An International Journal of Analytical Chemistry

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talanta

PERGAMON PRESS
LONDON NEW YORK PARIS LOS ANGELES

VOLUME 3 NUMBER 4 FEBRUARY 1960

Publishing Offices: Headington Hill Hall, Oxford (OXFORD 64881),

Published monthly—3 Volumes per year, each of 4 issues

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Talanta, 1960, Vol. 3, pp. 307 to 310. Pergamon Press Ltd. Printed in Northern Ireland

TITRIMETRIC ANALYSIS OF 3:5-DINITROBENZOATE DERIVATIVES

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(*Received* 10 *August* 1959)

Summary—The neutralization equivalents of 3:5-dinitrobenzoate ester derivatives of alcohols and ethers were ascertained by refluxing with pyridine followed by potentiometric titration of the pyridine solution with 0.01*N* tetrabutylammonium hydroxide.

INTRODUCTION

PERHAPS the most useful means of isolation and identification of alcohols is through the preparation of their 3:5-dinitrobenzoate derivatives. Although some of the 3:5-dinitrobenzoate esters have low melting points, they crystallize readily and are easily obtained in a pure form. Dinitrobenzoate derivatives are also employed to a lesser extent in the identification of some aliphatic ethers, phenols, mercaptans and amino acids. These derivatives have been identified by melting point data, elemental analysis, infrared and absorption spectroscopy and chemical microscopy.

Fritz, Moye, and Richard[1] demonstrated that anilines substituted in the 2:4 or 2:4:6 positions with at least two nitro groups, or with one nitro group and one or more chloro groups can be titrated as acids in pyridine with a quaternary ammonium hydroxide base, and Sensabaugh, Cundiff and Markunas[2] showed that 2:4-dinitrophenylhydrazones can be titrated as weak acids in pyridine with 0.01*N* tetrabutylammonium hydroxide.

In the present study, 3:5-dinitrobenzoates were found to be sufficiently acidic to be analyzed in a similar manner; however, refluxing of the pyridine solutions, before titration, was necessary to obtain stoichiometric values. If the proposed procedure is combined with the traditional qualitative analysis techniques, it can be a most valuable supplementary adjunct for the identification of unknown alcohols.

EXPERIMENTAL

Reagents and apparatus

Tetrabutylammonium hydroxide, 0.01*N*: Prepare 0.1*N* tetrabutylammonium hydroxide as described previously.[3] Add 30 ml of methanol to 100 ml of this solution and dilute to 1 litre with benzene. Standardize against benzoic acid in pyridine solution. The dilution contains approximately 25 parts of benzene to one part of methanol and is stable for at least 30 days.

Precision-Dow Recordomatic Titrometer (Precision-Scientific Company, Chicago, Illinois).

The remainder of the reagents and apparatus are as described in a previous article.[3]

Procedure

Accurately weigh 2 to 20 mg of the 3:5-dinitrobenzoate into a standard tapered 125-ml Erlenmeyer flask, dissolve in 50 ml pyridine and reflux for 30 minutes. Cool to room temperature, transfer to a 250-ml electrolytic beaker and titrate potentiometrically under nitrogen with 0.01*N* tetrabutylammonium hydroxide. Determine the potentiometric end-point and correct for the solvent blank.

RESULTS

Fig. 1 shows a typical potentiometric curve for titration of an alcohol 3:5-dinitrobenzoate. Table I lists the results obtained in the analysis of representative 3:5-dinitrobenzoates. *d*-Mannitol 3:5-dinitrobenzoate is hexabasic and diethylene glycol 3:5-dinitrobenzoate is dibasic, while the remainder of the compounds listed are monobasic. All results listed are the average of at least two determinations.

TABLE I.—ANALYSIS OF 3:5-NITROBENZOATES BY TITRATION WITH 0.01*N* TETRABUTYLAMMONIUM HYDROXIDE

3:5-Dinitrobenzoate of	Melting Point, °C	Neutralization Equivalent		% Purity
		Theoretical	Experimental	
d-Mannitol	90.5	224.46	224.88	99.82
Methyl alcohol	106–107	226.17	225.90	100.33
Ethyl alcohol	92.5–93	240.19	241.80	99.34
Diethylene glycol	152–154	247.16	248.96	99.37
Allyl alcohol	46.5–47	252.21	252.87	99.74
n-Propyl alcohol	71.5–72	254.19	253.01	100.47
*iso*Propyl alcohol	122.5–123	254.19	255.65	99.43
n-Butyl alcohol	61–61.5	268.23	268.30	99.98
*iso*Butyl alcohol	82–83	268.23	265.18	101.16
sec-Butyl alcohol	74.5–75.5	268.23	268.55	99.88
tert-Butyl alcohol	143.5–144	268.23	272.23	98.53
tert-Amyl alcohol	106–108	282.25	282.19	100.03
*iso*Amyl alcohol	58–59	282.25	285.05	99.20
Ethylene glycol mono-ethyl ether	73–74	284.22	283.50	100.25
*cyclo*Hexanol	111–111.5	294.26	300.41	97.96
Benzyl alcohol	114–114.5	302.23	302.68	99.86
β-Phenylethyl alcohol	106.5–108	316.26	320.25	98.76
n-Octyl alcohol	60.5–61	324.32	323.68	100.20
Phenylpropyl alcohol	85–86	330.29	330.91	99.82
n-Nonyl alcohol	49–50	338.85	333.55	101.45
l-Menthol	157.5–158	350.36	348.45	100.55
n-Decyl alcohol	55–56	352.38	347.78	101.34
l-Tetradecanol	62.5–63.5	408.48	402.93	101.38
l-Octadecanol	74–75	464.58	466.41	99.61
Solanesol[4]	61.5–63	825.14	800.33	103.10

DISCUSSION

Among the *m*-dinitrobenzenes and derivatives, only 1:3:5-trinitrobenzene and 3-dinitrobenzene have been reported as being sufficiently acidic to be titrated as acids in nonaqueous systems[1,5]. Brockman and Meyer[5] titrated 3-dinitrobenzene in ethylenediamine with sodium aminoethoxide and obtained two inflections in the titration curve. In this laboratory *m*-dinitrobenzene was titrated in pyridine with tetrabutylammonium hydroxide and found to be an exceedingly weak acid. The single inflection in the potentiometric titration curve was slight and the stoichiometry was erratic.

Since acidity is known to increase as other electron-withdrawing groups are

introduced into the aromatic ring, it seemed reasonable to expect that a 3:5-dinitrobenzoate would be a much stronger acid than 3-dinitrobenzene. This assumption was correct. In preliminary investigations the 3:5-dinitrobenzoates were titrated directly after solution in pyridine. Although suitable potentiometric curves were

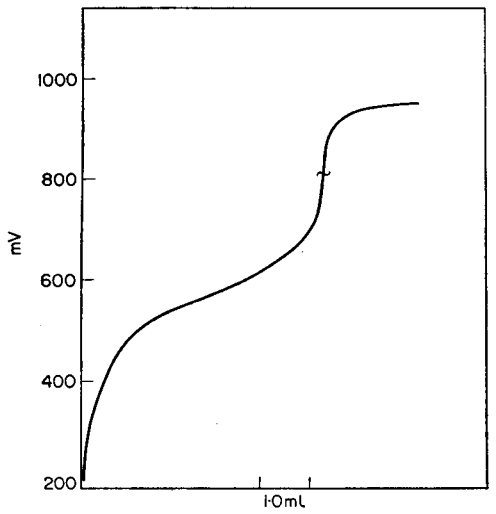

FIG. 1.—Titration of 3:5-dinitrobenzoate of *n*-butyl alcohol in pyridine with 0.01*N* tetrabutylammonium hydroxide.

realized, these titrations were not stoichiometric in that low neutralization equivalents were obtained. The most anomalous results were obtained on analysis of the dinitrobenzoates of the tertiary alcohols. If the solutions of dinitrobenzoates in pyridine were allowed to stand 48 hours, and then titrated, quantitative results were realized in most instances, although the precision was poor. Consistently accurate and precise results were obtained only when the dinitrobenzoates were refluxed in pyridine before titration.

Other solvents were substituted for pyridine in an effort to eliminate the refluxing time required with pyridine. These solvents included acetone, acetonitrile, dimethyl formamide, ethylenediamine, *iso*propyl alcohol and *n*-propyl alcohol. The lower molecular weight 3:5-dinitrobenzoates analyzed satisfactorily in acetone, but poor results were realized with the higher molecular weight derivatives. None of the other solvents were suitable in this analysis.

The method has been used also for the determination of 3:5-dinitrobenzoates of symmetrical ethers and some phenols. However, the phenol derivatives, especially those of the highly substituted phenols, do not titrate quantitatively and the present method is not recommended for their analysis. Although this procedure has not been tested for the analysis of the dinitrobenzoate derivatives of mercaptans and amino acids, there is no apparent reason why it should not be applicable to these derivatives also.

Indicators cannot be used in the discernment of the end-points, as all solutions were highly coloured.

Zusammenfassung—Die Neutralisationsäquivalente von Estern der 3:5-Dinitrobenzoesäure wurden bestimmt durch Erhitzen am Rückflusskühler mit Pyridin und anschliessende potentiometrische Titration der Pyridinlösung mit 0.01 n Tetrabutylammoniumhydroxyd.

Résumé—Les auteurs ont déterminé les "équivalents de neutralisation" des dérivés ester 3-5 dinitrobenzoate des alcools et des éthers par chauffage au reflux avec la pyridine suivi d'un titrage potentiométrique de la solution de pyridine avec l'hydroxyde de tétrabutylammonium 0,01 N.

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Talanta, 1960, Vol 3, pp. 311 to 317. Pergamon Press Ltd. Printed in Northern Ireland

COLORIMETRIC DETERMINATION OF BORON IN NITRATE SOLUTIONS

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(*Received* 10 *August* 1959)

Summary—A method has been developed for the determination of microgram amounts of boron in nitrate solutions. Nitrate is destroyed with formic acid and sulphuric acid under reflux conditions. As much as 3 millimoles of nitrate are reduced completely by refluxing 1 ml of the nitrate solution with 1 ml of 88% formic acid for 15 minutes. Boron is determined by the carminic acid method after forming the colored complex *in situ*. This method has been applied to the determination of boron in uranyl nitrate solutions after extraction of uranium with tri-*n*-octylphosphine oxide dissolved in *cyclo*hexane.

The colorimetric determination of boron in a variety of media has been the object of a considerable number of investigations during the past few years. In this laboratory, the carminic acid, spectrophotometric method[2] has been used frequently for the measurement of boron in aqueous solutions. Nitrate was found to bleach the colour of both carminic acid and the boron-carminic acid complex at room temperature in the presence of hydrochloric acid. Nitrate and strong oxidants interfere similarly with the other widely used chromogenic reagents (quinalizarin,[2] 1 : 1-dianthramide,[5] and curcumin[6]). Methods proposed for the removal of nitrate from boron solutions include: (1) ignition of an alkaline medium,[8] (2) reduction with ferrous sulphate or sodium sulphite.[3] The ignition method has been utilized successfully in the analysis of organic compounds wherein ashing of the sample is a requisite for dissolution; however, such a technique is inconvenient for the determination of boron in acidic solutions. Previous investigations in this laboratory have revealed that iron, in amounts greater than 1 g, interferes with the carminic acid method. Although quantitative reduction of nitrate can be achieved with the mercury cathode, the sample solution is diluted considerably during transfer from the electrolytic cell.

This study was undertaken to develop a method for the determination of boron in concentrations less than 100 ppm in 0.5*M* to 3*M* nitrate solutions. Carminic acid was chosen as the colorimetric reagent. Formic acid was selected as the most feasible reagent for destroying nitrate since only volatile products are formed in this redox reaction. The probable reactions involved are shown below.

$$HCOOH + 2NO_3^- + 2H^+ \rightleftharpoons CO_2 + N_2O_4 + 2H_2O \quad (1)$$

$$3HCOOH + 2NO_3^- + 2H^+ \rightleftharpoons 3CO_2 + 2NO + 4H_2O. \quad (2)$$

Since these reactions must be carried out at the boiling point of the solution, a reflux condenser is required in order to prevent loss of boron.

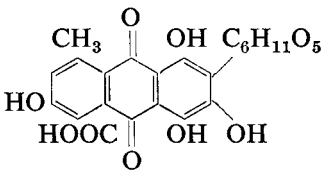
The maximum volume of the test solution was set at 2 ml. Larger volumes are impractical since inordinately large amounts of concentrated sulphuric acid would be

necessary in order for the reaction between carminic acid and boric acid to proceed to completion.[2]

The method was applied to the determination of boron in nitrate solutions of uranium.

Effect of nitrate on the absorbance of carminic acid

The bleaching effect of nitrate on carminic acid is postulated to be due to the destruction of the quinoidal structure of the carminic acid molecule, I.



I

The relationship between degree of bleaching and concentration of nitrate was established with a series of solutions that contained 0.001 to 1.6 millimoles of nitric acid. These solutions were prepared by adding two drops of hydrochloric acid, 10 ml of sulphuric acid, and 10 ml of carminic acid to 2 ml of the nitrate solution. The absorbance of each of these solutions was measured versus that of a solution that contained no nitrate. The bleaching effect of nitrate is readily observed in Fig. 1. The net absorbance of the carminic acid solution decreases logarithmically with increasing concentration of nitrate. As little as 0.001 millimoles of nitrate reduces the absorbance by 0.025 units. Even trace amounts of nitrate are thus detrimental to the development of the colour of carminic acid in sulphuric acid medium and must be removed before the addition of the chromogenic agent.

When N_2O_4 is produced from the reaction between nitric and hydrochloric acids, the colour of the carminic acid solution is initially green rather than deep red. In solutions that contain one millimole of nitric acid, the deep red colour is restored on waiting the customary 45-minute period; however, in the 1.6-millimole solution, the final colour of the carminic acid solution is yellow, not red.

