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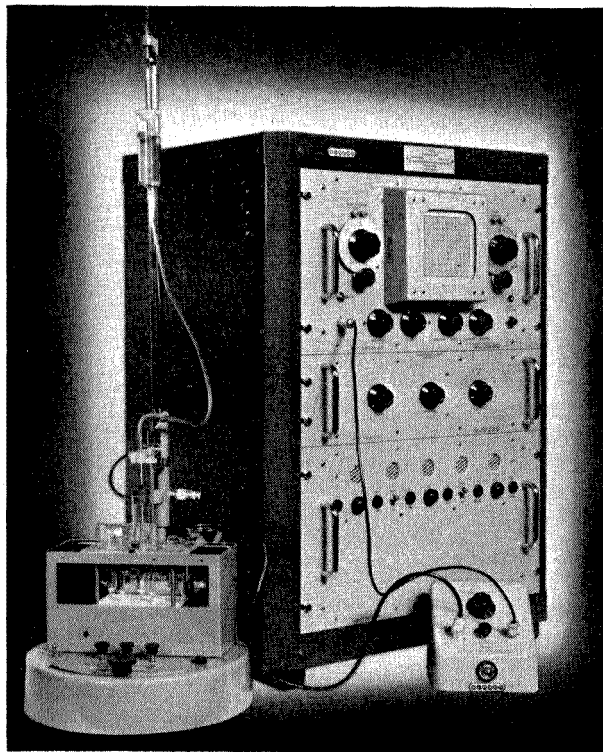
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THE DETERMINATION OF SULPHUR IN ORGANIC COMPOUNDS WITH METALLIC SILVER AS ABSORBENT

A CRITICAL EXAMINATION

JEAN P. DIXON

"Shell" Research Ltd., Thornton Research Centre,
P.O. Box 1, Chester, England

Summary—Interfering factors in the determination of microgram quantities of sulphur by the absorption on silver of the sulphur oxides produced during combustion of sulphur compounds have been isolated and eliminated. The method comprises "empty tube" oxidation, absorption of sulphur oxides on electrolytically prepared silver, and potentiometric titration of the silver ion equivalent to sulphur. The minimum limit of determination is 10–15 μg using a 25-mg sample, and the reproducibility about 3%.

INTRODUCTION

NUMEROUS methods have been reported in the literature for the determination of sulphur and chlorine, with metallic silver as the absorbing medium. The following recent references will provide an introduction to the literature on this subject. Stragend and Safford¹ describe procedures in which the sulphur is retained on silver gauze and determined gravimetrically. Kuck and Grim² extended the scope of the method by using a quartz-fibre balance to determine the small weight changes in the silver gauze when decimilligram samples were analysed. Removal of silver sulphate from the gauze by dissolving it in hot water, and subsequent titration of the silver ion with potassium iodide,³ offered a more sensitive and rapid method of assay for low sulphur contents. Papers describing the titration technique were published by Vecera and Snobl⁴, and Bladh, Karrman, and Andersson⁵. In both of these, experimental work led to the conclusion that the blank was too high and inconsistent to attempt the determination of sulphur in low concentrations. The method described by Kuck and Grim², however, does achieve determination in the sub-micro range (50–100 μg), although on a gravimetric basis. There seemed no reason, therefore, why the technique should not be capable of adaptation to the microgram range, using a titrimetric procedure, if the causes of the variable blank could be identified and eliminated. Mitsui and Sato⁶ describe a special preparation of silver for the quantitative absorption of chlorine, and claim that it has an activity fifty times that of silver wool or silver gauze. Other workers, *e.g.* MacNevin⁸, have reported that a similar preparation is necessary in the carbon and hydrogen determination to remove chlorine and sulphur. The information obtained from the literature is conflicting in that some workers report satisfactory results with silver gauze and others consider that specially prepared silver is necessary. With the exception of the method described by Kuck and Grim², the use of silver as an absorbent in the microgram range has not proved successful, because of the high and variable blanks obtained. The investigation was, therefore, based on isolating the causes of the blank, the reason for using specially prepared silver, and the sensitivity that could be obtained by the titrimetric potassium iodide procedure.

DEVELOPMENT OF METHOD

The first experimental work by the present author was carried out according to the publication by Zinneke³, in which the sample is oxidised by passage over platinum gauze (650–700°) in a stream of oxygen, and the sulphur oxides are absorbed on silver gauze (450–500°). The silver sulphate was extracted with hot water and the silver ions titrated potentiometrically with 0.01*N* potassium iodide solution, using a glass and silver electrode pair. Low results, of poor repeatability, were obtained on standard sulphur compounds, but the advantage of the extreme sensitivity of the potassium iodide titration procedure was realised. The low results could be attributed to one or more of the following factors, each of which will be treated separately:

- (a) Incomplete removal of silver sulphate from the gauze.
- (b) Incomplete oxidation of the sample.
- (c) Inefficient absorption of sulphur oxides on the silver gauze.

(a) *Extraction of silver sulphate from silver gauze*

The possibility of errors due to incomplete extraction of silver sulphate was not suspected since frequent extraction of the silver with boiling water after a determination had been made yielded washings in which silver ions were not detected.

(b) *Oxidation*

Classical methods for oxidising organic compounds include the use of heated silica chips, porous silica plates, platinum contacts and platinum gauzes. In all cases combustion is carried out in a stream of oxygen. Some sulphur compounds are difficult to oxidise and instances have occurred in which the use of platinum has been inadequate. On the other hand, the oxidation efficiency of the "empty tube" combustion technique^{7,9} is known to be good. In this procedure, the vapours of the sample are intimately mixed with oxygen in the turbulence caused by a series of quartz baffle plates inside the oxidation tube. The procedure is widely used in the determination of carbon, hydrogen, sulphur and halogens, and in practice it has been found that its reliability far exceeds that of other combustion-tube oxidation methods. Accordingly this technique was adopted, and its reliability for the oxidation of sulphur compounds merely checked by conventional titrimetric methods.

When the above technique was used in conjunction with silver gauze low results were again obtained. It was clear, therefore, that the silver gauze was not retaining sulphur oxides quantitatively.

(c) *Absorption of sulphur oxides by silver*

Literature references^{6,8} already quoted emphasise the need to use specially prepared silver for the absorption of sulphur oxides and chlorine in microchemical combustion work. We have found in practice that this is most important in the case of sulphur. Commercially manufactured silver wool and silver gauze retained chlorine quantitatively, but under similar conditions silver sulphate recoveries were low.

Electrolytic silver was prepared according to the method of Mitsui and Sato⁶. Using this preparation, in which the large surface area provides much greater efficiency, theoretical recoveries of silver sulphate were obtained. The results of these analyses are recorded in Table I, and confirm the author's belief that the extraction technique is satisfactory.

In order to make this procedure applicable to the determination of microgram amounts of sulphur, the manipulation of the silver during and after analysis and its effect on the blank were investigated further.

Extraction of silver sulphate and blank control

The operating blank is dependent on the technique used to extract the silver sulphate, and includes the effects of the atmosphere on the silver and the quality of water used. Previous workers in this field³⁻⁵ devised circulatory systems in which hot water flowed repeatedly over the gauze, and also made use of electric heating⁵ during extraction. The same authors reported that heating the silver gauze in the absence of sulphur oxides gave rise to soluble silver ions. The possibility of the formation of soluble silver oxide led to experiments in which the gauze was blanketed with nitrogen. Similar blanks were obtained, and the authors concluded that the procedure was not applicable to accurate determination of microgram concentrations of sulphur.

Previous investigators make no mention of the quality of distilled water used in the determination, or the preparation of the silver for individual analyses. Distilled water may contain traces of impurity and although samples tested with 0.1*N* potassium iodide may indicate a negligible blank (0.001 ml) this was found to be no criterion of suitability for the determination. The use of distilled water percolated over a mixed anion- and cation-exchange resin bed, and boiled before use, gave an immediate reduction in the blank. The only apparent explanation of this is that distilled water contains a small but variable amount of salts which react with silver to release soluble silver ion. Furthermore, if the silver was dried by heating directly after water washing, the blank increased. This again suggested the presence of traces of foreign ions left behind on the silver when the water evaporated, which would affect the next blank or determination.

Interference of this type was eliminated by using boiled percolated water, and by washing the silver with alcohol and ether between determinations.

Contrary to previous investigations we have found that the silver must be blanketed with nitrogen to prevent the formation of silver oxide during cooling from 450° to below 100°. This requirement in no way complicates the procedure, because the extraction technique uses nitrogen to agitate the wash water.

EXPERIMENTAL

Reagents

Ion-free water was obtained by percolating distilled water through a mixed-resin bed composed of Amberlite IR 120 and Amberlite IRA 400. *Electrolytic silver*⁶ was prepared by electrolysis in 1 litre of 0.5% nitric acid containing 7 g of silver nitrate, the anode (silver plate 0.5 mm thick, 10 × 5 cm) and the cathode (silver wire 1 mm diam. × 15 cm long, twisted into a spiral) being connected to a 1.5 V dry cell. The electrolysis was continued for some time (overnight) and the crystalline product washed, dried and stored in nitrogen. Conventional reagents included oxygen, nitrogen (oxygen free), "Carbosorb" (soda-lime) 14-20 mesh, and standard 0.1*N* solutions of silver nitrate and potassium iodide.

Apparatus

Fig. 1 shows the flow diagram of the apparatus.

Fill the preheater with wire-form copper oxide, and seal in the stopper. Connect the base of the rotameter to the oxygen line, and the top to one arm of the preheater. Insert the preheater in the back of the furnace. Fill the scavenging tube with "Carbosorb", seal the stopper with Kronig cement,

and attach the tube to the free side of the preheater. Attach a stainless steel lead from the scavenger to the end of the combustion tube through a fitting rubber bung.

Insert the baffle tube in the front of the furnace and connect to the combustion tube via the B10 quartz joint. Raise the temperature of the large furnace to 900° and the other to 400–450°.

Preparation of the silver absorber: fill the end of the tube next to the tap with glass beads to a depth of 1½ in. Insert the silver loosely but evenly to provide a layer 2½ in. long. Attach the side arm to the nitrogen supply with rubber tubing. Mount the tube vertically in a clamp and wash the silver repeatedly with boiling percolated water. Admit nitrogen at such a rate that the liquid in the tube is

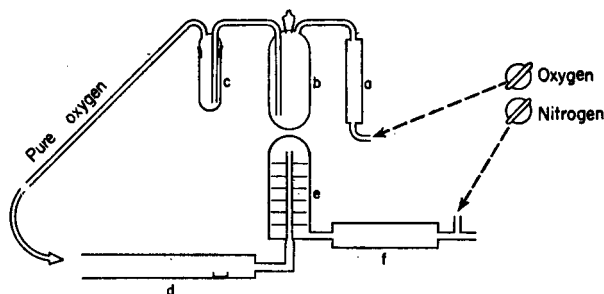


FIG. 1.—Flow diagram.

(a) Rotameter. (b) Preheater (900°). (c) Scavenger. (d) Combustion tube. (e) Baffle tube (900°). (f) Absorption tube (400°–450°).

agitated without overflowing. Drain off the final wash water, wash the silver with alcohol and ether and place it on top of the furnace to dry, maintaining the flow of nitrogen.

Insert the dry absorber in the small furnace, connect to the baffle furnace via the ground joint, and turn the tap to allow oxygen to pass through the tube. Adjust the oxygen flow to 50 ml/min.

Procedure

Weigh small samples (<10 mg) in platinum boats, and ignite in the normal way; for larger samples (10–25 mg) use a quartz sample tube. This consists of a small quartz test tube, 2 in. long and of such a diameter that it can be pushed into the combustion tube. Introduce the tube so that the open end faces the baffle furnace. Heat from the open end of the sample tube. Advance the burner towards the sample until decomposition begins. This will be indicated by deposition of carbon inside the sample tube. Do not advance the burner until the carbon begins to burn. Decompose the sample completely by moving the burner in this way until it reaches the closed end of the sample tube. Move the burner rapidly back along the combustion tube.

Two burners are used, one to ignite the sample and the other, which is attached to the furnace, to ignite the protruding end of the baffle tube. After the combustion, rotate the stationary burner to ignite the quartz between the baffle furnace and the silver absorber*.

Allow 5 minutes before detaching the absorber.

Turn the absorber tap to admit nitrogen, detach the absorber and mount it vertically in a small clamp. When the tube has cooled somewhat, cover the silver with boiling percolated water from the wash-bottle jet, using a pressure bulb, and allow the nitrogen to agitate the liquid. Drain into a 100-ml beaker. Repeat the washing until about 40 ml of water have been used.

Remove the beaker, cover the silver with alcohol and agitate, and repeat this operation with ether. Drain, and place on top of the furnace to dry. Maintain the flow of nitrogen.

Titrate the solution with 0.1N potassium iodide, using a micro glass and silver electrode pair, a magnetic stirrer and a syringe burette.

0.001 ml 0.1N KI \equiv 1.6 μ g of sulphur

DISCUSSION

The results shown in Tables I and II are typical of many obtained with the proposed method during routine use for over a year. In Table II sample sizes are included

* There is a tendency for SO₂ to condense.

with the results, which illustrate the reproducibility for low sulphur contents in small samples.

Interference from chlorine may be encountered in the microgram range, since the solubility of silver chloride in hot water may become significant. No effective method for overcoming this interference has been evolved.

TABLE I.—ANALYSIS OF STANDARD COMPOUNDS

Compound	Sulphur content	
	Theory %w	Found %w
Sulphonal	28.1	27.9 28.1
Di- <i>p</i> -tolyl disulphide	26.6	26.2 26.6
Thiacyclohexane	31.4	31.2 31.5
1:4-Dithiacyclohexane	53.4	52.8 53.6

TABLE II.—RESULTS OF ANALYSES SHOWING SAMPLE SIZE AND REPRODUCIBILITY

Material	Sample size, mg	Sulphur, %w	
Oil	A	9.9	3.24
		13.2	3.22
	B	18.4	3.57
		14.1	3.63
	C	13.6	3.74
		16.2	3.76
Oil fraction	A	23.4	0.62
		15.3	0.68
	B	12.9	0.322
		18.7	0.316
Olefin	A	10.6	0.48
		12.2	0.45
	B	18.2	0.193
		15.3	0.188
	C	12.6	0.114
		20.2	0.111

The advantage of using the quartz sample-tube technique for larger samples is twofold. The combustion is much faster, and the danger of explosions when igniting volatile samples is eliminated. Moreover, the reproducibility of results for low sulphur contents is much better when this type of combustion is employed.

CONCLUSION

A procedure has been developed which overcomes the high and variable blanks previously reported when the silver absorption/potassium iodide method was applied

to the microgram range of sulphur determinations. The blank is consistently low, and as little as 10–15 micrograms of sulphur can be determined. The use of boiled percolated water, and the drying of electrolytically prepared silver with organic solvents before use are recommended.

Acknowledgement—The author is indebted to the Directors of "Shell" Research Ltd. for permission to publish this article.

Zusammenfassung—Störungen bei der Bestimmung von Mikrogrammengen Schwefels nach der Silberabsorptionmethode wurden aufgezeigt und beseitigt. Die Methode verwendet Verbrennung im Leerrohr, Absorption des Schwefeldioxydes an elektrolytisch niedergeschlagenem Silber und potentiometrischer Titration de dem Schwefel äquivalenten Silbermenge. Die Mindestgrenze an bestimmbarem Schwefel liegt bei 10-15 Mikrogramm in einer Menge von 25 Milligramm Ausgangsmaterial.

Résumé—L'auteur a isolé et éliminé les facteurs gênants dans le dosage de microgrammes de soufre par la méthode d'absorption par l'argent. Cette méthode comprend une oxydation dans un tube sous vide, une absorption des oxydes de soufre sur de l'argent préparé électrolytiquement et un titrage potentiométrique de l'ion argent correspondant au soufre. La limite minimum du dosage est 10 à 15 μg en utilisant un échantillon de 25 mg.

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DETERMINATION OF ULTRAMICRO AMOUNTS OF SULPHATE AS METHYLENE BLUE—I

THE COLOUR REACTION

LILLY GUSTAFSSON

Department of Analytical Chemistry, University of Uppsala, Uppsala, Sweden

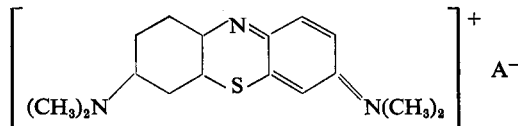
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Summary—Sulphate may be determined spectrophotometrically as methylene blue after reduction to sulphide, which is allowed to react with *p*-aminodimethylaniline and ferric iron to form the dye. This paper deals with the colour reaction.

The standard method for the colour development proposed is founded on an investigation of the following variables: hydrogen sulphide losses, acidity at reaction and measurement, reagent concentrations, temperature at reaction and measurement, concentration of traces of heavy metals, time, and air-oxidation. Previously found deviations from Beer's law are confirmed and discussed. The yield of the reaction is determined.

THE difficulty of finding a method for the determination of ultramicro amounts of sulphate has led to attempts to reduce this substance to hydrogen sulphide, which can be determined by sensitive titrimetric or colorimetric methods. Among the latter, the methylene blue (MB) method seems to deserve special attention; it is entirely specific for hydrogen sulphide and the colour reaction is one of the most sensitive. The method, however, has not been sufficiently investigated to permit its immediate application. This paper will deal with the colour reaction; the reduction of sulphate to hydrogen sulphide will be considered in a later paper.¹

Caro's MB reaction was recommended by Emil Fischer² for the identification of hydrogen sulphide. The solution containing hydrogen sulphide is mixed with an acidic solution of *p*-aminodimethylaniline, and ferric iron is added. The solution first becomes red from an intermediate compound but changes to blue as MB is formed. The formula of MB



where A⁻ represents an arbitrary anion, includes one atom of sulphur. The anion is chloride in commercial products of the dye.

This method was later used for quantitative determinations of sulphide by Mecklenburg and Rosenkränzer³ and by Almy⁴. Lorant⁵ developed a method for the reduction of microgram amounts of sulphate to hydrogen sulphide, which was determined colorimetrically as MB. Fogo and Popowsky⁶ used modern spectrophotometric instruments in their investigation of the MB method and applied it to the determination of hydrogen sulphide in gases. Lorant's method was further developed by Roth⁷ and by Johnson and Nishita.⁸ The results of these investigations will be discussed in their appropriate places.

According to Bernthsen,⁹ ferric iron together with *p*-aminodimethylaniline gives a red oxidation product, Wurster's red, which reacts in several ways with hydrogen sulphide. Among other products, sulphide green, leuco methylene blue and methylene red are said to be formed. The first two are easily transformed to MB, whereas methylene red is not. Lorant assumes that methylene red and MB are formed in the proportion 1:50. It is evident that hydrogen sulphide is not quantitatively transformed to methylene blue. In order to make full use of the reaction for quantitative purposes, a study of the effects of different factors on the yield and precision of the method is needed.

EXPERIMENTAL

Apparatus

In order to obtain accurate results, it is essential that all glassware used for the colour development should be kept free from traces of heavy metals. The glassware is washed with hydrochloric acid (1 + 1), then with water, and is finally rinsed with de-ionised, distilled water (see below).

The light absorption was determined with a Beckman DU spectrophotometer, the wavelength scale of which had been checked against Hg spectral lines. It proved necessary to use a water-cooled lamp-compartment to prevent temperature changes of the solutions during measurement; later on, a thermostated cell-compartment was used. Distilled water was used as a reference solution.

Reagents

Reagent-grade chemicals were used.

De-ionised water: distilled water was run through a 30-ml column of cation-exchange resin (Amberlite IR-120, H-form) at a rate not exceeding 0.5 litre/h.

Zinc acetate solution: 0.25M ZnAc₂; 0.10M NaAc. Remove traces of heavy metals by precipitating them as sulphides, with zinc sulphide as a carrier as follows: add drop by drop, with thorough shaking, 2 ml of freshly-prepared 0.05M sodium sulphide to 1 litre of the zinc acetate solution. Let stand overnight. Swirl up the precipitate, and filter through a quantitative paper of fine texture. Discard the first portion of the filtrate. A gradually developing turbidity is of no consequence.

"Amino" reagent: 0.005M NH₂C₆H₄N(CH₃)₂·½H₂SO₄; 3.50M H₂SO₄. Dissolve 0.93 g of the Eastman preparation No. 1333 in 750 ml of de-ionised water, add 3.50 moles of H₂SO₄, cool and dilute to 1 litre with de-ionised water. The reagent will keep at least 6 months.

Ferric solution: 0.25M NH₄Fe(SO₄)₂; 0.5M H₂SO₄. Use de-ionised water.

Preparation of the standard sulphide solution

Sulphide solutions are easily oxidised and must consequently be prepared and standardised immediately before use.

Standard solutions, 0.03–0.05M in sulphide, were prepared from large crystals of Na₂S·9H₂O. To remove traces of sulphite from the surface of the crystals, they were rapidly rinsed with water on a coarse glass filter before dissolution. Vacuum-boiled, de-ionised water was used for preparing the solutions.

Preliminary standardisations were made by iodimetric titration according to Bethge.¹⁰ The final standardisation was made as follows. Depending on the concentration, 20–50 ml of the sulphide solution were pipetted into a 250-ml beaker followed by 5 ml of 1M NaOH and 5 ml of 30% H₂O₂. The beaker was covered, and heated on a hot-plate until evolution of oxygen had ceased, and the solution was evaporated to about half the original volume. After cooling, the solution was passed through a cation-exchanger (Dowex 50, H-form) and boiled to expel carbon dioxide. The sulphuric acid formed was titrated with 0.1M NaOH. Blanks were carried out, but no blank exceeded 0.1% of the titrated acid.

In those series of experiments where only relative values were required, standardisation was omitted, and the approximate concentration was determined according to the standard procedure (see below), using the results of Table III for calculating the amount of sulphide.

Appropriate dilutions of the standard solution were made immediately before each series of experiments using vacuum-boiled, de-ionised water.

The standard procedure for colour development

It is assumed that the hydrogen sulphide to be determined in actual analyses has been absorbed in zinc acetate solution.

Pipette 10 ml of zinc acetate solution into a 100-ml glass-stoppered volumetric flask and add de-ionised water to make 80 ml after the addition of sulphide solution to follow. Mix and add the sulphide solution from a pipette, immersing its tip. Mix by gentle swirling and place the flask, together with the bottles containing amino reagent and ferric solution, in a thermostat at 20° for at least 10 minutes. Use rapidly-running pipettes for the next two additions. Add 10 ml of amino reagent so that the solution flows down the wall of the flask and forms a layer on the bottom. Mix

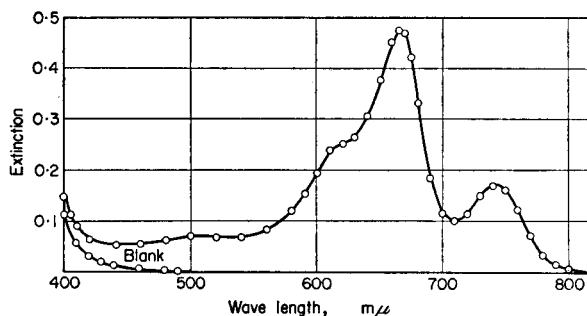


FIG. 1. Extinction-wavelength curve of a MB solution prepared from about 38 μg S according to the standard procedure. Cell length 1 cm.

by swirling, and immediately add 2 ml of ferric solution. Stopper the flask, and shake vigorously for about half a minute. Dilute to the mark, mix, and place the flask in subdued light at 20°. Measure the extinction at 20° and 667 $m\mu$ the same day, after 15 minutes or more. Perform a blank and apply the correction.

THE ABSORPTION CURVE

Fig. 1 shows the extinction-wavelength curve of a MB solution prepared according to the standard procedure. The wavelengths of maximum absorption are 667 and 743 $m\mu$. The higher peak, at 667 $m\mu$, is rather sharp, so that the extinction should be determined at a constant and preferably small slit-width, and care should be taken to reach the maximum, the position of which may vary for instruments of poorer spectral quality. The relation of the two absorption maxima to each other is discussed in connection with the acidity effect.

For comparison, the absorption curve of a commercial preparation, "Methylenblau B extra, Merck," was determined. It was dissolved in a solution containing the same amount of reagents as in the standard procedure. This curve was essentially the same as the one just discussed, with the exception that the latter had a stronger absorption at about 500 $m\mu$. This band is assumed to arise from methylene red formed during the colour development.

THE EFFECT OF VARIABLES

Hydrogen sulphide losses upon addition of reagents

The standard procedure for colour development proved to give the largest yield and the greatest precision. It seems that Roth⁷ and others mix the solution rather gently before and after the addition of the ferric solution by inverting the flask a few times. Mixing before the addition of the acid ferric solution brings part of the hydrogen sulphide into the gas phase; this part has no opportunity to react quantitatively after the addition of the ferric solution if the flask is only gently shaken.

The yield is consequently decreased, a fact that was experimentally confirmed in this laboratory. Gentle mixing without shaking before the addition of the ferric solution decreases the transfer of hydrogen sulphide to the gas phase; vigorous shaking after the addition of ferric solution facilitates the reaction of the hydrogen sulphide in the gas phase. That such a reaction really occurs a short time after the addition of the ferric solution was experimentally shown. Sulphide solution added 30 seconds after the ferric solution reacted to 90% of the normal yield.

Insufficient mixing before the addition of the ferric solution causes low results.

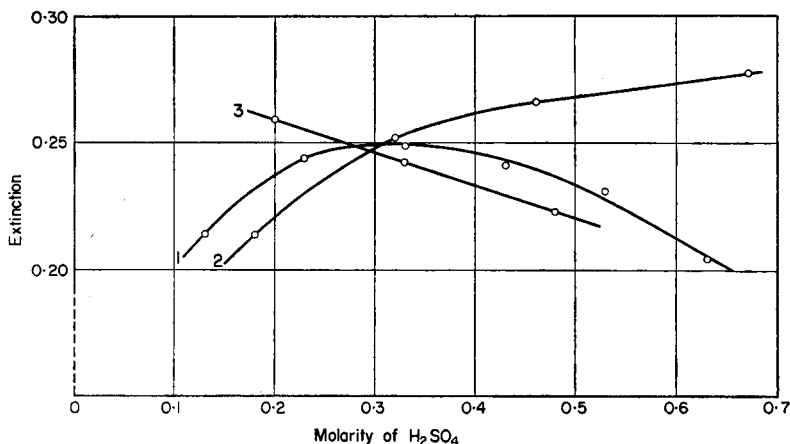


FIG. 2. Effect of acidity on light absorption and yield. Solutions prepared (see text) from about $18 \mu\text{g S}$ and extinction determined at $667 \text{ m}\mu$ in a 1-cm cell. Molarity of H_2SO_4 signifies concentration at

- (1) reaction and measurement
- (2) reaction; concentration at measurement $0.10M$
- (3) measurement; concentration at reaction $0.59M$

The acidity effect

The acid concentration may affect both the yield of the reaction and the extinction of MB. To elucidate this the following experiments were performed:

1. The colour reaction was performed according to the standard procedure with the exception that "amino" reagents of different acidities were used.
2. The colour reaction was performed with amino reagents of different acidities, but before measurement the solutions were brought to the same acidity by addition of the appropriate amount of ammonia. Special experiments showed that the presence of ammonium sulphate had no significant influence on the results.
3. The colour reaction was performed at constant acidity. Before measurement different amounts of ammonia were added, causing variable acidity at the extinction measurement.

