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SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM
WITH 1-NAPHTHYLAMINE-4,6,8-TRISULFONIC ACID

EDGAR L. STEELE AND JOHN H. YOE

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Charlottesville, Va. (U.S.A.)*

INTRODUCTION

In 1956 1-naphthylamine-3,5,7-trisulfonic acid was reported by this laboratory as a new reagent for the spectrophotometric determination of trace amounts of osmium[1]. The compound is more sensitive than the various thioureas previously reported for this determination. In addition to its higher sensitivity, the new reaction is carried out in weakly acid medium instead of in strong acid required in the thiourea methods. The chief disadvantage of the new method is that osmium must be in the osmate (OsVI) state of oxidation and 4 hours are required for maximum color development.

Recently we have investigated this reaction more fully[2] and found that by selecting the proper naphthylamine sulfonic acid isomer, adjusting the pH, and maintaining the proper temperature, the time required for complex formation is substantially reduced and the sensitivity slightly increased.

The reaction between 1-naphthylamine-4,6,8-trisulfonic acid and osmium, as the osmate ion, was investigated fully to determine whether the color produced could be utilized as the basis for a convenient, sensitive, and quantitative spectrophotometric method of analysis for trace amounts of osmium. The compound may also be used for ruthenium.

APPARATUS

All absorbance measurements were made with a Beckman spectrophotometer, Model DU, using matched 1.000-cm Corex cells. At wavelengths of 625 mμ or below, the ultraviolet-sensitive phototube was used; above 625 mμ, the red-sensitive phototube. The phototube circuit was kept at maximum sensitivity and under these conditions the slit width at 560 mμ was about 0.035 mm, corresponding to a band width of approximately 2 mμ.

A Beckman pH meter, Model G, was used for all pH measurements. The meter was calibrated daily with Fisher Certified Standard Buffers.

Temperature bath, accurate to $\pm$ 0.2°C.

The osmium still is essentially that of WESTLAND AND BEAMISH[3] with only a few minor changes[2].

REAGENTS

Standard osmium solutions

Solutions containing 100 p.p.m. osmium were prepared by dissolving 0.0194 g of potassium osmate ($K_2OsO_4 \cdot 2H_2O$), obtained from the American Platinum Works, in distilled water and diluting to the mark in 100-ml volumetric flasks. According to FRIEND[4] this solution is stable, but for maximum stability it is best stored in a refrigerator.

Reagent solution

1-naphthylamine-4,6,8-trisulfonic acid was purified by dissolving in a minimum amount of warm water and precipitated by the addition of isopropyl alcohol. Recrystallizations were continued until a solution gave the constant break in the mole-ratio determination experiment. The

number of recrystallizations required varies from 1 to 5 depending upon the purity of the compound. After purification, the reagent solution is prepared by dissolving the required amount in distilled water. The reagent may be obtained from the LaMotte Chemical Products Company, Chestertown, Md. (U.S.A.).

Buffer solution

A buffer solution (Clark and Lubs type) was prepared by mixing 97 ml of $0.2N$ HCl and 50 ml $0.2N$ KCl and diluting to 200 ml. The pH is 1.0.

Other reagents

All other reagents were analytical grade and were used without further purification.

EXPERIMENTAL

Effect of pH

Osmium, as the osmate (OsVI), reacts with 1-naphthylamine-4,6,8-trisulfonic acid to produce a water-soluble purple complex which changes to violet as the pH-1.0 buffer is added. The effect of the hydrogen-ion concentration on the absorbance of the complex was studied using a solution containing 3.55 p.p.m. osmium, excess reagent, and varying amounts of hydrochloric acid and sodium hydroxide. The results are given in Fig. 1 and show a maximum absorbance at 555 mμ with a pH between 1.0 and 1.5. It was found that 10 ml of pH-1.0 buffer per 25-ml aliquot is suffi-
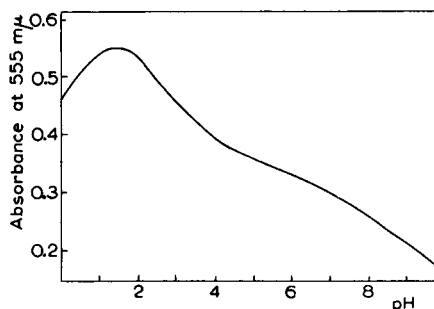
Fig. 1. Absorption *versus* pH for a 3.55 p.p.m. solution of osmium as the complex.
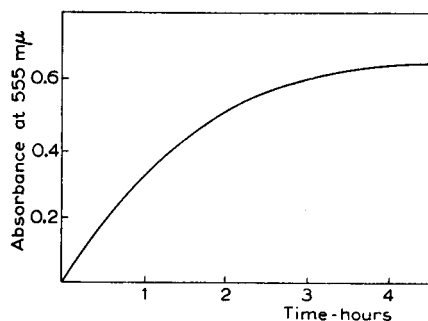
Fig. 2. Rate of complex formation *versus* time at 15°.

cient to give reproducible results. The purple color that forms at pH 3 changes to light blue at pH 6 and finally to a pale green above pH 8. Varying the hydrogen-ion concentration has no effect on the absorbance of the reagent at 555 mμ.

Stability of the complex

Absorbance measurements of a solution containing 4 p.p.m. osmium, excess reagent, and pH-1.0 buffer showed no appreciable change over a period of one month at room temperature. At 50° solutions of the complex are stable for 10 hours. The complex is destroyed by oxidizing agents such as hydrogen peroxide and sodium hypochlorite. An ethanol solution of the complex shows a slight decomposition after 12 hours at room temperature. Evaporation of an aqueous solution of the complex yields long monoclinic purple needles. A solution of the crystals shows a loss in absorbance (approx. 10%) indicating partial decomposition.

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Effect of reagent concentration

A study was made to determine the effect of the reagent concentration on the absorbance of the system. It was found that if enough reagent is present to complex all of the osmate ions, a further increase in the concentration does not produce a significant change in the absorbance value at 555 mμ. After standing a month some decomposition products begin to appear which absorb slightly at the maximum of the complex. For this reason, any reagent solution more than a month old should be limited to a 4 to 1 ratio of reagent to osmate ion.

Rate of color formation

The rate of color formation was investigated using an osmate solution containing 4 p.p.m. osmium, excess reagent and varying amounts of hydrochloric acid and sodium hydroxide. The rate was found to be dependent on two factors, namely, the temperature of the solution and the pH.

Holding the pH constant at 2.0 $\pm$ 0.1 solutions of osmate and reagent were kept at 15° for varying periods of time, then diluted with 10 ml of pH-1.0 buffer, made up to the mark with water and the absorbance measured at 555 mμ. The results are given in Fig. 2 and show that 4 h are required for maximum color development.

Runs were also made at 20°, 25°, 30°, 35°, 40° and 45°. Fig. 3 is a plot of absorbance *versus* temperature at the end of 1 h. It is seen that the reaction is practically complete at the end of 1 h at 35°. Higher temperatures were avoided to eliminate any chance of destroying the complex. 45 min at 40° is recommended.
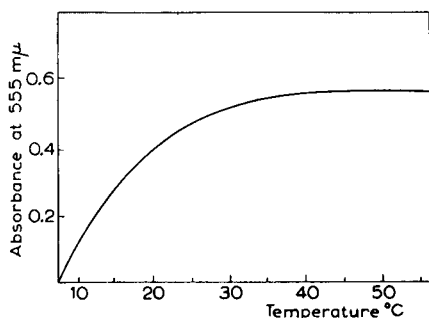
Fig. 3. Complex formed *versus* temperature at 1 hour.
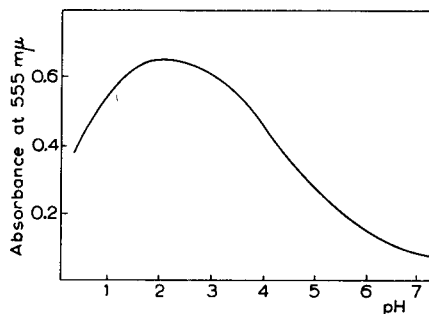
Fig. 4. Rate of complex formation *versus* pH at 35°.

Maintaining a constant temperature at 35°, solutions containing 4 p.p.m. osmium, excess reagent and varying hydrogen ion concentrations were allowed to react for 1 h. The solutions were then diluted with 10 ml of pH-1.0 buffer and water added to the mark. Absorbance readings were taken at 555 mμ. Fig. 4 shows that the solution must have a pH 1.5 to 2.5 for maximum rate of color formation.

Beer's law

In order to determine whether or not the system obeys Beer's law, a calibration curve was prepared. A series of solutions containing varying amounts of osmate ions and excess reagent, were allowed to react completely and then pH-1.0 buffer was added.

Absorbance measurements were made against a reagent blank at 555 mμ, and a plot of the data was made. In the absence of interfering substances, the complex concentration is proportional to the absorbed radiant energy between the concentration limits of $5.2 \cdot 10^{-7}$ and $3.4 \cdot 10^{-5} M$ osmium (0.1 to 6.5 p.p.m. osmium) as indicated by a straight line over this range.

SUGGESTED METHOD FOR DETERMINING OSMIUM(VI) IN ABSENCE OF INTERFERING SUBSTANCES

Pipette 5 ml of $5 \cdot 10^{-4} M$ reagent in the solution of osmate ions in a 25-ml volumetric flask and add $0.1 N$ hydrochloric acid dropwise until slightly acid (pH 2.5–3). Warm in a water bath at 40° for 45 min, then add 10 ml of pH-1.0 buffer and dilute to the mark with distilled water. Measure the absorbance at 555 mμ and convert absorbance units to osmium concentration with the aid of a previously prepared calibration curve.

Sensitivity and applicability of the method

At 555 mμ the molar absorptivity of the system is $2.98 \cdot 10^4$ liters $\cdot$ moles^{-1} $\cdot$ cm^{-1}. This corresponds to a sensitivity of 0.0068 μg/cm^2, i.e., 1 part of osmium in 140,000,000 parts of solution. A more practical value, however, is one in 20,000,000 because this value is reproducible within the limits of accuracy of the method.

A series of 10 determinations is given in Table I. The results show that the method is accurate to $\pm$ 2% over the concentration range $5.2 \cdot 10^{-7}$ to $5.2 \cdot 10^{-5} M$ osmium provided no interfering ions are present. Concentrations greater than $6 \cdot 10^{-5} M$ absorb too strongly at 555 mμ to be measured accurately.

TABLE I

RESULTS OF SEVERAL DETERMINATIONS

Reagent $= 1 \cdot 10^{-4} M$: pH $= 1.5$

Concentration of Osmium (VI) in p.p.m		
Added	Found	Error %
0.01	0.02	+ 100
0.05	0.06	+ 10
0.10	0.11	+ 2
0.50	0.51	+ 2
1.00	1.00	0
2.00	2.02	+ 1
3.00	3.00	0
4.00	3.87	— 0.8
6.00	6.07	+ 1.2
8.00	7.94	— 0.8

Accuracy and precision of the method

From the data in Table I it is apparent that the optimum concentration is between 0.1 and 8 p.p.m. osmium. The standard deviation was determined by preparing a set of solutions containing 4 p.p.m. osmium and excess reagent, heating at 40° for 45 min, adding pH-1.0 buffer and measuring the absorbance at 555 mμ. The data are given in Table II.

The absorbance value from the calibration curve is 0.620 abs. unit.

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TABLE II

RESULTS OF PRECISION AND ACCURACY DETERMINATIONS

Solution	Abs. at 555 mμ	Deviation	(Deviation)² × 10⁶
1	0.621	0.001	1
2	0.620	0.002	4
3	0.620	0.002	4
4	0.622	0.000	0
5	0.625	0.003	9
6	0.622	0.000	0
7	0.623	0.001	1
8	0.621	0.001	1
9	0.623	0.001	0
10	0.622	0.000	0
Av. 0.622			Total 21

Std. deviation 0.002 abs. unit, *i.e.*, 0.013 μg osmium

Effect of diverse ions

The specificity of the reaction was determined by preparing a solution containing 4 p.p.m. osmium, developed under optimum conditions, and varying amounts of the ionic species in question. An increase or decrease of 0.005 absorbance unit was taken as interference. The following ions were found to interfere in concentrations of 1:1 or less: RuO_4^{-2}, Ru^{+3}, Rh^{+3}, Ir^{+4}, Pd^{+2}, Pt^{+4}, Al^{+3}, V^{+2}, Cr^{+3}, Fe^{+3}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, Mn^{+2}, Mg^{+2} and Hg_2^{+2}. The results show that the reaction is not specific and that osmium must be separated from many common substances before it can be determined by this method.
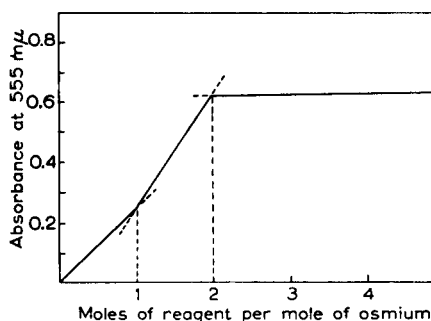
Fig. 5. Mole-ratio method applied to the osmium complex.

Nature of the complex in solution

Three methods were used to establish the empirical formula of the complex *in solution*. These were the mole-ratio method of YOE AND JONES[5], continuous variations method of JOB modified by VOSBURG AND COOPER[6] and the slope-ratio method of HARVEY AND MANNING[7]. Results of the three methods indicate a ratio of 2 moles of the reagent to 1 mole of the metallic ion. The mole-ratio curve in Fig. 5 indicates that with *excess* osmate ions a 1:1 complex is formed; the latter rapidly changes to the more stable 2:1 species as more reagent is added.

THE SEPARATION OF OSMIUM

Place the sample of osmium in the distillation apparatus[2,3] and regulate the flow of air so that, while the sample is being dissolved and during the distillation, the entire apparatus is continually swept with scrubbed air. Next, add $6N$ nitric acid, by means of the stopcock at the top of the distilling flask, until the sample just dissolves. Many alloys and some compounds containing osmium are not directly soluble in $6N$ nitric acid and must first be fused with ammonium persulfate or sodium peroxide. After the reaction has stopped, add more nitric acid (25 ml total) and slowly heat to boiling. Continue boiling for 30 min, distilling the osmium tetraoxide into the receiver containing 25 ml of $0.05N$ potassium hydroxide. Remove the basic distillate and analyze according to the procedure as outlined previously.

For small concentrations of osmium (less than 0.1 mg) the tetraoxide can be collected in 5 ml of $0.05N$ potassium hydroxide and thus increase the overall sensitivity of the method.

Results of analysis

Samples 1 through 5 were prepared by adding varying amounts of osmium to solutions, each containing approximately 1 mg of the following ions: Fe^{+3}, Cu^{+2}, Ni^{+2}, Co^{+2}, Pt^{+4}, Ir^{+4}, Ru^{+3}, Rh^{+3}, and Pd^{+2}. Samples 6 through 10 contained 1 mg Ru^{+3} and varying amounts of osmium. The samples were then treated with zinc dust and sulfuric acid to insure the lower oxidation state of osmium. No alloys were available to test the persulfate fusion, so this reagent was added to the reduced samples.

After the distillation was complete, aliquots of the basic distillate were pipetted into 25-ml volumetric flasks, neutralized and analyzed according to the proposed method.

The results of the ten distillations are given in Table III.

TABLE III

DISTILLATION OF OSMIUM

Sample	Os added (mg)	Os found (mg)	% Recovery
1	0.010	0.009	90
2	0.10	0.09	90
3	0.20	0.20	100
4	0.20	0.19	95
5	0.50	0.48	96
6	0.50	0.49	98
7	0.50	0.48	96
8	0.50	0.50	100
9	1.00	1.01	101
10	1.00	1.00	100

SUMMARY

This investigation was undertaken to determine if the naphthylamine sulfonic acid–osmate (OsVI) reaction is suitable for a spectrophotometric determination of osmium. The 1-naphthylamine-4,6,8-trisulfonic acid–osmate complex is water-soluble and forms a stable violet-colored system at pH 1 to 1.5 that is independent of reagent concentration. At 555 mμ the colored complex obeys Beer's law over a concentration range of 0.1 to 6.5 p.p.m. osmium and remains stable with respect to time and temperature. The effects of pH, temperature, reagent concentration, and diverse ions were studied. The nature of the organo–osmate complex *in solution* was studied by three techniques and the effect of temperature and pH on the rate of complex formation was

determined. A procedure for the removal of osmium from all interfering ions was developed based on well known distillation techniques.

A convenient, sensitive, reproducible and accurate method for the spectrophotometric determination of osmium has been developed.

RÉSUMÉ

Les auteurs ont étudié la réaction entre l'acide amino-1-naphtalène trisulfonique-4,6,8 avec l'osmium(VI). On obtient un complexe violet, stable, permettant un dosage spectrophotométrique de l'osmium à 555 mμ, pour des teneurs allant de 0.1 à 6.5 p.p.m. Une méthode de séparation de l'osmium d'avec les éléments gênants est proposée, en utilisant une technique par distillation.

ZUSAMMENFASSUNG

Die Reaktion zwischen Osmium-(VI) und 1-Amino-naphtalin-4,6,8-trisulfosäure wird als Grundlage zu einer spektrophotometrischen Bestimmung des Osmiums vorgeschlagen. In der Form des violetten Komplexes lässt sich das Osmium bei 555 mμ in einem Konzentrationsbereich von 0.1 bis 6.5 p.p.m. bestimmen. Die Abtrennung des Osmiums von störenden Metallen kann durch ein Destillationsverfahren erfolgen.

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SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH 1-NAPHTHYLAMINE-3,5,7-TRISULFONIC ACID

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INTRODUCTION

During a recent investigation of the naphthylamine sulfonic acid–osmate (OsVI) reactions, it was observed that additional chemical evidence might be obtained using the ruthenate ion[1]. It was thought that since many of the reactions of osmium and ruthenium are similar, the formation of a ruthenate–naphthylamine sulfonic acid complex would add much to our information concerning a reaction mechanism.

After studying several of the ruthenium complexes, the reaction between 1-naphthylamine-3,5,7-trisulfonic acid and ruthenium was investigated fully to determine the applicability of the color produced as the basis for a convenient, sensitive, and quantitative spectrophotometric method of analysis for trace amounts of ruthenium. The 4,6,8-isomer may be used equally well.

APPARATUS

All absorbance measurements were made with a Beckman spectrophotometer, Model DU, using matched 1.000-cm Corex cells. At wavelengths of 625 mμ or below, the ultraviolet-sensitive phototube was used; above 625 mμ, the red-sensitive. The phototube circuit was kept at maximum sensitivity and under these conditions the slit width at 530 mμ was about 0.035 mm, corresponding to a band width of approximately 2 mμ.

A Beckman pH meter, Model G, was used for all pH measurements. The meter was calibrated daily, using Fisher Certified Standard Buffers.

Temperature bath, accurate to $\pm$ 0.2°C.

The ruthenium still is essentially that of WESTLAND AND BEAMISH[2] with only a few changes[1].

REAGENTS

Standard ruthenium solutions

A solution of ruthenium chloride (RuCl$_3$) obtained from the American Platinum Works, was standardized by precipitating the ruthenium as the hydrated oxide and weighing as the oxide (Ru$_2$O$_3$). Unless the solution is acid, the ruthenium(III) will slowly undergo hydrolysis.

Reagent solution

1-naphthylamine-3,5,7-trisulfonic acid was purified by dissolving in a minimum amount of warm water and precipitated by the addition of isopropyl alcohol. The reprecipitations were continued until a solution of the reagent gave a constant break in a mole-ratio determination with a standard osmate solution. The number of recrystallizations necessary vary from 1 to 5 depending upon the state of purity of the compound available. After purification, the reagent solution is prepared by dissolving the required amount in distilled water. The reagent may be obtained from the LaMotte Chemical Products Company, Chestertown, Md. (U.S.A.).

Buffer solutions

Buffer solutions were the Clark and Lubs type, prepared by mixing 97 ml of 0.2N HCl and 50 ml 0.2N KCl and diluting to 200 ml. The pH is 1.0.

Other reagents

All other reagents were analytical grade and used without further purification.

EXPERIMENTAL

Absorbance curve

An absorbance curve of the reagent solution (5·10^{-4}M) and of the ruthenate complex (1.96·10^{-4}M) is shown in Fig. 1. Measurements were taken every 10 mμ except
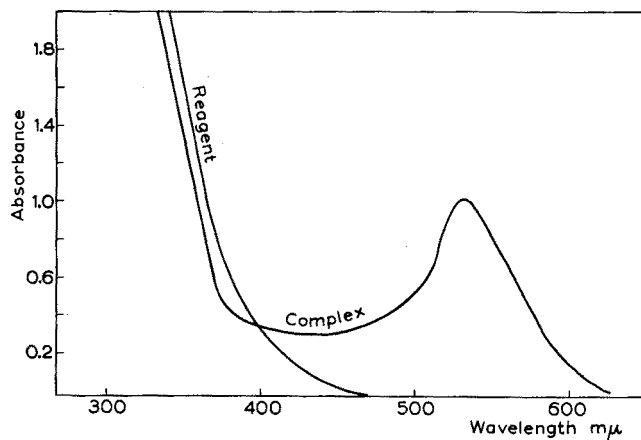
Fig. 1. Absorption spectra of reagent (5·10^{-4}M) and its ruthenium complex (1.96·10^{-4}M).

where maxima were encountered, then the readings were taken every 5 mμ. All measurements were made against a water blank, since the absorbance of the reagent at the maxima of the complex is negligible. Experiments show that a tolerance of 7-fold excess reagent is possible. The curve for the complex shows a sharp peak at 530 mμ.

Effect of pH

The effect of the hydrogen-ion concentration on the absorbance of the organo–ruthenate complex was studied using a $1.96 \cdot 10^{-4} M$ solution complex, excess reagent and varying quantities of hydrochloric acid and sodium hydroxide. As shown in Fig. 2, the maximum absorbance is at 530 mμ with a pH between 1.0 and 3.0. It was found that 10 ml of pH-1 buffer per 25-ml aliquot was sufficient to give reproducible results. Varying the hydrogen-ion concentration has no effect on the absorbance of the reagent at 530 mμ.

Rate of color formation

Unlike the osmate–naphthylamine sulfonic acid reaction[1] the ruthenate reacts almost instantaneously, when the pH is between 2.5 and 5. Above pH 7 and below pH 1.5 the complex is not formed.

Temperature has little noticeable effect on rate of complex formation since the reaction is rapid even at 15°.

Beer's law

The organo–ruthenium complex adheres to Beer's law up to a ruthenium concentration range of 20 p.p.m. The optimum range for the absorbance measurements on the spectrophotometer is 0.2 to 0.7 units. With the procedure outlined, these values correspond to a ruthenium concentration of 3 to 14 p.p.m.
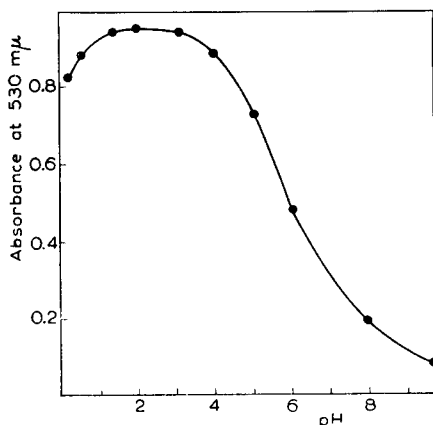
Fig. 2. Absorption *versus* pH for $1.96 \cdot 10^{-4} M$ solution of the ruthenium complex.
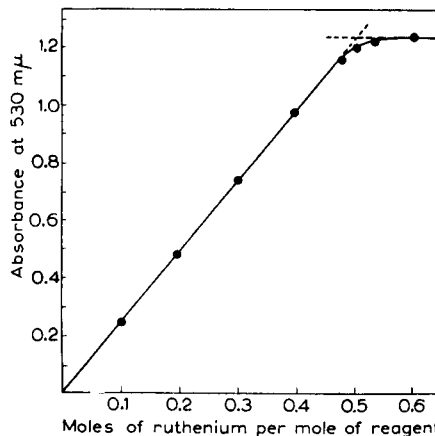
Fig. 3. Mole-ratio method applied to the ruthenium complex.

Sensitivity

According to SANDELL's[3] expression of sensitivity and using an absorbance value of 0.201 unit for a 4 p.p.m. ruthenium solution, the sensitivity is 0.02 $\mu g/cm^2$. For general use, however, the practical sensitivity is 0.1 $\mu g/cm^2$, *i.e.*, 1 part of ruthenium in 10,000,000 parts of solution.

Effect of order of adding solutions

As long as the ruthenium is in the valence state of the ruthenate ion, and the reagent solution is acid enough to have a proton on the amine group, the order of mixing is immaterial. It is essential, however, to maintain a pH during the reaction which will prevent the decomposition of the ruthenate ion, *i.e.*, pH 2.5 to 5.

Nature of the complex in solution

The empirical formula of the ruthenate complex was checked by the mole-ratio method of YOE AND JONES[4]. Since the procedures of analysis and reaction mechanism are so similar to the osmate system[1], it was felt that continuous variations and slope-ratio determinations would be unnecessary additions to the evidence already accumulated for the system. Fig. 3 shows the straight-line relationship between the absorbance and the amount of ruthenium added until the concentration reaches one-half that of the reagent. At this point, a sharp break occurs in the curve indicating no further complex formation. Hence, the formula of the complex is R_2RuO_4.

Effect of diverse ions

Because the mechanism of the proposed procedure eliminates all interfering materials known to interfere with the naphthylamine–osmate reaction, no systematic investigation of this effect was studied. It was found, however, that if these ionic species were added to the complex, an absorbance change was observed. If these substances were added to the distillation flask, no interference was noted in the procedure.

SUGGESTED METHOD FOR THE SEPARATION AND DETERMINATION OF RUTHENIUM

Place the sample in the distillation apparatus and dissolve it in 6N nitric acid. Boil the solution for 15 to 30 min to expel any osmium as the tetraoxide, add 20 ml of 0.1M $KMnO_4$ and again boil for 15 to 30 min depending upon the concentration of the ruthenium present. As in the case of osmium[5], ruthenium samples that do not dissolve in dilute nitric acid are first fused with $K_2S_2O_8$, Na_2O_2, or KOH–KNO_3 mixture and then treated with 6N nitric acid.

Collect the ruthenium tetraoxide that distills from the permanganate oxidation in 25 ml of $5 \cdot 10^{-4}M$ reagent solution (pH 2.5–3.0). After the ruthenium has been distilled and collected, add 5-ml aliquots of the organo–ruthenium complex to a 10-ml volumetric flask, dilute to the mark with pH-1 buffer, mix and measure the absorbance of the solution at 530 mμ against a reagent blank or a water blank. Read the ruthenium concentration from a preciously constructed absorbance *vs.* concentration graph (Beer's law curve).

For small concentrations of ruthenium (0.05 to 0.005 mg) the tetraoxide can be collected in 5 ml of the reagent solution to increase the overall sensitivity of the procedure.

Accuracy and precision of the method

6 samples containing 0.5 mg of ruthenium and varying quantities of osmium, were

distilled according to the previous section. Standard deviations for the distillation of ruthenium were determined by measuring the absorbance of the ruthenate complex formed after the osmium was boiled off. Table I shows the result of the 6 samples. The absorbance value for the concentration of ruthenium measured (10 p.p.m.) as taken from the Beer's law curve is 0.487 abs. unit.

TABLE I

Sample	Ru added (p.p.m.)	Os added (mg)	Abs. at 530 mμ	Ru found (p.p.m.)	(Deviations)² × 10⁶
1	10.00	0.10	0.484	9.94	9
2	10.00	0.20	0.482	9.90	25
3	10.00	0.30	0.493	10.12	36
4	10.00	0.50	0.491	10.08	16
5	10.00	0.70	0.483	9.92	16
6	10.00	1.00	0.487	10.00	0

S.D. = 0.004 Abs. unit, *i.e.*, 0.08 μg Ru.

SUMMARY

An investigation has been made to determine the applicability of the osmate–naphthylamine reaction to the ruthenate system. It was found that under proper conditions, ruthenium (RuVI) reacts with 1-naphthylamine-3,5,7-trisulfonic acid to form a water-soluble red complex ion with a maximum absorbance at 530 mμ. The complex was found to be stable and to obey Beer's law over a concentration range of 0.5 to 14 p.p.m. The effects of pH, reagent concentration, and diverse ions were studied. The nature of the complex in solution was investigated, and a standard procedure for analysis recommended. A procedure for the removal of ruthenium from all interfering materials was developed based on well known distillation techniques.

A rapid, sensitive, reproducible and accurate method for the spectrophotometric determination of ruthenium has been developed.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage du ruthénium au moyen de l'acide amino-1-naphtalène trisulfonique-4,6,8. On obtient un complexe stable, rouge, ayant une absorption maximum à 530 mμ. On sépare le ruthénium d'avec les éléments gênants par distillation.

ZUSAMMENFASSUNG

Die Reaktion zwischen Ruthenium und 1-Amino-naphtalin-4,6,8-trisulfosäure wird als Grundlage zu einer spektrophotometrischen Bestimmung des Rutheniums vorgeschlagen. Die erhaltene rote Komplexverbindung besitzt ein Absorptionsmaximum bei 530 mμ. Das Ruthenium wird von störenden Elementen durch ein Destillationsverfahren abgetrennt.

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A RAPID AND PRECISE MICRO-HETEROMETRIC DETERMINATION OF GOLD, PALLADIUM OR PLATINUM WITH NITRON IN THIOCYANATE SOLUTIONS

A STUDY OF THE REACTIONS AND OF THE COMPOUNDS

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INTRODUCTION

Nothing seems to be known about the reactions between the thiocyanato-complexes of gold(III), palladium or platinum(IV) and nitron. All three metal chlorides gave coloured solutions in the presence of excesses of potassium thiocyanate: gold gave an intense tea brown solution, palladium an orange one and platinum a yellow solution. The colour of the palladium and platinum solutions did not fade on dilution, whereas the gold solution became colourless under these conditions. Ammonia immediately decolourized the palladium thiocyanato-complex, but the corresponding platinum complex was less sensitive to the addition of ammonia. On the addition of nitron to the metal chloride solutions, *in the absence of thiocyanate*, no noticeable change occurred in the palladium or platinum solutions, which remained clear. In the case of gold chloride, a small amount of a flocculent yellowish precipitate appeared in hydrochloric acid solution; however, no change took place in sodium acetate solution.

Entirely different reactions were obtained when the heterometric reaction with nitron was carried out in the presence of *excesses of potassium thiocyanate*. Almost independently of the pH, insoluble compounds were obtained with all three metals. The compounds could be used for a *rapid* and *precise* heterometric determination of traces of each of the above metals. Ten minutes was entirely sufficient, in all normal cases, for a complete titration of these metals. Normally the error was between zero and 1%. The molar sensitivity of the reaction was approximately the same for all three metals (concentrations: $2 \cdot 10^{-4}M$ PdCl$_2$, $3 \cdot 10^{-4}M$ AuCl$_3$ and $4 \cdot 10^{-4}M$ H$_2$PtCl$_6$). The determination of palladium with nitron was more sensitive than any other heterometric method presented previously[1]. The amounts of the metals necessary for the analyses (in 20 ml solution) were about 1 mg gold, 0.8–1.6 mg platinum and 0.4 mg palladium.

It was very interesting to establish that, in the presence of potassium thiocyanate, even chloroplatinic acid reacted immediately with nitron, quantitatively giving an insoluble compound of definite composition. Another interesting feature was the remarkable insensitivity of the insoluble compounds obtained towards the most common complexing agents such as citrate, polyphosphates and ethylenediaminetetraacetate, at all pH's between 1 and 9. In contrast, potassium cyanide, when present in basic solution, dissolved all the insoluble compounds. In addition, the insoluble palladium compounds were dissolved in dilute ammonia; the platinum compounds

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required more concentrated ammonia for their solution. The gold compound gave an insoluble thiocyanato-complex of different composition in the presence of a large excess of ammonia. Besides the analytical study of the reaction, the composition of each of the compounds obtained was thoroughly investigated. The properties of all the compounds obtained and their structures will be discussed in a separate report.

EXPERIMENTAL

The same working conditions were observed as in previous heterometric investigations. The principles of heterometry have been discussed briefly in ref.[2]. Experience in dealing with problems in heterometry can be gained by studying the previous heterometric investigations, which were concerned with the study of complex compounds, of intermediates and of reactions in suspensions in general, as well as with the application of heterometry to microanalysis[3].

All chemicals used in this work were either AnalaR or chemical pure reagents. The special solutions were prepared as follows:

Nitron. (M.W. = 312.16) 0.7802 g nitron (Eastman Organic Chemicals, for chemical purposes) + 7 ml M CH$_3$COOH were dissolved in water to give 250 ml aqueous solution (= 0.01M).

Palladium chloride (Johnson Matthey). 1 g PdCl$_2$ + 56 ml M HCl were dissolved in water to give a volume of 562.8 ml (= 0.01M).

Gold chloride (brown) B.D.H. Laboratory reagent. 1 g HAuCl$_4$·3H$_2$O + 25 ml M HCl were dissolved in water to give a volume of 250 ml (approx. 0.01M HAuCl$_4$/0.1M HCl).