Decomposition of nitrate with formic acid

The degree to which nitrate is reduced when refluxed for 20 minutes with formic acid was investigated with synthetic solutions wherein the molar ratio of formic acid to nitric acid was varied from 1 to 13. Each solution contained 3 millimoles of nitric acid, 4 millimoles of sulphuric acid, and 3 to 40 millimoles of formic acid in a total volume of either 2 or 5 ml. After being refluxed for 20 minutes the solution was cooled and transferred to a 10-ml volumetric flask. The apparatus was rinsed with water and the rinse solution added to the sample. The amount of nitrate that remained after the solution had been refluxed was determined spectrophotometrically[1,7] by measurement of the absorbance of the solution versus water at 301 mμ. The effects of solution volume and ratio of the reactants on the percentage of nitrate destroyed are presented graphically in Fig. 2.

The reduction of nitrate with formic acid can be achieved with less formic acid if the solution volume is kept to a minimum. In the case of 2-ml test solutions, a molar

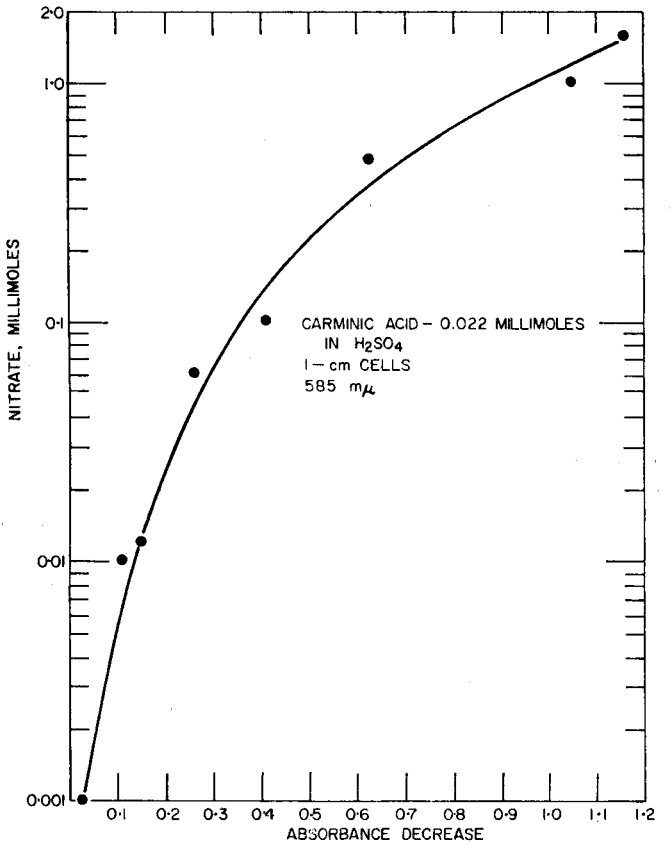


FIG. 1.—Effect of nitrate on the absorbance of carminic acid

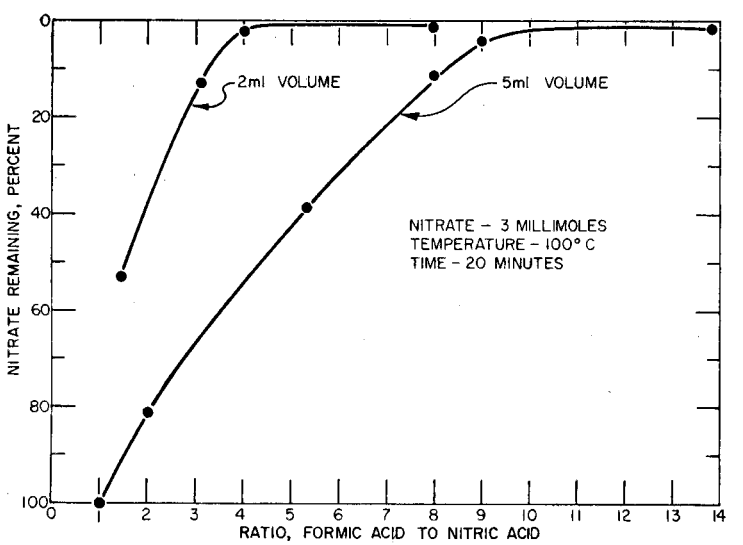


FIG. 2.—Reduction of nitrate with formic acid

ratio ($HCOOH:NO_3^-$) of four is sufficient to reduce, to an extent exceeding 99%, 3 millimoles of nitrate. For a similar ratio in 5-ml test solutions, the corresponding reduction was only 45% complete. In order to attain 99% reduction in 5-ml test volumes, the ratio of formic acid needed was approximately ten.

As shown in Fig. 2, complete reduction is approached asymptotically. Trace amounts of nitrate were found in every test conducted. This nitrate is assumed to be transported physically to the upper portion of the condenser during reflux and thus is not adequately contacted by the formic acid. The amount of nitrate that is so transferred is constant for practical purposes and does not vary appreciably with the shape and size of the apparatus or when the amount of nitrate originally present is reduced to as low as 0.75 millimoles. No enhancement in reduction of nitrate was achieved by doubling the concentration of sulphuric acid; however, slight impairment was observed when this acid was left out of the solution. Essentially no reduction occurred in solutions wherein the reactant ratio was 8 when 6 millimoles of sodium hydroxide were added. This amount of base was sufficient to neutralize the 3 millimoles of nitric acid present but insufficient to achieve neutralization of 23 millimoles of formic acid.

Although the amount of nitrate that remains after refluxing the solutions under optimum conditions is sufficient to cause partial bleaching of carminic acid, this source of error can be eliminated by rinsing the condenser with 10 ml of concentrated sulphuric acid followed by 10 ml of the carminic acid solution. This rinse, which in effect constitutes development of the boron-carminic acid complex, serves to complete the reduction of nitrate as a consequence of the exothermic reaction that takes place when the acids come in contact. For example, when 3 millimoles of nitric acid are refluxed with 24 millimoles of formic acid, in a total volume of 2 ml, for 20 minutes, and the carminic acid colour developed in the reaction, the absorbance of this solution does not vary from that of a reagent blank solution by more than 0.01 units.

Choice of wavelength

A selection of the optimum wavelength for measurement of the absorbance of the boron-carminic acid complex was made after carrying out a spectral study of this complex with a Cary recording spectrophotometer, Model 14M. Two lots of carminic acid were used in the preparation of reagents. The spectra of solutions that contained 1 μg of boron per ml (20 μg of boron per 22 ml) exhibited constant absorbance between 580 mμ and 615 mμ when measured versus a corresponding reagent reference solution. The slit width was smallest, 0.14 mm, in the spectral region of 585 mμ to 600 mμ and increased to 0.17 mm at 580 mμ and 610 mμ and to 0.18 mm at 615 mμ. A wavelength of 585 mμ was selected for this investigation primarily because this wavelength had been used in several previous methods for the determination of boron in this laboratory. The original choice of wavelength was based on the work of Hatcher and Wilcox.[8] Recently, Callicoat and Wolszon[4] have expressed a preference for 610 mμ as the optimum wavelength for measuring the intensity of the boron-carminic acid colour.

Effect of formic acid on the absorbance of carminic acid

Since the quinoidal structure of carminic acid can be reduced to the corresponding hydroquinone form by zinc in acetic acid,[9] the effect of formic acid, a much weaker reducing agent, was investigated to determine if carminic acid is reduced by relatively

large amounts of this reagent. The absorbance of carminic acid in solutions that contained 16 and 23 millimoles of formic acid was measured at 585 mμ versus an equivalent concentration of carminic acid in sulphuric acid. No change in absorbance was observed at either concentration of formic acid.

EXPERIMENTAL

Apparatus and reagents

A Beckman spectrophotometer, Model DU, and Cary recording spectrophotometer, Model 14 M, with 1-cm matched silica cells were used for measurement of absorbance.

Either Pyrex or Vycor flasks can be used without significant contamination if they are washed in hydrochloric acid and rinsed with water.

Boron: standard solutions. A stock solution that contained 500 μg of boron per ml was prepared by dissolving 440 mg of $Na_2B_4O_7 \cdot 10H_2O$ in 100 ml of water in a polyethylene bottle. Dilute solutions that contained 100, 50, 25, and 5 μg of boron per ml were prepared by diluting aliquots of the stock solutions with water.

Carminic acid solution: 0.1 % (w/v) in H_2SO_4. (Carminic acid is obtainable from National Aniline Division, Allied Chemical and Dye Corporation.)

Formic acid: 88 %. Analytical, reagent-grade.

Sulphuric acid. C. P. grade acid obtained from the General Chemical Division of Allied Chemical and Dye Corporation.

Procedure for the development of the boron-carminic acid colour

Two ml of aqueous solution that contains 40 μg of boron is transferred to a 50-ml Vycor beaker. Two drops of concentrated hydrochloric acid are then added to the beaker. The beaker is cooled in an ice bath, following which 10 ml of concentrated sulphuric acid and 10 ml of carminic acid solution are added by pipette and the solution is stirred thoroughly with a Teflon stirring rod. The beaker is then removed from the ice-bath and allowed to stand at least 45 minutes, after which the absorbance of the boron-carminic acid is measured at 585 mμ versus a reagent blank. The amount of boron in the solution is established by reference to a calibration curve or calculated by means of an empirical factor.

The colour of the complex attains maximum development in 30 to 40 minutes, remains constant for approximately 1·5 hours, and then fades slowly.

Determination of boron in synthetic nitrate solutions

Synthetic boron solutions that contained various amounts of nitrate were prepared by combining 1 ml of standard boron solution, 0·2 ml of sulphuric acid and 0·2 ml of various concentrations of nitric acid. The nitrate was reduced by the addition of 1 ml of formic acid in two, 0·5-ml increments. The boron-carminic acid colour was developed *in situ* by adding the necessary reagents through the condenser and subsequently was measured versus a reagent blank. The results are shown in Table I.

The coefficient of variation for the determination of 25 μg of boron is 1 %. This order of precision was obtained in the presence of varying concentrations of nitric acid. The precision for determining smaller amounts of boron is less, 5 % for 12.5 μg of boron. One of the contributiong factors to this decrease in precision is the presence of minute bubbles of carbon dioxide in the final solutions. These bubbles are formed by the decomposition of excess formic acid with concentrated sulphuric acid. Even on long standing, some gas remains which naturally affects the absorbance readings somewhat. The over-all effect is greatly minimized by frequent agitation of the solution while awaiting complete colour developement.

Determination of boron in synthetic solutions of uranyl nitrate

Because of its high capacity for absorbing neutrons, the concentration of boron in nuclear fuels must be kept to a minimum. The analysis of boron in uranium is thus one of the more common analyses in nuclear technology. Boron must generally be separated from uranium before its determination since at a weight ratio of 1000 (U : B) the error for the carminic acid method is about 15 %.

Table 1.—Determination of boron in nitrate solutions

NO_3, *Molarity*	Boron, μg			Coefficient of Variation, *Per Cent*
	Present	Found	Average	
0.4	12.5	11.4		
		12.4		
		12.8		
		12.0		
		11.4	12.0 ± 0.6	5
	25	24.8		
		26.0		
		24.8		
		24.0		
		25.6		
		24.7		
		25.0		
0.8	25	25.5		
		25.6		
1.5	25	27.4		
		26.8		
2.3	25	24.4		
3.0	25	24.4		
		24.9		
		24.8	25.2 ± 0.3	1

Boron is readily separated from uranium by ion-exchange resins;[10] however, this method results in considerable dilution of the sample so that concentration by evaporation is required. In order to avoid this step, liquid-liquid extraction separation was used with a *cyclo*hexane solution of tri-*n*-octylphosphine oxide (TOPO) as the reagent. This compound, dissolved in *cyclo*hexane, is an excellent extractant for uranium from either acidic nitrate or chloride solutions.[12] One millimole of TOPO in *cyclo*hexane can be used to extract 80 mg of uranium from 2*M* HNO_3.[11] Boron is not extracted and is retained in the aqueous phase.[12]

A series of synthetic solutions was prepared to contain 12 mg of uranium and 50 μg of boron in 5 ml of 2*M* HNO_3. These solutions were equilibrated with 5 ml of 0.1*M* TOPO for 10 minutes to extract uranium. One-ml aliquots of the aqueous phase were then transferred to a reflux flask, following which the nitrate in the solution was reduced with 1 ml of HCOOH, and boron was then determined by the carminic acid method. The average result of these determinations was 50.5 μg with a coefficient of variation of 1%. The extraction of uranium with *cyclo*hexane solution of TOPO, therefore, does not cause any error in the determination of boron in the resulting aqueous phase.

Procedure

Transfer 1 ml of the solution that contains 5 to 40 μg of boron to a 10-ml reflux flask and then add 0.2 ml of sulphuric acid and 0.5 ml of formic acid. Connect the flask to a water-cooled reflux condenser and heat the contents of the flask until all coloured oxides of nitrogen are expelled through the condenser. Cool the flask to <100° and then add 0.5 ml of formic acid to the flask through the condenser. Heat the solution to reflux temperature for 15 minutes and then cool in an ice bath. Add 2 drops of

hydrochloric acid, 10 ml of sulphuric acid, and 10 ml of carminic acid solution (in this order) to the flask by allowing these reagents to wash down the inner wall of the condenser. When the temperature of the solution is less than ~25°, remove the flask from the condenser, stir the solution and then transfer it to a 50-ml Vycor beaker. Set the solution aside for at least 45 minutes before measuring its absorbance at 585 mμ versus a reference solution that contains 2 ml of water, 2 drops of hydrochloric acid, 10 ml of sulphuric acid and 10 ml of carminic acid solution. Determine the concentration of boron by referring the absorbance to a calibration curve or calculate it by means of a calibration factor.

Work carried out under contract No. W-7405-eng-26 at Oak Ridge National Laboratory, operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

Zusammenfassung—Eine Methode zur Bestimmung von Mikrogrammengen Bor in Nitratlösungen wurde entwickelt. Nitrat wird mittels Ameisen-Schwefelsäure unterm Rückflusskühler zerstört. Bis zu 3 Millimolen Nitrat werden völlig reduziert wenn 1 ml der Nitratlösung mit 1 ml 88% iger Ameisensäure für 15 Minuten unter Rückfluss gekocht wird. Bor wird nach der Carminsäuremethode photometrisch bestimmt. Die methode wurde auf die Borbestimmung in Uranylnitratlösungen nach Extraktion des Urans mit Tri-*n*-octylphosphinoxyd in Cyclohexanlösung angewendet.