It was found (Fig. 2) that the yield of MB increases with increasing acidity, whereas its extinction at $667 \text{ m}\mu$ decreases. A combination of these two relations explains the maximum obtained in experiment 1. This result is opposed to the assumption made by Fogo and Popowsky⁶ that variable acidity of the "amino" reagent influences the light absorption rather than the reaction yield.

The optimal sulphuric acid concentration in the final solution is about $0.30M$.

There is a slight displacement of the extinction maximum towards longer wavelengths with increasing acidity. An increase in sulphuric acid concentration from $0.23M$

to 0.63M resulted in a displacement of the peak from 666 m μ to 668 m μ ; the extinction found at those peaks differed from the values at 667 m μ by less than 1%.

The absorption maximum at 743 m μ , which is absent in solutions of MB in distilled water, increases with the acidity, indicating the formation of another compound possibly produced by the addition of a proton to the MB cation. The decrease of the 667 m μ peak with increasing acidity is thus explained.

TABLE I. EFFECT OF TEMPERATURE ON THE EXTINCTION AT 667 m μ OF MB SOLUTIONS PREPARED AT 20° ACCORDING TO THE STANDARD PROCEDURE.

Temperature at measurement, °C	Extinction	Mean temp. coefficient in the interval, % per °C
<i>96 μg sulphide-S, 1-cm cell</i>		
15	1.049	
20	1.073	0.45
25	1.091	0.33
30	1.105	0.25
<i>19 μg sulphide-S, 5-cm cell</i>		
20	1.197	
25	1.200	0.05

In a series of experiments using hydrochloric acid instead of sulphuric acid for the "amino" reagent, a lower extinction was obtained even at the optimal concentration of this acid.

Effect of variable concentrations of zinc acetate, ferric ammonium sulphate and p-aminodimethylaniline

Varying the amounts of "amino" reagent as well as those of zinc acetate and ferric solutions will generally produce acidity effects. If, however, precautions are taken to keep the concentration of free sulphuric acid constant, only slight effects are produced by fairly large variations. Thus, varying the amount of ferric iron in the interval 0.1–1.0 millimoles of Fe (standard amount 0.5 millimole) gave deviations within 2% of the extinction; lower amounts as well as complexing by phosphoric acid delayed the reaction considerably. The amount of *p*-aminodimethylaniline should not be much less than the standard amount, 0.05 millimole; the use of 0.10 millimole increased the yield by about 1%.

Temperature effects

Mecklenburg and Rosenkränzer³ and others report a larger light absorption when the reaction is performed at a lower temperature. Temperature variations may, however, affect both the yield and the extinction of MB. These effects seem not to have been studied separately.

The temperature effect on the extinction was determined on two solutions prepared according to the standard procedure from 96 μ g and 19 μ g of sulphide-S. The extinction was determined at various temperatures (Table I), beginning and ending at

20° as a control. The temperature coefficient around 20° was found to be about +0.4% per degree for the higher concentration and 0.05% per degree for the lower one. This result agrees qualitatively with the observations made by Rabinowitch and Epstein¹¹ on MB solutions in water at pH 3.4, which will be further discussed later on.

To study the temperature effect on the yield of MB, all reagent solutions were brought to the same temperature in a thermostat and the colour development performed at this temperature. The extinction was determined at 20°.

From the results of Table II obtained with 106 μg S, it is seen that the yield is steadily lowered with increasing temperature; the negative temperature coefficient decreases further with increasing temperature and at 20° is about -0.5% per degree. Similar results were obtained with 20 μg S.

TABLE II. EFFECT OF TEMPERATURE ON THE YIELD OF MB.

MB solutions prepared from 106 μg sulphide-S according to the standard procedure, but at varying temperatures. Extinction is determined at 667 $m\mu$ and 20° in a 1-cm cell.

Temperature at reaction, °C	Extinction	Mean temp. coefficient in the interval, % per °C
10.1	1.209	-0.36
15.0	1.188	-0.46
20.0	1.161	-0.65
24.7	1.126	-0.74
30.0	1.083	

Using hydrochloric acid solutions, Fogo and Popowsky⁶ obtained a maximum yield of MB at 24°. They assume that the yield is decreased at higher temperatures because more hydrogen sulphide escapes from the acid solution into the gas phase; at lower temperatures little hydrogen sulphide escapes but the MB reaction becomes so slow that side reactions occur to a larger extent.

No such maximum was obtained in this investigation. The absorption coefficient for hydrogen sulphide in water decreases strongly with increasing temperature. Further, it was demonstrated that the capacity of the reaction mixture to react with further amounts of sulphide added after 10 or 30 seconds was strongly lowered with increasing temperature. These two facts combined will, at least qualitatively, explain the steadily decreasing negative temperature coefficient, though the influence of some side reaction cannot be excluded.

The opposite signs of the temperature coefficients of the yield and the extinction may, in isolated cases, cancel the errors. It is, however, obvious that the precision is much improved by keeping the temperature constant at both the reaction and the extinction measurement.

Colour stability

The colour was found to be fully developed after 15 minutes at 20°; the extinction was then constant for several hours if the solution was kept in subdued light. If kept overnight, a slight fading occurred (0.3% for a solution made from 100 μg S). It seems to be a commonly accepted fact that strong light will bleach the colour; no experiments to confirm this were performed.

Effects of traces of heavy metals

Water from a metal still often contains about 30–50 μg of Cu per litre. Preliminary experiments indicated that these traces in the water used for diluting the zinc acetate solution were responsible for certain anomalies in the yield of MB. In order to eliminate this source of error, the water had to be re-distilled in a glass apparatus or passed through a H^+ -saturated cation-exchanger. Also, the zinc acetate solution had to be purified as previously described.

Experiments where traces of copper sulphate were added to the diluted zinc acetate solution showed a nearly linear decrease of the extinction with increasing amounts of copper. As expected, addition of copper after the colour development had no effect. Addition of a constant amount of copper (3.0 μg Cu as sulphate) to the diluted zinc acetate solution produced the same losses (1.5–1.7 μg S) in the determination of 5–33 μg S. The molar ratio (copper added)/(loss of sulphur) is approximately 1:1. This supports the assumption that formation of copper sulphide is the cause of the interference. Addition of copper to the ferric solution had no effect, thus excluding the assumption that copper may serve as a catalyst for some harmful side-reaction appearing at the colour development.

While this work was being done, a short communication by Johnson and Arkley¹² appeared. They state that traces of copper in the water precipitate sulphide quantitatively, resulting in low yields of MB. This observation as to the low yields is confirmed in this laboratory; the formation of any precipitate was, however, never observed. It may be assumed that, at such small concentrations, copper sulphide remains in solution as a mononuclear complex.

Interference from lead and mercury was also studied. As expected from the ionic solubility of PbS , addition of 10–20 μg of Pb as nitrate had no effect. The interference from Hg was, however, serious. The molar ratio (Hg added)/(loss of S) was found to be about 1:2, indicating the formation of the complex $\text{Hg}(\text{SH})_2$. The interference was almost as large when Hg was present in the ferric solution as in the zinc acetate solution. This difference in behaviour from Cu^{II} may be explained by the fact that Hg^{II} forms complexes of greater stability with S^{2-} and SH^- .

Susceptibility of sulphide to air oxidation in zinc acetate solution

Two diluted zinc acetate solutions containing about 22 μg sulphide-S were treated with a stream of air, 50–100 ml per minute, for 1 hour before colour development. Losses of 1.1 and 1.8% were indicated. The sulphide in the zinc acetate solution is consequently unexpectedly stable.

THE RELATION TO BEER'S LAW

Different amounts of sulphide were treated according to the standard procedure (Table III). There is a noticeable decrease in specific extinction at 667 $\text{m}\mu$ at concentrations larger than about 25 μg S per 100 ml. This lack of linearity of the calibration curve has been observed by Johnson and Nishita⁸ and others. By diluting more concentrated solutions (50–100 μg S) with a blank solution and determining the extinction, Johnson and Nishita proved that this lack of linearity is caused by deviation from Beer's law and not by a decrease in the yield of MB; this has also been confirmed in this laboratory.

Rabinowitch and Epstein¹¹ have found that solutions of MB in water (pH 3.4) do not follow Beer's law even at very low concentrations ($<10^{-6} M$). They have proved that this deviation is quantitatively explained by the formation of dimeric ions $(MB)_2^{2+}$. The absorption spectrum of methylene blue consists of two overlapping absorption bands with maxima at 600 $m\mu$ and 656 $m\mu$. The former is more pronounced in more concentrated solutions, and is due to the dimeric ion; the latter, due to the monomeric ion, predominates in very dilute solutions. The dissociation of $(MB)_2^{2+}$ is increased by an increase in temperature as well as by diluting the solution. This explains the increase of the extinction at 667 $m\mu$ with increasing temperature illustrated in Table I.

TABLE III. THE RELATION OF EXTINCTION TO SULPHIDE-SULPHUR TREATED ACCORDING TO THE STANDARD PROCEDURE
The extinction, E, is determined at 667 $m\mu$ in a 1-cm cell. Cf also Table IV.

Sulphide-S, μg	Extinction	$E \times 10^2$ per μg sulphide-S	Yield of MB calcd. from Table IV, %
0	0.003	—	—
10.42	0.137	1.290	64.5
20.56	0.269	1.293	65.1
23.62	0.309	1.294	65.4
30.90	0.394	1.265	64.9
41.17	0.517	1.248	65.5
51.55	0.635	1.226	65.3
61.98	0.746	1.199	—
103.1	1.160	1.122	—

THE YIELD OF THE METHYLENE BLUE REACTION

According to Lorant,⁵ exactly 68.7% of the added sulphide is transformed to MB. The method used for standardising the sulphide solution is not stated, and the colorimetric determination, made by means of a Duboscq colorimeter, is performed with a solution of MB and methyl red (not methylene red) as a reference solution; Lorant seems to have mistaken methyl red for methylene red, the by-product reported by Bernthsen. The reported value for the yield of MB is, therefore, uncertain; however, it is evident that sulphide is not quantitatively transformed to MB. This is also assumed by several other authors, although no quantitative results are published.

The reaction yield can be determined by comparing the extinction of a MB solution made from a known amount of sulphide with the extinction of a solution containing a known amount of MB. The latter solution was prepared from "Methylenblau B extra, Merck" which was dissolved in a solution of the same composition as is obtained by performing a blank. The purity of the preparation used as calculated from nitrogen determinations was 97.5%, ash content 1.2%. Using the values given in Tables III and IV, and correcting for the purity, the reaction yield is calculated to 66.7% \pm 0.5% throughout the investigated interval.

No computation of the standard error has been made at this point in the investigation, but it will be found in a following paper¹ which also includes the reduction of sulphate to sulphide.

Acknowledgement—This work was suggested by Professor Folke Nydahl. The author wishes to thank him for his valuable discussions and the facilities placed at her disposal.

TABLE IV. THE EXTINCTION OF "METHYLENBLAU B EXTRA" AS A FUNCTION OF ITS CONCENTRATION

The preparation is dissolved in blank solutions prepared according to the standard procedure. The extinction, E , is determined at 667 $m\mu$ in a 1-cm cell. Cf also Table III.

MB sulphur, μg	Extinction	$E \times 10^2$ per μg MB sulphur
0	0.002	—
3.94	0.082	2.03
7.78	0.158	2.01
11.70	0.233	1.974
15.60	0.310	1.974
19.52	0.385	1.962
27.30	0.522	1.905
39.10	0.728	1.857

Zusammenfassung—Es existiert eine photometrische Bestimmung von Sulfat die auf folgender Reaktion beruht: Sulfat wird zu Sulfid reduziert und dieses in Gegenwart von Ferriionen mit p-Aminodimethylanilin zu Reaktion gebracht wobei Methyleneblau gebildet wird. Die vorliegende Abhandlung befasst sich mit der Farbreaktion. Die zur Bestimmung führende Farbreaktion ist abhängig von folgenden Faktoren: Schwefelwasserstoffverluste, Säuregehalt der Lösung während Reaktion und Messung, Temperatur während Reaktion und Messung, Spuren von Schwermetallen, Zeit, Oxydation durch Luftsauerstoff. Geeignete Berücksichtigung aller Faktoren führte zu einer vorgeschlagenen Standardmethode. Früher schon festgestellte Abweichungen vom Beer'schen Gesetz wurden bestätigt und diskutiert. Die Ausbeute der Reaktion wurde bestimmt.

Résumé—Les sulfates peuvent être dosés par spectrophotométrie à l'état de bleu de méthylène après réduction en sulfures, ce qui permet la réaction avec la p-aminodiméthylaniline et le fer ferrique pour former le colorant. Cet article est relatif à la réaction colorée.

La méthode étalon pour le développement de la couleur proposée ici est basée sur l'étude des paramètres suivants: pertes en H_2S , acidité pour la réaction et la mesure, concentration de traces de métaux lourds, oxydation par l'air et en fonction du temps. Les déviations à la loi de Beer, déjà signalées, sont confirmées et discutées. On détermine le rendement de la réaction.

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กระทรวงอุตสาหกรรม

DETERMINATION OF ULTRAMICRO AMOUNTS OF SULPHATE AS METHYLENE BLUE—II

THE REDUCTION

LILLY GUSTAFSSON

Department of Analytical Chemistry, University of Uppsala, Uppsala, Sweden

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Summary—Sulphate may be determined spectrophotometrically as methylene blue after reduction to sulphide, which is allowed to react with *p*-aminodimethylaniline and ferric iron to form the dye. A previous paper¹ dealt with the colour reaction; this paper deals with the reduction.

A method for the reduction of sulphate to sulphide by hydriodic and hypophosphorous acids in acetic acid solution is proposed. It is founded on an investigation of the following variables: composition of the reducing reagent, composition of the carrier gas and gas-washing liquid, temperature at reduction, and time. The yield of the reduction is found to be 100% within the experimental errors. The standard deviation of a single determination of 100 $\mu\text{g S}$ or 2 $\mu\text{g S}$ is found to be 0.14 $\mu\text{g S}$ or 0.05 $\mu\text{g S}$, respectively. Some interferences in connection with the application of the method for certain purposes are discussed.

In a previous paper¹ the reaction of sulphide with *p*-aminodimethylaniline and ferric iron to form methylene blue (MB) was investigated as part of an attempt to determine, spectrophotometrically, ultramicro quantities of sulphate after reduction to sulphide. The present paper deals with the reduction and the final method.

Lorant² seems to have been the first to employ the reducing properties of hydriodic acid for the quantitative determination of sulphate. The sulphate is reduced to sulphide by boiling with a mixture of hydriodic acid, formic acid and red phosphorus. More recently, some variants of this reduction method have been published. Thus Luke³ performs the reduction with hydriodic acid, hydrochloric acid and hypophosphorous acid, Roth⁴ with hydriodic acid, formic acid and hypophosphite, and Johnson and Nishita⁵ with a mixture similar to the one used by Lorant. Lorant states that sulphate is quantitatively reduced to sulphide. The basis for this statement is, however, not quite free from objections. Using a reducing agent of the same type as that employed by Luke, Bethge⁶ reports a quantitative yield in the reduction of centigram amounts of potassium sulphate.

In these methods, generally, the optimum range of several analytically important variables seems not to have been established, precluding their immediate application at least for ultramicro determinations.

EXPERIMENTAL

Apparatus

The apparatus (Fig. 1) used for the reduction is chiefly according to Johnson and Nishita.⁵ The sample, together with the reducing mixture, is boiled in the round-bottomed flask (*a*). Nitrogen, purified with permanganate solution, is introduced through the side-tube (*b*). This gas carries the hydrogen sulphide formed through the water-jacketed condenser (*c*) to the gas-washing column (*d*) where the gases are freed from hydriodic and acetic acid by washing with water. The gases are carried further through the delivery tube (*e*) dipping into a solution of zinc acetate which absorbs the

hydrogen sulphide; the solution is kept in a 100-ml volumetric flask with a ground-glass stopper. A small burner with a steady flame is used for the heating. The round-bottomed flask rests on an asbestos board fitted with a round hole to prevent overheating of the walls. The side tube (b) ends 1–2 mm from the bottom of the flask. The delivery tube (e) is constricted to an opening 1–2 mm in diameter at its lower end, and connected to the apparatus, glass-to-glass, with a short piece of latex tubing. The rate of the nitrogen flow is checked with a flowmeter (measuring the fall of gas pressure across a capillary tube). The ground-joints are greased with sulphur-free silicone lubricant.

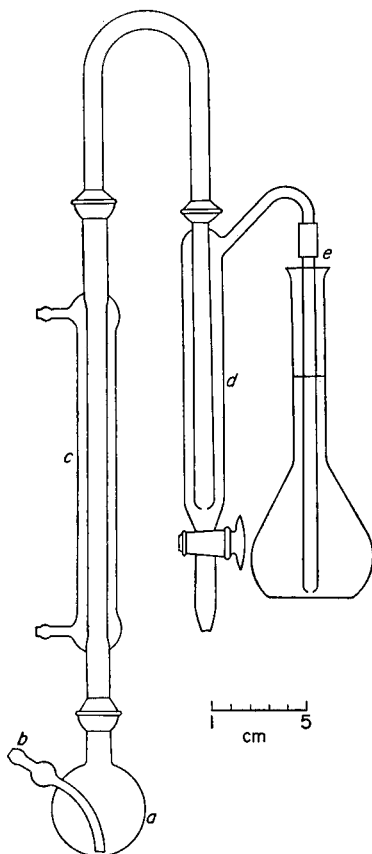


FIG. 1. Apparatus for the reduction of sulphate.

Concerning the importance of keeping the apparatus and other glassware free from traces of heavy metals as well as the spectrophotometer and thermostatic arrangements, *cf* Gustafsson.¹

Reagents

All reagents, except sodium hypophosphite, were of reagent-grade quality.

Concerning *de-ionised water*, *zinc acetate solution*, "*amino*" reagent and *ferric solution*, *cf* Gustafsson.¹

Reducing reagent: Dissolve 2.5 g $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ in 25 ml of glacial acetic acid and 100 ml of hydriodic acid (sp. gr. 1.7) in a 150–250-ml round-bottomed flask with a ground-in condenser and a gas delivery tube. The hydriodic acid should be taken from a newly-opened flask. Boil under reflux for 1 hour, bubbling a stream of nitrogen (about 50 ml per minute) through the solution; traces of sulphur are removed in this way, and iodine is reduced to iodide. Allow to cool in the nitrogen stream, close the flask with a glass stopper, and store in subdued light.

Sulphate-free water: If necessary, purify distilled water by passing it through a 20-ml column of an anion-exchange resin (Dowex 1, Cl-form) at a rate not exceeding 250 ml per hour.

Sulphate standard solution: Dissolve 5.435 g K_2SO_4 , dried at 105° for 2 hours, in distilled water to make 1 litre. This solution contains 1 mg of S per ml, and is used as a stock solution in preparing standard solutions of lower concentrations by diluting with sulphate-free water.

Nitrogen wash solution: 2% potassium permanganate solution, saturated with mercuric chloride.

Sulphur-free silicone lubricant: This is prepared according to Johnson and Nishita as follows: In a 100-ml beaker, mix about 5 g of Dow-Corning silicone lubricant with 10 ml of a solution consisting of equal volumes of hydriodic acid and hypophosphorous acid (30%). Boil for 45 minutes with occasional stirring. Use a round-bottomed flask filled with cold water as a condenser. Pour off the acid solution and wash the lubricant thoroughly with sulphate-free water.

Recommended procedure

The sample should not contain much more than $100 \mu\text{g S}$. If the sample is a solid, introduce it to the bottom of the reduction flask. If the sample is a solution, *e.g.* standard sulphate solution, add it with a pipette to the reduction flask and evaporate to dryness, preferably in a drying oven at 130° . The solution should contain bases equal to or in excess of sulphuric and other high-boiling acids in the sample. The evaporation can be accelerated by blowing a stream of air, washed with $4M$ potassium hydroxide, into the upper part of the flask. Allow the flask to cool to room temperature.

Lubricate all ground-joints of the apparatus with sulphur-free silicone lubricant. Add 10–15 ml of de-ionised water to the gas-washing column (*d*). Add 10 ml of zinc acetate solution and 68 ml of de-ionised water to the 100-ml volumetric flask and connect it to the apparatus with the delivery tube (*e*) reaching to the bottom of the flask.

Start the nitrogen flow through the gas-washing bottle containing nitrogen wash solution at a rate of 150–200 ml per minute. Pipette 3 ml of reducing reagent into the flask containing the sample, and connect it to the condenser and the nitrogen source. Heat to boiling in about 60 seconds with a small flame ending a few mm below the flask. Interrupt the heating after boiling for 10 minutes. Detach the delivery tube from the apparatus, but keep it in the volumetric flask.

The apparatus is now ready for another reduction. If there is more than a few minutes' delay between the reductions, iodine is formed in the apparatus, and this should be rinsed out with water before use. After 6–8 reductions, the water in the gas-washing column should be replaced.

Place the volumetric flask, together with the "amino" reagent and ferric solution bottles, in a thermostat at 20° for at least 10 minutes. Use rapid-running pipettes for the addition of the reagents to follow. Pipette 10 ml of "amino" reagent through the delivery tube so that the tube is rinsed and the reagent forms a layer on the bottom of the flask. Rinse the tube with 2 ml of de-ionised water, and remove it from the flask. Mix by gently swirling the flask, and immediately add 2 ml of ferric solution. Stopper the flask and shake it vigorously for half a minute. Dilute to 100 ml with water, mix, and place the flask in subdued light at 20° . Determine the extinction at the peak maximum, $667 m\mu$, at 20° the same day, after 15 minutes or more. Perform a blank and apply the correction. Determine the relation of extinction to amount of sulphur by performing the procedure on different amounts of sulphate standard solution (*cf.* Tables II and III).

EFFECTS OF VARIABLES

The composition of the reducing reagent

In the search for a reducing reagent able to give quantitative reduction of sulphate to sulphide and, moreover, one which was stable and easy to prepare, a systematic investigation was made of reducing mixtures of various compositions. The following mixtures were studied: (1) HI + P; (2) HI + P + HCOOH; (3) HI + P + HAc; (4) HI + P + H_3PO_2 ; (5) HI + H_3PO_2 ; (6) HI + H_3PO_2 + HCOOH; (7) HI + NaH_2PO_2 + HAc. The proportions of the constituents were also varied. Before use, the mixtures were refluxed for 1 hour with a stream of nitrogen bubbling through the solution to remove traces of sulphur.

As a result of these experiments, it was found that reagents made up of HI + NaH_2PO_2 + HAc gave the best precision and the lowest blanks. Varying the volume ratio HI:HAc from 10 to 1 did not affect the yield of the reduction. Using

formic instead of acetic acid, Roth⁴ obtained a constant yield only for reagents containing 43–53% of formic acid; he consequently recommends these proportions in spite of the fact that he had obtained as much as 20% higher yield with reagents containing less formic acid.

Reducing mixtures containing red phosphorus gave rather large and varying blanks (up to 0.3 μg S per ml). It seems probable that remaining sulphur compounds are slowly extracted from the solid particles.

Attempts to reduce the concentration of water in the reagent resulted in severe losses of gaseous hydrogen iodide during boiling.

With reagents composed of HI + P or HI + H_3PO_2 , the evolution of white fumes was sometimes observed to occur in a seemingly random way. These fumes were not wholly absorbed in the washing column and caused very large negative errors. As it seemed probable that this phenomenon was caused by overheating, a number of reductions were performed with the reaction vessel immersed in boiling water; but the errors remained. It is of great interest that such low and erratic results are not obtained if formic or acetic acid is added to the reaction mixture.

As a consequence of these results, the recommended reagent was finally chosen. It is of great advantage that interfering sulphur compounds can easily be removed by refluxing in a stream of nitrogen; at the same time free iodine is converted to iodide. Experiments showed that boiling for 10 minutes removed 99% of the sulphur contamination. After preparation, the reagent should not be transferred to another vessel, but should be stored in the same flask. Under these conditions, the reagent blank is found to have a low and constant value for at least several weeks; it is unnecessary to boil the solution each day before use as prescribed by Roth. If carefully prepared and handled, *e.g.* protected from contamination and undue exposure to light and air, the reducing solution is found to be stable for months. When the initially colourless or faintly yellow solution has turned brown from iodine formed by air-oxidation, it should be refluxed again before use.

Effect of temperature at reduction

According to Lorant², sulphate is reduced even at room temperature, though slowly. With a reducing mixture similar to that used by Lorant, the influence of temperature was studied. It was found that the reaction performed under boiling gave the highest yield, whereas no reduction could be observed at room temperature. At 50° reduction was slow; of 20 μg S added, only 4 μg was recovered in the first 20 minutes and 6 μg in the next 40 minutes. At 80° no more hydrogen sulphide was produced after 20 minutes, but the yield was considerably lower than at boiling. It seems probable that at lower temperatures part of the added sulphur escapes the reaction, presumably as sulphur dioxide. With regard to these losses at lower temperatures, the reducing mixture should be heated to boiling fairly rapidly.

The composition of the washing liquid

In order to prevent traces of iodine and hydriodic acid from being transferred to the zinc acetate solution, Lorant and others wash the gases with a solution of pyrogallol and sodium dihydrogen phosphate. Experiments proved, however, that de-ionised water could, with advantage, be substituted for this washing solution. This was usually replaced after about 6 reductions in succession, and then was found to

contain about 2 milliequivalents of acetic acid and very little hydriodic acid. No yellow colour from iodine was ever observed in the washing column.

The carrier gas

According to Lorant, not only hydrogen, nitrogen or carbon dioxide but also air may be used as carrier gas. This seems objectionable, as there may be losses of hydrogen sulphide by air oxidation. When performing a series of reductions with air instead of nitrogen as a carrier gas, the first reduction gave the same extinction as when nitrogen was used; the next reduction, made immediately after, gave an extinction that was 3–4% too low. The loss of hydrogen sulphide was evidently caused by iodine formed in the condenser. In consequence air should not be used as carrier gas. It is, however, not necessary to remove traces of oxygen from the nitrogen as many authors prescribe.

The time variable

Experiments showed that the reduction of sulphate is complete after a few minutes. The time necessary for the transfer of the hydrogen sulphide to the zinc acetate solution is obviously dependent on the rate of the nitrogen flow and the amount of the water in the washing column. When working according to the recommended procedure, the transfer is complete in 10 minutes.

Effect of diluting the reducing reagent with water

For practical reasons it would be of great advantage if the reduction method could be directly applied to sample solutions. Experiments proved, however, that addition of only 0.5 ml of water to the evaporated sulphate sample decreased the yield by 6%; when 2 ml of water was added the error amounted to –35%. This effect is not only obtained with the recommended reagent. Several other reducing mixtures prepared from HI + P or from HI + P + HAc were investigated in this respect. In all cases, diluting with water caused considerable losses, and boiling for a longer time did not increase the yield; the losses are therefore not due to a slower reduction. It seems as if part of the sulphur escapes the reaction, probably as sulphur dioxide.