Chloroplatinic acid, H$_2$PtCl$_6$·6H$_2$O, B.D.H. 1 g of the reagent was dissolved in water to give 500 ml solution (approx. 0.004M).

More dilute solutions were prepared from these standard solutions. In the case of nitron the diluted solutions were freshly prepared every few days and all the solutions were kept in dark brown bottles.

RESULTS AND DISCUSSION

General

The heterometric reaction of the chlorides of the noble metals with nitron in the presence of excesses of potassium thiocyanate, was studied at different pH's in the presence and in the absence of complexing agents. A selection of experiments, the composition of the solutions and the results obtained are compiled in Tables I, II and III. The course of the heterometric titrations in a few experiments is presented in Fig. 1. The same numeration is used in both cases. In Table IV and in Fig. 2 a selection of heterometric titrations is presented in which the noble metals were present in solution in a mixture. The aim was to see how far each of the metals present could be determined by a heterometric titration.

Reverse titrations, in which solutions of the noble metals were used as titrants, were also performed. These titrations were carried out with the purpose of obtaining further insight into the different complex compounds formed during these titrations. The information gathered did not provide much that was of value for the analytical aspect of the research.

A special study was carried out to determine palladium in the presence of large excesses of foreign metals. The results of this investigation will be presented separately.

Titrations of solutions of gold chloride

Compounds

In almost all cases the compound, which was calculated from the first maximum density point, had the exact composition Au$_1$N$_1$↓↓ (N = nitron). Only in solutions

TABLE I

Composition: a ml $PdCl_2$ + b ml KCNS + c ml supplements + ad 20 ml H_2O + x ml nM nitron.

T = 20°. Content Pd: 0.4268 mg; concn. $2 \cdot 10^{-4}M$.

Expt. No.	PdCl₂ ml	PdCl₂ Molarity	ml KCNS 2M	Supplements	Nitron* ml	Nitron* Molarity	Initial ppt. at ml	Max. density value	Titration time in min	Found % error	Remarks
1	4	0.001	1	—	i 3.93 h	0.0015	0.2	0.69	7	1.7	Bright brown ppt. End-point at Pd₂N₃
2	4	0.001	3	—	i 4.01 h	0.0015	0.6	0.58	7	0.3	,, ,,
3	4	0.001	1	3 ml M HCl	i 3.98 h	0.0015	0.2	0.66	8	0.5	,, ,,
4	4	0.001	1	3 ml M CH₃COOH	i 4.00 h	0.0015	0.2	0.67	7	0.0	,, ,,
5	4	0.001	1	1 ml M NH₄NO₃	i 3.97 h	0.0015	0.4	0.64	9	0.7	,, ,,
6	4	0.001	1	1 ml M CH₃COONa	i 4.00 h	0.0015	0.2	0.78	7	0.0	,,
7	4	0.001	1	4 ml 0.25M H₃PO₄	i 4.00 h	0.0015	0.2	0.81	9	0.0	,,
8	4	0.001	1	2 ml 0.5M Na₂HPO₄	i 4.00 h	0.0015	0.0	0.74	7	0.0	,,
9	4	0.001	1	1 ml M Na₃-citrate	i 4.02 h	0.0015	0.2	0.86	5	0.5	Bright brown ppt.
10	4	0.001	1	3 ml M Na₃-citrate	i 3.99 h	0.0015	0.2	0.69	7	0.3	,, ,,
11	4	0.001	1	3 ml M Na₂-tartrate	i 4.00 h	0.0015	0.4	0.73	5	0.0	,, ,,
12	4	0.001	1	8 ml 0.125M Na₅P₃O₁₀	i 4.01 h	0.0015	0.0	0.65	8	0.3	,, ,,
13	4	0.001	1	3 ml 0.2M Na₂-EDTA	i 4.00 h	0.0015	0.4	0.77	7	0.0	,, ,,
14	4	0.001	1	3 ml 0.2M Na₄-EDTA		0.0015	>5.0	0.0			
15	4	0.001	1	1 ml 0.2M KCN + 2 ml 0.5M Na₂HPO₄		0.0015	>5.0	0.0			
16	4	0.001	1	10 ml alcohol		0.0015	>5.0	0.0			
17	4	0.001	0.15	—	i 3.01	0.002	0.2	>0.40		0.3	Linear increase after the maximum
18	4	0.001	1	1 ml M NH₃		0.0015	0.0	0.0			
19	4	0.001	1	4 ml M NH₄NO₃	i.c. 3.00 h	0.002	0.0	0.69	5	0.0	End-point at Pd₂N₃
20	4	0.001	1	8 ml 0.125M Na₄P₂O₇	2.97	0.002	0.2	0.63	12	1.0	After the maximum linear increase

* i = intersection point; c = contact point; h = horizontal maximum density line.

TABLE II

Composition: a ml $HAuCl_4$ + b ml KCNS + c ml supplements + ad 20 ml H_2O + x ml nM nitron.

T = 20°. Content Au: 1.183 mg; concn. $3 \cdot 10^{-4} M$.

Expt. No.	HAuCl₄ ml	HAuCl₄ Molarity	ml KCNS 2M	Supplements	Nitron* ml	Nitron* Molarity	Initial ppt. at ml	Max. density value	Titration time in min	% error	Remarks
21	3	0.002	—	—	? 2.6	0.002	∿1.4	?0.18			Bright yellow floculant ppt.
22	3	0.002	—	1 ml M HCl	?	0.002	1.0	0.25	8		
23	3	0.002	—	1 ml M HNO₃	?	0.002	1.2	0.11	30		
24	3	0.002	—	1 ml M CH₃COONa	>5.0	0.002	>5.0	0.0	5		
25	3	0.002	1	—	i 3.00 h	0.002	0.6	0.56	6	0.0	White ppt. End-point at Au₁N₁
26	3	0.002	5	—	i 3.05 h	0.002	0.8	0.50		1.7	Short horizontal line. White ppt.
27	3	0.002	1	1 ml M HNO₃	i 2.99 h	0.002	0.2	0.61	8	0.3	End-point at Au₁N₁
28	3	0.002	1	1 ml M HCl	i 2.96 h	0.002	0.2	0.54	8	1.3	,, ,, ,,
29	3	0.002	1	1 ml M CH₃COONa	i 2.99 h	0.002	0.4	0.62	9	0.3	,, ,, ,,
30	3	0.002	1	1 ml M Na₃-citrate	i 3.00 h	0.002	0.4	0.61	7	0.0	,, ,, ,,
31	3	0.002	1	2 ml 0.2M Na₂-EDTA	i 3.00 h	0.002	0.4	0.60	5	0.0	,, ,, ,, White ppt.
32	3	0.002	1	5 ml 0.2M Na₂-EDTA	i 3.00 h	0.002	0.4	0.57	5	0.0	,, ,, ,,
33	3	0.002	1	2 ml 0.2M Na₂-EDTA + 2 ml 0.5M Na₂HPO₄	c 3.00 h	0.002	0.2	0.59	8	0.0	,, ,, ,,
34	3	0.002	1	3 ml 0.2M Na₄-EDTA	>5.0	0.002	0.2	>0.50	5	0.0	Linear increase without intersection point
35	3	0.002	1	8 ml 0.125M Na₄P₂O₇	i 2.84	0.002	0.0	0.50	15		Linear increase after intersection
36	3	0.002	1	8 ml 0.125M Na₅P₃O₁₀	i 3.00 h	0.002	0.2	0.45	37	0.0	Short horizontal line, then linear increase
37	3	0.002	1	2 ml 0.2M Na₂-EDTA + 2 ml M NH₃	c 3.00 h	0.002	0.0	0.52	12	0.0	End-point at Au₁N₁. White ppt.
38	3	0.002	1	2 ml M NH₃ + 1 ml 0.5M NH₄NO₃	c 3.00 h	0.002	0.0	0.57	9	0.0	White gelatinous ppt.
39	3	0.002	1	0.5 ml conc. NH₃	i 4.50 h	0.002	0.2	0.75	9	0.0	End-point at Au₂N₃. Yellow ppt.
40	3	0.002	1	1 ml M KCN + 2 ml 0.5M Na₂HPO₄	>5.0	0.002	>5.0	0.0		0.0	

* i = intersection point; c = contact point; h = horizontal maximum density line.

TABLE III

Composition: a ml H_2PtCl_6 + b ml KCNS + c ml supplements + ad 20 ml H_2O + x ml nM nitron.

T = 20°. Content Pt: 1.5618 mg; concn. $4 \cdot 10^{-4}M$.

Expt. No.	H_2PtCl_6 ml	H_2PtCl_6 Molarity	ml KCNS 2M	Supplements	Nitron* ml	Nitron* Molarity	Initial ppt. at ml (Found)	Max. density value	Titration time in min	% error	Remarks
41	2	0.004	1	—	i 2.98 h	0.002	0.0	0.66	8	0.7	End-point at Pt_4N_3 Yellow ppt.
42	4	0.002	5	—	i 2.99 h	0.002	0.4	0.79	7	0.3	„ „ „ „
43	4	0.002	1	1 ml M HCl	i 2.97 h	0.002	0.0	0.72	8	1.0	„ „ „ „
44	4	0.002	1	1 ml M CH_3COONa	i 3.00 h	0.002	0.2	0.62	12	0.0	Bright yellow powder
45	4	0.002	1	2 ml 0.5M Na_2HPO_4	c 3.0	0.002	0.0	0.57	5	0.0	End-point at Pt_4N_3
46	4	0.002	1	2 ml 0.2M Na_2-EDTA	i 3.02 h	0.002	0.0	0.80	8	0.7	„ „ „
47	4	0.001	1	5 ml 0.2M Na_2-EDTA	c 3.0 h	0.001	0.4	0.33	9	0.0	End-point at Pt_4N_3. Fine yellow ppt.
48	4	0.002	1	3 ml 0.2M Na_4-EDTA	i 2.6	0.002	0.8	⩾0.45	24		Intersection, then considerable linear increase
49	4	0.002	1	2 ml 0.2 M Na_2-EDTA + 2 ml 0.5M Na_2HPO_4	i 3.00 h	0.002	0.0	0.71		0.0	
50	4	0.002	1	1 ml M Na_3-citrate + 2 ml 0.5M Na_2HPO_4	c 3.00 h	0.002	0.0	0.60	6	0.0	
51	4	0.001	1	5 ml M Na_3-citrate	c 3.00 h	0.001	0.4	0.35	7	0.0	End-point at Pt_4N_3. Fine yellow ppt.
52	4	0.002	1	1 ml 0.2M KCN + 2 ml 0.5M Na_2HPO_4		0.002					Low density
53	4	0.002	1	2 ml M NH_3 + 5 ml 0.1M NH_4NO_3	i 2.97 h	0.002	0.0	0.66	10	1.0	Fine yellow ppt.
54	4	0.002	1	2 ml 2M pyridine	i 2.97 h	0.002	0.4	0.61	6	1.0	Fine yellow ppt.

* i = intersection point; c = contact point; h = horizontal maximum density line.

which contained large amounts of ammonia did the insoluble compound at the first maximum density point have the composition $Au_2N_3 \downarrow \downarrow$.

In the absence of other metals

Table II, presents the composition of the solutions together with the results obtained (see Fig. 1). All titrations, which were carried out in the *absence of potassium thiocyanate*, gave low densities, the initial precipitation occurred very late and no end-point was reached (Expts. 21–24). Successful titrations could be carried out *only* in solutions
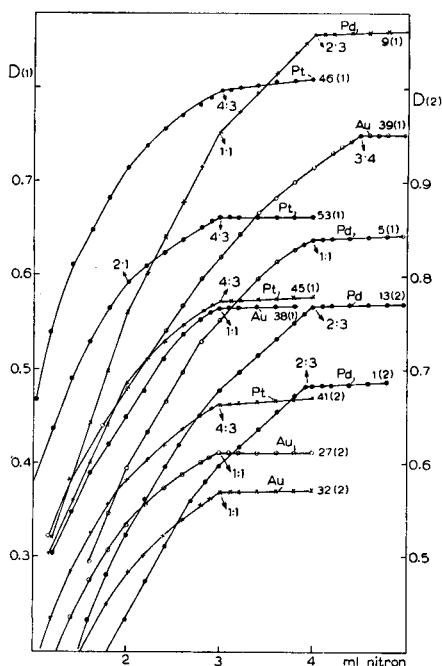
Fig. 1. Titrations of noble metal salts (= Me) with nitron (= N). Molar ratios [Me] : [N] at the critical points.
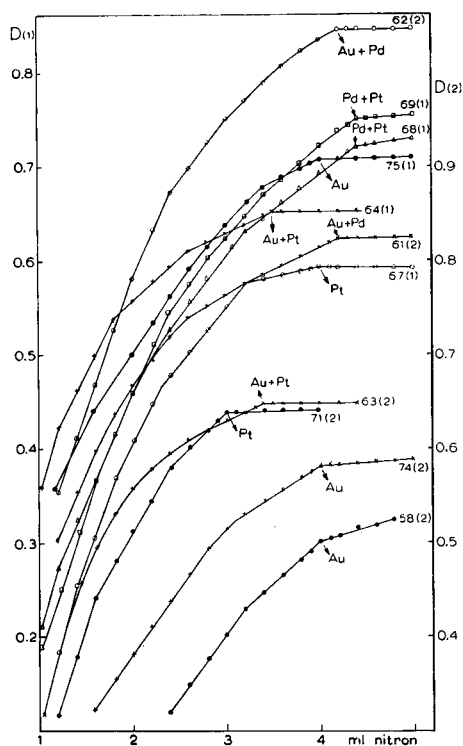
Fig. 2. Titrations of noble metal mixtures with nitron.

that contained sufficient potassium thiocyanate (conc. approx. = $0.1M$). Large *excesses of thiocyanate* made the end-point less certain (*cf*. Expts. 25 and 26). There were no essential differences between the results obtained in *nitric acid*, in *hydrogen chloride* or even in *sodium acetate* solutions (Expts. 27–29). Excesses of Na_3-*citrate* or Na_2-*EDTA* had no marked effect (Expts. 30–33). In the presence of excesses of Na_4-EDTA no end-point was reached (Expt. 34). The addition of excesses of polyphosphates caused an extension of the titration time and the end-point was less certain (Expts. 35–36). A *dilute ammonia* solution had hardly any influence on the end-point (Expts. 37 and 38). In the presence of a more *concentrated solution of ammonia* (conc. $0.4M$) the

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TABLE

Composition: a ml metal salts $+$ b ml KCNS $+$ c ml supplements

Expt. No.	$HAuCl_4$		$PdCl_2$		H_2PtCl_6		ml 2M KCNS	Supplements	Au
	ml	Mola-rity	ml	Mola-rity	ml	Mola-rity			
55	3	0.002	4	0.001	–	—	1	0.5 ml conc. NH_3	1.183*
56	3	0.002	–	—	–	—	1	1 ml M NH_3 + 1 ml M NH_4NO_3	1.183*
57	3	0.002	6	0.002	–	—	1	0.5 ml conc. NH_3 + 5 ml 0.2M Na_2-EDTA	1.183*
58	3	0.002	6	0.002	–	—	1	1 ml 2M NH_3 + 5 ml M Na_3-citrate	1.183*
59	3	0.002	–	—	2	0.002	1	0.5 ml conc. NH_3 + 3 ml 0.2M Na_2-EDTA	1.183*
60	3	0.002	4	0.001	2	0.002	3	0.5 ml conc. NH_3 + 3 ml 0.2M Na_2-EDTA	1.183*
61	2	0.002	3	0.001	–	—	1	3 ml M Na_3-citrate	0.7887*
62	2	0.002	3	0.001	–	—	1	3 ml 0.2M Na_2-EDTA	0.7887*
63	2	0.002	–	—	2	0.002	1	3 ml M Na_3-citrate	0.7887*
64	2	0.002			2	0.002	1	3 ml 0.2M Na_2-EDTA	0.7887*
65	3	0.002	–	—	2	0.002	1	0.5 ml conc. NH_3 + 3 ml M Na_3-citrate	1.183
66	–	—	6	0.002	4	0.002	1	1 ml M NH_3	
67	–	—	6	0.002	4	0.002	1	1 ml M NH_3 + 3 ml M Na_3-citrate	
68	–	—	2	0.002	2	0.002	1	—	
69	–	—	2	0.002	2	0.002	1	3 ml 0.2M Na_2-EDTA	
70	–	—	4	0.001	4	0.002	3	1 ml M NH_3	
71	–	—	6	0.002	4	0.002	1	1 ml M NH_3	
72	–	—	4	0.001	4	0.002	1	1 ml M NH_3	
73	3	0.002	–	—	3	0.002	1	0.5 ml conc. NH_3	1.183*
74	3	0.002	5	0.002	2	0.002	3	0.5 ml conc. NH_3 + 3 ml 0.2M Na_2-EDTA	1.183*
75	3	0.002	5	0.002	2	0.002	1	0.5 ml conc. NH_3	1.183*

* = the metal determined; i = intersection point; c = contact point; h = horizontal maximum.

titration took a different course: the reaction now became somewhat more sensitive towards gold and a higher maximum density value was obtained (Expt. 39). *The end-point was obtained at the point of quantitative formation of* $Au_2N_3 \downarrow \downarrow$. The precipitate was of a yellow colour instead of white $Au_1N_1 \downarrow \downarrow$. No precipitation at all occurred with nitron in the presence of excess potassium cyanide (Expt. 40). In most cases the *error* was close to zero. A normal titration lasted 5–10 minutes.

In mixtures

Table IV and Fig. 2 present some results of titrations of gold in mixtures with palladium or platinum or in mixtures containing both.

IV

+ ad 20 ml H_2O + x ml nM nitron (= N). T = 20°

Content mg		Nitron (x)		Initial ppt. at ml	Max. density value	Titration time in min	% error	Remarks
Pd	Pt	ml	Molarity					
0.426		i 4.50 h	0.002	0.2	0.74	10	0.0	End-point at Au_2N_3; yellow ppt.
		i 4.00 h	0.0015	0.2	0.49	20	0.0	End-point at Au_1N_1; white ppt.
1.279		i 3.9 h	0.0015	0.0	0.47	20	2.5	End-point at Au_1N_1; white ppt.
1.279		i 4.0 h	0.0015	0.2	0.50	15	0.0	End-point at Au_1N_1
	0.781	i.c.3.00h	0.002	0.0	0.55	14	0.0	End-point at Au_1N_1; yellowish ppt.
0.426	0.781	i 3.0 h	0.002	0.0	0.57	12	0.0	End-point at Au_1N_1
0.320*		i 4.20h	0.002	0.4	0.82	8	1.2	End-point at Au_1N_1 + Pd_2N_3; pink ppt.
0.320*		c 4.20h	0.002	0.4	0.85	7	1.2	End-point at Au_1N_1 + Pd_2N_3; pink ppt.
	0.781*	i 3.50h	0.002	0.4	0.65	10	0.0	End-point at Au_1N_1 + Pt_4N_3; yellow ppt.
	0.781*	i 3.50h	0.002	0.2	0.65	5	0.0	End-point at Au_1N_1 + Pt_4N_3
	0.781	i 4.40h	0.002	0.0	0.76	5	2.2	End-point at Au_1N_1 + Pt_4N_3; lemon yellow ppt.
1.279	1.562*	c 4.0 h	0.0015	0.4	0.41	12	0.0	End-point at Pt_4N_3; brown ppt.
1.279	1.562*	c 4.0 h	0.0015	0.2	0.59	9	0.0	End-point at Pt_4N_3; yellow ppt.
0.426*	0.781*	c 4.50h	0.002	0.2	0.90	10	0.0	End-point at Pd_2N_3 + Pt_4N_3
0.426*	0.781*	i 4.40h	0.002	0.2	0.95	8	2.0	End-point at Pd_2N_3 + Pt_4N_3
0.426	1.562*	i 3.00h	0.002	0.4	0.61	7	0.0	End-point at Pt_4N_3
1.067	1.562*	i 3.00h	0.002	0.2	0.64	7	0.0	End-point Pt_4N_3; bright yellow ppt.
0.426	1.562*	i 3.00h	0.002	0.6	0.54	9	0.0	End-point Pt_4N_3; bright yellow ppt.
	1.172	i 3.98h	0.0015	0.2	0.52	13	0.2	End-point at Au_1N_1; yellow ptt.
1.067	0.781	i 4.00h	0.0015	0.0	0.58	15	0.0	End-point at Au_1N_1; white ppt.
1.067	0.781	i 4.00h	0.002	0.2	0.71	11	0.0	End-point at Au_1N_1; lemon yellow ppt.

density line.

Gold + *palladium*. In the presence of *dilute ammonia* and excesses of Na_3-citrate (Expts. 58) a white precipitate was obtained and only the gold was titrated as $Au_1N_1\downarrow\downarrow$. In the presence of *concentrated ammonia*, the palladium remained dissolved while the gold alone was determined as $Au_2N_3\downarrow\downarrow$ (Expt. 55) just as in the absence of palladium (*cf.* Table II, Expt. 39). The maximum density value was high and therefore this procedure can be especially recommended. It was very interesting to establish that when an excess of Na_2-EDTA was added to the solution together with the concentrated ammonia, the maximum density value was lower than before and only the gold was determined as $Au_1N_1\downarrow\downarrow$ (Expt. 57). (The lower density could also be caused by the presence of excesses of palladium.)

In contrast to this, the sum of gold and palladium, as $Au_1N_1 + Pd_2N_3\downarrow\downarrow$ was always obtained when ammonia was absent and complexing agents such as citrate or Na_2-EDTA were present (Expts. 61 and 62).

Gold + platinum. When concentrated ammonia was added only the gold was determined as $Au_1N_1\downarrow\downarrow$ (Expt. 73). The same result was obtained when in addition to the concentrated ammonia Na_2-EDTA was present. Here too the gold was determined solely as $Au_1N_1\downarrow\downarrow$ (Expt. 59). In the *absence of ammonia* but in the presence of excesses of a complexing agent, such as Na_3-citrate or Na_2-EDTA, the *sum* of both metals was obtained at the first maximum point as $Au_1N_1 + Pt_4N_3\downarrow\downarrow$ (Expts. 63 and 64).

Gold + palladium + platinum. Only the gold was determined as Au_1N_1 while the platinum and palladium were masked when the solution being analysed contained concentrated ammonia $+ Na_2$-EDTA (Expts. 60 and 74).

Titrations of solutions of palladium chloride

Compounds

Using nitron as titrant, only one end-point was obtained in all cases at the point of the quantitative formation of $Pd_2N_3\downarrow\downarrow$. In reverse titrations using palladium chloride as titrant other compounds were obtained, amongst them the compound $Pd_1N_3\downarrow\downarrow$. No visible reaction whatsoever occurred between nitron and palladium chloride in the absence of potassium thiocyanate.

In the absence of other metals

Table I and Fig. 1 present a selection of such experiments, as well as the results obtained. Here too 1 ml $2M$ KCNS was entirely sufficient for a successful titration (Expts. 1 and 2) which lasted 5–10 minutes. However, when the solution contained very small amounts of *potassium thiocyanate* (Expt. 17) the density at the intersection point was lower and the density line showed a linear rise. 0.43 mg palladium (in 20 ml solution) was, in all cases, entirely sufficient for the analysis. The maximum density values were high (0.6 to 0.85) so that half the amount of palladium can, perhaps, still be analysed. The titrated solution may have a pH of $\sim$ 1–3 or $\sim$ 7–9 (Expts. 3, 4, 6, 7 and 8). The end-point was determined in all cases with equal accuracy. *Na_3-citrate* or *Na_2-tartrate* could be present in large excesses (Expts. 9–11). Even excesses of *tripolyphosphate* or *Na_2-EDTA* (Expts. 12 and 13) were without influence. In all cases a bright brown powder was obtained and the error was always near zero or less than 1%. Just as in the case of gold, no precipitation occurred in the presence of potassium cyanide (Expt. 15). No precipitation what all occurred when the solution contained *dilute ammonia* (Expt. 18) or excesses of Na_4-EDTA (Expt. 14). The compound Pd_2N_3 dissolved in 50% alcoholic solution (Expt. 16). The titration was normal even in a solution which contained a considerable amount of *ammonium nitrate* (conc. $= 0.2M$) (Expt. 19).

In mixtures

Palladium + gold. Palladium could be determined only from the *sum* of both metals (Table IV, Expts. 61 and 62), as $Au_1N_1 + Pd_2N_3\downarrow\downarrow$.

Palladium + platinum. In this case also, the *sum* of both metals, as $Pd_2N_3 + Pt_4N_3\downarrow\downarrow$,

was obtained at the end-point. The solution contained either no complexing agents at all (Expt. 68), or Na_2-EDTA in excess (Expt. 69). In the presence of even dilute *ammonia*, the palladium remained dissolved (Expts. 58, 66, 67, 70, 71 and 72); it could be determined in all cases by difference.

Titrations of solutions of chloroplatinic acid

Compounds

No visible reaction occurred between platinum and nitron in the absence of potassium thiocyanate. The composition of the compound, which was always obtained quantitatively when titrating chloroplatinic acid solution (containing potassium thiocyanate) with nitron was: $Pt_4N_3\downarrow\downarrow$. In reverse titrations, using the platinum solution as titrant, no precipitation occurred at pH's 7–9, while at lower pH's a compound $Pt_1N_3\downarrow\downarrow$ was obtained.

In the absence of other metals

The results are given in Table III. The platinum(IV) amounted in most cases to 1.562 mg, but in individual cases 0.78 mg was sufficient. The maximum density value was in the last case approximately equal to half the previous value. The presence of large excesses of potassium thiocyanate was not disadvantageous (Expts. 41 and 42). The compound Pt_4N_3 precipitated as a fine yellow powder.

From the experiments listed in Table IV it can be seen that no precipitation of platinum occurred in solutions containing more concentrated ammonia (0.5 ml conc. NH_3). But when the ammonia was diluted (Expt. 53) a regular precipitation of $Pt_4N_3\downarrow\downarrow$ occurred. The same compound was obtained quantitatively at pH's 1–9 in the presence and in the absence of complexing agents (Expts. 46, 47, 49, 50 and 51). Here also, no precipitation occurred in the presence of potassium cyanide (Expt. 52). In the presence of Na_4-EDTA a precipitate was formed, but the intersection point was not clear (Expt. 48). In all normal titrations the titration time was 5–10 minutes, and the error was less than 1%.

In mixtures

The experiments are presented in Table IV.

Platinum + palladium. It was easy to determine platinum alone in mixtures of platinum with palladium (Expts. 66, 67, 70, 71 and 72), by adding 1 ml M NH_3. The end-point always lay at the quantitative formation of $Pt_4N_3\downarrow\downarrow$. When *no complexing agent* at all was present, or when Na_2-EDTA was added in excess, the *sum* of both metals was measured as $Pt_4N_3 + Pd_2N_3\downarrow\downarrow$ (Expts. 68 and 69).

Platinum + gold. Only the sum of both metals could be determined as $Pt_4N_3 + Au_1N_1\downarrow\downarrow$; this could be carried out in solutions containing large excesses of Na_3-citrate or Na_2-EDTA (Expts. 63 and 64). But when the solution contained *concentrated ammonia* together with Na_2-EDTA (Expt. 59) or even concentrated ammonia alone (Expt. 73), the platinum remained dissolved and could be determined from the difference of two titrations.

ANALYTICAL ASPECTS

Gold(III), palladium(II) or platinum(IV) can be easily determined with precision within 10 minutes by a heterometric titration of the metal chloride in thiocyanate

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solution, with nitron. This solution may contain hydrochloric, nitric, acetic or phosphoric acid. The pH may be between 1 and 7. The solution may contain, in addition to the above, the following masking agents in excess: citrate, tartrate, Na_2-EDTA, pyro- or tripolyphosphate. The amounts of metal necessary for the analysis are: $\sim$ 0.5 mg palladium, $\sim$ 1 mg gold and $\sim$ 1.5 mg platinum. No filter is required. The error is always between zero and 1%. The end-point is always obtained from the intersection point of the following two lines: a line drawn through the optical density points of the last part of the titration curve (approximately the last quarter) and a line drawn through the horizontal density points *after* the end-point. In exceptional cases, the end-point is obtained from the contact point of the horizontal density line with the titration density curve.

In the case of gold, the sensitivity becomes somewhat higher (and the end-point is at $Au_2N_3\downarrow\downarrow$), when the heterometric titration is carried out in a solution that contains large excesses of ammonia (conc. $\sim$ 0.3M).

Composition of the compounds

The following compounds are quantitatively obtained at the end-point of the titration:

$$Au_1N_1\downarrow\downarrow; \ (Au_2N_3\downarrow\downarrow); \ Pd_2N_3\downarrow\downarrow; \ Pt_4N_3\downarrow\downarrow.$$
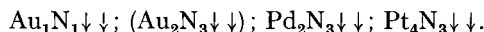
In strong ammoniacal solution the gold is precipitated as $Au_2N_3\downarrow\downarrow$. The structures of these and other compounds obtained will be discussed in a special report.

METHODS
Determination of gold
In the absence of other metals

I. (*as Au_1N_1*). 20 ml aqueous solution of gold chloride, which contains 1–1.5 mg gold, 1 ml 2M KCNS and may contain supplements, are titrated with 0.002M–0.0015M nitron.
Remark. The solution being analysed may contain the following supplements: 1 ml M HCl, 1 ml M HNO$_3$, 1–2 ml M CH$_3$COOH, 1 ml M H$_3$PO$_4$, 1 ml M Na-acetate, 1 ml M Na$_3$-citrate, 1 ml M Na$_2$-tartrate, 3 ml 0.2M Na$_2$-EDTA.
II. (*as Au_2N_3*). 20 ml aqueous solution of gold chloride, which contains $\sim$1 mg gold, 1 ml 2M KCNS and 0.5 ml conc. NH$_3$ are titrated with 0.002M–0.0015M nitron.

In mixtures of gold and palladium

III. (*as Au_1N_1*). 20 ml aqueous solution of gold chloride + palladium chloride, which contains $\sim$1 mg gold, 1 ml 2M KCNS and $\sim$1 ml M NH$_3$ are titrated with 0.002M–0.0015M nitron.
IV. (*as Au_2N_3*). As III, but the solution contains 0.5 ml conc. NH$_3$.
Remark. In both cases the palladium is masked by the ammonia. When the solution contains excesses of Na$_2$-EDTA in addition to the concentrated ammonia, the compound $Au_1N_1\downarrow\downarrow$ is obtained.

In mixtures of gold and platinum

V. (*as Au_1N_1*). 20 ml aqueous solution of gold chloride + chloroplatinic acid, which contains 1 ml 2M KCNS, $\sim$1 mg gold and 0.5 ml conc. ammonia are titrated with 0.002M nitron.

In mixtures of gold, palladium and platinum

VI. (*as Au_1N_1*). 20 ml aqueous solution of all three metals as chlorides, which contains $\sim$1 mg gold, 1 ml 2M KCNS, 0.5 ml conc. ammonia and 3 ml 2M Na$_2$-EDTA are titrated with 0.002M–0.0015M nitron.

Determination of palladium
In the absence of other metals

VII. (*as Pd_2N_3*). 20 ml aqueous solution of palladium chloride, which contains $\leqslant$ 0.5 mg palladium, 1 ml 2M KCNS and may contain supplements, are titrated with 0.0015M nitron.

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Remark. The solution being analysed may contain the following supplements: 1 ml M HCl, 1 ml M HNO$_3$, 1–2 ml M CH$_3$COOH, 1 ml M H$_3$PO$_4$, 1 ml M Na-acetate, 1 ml M Na$_3$-citrate, 1 ml M Na$_2$-tartrate, 3 ml 0.2M Na$_2$-EDTA.

Determination of platinum

In the absence of other metals

VIII. (as Pt$_4$N$_3$). 20 ml aqueous solution of chloroplatinic acid which contains ∼1.5 mg platinum, 1 or more ml 2M KCNS and may contain supplements, are titrated with 0.002M nitron.

Remark. The same supplements may be present as in (I).

In mixtures of platinum and palladium

IX. (as Pt$_4$N$_3$). 20 ml aqueous solution of platinum chloride + palladium chloride, which contains ∼1.5 mg platinum, 1 or more ml 2M KCNS, 1 ml M NH$_3$ and 1–2 ml Na$_3$-citrate are titrated with 0.0015M nitron.

Determination of the sum of two or three metals

X. (as Au$_1$N$_1$ + Pd$_2$N$_3$ + Pt$_4$N$_3$). 20 ml solution which contains 1–2 mg of the metals, 1 ml 2M KCNS and 3 ml 0.2M Na$_2$-EDTA or 1–2 ml Na$_3$-citrate are titrated with 0.002M nitron.

SUMMARY

Methods are presented for a rapid and precise determination of gold(III), palladium or platinum-(IV) either alone or in mixtures. The heterometric titrations were carried out in thiocyanate solutions with nitron. ∼1 mg gold, ⩽ 0.5 mg palladium or ∼1.5 mg platinum (dissolved in 20 ml aqueous solution) were necessary for a determination, which lasted 5–10 minutes. The error was mostly between zero and 1%.

