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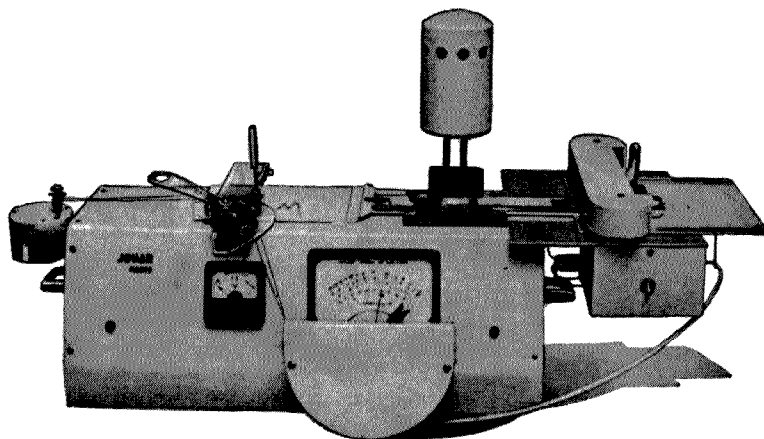
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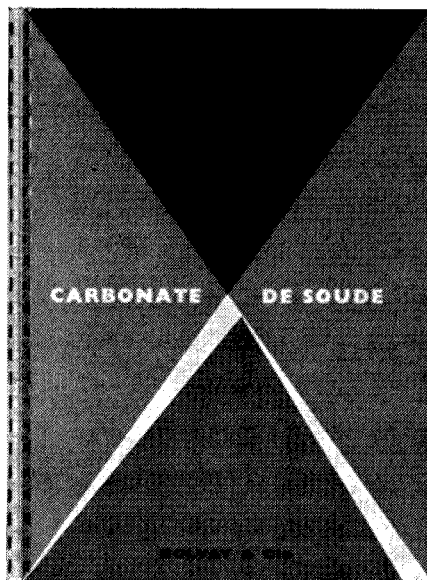
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THE USE OF SULFAMIC ACID AS A PRIMARY STANDARD
IN NONAQUEOUS TITRIMETRY*

SISTER MARGUERITE MIRIAM CASO** AND MICHAEL CEFOLA

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Since the choice of primary standards for use in nonaqueous titrimetry is limited, the possibility of using sulfamic acid in this field would be most acceptable. Sulfamic acid is an inorganic compound with a relatively simple structure. As a primary standard it has many advantages¹. It is cheap, readily available, and can be easily purified from the technical grade product, from which it separates as a non-hygroscopic, white crystalline material. It is a reliable standard when used in aqueous solutions. The reagent is soluble in the basic solvents currently used in nonaqueous titrations, and work described in this paper has sought to evaluate the possibilities of using sulfamic acid as a standard in these titrations.

In 1912 FOLIN AND FLANDERS² extracted benzoic acid with chloroform and succeeded in titrating it in benzene. Consequently, benzoic acid quite naturally came into use for the standardization of the alkoxides and amino-ethoxides with the advent of these titrants. This acid dissolves readily in dimethyl formamide and ethylenediamine and gives reproducible titrations. It has proved unsatisfactory for titrations in butylamine, however, since the formation of a gel produces erratic results. Crystalline phenols are used in place of benzoic acid for this latter solvent. These materials form the chief primary standards in use today for the nonaqueous titrations of bases. If sulfamic acid proved a good standard in the solvent, *n*-butylamine, it could then be recommended for use in nonaqueous titrations performed in the common basic solvents. This work has succeeded in titrating sulfamic acid in all of the commonly used basic solvents by both visual and potentiometric means.

One phase of the work has shown that it is possible to titrate sulfamic acid in an acidic solvent. By conductometric means, sulfamic acid was titrated with perchloric acid in a glacial acetic acid system.

One difficulty, presenting itself at the outset of this work, was the predictable low solubility of sulfamic acid — due to its highly polar nature — in the organic solvents frequently used in nonaqueous titrimetry. This prediction was justified and sulfamic acid proved practically insoluble in dioxane, benzene, carbon tetrachloride, methanol, ethanol, isopropanol and glacial acetic acid. However, it was found that sufficient

* (a) Presented in part before the Meeting-in-Miniature of the New York Section of the American Chemical Society, March 14, 1958. (b) Based on experimental part of thesis submitted by Sr. Marguerite Miriam Caso, S.C., to the Graduate School, Fordham University, June 1958, in partial fulfillment of requirements for the degree of doctor of philosophy.

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sulfamic acid dissolved in acetic acid, after refluxing the solid gently for 10 min, to give a 0.05 *N* solution basic to crystal violet indicator. Sulfamic acid was found to dissolve readily in the three basic solvents, dimethyl formamide, *n*-butylamine and ethylene-diamine, and in a fourth solvent, previously untried, dimethyl sulfoxide.

In the very beginning of the work in nonaqueous titrations, the lack of indicators with a suitable range for acid-base titrations was realized, and titrations were first performed potentiometrically. CONANT AND HALL³ used a chloranil indicator electrode with a calomel reference electrode for titrations in glacial acetic acid. The hydrogen-calomel pair and the antimony-antimony electrode pair were used successfully by MOSS, ELLIOTT AND HALL⁴ for titrations in ethylenediamine, and these authors reported that the glass electrode did not function well in this system. FRITZ AND LISICKI⁵ used the glass-antimony combination for titrations of acids in butylamine with sodium methoxide in benzene-methanol. LYKKEN⁶ *et al.* reported the use of the glass-calomel system, but warned that it required constant attention in order to achieve reproducible results. Platinum electrodes have been used for titrations in tetrahydrofuran⁷ and ethylenediamine^{8,9}. However, diverse opinions appear in the literature on both the use of the platinum electrode and the behavior of the glass electrode in basic solvents.

Preliminary investigations for this work revealed the sensitivity of the platinum-calomel system for titrations in basic media. Reproducibility was not good when an aqueous calomel electrode was used so further experiments were made in which the calomel electrode was filled with nonaqueous solutions of either potassium chloride or lithium chloride. In using the solvent, ethylenediamine, MOSS, ELLIOTT AND HALL⁴ had replaced the aqueous solution of potassium chloride with a solution of the same salt in ethylenediamine. RYAN¹⁰, working in dimethyl formamide, had replaced the aqueous solution with a saturated solution of lithium chloride in dimethyl formamide, lithium chloride was chosen because of its increased solubility over potassium or sodium chloride in the solvent. This electrode combination proved the most promising in the preliminary investigations, so work was continued with it.

The use of indicators in basic solvents is still empirical and a study of indicators was not attempted at this stage of the investigation. Thymol blue¹¹ was chosen because of its accuracy in titrations involving basic solvents in general, particularly dimethyl formamide¹².

EXPERIMENTAL

Apparatus

Potentiometric titrations were performed with a Shell-Precision Dual Titrometer equipped with a sleeve-type calomel electrode and an enlarged platinum electrode. The aqueous solution of the calomel electrode was replaced by a saturated solution of lithium chloride dissolved in dimethyl formamide. The titration assembly consisted of a 150-ml tall-form beaker, covered with a plastic lid to minimize pick-up of carbon dioxide and moisture during the titration. Three holes in the lid admitted the electrodes and buret tip into the titration beaker. The titrant was delivered from a 10-ml buret calibrated at 25° in the normal way. A magnetic stirrer and a glass-covered stirring bar were used to stir the solution during the titration.

Conductometric measurements were made with the Model RC-1B Conductivity Bridge manufactured by Industrial Instruments. The cell was the dipping type platinum electrode, the plates of which were of the approximate dimensions of 12 × 13 mm, separated by a glass bead at a distance of 2 mm. The plates were platinized by electrolysis of a 3% solution of chloroplatinic acid at an applied potential of 3 V for 10 to 15 min.

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Reagents

Sulfamic acid (Primary standard grade, Fisher), was recrystallized from water several times until it gave no opalescence with barium chloride. The reagent was dried at 105° for 3 h and its purity was assayed according to the method of BUTLER, SMITH AND AUDRIETH¹. Potassium acid phthalate (Primary standard grade, Merck), was dried at 145° for 3 h. *n*-Butylamine (Technical, Eastman), was dried over sodium hydroxide for several days, then dried over sodium for one day and finally distilled. Dimethyl sulfoxide (Technical, Stepan), was used, as received, without further purification. Ethylenediamine (95–100%, Eastman), was further purified by the method of MOSS, ELLIOT AND HALL⁴. Dimethyl formamide (technical grade, Dupont), was purified by simple distillation.

The titrants, lithium methoxide and perchloric acid, were prepared as described below.

The concentrations of the indicator solutions, thymol blue in dimethyl formamide and azo violet in benzene, were those normally used in analytical work.

All weighings were made with calibrated brass weights and were not corrected to vacuo.

Lithium methoxide solution

To make a 0.1 *N* solution of lithium methoxide, approximately 0.6 g of freshly cut lithium metal was dissolved in 150 ml of absolute methanol, cooling the flask during the addition. When the reaction was completed, 850 ml of dried benzene were added. Sufficient methanol was added to clarify the solution, the volume of methanol being kept at a minimum^{12,13}. The reagent was stored in a glass-stoppered bottle, protected from carbon dioxide and moisture.

Perchloric acid, 0.2 *N*

The titrant, 0.2 *N* perchloric acid, was prepared by mixing 17.0 ml of 72% perchloric acid with 200–300 ml of glacial acetic acid and adding 20 ml of acetic anhydride. The resulting solution was diluted to 1 l with glacial acetic acid and allowed to stand for at least 24 h to permit completion of the reaction between acetic anhydride and the water present¹¹.

Glacial acetic acid (Baker).

Benzene (anhydrous, reagent grade, Merck), was dried over sodium and distilled.

PROCEDURE

Visual titrations

Approximately 10 ml of solvent were placed in a 250-ml Erlenmeyer flask. A stirring bar was added and the solution was magnetically stirred. Three drops of thymol blue indicator solution were added and the solvent was titrated visually with 0.1 *N* lithium methoxide solution to the first appearance of a permanent, clear blue color. Less than 0.01 ml of titrant was usually required to neutralize the acidic impurities of the solvent. Approximately 0.1 g of primary standard was accurately weighed into the flask and the solution was titrated by passing 0.1 *N* lithium methoxide quickly into the flask. As the end-point was approached, one drop of base turned the solution a deep blue. The two standards, benzoic and sulfamic acids, were titrated alternately in a series of 10 determinations for each acid.

Potentiometric titrations

Exactly 0.50 mequiv. of primary standard was accurately weighed into a tall-form beaker and 10 ml of basic solvent, previously neutralized as above, were added to dissolve the sample. The beaker was mounted in the titration assembly described above and the titrant was added in small increments. The electrodes were permitted to come to equilibrium before the reading was recorded. The titration was continued several ml past the calculate end-point. The platinum-modified calomel electrode system was used for all titrations in basic solvents.

Conductometric titrations

Exactly 48.6 mg of sulfamic acid was dissolved in 40 ml of glacial acetic acid and

titrated conductometrically with 0.2 *N* perchloric acid using the apparatus specified above. The same quantity of sulfamic acid was also dissolved in 40 ml of dimethyl formamide and titrated with 0.2 *N* lithium methoxide. The platinum electrode was permitted to stand in the solution for approximately 10 min to allow the system to approach equilibrium before the titration was commenced.

RESULTS

A summary of the normalities found for lithium methoxide solutions in benzene-methanol using benzoic acid and sulfamic acid is given in Table I for both visual and potentiometric titrations.

TABLE I
STANDARDIZATION OF LITHIUM METHOXIDE SOLUTIONS IN BENZENE-METHANOL

<i>Solution A — Visual titrations</i> <i>Thymol Blue indicator</i>		<i>Solution B — Potentiometric titrations</i> <i>Platinum-calomel system</i>	
<i>vs. Sulfamic</i>	<i>vs. Benzoic.</i>	<i>vs. Sulfamic</i>	<i>vs. Benzoic</i>
0.1322	0.1317	0.1031	0.1010
0.1317	0.1321	0.1029	0.1002
0.1317	0.1314	0.1020	0.0980
0.1317	0.1314	0.1000	0.0986
0.1313	0.1320	0.1016	0.0986
0.1320	0.1327	0.1027	0.1004
0.1309	0.1318	0.1020	0.1002
0.1319	0.1319	0.1018	0.1000
0.1313	0.1310	0.1020	0.1010
0.1316	0.1313	0.1014	0.1002
Av. 0.1316	0.1317	0.1020	0.0999
Std. dev. 0.00027	0.00035	0.00086	0.00091
	(parts/1000)		

As a primary standard, sulfamic acid is seen to compare favorably with benzoic acid. No precipitates or gels were evident during the course of the titration with either of these standards. Previously to this investigation, a 50-ml buret had to be used and it was noted that the 4 mequivs. of sulfamic acid needed for the larger amount of titrant produced a precipitate slightly before the end-point. This precipitate, however, did not interfere with the results and the experimental values were in agreement with the theoretical values. Cutting down the amount to 1 mequiv., and using a 10-ml buret, obviated this difficulty.

Fig. 1 shows a comparison of two electrode systems for titrations in butylamine. The platinum-calomel pair was chosen for this investigation on the basis of the sharp potentiometric break produced at the end-point. Reproducibility of results was not good with the aqueous calomel electrode because a shifting of the potential break occurred. Replacing the standard aqueous potassium chloride solution with the dimethyl formamide solution of lithium chloride enabled greater reproducibility to be obtained. Fig. 2 shows the results of titrations in dimethyl formamide using duplicate samples of sulfamic acid.

Lithium methoxide was then standardized by visual means *vs.* sulfamic acid in

other solvent systems, dimethyl sulfoxide, *n*-butylamine and ethylenediamine. The results are listed in Table II. Thymol blue was used as the indicator for all the solvents except ethylenediamine. Azo violet was a better indicator for this latter solvent since thymol blue proved unsatisfactory¹⁴. Poorer precision with this solvent can be attributed to the predominance of benzene in the titrant, which interferes with the action of azo violet.

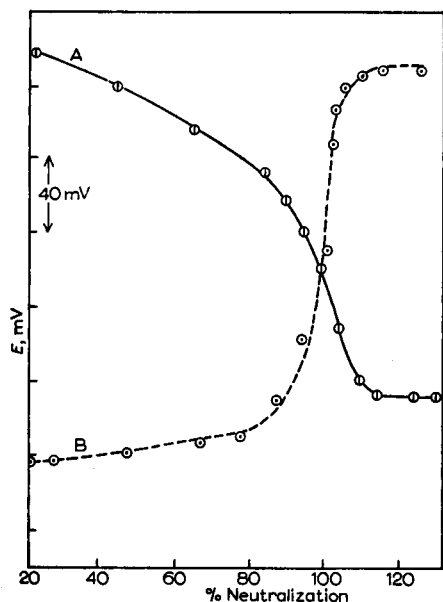


Fig. 1. Comparison of electrode systems in the solvent, *n*-butylamine. Curve A: platinum-glass electrode system. Curve B: platinum-aqueous calomel electrode system.

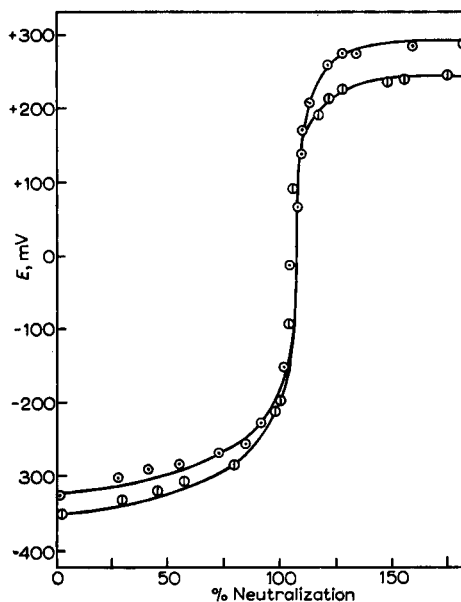


Fig. 2. Titrations in dimethyl formamide showing reproducibility of results. Electrode system: platinum-modified calomel. Solvent: dimethylformamide. Standard: 48.6 mg sulfamic acid. Titrant: 0.1031 *N* lithium methoxide.

TABLE II

NORMALITY OF LITHIUM METHOXIDE, SOLUTION A, vs. SULFAMIC ACID IN 4 BASIC SOLVENTS

Solvent	Indicator	Determinations	Normality	Deviation from mean	Standard deviation (parts/1000)
Dimethyl formamide	Thymol Blue	8	0.1316	0.00028	0.00027
Dimethyl sulfoxide	Thymol Blue	8	0.1315	0.00037	0.00039
<i>n</i> -Butylamine	Thymol Blue	8	0.1316	0.00029	0.00031
Ethylenediamine	Azo Violet	8	0.1315	0.00048	0.00050

A comparison of the potentiometric titrations of sulfamic acid in the four basic solvents is illustrated in Fig. 3. A large difference in the height of the potential break is evident with dimethyl formamide and dimethyl sulfoxide both of which surpass the other two. All of the solvents for this particular test were used, as received, without

further purification. The solvents were simply adjusted so that they were slightly basic before titration using the neutralization method described above.

Detection of the equivalence point

A major requirement for a volumetric standard is that the equivalence point be easily detected. The method used to determine the end-point for the potentiometric titrations is shown in Fig. 4. Since the titration curve appears to be symmetrical about the end-point, the end-point can be defined by the maximal value of dE/dV . A plot of dE/dV vs. V can then be used to determine the precise end-point of the titration.

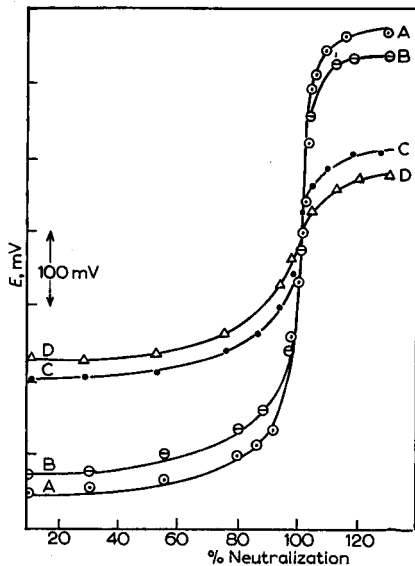


Fig. 3. Potentiometric titration of sulfamic acid in four basic solvents. Solvents: curve A — dimethyl formamide; curve B — dimethyl sulfoxide; curve C — ethylenediamine; curve D — *n*-butylamine. Standard: 48.6 mg sulfamic acid. Titrant: 0.1031 *N* lithium methoxide. Electrode system: platinum-modified calomel.

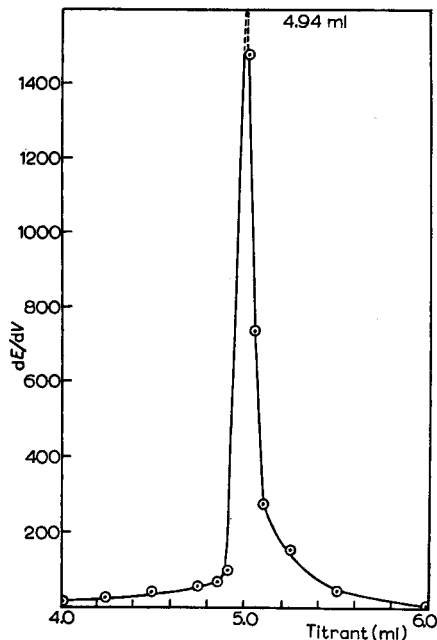


Fig. 4. Method for the detection of the end-point. Electrode system: platinum-calomel. Solvent: dimethyl formamide. Standard: 48.6 mg sulfamic acid. Titrant: 0.0998 *N* lithium methoxide.

Conductometric titrations

The titration curve for the standardization of lithium methoxide *vs.* sulfamic acid shown in Fig. 5 is interesting in so far as the conductance levels off after the end-point is reached, remaining unchanged as more titrant is added. Curves of this type were reported by MARYOTT¹⁵ for both di-*n*-butylamine and triethylamine, however, and are apparently characteristic of anhydrous systems for titrations in basic solvents. These titrations were very tedious due to the erratic behavior of the electrodes. The reproducibility of results ranged from 3 to 9%.

Conductometric titrations proved very sensitive to changes in acidity and a sul-

famic acid solution in glacial acetic acid could be titrated with perchloric acid in the same solvent. This titration curve is shown in Fig. 6. Reproducibility in acid medium was increased over that reported above and ranged from 2 to 4%.

Effect of water

The deleterious effects of water upon nonaqueous solvent titrations in general have been reported by many authors, and most basic solvents, including dimethyl

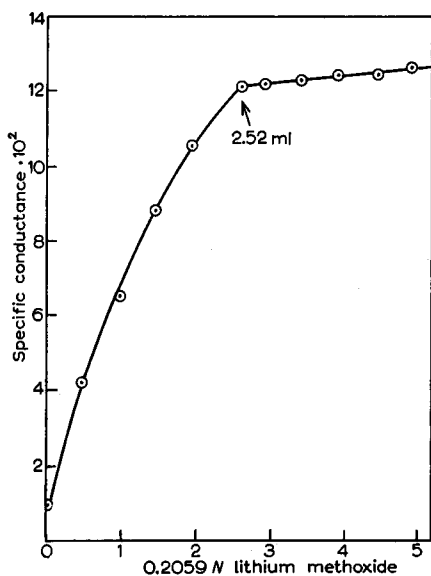


Fig. 5. Conductometric titration of sulfamic acid in dimethyl formamide. Standard: 48.6 mg sulfamic acid dissolved in 40 ml dimethyl formamide. Mequivs. sulfamic acid: calculated — 0.500, observed — 0.518.

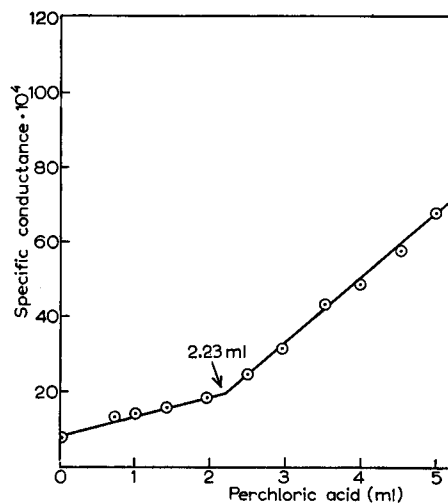


Fig. 6. Conductometric titration of sulfamic acid in glacial acetic acid. Standard: 48.6 mg sulfamic acid dissolved in 40 ml acetic acid. Titrant: 0.2250 N perchloric acid in acetic acid. Mequivs. sulfamic acid: calculated — 0.500, observed — 0.492.

formamide, have been known to be sensitive to moisture. FRITZ¹⁶ had reported the inability of the indicator to function properly in a dimethyl formamide system when 1% of water is exceeded. A series of titrations were subsequently performed, both visually and potentiometrically, in order to determine the exact effect as the water content in the solvent was increased to 5%. The results for visual titrations are listed in Table III. Poorer precision is attributed to the slowed response of the indicator as the water content is raised. Also noticeable is the change in the normality of the titrant. Apparently this is due to the hydrolysis of the dimethyl formamide splitting off formic acid¹⁶. The effect of water on a potentiometric titrations is shown in Fig. 7. The steep potential break exhibited in an anhydrous system gives way to a gradual slope as the water content was raised. Also evident is the noticeable depreciation of the height of the potential break at the end-point.

TABLE III
EFFECT OF WATER UPON THE STANDARDIZATION OF 0.1 N
LITHIUM METHOXIDE *vs.* SULFAMIC ACID

% Water	Determinations	Normality, Av.	Standard deviation
0	3	0.1066	0.00025
1	3	0.1067	0.00007
2	3	0.1066	0.00052
3	3	0.1061	0.00101
4	3	0.1050	0.00055
5	3	0.1053	0.00070

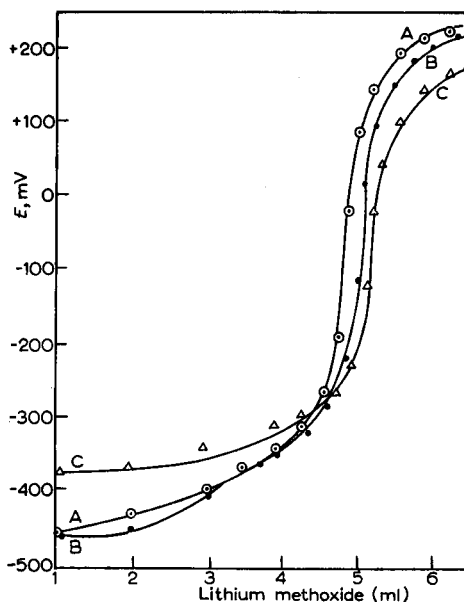


Fig. 7. Effect of increasing the water content in the solvent, dimethyl formamide. Curve A: 0% water; curve B: 2% water; curve C: 4% water. Solvent: dimethyl formamide. Standard: 48.6 mg sulfamic acid. Titrant: 0.1031 N lithium methoxide. Electrode system: platinum-modified calomel.

Effect of carbon dioxide

In order to ascertain the deleterious effects of carbon dioxide under ordinary laboratory conditions, visual titrations were performed after the titration solution was permitted to stand exposed to the air for intervals from 5 to 25 min. The titrations were then performed quickly, with magnetic stirring, at the close of the specified time interval, and the change in the normality of the titrant was noted. In the two series of experiments the greatest deviation up to 25 min exposure time was 5 parts per 1000, as seen in Table IV, given on the basis of deviation from the determined normality of the base.

From the results in Table IV, it seems that the rate of absorption of carbon dioxide

TABLE IV
EFFECT OF ATMOSPHERIC CARBON DIOXIDE UPON THE STANDARDIZATION OF 0.1 N
SOLUTIONS OF LITHIUM METHOXIDE *vs.* BENZOIC ACID

Time, min	Determinations	Series A		Series B	
		Normality	Dev. Mean	Normality	Dev. Mean
0	6	0.1082	0.0002	0.1102	0.0002
5	2	0.1081	0.0001	0.1098	0.0004
10	2	0.1081	0.0001	0.1096	0.0006
15	2	0.1084	0.0002	0.1096	0.0006
20	2	0.1081	0.0001	0.1097	0.0005
25	2	0.1088	0.0006	0.1103	0.0001

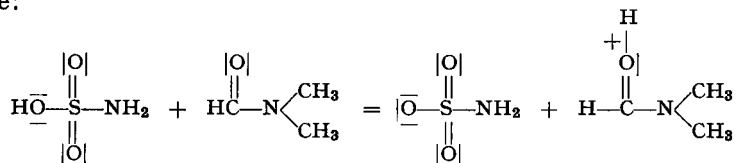
is quite slow, even under these extreme conditions. Apparently it can be concluded that dimethyl formamide can be safely used in the average laboratory with merely simple precautions taken to guard against carbon dioxide uptake.

DISCUSSION

Before performing the potentiometric titrations, the electrodes were permitted to stand in the solution for at least 10 min. It was found that this ten-minute period enabled the system to approach equilibrium and register a steady reading on the meter. The titrant was added in small increments and the electrodes again permitted to equilibrate before the reading was recorded. When this time was allowed at the start of the titrations, equilibrium was achieved within 30 to 60 sec upon the addition of each increment of titrant up to the stoichiometric point. Once this point was approached, longer intervals were required for the system to equilibrate. One of the great disadvantages of the platinum electrode can be seen here. However, the final result gave a large potentiometric break and somewhat offset this difficulty.

At first it was thought possible that the amount of water actually present in the solvent could be quantitatively estimated from the increase in the volume of titrant required for neutralization in a dimethyl formamide system. There was a definite shifting of the titration curve with the increase of water, added experimentally, but no reliable quantitative information could be established at this point in the investigation. Also, the electrode system used for these titrations approached equilibrium more slowly as the water content was increased, which made the procedure tedious. This application, in view of these difficulties, was abandoned since the Karl Fischer titration is easier to perform, either visually or potentiometrically.

The following mechanism can be proposed for titrations of sulfamic acid in dimethyl formamide:



CONCLUSION

In conclusion, the experimental behavior reported in this paper justifies the following assumptions:

1. Sulfamic acid can be titrated by both visual and potentiometric means with a

strong base, lithium methoxide, in several basic solvents. It can also be titrated with a strong acid, perchloric acid, in an acidic solvent by conductometric means, although the method is neither practical nor precise.

2. It is possible to use sulfamic acid as a primary standard in basic solvents for the standardization of lithium methoxide. When dissolved in dimethyl formamide, it standardized this base with a precision of 0.27%. Precision in other basic solvents ranged from 0.3 to 0.5%. Sulfamic acid can be used for titrations in *n*-butylamine without the formation of gels or precipitates which interfere with the titration.

ACKNOWLEDGEMENT

The authors wish to thank Doctor JOHN C. RYAN for his helpful suggestions concerning electrode systems in basic media.

SUMMARY

A method has been developed for the standardization of a typical nonaqueous base, lithium methoxide, with an inorganic primary standard, sulfamic acid. This acid was found to dissolve readily in four independent basic solvents, dimethyl formamide, ethylenediamine, *n*-butylamine and dimethyl sulfoxide. Sulfamic acid could be titrated in each of these solvents, by both visual and potentiometric means with lithium methoxide dissolved in benzene-methanol. No gels nor precipitates resulted in the course of the titrations and the accuracy of the method was comparable to that obtained using benzoic acid as the primary standard. Conductometric titrations were also performed using sulfamic acid dissolved in two systems, dimethyl formamide and glacial acetic acid. In the latter solvent it was possible to titrate sulfamic acid with perchloric acid in glacial acetic acid.

RÉSUMÉ

Une étude a été effectuée sur le titrage d'une base non-aqueuse, le méthoxyde de lithium, au moyen d'un étalon inorganique, l'acide sulfamique. La précision obtenue par cette méthode correspond à celle du titrage au moyen de l'acide benzoïque. Des titrages conductométriques de l'acide sulfamique ont été également effectués au moyen de l'acide perchlorique dans l'acide acétique glacial.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Standardisierung einer nicht-wässrigen Base (Lithium-methoxyd) mit Sulfaminsäure als anorganischer Ursubstanz. Die erreichbare Genauigkeit entspricht etwa der einer Titration von Benzoesäure. Ferner werden konduktometrische Titrationen von Sulfaminsäure mit Perchlorsäure in Eisessiglösung erwähnt.

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THE DETERMINATION OF SULPHATE IN SUPERPHOSPHATE

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INTRODUCTION

It is well known that the accuracy of the determination of sulphate by the classical technique of precipitation as barium sulphate, is dependent on the concentration and species of the various ions present in the solution. An accurate determination of the sulphate content of superphosphate, based on the quantitative collection of a chemically pure barium sulphate precipitate, would require prior removal of interfering ions and must consequently be extremely time consuming.

Furthermore, while interfering cations can be separated by cation exchange, phosphate is not readily separated without loss of sulphate. A rapid empirical method, taking cognisance of the effects of impurities contained in the barium sulphate precipitate, offers certain advantages.

EXPERIMENTAL

The method of preparing and collecting the barium sulphate precipitate was as described in text books^{1,2}. In the initial stages of the experiments the precipitate was separated and collected in a sintered glass crucible and dried at 110° and in later experiments in a sintered silica crucible and ignited at 900°.

Effect of quantity of barium chloride and hydrochloric acid on the yield of the barium sulphate precipitate

It is generally known that, for a given sample composition and a given analytical procedure the amount of sulphate found will vary with the amount of excess barium chloride reagent used and with the amount of hydrochloric acid added. In order to obtain a broad picture of the effects of varying amounts of excess barium chloride reagent and hydrochloric acid present on the yield of barium sulphate, the use of an economical factorial approach seemed an automatic choice. A factorial experiment results in a considerable saving of the time and material and also estimates each main effect with the same precision.

In this experiment, a solution equivalent in composition to that of a Morocco superphosphate, but of a known sulphate content, was analysed. The solution was prepared by extracting a weighed amount of Morocco rock with hot concentrated hydrochloric acid. A measured volume of standard sulphuric acid was added and the whole was diluted to a known volume. The accuracy with which the sulphate concn. of the solution could be calculated was not perturbed by the amount of sulphate introduced with the rock because this amount was relatively small. The following levels of reagent and hydrochloric acid were used in the experiment (see Table I).

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แผนกห้องสมุด กรมวิทยาศาสตร์
กระทรวงอุตสาหกรรม

The initial volume of solution, in which precipitation was carried out, was 250 ml. After dropwise addition from a 50-ml burette, at the rate of 8 ml per min of the barium chloride reagent, each mixture was made up, with water, to the same volume of 350 ml and digested for 1 h on a steam bath. Sintered glass crucibles were used.