It might be possible to reduce these losses to some extent by using a larger amount of reagent. Using a more concentrated reagent might also be considered, but then this reagent cannot be boiled to remove traces of sulphur without serious losses of gaseous hydrogen iodide. Dissolving the sample in acetic or formic acid might be possible in some cases. The safest way is, however, to evaporate the sample to dryness.

Conditioning the apparatus

When reducing 5 μg and smaller amounts of sulphate, it was observed that the first reduction of a series often gave a result too low by 0.1 – 0.2 μg S. This loss was presumably caused by absorption of hydrogen sulphide in the apparatus in spite of the precautions taken to keep the glass walls and the water in the washing column free from traces of metals. This error was eliminated by running the procedure on a small amount of sulphate before the actual series.

Magnitude of blanks

To indicate the magnitude of blanks to be expected, the following results are reported. The reducing reagent prepared on 4 different occasions in blank experiments gave the extinctions 0.008, 0.008, 0.010 and 0.011 (5-cm cell); blank experiments on the colour development alone gave 0.007. Sulphate-free water (10 ml) made alkaline with a few drops of 0.001M NaHCO₃ and evaporated to dryness gave no larger blank after reduction than the reagents alone.

THE YIELD OF THE REDUCTION

The yield of the reduction was determined by comparing the amounts of methylene blue obtained from known quantities of sulphate with those obtained by applying the colour development to known quantities of sulphide. The latter determinations were performed on freshly prepared and standardised solutions of sodium sulphide, *cf* Gustafsson¹. The uncertainty of the amount of sulphide is estimated to be less than 0.3%. Both the colour development and the photometric determination were performed at 20°. The results of Table I show that the yield of the reduction is quantitative well within the experimental errors.

RELATION TO BEER'S LAW AND PRECISION

It was confirmed in a previous paper¹ that the light absorption of methylene blue solutions does not follow Beer's law and that above 20 μg of S per 100 ml the deviations begin to be larger than the experimental errors. As the percentage yield of methylene blue from sulphide is constant and the yield of the reduction of sulphate is quantitative, the same deviations are obtained in the relation of amount of sulphate to extinction. (Table II. These values can only be compared approximately with those given in Table III of the previous paper¹ because the temperature constancy in the experiments of the latter table was not quite satisfactory.)

The serious deviations from linearity of the relationships of extinction to amount of sulphate make it advantageous to use a curve of specific extinction as a function of extinction for the calculations.

The precision in determining 100 μg of sulphate-S is obtained from the results of Table I; the standard deviation of a single determination is 0.14 μg of S.

Quantities of sulphate in the range 0-20 μg of S were determined using 5-cm cells for the absorption measurements (Table III). Assuming the extinction to be a linear function of the amount of sulphate, the method of least squares was applied to the results giving the curve

$$\text{Extinction} = -0.00019 + 0.06336 (\mu\text{g S}).$$

The constant term, corresponding to 0.003 μg of S, may be omitted as insignificant and the relation

$$\mu\text{g S} = 15.78 \times \text{Extinction}$$

was used for calculation of sulphur found.

It is apparent that Beer's law is valid up to 20 μg of S within the errors of the method. The standard deviation is calculated to be 0.12 μg of S, assuming it to be independent of the amount of S. This assumption is certainly not true, but the number will give an approximate conception of its magnitude.

TABLE I. THE YIELD OF THE REDUCTION OF SULPHATE TO SULPHIDE
As a mean of 7 determinations in each series, the following extinctions (667 $m\mu$, 1-cm cell, 100 ml, 20°) were obtained.

Starting from	Extinction	Standard deviation of	
		single result	mean
101.1 μg sulphide-S	1.120	0.0037	0.0014
101.1 μg sulphate-S	1.121	0.0016	0.0006

TABLE II. THE RELATION OF EXTINCTION TO AMOUNT OF SULPHATE, 0–100 μg S
Extinction, 667 $m\mu$, 1-cm cell, 100ml, 20°, corrected for blank.

Sulphate taken, μg S	Extinction	Extinction \times 100 per μg S
6.00	0.077	1.28
11.84	0.153	1.29
17.80	0.225	1.26
20.05	0.253	1.26
23.71	0.302	1.274
39.56	0.494	1.249
59.46	0.715	1.202
101.1	1.121	1.109

TABLE III. THE RELATION OF EXTINCTION TO AMOUNT OF SULPHATE, 0–20 μg S
Extinction, 667 $m\mu$, 5-cm cell, 100 ml, 20°, corrected for blank (0.008; 0.010). Sulphur
found is calculated as $15.78 \times$ Extinction.

Sulphate taken, μg S	Extinction	Sulphur found, μg S	Deviation, μg S
0.59	0.039	0.62	-0.03
1.20	0.081	1.28	+0.08
1.57	0.089	1.40	-0.17
2.36	0.143	2.26	-0.10
2.37	0.155	2.45	+0.08
3.94	0.246	3.88	-0.06
7.90	0.510	8.05	+0.15
11.87	0.751	11.85	-0.02
15.82	1.011	15.95	+0.13
18.98	1.196	18.87	-0.11
19.72	1.257	19.84	+0.12
19.72	1.239	19.55	-0.17

The standard deviation of a single result in the determination of 2 μg of S was found to be 0.05 μg of S from 9 determinations in 5-cm cells. The precision may possibly be improved by using apparatus and solutions of smaller volume.

APPLICATIONS AND INTERFERENCES

The method proposed has been used occasionally in this laboratory for a few years. The objects of analysis have essentially been fresh water samples and biochemical preparations. For water samples, 1–10-ml portions have been evaporated and analysed. In cases where there is a very small sulphate content, such as glacial stream waters which may contain less than 1 ppm, a sample size of 10 ml has been

used. Milligram samples of biochemical preparations with low percentages of sulphur (<1%) were burnt in oxygen according to Mikl and Pech⁷ (*cf* Schöniger⁸), the sulphur dioxide and trioxide formed was absorbed in 5–10 ml of dilute sodium hydroxide containing hydrogen peroxide, and an aliquot was then evaporated for analysis. This method worked well on standard samples. However, a limiting factor for its use on low-percentage samples is the varying sulphur content of the paper used for wrapping up the sample; the total blank amounted to about 2 μg of S.

Some interferences were studied in connection with these analyses. Oxidising agents as a rule interfere. Thus 3 mg of NO_3^- reduced the yield by 3%. Johnson and Nishita ascribe these losses to some volatile reduction product which is absorbed in the zinc solution and interferes with the colour reaction; our own results confirm this hypothesis. Iron^{III} in amounts up to at least 20 mg did not interfere.

Certain nitrogenous organic substances interfere, giving low results. The determination of sulphate in the presence of organic material by this method, without further investigation, is not recommended. Sulphur-containing organic material will give off varying amounts of its sulphur content.

Moderate amounts of alkalies or alkaline earths do not interfere; barium sulphate is rapidly reduced. Reduction of elementary sulphur, if newly formed, is quite rapid; reduction of flowers of sulphur, for example, proceeds slowly.

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Zusammenfassung—Im vorhergehenden Beitrag wurde die Farbreaktion bei der Bestimmung von Sulfat nach Reduktion zu Sulfid und Bestimmung dessen nach der Methylenblaumethode behandelt. Hier wird der Reduktionsschritt diskutiert. Es wird die Reduktion mittels Jodwasserstoffsäure und hypophosphoriger Säure in essigsaurer Lösung vorgeschlagen. Die Reduktion hängt von folgenden Faktoren ab: Zusammensetzung des Reduktionsreagens, Zusammensetzung des Trägergases und der Gaswaschflüssigkeit, Temperatur bei der Reduziert wird und schliesslich Zeit. Die Ausbeute der Reduktionsreaktion wurde zu 100% innerhalb der experimentellen Schwankungen gefunden. Die Standardabweichung einer Einzelbestimmung von 100 μg Schwefel wurde zu 0.14 μg und die von 2 μg Schwefel zu 0.05 μg S gefunden. Einige Störmöglichkeiten in Zusammenhang mit der Anwendung der Methode für bestimmte Zwecke werden diskutiert.

Résumé—Les sulfates peuvent être dosés par spectrophotométrie à l'état de bleu de méthylène après réduction en sulfures ce qui permet la réaction avec la p-aminodiméthylaniline et le fer ferrique pour former le colorant. Un précédent article traitait de la réaction colorée, celui-ci est relatif à la réduction.

On propose une méthode pour la réduction des sulfates en sulfures par les acides iodhydrique et hypophosphoreux en solution dans l'acide acétique. Elle est basée sur l'étude des paramètres suivants: composition du réactif réducteur, composition du gaz entraîneur et du liquide lavant le gaz, température de réduction et temps. Le rendement de la réduction est égal à 100% aux erreurs expérimentales près. L'écart type pour une seule détermination de 100 μg de S est de 0.14 μg S et pour 2 μg de S, elle est de 0,05 μg S. On discute l'influence de quelques interférences relatives à l'application de la méthode à certains objectifs.

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SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE USING LANTHANUM CHLORANILATE

KIYOKO HAYASHI, TAEKO DANZUKA and KEIHEI UENO*
Research Laboratory, Dojindo & Co., Ltd., Kumamoto, Japan

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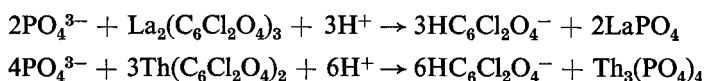
Summary—The spectrophotometric determination of phosphate using lanthanum chloranilate has been investigated. It is possible to determine 3–300 ppm of phosphate with an accuracy of $\pm 2\%$, if suitable conditions are chosen. Chloride or nitrate ions do not interfere up to 400 ppm. Interference from sulphate ion can be compensated for by adding a large amount of sulphate both to the sample and to the standard solutions. This method is simpler, has less critical reaction conditions, and develops a much more stable coloration than the conventional heteropolyacid methods.

INTRODUCTION

PHOTOMETRIC determinations of phosphate are based usually on the colour reaction of phosphate with molybdate or vanadomolybdate to form heteropolyacids or heteropoly blue. In all of these procedures, it is necessary, however, to carry out the colour reaction under critically controlled conditions to obtain reproducible results.

In a previous paper¹ the use of the lanthanum salt of chloranilic acid (2:5-dichloro-3:6-dihydroxy-*p*-benzoquinone) was proposed for the photometric determination of fluoride, the metathesis reaction between lanthanum chloranilate and fluoride ion to form insoluble lanthanum fluoride being utilised. As it was known that phosphate may be precipitated quantitatively by lanthanum or thorium ion, the uses of lanthanum chloranilate and thorium chloranilate were investigated in an analogous manner to the fluoride determination.

The reactions between phosphate and lanthanum or thorium chloranilate may be shown schematically as follows:



Insoluble lanthanum phosphate or thorium phosphate is precipitated, with the liberation of acid chloranilate ion, which is proportional to the amount of phosphate in the sample. After filtering excess reagent and metal phosphate, the liberated acid chloranilate ion in the filtrate is determined spectrophotometrically.

As reported earlier,¹ the spectrophotometric determination of acid chloranilate ion can be carried out either in the visible region (520–550 $m\mu$) or in the ultraviolet region (280–350 $m\mu$) of the spectrum. In the case of visible spectrophotometry, the instrument is less expensive and the determination will be less influenced by foreign materials, although the sensitivity is slightly lower.

This paper reports on the visible spectrophotometric determination of phosphate using lanthanum or thorium chloranilate, which is simpler in procedure, has less

* Present Address: Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka, Japan.

critical reaction conditions, and develops a much more stable coloration than the conventional heteropoly acid methods. With this procedure, it is possible to determine 3–300 ppm of phosphate with an accuracy of $\pm 2\%$.

EXPERIMENTAL

Reagents

Lanthanum chloranilate: Prepared as described previously.¹

Thorium chloranilate: Prepared in an analogous manner to lanthanum chloranilate from chloranilic acid and thorium nitrate. These reagents can be kept for an indefinite period without appreciable deterioration.

Standard phosphate solution (approximately 5,000 ppm as PO_4^{3-}): Prepared by dissolving 19 g of disodium hydrogen phosphate in 1 litre of distilled water. The phosphate ion concentration was determined by precipitating phosphate as MgNH_4PO_4 , followed by the EDTA titration of excess magnesium in the supernate.²

Buffer solutions: Acetate buffer pH 4 (sodium acetate and acetic acid) and succinate buffer pH 7 (sodium succinate), prepared according to standard practice. All other chemicals were reagent grade.

Apparatus

A Beckman Model DU spectrophotometer, equipped with a tungsten lamp and 1-cm Corex cells, was used for the spectrophotometric determinations. A glass electrode pH-meter (Horiba Model T) was used for all pH measurements, and a mechanical shaking apparatus with a time switch device was employed to ensure a constant reaction condition.

General procedure

The following general procedure was employed to investigate the influences of reaction conditions and of various interfering ions:

Pipette the standard phosphate solution, containing 0.15–5 mg of phosphate, into a 50-ml volumetric flask. Add 5 ml of buffer solution, 25 ml of water-miscible organic solvent and 0.1 g of lanthanum chloranilate (or thorium chloranilate) crystalline powder, and dilute the mixture to the mark with distilled water. After shaking the flask on a shaking machine for a given period, filter the solution through a filter paper. Discard the first portion of filtrate, then collect the middle portion into a Corex cell. Determine the absorbance of this solution at $530\text{ m}\mu$ against a reagent blank.

RESULTS AND DISCUSSION

Comparison of lanthanum chloranilate and thorium chloranilate

Both lanthanum chloranilate and thorium chloranilate were tried as reagents for the photometric determination of phosphate. When thorium chloranilate reacted with phosphate, however, thorium phosphate precipitated in a colloidal form which could not be removed by simple filtration; further, the colour intensity of the resulting solution was weaker than in the case of lanthanum chloranilate. On the other hand, the precipitate of lanthanum phosphate could be easily filtered, and lanthanum chloranilate was found to be a more suitable reagent for the photometric determination of phosphate. In the following investigations, only lanthanum chloranilate was employed.

Effect of organic solvents

As described previously¹, the use of a water-miscible organic solvent increased the sensitivity of the colour reaction. In the general procedure described above, ethanol, methanol, methylcellosolve, dioxan or acetone was added to the sample solution to give a final solvent concentration of 50%, and the results are shown in Fig. 1 and

Table I. With the same pH value and buffer solution, the order of decreasing sensitivity was 50% dioxan > 50% acetone, 50% methylcellosolve > 50% ethanol, 50% methanol > water. The absorbance of the reagent blank was, however, higher in 50% dioxan and in 50% methylcellosolve than in 50% ethanol and in water. The solvent system of 50% ethanol was therefore the most suitable, because it showed a fairly high sensitivity with a relatively low reagent blank.

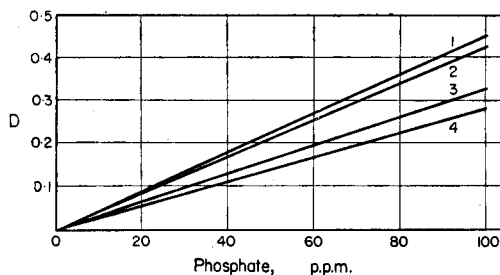


FIG. 1.—Effect of buffer and solvent on the absorption at 530 $m\mu$. (10 min shaking)

- 1: Acetate buffer, pH 4 and ethanol
- 2: Acetate buffer, pH 4 and methylcellosolve
- 3: Succinate buffer, pH 7 and methylcellosolve
- 4: Succinate buffer, pH 7 and ethanol.

TABLE I.—EFFECT OF ORGANIC SOLVENT ON SENSITIVITY AND ON REAGENT BLANK

Solvent	Absorbance		Absorbance difference
	Sample*	Reagent blank	
Water	0.227	0.026	0.201
50% Methanol	0.266	0.039	0.227
50% Ethanol	0.250	0.024	0.226
50% Methylcellosolve	0.319	0.059	0.260
50% Acetone	0.299	0.039	0.260
50% Dioxan	0.415	0.073	0.342

*Absorbance was determined on the sample containing 80 ppm of phosphate in the final solution at pH 7 (succinate buffer) after 10 min shaking.

Effect of pH and buffer solutions

The absorption spectrum of acid chloranilate ion in aqueous solution is greatly influenced by the pH of solution. The absorbance is at its maximum between pH 1 and 2, and it is progressively decreased with increasing pH value of the solution. The change in absorbance is less marked in the pH range of 5 to 12.³

If the colour reaction is carried out in the lower pH region, higher sensitivity will therefore be attained. At the same time, reproducible results will, however, hardly be obtained, and the interferences from anions are more marked in this pH region. The most suitable pH for the colour reaction was chosen as 7, where the absorbance was not appreciably influenced by pH and was less interfered by anions.

The composition of the buffer solution also affected the absorbance of acid chloranilate ion, as previously reported, and acetate and succinate buffers were found to be preferable for this procedure.

Reaction time

The condition of shaking was not so critical as in the case of fluoride determination. With the use of the shaking apparatus (350 strokes per min), the absorbance reached an almost constant value after 5 min, and no appreciable change in absorbance was observed by further shaking. The spectrophotometric determinations were therefore carried out after 10 min shaking.

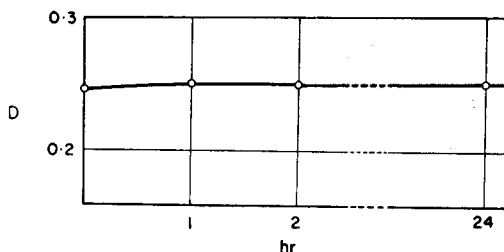


FIG. 2.—Stability of coloration. Determined on the sample containing 80 ppm of phosphate in the final solution, at pH 7 (succinate buffer) with 50% ethanol after 10 min shaking.

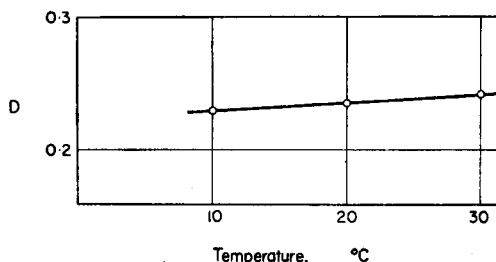


FIG. 3.—Effect of temperature. Determined on the sample containing 80 ppm of phosphate in the final solution, at pH 7 (succinate buffer) with 50% ethanol after 10 min shaking.

Stability of coloration and effect of temperature

The colour of the solution, once developed, was quite stable for many hours, and the absorbance after 24 h standing was almost the same as after 1 h, as shown in Fig 2. Hence, the absorbance can be measured at any time after the reaction.

The temperature during the reaction slightly affected the absorbance of the resulting solution, as shown in Fig. 3. The absorbance increased with increasing reaction temperature from 10° to 30°, but reproducible results could be obtained without taking any particular care for maintaining the reaction temperature constant.

Range of phosphate concentration

As Beer's law was obeyed for acid chloranilate ion up to 100 mg/100 ml, phosphate could be determined over a wide concentration range. The consumption of lanthanum chloranilate increased with increasing phosphate concentration in the sample solution, so that it was necessary to use an additional 0.1 g of the reagent for each 5 mg of phosphate present. With this procedure, it was possible to determine 0.15 to 15 mg of phosphate, or 3 to 300 ppm of phosphate in the final solution.

Interfering ions

Since almost all cations interfered in the determination, as in the case of fluoride

TABLE II.—INTERFERENCES BY ANIONS
(a) SULPHATE

Buffer	Solvent	Absorbance				
		Without sulphate	With sulphate			
			200 ppm	Error (%)	400 ppm	Error (%)
Succinate pH 7	Ethanol	0.226	0.248	+9.7	0.256	+13.3
Succinate pH 7	Methyl-cellosolve	0.260	0.293	+12.7	0.306	+17.7
Acetate pH 4	Ethanol	0.359	0.413	+15.0	0.423	+17.8

(b) CHLORIDE

Buffer	Solvent	Absorbance				
		Without chloride	With chloride			
			200 ppm	Error (%)	400 ppm	Error (%)
Succinate pH7	Ethanol	0.226	0.226	0	0.223	-1.3
Succinate pH 7	Methyl-cellosolve	0.260	0.259	-0.4	0.260	0
Acetate pH 4	Ethanol	0.359	0.339	-5.6	0.326	-9.2

(c) NITRATE

Buffer	Solvent	Absorbance				
		Without nitrate	With nitrate			
			200 ppm	Error (%)	400 ppm	Error (%)
Succinate pH 7	Ethanol	0.226	0.223	-1.3	0.221	-2.2
Succinate pH 7	Methyl-cellosolve	0.260	0.261	+0.4	0.263	+1.2
Acetate pH 4	Ethanol	0.359	0.333	-7.2	0.326	-9.2

The absorbances in the tables are the average of at least five determinations on a sample containing 80 ppm of phosphate in the final solution after shaking 10 min.

TABLE III.—COMPENSATION FOR SULPHATE INTERFERENCE

Sample composition	PO ₄ ³⁻ , ppm	80	80	80
	SO ₄ ²⁻ , ppm	800	1000	1200
Absorbance		0.274	0.272 (-0.7%*)	0.280 (+2.2%*)

* The difference from the value in the first column, %.

determination, it was necessary to remove previously all cations from the sample solution by means of ion-exchange. The only exception was ammonium ion which did not interfere, even in large amounts.

Interferences from anions such as sulphate, nitrate and chloride are summarised in Table II. With regard to nitrate and chloride, when the reaction was carried out at pH 7 with succinate buffer, no appreciable interference was observed up to 400 ppm of these anions.

The interference from sulphate was not negligible, even with small amounts. However, in the presence of amounts of sulphate greater than 800 ppm, the difference in absorbance due to the additional 200 ppm or 400 ppm of sulphate was found to be not more than $\pm 2\%$, as shown in Table III. Therefore, the interference due to sulphate could be compensated for by adding 800 ppm of sulphate both to the sample solution and to the standard phosphate solution.

Fluoride interfered seriously, even in small amounts, because it reacted with the reagent to form insoluble lanthanum fluoride.

Recommended procedure

After considering the results of the foregoing investigations, the following procedure is recommended for the determination of phosphate:

Place the sample solution, containing 0.15–5 mg of phosphate, in a 50-ml volumetric flask. To this, add 5 ml of 0.03M sodium succinate solution (pH 7), 25 ml of 95% ethanol and 0.1 g of lanthanum chloranilate crystalline powder, and dilute the solution to 50 ml with distilled water. Shake the flask for 10 min on a shaking machine (350 strokes per min), then filter the solution through a filter paper. Discard the first portion of the filtrate, and collect the middle portion in a cell for spectrophotometric measurement. Determine the absorbance at 530 m μ against a reagent blank. Obtain the phosphate concentration from a calibration curve which has been prepared from the standard phosphate solution by the same procedure.

Further study of this procedure and the practical applications is now being made, and the results will be published elsewhere.

Zusammenfassung—Die spectrophotometrische Bestimmung von Phosphat unter Verwendung von Lanthanchloranilat wurde untersucht. Es ist möglich 3–300 ppm Phosphat auf $\pm 2\%$ genau zu bestimmen, wenn geeignete Bedingungen gewählt werden. Chlorid- und Nitration stören nicht bis hinauf zu 400 ppm. Störungen durch Sulfat werden durch Zugabe einer grossen Menge Sulfats sowohl zu Probe als auch Vergleichslösung kompensiert. Die Methode ist einfacher, gestattet weinger strickte Reaktionsbedingungen und erzaugt eine stabilere Färbung als die conventionelle Heteropolysäuremethode.

Résumé—Les auteurs ont étudié le dosage spectrophotométrique du phosphate en utilisant le chloranilate de lanthane. Il est possible de doser 3 à 300 p.p.m. de phosphate avec une précision de $\pm 2\%$ en choisissant des conditions convenables. Les ions chlorure ou nitrate ne gênent pas jusqu'à 400 p.p.m. On peut compenser l'interférence du sulfate en ajoutant une grande quantité de sulfate aux deux solutions: solution standard et celle contenant l'échantillon. La méthode est plus simple, tient mieux compte des conditions de la réaction et donne une coloration plus stable que les méthodes conventionnelles mettant en jeu un hétéropolycide.

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ANALYTICAL CHEMISTRY OF α -BENZOINOXIME COMPLEXES OF MOLYBDENUM, TUNGSTEN AND VANADIUM

HENRY J. HOENES* and K. G. STONE

Department of Chemistry, Michigan State University,
East Lansing, Michigan, U.S.A.

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Summary—Molybdenum^{VI} is precipitated by α -benzoinoxime as $\text{MoO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})_2$ from acid solutions from pH 2 to 5% by volume sulphuric acid. The procedure of Knowles for molybdenum in steel is modified to yield precipitates which can be weighed without ignition to the oxide. In extraction of this molybdenum complex into chloroform the interference of tungsten and vanadium is eliminated by adding dihydrogen phosphate ion and ferrous ion. Tungsten^{VI} forms $\text{WO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})_2$ on addition of α -benzoinoxime to tungstate solutions freshly acidified with sulphuric acid. Precipitation of tungsten as this complex is not complete even in the presence of fluoride or phosphate ions. Extraction of the tungsten complex into chloroform is not feasible because of its limited solubility. Vanadium^V with α -benzoinoxime forms a yellow precipitate at pH 3, and on long standing at pH 1.5 a white precipitate. The yellow precipitate changes to the white precipitate with time. The white precipitate has the composition $\text{VO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})$ but is always contaminated with excess reagent. Using the α -benzoinoxime complex, vanadium^V can be extracted at pH 2.2 into chloroform and converted into the 8-quinolinol complex for measurement. Bismuth, antimony^{III} and uranyl ions interfere slightly. Chromium^{VI} in acid solution oxidises α -benzoinoxime so rapidly that studies were not possible.

INTRODUCTION

FEIGL¹ first used α -benzoinoxime as a reagent for the precipitation of copper. Knowles² found that α -benzoinoxime precipitates molybdenum^{VI} from acid solution. In this procedure tantalum, niobium, and silicon contaminate the precipitate by formation of insoluble hydrated oxides; tungsten^{VI} and palladium^{II} appear to be quantitatively precipitated; and the possible interference of chromium^{VI} and vanadium^V is prevented by reduction. Yagoda and Fales³ reported that molybdenum and tungsten are quantitatively precipitated together, provided that both are present. Variations of these procedures have been summarised by Flagg⁴, Blanco⁵, and Jensen and Weaver⁶. Recently Jeffrey⁷ and Goldstein, Manning, and Menis⁸ have used α -benzoinoxime as a reagent for the extraction of molybdenum into chloroform.

In all of these procedures molybdenum^{VI}, tungsten^{VI}, vanadium^V and chromium^{VI} are said to form complexes of some stability in acid solution or to interfere in the use of α -benzoinoxime as a precipitating reagent. With the exception of the palladium complex, the characterisation of the metal complexes formed from acid solution is incomplete. In addition, the nature of the metal ions in acid solution has been the subject of investigations for many years.

This paper presents an account of the composition of the complexes from extraction or precipitation studies; the effects of solvent composition, pH, and excess reagent on the precipitation of molybdenum^{VI}; the extraction of molybdenum and

* Present address: Columbia Southern Chemicals, Barberton, Ohio.

vanadium, and the effect of tungsten; and correlation of this work with the literature on the nature of molybdenum^{VI}, tungsten^{VI}, and vanadium^V in solution.