The insoluble compounds, which were quantitatively obtained at the end-points of the titrations, had the following compositions:

$$Au_1N_1; (Au_2N_3); Pd_2N_3 \text{ and } Pt_4N_3. (N = nitron)$$
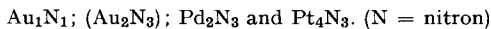
At pH 1–7 all these compounds were entirely insensitive to common masking agents, such as citrate, tartrate, ethylenediaminetetraacetate, pyro- and tripolyphosphate.

RÉSUMÉ

Des méthodes rapides et précises sont proposées pour le dosage de l'or, du palladium et du platine. Les titrages hétérométriques sont effectués en solutions thiocyaniques, au moyen de nitron. Les composés insolubles obtenus aux points finals des titrages sont les suivants: Au$_1$N$_1$; (Au$_2$N$_3$); Pd$_2$N$_3$ et Pt$_4$N$_3$ (N = nitron).

ZUSAMMENFASSUNG

Es werden rasche und genaue Methoden für die Bestimmung von Gold, Palladium und Platin vorgeschlagen. Die heterometrischen Titrationen werden in Thiocyanatlösung mit Nitron vorgenommen. Die beim Endpunkt der Titrationen erhaltenen unlöslichen Verbindungen haben folgende Zusammensetzungen: Au$_1$N$_1$; (Au$_2$N$_3$); Pd$_2$N$_3$ und Pt$_4$N$_3$ (N = Nitron).

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PHOTOMETRIC TITRATION OF IRON WITH
ETHYLENEDIAMINEDI(o-HYDROXYPHENYLACETIC ACID)

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The synthesis of ethylenediaminedi(o-hydroxyphenylacetic acid) or N,N'-ethylenebis[2-(o-hydroxyphenyl)-glycine], a compound analogous to ethylenediaminetetraacetic acid, was reported recently by KROLL *et al.*[1]. Stability constants of a

$$HOOC \qquad\qquad COOH$$
$$CH\ NH\ CH_2\ CH_2\ NH\ CH$$
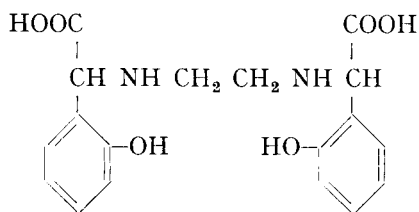
few of its metal chelates have been measured by FROST *et al.*[2], and a spectrophotometric method for determining iron in concentrations below about 10 p.p.m. has been described by UNDERWOOD[3], based upon the very stable, red ferric chelate. This new reagent is interesting because it possesses some of the attributes of ethylenediaminetetraacetic acid while it also bears chromophoric groups not found in EDTA. It is too early to predict what ultimate utility it will find as an analytical reagent; in the meantime, like all interesting reagents, it should be tested in a variety of situations. In this paper, it is shown that ferric iron in fractional mg amounts (or μg-amounts by scaling down the procedure) can be titrated with ethylenediaminedi(o-hydroxyphenylacetic acid), making use of a photometric end-point. Because only absorbance changes rather than absolute absorbance values are needed to fix such an end-point, certain interferences in an ordinary spectrophotometric method might be circumvented by the titration technique. The end-point should, moreover, be more accurate than isolated absorbance measurements. Further general information about photometric titrations may be found in the literature[4,5].

EXPERIMENTAL

Apparatus and reagents

Photometric titrations were performed using a Beckman Model DU spectrophotometer adapted as described previously[6]. The length of the light path through the titration cell was 1.7 cm. The titrant was delivered from a 10-ml buret graduated in 0.02-ml units. pH values were measured with a Beckman Zeromatic pH meter.

A standard ferric solution was prepared by dissolving 1.000 g of pure iron wire in 20 ml of 1:1 nitric acid, boiling the solution for a few minutes, and diluting to exactly 1 l with distilled water. Dilutions of this stock solution were prepared as required, with the addition of sufficient nitric acid to prevent hydrolysis of the iron.

As noted below, most of the titrations were performed at pH 3.5. Solutions were buffered at this pH value with a $1M$ chloroacetate buffer prepared by dissolving 48 g of monochloroacetic acid in 400 ml of distilled water, adjusting the pH to 3.5 by the addition of concentrated sodium hydroxide solution, and diluting the solution to 500 ml.

The reagent ethylenediaminedi(o-hydroxyphenylacetic acid) was obtained from the Geigy Industrial Chemicals Division of the Geigy Chemical Corporation, Ardsley, N.Y., under the trade name of Chel 138. As noted before[3], the reagent contains dark-colored impurities which probably result from air oxidation of the phenolic portions of the molecule. It was purified for this work by suspending it in water, adding the minimal amount of sodium hydroxide to effect solution, treating the solution with charcoal, and acidifying to pH 4 with hydrochloric acid. The white precipitate was washed with water and dried in a vacuum desiccator over silica gel. It remains white indefinitely when kept dry. A $0.01M$ solution of the reagent was prepared by suspending 2 g of the solid in 400 ml of water, slowly adding just enough sodium hydroxide to effect solution (the pH of the solution was about 8.8 at this point), and diluting to 500 ml with water. The solution was treated with charcoal to remove a small trace of colored material and filtered into a reagent bottle. Oxygen-free nitrogen was bubbled through the solution for about 30 min, and the bottle was tightly closed. The iron titer of this solution remained undiminished throughout daily checks over a period of 3 weeks.

Effect of pH

In developing the spectrophotometric method for iron using ethylenediamine-di(o-hydroxyphenylacetic acid), it was shown[3] that color development was maximal throughout the pH range of 2.5 to 9.5. However, excess reagent was used, whereas
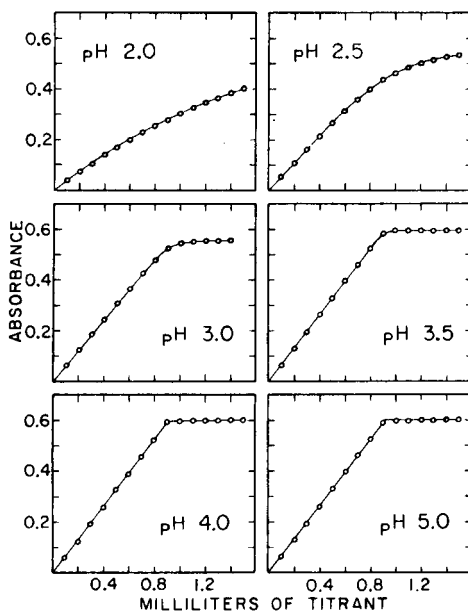
Fig. 1. Effect of pH.

a sharp photometric end-point requires that the chelation reaction go well toward completion with quantities of reagent more nearly stoichiometric. The effect of pH on the titration is shown in Fig. 1, where it may be seen that the pH should be at least 3 in order to obtain a reasonably good titration curve. The titrations shown in the figure were set up by adding 10 ml of the chloroacetate buffer to a solution con-

taining 0.5 mg of ferric iron, diluting to about 100 ml, and adjusting the pH to the desired value with drops of concentrated hydrochloric acid or sodium hydroxide solutions. (For pH values greater than 3.5, an acetate buffer was substituted for the chloroacetate.) As a compromise between staying on the safe side of the lower pH limit and retaining a pH as low as possible, all further titrations were performed at pH 3.5.

Reproducibility

Table I shows the results of a number of titrations involving small quantities of ferric iron in pure solution. 15 samples ranging from 0.2 to 1 mg show an average deviation of 5.5 μg, or about 1%. The volume in all cases was about 100 ml, so that the ferric concentrations titrated ranged from about $3.6 \cdot 10^{-5}$ to $1.8 \cdot 10^{-4}M$. The reproducibility is satisfying in this context. The results shown in the table include all of those obtained in a certain day's work; results from day to day are about the same. Certain statistical tests would permit one to discard a few of the results, leading to a much better apparent reproducibility. The end-points in the titrations are found by graphical extrapolation from a few points taken before and after the end-point. It is important to plot the data in such a way that the graphical process itself does not limit the reproducibility. This has been emphasized by GODDU AND HUME[4].

<div align="center">

TABLE I

TYPICAL RESULTS

</div>

Iron taken mg	Iron found mg	Deviation mg	Deviation %
0.2000	0.2043	0.0043	2.2
0.2000	0.2043	0.0043	2.2
0.3000	0.3078	0.0078	2.6
0.4000	0.4001	0.0001	0.0
0.4000	0.4029	0.0029	0.7
0.5000	0.4980	0.0020	0.4
0.5000	0.4897	0.0103	2.1
0.5000	0.4980	0.0020	0.4
0.6000	0.6044	0.0044	0.7
0.6000	0.6016	0.0016	0.3
0.7000	0.6939	0.0061	0.9
0.8000	0.7890	0.0110	1.4
1.0000	0.9961	0.0039	0.4
1.0000	0.9849	0.0151	1.5
1.0000	0.9933	0.0067	0.7

Average deviation: 0.0055 mg.

Iron concentration range

With the particular cell used for these titrations, 0.8 mg of iron in a volume of 100 ml leads to an absorbance value of about 1 at the end of the titration when the wave length is 470 mμ, the absorption maximum for the red ferric chelate[3]. To| titrate larger quantities of iron, it is desirable to change to a wave length where lower sensitivity obtains. This flexibility, indeed, is one of the attractive features of photo-

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metric titrations. 2 mg of iron in a volume of 100 ml led to an ultimate absorbance of about 0.95 at a wave length of 550 mμ. A series of titrations in this concentration range displayed an average deviation of about 0.6%. The larger volume of titrant may partly account for this improvement over the results shown in Table I for lesser quantities of iron.

Since a volume of 100 ml is not obligatory, much smaller quantities of iron can be titrated easily by scaling down the procedure. It is advisable then to employ a more dilute titrant so that the buret readings are sufficiently precise. For example, 0.1 mg of iron in 50 ml of solution is nicely titrated with 0.001M reagent with errors of less than 1%.

Effect of other metals

In a series of titrations of 0.5 mg of iron in 100 ml, 50-mg quantities of fourteen other metal ions were tested for interference. The following ions did not affect the titration in any way: magnesium, calcium, chromium(III), manganese(II), cobalt(II), zinc, cadmium, mercury(II), and lead. Thorium formed a precipitate when the solution was adjusted to pH 3.5 before the titration was started. Silver likewise formed a precipitate when the buffer was added, perhaps because of the presence of chloride in the chloroacetate solution. Aluminum caused slightly high results. With nickel, the results were correct but the titration took slightly more time than usual because of a drift in the absorbance values following each increment of titrant. In the case of copper, the drift was so persistent that the titration was considered non-feasible. Apparently a question of kinetics is involved: the titrant reacts with copper locally near the buret tip, and the shift to the more stable ferric chelate occurs very slowly after the solution has been mixed.

DISCUSSION

The titration of very dilute ferric iron solutions with the reagent ethylenediaminedi(o-hydroxyphenylacetic acid) using a photometric end-point works very well. A number of other metals do not interfere. The photometric titration can be performed easily and rapidly, employing a simple adaptation of ordinary spectrophotometric apparatus. It would be overly optimistic to envision wide general acceptance of this titration for determining iron, but one can easily imagine that it may be very useful in certain applications where particular interference problems must be circumvented.

SUMMARY

Fractional mg quantities of ferric iron in 100 ml of solution can be titrated at pH 3.5 with a solution of ethylenediaminedi(o-hydroxyphenylacetic acid). The end-point is found photometrically. Errors are generally under 1%, and a number of metals do not interfere. By scaling down the volume of the solution and the titrant concentration, the titration can be extended to μg quantities of iron, and mg quantities are also accessible by changing to a wave length where the sensitivity is not so great. The titration may be useful in certain applications.

RÉSUMÉ

Le fer(III) peut être titré par une solution d'acide éthylènediamine di(o-hydroxy-phénylacé-tique). Le point final est déterminé photométriquement. Les erreurs sont généralement inférieures à 1%. Plusiers métaux ne gênent pas.

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ZUSAMMENFASSUNG

Eisen-(3) kann mit einer Lösung von Äthylendiamin-di-(o-hydroxyphenylessigsäure) titriert werden. Der Endpunkt wird photometrisch bestimmt. Die Fehler liegen meistens unter 1%. Eine Reihe von Metallen zeigt keine Störung der Titration.

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U.V. ABSORPTION SPECTRA OF 8-OXYQUINOLINE
AND ITS COPPER CHELATE

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A comparative study of the absorption spectra of an organic ligand and its metal chelate can provide useful information regarding the nature of binding of the metal atom in the chelate. This has been shown by Basu and Chatterjee[1,2] for chelates of acetyl acetone and quinoline 8-carboxylic acid. In the present communication the same method has been applied to secure information regarding the structure of the copper complex of 8-oxyquinoline.

In solution, 8-oxyquinoline should exist as I; despite the presence of the basic N atom in the molecule a zwitterion structure II is less probable in view of the weakly acidic character of the phenolic group.

I   II
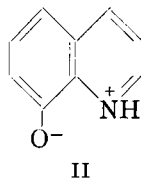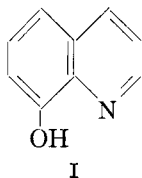
In acidic and alkaline media the molecule in all probability acquires the structures III and IV respectively.

III   IV
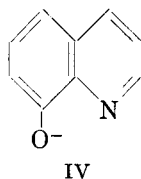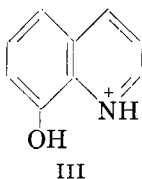
In 95% ethyl alcoholic solution the free ligand has two absorption maxima at 242 mμ and 310 mμ (Fig. 1). In 0.1N KOH in 95% alcohol, the band at 242 mμ shifts to 256 mμ. The second band is broad and diffuse and may be looked upon as made up of two overlapping bands with maxima at 340 mμ and 370 mμ respectively (Fig. 1). In 0.1N perchloric acid the ligand band shows absorption maxima at 255 mμ, 310 mμ, 320 mμ and 370 mμ (Fig. 2). The copper chelate of 8-oxyquinoline shows two absorption maxima at 258 mμ and 395 mμ respectively (Fig. 2). The nature of the absorption curve is similar to that of the ligand itself but the 310-mμ ligand band is shifted to 395 mμ.

The chelate cannot be ionic, for the characteristic absorption band of the ligand in the alkaline medium is absent in the chelate. It cannot have a simple covalent structure (V) for this will put a positive charge on the N atom and the characteristic band of the ligand in the acid solution should be present in the chelate, while contrary is the case.

It is also important to account for the shift of the ligand absorption band at 310 mμ to 395 mμ in the chelate. Obviously this indicates a larger resonating path of the
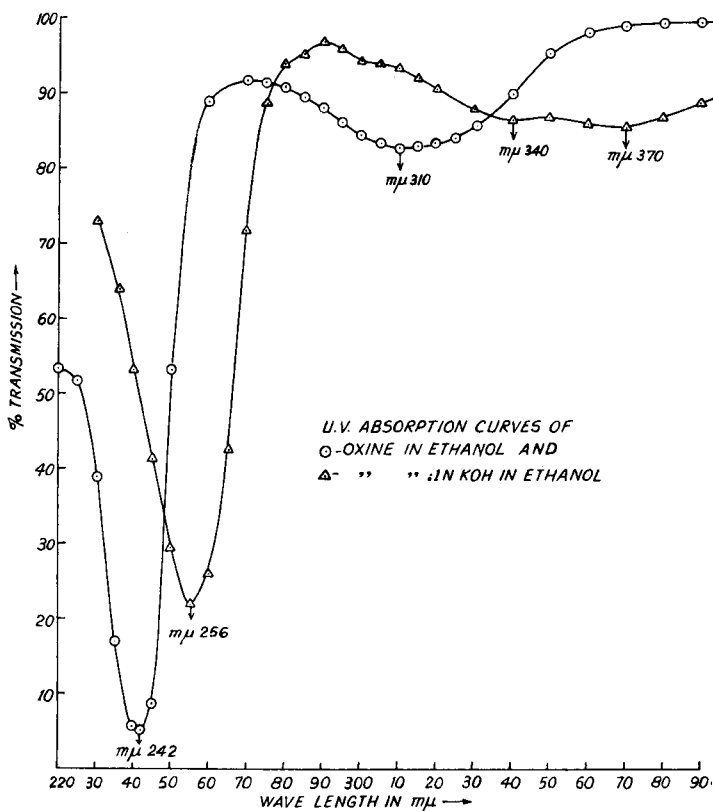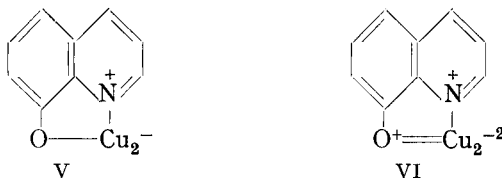

Fig. 1.

electrons in the chelate than in that of the ligand itself. All these characteristics can however be explained if the structure VI be accepted for the chelate.

In this structure Cu is doubly bonded to oxygen and since the double bond is in conjugation with the double bonds in the ring system, the structure shows characteristic absorption of its own which we attribute to the 295-mμ band.

The structure, however, presupposes a planar configuration, in which copper is in dsp^2-hybridised state; the additional pπ–dπ bond possibly confers further stability to the planar structure.

MERRITT, CADY AND MUNDY[3] have cited X-ray evidence in favour of a tetrahedral configuration of anhydrous copper oxinate. The space group P $2_1/a$ reported by the last named authors apparently indicates that the molecule is non-centrosymmetric but this is not quite conclusive. Also an outer level sp^3-configuration for the copper complex should have considerable contribution from the ionic structure and the characteristic absorption band of the oxinate ion should be present in the chelate which is not actually the case.

U.V ABSORPTION CURVES OF
(△) OXINE IN ;IN HClO₄ IN ETHANOL
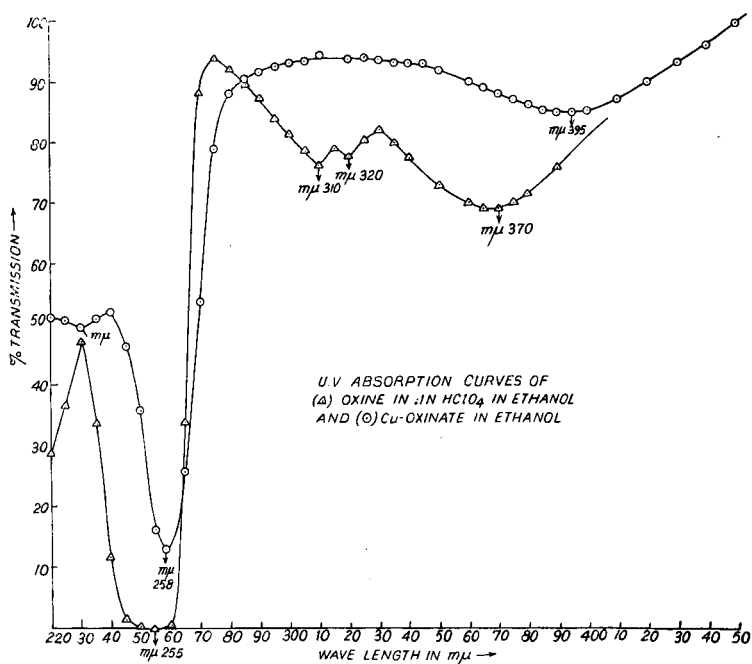AND (⊙) Cu-OXINATE IN ETHANOL

Fig. 2.

The structural analogy of zinc oxinate dihydrate and copper oxinate dihydrate as implied by the above workers is not tenable. In the zinc compound itself for which sp^3-d^2-configuration has been suggested there is considerable difference between the polar and equatorial Zn–O bond distances, indicating the non equivalence of these bonds. Such octahedral sp^3-d^2-structure for the hydrated copper complex will be still less probable, since in this case the water molecules are more loosely bound than that of the zinc complex. This is indicated by the fact that whereas the zinc compound loses water at 135°, the copper complex is completely dihydrated at 105°. Further, it has recently been shown by JONES et al.[4] that in all probability there is π-bonding between metal and ligand in nickel-8-oxyquinoline chelate, which evidently presupposes a planar structure for the chelate. The possibility for such a planar structure is even greater in copper chelates.

Ultraviolet absorption measurements were carried out with the help of Beckman model D.U. quartz spectrophotometer using 1-cm quartz absorption cells. The alcohol used was refluxed for 6–8 h with solid caustic soda and distilled. It showed complete transmission down to 220 mμ. The concentrations of the solutions employed were 10^{-4}–$10^{-5}M$.

SUMMARY

From a comparison of the U.V. absorption spectra of the copper chelate of 8-oxyquinoline in ethyl alcoholic solution with those of the ligand itself in the same medium and in the presence of $0.1N$ HClO$_4$ and $0.1N$ NaOH respectively, a probable structure for the former has been suggested. The structure presupposes a planar configuration for the complex and a metal–ligand double bonding.

RÉSUMÉ

Une étude a été effectuée en vue de déterminer la structure probable du chélate cuivre–hydroxy-8-quinoléine.

ZUSAMMENFASSUNG

Es wird eine Untersuchung zur Ermittlung der wahrscheinlichen Struktur des Kupfer–8-oxy-chinolats beschrieben.

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THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

VII. THE NITRONAPHTHOLS AS FLUORIMETRIC REAGENTS FOR STANNOUS TIN

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INTRODUCTION

In earlier papers of this series, the use of naphthalene compounds has been reported for the fluorimetric detection of various cations[1-6]. In particular, nitronaphthalene derivatives have been utilized for the fluorimetric detection[1,3-6] and determination[7] of stannous tin. For this paper, the nitro derivatives of 1-naphthol and 2-naphthol have been examined and found to be of importance in the detection of tin by fluorimetric methods. Spots of aqueous solutions of 49 metal salts were placed on No. 1 Whatman Chromatographic paper, air dried and then sprayed separately with 0.1 % solution of the reagents dissolved in a mixture of equal volumes of 96% ethyl alcohol and 10N hydrochloric acid. The paper was air dried, sprayed with 15N NH$_4$OH, again air dried and viewed under ultra-violet light. Under these conditions only stannous tin exhibited any marked fluorescence. The addition of 10N HCl to the alcoholic solutions of the nitronaphthols was found to increase the sensitivity of the test. The intensity of fluorescence was found to vary with the position of the nitro group in the naphthol nucleus.

EXPERIMENTAL

Synthesis of reagents

A summary of the methods of synthesis of the nitro-naphthols will be published in the near future by BRYSON[8]. All nitro-naphthols can be synthesized from the corresponding nitro-naphthylamines[4] by a diazotisation procedure and subsequent replacement of the diazo group by hydroxyl. The synthesis of 5-nitro-1-naphthol from 5-nitro-1-naphthylamine is an example of the procedure used for the preparation of the nitronaphthols.

5-Nitro-1-naphthol

5-Nitro-1-naphthylamine** (0.8 g) was warmed in a mixture of sulphuric acid (5 ml, sp.gr. ~ 1.84) and water (50 ml), then cooled to 0–5° so that the nitronaphthylamine was present in a finely divided state as the sulphate paste, the most suitable form for efficient diazotisation. A solution of sodium nitrite (0.5 g) in water (2.5 ml) was added from a dropping funnel over a period of 10 min at 0–5° and the presence of excess, nitrous acid confirmed by the starch–potassium iodide test. The mixture was stirred for 1 h at 0–5°, then urea (0.1 g) added to destroy excess nitrous acid. The diazo solution was now added slowly over a period of 10 min to 2N H$_2$SO$_4$ maintained just below the boiling point. After the addition was completed, the mixture was boiled for a further 10 min, filtered hot and the filtrate chilled. The flocculent yellow crystals of 5-nitro-1-naphthol were separated and recrystallised from boiling water using a trace of activated charcoal to remove the small amount of red dye which unavoidably forms during the sulphuric acid decomposition step.

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* On study leave at Birkbeck College, University of London.
** For the synthesis of this compound see GARNETT AND LOCK[4].

Yield 0.5 g; m.p. 171–2°; Literature 171°[8]

The same procedure was used for the synthesis of the remaining nitronaphthols, except 8-nitro-1-naphthol and 6-nitro-2-naphthol.

8-Nitro-1-naphthol

When the diazo compound from 8-nitro-1-naphthylamine was decomposed in $2N$ H_2SO_4, following the same procedure as previously reported, excessive coupling appeared to occur, resulting in bad tarring and a very poor yield (approx. 10%) of 8-nitro-1-naphthol. The yield was improved to 30% by using stronger sulphuric acid ($4N$) in the decomposition step. BRYSON[8] suggests that even better yields can be obtained if the diazonium solution is slowly added to the sulphuric acid at 50° (instead of 95°) and the solution slowly brought to the boil. This minimises the loss of 8-nitro-1-naphthol through the competing coupling reaction.

6-Nitro-2-naphthol

This compound can also be readily synthesized from the corresponding nitronaphthylamine by the diazotisation procedure[8], however the authors have used an alternative method of preparation which involves a pressure desulphonation of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid in $10N$ HCl.

A solution of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid* (1.0 g) in $10N$ HCl (10 ml) was carefully heated to 160° for 2 h in a sealed glass tube, then cooled. The solution was diluted with water (90 ml) and the precipitate filtered, dried and recrystallised from benzene in pale yellow needles.

Yield 0.48 g; m.p. 158–9°

This compound showed no depression of melting point when mixed with an authentic sample of 6-nitro-2-hydroxynaphthalene prepared from 6-nitro-2-naphthylamine by a diazotisation procedure.

The observed and reported melting points of the nitro-naphthols are listed in Table I and compared with those of the parent α- and β-naphthols.

TABLE I

MELTING POINTS OF THE NITRONAPHTHOLS

Substituent		Observed m.p.	Literature m.p.
NO_2	OH	°C	°C
	1	95.5	96
	2	122	122
2	1	127.5	128
3	1	168–9	167–8
4	1	166	164
5	1	171–2	171
6	1	181–2	181–2
7	1	212[a]	—
8	1	242[d]	212[d]
1	2	103	103
4	2	120	120
5	2	148	147
6	2	159	156–8
7	2	163	159
8	2	145	145

[a] 7-Nitro-1-naphthol is a new compound, the synthesis of which will be described elsewhere[8].

[d] decomposed without melting.

It will be noticed that the observed and reported melting points for 8-nitro-1-naphthol do not agree. BRYSON[8] discusses this anomaly and presents strong evidence to support the observed melting point.

From Table I, it can be seen that 13 of the theoretically possible 14 nitro-naphthols

* See ANDERSON, GARNETT AND LOCK[6] for the synthesis of this compound.

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are listed, 3-nitro-2-naphthol being the exception. This compound can be synthesized from 3-nitro-2-naphthylamine. However, this is the most difficult of all nitronaphthylamine preparations and was unavailable in sufficient quantity for the preparation of the corresponding nitronaphthol.

Technique of spot testing

The standard procedure reported in previous communications[1,3] was used. The reagents employed are listed in Table II. The results obtained are shown in Table III.

TABLE II

REAGENTS USED FOR SPRAYING METAL IONS

Reagent No.	Reagent 0.1% Solution in a mixture of equal volumes of 96% ethyl alcohol and 10N HCl	Reagent No.	Reagent 0.1% Solution in a mixture of equal volumes of 96% ethyl alcohol and 10N HCl
1	2-Nitro-1-naphthol	8	1-Nitro-2-naphthol
2	3-Nitro-1-naphthol	9	4-Nitro-2-naphthol
3	4-Nitro-1-naphthol	10	5-Nitro-2-naphthol
4	5-Nitro-1-naphthol	11	6-Nitro-2-naphthol
5	6-Nitro-1-naphthol		
6	7-Nitro-1-naphthol	12	7-Nitro-2-naphthol
7	8-Nitro-1-naphthol	13	8-Nitro-2-naphthol

TABLE III

FLUORESCENCE OBTAINED ON SPRAYING SPOTS OF IONS WITH VARIOUS REAGENTS, BEFORE (B) AND AFTER (A) QUENCHING WITH 15N NH₄OH

	Reagent																									
	1		2		3		4		5		6		7		8		9		10		11		12		13	
Ion	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A
Sn+2	F(s)	F(s)	F	F	F	F	F	F	F(s)	F	F(s)	F	F(s)	F(h)	F(s)	F	F	F	F(s)	F	F(s)	F	F(s)	F(s)	F(s)	F
Sn+4															F(t)											
As+5								F(t)																		
Al+3															F(t)								F(t)			
Li+																				F(t)						
Be+2				F(t)				F(t)						F(t)	F(t)		F(t)		F(t)		F(t)		F(t)			
Th+4																			F(t)							
ZrO+2								F(t)							F(t)		F(t)						F(t)		F(t)	
Ti+4																							F(t)			
In+3																				F(t)			F(t)			

Other ions tested included: Fe+2, Fe+3, Hg+, Hg+2, As+3, Sb+3, Bi+3, Cr+3, Mn+2, Zn+2, Sr+2, Ca+2, Ba+2, Mg+2, Cu+2, Co+2, Ni+2, Pb+2, Na+, K+, Rb+, Cs+, Ce+3, Ce+4, Mo+6, Pt+2, Pt+4, Au+3, Pd+2, Tl+, Tl+3, W+6, UO₂+2, VO+2, V+5, Ru+3, Ti+3, Cd+2, Ag+.

These ions gave either no fluorescence or coloured spots with only a faint trace of fluorescence.

B = Before quenching with 15N NH₄OH	F(s) = Slight fluorescence
A = After quenching with 15N NH₄OH	F(t) = Trace of fluorescence
F = Fluorescence	F(h) = Coloured spot with faint fluorescent ring

Effect of acid upon the test

Two series of sensitivity tests were performed using (a) the nitronaphthols dissolved in 96% ethyl alcohol and (b) the nitronaphthols dissolved in equal volumes of 96% ethyl alcohol and $10N$ HCl. The results are summarised in Table IV.

TABLE IV

EFFECT OF ACID UPON THE INTENSITY OF FLUORESCENCE

Reagent	*Reaction with Sn^{+2}*		*Reagent*	*Reaction with Sn^{+2}*	
Series I *0.1% in 96% ethyl alcohol*	*B*	*A*	*Series II* *0.1% in equal volumes of 96% ethyl alcohol and 10N HCl*	*B*	*A*
2-Nitro-1-naphthol	WF	WF	2-Nitro-1-naphthol	WF	WF
3-Nitro-1-naphthol	F	F	3-Nitro-1-naphthol	F	SF
4-Nitro-1-naphthol	WF	F	4-Nitro-1-naphthol	F	F
5-Nitro-1-naphthol	WF	WF	5-Nitro-1-naphthol	F	F
6-Nitro-1-naphthol	WF	WF	6-Nitro-1-naphthol	WF	F
7-Nitro-1-naphthol	WF	F	7-Nitro-1-naphthol	WF	F
8-Nitro-1-naphthol	WF	F(h)	8-Nitro-1-naphthol	WF	F(h)
1-Nitro-2-naphthol	WF	WF	1-Nitro-2-naphthol	WF	F
4-Nitro-2-naphthol	F	F	4-Nitro-2-naphthol	F	SF
5-Nitro-2-naphthol	F	F	5-Nitro-2-naphthol	WF	SF
6-Nitro-2-naphthol	WF	WF	6-Nitro-2-naphthol	WF	F
7-Nitro-2-naphthol	WF	WF	7-Nitro-2-naphthol	WF	WF
8-Nitro-2-naphthol	WF	F	8-Nitro-2-naphthol	WF	SF

SF	= Strong fluorescence	F(h)	= Coloured spot surrounded by a faint fluorescent ring
F	= Fluorescence	B	= Before quenching with $15N$ NH_4OH
WF	= Weak fluorescence	A	= After quenching with $15N$ NH_4OH

The above results are in agreement with the data reported for the nitronaphthylamines[4] where the presence of strong hydrochloric acid in the reagent solution improved the fluorescent properties of the particular reagent in the detection of stannous tin.

Sensitivity tests

Sensitivity tests were carried out on freshly prepared dilute solutions of stannous chloride containing 2 ml of 30% hypophosphorous acid per 100 ml of solution[3]. All the nitronaphthols exhibited a blue fluorescence under the conditions of test except reagent No. 7 which yielded a purple spot with a fluorescent ring. Reagent Nos. 1, 8 and 12 gave only slight fluorescence. Reagent Nos. 2, 9, 10 and 13 gave the most intense fluorescence of the series and were capable of detecting 10^{-5} g stannous tin whilst the remaining reagents were sensitive to 10^{-4} g stannous tin. The nitro derivatives of 2-naphthol produced more intense fluorescence than the corresponding derivatives of 1-naphthol. Blank experiments were performed on the dilute hypophosphorous acid solutions described previously and were found to yield no fluorescence.

DISCUSSION

In earlier papers of this series, it has been shown that both the nitronaphthylamines[4] and nitro-aminonaphthalene monosulphonic acids[1,3,5] can be used as fluorimetric reagents for stannous tin, the species responsible for the fluorescence being the excited

state of the naphthylammonium ion. More recent evidence indicates that the test will also be given by other nitronaphthalene derivatives, in particular 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid[5] and the reagents reported in this paper, the nitro-naphthols.