TABLE I
10% w/v Barium chloride reagent

Levels	Added (ml)	Excess (ml)
x ₁	16	3
x ₂	58	45
x ₃	100	87

Hydrochloric acid	
Levels	Weight (g)
y ₁	4.563 (12.5 ml of 10 N HCl)
y ₂	6.844 (18.75 ml of 10 N HCl)
y ₃	9.125 (25 ml of 10 N HCl)

The experiment, randomized and replicated 3 times, involved 27 separate determinations of barium sulphate. The mean results of the three replicates, expressed in grams and percentage yields, are shown in Table II and Fig. 1. A result of 1.2075 g would have been quantitative.

TABLE II
YIELDS OF BaSO₄ FROM SIMULATED SUPERPHOSPHATE SOLUTION

Levels	x ₁		x ₂		x ₃	
	g	%	g	%	g	%
y ₁	1.205	99.77	1.215	100.55	1.215	100.61
y ₂	1.211	100.26	1.222	101.18	1.227	101.58
y ₃	1.201	99.40	1.220	101.02	1.228	101.67

Statistical analysis of these results showed that the excess of barium chloride and the amount of hydrochloric acid had a significant effect on the quantity of barium sulphate found. The curvilinearity of yield surface has been established by the significance of linear and quadratic effects of investigated factors in the analysis of variance. The standard deviation was found to be 0.0045 g of barium sulphate. As differences in yield equal to or in excess of 0.0082 g BaSO₄ become significant at the 5% level there exists a virtual horizontal plane on the yield surface, because within this area all differences in yield are less than the significant amount. In the factorial experiment this area proved to be within the limits 45–87 ml BaCl₂ solution and 6.84–9.13 g HCl respectively. This region is therefore one in which it is not necessary for the analyst to exercise particular care in measuring out prescribed quantities of hydrochloric acid and barium chloride solution. Quantitatively, how-

ever, this region would have overestimated sulphate content and consequently had to be abandoned in further experimentation involving use of sintered glass crucibles.

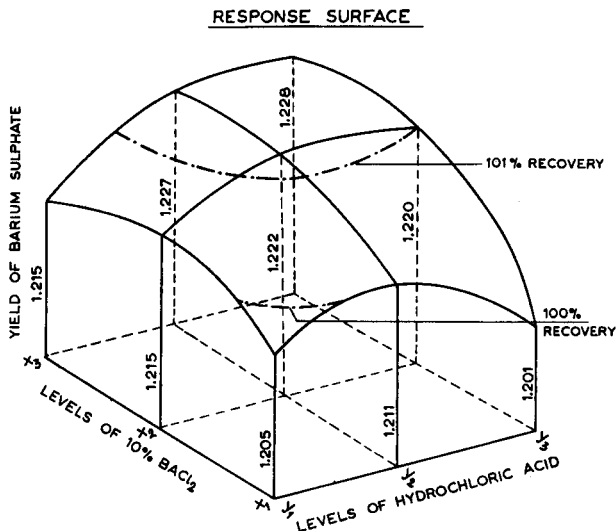


Fig. 1. Response surface (using sintered glass crucibles).

Effect of volume on precision and accuracy

The possibility existed that a greater precision could have been obtained if larger volumes of solutions had been used. This effect was therefore investigated at three levels of volume, V_1 , V_2 and V_3 , corresponding to 250, 450 and 650 ml respectively, prior to the addition of precipitating reagent.

The quantities of reagent are shown in Table III:

TABLE III
10% w/v Barium chloride

Levels	Added (ml)	excess (ml)
x ₁	16	3
x ₂	58	45

Hydrochloric acid

Levels	N	Abs. weight (g)		
		V ₁	V ₂	V ₃
y ₁	0.50	4.562	8.212	11.862
y ₂	0.75	6.844	12.319	17.794

Mean yields of barium sulphate in grams and corresponding percentages are given in Table IV. A quantitative yield would have been 1.2105 g.

TABLE IV

MEAN YIELDS OF 3 DETERMINATIONS OF BARIUM SULPHATE AT VARYING VOLUMES OF SOLUTION OF SUPERPHOSPHATE

Levels	V_1		V_2		V_3	
	g	%	g	%	g	%
y_1x_1	1.2006	99.18	1.1876	98.11	1.1537	95.31
y_1x_2	1.2075	99.75	1.2200	100.78	1.2220	100.95
y_2x_1	1.2055	98.59	1.1697	96.63	1.1109	91.77
y_2x_2	1.2161	100.46	1.2251	101.21	1.2165	100.50

No statistically significant differences in precision between the three volumes considered were found, but numerically the best precision was obtained for the volume of 250 ml under the conditions of this experiment.

Since the 250-ml volume also yielded the best quantitative amount of barium sulphate, it was decided to use this volume in further experiments:

Effect of sintered silica crucible and ignition temperature on accuracy and precision

It appeared that the precision could be improved by igniting the barium sulphate precipitate in a sintered silica crucible at 900°. The standard errors of barium sulphate yields obtained from simulated superphosphate, using both sintered glass and sintered silica crucibles, were therefore compared and gave the results summarized in Table V.

TABLE V

STANDARD ERROR AND ACCURACY WITH SINTERED SILICA AND SINTERED GLASS CRUCIBLES (calculated yield = 1.2135 g of barium sulphate)

	Silica	Glass
Number of determinations	6	6
Standard error	0.0018 g of barium sulphate	0.0053 g of barium sulphate
Yield of barium sulphate	1.2010 g	1.2123 g
% recovery	98.97	99.90

Since the difference between the standard errors obtained by the two procedures had been found significant at the 2% level, it was concluded that the use of sintered silica crucibles has improved the precision of the analysis. Consequently, in all further experiments, sintered silica crucibles were used.

Table V reveals also that the new procedure has depressed the barium sulphate yield by 0.0125 g. The decrease in yield was found to be significant at 0.1% level and to achieve the quantitative recovery of barium sulphate the conditions of precipitation had to be altered. This can be done by reference to the yield surface (Fig. 1) where the required set of conditions are shown by the dotted contour at 100% recovery, on the assumption that this surface also applies to the use of the ignition procedure with sintered silica. The following new levels of reagents were selected from the contours:

10% w/w barium chloride	50 ml
hydrochloric acid	6.3875 g

It must be noted that this particular set of levels, required to give a quantitative

yield of barium sulphate, was one of many possible values along a contour of the yield surface. The above choice was made because it is convenient to pipette exactly 50 ml of barium chloride and because it was observed that a high level of excess reagent gave a dense precipitate, consisting of larger barium sulphate crystals than were obtained using smaller quantities of reagent. The larger crystals settled more rapidly and were consequently easier to wash.

Effects of constituents of superphosphate

Simulated superphosphate solutions of a known sulphate content were prepared as before from Morocco (M), Saafi (S) and Phalaborwa (P) rocks: These rocks were chosen because they represent a wide range of raw materials available for superphosphate manufacture. Six determinations as described in the recommended procedure, were made on each superphosphate and gave the following results:

TABLE VI
YIELDS OF BARIUM SULPHATE FROM VARIOUS SUPERPHOSPHATES

Rock	Calculated result (g)	Result found (g) (Mean of 6 determinations)	Yield (%)
M	1.1973	1.2004	100.26
P	1.1815	1.1806	99.92
S	1.2041	1.2036	99.95

The standard deviation was found to be 0.002 g of barium sulphate. The highest deviation observed between calculated and found, namely 0.0031 g for Morocco rock, was found not significant, since the difference must attain the value of 0.0048 g to be significant at a 5% level.

Application of method to commercial superphosphate

A sample of approximately 200 g superphosphate was crushed in a mortar to pass through a 20-mesh sieve (Gallenkamp's specification). Sixteen identical samples were taken from a sample splitter, of which 10 samples were selected randomly. The superphosphate was then analysed in duplicate as described later and gave the following results: Mean sulphate content 40.1%, Standard deviation 0.08.

RECOMMENDED PROCEDURE

Digest approximately 2.5 g of superphosphate with 25 ml of 10 *N* conc. hydrochloric acid and 125 ml of water for 1½ h, replacing from time to time the water lost during the digestion. Cool the solution and transfer it quantitatively to a 250-ml volumetric flask. Filter the solution through a Whatman No. 40 filter paper. To exactly 100 ml of the filtrate, add 7.5 ml of conc. hydrochloric acid and 150 ml of water. Bring the solution to the boil and add dropwise from a burette at the rate of about 8 ml per min 50 ml of 10% w/v barium chloride solution, stirring at about

200 r.p.m. with a glass rod bent at one end. Digest the precipitate for 1 h on a steam bath and collect it on a sintered silica crucible.

Wash in the usual manner, dry in an oven at 110° and ignite at 900° in a muffle furnace.

DISCUSSION

The curvilinearity of equal yield contours can only be accounted for by phenomena such as occlusion, coprecipitation, post-precipitation etc. It was never the intention of the authors to fit mathematically a surface to the points observed. The required quantities of barium chloride and hydrochloric acid to give a quantitative yield were obtained by interpolation. The mathematical fitting of a barium sulphate yield surface would call for a central composite design which is fully discussed by BOX AND WILSON².

Additional experiments carried out on solutions, differing in volume by not more than 50 ml, showed no detectable changes in barium sulphate yields. This is encouraging to the analyst as it relaxes somewhat the analytical procedure.

It must be noted that the standard error of barium sulphate determinations are quoted in grams of barium sulphate. It is obvious that the standard error expressed in percentages is erroneous if the barium sulphate yields happen to differ amongst themselves considerably.

The importance of the accuracy and precision of the method while establishing the yield surface, cannot be too strongly emphasized, since any possible bias in the analytical work, due either to operator or to a change in the technique, can only be detected by referring back to the original yield surface.

The method is considered to be suitable for determining the percentage sulphate content of superphosphates made from raw phosphate rocks differing in silica contents as exemplified by the Morocco and Saafi (low grade Morocco) rocks used.

It is well known^{1,2} that the accuracy of the determination of sulphate by precipitation as barium sulphate is dependent on the concentrations and species of the various ions present in the solution in which precipitation is carried out.

In the case under consideration the major sources of interference in addition to those arising from the reagents will come from the calcium, silica and phosphate present in the superphosphate. Any coprecipitation of calcium sulphate will tend to give low recoveries of sulphate while coprecipitation of barium or calcium phosphate and silicate will tend to give high recoveries. Increase of acid concentration at any given volume will lead to low recoveries of sulphate since the solubilities of both calcium and barium sulphates increase with increasing acid concentration, due to the formation of bisulphate ion. The excess of chloride will tend however to compensate for this, since barium chloride is readily coprecipitated. The large excess of barium chloride will decrease the solubility of barium sulphate due to the common ion effect.

Qualitative spectrographic examination of a few of the precipitates showed the presence of calcium, phosphate and silica, while chemical examination proved the presence of chloride ion. Quantitative determination of these impurities was not undertaken. It does therefore appear fairly certain that the quantitative recovery of sulphate obtained by the suggested method is due to compensation of errors such as have been suggested above.

ACKNOWLEDGEMENTS

We wish to express our thanks to Dr. E. L. TIETZ for continued advice and guidance during the course of this work, and African Explosives and Chemical Industries, Limited, for their permission to publish this paper.

SUMMARY

An accurate method developed by means of a statistical approach, has been devised for the quantitative determination of sulphate in superphosphate fertilizer. The method proved to be independent of the source of raw phosphate used in the preparation of the superphosphates examined. A standard error of two parts per thousand has been obtained and it is claimed that the method is capable of determining the existence of sources of bias, if any.

RÉSUMÉ

Une méthode est proposée pour le dosage du sulfate dans des engrais superphosphatés.

ZUSAMMENFASSUNG

Beschreibung einer Bestimmungsmethode von Sulfat als Bariumsulfat in Superphosphat.

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THIODIGLYCOLIC ACID AS A REAGENT FOR ZIRCONIUM

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Of the several organic precipitating reagents suggested for zirconium¹, mandelic acid is by far the most useful. This reagent and several of its derivatives particularly *p*-bromo- and *p*-chloro-mandelic acids are specific, precipitations can be effected in fairly high acid concentrations and the formation of tetramandelates offers a special advantage when handling small quantities of zirconium². VENKATRAMANIAH AND RAO³ reported the use of *m*-cresoxyacetic acid for the precipitation and separation of zirconium from a considerable number of cations.

Preliminary experiments revealed that an aqueous solution of thiodiglycolic acid, HOOC-CH₂-S-CH₂-COOH, gives a white precipitate when boiled with a zirconyl salt solution. This suggested a study on the utility of thiodiglycolic acid as a reagent for

zirconium. In the present communication, optimum conditions are described for the quantitative determination of zirconium by thiodiglycolic acid. The analysis is completed by igniting the zirconium-complex and weighing as ZrO_2 . Several metal ions do not interfere in the present method.

EXPERIMENTAL

Reagents

Zirconyl nitrate: Reagent grade zirconyl nitrate supplied by A. D. Mackay Inc., was used to prepare its aqueous solution. The total acidity was maintained at 0.2 *N* with respect to nitric acid and the zirconium content was ascertained by the standard *m*-nitrobenzoic acid method².

Thiodiglycolic acid: A stock 5% solution of thiodiglycolic acid was prepared in water from a pure sample obtained from Evans Chemetics Inc.

Procedure

To an aliquot of zirconyl nitrate solution enough nitric or hydrochloric acid to maintain its final acidity 0.2–0.4 *N* were added and the solution diluted to 100 ml; 15–20 ml of 5% thiodiglycolic acid were now added and the system heated on a steam bath for about 20 min. After an hour, the precipitate was filtered through Whatman No. 42 and washed a few times with hot water. The precipitate and the wet filter paper were placed in a silica or a platinum crucible, dried, ignited, cooled and the zirconium weighed as ZrO_2 . A representative set of data is given in Table I.

DISCUSSION

Precipitation of zirconium-thiodiglycolate carried out in presence of mineral acids of different concentrations revealed that while sulfuric acid cannot be used, hydrochloric or nitric acid can be used provided its overall normality in the system does not exceed 0.4 *N*. In the acidic medium, the precipitate is crystalline and hence easy to filter and wash. It was observed that the presence of 0.1 g of elements Co, Ni, Zn, Mg, Cd, Mn, Al, Pb, Ti, Be, and alkaline earths as chlorides or nitrates causes no

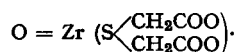
TABLE I

<i>ZrO₂</i> , g		Diff.
By thiodiglycolic acid	By <i>m</i> -nitrobenzoic acid	
0.0428	0.0429	– 0.0001
0.0514	0.0512	+ 0.0002
0.0856	0.0858	– 0.0002
0.1027	0.1024	+ 0.0003
0.1115	0.1116	– 0.0001
0.1289	0.1287	+ 0.0002
0.1540	0.1536	+ 0.0004
0.2141	0.2145	– 0.0004

interference in the present method of estimating zirconium. Although the presence of vanadyl, uranyl, iron(II) and chromium(III) gives a positive error of 0.5–2% when zirconium is precipitated in an aqueous medium, the error is negligible by effecting the precipitation in the higher permissible acid concentration of 0.4 *N*.

Cerium(IV) also gives a precipitate with thiodiglycolic acid but its interference is easily avoided by reducing it initially to cerium(III) with hydrogen peroxide or thiocyanate. Thorium which is not precipitated in acidic medium tends to give high results to an extent of about 2% due presumably to coprecipitation and/or adsorption. However, by carrying out the precipitation in 0.4 *N* nitric acid medium and using warm 0.15–0.2 *N* nitric acid as the wash liquid, it was found that the sparingly soluble zirconium thiodiglycolate can be freed completely of thorium.

An attempt was made to weigh the zirconium-complex of thiodiglycolic acid to find out its composition. The precipitate was filtered through sintered glass crucible, washed with hot water and dried at 110° for several hours. The results, within a variation of 2–5%, correspond to the formation of zirconyl thiodiglycolate:



Further work on the use of thioglycolic acid, iminodiacetic acid and other organic reagents for the quantitative precipitation of zirconium is in progress.

ACKNOWLEDGEMENT

We are indebted to Professor LUCY W. PICKETT and Professor PHILIP W. WEST for research facilities and interest in the work. One of us (S.B.S.) is grateful for the award of a Special Skinner Fellowship. We wish to acknowledge the gift sample of thiodiglycolic acid given by Evans Chemetics Inc., New York.

SUMMARY

Thiodiglycolic acid is shown to be a suitable precipitating reagent for zirconium. The analysis is completed by igniting the precipitate and weighing the ZrO_2 . Several metal ions do not interfere. Interference due to cerium(IV) is avoided by reducing it initially to cerium(III). Estimation of zirconium can be carried out in presence of thorium. The composition of the complex is slightly variable but corresponds to zirconyl thiodiglycolate: $O = Zr \left(S \begin{array}{l} \langle CH_2COO \rangle \\ \langle CH_2COO \rangle \end{array} \right)$.

RÉSUMÉ

L'acide thioglycolique est proposé comme réactif pour le dosage gravimétrique du zirconium. Le précipité obtenu est calciné; on pèse finalement l'oxyde ZrO_2 . Ce dosage peut s'effectuer en présence de thorium et de cérium.

ZUSAMMENFASSUNG

Zur gravimetrischen Bestimmung von Zirkonium kann Thioglycolsäure verwendet werden. Der gebildete Niederschlag wird zum Zirkoniumdioxid verglüht und gewogen. Eine Störung durch Cer und Thorium kann verhindert werden.

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AN ULTRAVIOLET SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF VANADIUM IN ORES AND STEEL

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A spectrophotometric procedure has been developed for the determination of small amounts of vanadium in ores and steels. The method depends upon the absorption of the orthovanadate ion at 270 $m\mu$ in a 1 *N* sodium hydroxide solution. A study has been made of the ions that might interfere, and a method described for the removal of the interfering ions with an ion-exchange resin. This method avoids a number of operations described previously¹ such as repeated extraction with an organic solvent, evaporation, fusion with sodium carbonate and filtration.

Preparation of a calibration curve

A 2.0000 g sample of ammonium vanadate was dissolved in water and transferred to a 1-l volumetric flask and diluted to the mark. 10 ml of the stock solution were pipetted into a 100-ml volumetric flask and diluted to the mark with 1 *N* NaOH. 5, 4, 3 and 2 ml, respectively, of this solution were pipetted into separate 100-ml volumetric flasks which were then diluted to the mark with 1 *N* NaOH solution. The spectra of these solutions were obtained from 300 to 250 $m\mu$ on a Cary model 11 spectrophotometer using 1-cm cells and 1 *N* sodium hydroxide solution in the reference cell. The absorbance was read at 270 $m\mu$ and a Beer's Law curve was made by plotting absorbance vs. concn.

Determination of vanadium in ores

Transfer a 1.0000 g sample of the ore to a platinum crucible and mix with 5 g of anhydrous sodium carbonate. Spread over the mixture another 0.5 g of sodium carbonate. Fuse the mixture and allow to cool to room temperature. Transfer the crucible and contents to a 400-ml pyrex beaker and add a few ml of water. Heat to boiling in order to loosen the residue in the crucible and crush any large particles with a flattened stirring rod. Remove the crucible, wash with water and add the washings to the beaker. Add 3-5 ml of reagent grade methyl alcohol to reduce the manganate, boil for 5 min and filter hot through a filter paper (Whatman no. 42) into a small Erlenmeyer flask. Wash the residue with hot water and add the washings to the filtrate. Allow to cool, acidify to pH 2 with HCl, transfer to a 100-ml flask and dilute to the mark. Pipet 20 ml of the solution into an ion-exchange column containing amberlite IRA-400. Adjust the rate of flow of the sample through the column to approximately 30 drops per min and collect the eluate in a 100-ml volumetric flask. Rinse the column

with several portions of water. Add enough NaOH solution to the flask in order to make the contents 1 *M* after diluting to the mark. Obtain the ultraviolet absorbance at 270 $m\mu$ on a spectrophotometer (Cary Model 11) using 1-cm cells and 1 *N* NaOH as reference. Read the concentration of vanadium from a standard working curve.

Determination of vanadium in steel

Weigh a 1.0000 g sample of the steel shavings into a small beaker and add 10 ml of 6 *N* HCl. Place the beaker on a steam bath and allow it to heat until the sample is dissolved completely. Evaporate the solution to a few ml, being careful not to evaporate to dryness, and add 2 or 3 drops of nitric acid. Heat for a few min and transfer to a 100-ml volumetric flask containing 40 ml of hot 2.5 *N* NaOH. The iron will precipitate and the vanadium remain in solution as sodium vanadate. After allowing the solution to cool to room temperature, dilute to the mark with water. Filter the solution or allow it to stand for a few min during which time the precipitate will settle out. Remove a 10 or 20-ml aliquot depending on the concentration of vanadium. Acidify to pH 2 or less and continue as given under the determination of vanadium in ores.

TABLE I
RESULTS OF THE DETERMINATIONS CARRIED OUT BY THE PROPOSED METHOD COMPARED TO PREVIOUSLY REPORTED VALUES ARE AS FOLLOWS:

Ore number	% Vanadium	
	Proposed method values	Previously reported values
1	0.29	0.28
	0.27	
	0.30	
	0.31	
	0.27	
2	0.19	0.19
	0.17	
	0.21	
3	0.54	0.59
	0.58	
	0.56	
	0.56	
4	0.058	0.053
	0.068	
	0.058	
5 Steel-containing chromium and vanadium	0.16	0.18
	0.16	
	0.21	
	0.19	

INTERFERING IONS

A study of the interfering elements found in ores and steel indicated that chromium was the greatest offender. Chromate ions have a strong absorption at 275 $m\mu$ and cause

serious interference. Separation of chromate was accomplished by use of an ion-exchange resin. In concentrated acid solutions vanadium is present in the form of $(VO)_2^+$ and $(VO)^{+3}$ while the chromium is in the form of dichromate. The vanadium can be adsorbed as a cation on a cation-exchange resin or the chromium can be adsorbed as an anion on an anion-exchange resin. The latter was found to be most satisfactory for two reasons. The vanadium was difficult to elute from the cation resin and the chromate reacted with the cation resin and caused erroneous results. The procedure was tried first with standard solutions in the following manner. A standard vanadate solution was adjusted to pH 1. 20 ml of the solution was passed through an anion-exchange column consisting of Amberlite IRA-400 in the chloride form. This was followed by 50 ml of dilute HCl of the same pH. The solution and washings were collected in a 100-ml volumetric flask and made alkaline with sodium hydroxide. The ultraviolet spectrum was obtained and compared to that of a standard not passed through the column. They were identical indicating none of the ion had been adsorbed or reacted with the resin. The procedure was repeated using a solution consisting of a mixture of vanadate and chromate ions. The resulting spectrum showed absence of chromate and full recovery of the vanadium.

RESULTS

The ores used in the determinations of vanadium were of the same general type as Ore no. 1, the composition of which was as follows: Fe 67.5%; Ni 0.016%; Cr 0.004%; Mn 0.08%; SiO_2 2.40%; Al_2O_3 0.61%; MgO 0.97%; CaO 0.64%; TiO_2 0.36%; Cu 0.007%; V 0.24%.

SUMMARY

The method proposed is suitable for a quick routine determination of small amounts of vanadium in certain ores and steel. The interference of chromium in the final determination of vanadium using the ultraviolet spectra was eliminated by the use of an ion-exchange resin. Reproducibility of results was found to be acceptable for a colorimetric method.

RÉSUMÉ

Une méthode colorimétrique est proposée pour le dosage du vanadium. Elle permet un dosage rapide de cet élément dans des minerais et des aciers. Le chrome gêne; il peut être séparé par adsorption sur une résine d'échange d'ions.

ZUSAMMENFASSUNG

Es wird eine colorimetrische Schnell-Bestimmung von kleinen Mengen Vanadium in Erzen und Stahl beschrieben. Chrom, das die Bestimmung stört, kann mit einem Ionenaustauscher entfernt werden.

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COULOMETRIC TITRATION OF +2 COPPER WITH
ELECTROGENERATED +2 TIN

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The use of electrogenerated +2 tin as a coulometric titrant – especially for “coulometric iodometry” – has been described in previous papers from this laboratory¹. The present study is concerned with the direct titration of +2 copper to the +1 state in an acidic bromide medium. Very probably +2 copper could be titrated by the coulometric iodometric technique previously described¹. However the direct titration described herein has the advantage of greater selectivity. In principle, it is applicable to the determination of +2 copper in the presence of other oxidants, provided their oxidation potential is a few tenths of a V greater than that of the cupric-cuprous couple and provided their concentration is of the same order of magnitude (or smaller) than the copper concentration.

EXPERIMENTAL

The titration cell was the same as that depicted on p. 396, Vol. 19, (1958) of this journal, except that a platinum rather than gold generating electrode was used. The area of the platinum generator electrode was 10 cm² and the volume of solution titrated was 75 to 90 ml.

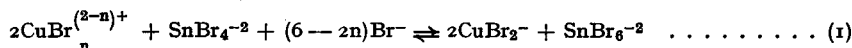
The supporting electrolyte was 4 M sodium bromide–0.2 M stannic chloride–0.2 N hydrochloric acid, because previous experience had shown that this composition was optimum for the generation of +2 tin with 100% current efficiency. Dissolved air was removed from the solution with nitrogen. Complete exclusion of air is required because the bromide complexes of +1 copper and +2 tin are both rapidly oxidized by dissolved oxygen.

The generating current was controlled automatically to $\pm 0.01\%$ by the amperostat previously described². The generating current density can be as large as 80 mA/cm². It must not be smaller than about 5 mA/cm², because this causes the current efficiency for generation of +2 tin to fall below 100%.

Generation of +2 tin at a platinum cathode in an acidic bromide medium proceeds with practically 100% current efficiency only in virtue of the fact that the electrode acquires a film of hydrous stannic oxide which increases the overpotential required for reduction of hydrogen ion. Although this film is persistent, and is removable only by drastic solvents for hydrous stannic oxide, its effectiveness is maximal when freshly formed. Consequently the platinum cathode should be freshly cathodized in the supporting electrolyte before the sample is added. Ordinarily this is accomplished by pre-titration to the e.p. potential.

TITRATION CHARACTERISTICS

In the 4 *M* bromide solution used +2 and +4 tin very probably exist as SnBr_4^{-2} and SnBr_6^{-2} , and +1 copper is present chiefly as CuBr_2^- . The state of the +2 copper is less certain; the fact that its color is reddish brown shows that it is complexed with bromide ion, but which of the several bromo complexes predominates in a 4 *M* bromide solution is not known. Evidence discussed by KRUIH³ indicates that with about 1 *M* bromide ion the predominant species are CuBr^+ and CuBr_2^- . With 4 *M* bromide ion it seems very probable that considerable concentrations of CuBr_3^- and CuBr_4^{-2} will also be present. Hence we shall indicate the +2 copper species as $\text{CuBr}_n^{(2-n)+}$, and accordingly the titration reaction may be written as



At the temperature of 55–60° used in the titrations, and with 4 *M* bromide ion and 0.2 *M* hydrogen ion, the formal potential of the stannic–stannous couple was found to be -0.017 ± 4 V vs. S.C.E. ($+0.201$ V vs. N.H.E.). Under the same conditions the formal potential of the cupric–cuprous couple is $+0.442 \pm 7$ V vs. S.C.E. ($+0.660$ V vs. N.H.E.). Hence the formal e.m.f. of the titration reaction is $+0.459$ V and its equilibrium constant (at 55–60°) is

$$K = \frac{(\text{Cu}^{+1})^2 (\text{Sn}^{+4})}{(\text{Cu}^{+2})^2 (\text{Sn}^{+2})} = 7 \cdot 10^{12} \quad \dots \dots \dots (2)$$

At room temperature the reaction is somewhat slow, and with either potentiometric or amperometric detection about 10 min is required for attainment of steady potential or indicator current in the immediate vicinity of the equivalence point. However at 55–60° equilibrium is reached in a few seconds prior to the e.p. and in about 2 min right at the e.p.

Fig. 1 shows the course of the potential change, and the time required to reach steady potentials after each increment of generation, in the titration at 57° of 1.59 mg of +2 copper in a volume of 100 ml. A platinum indicator electrode was used in

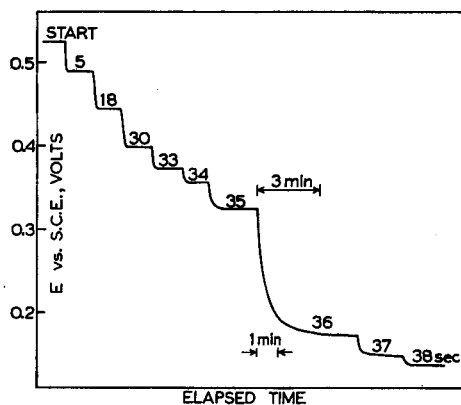


Fig. 1. Potential change of platinum indicator electrode during coulometric titration of 1.59 mg of +2 copper at 57° with a generating current of 67.6 mA. Recorded automatically with recording potentiometer. Total elapsed time on abscissa. Numbers on each step are the cumulative generation time (sec). The theoretical e.p. time is 35.6 sec.

conjunction with a saturated calomel reference electrode. The curve was recorded with a recording potentiometer and the cumulative generation time is indicated by the number on each incremental step. The theoretical e.p. time is 35.6 sec, and up to 35 sec it is seen that the potential becomes constant almost immediately after each generation increment. At 36 sec 3 min was required for the potential to become constant to ± 2 mV, but it was within 20 mV of its final value after 1 min. The error in the e.p. time would have been only +0.05 sec if the 36 sec reading had been taken after only 1 min.

The fact that the +2 copper and +2 tin react in a 2:1 mole ratio causes the titration curve to be asymmetrical. Consequently the point of maximum slope occurs somewhat ahead of the true e.p. If no excess +4 tin were present (*i.e.*, if the titration were performed in the classical manner with a standard solution of +2 tin) the e.p. potential would be constant and independent of the quantity of +2 copper titrated. However, in the coulometric titration the fact that a large excess of +4 tin necessarily must be present causes the e.p. potential to depend on the concentration of copper titrated (*i.e.*, on the concn. of +1 copper present at the e.p.).

If no excess of +4 tin were present it follows from equation 1 that at the equivalence point $(\text{Cu}^{+2})_{\text{e.p.}} = (\text{Sn}^{+2})_{\text{e.p.}}$ and $(\text{Cu}^{+1})_{\text{e.p.}} = (\text{Sn}^{+4})_{\text{e.p.}}$. Hence from equation 2

$$\frac{(\text{Cu}^{+1})_{\text{e.p.}}}{(\text{Cu}^{+2})_{\text{e.p.}}} = \frac{(\text{Sn}^{+4})_{\text{e.p.}}}{(\text{Sn}^{+2})_{\text{e.p.}}} = K^{1/2} \dots \dots \dots (3)$$

and since (at 57°)

$$E_{\text{e.p.}} = E_{\text{Cu}^{+2}, \text{Cu}^{+1}}^{\circ} - 0.0714 \log \frac{(\text{Cu}^{+1})_{\text{e.p.}}}{(\text{Cu}^{+2})_{\text{e.p.}}}$$

and

$$\frac{0.0714}{2} \log K = E_{\text{Cu}^{+2}, \text{Cu}^{+1}}^{\circ} - E_{\text{Sn}^{+4}, \text{Sn}^{+2}}^{\circ}$$

the e.p. potential would correspond to any of the three relations

$$E_{\text{e.p.}} = E_{\text{Cu}^{+2}, \text{Cu}^{+1}}^{\circ} - \frac{0.0714}{3} \log K \dots \dots \dots (4)$$

$$E_{\text{e.p.}} = E_{\text{Sn}^{+4}, \text{Sn}^{+2}}^{\circ} - \frac{0.0714}{6} \log K \dots \dots \dots (5)$$

$$E_{\text{e.p.}} = \frac{E_{\text{Cu}^{+2}, \text{Cu}^{+1}}^{\circ} + 2E_{\text{Sn}^{+4}, \text{Sn}^{+2}}^{\circ}}{3} \dots \dots \dots (6)$$

From the formal potentials of the cupric-cuprous and stannic-stannous couples quoted above the e.p. potential in this case would be +0.136 V *vs.* S.C.E.