EXPERIMENTAL

All chemicals used were C. P. or reagent-grade with the following exceptions. The α -benzoinoxime used was obtained from Paragon Testing Laboratories, and was recrystallised from ethanol where high purity was required. The quercetin, m.p. 195°, was a special student preparation. The pH measurements were made with a Beckman model H2 pH meter with glass and calomel electrodes. Spectra and single wavelength measurements were taken with a Beckman model DK2 automatic recording spectrophotometer or a Beckman model DU spectrophotometer.

The following general methods were used. Where specific details are important, these will be provided in the discussion. Any variations will be noted also.

Precipitation studies were done as follows. Solution containing the desired amount of the element being studied was pipetted using a calibrated pipette into a 150- or 250-ml beaker. The acidity was adjusted and any additional materials were added. The desired amount of α -benzoinoxime dissolved in 50% acetone, or in some cases in ethanol, was then added from a burette equipped with a Teflon stopcock. The solution was stirred during the addition of the reagent. After the precipitates had stood for the required time, they were collected on weighed, 30-ml, medium porosity, sintered-glass crucibles. They were then washed, care being taken to wash down the sides of the crucibles, and were dried to constant weight at 105°.

To determine the amount of metal in the complex, some of the previously dried complex was ignited at 500–550° in silica crucibles, and the metal content was calculated from the weight of oxide obtained.

All extractions were done batchwise. The solution to be extracted was placed in a 60-ml separatory funnel and additional materials in solution were added. Acidity was controlled by adding acid to the separatory funnel, except that where close pH control was required, the pH was adjusted before adding the solution to the funnel. Extractions were carried out by adding controlled amounts of α -benzoinoxime in chloroform solution from a burette equipped with a Teflon stopcock and shaking the separatory funnels in a mechanical shaker. The chloroform layer was drawn off into a volumetric flask, the aqueous layer was extracted with chloroform which was added to the previous extract, and the chloroform was made to volume. Metals were determined in aliquots of this solution or in the whole solution by adding the reagents and measuring the colour intensity.

The method of continuous variations could not be used to establish the metal:reagent ratio in the complexes because no difference in absorption between the reagent and the complex was found. The metal:reagent ratio was derived from extraction or precipitation results.

RESULTS AND DISCUSSION

1. Molybdenum complex with α -benzoinoxime

The exact nature of the molybdenum^{VI} species in acid solution is not clear. In the review of the literature by Huckel⁹ it is stated that at pH 0.9 polymerised molybdenum trioxide precipitates, but in more acid solution molybdenum trioxide is depolymerised and redissolves. Other workers^{10,11,12,13} have reported that MoO₂²⁺ ion appears to be the major species in hydrochloric and sulphuric acid solution. Molybdenum^{VI} is precipitated by 8-quinolinol from slightly acid solution as bis(8-quinolinolo)dioxomolybdenum¹⁴.

When α -benzoinoxime in 50% aqueous acetone is added to solutions of molybdenum^{VI}, no precipitation occurs in the range pH 2.5–7. At pH 1.5 and 2.5 a slight cloudiness is observed, and in solutions more acid than pH 1 a heavy, white, flocculent precipitate is formed. This behaviour suggests that the complex is formed from the MoO₂²⁺ ion. Since α -benzoinoxime is not soluble in water, the solubilities had to be determined for various alcohol-water and acetone-water compositions and are

summarised in Table I. The solubility of the molybdenum- α -benzoinoxime complex in the same media is included here for conciseness.

As mentioned previously, when the method of continuous variations was tried in 50% ethanol containing 5% hydrochloric acid, solutions containing α -benzoinoxime or the molybdenum complex in equivalent concentration gave the same spectra. In order to establish the ratio of molybdenum to α -benzoinoxime in the complex, a variation of the extraction method of Goldstein, Manning, and Menis⁸ was used.

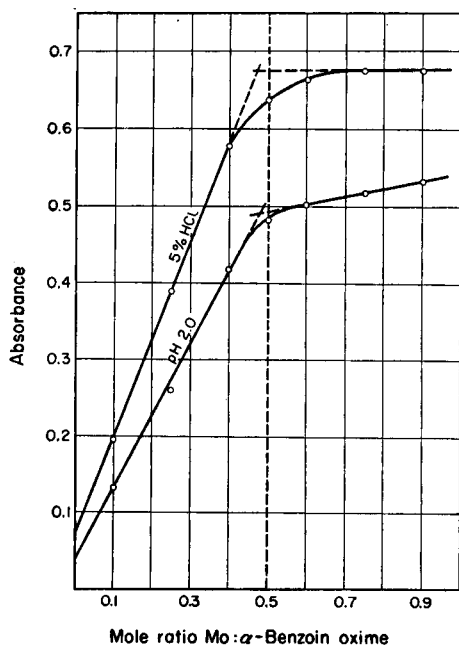


FIG. 1. Determination of molybdenum: α -benzoin oxime ratio by extraction procedure.

A series of 10-ml portions of 5% hydrochloric acid solutions containing 0.2 – $1.8 \times 10^{-3}M$ molybdenum^{VI} were extracted with 20 ml of $1 \times 10^{-3}M$ α -benzoinoxime in chloroform, and the aqueous layer was washed with 10 ml of chloroform using a 15-min shaking time in both cases. The combined chloroform extracts were diluted to 50 ml. A 2-ml aliquot plus 3 ml of 0.1% quercetin in ethanol was diluted to 25 ml with ethanol and measured at $420 m\mu$ against a quercetin blank. The results are shown in Fig. 1. There is a break in the curve where the ratio of Mo to α -benzoinoxime is slightly less than 1:2, which indicates that the precipitate in the absence of chloroform should have this composition. The extractions were repeated with the water layer adjusted to pH 2. The results are also shown in Fig. 1. It is clear that 1:2 composition is still present, but that the extraction is incomplete. This is in agreement with the suggestion that formation of the MoO_2^{2+} species is not complete until the acidity is greater than pH 0.9.

Preliminary experiments to determine the composition of the molybdenum^{VI}- α -benzoinoxime complex indicated that the blue colour noted by previous workers⁴ was caused by reduction of molybdenum by excess α -benzoinoxime in the precipitate. To prepare a sample of pure complex, 20 ml of $0.0156M$ α -benzoinoxime in ethanol was added dropwise to 40 ml of ice-cold $0.0052M$ molybdenum^{VI} in 5% sulphuric

acid. After 15 minutes standing the precipitate was filtered, washed twice with 5 ml of ethanol to remove excess reagent, and dried at 105°. The white precipitate did not turn blue, and in a separate test it melted sharply at 158–9°. Three more samples were prepared in the same way. These were dried at 105° and weighed, and on ignition to MoO₃ they gave 16.40, 16.52, and 16.45% Mo in the dried precipitate.

Since molybdenum^{VI} exists in acid solution as MoO₂²⁺ and the complex contains

TABLE I. SOLUBILITY OF α -BENZOINOXIME (ABH) AND MOLYBDENUM COMPLEX OF α -BENZOINOXIME (Mo-ABH)

Solvent, Volume %	ABH, g/100 ml	Mo-ABH, g/100 ml
Water-Ethanol		
25	0.20	
50	0.30	
75	1.25	
Water-Acetone		
25	0.20	0.004
50	1.90	0.006
100	13.50	0.014

molybdenum: α -benzoinoxime in a 1:2 ratio, it appears that the molybdenum^{VI}- α -benzoinoxime complex should be described as bis(α -benzoinoximato)dioxomolybdenum^{VI}, MoO₂(C₁₄H₁₂O₂N)₂. This complex contains 16.51% Mo, is based on MoO₂²⁺, and has the correct ratio of molybdenum to α -benzoinoxime.

TABLE II. EFFECT OF ACETONE CONCENTRATION

% Acetone at end	Mo taken, mg	Mo found, mg	Error, mg
33	12.5	12.1	-0.4
25	12.5	12.3	-0.2
20	12.5	12.4	-0.1
20	12.5	12.5	—
15	12.5	12.5	—
15	12.5	12.6	+0.1

Quantitative precipitation of molybdenum

Quantitative precipitation of the complex was attempted. Based on the results in Table I, acetone was used as the solvent for the reagent. From preliminary experiments it was clear that the acetone concentration was critical and that the precipitate matted on the crucible if it was not covered with wash liquid. The results in Table II show that up to 20% acetone can be present in the final solution without affecting the results. With some acetone present, precipitation of excess reagent is not a factor. Since it is very difficult to tell when enough reagent has been added, another series of experiments was run to check the effect of excess reagent. In all cases the final acetone concentration was held to 15–20% by addition of water. The results are summarised in Table III. Further experiments using 25, 50, and 100 mg of Mo showed

that up to 100 mg of Mo could be precipitated. However, 25 mg is the largest convenient amount because above this the washing and handling of the precipitate becomes difficult. With 50 mg the precipitate mats together, and washing becomes extremely slow.

In previous work¹⁵ niobium, silicon, tantalum, palladium, tungsten^{VI}, vanadium^V, and chromium^{VI} interfered in the precipitation of molybdenum^{VI}. The precipitation of palladium by the reagent cannot be avoided and palladium must be absent.

TABLE III. EFFECT OF EXCESS REAGENT

% Excess of Oxime	Mo taken, mg	Mo found, mg	Error, mg
10	12.5	12.4	-0.1
25	12.5	12.5	—
50	12.5	12.4	-0.1
100	12.5	12.4	-0.1

Niobium, silicon, and tantalum are precipitated as hydrated oxides by the acid and can be separated, provided that no molybdenum is carried down by the hydrated oxide. Tungsten^{VI} is precipitated by the reagent and must be absent.³ The interference of vanadium^V and chromium^{VI} is avoided¹⁵ by reduction with sulphur dioxide or ferrous ammonium sulphate. In the regular procedure for determining molybdenum in steel,² vanadium and chromium do not interfere. It was necessary to

TABLE IV. EFFECT OF Fe, Cr, AND V ON Mo^{VI} PRECIPITATION

Added			Mo taken, mg	Mo found, mg	Error, mg
Fe ₂ (SO ₄) ₃ ·XH ₂ O, g	CrO ₃ , g	V ₂ O ₅ , g			
2.5			25.0	25.0	—
2.5			25.0	24.9	-0.1
	0.02		25.0	24.8	-0.2
	0.02		25.0	25.1	+0.1
		0.04	25.0	25.1	+0.1
		0.04	25.0	25.1	+0.1
2.5	0.02	0.04	25.0	25.0	—
2.5	0.02	0.04	25.0	24.9	-0.1

check the interference of Fe^{III}, Cr^{III}, and V^{IV} in precipitation of the complex. When the precipitate from a sulphuric acid solution containing both Mo^{VI} and Fe^{III} was washed with aqueous acetone to remove reagent, the precipitate turned brown showing hydrolysis of the iron. This difficulty is eliminated by using 1% sulphuric acid to transfer the precipitate to the crucible and to wash the precipitate before the 50% acetone wash. Cr^{VI} and V^V were added to Mo^{VI} solutions and then excess ferrous ammonium sulphate was added to form Cr^{III} and V^{IV}. The precipitation of Mo^{VI} was then carried out as described using the sulphuric acid wash. Typical results of all these experiments are summarised in Table IV. It is apparent that Fe^{III}, Fe^{II}, Cr^{III}, and V^{IV} do not interfere in the determination of Mo^{VI} by the following recommended procedure.

Procedure: To 25 ml of 5% sulphuric acid containing 8–20 mg of Mo^{VI} add excess ferrous ammonium sulphate to reduce chromium and vanadium, and then dropwise, with stirring, 10 ml 0.05M α -benzoinoxime in 1:1 aqueous acetone. After 10 min decant into weighed sintered-glass crucibles. Wash by decantation with 5 ml of 1% sulphuric acid and transfer the precipitate using water. Do not allow all the solution to be drawn out of the crucible or the precipitate will mat. Wash the walls of the crucible and the precipitate with two 5-ml portions of 1:1 aqueous acetone. Dry at 105° for 1 h and then for 0.5-h periods to constant weight. The precipitate contains 16.51% Mo.

TABLE V. DETERMINATION OF MO IN NBS STEELS

NBS No.	Mo, %	Sample, g	Complex, g	Mo found, %
106	0.164	5.0620	0.0497	0.162
		5.0063	0.0493	0.163
		4.9964	0.0492	0.163
139	0.178	5.0135	0.0547	0.180
		5.0685	0.0565	0.182
		5.1698	0.0549	0.175
159	0.414	3.9952	0.1007	0.416
		3.9921	0.0996	0.412
		4.1141	0.1049	0.420
36	1.01	2.1918	0.1335	1.014
		2.1219	0.1290	1.004
		1.9974	0.1217	1.006

This procedure was then used to determine Mo in some NBS steels which contained no tungsten. The procedure of Knowles² was used to dissolve the samples, oxidise the carbon, and remove insolubles. Since the volume was large, acetone was added to give 15–20% acetone by volume after the reagent was added. These results are summarised in Table V.

Extraction of molybdenum

Goldstein, Manning, and Menis⁸ determined small amounts of molybdenum by extraction with α -benzoinoxime followed by determination with quercetin. Both vanadium and tungsten were found to interfere in the determination. Since the interference of vanadium^V in the precipitation of molybdenum was prevented by reduction with ferrous ion, the reduction of vanadium^V was tried in the extraction. In a later section it will be shown that phosphate ion prevents the precipitation of tungsten^{VI} by α -benzoinoxime. This was tried in the extraction. The solubility of the molybdenum complex in the extracts was improved by dilution with ethanol rather than chloroform as previously suggested.

Revised procedure: 1. Add 5 ml of KH₂PO₄ solution (1 ml = 1 mg KH₂PO₄) and 100 mg of ferrous ammonium sulphate hexahydrate to the 5% hydrochloric acid solution containing the molybdenum before extraction. Up to 4 mg of W^{VI} and 2 mg of V^V may be present when determining 1 mg of Mo^{VI}.

2. Dilute the washed chloroform extracts to 100 ml with 95% ethanol rather than with chloroform. The molybdenum complex dissolves in the ethanol.

3. Use 2 ml of the diluted extract to measure 1 mg of Mo^{VI}.

The results of the procedure using these changes are summarised in Table VI. It is seen that V^V requires a higher concentration of Fe^{II} for reduction in the absence of phosphate ion than in the presence of phosphate ion. Also there is a slight negative error caused by V^V plus phosphate ion in the absence of W^{VI} . It appears that our knowledge of the chemistry of complex ions is inadequate to explain these cases.

2. Tungsten complex with α -benzoinoxime

The nature of the tungsten^{VI} species in solution has been summarised by Huckel⁹ and by Bettinger and Tyree¹⁶. All workers agree that either H_2WO_4 or $H_2WO_4 \cdot 2H_2O$

TABLE VI. ELIMINATION OF INTERFERENCE OF VANADIUM AND TUNGSTEN IN THE EXTRACTION OF MOLYBDENUM

Interference, mg		Inhibitor, mg		Molybdenum, mg		
W^{VI}	V^V	KH_2PO_4	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Present	Found	Error
				1.00	0.98	-0.02
					1.00	—
					0.99	-0.01
1.0					1.45	+0.45
	1.0				1.15	+0.15
1.0		2.5			0.99	-0.01
1.0		2.5			0.99	-0.01
2.0		2.5			0.99	-0.01
	1.0		50		1.05	+0.05
	2.0		100		1.04	+0.04
	1.0		100		1.00	—
	1.0	2.5	100		0.95	-0.05
1.0	1.0	2.5	50		1.00	—
1.0	1.0	2.5	50		0.99	-0.01
2.0	2.0	5.0	100		1.01	+0.01

is precipitated from acid solutions. Phosphoric acid forms phosphotungstic acid with tungsten^{VI} but the exact nature and molecular weight of this compound in aqueous solution are unknown.¹⁷ The limiting composition in the solid state is $12W:1P$.⁹ A complex ion, $WO_2F_4^{2-}$, keeps tungsten^{VI} in solution in the presence of fluoride ion.^{18,19} From this point of view it is interesting that tungsten^{VI} is precipitated by 8-quinolinol from acid solution as $WO_2(C_9H_6ON)_2$.²⁰

To determine the ratio of tungsten to α -benzoinoxime in the complex the extraction procedure used for the molybdenum complex appeared to be applicable. Since tungsten was an interference in the quercetin method for molybdenum⁸ but no further work was done, the spectrum of the tungsten-quercetin complex was studied. Some tungsten- α -benzoinoxime complex was prepared by adding α -benzoinoxime in acetone to freshly acidified tungstate solution and washing out excess reagent from the precipitate with acetone. The precipitated complex was dissolved in ethanol and 0.1% quercetin in chloroform was added. The absorption spectrum is shown in Fig. 2. In addition to the peak at $425 m\mu$ a second broad absorption ($370-380 m\mu$) was found for tungsten. Molybdenum gave only a peak at $420 m\mu$ so that tungsten could be measured at $375 m\mu$ even in the presence of molybdenum. When the extraction of the tungsten- α -benzoinoxime was attempted, it was found that almost

no tungsten was extracted in spite of the appearance of a white precipitate at the water-chloroform interface. The addition of sodium dihydrogen phosphate decreased the amount of tungsten extracted. Since the tungsten- α -benzoinoxime complex appeared to be soluble in chloroform, the solubility was determined by evaporating a saturated solution to dryness and weighing the residue. The solubility was 0.12 mg of complex per ml of chloroform at room temperature. This solubility is too low to be of practical use for quantitative extraction, so the extraction experiments were abandoned.

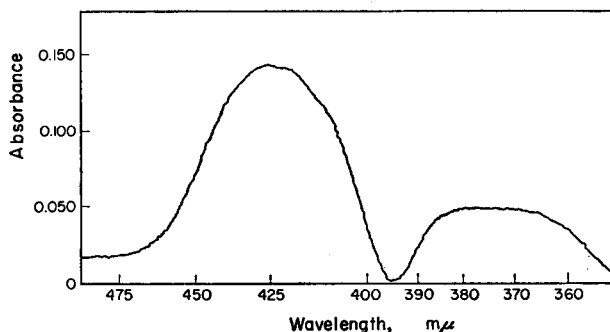


FIG. 2. Absorption spectrum of tungsten-quercetin complex versus quercetin.

Next, a series of solutions containing 0.1 millimole of tungstate ion in 10 ml of 4% sulphuric acid and 0.001M sodium dihydrogen phosphate were precipitated with α -benzoinoxime in 50% acetone as described for molybdenum. The samples using 0.04–0.4 millimole of α -benzoinoxime gave precipitates weighing from 1.4 up to 4.7 mg. These results suggest that phosphoric acid prevents the precipitation of the tungsten- α -benzoinoxime complex. The experiments were repeated omitting the phosphate addition but making the solution 0.1M in potassium fluoride to prevent precipitation of the tungsten. As the amount of α -benzoinoxime was increased, the weight of precipitate increased up to the mole ratio of tungsten to α -benzoinoxime of 0.5 as shown in Fig. 3. Thus it is seen that the precipitated complex contains one mole of tungsten to two moles of α -benzoinoxime.

Portions of a tungsten solution were made 15% in acetone and slightly more than 2 moles of α -benzoinoxime in 50% acetone per mole of tungsten were added. The precipitates were filtered, washed with small portions of 50% acetone to remove excess reagent and with water, and dried at 110°. The dried material was ignited at 500° and weighed as tungstic oxide. The results are listed in Table VII. Since the precipitate was expected to be $WO_2(C_{14}H_{12}O_2N)_2$, which contains 27.51% tungsten, the average of 27.58% tungsten found combined with the proper ratio supports the formula expected from analogy with the molybdenum complex as well as the 8-quinolinol-tungsten precipitate.

Attempted precipitation of tungsten

Since it was found that tungsten gave an α -benzoinoxime precipitate of definite composition, the gravimetric determination of tungsten by a procedure analagous to that for molybdenum was tried. The solubility of the complex in acetone solutions was checked by evaporating 150-ml portions of solutions saturated at 25° and

weighing the residues. From the results in Table VIII it is seen that the tungsten complex is only sparingly soluble in dilute acetone and that no great losses will result using 15% acetone as the solvent, as was done with the molybdenum.

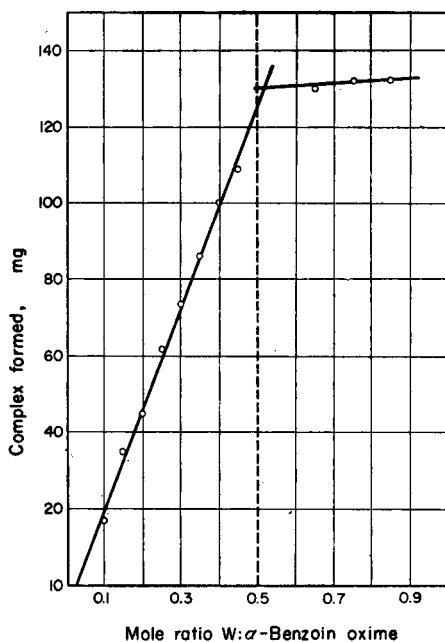


FIG. 3. Precipitation of tungsten complex with varying amounts of α -benzoin oxime.

TABLE VII. TUNGSTEN IN THE α -BENZOINOXIME COMPLEX

Complex, g	0.1848	0.1949	0.2073	0.1987	0.1720
WO ₃ , g	0.0645	0.0681	0.0715	0.0689	0.0691
% W in Complex	27.68	27.70	27.42	27.50	27.59
Average	27.58				

TABLE VIII. SOLUBILITY OF TUNGSTEN- α -BENZOINOXIME COMPLEX

Acetone, Volume %	Complex mg/ml
50	0.30
25	0.19
15	0.02

The original precipitation was made by acidifying a tungstate solution with sulphuric acid and adding α -benzoinoxime in 50% acetone. The precipitate obtained weighed only half as much as expected and by visual inspection contained tungstic oxide. When the tungstate solution was acidified with hydrochloric acid, and potassium fluoride was added to keep the tungsten in solution, again only half the expected weight of α -benzoinoxime precipitate was found. On acidification of the tungstate solution with sulphuric acid and adding a 20% excess of potassium fluoride based on the $\text{WO}_2\text{F}_4^{2-}$ ion, the α -benzoinoxime precipitates obtained were always slightly less

than expected. In addition, anything which consumed fluoride ion, such as ferric ion, caused low precipitate weights. It appears that the fluoride:tungsten ratio is quite important.

A series of equal samples of tungstate solution were mixed with varying amounts of potassium fluoride, acidified with sulphuric acid, and precipitated with α -benzoinoxime, and the precipitates were weighed and calculated as $\text{WO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})_2$.

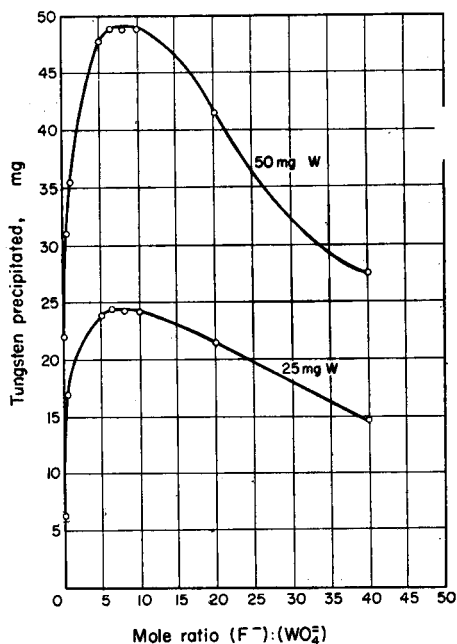


FIG. 4. Effect of fluoride ion concentration on tungsten precipitation.

From the results in Fig. 4 it is seen that the ratio of fluoride ion to tungsten must be controlled more closely than is reasonable for unknown samples. Therefore further investigations were abandoned.

Yagoda and Fales³ reported the simultaneous precipitation of molybdenum and tungsten by α -benzoinoxime. Based on the preceding experiments it is clear that Yagoda and Fales were successful because the mixture was ignited to oxides and that the precipitate probably contained molybdenum- α -benzoinoxime complex, tungsten- α -benzoinoxime complex, and tungstic oxide.

3. Vanadium complexes with α -benzoinoxime

The literature on the vanadium^V species in acid solution has been thoroughly reviewed by Rossotti and Rossotti²¹. Using spectrophotometric and potentiometric measurements VO_2^+ ion was found to be the sole species in the pH range ± 0.5 to 1.3. In the pH range 2.5–3.5, $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ ion was the predominant species. From pH 1.3 to 2.5 both ions were present in varying proportions. When an acetone solution of α -benzoinoxime was added to vanadium^V solutions, the following results were found. Above pH 4 no precipitate formed. At pH 2.8 and 2.0 a yellow precipitate formed, with much more at pH 2.0. At pH 1.5 a white precipitate formed only after long standing.

In an attempt to characterise the yellow precipitate, portions were washed with 1:1 aqueous acetone, dried under various conditions and ignited to vanadium pentoxide. The vanadium content was found to vary widely; the yellow precipitate changed colour from 115–130°, and the crystals did not melt sharply. It was concluded that the yellow precipitate was not a pure compound. Quite accidentally it was discovered that when the yellow precipitate stood in the mother liquor for several hours, it was converted to a flocculent white precipitate which was not α -benzoinoxime. When portions of this were washed with acetone to remove excess reagent, dried at 105°, and ignited to vanadium pentoxide, successive samples of

TABLE IX. pH EFFECTS ON VANADIUM- α -BENZOINOXIME PRECIPITATION

pH	Precipitate	
	Immediate	After 2 days
3	yellow	yellow
2	yellow	white
1.5	none	white

white precipitate were found to contain 16.43, 16.53, 16.40, and 16.56% vanadium. The expected precipitate, $\text{VO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})$, contains 16.47% vanadium. Additional experiments were conducted at different pH values. All of the experiments are summarised in Table IX. Qualitatively these results follow the experiments of Rossotti and Rossotti. At pH 3 the yellow precipitate would be based on a complex decavanadate which would not change. At pH 1.5 the white precipitate would be based on the VO_2^+ ion. At pH 2 the yellow precipitate changing to a white precipitate implies that the yellow precipitate dissolves to change to the less soluble, less complex white precipitate. A qualitative test showed that the yellow form was much more soluble in 1:1 aqueous acetone than the white form.

In an attempt to determine vanadium gravimetrically precipitations were made at pH 3 and allowed to stand, to change to the white precipitate, or precipitations were made by long standing at 1.5. In all cases the white precipitates were contaminated with excess reagent. If sufficient acetone was included to hold the excess reagent in solution, then the precipitation of vanadium was not quantitative. As a result, gravimetric studies were discontinued.

Extraction of the vanadium- α -benzoinoxime complex

Since the extraction of molybdenum^{VI} using α -benzoinoxime had been successful, the same process for vanadium^V was investigated. Preliminary experiments showed that the yellow complex was easily extracted into chloroform. Several difficulties soon became apparent. The extraction is dependent on the pH, with best results obtained at pH 2.2. The extraction is time dependent, with the best results found by 10-min shaking on an automatic shaker. The yellow complex is not stable, but fades with time. The last two difficulties may be attributed to the conversion of the yellow form to the white form which is less soluble in chloroform and colourless in solution. With larger amounts of vanadium the colour change was from yellow to greenish-blue, indicating reduction of the vanadium. One way to minimise these difficulties would be to transform the vanadium to a more tightly bound complex following extraction into chloroform.