Résumé—Les auteurs ont mis au point une méthode pour le dosage de microgrammes de bore dans des solutions de nitrate. Le nitrate est détruit par l'acide formique et l'acide sulfurique par chauffage au reflux. On réduit des quantités aussi importantes que 3 millimoles de nitrate par chauffage au reflux de 1 ml de solution de nitrate avec 1 ml d'acide formique à 88% pendant 15 minutes. Le bore est dosé par la méthode de l'acide carminique après formation du complexe coloré "in situ". On a appliqué cette méthode au dosage du bore dans des solutions de nitrate d'uranyle après extraction de l'uranium par l'oxyde de tri-*n*-octylphosphine dissous dans le cyclohexane.

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Talanta, 1960, Vol. 3, pp. 318 to 323. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC ESTIMATION OF PHENOL IN SOLUTIONS CONTAINING TYROSINE, TRYPTOPHANE, HISTIDINE OR CHYMOTRYPSIN

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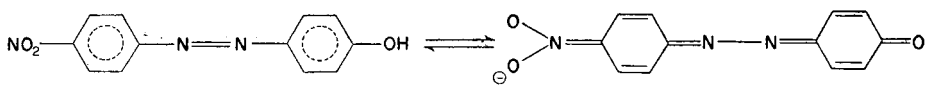
(*Received* 21 *August* 1959)

Summary—A sensitive spectrophotometric method for the estimation of phenol ($10^{-5}M$) in solutions containing tyrosine, tryptophane, histidine or chymotrypsin is described. The method employs diazotised *p*-nitroaniline as reagent.

THE direct estimation of low concentrations of phenol in alkaline solution by measurement of the intensity of absorption of phenoxide ion at 234 mμ has been described earlier.[1] This method is unsuitable for the estimation of phenol in the presence of alkali-labile phenyl esters. Furthermore it is difficult to apply accurately in the presence of low concentrations of aromatic amino-acids (particularly tyrosine) or proteins, on account of their high background absorption in the ultra-violet.[2,3]

The present method avoids these difficulties by utilising a sensitive colour reaction of phenol.[4] When dilute aqueous phenol solutions are treated with diazotised *p*-nitroaniline at pH 8, 4-(4′-nitrobenzene-azo) phenol (I) is formed.[5] The latter gives rise to the intensely red anion (II) in alkaline solution.[6]



I II

The intensity of absorption of the species II, which shows a prominent maximum in the visible region[7,8] (λ_{max} 480 mμ, ε_{max} 2,000; Fig. 1), may be conveniently determined spectrophotometrically, thereby affording the concentration of phenol in the original solution.

Coupling of the diazo reagent with phenol is optimal in the neutral pH region. At the same time this pH region favours decomposition of the diazo species into *p*-nitrophenol and nitrogen.[9–11] The *p*-nitrophenol reacts with more diazo reagent forming coloured products which tend to increase the background absorption of the solution. These undesirable side-reactions may be largely eliminated by reducing the reaction time to a minimum. In practice a small excess of diazotised *p*-nitroaniline is allowed to react with the phenol solution in phosphate buffer (pH 8) for one minute, and the product is then made strongly alkaline. The strongly alkaline conditions at once check further coupling,[9] and give rise to the desired red ion II.

It is evident (Fig. 5) that phenol couples almost instantaneously with the diazo solution at pH 8. This behaviour makes it possible to estimate phenol in the presence of tyrosine, tryptophane or histidine, which are found to react with the diazo solution

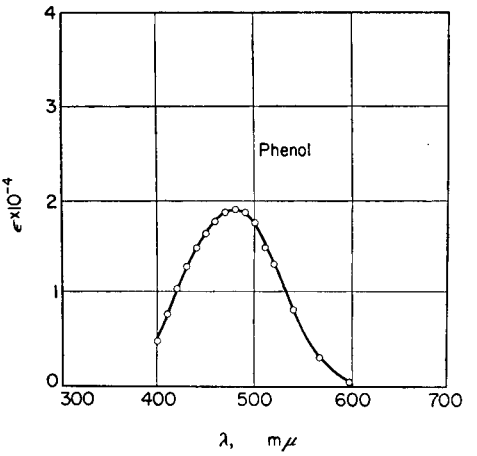


FIG. 1.—Absorption maximum produced by treatment of buffered phenol solution with diazo reagent, and making alkaline after 30 min.

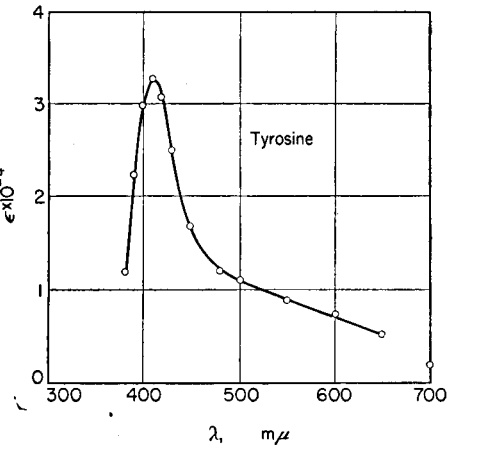


FIG. 2.—Absorption maximum produced by treatment of buffered tyrosine solution with diazo reagent, and making alkaline after 30 min.

much more slowly (Fig. 5). Proteins themselves are known to undergo coupling with diazo solutions,[12,13] but the presence of low concentrations of protein does not seriously interfere with phenol estimation under the experimental conditions of this method. Linear dependence of optical density at 480 mμ on phenol concentration, in the presence of the enzyme-protein chymotrypsin ($2.14 \times 10^{-5} M$) is shown in Fig. 6.

EXPERIMENTAL

Apparatus and reagents

Measurements were carried out using a Unicam S.P. 500 spectrophotometer (Cambridge, Instrument Co.), with 1-cm silica cells. Small volumes of solution were measured using a micrometer syringe.

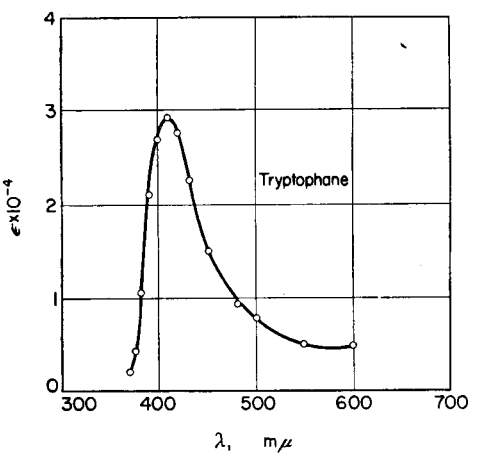


FIG. 3.—Absorption maximum produced by treatment of buffered tryptophane solution with diazo reagent, and making alkaline after 30 min.

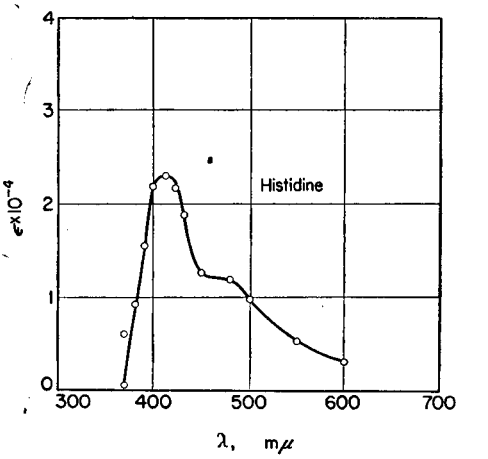


FIG. 4.—Absorption maximum produced by treatment of buffered histidine solution with diazo reagent, and making alkaline after 30 min.

Diazo reagent: *p*-Nitroaniline (1·5 g) was dissolved in concentrated hydrochloric acid (40 ml) and made up to 500 ml with distilled water. For phenol estimations, 5-ml portions of this stock solution were withdrawn and cooled in ice, and solid sodium nitrite was gradually added until a slight excess of nitrous acid persisted. Solutions of *p*-nitrobenzene diazonium chloride prepared in this manner, were stored for minimum periods in the dark.

Procedure

Determination of optimum concentration of diazo reagent required: Increasing amounts of diazo reagent were added to 3 ml of $3 \times 10^{-5}M$ phenol in $0{\cdot}1M$ aqueous sodium phosphate buffer (pH 8·0).

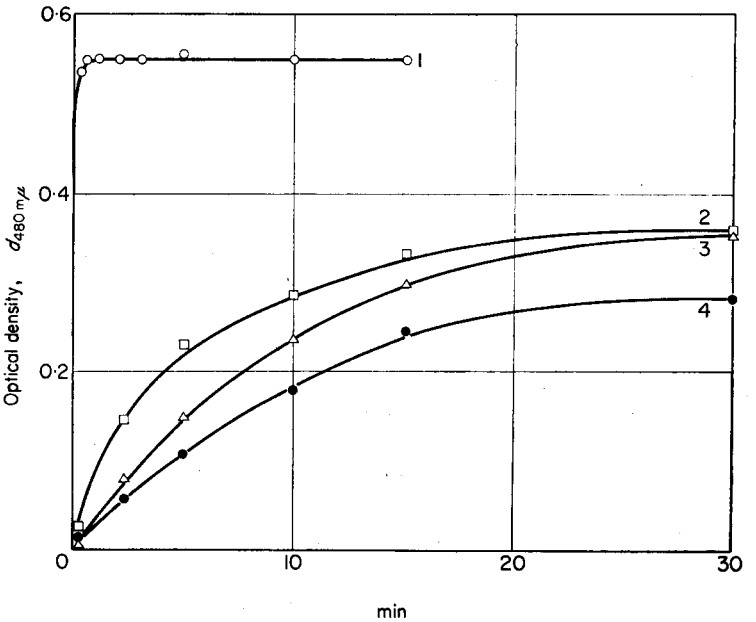


FIG. 5.—Comparison of rates of colour development on treatment of buffered solutions of phenol (1), tyrosine (2), tryptophane (3), and histidine (4) ($3 \times 10^{-5}M$) with diazo reagent, and subsequently making alkaline.

After maintaining at 20° for one minute, 1 ml of $0{\cdot}2N$ aqueous sodium hydroxide was added, and the optical density at 480 mμ was measured. (Table I.) Maximum optical density was obtained by the addition of only 0·02 ml of reagent. To ensure an excess of reagent 0·03 ml was added in subsequent estimations.

TABLE I.—DEPENDENCE OF OPTICAL DENSITY (d_{480}) ON VOLUME OF DIAZO REAGENT ADDED TO 3 ml OF BUFFERED PHENOL SOLUTION ($3 \times 10^{-5}M$) UNDER THE PRESCRIBED CONDITIONS

Diazo reagent, *ml*	$d_{480\,m\mu}$
0·01	0·265
0·02	0·555
0·03	0·550
0·05	0·540
0·10	0·555
1·00	0·545

Dependence of optical density (480 mμ) *on phenol concentration:* Three ml of solutions of phenol in 0·1*M* sodium phosphate buffer were treated with 0·03 ml of diazo reagent, and set aside for one minute at 20°. After making alkaline with 1 ml of 0·2*N* aqueous sodium hydroxide, the optical density at 480 mμ was measured. A linear plot of $d_{480\,m\mu}$ against phenol concentration over the range $1 \times 10^{-5}M$ to $5 \times 10^{-5}M$ phenol was obtained (Fig. 6).

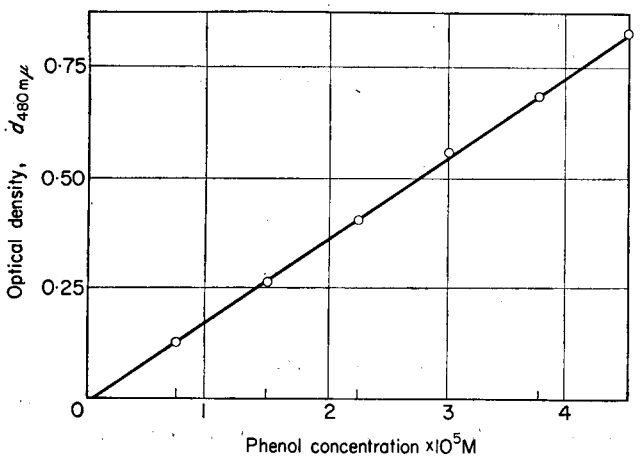


FIG. 6.—Dependence of optical density (d 480 mμ) on phenol concentration in buffered solutions, after treatment with diazo reagent, and making alkaline.

Stability of colour: Solutions of phenol, treated with the diazo reagent in the foregoing manner, showed no change in optical density after standing overnight. Similar preparations in the presence of chymotrypsin ($3 \times 10^{-5}M$) showed a slow decrease of optical density at 480 mμ (Table II) with time.

TABLE II.—TIME DEPENDENT EFFECT OF CHYMOTYPSIN (3×10^{-5} *M*) ON THE OPTICAL DENSITY (d_{480}) PRODUCED ON TREATMENT OF PHENOL SOLUTIONS ($3 \times 10^{-5}M$) WITH DIAZO REAGENT AND MAKING ALKALINE IN THE PRESCRIBED MANNER

Time, *min*	$d_{480\,m\mu}$
5	0·430
16	0·420
31	0·412
60	0·410
overnight	0·320

Reaction of phenol, tyrosine, tryptophane and histidine solutions with the diazo reagent: Solutions of phenol, tyrosine, tryptophane and histidine ($3 \times 10^{-5}M$) were prepared in 0·1*M* sodium phosphate buffer and 0·03 ml of the diazonium reagent was added to 3 ml of each. The mixtures were maintained at 20° for 30 minutes, made alkaline by the addition of 1 ml of 0·2*N* aqueous sodium hydroxide and their absorption spectra in the visible region measured against a blank cell containing sodium phosphate buffer treated in the same manner as the reactant solutions (Figs. 1–4).