However with stannic tin present at a constant concentration of 0.2 *M* it follows from equation 2 that at the e.p.

$$\left[\frac{(\text{Cu}^{+1})^2}{(\text{Cu}^{+2})^2 (\text{Sn}^{+2})} \right]_{\text{e.p.}} = \frac{K}{0.2}$$

and since $(\text{Cu}^{+2})_{\text{e.p.}} = 2(\text{Sn}^{+2})_{\text{e.p.}}$ we have instead of equation 3

$$\frac{(\text{Cu}^{+1})_{\text{e.p.}}^2}{(\text{Cu}^{+2})_{\text{e.p.}}^3} = \frac{5K}{2} \dots \dots \dots (7)$$

from which

$$(\text{Cu}^{+2})_{\text{e.p.}} = \frac{2^{1/3}}{5} K^{-1/3} (\text{Cu}^{+1})_{\text{e.p.}}^{2/3} \dots \dots \dots (8)$$

The concentration of +1 copper present at the e.p. is very nearly equal to the initial

concentration of +2 copper titrated, and if we denote this concentration by C it follows as a very good approximation that instead of equation 6

$$E_{e.p.} = +0.136 - \frac{0.0714}{3} \log \frac{5}{2} - \frac{0.0714}{3} \log C \dots\dots\dots (9)$$

or

$$E_{e.p.} = +0.127 - 0.024 \log C \dots\dots\dots (10)$$

Thus the e.p. potential decreases by 24 mV for a ten-fold increase in the concentration of copper titrated.

These characteristics are demonstrated in Fig. 2, in which 1 is the theoretical titration curve for the classical titration without excess +4 tin present, 2 is the theoretical coulometric titration curve of $5 \cdot 10^{-3} M$ copper in $0.2 M$ stannic chloride-

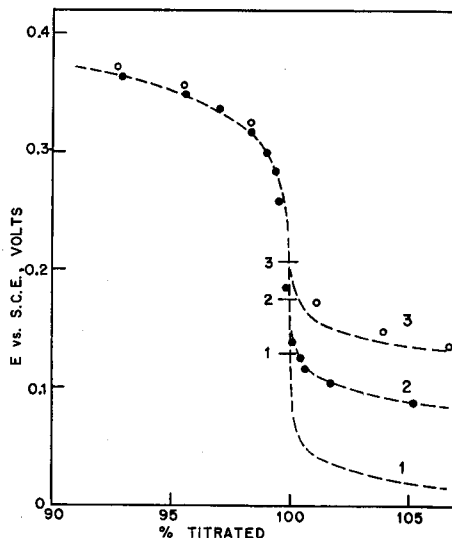


Fig. 2. Theoretical titration curves at 57° : (1) with no excess of +4 tin; (2) with $0.2 N$ stannic chloride and 32.6 mg of +2 copper per 100 ml ; (3) as 2, except only 1.59 mg of +2 copper. The circles are experimental points with a generating current of 67.63 mA . The short horizontal bars on each curve mark the theoretical equivalence point potentials.

$4 M$ sodium bromide- $0.2 N$ hydrochloric acid, and 3 is the theoretical coulometric titration curve of $2.5 \cdot 10^{-4} M$ copper. The circles are experimental points obtained with the corresponding quantities of copper, and their good agreement with the theoretical curves is evident.

In practice the point of maximal slope is taken as the end-point. Under the extant conditions, and with 1 to 35 mg of copper per 100 ml , the point of maximal slope precedes the true equivalence point by 30 to 35 mV . With 1 mg of copper per 100 ml this discrepancy corresponds to a titration error of approximately -0.7% , and with 35 mg of copper per 100 ml the corresponding titration error is -0.1% . However this negative titration error is more or less compensated by the fact that the current efficiency for generation of +2 tin is 0.2 to 0.3% short of 100% , which produces a corresponding positive titration error.

Successive samples can be titrated in the same batch of supporting electrolyte, but when this is done two facts should be kept in mind. Firstly, each sample after the first must be freed from dissolved air before it is added, as otherwise some of the $+1$ copper already present from the previous titration will be oxidized and a positive error will result. Secondly, when in each case the point of maximal slope is taken as the e.p., a negative titration error appears, which increases with each succeeding sample, due to the circumstance that the true e.p. potential shifts progressively to a less positive (more reducing) value as $+1$ copper accumulates (eq. 10). The rate of potential change at the e.p., and hence the precision, also decreases in the presence of an increasing concentration of $+1$ copper. Consequently, if maximal accuracy is needed, no more than two or three successive samples should be titrated in the same batch of supporting electrolyte.

The end-point can also be detected amperometrically, by observing the change in current between two small platinum electrodes which are subjected to a small, constant applied voltage (50 to 150 mV). The principle of two electrode amperometry has been discussed in detail elsewhere². As expected, the amperometric titration curve is V-shaped and the point of minimum current occurs very close to the equivalence point. However, amperometric detection is no more precise than potentiometric detection, and it is slower and less convenient because it requires a graphical plot. With potentiometric detection one simply titrates to the known e.p. potential.

PERFORMANCE DATA

The data in Table I demonstrate that the titration of 1.5 to 33 mg of copper in a volume of 75 to 90 ml, with potentiometric e.p. detection, can be performed with an average error of $\pm 0.3\%$.

In these trials the supporting electrolyte was freed from dissolved air with nitrogen, and then adjusted (by cathodic generation) to an indicator electrode potential of

TABLE I

TITRATION OF $+2$ COPPER WITH ELECTROGENERATED $+2$ TIN

The supporting electrolyte was 4 *M* sodium bromide–0.2 *M* stannic chloride–0.2 *N* hydrochloric acid, and the volume was 75 to 90 ml. Air was removed with nitrogen. The temperature was $57 \pm 2^\circ$, the generating current was 67.63 ± 1 mA, and the area of the platinum generating cathode was 10 cm^2 .

Trial No.	Cu taken mg	Time Sec	Cu found mg	Error mg	Error %
1	1.587	35.5	1.581	–0.006	–0.4
2	1.587	35.9	1.598	+0.011	+0.7
3	1.587	35.7	1.589	+0.002	+0.1
4	1.587	35.5	1.581	–0.006	–0.4
5	1.587	35.4	1.578	–0.009	–0.6
6	3.169	71.3	3.178	+0.009	+0.3
7	6.52	146.4	6.52	0.00	0.0
8	6.52	146.7	6.53	+0.01	+0.2
9	6.52	147.1	6.55	+0.03	+0.5
10	13.01	291.7	12.99	–0.02	–0.2
11	32.63	730.4	32.55	–0.08	–0.2
12	32.63	730.9	32.57	–0.06	–0.2

0.25 \pm 0.03 V vs. S.C.E. before the sample solution was added. The sample solution was not freed from dissolved air before it was added (except when it was added to a previously titrated solution), but a few minutes was allowed for the nitrogen stream to flush out the oxygen thus introduced before the titration was begun. The point of maximum slope of the titration curve was taken as the end-point.

In trials 3, 4, and 5 successive samples (air-free) were added to the previously titrated solution. In trial 2 the generation had been carried beyond the e.p. to obtain the data necessary for determining the point of maximum slope of the titration curve. Therefore the solution was adjusted back to the e.p. potential (point of maximum slope) by anodic generation before sample 3 was added. A similar procedure was followed in the successive trials 4 and 5. Each sample solution after the first was freed from dissolved air before it was added. Note that the titration error became progressively more negative. This happened because as +1 copper accumulated the discrepancy between the point of maximal slope (used as the end-point) and the true equivalence point increased. Although this effect will be smaller with the larger amounts of copper, these trials demonstrate the inadvisability of titrating more than two or three successive samples in the same batch of electrolyte.

Most of the elements commonly associated with copper, such as zinc, tin, lead, nickel, manganese, cobalt, aluminum, silver, and mercury, do not interfere. Ferric iron will interfere because it is reduced concomitantly with the +2 copper, but ferrous iron should not interfere.

Gold, when present in the +3 state, is titrated along with the copper and only a single e.p., corresponding accurately to the sum of the two metals, is observed. It should be possible to analyze copper-gold alloys by first determining the sum of the two metals by the present titration, and then determining the gold by coulometric titration with electrogenerated chlorocuprous ion by a method previously described⁴.

SUMMARY

Using a supporting electrolyte composed of 4 M sodium bromide-0.2 N hydrochloric acid-0.2 M stannic chloride, and a platinum generator cathode, +2 copper can be titrated accurately to the +1 state with electrogenerated +2 tin. With potentiometric end-point detection, quantities of copper from about 1 to 35 mg in a volume of 90 ml are titratable with an error of \pm 0.3%. The titration is applicable in the presence of most of the elements that are commonly associated with copper.

RÉSUMÉ

Une méthode précise est proposée pour le dosage coulométrique du cuivre(II), par réduction en cuivre(I) au moyen de l'étain(II) formé au cours du titrage. Ce dosage peut s'appliquer en présence de la plupart des éléments accompagnant généralement le cuivre.

ZUSAMMENFASSUNG

Kupfer(II) lässt sich coulometrisch mit Zinn(II) bestimmen, wobei Kupfer(I) entsteht. Die meisten anderen Elemente, die häufig mit Kupfer zusammen vorkommen, stören nicht.

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VOLTAMMETRIC, POTENTIOMETRIC AND AMPEROMETRIC STUDIES
WITH A ROTATED ALUMINUM WIRE ELECTRODE

III. AMPEROMETRIC DETERMINATION OF FLUORIDE WITH THE RAIE

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Examples of the anodic depolarization of the RAIE by fluoride in acid medium have been presented in previous papers^{1,2}. Fluoride yields an anodic diffusion current which is proportional to its concentration. The present paper is concerned with the development of a rapid, simple, and fairly selective amperometric method for the determination of fluoride which is based on the measurement of its anodic diffusion current at a given applied potential. In a subsequent paper the use of the RAIE in the amperometric titration of fluoride with suitable cations will be described.

A few years ago BAKER AND MORRISON³ recommended a simple cell for the rapid amperometric determination of fluoride. The cell was composed of a straight piece of aluminum wire (0.125 inch in diameter) as anode and a 10-inches long and 0.03-inch diameter platinum spiral as cathode. The cell was short-circuited, the contents stirred with a magnetic stirrer and the current measured after 2 min. The current is claimed to be proportional to the fluoride concentration. The size of the aluminum wire as stated by the authors (0.5 inch of exposed length) indicates that its surface area was several times larger than that of our RAIE¹. The above authors observed a fairly large and fluctuating current upon short-circuiting the cell. When fluoride was added, the current increased rapidly to a maximum value, then decreased continuously with time, and became almost zero after about 80 min. The current measured after 2 min was found to be approximately proportional to the fluoride concentration. It is stated that chloride causes serious interference, phosphate and sulfide cause some, while nitrate, sulfate and cyanide do not interfere. In order to eliminate chloride interference MEGREGIAN⁴ tried several electrodes other than aluminum and found zirconium suitable. In a brief note on the amperometric titration of traces of fluoride with thorium nitrate JOHANNESON⁵ used a cell composed of a rotated aluminum electrode and a stationary platinum wire electrode. The cell used by us differs in three important respects from that used by previous authors^{3,4}. Firstly, the electrode is rotated at a constant speed which provides reproducible stirring conditions. Secondly, the size of the RAIE (0.15 cm² of exposed area) is such that exhaustion of fluoride as a result of the electrolysis is very slow and amounts to a loss of the order of 1% per 10 min electrolysis (see Fig. 2). This slow exhaustion is very important in our procedure because a time lapse of 5 to 10 min for obtaining a constant current was required (*vide infra*) after placing a "cleaned" electrode in the fluoride solution.

* On leave of absence from Atomic Energy Commission - Argentina

Thirdly, by using the saturated calomel electrode (SCE) as a depolarized reference electrode, it was possible to select the appropriate applied potential at which no interference by chloride and many other anions is observed.

Various factors which affect the fluoride diffusion current have been studied systematically and the results are described in this paper. The recommended procedure for the amperometric determination of fluoride is independent of the reproducibility of the surface area of the electrode since the "method of standard addition" could be used⁶ which is based on the proportionality between diffusion current and concentration of fluoride. It is of great practical consequence that the recommended procedure is not interfered with by relatively large concentrations of phosphate. The method has been found eminently suitable for the rapid determination of fluoride in potable and natural waters in a concentration region between 10^{-5} and $3 \cdot 10^{-4} M$ (0.2 to 6 p.p.m. fluoride).

EXPERIMENTAL

Materials

Sodium fluoride (Baker's analyzed) was dried at 150° and cooled in desiccator. A stock solution was prepared which contained 2.206 g of the salt per l. It was standardized gravimetrically by the lead chlorofluoride method using the procedure described by HILLEBRAND AND LUNDELL⁷. By proper dilution a $10^{-3} M$ solution was then prepared. Fluoride solutions were kept in polyethylene bottles. All other reagents were C.P. products. Conductivity water was used for the preparation of all solutions. Oxygen was removed by bubbling through 99.99% pure Linde nitrogen.

Apparatus

The electrode, electrolysis cell, etc. have been described previously¹.

Current-time curves

Such curves in fluoride solutions were determined (a) using the saturated calomel electrode (SCE) as a reference electrode without applying a potential; (b) as (a) at an applied potential of $-0.75 V$, and (c) using a platinum spiral (0.1 cm diameter, 2 cm in length) without applying a potential. Before each experiment the electrode was pretreated in the EDTA buffer solution as described in previous paper^{1,2}. Since fluoride induces the cathodic reduction of oxygen at the RAIE², measurements were made in a nitrogen atmosphere after the solution had been deaerated by bubbling through nitrogen for 10 min. When the electrode was short-circuited against the SCE in a supporting electrolyte composed of 0.2 *N* acetic acid or an acetate buffer of pH 3.6, a large residual current was observed in the absence of fluoride which diminished within 5 min (curve A, Fig. 1) to a small constant value of $0.3 \mu A$. Curve B in Fig. 1 represents the change in current with time when fluoride was added to the solution after the residual current had become constant. The fluoride current increased very rapidly and became equal to the diffusion current within 10 min. From then on the current decreased only slightly (3% in 30 min) as a result of decrease of the fluoride concentration in the solution caused by the continuous electrolysis. A similar current-time plot was obtained by applying $-0.75 V$ (*vs.* SCE) as shown in curve A of Fig. 2. Curve B in Fig. 2 illustrates the fact that the limiting current is proportional to concentration up to a fluoride concn. of $3 \cdot 10^{-4} M$. Upon the first addition of fluoride to the supporting electrolyte about 10 min were required to attain the diffusion current. After successive additions of fluoride the corresponding limiting current reached a constant value within less than 5 min. When the RAIE was short-circuited against the

platinum spiral (instead of the SCE) the residual currents became larger, of the order of 1 to 1.5 μA , and less reproducible. Also the fluoride currents became less reproducible and exhibited irregular variations with time of electrolysis. The platinum spiral anode cannot be recommended as a reference electrode.

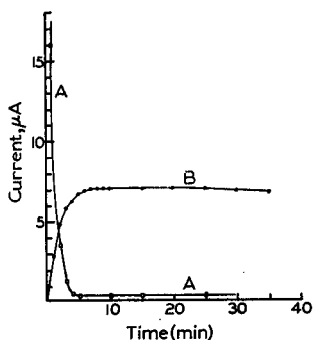


Fig. 1. Current-time curves in 0.2 *N* acetic acid (pH 2.80), short-circuited against SCE. (A) Residual current in absence of fluoride; (B) solution made $5.6 \cdot 10^{-5} M$ in fluoride.

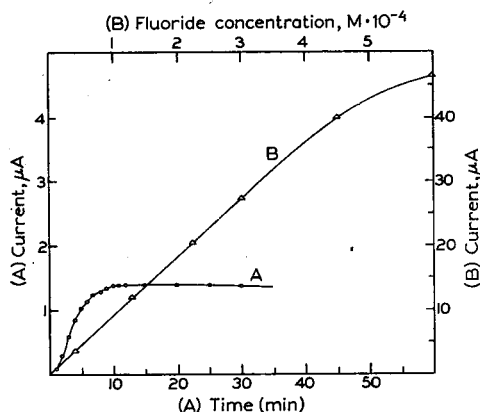


Fig. 2. Current-time curves in acetate buffer (pH 3.60) at *E* applied of $-0.75 V$. (A) $1.5 \cdot 10^{-5} M$ fluoride. (B) Proportionality between current and fluoride concentration. Lower abscissa and left hand ordinate refer to curve A.

Sensitivity of the electrode for fluoride

A diffusion current at a rotated electrode of given dimensions is proportional to the concentration of the diffusing species:

$$i_d = k C$$

in which *C* is the molar concentration in the solution. The value of *k* for an electrode of given surface area varies with the speed of rotation. For a given electrode at a constant rate of rotation the sensitivity may be expressed by

$$k = \frac{i_d}{C}$$

For an electrode of the usual dimensions *k* is expressed in μA for a millimolar solution.

In the following section is reported the reproducibility of the value of *k* for fluoride ions in buffers of varying pH. Also the effect of several anions on the value of *k* (and hence on the diffusion current of fluoride) is reported.

Effect of pH on the electrode sensitivity

After a systematic study it was decided to measure the fluoride diffusion current at an applied potential of $-0.75 V$ (*vs.* SCE). The selection of this potential eliminates the interfering effect of such anions like chloride, bromide and perchlorate which cause depolarization when the potential of the aluminum electrode is less negative than about $-0.6 V$ (*vs.* SCE)¹. The residual current was measured first in the particular medium and then increasing amounts of fluoride were added and the diffusion current

TABLE I
EFFECT OF pH ON k AND ON REPRODUCIBILITY; APPLIED POTENTIAL -0.75 V vs. SCE

Electrolyte	NaF concn.	i_a (μA)	k $\mu A/mM/l. \cdot 10^{-3}$	Duplic.*
0.1 M HClO ₄ pH 1.1 $i_r = 1.50 \mu A$	$2.00 \cdot 10^{-5}$	3.45	1.71	1.72
	$5.60 \cdot 10^{-5}$	9.60	1.71	1.72
	$9.00 \cdot 10^{-5}$	15.10	1.66	1.71
	$1.50 \cdot 10^{-4}$	25.30	1.70	1.71
	$3.10 \cdot 10^{-4}$	47.80	1.54	1.65
0.01 M HClO ₄ pH 2.1 $i_r = 0.50 \mu A$	$2.00 \cdot 10^{-5}$	3.20	1.60	1.66
	$5.60 \cdot 10^{-5}$	9.10	1.62	1.66
	$9.00 \cdot 10^{-5}$	14.50	1.61	1.63
	$1.50 \cdot 10^{-4}$	23.20	1.54	1.63
	$3.50 \cdot 10^{-4}$	48.80	1.40	1.63
Acetic acid-sodium acetate pH 3.60 $i_r = 0.3 \mu A$	$2.00 \cdot 10^{-5}$	1.98	0.99	0.97
	$5.60 \cdot 10^{-5}$	5.60	1.00	0.96
	$9.00 \cdot 10^{-5}$	8.75	0.97	0.96
	$1.50 \cdot 10^{-4}$	14.30	0.95	0.96
	$2.30 \cdot 10^{-4}$	22.60	0.98	0.96
Acetic acid-sodium acetate pH 4.60 $i_r = 0.25 \mu A$	$3.90 \cdot 10^{-4}$	35.10	0.89	0.85
	$5.10 \cdot 10^{-4}$	39.00	0.76	
	$2.00 \cdot 10^{-5}$	1.60	0.80	0.80
	$5.60 \cdot 10^{-5}$	4.50	0.80	0.81
	$9.00 \cdot 10^{-5}$	7.20	0.80	0.81
	$1.50 \cdot 10^{-4}$	12.25	0.81	0.81
	$3.10 \cdot 10^{-4}$	22.90	0.74	0.78
	$4.50 \cdot 10^{-4}$	32.15	0.71	0.76

* The duplicate determinations were not made consecutively. After running a series of experiments from pH 1.1 to 4.60 the constancy of the k value was checked by running the set in the reverse order from pH 4.60 to pH 1.1.

measured after the appropriate time (5 to 10 min). All current data reported have been corrected for the residual current. As is illustrated by Fig. 3 and in Table I, the sensitivity of the electrode reaction increases as the pH is decreased. It is interesting to note that the sensitivity in 0.1 to 0.01 *N* perchloric acid is about twice as great as that at pH 4.6. This result was quite unexpected considering that 10^{-4} *M* aluminum ions hardly interfere with the amperometric fluoride determination at a pH of 1 but very seriously at a pH of 3.6 (*vide infra*). From Table I it is noticed that the residual current increases with increasing acidity. In spite of the higher sensitivity of the electrode at lower pH it is recommended to carry out the determination of fluoride in an acetate buffer (pH 3 to 3.6) because the residual current was found much smaller and reproducible between 0.3 to 0.35 μA .

Effect of phosphate on the fluoride current

The fluoride limiting current is decreased by the presence of phosphate ions. From the analytical point it is important that small concentrations of phosphate of the order of 10^{-3} *M* or less have little effect. Even though the decrease in current becomes greater at higher phosphate concentrations, the proportionality between current and concentration is still maintained. The effect of phosphate is also dependent on the pH of the solution. In perchloric acid solution of pH 1.1 the value of k in the absence

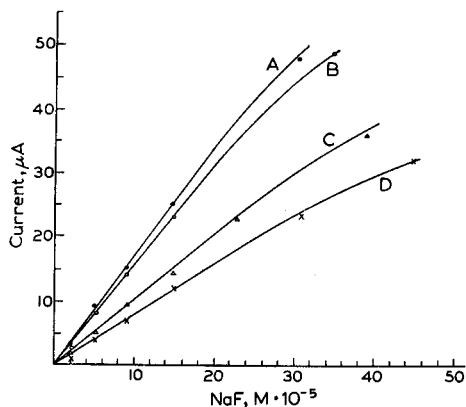


Fig. 3. Fluoride current vs. concentration at various pH. (A) 0.1 *M* HClO₄; (B) 0.01 *M* HClO₄; (C) acetate buffer pH 3.60; (D) acetate buffer pH 4.60.

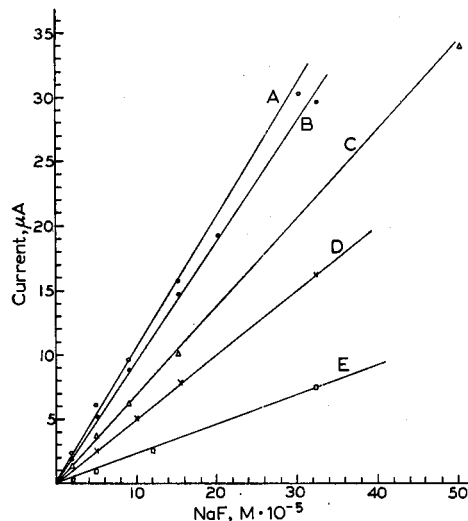


Fig. 4. Effect of $2 \cdot 10^{-3}$ *M* KH₂PO₄ at various pH. (A) 0.1 *M* HClO₄; (B) 0.01 *M* HClO₄; (C) acetate buffer pH 3.60; (D) acetate buffer pH 4.0; (E) acetate buffer pH 4.60.

of phosphate was found to be $1.7 \cdot 10^2$; $1.0 \cdot 10^2$ in the presence of 10^{-3} *M* phosphate and $0.75 \cdot 10^2$ in 0.01 *M* phosphate. At pH 2.0 these values were $1.6 \cdot 10^2$, $1.0 \cdot 10^2$ and $0.65 \cdot 10^2$; while in acetate buffer pH 3.6, they were $0.98 \cdot 10^2$, $0.70 \cdot 10^2$ and $0.55 \cdot 10^2$, respectively. The interference by phosphate greatly increases at pH 4.6; the value of the proportionality constant at this pH was found to decrease from $0.8 \cdot 10^2$ in the absence of phosphate to about $0.15 \cdot 10^2$ in the presence of $2 \cdot 10^{-3}$ *M* phosphate. Many of the data are reported in Table II. The effect of 0.002 *M* monopotassium dihydrogen phosphate on i_a at different fluoride concentrations and varying pH is illustrated in Fig. 4.

TABLE II

EFFECT OF PHOSPHATE ON THE FLUORIDE CURRENT AT VARIOUS pH; APPLIED POTENTIAL: -0.75 V vs. SCE

Electrolyte	NaF concn. <i>M</i>	i_a (μ A)	$\frac{i_a/C}{\mu A/mM/1 \cdot 10^{-2}}$
<i>0.1 M HClO₄; pH 1.1</i>			
KH ₂ PO ₄ concn. = 0 $i_r = 1.50 \mu$ A	$2.00 \cdot 10^{-5}$	3.45	1.72
	$5.60 \cdot 10^{-5}$	9.60	1.71
	$9.00 \cdot 10^{-5}$	15.10	1.68
	$1.50 \cdot 10^{-4}$	25.30	1.69
	$3.10 \cdot 10^{-4}$	46.80	1.50
$2 \cdot 10^{-3}$ <i>M</i> KH ₂ PO ₄ $i_r = 1.90 \mu$ A	$2.00 \cdot 10^{-5}$	2.10	1.05
	$5.60 \cdot 10^{-5}$	6.00	1.07
	$9.00 \cdot 10^{-5}$	9.65	1.07
	$1.50 \cdot 10^{-4}$	15.80	1.06
	$3.10 \cdot 10^{-4}$	30.85	0.99
10^{-2} <i>M</i> KH ₂ PO ₄ $i_r = 5.50 \mu$ A	$2.00 \cdot 10^{-5}$	1.50	0.75
	$5.60 \cdot 10^{-5}$	4.10	0.73
	$9.00 \cdot 10^{-5}$	7.00	0.77
	$1.50 \cdot 10^{-4}$	11.90	0.78
	$3.10 \cdot 10^{-4}$	25.60	0.82

TABLE II (continued)

<i>Electrolyte</i>	<i>NaF concn. M</i>	<i>i_a (μA)</i>	<i>i_a/C</i> <i>μA/mM/l. · 10⁻²</i>
<i>0.01 M HNO₃; pH 2.0</i>			
<i>KH₂PO₄ concn. = 0</i> <i>i_r = 0.55 μA</i>	$2.00 \cdot 10^{-5}$	3.20	1.60
	$5.60 \cdot 10^{-5}$	8.70	1.55
	$9.00 \cdot 10^{-5}$	14.20	1.57
	$1.50 \cdot 10^{-4}$	22.90	1.53
	$3.10 \cdot 10^{-4}$	39.00	1.25
10^{-3} M <i>KH₂PO₄</i> <i>i_r = 1.20 μA</i>	$2.00 \cdot 10^{-5}$	2.00	1.00
	$5.60 \cdot 10^{-5}$	5.90	1.05
	$9.00 \cdot 10^{-5}$	9.30	1.05
	$1.5 \cdot 10^{-4}$	15.30	1.02
	$3.10 \cdot 10^{-4}$	30.00	0.96
10^{-2} M <i>KH₂PO₄</i> <i>i_r = 5.10 μA</i>	$2.00 \cdot 10^{-5}$	1.28	0.64
	$5.60 \cdot 10^{-5}$	3.90	0.65
	$9.00 \cdot 10^{-5}$	6.10	0.66
	$1.50 \cdot 10^{-4}$	10.90	0.72
	$3.10 \cdot 10^{-4}$	23.30	0.75
<i>Acetate buffer pH 3.60</i>			
<i>KH₂PO₄ concn. = 0</i> <i>i_r = 0.30 μA</i>	$2.00 \cdot 10^{-5}$	1.98	0.99
	$5.60 \cdot 10^{-5}$	5.60	1.00
	$9.00 \cdot 10^{-5}$	8.75	0.97
	$1.50 \cdot 10^{-4}$	14.30	0.95
	$3.90 \cdot 10^{-4}$	33.00	0.84
10^{-4} M <i>KH₂PO₄</i> <i>i_r = 0.30 μA</i>	$2.00 \cdot 10^{-5}$	1.75	0.87
	$5.60 \cdot 10^{-5}$	4.70	0.84
	$9.00 \cdot 10^{-5}$	7.70	0.85
	$1.50 \cdot 10^{-4}$	12.80	0.85
	$2.00 \cdot 10^{-4}$	16.60	0.83
$2 \cdot 10^{-3}$ M <i>KH₂PO₄</i> <i>i_r = 0.35 μA</i>	$2.00 \cdot 10^{-5}$	1.39	0.70
	$5.60 \cdot 10^{-5}$	3.85	0.70
	$9.00 \cdot 10^{-5}$	6.25	0.70
	$1.50 \cdot 10^{-4}$	10.00	0.67
	$5.00 \cdot 10^{-4}$	34.90	0.69
0.01 M <i>KH₂PO₄</i> <i>i_r = 0.50 μA</i>	$2.00 \cdot 10^{-5}$	1.18	0.59
	$5.60 \cdot 10^{-5}$	3.00	0.53
	$9.00 \cdot 10^{-5}$	5.20	0.57
	$1.50 \cdot 10^{-4}$	9.00	0.60
	$2.00 \cdot 10^{-4}$	12.10	0.60
<i>Acetate buffer pH 4.0</i>			
$1 \cdot 10^{-4}$ M <i>KH₂PO₄</i> <i>i_r = 0.25 μA</i>	$2.00 \cdot 10^{-5}$	1.40	0.70
	$5.00 \cdot 10^{-5}$	3.35	0.67
	$1.00 \cdot 10^{-4}$	6.70	0.67
	$1.50 \cdot 10^{-4}$	10.00	0.66
$2 \cdot 10^{-3}$ M <i>KH₂PO₄</i> <i>i_r = 0.20 μA</i>	$5.60 \cdot 10^{-5}$	2.55	0.45
	$1.10 \cdot 10^{-4}$	5.10	0.45
	$1.50 \cdot 10^{-4}$	7.90	0.52
	$3.20 \cdot 10^{-4}$	16.85	0.52

TABLE II (continued)

Electrolyte	NaF concn. <i>M</i>	<i>i_a</i> (μ A)	$\frac{i_a/C}{\mu A/mM/l \cdot 10^{-2}}$
<i>Acetate buffer pH 4.0</i>			
0.01 <i>M</i> KH ₂ PO ₄ <i>i_r</i> = 0.20 μ A	$2.00 \cdot 10^{-5}$	0.69	0.34
	$5.00 \cdot 10^{-5}$	1.85	0.37
	$1.00 \cdot 10^{-4}$	3.80	0.38
	$1.50 \cdot 10^{-4}$	5.80	0.39
<i>Acetate buffer pH 4.60</i>			
KH ₂ PO ₄ = 0 <i>i_r</i> = 0.20 μ A	$2.00 \cdot 10^{-5}$	1.60	0.80
	$5.70 \cdot 10^{-5}$	4.50	0.80
	$9.20 \cdot 10^{-5}$	7.30	0.79
	$1.50 \cdot 10^{-4}$	12.20	0.81
	$3.10 \cdot 10^{-4}$	22.90	0.73
$2 \cdot 10^{-3}$ <i>M</i> KH ₂ PO ₄ <i>i_r</i> = 0.20 μ A	$2.00 \cdot 10^{-5}$	0.20	0.10
	$5.60 \cdot 10^{-5}$	0.79	0.14
	$1.20 \cdot 10^{-4}$	2.70	0.22
	$3.20 \cdot 10^{-4}$	7.65	0.23

Between pH 1 and 3.6 the relative effect of a given concentration of phosphate upon the sensitivity *k* is only slightly affected by pH. The effect is somewhat greater at pH 1 to 2 than at pH 3.6. For example, at pH 1 to 2 the sensitivity decreased about 1.6 times when a phosphate-free fluoride solution was made 0.001 *M* in phosphate and 1.4 times under the same circumstances at a pH of 3.6. In 0.001 *M* phosphate the ratios were 2.3 and 1.75 respectively. From the analytical point of view it is important to note from Table II that the residual current at pH 1 to 2 increases much more by a given concentration of phosphate than at pH 3.6. In 0.01 *M* or more concentrated perchloric acid phosphate has an anodic depolarizing effect on the RALE as is illustrated in Fig. 5. Apparently some highly dissociated or complex aluminum phosphate

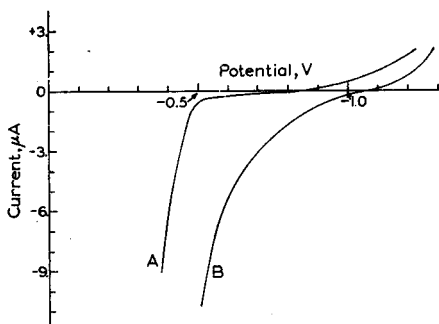


Fig. 5. Effect of phosphate on the electrode depolarization in 0.01 *M* perchloric acid. (A) no addition; (B) plus 0.01 *M* KH₂PO₄.