A survey of the literature on vanadium complexes suggested that the vanadium 8-quinolinol complex²² was stable and had the advantage that the red colour (550 $m\mu$) was in a region where molybdenum and tungsten did not absorb. It was found that the complex formed readily on adding the chloroform solution of the vanadium- α -benzoinoxime complex to an ethanol solution of 8-quinolinol. To check this method the following procedure was used.

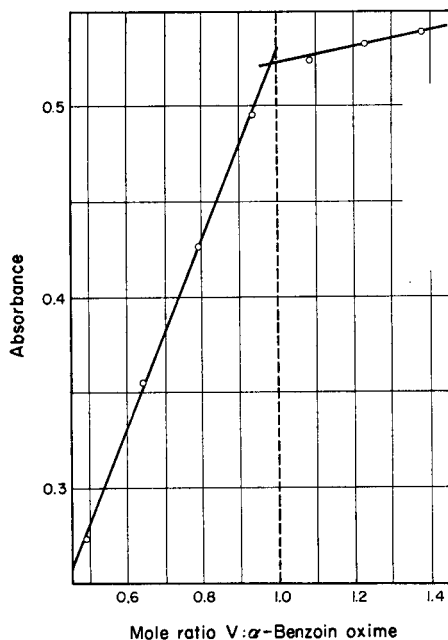


FIG. 5. Determination of vanadium: α -benzoin oxime ratio by extraction.

Procedure: A 10-ml portion of vanadium^V solution was adjusted to pH 2.2 with hydrochloric or sulphuric acid and extracted for 1 min with 10 ml of 0.1% α -benzoinoxime in chloroform. The chloroform extract was drawn off into a 100-ml volumetric flask containing 10 ml of 0.1% 8-quinolinol in 95% ethanol. The aqueous layer was extracted with two more 10-ml portions of α -benzoinoxime solution and finally with one 10-ml portion of chloroform. Twenty ml of 95% ethanol were added and the flask was filled to the mark with chloroform. After mixing, the absorption was measured at 550 $m\mu$ against a blank containing everything except the vanadium. It was found that Beer's law was followed for 5–80 μg of vanadium per ml of the starting aqueous solution. The extraction of the vanadium was complete as shown by a negative Feigl test.²³

This extraction method was used to establish the ratio of vanadium^V to α -benzoinoxime in the complex extracted. Solutions containing 0.01–0.0275 millimole of vanadium^V were extracted with two 10-ml portions of $1 \times 10^{-3}M$ α -benzoinoxime in chloroform (total 0.02 millimole) and the colour was developed and measured as before. The results are shown in Fig. 5. It is seen that the complex has a 1:1 composition and that excess reagent is needed to get quantitative extraction.

Determination of vanadium

The determination of vanadium^V by extraction with 8-quinolinol proposed by Talviti²² requires the removal of iron^{III} before extraction. Using α -benzoinoxime as previously described eliminates the effect of iron^{III} and does not introduce any other

difficulties. The vanadium in 10 ml of solution containing 0.049 mg per ml was determined as previously described. A variety of possible interfering ions was added. The results are summarised in Table X. The interference by antimony was caused by precipitation of a white substance which turned yellow with time, suggesting the adsorption of vanadium. This is supported by the decrease in vanadium found when the acid solution stands 24 h before extraction. The other low results are found with ions which form heteropoly acids with vanadium^V.

TABLE X. EFFECT OF IONS ON THE DETERMINATION OF VANADIUM

Ion, mg	Vanadium, mg		
	Present	Found	Difference
Mo ^{VI} 2.50	0.49	0.48	-0.01
W ^{VI} 2.50	0.49	0.47	-0.02
Cr ^{VI} 2.50	0.49	0.49	—
Mn ^{VII} 2.50	0.49	0.49	—
Cu ^{II} 2.50	0.49	0.49	—
Si ^{IV} 2.50	0.49	0.47	-0.02
Bi ^{III} 2.50	0.49	0.45	-0.04
U ^{VI} 2.50	0.49	0.46	-0.03
Sb ^{III} 2.50	0.49	0.43	-0.06
after 24 h		0.35	-0.14
H ₃ PO ₄ 1.25	0.49	0.49	—
Fe ^{III} 2.50	0.49	0.49	—
Al ^{III} 2.50	0.49	0.49	—

4. Chromium^{VI} complex with α -benzoinoxime

Since there is some evidence for the existence of CrO₂²⁺ in acid dichromate solution,⁹ experiments were run to determine if an α -benzoinoxime complex was formed. When α -benzoinoxime in 1:1 aqueous acetone was added to potassium dichromate in 5% by volume hydrochloric acid, a bright orange precipitate formed. Within minutes, however, the precipitate changed to a greenish-brown gummy mass. It appears that the reagent is oxidised by the chromium^{VI} so that no useful precipitations are possible. An attempt was made to extract chromium^{VI} from 5% hydrochloric acid using the procedure as described for vanadium. To test for chromium, diphenylcarbazide⁶ was used. The largest amount of chromium found was only 1% of that put into the solution to be extracted. It was therefore concluded that further work at this time was not worth while.

Acknowledgment—The financial support of the Socony Mobil Oil Company and the Renaud Foundation which made this work possible is gratefully acknowledged.

Zusammenfassung—Molybdän(VI) wird durch α -benzoinoxim als MoO₂(C₁₄H₁₂O₂N)₂ aus Lösungen von pH 2 bis hinauf zu 5 Volumpercent Schwefelsäure gefällt. Die Methode von Knowles zur Bestimmung von Molybdän in Stahl wird modifiziert, sodass der Niederschlag gewogen werden kann ohne erst zum Oxyd verglühen worden zu sein. Die bei der Extraktion des Komplexes mit Chloroform auftretende Störung durch Wolfram und Vanadin wird durch Zusatz von Dihydrogenphosphat und Eisen(II)-Lösung ausgeschaltet. Wolfram bildet eine analoge Komplex und fällt auf Zusatz des Reagens zu einer frisch mit Schwefelsäure angesäuerten Wolframsalzlösung aus. Die Fällung des Wolframs ist jedoch nicht komplett, selbst nicht in Anwesenheit von Fluorid- oder Phosphationen. Die Extraktion des Wolframkomplexes ist nicht anzuraten, da seine Löslichkeit zu gering ist. Vanadin(V) formt mit Benzoinoxim bei pH 3 einen gelben Niederschlag und bei

pH 1.5 nach langem Stehen einen weissen Niederschlag. Der gelbe Niederschlag geht bei längerem Stehen in die weisse Form über. Der weisse Niederschlag hat die Zusammensetzung $\text{VO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})_2$ enthält aber stets erhebliche Mengen von Fällungsmittel. Der Vanadinkomplex kann bei pH 2.2 mit Chloroform extrahiert werden und wird zur Messung in den Oxinkomplex übergeführt. Wismut, Antimon(III) und Uranyl verursachen leichte Störung. Chrom(VI) oxydiert das Reagens so rasch, dass keine Studien möglich waren.

Résumé—Le molybdène VI est précipité par l' α benzoïne oxime sous forme de $\text{MoO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})_2$ dans des solutions acides de pH 2 contenant jusqu'à cinq pour cent en volume d'acide sulfurique.

Le procédé de Knowles pour le dosage du molybdène dans les aciers est modifié afin d'obtenir des précipités qui peuvent être pesés sans calcination à l'état d'oxyde. Dans l'extraction de ce complexe du molybdène par le chloroforme, l'interférence du tungstène et du vanadium est éliminée par addition d'ion H_2PO_4^- et d'ion ferreux. Le tungstène VI forme $\text{WO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})_2$ par addition d' α benzoïne oxime à des solutions de tungstate fraîchement acidifiées par l'acide sulfurique. La précipitation du tungstène sous forme de ce complexe n'est pas complète même en présence d'ions fluorure ou phosphate. L'extraction du complexe du tungstène par le chloroforme n'est pas faisable à cause de sa solubilité limitée. Le vanadium V forme avec l' α benzoïne oxime un précipité jaune à pH 3 et, après un temps assez long, un précipité blanc à pH 1,5. Le précipité jaune se transforme à la longue en précipité blanc.

Le précipité blanc a la composition suivante: $\text{VO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})$ mais il est toujours contaminé par un excès de réactif. En utilisant le complexe avec l' α benzoïne oxime, le vanadium V peut être extrait à pH 2,2 par le chloroforme et transformé en un complexe avec le 8-quinolinol pour permettre des mesures. Le bismuth, l'antimoine III et les ions uranyl gênent légèrement. Le chrome VI en solution acide oxyde l' α benzoïne oxime si rapidement qu'aucune étude n'a été possible.

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THE ESTIMATION OF THE STABILITIES OF BIVALENT TRANSITION METAL COMPLEXES AND DEVIATIONS FROM THE IRVING-WILLIAMS ORDER

D. L. LEUSSING

Department of Chemistry, University of Wisconsin, Madison, Wisconsin, U.S.A.

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Summary—The free energies of formation of a range of ligands with Mn^{II} , Fe^{II} , Co^{II} and Zn^{II} have been related to ligand field stabilisations, and it has been found possible to predict on theoretical grounds deviations from the Irving-Williams order.

THE ligand field stabilisations in complexes of a given ligand with Fe^{II} , Co^{II} and Ni^{II} have been shown^{1,2} to be approximately proportional to the difference, Δ , in the free energies of formation of the complexes of Mn^{II} and Zn^{II} with the ligand. The free energies are corrected for the hydration energies of the metal ions. Thus, the course of the formation constants in the series Mn^{II} to Zn^{II} (with the possible exception of Cu^{II}) can be represented by such simple expressions that it is possible to calculate the constants for unknown members of the series if any two are known. With the aid of additional data taken from a recent compilation³ and results obtained in our laboratories⁴ it is possible to present more exact relationships covering a wider range of Δ values.

As before, the monotonic function which describes the increase in stabilities through the series Mn^{II} to Zn^{II} in the absence of any ligand field stabilisation is assumed to be linear. Some justification for this is given by the results of Holmes and McClure⁵ who show a linear increase in the resulting hydration energies of the bivalent transition metals after corrections are made for the spectroscopic ligand field stabilisation energies. Then from this assumption and definition of Δ the following equations can be set up:

$$\begin{aligned}\Delta &= \Delta F_{Zn} + \Delta H_{h_{Zn}} - \Delta F_{Mn} - \Delta H_{h_{Mn}} \\ \Delta F_{Ni} &= \frac{3}{5}\Delta + \Delta F_{Mn} + \Delta H_{h_{Mn}} - \Delta H_{h_{Ni}} + E_{lf_{Ni}} \\ \Delta F_{Co} &= \frac{2}{5}\Delta + \Delta F_{Mn} + \Delta H_{h_{Mn}} - \Delta H_{h_{Co}} + E_{lf_{Co}} \\ \Delta F_{Fe} &= \frac{1}{5}\Delta + \Delta F_{Mn} + \Delta H_{h_{Mn}} - \Delta H_{h_{Fe}} + E_{lf_{Fe}}\end{aligned}$$

where ΔF_M is the free energy of formation of a complex from the aquo ion, M^{2+} , ΔH_{h_M} is the hydration energy of M^{2+} and E_{lf_M} is the ligand field stabilisation energy of the complex.

Using the Benjamin and Gold hydration energies⁶ the equations became

$$\begin{aligned}\Delta &= \Delta F_{Zn} - \Delta F_{Mn} - 47.6 \text{ kcal} \\ \Delta F_{Ni} &= \frac{3}{5}\Delta + \Delta F_{Mn} + 62.3 + E_{lf_{Ni}} \text{ kcal} \\ \Delta F_{Co} &= \frac{2}{5}\Delta + \Delta F_{Mn} + 50.0 + E_{lf_{Co}} \text{ kcal} \\ \Delta F_{Fe} &= \frac{1}{5}\Delta + \Delta F_{Mn} + 17.9 + E_{lf_{Fe}} \text{ kcal}.\end{aligned}$$

These equations can be used to obtain the E_{lf} if the free energies are known or can be used to calculate unknown ΔF_M using two known values and the equations given below.

Simple proportionalities do not exist as first given,^{1,2} but the relationships between the E_{lf} and Δ can be described by linear equations, the parameters of which depend on the metal ion and the type of complex. For the Ni^{II} complexes three equations are sufficient. These represent straight lines which intersect at the point for the aquo ion. The octahedrally symmetrical complexes (Ni[H₂O]₆)²⁺, Ni en₃²⁺ and Ni[1:10-phen]₃²⁺ give the relationship

$$E_{lf} = 1.13\Delta + 20.3.$$

Those complexes with ligands that co-ordinate only through oxygen (oxalate, malonate and salicylaldehyde) also obey this relationship. It is thus indicated that not much difference exists in the behaviour of oxygen as a charged or uncharged donor, in this respect. Values of E_{lf} for the pyridine and 8-hydroxyquinoline-5-sulphonate complexes are also given by this equation.

For those mixed complexes in which both amino nitrogen and oxygen are co-ordinated, lower values of E_{lfNi} are given by

$$E_{lfNi} = 0.88\Delta + 8.1.$$

These complexes are represented by Ni(glycinate)(H₂O)₄⁺, Ni(glycinate)₂(H₂O)₂, Ni(EDTA)²⁻, Ni en(H₂O)₄²⁺, Ni en₂(H₂O)₂²⁺, Ni(nitrilotriacetate)(H₂O)₂⁻, Ni(2:2-diaminodiethylamine)(H₂O)₃²⁺, Ni(ethylenediamine-N:N-diacetate)(H₂O)₂ and Ni(2-methylthioethyliminodiacetate)(H₂O)_x. The complex Ni[N:N:N':N'-tetrakis (2-aminoethyl) ethylenediamine] also obeys this relationship. This may be an indication that all of the nitrogen atoms are not co-ordinated with this latter ligand. The lower stabilisation in this series probably results from the lower symmetry of the ligand field about the nickel ion.

The lowest values of E_{lfNi} are obtained with the complexes Ni(mercaptoacetate)₂²⁻¹ and Ni(2:3-dimercapto-1-propanolate)₂⁻.^{*7} Here the relationship is

$$E_{lfNi} = 0.35\Delta - 17.3.$$

The octahedral cobalt^{II} complexes give the result

$$E_{lfCo} = 0.84\Delta + 8.7$$

while in the mixed complexes (oxygen, nitrogen, sulphur) the relationship simply is

$$E_{lfCo} = 0.66\Delta.$$

The values of E_{el} for Fe^{II} are relatively small and for both octahedral and mixed complexes one equation suffices. This is

$$E_{lfFe} = 0.27\Delta + 4.2.$$

A departure from this occurs with the well known 1:10-phenanthroline. The observed value of E_{lfFe} for the tris-(1:10-phenanthroline) iron^{II} ion is much greater than

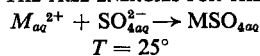
* The value of Δ was calculated using the formation constants of Mn(DMP)₂²⁻ and Zn(DMP)₂²⁻ which have been found to be $3 \times 10^{+10}$ and $1.8 \times 10^{+23}$ at 30° (ref. 4). These give the largest value of Δ so far observed.

would appear likely from the stabilities of the Mn^{II} , Ni^{II} and Zn^{II} complexes. This is a consequence of the fact that in the diamagnetic Fe^{II} complex all the electrons are in the t_{2g} orbitals and enter into π bonding with the ligand molecules.

In the absence of steric or other abnormal factors these equations give an uncertainty in ΔF of about ± 1 kcal for the larger Δ values. The uncertainty is less for small values of Δ . If a more accurate value of a constant is needed, be it is, of course, better to measure it under the prescribed set of conditions to be met in practice.

In addition to the case of tris-(1:10 phenanthroline) iron^{II} mentioned above, other deviations from the Irving-Williams order of complex stabilities are observed.

TABLE I.—THE FREE ENERGIES FOR THE REACTION



M	ΔF_{298} ^a obs, kilocalories	ΔF_{298} calc, kilocalories
Mn^{2+}	-3.07	(-3.07)
Fe^{2+}	—	-3.5
Co^{2+}	-3.21	-3.6
Ni^{2+}	-3.16	-3.2
Zn^{2+}	-3.25	(-3.25)

^a From Reference 9.

One deviation is found with the mercaptides where the Ni^{II} complexes are appreciably less stable than those of Zn^{II} . It appears that this is the result of abnormalities in the Ni^{II} complexes rather than in the Δ values as given by the Mn^{II} and Zn^{II} complexes. The Ni^{II} complexes are diamagnetic and the lower values of $E_{I/Ni}$ can be attributed to the electron repulsion energy which is lost in pairing up the electrons. If no delocalisation of electrons occurs through π bonding this energy is not regained and net lower stability results.

Another deviation from the Irving-Williams order occurs with the weak complexes. In the sulphates, for example, the Ni^{II} complex has been found⁹ to be less stable than even that of Co^{II} . The effect can be attributed primarily to the hydration energies, which are the largest in this series for the Ni^{II} ion. An analogy, in this respect, exists with the solubilities of the transition metal salts where an inversion of nickel also sometimes occurs¹⁰.

Calculated values of the free energies of formation of the sulphate complexes are given in Table I, together with those observed. It is seen that the relationships presented in this paper, which were obtained from systems in which the Irving-Williams order is obeyed, correctly predict the inversion with the Ni^{II} sulphate complex. The calculated free energies of formation compare favourably with those observed and the order of stability of the Ni^{II} complex is correctly placed.

Another deviation of this type must also occur with the chloride complexes. Here it is found that nickel^{II} is not extractable from solutions as an anionic chloro complex with ion-exchange resins even though media up to 10M-11M in hydrochloric acid have been used. The other metal ions in this series are, on the other hand, easily extractable.

Zusammenfassung—Die freie Energie der Komplexbildung einer Reihe von Liganden mit Mn(II), Fe(II), Co(II) und Zn(II) wurde zur Stabilisierung des Lignadfeldes in Bezuggesetzt. Es wurde gefunden dass es derart möglich ist auf Grund theoretischer Gründe Abweichungen von der Irving-Williams-Reihe vorauszusagen.

Résumé—Les énergies libres de formation d'une série de composés de Mn(II) Fe(II), Co(II) et Zn(II) ont été reliées aux "stabilisations du champ du composé" et l'auteur a trouvé qu'il était possible de prédire sur des bases théoriques, les écarts à l'ordre de Irving-Williams.

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A NEW METHOD FOR "FERROUS IRON" AND "EXCESS OXYGEN" IN ROCKS, MINERALS, AND OXIDES*

C. OLIVER INGAMELLS

Mineral Constitution Laboratories, The Pennsylvania State University
University Park, U.S.A.

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Summary—A new method is given whereby oxygen excess or deficiency in many minerals and oxides may be simply determined. The method depends on the stability in phosphoric acid-pyrophosphate mixtures of both Mn^{III} and Mn^{II} . The sample is dissolved in a phosphoric acid mixture containing excess Mn^{II} , with or without the addition of standard oxidant, and Mn^{III} remaining in solution or produced by reaction with the sample is titrated with ferrous ammonium sulphate, using barium diphenylamine sulphate as indicator. The method is useful in many cases where existing methods are inapplicable or unsatisfactory. Accurate results can be obtained using relatively small samples.

IN presenting the results of silicate rock and mineral analyses, it is standard practice to report both ferrous and ferric oxides. "Ferrous iron" is determined by solution of the sample in acid and titration with standard oxidant: the titration is assumed to be proportional to the ferrous iron content (after making certain corrections, e.g. for sulphides and insoluble material such as chromite), and it is calculated to FeO and reported as such. Ferric oxide is obtained by subtracting the equivalent of the FeO from the total Fe_2O_3 . Ferrous iron determination is discussed at length by Hillebrand *et al.*⁴

Although in most instances the volume of oxidant consumed by its acid solution is indeed a measure of the ferrous iron content of the sample, this is not always the case. The amount of ferrous iron in solution does not necessarily bear any relation to the number of Fe^{II} atoms in the sample itself. For instance, an equimolecular mixture of Fe_3O_4 and CeO_2 would show no ferrous iron by the usual procedures; neither would the oxide $Fe^{II}Fe^{III}Mn^{III}O_4$, though in each case Fe^{II} is an essential constituent.

It would thus seem that there are occasions when FeO should not be reported as such but, instead, a figure for "oxygen deficiency" should be given, just as "oxygen excess" is reported, for example, in the analyses of certain manganese ores. In interpreting such results, it should be understood that the figure reported represents the oxygen loss or gain necessary to bring all the elements in the sample to specified valency states. These valences need not be the maximum stable valences; for example, though manganese exists naturally in both the ter- and quadrivalent condition, it will invariably finish bivalent in the ferrous iron determination.

In certain mixed oxides, in particular Fe_2MnO_4 , there may be either an excess or deficiency of oxygen, and it would be highly desirable to have a method whereby either could be determined with accuracy: such a method is presented here.

The method depends on the stability, over a wide temperature range, of both bi- and tervalent manganese in a phosphoric acid-pyrophosphate mixture. Many

* Contribution No. 59-67, College of Mineral Industries, The Pennsylvania State University, University Park, Penna., U.S.A.

oxides and silicates are soluble in this mixture and, if these contain excess oxygen in the sense indicated above, they have only to be dissolved in the presence of a large excess of bivalent manganese; the resulting Mn^{III} may then be quite simply titrated with standard ferrous solution, using barium diphenylamine sulphonate as indicator. For "ferrous iron" or oxygen deficiency, a measured excess of oxidant, either permanganate or dichromate, is added to the acid mixture before dissolving the sample. The excess is then titrated as before with standard ferrous solution. The addition of either Mn^{VII} or Cr^{VI} to a phosphoric acid-pyrophosphate solution of Mn^{II} results in immediate oxidation of the latter to Mn^{III} .

The procedure is similar in its essentials to one described earlier⁵ for the determination of manganese. It resembles, in some respects, certain modifications of the Seil method⁶ for the determination of ferrous iron in chromite, particularly those of Shein⁷ and Goswami,² who used V^{V} and Ce^{IV} respectively as intermediate oxidants. These procedures have been discussed and evaluated by Dinnin.¹ In the author's experience, Mn^{III} , produced when dichromate or permanganate is added to phosphoric acid-pyrophosphate solutions of bivalent manganese, is more satisfactory than either V^{V} or Ce^{IV} for this purpose, provided that certain precautions are taken in the preparation of the reagents.

The new method is not universally applicable, being limited to samples which dissolve directly in phosphoric acid-pyrophosphate, do not contain elements (notably sulphur and organic carbon) which oxidise variably, and do not yield peroxides on solution in acid. Peroxide reduces Mn^{III} immediately. Among materials which do not dissolve readily under the conditions of the procedure must be listed silicates low in iron and some oxides containing Mn^{IV} .

Despite its limitations, the method has proved very useful, particularly in cases where other methods are inapplicable or unsatisfactory. It has been used successfully with chromite, various silicate minerals, and rocks, and for the determination of excess oxygen in various oxides. A good determination of either excess oxygen or ferrous iron can be made on a relatively small sample: 100 mg or less is often sufficient. This is of importance when only a small amount of material is available.

In most cases where both have been used, the new and older methods agree quite satisfactorily; however, with some silicates (samples 5, 8, Table I) results for ferrous iron by the new method appear low. Further, the excess oxygen in some oxides is not completely recovered (Table II). Thus its indiscriminate application is inadvisable.

EXPERIMENTAL

Reagents

Ferrous ammonium sulphate: 0.01N in 0.5% (V/V) sulphuric acid.

Manganous sulphate: Dissolve 100 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 100 ml of water. Filter through glass-fibre paper to remove small particles of organic material.

Sodium dihydrogen phosphate: Dissolve 200 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 200 ml of water. Filter through glass-fibre paper.

Phosphoric acid: Reagent-grade, 85% H_3PO_4 .

Potassium permanganate: 0.1N, accurately standardised.

Potassium dichromate: 0.1N.

Barium diphenylamine sulphonate: 0.2% aqueous solution.

Prepare a reagent solution for each sample as follows: add 20 ml of phosphoric acid, 5 ml of sodium dihydrogen phosphate solution, and about 0.5 ml (more if necessary to oxidise organic impurities in the reagents) of 0.1N potassium dichromate to a 250-ml wide mouth conical flask. Mix,

TABLE I.—COMPARISON OF RESULTS FOR FERROUS IRON

Sample	Description	Weight, <i>mg</i>	KMnO ₄ , <i>ml 0.1N</i>	FeO found	
				New method	Other methods
1	Shonkinite	250	5	12.94	13.19*
2	Chromite	150	5	21.23	21.32† 21.25‡
3	Garnet	200	2	6.09 6.10	5.71*
4	Grunerite	250	10	27.86	27.16*
5	Amphibole	100	3	17.86 17.85	18.48*
6	Pyroxene	200	5	17.29	17.27*
7	Biotite	200	10	29.53	29.22
8	Olivine	100	10	59.72	60.36* 60.44*
9	Ilvaite	200	10	31.14	31.16*
10	Granite G-1	500	1	0.94	0.97§
11	Diabase W-1	200	1	8.75	8.71§
12	Olivine	200	3	7.51	7.21*

* Solution in HF-H₂SO₄, titration with KMnO₄ in presence of H₃BO₃.

† Closed tube method.

‡ Method of Seil⁹.

§ Value reported by Goldich and Oslund⁸.

|| Result uncorrected for about 1% of chromite which remained largely unattacked.

TABLE II.—COMPARISON OF RESULTS FOR EXCESS OXYGEN

Sample	Description	Weight, <i>mg</i>	Excess oxygen, %	
			New method	Other methods
1	Iron-manganese oxide, Fe ₂ MnO ₄	500	0.202 0.202	
2	Iron-manganese oxide, Fe ₂ MnO ₄	500	0.340 0.341	
3	Manganese oxide, Mn ₃ O ₄	100	6.91 6.92	6.94* 6.97* 6.99†
4	Manganese oxide, Mn ₃ O ₄	100	6.94	6.93* 6.96* 6.99†
5	Manganese oxide, MnO	500	0.00	0.00
6	Manganese oxide	100	1.54	1.54†
7	Manganese oxide	100	3.06	3.04†
8	Ceric oxide	100	4.64	4.65†
9	Praseodymium oxide	173	2.76 2.65	3.13‡
10	Terbium oxide	100	1.84	2.14‡
11	Red lead	260	1.98	2.33‡
12	Cobalt oxide	120	4.02	6.64‡

* Solution in H₂SO₄-Fe^{II}, back titration with KMnO₄.

† Well-established calculated value.

‡ Calculated value, composition not certain.

and heat slowly, without boiling, gradually increasing the temperature until water is expelled and the excess chromate is destroyed. A final temperature exceeding 250° is required to remove excess chromate completely, but heating must not be continued to the point where insoluble polyphosphates separate. The solution should not be allowed to boil because of an extreme tendency to spatter.

Cool until the flask can be handled, then add about 2 ml of cold water. Mix, and cool to room temperature.

Add 1.0 ml of manganous sulphate solution, rinse down the sides of the flask with a very small volume of water, mix thoroughly, and add a measured excess of standard (0.1N) permanganate, sufficient to oxidise the ferrous iron expected and provide a small excess. It is essential that the manganous sulphate solution be thoroughly mixed with the acid before the permanganate addition. Dichromate may be used instead of permanganate if desired: in either case the effect is to add Mn^{III}. Dichromate has the disadvantage of imparting a green colour to the final solution which obscures the end-point somewhat.