In general, the trend of the results with the nitronaphthols confirms the earlier work reported for the nitronaphthylamines, bearing in mind that the nature of the tests enables only a semi-quantitative study to be made of the type and intensity of the fluorescence exhibited by each compound.

From evidence available at present, the following conclusions can be made when attempting to correlate the effect of structure of reagent with intensity of fluorescence.

(1) Those substituted naphthalene derivatives (either naphthylamines or naphthols) containing a nitro group in the second ring appear to yield a more intense fluorescence than the corresponding homonuclear substituted nitro compounds.

(2) The nitro derivatives of the β-substituted naphthalenes (naphthylamines or naphthols) produce a more intense fluorescence than the corresponding nitro derivatives of the α-substituted compounds.

These results are in agreement with the data reported by ALLEN and his co-workers[9] who studied the effect of substituents in the naphthalene ring upon the fluorescent properties of the individual compounds, also the results of TOMASCHEK[10] who reports that the presence of substituents —OH and —NH$_2$ intensify the fluorescence of a particular compound and displace it towards the longer wavelengths.

The exceptions to the above conclusions are the 8-nitro-1-substituted naphthalene derivatives which exhibit poor reactivity in the stannous tin test when compared with the remaining isomers of each particular series. Both 8-nitro-1-naphthylamine[4] and 8-nitro-1-naphthol, in either weakly or strongly hydrochloric acid solution yield poor fluorescence with stannous tin. It is suggested that hydrogen bonding is responsible for this phenomenon, *i.e.* the ease of reduction of the nitro group is impaired by a hydrogen bond to, either the amino group in the case of 8-nitro-1-naphthylamine[4], or to the hydroxyl group in the case of 8-nitro-1-naphthol. This hydrogen bonding will be exhibited by both the free base and the acidic forms of the compounds as figures (I, II and III) illustrate.

E.g.

(I)   (II)   (III)
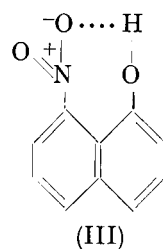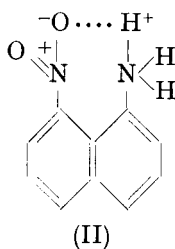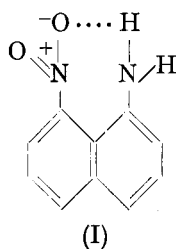
Further support for the presence of an intramolecular hydrogen bond in these compounds is shown by the relatively poor reactivity already observed when 8-nitro-1-naphthylamine[4] is diazotised and the diazonium group replaced by hydroxyl. 8-Nitro-1-naphthylamine[4] exhibits the least reactivity of the nitronaphthylamine series in this

reaction and the slow rate of diazotisation may be attributed to the existence of a hydrogen bond between the nitro and amino groups.

In the *ortho*-substituted compounds (*i.e.* 2-nitro-1- and 1-nitro-2-derivatives) this same lack of reactivity is not as appreciable as with the 8-nitro-1-compounds. Both *ortho* derivatives are readily diazotised and yield a positive stannous tin test, although the fluorescence is not so intense as with the remaining isomers of the series (except for the 8-1 derivative). Obviously the hydrogen bonding in the *ortho* derivatives (IV, V) does not influence the ease of reduction of the compounds as markedly as the hydrogen bonding does in the 8-1 derivative.

This observation is consistent with the effect of *ortho* nitro substituents on the acidity of phenols and anilinium ions[11]. With these systems, it is found that such factors do not appreciably affect the basic strength except in N-substituted anilines. Some indication of this effect can be seen from an analysis of Table V[11].

TABLE V

IONIZATION CONSTANTS OF SOME PHENOLS IN WATER SOLUTION

Compound	K
Phenol	$1.2 \cdot 10^{-10}$
o-Nitrophenol	$6.8 \cdot 10^{-8}$
m-Nitrophenol	$5.0 \cdot 10^{-9}$
p-Nitrophenol	$7.0 \cdot 10^{-8}$
2-Nitroresorcinol	$1.59 \cdot 10^{-6}$
4-Nitroresorcinol	$1.04 \cdot 10^{-6}$

It will be observed that it makes relatively little difference to the K value whether a nitro group is placed *ortho* or *para* to a hydroxyl group. This indicates two significant features.

Firstly, it might have been expected that hydrogen bonding in the *ortho* compounds such as (VI) might preferentially stabilize the neutral forms of the *ortho* compounds.

(IV)   (V)   (VI)
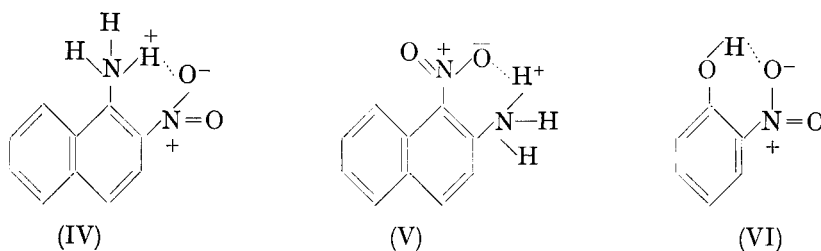
Secondly, there is a possibility that the *ortho* nitro group will be forced out of the plane of the benzene ring and thus lose part of its potency as an acid-strengthening substituent. The results indicate that neither effect is large. This conclusion is fortified by the comparison of 2- and 4-nitro-resorcinol. In the former compound both hydroxyl groups are *ortho* to the nitro function and so distortion from planarity should be increased if it were of measurable significance.

By comparison, recent unpublished work[8] in the naphthalene series indicates that

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small *"ortho"* effects do occur with the nitro-naphthylamines and nitronaphthols. In each particular series, infrared studies and pK_a determinations show that intramolecular hydrogen bonding is present to a small degree with the 1-2 and 2-1 compounds, and to a more appreciable extent with 8-1 derivatives. These observations are confirmed by our stannous tin tests where the relative magnitude of the hydrogen bonding appears to be slightly greater with the 8-1 derivative than with either of the 1-2 or 2-1 compounds.

SUMMARY

Thirteen nitronaphthols have been examined and found to be of use in the fluorimetric detection of stannous tin. The reagents were capable of detecting 10^{-4} to 10^{-5} g stannous tin whilst the nitro derivatives of 2-naphthol produced more intense fluorescence than the corresponding derivatives of 1-naphthol. Of the series examined, 8-nitro-1-naphthol was the least reactive, and this was attributed to the presence of intramolecular hydrogen bonding between the nitro and hydroxyl groups in this compound.

RÉSUMÉ

Les nitronaphtols ont été examinés en vue de leur utilisation comme réactif fluorimétrique de l'étain(II). On peut déceler ainsi jusqu'à $10^{-4} - 10^{-5}$ g de cet élément. Les dérivés nitrés du β-naphtol donnent une fluorescence plus intense que les dérivés de l'α-naphtol.

ZUSAMMENFASSUNG

Eine Anzahl Nitronaphtole wurden auf ihre Eignung als fluorimetrisches Nachweisreagenz für Zinn(II) geprüft. Es lassen sich hiermit noch $10^{-4} - 10^{-5}$ g Zinn nachweisen. Die Nitroderivate von β-Naphtol zeigen eine intensivere Fluoreszens als die entsprechenden Derivate des α-Naphtols.

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PROPERTIES OF RIBOFLAVIN PHOSPHATES

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Recently we have described[1,2] methods by which pure preparations of flavins can be obtained, and by which microgram quantities can be analysed. In the present investigation, the absorption spectra and the fluorescence of flavin phosphates were studied and their dissociation constants determined.

EXPERIMENTAL

Materials

Riboflavin-5'-phosphate (flavin mononucleotide, FMN) was prepared according to VISCONTINI *et al.*[3]. Riboflavin-5'-pyrophosphate (RPP) was a commercial preparation obtained from F.F. Firma, Florence. These substances were ultimately purified by several passages through a cation exchanger[1]. All manipulations were done in the dark.

Criteria of purity. The quantitative determination of FMN and RPP was routinely carried out by measuring the optical density at 260 and 450 mμ of the solutions under study. The qualitative determination was done by paper electrophoresis[2], and, in the experimental conditions used, the comparison of these two sets of data constituted an adequate criterion of purity.

Spectra, extinction coefficients and fluorescence

The absorption spectra (Fig. 1) were determined in a Beckman D.U. spectrophotometer, in 0.1M phosphate buffer pH 7.0. Readings were made every 2 mμ in the regions of the maxima and every 5 mμ elsewhere.

The extinction coefficients were determined on samples of the dry substances which had been kept in a desiccator *in vacuo* for several days, weighed and then dissolved to a suitable concentration. The values obtained are:

wavelength (mμ)	224	260	268	375	450	
ε (cm^2/mole $\cdot$ 10^3)	30.9	27.1	31.0	10.6	12.2	RPP
		27.1	30.6	10.4	12.2	FMN

The infrared spectra (Fig. 2) have been obtained in a Perkin Elmer IR spectrograph, Nujol medium. The effect of pH on the fluorescence of FMN and RPP was investigated in 0.1M phosphate–acetate–borate buffer[4] in the pH range from 2.0 to 12.0 Measurements were made in a Klett fluorimeter, lamp filter Corning glass 5543 and photocell filter Corning 3385. Results are shown in Fig. 3.
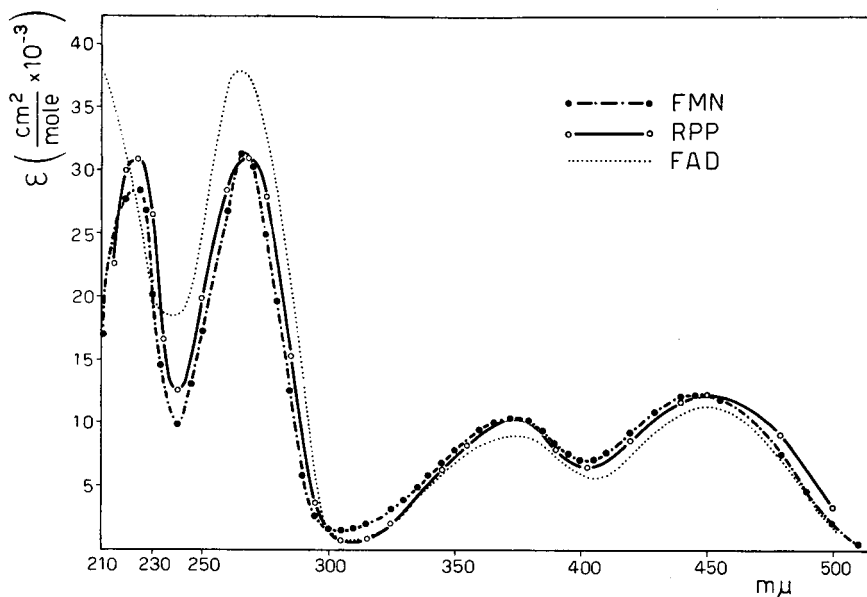
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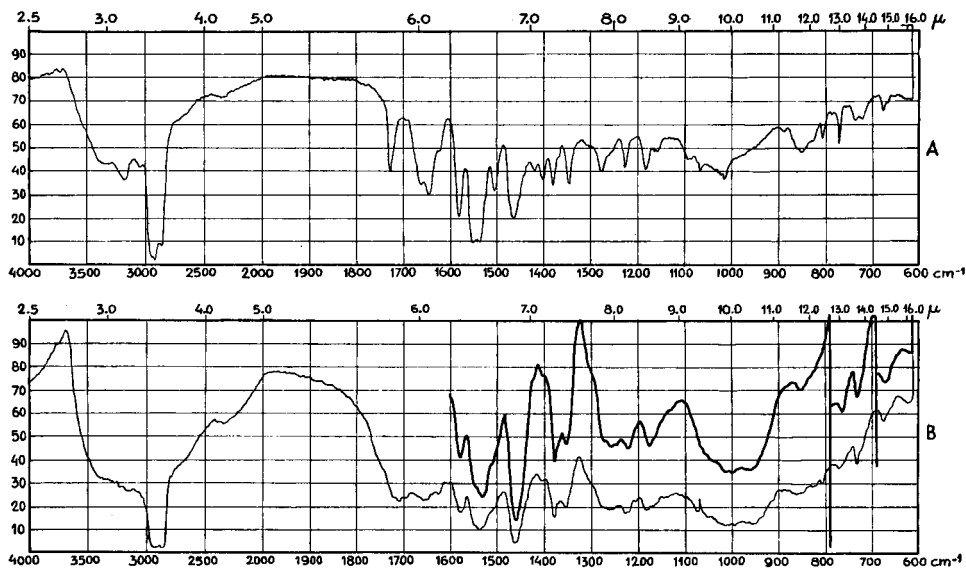Fig. 1. Absorption spectra of RPP, FMN and FAD in 0.1 M
phosphate buffer pH 7.0.

Fig. 2. Infrared spectra of FMN (A) and RPP (B).

Titration of FMN and RPP

Titrations were carried out with a Beckman or a Metrohm pH meter equipped
with a glass electrode, at 18–20°. A microburette with a capacity of 1 ml was used.
A magnetic stirrer kept the solution vigorously agitated. Back titration with HCl

of the same normality as the NaOH used, was carried out in all experiments. Several samples were titrated for each substance. By keeping the volume small and using a fairly concentrated titrant, the corrections for the free hydrogen and hydroxyl ions in the pH range studied were kept quite small. Blank titration was carried out
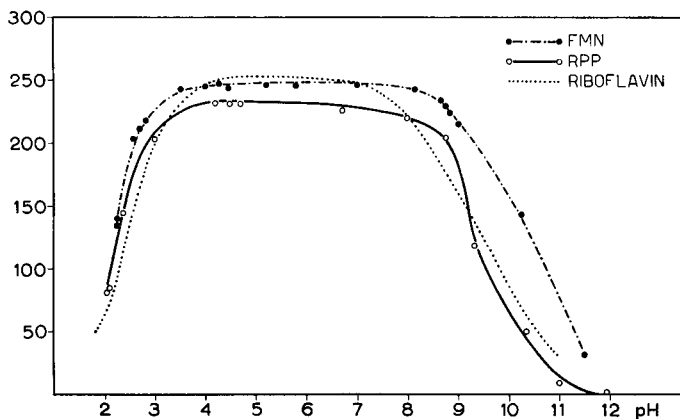

Fig. 3. Fluorescence of RPP, FMN and riboflavin at various pH. Ordinates give the per cent fluorescence as referred to a fluorescein standard.

by collecting from the tubes which preceded and followed the peak of the sample in the last chromatographic passage, a volume of eluate identical to that of the sample and submitting it to the same treatment as the sample itself. The blank curve was substracted by volume from the sample curve, the difference curve representing the hydrogen ion-binding capacity of the samples as a function of the pH[5].

FMN. The titration curve of FMN corrected for blank titration is shown in Fig. 4. It was obtained by titrating 9 ml of 0.0038M FMN with 0.3N NaOH and HCl. No hydrolysis occurred during titration. The curve shows two inflections with midpoints
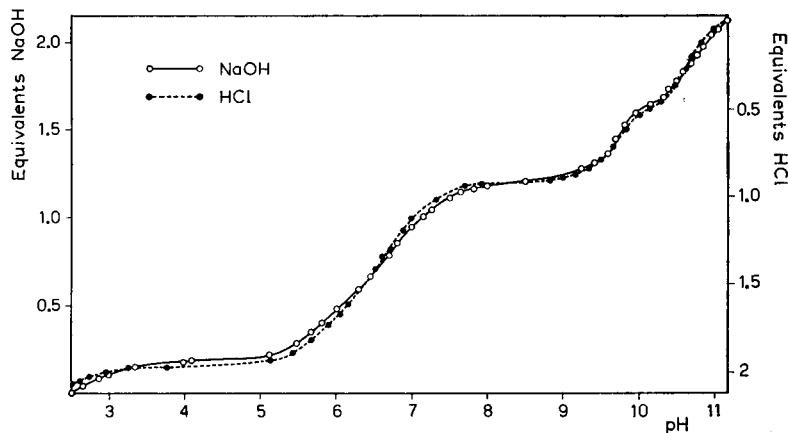

Fig. 4. Titration curve of FMN, corrected for a blank titration.

at pH 6.6 and 9.8. About 2.2 equivalents of titrant are needed to raise the pH from 2.52 to 11.16. A single clear equivalence point is seen, after addition of 1.15 equivalents. FMN has two ionizing groups in the isoalloxazine ring, with pK_a values of 9.8 and —0.2 in free riboflavin[6,7], and two acid functions in the phosphate moiety with pK_a values of 7.1 and 11.75 in free orthophosphoric acid. This last value is too high to be determined by direct titration[8].

At the initial pH of our solution a function with pK_a—0.2 is practically undissociated so that one may assume that the 2.3 equivalents of titrant are completely used for the other functions of FMN, one of which, having a $pK_a > 11$, is only partially titrated. The first inflection with midpoint at pH 6.7, is therefore ascribable to a function in the phosphoric radical while the inflection at pH 9.8 is due to one CO–NH group in the alloxan part of the isoalloxazine ring.
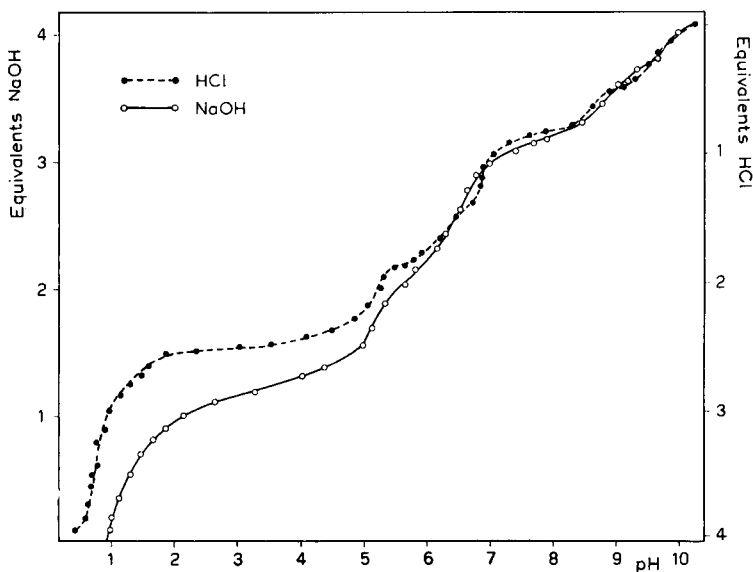

Fig. 5. Titration curve of RPP, corrected for a blank titration.

RPP. Fig. 5 shows the corrected titration curve of RPP, obtained by titrating 8 ml of 0.0065M RPP with 1N NaOH and HCl. No hydrolysis occurred during titration. The inflections, although not very sharp, are quite significant if considered in connection with the volumes of titrant. In the NaOH titration curve, four inflections are observed; only three reliable midpoints can, however, be fixed: about pH 6.2 (1.8 equiv.), pH 7.7 (2.8 equiv.) and pH 10.2 (3.5 equiv.). Equivalence points are distinct only after 1.2 and 3.2 equiv. A further equivalence point can however be discerned after 2.4 equiv. if the single hump due to overlapping groups in the region of pH 6.2 and pH 7.7 is resolved into two distinct curves according to PARKE AND DAVIS[6].

In the back titration diagram with HCl, four inflections are seen with midpoints at pH 9.85 (0.5 equiv.), pH 7.9 (1.2 equiv.), 6.2 (2.1 equiv.). A fourth possible midpoint can be placed at pH 1.8 (3.4 equiv.): it is known that an acid group with $pK_a < 2$

is titrated with difficulty using glass electrodes[9]. It is therefore possible that this last midpoint, which is not clearly seen in the NaOH titration curve, might have been missed during the titration with alkali.

Equivalence points are found after 0.85 and 2.6 equiv., and by resolving the straight line in the region from pH 6.5 to pH 8, also after 1.7 equiv. The inflections with midpoint at pH 1.8, 5.2, 7.8 − 7.9 can be ascribed to the acidic functions of the pyrophosphate radical, while the inflection with midpoint at pH 9.85 − 10.2 is probably due to the NH in the isoalloxazine ring, as in FMN.

CALCULATION OF THE DISSOCIATION CONSTANTS

Although theoretically all of the anionic species of a polybasic acid will be present at a given pH, the concentrations of one or more of the species will always be small enough at that pH to be neglected in a first approximation[8]. It is therefore possible to estimate the dissociation constants of a polybasic acid by a method of successive approximations utilizing the data obtained from an electrometric titration, the acid being dealt with at each pH as a monobasic acid[8]. The values thus obtained may then be used to estimate the concentrations of the components which were neglected in the first approximation. The appropriate corrections may then be made and the dissociation constants estimated a second time.

At the equivalence points only one species predominates, while, at intermediate points between them, two of the species predominate and it is in these regions that the most accurate estimations of the dissociation constants may be obtained. The method of calculation also permits the inclusion of one minor component in obtaining the first approximation of all the constants except the first one to be calculated.

The pH ranges chosen and the anionic species assumed to be present in first approximation calculations are given in Table I, the major components being printed in bold face type.

TABLE I

pH range	Anionic species assumed present				Dissociation constant
<5.5	**HRPO$_4$H$_2$**	**HRPO$_4$H$^-$**	$^-$RPO$_4$H$^-$		K_1
9-10	HRPO$_4$H$_2$	**HRPO$_4$H$^-$**	**$^-$RPO$_4$H$^-$**	$^-$RPO$_4^{-2}$	K_2
>10.5		HRPO$_4$H$^-$	$^-$RPO$_4$H$^-$	$^-$RPO$_4^{-2}$	K_3
<2	**HRP$_2$O$_7$H$_3$**	**HRP$_2$O$_7$H$_2^-$**			K_1
5-7	HRP$_2$O$_7$H$_3$	**HRP$_2$O$_7$H$_2^-$**	**HRP$_2$O$_7$H^{-2}** HRP$_2$O$_7^{-3}$	$^-$RP$_2$O$_7^{-3}$	K_2
7.8 − 8.6			**HRP$_2$O$_7$H^{-2}** **HRP$_2$O$_7^{-3}$**	$^-$RP$_2$O$_7^{-3}$	K_3
>9.6			HRP$_2$O$_7$H^{-2} **HRP$_2$O$_7^{-3}$**	**$^-$RP$_2$O$_7^{-3}$**	K_4

HRPO$_4$H$_2$ and HRP$_2$O$_7$H$_3$ indicate the undissociated molecule of FMN and RPP respectively, HRPO$_4$H$^-$, HRP$_2$O$_7$H$_2^-$, HRP$_2$O$_7$H^{-2}, HRP$_2$O$_7^{-3}$ the anions deriving from the dissociation of the acid functions in the phosphate or pyrophosphate radical and $^-$RPO$_4$H$^-$, $^-$RPO$_4^{-2}$, $^-$RP$_2$O$_7^{-3}$ the anions originating from the dissociation of the acidic group in the isoalloxazine ring and of the acid functions in the phosphate or pyrophosphate radical.

The NaOH titration curve has been chosen for calculating the dissociation constants of FMN, since at the highest pH reached, one of the acid functions had not been fully titrated.

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The initial solution of FMN is in the pH range where $HRPO_4H_2$ and $HRPO_4H^-$ are the only anionic species present in significant amounts.

Therefore, to a first approximation, at any given pH in that range,

$$A_0 + A_1 = RP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where A_0 and A_1 are the amounts in micromoles of $HRPO_4H_2$ and $HRPO_4H^-$ present at the pH chosen, and RP the total amount of FMN used in the titration. OH_a equivalents of alkali are now added, which raise the pH of the solution but do not take it out of the range where $HRPO_4H_2$ and $HRPO_4H^-$ are the only major components. However the alkali does convert an equivalent amount of $HRPO_4H_2$ to $HRPO_4H^-$ (eqn. 4), the amounts of the two species becoming $(A_0—OH_a)$ and (A_1+OH_a) respectively.
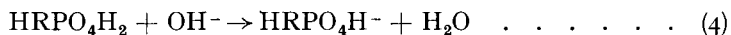
Therefore, if $[H^+]_i$ and $[H^+]_f$ are the initial and final hydrogen ion concentrations,

$$K_1 = [H^+]_i \, A_1/A_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

before adding acid and

$$K_1 = [H^+]_f \, (A_1 + OH_a) \, / \, (A_0 - OH_a) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

after adding acid. Equating (2) and (3) and substituting $(RP—A_1)$ for A_0, a quadratic in A_1, is obtained. Although both solutions are positive, only one gives reasonable results in the calculation of K_1. Having now a value for K_1 it is possible to determine K_2 using much the same procedure as in estimating K_1. A quantity OH_b of alkali is added to the initial solution of FMN such that the resulting pH of the solution lies in the range 9–10, where $HRPO_4H^-$ and $^-RPO_4H^-$ are the major components, and $HRPO_4H_2$ the largest minor component. The alkali added is consumed in two reactions:

$$HRPO_4H_2 + OH^- \rightarrow HRPO_4H^- + H_2O \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$HRPO_4H^- + OH^- \rightarrow {}^-RPO_4H^- + H_2O \quad . \quad . \quad . \quad . \quad . \quad (5)$$
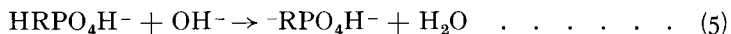
If an amount B of alkali is consumed in reaction (4), then $(OH_b—B)$ is consumed in reaction (5). If the hydrogen ion concentration at this point is designated by $[H^+]_{f2}$ then the following expressions are obtained for K_1 and K_2.

$$K_1 = [H^+]_{f2} \, (A_2 + OH_b + 2B) \, / \, (RP—A_1 — B) \quad . \quad . \quad . \quad . \quad (6)$$

$$K_2 = [H^+]_{f2} \, (OH_b — B) \, / \, (A_1 — OH_b + 2B) \quad . \quad . \quad . \quad . \quad (7)$$

The third dissociation constant is extremely small and titration in the pH range which should be considered does not give reliable values, the substance being strongly hydrolyzed. The equations for calculating the dissociation constants of RPP are obtained in the same way using the HCl titration curve and making the appropriate assumptions with regard to the anionic species present (see Table I). On substituting the experimental data into approximate equations developed as described above, the following dissociation constants were obtained for FMN:

$$K_1 = 2.5 \cdot 10^{-7} \qquad pK_{a1} = 6.60$$
$$K_2 = 7.6 \cdot 10^{-11} \qquad pK_{a2} = 10.12$$

and for RPP, in a second approximation:

$$K_1 = 8.9 \cdot 10^{-3} \qquad pK_{a1} = 2.04$$
$$K_2 = 5.6 \cdot 10^{-7} \qquad pK_{a2} = 6.25$$
$$K_3 = 1.6 \cdot 10^{-8} \qquad pK_{a3} = 7.80$$
$$K_4 = 1.3 \cdot 10^{-10} \qquad pK_{a4} = 9.87$$

DISCUSSION

The extinction coefficients of RPP at the wavelengths of the maxima and at 260 mμ are in good agreement with those found for FMN and riboflavin by previous authors. The "flat" shape of the IR spectrum of RPP and the greater intensity of its bands at 1225 and 1260 cm^{-1}, as compared to FMN, reflect the presence of a pyrophosphate. The specific absorption of the P-O-P group, which is placed by some authors at about 970–940 cm^{-1}, is however masked by the absorption of the phenyl group, and the free OH groups of the phosphoric and pyrophosphoric radicals do not allow the study of bands in the 1000 cm^{-1} region where the P-O-C alkyl bond should absorb. The pH–fluorescence curves of FMN and RPP are quite similar to those found for riboflavin by previous authors[7,10–12].

According to KUHN AND MORUZZI[12] the fluorescent form of riboflavin is the dipolar ion. The dissociation constants of the CO-NH group in the alloxan ring of FMN and RPP, as determined from the slopes in the alkaline range of the fluorescence curves, correspond to the values obtained by titrimetric methods.

The pK_a for the imino group is much higher in FMN than in RPP and riboflavin, where the values are nearly the same. This is probably due to the influence of a weakly acid function, with pK_a >11, which is found in FMN but not in RPP or riboflavin. The value of the dissociation constants of RPP and FMN found in the present investigation, are in good agreement with those given for free ortho- and pyrophosphoric acid and for riboflavin by previous authors[6,7,12,13]. The data presented are apparent ionization constants (K_a'): they can however be directly compared to true dissociation constants (K_a) since in the present case the ionic strength of the solution at the end of the titration was sufficiently low[5,14] to keep the deviation from K_a within the experimental error.

It should be noted that K_1 in FMN and K_3 in RPP have higher values than the corresponding constants of the free inorganic acid. This effect may reasonably be ascribed to the lack of one of the acid functions existing in the free acid, which in RPP and FMN forms an ester linkage with ribitol.

SUMMARY

The u.v., visible, and i.r. spectra, the extinction coefficients, fluorescence, and dissociation constants of pure riboflavin-5'-phosphate and riboflavin-5'-pyrophosphate are studied and discussed.

RÉSUMÉ

On a étudié les spectres d'absorption u.v., visible et infrarouge, les coefficients d'extinction molaire, la fluorescence et les constantes de dissociation de phosphates de riboflavine.

ZUSAMMENFASSUNG

Es wurden die u.v.-, sichtbaren- und i.r.-Absorptionsspektren sowie die Fluoreszenz von reinem Riboflavin-5'-phosphat und Riboflavin-5'-pyrophosphat untersucht und deren Extinktions-koeffizienten und Dissoziationskonstanten bestimmt. Die Ergebnisse werden diskutiert.

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POLAROGRAPHY OF 4-BENZOTHIAZOLOL

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A study of the analytical chemistry of 4-benzothiazolol was undertaken in order to determine the usefulness of this reagent and to compare its analytical behaviour with structurally similar compounds such as 8-quinolinol. As a part of this study, the reduction of 4-benzothiazolol at the dropping mercury electrode was investigated mainly to establish the conditions under which it could be used as a reagent for the amperometric titration of metal ions.

EXPERIMENTAL

Preparation of compound

4-Benzothiazolol was prepared by the method described by Erlenmeyer and Überwasser[1], and recrystallized several times from ethanol: m.p. 143°. The infrared absorption spectrum of the compound was determined for purposes of characterization. A Perkin-Elmer Model 21 recording spectrophotometer with sodium chloride optics was used to record the spectrum of the compound in KBr pellets. Fig. 1 and Table I give results obtained.
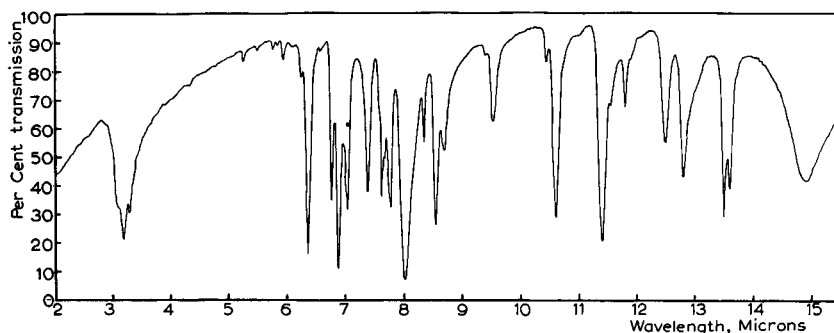

Fig. 1. Infrared spectrum of 4-benzothiazolol.

Apparatus

All polarograms were recorded on a Leeds and Northrup Model E Electrochemograph. A voltage span of 2 V was used in all experiments with the damping switch at zero. Nitrogen was used to remove dissolved oxygen from the solutions. One arm of an H-type cell was used as the electrolysis vessel and was separated from the reference saturated calomel electrode by means of a fritted glass disc and an agar plug saturated with KCl. No corrections were made for the iR drop since the resistance of the cell was small. All polarograms were recorded at $25° \pm 0.05°$, except those used for determining temperature coefficients. The capillary used had a drop time of 2.64 seconds and a mass rate of flow of 2.94 mg/sec in a Na_2HPO_4–citric acid buffer at pH 6.90, at an applied potential of 1.55 V under a corrected mercury head of 44.24 cm. pH values were determined with a Beckman Model G pH meter standardized with a potassium acid–phthalate buffer of pH 4.01.