Comparison of rates of colour development of phenol, tyrosine, tryptophane and histidine: Solutions of phenol, tyrosine, tryptophane and histidine ($3 \times 10^{-5}M$), in 0·1*M* sodium phosphate buffer, were treated with the diazo reagent as in the previous experiment. The solutions were made alkaline with 1 ml of 0·2*N* aqueous sodium hydroxide, after increasing time intervals, and optical densities were measured at 480 mμ against a blank phosphate-diazo solution. The rate curves are shown in Fig. 5.

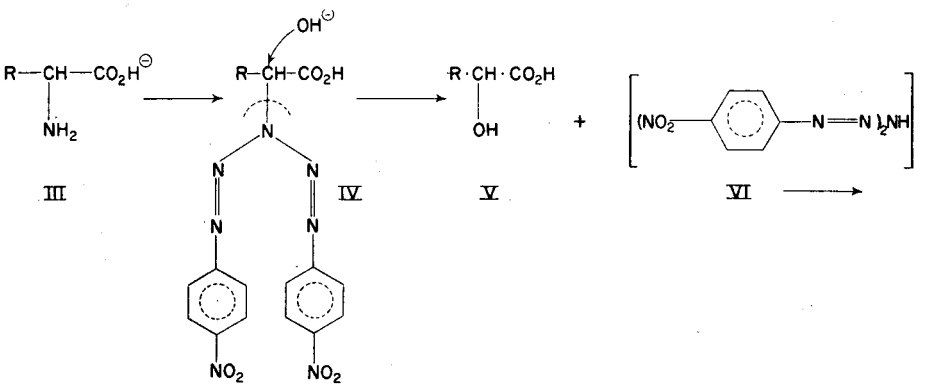
Rate of colour production in phenol solutions at 0°: Solutions of phenol (3-ml portions, $3 \times 10^{-5}M$) in 0·1*M* sodium phosphate buffer, were maintained in an ice-bath. To each portion, 0·03 ml of diazonium reagent was added, followed by 1·0 ml of 0·2*N* aqueous sodium hydroxide after increasing time intervals. The optical densities were measured at 480 mμ. (Table 3). This information is useful when phenol estimations are required for kinetic studies at 0°.

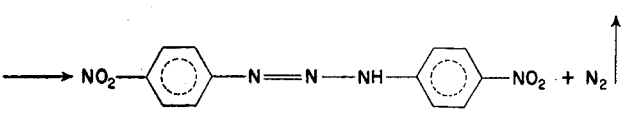
TABLE III.—RATE OF COLOUR PRODUCTION AT 0° IN PHENOL SOLUTIONS ($3 \times 10^{-5}M$) TREATED WITH DIAZO REAGENT IN THE PRESCRIBED MANNER

Reaction time (*sec*)	$d_{480 m\mu}$
15	0·360
30	0·526
60	0·618

DISCUSSION

Comparison of the visible absorption spectra of phenol, tyrosine, tryptophane and histidine solutions, after the standard treatment with diazotised *p*-nitroaniline, reveals interesting features. Phenol solutions, on the one hand, show the absorption maximum of the ion II at 480 mμ (Fig. 1). Tyrosine, tryptophane and histidine solutions, on the other hand show a distinctly different absorption maximum 410 mμ (Figs. 2-4) which is apparently common to all three amino-acids. A closely similar maximum (410 mμ) was obtained from a solution of 4:4′-dinitrodiazoaminobenzene[14] (VII) buffered similarly to pH 8. It would appear that tyrosine, tryptophane and histidine do not undergo appreciable nuclear coupling with the diazo solution under these conditions, for this would yield different chromophoric species.[15,16] Instead, these amino-acids





VII

evidently react with diazotised *p*-nitroaniline affording the dinitrodiazoaminobenzene (VII) and the corresponding α-hydroxy acids (V).[17–19] In line with earlier work we suggest that this reaction proceeds through the α-amino-bis-diazo compound (IV). The latter may then undergo subsequent nucleophilic attack by OH^- yielding the α-hydroxy acid and the unstable pentazine[20–22] (VI) which immediately decomposes into nitrogen and the dinitrodiazoaminobenzene.

Acknowledgement—Thanks are due to Mr. P. M. Newman for helpful discussion.

Zusammenfassung—Eine empfindliche spectrophotometrische Methode zu Bestimmung von Phenol (10^{-5} m) in Lösungen, die Tyrosin, Tryptophan, Histidin oder Chymotrypsin enthalten, wird beschrieben. Diazotiertes *p*-Nitroanilin wird als Reagenz verwendet.

Résumé—Les auteurs décrivent une méthode spectrophotométrique sensible pour le dosage du phénol ($10^{-5}M$) dans des solutions contenant de la tyrosine, du tryptophane, de l'histidine ou de la chymotrypsine. La méthode utilise comme réactif la *p*-nitroaniline diazotée.

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Talanta, 1960, Vol. 3, pp. 324 to 329. Pergamon Press Ltd. Printed in Northern Ireland

THE ANALYTICAL CHEMISTRY OF THE PYRIDINE THIOCYANATES—II

THE SEPARATION OF RUTHENIUM AND PALLADIUM

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(*Received* 22 *August* 1959)

Summary—A procedure is described for the separation and subsequent colorimetric determination of ruthenium and palladium as complex and ammine-type thiocyanates respectively, using solvent extraction. Suggestions are put forward as to the nature of the ruthenium complex occurring in solution.

A NUMBER of organic reagents have been employed in the solvent extraction of the platinum metals, but the use of these has been largely restricted to palladium and platinum. One difficulty in the way of easy formation of chelate compounds is the fact that the commonest form for these metals is in stable complex ions such as $(PtCl_6)^{2-}$, $(RuCl_5OH)^{3-}$. This class of compounds, involving hexachloro-complexes etc., is presumably essentially ionic in character and will exist as entities only in the solid state; reagents forming such compounds would not be expected to assist the solvent extraction of the platinum metals. A second category, however, apparently consists of non-ionic substances related to $Pd(NH_3)_2Cl_2$, and solubility in organic solvents may be expected. Thus Ryan[1] extracted the *p*-nitrosodiphenylamine complex, $Pd(C_{12}H_{10}N_2O)_2Cl_2$, into ethyl acetate, ether and chloroform, while Yoe and Kirkland[2] used *p*-nitrosodimethylaniline for a similar purpose. The covalent complex $Pd\,py_2Cl_2$ (py = pyridine) has been known for many years,[3,4] but the analytical possibilities of similar complexes with thiocyanate ion in place of halogen appear either not to have been noted in the literature or to have been completely neglected, although Rubinshtein[5] prepared a series of substituted pyridino-chlorides of palladium, without investigating their extractability into organic solvents.

A survey of the literature reveals that little attention has been paid to the solvent extraction of thiocyanate complexes of the platinum metals. Ogburn[6] first noted the formation by Ru^{III} of a red colour with thiocyanate ion, which is extracted by suitable organic solvents.[7] Recently[8] the red complex $[Pd(SCN)_4]^{2-}$ has been extracted with butyl alcohol or *iso*-amyl alcohol at pH below 5, in the presence of Pt^{IV} and Ir^{IV}. Apart from such investigations, however, it would appear that the analytical value of the complex and ammine-type thiocyanates of ruthenium and palladium has not been examined to any extent.

This paper describes a procedure for the separation and determination of ruthenium and palladium through the formation of compounds of both the above types.

PRELIMINARY INVESTIGATIONS

The replacement of Cl by SCN in $Pd\,py_2Cl_2$ was undertaken and the conditions under which a pyridine thiocyanate of palladium is formed were examined. It was

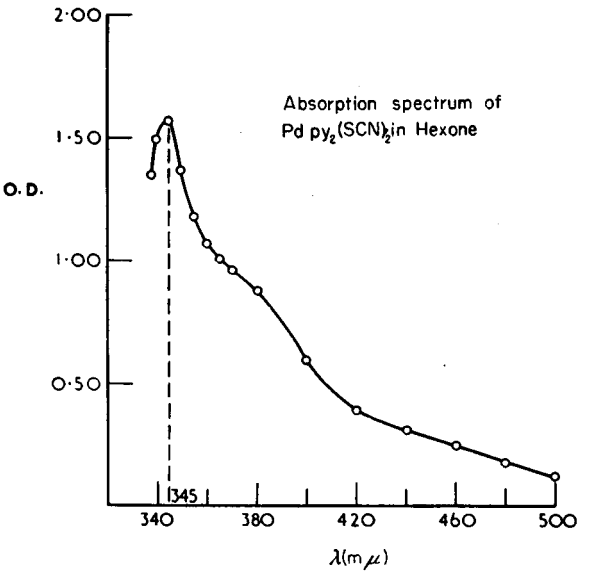
found that if excess thiocyanate is added to a palladous chloride solution and the pH adjusted to between 4 and 6, the addition, dropwise, of pyridine causes the red-brown solution to become pale yellow in colour. After a moment the solution becomes completely colourless with the formation of a yellow flocculent precipitate, which is only obtained from solutions containing palladium alone. In the presence of other platinum metals no precipitate is obtained from the pale yellow solution and this effect is also observed in the presence of excess pyridine or in alkaline solution. The yellow precipitate was analysed both by ignition to PdO and by C, H and N determinations; all results accorded with the formula Pd $py_2(SCN)_2$. Both this precipitate and the pale yellow aqueous solution from which it is obtained were found to be very readily and completely extracted, even from solutions of pH up to 12, by organic solvents such as chloroform, ethers, ketones and tributyl phosphate, in all cases yielding a pale yellow solution in the organic phase. The species extracted was thought to be the molecular species Pd $py_2(SCN)_2$, since both chloroform and hexone (methyl *iso*-butyl ketone) yield similarly coloured solutions, very different in colour from that of the palladium thiocyanate complex extracted into hexone from acid solutions. Palladium here closely resembles nickel in the behaviour of its complex and ammine-type thiocyanates.[9]

The behaviour of ruthenium complex thiocyanates was next investigated. Ruthenium was present in the tervalent state as the complex $[Ru(H_2O)Cl_5]^{2-}$, soluble in water or dilute hydrochloric acid. In 0·1*N* acid solution, on the addition of excess thiocyanate, a crimson extractable complex is obtained, which is stable provided that the solution is not heated. On heating the solution, however, the colour changes to deep blue, this process being complete at about 50° in 0·1*N* acid solution and being independent of the particular acid used. In neutral solution it is necessary to maintain the temperature near to the boiling point for a few moments in order to bring the reaction to completion, but in both cases an odour of hydrogen sulphide is observed. The blue colour obtained is considerably intensified if the solution is made 1*N* or more in acid concentration, when it appears very stable and showed no fading after standing for one week.

From neutral or only weakly acid solutions this blue complex is extracted only partially by hexone or a 1 : 5 tributyl phosphate/*cyclo*hexane mixture and not at all by chloroform, ethers or acetates. From a 2*N* hydrochloric acid solution, however, it is rapidly and completely extracted by the first two solvents mentioned above, partially extracted by ethers and acetates, and not at all by chloroform.

On the basis of these preliminary observations it was found possible to effect a separation of ruthenium and palladium. It was decided to employ an absorptiometric method for the determination of the metals and as a first step the absorption spectrum of Pd $py_2(SCN)_2$ in hexone was determined. This is shown in Fig. 1. The maximum at 345 mμ is very suitable for measurement and was used throughout. For known amounts of palladium a calibration curve was prepared, from which the minimum amount which could be determined with certainty was 25 μg.

The absorption spectrum of the dark blue ruthenium thiocyanate complex in hexone is shown in in Fig. 2, the maximum at 570 mμ being employed in subsequent measurements. For known amounts of ruthenium a calibration curve was prepared, from which the minimum amount which could be determined with certainty was 25 μg.


2·00
1·50
O.D.
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Absorption spectrum of
Pd py2(SCN)2 in Hexone
345
340
380
420
460
500
λ(mμ)

FIG. 1.

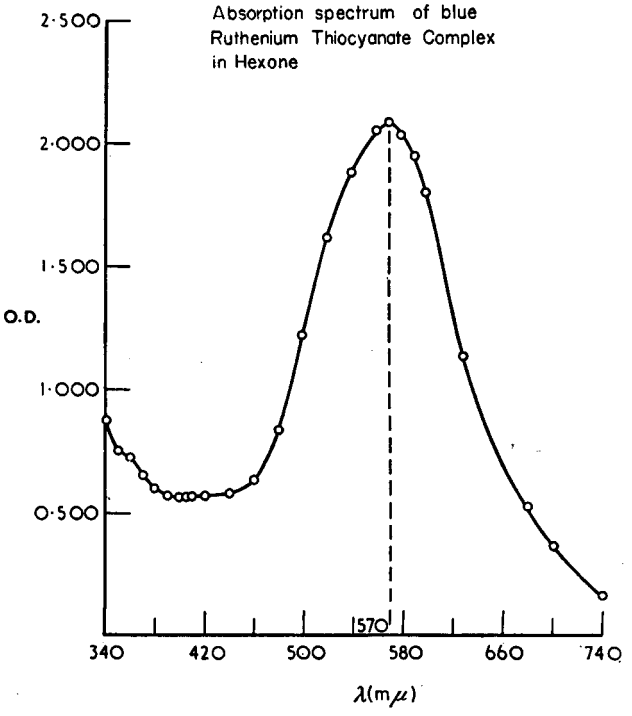
2·500
2·000
1·500
O.D.
1·000
0·500
Absorption spectrum of blue
Ruthenium Thiocyanate Complex
in Hexone
570
340
420
500
580
660
740
λ(mμ)

FIG. 2.

PROCEDURES

To about 20 ml of the solution for analysis, which should contain not less than 25 μg palladium and 25 μg ruthenium and have pH 1·5–2·0, add 10*N* sodium hydroxide solution rapidly until the pH is 11 to 12. It is essential that this adjustment should be made quickly with a strong alkali solution.

Transfer the solution to a separating funnel and use 0·05*N* sodium hydroxide to rinse the beaker, adding these washings to the main solution. To the pale green solution add 0·5 ml (excess) of a 40% solution of potassium thiocyanate, followed by 5 drops of pyridine. The solution becomes pale yellow in colour due to the formation of the pyridine thiocyanate of palladium.