Again evaporate the solution to remove most of the extra water added with the standard oxidant. This step may be omitted if water additions were kept to a minimum, and no more than 2.00 ml of the standard oxidant were used. If the sample is dissolved in a mixture containing much water, the pyrophosphate is depleted during solution to the point where Mn^{III} is no longer stable, and air oxidation of ferrous iron may occur.

If the sample contains excess oxygen, no addition of standard oxidant is required.

Sample

The sample weight should be chosen so that no more than 10 ml of standard (0.1N) oxidant need be used. If excess oxygen is to be determined, not more than 0.5 to 1.0 milliequivalents should be present.

Most samples require grinding to -115 mesh or finer. Chromite should be -325 mesh.

Procedure

To the prepared mixture, add the sample and shake or swirl until it is uniformly distributed. Rinse down the sides of the flask with a very small volume of water, and heat on the hot plate, without boiling, gradually increasing the temperature until attack is complete. Some materials dissolve rapidly even before water is expelled: others, chromite for example, do not react until the temperature of the mixture approaches or exceeds 300°. Some leave an insoluble fraction which may be ignored. With silicates, it is important that the sample be well dispersed, for particles which clump together and become coated with silicic acid may escape attack. Not more than 0.2 to 0.5 g of silicate mineral should be used under the conditions described, but with silicious rocks, up to 1 g will usually give no trouble.

When solution is complete, cool until the flask can be handled, add 5 ml of cold water, mix thoroughly, and cool in running water. Dilute to about 20% in phosphoric acid, cool to room temperature, and titrate with 0.01N ferrous ammonium sulphate solution, adding 1-2 drops of barium diphenylamine sulphonate indicator just before the end-point. It is best to delay the indicator addition until the pink colour of Mn^{III} is nearly discharged.

A blank determination should be made using a small volume of standard oxidant (say 0.100 ml of 0.1N permanganate). A small negative blank (about 0.2 ml of 0.01N solution) is always obtained. For example, 0.100 and 1.994 ml of 0.1001N permanganate gave titrations of 0.81 and 19.93 ml of 0.00993N ferrous ammonium sulphate solution when carried through the procedure, and 0.99 and 20.13 ml when titrated directly. The actual indicator blank is very small: about 0.02 ml of 0.01N solution.

If the reagents are not subjected to a preliminary treatment to remove oxidising and reducing impurities, the blank is very large and non-reproducible.

DISCUSSION

The procedure described for the preliminary treatment of the reagents to remove oxidising and reducing impurities is more effective than several others tried. Preparation of the reagent in bulk is possible, but has serious disadvantages: a high

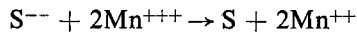
temperature is necessary to decompose chromate completely, and the resulting mixture tends to freeze into a glass on standing.

Because of the relative ease with which Mn^{II} is oxidised in phosphoric acid solution, the possibility of air oxidation was investigated, and it is certain that no such oxidation takes place under the conditions of the procedure. Likewise the stability of Mn^{III} has been established, though there is a possibility of slight loss of oxygen when heating is continued for several hours above 360° .

When determining ferrous iron, especially in samples which dissolve readily, it is essential that most of the water be evaporated from the reagent mixture before adding the sample. Failure to do this often leads to low results (presumably because the pyrophosphate formed in the early stages of reagent preparation becomes depleted, leaving the sample liable to air oxidation). With a ferrous olivine (sample 8, Table I) 57.18, 57.23, and 56.54% FeO were found when this step was omitted, as compared to 59.72% when the reagent was evaporated as directed. With chromite, which is unattacked below about 250° , the removal of excess water before addition of the sample makes very little difference to the results.

In the course of the titration, vanadium is reduced to V^{IV} ; when this element is present, a correction must be made if results are to be compared with those obtained by methods in which vanadium finishes in the quinquevalent condition.

The behaviour of sulphur and sulphides is not stoichiometric. Most metallic sulphides are completely attacked by the phosphate mixture containing excess Mn^{III} : some of the sulphur is volatilised in the elemental state; some is presumably oxidised to sulphate. The possibility of using an empirical correction based on the sulphide content of the sample was investigated, but results were not very satisfactory. If minor amounts of sulphide are present, a correction based on the relation



may be applied with fairly good results.

Most silicate minerals to which the method can be applied dissolve readily if passed through a 115-mesh screen, though amphiboles and pyroxenes must usually be -200 mesh. Chromite should be -325 mesh. Grinding is best done by hand in an agate mortar, with frequent screening to remove fines so that air oxidation is minimised. The samples should always be passed through the appropriate screen, then thoroughly mixed before the determination is attempted. Grinding without screening is certain to be unsatisfactory.

The heating period necessary for solution of the sample varies greatly. It does no harm to heat for 2 h or more at $200\text{-}250^\circ$ if attack is slow. At higher temperatures, Pyrex is attacked rapidly, and much silica is thereby introduced. Polyphosphates may separate on prolonged heating at elevated temperatures. It is best to heat at the lowest effective temperature, for if polyphosphates separate because of too rapid heating, these tend to coat particles of sample, greatly slowing the rate of solution. The use of Vycor flasks may be desirable with chromites.

During solution of some oxide samples, the Mn^{III} colour may fade after a preliminary development, sometimes with the deposition of dark-coloured oxides. This is presumably due to depletion of the pyrophosphate in solution. On further heating to remove water, the colour reappears, and the determination proceeds normally.

The behaviour of the rare earth oxides is of interest. Ignited ceric oxide dissolves readily in the hot phosphoric acid mixture, and the excess oxygen is quantitatively retained and titrated. Praseodymium oxide dissolves with the evolution of gases: whether this is due to peroxide formation or liberation of oxygen from solid solution is in doubt. Terbium oxide dissolves without perceptible gas evolution, but the values obtained for excess oxygen are less than indicated by the formula Tb_4O_7 .

Higher oxides of cobalt and lead (Co_3O_4 and Pb_3O_4) dissolve with the evolution of oxygen, and results for excess oxygen are low.

Acknowledgment—Thanks are due to A. I. Muan for supplying oxide samples of known composition, to R. O'Neil for helpful criticism, and to Marilyn Grender, who carried out many of the determinations during the development of the method.

Zusammenfassung—Eine neue Methode wird beschrieben, um Überschuss oder Mangel an Sauerstoff in Mineralen oder Oxyden einfach zu bestimmen. Die Methode beruht darauf, dass sowohl Mn(III) als auch Mn(II) in einer Mischung von Phosphorsäure und Pyrophosphate beständig sind. Die Probe wird in gegenwart oder Abwesenheit von Standard-Oxydans in einer Phosphorsäuremischung gelöst, die überschüssigess Mn(II) enthält. Das in Lösung vergleichende oder durch Reaktion mit der Probe gebildete Mn(III) wird mit Ferro-ammonsulfat gegen Diphenylamin als indicator titriert. Die Methode kann in vielen Fällen angewendet werden, in denen übliche Methoden versagen oder unbefriedigende Resultate liefern. Genaue Ergebnisse werden mit relativ kleinen Probemengen erhalten.

Résumé—L'auteur donne une nouvelle méthode par laquelle l'excès ou le manque d'oxygène peut être dosé simplement dans de nombreux minerais et oxydes. La méthode dépend de la stabilité de Mn(III) et Mn(II) dans les mélanges acide phosphorique-pyrophosphate. L'échantillon est dissous dans un mélange d'acide phosphorique contenant un excès de Mn(II), avec ou sans addition d'un oxydant standard; Mn(III) restant en solution ou produit par réaction avec l'échantillon est titré avec du sulphate d'ammonium et de fer ferreux, en utilisant la diphenylamine sulfonée comme indicateur. La méthode est utile dans de nombreux cas où les méthodes existantes sont inapplicables ou ne sont pas satisfaisantes. Des résultats précis peuvent être obtenus en utilisant des échantillons relativement petits.

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RADIO-FREQUENCY METHODS IN ANALYTICAL CHEMISTRY

M. F. C. LADD and W. H. LEE

Chemistry Department, Battersea College of Technology, London, S.W.11, England

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Summary—The theory of radio-frequency measurements of chemical importance is outlined, and suitable apparatus is discussed. The applications, especially to analytical chemistry, are reviewed.

INTRODUCTION

The first applications of radio-frequency (RF) measurements were concerned with dielectric constant determination. For example, the moisture content of powdered materials has been measured by packing them between the plates of a capacitor in an oscillatory circuit and observing the change in frequency by a heterodyne-beat method.^{1,2} The separation of organic mixtures by fractional distillation may be controlled by such dielectric measurements.² The classical work of Debye and Falkenhagen showed that ionic-atmosphere effects decreased with increase in frequency; a considerable change in equivalent conductance was observed³ above 30 Mc/sec. The absorption of higher frequencies (300–500 Mc/sec) by electrolyte solutions shows that the product of the wavelength for maximum absorption and the concentration of the solution in g-equiv/litre is a constant.⁴

Radio-frequency measurements were first used for the determination of titrimetric end-points in 1946,^{5,6} and since that time over one hundred and fifty publications have appeared on this subject. The apparatus used in these determinations has been of two main types: standard electronic measuring equipment adapted for this purpose; and specifically designed instruments (generally much simpler). Some commercial apparatus is now available. Operating frequencies have varied within the range 0.1–415 Mc/sec.

The conductivity cells in general use are distinguished from those employed in low-frequency conductivity work by having the electrodes on the outer wall of the cell or even dispensing with them altogether. The electrodes cannot, therefore, become polarised or contaminated by precipitation occurring within the cell; this is one of the principal advantages of the radio-frequency technique. Furthermore, changes which affect mainly the dielectric constant of the cell contents rather than its electrical conductance may be followed just as easily. To gain these advantages, however, it is necessary to operate at frequencies within the above mentioned range instead of at audio-frequencies.

Many attempts have been made to formulate a theory of the observed changes in terms of parameters of the oscillatory circuit, and to produce an electrical "equivalent circuit" for the cell used. The effects of change of frequency and concentration upon the shape of titration curves have been predicted from "transfer-plots."⁷

Applications of the radio-frequency technique fall conveniently into two classes: those which follow conductance changes within the cell as in conductimetric titrations, and those recording changes in dielectric constant of non-conducting solutions. The

technique has been applied also to flame-detection and measurement of flame speeds.⁸

A number of short reviews of this subject have appeared;⁹⁻¹⁵ accounts have been given in standard texts on instrumental chemical analysis;¹⁶⁻¹⁹ and monographs dealing specifically with the radio-frequency technique have been published.²⁰⁻²²

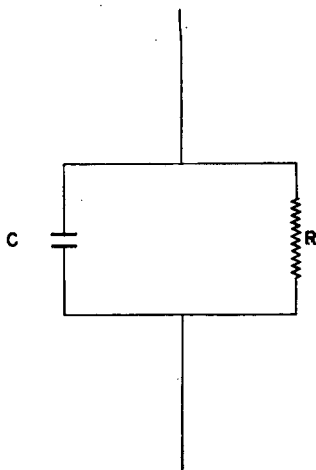


FIG. 1. Equivalent electrical circuit of LF conductivity cell.

THEORY

The conventional low-frequency conductivity cells with internal electrodes may be represented electrically by the circuit of Fig. 1. The resistance R is the parameter measured and C represents the capacity between the plates with the cell solution as dielectric together with the stray capacities between the bridge components and earth. In practice, C is balanced-out by a variable capacitor across the appropriate arm of the bridge.

The usual radio-frequency conductivity cell, a glass tube with band-electrodes on the outer wall, may be represented electrically^{23,24,7} by Fig. 2. C_2 is the capacity from the electrodes to the solution; the dielectric of this capacitor is the glass or ceramic cell-wall. C_1 and R_1 are respectively the capacitance and resistance of that part of the path between the electrodes through the cell-solution; this solution is, therefore, the dielectric of C_1 . The resistance through the cell-wall which shunts C_2 is normally so large that its effect is negligible. Typical values for the components in Fig. 2 relating to a cell of volume 100 ml and having band-electrodes of width $\frac{1}{4}$ in. spaced 1 in. apart are: $C_1 = 100$ pf, $C_2 = 30$ pf. If the cell be filled with 0.1N KCl solution, then R_1 is approximately 5 ohm.

Changes occurring within the cell affect C_1 and/or R_1 ; so that these fluctuations may influence the supply or detector circuits connected across AB , the reactance of C_2 must be relatively small. This is why it is necessary to make measurements with this type of cell at radio-frequencies; the reactance of C_2 at 1000 c/sec is about 5×10^6 ohm but at 10 Mc/sec this is reduced to 500 ohm. Again, increasing the capacity of C_2 by decreasing the cell wall-thickness or by using high-permittivity ceramic in place of glass improves the sensitivity by reducing the reactance of C_2 .²⁵ The impedance of the cell depends upon the frequency, which must therefore be maintained constant during an experiment.

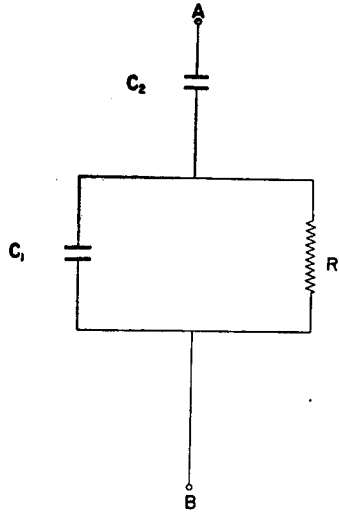


FIG. 2. Equivalent electrical circuit of RF conductivity cell.

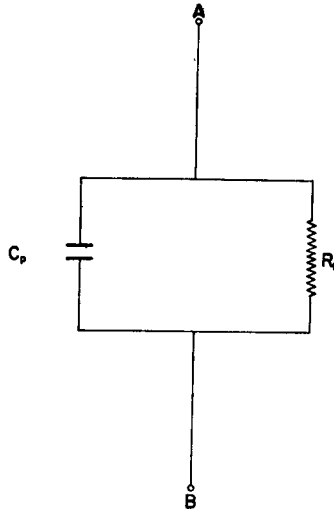


FIG. 3. Reduced equivalent circuit of RF conductivity cell.

The circuit of Fig. 2 may be simplified to that of Fig. 3 by equating the real and imaginary components of the reactance of each circuit; at a frequency of ω radian/sec these circuits are equivalent if

$$R_p = \frac{\kappa^2 + \omega^2(C_1 + C_2)^2}{\kappa^2\omega^2C_2^2} \quad (1)$$

and

$$C_p = \frac{\kappa^2C_2 + \omega^2C_1C_2(C_1 + C_2)}{\kappa^2 + \omega^2(C_1 + C_2)^2} \quad (2)$$

where $\kappa = 1/R_1$, *i.e.* the conductivity of the cell contents in ohm^{-1} .

The apparatus connected across *AB* responds to the parallel combination of Fig. 3; changes in C_1 and/or R_1 affect both C_p and R_p . Electronic impedance bridges (for example, the Twin-T Test Bridge²⁶ or the Wayne-Kerr Impedance Bridge²⁷) enable the

components C_p and R_p to be separately determined; actually C_p and $G_p (=1/R_p)$ are the quantities directly measured. Such test equipment can be used to follow the course of reactions within the cell, but it has been used mainly in fundamental investigations attempting to relate the measurements to the absolute specific conductance κ_0 and to the dielectric constant ϵ .

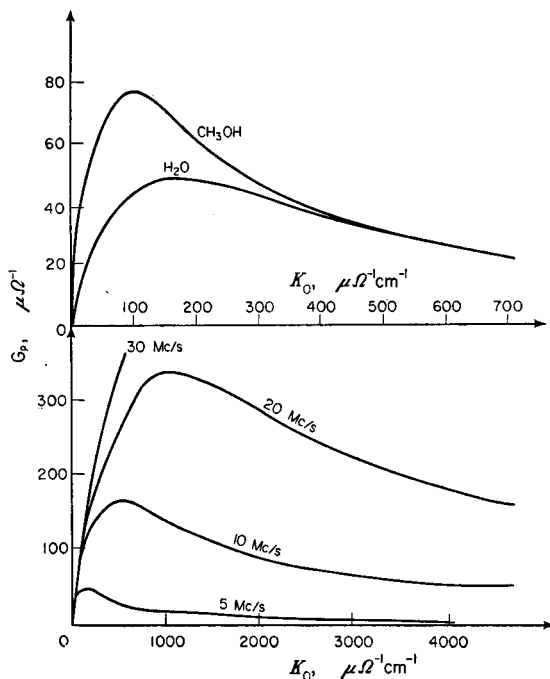


FIG. 4. Variation of G_p with κ_0 for change in dielectric constant and frequency (after ref. 7).

The variations of G_p and C_p with the low-frequency specific conductance κ_0 depend on frequency, Fig. 4, and upon the dielectric constant of the medium,⁷ Fig. 5. To determine κ from the equation,

$$G_p = \frac{\kappa \omega^2 C_2^2}{\kappa^2 + \omega^2 (C_1 + C_2)^2} \quad (3)$$

i.e. from the inverse of equation (1), or from equation (2), we require C_1 and C_2 for the cell. If the cell is filled with mercury, then $R_1 = 0$, $\kappa = \infty$ and from equation (2) C_p (Hg) = C_2 . Replacing the mercury with conductivity water, $\kappa = 0$, and C_p (H₂O) = $C_1 C_2 / (C_1 + C_2)$. With the cell previously considered, C_p (Hg) = 30 pf, C_p (H₂O) = 23 pf. C_1 and C_2 may then be determined and used in equation (2) or (3) to obtain κ at a known frequency, ω radian/sec.

For a cell in which the electrode area and spacing are effectively A and d respectively, the conductivity is related to the specific conductance of the solution in the cell by:

$$\kappa = \kappa_0 A/d.$$

The capacitance of the same cell filled with a liquid of dielectric constant ϵ is:

$$C_1 = \frac{\epsilon \cdot A}{4 \cdot 4\pi d} \text{ pf.}$$

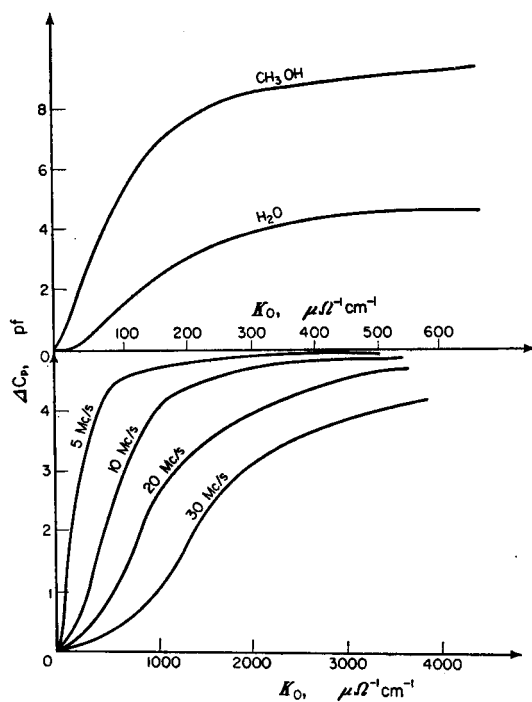


FIG. 5. Variation of ΔC_p with κ_0 for change in dielectric constant and frequency (after ref. 7).

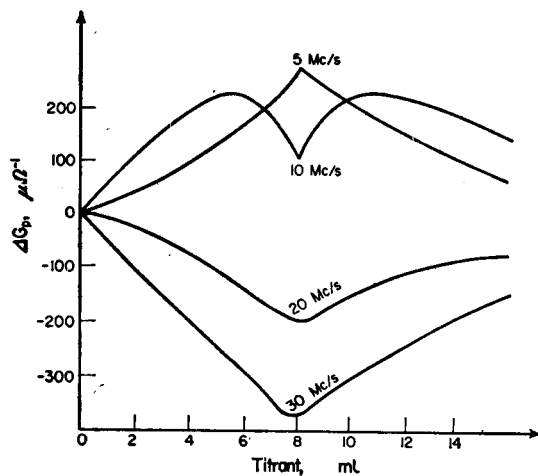


FIG. 6. Effect of change of frequency upon titration curves. HCl v NaOH (after ref. 28).

Hence, A/d , the cell-constant, = $\frac{4 \cdot 4\pi C_1}{\epsilon}$

and

$$\kappa = \kappa_0 \cdot \frac{4 \cdot 4\pi C_1}{\epsilon}$$

so that κ_0 may be determined from κ . For a given electrolyte, solvent and temperature, κ_0 is a function of concentration; thus, from Fig. 4 or 5, the corresponding variations of G_p or C_p with concentration may be derived for a given electrolyte.

The widely varying shapes of the curves representing G_p and C_p during the course of a titration are characteristic of the high-frequency method; typical response curves of G_p and C_p , at various frequencies, are shown in Fig. 6 and 7 for the titration of HCl with NaOH. The usual V-shaped conductimetric titration curves may, with change in frequency or concentration, become S- or M-shaped. These have been explained by "transfer-plots",⁷ which relate low-frequency conductances over a range of concentration to the corresponding high-frequency conductances. By differentiation of G_p with respect to κ , it is found that, for a given cell, the concentration for maximum

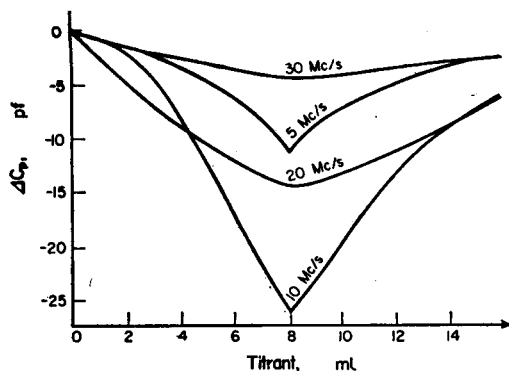


FIG. 7. Effect of change of frequency upon titration curves. HCl v NaOH (after ref. 28).

sensitivity (maximum $dG_p/d\kappa$) varies directly as the frequency, ω radian/sec. The highest frequencies used in this procedure have been adopted in order to extend the concentration range.^{29,30}

With regard to C_p , maximum sensitivity $dC_p/d\kappa$ is obtained for $C_2 \gg C_1$. This may be achieved as already indicated by decrease in cell-wall, increase in electrode area, or by use of a high permittivity ceramic cell. Reduction in ϵ (e.g. by the addition of EtOH to the aqueous solution) reduces C_1 , and this increases its reactance; the sensitivity of both G_p and C_p measurements is thus increased.

In following the course of titrations or precipitations it is unnecessary to derive κ_0 from the measurements or even to obtain G_p and C_p separately. An oscillator connected across AB will experience some change in loading upon its oscillatory circuit because of changes within the cell and this may be followed as a variation in anode or grid current or in the oscillator frequency. A frequency change is easily measured by mixing the cell oscillator output with that of a second oscillator of constant frequency and observing the beat-frequency audibly or upon the screen of a cathode-ray oscilloscope. Alternatively, if the oscillator is restricted to operation within a few hundred cycles of its nominal frequency, e.g. by piezo-electric crystal control, changes within the cell may cause oscillations to die away. The variation of a tuning capacitor necessary to restore oscillation may then be followed.

Changes in grid-current may be measured directly by a micro-ammeter, or a lamp-and-scale galvanometer connected in series with the grid resistor. It might be thought that the changes in anode current would be less sensitive than those in grid current, since they are of the order of 10–100 microamps in a steady anode current of 5–10

milliamps. However, the changes may be recorded on a micro-ammeter by "backing-off" the steady current with a reverse-connected variable voltage source. The "zero-shunt" circuit was described in this connection by Blake²⁰ and we have adopted it in a satisfactory instrument of our design. Under these conditions the anode current variations afford the greater sensitivity.³¹

The magnification factor, or "Q"-factor, of the oscillatory circuit *i.e.* the ratio of its impedance at resonant frequency to its resistance, evidently depends upon external resistance connected in parallel with it. If this resistance is supplied by the cell, changes in it are reflected in the "Q" of the circuit, and these may be measured directly on a commercial "Q"-meter.³²

Advantages are claimed for differential measurements in RF titrimetry.³³

APPARATUS

Considering firstly apparatus specifically designed for RF titrimetry, the principles of stable oscillator construction have been followed.³⁴⁻³⁷ The earliest apparatus for analytical purposes⁵ appeared in 1946 and used a tuned-anode tuned-grid (TATG) oscillator with the cell inside the anode-circuit inductance ("tank coil") working at frequencies between 15 and 20 Mc/sec; variations in anode current were followed. Simple feed-back oscillators have also been used.⁶

The TATG oscillator has frequently been used;³⁸⁻⁴¹ improved sensitivity is claimed for a modification which encloses the cell by a capacitor in the oscillatory circuit,⁴² and for the inclusion of a metal plate in the coil.⁴³ The cell has been used to couple the anode and grid coils⁴⁴ and a similar circuit has been adapted for battery operation in a portable instrument.^{45,46} The course of titrations has been followed by changes in grid voltage,⁴⁷ in screen current⁴⁸ and in the resistance in the anode circuit necessary to maintain constant anode current.⁴⁹

The Clapp oscillator⁵⁰ has been used in a number of titrimeter circuits covering the frequency range 5 to 30 Mc/sec. Anode current,^{51,31} grid current³¹ and oscillatory voltage⁵² have been followed. The Clapp oscillator has been incorporated in a heterodyne-beat circuit, the beat-frequency being measured by a frequency meter,^{29,53,54} or by an oscilloscope.⁵⁵ The Colpitts circuit has been used at 14 Mc/sec with the cell in the capacitor between anode and cathode.⁵⁶ It has also been used as a blocking oscillator at 100 Mc/sec.⁵⁷

A tuned transmission-line oscillator at 350 Mc/sec uses the heterodyne-beat method of measurement.⁵⁸ Advantages are claimed for modulation of the oscillator frequency (2.5 or 6 Mc/sec) at 1000 c/sec, the audio-frequency being detected.^{59,60} Crystal-controlled oscillators may be tuned by a variable capacitor for maximum amplitude of oscillation.^{61,62} The "grid dip" or sudden decrease in grid current has been followed⁶³ in a Clapp oscillator at 8, 22 and 35 Mc/sec; the circuit was later modified.⁶⁴ A crystal oscillator of frequency 2 Mc/sec indicates the position of oscillation by means of a "magic-eye" tube, conductance changes being followed by a valve-voltmeter.^{65-67,162} A Pierce crystal oscillator employs frequency doubling up to 14 Mc/sec.⁶⁸ The differential method of measurement^{33,69} follows the rate of change of beat-frequency with the volume of titrant added. Oscillators of higher frequency have been designed for use with more concentrated electrolyte solutions.^{30,37,58,70-72} The Franklin two-valve oscillator has been used, and the rectified oscillatory voltage measured.⁷³ Other stable-oscillator instruments have been described.⁷⁴⁻⁷⁸

Commercially available electronic test equipment which has been adapted for radio-frequency titrimetry and for the determination of specific conductances includes the Twin-T Impedance Measuring Bridge,^{7,26,28} and the Magnification ("Q") Meter.^{32,79} The use of any available stable oscillator with diode detector and "backed-off" meter has been discussed.^{80,81}

It should be noted that the Twin-T Bridge requires auxiliary equipment in the form of a stable, variable-frequency oscillator and a "communications" radio-frequency receiver as detector. The complete apparatus is thus bulky and expensive.