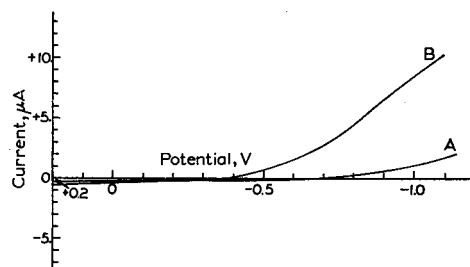


Fig. 6. Voltammograms of copper(II) in acetate buffer pH 3.60. (A) Residual current; (B) presence of $1 \cdot 10^{-4}$ *M* Cu(NO₃)₂.

is being formed. It has been mentioned that in the absence of phosphate the residual current is smaller and better reproducible at pH 3.6 than at pH lower than 2. This, combined with the fact that the residual current increases considerably in the presence of phosphate at a pH lower than 2 while it is not affected by 0.001 *M* phosphate at

pH 3.6, makes it evident that for the amperometric determination of fluoride a pH of about 3.5 is most suitable. With our electrode the residual current at pH 3.6 was found equal to 0.30-0.35 μA , even in the presence of 0.005 M phosphate. In the fluoride determination in a phosphate containing unknown the residual current can be determined in the supporting buffer, whereas at a pH less than 2 the residual current is unknown and could be estimated only if the phosphate concentration were known.

Effect of other substances

Experiments similar to those in Table II at different fluoride concentrations and in a buffer of pH 3.6 were repeated in the presence of 0.01 M alkali salts of nitrate, chloride and sulfate and 0.002 M calcium salts. No effect on the fluoride current was observed. Similarly, boric acid in a concentration of 0.01 M had no effect. On the other hand, ethylene diaminetetraacetic acid (EDTA) decreased the diffusion current, the effect being considerably greater at a pH 2 than in an acetate buffer of pH 3.6 (Table III). For example, the value of i_d/C at pH 2 decreased from $1.50 \cdot 10^2$

TABLE III
EFFECT OF EDTA ON THE FLUORIDE CURRENT AT -0.75 V vs. SCE

	NaF concentration	i_d (μA)	$i_d/C \cdot 10^2$
(1) 0.01 M nitric acid (pH 2.1) + 10^{-3} M EDTA			
$i_r = 0.25 \mu\text{A}$	$2.00 \cdot 10^{-5}$	1.50	0.75
	$5.60 \cdot 10^{-5}$	4.50	0.80
	$9.00 \cdot 10^{-5}$	7.55	0.83
	$1.50 \cdot 10^{-4}$	12.30	0.82
	$2.00 \cdot 10^{-4}$	16.70	0.83
(2) Acetate buffer (pH 3.60) + 10^{-3} M EDTA			
$i_r = 0.30 \mu\text{A}$	$2.00 \cdot 10^{-5}$	1.36	0.68 ^a
	$5.60 \cdot 10^{-5}$	4.60	0.82
	$9.00 \cdot 10^{-5}$	7.45	0.82
	$1.50 \cdot 10^{-4}$	12.20	0.81
	$2.00 \cdot 10^{-4}$	16.75	0.83

^a Current increases very slowly and reaches constancy after waiting 20 min.

in the absence of EDTA to $0.80 \cdot 10^2$ in the presence of 0.001 M EDTA. At a pH of 3.6 the corresponding figures were $1.00 \cdot 10^2$ and $0.82 \cdot 10^2$. From the analytical view point it is significant that the value of i_d/C in the presence of EDTA remains constant over a wide range of fluoride concentrations. In 0.001 M EDTA at pH 3.6 it was necessary to wait after the first addition of fluoride for about 20 min before the fluoride current had attained its constant value. Upon additions of successive amounts of fluoride the final value of the current was attained within 5 min.

Aluminum ions form stable complexes with fluoride at pH 3.6 and interfere seriously with the amperometric determination of fluoride. The effect of 10^{-4} M aluminum nitrate at a pH of 3.6 is illustrated in Table IV. As was to be expected, the i_d/C values increase with fluoride concentration. The aluminum can be made almost harmless by the addition of EDTA. Under these conditions the sensitivity of the electrode is about one half of that in the absence of aluminum and EDTA. The stability of aluminum fluoride complexes decreases with increasing hydrogen ion concentration. It is inter-

TABLE IV

EFFECT OF ALUMINUM IONS ON THE FLUORIDE CURRENT AT -0.75 V vs. SCE

	NaF concentration	i_a (μA)	$i_a/C \cdot 10^{-2}$
<i>0.1 M HClO₄ + 10⁻⁴ M Al(NO₃)₃</i>			
$i_r = 1.40 \mu A$	$2.00 \cdot 10^{-5}$	3.50	1.75
	$5.60 \cdot 10^{-5}$	9.38	1.68
	$9.00 \cdot 10^{-5}$	14.69	1.63
	$1.20 \cdot 10^{-4}$	19.25	1.60
<i>Acetate buffer (pH 3.60) + 10⁻⁴ M Al(NO₃)₃</i>			
$i_r = 0.25 \mu A$	$2.00 \cdot 10^{-5}$	0	0
	$5.00 \cdot 10^{-5}$	0.20	0.04
	$8.00 \cdot 10^{-5}$	0.60	0.07
	$1.00 \cdot 10^{-4}$	0.76	0.07
<i>Acetate buffer (pH 3.60) + 10⁻⁴ M Al(NO₃)₃ + 10⁻³ M EDTA</i>			
$i_r = 0.10 \mu A$	$5.60 \cdot 10^{-5}$	2.80	0.50
	$9.00 \cdot 10^{-5}$	4.55	0.50
	$1.10 \cdot 10^{-4}$	6.61	0.59
	$1.50 \cdot 10^{-4}$	8.79	0.59

TABLE V

EFFECT OF IRON(III) AND IRON(II) AT -0.75 V

	NaF concentration	i_a (μA)	$i_a/C \cdot 10^{-2}$
<i>0.01 M nitric acid (pH 2.1); absence of iron; $i_a/C = 1.6 \cdot 10^2$ with 10⁻³ M Fe(NO₃)₃</i>			
$i_r = 0.45 \mu A$	$2.00 \cdot 10^{-5}$	0.20	0.10
	$5.60 \cdot 10^{-5}$	0.65	0.11
	$9.10 \cdot 10^{-5}$	0.90	0.10
	$1.50 \cdot 10^{-4}$	2.10	0.14
<i>Acetate buffer (pH 3.60); absence of iron: $i_a/C = 0.98 \cdot 10^2$ with 10⁻³ M Fe(NO₃)₃</i>			
$i_r = 0.25 \mu A$	$2.00 \cdot 10^{-5}$	1.00	0.50
	$5.60 \cdot 10^{-5}$	3.70	0.65
	$9.00 \cdot 10^{-5}$	6.35	0.70
	$1.50 \cdot 10^{-4}$	10.90	0.72
<i>with 10⁻³ M Fe(NO₃)₃ + 0.01 M NH₂OH · HCl</i>			
$i_r = 0.35 \mu A$	$2.00 \cdot 10^{-5}$	2.35	1.10
	$5.60 \cdot 10^{-5}$	6.10	1.07
	$9.10 \cdot 10^{-5}$	9.90	1.07
	$1.50 \cdot 10^{-4}$	15.40	1.02

esting to note in Table IV that aluminum in a concentration of 10^{-4} M does not have an effect at all on the fluoride current in 0.1 N perchloric acid, even though the depolarization of the electrode at this pH is attributed to formation of aluminum fluoride complexes. This anomalous behavior may be related to the permeability for fluoride ions and hydrofluoric acid of a film on the electrode whereas the film is impermeable to hydrogen ions.

Contrary to the behavior of aluminum ions it was found that ferric iron even in a

concentration as high as 0.001 M has relatively little effect on the fluoride current at pH 3.6. It is seen in Table V that the sensitivity of the electrode for fluoride drops is relatively little under these conditions. The ferric iron can be made entirely harmless by reducing agents like hydroxylamine hydrochloride (Table V). The interference by 0.001 M ferric iron at pH 2 is very great as is illustrated in Table V. In an acetate buffer of pH 3.6 the ferric iron apparently is almost completely hydrolyzed or present in the form of fairly stable acetate complexes. On the other hand, at a pH of 2 it is mainly present in the form of ferric iron which forms stable complexes with fluoride.

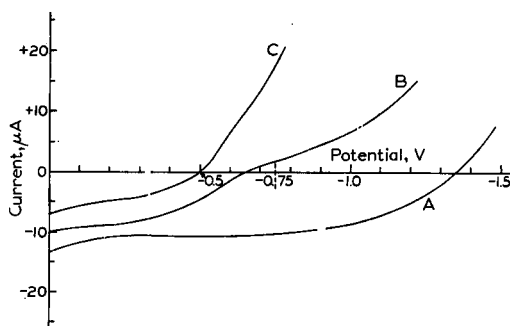


Fig. 7. Effect of copper(II) on voltammogram of fluoride (oxygen-free) at pH 3.6. (A) $1 \cdot 10^{-4} M$ fluoride; (B) as (A) with $10^{-4} M$ copper (II); (C) as (A) with $5 \cdot 10^{-4} M$ copper (II).

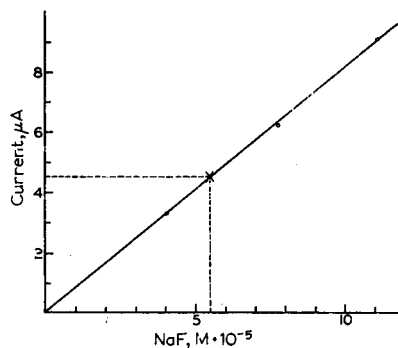


Fig. 8. Determination of fluoride in Minneapolis water by the standard addition technique. X presents the current of the unknown (corrected for residual current); fluoride content: 1.04 p.p.m.

As can be seen from Fig. 6, copper(II) cathodically depolarizes the aluminum electrode and yields a drawn-out irreversible reduction wave with the formation of metallic copper. Since the amperometric determination of fluoride is carried out at -0.75 V (*vs.* SCE), copper(II) interferes seriously because these ions yield a considerable reduction current at this potential. The situation is made clear in Fig. 7. The interference of copper can be eliminated to a large extent by making the solution 0.001 M in EDTA. But even then, a slight reduction current of copper is observed at -0.75 V. Although the fluoride current at this potential was found to be proportional to concentration in the presence of copper(II) and EDTA, the difficulty remains to find out the proper correction in the residual currents of unknowns for the presence of copper(II).

Quite generally, oxidizing substances like oxygen, silver ions, ceric cerium etc. all interfere for the same reason as copper(II) does. They must be removed from solution prior to the amperometric determination of fluoride. This is actually a simple matter and it can be accomplished by classical methods.

AMPEROMETRIC DETERMINATION OF FLUORIDE

Application to fluoride analysis in water

In order to be independent of the reproducibility of the electrode, the method of

"standard addition"⁶ is recommended; it has been used by us in all our fluoride determinations. No effort has been made to develop a technique using semimicro or micro volumes of fluoride. In general, we used 50 ml of the sample in the electrolysis cell. The recommended procedure has been tested with various samples of potable water.

PROCEDURE

Residual current. For the determination of the residual current transfer 50 ml of distilled water into the electrolysis cell, add 1 ml of 1 *M* sodium acetate and 0.5 ml of glacial acetic acid, place the RAIE in position, rotate at 600 r.p.m. and measure the residual current at -0.75 V vs. SCE.

Unknown. Place a suitable volume of the sample into a 50-ml volumetric flask and adjust to pH 3.6 by addition of 1 ml of 1 *M* sodium acetate and 0.5 ml of glacial acetic acid, then dilute to 50 ml. Transfer the solution to the electrolysis cell and remove oxygen by bubbling nitrogen for at least 5 min. While nitrogen is passed through, introduce the RAIE and start its rotation at 600 r.p.m. Care must be taken to avoid formation of gas bubbles at the electrode which tend to disturb the diffusion layer and cause irregular readings. Apply a potential of -0.75 V and record the current after it has attained a constant value (usually less than 10 min). Add known amounts of fluoride from a microburet, continue passage of nitrogen and record the steady current after each increment addition. Plot the increase in current after each successive addition of fluoride vs. the concentration of added fluoride (consider volume correction) and construct a straight line as illustrated in Fig. 8. Correct the current measured in the unknown for the residual current and read the fluoride concentration from the graph.

Example

Minneapolis city water was analysed by the above procedure. The residual current was $0.3 \mu\text{A}$ (anodic). Sodium acetate and acetic acid were added to the undiluted sample. The fluoride current measured was $4.8 \mu\text{A}$. After correction for the residual current, a value of $4.5 \mu\text{A}$ is found. According to the plot in Fig. 8 this current corresponds to a fluoride concentration of $5.5 \cdot 10^{-5}$ *M* or 1.04 p.p.m. is found.

Notes

1. The linear relation between current and fluoride concentration holds up to a concentration of about $3 \cdot 10^{-4}$ *M* or about 6 p.p.m. of fluoride. The original sample need not to be diluted when the fluoride concentration is less than about 2 p.p.m.

2. The precision obtained by running 5 separate experiments with Minneapolis city water was 3%. The precision and accuracy decrease with decreasing fluoride content. However, concentrations of 0.2 p.p.m. fluoride still could be estimated with an accuracy and precision of 10%. At such low concentrations of fluoride the error is caused mainly by the uncertainty in the residual current of the unknown.

3. Moderate amounts of phosphate and sulfate do not interfere. Thus the method has great advantages over colorimetric or spectrophotometric methods which require distillation.

4. When the order of magnitude of the fluoride concentration in the sample is not known it can be estimated by measuring the current at -0.75 V *vs.* SCE (absence of oxygen). From the known sensitivity of the electrode the fluoride content is readily estimated with fair accuracy.

5. The RAIE could be installed in water works in which water is being fluorinated so that constancy of the fluoride content of the water could be tested.

Results of analyses

Some 20 samples of known fluoride content (but unknown to the analyst) were prepared in which the fluoride concentration varied between 0.2 and 2 p.p.m. Some samples contained 0.001 *M* phosphate, others 0.005 *M* sulfate or 0.01 *M* chloride or combinations. The fluoride content found checked within 10% (and usually better) with the known content.

One sample of potable water was analyzed for fluoride in order to test the reliability of the method. Minneapolis city water: found 1.06 ± 0.02 p.p.m. (average of 5 determinations). The same sample was analyzed by Dr. L. SINGER of the Department of Physiological Chemistry of the University of Minnesota, using the method of MEGREGIAN⁸ which involves distillation, with the following results: 1.04; 1.09; 1.11; 1.13; 1.18; 1.28. If the last value is omitted, the average is 1.11 p.p.m.

Eight samples of raw, non-potable natural waters were obtained from the Minneapolis Health Department. These samples from different parts of the State of Minnesota were of widely different composition and had been analyzed by the Health Department using a slight modification of the procedure of MEGREGIAN⁸. Some of the samples, contained considerable amounts of solids. The results of our method are compared in Table VI with those reported by the Department of Health. The agreement is gratifying.

TABLE VI
FLUORIDE ANALYSIS OF WATER SAMPLES FROM THE MINNESOTA HEALTH DEPARTMENT

Sample number	Fluoride in p.p.m.	
	RAIE ^a	Colorimetric method
8284	0.25 0.28	0.30 (without distillation)
8712 ^b	0.40 0.43	0.25 (without distillation)
8136	1.06 1.10	1.10 (without distillation)
8285	1.35 1.35	1.20 (without distillation)
8408	1.10 1.19	1.10 (without distillation)
8380 ^b	0.28 0.30	0.40 (after distillation)
8625 ^b	0.20 0.25	0.42 (without distillation) 0.32 (after distillation)
8286	0.22 0.26	0.20 (without distillation)

^a Results of two independent analyses.

^b Samples contained large quantities of solid.

ACKNOWLEDGEMENTS

This work has been supported by a grant from the United States Public Health Service. — We wish to thank Mr. R. R. CARR of the Minnesota Public Health De-

partment and Dr. L. SINGER of the Department of Physiological Chemistry of the University of Minnesota for their cooperation.

SUMMARY

A simple and rapid amperometric method is described for the determination of traces of fluoride by measuring the anodic current at the RAIE at -0.75 V vs. SCE. In order to be independent of varying sensitivity of the RAIE, use is made of the standard addition technique.

Proportionality between current and concentration is found between 0.2 and 6 p.p.m. of fluoride. Chloride, sulfate, nitrate, alkali and earth alkali ions do not interfere. Phosphate decreases the sensitivity but does not interfere. Aluminum ions interfere but can be made harmless by EDTA. Oxidizing agents (including oxygen) must be removed. The method gives excellent results in potable and natural waters.

RÉSUMÉ

Une méthode ampérométrique simple et rapide est proposée pour le dosage de traces de fluorure, en mesurant le courant anodique à l'électrode tournante d'aluminium à -0.75 V (vs. ECS). Ce procédé peut être appliqué à l'analyse de l'eau.

ZUSAMMENFASSUNG

Es wird eine einfache und schnelle ampérometrische Methode beschrieben zur Bestimmung von Spuren von Fluorid durch Messung des anodischen Stromes einer drehenden Aluminium Elektrode bei -0.75 V gegen ECS. Diese Methode kann bei der Wasseranalyse verwendet werden.

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DIRECT ESTIMATION OF NIOBIUM BY N-BENZOYL-N-PHENYLHYDROXYLAMINE

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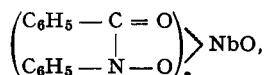
The preparation of various complexes of niobium and tantalum with a number of organic reagents has been attempted^{1,2}. None of the experiments, however, have resulted in the formation of a compound of definite composition, suitable for analytical work. SÛE³, on the other hand, claims to have isolated an oxine complex of niobium which apparently corresponds to the composition $Nb_2O_5 \cdot 5.5 C_9H_7ON \cdot 4 H_2O$.

In a previous paper⁴, N-benzoyl-N-phenylhydroxylamine was shown to be an

effective reagent not only for the separation of niobium and tantalum from each other by the control of pH but also for the separation of the former element from other interfering ions by the proper control of conditions in the presence of sequestering agents. In that work, the precipitates of niobium and tantalum were ignited to their respective oxides before their final weighing.

Further study reveals that the buff-coloured precipitate of niobium, obtained after digestion on the boiling water bath at a pH lower than 6.5, is insoluble in water, ethyl and amyl acetates, acetone, carbon tetrachloride and benzene, but highly soluble in chloroform. Niobium's excellent solubility in chloroform classifies it as a member of the internal complex salts, whose molecules contain no free acid and basic groups.

The complex dried at 110° indicates the composition to be



where the percentage of niobium is only 12.46%. This complex, even when air-dried, is stable up to a temperature of about 229° which implies its formation by the elimination of water, during the reaction of the niobic acid with the reagent on the boiling water bath.

Owing to its stability to heat and insolubility in hot water, the niobium complex, after being filtered, washed and dried, can be directly weighed for its gravimetric estimation.

The tantalum precipitate, however, is of indefinite composition and loses weight with the rise of temperature. Both the niobium and tantalum precipitates are converted to their oxides at about 500°.

EXPERIMENTAL

All the chemicals and standard solutions used were the same as previously reported⁴.

Composition

The niobium complex after precipitation, according to the procedure described earlier⁴, was washed with hot water and dried at 110°. A portion of the complex was ignited to oxide to determine the percentage of niobium present, and from the other portion, the nitrogen content of the complex was estimated by the Kjeldahl method.

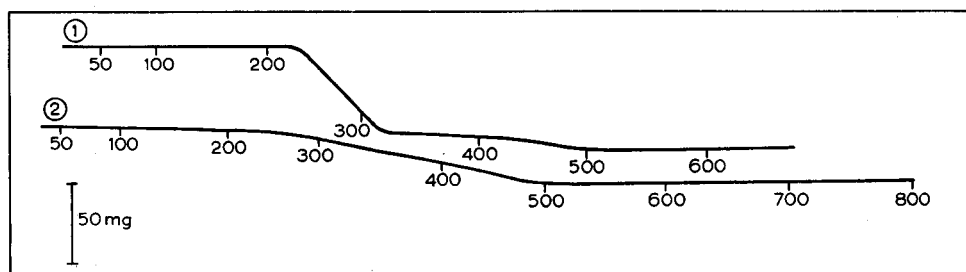


Fig. 1. Thermolysis curves: (1) Niobium complex. (2) Tantalum complex.

Thus the composition was found to be $\text{NbO}(\text{C}_{13}\text{H}_{10}\text{NO}_2)_3$ [% Nb calc. 12.46, % N_2 calc. 5.64; % Nb found 12.42, 12.44, % N_2 found 5.58, 5.62].

The thermolysis curves (Fig. 1) show that the niobium complex, dried at 110° , is stable up to about 229° , but that the tantalum complex loses weight with the increase of temperature; both complexes are completely changed to their oxides at about 500° .

Procedure

The niobium, after precipitation by the reagent solution, as described in the previous paper⁴, was digested on the boiling water bath for about an hour and was then filtered through a weighed, sintered Gooch crucible, washed thoroughly with hot water, dried at 110° and weighed. The weight of complex multiplied by the factor 0.1783 gave the weight of Nb_2O_5 . Tantalum, when present, was estimated from the filtrate of niobium. The tantalum precipitate, however, was ignited to oxide before weighing. The results are given in Table I.

For the separation of niobium from other ions in the presence of EDTA, a procedure similar to that discussed previously⁴ was followed.

TABLE I

Nb_2O_5 taken mg	Ta_2O_5 taken mg	Wt. of Nb-complex mg	Nb_2O_5 found mg	Ta_2O_5 found mg
9.6	—	53.2	9.5	—
24.0	—	135.7	24.2	—
48.0	8.6	(i) 271.0	(i) 48.3	(i) 8.2
		(ii) 270.3	(ii) 48.1	(ii) 8.2
9.6	43.0	(i) 55.2	(i) 9.8	(i) 42.7
		(ii) 55.5	(ii) 9.8	(ii) 42.6

SUMMARY

N-benzoyl-N-phenyl hydroxylamine, with niobium, forms a complex of composition $\text{NbO}(\text{C}_{13}\text{H}_{10}\text{NO}_2)_3$ which is stable up to a temperature of 229° . Niobium, thus, can be separated from tantalum and other elements as this complex and weighed directly after being dried at 110° .

RÉSUMÉ

La N-benzoyl-N-phénylhydroxylamine est proposée comme réactif pour le dosage gravimétrique du niobium. On peut ainsi séparer le niobium d'avec d'autres éléments, en particulier d'avec le tantale.

ZUSAMMENFASSUNG

N-Benzoyl-N-phenylhydroxylamin eignet sich als Fällungsreagenz zur gravimetrischen Bestimmung von Niob, das sich damit von Tantal und anderen Elementen trennen lässt.

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PHOTOMETRIC DETERMINATION OF QUATERNARY AMMONIUM COMPOUNDS WITH HEXANITRODIPHENYLAMINE. I.

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Many recent methods for the determination of amines and quaternary ammonium compounds are based on the use of reagents which yield compounds extractable from aqueous solutions with chloroform or similar solvents. The majority of the published methods employ acid-base indicators of the sulphophthalein type. The extracted compounds have high molar extinctions and can be directly determined photometrically. For the determination of quaternary ammonium compounds bromothymol blue¹, bromocresol purple^{2,3}, and bromophenol blue⁴⁻⁶ have been used. The literature has been summarized by BALLARD *et al.*⁷. Similar methods have been used for the determination of amines^{8,9}.

The indicator methods appear in general to be strongly dependent on the experimental conditions and are only applicable for the determination of certain kinds of quaternary ammonium compounds.

A few other extraction methods have also been used. High molecular quaternary ammonium compounds yield iodides, which are extractable with chloroform; the extracted iodide can be determined photometrically after oxidation to free iodine¹⁰. Atropine can be determined by extracting atropine picrate with chloroform; the picrate is reduced to picramic acid and determined photometrically¹¹.

We have found that hexanitrodiphenylamine with quaternary ammonium compounds yields compounds which can be extracted from aqueous solution with organic solvents such as chloroform or methylene chloride. The compounds have high molecular extinctions and therefore very small amounts of quaternary ammonium compounds can be determined by direct photometric measurements.

In the present paper investigations of the reagent and of the general experimental conditions for the determination of quaternary ammonium compounds are described.

Little information is available concerning the physico-chemical properties of hexanitrodiphenylamine (dipicrylamine). SCHROEDER *et al.*²¹ reported the spectra in acid and basic ethanol solution as well as the molar extinction at the maxima. KERTES AND GOLDSCHMIDT¹² determined the corresponding spectra in dioxane-water solution. On the basis of potentiometric measurements they found the apparent $pK_a = 0.35$ (dioxane). TREADWELL AND HEPENSTRICK¹³ found $pK_a = 8.15$ (water).

Hexanitrodiphenylamine yields slightly soluble compounds with organic bases and has been used as a precipitant for alkaloids and other bases^{14,15}. ACKERMAN AND MAUER¹⁶ found that quaternary ammonium compounds gave precipitates which were soluble in acetone, thus permitting their photometric determination. SAMUELS-

SON¹⁷ determined choline and choline esters according to this principle and SIMON-DORLET¹⁸ determined divalent quaternary ammonium compounds. The compounds formed contained hexanitrodiphenylamine in the form of univalent anions.

KERTES^{19,20} has studied reactions between hexanitrodiphenylamine and organic bases in dioxane solution and has also given a method for the determination of pyridine.

EXPERIMENTAL

Purification of the reagent

A saturated chloroform solution of dipicrylamine (pro analysi, Merck) was applied to a chromatographic column containing kieselguhr (Hyflo Super Cel) as the supporting phase, phosphate buffer (pH = 7) as the stationary phase and chloroform as the mobile phase. The column was eluted with chloroform, and the eluate was collected in 5-ml portions. The concentration of solute in the eluate was determined by measurement of the extinction at 380 m μ . Results are shown in Fig. 1.

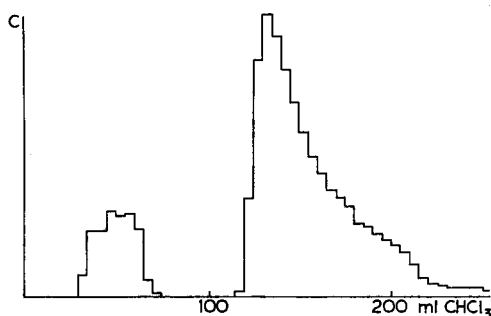


Fig. 1. Chromatogram of dipicrylamine (analytical grade) containing hexa- and pentanitrodiphenylamine.

The eluate fractions were evaporated and the residues were dissolved in ethanol. The absorption spectra of the ethanolic solutions were determined after addition of acid (0.05 ml of 5 *N* HCl per 100 ml) and base (0.05 ml of 5 *N* NaOH per 100 ml). The fractions 30–75 ml were found to yield identical spectra; comparison with SCHROEDER *et al.*²¹ indicated that they contained 2,2',4,4',6-pentanitrodiphenylamine. The fractions after 115 ml were found to contain 2,2',4,4',6,6'-hexanitrodiphenylamine by similar methods.

Determination of dissociation constants

The dissociation constants of the pure substances obtained by the foregoing procedure were determined according to SAGER *et al.*²². The photometric determinations were carried out with a Uvispek spectrophotometer using a band width of 5 Å at a temperature of 20° ± 1°. The pH determinations were performed at the same

temperature with a glass electrode calibrated against potassium biphthalate 0.05 *M*. The readings are believed to be correct within ± 0.01 pH unit.

All determinations were carried out in phosphate buffers with an ionic strength of about $6 \cdot 10^{-3}$ using the same concentration of substances (2 mg per 1000 ml). The only exception was the determination at pH 0.22, which was done in hydrochloric acid. In order to obtain sufficiently high extinction a layer thickness of 4 cm was employed. The buffer solutions were used as blanks. The phosphate has no absorption in the wavelength region used for the calculations, and as the isosbestic point is well-defined there is probably no other disturbing effect from the buffer system.

The constants determined were the apparent dissociation constants which are defined:

$$\frac{a_{\text{H}_3\text{O}^+} \cdot c_b}{c_a} = K_a$$

where $a_{\text{H}_3\text{O}^+}$ = hydronium ion activity, c_b = concentration of base, and c_a = concentration of acid.

At constant concentration of nitro compound the following expression for pK_a is obtained:

$$pK_a = \text{pH} - \log \frac{E - E_a}{E_b - E}$$

where E = extinction found, E_a = extinction with the compound in acid form, and E_b = extinction with the compound in basic form.

The calculations were carried out using extinction values at wavelengths where the extinction of the base had a rather flat maximum while the extinction of the acid was very low. The results for hexanitrodiphenylamine appear in Fig. 2 and Table I and for pentanitrodiphenylamine in Fig. 3 and Table II.

TABLE I
PHOTOMETRIC DETERMINATION OF APPARENT DISSOCIATION
CONSTANT OF HEXANITRODIPHENYLAMINE

pH	E^{480}	pK_a
0.22	0.038	—
2.60	0.252	2.80
2.74	0.297	2.80
2.80	0.311	2.81
3.07	0.393	2.82
6.96	0.591	—

Determination of partition coefficients

10.00 ml of approximately $4 \cdot 10^{-5}$ *M* solutions of the nitro compounds in the organic solvent (chloroform, methylene chloride or ethylene chloride) were shaken to equilibrium with 10.00 ml of the aqueous phase. The concentration of the nitro compound was determined spectrophotometrically in the organic phase. The pH of

the aqueous phase was determined after the shaking was completed. The temperature and error in the pH determinations were the same as in the determination of the dissociation constants. The spectrophotometric determinations were carried out with a Beckman spectrophotometer model B.

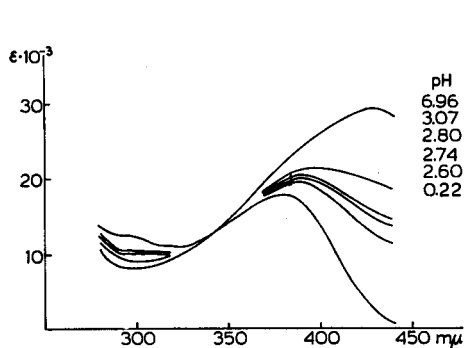


Fig. 2. Absorption spectra of hexanitrodiphenylamine in water of varying acidity.

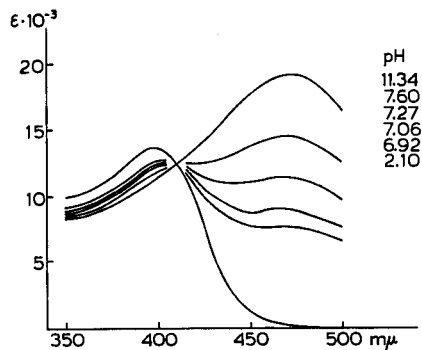


Fig. 3. Absorption spectra of pentanitrodiphenylamine in water of varying acidity.

TABLE II

PHOTOMETRIC DETERMINATION OF APPARENT DISSOCIATION CONSTANT OF
PENTANITRODIPHENYLAMINE

pH	E^{470}	pK_a
2.10	0.005	—
6.92	0.138	7.11
7.06	0.161	7.13
7.27	0.204	7.12
7.60	0.261	7.11
11.34	0.343	—

TABLE III

PARTITION COEFFICIENTS

System	K_a	
	Hexanitro- diphenylamine	Pentanitro- diphenylamine
$CHCl_3/H_2O$	$6.5 \cdot 10^3$	$3.2 \cdot 10^3$
CH_2Cl_2/H_2O	$4.9 \cdot 10^4$	$2.0 \cdot 10^3$
$CH_2Cl \cdot CH_2Cl/H_2O$	$5.5 \cdot 10^4$	—

The chloroform used was of pharmaceutical grade. The methylene chloride and ethylene chloride were purified by shaking with sodium carbonate solution and

water and by distillation after drying. As aqueous phases 0.05 *M* phosphate buffers were employed.

The partition coefficients are defined as:

$$\frac{c_{a(\text{org})}}{c_{a(\text{H}_2\text{O})}} = K_d$$

In the organic phase the nitro compounds occur only as acids; in the aqueous phase they are protolyzed to a varying degree. Since the organic and aqueous phases are of equal volume the following equations are obtained:

$$c_{a(\text{org})} = E \cdot K$$

$$c_{a(\text{H}_2\text{O})} + c_{b(\text{H}_2\text{O})} = (E_{\text{tot}} - E) \cdot K$$

$$K_d = \frac{E}{E_{\text{tot}} - E} \left(1 + \frac{K_a}{a_{\text{H}_3\text{O}^+}} \right)$$

where *E* = extinction of the organic phase after shaking, and *E*_{tot} = extinction of the organic phase before shaking. The results are given Table III.