Extract the solution twice with 10-ml portions of hexone and make up to 25 ml. The hexone solution contains all the palladium present in the original aqueous solution. Under these conditions a thiocyanate complex of ruthenium is not formed, or, if formed, is not extracted.

Filter the hexone extract and pour into the absorption cell of the spectrophotometer. This operation removes tiny globules of air or water which may be present. Measure the optical density of this solution at 345 mμ, with reference to hexone as standard, and read off the concentration of palladium present from the prepared calibration curve.

Determination of ruthenium

Transfer the pale green aqueous solution remaining after the extraction of palladium to a 50-ml beaker. This solution contains potassium thiocyanate (excess), a trace of pyridine, ruthenium, if present, and has a pH of approximately 11.

Add 1 ml of concentrated (11*N*) hydrochloric acid rapidly with stirring and heat the solution to about 90°, when an odour of hydrogen sulphide is observed. The time taken to reach this temperature should be about 4 minutes. While still hot, add a further 5 ml of concentrated hydrochloric acid down the sides of the beaker. This has the effect of intensifying the colour of the blue complex and, allowing for wash liquor, renders the solution approximately 2*N* in hydrochloric acid. Cool the beaker and contents to about 20°.

When cool, transfer solution to a separating funnel, extract twice with 10-ml portions of hexone and make up to 25 ml. This solution will contain all the ruthenium present in the original aqueous sample.

Filter the hexone extract and pour into the absorption cell of the spectrophotometer. Measure the optical density of this solution at 570 mμ, with reference to hexone as standard, and read off the concentration of ruthenium present from the prepared calibration curve.

Notes

It is necessary to carry out the extraction of $Pd\ py_2(SCN)_2$ at pH above 11, since this is not formed below pH 4, while at pH 4–8 a hydrous oxide of ruthenium is precipitated. It cannot be too strongly emphasised that the initial adjustment to pH 11 of the ruthenium–palladium mixture must be made very rapidly using a concentrated alkali solution, under which conditions no precipitation is observed. The same precaution is also necessary on later acidification *i.e.* concentrated hydrochloric acid must be rapidly added.

RESULTS

To test the validity of the proposed method, a number of "unknown" mixtures were analysed by one of us (J. H. W. F.). The results are recorded in Table I. Where the experimental results differ from the actual composition, the latter is recorded in parentheses.

These results were extremely satisfactory, especially for palladium. The method shows great promise in the separation and subsequent concentration and determination of small amounts of ruthenium; results are easily reproducible and precision is very good.

DISCUSSION

In 1952 Yaffe and Voigt,[10] through a spectrophotometric study, claimed to have established the formula $Ru(SCN)^{2+}$ for the deep blue complex formed by the reaction

of Ru^{III} and Ru^{IV} perchlorates with thiocyanate ion. In the case of Ru^{IV}, reduction to Ru^{III} occurred at the expense of the thiocyanate, and no evidence was found for higher complexes. However, during the present investigations it was found that both the crimson Ru^{III} thiocyanate complex and the blue complex later obtained were, in fact,

TABLE 1

No. of Sample	Palladium, μg	Ruthenium, μg
1	450	30 (25)
2	295 (300)	155 (150)
3	97·5 (100)	405 (400)
4	—	250
5	745 (750)	25
6	50	495 (500)
7	247·5 (250)	—

anionic in nature, being readily adsorbed on the anionic-exchange resin Amberlite IRA-410. In neither case did any adsorption take place on the cationic-exchange resin Dowex 50. These observations conflict directly with the findings mentioned above.

From their experimental data, for the reaction,

$$A + nB \rightleftharpoons AB_n$$

Yaffe and Voigt obtained best agreement with experiment when n was chosen as unity. They endeavoured to fit their results to other values for n, but found these to be less satisfactory. From their published curve, the deduction must be that at least some of their results were capable of being fitted to the assumption that n could equal 2, 3, or even 4. The formation of a negatively charged Ru^{III} thiocyanate complex capable of being adsorbed on an ionic-exchange resin, as observed in the present work, would require it to be formulated as $Ru(SCN)_4^-$ or $Ru(SCN)_5^{2-}$, *i.e.* $n = 4$ or 5; and this may be regarded as at least a possibility, if the behaviour of Fe^{III} thiocyanate[11,12] is taken into account. It is, therefore, suggested that the crimson Ru^{III} thiocyanate may be represented by one or both of the above formulae, at high thiocyanate concentration.

Again it is known,[13,14] that aqueous solutions of Ru^{III} chloride turn deep blue when treated with strong reducing agents, ruthenium being reduced to the Ru^{II} state. It is suggested that the odour of hydrogen sulphide observed on formation of the blue thiocyanate complex is due to the reduction of Ru^{III} to Ru^{II} at the expense of the thiocyanate, catalysed by the metal. $Ruthenium^{II}$ then forms the blue anionic thiocyanate complex, which could be formulated as $Ru(SCN)_4^{2-}$ or $Ru(SCN)_3^-$, and would be capable of adsorption on anionic-exchange resins. At very low thiocyanate concentrations the formation of the complex $Ru(SCN)^+$ would be possible. Investigation with such solutions showed that it was, in fact, possible to form a blue ruthenium thiocyanate complex which was not completely adsorbed on anionic-exchange resins, and this is considered evidence for the existence of one or both of the complexes $Ru(SCN)^+$, $Ru(SCN)_2$. Yaffe and Voigt evidently failed to take into consideration the possibility of such a reduction to Ru^{II}, or the possibility of the existence of a whole series of cationic and anionic complexes at different thiocyanate concentrations, as in

the case of iron^{III}. Babko[12] has postulated the coexistence at the same thiocyanate concentration of two complexes of iron^{III} and the incomplete adsorption referred to above indicated the probability of a similar phenomenon in the case of ruthenium^{II}. Although ruthenium^{II} is certainly unstable in alkaline solution, as instanced by the apparent non-existence of the oxide RuO,[14] yet under the fairly strongly acid conditions in which the most intense colour of the blue thiocyanate complex is observed, stabilisation of this relatively unfamiliar oxidation state appears to be possible.

Acknowledgement—One of us (J. H. W. F.) gratefully acknowledges a research grant from the Imperial Chemical Industries Ltd., (Billingham Division), which enabled him to take part in this work.

Zusammenfassung—Eine Methode zur Trennung und nachfolgenden kolorimetrischen Bestimmung von Ruthenium und Palladium als Komplex bzw. Thiocyanate des Ammintyps unter verwendung von Solventextraktion wird beschrieben. Die Natur der in der Lösung auftretenden Rutheniumkomplexe wird diskutiert.

Résumé—On décrit un procédé pour la séparation puis la déterminationcolor imétrique du ruthénium et du palladium à l'état de complexes amminés et thiocyanates respectivement, en utilisant l'extraction par solvant. On a proposé quelques hypothèses sur la nature du complexe du ruthénium en solution.

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THE ANALYTICAL CHEMISTRY OF THE PYRIDINE THIOCYANATES—III

THE SEPARATION OF RHODIUM, PALLADIUM AND PLATINUM

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(*Received* 22 *August* 1959)

Summary—A procedure is described for the separation and subsequent colorimetric determination of rhodium, palladium and platinum through the formation of complex and ammine-type thiocyanates, using solvent extraction. Suggestions are put forward as to the nature of the complexes in solution.

PART II[1] of this series of papers outlined a procedure for the separation of ruthenium and palladium through the formation of their complex and ammine-type thiocyanates respectively, using solvent extraction. The success achieved in this manner led to further investigations of such compounds, with a view to including other platinum metals within the scheme. In this connection, the thiocyanate system appears to have been completely neglected, even McBryde's comprehensive review[2] making no reference to it.

For platinum, at least, the possibility arises of forming non-ionic compounds, $R_2M^{IV}X_2$, resembling those formed by palladium, with a high probability of successful extraction into organic solvents. Thus, in the cold, platinum^{IV} does not react with such organic reagents as *p*-nitrosodiphenylamine, but, on warming, a coloured extractable product is obtained.[3] It is believed that the effect of heating is to cause reduction of platinum^{IV} to the II state, in which it does react with this and certain other reagents in the same manner as palladium. Complexes of platinum containing thiocyanate ion do not appear to have been investigated in this context.

Little information is available on the behaviour of rhodium in thiocyanate solution, although it has been stated[4] that the action of potassium thiocyanate on potassium chlororhodite yields the stable complex $K_3Rh(SCN)_6$ and that the addition of dilute sulphuric acid to a solution of this salt liberates the free acid, $H_3Rh(SCN)_6$, which may be extracted by amyl alcohol.

This paper describes a procedure for the separation and determination of rhodium, palladium and platinum through the formation of both complex and ammine-type thiocyanates.

PRELIMINARY INVESTIGATIONS

The conditions for formation of the ammine-type thiocyanate of palladium, $Pd\ py_2(SCN)_2$, have been discussed in Part II of this series.[1] It was found that this procedure can be applied for the removal of palladium by extraction with hexone (methyl *iso*-butyl ketone) in presence of both rhodium and platinum, with the advantage that it is unnecessary to use strong alkali for rapid pH adjustment. If pyridine is used instead to adjust the pH to 6·0–6·5, the $Pd\ py_2(SCN)_2$ compound is formed in solution,

while, in the cold, the complexes of rhodium^{III} and platinum^{IV}, if formed at all, are not extracted.

In the cold, platinum^{IV}, present as $PtCl_6^{2-}$, is not extracted, even from acid solution, in the presence of excess thiocyanate, by any of the usual organic solvents. However, if such a solution, approximately 0·1*N* in hydrochloric acid concentration, is heated almost to boiling point, an odour of hydrogen sulphide is observed and the solution becomes golden yellow in colour. This colour is quite stable and is readily extracted by hexone at pH below 6·5, giving a golden yellow colour in the organic layer. The process occurring here is presumably reduction of platinum^{IV} to platinum^{II}, with formation of an extractable thiocyanate complex. As in the case of ruthenium, this complex is anionic in nature, as shown by its ready adsorption on the anionic-exchange resin Amberlite IRA-410. This is the case even in the presence of pyridine or acids other than hydrochloric, the rate of formation of the complex being to some extent dependent on acid concentration. It is possible that this species could be formulated as $Pt(SCN)_4^{2-}$, although Ayres[5] has shown the danger of assuming simplified structures for platinum complexes.

Solutions of ammonium chlororhodite or chlororhodate behave very similarly to the $PtCl_6^{2-}$ ion in their reaction with potassium thiocyanate, a golden yellow colour being developed on heating. This, however, is only completely extracted from about 3*N* hydrochloric acid solution by hexone or oxygen-containing solvents and is not extracted from solutions of pH above 1·5. Once again, the rhodium thiocyanate complex is anionic in nature.

On the basis of these observations it was found possible to effect a separation of rhodium, palladium and platinum and to employ an absorptiometric method for their determination. The absorption spectrum of $Pd\,py_2(SCN)_2$ in hexone is shown in Part II of this series.[1] For known amounts of palladium a calibration curve was prepared, from which the minimum amount which could be determined with certainty was 25 μg.

The absorption spectrum of the platinum^{II} thiocyanate complex in hexone is shown in Fig. 1, the maximum at 385 mμ being employed in subsequent measurements. For known amounts of platinum a calibration curve was prepared, from which the minimum amount of platinum which could be determined with certainty was 50 μg.

Fig. 2 shows the absorption spectrum of the rhodium thiocyanate complex in hexone, subsequent optical density measurements being made at 380 mμ. From the calibration curve prepared, the minimum amount of rhodium determinable was 50 μg.

PROCEDURE

Determination of palladium

To about 20 ml of the solution for analysis, which should contain not less than 25 μg palladium, 50 μg platinum, 50 μg rhodium, and should have a pH about 2·5, add pyridine dropwise with stirring until the pH reaches 6·0–6·5.

Transfer the pale yellow solution to a separating funnel, add 0·5 ml (excess) of a 40% potassium thiocyanate solution, swirl the mixture and allow to stand for two minutes. Extract the solution twice with 10-ml portions of hexone and make up to 25 ml. The hexone solution contains all the palladium present in the original aqueous solution. Under these conditions, thiocyanate complexes of platinum and rhodium are not formed, or, if formed, are not extracted.

Filter the hexone extract and pour into the absorption cell of the spectrophotometer. This operation removes tiny globules of air or water which may be present. Measure the optical density of

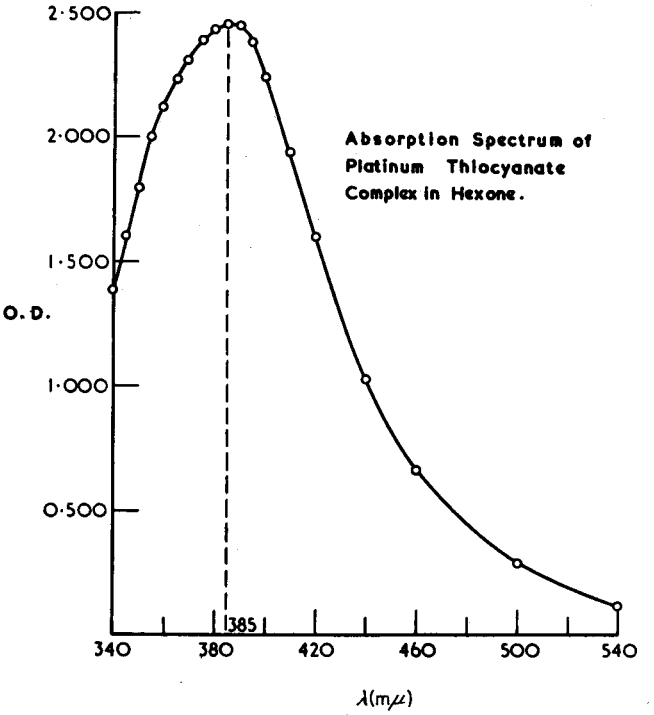
2·500
2·000
1·500
O. D.
1·000
0·500
385
340
380
420
460
500
540
λ(mμ)
Absorption Spectrum of
Platinum Thiocyanate
Complex in Hexone.

FIG. 1.