Some commercial titrimeters are available. The Model V Oscillometer²² operates at 5 Mc/sec and employs a frequency discriminator circuit to follow the heterodyne beat-frequency. Special conductivity cells are normally used but adaptors for the band-electrode type of cell have been described.^{82,83} The Fischer titrimer⁸⁴ is a modification of the apparatus of Hall.⁶⁵ The HFT30C titrimer⁸⁵ operates at 30 Mc/sec and incorporates a precision variable capacitor tuning for maximum response; the apparatus and some applications have been described.⁸⁶

The heterodyne-beat apparatus would appear to be the most sensitive; it may be combined with a null indicator if a tuned frequency discriminator is incorporated, as in the Model V Oscillometer. However, the circuit is relatively complicated and very careful screening is required. Crystal-controlled oscillators in which oscillations are maintained at maximum amplitude by adjustment of a tuning capacitor may be very simple and reliable. However, we have found that the type of circuit in which changes in the loading of the oscillator are followed by changes in grid or anode current is generally more sensitive. It should be pointed out that in a steady anode current of 5 milliamps, for a variation of 1 microamp to be significant, very careful mains and HT voltage stabilisation is required. The "reliable-series" valves are sometimes found to improve the stability.⁸⁷ There seems little advantage in operating at frequencies higher than about 30 Mc/sec except in the study of very concentrated electrolyte solutions.

Cell design

The first cells used in this work were of the pipette type.^{81,88-90,91} Aluminium sleeve electrodes⁵¹ and a central wire⁸⁰ or spigot²² electrode were subsequently introduced. The cell may be designed to minimise changes due to dielectric constant variations;⁹² on the other hand, disc-shaped cells are sensitive towards such variations.⁸²

Recent workers have preferred cells with external bands to the "electrodeless" cell placed inside the tank coil. Band-electrodes of silver or gold fired on to a glass or ceramic cell avoid having a layer of air between the electrodes and the cell wall. They may be protected by embedding in a thermosetting resin and terminated in plugs for direct connection to the oscillatory circuit.³¹ Thermostatted cells have been described.^{79,93,94}

PRACTICAL APPLICATIONS

Several investigators have given the range of concentration over which their apparatus is sensitive; some of these concentrations are listed in Table I.

The radio-frequency technique has been extensively employed in acid-base titrations; these are summarised in Table II.

The RF method is thus applicable to acid-base titrations over a wide range of concentrations. Except in the case of weak acid-weak base titrations,⁶³ the technique appears to offer no advantage over potentiometric titrations, which may now be made fully automatic.

TABLE I.—REPRESENTATIVE CONCENTRATION RANGES FOR ADEQUATE SENSITIVITY

Electrolyte	Concn. range, <i>g-equiv/litre</i>	Freq. range, <i>Mc/sec</i>	Refs.
HCl	1.0×10^{-4} to 5.0	1 to 40	43, 59, 77, 79, 92
H ₂ SO ₄	1.0×10^{-4} to 2.0×10^{-3}	16	95
CH ₃ COOH	1.0×10^{-4} to 1.0	2 to 6	59
NaOH	1.0×10^{-4} to 2.0	1 to 30	79, 95, 96
NaCl	1.0×10^{-4} to 2.0	1 to 14	68, 96
KCl	4.0×10^{-4} to 1.0×10^{-2}	20 to 30	79

TABLE II.—ACID-BASE TITRATIONS

Acid	Base	Concn. range, <i>g-equiv/litre</i>	Freq. range, <i>Mc/sec</i>	Comments	Refs.
HCl	NaOH	3.0×10^{-4} to 5.0	0.5 to 120	(Normal monobasic behaviour)	5, 6, 28, 52, 61, 72, 75, 88, 89, 90, 95, 97-100, 101
HCl	KOH	5.0×10^{-3} to 0.5	4	„	53, 76
HCl	Ba(OH) ₂	0.025	30	„	29
H ₂ SO ₄	NaOH, KOH	0.1	1 to 40	„	101
				Suggestion of break at NaHSO ₄	63
H ₂ SO ₄	NH ₄ OH	2.0×10^{-5} to 2.0×10^{-4}	30	—	42
HCl	Na ₂ CO ₃	1.0×10^{-3} to 1.0	1 to 30	Two breaks on adding Na ₂ CO ₃ to acid	5, 28, 56, 66, 97
HNO ₃	Na ₂ SiO ₃	0.1 to 0.25	2	—	98
CH ₃ COOH	NaOH	0.01 to 0.60	10 to 130	—	71, 102, 103
CH ₃ COOH	Ba(OH) ₂	0.025	30	—	29
CH ₃ COOH	NH ₄ OH	5.0×10^{-3} to 1.0	1 to 35	Excellent end-point obtained	6, 63
Picric Phthalic Malonic Tartaric	NaOH	1.0×10^{-3} to 3.0×10^{-2}	5	One break corresponding to the first H atom	104
H ₃ PO ₄	NaOH	—	8 to 20	Three breaks	97
H ₃ PO ₄	NaOH	0.025 to 0.25	130	Two breaks	71
H ₃ PO ₄	NaOH	0.2	10, 20, 30	One break	31
H ₃ PO ₄	KOH	3.0×10^{-4}	4 to 7	Three breaks, estimated K ₁ , K ₂ and K ₃	48

Various phenols, enols, and imides have been titrated with 0.05*N* lithium hydroxide at a frequency between 15 and 20 Mc/sec.¹⁰⁵ Glycine was satisfactorily determined by dissolving in excess standard sodium hydroxide, and back-titrating with hydrochloric acid.¹⁰⁶ Salts of alkaloids and other weak organic bases have been titrated with 0.1*N*

sodium hydroxide at 27 Mc/sec in water and in aqueous alcohol as solvents; the method is satisfactory¹⁰⁷ if K_b is not less than 10^{-9} .

It has been frequently observed that potentiometric and conductimetric titrations in which a precipitate is formed are liable to errors due to contamination of the electrodes. The "external electrode" technique has been fully explored for such reactions, and the results are summarised in Tables III and IV.

TABLE III.—CHLORIDE* DETERMINATIONS

Chloride	Titrant	Concentration range, g-equiv/litre	Freq. range, Mc/sec	Refs.
NaCl KCl	AgNO ₃	1.0×10^{-4} to 1.0	0.1 to 350	5, 28, 29, 45, 58, 61, 63, 66, 71, 81, 97, 108
HCl	AgNO ₃	1.0×10^{-4} to 0.1	4 to 30	31, 48
Cl ⁻	Hg(NO ₃) ₂	0.025	30	29
Cl ⁻	Hg(ClO ₄) ₂	0.01	30	69, 109†

* Bromide and iodide ions could doubtless be determined by similar titrations, as has indeed been found for the reverse titrations.⁶⁷

† The method described is claimed to be superior to potentiometric or conductimetric titration.

TABLE IV.—SULPHATE DETERMINATIONS

Sulphate	Titrant	Concentration range, g-equiv/litre	Freq. range, Mc/sec	Refs.
(NH ₄) ₂ SO ₄	BaCl ₂	0.05 to 0.10	8 to 20	97
Na ₂ SO ₄	BaCl ₂	1.0×10^{-4} to 0.1	0.5 to 18.5	52, 61, 76 110,* 111*
MgSO ₄	BaCl ₂	0.01	10 to 30	31*
SO ₄ ²⁻	(CH ₃ COO) ₂ Ba	0.015	5	112*
SO ₄ ²⁻	(CH ₃ COO) ₂ Ba	0.005 to 0.05	15 to 20	113
SO ₄ ²⁻	Pb(NO ₃) ₂	0.005 to 0.05	15 to 20	113
SO ₄ ²⁻	octa-ammino- μ -amino- μ -nitrodicobalt ^{III}	0.005 to 0.05	15 to 20	113
SO ₄ ²⁻	tetranitrate Hexamminocobalt ^{III} bromide	0.005 to 0.05	15 to 20	113

* The use of 30 to 50% by volume of ethanol, together with seed crystals of barium sulphate, has been recommended in these titrations. Such additions had been found advantageous in similar low-frequency determinations.¹¹⁴

The RF titration has been applied to the determination of fluoride ions, an analysis which is difficult to carry out by more conventional precipitation methods. Although objection has been raised to the use of thorium nitrate as a titrant,¹¹⁵ this reagent has been reported to be satisfactory for titration at 5 Mc/sec over a wide range of fluoride ion concentration.^{116,117} Lanthanum acetate has been used as titrant at frequencies within the range 2 to 20 Mc/sec and at concentrations between 0.01 and 0.025 g-equiv/litre of fluoride.^{45,102,118} The stoichiometry of this reaction has been confirmed by independent standardisations of the fluoride and lanthanum solutions,¹⁰² the fluoride in the form of hydrofluoric acid was neutralised by standard sodium hydroxide and

the lanthanum acetate solution titrated with disodium EDTA at pH 4.0 to 5.5 using Xylenol Orange as indicator.

A few applications have been made to redox titrations. Ferrous ammonium sulphate has been titrated with potassium permanganate at frequencies from 4 to 20 Mc/sec, and concentrations within the range 0.01 to 0.1 g-equiv/sec.^{5,48,76} More

TABLE V.—MISCELLANEOUS RF TITRATIONS

Ion determined	Titrant	Concn. range <i>g-equiv/litre</i>	Freq. range, <i>Mc/sec</i>	Notes	Refs.
CNS ⁻	AgNO ₃	2.5 × 10 ⁻⁴ to 1.0	1 to 30	—	28, 29, 69, 119
CNS ⁻	Hg(NO ₃) ₂	2.5 × 10 ⁻⁴ to 0.1	5, 30, 350	0.1% error*	29, 58, 119
CrO ₄ ²⁻	BaCl ₂	0.1	2, 5, 11	—	66
C ₂ O ₄ ²⁻	Th ⁴⁺	0.05 to 0.25	2, 350	—	58, 65
Th ⁴⁺	C ₂ O ₄ ²⁻	0.025 to 0.05	30	0.04% error	120†
KCN	AgNO ₃	0.05	6	sharp break at KAg(CN) ₂	67
KI	Na ₂ S ₂ O ₃ (HCl)	0.025	30	—	29
Be(HCl soln)	NaOH or NH ₄ OH	0.01 to 0.03	2, 22	CO ₂ ⁻ free re- agents and N ₂ atmosphere	118, 121
Ca ²⁺	C ₂ O ₄ (NH ₄) ₂	—	100	Used for lime in slag. pH 5.2-5.4 and 50% MeOH.	57
Ca ²⁺	C ₂ O ₄ (NH ₄) ₂	0.01	6	pH 6-6.5	122
Mg ²⁺ , Ca ²⁺ , Ba ²⁺ and mixtures.	C ₂ O ₄ (NH ₄) ₂	1.0 × 10 ⁻³ to 3.0 × 10 ⁻³	6.5	2% error in presence of EtOH	111
Mg ²⁺	NaOH	8.0 × 10 ⁻⁴ to 5.0 × 10 ⁻³	6.5	Ca does not interfere	111
Pb ²⁺ , Tl ⁺ , Ba ²⁺	Cr ₂ O ₇ ²⁻	0.01	6	pH 6-6.5	122
Zn ²⁺ , Cu ²⁺ , Cd ²⁺	NaHS	0.001 to 0.1	8	—	40
Tl ⁺	Na(C ₆ H ₃) ₄ B	0.1	25 to 30	0.5% error	123‡
Ce ⁴⁺	C ₂ O ₄ (NH ₄) ₂	0.01	6	pH 6-6.5	122
Ag ⁺ , Cu ²⁺	K ₄ Fe(CN) ₆	0.01	6	pH 6-6.5	122
Ag ⁺	KCl, KBr, KI, NH ₄ CNS, 2- mercapto benzo- thiazole, Bismuthiol II	0.05	6	—	67

* One break was observed in the titration of Hg²⁺ with CNS⁻; two breaks for the reverse titration (Hg[CNS]⁺).

† Of several ions considered for titrant, oxalate was found most satisfactory; the interference of several ions was investigated.

‡ The interference of several ions was studied.

recently ferrous ethylenediamine sulphate has been titrated with potassium dichromate.³¹

A very large number of miscellaneous determinations, mainly precipitation methods, have been reported and these are conveniently summarised in Table V. Water hardness determination by titration with "soap solution" has been reported,¹²⁴ and the precipitation of many ions with cupferron reagent¹²⁵ studied over the concentration range 5.0 × 10⁻⁴ to 1.0 × 10⁻³N. Complex formation between various cations and glycine has been investigated,³⁹ and several bivalent and trivalent cations titrated at a frequency of 100 Mc/sec with 0.02M solution of 8-hydroxyquinoline. With the latter it was found that for sharp breaks, the pH of the electrolyte solution needed careful adjustment. For example, with a 0.02M solution of iron a definite

end-point was obtained at pH 3.4 whereas at pH 4.8 the curve, under similar experimental conditions, was a straight line.¹²⁶

In addition to the numerous examples of titrations listed in the previous Table, the RF technique has been extensively applied in complexing reactions involving EDTA, dimethylglyoxime, pyridine and many other reagents. Table VI lists the work reported with EDTA.

TABLE VI.—RF TITRATIONS INVOLVING EDTA

Cations determined	Concn. range, <i>g-mole/litre</i>	Freq., <i>Mc/sec</i>	Comments	Ref.
Cu ²⁺ , Zn ²⁺ , Ca ²⁺ , Mg ²⁺ . UO ₂ ²⁺	0.01 0.01	30 30	0.1% error NaOH via EDTA pH 3.5 to 4.0, and direct titrn.	127 128
La ³⁺	3×10^{-4} to 0.01	30	NaOH via EDTA, and direct, pH 2.8 to 3.0	129
Gd ³⁺ , Ce ³⁺	3×10^{-4} to 0.01	30	Direct, pH 10	129
Pr ³⁺ , Nd ³⁺ , Ce ³⁺	3×10^{-4} to 0.01	30	In HAc/Ac ⁻ buffer at pH 5.3	129
"Ca Bentonite"	0.1 to 3.0	0.1 and 3	0.5 to 1.0% error Colloidal	81
Ni ²⁺	0.01 to 0.05	5	NaOH via EDTA	130
Cu ²⁺	1.0×10^{-4} to 0.01	5	Direct	130
La ³⁺	0.01 to 0.1	10 to 30	—	102

In general, RF titrimetry is found to give qualitative evidence regarding the ability of cations to chelate with EDTA¹³¹ which is in agreement with the order of "formation constants".¹³² The method is not suitable where weak EDTA complexes are formed, e.g. with Tl^I or Ag^I; because of the low selectivity of the reagent, few separations are feasible.¹³⁰

Other complexing agents have been studied and information regarding complex formation in solution has been deduced. Thus, in RF titration at 30 Mc/sec with pyridine, copper, nickel and zinc show breaks in the titration curve at mole ratios of 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6; nickel titrated with dimethylglyoxime showed breaks¹³³ at 1:1.1, 1:2, and 1:3.3

However, it seems probable that some of the very indistinct breaks recorded may represent instrument fluctuations; further evidence is required before the breaks representing hitherto unknown co-ordination numbers may be safely interpreted.

We consider next applications of the RF technique to non-aqueous solutions; most of these are acid-base reactions and are reported in Table VII.

Sulphuric acid titrated by potassium acetate in glacial acetic acid at 5 Mc/sec behaves as a monobasic acid.¹⁴⁴ The lithium halides may be titrated by KCNS in pyridine solution.¹⁴⁴

Applications to dielectric constant measurement

The measurement of dielectric constants was one of the earliest applications of radio-frequencies to the study of chemical systems, and the RF technique just described can

equally well follow changes in dielectric constant as in conductance during the course of a reaction. Mixtures may be analysed by measurement of dielectric constant if a calibration curve relating to the components has previously been constructed.

The heterodyne-beat method for determining dielectric constants, using a fixed-frequency crystal oscillator at 500 kc/sec, has been described.¹⁴⁵ The resonance method employing a 3.5-Mc/sec crystal oscillator, is claimed to be satisfactory over the dielectric constant range 1–80.¹⁴⁶ A frequency-deviation method, calibrated by observing

TABLE VII.—ACID-BASE TITRATIONS IN NON-AQUEOUS SOLVENTS

Acid	Base	Solvent	Concn. range, mole/litre	Freq. range, Mc/sec	Refs.
Phthalic	Na methoxide	Methanol/acetone	0.01 to 0.1	15 to 20	5
Phthalic	Methylamine	Aniline	—	30	64
HClO ₄ (0.1N) in glacial acetic acid	Aniline and substituted anilines*	Glacial acetic acid	1.0 × 10 ⁻³ to 1.0 × 10 ⁻²	130	134
HClO ₄ (0.1N) in glacial acetic acid	Various organic bases†	Glacial acetic acid	0.1	5 to 20	45, 104, 135, 165
HClO ₄ (0.1N) in glacial acetic acid	Various organic bases†	Benzene/methanol/glac. acetic acid	1.0 × 10 ⁻⁴ to 1.0 × 10 ⁻²	2 to 15	136, 137
HClO ₄ (0.1N) in glacial acetic acid	Salts of various carboxylic acids	Glacial acetic acid	0.1	—	138
HClO ₄ (0.1N) in glacial acetic acid	Amino acids, teramycin, actinomycin	—	—	30‡	139, 140
Various weak carboxylic acids and phenols¶	Na methoxide K methoxide	—	—	5	141, 142
Oxine	Na methoxide	Dimethyl formamide	0.1	15 to 20	45
NH ₄ ⁺ halides	Na methoxide	Dimethyl formamide	1.0 × 10 ⁻⁴	5	143
Salicylic o-nitro phenol Benzoic Lactic Tartaric**	Alcoholic KOH	Pyridine	0.001	5	104

* Pairs of such amines can be determined when their molecular weights differ by about 20.

† Lower limit of $K_b = 10^{-12}$; poor indication if K_b less than 10^{-10} .

‡ Using a ceramic cell of permittivity about 80.

¶ Two breaks with oxalic and similar dibasic acids; each OH group of polyhydric phenols is observed.

** Lactic and tartaric acids showed one break only.

the deviations produced by a standard capacitor, uses a 1-Mc/sec crystal oscillator.¹⁴⁷ A 10-Mc/sec oscillator, with concentric-cylinder cell, operates a pen recorder by its anode current.¹⁴⁸

The Hall RF Titrimeter circuit has been modified specifically for the determination of dielectric constant; this uses the normal external-band electrodes, at frequencies of 2, 5 and 11 Mc/sec.⁶⁶ Many other titrimeter circuits are amenable to this type of measurement.

Apparatus and methods for the determination of dielectric constant have been reviewed,^{149,150} and the applications of the technique to the analysis of mixtures are recorded in Table VIII.

Miscellaneous chemical applications

The position of absorption bands in a column of ion-exchange resin may be determined by the RF technique;^{155,156} and chromatographic zones may be followed in a similar manner.^{47,157} The rate constants for ester hydrolyses have been determined by following conductance changes during the course of the reaction. A calibration curve, the titration of acetic acid with sodium hydroxide, is used and the method is applicable

TABLE VIII.—ANALYSIS OF MIXTURES BY MEASUREMENT OF DIELECTRIC CONSTANT

System	Freq., Mc/sec	Comments	Ref
H ₂ O/MeEtCO/C ₆ H ₆	4	H ₂ O content within 0.2% error	151
H ₂ O/EtOH	10 to 30	—	31
H ₂ O/mono-, di- and tri-hydric alcohols	4,5	particularly sensitive to EtOH/H ₂ O	152
H ₂ O/Me ₂ CO	5	accurate temp. control required	82
H ₂ O/ powdered materials	7	—	2
H ₂ O/salts/MeOH/dioxan	9	water content to 0.2% at optimum % dioxan <i>e.g.</i> NaCl . . . 35% dioxan NH ₄ NO ₃ . . . 69% dioxan	51
H ₂ O/dioxan/KCl	Various	—	153
H ₂ O/oil emulsion*	10	salinity does not interfere but suspended solids must be absent	148
acetone/toluene/ benzene,	7	—	2
<i>o</i> - and <i>m</i> -xylenes			
hexane/benzene, <i>o</i> - and <i>p</i> -xylenes	5	accurate temp. control required	82
continuous monitoring of toluene in distillation	2	toluene content to within ±1%.	154

* Sodium chloride has been determined in such emulsions by titration with 0.1*N* AgNO₃ at 20 Mc/s.¹⁰⁹

to reactions of half-life of 10 sec or less.^{74,93,158} The rate of precipitation of barium sulphate in aqueous solution has been determined as a function of the concentrations of the ions and of the number of moles of precipitate already formed.¹⁵⁹ The RF titration of lead with potassium dichromate solution has been studied, with particular regard to co-precipitation of other ions. Using the differential method an error of less than 0.2% is claimed. In this investigation the Beckmann Conductometer was used.¹⁶⁰

CONCLUDING REMARKS

The main advantage of having external electrodes is that precipitation reactions may be followed more easily than with the conventional cell. It has been pointed out²⁴ that for a given conductance change within the cell the RF indication will be less than the LF resistance change; however, if the measuring technique under RF conditions is better, the overall accuracy may be improved. The conductance at radio-frequency is a function of the LF conductance, and not a measure of some new property. It is,

perhaps, worth mentioning that any beaker or test-tube may be used as a conductivity cell in the RF method and that accurate results can be obtained with quite simple apparatus. Moreover, the same apparatus may often be used to follow changes in dielectric constant.

Note added in proof

The out-of-balance voltage of a Twin-T Bridge, powered by a General Radio signal generator at frequencies between 10 and 30 Mc/sec, has been measured to follow the course of titrations. Transfer plots relate this voltage to the low-frequency conductance of the solution, κ_0 . The equation: $\Delta E_p = (EZ) \cdot \Delta Y_{ac}$ is obtained, where ΔE_p is the out-of-balance voltage, and ΔY_{ac} the change in admittance of the cell-equivalent circuit; E is the generator voltage, and Z the detector impedance.¹⁶¹

The importance of a correctly-designed cell has again been emphasised, and several types have been described.¹⁶²

A 130-Mc/sec oscillator is described, in which changes in grid-current are followed; a band-electrode cell is used.¹⁶³ The lower limits of concentration with this oscillator are as follows:¹⁶⁴

HCl v. bases, 1 $\mu\text{g/ml}$ of HCl.

CH_3COOH v. bases, 20 $\mu\text{g/ml}$ of CH_3COOH .

Cl^- v. AgNO_3 , 2 $\mu\text{g/ml}$ of Cl^- .

SO_4^{2-} v. BaAc_2 , 10 $\mu\text{g/ml}$ of SO_4^{2-} .

A heterodyne beat oscillator for the accurate determination of dielectric constants is described; it uses a Pierce crystal oscillator, beating with a Clapp variable oscillator, the mean frequency being 1 Mc/sec. Cells with rigid electrode assemblies are described, and measurements on benzene and chlorobenzene solutions are reported.¹⁶⁶

Zusammenfassung—Die Theorie radiofrequenter Messungen, die von Bedeutung für die Chemie sind, wird dargelegt und ein geeigneter Apparat diskutiert. Anwendungen, besonders auf dem Gebiete der analytischen Chemie, werden zusammenfassend behandelt.

Résumé—Les auteurs donnent un aperçu de la théorie des mesures de fréquence radio d'importance chimique, et discutent l'appareillage convenable. Les applications sont passées en revue, spécialement en chimie analytique.

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PRELIMINARY COMMUNICATION

A new reducing agent: Reduction of vanadium^{IV} and uranium^{VI} with ferrous ion in catechol solutions

(Received 25 April, 1960)

In a study of the polarographic behaviour of vanadium, iron, and uranium as their catechol complexes a powerful reducing system has been observed. When a ferrous solution is added to an ammoniacal solution containing either the vanadyl- or uranyl-catechol complex in the presence of excess catechol, the vanadium and uranium are reduced rapidly to V^{III} and U^{IV} species, respectively. The analytical application of this reaction has been examined briefly. The direct titration of uranyl-catechol with ferrous ion to a potentiometric or amperometric end-point indicated the above stoichiometry. Similar behaviour was also noted for the vanadyl-catechol complex.

Polarographic data indicate that the reduction potential of the ferrous-catechol/ferric-catechol couple in ammoniacal medium (pH9.5) is -0.97 volts v. Ag/AgCl. Ferrous-catechol is very unstable in a de-gassed solution containing no reducible materials. It appears that the ferrous complex will readily reduce water. The reducing strength exceeds that of chromous ion in acid solution. By employing a standard ferrous solution this strong reducing agent is readily available for titrations. The strong reducing power is attributed to the high stability of the ferric-catechol complex as compared with that of the ferrous-catechol complex.¹ Undoubtedly, the existence of vanadium- and uranium-catechol complexes contributes to the favourable titration. This behaviour is similar to the titration of bivalent cobalt with ferric chloride in the presence of 1:10-phenanthroline.²

The stoichiometry of the reduction for vanadium and uranium was checked by the potentiometric titration of standard solutions of each ion. The results are shown in Table I.

TABLE I. TITRATION OF VANADIUM AND URANIUM WITH FERROUS IN CATECHOL SOLUTION

Material titrated	Milliequivalents		Titration reaction
	Taken	Found	
VO ²⁺	0.238	0.237	V ^{IV} → V ^{III}
VO ²⁺	0.245	0.244	V ^{IV} → V ^{III}
V ^V	0.228	0.227*	V ^{IV} → V ^{III}
UO ₂ ²⁺	0.262	0.262	U ^{VI} → U ^{IV}

* All results indicate that vanadium^V is reduced to vanadium^{IV} by catechol before the titration.^{3,4}

The potentiometric titration curves and appropriate data are shown in Fig. 1.

Mixtures of vanadium^{IV} and uranium^{VI} cannot be differentiated so that it is necessary to remove the vanadium before titrating the uranium. The molybdate-catechol complex is also reduced under these conditions.

This is the first direct reduction that has been reported of uranium^{VI} with a stable titrant. Titanium^{III} is more difficult to prepare and use.^{5,6} Further applications of this reagent are under study. The polarographic results will be published elsewhere.

Acknowledgement—I wish to thank Dr. D. D. DeFord for his interest in this work.

Research Division
Phillips Petroleum Company
Bartlesville, Oklahoma, U.S.A.

JOHN W. MILLER

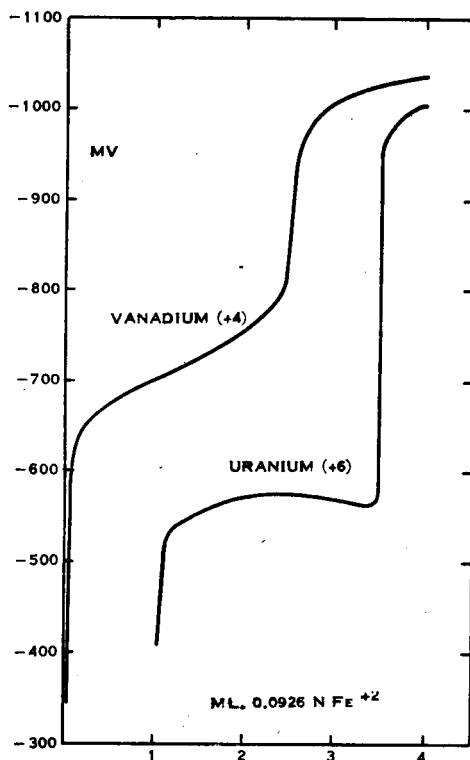


FIG. 1.—Titration curves of vanadium and uranium with ferrous in catechol solution

Vanadium titration: 60 ml 1M NH_4Cl –1M NH_3 –0.1M Na_2SO_3

2400 mg catechol

5 ml 0.046N vanadate solution

Titrated with 0.0926N ferrous; mercury pool versus Ag/AgCl.