Spectra in chloroform and methylene chloride solutions

The absorption spectra of the nitro compounds were determined after addition of acid (1 mg of trichloroacetic acid per 10 ml) and of base (1 mg of piperidine per 10 ml). Spectra were also determined for the complex formed between the nitro compounds and a quaternary ammonium compound (tetraethylammonium bromide).

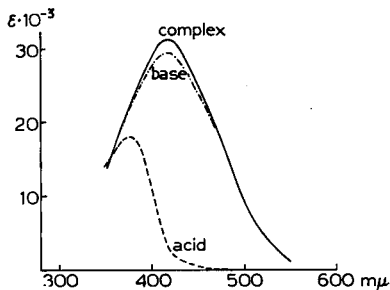


Fig. 4. Absorption spectra in methylene chloride of hexanitrodiphenylamine after addition of acid (trichloroacetic acid) and base (piperidine) and of its complex with tetraethylammonium ion.

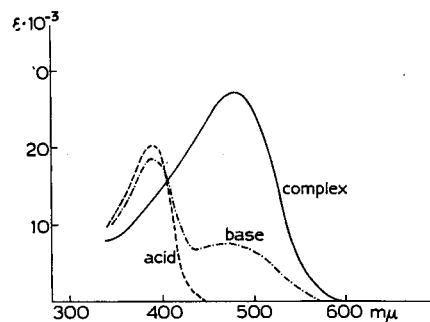


Fig. 5. Absorption spectra in chloroform of pentanitrodiphenylamine after addition of acid (trichloroacetic acid) and base (piperidine) and of its complex with tetraethylammonium ion.

The solution of this complex was obtained by extraction with methylene chloride or chloroform from an aqueous solution at pH 11 for hexanitrodiphenylamine and at pH 13–14 for pentanitrodiphenylamine. The results are shown in Fig. 4 (hexanitrodiphenylamine) and Fig. 5 (pentanitrodiphenylamine). There are only small differences between the spectra in chloroform and in methylene chloride.

DISCUSSION

The chromatographic investigation showed that commercially available hexanitrodiphenylamine (dipicrylamine p.a. Merck) is contaminated with pentanitrodiphenylamine. Only experiments at pH 7 are described above, but corresponding experiments at pH 8, 9, 10 and 11 showed no further components. At the higher pH values the elution of the hexanitro compound takes place very slowly.

The great difference in elution rate is caused primarily by the difference in the pK_a values (Tables I and II). The value found for hexanitrodiphenylamine diverges very remarkably from that reported in the literature¹³. However, this is probably due to the fact that the latter value was determined as the half-titre point in the titration of the sodium salt of the compound with hydrochloric acid. Since hexanitrodiphenylamine is very slightly soluble, precipitation occurs during the titration.

The remarkably strong acidic properties of hexanitrodiphenylamine as well as the difference in strength between the hexa- and pentanitro compounds are, of course, connected with the positively polarized nitro groups of the molecules (*cf.* 4-nitrophenol: $pK_a = 7.2$, 2,4-dinitrophenol: $pK_a = 4.0$ and 2,4,6-trinitrophenol: $pK_a = 0.8$).

The partition coefficients for the hexa- and pentanitro compounds differ only slightly (Table III), but because of the great difference in the dissociation constants, the compounds are very easily separated (Fig. 6). The values shown in the figure

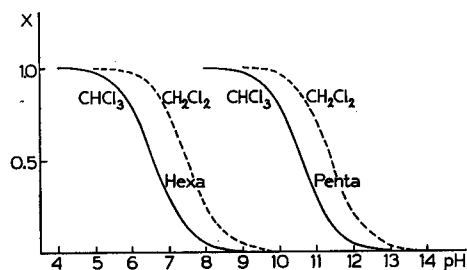


Fig. 6. Distribution of hexa- and pentanitrodiphenylamine between aqueous and organic phases (chloroform or methylene chloride) at different pH values. (X = part of total amount in the organic phase. Both phases have equal volumes)

have been calculated from the pK_a and K_a values obtained for the two nitro compounds.

The difference in the absorption spectra of the complexes formed from the hexa- and pentanitro compounds and a compound containing tetraethylammonium ion is striking. Hexanitrodiphenylamine yields a complex with the extinction maximum at $420 m\mu$ and the molar extinction at the maximum is $3.1 \cdot 10^4$ (Fig. 4). The complex containing the pentanitro compound has its extinction maximum at $480 m\mu$ and the molar extinction at the maximum is $2.7 \cdot 10^4$. At $420 m\mu$ this complex has the molar extinction $1.7 \cdot 10^4$ (Fig. 5).

From Fig. 4 it can be seen that free acid (hexanitrodiphenylamine) has a significant extinction at the extinction maximum of the complex ($420 m\mu$). It is therefore necessary to extract the complex at such a pH that practically no free acid is extracted.

The pH should exceed 10 when chloroform is used and 11 when methylene chloride is used.

The necessity of employing a reagent which is free from pentanitrodiphenylamine is also clear from Figs. 4, 5 and 6. At a pH of less than 12 more or less of the pentanitrodiphenylamine is extracted with chloroform (with methylene chloride at pH below 13) and this contaminates the complex of hexanitrodiphenylamine extracted at the same time. Pentanitrodiphenylamine interferes in the spectrophotometric determination because it has a relatively high extinction at the extinction maximum for the complex (420 m μ).

SUMMARY

Dissociation constants, partition coefficients and absorption spectra have been determined for hexanitrodiphenylamine and pentanitrodiphenylamine. The two compounds have quite different dissociation constants and can be easily separated. Both substances give compounds with quaternary ammonium ions which can be extracted with chloroform or methylene chloride from an aqueous solution. To obtain a pure hexanitrodiphenylamine compound the reagent must be free from pentanitrodiphenylamine and the extraction made at high pH.

RÉSUMÉ

Des déterminations de constantes de dissociation, de coefficients de partage et de spectres d'absorption ont été effectuées pour l'hexanitrodiphénylamine et la pentanitrodiphénylamine. Ces deux substances donnent avec les ions ammonium quaternaires des composés que l'on peut extraire dans le chloroforme ou le chlorure de méthylène.

ZUSAMMENFASSUNG

Es wurden die Dissoziationskonstanten, Verteilungskoeffizienten und Absorptionsspektren von Hexanitrodiphenylamin und Pentanitrodiphenylamin bestimmt. Diese beiden Substanzen bilden mit quaternären Ammonium Ionen Verbindungen, die sich mit Chloroform oder Methylenchlorid aus einer wässrigen Lösung extrahieren lassen.

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THE POLAROGRAPHY OF LEAD STYPHNATE*

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INTRODUCTION

In the course of a recent study of styphnate materials it became necessary to determine the lead-styphnate ratio existing in the same solution. This was required to provide information regarding the presence of free styphnic acid, or other styphnates in lead styphnate solutions. Since both lead and styphnic acid are reducible at the dropping mercury electrode it appeared that the determination of these two species might conveniently be made by polarography. This paper describes the work carried out to develop a method for this determination.

EXPERIMENTAL AND DISCUSSION

All polarography described in this paper was carried out on a Cambridge Pen Recording Polarograph and *versus* the mercury pool anode. A Cambridge Univector Unit¹ was used in conjunction with this instrument to provide derivative-type curves by A.C. polarography. All potentials quoted are given on the European sign convention. On this convention the potential of the saturated calomel electrode (S.C.E.) has been taken as + 0.246 V *versus* the normal hydrogen electrode (N.H.E.). The electrode employed had a drop time of 3.90 sec and a mass-drop time ($m^{\frac{2}{3}} \cdot t^{\frac{1}{3}}$) value of 1.79 (in water at zero volts applied potential).

Styphnic acid is known to yield three steps of half-waves potentials which vary considerably with pH. PEARSON² has reported the half-wave potentials of a number of nitro compounds, including styphnic acid, over a wide range of pH values. Those relating to the three steps due to styphnic acid, determined in an 8% ethanol solution, are summarized in Table I below.

TABLE I

pH	<i>Styphnic acid half-wave potentials (vs. S.C.E.) in V</i> (PEARSON)		
	<i>1st step</i>	<i>2nd step</i>	<i>3rd step</i>
2.0	— 0.07	— 0.12	— 0.23
4.0	— 0.15	— 0.24	— 0.48
6.0	— 0.25	— 0.38	— 0.55
8.0	— 0.38	— 0.66	— 0.82
9.2	— 0.57	— 0.89	— 1.17
10.0	— 0.70	— 1.05	— 1.30

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References p. 260

It was desirable that the present work should be carried out in purely aqueous solution and experiments were therefore conducted over the range of pH 6 to 9 using an aqueous sodium citrate-hydrochloric acid buffer³. The results obtained are given in Table II. A typical polarogram is shown in Fig. 1.

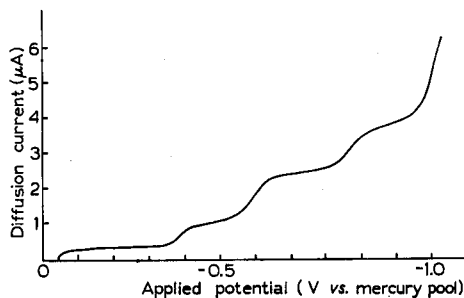


Fig. 1. Styphnic acid in sodium citrate-hydrochloric acid buffer. pH 7.0.

These values were closer to those of PEARSON than might have been expected in view of the changes in reference electrode. It was considered that on this basis the values of Table I could be used as a guide for further work.

TABLE II

pH	Styphnic acid half-wave potentials (vs. mercury pool) in V		
	1st step	2nd step	3rd step
6.0	— 0.18	— 0.33	— 0.60
7.0	— 0.38	— 0.72	— 0.95
9.0	— 0.52	— 0.92	— 1.30

Lead reduces reversibly in aqueous solutions of all the common base electrolytes. It was not considered necessary to obtain half-wave potential values over the range pH 2 to 9 in this solution since the values listed by LINGANE⁴, (see Table III) provide sufficient data on which to base predictions of the behaviour of this element under the above conditions.

TABLE III

Base electrolyte	Lead half-wave potential (V vs. S.C.E.)
0.1 N hydrochloric acid	— 0.396
N hydrochloric acid	— 0.435
0.5 M tartrate pH 4.5	— 0.48
0.5 M tartrate pH 9.0	— 0.50
N sodium hydroxide	— 0.755

It was evident from the values quoted in the above tables that separation of the wave due to the lead from those of styphnic acid would be greatest at pH values of 2

or below. At all values above this interference occurs with one or other styphnic acid step. A solution containing $8.8 \cdot 10^{-5} M$ lead styphnate in sodium citrate-hydrochloric acid buffer of pH 1.8 and containing 0.005% proteose peptone (maximum suppressor) was therefore prepared and polarographed. The polarogram obtained, which consisted of a large "styphnate" step followed by a smaller step, due to lead, is shown in Fig. 2.

Examination of the polarographic wave of Fig. 2 indicated that the first step was composite and probably contained the three styphnate steps which usually occur. In order to check this the Ilkovic equation was used to obtain a value for n , the number of electrons transferred in the reduction. For this purpose the limiting diffusion current was taken as $6.8 \mu A$ and the concentration of styphnate ion as $8.8 \cdot 10^{-2}$ mmoles. The value of the mass drop time of the electrode ($m^2 \cdot t$) in this solution at $-0.3 V$ was found to be 1.81. No value for the diffusion coefficient of the styphnate ion is known but, by analogy with similar compounds, it was assumed to be $0.5 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. The value obtained for " n " by this calculation was 31.5, indicating that this reduction is highly irreversible. KOLTHOFF AND LINGANE⁵ have reported values of 6, 12 and 17 electrons transferred for the first, second and third steps of styphnic acid respectively, giving a total of 35 electrons transferred. The value obtained above is in agreement with this and supports the suggestion that all three waves are combined in the styphnate step obtained by us at pH 1.8.

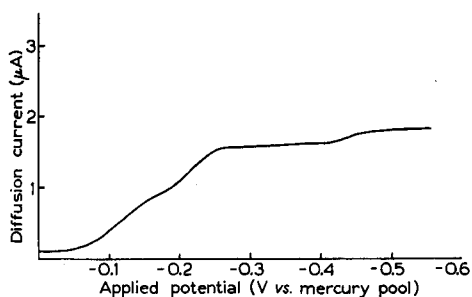


Fig. 2. D.C. Polarogram: lead styphnate $8.8 \cdot 10^{-5} M$ in sodium citrate-hydrochloric acid buffer, pH 1.8.

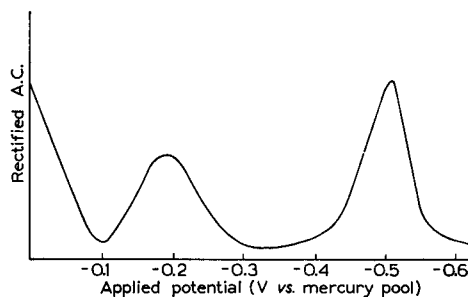


Fig. 3. A.C. Polarogram: lead styphnate $8.8 \cdot 10^{-5} M$ in sodium citrate-hydrochloric acid buffer, pH 1.8.

The ratio of the step height due to lead to that due to styphnate was 1:9 and since the styphnate wave preceded the lead it was not possible to obtain a sufficiently large and undistorted lead step. In order to overcome this difficulty it was decided to take advantage of the irreversible nature of the styphnate wave as it was known⁶ that polarography of irreversible systems by the A.C. superimposition method gives rise to relatively much smaller peaks than those due to reversible reactions at similar concentration. Polarography of the above solution was therefore repeated using the Cambridge Univector attachment set for A.C. working. The wave obtained is shown in Fig. 3. On this polarogram it is seen that the large styphnate step obtained on normal working (Fig. 2) has become a broad peak characteristic of an irreversible reduction. The lead step has been converted to a well-defined, sharp peak of greater height than that due to the styphnate ion.

It was considered that, on the basis of the above results, a determination of both lead and styphnate ions in the same solution could be made by carrying out polarography on normal and derivative working successfully and following method was therefore prepared.

METHOD

Place 14 ml of a sodium citrate-hydrochloric acid buffer of pH 1.8 (note 1) in a 25-ml graduated flask and add 0.5 ml of 0.1% proteose peptone in 0.2% phenol solution (maximum suppressor) and 10 ml of the sample solution (note 2). Make up to volume with water.

Transfer an aliquot of the prepared solution to a polarographic cell, deoxygenate for 5 min by bubbling hydrogen or nitrogen through it and record the following two polarograms at 25°, using a Cambridge pen writing polarograph equipped with a Univector unit (note 3).

1. A polarogram on normal working over the voltage range 0.0–0.7 V using the mercury pool as anode. Measure the height of the extended wave which occurs over the range —0.1 to —0.3 V.

Calculate the concentration of styphnic acid by reference to graph 1, prepared as described under “*Calibration*” below, making the appropriate corrections for the sensitivity setting of instrument.

2. A polarogram, with the Univector set for A.C. working, over the range 0.0 to —0.7 V using the mercury pool as anode.

Measure the height of the peak which occurs at about —0.5 V.

Calculate the concentration of lead by reference to graph 2, prepared as described under “*Calibration*” below, making the appropriate correction for the sensitivity setting of the instrument.

Calibration

Prepare an aqueous solution of lead styphnate containing 0.6 g/l (note 4). Carry out four determinations as described in the method, using aliquots of 0, 3, 7 and 10 ml respectively of the prepared lead styphnate solution instead of the sample. Measure the wave and peak heights due to the styphnic acid and lead obtained with each solution. Plot calibration graphs of:

1. Styphnic acid step height against the concentration given in Table IV column 3.
2. Lead peak height against the concentration given in Table IV column 4.

TABLE IV

Lead styphnate added (ml)	Concentration (g/l)		
	Lead styphnate	Styphnic acid	Lead
0	0.0	0.0	0.0
3	0.072	0.039	0.033
7	0.168	0.091	0.077
10	0.240	0.130	0.110

Notes

1. The buffer solution is prepared by dissolving 21 g of citric acid in water, adding 200 ml of *N* sodium hydroxide. 5 ml of this solution is titrated with 0.1 *N* hydrochloric acid until the pH is 1.8. This gives a final volume of about 20 ml.
2. The volume of the sample solution may be varied if the concentration of lead styphnate is such that the step heights obtained fall outside the calibration ranges.
3. The Univector Unit produces derivative-type waves by the method of A.C. superimposition. Derivative circuits not of this type are unsuitable for this determination.
4. This compound is a highly sensitive explosive. Great care in handling is necessary.

TRIAL OF THE METHOD

In order to study the accuracy and reproducibility of the method detailed above a number of determinations were made on solutions containing varying amounts of lead and styphnic acid. The results obtained are given in Table V below.

TABLE V

Solution	Styphnic acid (mg per 25 ml)		Lead (mg per 25 ml)	
	Added	Found	Added	Found
A	3.24	3.3	2.76	2.8
	3.24	3.3	2.76	2.75
	3.24	3.4	2.76	2.8
B	3.24	3.4	3.26	3.4
	3.24	3.2	3.26	3.2
	3.24	3.2	3.26	3.35
C	3.74	3.75	2.76	2.8
	3.74	3.9	2.76	2.85
	3.74	3.7	2.76	2.85

CONCLUSIONS

The results given in Table V show that both lead and styphnic acid can be determined in the same solution, when either are in excess of the stoichiometric amounts corresponding to lead styphnate. Recoveries should be better than $\pm 5\%$.

The method of determination of an organic radical and a metal ion in the same solution by successive applications of direct and A.C. polarography is novel and should have wide application, with consequent avoidance of separation procedures.

SUMMARY

A study of the polarographic behaviour of lead styphnate has been made. It has been shown that by use of a combination of normal polarography and derivative polarography using an alternating current method it is possible to determine both lead and styphnate ions in the same solution.

RÉSUMÉ

Une étude du comportement polarographique du styphnate de plomb a été effectuée. En combinant la polarographie normale et une polarographie à courant alternatif, il a été possible de doser le plomb et les ions styphnates dans une même solution.

ZUSAMMENFASSUNG

Blei- und Styphnat Ionen lassen sich in der gleichen Lösung bestimmen durch Anwendung einer Kombination von normaler Polarographie und Polarographie mit Wechselstrom.

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SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

II. SULPHANILIC ACID AS A REAGENT

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In our previous communication¹, we have fully discussed the nature, stability and the analytical aspects of the colour reaction that traces of osmium, in different valency states, give with anthranilic acid in faintly acid medium. In this paper, the results of similar studies on the colour reaction between osmium and sulphanilic acid in acid medium, have been recorded.

In both the hexavalent and octavalent state, osmium reacts in the pH range 1.8–3.5 with an excess of sulphanilic acid to form a stable dark-violet complex with an absorption maximum at 490 m μ .

The results obtained on applying the method of continuous variations and the molar ratio method to determine the composition of the complex, indicated that in the case of osmium(VI) the complex is formed when the ratio between the moles of metal and reagent is 1 : 2; in the case of osmium(VIII), however, no definite indication as to the ratio was observed. This may be due to the fact that osmium(VIII) has oxidising properties, so that it slowly oxidises the entire reagent when this is present in small quantities. That the coloured products obtained from osmium(VI) and osmium(VIII), in the presence of an excess of the reagent, are the same is evident from their identical colour reaction, same region of maximum absorption and similar tolerance to pH variation.

The osmium(VI) complex is stable in water and alcohol, and has an average dissociation constant of $1.2 \cdot 10^{-7}$.

In the tetra-, tri- and bi-valent states, osmium does not react with the reagent.

EXPERIMENTAL

Apparatus

All O.D. measurements were carried out with a Hilger Uvispek Spectrophotometer, using a tungsten filament lamp and quartz absorption cells of 1-cm thickness.

A Cambridge pH indicator was used for all pH measurements.

Standard osmium solutions

A standard stock solution of osmium(VIII) was prepared from a 0.1-g ampoule of osmic acid (OsO_4) of Dr. THEODOR SCHUCHARDT, according to the method reported in the previous communication¹.

A standard solution of osmium(VI) was obtained by reducing a 10^{-8} M stock solution of osmic acid in a measuring flask with 1 : 2 alcohol (v/v), adding 0.1 ml alcohol for every 10 ml of stock solution, and then making up volume with distilled water. When not in use, this solution was kept in a refrigerator where it was found to be stable for about a fortnight.

Reagent solution

A 1% solution of sulphanilic acid was prepared by suspending in water 1 g of B.D.H. AnalaR grade reagent and dissolving it by the addition of the required quantity of sodium carbonate. When the reagent was completely dissolved, the solution was made up to 100 ml with distilled water.

Buffer solution

Buffer solutions with pH values ranging from 3.42-5.89 were obtained by mixing 0.2 N acetic acid and 0.2 N sodium acetate in different proportions.²

Other reagents

Test solutions of palladium(II), ruthenium(III), rhodium(III), platinum(IV) and iridium(IV) were prepared by the methods reported previously¹.

All other metal solutions were prepared by dissolving their analytical grade chlorides, sulphates, nitrates or oxides in water or hydrochloric acid.

Absorbance curves

For osmium(VI) or osmium(VIII), the colour was developed by adding osmate (OsO_4^{-2}) or osmium tetroxide solution, respectively, to 5 ml of the reagent solution in a 25-ml flask. After allowing the mixture to stand for 2 h it was made up to volume with sodium acetate-acetic acid buffer of pH 3.42. The optical density of the solution was then measured against a reagent blank prepared in the same way, but omitting the osmium.

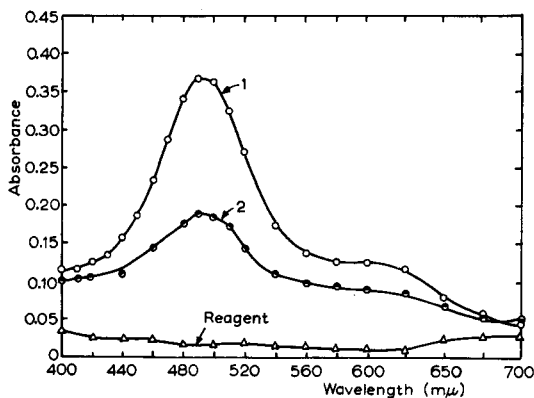


Fig. 1. Absorbance curves for sodium sulphanilate and its osmium complex at pH 3.4. Curve 1: 3.97 p.p.m. osmium(VIII) + 5 ml of 1% reagent. Curve 2: 3.87 p.p.m. osmium(VI) + 5 ml of 1% reagent.

Optical density–wavelength curves of osmium(VIII) and osmium(VI) against the reagent blank, and of the reagent against water at the same pH are represented in Fig. 1. For both the valence states, the colour of the solutions and the nature of the absorption spectra are the same and both show maximum absorption at 490 $m\mu$. In this region the reagent has negligible absorption. Hence an excess of the reagent does not appreciably increase the absorbance of the solution. The depression of the peak in the case of osmium(VI) is due to the presence of alcohol in the solution.

Effects of pH, reagent and time

The pH's of the solutions, prepared by mixing a definite amount of osmium with an excess of the reagent, were adjusted to different values (3.4–5.9) with sodium acetate–acetic acid buffer. Higher and lower pH values were obtained by adding sodium hydroxide and sulphuric acid, respectively. It was found that with increasing pH the optical density of the solutions increased up to pH 1.8 and then remained constant up to 3.5, after which it decreased continuously up to pH 10. Therefore all subsequent measurements were carried out in the pH range 1.8–3.5.

5 ml of the reagent solution were required for maximum development of colour with either 0.5 to 8 p.p.m. of osmium(VIII) or 1 to 18 p.p.m. of osmium(VI). Addition of more reagent did not appreciably alter the density of the colour.

The colour developed very rapidly with the reagent solution, and a stable colour with maximum density was obtained on keeping for 2 h in the cold. The density values of the coloured systems thus produced do not undergo any change even after 24 h. With very dilute solutions of reagent, the colour does not develop at a pH higher than 3.5, even on long standing, but readily does so if a drop or two of dilute sulphuric acid is added to lower the pH to about 1.8 to 3.0.

Beer's law

The complex obeys Beer's law for osmium(VIII) concentrations of 0.5 to 9 p.p.m. and osmium(VI) concentrations of 1 to 18 p.p.m. (*cf.* Fig. 2), when measurements are made against a reagent blank.

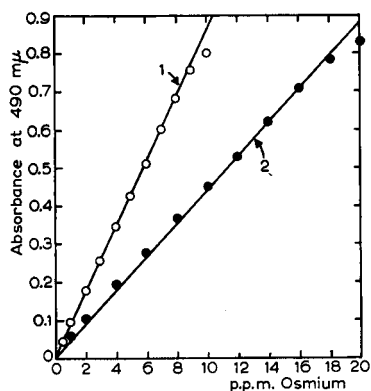


Fig. 2. Beer's law plots for (1) osmium(VIII) and (2) osmium(VI); pH 3.4.

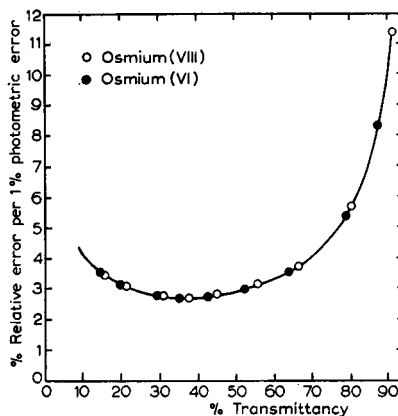


Fig. 3. Evaluation of per cent relative error ($dc/c \times 100$) relative to 1% absolute photometric error.

Optimum range and accuracy

The % relative error per 1% absolute photometric error was calculated by means of the equation reported previously¹, and plotted against transmittancy (Fig. 3) to show how the analytical error varies with the transmittancy.

On plotting % absorbancy (100 — % transmittancy) at 490 m μ as the ordinate against log concentration as the abscissa, the optimum concentration ranges were found to be between 2 and 8 p.p.m. of osmium(VIII) and between 4 and 16 p.p.m. of osmium(VI), the curves having the steepest slopes there (Fig. 4). For these regions, the % relative errors per 1% absolute photometric error are 3.02 for osmium(VIII) and 3.1 for osmium(VI), as evaluated by means of the equation described in a previous paper¹.

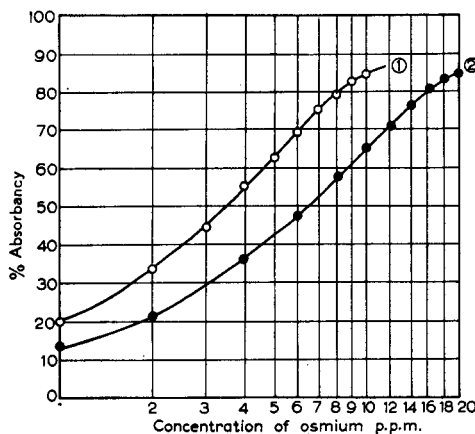


Fig. 4. Calibration curves for (1) osmium(VIII) and (2) osmium (VI) at 490 m μ .

Sensitivity

The spectrophotometric sensitivities, as calculated from Beer's law curves, were found to be 0.01 $\mu\text{g}/\text{cm}^2$ for osmium(VIII) and 0.02 $\mu\text{g}/\text{cm}^2$ for osmium(VI) (cf. SANDELL³).

Effect of diverse ions

To determine the interference of diverse ions, solutions were prepared with 4.2 p.p.m. of osmium(VI), 5 ml of 1% reagent and varying concentrations of each ionic species being tested. An increase or decrease of 0.005 unit in absorbance was taken as an interference. The following ions were found to interfere even in a ratio of 1 : 1 Pd⁺², Pt⁺⁴, Ru⁺³, Rh⁺³, Ir⁺⁴, Cu⁺², Ag⁺, Zn⁺², Cd⁺², Hg⁺², Al⁺³, Th⁺⁴, Zr⁺⁴, As⁺³, Sb⁺³, Cr⁺³, W⁺⁶, U⁺⁶, Mn⁺², Co⁺², Ni⁺². It is preferable to separate osmium as osmic acid by nitric acid oxidation and distillation³ in order to avoid the interference of other ions.

Nature of the complex in solution

Two methods were employed to ascertain the empirical formula of the osmium(VI)–sulphanilic acid complex in solution. These were the method of continuous variations and the molar ratio method, which we have also applied in a previous investigation¹.

The results obtained with these two methods indicate that in solution osmium(VI) forms a 1 : 2 complex with the reagent. As in the case of anthranilic acid¹, difficulties were encountered when excess of osmium and smaller amounts of reagent were present, owing to black osmium dioxide and metallic osmium separating from the solution.

In both methods, solutions of osmium(VI) and the reagent were mixed and treated with two drops of 6 *M* sulphuric acid. After 2 h, when the colour had developed, the volume of the mixed solution was made up to 25 ml with a buffer of pH 3.42. It was then allowed to stand overnight, and afterwards the optical density was measured. With dilute equimolecular solutions, no colour developed until the pH of the mixture had been adjusted to a value between 1.8 and 3.0; further, it was found that for full colour development a period of 24 h was absolutely necessary. Results of such experiments are given in Figs. 5 and 6.

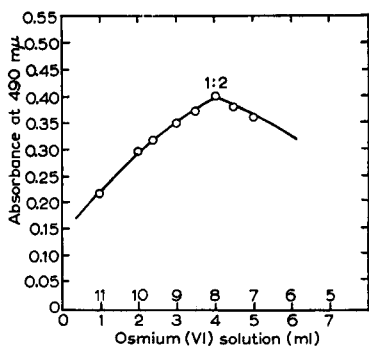


Fig. 5. Determination of the ratio of reagent to osmium(VI) by Job's method. Concn. osmium(VI) = concn. sulphanic acid (sodium salt) = $0.8935 \cdot 10^{-8} M$.

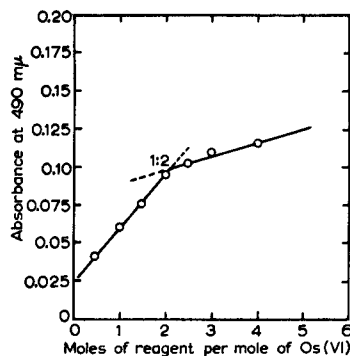


Fig. 6. Determination of ratio of reagent to osmium(VI) by the molar ratio method. Concn. osmium(VI) = concn. sulphanic acid = $0.8935 \cdot 10^{-8} M$.

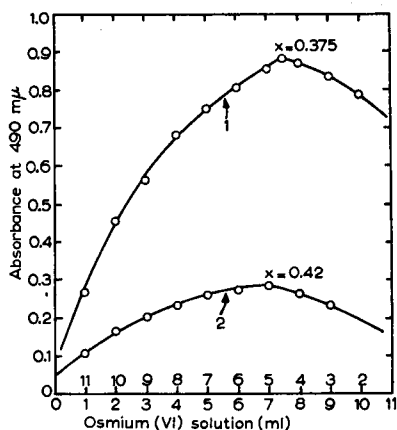


Fig. 7. Absorbance of mixtures of non-equimolecular solutions. Curve 1: $1.15 \cdot 10^{-8} M$ osmium(VI) solution, $5.75 \cdot 10^{-8} M$ sulphanic acid (sodium salt) solution. Curve 2: $0.575 \cdot 10^{-8} M$ osmium(VI) solution, $2.875 \cdot 10^{-8} M$ sulphanic acid (sodium salt) solution.

Dissociation constant of the osmium(VI)-sulphanilic acid complex

For the evaluation of the dissociation constant of the complex, mixtures of non-equimolecular solutions of reagent and osmate (OsO_4^{-2}) were treated with a drop of 12 N sulphuric acid and allowed to stand for 2 h. After making up their volumes to 25 ml with buffer of pH 3.42, their absorbances were measured at 490 m μ . Experimental data are given in Fig. 7 where absorbances have been plotted against the volumes of osmium(VI) solution added. Owing to the higher concentration of the reagent, it was not necessary to let the solution stand overnight for maximum colour development.

From the data obtained (*cf.* Fig. 7) the dissociation constant was calculated, using Job's equation¹; it was found to be $1.2 \cdot 10^{-7}$.

ACKNOWLEDGEMENT

Our thanks are due to the University Grants Commission for providing us with funds to purchase the spectrophotometer used in this work.