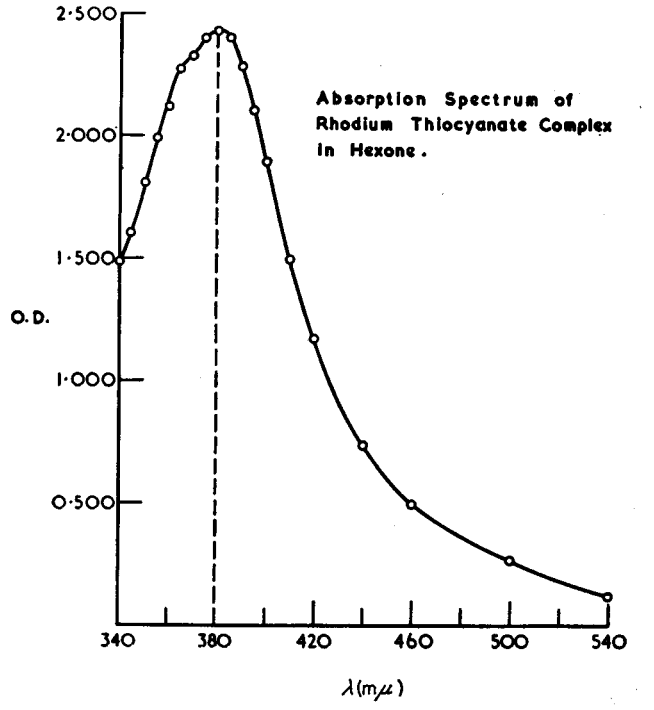
2·500
2·000
1·500
O. D.
1·000
0·500
340
380
420
460
500
540
λ(mμ)
Absorption Spectrum of
Rhodium Thiocyanate Complex
in Hexone.

FIG. 2.

this solution at 345 mμ with reference to hexone as standard and read off the concentration of palladium present from the prepared calibration curve.

Determination of platinum

The colourless solution remaining after the extraction of palladium contains potassium thiocyanate (excess), a little pyridine, platinum and rhodium, if present, and has a pH approximately 6·0. Adjust the pH to 2·0–2·5 using hydrochloric acid and heat the solution. On first heating a cloudiness appears at about 40°, a golden yellow colour being developed. The reaction is complete at about 90° and the time taken to reach this temperature should be about 4 minutes. Cool the beaker and contents to about 20°.

When cool, transfer the solution to a separating funnel, extract twice with 10-ml portions of hexone and make up to 25 ml. This hexone solution will contain all the platinum present in the original aqueous sample. Under these conditions the rhodium thiocyanate complex, although present in solution, is not extracted.

Filter the hexone extract and pour into the absorption cell of the spectrophotometer. Measure the optical density of this solution at 385 mμ, with reference to hexone as standard, and read off the concentration of platinum present from the prepared calibration curve.

Determination of rhodium

To the yellow aqueous solution remaining after the extraction of palladium and platinum add 0·5 ml (excess) of 40% potassium thiocyanate solution, followed by concentrated hydrochloric acid until the acid concentration of the solution is 3–4*N*. Cool the beaker and contents to about 20°.

When cool, extract the solution twice with 10-ml portions of hexone and make up to 25 ml. This hexone solution will contain all the rhodium present in the original aqueous sample.

Filter the hexone extract and pour into the absorption cell of the spectrophotometer. Measure the optical density of this solution at 380 mμ with reference to hexone previously saturated with 2*N* hydrochloric acid as standard and read off the concentration of rhodium present from the prepared calibration curve.

RESULTS

To test the validity of the proposed method a number of "unknown" mixtures were analysed by one of us (J. H. W. F.). The results are recorded in Table I. Where the

TABLE I.

No. of sample	Palladium	Platinum	Rhodium
1	100	110(100)	95(100)
2	202·5(200)	260(250)	65(50)
3	50	105(100)	90(100)
4	52·5(50)	245(250)	215(200)
5	255(250)	55(50)	210(200)
6	205(200)	260(250)	50(50)
7	100	100	75
8	100	105(100)	220(225)

experimental results differ from the actual composition, the latter is recorded in parentheses.

The results, especially for palladium, are extremely satisfactory. The procedure described is rapid in application, a complete separation and determination of the three elements taking about 1½ hours.

DISCUSSION

Although ruthenium forms two thiocyanate complexes, one of which is thought to result from reduction from the III to the II state, rhodium forms only a single complex, and this fact operates against the hypothesis of reduction of rhodium to the II state. The fact that platinum also forms only one observed thiocyanate complex is no bar to the hypothesis of the reduction of platinum^{IV} since the bivalent state is also stable. Rhodium presents the important difference that, although the ion Rh^{2+} is probably stable, yet in the presence of chloride it is readily oxidised[6] to $RhCl_6^{3-}$. From these considerations it is probably safest to assume that the extracted species is a thiocyanate complex of rhodium^{III}. On the other hand, although the sulphide Rh_2S_3 is normally precipitated from acid solutions by hydrogen sulphide, yet under the conditions described this is not the case. Very recently Jackson[7] separated rhodium from iridium by precipitation with thioacetanilide after treatment with chromous chloride and suggested that a bivalent complex was formed by rhodium. In either case, some evidence exists for the formation of more than one complex in a varying range of thiocyanate concentration.

Acknowledgement—One of us (J. H. W. F.) gratefully acknowledges a grant from the Imperial Chemical Industries Ltd., (Billingham Division), which enabled him to take part in this work.

Zusammenfassung—Eine Methode zur Trennung und anschliessenden kolorimetrischen Bestimmung von Rhodium, Palladium und Platin durch Bildung von Thiocyanaten des Ammintyps, unter Verwendung von Solventextraktion wird beschrieben. Die Natur der in der Lösung auftretenden Komplexe wird diskutiert.

Resume—On décrit un procédé pour la séparation puis la détermination colorimétrique du rhodium du palladium et du platine par la formation de complexes amminés et thiocyanates en utilisant l'extraction par solvant. On a proposé quelques hypothèses sur la nature des complexes en solution.

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THE EFFECT OF PLATINUM OXIDE FILMS ON REACTION KINETICS AT PLATINUM ELECTRODES

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(*Received* 24 *August* 1959)

Summary—It has been known for some time that the pre-treatment of platinum electrodes often effects subsequent electrochemical reactions. Part of the effect of pre-treatment is due to the fact that anodized or chemically oxidized platinum electrodes become coated to some degree with a film of platinum oxide. This work was concerned with quantitative measurement of kinetic parameters as a function of the extent of oxide film formation. Whenever possible, variations in reaction mechanisms are proposed.

Most of the experimental evidence has been taken from current-potential curves but the techniques of chronopotentiometry and microscopy were also used.

The reduction of vanadium^{V}, chromium^{VI}, arsenic^{V}, iodate and oxygen were investigated as well as the oxidation of vanadium^{IV}, arsenic^{III}, oxalic acid, and formic acid. The presence of the platinum oxide film effected the reactions studied in a variety of ways but in every case some variation in the kinetic parameters of the reactions studied was recorded. For a number of cases, a modified oxygen bridge theory was found useful.

INTRODUCTION

MANY workers have found that a platinum electrode which has a coating of platinum oxides exhibits quite different behaviour from an unoxidized electrode.[1–7] Kolthoff and Nightingale[6] have shown that the ferrous-ferric couple acts more reversibly at an oxidized electrode than at an unoxidized one. They have proposed the formation of oxygen bridges between the oxidized electrode and the reacting ions to account for this fact. Similarly Anson[7] has proposed that the enhancement of the reduction of iodate ion by platinum oxide films is due to the fact that "the first step in the reduction of iodate ion at an oxidized electrode can be imagined to consist of the transfer of an electron to iodate from the electrode by means of a platinum oxide bridge which can only serve as an electron-carrying bridge at potentials where the platinum oxide itself begins to be reduced."

Although the oxide-bridge theory explains the more nearly reversible behaviour of many reactions at oxidized electrodes, some reactions, especially those of anions, are rendered less reversible and are sometimes completely suppressed by a coating of oxide film on the working electrode.[2,3] Inhibition of the oxidation of ferrous and arsenious ions by oxide films has been reported by Baker and MacNevin.[4]

This work was undertaken in an effort to measure quantitatively the effect of oxide film formation and to discover some of the causes of the various effects observed. Wherever possible the approach was to measure the kinetic parameters α and $k_{s,h}$ (the electron transfer coefficient and the heterogeneous rate constant respectively)[8] as a function of the extent of oxidation of a platinum electrode. As many chemical systems as possible were investigated but only a limited number yielded useful results

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since the values of $k_{s,h}$ and α must be within certain limits for reasonably accurate results to be obtained with the technique used. In addition, strong reducing or oxidizing agents had to be avoided so that the oxide coating on the electrode would not be too greatly affected by chemical action alone. Although it seems that each reaction must be considered individually, the presence of an oxide film on the electrode seems to effect either the heterogeneous rate constant alone or both the rate constant and the transfer coefficient. In the latter case it is quite probable that the rate determining step is completely altered.

EXPERIMENTAL

The current-potential curves, from which the log i versus E plots were derived, were obtained with a potentiostat and a current integrator[9] secured from Analytical Instruments, Inc., Bristol, Connecticut, U.S.A. The method of measurement and the treatment of results have been described by Meites.[10] In this work each point on the current-potential curves was obtained by reading the current integrator at the beginning and at the end of a 100-second period of time. A period of 50 seconds was allowed after each change in potential to assure steady readings. The reading of millifaradays per 100 seconds at each potential was then easily converted to microamperes since the value of the faraday is accurately known. Some typical log i versus E plots are shown in Fig. 1.

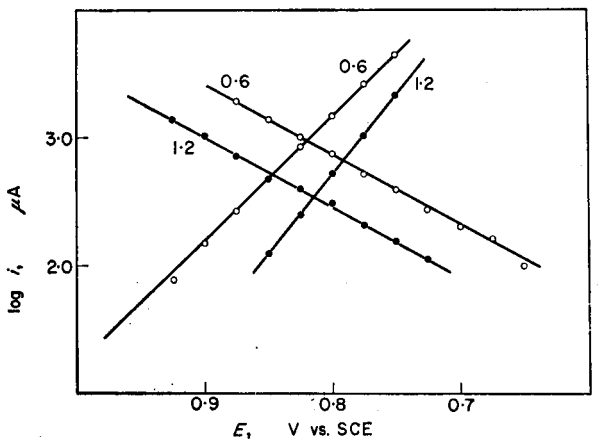

FIG. 1.—Log i versus E curves for the Vanadium^{V}–Vanadium^{IV} couple.
Open circles—Electrode pre-reduced at +0.60 v. vs. S.C.E. after oxidation.
Closed circles—Electrode pre-reduced at +1.20 v. vs. S.C.E. after oxidation.

A large H-type cell with a working electrode compartment of 100-millilitre capacity was used. A platinum-foil working electrode, whose area was 71.4 cm^2 (both sides), was held in the cell by means of a hole in a rubber stopper. The stopper also contained holes which held an ordinary Beckman asbestos-fibre saturated calomel reference electrode and a glass tube through which purified, oxygen-free nitrogen could be passed. The platinum wire auxiliary electrode was placed in the smaller side of the H-cell and was thus separated from the working electrode compartment by a sintered-glass disk. Stirring was provided by a magnetic stirrer.

The platinum working electrode was pre-treated by oxidation in a solution of argentic oxide in 6M nitric acid and then reduction at controlled potential in a 1M sulphuric acid solution. The treatment with an argentic solution not only oxidized the electrode but also removed oxidizable impurities. The reduction of the electrode by means of the potentiostat was continued for ten minutes after the current integrator stopped registering when set at its most sensitive range (until the current dropped below about 10 microamps). This method of electrode treatment gave a reproducible amount of oxide on the electrode surface provided that the electrode was well soaked in the argentic solution previous to reduction. Sometimes the electrode became "fouled" by being reduced at potentials

below about +0.2 volts versus S.C.E. but the electrode could always be restored to the desired conditions provided it was soaked in the oxidizing solution for a long enough time. Several hours was the maximum found necessary.

Experimental conditions were chosen such that the rate of reaction was independent of diffusion. Relatively concentrated solutions of reactants were used (approximately 0.01M) together with a low current density which rarely exceeded 30 microamps per cm^2. The fact that the current was indeed independent of diffusion was verified by changing the rate of stirring over about a ten-fold range. The current was found to be independent of the stirring rate. Each run was performed with a fresh solution to avoid depletion of substance undergoing reaction even though less than 1% was oxidized or reduced during a run. This method may be thought of as measuring a very small section at the foot of a typical polarographic wave.

The experimental arrangement for chronopotentiometric measurements was similar to that described by Anson and Lingane,[11] except that a Sargent Potentiometric Recorder was used.

Pictures of the surface of the platinum electrode were obtained with a Zeiss Standard Metallurgical Microscope. A magnification of about 600× was achieved by the appropriate selection of objective lens supplied with the instrument. The electrode was treated exactly as it had been for the electrochemical experiments, that is, oxidation was accomplished in an argentic ion solution and the electrode was reduced at controlled-potential in 1M sulphuric acid.

The chemicals used in this work were reagent grade or better and were used as obtained without further purification. The arsenic solutions were prepared from National Bureau of Standards arsenious oxide (100.00%) especially to avoid the difficulties due to antimony observed by Baker and MacNevin.[4] Only when the working electrode was strongly reduced was any effect of impurities apparent. Potentials below +0.2 volts versus S.C.E. were therefore avoided and the electrode was cleaned by oxidation between each run.

One molar sulphuric acid was used as the medium for all experiments except the reduction of iodate, which was carried out in 1M acetic acid—1M sodium acetate buffer.