Uranium titration: 60 ml 1M NH_4Cl –1M NH_3 –0.1M Na_2SO_3

2400 mg catechol

2 ml 0.131N uranyl acetate

Titrated with 0.0926N ferrous; mercury pool versus Ag/AgCl.

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BOOK REVIEWS

Quantitative Inorganic Analysis. R. BELCHER and A. J. NUTTEN. Second Edition, Butterworths Scientific Publications, London, 1960. Pp. x + 390. 35s.

THIS book is intended mainly as a practical teaching manual. It gives up-to-date instructions, with many references to the original literature, for a good selection of gravimetric and titrimetric analyses, and for a few instrumental determinations. The background and limits of applicability of each method are fully and completely discussed. It is suitable for use at all levels of undergraduate training. The Second Edition differs from the First Edition mainly in the expansion of the sections on EDTA titrations, and on balances and weighing (aperiodic and single-pan balances are now covered). Other minor improvements, resulting from new publications and from experience with the determinations, have also been made.

The cheapness of this book, and its compact presentation of detailed laboratory instructions in a form suitable for immediate use at the bench, are attractive, but it has serious faults. In concentrating on "classical" quantitative analysis, the authors fail to give their readers, most of whom will be students unable or unwilling to buy any other textbook of quantitative analysis, a balanced picture of the present state of the subject. "Microanalysis", for instance, does not even appear in the Index nor does "Ion-Exchange", although an ion-exchange method receives passing mention in the text. In spite of the authors' admonition to read up the physicochemical theory of the methods elsewhere, many student readers are likely to take the partial omission of theory from this book as evidence that the theory is not really important.

The treatment of practical techniques is, on the whole, sound and detailed, but is not free from defects. The First Edition of this book must be almost unique in the literature of analytical chemistry in containing a diagram of a chemical balance which does not show knife edges, planes, or pan stops. The Second Edition has a revised version showing the pan stops. There is a serious omission from the instructions for use of the pipette which has not been corrected in the Second Edition.

The weakest feature of the book, however, is the section on the calculations of titrimetric analysis. This is marred in parts by a reluctance to use simple mathematical equations which would have shortened and clarified the explanations. There are references to "molecules" of KMnO_4 and FeSO_4 , and the term "molecular weight" is persistently used in connection with ionic compounds, although a perfectly good term, "formula weight", has long been current for this case. The account of oxidation numbers is not very clear, and is not as good as can be found in some older texts. The statement on p. 160 to the effect that the equivalent weight of a base is determined by the "number of replaceable hydroxyl groups in the molecule" is unsatisfactory; hydroxylic bases are composed of ions, not molecules, and many bases of importance in analysis, such as sodium carbonate, borax and ammonia, are not hydroxylic compounds at all. This difficulty can be overcome by defining the equivalent weight in terms of the number of protons accepted by the base formula. Another sentence on p. 160 deserves to be quoted: "The molar weight of a substance is a constant, and must not be confused with a normal solution, although in many instances a normal solution contains a mole of solute and the concentrations become identical." (This is the *revised* version of the Second Edition.) It is only fair to state that this is an example of the worst writing in the book, and is not typical. It seems to show, however, how little comfort the puzzled student is likely to derive from this section. Faults like these can, it is true, be found in many other textbooks of quantitative analysis, but it is disappointing to find them so unnecessarily repeated in the second edition of a new book.

To summarise, this is a useful and, in some respects excellent book, but one which cannot be given unqualified approval as a student text.

HENRY G. HEAL

Analytical Chemistry in Nuclear Reactor Technology, 2nd Conference 1958. U.S. Atomic Energy Commission, Office of Technical Services. Department of Commerce, Washington 25, D.C. Part I Pp. vii + 298, Part II Pp. vi + 236.

THESE two paper-bound volumes contain 55 of the 70 papers presented at the second conference on analysis in reactor technology held in September 1958 at Gatlinburg, Tennessee. This conference was concerned with the problems of the analyst during the commissioning and operation of reactors; it will be recalled that the first conference in 1957 concentrated on reactor materials analysis.

Part 1 contains fourteen contributions mainly dealing with fuel alloy analyses and the range of control analyses called for in operating some experimental reactors; five papers on boron and other special determinations; a group of five papers on applications of flame photometry and polarography and finally six contributions concerned with applications of X-ray and emission spectroscopy. There are four abstracts of papers published in full elsewhere.

Part 2 contains seven papers on instrumentation (laboratory and "in-line"), nine reports on remote-control techniques, and concludes with nine papers under the heading "Nucleonics" including several dealing with radiochemical and gamma-spectrometric analysis.

The prospective reader should perhaps be warned against being misled by the title into thinking that this useful compilation is a systematic and comprehensive attempt to survey the whole field; as indicated by the editors in their preface, the objective of the conference was "to provide a forum for the exchange of information" and consequently the collected papers are in the nature of a miscellany, some indeed being rather remotely connected with reactor start-up and operation. One feels that the inclusion of a few review papers aimed at establishing trends in techniques and attempting to summarise philosophies would have increased the overall value of the conference record as now presented. If one were to try to summarise impressions, no doubt one would have to note the ever increasing activity levels the analyst must needs work at and the ingenuity and skill which have been used to adapt many of his conventional physical instrumental techniques to operation at high radiation levels; indeed, if we want to single out a group of papers, perhaps one of the most impressive presented at this symposium is that dealing with remote control developments. Other significant trends are the steadily increasing importance and widening application of such techniques as X-ray fluorescence and gamma spectrometry and the successful extensions of flame photometry to alkaline earth determination without separation in uranic solutions.

These volumes are well printed and adequately illustrated with more than 250 diagrams and reproductions from photographs, and are useful reference works to set beside the earlier volume covering the first conference.

F. J. WOODMAN

Solution of Multistage Separation Problems by Using Digital Computers. JOHN H. DUFFIN. *University of California, Radiation Laboratory. Report UCRL 8787.* U.S. Department of Commerce, Washington, D.C. 1959. pp. 266. \$4.00.

THIS report is in thesis form, its object being to indicate, with appropriate detailed examples, the conditions under which digital computers may be programmed to solve multistage separation problems. Various approaches to the solution of such problems *e.g.* using mass balance, energy balance etc. are critically examined as to their range of usefulness and to the type of resulting computer programmes. The procedures are mostly iterative and the document is valuable in that it provides cross-checking of the computer data derived from the different approaches. The volume may well prove useful to chemical engineers associated with distillation and similar problems but it falls outside the working range of the majority of analytical chemists.

J. K. FOREMAN

NOTICES

The following meetings have been arranged:

Sunday–Friday 11–16 September 1960: New York Meeting of Division of Analytical Chemistry, American Chemical Society.

Four symposia are being presented: *Resonance Methods for Analysis and Characterisation: (a) Nuclear Magnetic Resonance, (b) Electron Paramagnetic Resonance*, organised by HARLAN FOSTER. *Infrared Methods of Chemical Analysis*, organised by RICHARD C. LORD Jr. and BRYCE CRAWFORD, in conjunction with the Division of Physical Chemistry. *X-ray Absorption and Emission in Chemical Analysis*, organised by HERMAN A. LIEBHAFSKY. *Recent Advances in Analytical Chemistry*, organised by CLARK BRICKER, in conjunction with the Division of Chemical Education.

Further information may be obtained from LOCKHART B. ROGERS, Secretary-Treasurer of the Division of Analytical Chemistry, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A.

Wednesday 21 September 1960: Polarographic Society: The Application of Polarography in Metallurgical Analysis: Wolverhampton and Staffordshire College of Technology, Wolverhampton. 2.30 p.m.

Further details concerning the meeting may be obtained from Mr. R. C. ROONEY, A.R.I.C., British Cast Iron Research Association, Bordesley Hall, Alvechurch, Birmingham.

Thursday–Saturday, 6–8 October 1960: Austrian Microchemical Society: Emich-Commemoration and Microchemical Conference.

On behalf of the Austrian Microchemical Society and under the direction of Professor Dr. Ing. G. Gorbach, the Emich Group has arranged an Emich-Commemoration and Microchemical Conference at the Technical University of Graz on October 6, 7 and 8, 1960.

The provisional programme is as follows:

Thursday 6 October

Arrival and reception of the visitors in the Hotel Steirerhof.

Friday 7 October

Morning—Reception speech, commemoration speech and plenary lectures.

Visit to the birthplace and the grave of Emich, with the laying of a wreath at both places.

Visit to the "Emichplatzl" and lunch at the Schloßberg.

Afternoon—Individual lectures.

Saturday 8 October

Morning—Individual lectures.

Simultaneously with the lectures there will be demonstrations of microchemical apparatus at the Technical University of Graz as well as a visit to the Pregl-Laboratories of the University of Graz under the direction of Professor Dr. H. Lieb.

The fee for the Conference is ö.s.60,— for members or ö.s.100,— for non-members.

Those people who wish to participate in the proceedings are asked to write as soon as possible to Professor Dr. Ing. G. GORBACH, Institut für Biochemische Technologie, Lebensmittelchemie und Mikrochemie, Technische Hochschule, Graz, Schlegelgasse 9, Austria.

Thursday 3 November 1960: Royal Dutch Chemical Society: Symposium on Organic Analysis.

The Section for Analytical Chemistry of the Royal Dutch Chemical Society is arranging a Symposium on Organic Analysis in the Laboratorium voor Algemeen Anorganische Chemie der Universiteit te Amsterdam on November 3, 1960.

The tentative programme is as follows:

General Introduction: Dr. Ir. E.A.M.F. DAHMEN (Kon./Shell Lab., Amsterdam);

Qualitative Detection of Elements and Functional Groups: Dr. W. I. STEPHEN (University of Birmingham, England);

Identification of Specific Organic Compounds: Mej. Dr. P. HAVERKAMP-BEGEMANN (Unilever Research Lab., Vlaardingen);

Quantitative Elementary Analysis: P. GOUVERNEUR (Kon./Shell Lab., Amsterdam);

Quantitative Determination of Groups and Specific Compounds: Dr. L. BLOM (Centraal Lab., Staatsmijnen, Geleen).

Further information can be obtained from Mej. Ir. E. HOEKSTRA, p/a Willem Smit & Co's Transformatoren fabriek N.V., Groenestraat 336, Nymegen, Netherlands.

The Polarographic Society now has a permanent address for mail; enquiries concerning the Society should be addressed to:—

The Polarographic Society, c/o Lloyds Bank Ltd., 36 High Street, Wealdstone, Middlesex.

PAPERS RECEIVED

- Contributions to the basic problems of complexometry—III: Some advantages of acetate buffer.** W. BERNDT and J. ŠÁRA. (2 May 1960).
- A study of the reduction waves of the three isomers of nitrophenol by means of the alternating current polarograph.** TAKEO TAKAHASHI and HIDEKO SHIRAI. (2 May 1960).
- Precipitation of nickel dimethylglyoximate from homogeneous solution.** EUGENE D. SALESIN and LOUIS GORDON. (5 May 1960).
- Detection of monobasic phosphorus acid esters by conversion to cholinesterase inhibitors.** HARVEY W. YUROW, DAVID H. ROSENBLATT and JOSEPH EPSTEIN. (11 May 1960).
- Radiometric trace analysis—I: Determination of lead with phosphate-³²phosphorus on filter paper without preliminary separations.** P. C. VAN ERKELENS. (6 May 1960).
- Radiometric trace analysis—II: Quantitative paper chromatography of lead with phosphate-³²phosphorus.** P. C. VAN ERKELENS. (16 May 1960).
- Radiometric trace analysis—III: Determination of lead with diethyldithiocarbamate and ²⁰⁴thallium⁺ ions.** P. C. VAN ERKELENS. (16 May 1960).
- Radiometric trace analysis—IV: Determination of lead with ²⁰⁴thallium-diethyldithiocarbamate.** P. C. VAN ERKELENS. (16 May 1960).
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LIST OF CONTENTS

Volume 4

SUBJECT INDEX

8-Acetoxyquinoline, Preparation	75
3-Acetyl-4-hydroxycoumarin for the gravimetric determination of uranium and thorium	13
Acid chlorides for determination of water	166
— —, Titrimetric determination in carboxylic acid chlorides	120
Alizarin-Red S for spectrophotometric determination of zirconium	108
Aluminium, Complexometric determination	133, 141
— oxide precipitates, Minimum ignition temperature	115
Amines, Determination with cationite paper	174
α -Benzoinoxime complexes of molybdenum, tungsten and vanadium	250
Beryllium and beryllium oxide analysis	61, 101, 104
Blood sugar, Spectrophotometric determination with 3:6-dinitrophthalic acid	33
Book Reviews:	
<i>Analytical Chemistry in Nuclear Reactor Technology: 2nd Conference, 1958</i>	295
<i>Automatic Titrators: J. P. Philips</i>	217
<i>Chemical Analysis, Vol. 9: Analytical Chemistry of Titanium Metal and Compounds:</i> Maurice Codell	148
<i>Contributi Teorici e Sperimentale di Polarografia, Vol. IV</i>	213
<i>Instrumental Methods of Chemical Analysis: Galen W. Ewing</i>	214
<i>Optics and Spectroscopy, Vol. VI, No. 1</i>	149
<i>Proceedings of the International Symposium on Microchemistry</i>	215
<i>Quantitative Inorganic Analysis: R. Belcher and A. J. Nutten</i>	294
<i>Reactor Technology, Report No. 10: Chemistry</i>	149
<i>Separation and Identification of Food Colours Permitted by the Colouring Matters in Food</i> <i>Regulations</i>	216
<i>Solution of Multistage Separation Problems by Using Digital Computers: John H. Duffin</i>	295
<i>The Analysis of Titanium and its Alloys</i>	148
<i>Trace Techniques using the K-1000 Cathode Ray Polarograph: J. Hetman</i>	213
Bubble-type gas absorbers, Estimation of efficiency	89
Calcein Blue as metal fluorechromic indicator	182
Carbon disulphide, Titrimetric determination with chloramine-T	206
Cationite paper for determination of amines	174
Chloramine-T for titrimetric determination of carbon disulphide	206
Chromatography, Salting-out	67
Complexometric determination of aluminium	133, 141
— — — mercury ^{II}	133
— — — thorium	8
Copper, Spectrophotometric determination in beryllium by neocuproine	101
2:5-Dihydroxy- <i>p</i> -benzoquinone for gravimetric determination of thorium and zirconium	178
"Excess oxygen" in rocks, Titrimetric determination by manganese ^{III}	268
"Ferrous iron" in rocks, Titrimetric determination by manganese ^{III}	268
Fluorescent indicators, Calcein Blue	182

—, Umbellicomplexone and Xanthocomplexone	38
Fluoride, Spectrophotometric determination with lanthanum chloranilate	126
Gas absorbers Estimation of efficiency	89
Glutaric acid derivatives for determination of water	166
Gravimetric determination of thorium with 3-acetyl-4-hydroxycoumarin	13
— — — — — 2:5-dihydroxy- <i>p</i> -benzoquinone	178
— — — uranium with 3-acetyl-4-hydroxycoumarin	13
— — — zirconium with 2:5-dihydroxy- <i>p</i> -benzoquinone	178
8-Hydroxyquinolates, Precipitation from homogeneous solution	75
Homogeneous solution, Precipitation of 8-hydroxyquinolates from	75
Identification of isatin	209
— — manganese	17
— — molybdenum	17
— — rhenium	17
— — ruthenium	17
— — technetium	17
Ignition temperature of aluminium oxide precipitates	115
Indicator tube, Self-sampling, for oxygen	203
Indicators, Fluorescent, N:N':N'-tetracarboxymethylbenzidines	78
— — Umbellicomplexone and Xanthocomplexone	78
—, Metalfluorechromic	80
—, Metallochromic, Thiazolyl analogues of 1-(2-pyridylazo)-2-naphthol	201
—, Metallofluorescent, N:N':N'-tetracarboxymethylbenzidines	78
— —, Umbellicomplexone and Xanthocomplexone	38
Indium, Polarographic determination	158
Ion-association complexes in analytical chemistry	158
Ion-exchange columns, Oxidation-reduction on	25
— — resins in salting-out chromatography	67
— — separation of ²³⁴ thorium from uranium	153
Iridium-rhodium separation	44
Iron, Spectrophotometric determination in beryllium with <i>o</i> -phenanthroline	61
—, Titrimetric determination after reduction on an ion-exchange column	25
Irving-Williams order, Deviations from	264
Isatin, Identification	209
Lanthanum chloranilate for spectrophotometric determination of fluoride	126
— — — — — phosphate	244
Liquid-fire reaction	185
Lithium chloride in non-aqueous potentiometric titrations	205
Manganese, Identification on ultramicroscale	17
— for titrimetric determination of "ferrous iron" and "excess oxygen" in rocks	268
Mercury, Complexometric determination	133
Metal fluorechromic indicators	80
— —, Calcein Blue	182
Metallochromic indicators, Thioazolyl analogues of 1-(2-pyridylazo)-2-naphthol	201
Metallofluorescent indicators, N:N':N'-tetracarboxymethyl benzidines	78
— —, Umbellicomplexone and Xanthocomplexone	38
Methylene blue for spectrophotometric determination of sulphate	227, 236
Molybdenum, α -Benzoioxime complex	250
—, Identification on ultramicro scale	17
— in beryllium, Spectrophotometric determination as thiocyanate	104
Molybdosilicic acid, Titrimetric determination of silica as	1
Neocuproine for spectrophotometric determination of copper in beryllium	101
Neutron activation determination of silver and thallium in rocks	51

— — — tantalum in rocks	194
Non-aqueous potentiometric titrations, Lithium chloride in	205
Oxidation at low temperature with perchloric-periodic acids	185
— by potassium ferricyanide	211, 212
— -reduction on an ion-exchange column	25
Oxygen, Self-sampling indicator tube	203
Perchloric-periodic acids as oxidant	185
Periodic acid liquid fire reaction	185
<i>o</i> -Phenanthroline for spectrophotometric determination of iron in beryllium	61
Phosphate, Spectrophotometric determination with lanthanum chloranilate	244
Platinum metals, Isolation from concentrates	44
Polarographic determination of indium	158
Potassium ferricyanide as oxidant	211, 212
Potentiometric titration of uranium with ferrous iron	292
— — — vanadium with ferrous ion	292
— — —, Non-aqueous, lithium chloride in	205
Precipitates of aluminium oxide, Minimum ignition temperature	115
Precipitation from homogeneous solution of 8-hydroxyquinolates	75
1-(2-Pyridylazo)-2-naphthol, Thioazolyl analogues as metallochromic indicators	201
Radiofrequency methods in analytical chemistry	274
Rhenium, Identification on ultramicro scale	17
Rhodium, Separation from iridium	44
Rocks, Determination of "ferrous iron" and "excess oxygen"	268
— — — silver and thallium by neutron activation	51
— — — tantalum by neutron activation	194
Ruthenium, Identification on ultramicro scale	17
Salting-out chromatography	167
Sampling tube, Indicating, for oxygen	203
Separation of manganese, technetium, rhenium, ruthenium and molybdenum	17
— — rhodium and iridium	44
— — ²³⁴ thorium from uranium by ion-exchange	153
Silica, Titrimetric determination as molybdosilicic acid	1
Silver as absorbent of sulphur in organic compounds	221
—, Determination in rocks by neutron activation analyses	51
Spectrophotometric determination of fluoride with lanthanum chloranilate	126
— — — iron in beryllium by <i>o</i> -phenanthroline	61
— — — molybdenum in beryllium as thiocyanate	104
— — — phosphate with lanthanum chloranilate	244
— — — sugars with 3:6-dinitrophthalic acid	33
— — — sulphate as methylene blue	227, 236
— — — zirconium with Alizarin-Red S	108
Spot test for isatin	209
Stabilities of bivalent transition metal complexes	204
Sulphate, Spectrophotometric determination as methylene blue	227, 236
Sulphur in organic compounds, Determination by absorption on silver	221
Sugars, Spectrophotometric determination with 3:6-dinitrophthalic acid	33
Tantalum, Determination by neutron-activation	194
Technetium, Identification on ultramicro scale	17
N:N':N'-Tetracarboxymethyl benzidines as metalfluorechromic indicators	78
Thallium, Determination in rocks by neutron-activation	51
Thioazolyl analogues of 1-(2-pyridylazo)-2-naphthol as metallochromic indicators	201
Thiocyanate for spectrophotometric determination of molybdenum in beryllium	104
Thorium, Complexometric determination	8
—, Gravimetric determination with 3-acetyl-4-hydroxycoumarin	13
— — — — 2:5-dihydroxy- <i>p</i> -benzoquinone	178

—, Separation from uranium by ion-exchange	153
Titrimetric determination of acid chlorides in carboxylic acid chlorides	274
— — — aluminium complexometrically	120
— — — carbon disulphide with chloramine-T	133, 141
— — — “ferrous iron” and “excess oxygen” in rocks	206
— — — mercury complexometrically	268
— — — silica as molybdosilicic acid	133
— — — thorium complexometrically	1
— — —, Potentiometric, of uranium with ferrous ion	8
— — — — vanadium with ferrous ion	292
Transition metal complexes, Estimation of stabilities	292
Tungsten, α -Benzoinoxime complex	264
Umbellicomplexone as fluorescent indicator	250
Uranium alloys, Spectrophotometric determination of zirconium in	38
—, Gravimetric determination with 3-acetyl-4-hydroxycoumarin	108
—, Reduction with ferrous ion	13
Urine sugar, Spectrophotometric determination with 3:4-dinitrophthalic acid	292
Vanadium, α -Benzoinoxime complex	33
—, Reduction with ferrous ion	250
Wännigen-Ringbom method	292
Water, Determination with acid chlorides	141
Xanthocomplexone as fluorescent indicator	166
Zirconium, Gravimetric determination with 2:5-dihydroxy- <i>p</i> -benzoquinone	38
—, Spectrophotometric determination with Alizarin-Red S	178
	108

AUTHOR INDEX

(Names of authors of books reviewed are in italics)

- Bányai, É. 133
 Beamish, F. E. 44
 Bednas, M. E. 153
 Berman, S. S. 153
 Belcher, R. 78, 166
Belcher, R. 294
 B.-Gere, É. 133
 Bhat, A. N. 13
 Breyer, Arthur 67
 Burger, K. 8, 120
 Burgess, J. 148

 Calvert, Seymour 89
Codell, Maurice 148

 Danzuka, Takeo 126, 244
 Davis, W. F. 61, 101, 104
 Diehl, Harvey 185
 Dixon, B. E. 203
 Dixon, Jean P. 221

 Eggers, J. H. 38
 Erdey, L. 25, 133
Ewing, Galen W. 214

 Feigl, F. 209
 Firsching, F. H. 148
 Foreman, J. K. 149, 295

 Goldstein, D. 209
 Gordon, Louis 75, 115
 Greenfield, S. 147
 Grove, E. L. 205
 Gustafsson, Lilly 227, 236

 Hayashi, Kiyoko 126, 244
 Headridge, J. B. 215
 Heal, Henry G. 294
Hetman, J. 213

 Hibbits, J. O. 61, 101, 104
 Hoenes, Henry J. 250
 Howard, A. J. 216

 Inaba, Akira 33
 Inczédy, J. 25
 Ingamells, C. Oliver 268

 Jain, B. D. 13, 178
 Jarczewski, A. 174
 Jasim, Fadhil 17

 Kallmann, S. 104
 Kesser, Gwendolyn 108
 Kiff, P. R. 203
 Killick, R. A. 51
 Kopanica, Miloslav 158

 Ladd, M. F. C. 274
 Larsen, R. P. 108
 Lee, W. H. 274
 Leussing, D. L. 264
 Lewandowski A. 174

 McKinney, Lorna E. 153
 Magee, Robert J. 17
 Markovits, I. 25
 Menke, M. R. 61, 101, 104
 Milner, Oscar I. 115
 Miyake, Shingo 1
 Momose, Tsutomu 33
 Morris, D. F. C. 51, 194
 Mukai, Yoshiko 33
 Murthy, A. R. Vasudeva
 206
Nutten, A. J. 294
 Nydahl, Folke 141

 Olya, A. 194
 Ottendorfer, L. 166

 Pearson, R. M. 217
Phillips, J. P. 217
 Přibil, Rudolf 8, 158
 Pullin, David 149

 Rao, V. R. Satyanarayana
 206
 Rees, D. I. 78
 Reynolds, G. F. 213
 Rieman, Wm., III, 67
 Ross, L. E. 108

 Salesin, Eugene D. 75
 Sant, Bharat R. 212
 Sant, Suseela B. 212
 Schulek, E. 120
 Singhal, S. P. 178
 Smith, G. Frederick 185
 Solymosi, F. 211
 Stephen, W. I. 78
 Stone, K. G. 250
 Svoboda, V. 201

 Takahashi, Takeo 1

 Ueno, Keihei 126, 244

 Watanabe, Mitsuko 33
 West, T. S. 166
 Wilkins, Donald H. 80,
 182
 Wilson, Cecil L. 17
 Wilson, H. N. 214
 Woodman, F. J. 295
 Workman, Walter 89

 Zachariasen, H. 44

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- ² S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
- ³ A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
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JUNE 1960

VOLUME 4

NUMBER 4

CONTENTS

JEAN P. DIXON: The determination of sulphur in organic compounds with metallic silver as absorbent: A critical examination - - - - -	221
LILLY GUSTAFSSON: Determination of ultramicro amounts of sulphate as methylene blue—I: The colour reaction - - - - -	227
LILLY GUSTAFSSON: Determination of ultramicro amounts of sulphate as methylene blue—II: The reduction - - - - -	236
KIYOKO HAYASHI, TAEKO DANZUKA and KEIHEI UENO: Spectrophotometric determination of phosphate using lanthanum chloranilate - - - - -	244
HENRY J. HOENES and K. G. STONE: Analytical chemistry of the α -benzoinoxime complexes of molybdenum, tungsten and vanadium - - - - -	250
D. L. LEUSSING: The estimation of the stabilities of bivalent transition metal complexes and deviations from the Irving-Williams order - - - - -	264
C. OLIVER INGAMELLS: New method for "ferrous iron" and "excess oxide" in rocks, minerals and oxides - - - - -	268
M. F. C. LADD and W. H. LEE: Radio-frequency methods in analytical chemistry - - - - -	274
Preliminary Communication:	
JOHN W. MILLER: A new reducing agent: Reduction of vanadium ^{IV} and uranium ^{VI} with ferrous ion in catechol solution - - - - -	292
Book Reviews - - - - -	294
Notices - - - - -	296
Papers Received - - - - -	298
Publications Received - - - - -	298
Indexes to Volume 4	

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