SUMMARY

Sulphanilic acid has been found to be a very effective reagent for the spectrophotometric determination of hexavalent and octavalent osmium in the pH range between 1.8-3.5. In these two valence states, the element forms a dark-violet complex with the reagent, the absorption maximum of the complex being at 490 m μ . As most of the other ions interfere in the determination, the element must be separated as osmic acid by nitric acid distillation. Beer's law is obeyed in the case of 0.5 to 9 p.p.m. of osmium(VIII) and 1 to 18 p.p.m. of osmium(VI); the optimum concentration ranges are from 2 to 8 p.p.m. for osmium(VIII) and from 4 to 16 p.p.m. for osmium(VI). In these ranges, the % relative errors per 1% absolute photometric error are 3.02 for osmium(VIII) and 3.1 for osmium(VI). Application of the method of continuous variations and the molar ratio method indicates that in solution hexavalent osmium and the reagent form a 1 : 2 complex, with an average dissociation constant of $1.2 \cdot 10^{-7}$.

RÉSUMÉ

L'acide sulfanilique est proposé comme réactif pour le dosage spectrophotométrique de l'osmium(VI) et (VIII). Le complexe formé est violet foncé. La plupart des autres ions gênent; il faut alors séparer l'osmium par distillation.

ZUSAMMENFASSUNG

Als Reagens zur spektrophotometrischen Bestimmung von Osmium(VI) und (VIII) wird Sulfanilsäure vorgeschlagen, die damit einen dunkel-violett gefärbten Komplex bildet. Da die meisten Fremd-Ionen stören, muss das Osmium durch Destillation abgetrennt werden.

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THE DETERMINATION OF URANIUM BY SQUARE WAVE POLAROGRAPHY

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INTRODUCTION

Conventional polarography is a useful technique for the determination of uranium, but it is not suitable for very low concentrations. SHALGOSKY¹ used the step from a sulphuric acid-perchloric acid-tartrate supporting electrolyte for the determination of uranium concentrations in the range from 20 to 200 $\mu\text{g/ml}$. A linear calibration graph of step height against concentration was obtained over this concentration range, but a non-linear graph resulted for lower uranium concentrations.

The advantage of the square wave polarography for the determination of trace amounts of several elements² is now well established and a study of the potentialities of this instrument for the determination of very small amounts of uranium was therefore desirable. Brief reference to the determination of uranium by square wave polarography was made by FERRETT AND MILNER³. They used a 0.1 *N* hydrochloric acid supporting electrolyte and reported two peaks at -0.18 and -0.86 V *vs.* the mercury pool anode respectively. The first peak coalesced with a copper peak and was unsuitable for the determination of uranium in the presence of copper. For the determination of traces of uranium in effluents, MILNER AND FERRETT⁴ found a molar perchloric acid supporting electrolyte to be most satisfactory. The uranium peak occurred at about -0.55 V *vs.* the mercury pool anode and it proved suitable for the determination of uranium at the level of a few tenths of a microgram per ml of final solution. Any organic matter in the samples was first destroyed by evaporation to fumes of perchloric acid followed by the dropwise addition of conc. nitric acid.

EXPERIMENTAL

In view of the satisfactory results obtained by MILNER AND FERRETT⁴ with mineral acid supporting electrolytes for the determination of small amounts of uranium, a more detailed investigation of this type of supporting electrolyte was carried out and the results obtained are summarized below:

(a) *Hydrochloric acid*

In studying the behaviour of uranium in this supporting electrolyte, 1-ml aliquots of a standard solution in dilute perchloric acid containing 50 μg of uranium were taken and evaporated just to dryness. Each residue was dissolved in the requisite volume of 10 *N* hydrochloric acid before dilution to a volume of 5 ml with water. A well-defined peak was obtained from solutions in the range 0.5 to 1.5 *M* in HCl, and the $E_{\frac{1}{2}}$ value of the peak, as determined by conventional methods, varied with the acid concentration as follows:

Molarity of HCl	0.5	1.0	1.5
$E_{\frac{1}{2}}$ vs. S.C.E.	-0.20 V	-0.20 V	-0.196 V

From 2 *N* HCl solutions the definition of the uranium peak was unsatisfactory due to abnormal responses of the instrument. Although the $E_{\frac{1}{2}}$ value of the peak moved to slightly more positive value with increase in the acid concentration, the most important effect was the considerable decrease in the height of the peak (See Fig. 1). From this behaviour strict control of the hydrochloric acid concentration is essential for the use of this peak in quantitative analysis. When this is done, the height of the peak is proportional to the concentration of uranium.

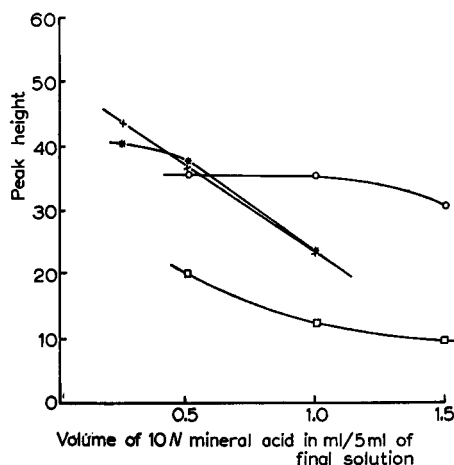


Fig. 1. Influence of the nature and concentration of mineral acid on the peak height for uranium. Tartrate absent. Uranium concentration 10 $\mu\text{g/ml}$. \circ HClO₄; \times HCl; $*$ HNO₃; \square H₂SO₄.

(b) Nitric acid

Uranium was found to give a well-defined peak in this supporting electrolyte. In experiments to study any possible effects of variations in the nitric acid concentration, 1-ml aliquots of a standard uranium solution in dilute nitric acid containing 50 μg of U per ml were evaporated to dryness. Each residue was dissolved in the requisite volume of 10 *M* nitric acid before dilution to 5 ml with water.

With an increase in the nitric acid concentration the uranyl peak moved to more positive potentials, as shown by the following $E_{\frac{1}{2}}$ values for solutions up to 1.5 *M* in nitric acid:

Molarity of HNO ₃	0.25	0.5	1.0	1.5
$E_{\frac{1}{2}}$ vs. S.C.E.	-0.235 V	-0.21 V	-0.175 V	-0.16 V

In 1.5 *M* nitric acid solutions the mercury is attacked fairly rapidly and it is necessary to record the polarogram within 30 min of pouring the solution into the cell.

Over the range examined, the relationship between the half-wave potential and the logarithm of the acid concentration is given by the equation:

$$E_{\frac{1}{2}} = -0.175 - 0.096 \log_{10} (\text{acid concentration}) \\ \approx -0.175 + 0.096 \text{ pH}$$

As in the experiments with hydrochloric acid, the height of the peak decreased appreciably with increase in the nitric acid concentration (See Fig. 1). The acidity of the final solution must therefore be carefully controlled in using this peak in analysis and then the peak height is proportional to the concentration of uranium.

(c) *Sulphuric acid*

In a study of this supporting electrolyte the procedure of evaporating the uranium solution to fumes of sulphuric acid before recording the uranyl peak was avoided because of the difficulties experienced by SHALGOSKY¹. Aliquots (1 ml) containing 50 μg of uranium in 0.1 *M* perchloric acid were taken and mixed with the requisite volumes of 5 *M* sulphuric acid before dilution to 5 ml with water. Under these conditions the height of the uranium peak was much smaller than that for the same concentration of uranium in HCl and HNO₃ solutions respectively (See Fig. 1). The peak height also decreased with increase in sulphuric acid concentration over the range studied. The half-wave potential of the peak became more positive with increase in acidity, in accordance with the following values:

Molarity of H ₂ SO ₄	1.0	2.0	3.0
$E_{\frac{1}{2}}$ vs. S.C.E.	-0.205 V	-0.175 V	-0.155 V

Again a linear relationship exists between the $E_{\frac{1}{2}}$ value and the logarithm of the acid concentration and is given by the equation: $E_{\frac{1}{2}} = -0.205 - 0.111 \log_{10} (\text{acid concentration})$.

(d) *Perchloric acid*

A well-defined peak was obtained from perchloric acid solutions up to 3 *M* in this acid. Variations in the acid concentration had only a small effect on the peak height and the position of the peak, the $E_{\frac{1}{2}}$ values being as follows:

Molarity of HClO ₄	1.0	2.0	3.0
$E_{\frac{1}{2}}$ vs. S.C.E.	-0.21 V	-0.225 V	-0.23 V

This supporting electrolyte proved to be the only one not requiring careful control of the final acid concentration. The peak height for a concentration of uranium of 10 $\mu\text{g}/\text{ml}$ in *M* HClO₄ was much greater than that for the same concentration in sulphuric acid, but approximately the same as that in *N* HCl and *M* HNO₃ solutions. Perchloric acid appeared potentially more useful than the others for application in analytical chemistry and was therefore examined in more detail. The relationship of peak height vs. concentration was studied over a very wide range of uranium concentrations in *M* HClO₄ and was found to be linear over the range from 1 to at least 2,500 μg of uranium per ml of final solution. Small peaks were obtained for uranium

concentrations less than $1 \mu\text{g/ml}$, but these would not be very suitable for analytical purposes because of the poor precision in measuring such small peak heights.

The effects on the uranium peak of peaks produced by several other elements were examined. Cupric ions give a peak just preceding that for uranium which causes little difficulty for ratios of copper to uranium of 1 : 1. Serious interference occurs, however, for higher ratios. Lead gives a peak following the uranium peak which is less troublesome than the copper peak. The peak for bismuth occurs very close to the uranium peak and the resolution of these peaks is very poor for bismuth to uranium ratios of 1 : 1. Similarly molybdenum gives an interfering peak with an $E_{\frac{1}{2}}$ value of -0.20 V vs. S.C.E. in $M \text{ HClO}_4$. Several elements, including Ni, Mn and ferric iron, cause no interference.

ACIDIC-TARTRATE SUPPORTING ELECTROLYTES

This type of supporting electrolyte was studied because of the interferences occurring with the uranium peak in the perchloric acid solutions. From results in conventional polarography, mineral acid-tartrate¹ and -oxalate² supporting solutions appeared to be the most suitable for the removal of interferences in the polarographic determination of uranium. SHALGOSKY, for example, recommended a sulphuric acid-perchloric acid-tartrate supporting electrolyte and concluded that the addition of tartrate assisted mainly in the separation of interfering steps from the uranium step and hardly affected the diffusion current or the mechanism of the reaction at the dropping mercury electrode. From this supporting electrolyte the steps for copper, bismuth and lead were well-separated from the uranium step. However, the step height-concentration graph was not linear for low uranium contents.

In the investigations of the suitability of the tartrate base for the determination of uranium by square-wave polarography, a solution of the supporting electrolyte was prepared by dissolving 6 g of sodium tartrate and 0.15 g of sodium chloride in water followed by dilution to a volume of 50 ml. A standard uranium solution was prepared by dissolving 100 mg of U_3O_8 , previously ignited at 800° , in about 2 ml of hot concentrated perchloric acid (60%). After cooling, the solution was transferred to a 100-ml volumetric flask and diluted to volume with water. Suitable dilutions of this standard solution were made, perchloric acid being added as required to maintain the solutions about 0.1 M with respect to this acid. Results obtained on investigating solutions of this tartrate supporting electrolyte in conjunction with different mineral acids are summarized below:

(a) Hydrochloric acid-tartrate

In the study of the hydrochloric acid supporting electrolyte, a well-defined peak was obtained for uranium in solutions molar in this acid and these conditions were therefore used to investigate the effects of different tartrate concentrations. Aliquots of the standard uranium solution containing $50 \mu\text{g}$ of this element were taken and evaporated to remove perchloric acid. Then the requisite volume of the tartrate base was added and the solution warmed. After cooling, 0.5 ml of 10 N hydrochloric acid was added and the solution diluted to 5 ml with water. With volumes of tartrate base varying from 0 to 2.0 ml, negligible effect was obtained on the peak height and also on the position of the peak. In experiments to study the effect of hydrochloric acid

concentration, the volume of tartrate solution was fixed at 0.5 ml and varying amounts of 10 *N* HCl were added after the tartrate, as before. Abnormal instrumental responses were obtained from solutions 2 *M* in HCl, but in the range from 0.5 to 1.5 *M* well-defined peaks were obtained, the peak height decreasing appreciably with increase

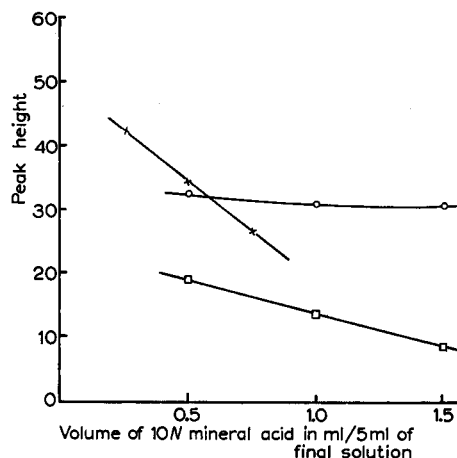


Fig. 2. Influence of the nature and concentration of mineral acid in an acid-tartrate supporting electrolyte on the peak height for uranium. Tartrate present. Uranium concentration 10 $\mu\text{g}/\text{ml}$. ○ HClO₄; × HCl and HNO₃; □ H₂SO₄.

in acidity (See Fig. 2). Changes in acidity had little effect upon the half-wave potential of the peak, as shown by the following values:

Molarity of HCl	0.5	1.0	1.5
$E_{\frac{1}{2}}$ vs. S.C.E.	-0.21 V	-0.205 V	-0.20 V

The close similarity between these values and those for HCl alone suggests that the same species is being reduced with or without the presence of tartrate. The quantitative behaviour of this peak was studied in solutions containing 0.5 ml of tartrate solution and 0.5 ml of 10 *N* HCl in 5 ml of final solution. A linear relationship was obtained between peak height and uranium concentration over the range from 5 to at least 20 μg of uranium per ml of final solution. Very unsatisfactory results were obtained, however, for concentrations less than 5 $\mu\text{g}/\text{ml}$. The peak was incompletely developed and the base line was unstable.

(b) Nitric acid-tartrate

The effects of acidity and tartrate concentration on the uranyl peak in this supporting electrolyte proved to be very similar to those occurring in HCl-tartrate solutions. In experiments with varying amounts of tartrate base, 0.5 ml of 10*M* nitric acid was included in 5 ml of final solution. As before, variations in the volume of tartrate solution from 0.5 to 2.0 ml had negligible influence on the peak height and the position of the peak remained fairly constant. Similarly, in experiments to study the influence of the nitric acid concentration, the volume of tartrate solution was

kept constant at 0.5 ml in 5 ml of final solution. The peak height for 50 μg of uranium decreased appreciably with increase in acidity from 0.5 to 1.5 M and strict control of acidity must therefore be enforced in applying this supporting electrolyte to analytical determinations. The half-wave potential of the peak moved to slightly more positive potentials with an increase in acidity, according to the following results:

Molarity of HNO_3	0.5	1.0	1.5
$E_{\frac{1}{2}}$ vs. S.C.E.	-0.21 V	-0.205 V	-0.19 V

The $E_{\frac{1}{2}}$ value in the 0.5 M HNO_3 -tartrate solution agrees with that in the 0.5 M HNO_3 supporting electrolyte. This suggests that the same uranium species is reduced at the dropping mercury electrode in each case. It is significant that an increase in the nitric acid concentration has a smaller effect in the presence of tartrate than in its absence.

The quantitative behaviour of the peak was studied on maintaining the volume of tartrate solution and 10 M HNO_3 each at 0.5 ml per 5 ml of final solution. As with HCl -tartrate solutions, a linear relationship was obtained on plotting peak height against concentration over the range 5 to 20 μg of uranium per ml. The peaks for smaller concentrations of uranium were also completely developed, a linear calibration graph being obtained over the range 0.5 to 2.0 μg of uranium per ml.

(c) *Sulphuric acid-tartrate*

The influence of the tartrate concentration on the uranium peak was investigated with the H_2SO_4 concentration fixed at 1 ml of 5 M acid per 5 ml of final solution. The peak height remained fairly constant for amounts of tartrate from 0.5 to 2.0 ml and there was negligible influence on the position of the peak. In studying the effect of H_2SO_4 concentration, experiments were carried out with the volume of tartrate solution constant at 0.5 ml. As before the peak height depended on the H_2SO_4 concentration and decreased appreciably with an increase in acidity (see Fig. 2). There was also some loss in sensitivity in this solution as compared with the other acidic-tartrate supporting electrolytes. The half-wave potential value of the peak moved to slightly more positive potentials with an increase in acidity, according to the following values:

Molarity of H_2SO_4	1.0	2.0	3.0
$E_{\frac{1}{2}}$ vs. S.C.E.	-0.20 V	-0.20 V	-0.185 V

With this supporting electrolyte, the half-wave potential value in 1 M H_2SO_4 is the same as that measured in the absence of tartrate. Again an increase in acidity has a smaller effect in these solutions than in supporting electrolytes containing only sulphuric acid.

On using 0.5 ml of tartrate solution and 1 ml of 5 M H_2SO_4 per 5 ml of final solution, quantitative peaks were obtained for uranium concentrations in the range 5 to 20 $\mu\text{g}/\text{ml}$. For lower uranium concentrations fully-developed peaks were produced, but the maximum sensitivity of the instrument had to be used and some interference from variations in the capillary response results.

(d) Perchloric acid-tartrate

With the volume of tartrate solution constant at 0.5 ml per 5 ml of final solution, the height of the uranyl peak was found to be fairly constant in solutions ranging from 1 to 3 *M* in HClO₄. Also the shift in the half-wave potential was insignificant in the range covered:

Molarity of HClO ₄	1.0	2.0	3.0
$E_{\frac{1}{2}}$ vs. S.C.E.	-0.225 V	-0.23 V	-0.225 V

On studying the effect of varying the tartrate concentration, all solutions were adjusted to be 2 *M* in HClO₄ and for variations of tartrate from 0.5 to 2.0 ml, the height of the peak showed negligible variation. The quantitative behaviour of the uranium peak was studied in solutions containing 1 ml of 10 *M* HClO₄ and 0.5 ml of tartrate solution per 5 ml of final solution. Linear calibration graphs of peak height against concentration were obtained over the concentration range from 0.6 to at least 50 μ g per ml. A second uranium peak occurring at about -1.2 V vs. the mercury pool anode was also observed in this supporting electrolyte, but it suffered some interference probably from the reduction of hydrogen ions at the cathode.

This supporting electrolyte appeared to be the most useful of the acid-tartrate solutions studied for the determination of uranium and the behaviour of other elements and it was therefore examined in some detail. Bismuth was studied first because of the serious interference caused by this element to the uranium peak in perchloric acid solutions. Bismuth ions gave a peak in a 1 *M* HClO₄-tartrate solution with an $E_{\frac{1}{2}}$ value of -0.024 V vs. S.C.E. and well separated from the uranium peak (see Fig. 3). Moreover, the $E_{\frac{1}{2}}$ value shifted to slightly more positive values with increase in the acid concentration. The peak for copper in this supporting electrolyte occurred at a still more positive potential. Also the half-wave potential for the reduction of ferric iron occurred at a potential more positive than +0.10 V vs. S.C.E. Interference from any of these elements in the uranium determination would only occur with very high ratios of each element to uranium.

Molybdate ions gave a peak at -0.19 V vs. S.C.E. in a *M* HClO₄-tartrate solution. This peak caused serious interference with the uranyl peak, even for low concentrations of molybdenum. Similarly the reduction of vanadic ions gave an interfering peak at -0.15 V vs. S.C.E. A peak for chromic ions occurred at -0.43 V vs. S.C.E. and difficulties resulted in the determination of uranium for high unfavourable ratios of chromium to uranium. Similar conclusions apply to lead which give a peak at about the same potential. Elements found to cause no interference include zinc, nickel, cadmium, indium, cobalt and manganese.

ANALYTICAL APPLICATION OF THE URANIUM PEAK IN THE PERCHLORIC ACID-TARTRATE SUPPORTING ELECTROLYTE

Mineral analysis — Determination of uranium

The determination of the uranium content of minerals is frequently required and several methods of analysis are already available. A neutron activation method⁶ is available for laboratories with facilities for radiochemical work. In chemical methods for this determination, preliminary separation and concentration of the uranium is

required before the determination is completed either polarographically or absorptiometrically^{7,8}. The chromatographic method of separation is usually employed and the step for uranium from an acidic oxalate or acidic tartrate supporting electrolyte is used in the polarographic determination. It was considered that the application of the square-wave polarograph instead of the conventional polarograph might improve this determination. With the improved sensitivity of this instrument, it should be possible to eliminate the lengthy separation and concentration of the uranium and experiments were therefore carried out to investigate the applicability of the uranium peak from the tartrate-perchloric acid supporting electrolyte to the direct determination of the uranium content of minerals.

The most reliable method for producing the solution of mineral samples involves sintering with sodium peroxide followed by extraction into water. After this solution procedure it would be necessary to destroy any peroxide in the aqueous extract before proceeding with the polarographic determination because of the interfering reduction of peroxide at the dropping mercury electrode. Preliminary experiments showed that, if the aqueous extract of sodium peroxide used in a sinter was acidified with hydrochloric acid and then evaporated to dryness, decomposition of the peroxide took place rapidly. After re-solution of the salts, aliquots of the resultant solution were evaporated to fumes of perchloric acid before the addition of the tartrate supporting electrolyte. Normal polarographic traces were obtained without any indication of interference from the reduction of peroxide. The polarograms showed a peak for lead present as an impurity in the sodium peroxide, but no peaks or irregularities in the applied voltage range for the uranium peak. Based on these findings, a direct procedure was developed for the analysis of minerals for uranium and further details are as follows:

Procedure for uranium in minerals

Transfer 100 mg of finely-ground sample to a small platinum crucible and intimately mix with 0.8 g of pure sodium peroxide (B.D.H. micro reagent grade). Cover the mixture with a further 0.2 g of sodium peroxide and place the crucible in a muffle furnace at $480 \pm 20^\circ$ for 20 min. After cooling, detach the peroxide sinter from the crucible and dissolve in a small volume of water. Add 10 ml of hydrochloric acid ($d = 1.18$) to the aqueous solution in the beaker and heat to boiling on a hot plate. Gradually evaporate the solution to dryness, using infra-red heating to complete the evaporation. Then bake for about 20 min on a hot plate to dehydrate the silica. Redissolve the salts in 20 ml of hydrochloric acid ($d = 1.18$) with boiling and then dilute with an equal volume of water. Filter the cooled solution through a Whatman No. 40 filter paper, washing with dilute hydrochloric acid and collecting the filtrate in a 100-ml volumetric flask (see Note). Dilute the solution to volume, then transfer 5 ml to a small beaker followed by 1 ml of 10 *N* perchloric acid (lead-free) and evaporate the solution just to fumes of perchloric acid. Rinse the beaker sides with a small volume of water and again evaporate the solution just to fumes of perchloric acid. To the cooled solution add 0.50 ml of the tartrate supporting electrolyte and dilute to 5 ml in a volumetric flask with water. After mixing, transfer this solution to a polarograph cell, de-aerate and record the uranium peak by scanning from -0.1 to -0.6 V vs. the mercury pool anode. Then make an addition of a standard uranium solution, de-aerate and record the peak.

Note. If the silica content of the sample is high, transfer the filter paper plus contents to a platinum dish and ignite. Add 2–3 drops of concentrated sulphuric acid to the residue, followed by a few ml of hydrofluoric acid and evaporate to remove silica. Then heat to remove the sulphuric acid and continue heating until no more fumes of this acid are visible. Dissolve any residue in hydrochloric acid and add to the main sample solution before dilution to 100 ml with water.

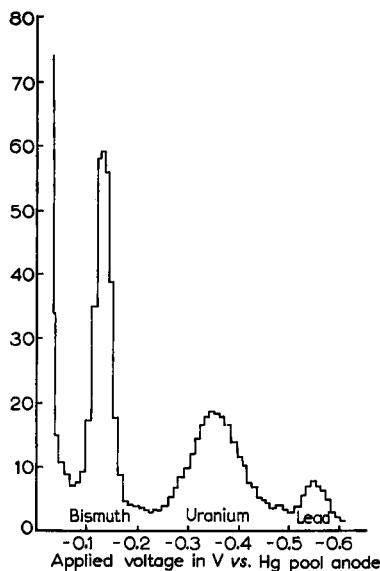


Fig. 3. Polarogram of bismuth, uranium and lead in the 2 N HClO₄-tartrate supporting electrolyte.

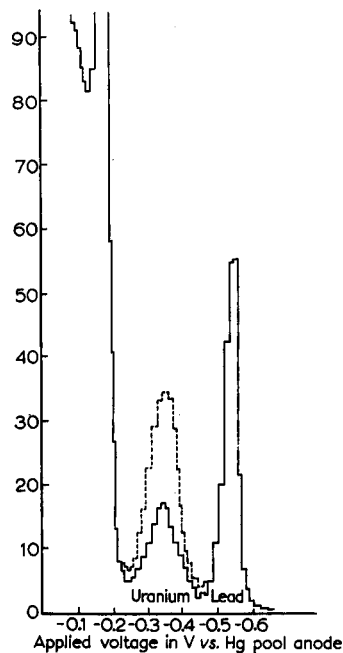


Fig. 4. Polarogram for monazite sand sample.-----: after standard addition of uranium.

Results

The suitability of this procedure was tested on samples which had been analysed by other methods and the results are given in Table I. Samples 1 and 2 were produced in the mineral dressing study of a quartz-iron oxide ore containing small amounts of pyrites, marcasite, sphalerite, galena, pitchblende and mica. The results for uranium reported in the last column were obtained by conventional polarography after the separation of the uranium from other sample constituents by paper chromatography. The remaining samples in Table I were pitchblende and monazite samples previously analysed for uranium by the neutron activation method. Fairly good agreement was obtained between the results by direct polarography and those by other methods. The square-wave polarographic method proved fairly rapid compared with the other methods for this determination, because chemical separations were unnecessary on the samples examined. A typical polarogram for a monazite sample is given in Fig. 4.

TABLE I
RESULTS FOR URANIUM IN MINERALS BY SQUARE-WAVE POLAROGRAPHY

Nature of sample	Uranium %	
	By square-wave polarography	By other methods
1. Quartz-iron oxide	0.295	0.29
2. Quartz-iron oxide	0.295	0.31
3. Pitchblende-dunite	0.093	0.097, 0.093, 0.10
4. Pitchblende-dunite	0.017	0.02, 0.018
5. Monazite-dunite	0.034	0.038
6. Monazite	0.28	0.30, 0.29

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Thanks are due to Mr. J. M. HALE for carrying out many of the halfwave potential measurements.

SUMMARY

Mineral acid supporting electrolytes, both in the presence and absence of tartrate ions, have been examined for use in the determination of small amounts of uranium by square wave polarography. A perchloric acid-tartrate supporting electrolyte is most suitable for analytical work and has been used for the determination of uranium in mineral samples.

RÉSUMÉ

Les auteurs ont examiné divers acides minéraux, comme électrolytes de base pour le dosage de l'uranium par polarographie „square-wave”. L'acide perchlorique, en présence de tartrate est recommandé. Une méthode est proposée pour le dosage de l'uranium dans ses minéraux.

ZUSAMMENFASSUNG

Die Anwendbarkeit der „square-wave” Polarographie auf die Bestimmung von Uran in Gegenwart von verschiedenen Mineralsäuren als Elektrolyte wurde untersucht. Perchlorsäure unter Zusatz von Tartrat ist besonders geeignet und wurde zur Bestimmung von Uran in Mineralien angewandt.

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POLAROGRAPHIC DETERMINATION OF MIXTURES
OF ALUMINUM AND GALLIUM

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INTRODUCTION

Aluminum and gallium, when present together, are difficult to determine quantitatively. COLLAT AND ROGERS¹ have proposed a fluorometric method for determining microgram quantities from mixtures of the oxinates in chloroform solution. WILLARD AND DEAN² have introduced a polarographic method for determining aluminum using the di-*o*-hydroxyazo dye, Pontachrome Violet SW (C.I. 169), which is the sodium salt of 5-sulfo-2-hydroxy- α -benzene-azo-2-naphthol. These investigators observed that reaction between the dye and aluminum(III) resulted in a new wave, the diffusion current of which was directly related to the concentration of aluminum present. This method can be used to determine $8 \cdot 10^{-6} M$ to $2.2 \cdot 10^{-4} M$ aluminum within 5%. The method has been further studied by PERKINS AND REYNOLDS³. LATIMER AND HOUSTON⁴ showed that the chelate of Pontachrome Violet SW with gallium(III) has similar polarographic behavior. The diffusion current of the chelate reduction wave is a linear function of gallium in solution. They determined $1.4 \cdot 10^{-5} M$ to $1.4 \cdot 10^{-4} M$ gallium by this method. SAYLOR AND CASTOR⁵ developed an amperometric method for the determination of fluoride using the reactions of aluminum with Superchrome Garnet Y (C.I. 168), the sodium salt of 5'-sulfo-2,4,2'-trihydroxyazobenzene. ADCOCK⁶ used the polarographic reduction of the aluminum-Superchrome Garnet Y chelate to determine concentrations of aluminum from $2 \cdot 10^{-6} M$ to $3 \cdot 10^{-3} M$. Gallium also reacts with Superchrome Garnet Y (SGY) giving similar polarographic behavior⁷. However, in addition to the usual two waves observed for the aluminum-SGY system, the gallium-SGY system produces a third polarographic wave having a halfwave potential of approximately $-1.05 V$ versus the saturated calomel electrode. The diffusion current of the third wave is also a linear function of the concentration of gallium present, but it is considerably smaller than that of the more positive chelate wave.

The work described here was undertaken to provide a polarographic method for determining mixtures of aluminum and gallium as part of a more general study of aluminum, gallium, and indium chelates of azo compounds.

EXPERIMENTAL AND RESULTS

Apparatus and procedure

A Sargent polarograph, Model XXI, was used to obtain all current-voltage curves. All potentials were referred to the saturated calomel electrode (S.C.E.). Measurements of pH were made to ± 0.05 pH unit with a Beckman Model G pH meter calibrated with standard buffer solution.

* Taken in part from the thesis submitted by BARBARA A. COONEY in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at Duke University, June, 1959.

Sample solutions were prepared at pH 5.53 with acetic acid-sodium acetate buffer. The sample solutions consisted of 0.1 *M* potassium chloride, 0.2 *M* buffer, and gelatin. For dye concentrations of $1 \cdot 10^{-3}$ *M* and less, 0.008% gelatin was sufficient as maxima suppressor, but 0.018% gelatin was necessary for $5 \cdot 10^{-3}$ *M* dye. The prepared sample solutions were allowed to stand for 10 to 12 h or were heated at 70° for 15 min to insure complete chelation. The solutions were deaerated by bubbling purified nitrogen through them for 15 min. All measurements were carried out in a thermostat at $25 \pm 0.01^\circ$.

Reagents

Superchrome Garnet Y was synthesized by coupling diazotized 2-aminophenol-4-sulfonic acid with resorcinol. The dye was purified by continuous extraction with ethanol. The dye was determined to be $82.8 \pm 2.6\%$ pure from a quantitative determination of azo nitrogen by reduction with standard titanium trichloride solution according to the method of KOLTOFF AND ROBINSON⁸. A stock solution of dye was prepared to be $1 \cdot 10^{-3}$ *M* with respect to available azo nitrogen.

The aluminum stock solutions were $1.007 \cdot 10^{-2}$ *M* prepared with 99.997% aluminum metal furnished by the Aluminum Company of America and $5.00 \cdot 10^{-3}$ *M* and $1.00 \cdot 10^{-2}$ *M* prepared with $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (Mallinkrodt Chemical Works). The gallium stock solution was $4.99 \cdot 10^{-3}$ *M* prepared with gallium metal (Fisher Scientific Company) which was $99.5 \pm 0.3\%$ pure by analysis with 5,7-dibromo-8-hydroxyquinoline⁹.

Calibration curves

Calibration curves of diffusion currents *versus* concentration of metal were prepared for each metal ion using a constant amount of dye and varying concentrations of metal. The diffusion current of the resulting polarographic waves for a given metal-dye system were linear functions of the metal ion present if sufficient dye were present to insure complete chelation. Calibration curves were prepared for aluminum and for gallium determinations using $1 \cdot 10^{-4}$ *M* SGY, $5 \cdot 10^{-4}$ *M* SGY, $1 \cdot 10^{-3}$ *M* SGY, and $5 \cdot 10^{-3}$ *M* SGY. The lower limit of dye concentration was determined by inherent fluctuations in the recorder circuit and the upper limit, by the solubility of the dye. The half-wave potentials of the first two waves of the aluminum-dye and gallium-dye systems were approximately -0.34 and -0.54 V respectively, and the half-wave potential of the third wave from the gallium-dye system was approximately -1.05 V. The half-wave potentials vary slightly with the concentration of dye.