RESULTS AND DISCUSSION

The log current versus potential diagrams were interpreted by means of the following relationships:

$$\log i_c = \log nFAC_0k^\circ_{f,h} - \frac{1}{2{,}3}\frac{\alpha nF}{RT}E \tag{1}$$

$$\log i_a = \log nFAC_Rk^\circ_{b,h} + \frac{1}{2{,}3}\frac{(1-\alpha)nF}{RT}E \tag{2}$$

$$k_{s,h} = k^\circ_{f,h}\exp\left[-\frac{\alpha nF}{RT}E^\circ_c\right] = k^\circ_{b,h}\exp\left[\frac{(1-\alpha)nF}{RT}\right]E^\circ_e \tag{3}$$

These symbols are those in general use and are defined by Delahay.[8] The values of the current are given by i; the electron change, by n; the faraday, by F; the electrode area by A; the gas constant, by R; the absolute temperature, by T; the potential, by E; the heterogeneous rate constants, by k; and the transfer coefficient, by α. Experimental conditions were chosen so that it was reasonable to assume that E differs considerably from the equilibrium potential and that C_0 or C_R may be set equal to the analytical concentration of the substance under investigation. The values of α and $1-\alpha$ were easily found from the slope of the log i versus E plots. The question of how to interpret the heterogeneous rate constants is not easily answered. One difficulty is that the values of $k^\circ_{b,h}$ and $k^\circ_{f,h}$ depend on the potential scale used (in this work the saturated calomel electrode) and show wide variation in absolute value depending on the reaction under investigation. Ideally $k_{s,h}$'s are more useful, since they are truly characteristic of the reaction being studied. However, the value of E°_c must be known or must be able to be accurately determined.

Another difficulty is the problem of what value to use for the electrode area in the calculation of the rate constants. At first thought the gross area would seem sufficient but even a polished platinum electrode is not even approximately smooth as can easily be seen from Fig. 3. It is also possible that even with solid electrodes the "effective area" might be variable as will be discussed later. For these reasons the product of the area and $k_{s,h}$'s are reported since it is not absolutely certain which of these is caused to vary by the presence of the oxide film. When the value of E°_c (see equation 3) is not known, values of $Ak_{s,h}(E)$ are reported, where E is some arbitrary potential selected for convenience only, but whose value is recorded so that the appropriate calculations could be made if the value of E°_c is ever determined.

Variation of the Area—Rate Constant Product

When vanadium^{V} was reduced and vanadium^{IV} or arsenic^{III} was oxidized, variation of the extent of oxidation of the electrode surface seemed to mainly effect the area-rate constant product. The values of α and $1 - \alpha$ showed only slight variations. Tables I and II show the values obtained with the working electrode oxidized, and then reduced at various potentials. Only in the case of the vanadium^{V}–vanadium^{IV} couple was it possible to study the reaction in both directions. For some unknown reason the log i versus E plots for the reduction of arsenic^{V} were not straight lines

TABLE I.—THE EFFECT OF ELECTRODE OXIDATION ON THE KINETICS OF THE VANADIUM^{IV}—VANADIUM^{V} COUPLE

Treatment (E vs. SCE)	$Ak_{s,h} \times 10^7$ (a)	α	$1 - \alpha$	Sum	$E_{1/2}$ vs. S.C.E.
0.40	2.6	0.74	0.32	1.06	0.818
0.50	2.9	0.52	0.41	0.93	0.786
0.55	11.9	0.59	0.47	1.06	0.792
Red. (Fe^{2+})	13.2	0.67	0.29	0.96	0.810
0.60	7.9	0.59	0.32	0.91	0.815
0.75	5.5	0.70	0.34	1.04	0.812
0.90	4.4	0.67	0.38	1.05	0.820
1.20	3.3	0.73	0.32	1.05	0.812
Ox (Ag^{2+})	2.7	0.74	0.30	1.04	0.825
Average		0.64	0.35	1.005	0.809

(a) Units of $cm^3\ sec^{-1}$.

and no conclusions could be drawn from them. Fig. 1 shows two sets of log i versus E plots for vanadium. Since the concentrations and other experimental conditions were identical for both reduction and oxidation, the values of the potential and the current at the intersection of the reduction line and the oxidation line were used to calculate $Ak_{s,h}$ and the formal potential of the couple. The value of the latter is in fair agreement with that reported by Swift[12] for $1M$ sulphuric acid.

The values of $A\,k_{s,h}$ for the vanadium^{V}–vanadium^{IV} couple increase as the oxide film is removed, reach a maximum, and then decrease again. By examination of Tables I and III it is possible to notice that the variation of $A\,k_{s,h}$ follows closely the

removal of the oxidized film. The maximum value of $A\,k_{s,h}$ occurs with the electrode from which most, but not all of the film is removed. Several explanations for this behaviour are possible.

It could be that the reduction or oxidation of the electrode serve simply to increase the measured values of the current. This possibility can be rejected at once on the grounds that the current for the oxidation or reduction of the electrode alone is very

TABLE II.—EFFECT OF ELECTRODE OXIDATION ON THE KINETICS OF THE OXIDATION OF ARSENIC^{III}

Treatment (E vs. SCE)	$Ak_{s,h}$(+0.475 v. vs. SCE) × 10^8 (a)	$(1-\alpha)n_a$
0.30	2.5	0.76
0.40	4.2	0.77
0.50	5.2	0.81
0.55	17.5	0.80
0.60	53.0	0.71
0.70	66.8	0.70
0.80	66.7	0.71
Oxidized (Ag^{2+})	66.6	0.71

(a) Units of $cm^3\ sec^{-1}$.

small (less than 1% of the currents measured for the reduction or oxidation of vanadium). Also curved log i versus E plots should be observed if the two different reactions were making a significant contribution to the total current.[13]

A mechanism involving the induction of the vanadium oxidation or reduction by the simultaneous oxidation or reduction of the electrode must also be considered. However, one would expect the maximum value of $Ak_{s,h}$ to be found when the electrode was the most completely oxidized for reductions, and the most completely reduced for oxidations.

The most logical explanation seems to be a slight modification of the oxide bridge theory, which proposes that the greater ease of reduction (or oxidation) at an oxide-coated electrode can be attributed to the formation of a bridge between oxygen of the film and the ion undergoing reaction, thus facilitating the electron transfer between the electrode and the ion.[6,14] Since the theory as originally stated cannot account for the decrease in $Ak_{s,h}$ when the electrode is fairly strongly oxidized (Table I) it should be modified to state that oxygen bridges can form only when a slight or very thin coating of oxide is present.

The proposed change in the oxygen bridge theory can be used to explain several other experimental observations as well as the variations of $Ak_{s,h}$ with the extent of electrode oxidation. Fig. 2 shows a chronopotentiogram of vanadium^V in $1M$ sulphuric acid taken with an oxidized platinum electrode. When the current is first applied, the potential changed rapidly in a reducing direction but then reversed itself forming a small "dip" before the potential hold up for the reduction of vanadium^V occurred. The "dip" was not observed if a reduced platinum electrode was used. This "dip" is due to the fact that the oxide on the electrode is first partly reduced but, when the oxide coating is such that oxygen bridges can form and facilitate

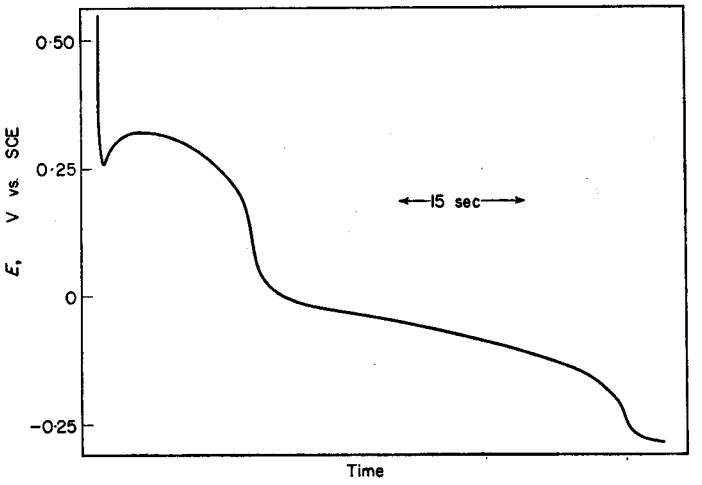

FIG. 2.—Chronopotentiogram for the reduction of 0.1*M* vanadium^{V} in 1*M*.
Sulphuric acid.
Electrode area, 0.2 square centimeters.
Current, 1.0 milliampere.

electrode exchange, the potential shifts anodically to a value determined by the reduction of vanadium^{V}. Exactly the same behaviour was noticed when iron^{III} was reduced in 1*M* sulphuric acid with an oxidized electrode.

Apparently a heavy oxide film has the ability to suppress rather than enhance the electrode reaction of the iron^{III}–iron^{II} couple as well as the vanadium^{V}–vanadium^{VI} couple. Indeed this has been noticed by Baker and MacNevin[4] in the process of investigating the oxidation of iron^{II} by controlled-potential electrolysis. Their findings were confirmed in this laboratory.

TABLE III.—REDUCTION OF AN OXIDIZED ELECTRODE BY CONTROLLED-POTENTIAL ELECTROLYSIS IN AIR-FREE 1*M* SULPHURIC ACID

E vs SCE	Total milliequivalents × 10^{5}
1.00	1
0.90	0
0.80	3
0.75	2
0.70	2
0.65	6
0.60	8
0.55	26
0.50	8
0.40	6

Evidently only a slight amount of oxide is necessary—or in fact desirable—for oxygen bridge formation. The amount seems to be something less than a monolayer. (Table III and Reference 15). With these facts in mind a microscopic study of the

surface of the working electrode was undertaken. Some typical photographs are shown in Fig. 3. The only noticeable difference between the surface of an oxidized and a reduced electrode is that the grain boundaries are darker in the former case. The results of this study seem to indicate that the PtO and PtO_2 form principally at the grain boundaries. Quite possibly the condition of maximum effectiveness of a platinum electrode occurs when the grain boundaries and possibly other areas, which may be considered active sites, are completely covered with a monolayer of PtO. More than a monolayer can undoubtedly form but the oxide then loses its ability to make electron transfer easier.

Fig. 2 also shows a second wave just following the one attributed to the reduction of vanadium^{V}. This second wave was found to be absent when a reduced electrode was used. Apparently the power of the oxide film to facilitate electron transfer is so great that the notoriously irreversible vanadium^{IV}–vanadium^{III} couple is made quite reversible. The belief that this second wave is truly due to the reduction of vanadium^{IV} to vanadium^{III} is supported by the fact that $\frac{(\tau_1 + \tau_2)^{1/2}}{\tau_1^{1/2}}$ was found to be equal to 1.9. The theoretical value for this fraction would be 2.0 if the vanadium^{V} were reduced in two consecutive one-electron steps.[16]

When vanadium^{IV} is reduced at an oxidized electrode a wave similar to the second wave in Fig. 2 is obtained. If the chronopotentiogram is retaken without re-oxidizing the electrode the wave for the reduction of vanadium^{IV} becomes smaller and smaller and, after about four or five runs, the potential drops immediately to the value at which hydrogen ion is reduced.

It is convenient then to think of an oxidized electrode as possessing a variable "effective area." An electrode which is just sufficiently oxidized so that a monolayer of PtO is covering the grain boundaries and other active sites, may be said to possess maximum "effective area." A heavier oxide film tends to inhibit electron transfer, and likewise when part of the monolayer is reduced the "effective area" is decreased. It is rather difficult to reduce the last bits of PtO from an oxidized electrode as is apparent from the fact that several repeated runs still give waves for the reduction of vanadium.^{IV}

Variation of Reaction Mechanism

Iodate: Several of the reactions studied showed not only variation of the area–rate constant product but also variation in the value of $n_a\alpha$, where n_a is the number of electrons involved in the rate determining step. Apparently the presence of the oxide film changes the whole reaction mechanism, and does not just facilitate the electron transfer process.

The results for the reduction of iodate ion, shown in Table IV, seem to confirm the proposal of Anson.[7] The reduction of iodate is facilitated by the simultaneous reduction of the platinum oxide on the electrode. The current densities measured $+0.450$ volts versus SCE are greater, the greater the amount of oxide. When the oxide is completely removed from the electrode—reduced below about $+0.25$ volts—there is an abrupt shift in $n_a\alpha$ from 0.79 to 0.35. If it is assumed that α is about 0.35, then this shift may be interpreted to mean that the rate-determining step has changed from a two-electron to a one-electron one. It is also possible that α is equal to 0.16 or 0.17 making the rate-determining step for the oxidized electrode a

five-electron reduction, whereas a two-electron step would occur at a reduced electrode. Generally α is considered to be larger than 0.16, however.

Delahay and Strassner[17] have studied the reduction of iodate at a dropping mercury electrode but they propose an n_a value of 2 and an α of 0.3 in the pH range studied here. DeMars and Shain have found $n_a\alpha$ to be 0.39, also with a mercury electrode,[18] which is in good agreement with the values determined with a reduced platinum electrode.

TABLE IV.—THE EFFECT OF ELECTRODE OXIDATION ON THE KINETICS OF THE REDUCTION OF IODATE (1*M* ACETIC ACID—1*M* SODIUM ACETATE, pH = 4.7)

Treatment (*E* vs SCE)	Current density at +0.450 v. vs. SCE, microamps per cm²	$n_a\alpha$
0.15	0.0025	0.35
0.30	0.79	? (curved line)
0.45	7.88	0.79
0.60	11.7	0.79
0.90	65.6	0.77
Oxidized (Ag^{2+})	111.0	0.69

Oxalic acid: The rate-determining step of oxidation of oxalic acid appears to be different depending on whether the electrode is oxidized or not. (See Table V.) If one assumes that $1 - \alpha$ is about 0.5, as is generally the case, then $n_a = 1$ with an oxidized electrode, but $n_a = 2$ with a reduced one. In addition, there is a maximum in the $Ak_{s,h}$ at the

TABLE V.—THE EFFECT OF ELECTRODE OXIDATION ON THE KINETICS OF THE OXIDATION OF OXALIC ACID

Treatment (*E* vs SCE)	$Ak_{s,h}$(+0.675 v. vs. SCE) × 10^7 (a)	$n_a(1 - \alpha)$
0.40	6.9	1.02
0.50	6.8	1.02
0.60	15.3	0.70
0.80	3.12	0.70
1.00	1.21	0.49
Oxidized (Ag^{2+})	1.56	0.49

(a) Units of $cm^3\ sec^{-1}$.

electrode which has just a small amount of surface oxidation. It is possible that there is some sort of bridge formation between the oxygen of the platinum oxide and oxalic acid or one of its intermediate oxidation products. In any case the partially oxidized electrodes (treatment 0.60 and 0.70 volts) have $n_a(1 - \alpha)$ values intermediate between those of the strongly oxidized and strongly reduced electrodes. The reason for this behaviour is not apparent from this work.