Buffer solutions

McIlvaine buffers in the pH range $2-8$ were made up from $0.2M$ Na_2HPO_4 and $0.1M$ citric acid. The composition of the buffer solutions used is given in Table II. Less than 1% ethanol was

TABLE I

INFRARED ABSORPTION SPECTRUM OF 4-BENZOTHIAZOLOL

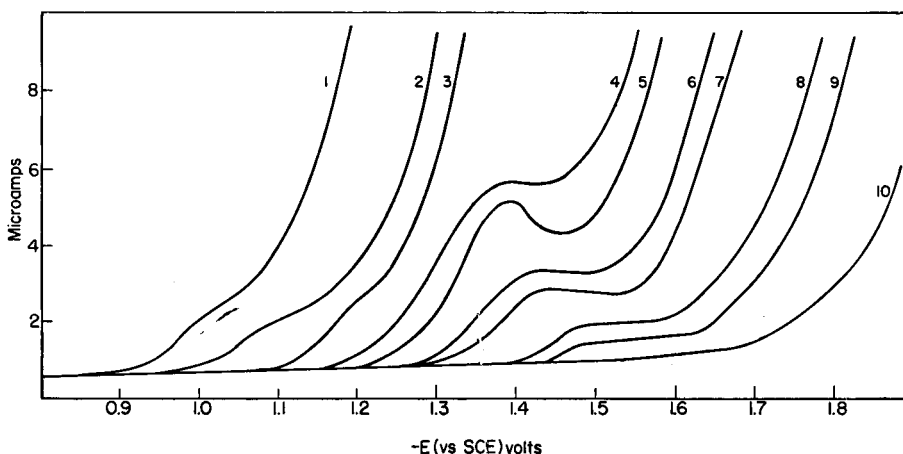| Intensity:	Strong cm^{-1}	Medium cm^{-1}	Weak cm^{-1}	Very weak cm^{-1}
	3125	1480	3050	1905
	1600	1420	1150	1820
	1570	1355	955	1735
	1450	1320	848	1715
	1245	1285		1685
	942	1200		1520
	878	1170		866
		1050		
		802		
		782		
		743		
		736		
		670		

Fig. 2. Polarograms of $1 \cdot 10^{-4}M$ 4-benzothiazolol. (1) pH 2.25; (2) pH 3.30; (3) pH 4.25; (4) pH 4.88; (5) pH 5.30; (6) pH 5.61; (7) pH 6.00; (8) pH 6.82; (9) pH 7.30; (10) pH 8.10.

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TABLE II

VARIATION OF THE HALF-WAVE POTENTIAL WITH pH

pH	Buffer components		$-E\frac{1}{2}$ V vs. S.C.E.
	Na_2HPO_2 M	Citric acid M	
2.25	0.004	0.088	1.06
2.70	0.020	0.080	1.09
3.09	0.040	0.070	1.11
3.30	0.050	0.065	1.14
3.55	0.060	0.060	1.15
4.00	0.070	0.055	1.24
4.25	0.077	0.052	1.27
4.40	0.080	0.050	1.31
4.60	0.084	0.048	1.34
4.88	0.090	0.045	1.38
5.30	0.100	0.040	1.43
5.45	0.102	0.039	1.45
5.61	0.106	0.037	1.45
6.00	0.111	0.035	1.48
6.20	0.120	0.030	1.49
6.70	0.130	0.025	1.54
6.80	0.140	0.022	1.55
6.90	0.143	0.020	1.55
7.09	0.147	0.017	1.57
7.30	0.160	0.010	1.58

added to all solutions in order to ensure that the 4-benzothiazolol was in solution. The buffer components were examined for polarographically reducible impurities before use. The concentration of 4-benzothiazolol was $1 \cdot 10^{-4}M$, except in those cases in which the dependence of the diffusion current on concentration was determined.

RESULTS AND DISCUSSION

Fig. 2 shows that solutions of 4-benzothiazolol were reducible at pH values greater than 5.3. In general, the behaviour of this compound is less complicated than that
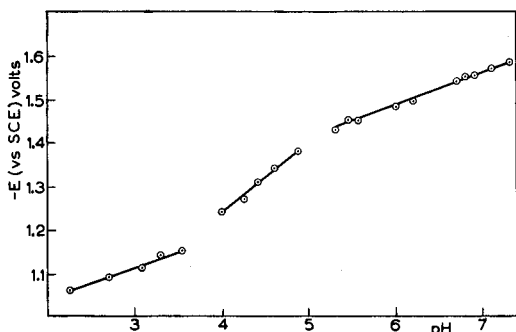

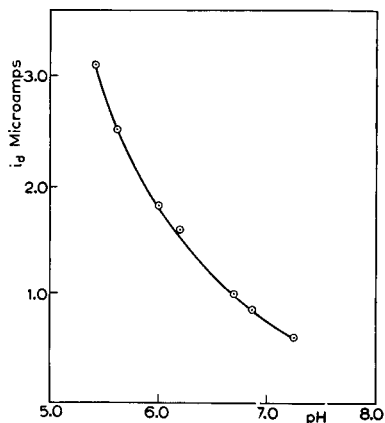Fig. 3. Effect of pH on the half-wave potential of $1 \cdot 10^{-4}M$ solutions of 4-benzothiazolol.

Fig. 4. Effect of pH on the diffusion current of $1 \cdot 10^{-4}M$ solutions of 4-benzothiazolol.

of 8-quinolinol[2]. In acid solutions, between pH 2 and 5, a small wave appears and its height increases with increase in pH. This is probably a catalytic wave similar to that observed in acid solutions in the reduction of several 8-quinolinols[3]. Analysis of this wave was made difficult by hydrogen discharge in acid solutions and also by the appearance of a pronounced maximum at a pH of about 4.5. This maximum can be suppressed with small amounts of Triton X-100, but the wave height and half-wave potential are altered. The half-wave potential of this wave in acid solutions shifts to more negative potentials with increasing pH. Fig. 3 and Table II show the effect of pH on the half-wave potential, over the complete pH range examined. At a pH of about 6 a well-defined wave is obtained; the height of this wave decreases, and the half-wave potential becomes more negative, with increase in pH.

4-Benzothiazolol consists of a mixture of the protonated ion, the neutral molecule, and the anion in solution as shown in eqn. (1). The dissociation constants K_{NH} and

K_{OH} have been found by a spectrophotometric method to be 1.20 ± 0.05 and 8.85 ± 0.05 respectively[4]. From these values it can be shown that at a pH of 2.2, 91% of the 4-benzothiazolol exists in the neutral form, and at a pH of 9.85 only 9% of the 4-benzothiazolol remains as the neutral species. Fig. 2 shows that at a pH of 8.1 no appreciable reduction wave was observed at an instrument sensitivity of 20 μA per 100 chart divisions. Fig. 4 shows the manner in which the wave height decreases with increase in pH. It is therefore reasonable to infer that at pH values greater than 5.3, it is the neutral species (b) of 4-benzothiazolol that undergoes reduction at the dropping mercury electrode. Although it would be reasonable to expect that the protonated ion (a) would be more easily reduced, hydrogen discharge precluded direct observation of this. Of course, the negative charge in the anionic species (c) would increase the difficulty of reduction of this form.

The well-defined reduction wave obtained at a pH of 6.9 was free of maxima, and its characteristics were studied in greater detail. The diffusion current at pH 6.9 was determined at various heights of the mercury column. The wave height was corrected for residual current variation with the mercury head, and the height of the mercury column was corrected for back pressure. The determination of $i_d/(h_{corr.})^{0.5}$ at six different values of $h_{corr.}$ between 30 and 53 cm of mercury, gave an average value of 0.0528 ± 0.001. This indicates that the reduction wave obtained at this pH is governed by diffusion.

The diffusion currents at pH 6.9 were also determined over a temperature range from 10° to 47°; the temperature coefficient calculated from the compound in-

terest formula is $+1.6\%$ per degree. This confirms the fact that the wave is diffusion controlled.

The number of electrons involved in this reduction can be calculated by means of the Ilkovic equation. Assuming that the diffusion coefficient of the compound is the same as that of quinaldinic acid[2], *i.e.*, $0.80 \cdot 10^{-5}$ cm^2/sec, the number of electrons involved in the reduction is 2. The reduction process that is most probable is shown in eqn. (2).
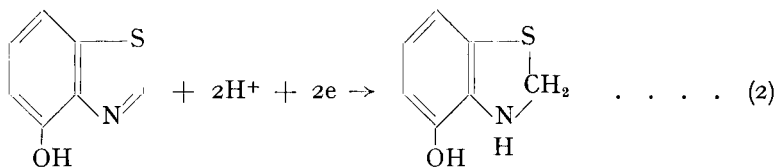
A plot of the applied potential against log $\{i/(i_d - i)\}$ for the reduction wave at pH 6.9 did not give a straight line, thereby indicating that the above reduction process is probably irreversible.

Attempts were made to identify the reduction product formed at the dropping mercury electrode. A $1 \cdot 10^{-4} M$ solution of 4-benzothiazolol was reduced at the dropping mercury cathode for 8 hours at an applied potential of -1.6 V and at a pH of 6.9 with a nitrogen atmosphere maintained over the solution. The ultraviolet absorption spectrum was determined before and after the polarographic reduction; the absorption spectrum of the compound and its reduced form were identical from 220 mμ to 240 mμ and 260 mμ to 320 mμ. Between 240 mμ and 250 mμ small differences were observed; a new peak appeared in the reduced solution and the peak at 257 mμ underwent a small hypsochromic shift. A controlled cathode potential reduction was carried out on a large scale at a mercury pool cathode separated from the anode compartment by means of a salt bridge. The potential of the mercury cathode was maintained manually at -1.6 V, measured against an external saturated calomel

TABLE III

PROPORTIONALITY BETWEEN DIFFUSION CUR-
RENT AND CONCENTRATION OF 4-BENZOTHIA-
ZOLOL AT pH 6.80

Concentration (C) mmoles/l	Diffusion current (i_d) μA	i_d/C
0.10	0.87	8.70
0.20	1.74	8.70
0.24	2.08	8.67
0.30	2.60	8.67
0.32	2.77	8.66
0.36	3.12	8.67
0.40	3.45	8.63
0.48	4.15	8.65
0.56	4.82	8.61

electrode. A nitrogen atmosphere was maintained above the solution during the electrolysis. The ultraviolet absorption spectrum of the 4-benzothiazolol solution before and after reduction was essentially the same as that observed in the polarographic reduction. Even after prolonged reduction, no further changes in the spectrum were observed. However, these differences between 240 mμ and 260 mμ were not sufficiently marked to warrant interpretation.

The height of the well-defined reduction wave at pH 6.9 was proportional to the concentration of 4-benzothiazolol from 0.1 to 0.6 mmoles/l, and the diffusion current constant for this wave was 2.86 (Table III). This wave could therefore be used for the amperometric titration of metal ions such as Fe^{+3}, Co^{+2}, Ni^{+2}, Zn^{+2}, Cu^{+2}, Hg^{+2}, and Ag^+, which were found to form precipitates with 4-benzothiazolol in an acetate–acetic acid buffer at pH 4.6. The usable reduction wave for 8-quinolinol is obtained at pH values greater than 9, and in this respect, 4-benzohiazolol seems to be more suitable than 8-quinolinol for the amperometric titration of metal ions.

SUMMARY

The polarographic behaviour of 4-benzothiazolol at the dropping mercury electrode has been compared with that of 8-quinolinol. A well-defined, irreversible cathodic wave, suitable for the determination of 4-benzothiazolol, was obtained at pH 6.8. The characteristics of this wave indicated that it was due to a two-electron reduction of 4-benzothiazolol to 2,3-dihydro-4-benzothiazolol.

RÉSUMÉ

Le comportement polarographique de l'hydroxy-4-benzothiazol, à l'électrode à gouttes de mercure, a été comparé à celui de l'hydroxy-8-quinoléine. On obtient au pH 6.8 une vague cathodique bien définie, irréversible, pouvant servir au dosage de ce composé.

ZUSAMMENFASSUNG

Das polarographische Verhalten von 4-Hydroxybenzothiazol an der Quecksilbertropfelektrode wurde mit dem von 8-Oxychinolin verglichen. Bei pH 6.8 wurde eine gut definierte, irreversible kathodische Welle erhalten, welche zu dessen Bestimmung verwendet werden kann.

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[3] Q. Fernando and J. P. Phillips, *J. Am. Chem. Soc.*, 74 (1952) 3103.
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RAPID DETERMINATION OF CHLORIDE IN SILICA OR OTHER SOLIDS

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INTRODUCTION

A rapid procedure was required for the determination of inorganic chloride in silica and other solids. Chloride can be determined rapidly after it is separated from interfering elements, but the separation step is usually lengthy and requires considerable attention. It was decided, therefore, to develop a method which would enable rapid separation of the chloride by evolution from the rest of the sample.

Proposed method

It is known that if a solid is treated with a sulfuric–nitric acid mixture and heated to fumes, any inorganic and most organic chlorides will be evolved. The evolved chloride can be collected in a scrubber and determined by titration or colorimetrically. It was hoped that the procedure would be rapid and precise. It was also anticipated that this procedure could be extended to the analysis of other halides and work is in progress to develop such procedures.

RESULTS

Evolution procedure

A method was developed using the principles outlined above. A diagram of the apparatus is shown in Fig. 1. The procedure was found to be rapid (total time, 20 min) and to give good precision as illustrated in Table I.
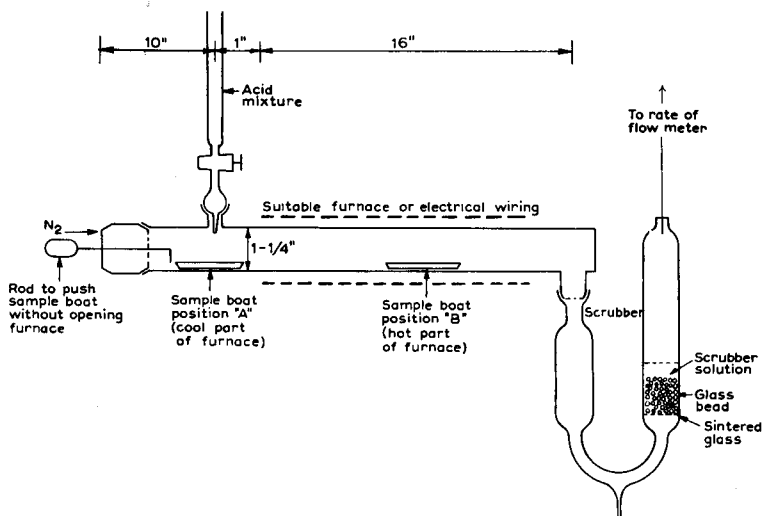

Fig. 1. Chloride evolution procedure.

TABLE I

RESULTS OBTAINED ON REPETITIVE ANALYSIS OF A SAMPLE
CONTAINING APPROXIMATELY 0.6% Cl

(1) 0.618	(5) 0.590	(8) 0.602	(11) 0.598
(2) 0.626	(6) 0.598	(9) 0.620	(12) 0.600
(3) 0.615	(7) 0.605	(10) 0.618	(13) 0.610
(4) 0.598			

$2 = 0.022\%$, 95% confidence.
Average = 0.61 wt. %.

A significant advantage of the method is that samples up to 1.5 g can be taken. This is particularly useful when the homogeneity of the sample is in doubt.

Scrubber

Dilute sodium carbonate solutions or deionised water were both successfully used as scrubbing agents. The chloride content of the scrubber was determined satisfactorily either by a potentiometric silver nitrate titration, or by a colorimetric procedure. These enabled the procedure to be used for wide ranges of chloride content, *i.e.*, from the part per million level to the high wt.% level. The majority of interfering elements are eliminated by this procedure because they form non-volatile sulfates.

RECOMMENDED PROCEDURE

A typical procedure is as follows:

Reagents

Sulfuric acid + nitric acid. 90 ml sulfuric acid (conc.) + 10 ml nitric acid (conc.). *Sodium carbonate solution.* 2% AnalaR sodium carbonate in deionized water. *Deionized water.* Water deionized with a resin column. *Silver nitrate solution.* 0.0282N AgNO$_3$. 1 ml = 1 mg Cl made from Aculates. *Nitrogen.* Cylinder nitrogen. *Acetone.* AnalaR acetone.

For the analysis of a silica sample containing 0.5% chloride, weigh out approximately 1 g of sample into a porcelain boat. Insert the boat into the furnace tube beneath the acid dropper. Add the acid dropwise to the sample, traversing the full length of the boat until the sample is just wetted.

Allow the sample to soak for 1 min in the cool zone of the furnace. Push the sample into the hot part of the furnace, and beat for 15 min. Temperature of the hot zone of the furnace is 590°F.

Nitrogen is passed down the tube throughout the entire operation at a rate of 1 l/min.

Evolved chloride is collected in 100 ml of scrubbing solution.

At the end of the run, the contents of the scrubber are transferred to a beaker, the scrubber is washed several times with a few ml of fresh scrubber solution. The combined scrubber and wash solutions are adjusted to pH 2 with HNO$_3$. An equal volume of acetone is added to the beaker and the chloride is titrated potentiometrically with standard silver nitrate solution. For samples with low chloride content, *i.e.* 1 mg, a small amount of chloride (about 1 mg) may be added to the scrubber

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prior to titration and subsequently substracted during the calculation. This gives a sharper potentiometric break and makes the end-point easier to determine.

Blank

A blank determination can be run by going through the entire procedure but leaving out the sample. This enables the chloride content of the nitrogen and other reagents to be determined and subtracted from the apparent chloride content of the sample.

Colorimetric procedure

For very low chlorides, a suitable sample weight is treated as described above. The chloride content of the scrubber is determined colorimetrically using mercuric thiocyanate and ferric ammonium sulfate[1].

CALCULATIONS

$$\% \ Cl^- = \frac{\text{wt. chloride (g)} \times 100}{\text{wt. sample (g)}}$$

Titration procedure:

$$\text{Wt. chloride} = \frac{\text{No. ml AgNO}_3 \text{ taken}}{1000} \quad (1 \text{ ml AgNO}_3 = 1 \text{ mg Cl}^-)$$

Colorimetric procedure:

$$\text{Wt. chloride} = \text{Concn. of Cl}^- \text{ solution (from calibration chart)} \times$$
$$\text{volume scrubber solution}$$

ACKNOWLEDGEMENTS

The author wishes to express thanks to A. F. DE CASTRO, JULIA ELLERBE, L. J. JONES, J. R. WAGNER for suggestions used in completing this project.

SUMMARY

A rapid evolution method has been developed for the determination of chloride. This procedure can be applied to a wide range of chloride concentrations.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage des chlorures à des concentrations variées.

ZUSAMMENFASSUNG

Es wird eine Schnellmethode zur Bestimmung von Chloriden bei verschiedenen Konzentrationen beschrieben.

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HIGH FREQUENCY TITRATIONS

II. THE MERCURY(II)–THIOCYANATE REACTION

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In a previous communication[1], it has been shown that the high frequency (oscillo-metric) technique can be suitably employed for the end-point detection in a precipitation reaction between Ag^+ and SCN^-. The chief advantage of this procedure is the ability to determine milligram-quantities of silver or thiocyanate in dilute solutions.

Because mercury(II) thiocyanate is slightly dissociated, it was thought interesting to study this reaction oscillometrically. Volumetrically, the titrations are performed either way using ferric iron as the indicator. During the titration, $Hg(SCN)^+$ is usually present and at the end-point precipitation of $Hg(SCN)_2$ is likely to occur. The end-point is less sharp than in the corresponding silver–thiocyanate reaction owing to the complexation of excess thiocyanate ion as $Hg(SCN)_3^-$ and $Hg(SCN)_4^{-2}$. As such titrations have a comparatively low accuracy in dilute solutions[2], KOLTHOFF[3] has shown that at low temperatures the results are scarcely influenced by the nitric acid concentration of the solution although it is preferable to keep it low. Notwithstanding, the mercury(II)–thiocyanate reaction is widely used for ordinary precision work in organic and inorganic analysis provided not too dilute solutions are used.

In general, instrumental methods for end-point detection are superior in being independent of visual observation of color changes, and the high frequency technique possesses an additional advantage due to the absence of contact between the electrodes and the solution without sacrificing the sensitivity in measuring characteristic changes in the composition of the system. The present paper describes the high frequency end-point in the titration of Hg(II) with thiocyanate and *vice versa*, for the microdetermination of either of these ions in dilute solutions.

EXPERIMENTAL

Apparatus

A Sargent model V Oscillometer, operating at 110–120 V and 60 cycles, was used in the present work. The titrations were carried out in a Type B (100-ml) cell.

Reagents

All the chemicals used were of reagent grade. In the mercury(II) nitrate solution the nitric acid concentration was kept minimum. The mercury(II) solution was titrated with 0.1 N KSCN or NH_4SCN using ferric alum indicator. Low concentration solutions were obtained by successive dilution.

Procedure

The instrument was allowed to stabilize for 30–60 min before use. The clean dry cell was placed in the cell holder and the needle pointer adjusted to center zero scale

position. A desired volume of mercuric nitrate solution was transferred into the cell and the total volume brought to 100 ml with water. After the initial instrument (capacitance) reading was recorded, small increments of ammonium or potassium thiocyanate solution were added from the buret. The system was stirred carefully after each addition of the reagent. Readings were taken before and after the equivalence point and the experimental end-point obtained from a plot of volume of the reagent added *versus* the instrument reading. Reverse titrations were carried out in an exactly similar manner.

Representative curves are shown in Figs. 1–4 and the experimental results for the estimation of mercury and thiocyanate are entered in Tables I and II.

TABLE I

HIGH FREQUENCY TITRIMETRIC DETERMINATION OF MERCURY(II) BY THIOCYANATE

Final molarity of $Hg(NO_3)_2$ *solution, M*	*Mercury (mg)*		
	actual	*found*	*difference*
1/1,596	12.5975	12.7300	0.1325
1/3,186	6.2951	6.2550	0.0401
1/6,372	3.1475	3.1275	0.0200
1/10,621	1.8885	1.8755	0.0130
1/15,933	1.2585	1.2340	0.0245
1/31,866	0.6295	0.6055	0.0240

TABLE II

HIGH FREQUENCY TITRIMETRIC DETERMINATION OF THIOCYANATE BY MERCURY(II)

Final molarity of *KSCN solution, M*	*KSCN (mg)*		
	actual	*found*	*difference*
1/1,523	6.3651	6.4860	0.1209
1/3,047	3.1820	3.1910	0.0090
1/15,239	0.6365	0.6335	0.0030
1/30,385	0.3192	0.3070	0.0122

DISCUSSION

Fig. 1 shows that during the course of a straight titration of mercury(II) nitrate *versus* thiocyanate, the instrument (capacitance) reading first decreases and then rises continuously. The single inflection denotes the quantitative formation of mercuric thiocyanate. These titrations could be performed in the presence of nitric acid provided its overall normality did not exceed about $1/300N$. In the reverse titration also, the instrument reading exhibits a slight initial decrease and then a continuous increase. The magnitude of increase is small in the beginning and larger thereafter (*cf.* Fig. 2). Here, the reaction appears to take place in two stages, the first break corresponding approximately to the stoichiometry of $Hg^{+2}:SCN^-$ as 1:1 and hence to the formation of $Hg(SCN)^+$. The second break indicates the normal mercuric thiocyanate, $Hg(SCN)_2$. The occurrence of the first break is perhaps due to the tendency of $Hg(SCN)^+$ complex to be comparatively more stable in the presence of excess thiocyanate, which is not the case in the straight titration. A few experiments were carried out using mercury(II) acetate solution. Fig. 3 shows that during the titration

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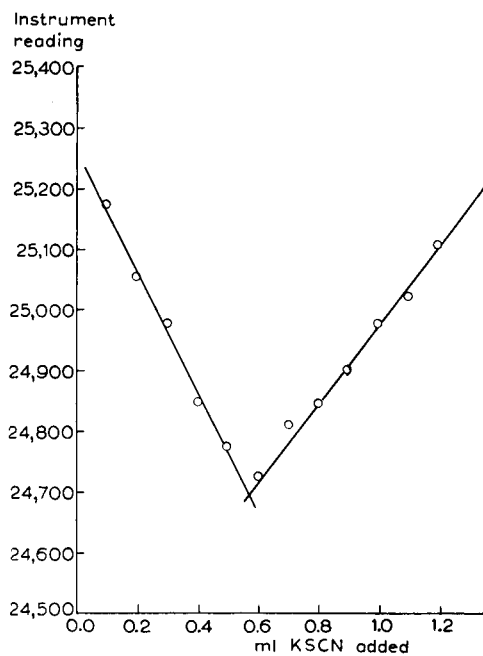
Instrument
reading

Fig. 1. High frequency titration of 100 ml of $1/10,621M$ $Hg(NO_3)_2$ with $0.03281M$ KSCN. End-point: theoretical 0.574 ml, from graph 0.570 ml.

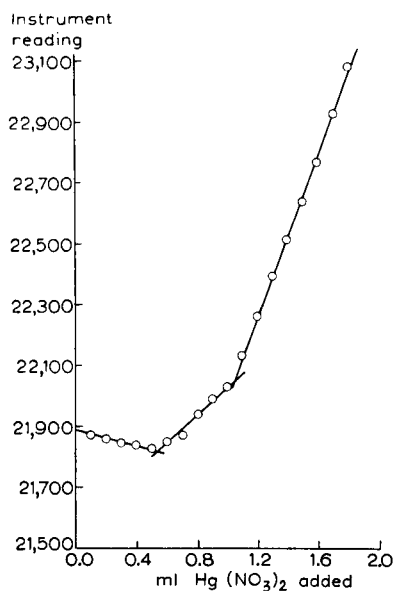

Fig. 2. High frequency titration of 100 ml of $1/15,239M$ KSCN with $0.003125M$ $Hg(NO_3)_2$. End-point: theoretical 1.050 ml, from graph 1.045 ml.
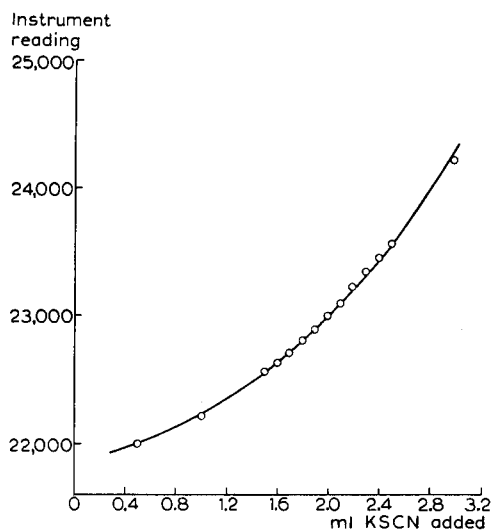

Fig. 3. High frequency titration of 100 ml of $1/2,000M$ $Hg(CH_3COO)_2$ with $0.050M$ KSCN. End-point: theoretical 2 ml.
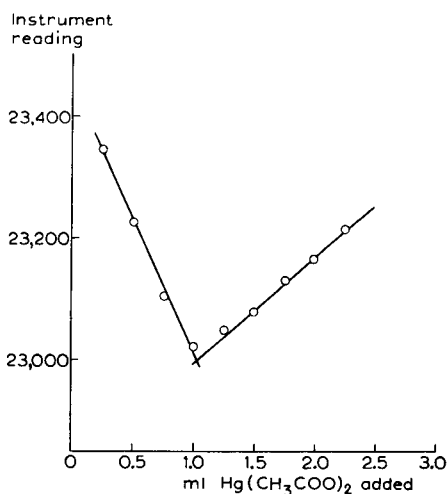

Fig. 4. High frequency titration of 100 ml of $1/1,995M$ KSCN with $0.0514M$ $Hg(CH_3COO)_2$. End-point: theoretical 1.025 ml, from graph 1.025 ml.

of mercury(II) acetate against thiocyanate, the instrument characteristics change uniformly with no means of determining the end-point. However, mercury(II) acetate can be used as a titrant for the determination of thiocyanate, the inflection point corresponding to the formation of neutral mercuric thiocyanate (cf. Fig. 4). In all the experiments, there was no visible precipitate at or near the end-point. Under the present conditions of ionic concentrations and dilution, it is difficult to say conclusively whether or not the complexes $Hg(SCN)^+$, $Hg(SCN)_3^-$ and $Hg(SCN)_4^{-2}$ are formed. Only in one case is the existence of $Hg(SCN)^+$ suspected (*vide supra*), whereas in no case is there an indication of the formation of negatively charged complexes. Hence either these complexes are only transiently formed, or the high frequency method, like other electrometric methods, is unsuitable to record their step-wise formation.

Data in Tables I and II show that very small quantities of mercury or thiocyanate may be determined with a reasonable accuracy. Only in the dilution ranges 1/16,000 and 1/32,000M, does the error become about 2 and 4% respectively. The mercury(II)–thiocyanate reaction, employing the high frequency end-point, can therefore be adopted for a rapid titrimetric analysis in high dilutions — a circumstance in which the indicator method generally fails.

Further work on the halide and the cyanide complexes of mercury(II) is in progress.

SUMMARY

Soluble complex-formation of mercury(II) thiocyanate has been studied oscillometrically. The titration of mercury(II) nitrate with thiocyanate gives one inflection corresponding to the formation of $Hg(SCN)_2$, while in the reverse titration the formation of $Hg(SCN)^+$ is also indicated. The method is useful for a rapid determination of very small quantities of mercury or thiocyanate in highly dilute solutions. The titrations can be effected in presence of nitric acid provided its total acidity in the system does not exceed about 1/300N. Further work on the mercury(II)–halide and mercury(II)–cyanide reactions is in progress.

RÉSUMÉ

La formation du complexe soluble mercure(II)–thiocyanate a été étudiée par oscillométrie. La méthode peut être utilisée pour le dosage rapide de très petites quantités de mercure ou de thiocyanate. Le titrage peut s'effectuer en présence d'acide nitrique, si l'acidité totale du système ne dépasse pas 1/300N environ.

ZUSAMMENFASSUNG

Die Bildung des löslichen Quecksilber(II)–Thiocyanat Komplexes wurde oszillometrisch untersucht. Diese Methode kann zur Schnellbestimmung sehr kleiner Mengen Quecksilber oder Thiocyanat angewandt werden. Die Titration kann in Gegenwart von Salpetersäure ausgeführt werden, wobei aber die Gesamt-Acidität des Systems 1/300N nicht überschreiten darf.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES VII*

CLÉMENT DUVAL

avec la collaboration technique de

COLETTE WADIER ET YVETTE SERVIGNE

*Laboratoire de Recherches micro-analytiques, Paris (France)***

Dans cette septième série, nous présentons une étude relative aux 12 corps suivants: iodate de baryum, saccharose, tartrate de sodium, oxalate neutre de potassium, acétate de cuivre, chlorure de cadmium, sulfate d'ammonium, nitrate ferrique, persulfate d'ammonium, carbonate de thallium, acétate d'uranyle, carbonate de potassium.

Toutes ces substances ont été chauffées sur l'une des thermobalances à enregistrement photographique, avec montée linéaire à raison de 300° par heure et avec des poids de substance de l'ordre de 200 mg. Les spectres infrarouges ont été réalisés sur poudre, avec de la vaseline comme agglomérant, entre 6 et 15 μ, sur le spectromètre Perkin-Elmer 12C avec optique de chlorure de sodium.

Iodate de baryum

Ce corps, cristallisé avec une molécule d'eau, a été préconisé comme étalon pour le dosage par la méthode de Karl Fischer. La courbe représentative de la thermolyse (Fig. 1) avait déjà été tracée[1] mais les vitesses d'échauffement n'étant pas les mêmes, nous observons aux hautes températures une divergence que nous voulons préciser. La déshydratation commence à 43°; elle est à peine sensible à 60°, s'accentue vers 79°, puis on observe un changement de courbure lorsque les trois quarts de l'eau de cristallisation ont disparu. La perte du reste de l'eau s'effectue beaucoup plus paresseusement et n'est vraiment terminée qu'à 320°. De 320° à 476° se présente le palier horizontal relatif à l'iodate anhydre, puis la réaction de Rammelsberg se manifeste:

$$5\ Ba(IO_3)_2 \rightarrow Ba_5(IO_6)_2 + 9\ O_2 + 4\ I_2$$
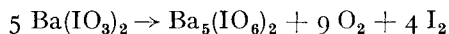
avec violence, notamment à 610°, pour s'achever à 666°; alors commence le palier du paraperiodate de baryum qui est stable au moins jusqu'à 960°, limite de notre expérience.

Le spectre infrarouge présente les bandes suivantes: 728 (F), 784 (épaulement), 801 (f), 811 (aF) cm^{-1}.

Saccharose

Nous avons chauffé ce corps à plusieurs reprises en nous servant de produits commerciaux divers (sucre de canne, sucre de betterave, en morceaux, cristallisé,

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* Pour le sixième mémoire de cette série, voir *Anal. Chim. Acta*, 20 (1959) 20.
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en poudre, sucre d'érable, etc.). Les courbes tracées sont toutes identiques et ressemblent beaucoup à celle de l'amidon, du coton hydrophile, du papier, etc.

En ce qui concerne le saccharose (Fig. 2), on observe un poids constant jusqu'à 231°, le produit ayant déjà bruni à cette température, puis le dégagement gazeux, la combustion commencent, se montrent en pleine activité à 327° et les réactions s'achèvent vers 619°, le creuset étant sensiblement vide. A 900°, il ne reste qu'une minime particule d'une substance minérale (chaux?) et de charbon non brûlé.

Le spectre infrarouge présente un assez grand nombre de bandes: 849 (F), 865 (F), 907 (TF), 919 (épaulement), 939 (F), 988 (TF), 1001 (aF), 1039 (f), 1050 (f), 1069 (f), 1104 (f), 1121 (f), 1158 (f), 1204 (f), 1233 (aF), 1273 (aF), 1318 (aF), 1347 (aF) cm⁻¹.