By means of these calibration curves, concentrations of aluminum from $4.0 \cdot 10^{-6}$ *M* through $1.6 \cdot 10^{-3}$ *M* and concentrations of gallium from $4.0 \cdot 10^{-6}$ *M* through $2.0 \cdot 10^{-3}$ *M* can be determined with an accuracy of 3 to 5% using the first chelate wave (-0.54 V). Gallium can be determined from the third wave in the concentration range of $8 \cdot 10^{-6}$ *M* to $1.4 \cdot 10^{-3}$ *M* with an average precision of 4%. Figs. 1 and 2 show typical calibration curves for aluminum and for gallium respectively.

The effect of diverse ions was studied using 50-ml samples containing 10 mg of each ion. Foreign ions which were found to seriously interfere with this method of determining aluminum and gallium at pH 5.53 are zinc, manganese(II), cerium(IV), iron(III), vanadium(IV), and nickel. Cadmium and lead interfere with the determination of aluminum but not with the determination of gallium. Ions which were not found to interfere with the determination of aluminum or of gallium at pH 5.53 are magnesium, calcium, potassium, sodium, cesium, phosphate, nitrate, sulfate, and acetate.

Simultaneous determination of aluminum and gallium

Sample solutions for polarographic measurement were prepared with mixtures of aluminum and gallium and sufficient dye to insure complete chelation. The resulting

polarograms exhibited, in most instances, three polarographic waves. The first or most positive wave results from the reduction of unchelated SGY, the second wave results from the reduction of chelated SGY, and the third or most negative wave appears to result from the reduction of gallium in the gallium-SGY chelate.

The metal ion concentrations were determined by assuming that all of the aluminum and gallium in the solutions are present as the metal-SGY chelates, that the third wave resulting from the gallium-SGY system is independent of the presence of aluminum, that the second waves from the aluminum-SGY system and from the gallium-SGY system have the same half-wave potential, and that the diffusion current of the second wave when both metals are in solution is equal to the sum of the diffusion currents of the individual metal chelates. The sample solutions were polarographed and then the concentration of aluminum and of gallium was determined as follows:

1. The concentration of gallium corresponding to the measured diffusion current of the third wave was determined from the appropriate calibration curve.
2. The diffusion current of the second wave for that concentration of gallium was read from the calibration curve.
3. The concentration of aluminum was determined using the diffusion current of the second wave resulting from electrolysis of the mixture. The diffusion current resulting from the reduction of aluminum-SGY chelate was determined by subtracting the diffusion current of the first gallium-SGY chelate wave (as determined in 2) from the diffusion current of the wave which results from the reduction of both metal chelates. The aluminum concentration corresponding to this diffusion current was found from the appropriate calibration curve.

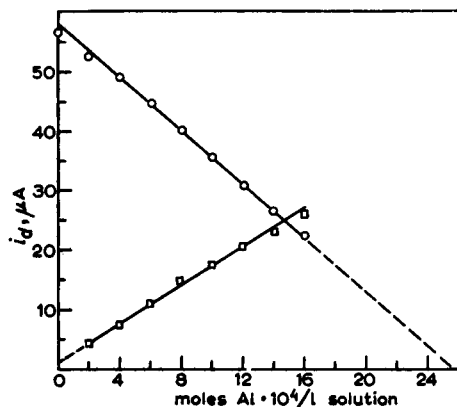


Fig. 1. Calibration curves for aluminum at pH 5.53 using $5 \cdot 10^{-3}$ M SGY.

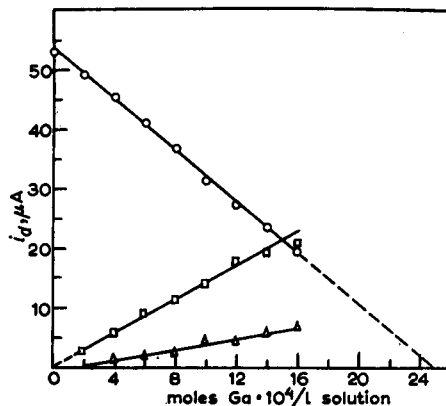


Fig. 2. Calibration curves for gallium at pH 5.53 using $5 \cdot 10^{-3}$ M SGY.

The results of analysis of mixtures of aluminum and gallium by this method are given in Table I. Aluminum was determined in all the mixtures with an average precision of $\pm 6.0\%$. Gallium was determined with an average precision of $\pm 7.8\%$, provided the aluminum concentration is less than five times that of the gallium. Aluminum, but not gallium, can be determined when the concentration of aluminum is more than five times that of gallium. This failure is caused in part by a small

TABLE I
SIMULTANEOUS DETERMINATION OF ALUMINUM AND GALLIUM

Concn. SGY moles/l	Aluminum(moles/l)		Gallium(moles/l)		% error
	Taken	Found	Taken	Found	
1.00·10 ⁻⁴	1.00·10 ⁻⁵	1.07·10 ⁻⁵	1.00·10 ⁻⁵	1.03·10 ⁻⁵	+ 3.0
1.00·10 ⁻⁴	3.00·10 ⁻⁵	2.83·10 ⁻⁵	1.00·10 ⁻⁵	0.93·10 ⁻⁵	- 7.0
5.00·10 ⁻⁴	5.00·10 ⁻⁵	5.20·10 ⁻⁵	1.00·10 ⁻⁵	1.17·10 ⁻⁵	+ 17.0
5.00·10 ⁻⁴	1.00·10 ⁻⁴	1.10·10 ⁻⁴	1.00·10 ⁻⁵	no measurable wave	—
1.00·10 ⁻³	1.00·10 ⁻⁴	0.96·10 ⁻⁴	1.00·10 ⁻⁴	1.05·10 ⁻⁴	+ 5.0
1.00·10 ⁻³	2.00·10 ⁻⁴	1.88·10 ⁻⁴	1.00·10 ⁻⁴	0.92·10 ⁻⁴	- 8.0
1.00·10 ⁻³	3.00·10 ⁻⁴	2.85·10 ⁻⁴	1.00·10 ⁻⁴	0.93·10 ⁻⁴	- 7.0
5.00·10 ⁻³	5.00·10 ⁻⁴	5.20·10 ⁻⁴	1.00·10 ⁻⁴	no wave	—
1.00·10 ⁻³	2.00·10 ⁻⁴	1.85·10 ⁻⁴	2.00·10 ⁻⁴	2.13·10 ⁻⁴	+ 6.5
1.00·10 ⁻³	2.00·10 ⁻⁴	2.15·10 ⁻⁴	3.00·10 ⁻⁴	2.75·10 ⁻⁴	- 8.3

TABLE II
SEPARATION AND DETERMINATION OF ALUMINUM - GALLIUM MIXTURES

Mixture No.	Aluminum(moles/l)		Gallium(moles/l)		% error
	Taken	Found	Taken	Found	
1	5.00·10 ⁻⁵	5.00·10 ⁻⁵	1.00·10 ⁻⁵	1.00·10 ⁻⁵	± 0
2	1.00·10 ⁻⁴	1.08·10 ⁻⁴	1.00·10 ⁻⁵	0.92·10 ⁻⁵	- 8
3	1.00·10 ⁻⁴	1.02·10 ⁻⁴	1.00·10 ⁻⁴	1.05·10 ⁻⁴	+ 5
4	1.00·10 ⁻⁴	0.54·10 ⁻⁴	1.00·10 ⁻³	0.96·10 ⁻³	- 4
5	1.00·10 ⁻³	0.89·10 ⁻³	1.00·10 ⁻⁵	1.09·10 ⁻⁵	+ 9
6	1.00·10 ⁻³	0.48·10 ⁻³	1.00·10 ⁻⁴	1.10·10 ⁻⁴	+ 10
7	1.00·10 ⁻³	0.89·10 ⁻³	1.00·10 ⁻³	0.98·10 ⁻³	- 2

anomalous wave appearing at -0.9 V in the aluminum-SGY system. This wave does not affect the diffusion currents of the two more positive waves, nor does it affect the third gallium wave directly. However, when the aluminum conc. is much greater than that of gallium, the diffusion current of the anomalous wave masks that of the third gallium wave. For the mixture of $5 \cdot 10^{-4}$ M aluminum and $1 \cdot 10^{-5}$ M gallium, the diffusion current of the third wave is too small for accurate measurement. This third wave failed to appear for $1 \cdot 10^{-4}$ M gallium in the presence of $5 \cdot 10^{-3}$ M SGY. (Fig. 2).

Separation and determination of mixtures of aluminum and gallium

Since the simultaneous determination of aluminum and gallium is limited to mixtures in which the ratio of aluminum to gallium does not exceed 5 to 1, a simple method of separating the cations before their polarographic determination was investigated. The method used, developed by SWIFT¹⁰, depends upon the fact that gallium(III) chloride is soluble in diethyl ether while aluminum chloride is not. Mixtures of aluminum and gallium were prepared in 6 N hydrochloric acid. Volumes of 100 ml were extracted twice with 50 ml cold diethyl ether and twice with 40 ml ether. The ether portions were combined and extracted with 30 ml 3 N hydrochloric acid, which was prepared from purified hydrochloric acid. This final aqueous layer was combined with the other aqueous portion containing the aluminum. To the ether layers was added 5 ml distilled water and the ethereal and aqueous layers were evaporated almost to dryness. The respective residues were used in preparing the sample solutions to be polarographed. The concentrations of the metal ions were determined by means of the appropriate calibration curve. Typical results for such determinations are given in Table II.

The determination of gallium in these mixtures is satisfactory, but the determination of aluminum is poor. Further investigation of the procedure was made in an effort to improve the determination of aluminum, but without success.

Determination of aluminum and gallium in an aluminum alloy

The alloy used was from the National Bureau of Standards, Sample 85B, Aluminum Alloy (wrought), and contained 93.308% aluminum and 0.019% gallium. Other constituents of the alloy were copper, magnesium, manganese, iron, silicon, nickel, zinc, titanium, lead, and vanadium. All constituents except vanadium were present in larger quantity than gallium. Copper, iron, nickel, zinc, titanium, and lead were removed by reduction of a solution of the alloy at a mercury cathode at a potential of -1.1 to -1.2 V.

The alloy was first treated with 40 ml 1:1 hydrochloric acid and the remaining black residue was dissolved with 20 ml 6% hydrogen peroxide resulting in a clear, bright green solution. The solution was heated to remove excess hydrogen peroxide and was transferred to the electrolysis vessel. The solution was electrolyzed for 20-, 20-, 20-, 30-, and 30-min intervals at a stirred mercury cathode. The solution was then evaporated to 50 ml. An aliquot of this solution was used to prepare a sample solution which was approximately $1.4 \cdot 10^{-4}$ M aluminum. At this concentration of aluminum, the concentrations of interfering ions, including gallium, were negligible. The alu-

minimum concentration was determined from the resulting polarogram and the appropriate calibration curve.

Another aliquot of the electrolyzed solution was extracted with cold diethyl ether as previously described. A sample solution was prepared for the polarographic determination of gallium from the residue of the combined ethereal layers. The concentration of gallium in the sample solution was of the order of $10^{-5} M$.

The aluminum and gallium content of three samples of the alloy was determined by this method, and the results are given in Table III.

TABLE III
ALUMINUM AND GALLIUM DETERMINATIONS IN STANDARD ALLOY

Sample grams	Aluminum		% Error	Gallium		% Error
	mg taken	mg found		mg taken	mg found	
1.0025	935.4	979.0	+ 4.6	0.190	0.175	- 7.9
1.0053	938.0	904.5	- 3.6	0.191	0.208	+ 8.9
1.0042	937.0	898.0	- 4.2	0.191	0.205	+ 7.3
		Average	± 4.1		Average	± 8.0

Mixtures of aluminum, gallium, and indium

Preliminary investigations indicate that these metals can be determined over a limited concentration range from polarograms of the mixtures. A polarogram of the indium-SGY system shows two waves with essentially the same half-wave potentials as for the aluminum-SGY and gallium-SGY systems. However, a third wave appears at a half-wave potential of $-0.64 V$ which is the half-wave potential of indium reduced in the absence of dye. In the presence of a three-fold excess of dye, the diffusion current of the third wave is a linear function of indium concentration.

Mixtures of aluminum, gallium, and indium can be determined if the unreacted SGY present exceeds the total metal ion concentration three-fold or more. The reduction of such a mixture of metal ions and SGY produces four polarographic waves. The gallium concentration is determined from the fourth (most negative) wave; the indium concentration from the third wave; and the aluminum concentration from the second wave after subtracting the contributions of the other two metal chelates from the total diffusion current.

ACKNOWLEDGEMENT

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SUMMARY

Methods have been described for determining mixtures of aluminum and gallium when the ions are present in approximately the same concentration and when the concentration of aluminum exceeds the concentration of gallium by at least a factor of five. The average error of the determination of aluminum is ± 4 to 8% and that of gallium is ± 6 to 8% .

RÉSUMÉ

Une méthode est proposée pour le dosage polarographique de l'aluminium et du gallium, en présence l'un de l'autre. Erreur moyenne: ± 4 à 8% pour l'aluminium et ± 6 à 8% pour le gallium.

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ZUSAMMENFASSUNG

Es wird eine polarographische Methode beschrieben, mit welcher Aluminium und Gallium nebeneinander bestimmt werden können. Mittlerer Fehler für Aluminium: ± 4 bis 8%, für Gallium: ± 6 bis 8%.

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EXTRACTION OF ZINC WITH TRI(ISO-OCTYL)AMINE IN METHYL ISOBUTYL KETONE AND COLORIMETRIC DETERMINATION WITH ZINCON IN THE ORGANIC PHASE*

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The aim of this investigation was to develop a colorimetric procedure for zinc after extraction from many interfering ions with an organic solution of a long chain aliphatic or aromatic amine. The effect of acid concentration in the aqueous phase and the time required for extraction were studied. The optimum conditions of basicity and time for the development of full, stable color were determined. The data thus obtained enabled a satisfactory colorimetric procedure for the determination of zinc *in situ* after extraction from aqueous solution to be established.

MAHLMAN, LEDDICOTTE and MOORE¹ found that methyldioctylamine and tribenzylamine are efficient extractants for zinc in hydrochloric acid solutions. The amines were dissolved in xylene, trichloroethylene and chloroform. Methyldioctylamine 8% (w/v) in trichloroethylene extracts zinc quantitatively from solutions containing hydrochloric acid above 3.0 *N*. Tribenzylamine 5% (w/v) in chloroform extracts less than threefourths of the zinc from solutions above 2.0 *N* in hydrochloric acid. MOORE², in using 5% (w/v) tri(iso-octyl)amine in xylene and methyl isobutyl ketone for the extraction of uranium and plutonium, noted that zinc would be extracted also, along with other elements that form anionic chloride complexes.

Dithizone (diphenylthiocarbazon) extractions of heavy metals, including zinc, from a water phase into chloroform or carbon tetrachloride have become standard

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practice in the determination of such metals. However, dithizone is not selective and solutions of the reagent and its salts are very unstable. These characteristics of the reagent, along with the necessity of using very pure reagents and water, are disadvantages in dithizone determinations³. RUSH AND YOE⁴ found that 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene (Zincon) gave a dark blue precipitate (blue solution at high dilution) with zinc and developed a colorimetric method for zinc and copper in the presence of each other. An anion-exchange resin was used to separate zinc from a large number of common metal ions. The large amount of time required for such an ion-exchange separation is a disadvantage.

APPARATUS AND REAGENTS

Spectrophotometer and colorimeter

Preliminary studies were done using a Beckman Model DU quartz spectrophotometer employing 1-cm, corex-glass, absorption cells. A Bausch and Lomb Spectronic 20 colorimeter with one-half inch (1.33 cm) cylindrical cells was used for subsequent work.

Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene) solution

Zincon solutions were prepared by dissolving 0.130 g of finely powdered Zincon in 2 ml of 1*N* sodium hydroxide and diluting to 100 ml with 95% ethanol. This gives a solution which is 0.002 *M*, based on a purity of 68% for the reagent. Zincon was obtained from LaMotte Chemical Products Co., Baltimore, Maryland. A fresh solution should be prepared weekly.

Standard zinc solutions

A standard zinc solution was prepared by dissolving 0.2500 g of reagent grade zinc metal in 1 ml of conc. hydrochloric acid and diluting to 250 ml with deionized water. This gives a solution containing 1000 μg of zinc per ml. A solution containing 100 μg of zinc per ml was prepared by diluting 10.0 ml of the stock solution to 100 ml with deionized water.

Tri(iso-octyl)amine-methyl isobutyl ketone

A solution containing 5% (w/v) tri(iso-octyl)amine in methyl isobutyl ketone was prepared. All organic solvents were practical grade and were used without further purification. All aqueous solutions were prepared from reagent grade chemicals and using deionized water which was prepared by passing ordinary distilled water through a bed of Amberlite MB-3 ion-exchange resin.

EXPERIMENTAL

Extraction of zinc from hydrochloric acid solutions with various amines in organic solvents

The percent of extraction of zinc from aqueous solutions of various hydrochloric acid concentrations with methyldioctylamine and tri(iso-octyl)amine in methyl

TABLE I
EXTRACTION OF ZINC WITH METHYLDIOCTYLAMINE AND
TRI(ISO-OCTYL)AMINE IN METHYL ISOBUTYL KETONE AS A
FUNCTION OF HYDROCHLORIC ACID CONCENTRATION

HCl, <i>N</i>	% Zinc extracted with various extractants	
	Methyldioctylamine ^a	Tri(iso-octyl)amine ^b
1.0	92.00	100.00
2.0	100.00	100.00
3.0	100.00	97.75
4.0	95.50	100.00
5.0	94.25	100.00

^a 8% (w/v) methyldioctylamine in methyl isobutyl ketone.

^b 5% (w/v) tri(iso-octyl)amine in methyl isobutyl ketone.

isobutyl ketone is shown in Table I. Solutions containing 100 μg of zinc in 5.0 ml of aqueous phase were shaken with 10.0 ml of the amine solution for 3 min at room temperature. The amount of zinc remaining in the aqueous phase after extraction was determined colorimetrically using the procedure developed by RUSH AND YOE⁴.

Although both methyldioctylamine and tri(iso-octyl)amine extract zinc quantitatively from hydrochloric acid solutions, a 5% (w/v) solution of the latter amine in methyl isobutyl ketone was chosen for all subsequent study, since it is less expensive and obtained more easily. Non-equilibrated organic phases were used in all extractions. A 2.0 *N* concentration of hydrochloric acid gave sufficient acid to form the extractable anionic zinc complex and to obtain efficient extraction even though acid is extracted by the tertiary amine-organic solvent phase.

The extraction of zinc as a function of extraction time at 25° is shown in Table II. The amount of zinc remaining in the aqueous phase after extraction was determined colorimetrically as before.

While the extraction of zinc is shown in Table II to be quantitative after 1 min of shaking, it was found later that 3 min were required to remove all of the zinc from a solution containing large quantities of magnesium.

TABLE II
EXTRACTION OF ZINC FROM 2.0 *N* HYDROCHLORIC ACID
WITH 5% TRI(ISO-OCTYL)AMINE-METHYL ISOBUTYL
KETONE AS A FUNCTION OF EXTRACTION TIME

Extraction time (min)	Zinc extracted (%)
0.5	98.75
1.0	100.00
2.0	100.00
3.0	100.00

Extraction and colorimetric determination of zinc in situ

Attempts were made to correlate the determination of zinc in the organic phase with Zincon reagent to the determination in the aqueous phase. The reagents and the ketone phase from the extraction step were made to form a single phase by dilution with 95% ethanol. A homogeneous solution was observed, but inconsistent absorbancies were noted for replicate determinations on solutions containing known zinc concentrations. The difficulties seemed to lie in the buffer solution used. In order to

TABLE III
ABSORBANCY AS A FUNCTION OF THE POTASSIUM
HYDROXIDE CONCENTRATION^a

KOH, <i>N</i>	Absorbancy		
0.10	0.568	0.570	0.570
0.20	0.277	0.277	0.274
0.30	0.139	0.128	0.131
0.40	0.073	0.068	0.080
0.50	0.053	0.046	0.066

^a Absorbancies of solutions containing 2 μg of zinc per ml measured at 620 $m\mu$ against a reagent blank.

surmount these difficulties, various volumes of 5.0 *N* potassium hydroxide were added to the ketone layer containing the zinc with no attempt to buffer the solutions. The effect of the potassium hydroxide concentration in the final 50-ml volume on the absorbancy of a series of solutions containing the same amount of zinc is shown in Table III. Solutions whose final concentration were 0.10 *N* in potassium hydroxide gave the maximum absorbancies. For this reason and because solutions treated in this manner gave reproducible values of absorbancy, this concentration of potassium hydroxide was adopted in the final procedure.

In order to determine the length of time required for full color development and the stability of the color, a time study was carried out: Table IV. The time was measured in min after mixing and the absorbancy was measured at 620 *mμ* against a reagent blank. The absorbancy of the blank became constant immediately, but full color development required 8 min. The absorbancy increased only 2% after standing for 24 h.

TABLE IV
ABSORBANCY AS A FUNCTION OF TIME AFTER MIXING^a

<i>Time (min)</i>	<i>Absorbancy</i>	<i>Time (min)</i>	<i>Absorbancy</i>
1.0	0.250	14.0	0.560
2.0	0.368	16.0	0.560
3.0	0.455	18.0	0.560
4.0	0.510	20.0	0.560
5.0	0.539	25.0	0.560
6.0	0.545	30.0	0.560
7.0	0.555	35.0	0.560
8.0	0.560	40.0	0.560
9.0	0.560	45.0	0.560
10.0	0.560	50.0	0.560
11.0	0.560	55.0	0.560
12.0	0.560	60.0	0.560

^a Absorbancy of a solution containing 100 μg of zinc measured at 620 *mμ* against a reagent blank.

RECOMMENDED PROCEDURES

Calibration curve

To suitable aliquot portions of a standard zinc solution, add 1.0 ml of 10 *N* hydrochloric acid and enough water to give a total volume of 5.0 ml. Shake with 10.0 ml of 5% (w/v) tri(iso-octyl)amine-methyl isobutyl ketone in a 30-ml separatory funnel for 3 min. Remove and discard the aqueous phase. Dry the stem of the funnel with a strip of filter paper. Drain the ketone layer into a 50-ml volumetric flask. Add 5.0 ml of 1.0 *N* potassium hydroxide, 5.0 ml of methyl isobutyl ketone, and 3.0 ml of Zincon solution. Dilute to the mark with 95% ethanol and mix thoroughly. After 8 min standing, measure the absorbancy at 620 *mμ* against a reagent blank. Plot absorbancies against concentration expressed as μg of zinc per ml.

Procedure for magnesium-base alloys

Dissolve a suitable size sample in dilute hydrochloric acid and dilute to a known

volume. Transfer a suitable aliquot portion to a 30-ml separatory funnel. Add 1.0 ml of 10 *N* hydrochloric acid and enough water to give a total volume of 5.0 ml. Extract, develop the color, and measure as described under *calibration curve*. Determine the zinc concentration from a calibration curve.

Procedure for aluminum-base alloys

To the sample add 3 ml of 19 *N* sodium hydroxide. After 3 min, add 3 ml of water. After the reaction subsides, heat the solution to boiling and boil for 3 min. Cool to room temperature and acidify with hydrochloric acid. Transfer the solution to a volumetric flask and dilute to a known volume. Transfer a 4.0-ml aliquot to a 30-ml separatory funnel and add 1.0 ml of 10 *N* hydrochloric acid. Shake for 2 min with 10.0 ml of 5% (w/v) tri(iso-octyl)amine–methyl isobutyl ketone. Remove and discard the aqueous phase. Wash the ketone layer with a fresh 5.0-ml portion of 2.0 *N* hydrochloric acid and discard the aqueous phase. Back-extract the zinc by shaking the ketone layer for 1 min with two 5.0-ml portions of 0.05 *N* hydrochloric acid. Combine the aqueous phases and transfer a 4.0-ml aliquot to a clean 30-ml separatory funnel. Add 1.0 ml of 10 *N* hydrochloric acid. Extract for 2 min with 10.0 ml of 5% (w/v) tri(iso-octyl)amine–methyl isobutyl ketone. Remove and discard the aqueous phase. Dry the stem of the funnel with a strip of filter paper. Transfer the ketone layer to a 50-ml volumetric flask. Proceed with the color development and measurement as described under *calibration curve*. Determine the zinc concentration from a calibration curve.

DISCUSSION

Nature of the extraction

Zinc is extracted by tri(iso-octyl)amine–methyl isobutyl ketone as the chloroanionic complexes trichlorozincate(II) or tetrachlorozincate(II). The extraction probably proceeds through hydrogen-bonding and ion association between the negatively-charged $ZnCl_3^-$ or $ZnCl_4^{2-}$ and the tri(iso-octyl)ammonium ion or the solvonium ion of the ketone.

Chromogenic system

The potassium hydroxide necessary to give full color development probably slowly converts the extracted ion association complex to the zinc(II) ion, which then reacts with the Zincon.

The actual pH of the solutions at the time of color development was not ascertained. The potassium hydroxide concentration for best results is given as 0.1 *N*, but of necessity the actual concentration is less than this, since some of the hydroxide reacts with co-extracted acid.

Following AYRES' treatment⁵, the concentration range of best accuracy extends from 0.6 to 3.0 μg of zinc per ml when using the 1.33-cm cylindrical cells supplied with the colorimeter. This corresponds to from 30 to 150 μg of zinc in the initial 5.0 ml sample volume. Two solutions containing 0.02 μg of zinc per ml gave an average absorbancy of 0.005 unit, which gives about 0.004 μg per ml as the minimum detection limit. The method gives 3.39% relative analysis error per 1% absolute photometric error. The molar absorbancy index, calculated on the basis of the molarity of the zinc solution, is 14,000 at 620 $m\mu$.

The blank value is rather large (usually about 0.14 absorbancy unit) because the reagent absorbs to some extent at 620 $m\mu$ and because exhaustive purifications of the reagents were not attempted. An absorbancy *versus* wavelength curve, similar to the curve given by RUSH AND YOE⁴, was obtained for solutions analyzed by the recommended procedure.

Effect of diverse ions

The effect of added diverse ions on the analysis of zinc solutions by the recommended procedure is shown in Table V. Copper(II) is by far the most serious interferent.

TABLE V
EFFECT OF DIVERSE IONS ON THE ANALYSIS OF ZINC SOLUTIONS^a

Element	Amount present (μg total)	Zinc recovered (%)	Tolerance limit (μg total)
Al(III)	10,000	109	1,100
Cd(II)	1,000 ^b		
Cr(III)	10,000	57	230
Cr(VI)	1,000	102	500
Co(II)	3,800 ^c		
Cu(II)	250	199	
	100	134	< 10
Fe(II)	500	84	30
Fe(III)	1,000	74	40
Pb(II)	2,000	102	1,000
Mn(II)	10,000	102	5,000
Mo(VI)	1,000	100	> 1,000
Ni(II)	10,000	88	830
Sn(IV)	1,000	108	120
V(V)	1,000	115	70

^a Each solution contained 100 μg of zinc.

^b Solutions containing Cd(II) gave insoluble precipitates.

^c Solutions containing Co(II) were cloudy.

TABLE VI
ZINC ANALYSES ON NATIONAL BUREAU OF STANDARDS ALLOYS

Sample	Zinc value, %		
	Certified	Found	
Magnesium-base alloy 171	1.05 ± 0.01^a	1.00 1.06	
		1.04 0.98	
		1.02 1.06	
		Average	1.03
		S. D.	0.03
Aluminum-base alloy 87	0.077 ± 0.007^a	0.075 0.078	
		0.075 0.080	
		0.072 0.076	
		Average	0.076
		S. D.	0.003

^a Values given are mean of certificate values, with associated standard deviation.

The interference of copper and of many other ions can be removed, or at least minimized, by the back-extraction of zinc into 0.05 *N* hydrochloric acid and re-extraction. Cadmium(II) and cobalt(II) tend to give precipitates in the final solutions, indicating that these ions are also extracted, but that they are insoluble at the final pH. Many interferences can be removed by prior extractions. For instance, chromium(VI) is completely extracted from solutions 1 *N* in hydrochloric acid with methyl isobutyl ketone^{6,7}, and iron (III) from solutions 5.0 *N* in hydrochloric acid with methyl isobutyl ketone⁸ or from solutions 8.0 *N* in hydrochloric acid with isopropyl ether¹.

Analysis of National Bureau of Standards Alloys

Analysis of two National Bureau of Standards samples of magnesium- and aluminum-base alloys was carried out using a Bausch and Lomb Spectronic 20 colorimeter with one-half inch (1.33 cm) cylindrical cells. The results of the analyses are given in Table VI.

SUMMARY

A study was made of the extraction of zinc from hydrochloric acid solutions with solutions of methyldiethylamine and tri(iso-octyl)amine in methyl isobutyl ketone. Quantitative extraction was accomplished from 2 *N* hydrochloric acid with 5% (w/v) tri(iso-octyl)amine-methyl isobutyl ketone. A procedure was developed for the colorimetric determination of zinc in the organic phase after extraction using 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene (Zincon).

RÉSUMÉ

Une étude a été effectuée sur l'extraction du zinc, en solution chlorhydrique, au moyen de solutions de méthyldiéthylamine et de tri(iso-octyl)amine dans la méthylisobutylcétone. Une méthode est proposée pour le dosage colorimétrique du zinc au moyen de zincon(2-carboxy-2'-hydroxy-5'-sulfo-formazylbenzène).

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Extraktion von Zink aus salzsaurer Lösung mit Hilfe von Methyl-diäthylamin oder Tri-(iso-octyl)-amin in Methylisobutylketon. Die quantitative Bestimmung des Zinks im organischen Lösungsmittel erfolgt colorimetrisch mit Zincon (2-Carboxy-2'-hydroxy-5'-sulfo-formazyl-benzol).

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THE DETERMINATION OF NITROGEN IN METALS BY ISOTOPE DILUTION*

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INTRODUCTION

Isotope dilution procedures have been developed for the determination of oxygen in some metals by KIRSHENBAUM, *et al.*¹⁻⁴ The technique was also extended to the determination of carbon in steels and related metals by HICKAM⁵. In general, the basis of these procedures is one of vacuum heating or vacuum fusion of the samples along with a 'master alloy' containing the enriched isotopic tracer. KIRSHENBAUM, HINDIN and GROSSE used the isotope dilution technique to determine the nitrogen content of organic compounds⁶, the method developed involving principles employed in the classical Dumas determination. Generally speaking, the procedures described by these authors have not been applied to sample material that contained very small amounts of the impurity being determined in spite of the fact that in principal the technique should be amenable to such assays.

Despite these applications of the general techniques to the assay of the above non-metallic elements, no similar approach has been applied to the problem of assaying metals for their nitrogen content, especially in the very low concentration range. An attempt in these laboratories several years ago to develop a 'master alloy'-vacuum fusion procedure for nitrogen determinations failed to give satisfactory results. In a general sense, this procedure is not simple nor is it very convenient. Furthermore, the time required to do an analysis is long and one has all the problems associated with the vacuum fusion procedure. In spite of the simplicity of the Dumas procedure which makes it an enticing one, it is not applicable to metal systems.

Two principal methods are used to determine nitrogen in metals, the vacuum fusion method and the Kjeldahl method. Many different variations of the general procedures are used primarily involving the final handling of the evolved nitrogen gas. In vacuum fusion procedures, if the only gas evolved is nitrogen, a simple volumetric measurement is sufficient to obtain the desired result⁷. When gas mixtures are evolved, some analytical procedure must also be employed which will give proper results with small amounts of gas sample. Mass spectrometric methods have been used for such analyses⁸. In the Kjeldahl method, after the samples have been dissolved and the ammonia separated from the solution, some appropriate titration procedure⁹ or photometric method is generally applied¹⁰.

The isotope dilution method for nitrogen described in this paper was developed in

* Contribution No. 719. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

order to determine trace amounts of nitrogen in metals more conveniently than by vacuum fusion and more accurately and precisely than by the Kjeldahl method. In principle, the method consists of adding a known amount of ammonium sulfate of known ^{15}N content, which is different from normal, to a weighed amount of metal, dissolving the metal in some appropriate acid and determining the final amount of ^{15}N in the resultant mixture. The amount of nitrogen in the metal can be calculated from this information. Except for the isotope determination with the mass spectrometer, all of the operations involved in handling the samples are classical ones for which chemists have a long standing tradition. Quantitative manipulation of small amounts of gas under high vacuum conditions are unnecessary.