Tartrate neutre de sodium

Le tartrate de sodium actif renferme au départ deux molécules d'eau qu'il conserve jusqu'à 57°. Il fond alors dans son eau de cristallisation, puis cette eau est évacuée progressivement jusqu'à 154° avec changement de direction quand une molécule d'eau a disparu. Le sel anhydre est stable jusqu'à 255°; alors commence une perte brutale d'oxyde de carbone, d'eau de constitution; vers 309° on a un mélange de charbon et de carbonate de sodium. Ce charbon brûle progressivement jusqu'à 700° environ. Le carbonate de sodium résiduel commence à son tour à se dissocier vers 875° (au lieu de 840° lorsque ce corps est chauffé seul à la même vitesse) (Fig. 3).

Dans son spectre infrarouge nous relevons les bandes suivantes: 770 (large), 804 (aF), 849 (aF), 885 (F), 919 (TF), 990 (TF), 1064 (F), 1110 (F), 1203 (aF), 1239 (aF), 1273 (aF), 1337 (f), 1408 (f), 1603 (TF) cm⁻¹.

Oxalate neutre de potassium

Ce sel contient exactement une molécule d'eau de cristallisation qu'il n'abandonne qu'au-dessus de 100° et jusqu'à 168°. Alors s'étend le palier horizontal de l'oxalate anhydre $K_2C_2O_4$, jusqu'à 500°. La dissociation se produit alors libérant une molécule d'oxyde de carbone suivant:

$$K_2C_2O_4 \rightarrow CO + K_2CO_3$$
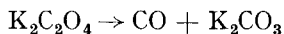
Ce carbonate de potassium fournit un palier horizontal jusqu'à 914° au moins (Fig. 4).

Dans la région du sel gemme nous relevons les bandes suivantes: 772 (TF), 1308 (F), 1587 (TF) cm⁻¹.

Acétate de cuivre

Ce sel cristallise avec une molécule d'eau qu'il commence à perdre à 107°. La déshydratation se produit ensuite progressivement jusqu'à 167°. Là, le sel anhydre n'est pas stable; il commence tout de suite à perdre de l'oxyde de carbone, puis une explosion se manifeste vers 270° et donne naissance à un mélange de cuivre et d'oxyde cuivreux qui se réoxyde progressivement à partir de 296°. On arrive à l'oxyde cuivrique CuO, noir, dont le poids se maintient constant au-dessus de 510° (Fig. 5).

Son spectre infrarouge présente trois bandes: 1031 (aF), 1050 (aF), 1600 (TF) cm⁻¹.

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Chlorure de cadmium

Le chlorure de cadmium $CdCl_2 \cdot 2.5H_2O$, n'est pas stable sous cet état d'hydratation; dès 35° il perd progressivement cette eau jusqu'à 210°. Vient alors le palier du chlorure anhydre qui s'étend jusqu'à 600°. Alors commence la dissociation avec oxydation, donnant naissance à l'oxyde CdO qui se sublime à son tour et vers 1012° le creuset est vide (Fig. 6).

Le chlorure de cadmium est transparent dans la région spectrale étudiée.

Sulfate d'ammonium

Lorsque ce sel est tout seul, il commence à se sublimer et à se détruire à 266°. Il n'en est pas de même, comme nous le savons (voir le VIème mémoire de cette série), lorsque ce sulfate provient de la dissociation du sel de Mohr ou de l'alun ferrique. La dissociation se fait en deux temps: de 266° à 446° environ, départ d'ammoniac, puis de 446° à 514°, départ explosif d'anhydride sulfurique ou de ses produits de dissociation. Le creuset est complètement vidé à 514° (Fig. 7).

Le spectre infrarouge, dans la région étudiée, présente les bandes suivantes: 1050 (F), 1099 (épaulement), 1387 (F) (confondue avec une bande de la vaseline).
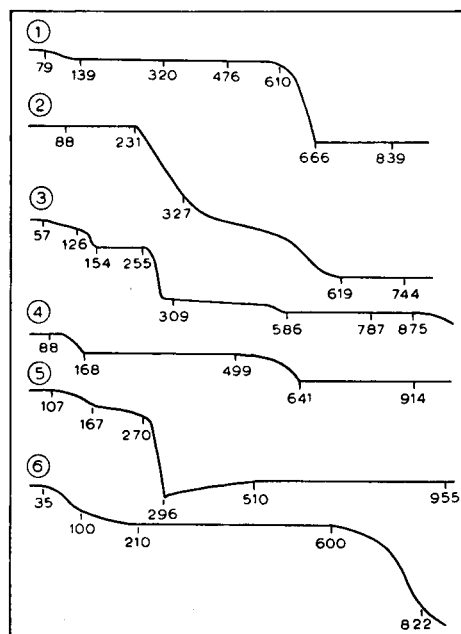
Figs. 1-6.
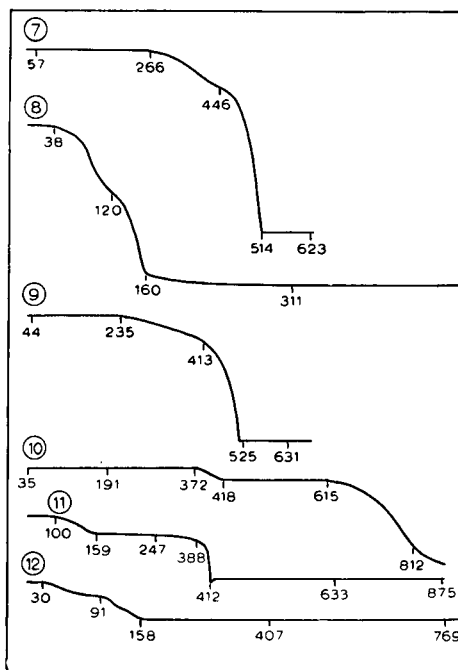
Figs. 7-12.

Nitrate ferrique

Il est à peu près impossible de faire directement une liqueur titrée avec ce sel car il perd son eau de cristallisation dès 38°. A 120° il commence à se dissocier en perdant les vapeurs rutilantes et la réaction est même explosive vers 144°. Elle se ralentit

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ensuite vers 160° et les dernières traces d'oxydes de l'azote étant enlevées progressivement, on arrive à l'oxyde de fer vers 311°, poids constant qui se maintient ensuite jusqu'à 1000°. Quoique d'apparence hygroscopique, le sel initial renferme, suivant les calculs effectués sur le graphique, environ 9 molécules d'eau (poids moléculaire calculé 392 pour un poids théorique de 398, correspondant à $Fe(NO_3)_3 \cdot 9H_2O$, l'oxyde final étant Fe_3O_4) (Fig. 8).

Le spectre infrarouge présente trois bandes: 837 (TF), 1040 (épaulement), 1327 (F et large) cm^{-1}.

Persulfate d'ammonium

Ce sel est anhydre et stable jusqu'à 235°. Il se transforme alors en sulfate d'ammonium et le reste de la courbe est identique à celui de la Fig. 7. Le creuset est vidé à 514°, après départ explosif de SO_3 (Fig. 9).

Dans son spectre infrarouge nous relevons les bandes suivantes: 859 (F), 1050 (F) (sulfate), 1183 (TF), 1407 (aF) cm^{-1}.

Carbonate de thallium

Ce sel est anhydre et stable jusqu'à 372° (température plus élevée que celles données par différents auteurs.) Après cela, le thallium s'oxyde et il y a simultanément perte de gaz carbonique et brunissement du résidu. Il apparait le composé $CO_3Tl_2 \cdot Tl_2O_3$ qui a déjà été signalé parmi les carbonates basiques de thallium. Ce dernier composé offre un palier horizontal allant de 418° à 615°. Alors commence une nouvelle décomposition assez compliquée: le carbonate de thallium restant se dissocie, l'oxyde de thallium trivalent Tl_2O_3 se réduit et l'oxyde de thallium monovalent résultant Tl_2O se sublime. Le creuset n'est pas encore complètement vidé à 1000° (Fig. 10).

Le spectre infrarouge accuse les bandes suivantes: 844 (aF), 1033 (aF), 1059 (f), 1327 (f) cm^{-1}.

Acétate d'uranyle

L'acétate d'uranyle répond bien à la formule $UO_2(CH_3CO_2)_2 \cdot 2H_2O$; il est stable jusqu'à 100°. L'eau de cristallisation s'échappe jusqu'à 159°. Alors commence le palier du sel anhydre qui s'étend jusqu'à 247°. La dissociation de l'acétate se produit alors très lentement jusqu'à 388°, puis d'une manière explosive ensuite et à 412° il ne reste plus que l'oxyde U_3O_8 mélangé sans doute d'un peu d'oxyde UO_2, car la courbe de thermolyse (Fig. 11) accuse un petit crochet et une légère réoxydation.

Le spectre infrarouge, entre 6 et 15 μ présente les bandes suivantes: 937 (épaulement), 944 (F), 971 (f), 1028 (aF), 1059 (aF), 1375 (F), 1475 (F) cm^{-1}.

Carbonate de potassium hydraté

Les cristaux d'hydrate sont habituellement comptés à 1.5 H_2O. L'échantillon que nous avons eu en mains était probablement un mélange de ce dernier et d'hexahydrate. Les calculs effectués sur la courbe (Fig. 12) s'accordent avec la formule $K_2CO_3 \cdot 3H_2O$. Cette eau disparait progressivement et sans former de palier jusqu'à 158°. Alors commence le palier du carbonate anhydre qui s'étend jusque vers 875°.

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Son spectre infrarouge révèle les bandes suivantes: 846 (F), 881 (aF), 1022 (F), 1059 (F), 1151 (F), 1604 (TF) cm^{-1}.

RÉSUMÉ

Nous avons donné la courbe de thermolyse et le spectre infrarouge entre 6 et 15 μ, pour 12 substances proposées jusqu'ici comme étalons en chimie analytique.

SUMMARY

The thermolysis curves and infra-red spectra between 6 and 15 μ are given for 12 substances that are used as standards in analytical chemistry.

ZUSAMMENFASSUNG

Der Verlauf der Thermolyse und die IR-Spektren zwischen 6 und 15 μ werden für 12 Ursubstanzen der analytischen Chemie beschrieben.

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THE THERMOLYSIS OF AMMONIUM 12-MOLYBDOPHOSPHATE

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There is some question as to the composition and drying temperature for ammonium 12-molybdophosphate. DUVAL[1] found that the precipitated compound corresponded to the formula, $(NH_4)_3(MoO_3)_{12}PO_4 \cdot 2HNO_3 \cdot H_2O$. On studying the pyrolysis of this compound, he found that nitric acid and water were evolved up to 180° and that from 180° to 410° the compound, $(NH_4)_3(MoO_3)_{12}PO_4$, was obtained. Above 410°, ammonia and water were lost with subsequent formation of the $24MoO_3 \cdot P_2O_5$ level at 812°. However, an oxide ignition temperature of 600–850° was deemed permissible.

The thermal decomposition of $(NH_4)_3PO_4 \cdot 12MoO_3$ *in vacuo* was investigated by GREGG AND STOCK[2]. They found that after heating the sample to constant weight at 180°, the rate of weight loss increased gradually up to 380° and then became very rapid above 470°. At 630°, the oxide level, $24MoO_3 \cdot P_2O_5$, was obtained. In many respects, this work was similar to that of DUVAL except for the thermal decomposition of the compound below 180°.

The recent work of STOCKDALE[3] revealed that the composition of ammonium 12-molybdophosphate depended upon the precipitate washing conditions. If the precipitate was washed with dilute nitric acid and dried at 140°, it corresponded to the formula, $(NH_4)_2H[P(Mo_3O_{10})_4] \cdot H_2O$; if washed with a dilute solution of ammonium nitrate and dried at 280°, the composition corresponded to the formula, $(NH_4)_3[P(Mo_3O_{10})_4]$. There was little difference in the gravimetric factors for the two com-

positions, hence, either of the two compounds could be used in gravimetric analysis.

Since the studies of STOCKDALE[3] differ from previous work on ammonium 12-molybdophosphate, it was of interest to reinvestigate this compound on the thermobalance.

<div align="center">EXPERIMENTAL</div>

Reagents

All chemicals used were of analytical reagent grade quality.

Preparation of ammonium 12-molybdophosphate

The same procedure as described by STOCKDALE[3] was followed. Samples of the dilute HNO_3 and dilute NH_4NO_3 washed precipitates were either air dried at room temperature for 24 h or dried in an oven at 160° for 2 h.

Thermobalance

An automatic recording thermobalance as previously described was used[4]. Sample sizes ranged from 70 to 90 mg and were run in duplicate or triplicate. A linear heating rate of 5.0° per minute was employed. During the pyrolyses, a slow stream of air was passed through the furnace.

<div align="center">DISCUSSION</div>

The thermograms of the compounds are given in Fig. 1.

Ammonium 12-molybdophosphate, HNO_3 washed

The air-dried compound (Fig. 1/A) began to evolve loosely held water at 60°. After a fairly rapid weight loss, a horizontal weight level was observed from 160° to
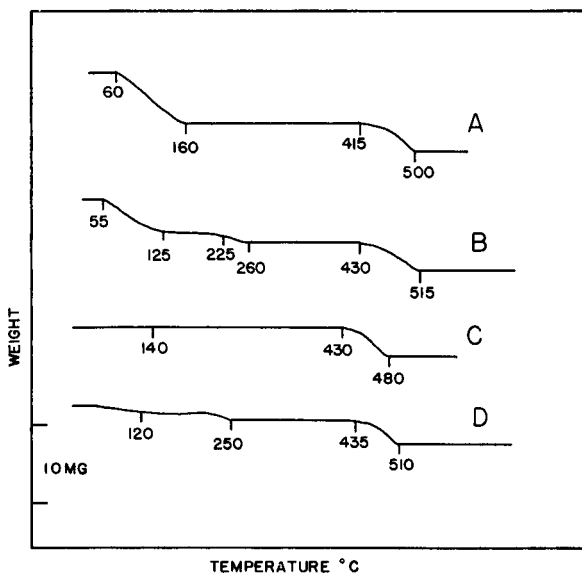

Fig. 1. Thermograms of ammonium 12-molybdophosphate.
A. HNO_3 washed, air dried.
B. NH_4NO_3 washed, air dried.
C. HNO_3 washed, oven dried.
D. NH_4NO_3 washed, oven dried.

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$415°$ which corresponded to the formula, $(NH_4)_2H[P(Mo_3O_{10})_4]\cdot H_2O$. Beyond $415°$, additional weight loss occurred to give the oxide level, $P_2O_5\cdot 24MoO_3$, beginning at $500°$. The drying temperature of $140°$ cited by STOCKDALE[3] appears to be a little too low to effectively dry the compound.

The oven-dried (at $160°$) compound (Fig. $1/C$) gave a thermogram similar to that of the air-dried compound, but did not show the loss of the loosely held water. Decomposition of the compound to the oxide began at $430°$ and was complete at $480°$.

Ammonium 12-molybdophosphate, NH_4NO_3 washed

The air-dried compound (Fig. $1/B$) began to evolve loosely held water at $55°$. The rate of weight loss was rapid at first, but became much slower between $125°$ and $225°$. However, a horizontal weight level was not obtained so that this region of the curve could not be used for drying temperature. Apparently, the compound is slowly losing NH_4NO_3 left by the wash liquid. Above $225°$, the NH_4NO_3 is evolved more rapidly, resulting in a horizontal weight level from $260°$ to $430°$, which corresponded to the formula, $(NH_4)_3[P(Mo_3O_{10})_4]$. Total decomposition of the compound began at $430°$, resulting in the $P_2O_5\cdot 24MoO_3$ level at $515°$. The drying temperature of $280°$ recommended by STOCKDALE[3] appears to be suitable, but slightly higher temperatures may be employed.

The oven-dried (at $160°$) compound (Fig. $1/D$) exhibited a pyrolysis curve which was similar to that of the air-dried compound except for the initial loss of water. Ammonium nitrate was slowly evolved up to $250°$, the temperature at which the anhydrous triammonium 12-molybdophosphate level began. Total disruption of the compound began at $435°$, resulting in the $P_2O_5\cdot 24MoO_3$ level at $510°$.

General

The results of this study differ from the pyrolysis curve as previously reported by DUVAL[1]. However, this may be due to the different methods used to precipitate the ammonium 12-molybdophosphate. A similar situation was found in the case of oxine molybdophosphate[5]. The precipitation process is no doubt very complex and still requires further study. However, if the method of STOCKDALE[3] is employed, then the pyrolysis curves reported in this study should apply. Any deviation from this procedure may seriously affect the composition of the precipitate and also the drying temperature.

SUMMARY

The thermal decomposition of ammonium 12-molybdophosphate, prepared under various conditions was studied on the thermobalance. For the HNO_3 washed precipitate, a drying temperature of $160°$ to $415°$ was recommended; for the NH_4NO_3 washed compound, a drying temperature of $260°$ to $430°$ should be employed.

RÉSUMÉ

L'auteur a examiné, à l'aide d'une thermobalance, la décomposition thermique du phosphomolybdate d'ammonium, préparé dans diverses conditions.

ZUSAMMENFASSUNG

Die thermische Zersetzung von Ammonium-phosphormolybdat, unter verschiedenen Bedingungen hergestellt, wurde mit Hilfe einer Thermowaage untersucht.

References p. 270

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REMARQUES SUR LA COMMUNICATION PRÉCÉDENTE DE M. WENDLANDT

CLÉMENT DUVAL

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1. Lorsque j'ai entrepris en 1946 l'étude de thermogravimétrie publiée dans *Analytica Chimica Acta* je me suis servi des modes opératoires publiés jusqu'en 1945. Je ne peux donc pas avoir étudié le précipité préparé par STOCKDALE en 1958.

2. Même en utilisant un mode opératoire semblable, les courbes de thermobalance ne sont comparables que si l'on s'en tient aux mêmes vitesses de chauffage, au même poids, à la même épaisseur de précipité et à la même nature de creuset, à la même forme de celui-ci, etc.; les résultats ne sont pas les mêmes dans un appareil de silice ou de nickel; de plus, comme nous l'avons reconnu récemment, la thermobalance doit être corrigée de courants de convection pour éviter la ,,montée du creuset vide''. Toutes ces causes d'erreur qui étaient déjà bien étudiées par GUICHARD et ses élèves ne nous avaient pas échappé dès le début de notre étude; c'est pourquoi, tout au long de celle-ci, nous avons beaucoup plus recherché pour un précipité donné, l'existence d'un palier devant nous servir, par voie de comparaison pour effectuer un dosage automatique que la connaissance exacte des températures du début et de la fin puisque, en fin de compte, nous utilisons la température du milieu du palier.

3. Jusqu'en 1949, nous avons utilisé avec la thermobalance Chevenard un mode de chauffage avec rhéostat muni d'un mouvement d'horlogerie et dont les vitesses sont indiquées page 20 du livre *Inorganic Thermogravimetric Analysis*. Depuis cette date, nous avons installé sur nos thermobalances les fours à cycle thermique imposé qui donnent des échauffements linéaires. Comme M. WENDLANDT opère avec un autre mode d'échauffement que nous, ses résultats sont tout aussi acceptables que les nôtres; tout dépend de ce qu'il veut en faire.

4. La courbe de thermolyse du phosphomolybdate d'ammonium réalisée à plusieurs exemplaires en 1946 en s'inspirant des données du traité de TREADWELL a été recommencée ces jours-ci et nous a donné le même résultat en creuset d'aluminite, sur 200 mg et avec la première vitesse de chauffe. Nous maintenons donc nos résultats de 1946.

5. Le spectre d'absorption infrarouge du précipité de phosphomolybdate d'ammonium, même réalisé par la technique de STOCKDALE accuse sans cesse la présence de groupes PO_4 et de groupes MoO_3 à l'exclusion de groupes Mo_3O_{10}, c'est pourquoi, dans nos calculs, nous continuons d'employer la formule habituelle $(NH_4)_3(MoO_3)_{12}PO_4$.

THE DETERMINATION OF NICKEL, COBALT, IRON AND ZINC IN FERRITES

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Ferrites are soft magnetic materials which are used in computers, television sweep cores, microwave gyrators, etc. The basic material is essentially magnetic iron oxide in which part of the ferrous iron has been replaced with zinc. Attempts have been made to improve the magnetic properties by the addition of other elements. This investigation was undertaken to develop an analytical method which could be used to analyze the base material for total iron and zinc as well as for nickel and cobalt in materials to which they had been added.

The successful application of ion exchange separations to Alnico[1] indicated that an improved method for the analysis of ferrites could be developed by a similar approach. The methods usually used for the separation of iron, nickel, cobalt and zinc are time-consuming and are not suitable for rapid routine work.

EXPERIMENTAL

The investigation of the application of ion exchange resins to the analysis of Alnico[1] showed that an excellent separation of iron, cobalt, and nickel could be attained on a strongly basic anion exchange resin. The data on the adsorption characteristics of zinc in HCl[2] indicated that zinc would remain in the column during the elution of nickel, cobalt, and iron.

Since the separation of mixtures of iron, cobalt and nickel had already been accomplished, the preliminary experimental work was confined to insuring that the zinc would not pass through the column while these elements were being eluted, and to selecting optimum conditions for the elution of zinc.

A previously analyzed sample was used as a standard material in this investigation. A 1-g sample was dissolved in $9N$ HCl and 0.5 ml of 30% H_2O_2 and transferred to a column (1 cm I.D. × 50 cm long) containing 28 g of a 100–150 mesh strongly basic type anion exchange resin. The sample solution was washed into the resin, and the nickel eluted with 80 ml of $9N$ HCl. The cobalt was then eluted with 75 ml of $4N$ HCl and the iron with 100 ml of $0.5N$ HCl. Each fraction was evaporated to dryness and each element determined by the back titration of an excess of EDTA with a standard $0.03M$ copper sulfate solution. The results of these analyses are shown in Table I. The agreement between the values by the ion exchange method and the previous analyses by independent methods indicate that zinc was not passing through the column. In order to confirm this a standard zinc solution was introduced into the column and the quantities of HCl given above were passed through the column. Zinc was not found in any of these fractions.

The elution of zinc by dilute HCl was not attempted because of the strong absorption of zinc chloride complexes even in dilute HCl[2]. Attempts were made to elute zinc with ammonium hydroxide, perchloric acid, and nitric acid. It was possible to elute the zinc with all of these reagents; however, $3N$ nitric acid was most suitable for the subsequent treatment of the zinc fraction. The results for zinc, also given in Table I, were obtained by eluting with $3N$ nitric acid.

TABLE I

Sample No.	% Ni Present	% Ni Found	% Co Present	% Co Found	% Fe Present	% Fe Found	% Zn Present	% Zn Found
1	8.2	8.33	0.33	0.33	53.3	53.2	10.4	10.7
2	8.2	8.31	0.33	0.33	53.3	53.2	10.4	10.7
3	8.2	8.31	0.33	0.34	53.3	53.3	10.4	10.7
4	8.2	8.33	0.33	0.33	53.3	53.3	10.4	10.7
5	8.2	8.29	0.33	0.34	53.3	53.2	10.4	10.6

PROCEDURE

Dissolve a 1-g sample in 20 ml of $9N$ HCl and 0.5 ml of 30 vol. % hydrogen peroxide. Transfer the solution of the sample to an ion exchange column with $9N$ HCl. Elute the nickel with 80 ml of $9N$ HCl, the cobalt with 75 ml of $4N$ HCl, the iron with 100 ml of $0.5N$ HCl and the zinc with 100 ml of $3N$ nitric acid. Evaporate each fraction to 5–10 ml. Take a suitable portion of each fraction for the EDTA determination.

All four elements were determined in an identical manner as follows:

Add a 5–10 ml excess of EDTA, 10 ml of acetate buffer (pH ~ 4.8), and back titrate with a standard copper solution using PAN [1-(2-pyridylazo)-2-naphthol] as an indicator.

DISCUSSION

The volumes used for elution were suitable for the columns and resin used in this investigation. The application of this procedure with a different column size or a different resin particle size will require somewhat different elution volumes.

The addition of hydrogen peroxide during dissolution is necessary to insure complete oxidation of iron to the ferric condition. Ferrous iron is only slightly absorbed in $9N$ HCl and would contaminate the nickel and cobalt fractions.

After the elution of zinc with nitric acid, 25 ml of water is added before regenerating the column with $9N$ hydrochloric acid. This precaution is taken to diminish the possibility of generating chlorine in the column. Both the elution of zinc with nitric acid and the regeneration of the column with HCl must be completed without allowing the column to stand for an extended period of time (several hours). The generation of chlorine causes gas bubbles to appear in the column, which necessitates removing the resin and refilling the column.

SUMMARY

An anion exchange technique has been developed for the determination of iron, nickel, cobalt and zinc in a ferrite type material. The constituents are separated by utilizing the differences in the adsorption of their chloride complexes on a strongly basic anion exchange resin. Each constituent is determined by the back titration of an excess of EDTA with a standard copper solution, using PAN as an indicator.

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RÉSUMÉ

Une méthode par échange d'anions est proposée pour le dosage du fer, du nickel, du cobalt et du zinc. La séparation est basée sur les adsorptions différentes des chlorures complexes. Chaque constituant est ensuite dosé par titrage indirect de l'EDTA au moyen d'une solution étalon de cuivre.

ZUSAMMENFASSUNG

Es wird eine Trennung und Bestimmung von Eisen, Nickel, Kobalt und Zink mit Hilfe von Jonen-Austauschern und indirekter EDTA Titration mit einer Standard-Kupferlösung beschrieben. Die Trennung beruht auf der unterschiedlichen Adsorption der komplexen Chloride an stark basischem Anionenaustauscher.

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DETERMINATION OF NICKEL IN GOLD–NICKEL ALLOYS

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The determination of nickel in gold–nickel alloys is complicated by the fact that the dioximes usually used for the precipitation of nickel will reduce gold to the metal. In order to avoid a sulfide precipitation for the separation of gold the possibility of using anion exchange as a rapid means of separation was investigated. It has previously been indicated that gold chloro complexes are strongly adsorbed from a hydrochloric acid solution on a strongly basic anion exchange resin whereas nickel exhibits no adsorption in chloride solutions[1,2]. Investigations with synthetic mixtures of nickel and gold showed that nickel is not noticeably retarded in the column while the gold complex is retained at the top of the column in hydrochloric acid solutions from 2 to 12N.

The determination of nickel was concluded by the back titration of an excess of standard EDTA with a standard copper solution[3].

PROCEDURE

Dissolve a sample in aqua regia to give 15 to 50 mg of nickel. Remove the nitric acid by evaporation to dryness several times on a steam bath. Take up the chlorides with 2N HCl and transfer the solution to an ion exchange column (1-cm diameter) containing 5 g of Dowex 1-X8, 100–200 mesh, chloride form. Wash the sample solution down the sides of the column and elute the nickel into a 250-ml beaker with 2N HCl. Neutralize the eluent with 50% potassium hydroxide until a permanent precipitate just forms. Redissolve the precipitate of nickel hydroxide with 0.1N hydrochloric acid. Add a measured excess of standard EDTA (0.03M), 10 ml of a sodium acetate–acetic acid buffer (0.5M sodium acetate–0.5M acetic acid) and sufficient water to give approximately 300 ml of solution. Heat to 70–90°, add 3 to 4 drops of PAN[4,5] and back titrate with a standard copper solution (0.03M). Calculate per cent nickel from the following expression:

$$\%\text{Ni} = \frac{(V_{\text{EDTA}} \times F - V_{\text{Cu}})\,92.37 M_{\text{Cu}}}{\text{mg of sample}}$$

where V_{EDTA} and V_{Cu} represent the volumes of EDTA and standard copper solution in ml and F represents the volume (in ml) of standard copper whose molarity is M_{Cu} equivalent to 1 ml of EDTA solution.

DISCUSSION

The separation of nickel from gold is simplified by the use of anion exchange resins. The gold(III) chloride complex is adsorbed so strongly by the resin that it is not practical to remove the gold from the column after each sample. Successive samples are separated in the column until the gold complex is within a few centimeters of the bottom of the column as indicated by the bright orange color of the adsorbed complex. The resin is then removed and the column recharged.

The results given in Table I are from a synthetic solution made up of pure gold and nickel.

TABLE I

Sample No.	Gold added mg	Nickel added mg	Nickel found mg	Error mg
1	—	19.50	19.54	0.04
2	—	19.50	19.48	0.02
3	—	19.50	19.48	0.02
4	—	19.50	19.50	0.0
5	80	19.50	19.50	0.0
6	80	19.50	19.54	0.04
7	80	19.50	19.59	0.09
8	80	19.50	19.61	0.11
9	80	19.50	19.55	0.05

SUMMARY

An ion exchange separation based on the difference in adsorption from a chloride solution combined with an EDTA titration is suggested as a rapid and accurate method for the determination of nickel in nickel–gold alloys.

RÉSUMÉ

Une séparation par échange d'ions est proposée comme méthode rapide et précise pour le dosage du nickel dans les alliages nickel–or.

ZUSAMMENFASSUNG

Es wird eine schnelle und genaue Methode zur Bestimmung von Nickel in Nickel–Gold Legierungen mit Hilfe von Jonen-Austauschern und einer EDTA Titration beschrieben.

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ELECTROCHROMATOGRAPHY IN THE SEPARATION OF IONS

VII. SEPARATION OF ALKALINE EARTH METALS

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In previous communications to this Journal attempts to separate common elements belonging to the groups occurring in the analytical table have been described. The ions of the silver group[1] separate into distinct zones with a decinormal solution of sodium chloride, potassium chloride or potassium cyanide. The elements of the copper group[2] form separate bands in the presence of potassium chloride. Such a separation into distinct bands also occurs in the case of members of the zinc group[3] in the presence of potassium cyanide at pH 6.0.

The separation of alkaline earth metals from mixtures of two such elements, with metaphosphate as the electrolyte, has recently been reported by MAKI[4], who has also suggested the possibility of separating a ternary mixture, Ca, Ba(Sr) and Mg, with the aid of a mixture of ethylenediamine or triethanolamine and ammonium tartrate. EVANS AND STRAIN[5] have found that citric, tartaric and lactic acids, but not their ammonium salts, are effective for the separation of Ca, Sr and Ba from a mixture.

The investigation of the separation of the ions of the alkaline earth metals, reported here, shows that separation of ternary mixtures of Ca, Mg and Sr or Ba and of a few binary mixtures are quite feasible even when the most common electrolytes such as ammonium nitrate and chloride are used.

EXPERIMENTAL

The solutions of the ions of calcium, magnesium, strontium and barium were prepared from the nitrates; a small drop (0.01 ml) of the mixtures contained about 20 μg of each ion. The electrolytes used were all decinormal in strength. Solutions of sodium rhodizonate ($M/100$) and 8-hydroxyquinoline ($M/10$) were prepared in distilled water and in N acetic acid respectively.

The experimental technique was exactly the same as reported in earlier papers and here also the signs $+$ and $-$ signify migrations towards anode and cathode respectively. In Table I the movements of the ions in cm are recorded.

An attempt was made to carry out those separations that, on the basis of the migration values, appeared to be fairly feasible. Only a few separations, which are reported in Table II, were found to be successful; in a large number of cases the bands fused together due perhaps to some sort of influence exerted by the ions on each other. The square brackets indicate that the ions enclosed have a portion of their migration zone in common although they can easily be detected. Failure to locate the bands is shown in Table I by dashes.

DISCUSSION

From the movements of the ions of the calcium group it is clear that they have a low tendency to complex formation; in a number of cases owing to complex formation or precipitation reactions the chromogenic reagents fail to locate the bands. Only in

the presence of sodium citrate are all the four ions anionic while in all other electrolytes they behave as cations.

Separation of barium and strontium from each other with electrolytes such as hydrochloric acid and potassium iodide was found not to be possible, in spite of the quite large difference between the migration values; the bands invariably fused together.

TABLE I

Ions	HNO_3	NH_4NO_3	H_3PO_4	$HClO_4$	HCl	NH_4Cl	$NaCl$	KCl	$NaBr$
Mg^{+2}	—3.4	—6.7	–	—5.4	—4.0	—6.1	—11.0	—9.6	—11.0
Ca^{+2}	—3.5	—3.0	—4.7	—5.0	—5.7	—0.5	—13.5	—8.0	—12.3
Sr^{+2}	—6.0	—8.1	—5.5	—6.0	—5.4	—9.0	—10.1	—9.9	—11.8
Ba^{+2}	—5.8	—8.3	—5.8	—6.5	—3.7	—8.5	—10.0	—10.0	—10.9

Ions	KI	CH_3CO_2H	NH_4 acetate	$NaNO_2$	$Na_2S_2O_3$	NH_4CNS	$KCN(aq.)$	Thiourea (aq.)
Mg^{+2}	—8.7	—9.2	—9.0	—6.2	—6.0	—7.5	—0.3	—1.7
Ca^{+2}	—9.5	—2.1	—8.2	—3.2	—5.7	—5.6	—0.3	—0.7
Sr^{+2}	—4.2	—17.1	—11.0	—7.5	—5.1	—7.4	—0.4	—8.5
Ba^{+2}	—10.9	—18.4	—11.8	—7.3	—3.7	—6.6	—0.2	—8.5

Ions	Thiourea (pH 5.8)	Thiourea (0.1N HCl)	Tartaric acid	Citric acid	Na K tartrate	Na citrate	Na rhodizonate ($M/100$)	Oxine ($M/10$) in N acetic acid
Mg^{+2}	—8.9	—5.2	—11.7	—8.0	–	+2.6	—2.9	—6.5
Ca^{+2}	—8.0	—2.0	—13.6	–	–	+7.6	—3.0	—8.5
Sr^{+2}	—10.6	—3.5	—7.1	—13.2	—4.5	+1.8	0.0	—1.7
Ba^{+2}	—8.8	—5.5	—6.5	–	—4.6	+2.5	0.0	—1.0

TABLE II

Electrolyte	Sequence of separation
HCl	: [Mg, Sr] —; : Ba, Ca—
HNO_3	: Ca, Ba—; : Ca, Sr—; : Mg, Sr—; : Mg, Ba—
NH_4NO_3	: Ca[Mg, Ba]—; : Ca[Mg, Sr]—
CH_3CO_2H	: Ca, Ba—; : Ca, Sr—
NH_4Cl	: Ca, Mg, Sr—; : Ca, Mg, Ba—
NaCl	: Sr, Ca—; : Ba, Ca—; : Mg, Ca—
$NaNO_2$	: Ca, Ba—; : Ca, Mg—; : Ca, Sr—
Thiourea (aq.)	: Ca, Mg—; : Ca, Ba—; : Ca, Sr—
Na rhodizonate or oxine	: Sr, Mg—; : Sr, Ca—; : Ba, Ca—; : Ba, Mg—

SUMMARY

Complete separation of ternary mixtures of Ca, Mg and Sr or Ba ions with ammonium chloride and less complete but detectable separation of the same mixtures with ammonium nitrate have been achieved, as well as a few binary separations of the type Ca–Ba, Ca–Sr, Ca–Mg, Mg–Sr and Mg–Ba.

RÉSUMÉ

Les auteurs ont pu effectuer, par électrochromatographie, des séparations Ca–Mg–Sr (ou Ba) et des séparations binaires: Ca–Ba, Ca–Sr, Ca–Mg, Mg–Sr et Mg–Ba.

ZUSAMMENFASSUNG

Es wird eine elektrochromatographische Methode zur Trennung von Ca, Mg und Sr (oder Ba) sowie die Trennung binärer Gemische von Ca–Ba, Ca–Sr, Ca–Mg, Mg–Sr und Mg–Ba beschrieben.

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DETERMINATION OF Ni, Zn AND Al IN BRONZES AND BRASSES AFTER DETERMINING Cu-Pb-Sn-Sb BY CONTROLLED-POTENTIAL ELECTROLYSIS

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A method for the determination of copper, lead, tin and antimony by controlled-potential electrolysis and the applications of this method to the analysis of some alloys, particularly bronzes and brasses, have been described in previous papers[1-3].

Further investigations have led to the elaboration of a method for the successive determination of nickel, zinc and aluminium using the solution remaining after the electrolytic separation of the four metals mentioned above. The solution is acid because of its hydrochloric acid content, and contains tartaric and succinic acids. Ammonium salts of all three of these acids are present and, if the alloy to be analysed contains antimony, potassium iodide is also present in the solution.

PRINCIPLE OF THE METHOD

Nickel is precipitated by dimethylglyoxime in slightly ammoniacal medium; in the filtrate zinc is separated by controlled-potential electrolysis. The solution is subsequently treated with 8-hydroxyquinoline to separate the aluminium which, after filtration and dissolution of the oxinate, is precipitated with ammonium benzoate.

Reagents (Merck, pro analysi)
  Concentrated ammonia, sp.gr. = 0.88.
  Dilute ammonia (1 + 1).
  Concentrated sulphuric acid, sp.gr. = 1.83.
  Concentrated nitric acid, sp.gr. = 1.38.
  Dilute nitric acid (1 + 1).
  Perchloric acid (60% solution).
  Thioglycollic acid (76% solution).
  Hydrazine hydrochloride.
  Solution of dimethylglyoxime: dissolve 10 g of KOH in 400 ml of distilled water, add 10 g of dimethylglyoxime and stir until solution is complete, then bring to 1 l with distilled water.

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Solution of gelatine: dissolve 0.2 g of gelatine in 70 ml of warm distilled water and bring to 100 ml with distilled water.

10% aqueous solution of KCNS.

Solution of 8-hydroxyquinoline: dissolve 2 g of 8-hydroxyquinoline in 70 ml of distilled water containing 6 ml of glacial acetic acid and bring to 100 ml with distilled water.

Solution of ammonium benzoate: dissolve 10 g of ammonium benzoate in 70 ml of warm distilled water and bring to 100 ml with distilled water (if the benzoate precipitates when the solution is cold, heat it before use).

Benzoate wash solution: dissolve 2 g of ammonium benzoate in 170 ml of distilled water, add 4 ml of glacial acetic acid and bring to 200 ml with distilled water.

DETERMINATION OF NICKEL

Neutralize the solution remaining after the determination of copper, lead, tin and antimony, with ammonia until a pH of 6–7 is obtained and add a slight excess of dimethylglyoxime solution; 10 ml are usually sufficient. Then bring the pH to 7.5–8 (check with narrow range test papers) with ammonia while stirring the solution during the precipitation; heat to 45–50°, but not beyond this temperature, set aside for 10–15 minutes and then filter at the pump on a weighed Gooch or sintered glass crucible collecting the filtrate in a tall-form 600 ml beaker, wash with distilled water, dry for two hours at 110°, cool in a desiccator and then weigh:

$$\text{Ni \%} = \frac{\text{weight of the nickel dimethylglyoxime} \times 20.32}{\text{sample weight}}$$

Nickel precipitates equally well if an alcoholic solution of dimethylglyoxime is used, but the presence of alcohol in the filtrate adversely affects the subsequent precipitation of aluminium, the oxinate of which is rather soluble in the presence of alcohol; the precipitation of nickel is not disturbed by the presence of tin and antimony and may be carried out without previously separating these elements.

If the iron present in the solution exceeds 20 mg it is advisable to add some drops of 3% hydrogen peroxide before precipitating the nickel. Before filtration, the solution containing the precipitate must not be heated above 50°, otherwise the subsequent determination of zinc will prove difficult.

DETERMINATION OF ZINC

To the dimethylglyoxime filtrate add 2 g of hydrazine hydrochloride, 20 ml of concentrated ammonia and 10 ml of the gelatine solution, then electrolyse the solution at controlled cathode potential to deposit the zinc. The electric circuit, the electrodes and the apparatus have already been described in a previous paper[1].

The electrolysis of zinc is disturbed by iron which, if present in amounts smaller than 10 mg will partially co-deposit with the zinc, while, if present in greater amounts, will also prevent the complete deposition of the zinc itself. An attempt has been made to overcome these difficulties by complexing the iron with CN^- ions in ammoniacal solution or with F^- ions in a solution either weakly acid or ammoniacal, but no advantage was obtained; zinc deposition in formic acid medium has also not proved satisfactory. Therefore, it is necessary to avoid determining the zinc by electrolysis when the amount of iron exceeds 10 mg, while when the iron present in the solution is less than 10 mg, a determination of the iron co-deposited with zinc must be made.

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Zinc deposition is always accompanied by a considerable evolution of hydrogen, and if this evolution ceases it means that the zinc deposition has also ceased.

During the electrolysis the solution assumes a pink or red colour owing to the reaction of the ferrous iron with the dimethylglyoxime previously added for the separation of nickel.

Some manganese dioxide may separate at the anode when the electrolysis is approaching completion; this oxide may be redissolved, if desired, simply by immersing the anode in the electrolyte after the electrolysis is finished and the cathode has been removed.

Zinc is deposited by passing a current through the solution (usually 0.4 to 0.8 A) to which a cathode potential ranging from —1.2 to —1.3 V vs. S.C.E. corresponds. The cathode potential has a tendency to become immediately more negative.

If manual apparatus is used for potential control, the cathode potential should be allowed to reach —1.50 to —1.55 V vs. S.C.E. during the electrolysis; if potassium iodide is present in the solution it is preferable not to let the cathode potential exceed —1.50 V vs. S.C.E.

However, some cases are met with — specially when iron exceeds 3–4 mg — where the cathode potential does not spontaneously become more negative down to —1.45 and —1.50 V vs. S.C.E.; it is therefore necessary to lower it first to —1.45 V vs. S.C.E. (10–15 min after the electrolysis has started) and then to —1.50 V vs. S.C.E. (20–30 min before the electrolysis ends).

If automatic apparatus is used, start the zinc electrolysis with a cathode potential (about —1.2 to —1.3 V vs. S.C.E.) to which a current intensity of 0.4–0.8 A corresponds; then gradually raise the cathode potential to —1.5 to —1.55 V vs. S.C.E.

The electrolysis takes 50–60 min for bronzes and from 1 h 15 min to 1 h 20 min for brasses; after the electrolysis is finished the zinc deposit is washed with distilled water containing a drop of ammonia per liter and then with alcohol and ether; finally, it is dried at 100° and weighed.

A noticeable amount of the current flowing through the solution is used up by secondary reactions such as the evolution of hydrogen at the cathode and the cyclic oxidation and reduction of iron, at the anode and the cathode respectively. As a consequence, the deposition of the last traces of zinc is slow. Furthermore, when the amount of zinc is less than 10 mg it is not advisable to bring the cathode to a potential more negative than —1.48 to —1.50 V vs. S.C.E. because the only result would be an increased evolution of gas.

When the electrolyte contains potassium iodide (added if antimony has been previously determined) and the amount of iron is less than about 3 mg, the cathode potential must not be adjusted to values more negative than —1.48 to —1.50 V vs. S.C.E., because otherwise a rise in the anodic potential will also occur, causing the separation of iodine, which partially clings to the zinc deposit; this then assumes a blackish appearance. However, if the iron present in the solution exceeds 3 mg, this will prevent the separation of iodine even if the cathode is more negative than —1.50 V vs. S.C.E.

If the amount of iron present in the solution is greater than 9–10 mg, then the deposition of zinc is incomplete in any case; this limitation restricts the possible applications of the method, but, in the numerous cases in which it is applicable, the results

agree with those obtained with methods that are more complex and time-consuming. Table I shows the results of the determinations carried out on seven samples of known composition; the range of their compositions covers the more usual cases met with in current analysis, excepting those alloys that contain more than 1% of iron.

To evaluate the iron co-deposited with the zinc (from a few tenths to 30–40 tenths of a mg, depending on the total amount of iron present in the electrolyte) several methods may be followed; the method used by the author is as follows[4]: dissolve the zinc deposit in 15 ml of lukewarm HNO_3 (1+1), boil and bring to 250 ml; transfer 25 ml of the solution to a 100-ml flask, heat at approximately 50°, add 10 ml of the KCNS solution, let stand for 1 min, cool to 20°, bring to volume and take a photometric measurement against distilled water (check that reagents and vessels are free from iron). A Pulfrich photometer, 546 Hg filter, was used. The percentage of iron so found is subtracted from that of zinc.

$$Fe \% = 1.518 \, k \text{ (for 1 g sample)}$$

$$k = \text{extinction coefficient}$$

DETERMINATION OF ALUMINIUM

The aluminium possibly present in the solution remaining after the zinc electrolysis may be separated by means of hydroxyquinoline. If the zinc deposition was not quantitative, owing to the presence of too large an amount of iron, this does not affect the determination of aluminium.

The hydroxyquinoline also precipitates the iron and most of the manganese; in the presence of potassium cyanide the co-precipitation of these two elements is prevented, but if manganese is present in amounts greater than 5 mg, manganese ferrocyanide will separate, which is very difficult to filter. Also if manganese is absent, or present in amounts of not more than 5 mg, the precipitation of pure aluminium oxinate of stoichiometric composition requires some special conditions[5], which cannot be applied to this particular test-solution. Therefore the hydroxyquinoline is used for a preliminary separation, while the quantitative determination of aluminium is carried out by precipitation with ammonium benzoate.

Heat the solution from which zinc has been separated to 60° and do not exceed 70°. While continuously stirring, add drop by drop an excess of the hydroxyquinoline solution; at least 1 ml of the precipitating solution is required for every mg of aluminium, iron and manganese; it is always inadvisable to use less than a total of 15 ml. Allow to cool, filter on Whatman No. 40 paper and wash with distilled water. (If it is desired to prevent the co-precipitation of iron, add 3 g of potassium cyanide to the solution before heating to 60°.)

Transfer both the filter and the precipitate to the beaker in which the precipitation has been carried out and add 10 ml of conc. sulphuric acid; let the paper carbonize, add 10 ml of conc. nitric acid, cover with a watch glass and heat until all nitrous vapors are eliminated. Remove the watch glass and bring to sulphuric acid fumes; take the beaker off the plate, add 3 ml of perchloric acid and then bring to perchloric acid and subsequently sulphuric acid fumes.

Allow to cool, dilute with distilled water to approximately 70 ml, boil to dissolve the aluminium sulphate and allow to cool.

TABLE I

RESULTS OF THE ANALYSES OF SAMPLES WITH KNOWN COMPOSITION

Sample		*Values found**				
		1	*2*	*3*	*4*	*5*
N. 207 Bronze C (B.Ch.S.)	Cu	86.82	86.72	86.64	86.73	86.88
Cu = 89.65–87.00; Ni = 0.09	Pb	0.36	0.41	0.38	0.38	0.38
Pb = 0.41; Zn = 2.53; Fe = 0.06	Sn	9.82	9.80	9.92	9.80	9.74
Sn = 9.71–9.97; Ag = 0.02	Sb	n.d.	n.d.	n.d.	n.d.	n.d.
Sb = 0.04; As = 0.05; S = 0.005	Ni	0.11	0.08	0.07	0.10	0.09
	Zn	2.54	2.52	2.55	2.59	2.53
Al added: to 2 = 0.20%; to 3 = 0.10%	Al	—	0.18	0.095	—	—
N. 52 c Cast Bronze (N.B.S.)	Cu	89.26	89.21	89.22	89.21	89.26
Cu = 89.25; Ni = 0.76; S = 0.002	Pb	n.d.	n.d.	n.d.	n.d.	n.d.
Pb = 0.011; Zn = 2.12; P = 0.001	Sn	7.77	7.81	7.76	7.78	7.79
Sn = 7.85; Fe = 0.004	Ni	0.75	0.77	0.78	0.78	0.75
	Zn	2.12	2.10	2.15	2.10	2.14
Al added: to 2 = 0.50%; to 3 = 0.30%	Al	—	0.49	0.28	—	—
N. 63 b Phosphor Bronze (N.B.S.)	Cu	77.88	77.92	77.89	77.88	77.87
Cu = 77.94; Ni = 0.33; P = 0.44	Pb	9.27	9.26	9.28	9.25	9.35
Pb = 9.36; Zn = 0.71; S = 0.16	Sn	9.77	9.76	9.81	9.76	9.78
Sn = 9.78; Fe = 0.47; Ag = 0.04	Sb	0.50	0.52	0.48	0.46	0.49
Sb = 0.54; Si = 0.12; Al = 0.05	Ni	0.33	0.34	0.32	0.30	0.36
	Zn	0.67	0.75	0.74	0.70	0.73
Al added: to 3 = 0.50%; to 4 = 0.20%	Al	n.d.	n.d.	0.54	0.24	n.d.
N. 124 c Ounce Metal (N.B.S.)	Cu	84.21	84.18	84.18	84.17	84.19
Cu = 84.22; Ni = 0.60; S = 0.048	Pb	4.70	4.70	4.68	4.69	4.78
Pb = 4.74; Zn = 4.93; P = 0.024	Sn	5.10	5.12	5.12	5.07	5.07
Sn = 5.13; Fe = 0.107	Sb	0.18	0.20	0.20	0.19	0.18
Sb = 0.20; Si = 0.002	Ni	0.58	0.59	0.60	0.57	0.61
	Zn	5.01	5.02	4.94	4.99	4.91
Al added: to 3 = 0.10%; to 4 = 0.20%	Al	—	—	0.10	0.21	—
N. 37 d Sheet Brass (N.B.S.)	Cu	70.79	70.72	70.79	70.85	70.76
Cu = 70.78; Ni = 0.58	Pb	0.92	0.93	0.87	0.94	0.93
Pb = 0.94; Zn = 26.65	Sn	0.94	0.95	0.95	0.95	0.92
Sn = 0.97; Fe = 0.076	Ni	0.57	0.59	0.57	0.55	0.60
	Zn	26.68	26.65	26.66	26.67	26.70
Al added: to 3 = 0.30%; to 4 = 0.50%	Al	—	—	0.28	0.52	—
N. 62 b Manganese Bronze (N.B.S.).	Cu	57.45	57.40	57.38	57.37	57.43
Cu = 57.39; Ni = 0.27; Mn = 1.29	Pb	0.23	0.24	0.22	0.25	0.22
Pb = 0.28; Zn = 37.97; Si = 0.048	Sn	0.89	0.87	0.88	0.92	0.92
Sn = 0.96; Al = 0.97; As = 0.004	Ni	0.24	0.25	0.28	0.27	0.30
Sb = 0.005; Fe = 0.82; Ag = 0.005	Zn	37.92	37.88	38.03	37.90	37.96
	Al	0.95	0.94	0.95	0.92	0.99
N. 62 c Manganese Bronze (N.B.S.)	Cu	59.18	59.19	59.16	59.17	59.14
Cu = 59.16; Zn = 37.24	Pb	0.20	0.18	0.18	0.25	0.22
Pb = 0.24; Al = 1.22	Sn	0.37	0.36	0.37	0.35	0.37
Sn = 0.39; Fe = 0.74	Ni	0.27	0.27	0.27	0.29	0.31
Ni = 0.28; Mn = 0.66	Zn	37.24	37.19	37.26	37.20	37.27
Si = 0.068	Al	1.21**	1.21	1.23**	1.22	1.26

* n.d. = not determined.

** Al precipitated with 8-hydroxyquinoline in the presence of KCN.

A possible violet colour is due to the presence of manganese oxidized to permanganate by the perchloric acid; this coloration is eliminated with some hydrazine hydrochloride or sulphate.

Filter to separate the silica which, though almost invisible, is always present; wash the filter with distilled water. Add 2 ml of thioglycollic acid to the filtrate, heat and add little by little while stirring 20 ml of the ammonium benzoate solution and then neutralize first with conc. ammonia and subsequently with dilute ammonia to pH 3.6–4.2. If necessary, correct with dilute sulphuric acid and ammonia (check with narrow range pH test papers or use bromophenol blue as indicator). Heat and boil for a few minutes while stirring the solution occasionally. Allow to settle, filter on Whatman No. 40 paper, wash with warm benzoate wash solution, ignite and weigh.

$$Al \% = \frac{\text{weight of } Al_2O_3 \times 52.91}{\text{sample weight}}$$

In Table I the results obtained in the analysis of some samples of known composition are listed; copper, lead, tin and antimony were determined according to the method described in previous papers[1,2] and nickel, zinc and aluminium according to the method described here. Besides supporting the method outlined here, the values found are a further confirmation of the suitability of the method previously described.

SUMMARY

A method is given, which allows nickel, zinc and aluminium to be determined in the solution remaining after the determination of copper, lead, tin and antimony by controlled-potential electrolysis. Nickel is precipitated by dimethylglyoxime, zinc is deposited by controlled-potential electrolysis and aluminium is precipitated first by oxine and then by ammonium benzoate.

RÉSUMÉ

Une méthode est proposée pour le dosage du nickel, du zinc et de l'aluminium dans la solution résultant du dosage du cuivre, du plomb, de l'étain et de l'antimoine par électrolyse à potentiel contrôlé.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Nickel, Zink und Aluminium in einer Lösung, die nach der Bestimmung von Kupfer, Blei, Zinn und Antimon mittels Elektrolyse bei kontrolliertem Potential übrig bleibt.

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PRECISION NULL-POINT POTENTIOMETRY

A SIMPLE, RAPID AND ACCURATE METHOD
FOR LOW CONCENTRATION CHLORIDE DETERMINATIONS

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Chloride determinations have been performed by a variety of methods, but the most generally used are the titration methods, using visual, potentiometric, ampero-metric and other end-point detection systems. The titration procedure is capable of good accuracy except when the chloride concentrations are too low. At low chloride concentrations, absolute potential measurements in a concentration cell containing two silver–silver chloride electrodes can yield satisfactory quantitative results as demonstrated by FURMAN AND LOW[1,2] and others[3,4]. This method is rapid and provides good chloride results if the equipment is properly set up and all samples adjusted to about the same over-all ionic strength.

Unfortunately, with the regular concentration cell method it is necessary to maintain the reference and samples at the same and constant known temperature, and this requires an inconvenient temperature controlling system. Also, in dilute chloride solutions it is necessary to correct for chloride contribution by the Ag–AgCl electrode solubility and for the chloride content of any reagents used. These calculations can be quite time-consuming, and even with care the relative accuracy is seldom better than 1%, regardless of the concentration range. The accuracy by the regular concentration cell method is better than obtainable by the titration procedure for dilute solutions (about $10^{-4}M$ and below), but less for the higher concentrations, where 0.1% relative accuracy is often possible by the titration method.

In order to eliminate the difficulties inherent in the regular concentration cell method and readily provide results of better accuracy, a new technique was developed which is herein referred to as Precision Null-Point Potentiometry. The new method can be applied for determinations of chloride over a wide concentration range, as low as $10^{-6}M$ and as high as necessary if the sample can be diluted to at least $0.1M$. The method does not require a temperature controlling system, and calculation corrections are not necessary for electrode solubility and chloride contributions by reagent impurities. The only calculation necessary for determining chloride concentration is either a simple addition or subtraction of two numbers. The method is especially applicable where the chloride concentrations for a series of samples vary over a relatively small range. In this case, even though the chloride concentration is sufficiently high so that a titration would be satisfactory, the precision null-point potentiometric method can be more rapid and accurate. For example, the chloride concentration of a prepared solution sample could be determined in less than a

minute with an accuracy of 0.1%, and sample preparation for some samples would require only a few seconds.

The precision null-point potentiometric method consists simply of changing the chloride concentration of the unknown solution, while maintaining the ionic strength constant, until it is of identical concentration to a known reference solution. This can be accomplished experimentally in such a way that temperature control and calculation corrections are not necessary. The general principles and simple experimental techniques are described and results for chloride presented.

GENERAL PRINCIPLES OF THE METHOD

If the liquid junction potential of a concentration cell is negligible, which is the case if the ionic strength is the same on both sides of the junction, then the e.m.f. of the cell is given by equation (1),

$$E = kT \log \frac{a_u}{a_R} = kT \log \frac{C_u}{C_R} + kT \log \frac{v_u}{v_R} \quad \ldots \ldots \ldots \quad (1)$$

where a_u, C_u, v_u and a_R, C_R, v_R are the activity, concentration and activity coefficient for the potential determining species in the unknown and reference solutions, respectively. It is already assumed that the ionic strengths in both solutions are essentially equal so the activity coefficients are equal and the second term of equation (1) drops out and

$$\frac{C_u}{C_R} = 10^{E/kT} \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (2)$$

Since the method to be described has been used for the determination of chloride, the following discussion and equations will refer to chloride specifically, but the method is general and should be applicable for other determinations.

Assume the following conditions: (a) It is possible to set up a concentration cell, as shown in Fig. 1, consisting of an unknown chloride solution in a beaker and a chloride reference solution in a small glass isolation compartment which provides electrical contact but prevents any significant mixing of the two solutions; (b) there is zero or a small constant potential across the electrode pair when the solutions in the isolation compartment and beaker are the same concentration; (c) a pair of Ag–AgCl electrodes having nearly identical characteristics is available, with one placed in the reference and the other in the unknown solution; (d) the chloride concentration of the unknown can be easily and rapidly changed by either dilution or addition of a more concentrated standard chloride solution while maintaining the ionic strength of the unknown equal to the reference solution and stirring the unknown solution continuously with a motor-driven paddle stirrer; (e) both reference and unknown solutions rapidly come to the same temperature under experimental conditions.

Under these conditions it is apparent from equation (2) that when $E = 0$ the concentrations of the adjusted unknown solution, C_{uA}, and the reference solution, C_R, are the same, *i.e.*,

$$C_{uA} = C_R \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (3)$$

and independent of the temperature. The procedure consists simply of changing the original volume, V_o, of unknown chloride solution of concentration C_u, until the null potential is reached, at which point the solution has a new total volume $(V_o + V_a)$ and a concentration equal to the known reference C_R.
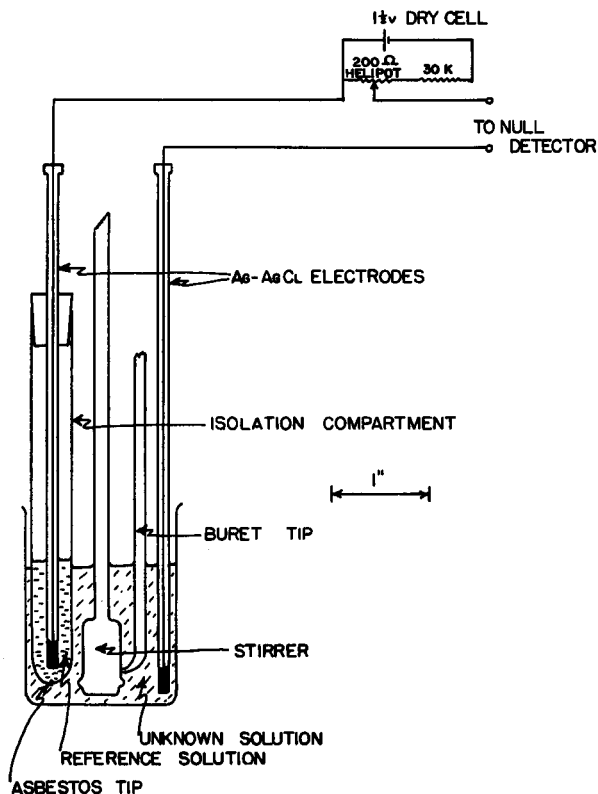
Fig. 1. Precision null-point potentiometric apparatus for chloride determinations.

If the original unknown solution is diluted by adding a volume, V_a, of a solution containing no chloride, but of essentially the same electrolyte concentration as the reference, then at the null point the quantity of chloride in the unknown, Q_u, is given by equation (4),

$$Q_u = C_R(V_o + V_a) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ (4)$$

If C_R is some exact fraction or multiple of ten, the unknown quantity of chloride, Q_u, can be calculated by adding two numbers, the volume of the original sample aliquot plus the volume of electrolyte added from the buret, and moving the decimal point in accordance with C_R.

If the unknown chloride solution is originally more dilute than the reference, it is made more concentrated by adding a chloride solution more concentrated than the reference, for example, exactly $2C_R$. In this case at the null point the total quantity

of chloride present in a volume $(V_o + V_a)$ is the sum of the chloride in the unknown, Q_u, and the quantity added, Q_A, and

$$\frac{Q_u + Q_A}{V_o + V_a} = C_R \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (5)$$

Since $Q_A = 2C_R V_a$, it follows from equation (5) that,

$$Q_u = C_R(V_o - V_a) \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (6)$$

Although it is assumed in the above discussion that no chloride is contributed by the electrolyte and other reagents or the electrodes, it can be readily shown that such contributions of chloride will not enter into the final calculations if the reference solution is made up with the same reagents and same concentration as for the unknown samples and both reference and unknown electrodes have similar characteristics. This is generally easy to attain in practice, but too large a chloride contribution by the reagents and electrodes obviously decreases sensitivity of null detection.

<div align="center">APPARATUS</div>

Electrodes

The Ag−AgCl electrodes were prepared by using the plating procedure of BROWN AND MACINNES[5] and the chloridizing procedure of FIANDA AND NAGEL[6]. Platinum plate electrodes (2 × $^1/_2$ cm, 1 × $^1/_2$ cm, $^1/_2$ × $^1/_2$ cm, and $^1/_2$ × $^1/_5$ cm) and wire electrodes, (1 cm long and 1 mm diameter) were used. All electrodes were plated and chloridized in pairs. It was possible to easily prepare electrode pairs having asymmetry potentials, *i.e.*, the potential between two electrodes in the same reference solution, less than 0.1 mV, and negligible drift. These electrodes were stable for months when kept in the reference solution and never allowed to dry out. The potential between the two electrodes when in solutions of same concentration and separated by the isolation compartment, as shown in Fig. 1, was also usually less than 0.1 mV.

Isolation compartment

Several methods for isolating the reference solution were found satisfactory and are referred to as the asbestos fiber type, cracked glass type, and porous unglazed vycor type. The asbestos fiber type was made from a Beckman fiber type calomel electrode, number 4970, by cutting away the plastic cap and cleaning the tube thoroughly and soaking for several hours in distilled water to remove all traces of potassium chloride. The tube was then filled with the appropriate reference solution and after about an hour was ready for use. The cracked glass type was made by sealing a bead of soft glass in a small hole in the bottom of a pyrex test tube. As the soft glass cooled it produced many small cracks providing electrical contact, but preventing any significant mixing of reference and unknown solutions. The cracked glass type usually has a larger electrical resistance than the asbestos fiber type. The unglazed vycor type, which is made from Corning porous glass 7930 and described by CARSON *et al.*[7] has a lower resistance than the other two types and prevents mixing of the two solutions. However, it must be filled with reference solution for at least one day before it can be used.

Stirring equipment

The stirrer setup for the Sargent-Malmstadt automatic titrator[8] was used to assure efficient stirring and to provide a means of holding the beaker and isolation compartment and of allowing a simple and rapid changing of beakers. To obtain the most efficient mixing of the solution being added by the buret and the solution in the beaker, the buret tip is pointed at and nearly in contact with the enlarged end of the Sargent stirrer as shown in Fig. 1. The electrode outside the isolation compartment is held firmly in place by means of one of the clips on the side of the Sargent-Malmstadt titrator stand. The isolation compartment is held in place by the other clip, and the electrode inside the compartment is held in place by means of a split one-holed cork which fits into the tube as shown in Fig. 1.

Zero-suppress

In order to use zero as the null potential, it was necessary to buck out the small potential

between the electrodes when the solution in the beaker was the same concentration as that in the isolation compartment. This was accomplished by using a ten-turn Helipot in series with a resistor across a 1.5 V dry cell so that a 0 to 10 mV bucking voltage could be applied. However, if more than 1 mV exists across the electrodes in the above case, something is probably wrong, and the system should be checked.

Null detector

For expediency in studying the characteristics of the system, a Leeds and Northrup 10 mV Speedomax recording potentiometer was used as the null detector. Other types of null detectors could be used, the sensitivity depending on the required precision. Systems for automatically terminating the addition of reagent at the null potential could also be easily applied.

Burets

Fischer-Porter automatic self-zeroing, 25 ml, precision-bore, teflon stopcock burets were used for adding the reagent. Each buret was filled through a sidearm fitted with a teflon stopcock connected to a large reservoir of appropriate reagent.

PREPARATION OF SOLUTIONS

The most suitable chloride concentration for the reference depends on the concentration range of chloride in the unknowns, and the reference is made up so that the final chloride results can be obtained in suitable units, such as milliequivalents, parts-per-million, or per-cent, by simple addition or subtraction of volume of reagent added from the buret and volume of sample aliquot or some multiple of it. The reference solutions, solutions added, and unknown solutions used for the experimental work were $1.000 \cdot 10^{-2}$ to $1.000 \cdot 10^{-6} M$ chloride made from reagent grade sodium chloride.

The ionic strength of different unknown samples might vary considerably, and since it is necessary that all samples and reference solution have essentially the same ionic strength, it is desirable to add a large known quantity of electrolyte to all solutions so that the contribution to the ionic strength of ionic constituents in the sample is insignificant. Of course, at the null point the chloride contribution to the ionic strength is the same in both solutions. All solutions used for the experimental work described herein were prepared to be $1 M$ sulfuric acid, by pipetting suitable aliquots of 5 or $10 M$ sulfuric acid and diluting to correct volume. To assure that the same amount of chloride is added to all solutions by the H_2SO_4, a large volume (20 l) of 5 or $10 M$ H_2SO_4 was prepared and used in making the reference and in preparing samples for analysis.

Although the chloride concentration from the added electrolyte does not enter into the final calculation, since it is the same in the reference and unknown solutions, it is desirable to use an electrolyte containing a very small amount of chloride to prevent a decrease in sensitivity of null detection. This becomes important when the chloride contribution from the electrolyte is large compared to the chloride contribution from the unknown. For this reason sulfuric or nitric acids are good to use because of their commercial availability with low chloride content.

PROCEDURE

Establishment of null point

At the beginning of each day the isolation compartment is emptied and filled to at least a few millimeters above the top of the Ag–AgCl plate with fresh reference solution. The isolation compartment is positioned in the beaker as shown in Fig. 1;

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the reference solution is also placed into the beaker and the stirrer started. In order to have a null point at zero, any small potential between the electrodes is bucked out by means of the zero-suppress control. About every hour or two it is a good idea to recheck the null point using reference solution in the beaker and readjusting to zero by means of the zero-suppress. Usually it has not varied by more than $\pm$ 0.05 mV upon rechecking unless some unexpected interference fouled the electrodes.