EXPERIMENTAL PROCEDURE

Five to seven grams of the metal sample are weighed to one-tenth of a mg. At least three tenths of a mequiv. of tracer ammonium ion is added from a weight buret. The sample is then dissolved in as little acid as possible, using conventional dissolution procedures where they apply to the various metals. The solution is transferred to a Kjeldahl flask, made alkaline and distilled for 3 min into 10 ml of 0.1 *N* hydrochloric acid. The NH_4^+ in the distillate is then oxidized to N_2 by alkaline sodium hypobromite in an appropriate gas generating and collecting apparatus¹¹. The gas is then introduced into a dual-collector, isotope-ratio mass spectrometer and assayed for ^{15}N by determining the $29^+/28^+$ ion current ratio. The $^{40}\text{Ar}^+$ ion peak in the sample gas is monitored to check for contamination due to air, in which case proper corrections are applied¹².

CALCULATIONS

The general equation used to calculate the percent nitrogen in the metal sample is:

$$\% \text{ N} = \frac{(14.008) (\text{mequiv. tracer } \text{NH}_4^+)}{\text{mg of sample}} \times \frac{\text{at. } \% \text{ tracer } ^{15}\text{N} - \text{at. } \% \text{ mixture } ^{15}\text{N}}{\text{at. } \% \text{ mixture } ^{15}\text{N} - \text{at. } \% \text{ sample } ^{15}\text{N}} \times 100 \quad (1)$$

where a value of 0.3649 is used for the "at. % sample ^{15}N ". The "at. % ^{15}N " in the sample gas is calculated by using the formula:

$$\text{at. } \% ^{15}\text{N} = \frac{R}{2 + R} \times 100 \quad \dots \dots \dots (2)$$

where *R* is the $29^+/28^+$ ion current ratio obtained from the mass spectrometer. This ratio is corrected for air leaks if necessary, and for the background of the mass spectrometer and then normalized by comparing with a standard nitrogen tank sample whose absolute isotopic abundances have been previously determined¹³.

RESULTS

A variety of metals were obtained from the Ames Laboratory of the U. S. Atomic Energy Commission and from several commercial producers. Where previous analyses were available, comparisons were made between this procedure and ones previously employed. Unfortunately, no information regarding the precision of most of the

independent analyses was available. However, the precision of the results of the present study are reported here as an indication of what might be expected from the isotope dilution procedure. Tables I and II contain summaries of the results obtained on a variety of metals and alloys. In all cases cited, hydrochloric acid was the principal reagent used to dissolve the sample. Variations involving the addition of other reagents were applied in appropriate cases. The determinations of the nitrogen content in reagent grade conc. hydrochloric acid is also reported in Table I.

TABLE I

DETERMINATION OF THE NITROGEN CONTENT OF NON-FERROUS METALS AND ALLOYS

<i>Metal sample</i>	<i>Previous analysis in p.p.m. nitrogen ^a</i>	<i>Isotope dilution in p.p.m. nitrogen</i>	<i>No. of determs. ^b</i>	<i>Deviation \pm %</i>
Thorium ^c	100	57	8	3
Lanthanum 1 ^c	—	271	5	5
Lanthanum 2 ^c	—	154	5	8
Yttrium XC-123t ^c	385	164	3	8
Yttrium XC-123b ^c	332	248	5	6
Yttrium XC-120b ^c	138	87	6	9
Yttrium XC-128b ^c	87	114	3	5
Yttrium XC-129t ^c	55	88	3	4
Yttrium XC-119b ^c	107	95	4	9
Yttrium C-174-B-t ^c	214	254	3	2
Nichrome, heat 7444 ^d	265 \pm 15 (Kjeldahl) 237 \pm 44 (Vac. fusion)	387	3	0.5
Ferrotitanium, 70% Ti ^e	1300	1366	4	2
Ferrotitanium, 30% Ti ^e	210	150	4	12
Ferromanganese, med C ^e	460	497	4	2
Manganese, electrolytic, nitrided, 94% Mn ^e	5.16%	5.69%	4	1
Ferrochrome, low C, 71% Cr ^e	770	848	4	12
Chromium, low C, 97.5% Cr ^e	370	408	4	6
Chromium, electrolytic, 97.5% Cr ^e	50	29	4	6
Titanium 99.8% Ti ^e	60	77	1	—
Aluminum 40 ^e				
Vanadium 60 ^e	350	353	3	6
Vanadium (crystal bar) CO-2-108 ^e	150	194	3	4
Concentrated hydrochloric acid ^f	3	2.4	2	6

^a Analytical results obtained from source of samples.

^b Each determination represents a separate portion of the sample treated individually. No aliquots of solutions were taken.

^c Ames Laboratory of the U. S. Atomic Energy Commission, Ames, Iowa.

^d The Driver-Harris Co., Harrison, New Jersey.

^e Electrometallurgical Co., Niagara Falls, New York.

^f E. I. Dupont de Nemours & Co., Wilmington, Delaware.

TABLE II
DETERMINATION OF THE NITROGEN CONTENT OF FERROUS METALS AND ALLOYS

<i>Metal sample</i>	<i>Previous analysis in p.p.m. nitrogen^a</i>	<i>Isotope dilution in p.p.m. nitrogen</i>	<i>No. of determs.^b</i>	<i>Deviation \pm %</i>
Steel A9 ^c	2400	2415	3	2
Steel 84 ^c	200	180	2	12
Steel A2a ^c	7500	7469	10	0.5
Cast Iron 8h ^d	170	191	2	5
Steel I-335 ^e	8 (v.f.)	2	3	3
Steel 1020 ^e	24 (v.f.)	48	3	0.6
Steel E ^e	4 (v.f.)	52	2	5
Steel RH1081 ^e	20 (v.f.)	40	3	5
Steel 1296-1 ^e	50 (v.f.)	42	3	7
Steel RH836 ^e	34 (v.f.)	61	3	2
Steel 154082 ^e	64 (v.f.)	72	2	3
Steel 84997 ^e	172	172	3	1
Steel 92171 ^e	226	247	3	1
Steel J-3245 ^f	4 (v.f.)	35	3	9
Steel J-3049 ^f	4 (v.f.)	29	3	3
Steel K-4115-2 ^f	430	427	3	1.2
Steel K-4116-1 ^f	70 (v.f.)	71	3	9.4
Steel K-4320-1 ^f	140	107	4	7.4
Steel K-4323-1 ^f	3900	3996	3	1.8
Steel K-4329-1 ^f	2200	2277	3	0.6
Steel K-4331-1 ^f	1600	1749	3	2
Steel K-4332-1 ^f	2100	2201	3	1.5
Steel K-4335-1 ^f	70 (v.f.)	79	3	1.4
Iron, electrolytic ^g	—	31	3	6
Iron, electrolytic, fired in moist H ₂ ^g	—	22	3	2

v.f. = vacuum fusion.

^a Analytical results obtained from supplier of samples.

^b Each determination represents a separate portion of the sample treated individually. No aliquots of solutions were taken.

^c Ford Motor Co. Research Laboratory, Dearborn, Michigan.

^d National Bureau of Standard, Washington, D. C.

^e Jones and Laughlin Steel Corp., Pittsburg, Pa.

^f U.S. Steel Corp., Pittsburgh, Pa.

^g The G. Fredrich Smith Chemical Co., Columbus, Ohio.

DISCUSSION OF FACTORS AFFECTING RESULTS

In a strict sense, any variation in the isotopic abundance of an impurity in a material, compared with the isotopic abundance in the principal source of the impurity may introduce errors into an analytical procedure based on isotope dilution. In the case of a nitrogen impurity in metals, the principal source of contamination is the atmosphere or chemicals used in nitriding operations. Thus the isotopic abundance of ¹⁵N in the metals should be expected to be that of the atmosphere or not very far from it. Examination of equation (1) indicates that if the ¹⁵N content of the tracer is at least ten-fold enriched over that of the atmosphere, then under the ordinary conditions of this procedure, variation of as much as $\pm 3\%$ in the isotope abundance of nitrogen from the metal samples will not introduce an error greater

than $\pm 0.4\%$ in the final result. As a check on what variations may reasonably be expected in representative materials, the ^{15}N abundance was measured in reagent grade ammonium sulphate and in the hydrolysates of a $\text{Mg}_3\text{N}_2\text{-MgO}$ mixture made by burning Mg in air, of thorium nitride in the presence of a large excess of thorium metal and in titanium nitride. These nitrides were prepared by the reaction of air, nitrogen or ammonia with the metal involved. The absolute ^{15}N abundance for these materials was found to vary from 0.365 to 0.375 at. %; therefore, any error introduced into the determination from this source is negligible compared to other possible sources of errors.

The method described in this paper depends upon the conversion to NH_4^+ of all the nitrogen held as an impurity in a metal when the metal is dissolved in an acid. In discussions with several metallurgists*, the possible existence of free nitrogen in certain nitrided steels which were austenitic in character was cited. Also, the possibility of nitrogen-carbon combinations in metals of high carbon and nitrogen content was given. If the former is true, then N_2 gas might be liberated among the other gases when these metals are dissolved. In the latter case, hydrogen cyanide, complexed CN^- or amines formed as hydrolysis products might be expected to be present either in the evolved gases or in the solution.

A high nitrogen, austenitic type steel (A2a, Table II) was dissolved in hydrochloric acid and all the evolved gas collected. No free N_2 was detected in this gas by mass spectrometric methods. The gas from the same sample was passed through a solution of sodium hydroxide which was subsequently analysed for the presence of CN^- . No cyanide was detected in the alkali solution nor was any complexed cyanide found in the acid solution containing dissolved iron. Attempts to detect simple amines in gases evolved when solutions of this steel were made alkaline, failed. However, because the mass spectrometer is not too sensitive to these substances other corroborating experiments were performed. Dissolving this steel in H_2SO_4 followed by fuming to SO_3 in the conventional Kjeldahl manner resulted in nitrogen assays that were identical with those made when other acid solvents were used. Thus the presence of simple amines as products of reaction in materials similar to this particular steel is unlikely. Repetition of these experiments on other metal samples gave identical results. The weight of the evidence is that only NH_4^+ is produced when nitrogen-containing metals are dissolved in acids. On the basis of this evidence the isotope dilution method for assaying the nitrogen content of metals and alloys appears to be sound and reliable.

The Kjeldahl-type distillation indicated in the experimental procedure is not necessary but has many advantages. Because of the design of the apparatus employed, a small volume of solution was needed to oxidize the NH_4^+ solution to N_2 gas. Concentration of ammonia by distillation resulted in considerable time saving. It also served as a convenient means of reducing the amount of acid because the evolved ammonia was caught in 10 ml of 0.1 *N* hydrochloric acid. This greatly simplified the alkaline hypobromite oxidations. Separation of the ammonia from certain heavy metal ions also aided the oxidation step inasmuch as their presence causes undesirable side reactions, notably the production of gaseous O_2 which interferes with the mass spectrometry by decreasing instrument stability.

* Private Communication, members of Ames Laboratory Nuclear Metallurgy School, July 1-August 24, 1957, Iowa State College Ames, Iowa.

A ten-fold enriched ^{15}N tracer in the form of an ammonium sulfate solution was used in most of the work reported here. This was assayed by careful Kjeldahl titrations employing electrometric methods to determine the end-points. As a check, the solutions were also assayed by an isotope dilution method using as the standard, recrystallized, reagent-grade ammonium sulphate which had been compared with atmospheric nitrogen for its isotope abundance. Weighed amounts of vacuum dried crystals were mixed with a weighed amount of the tracer solution. Excellent agreement with the titrations were obtained in this manner.

Although tracers either enriched or depleted in ^{15}N were used during the course of the work, the enriched tracer gave more consistent and precise results. This was primarily because of the limit placed on any depleted material due to the small amount of ^{15}N existing in natural sources. The absolute abundance of ^{15}N in atmospheric nitrogen is 0.3649 at. % which gives a $29/28$ ratio of 0.007325. Ratio measurements considerably below this figure are difficult to make with great precision. On the other hand, employing a ten-fold enriched tracer gives a value for this ratio of about 0.073250 which can be easily measured to four significant figures thereby allowing for considerable improvement in the overall precision for the nitrogen analyses. It should be pointed out that when more highly concentrated tracers are employed a point of diminishing returns is reached because of the effect of the 30^+ ion current on the ^{15}N assays. For an approximately ten-fold enriched tracer, only the $29^+/28^+$ ratio must be measured. At greater ^{15}N concentrations the 30^+ ion current must also be measured, adding to the time consumed in making the measurement without contributing greater precision.

Ideally, half of the nitrogen in the mixture should come from the metal sample and half from the tracer. For a low-nitrogen impurity this would necessitate a prohibitively large sample. Using a ten-fold enriched tracer, very good precision was obtained when a nitrogen ratio of one part from the sample to fifteen parts from the tracer was attained. For less favorable dilutions, only the precision of the analysis suffered, since it was still possible to get an estimate of the N present. More precise results were then obtainable if warranted, by adjustment of the amount of sample taken.

In the outlined procedure, it was stated that three-tenths of a mequiv. of tracer ammonium ion was always added. This produced the minimum amount of nitrogen gas needed to give enough pressure in the sample system of the mass spectrometer used in the work. Thus the operator was always assured of enough gas to assay in the instrument. Some variation is reported here between results obtained by this method and those obtained by others. No reasons for these are apparent. It is the feeling of the authors that some of the questions involving the fate of nitrogen when metal samples are dissolved in acids has been clarified. No claim is made that exceptions to our findings cannot exist but the large variety of sample materials chosen and tested justifies confidence in the reported results. The discrepancy between these data and some of the samples previously analysed by the vacuum fusion technique is not surprising inasmuch as similar findings have been observed by a great number of workers.

With a few slight changes in the experimental procedure, the isotope dilution method as described here can be applied to many different types of nitrogen analyses in inorganic and organic compounds.

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The authors wish to acknowledge the fine cooperation of all the commercial laboratories listed in Tables I and II that supplied metal and alloy samples which had previously been analysed for nitrogen. The analytical group of the Ames Laboratory also deserves special mention.

SUMMARY

A wet chemical procedure for determining the amount of nitrogen in a metal or alloy has been developed which utilizes the isotope dilution technique. Ammonium sulfate, either enriched or depleted in ^{15}N , is added to the metal sample during solution procedures. Ammonium ions resulting from the hydrolysis of bound nitrogen in the metals mix with that of the tracer and the total is then oxidized to N_2 in which form the element is analyzed in the mass spectrometer. The method has been tested on a variety of metals and alloys including thorium, lanthanum, yttrium, titanium, chromium, manganese, various steels, nickel-chromium, ferrotitanium, ferromanganese and ferrochromium. The range of nitrogen in these materials was from 2 ppm to almost 6%. Average precision was generally better than $\pm 5\%$.

RÉSUMÉ

Une méthode par dilution isotopique est proposée pour le dosage de l'azote dans un métal ou dans un alliage. On ajoute à l'échantillon à analyser du sulfate d'ammonium avec une teneur en ^{15}N connue (et différente de la normale). Le total des ions ammonium (ceux qui ont été additionnés et ceux provenant de l'azote à doser) est oxydé en N_2 , que l'on analyse au spectromètre de masse

ZUSAMMENFASSUNG

Es wird ein Verfahren beschrieben zur Bestimmung von Stickstoff in Metallen und Legierungen durch Anwendung der Isotopen-Verdünnungsmethode. Zur Analysenprobe wird eine gemessene Menge Ammoniumsulfat mit bekanntem N^{15} Gehalt gegeben. Die Gesamtmenge der Ammonium-Ionen wird zu Stickstoff oxydiert und dieser im Massenspektrometer analysiert.

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Short Communications

Separation and micro determination of formaldehyde and methanol in excess azoalkanes, methylal and lower esters

Formaldehyde and methanol are major products in the gas phase photo-oxidation of methyl radicals. In kinetic work, with azomethane as a source of methyl radicals, the problem was to analyse both substances quantitatively in a 300-fold excess of azomethane.

All the methods described in the literature lead, in the aqueous phase, to hydrolysis of the azomethane producing formaldehyde and methyl hydrazine¹ and cannot therefore be used. It was found that the azomethane could be separated from the formaldehyde and methanol simply by blowing nitrogen through an aqueous solution of the mixture. Azomethane is removed quantitatively whereas formaldehyde and methanol are kept back.

The procedure described has been applied also to the separation of a few other substances which are of some interest to the gas kineticist and was successful in the case of azoethane, methylal, and esters like methyl formate.

A sample containing not more than 120 μg formaldehyde and 450 μg methanol in the presence of excess azomethane is dissolved in 2 ml water and placed in a convenient flask. Nitrogen which has been very carefully saturated with water is led through the solution for 10 min at room temperature by means of a capillary tube.

The saturation of nitrogen with water is attained by bubbling it through two wash bottles, the first containing hot water to ensure saturation.

Methanol is separated from formaldehyde by distillation in the presence of chromotropic acid and is determined as formaldehyde after oxidation². The formaldehyde content in the residue is then established by the method published by BRICKER AND VAIL³.

No attempt was made to determine how much formaldehyde and methanol could be retained by the water. However, in an experiment in which 120 μg formaldehyde and 450 μg methanol were present, formaldehyde was kept back quantitatively whereas about 3% of the methanol was removed by the stream of nitrogen.

In our specific experiments (to be published elsewhere) it was found necessary to trap the reaction products in a solution of 200 mg of trisodium salt of chromotropic acid instead of in pure water. The reagent acts purely as a buffer for acids present in the mixture which would otherwise cause hydrolysis of the azomethane. The distillation of the methanol is then carried out after acidifying the solution.

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¹ F. C. WHITMORE, *Organic Chemistry*, D. van Nostrand Co., New York 1951.

² R. N. BOOS, *Anal. Chem.*, 20 (1948) 964.

³ C. E. BRICKER AND W. A. VAIL, *Anal. Chem.*, 22 (1950) 720.

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Plasmocorinth B als Indikator bei komplexometrischen Titrationen

Seitdem die komplexometrische Titration entdeckt wurde¹ bedeutete das Auffinden eines entsprechenden Indikators ein ständiges Problem. Das Murexid entsprach den Erwartungen nicht: die Farbe des Überschlages ist nicht scharf und kann daher mit freiem Auge nicht gut beurteilt werden; deshalb scheint Murexid für einfache Bestimmungen in biologischen Flüssigkeiten nicht geeignet. Neuerdings wurden einige Naphthyl-azo-naphthalin Derivate als Indikatoren bei der Serumkalzium-Bestimmung mit Erfolg verwendet²⁻⁴.

YANAGISAWA⁵ und später KINGSLEY UND ROBNETT⁶ teilten eine kolorimetrische Bestimmung für Serumkalzium mittels des Farbstoffes Plasmocorinth B (Inabata Industry & Co., Ltd., Osaka, Japan) mit. Dieser Farbstoff ist dem neuerdings beschriebenen Ca-Indikatoren ähnlich mit dem Unterschied, dass dies ein Phenyl-azonaphthalin Derivat (Plasmocorinth B = Dinatrium Salz der 1-Oxy-4-chlorbenzol-(2-azo-2)-1,8-dioxynaphthalin-3,6-disulfonsäure) ist. Daher wurden Untersuchungen unter der Verwendung dieses Farbstoffes vorgenommen und es konnte festgestellt werden, dass er als Indikator für die komplexometrische Titration von Kalzium und Magnesium sehr gut geeignet ist.

In alkalischem Medium bildet das rote Plasmocorinth B einen farbigen Komplex mit Äthylendiamintetraessigsäure (EDTA); und zwar in der Anwesenheit von Natriumhydroxyd gibt es eine blau-violette, und in derjenigen von Ammoniumhydroxyd, eine

TABELLE I

WIRKUNG VERSCHIEDENER Ca, Mg UND EDTA MENGEN AUF DAS ABSORPTIONSMAXIMUM DES PLASMOCORINTH B

Die Konzentration der verwendeten Ca-, Mg- und EDTA-Lösungen wurde so gewählt, dass gleiche Volumen äquivalente Mengen enthalten sollen.

	10 mg % Plasmocorinth ml	0,5 N NaOH ml	NH ₄ - puffer* ml	0,001 M Ca ml	0,001 M Mg ml	0,001 M EDTA ml	Dest. wasser ml	E max. μμ
1.	I	—	—	—	—	—	11	546
2.	I	I	—	—	—	—	10	554
3.	I	I	—	2	—	—	8	546
4.	I	I	—	2	2	—	6	546
5.	I	I	—	—	—	I	9	572
6.	I	I	—	2	2	I	5	546
7.	I	I	—	2	2	3	3	572
8.	I	I	—	2	2	5	I	572
9.	I	—	I	—	—	—	10	550
10.	I	—	I	—	2	—	8	548
11.	I	—	I	2	2	—	6	548
12.	I	—	I	—	—	I	9	594
13.	I	—	I	2	2	I	5	548
14.	I	—	I	2	2	3	3	548
15.	I	—	I	2	2	5	I	594

* Die Zusammensetzung des HN₄-Puffers ist: 0.83 g NH₄Cl + 12 ml conc. NH₄OH + dest. Wasser ad 100 ml.

intensiv blaue Farbe. Wenn eine Ca und Mg enthaltende Lösung in der Anwesenheit von NaOH mit EDTA titriert wird, so reagiert das EDTA nach Bindung der äquivalenten Menge des Kalziums mit Plasmocorinth B; diese Reaktion wird durch die Anwesenheit von Mg nicht gestört. In der Anwesenheit von NH_4OH dagegen, bildet das Plasmocorinth B mit dem EDTA erst nach der gemeinsamen Bindung der äquivalenten Menge von Ca und Mg (Tabelle I). In erstem Falle kann durch die Zugabe von überschüssigem Ca, und in dem zweiten, durch diejenige von überschüssigem Ca oder Mg die ursprüngliche Farbe des Indikators zurückgewonnen werden. (Ähnlicherweise kann der labile Indikator-EDTA Komplex gespalten werden wenn das pH des Mediums herabgesetzt wird). In beiden Fällen ist die Farbe des Überschlages scharf; zwischen der eigenen Farbe des Indikators und derjenige des Plasmocorinth B-EDTA Komplexes besteht ein leicht beurteilbarer Unterschied (Fig. 1 und 2).

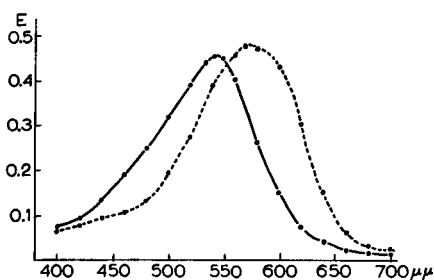


Fig. 1. Die Absorptionskurve des Plasmocorinth B und des Plasmocorinth B-EDTA Komplexes in NaOH-Medium. (— · — · — = Plasmocorinth B + NaOH + Ca + Mg, · · · · · = Plasmocorinth B + NaOH + Ca + Mg + überschüssiges EDTA).

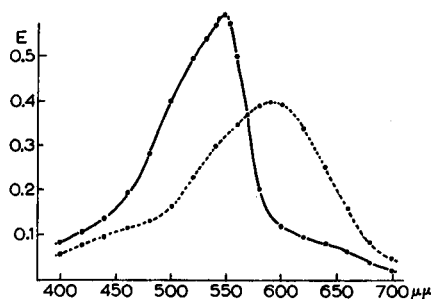


Fig. 2. Die Absorptionskurve des Plasmocorinth B und des Plasmocorinth B-EDTA Komplexes in NH_4OH -Medium. (— · — · — = Plasmocorinth B + NH_4OH + Ca + Mg, · · · · · = Plasmocorinth B + NH_4OH + Ca + Mg + überschüssiges EDTA).

Mit der Verwendung dieses Prinzips gelang es uns eine einfache Methode auszuarbeiten, mit welcher der Ca- und Mg-Gehalt des Serums, des Liquors und des Harns in kurzer Zeit genau bestimmt werden kann.

Verfasser sprechen der Firma Inabata Industry & Co., Ltd., ihren aufrichtigen Dank für die Überlassung des benötigten Plasmocorinth B aus.

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- 1 G. SCHWARZENBACH, W. BIEDERMANN UND F. BANGERTER, *Helv. Chim. Acta*, 29 (1946) 811.
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Received March 10th, 1959

REVUES DE LIVRE

Handbuch der Papierchromatographie. 2 Bände. Herausgegeben von DR. IVO M. HAIS und DR. KAREL MACEK, beide Forschungsinstitut für Pharmazie und Biochemie Prag. Uebersetzung nach der zweiten, überarbeiteten und erweiterten tschechischen Auflage von J. LIEBSTER, Prag.

Band I: Grundlagen und Technik. Unter Mitarbeit von 20 Fachwissenschaftlern. VEB Gustav Fischer Verlag, Jena 1958, mit 242 zum Teil farb. Abb. im Text. XXIV + 860 S. gr. 8°. Ganzleinen DM 58,40.

La chromatographie sur papier a déjà fait l'objet d'assez nombreux traités, écrits par d'éminents spécialistes. Aussi, la publication d'un livre nouveau dans ce domaine demande-t-elle bien de qualités à son auteur, si ce dernier désire obtenir quelque succès auprès du public.

Or, voici qu'un comité de vingt-deux savants tchécoslovaques a entrepris la préparation d'un traité de chromatographie sur papier, dans l'ambition que leur oeuvre, dépassant les limites d'un simple exposé théorique et pratique du sujet, puisse permettre aux chimistes non initiés de se familiariser avec les différentes techniques actuelles et leur offrir la possibilité de les appliquer sans trop de difficultés.

Ce but fort louable par ailleurs est-il atteint? Nous croyons pouvoir répondre oui. En effet, cet excellent ouvrage contient un choix très judicieux des méthodes les plus importantes au point de vue théorique et pratique. La bibliographie a été consultée jusqu'à la fin de 1955, mais les principales publications parues en 1956 y figurent également. De toute manière, un répertoire bibliographique complet fera l'objet d'un second volume annoncé pour le début 1960.

Après une brève introduction historique, un exposé, clair, sur la théorie de la méthode permet d'aborder les principes fondamentaux avec un minimum de formules mathématiques et d'une manière absolument satisfaisante. Vient ensuite le chapitre concernant la technique générale; les opérations sont décrites successivement dans le même ordre que lors de la préparation d'un chromatogramme. A la fin de la partie générale, l'on trouve encore deux petits chapitres consacrés à la chromatographie des produits radioactifs et à la chromatographie préparative sur papier et sur colonne de cellulose.

Suit la partie spéciale, traitant de très nombreuses classes de corps organiques et donnant la préférence aux dérivés d'importance biologique ou pharmaceutique. A la fin, un petit chapitre s'occupe des colorants et 90 pages seulement sont consacrées à l'analyse minérale. C'est peut-être l'unique point faible du livre.

L'exposé pratique est encore suivi de deux listes: la première contient les réactifs servant à identifier les „spots"; la seconde, un recueil de méthodes concernant les traitements divers du papier, un choix de solvants et plusieurs exemples d'analyse quantitative.

Ajoutons encore deux mots sur la présentation parfaite de l'ouvrage et félicitons le traducteur qui le rend ainsi accessible à un public beaucoup plus large. Persuadés de sa valeur, nous recommandons ce livre à tous ceux qui travaillent en chimie organique croyant qu'il constituera une aide précieuse pour leurs recherches.

I. KAPÉTANIDIS (Genève)

Besser spat als nie, par CLÉMENT DUVAL, cours d'allemand scientifique pour les débutants. 6° Éd. - Edition CNRS, Paris 1958, 103 pages, Fr. 500.—

Ce cours d'allemand scientifique, conçu en 1945-'46 pour l'instruction des chercheurs et aides techniques, et qui est devenu depuis cette époque un cours régulier comprenant 25 leçons en est aujourd'hui à sa sixième édition, complètement remanié. Ceci prouve d'une part qu'il répond à un besoin réel, et d'autre part, que par suite de l'élargissement considérable du vocabulaire le livre est d'une utilité incontestable aussi bien pour les chimistes, que pour les physiciens, les botanistes, les pharmaciens, etc.

Chacune des 25 leçons ne demande, au dire de l'auteur, que 3 heures d'étude. Ceci permet de s'approprier en peu de temps les bases essentielles de la grammaire, de la syntaxe et un vocabulaire technique suffisant pour la lecture des périodiques allemands et pour la traduction de textes techniques, comme celui de la page 100 qui forme l'examen de fin de cours.

Le livre peut être recommandé vivement à tous ceux, qui par leurs travaux de recherches éprouvent le besoin d'améliorer leurs connaissances de la langue allemande.

G. VAN DER KELEN (Gand)

REVUE DE LIVRE

Electroanalytical Chemistry, par JAMES J. LINGANE. 2nd Ed., revised and enlarged. Interscience Publishers Inc., New York 1958, 669 pp., \$ 14.50.

Le Prof. LINGANE vient de faire paraître la seconde édition de son livre „*Electroanalytical Chemistry*”. Considérablement augmenté, 669 pp. au lieu de 448, il renferme plusieurs chapitres nouveaux.

Citons l'analyse polarographique avec comme paragraphes: Appareillage et technique, caractérisation du courant limite avec l'électrode à goutte, calibrage de l'électrode à goutte en polarographie, équations des ondes polarographiques et potentiel de demi-onde. L'ampérométrie et les titrations ampérométriques font aussi l'objet d'un nouveau chapitre dans lequel l'auteur traite de l'ampérométrie avec une ou deux électrodes polarisables. Signalons encore le chapitre ayant pour objet la titration coulométrique à courant constant et la chronopotentiométrie, théorie, méthodologie, appareillage et applications analytiques. La plupart des anciens chapitres ont été complétés. L'auteur ne donne pas une bibliographie complète, il a choisi parmi les très nombreuses publications de ces dernières années (jusqu'en 1958) celles qui sont susceptibles d'illustrer son exposé. Celui-ci est présenté de façon claire, avec un souci constant de simplification. Il est accompagné de nombreuses applications décrites avec le plus grand soin. La partie théorique est traitée de façon originale et suggestive et ne fait appel qu'à des considérations physico-chimiques élémentaires. On pourrait reprocher à l'auteur d'avoir surchargé son ouvrage d'une série de schémas qui présentent peu d'intérêt pour la plupart des chimistes analystes, mais ceci n'enlève rien à la valeur de ce livre de choix qui est fort bien présenté et illustré de nombreuses figures.

D. MONNIER (Genève)

BUCHBESPRECHUNG

Handbuch der Analytischen Chemie, herausgegeben von W. FRESENIUS UND J. JANDER, Springer Verlag, Berlin 1958, Dritter Teil: Quantitative Bestimmungs- und Trennungsmethoden, Band VI b₂, Elemente der sechsten Nebengruppe (Chrom), LV, 411 S., DM 104.—, Ganzleinen DM 108.—.

Die Verfasser behandeln zuerst die Bestimmungsmöglichkeiten des Chroms und orientieren über deren Eignung. Besondere Berücksichtigung erhalten einzelne theoretische Betrachtungen z.B. die der modernen Oxydationsmethoden durch Überchlorsäure.

Das Buch fährt fort mit den Kapiteln der gravimetrischen Bestimmungsmethoden des 3- und 6-wertigen Chroms. Die genauen Arbeitsvorschriften machen das Buch für den Praktiker und für den Theoretiker interessant.

Auf den gleichen Principien sind auch die Kapitel der titrimetrischen Chrombestimmung aufgebaut. Speziell sorgfältig werden dabei die direkten und indirekten iodometrischen und ferrometrischen Titrationsmethoden behandelt. Der Benutzer des Buches wird dabei auch auf die, in dem Falle des Chroms, so wichtige Frage der Endpunktbestimmung durch Redoxindikatoren und elektrometrische Methoden aufmerksam gemacht. Die Bemerkungen bezüglich der Genauigkeit der Methoden, der eventuellen Indikatorenkorrekturen und der störenden Stoffe sind nach unserem Dafürhalten besonders wertvoll.

Sehr modern sind auch die folgenden Kapitel der physikalisch-chemischen Methoden; der Kolorimetrie, Photometrie, Polarographie und der spektral-analytischen Analyse. Auch hier begrüßen wir ganz besonders die genauen detaillierten und sehr vollständigen Angaben.

Der letzte Teil des Buches behandelt die Trennungen des Chroms (Eisen, Aluminium, Nickel, Titan, usw.) und die speziellen Methoden der Chrombestimmung in Stahl, den verschiedensten Legierungen, den Erzen, im Abwasser, in organischen Verbindungen in Gasen und Stauben usw.

Abschliessend können wir sagen, dass das Buch ein modernes und wohl vollständigste Werk der Chromanalyse darstellt. Wir können es wegen seinem klaren Aufbau und Vollständigkeit allen analytisch Interessierten bestens empfehlen.

H. KELLER (Genf)

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