Determination of the unknowns

After setting the null point, the reference solution in the beaker is removed, and the beaker lip is touched to the bottom of the stirrer and isolation compartment to remove the adhering solution. A measured aliquot of the unknown chloride solution is pipetted into a clean, dry, tall-form beaker and the stirrer is started. For example, a 20-ml aliquot is added to a 50-ml beaker, or a 50-ml aliquot to a 100-ml beaker. If the unknown solution is more concentrated in chloride than the selected reference solution, the unknown is diluted by adding $1M$ H_2SO_4 containing no added chloride. This reagent is added at a rate of about 15 ml/min from a teflon stopcock buret with vigorous stirring until the null point is reached. Because a pair of electrodes may not respond instantaneously, about five to thirty seconds are allowed for equilibration, and the addition of reagent is continued if necessary to establish the null point. The buret reading is recorded and the quantity of chloride is expressed in appropriate units as given by equation (4). The entire determination requires from about a few seconds to 2 minutes depending on the volume added.

If the unknown solution is less concentrated in chloride than the selected reference solution, a solution exactly twice the chloride concentration of the reference solution is added from a teflon stopcock buret until the null point is reached. Again five to thirty seconds are allowed for equilibration, and the addition of reagent is continued if necessary to re-establish the null point. The buret reading is recorded, and the quantity of chloride is calculated by equation (6).

After each determination the beaker rim is touched to the bottom of the stirrer and isolation compartment to remove adhering solution. Another beaker containing a new aliquot of chloride is put into place, and the determination is carried out as above.

RESULTS

Several thousand samples were determined having chloride concentrations both larger and smaller than the reference solution. Table I shows results for a typical series of ten identical samples which were twice the chloride concentration of the $1.000 \cdot 10^{-4}M$ chloride reference solution, and required the addition of about 20 ml of sulfuric acid electrolyte reagent to dilute the 20 ml samples to the null point. Similar results were obtained using the asbestos fiber or cracked glass isolation compartments, but the results were not quite as good with the unglazed vycor compartment. Results of equal precision and accuracy were obtained using various sizes and shapes of electrodes, and other samples requiring up to a two-fold dilution.

Results for a typical series of 10 indentical samples which were 10 times more dilute than the reference are shown in Table II. In this case the reagent added is exactly twice the chloride concentration of the $1.000 \cdot 10^{-4}M$ chloride reference solution, and about 18 ml of reagent are added to each 20-ml aliquot of sample to

TABLE I

DETERMINATION OF CHLORIDE BY THE PRECISION NULL-POINT
POTENTIOMETRIC METHOD FOR A SAMPLE TWICE THE
REFERENCE CONCENTRATION

Millimoles chloride taken	Millimoles chloride found	Deviation
0.004000	0.004000	0.000000
0.004000	0.004000	0.000000
0.004000	0.003998	0.000002
0.004000	0.003997	0.000003
0.004000	0.004004	0.000004
0.004000	0.004000	0.000000
0.004000	0.003997	0.000003
0.004000	0.003998	0.000002
0.004000	0.003994	0.000006
0.004000	0.003999	0.000001
Ave. 0.004000	0.003999	0.000002

Coefficient of variation: 0.07%

TABLE II

DETERMINATION OF CHLORIDE BY THE PRECISION NULL-POINT
POTENTIOMETRIC METHOD FOR A SAMPLE ONE-TENTH THE
REFERENCE CONCENTRATION

Millimoles chloride taken	Millimoles chloride found	Deviation
0.000200	0.000195	0.000003
0.000200	0.000200	0.000002
0.000200	0.000197	0.000001
0.000200	0.000200	0.000002
0.000200	0.000201	0.000003
0.000200	0.000194	0.000004
0.000200	0.000198	0.000000
0.000200	0.000195	0.000003
0.000200	0.000196	0.000002
0.000200	0.000200	0.000002
Ave. 0.000200	0.000198	0.000002

Coefficient of variation: 1.3%

reach the null point. The buret reading error in this case is relatively large compared to the volume difference $(V_o - V_a)$, and the relative deviation is considerably larger than for the results shown in Table I. However, it is possible to cover a greater concentration range by the addition of chloride to the sample than by dilution of the sample. Results would, of course, be better with a more precise buret.

Many results were also obtained for even smaller quantities of chloride than those illustrated in Tables I and II. For example, a series of ten identical samples containing 0.100 parts per million chloride was determined with a standard deviation of 0.002 p.p.m. using a 1-p.p.m. reference solution.

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DISCUSSION OF RESULTS

Because of the size of the beaker, only a two-fold range of concentration can be covered when determining an unknown chloride solution by dilution with $1M$ H_2SO_4 containing no added chloride, but a ten-fold range of concentration can be covered with good precision and accuracy when determining an unknown solution by addition of a solution twice as concentrated in chloride as the reference solution and $1M$ in sulfuric acid. It is possible to cover greater than a ten-fold range with the same reference, but the relative precision of results is more than 1% because of the buret reading errors, as can be seen from equation (6) and the results in Table II. Therefore, it is advisable to either change the reference solution or sample preparation method so that the unknowns and reference do not vary in concentration by more than ten-fold.

The temperature of some reference samples was raised several degrees above the reference solution in the isolation compartment and the samples then placed into position for measurement to determine the time required for reference and unknown solutions to reach the same value and the potential to reach the null point. The time required to equilibrate to within 0.1 mV of the null potential was about 1 min for a $3°$ change in temperature. Therefore, the sample and reference solutions are essentially at the same temperature by the time the addition of reagent is completed. This, of course, fulfills one of the basic requirements of the method as stated in the initial assumptions. It is important, of course, for rapid temperature equilibrium that the height of reference solution in the isolation compartment be not much above the height of the solution in the beaker.

The effect of ionic strength was also tested, and it was determined that a 1% difference in ionic strength between samples and reference solution caused about a 0.1-mV shift of the null potential. Therefore, the ionic strength in samples and reference solutions must be carefully controlled, but this is easily accomplished using large quantities of electrolyte pipetted accurately as previously described.

Interferences were not studied in detail, but appear to be the same as previously investigated for the absolute potentiometric method for chloride[1-4]. Again, the only abnormal divergence from predicted behavior is brought about by bromide which causes a drifting of the electrode when present in even small concentrations, such as 0.02 p.p.m. In fact, a drifting of electrode potential is a good indication that bromide is present. Errors caused by the slow drifting of electrode potential due to the presence of small bromide concentrations can be overcome by frequent checking and re-establishment of the null point with reference chloride solution.

SUMMARY

A new, rapid and accurate potentiometric technique is described for the determination of chloride in the concentration range 10^{-6} to $10^{-1}M$. For many samples results can be obtained in less than a minute with 0.1% accuracy. The method consists simply of changing the chloride concentration of an unknown solution, while maintaining the ionic strength constant, until it is of identical concentration to a known reference solution. This can be accomplished experimentally in such a way that temperature control and calculation corrections for chloride from reagents or

electrodes are not necessary. The procedure can be set up so that the calculation for the result is merely an addition or subtraction of two numbers. The general principles and simple experimental techniques are described and results for chloride presented.

RÉSUMÉ

Une nouvelle technique potentiométrique est proposée pour le dosage des chlorures (10^{-6} à $10^{-1}M$). Cette méthode consiste simplement à faire varier la concentration en chlorure de la solution à analyser pour arriver à une concentration identique à celle de la solution de référence, tout en maintenant la force ionique constante.

ZUSAMMENFASSUNG

Es wird eine neue potentiometrische Methode zur Bestimmung von Chlorid im Konzentrationsbereich von 10^{-6} bis $10^{-1}M$ beschrieben. In der zu untersuchenden Lösung wird die Chlorid-Konzentration unter Konstanthaltung der ionischen Stärke der Lösung so variiert, bis sie mit derjenigen einer Referenz-Lösung identisch ist.

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CONFORMATION ET CINÉTIQUE D'OXYDATION
DES α,β-AMINO-ALCOOLS ALIPHATIQUES DIASTÉRÉOISOMÈRES

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CRIEGEE a montré que le clivage tétracétique des *α,β-glycols* était fortement influencé par la distance séparant les deux groupes fonctionnels. Dans le cas des cyclane-diols[1-4], bien que le mécanisme intime soit encore discuté, la coupure est plus rapide pour la forme *cis* que pour la forme *trans*. Il en est de même pour les aminocyclanols[5].

En série linéaire, CRIEGEE a également observé une notable différence de réactivité entre des diols diastéréoisomères *dl* et *méso*[2-4] que l'on peut attribuer, comme précédemment, à une variation de la distance entre les hydroxyles. On sait, en effet, que la rotation entre les atomes de carbone n'est pas entièrement libre et qu'il existe pour les structures linéaires des conformations privilégiées[6]. Dans la conformation favorisée où les radicaux les plus volumineux sont opposés, les groupes fonctionnels se trouvent rapprochés en série *thréo* ou *dl* et éloignés en série *érythro* ou *méso*.

Nous avons tenté de distinguer les *α,β-amino-alcools* aliphatiques diastéréoisomères par clivage tétracétique. On avait déjà observé une différence entre les formes *thréo*

et *érythro* de ces composés lors de la mesure des vitesses de la migration des acyles de l'azote à l'oxygène. La transformation est alors plus rapide pour la *pseudo*-noréphédrine (*thréo*), I, que pour la noréphédrine (*érythro*), II[7-13].
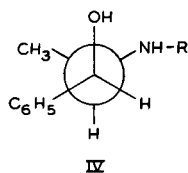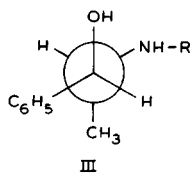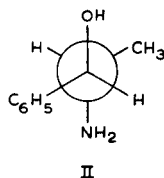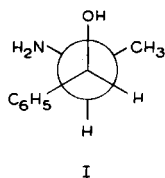
L'emploi du clivage tétracétique offre l'avantage d'une prise d'essai réduite en amino-alcool car il est possible de doser par voie spectrographique le sel de plomb tétravalent non consommé. Celui-ci, contrairement à l'acétate divalent, offre en effet un spectre d'absorption continu entre 2,500 et 3,000 Å. L'oxydation par le réactif tétracétique s'effectue selon le schéma (a) pour les amines β-hydroxylées et selon le schéma (b) pour les amines β,β'-dihydroxylées.

$$\text{(a)} \quad R\text{-CHOH-CH(NH}_2\text{)-}R'' \xrightarrow{1/2\ O_2} R\text{-CHO} + R''\text{-CHO} + NH_3$$

$$\text{(b)} \quad R\text{-CHOH-CH(NH}_2\text{)-CH}_2\text{OH} \xrightarrow{O_2} R\text{-CHO} + HCHO + HCOOH + NH_3$$
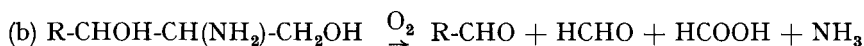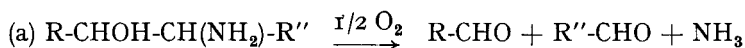
Dans les conditions opératoires ci-après décrites, les différences d'oxydabilité entre la thréonine (*thréo*) et *l'allo*-thréonine (*érythro*) sont confirmées, la forme

TABLEAU I

VITESSE D'OXYDATION D'α,β-AMINO-ALCOOLS DIASTÉRÉOISOMÈRES PAR
LE TÉTRACÉTATE DE PLOMB

Temps de contact	Oxygène consommé (en atomes par molécule d'amino-alcool)							
	Thréonine	Allo-thréonine	Pseudo-nor-éphédrine	Noréphé-drine	1-Phényl 2-amino propane 1,3-diol		1-p-Nitrophényl 2-amino propane 1,3-diol	
	(Thréo)	(Erythro)	(Thréo)	(Erythro)	(Thréo)	(Erythro)	(Thréo)	(Erythro)
30 minutes			0.73	0.38				
1 heure			0.86	0.52	1.27	0.10	0.80	0.20
2 heures	1.31	0.19	0.98	0.86	1.55	0.14		
3 heures	1.59	0.32	1.00	1.06	1.80	0.17	1.50	0.32
4 heures	1.80	0.45			1.94	0.19		
5 heures	2.0	0.51			2.10		1.83	0.45
6 heures	2.0	0.65						
7 heures	2.1	0.79						

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thréo étant oxydée plus rapidement[14]. La valeur stoechiométrique (schéma a) est atteinte pour la thréonine en 15 minutes. La quantité d'oxydant consommée augmente ensuite dans le temps par suite de l'oxydation de l'acide glyoxylique formé pour atteindre 2 atomes d'oxygène par molécule après une heure. L'*allo*-thréonine, oxydée beaucoup plus lentement, consomme respectivement 1 et 2 atomes d'oxygène en 45 minutes et 2 heures. En présence de faibles quantités d'acide perchlorique, l'oxydation est ralentie et les différences sont encore plus accentuées (Tableau I).

L'oxydation de la *pseudo*-noréphédrine (*thréo*) est également plus rapide que celle de son isomère *érythro*, la noréphédrine. La consommation limite d'oxygène correspond, après 3 heures, à un atome par molécule d'amino-alcool. Les différences d'oxydabilité entre les diastéréoisomères sont encore notables si les bases sont salifiées par un acide fort, tel que l'acide perchlorique. Avec les acétates, par contre, les différences sont beaucoup moins importantes.

L'oxydation des formes *thréo* et *érythro* du 1-phényl 2-amino propane 1,3-diol et du 1-*p*-nitrophényl 2-amino propane 1,3-diol répond au schéma (b). L'étude cinétique de l'oxydation montre encore une oxydation plus rapide des formes *thréo*.

$$CH_3\text{-CHOH-CH-COOH} \qquad\qquad C_6H_5\text{-CHOH-CH-CH}_3$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$NH_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad NH_2$$

Thréonine   Noréphédrine

$$C_6H_5\text{-CHOH-CH-CH}_2OH$$
$$|$$
$$NH_2$$
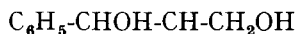
1-Phényl 2-amino propane
1,3-diol

Dans le cas des dérivés N-substitués des α,β-amino-alcools, les vitesses d'oxydation des diastéréoisomères sont sensiblement égales, aux erreurs expérimentales près.

Ce phénomène a été observé sur les couples:
— *pseudo*-éphédrine (*thréo*) et éphédrine (*érythro*)
— N-benzyl *pseudo*-noréphédrine (*thréo*) et N-benzyl
noréphédrine (*érythro*).

Il peut être interprété par l'intervention de nouvelles conformations dans lesquelles l'un des groupes volumineux extrême est l'azote substitué, III et IV. Les diastéréoisomères *thréo* et *érythro* n'offrent alors plus de différence dans les distances azote–oxygène.

PARTIE EXPÉRIMENTALE

(avec Mlle G. CLEMENT)

Réactif

Le réactif est une solution 0.05M obtenue en dissolvant 2.22 g de tétracétate de plomb[15] dans 100 ml de mélange à parties égales de chloroforme et d'acide acétique.

Oxydation quantitative

On pratique l'oxydation de la thréonine et de l'*allo*-thréonine sur des solutions 0.5*M* dans l'eau ou l'acide perchlorique 0.5*N*. L'éphédrine, la *pseudo*-éphédrine, la noréphédrine et la *pseudo*-noréphédrine ont été oxydées en solution *M* dans l'acide perchlorique *N*. Pour les isomères de la base du chloramphénicol et leurs analogues non nitrés, les solutions sont 0.5*M* dans l'acide perchlorique 0.5*N*.

A 20 ml de réactif tétracétique on ajoute 0.5 ml de solution d'amino-alcool et on maintient à 20°. Après un temps variable, on prélève 1 ml du mélange et dilue à 100 ml avec le mélange à parties égales chloroforme–acide acétique. La lecture est effectuée à 3,000Å sur spectrophoto-mètre Beckman DU.

RÉSUMÉ

L'étude de la scission des α,β-amino-alcools diastéréoisomères par le tétracétate de plomb permet de différencier les séries *thréo* et *érythro*. Un dosage spectrophotométrique du sel de plomb tétravalent montre que la thréonine, la *pseudo*-noréphédrine, le 1-*p*-nitrophényl 2-amino propane 1,3-diol *thréo* (base du chloramphénicol) et son analogue non nitré sont en effet oxydés plus rapidement que leurs isomères *érythro*. Les différences de vitesses d'oxydation s'annulent lorsqu'il y a substitution sur l'azote.

SUMMARY

A study of the splitting of the diastereoisomers of α,β-aminoalcohols with lead tetraacetate makes it possible to differentiate between the *threo*- and *erythro*-forms. Spectrophotometric analyses of the lead(IV) salts have shown that threonine, *pseudo*-norephedrine, *threo*-1-*p*-nitro-phenyl-2-amino-propane-1,3-diol (ground substance of chloramphenicol) and its non-nitrated analogue are more rapidly oxidized than the isomers of the *erythro*-series. There is no difference in the rate of oxidation when substituents are attached to the nitrogen.

ZUSAMMENFASSUNG

Das Studium der Spaltung der Diastereoisomere der α,β-Amino-alkohole mit Bleitetraacetat ermöglicht die Unterscheidung zwischen den *threo*- und *erythro*-Formen. Eine spektrophoto-metrische Bestimmung des Blei(IV)salzes zeigt, dass Threonin, *pseudo*-Norephedrin, *threo*-1-*p*-Nitrophenyl-2-amino-propan-1,3-diol (Grundkörper des Chloramphenicols) und dessen nicht-nitriertes Analogon rascher oxydiert werden als die Isomeren der *erythro*-Reihe. Der Unterschied in der Oxydationsgeschwindigkeit verschwindet, wenn am Stickstoff Substitutionsgruppen sitzen.

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COULOMETRIC TITRATION WITH QUINQUEVALENT URANIUM

DETERMINATION OF VANADIUM(V)

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INTRODUCTION

Quinquevalent uranium was recently employed by EDWARDS AND KERN[1] as a generated reagent for the reduction of ferric ion. The reducing power of the U(VI), U(V) couple ($E° = +0.06$ V *vs.* S.H.E.) is surpassed only by that of Ti(III)[2] and Fe(II)EDTA[3] among coulometric reagents investigated to date. The danger of simultaneous hydrogen evolution prevents the generation of significantly stronger reducing agents at solid electrodes.

Uranium(V) is unstable with respect to disproportionation to U(VI) and U(IV); the rate is directly proportional to the hydrogen ion concentration[4]. The U(IV) produced in this reaction is neither as strong nor as rapid a reducing agent as U(V)[5]. Consequently the pH is preferably kept greater than 1 during coulometric titrations with this ion, in order that the disproportionation reaction should not compete with the titration reaction. This requirement is a disadvantage in the titration of such substances as hydrogen peroxide and dichromate ion, whose oxidizing power is much dependent on the acidity; in fact, U(V) cannot be used to titrate these two substances coulometrically. Vanadate, however, is reduced very well, no doubt because of the reversible nature[6] of the V(V), V(IV) couple ($E° = +1.0$ V). The coulometric titration described in this paper provides a simple and reliable method for its determination. In particular, it permits the determination of vanadium in uranium samples without the addition of any reagent except what is required to adjust the pH within the limits 1–3. Iron and other rapid oxidizing agents are titrated along with the vanadium. This titration can be used to correct the coulometric uranium assay of LINGANE AND IWAMOTO[2] for the presence of oxidizing impurities. These authors used Ti(III) as the generated reagent, which reduces iron and vanadium as well as uranium.

The problem of determining vanadium coulometrically in the presence of uranium was treated earlier by FURMAN, REILLEY AND COOKE[7]. These authors used ferrous ion as their reducing agent, generated from a ferric salt added to the uranium in large excess. Actually, the potentials are more favorable and the end-points sharper if the ferric ion is omitted, and the uranium employed as the source of reductant. Their method is useful for the selective determination of vanadium impurities. It can also be carried out in the presence of air, which must be carefully excluded when U(V) is the titrant because of its rapid air oxidation.

EXPERIMENTAL

Circuitry

The constant current source has been described previously[1]. A small drift in the

line voltage was corrected by the use of a current stabilizer similar to that described by LINGANE[8]. This consisted of a Brown Electronik amplifier Type 358816 with associated 130-r.p.m. motor, which operated a 500-ohm Beckmann Type A Helipot resistor. The potential drop across a decade resistor in the constant current circuit was balanced against the E of a 1.5-V dry cell. Slight deviations in the generating current produced a net E which operated the motor and produced compensating changes in the Helipot resistor, which was likewise in the main current circuit. Total applied voltage in this circuit varied between 50 and 300 V. The current was held constant to within $\pm$ 0.02%.

For currents less than 0.1 mA, this entire apparatus could be replaced by a pair of 45-V B batteries, which gave currents that varied by less than 0.1% during the period required to carry out a titration.

Cells

Two cells were used, which are described fully elsewhere[1]. In the larger cell the cathode was a 20-cm^2 platinum sheet immersed in 0.03M UO_2Cl_2, the anode a platinum wire in 0.5M Na_2SO_4 solution. The two were separated by a glass frit and an agar plug.

For samples of less than 100 μg of vanadium, a smaller cell and cathode were employed. The anode consisted of a silver wire sealed in a tube completely filled with saturated KCl. The tube was suspended in the cathode compartment and made electrical contact with it through an upturned capillary of 0.5 mm diameter. This anode could not be used with currents exceeding 2 mA. Current fluctuations appeared which were ascribed to the small cross section of the wire and the capillary.

Reagents

We were fortunate in having a very pure sample of $VOSO_4 \cdot 3H_2O$ prepared by JONES AND COLVIN[9]. The salt had been dissolved in 0.6N H_2SO_4 and made up to 0.1000M in 1953. Titration with ceric sulfate and potassium permanganate in 1958 yielded concordant results, the average being 0.09987M. This result attests the stability of V(IV) solutions in stoppered soft glass bottles. Several aliquots were given a preliminary treatment with SO_2 before titration, to insure that all vanadium was present as V(IV). This treatment did not alter the titer. Vanadium(V) was therefore absent.

In addition, a second sample of $VOSO_4 \cdot 3H_2O$ was prepared in the manner of JONES AND COLVIN. The starting material was an impure $VOSO_4$ sample from A.D. Mackay Inc. The crystals were washed with acetone rather than alcohol, as the latter reagent gave an unmanageable sticky mass. This sample proved to have a slight excess of water, but was a satisfactory source of stock vanadium solution.

Uranyl chloride was prepared from Mallinckrodt uranyl nitrate by fuming with conc. HCl. The interference of nitrate in U(V) titrations has been discussed previously[1].

End-point determination

An amperometric method was used. About 0.25 V were applied across two small platinum gauze electrodes immersed in the catholyte. The electrodes were about 1 cm apart, and were placed outside the field between the generator electrodes. In the course of the titration the current rose and then fell to a sharp minimum at the end-point, followed by a steady increase thereafter. This type of indicator current curve is characteristic of reaction between two reversible couples[6].

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Procedure

50-ml aliquots of stock vanadium(IV) solution were oxidized with Cl_2. The solution was boiled at length to remove excess oxidant. The volume of the solution was not permitted to shrink during this operation, since vanadium(V) readily precipitates as a basic salt on boiling, and redissolves only very slowly even if more H_2SO_4 is added to the solution. The resultant vanadium(V) solutions were diluted to strength and aliquots used for the titrations.

100 ml 0.03M UO_2Cl_2 served as the catholyte*. The acidity was adjusted to about pH = 1.5 by the dropwise addition of conc. HCl, and the solution then deaerated with nitrogen gas for 15 min. The vanadium solution was likewise deaerated with nitrogen that had been equilibrated by prior passage through a portion of the same solution.

Following a blank run with a few drops of vanadium solution, a series of 0.5-ml aliquots from a calibrated micropipet were analyzed in succession. During a run, U(V) was generated continuously until the indicator current showed that the end-point was near. The end-point was then reached by a series of small current increments. The first 0.1-sec excess of U(V) showed a clear and permanent increase in indicator current. Time was measured with an electric timer. Bubbling with nitrogen and magnetic stirring continued throughout the titrations.

RESULTS

The results for the titration of 0.014–2.5 mg samples are presented in Table I. The pH was in the range 1.5–1.9. The error curve was slightly displaced, the most probable error being +0.10%.

TABLE I

TITRATION OF VANADIUM(V) SAMPLES WITH GENERATED URANIUM(V)

mg Vanadium	Current mA	Time sec	No. of trials	Limits of error, %	Average deviation from theoretical, %
2.5	8–9	500–600	21	+0.47 −0.32	0.17
1.8	6–9	380–600	11	+0.39 +0.08	0.30
1.3	8	330	3	+0.1 −0.1	0.03
0.25	1	200–250	4	+0.20 −0.23	0.16
0.20	1	300–500	6	+0.43 +0.16	0.29
0.025	0.08–0.16	300–600	12	+0.33 −0.47	0.21
0.014	0.09	300	7	+0.90 −1.00	0.51

Effect of pH

The permissible upper limit is determined by the hydrolysis of uranyl ion, the lower by the disproportionation of U(V). Successful runs were made in the pH range 1.00–2.67. At pH = 3.28 no end-point was observed. The influence of more strongly acid solutions was not studied.

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* When the small cell was used, the volume of catholyte was 20 ml.

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Mixtures of Fe(III) and V(V)

Titrations of mixtures were carried out at pH 1.5. The results are given in Table II. The two ions were reduced together, yielding an indicator current curve similar to that of vanadium alone. Assuming the species making up the vanadium couple to

TABLE II

TITRATION OF Fe(III)–V(V) MIXTURES

	Current mA	Time sec	Error, %
3 mg Fe + 5 mg V	15	1000	+0.6, +0.1, +0.3
3 mg Fe + 0.8 mg V	15	400	+0.2, —0.2, +0.4
3 mg Fe + 0.4 mg V	15	400	—0.1, +0.1

be VO_2^{+2} and VO^{+2}, it is easily shown that the formal potential of the couple is about 0.82 V at pH 1.5, which does not differ materially from the 0.78 V value of the ferric–ferrous couple. The titration of ferric ion with U(V) is unsatisfactory[1] at acidities at which the couples might have sufficiently dissimilar potentials to yield two minima in the indicator current curve. Reduction of the indicator voltage to 0.01 did not change the shape of the curve.

SUMMARY

Vanadium(V) has been determined by reduction with generated uranium(V) with an accuracy of about ± 0.3%. Amounts as small as 15 μg were successfully titrated. The suggested pH range is 1–2.5. Iron(III) is reduced simultaneously with vanadium(V).

RÉSUMÉ

Une méthode coulométrique est proposée pour le dosage du vanadium(V), à l'aide d'uranium(V).

ZUSAMMENFASSUNG

Es wird eine coulometrische Methode zur Bestimmung von Vanadium(V) mit Hilfe von Uranium(V) beschrieben.

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REVUES DE LIVRE

Tratado de Quimica Analitica Cuantitativa, par Prof. Dr. F. BERMEJO MARTINEZ. Imprenta del Seminario Conciliar Santiago de Compostela, 1958, 1079 pages, 300 fig., 58 tables. Prix: 600 Ptas.

Le Professeur F. BERMEJO vient de publier un remarquable ouvrage de chimie analytique quantitative donnant une excellente vue d'ensemble de cette science et destiné tout spécialement à l'étudiant. En effet, ce dernier y trouvera d'utiles et précieux renseignements lui permettant d'acquérir les principes fondamentaux, les connaissances indispensables de l'analyse classique et les bases des techniques les plus récentes. Il y apprendra également comment apprécier les limites et déterminer les erreurs possibles des méthodes utilisées.

Voici, brièvement donné, un aperçu des différents chapitres traités, montrant l'importance de ce traité:
– classification des méthodes et opérations préliminaires,
– balance et pesée,
– analyse gravimétrique: théorie (produit de solubilité, effet de sel, coprécipitation, électrolyse, électrolyse à potentiel contrôlé, etc.), appareillages et méthodes, description de dosages classiques,
– théorie des séparations (par précipitation, distillation, électrolyse, extraction, échange ionique, chromatographie),
– description de quelques séparations,
– analyse volumétrique: théorie (oxydo-réduction, acide-base, formation de complexes), appareillage et méthodes, dosages par oxydo-réduction (permanganométrie, dichromatométrie, cérimétrie, iodométrie, titanométrie, vanadométrie, etc.), dosages alcali-acidimétriques (également en milieu non aqueux), dosages par précipitation et formation de complexes,
– conductométrie et potentiométrie,
– polarographie, ampérométrie, coulométrie,
– spectrophotométrie par absorption (absorption dans le visible, l'ultra-violet, l'infra-rouge, les ondes ultra-courtes, spectres Raman, fluorométrie, néphélométrie, turbidimétrie, hétérométrie, etc.),
– spectrophotométrie par émission,
– application des rayons X et de la radioactivité à l'analyse,
– spectrométrie de masse,
– méthode de diffraction des électrons,
– microanalyse,
– calcul d'erreurs.

Signalons encore quelques tables (poids atomiques, logarithmes, concentrations, solutions tampons) et de nombreuses références bibliographiques.

C'est donc un ouvrage complet et moderne; bien que volumineux (1079 pages), il est bien ordonné, très clair et facile à consulter.

Le Professeur BERMEJO montre ainsi toute l'importance que prend à l'heure actuelle la chimie analytique, discipline indispensable à la formation du futur chimiste, qu'il se destine à l'analyse, à la recherche ou à l'industrie.

Nous félicitons l'auteur et nous sommes heureux de pouvoir recommander son traité.

Y. RUSCONI (Genève)

Spot Tests in Inorganic Analysis, par FRITZ FEIGL, traduit par RALPH E. OESPER, cinquième édition anglaise entièrement revue et augmentée, Elsevier Publishing Company, Amsterdam, 1958, 6 × 9, xiii + 600 pp., £ 3.5.–.

Il y a quelque temps, nous avions le plaisir d'annoncer aux lecteurs des ,,*Analytica Chimica Acta*'' la cinquième édition du fameux ,,*Spot Tests in Organic Analysis*''.

Infatigable dans sa tâche et fidèle à son but, M. FEIGL nous présente aujourd'hui la première partie de cette oeuvre, le ,,*Spot Tests in Inorganic Analysis*'', en cinquième édition également.

Le livre, un classique dans son genre, est suffisamment connu des chimistes pour que nous n'insistions pas sur ses mérites. Nous ne saurions néanmoins passer sous silence les avantages qu'offre cette nouvelle édition vis-à-vis de la précédente. Ayant procédé à une revision complète de son oeuvre, M. FEIGL l'a enrichie de nombreuses nouvelles réactions et techniques améliorées, résultant pour la plupart de ses recherches personnelles. Le nombre des pages est ainsi porté à 600 contre les 451 de l'édition précédente. La disposition des chapitres est la même: Introduction, techniques à la touche (par M. P. W. WEST), réactions des cations, réactions des anions, réactions des éléments libres, analyse systématique des mélanges, applications pratiques, tableau résumant les réactions.

Nous tenons à recommander vivement ce livre à tous les chimistes, persuadés qu'il leur sera un guide des plus utiles, lorsqu'ils auront à effectuer un contrôle qualitatif quelconque.

I. KAPÉTANIDIS (Genève)

ANNOUNCEMENTS

XVe CONGRÈS INTERNATIONAL DE CHIMIE PURE ET APPLIQUÉE

Les nombreuses communications présentées au XVe Congrès International de Chimie Pure et Appliquée (Chimie Analytique) seront publiées en trois volumes.

Un premier volume, concernant les ,,Discours'', les ,,Allocutions'' et les ,,Communications'' jusqu'à la fin de la 3ème Section est déjà imprimé. Les deux autres volumes, se rapportant aux autres sections, pourront être obtenus dans un court délai.

Ce volume I peut être commandé à l'adresse suivante:

Secretario-Geral do XV Congresso Internacional de Quimica Pura e Aplicada, Instituto Superior Tecnico, Avenida Rovisco Pais, Lisboa, Portugal,

Le prix des trois volumes est de 320 escudos (par poste ordinaire, y inclus emballage et poste); par avion, le prix est de 330 escudos.

Le paiement pourra être effectué par n'importe quelle banque de Lisbonne.

LUIS ACCIAIUOLI
Secrétaire Général du Congrès

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An International Symposium on Inhaled Particles and Vapours, organized by the British Occupational Hygiene Society, will be held in Oxford in April 1960. The Symposium will be concerned with the physical, chemical and physiological factors governing the entry of harmful substances into the body via the respiratory system.

The subjects of the Symposium have a bearing on many hygiene problems including silicosis, asbestosis and the other pneumoconioses, and on the damage to health produced by smog, tobacco smoke, radioactive gases and dusts, airborne bacteria and toxic vapours. The Society believes that the Symposium will meet a real need in providing an opportunity for the comprehensive discussion of recent research in this field and that the published proceedings will be of value not only to research workers, but also to those concerned with the practical problems of establishing and maintaining safe environments.

Contributions to the Symposium will be welcomed from all countries. The main language of the Symposium will be English and it is intended to circulate the papers in advance in this language, but it is hoped to be able to provide interpretation for those oral contributions to the discussion which may have to be made in French or German. Papers submitted will be subject to scrutiny by the Society's Honorary Editor, Dr. C. N. Davies, assisted by a panel of referees.

Those wishing to contribute are requested to notify the Chairman of the Organizing Committee, Mr. W. H. Walton, Assistant Director, Mining Research Establishment, National Coal Board, Worton Hall, Worton Road, Isleworth, Middlesex, as soon as possible, indicating the subject of their papers.

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