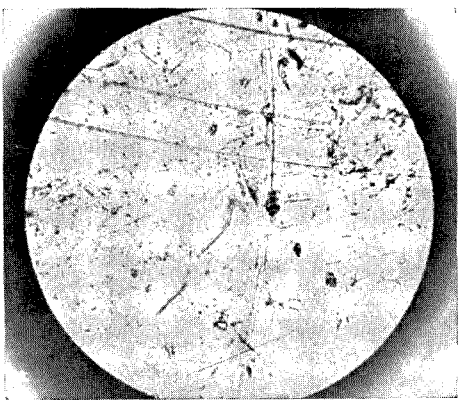

FIG. 3a.

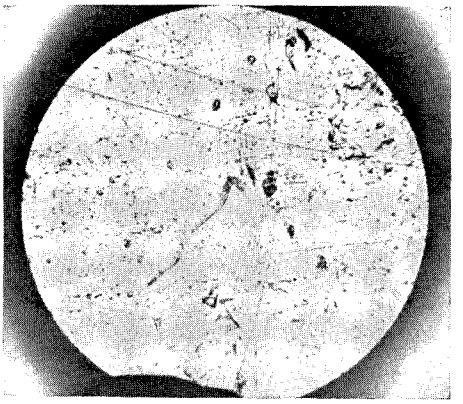

FIG. 3b.

FIG. 3.—Photomicrograph of the surface of the platinum working electrode.
Magnification—600×
A—Oxidized
B—Reduced.

Chronopotentiometric studies[2] have shown that the wave due to the oxidation of oxalic acid could be suppressed by oxidation of the electrode, which is in general agreement with this study.

Oxygen: Values for $n_a\alpha$ for the reduction of oxygen are reported in Table VI. No values of $Ak_{s,h}$ are reported since they proved to be rather variable due to the difficulty of controlling the oxygen concentration. However, oxidation of the electrode

TABLE VI.—THE EFFECT OF ELECTRODE OXIDATION ON THE REDUCTION OF OXYGEN

Treatment (E vs. SCE)	$n_a\alpha$
0.30	0.54
0.40	0.53, 0.59
0.50	0.61
0.55	0.67
0.60	0.61, 0.65
0.70	1.21, 1.19, 1.29
0.80	1.29, 1.26
0.90	1.25
Oxidized (Ag^{2+})	1.26

appears to facilitate the reduction of oxygen. The sudden shift in the values of $n_a\alpha$ indicates that a change in mechanism occurs when the electrode becomes fairly well oxidized. If α is taken as about 0.6 then $n_a = 2$ for oxidized electrodes but only 1 for reduced electrodes. It is proposed that with an oxidized electrode, oxygen is reduced directly to hydrogen peroxide, but at a reduced electrode the rate determining step is:

$$H^+ + O_2 + e = HO_2$$

The results at a reduced electrode serve to confirm the results of several workers.[19]

Other reactions: Several other reactions were studied but the results were inconclusive. The oxidation of thallous ion seemed little affected by the presence or absence of an oxide film. Although the log i vs. E plots were not very good $n_a(1 - \alpha)$ was apparently very close to unity.

A study of the oxidation of formic acid[20] was found to give no useful information apparently due to its great irreversibility. The reduction of dichromate proved to be so greatly suppressed at a platinum electrode that no measurements are reported. However, the reduction of dichromate was studied with a gold electrode by the same methods used for the platinum electrode and straight log i versus E plots were obtained, which gave a value of $n_a\alpha = 1.00$. This value of $n_a\alpha$ is in good agreement with the values determined by Baumann and Shain.[13]

CONCLUSIONS

The results of the study indicate that the participation of platinum oxide films in electrochemical reaction is undoubtedly rather complex. The theory that a monolayer of platinum oxide residing on the grain boundaries and other active sites can facilitate electron transfer by means of oxygen bridge formation seems to account for

the increase in reversibility observed for a number of reactions. In many other cases the mechanism of the reactions is completely altered by the presence of the oxide film.

Analytical chemists should exercise extreme care when using platinum electrodes in conjunction with controlled-potential electrolysis, chronopotentiometry and other electroanalytical techniques. Corrections for the current used to oxidize or reduce the electrode must be made in many cases.[11,15,21] In addition, the effect on the electrode kinetics must be considered. In many cases advantage may be taken of the increase in reversibility or of the rate constant for a particular reaction. For instance it is advantageous to titrate an oxidant with a reductant, rather than the reverse, when the end-point is located by means of "two electrode" amperometry.[6] Likewise, if iodate ion is to be determined by controlled-potential electrolysis, an oxidized electrode would allow a more rapid and possibly more complete reduction. Oxalic acid should be oxidized with a reduced electrode, in so far as is possible, as should iron^{II}.[4]

Acknowledgements—The author wishes to express his thanks to the Research Corporation for financial aid in securing the potentiostat and current integrator and to the National Science Foundation for the recorder. Thanks are also due to Mr. John Ganchoff and Mr. Harris Burns who participated in the experimental work.

Zusammenfassung—Es ist seit geraumer Zeit bekannt, dass die Vorbehandlung von Platinelektroden häufig von Einfluss auf die elektrochemischen Reaktionen ist. Zum Teil lässt sich der Effekt auf die Tatsache zurückführen, dass anodisch oder chemisch oxydierte Platinelektroden zu einem gewissen Grade mit einem Film von Platinoxyd überzogen sind. Die vorliegende Arbeit beschäftigt sich mit der quantitativen Beziehung zwischen kinetischen Parametern und Ausmass der Oxydfilmbildung. Wo immer möglich werden Änderungen des Reaktionsmechanismuss es vorgeschlagen. Die meisten experimentellen Daten wurden aus Strom-Potential-Kurven gewonnen, doch wurde auch de Technik der Chronopotentiometrie und Mikroskopie angewandt.

Die Reduktion von Vanadin (V), Chrom(VI), Arsen(V) Iodate und Sauerstoff wurden untersucht. Desgleichen die Oxydation von Vanadin(IV), Arsen(III), Oxalsäure und Amseisensäure. Die Anwesenheit von Oxydfilmen beeinflusste die Reaktionen in verschiedenster Weise. Jedoch wurde in jedem Falle eine Änderung der kinetischen Parameter der studierten Reaktionen festgestellt. Für einige Fälle war die Anwendung einer modifizierten Sauerstoffbrückentheorie nützlich.

Résumé—On sait depuis quelques temps que le pté-traitement des électrodes de platine affecte souvent les réactions électrochimiques ultérieures. Une partie de l'effet du pré-traitement est due au fait que des électrodes de platine oxydées anodiquement ou chimiquement se recouvre plus ou moins d'un film d'oxyde de platine. Ce travail est relatif à la détermination quantitative de paramètres cinétiques en fonction de l'importance du film d'oxyde. Lorsque cela a été possible, on a proposé des changements dans les mécanismes des réactions.

La plupart des phénomènes expérimentaux ont été empruntés aux courbes intensité-potentiel, mais les techniques de la chronopotentiométrie et de la microscopie ont été aussi employées. On a étudié la réduction du vanadium (V), du chrome (VI), de l'arsenic (V), de l'iodate et de l'oxygène ainsi que l'oxydation du vanadium (IV), de l'arsenic (III), de l'acide oxalique et de l'acide formique. La présence d'un film d'oxyde de platine affecte différemment les réactions étudiées, mais dans chaque cas, on a enregistré la variation de paramètres cinétiques de la réaction étudiée. Dans un grand nombre de cas, une théorie modifiée du pont d'oxygène a donné satisfaction.

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THE DETERMINATION OF COBALT BY OXIDATION WITH POTASSIUM MOLYBDICYANIDE

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(*Received* 1 *September* 1959)

Summary—Cobalt has been determined titrimetrically and coulometrically by oxidation of the bivalent ion with potassium molybdicyanide, $K_3Mo(CN)_8$, in ammoniacal medium. The break in potential at the equivalence-point is approximately 0.6 volt. Manganese is not oxidized stoichiometrically in citrate media, but the total of cobalt and manganese may be obtained in the presence of fluoride. Iron interferes when fluoride, but not when citrate is used as the complexing agent. The method, therefore, is not directly applicable to steels where both iron and manganese are present.

OF the various methods which have been devised for the titrimetric determination of cobalt, the one most widely used is that proposed almost simultaneously by Dickens and Maasen[1] and by Tomicek and Freiberger[2]. In this procedure bivalent cobalt is oxidized to the tervalent state in the presence of ammonia and an ammonium salt by potassium ferricyanide, the end-point being determined potentiometrically. The method suffers the disadvantage that the break in potential at the equivalence-point is only about 0.2 volt, making it necessary that the end-point of inflection be obtained from a plot of the titration curve.

Substitution of ethylenediamine for ammonia lowers the reduction potential of the $cobalt^{III}$–$cobalt^{II}$ system some 0.5 volt to about −0.55 volt versus the saturated calomel electrode, giving a greatly improved potential break of 0.7 volt at the end-point.[3] However, because the $cobalt^{II}$ ethylenediamine ion is readily oxidized by atmospheric oxygen, careful precautions must be taken to exclude air from the titration vessel and the titrant.

Potassium molybdicycanide, $K_3Mo(CN)_8$, with a reduction potential of 0.73 volt versus the saturated calomel electrode,[4] is a more powerful oxidizing agent by some 0.4 volt than is potassium ferricyanide. The solid compound decomposes rapidly upon exposure to light, but is more stable in solution. Solutions may be readily prepared by oxidation of a solution of the corresponding potassium molybdocyanide, $K_4Mo(CN)_8$, which as the solid is stable in light. This oxidation is most conveniently performed by stirring with lead dioxide in dilute sulphuric acid solution. Solutions of the molybdicyanide prepared in this manner may be kept and used for two to three days if stored away from light and standardized at the time of use.

Using this reagent in place of potassium ferricyanide, cobalt has been successfully determined under conditions similar to those employed in the ferricyanide titration. The break in potential at the equivalence-point is approximately 0.6 volt.

Also, a procedure for the application of the system to constant-current coulometry has been developed which eliminates the necessity for preparation and frequent standardization of potassium molybdicyanide solutions. By adding solid potassium molybdocyanide to a solution containing $cobalt^{II}$ in the presence of ammonia and an ammonium salt and oxidizing the cobalt and/or the molybdocyanide at a platinum

electrode under conditions of one hundred percent current efficiency, the amount of cobalt present may be determined from the total current required to effect the oxidation. The end-point may be found by following the potential with a pH meter, using a platinum-calomel electrode system as was done in the titrimetric procedure.

EXPERIMENTAL WORK

Titrimetric Method

Reagents

Potassium Molybdicyanide Solution: A solution of approximately 0.05*M* potassium molybdicyanide was prepared by dissolving 36 g of potassium molybdocyanide, prepared by the method of Willard and Thielke[5], in 500 ml of distilled water. About 10 g of lead dioxide and 4 ml of concentrated sulphuric acid were added and the solution stirred vigorously for 5 minutes. After the addition of the lead dioxide the solution was protected from exposure to light as much as possible. The lead sulphate and unreacted lead dioxide were filtered off on a medium-porosity fritted-glass funnel, the solution diluted to approximately one litre and stored in a dark bottle away from the light. It was standardized potentiometrically against cobalt^{II} sulphate.

Cobalt^{II} sulphate: A standard solution of 0.05*M* cobalt^{II} sulphate was prepared by weighing out accurately 16.617 g of potassium cobalticyanide into a 500-ml conical flask, adding 50 ml of concentrated sulphuric acid and heating gently at first and then strongly until all the cyanide was driven off and about 10 ml of solution remained[6]. After cooling, the solution was transferred quantitatively to a litre volumetric flask and diluted to volume. It was stored in a polyethylene bottle.

Apparatus

A Beckman Model H–2 pH meter with a bright platinum-saturated calomel electrode system was used for the titrations. The titration vessel was a 250-ml beaker with the exterior covered with aluminium foil. Magnetic stirring was used.

Standardization of potassium molybdicyanide solutions

It has been shown by Kolthoff and Tomsicek[4] that decomposition of potassium molybdicyanide in solution is less rapid if the solution is made acid. In the procedure given above for the preparation of molybdicyanide solutions a sufficient excess of sulphuric acid is present to provide the required acidity. A solution prepared by the method given above was stored away from direct light and portions were withdrawn and titrated over a period of eight days. A plot of concentration versus time is shown in Fig. 1. The rate of decomposition may be seen to increase with time. For this work fresh solutions were prepared every two or three days.

Determination of cobalt

For the determination of cobalt a known excess of standard potassium molybdicyanide solution was pipetted into a solution containing up to 50 mg of cobalt to which had been added 15 ml of ammonium citrate and 25 ml of concentrated ammonia. The excess molybdicyanide was then back-titrated immediately with standard cobalt^{II} sulphate. Back-titration is recommended, as equilibrium is reached rapidly after the addition of each increment of titrant. With direct titration it is necessary to wait 30 seconds or so after the addition of each quantity of titrant when in the neighborhood of the end-point to allow the system to come to equilibrium. A titration plot is shown in Fig. 2.

Effect of iron and manganese

Iron^{III} does not interfere, as it is held in solution by the high concentration of citrate present. Iron^{II} if present must be oxidized to the tervalent state. This may be done with hydrogen peroxide, the excess oxidizing agent being removed by boiling.

In the presence of citrate, manganese^{II} was oxidized by molybdicyanide to a mixture of the three and four oxidation states, so that stoichiometric results could not be obtained. Other complexing agents were investigated in an effort to find one in whose presence manganese would be oxidized to some definite oxidation state. Those studied included tartrate, sulphosalicyclate, pyrophosphate, ethylenediaminetetraacetate, N-hydroxyethylene-diaminetriacetate and fluoride. Of this number

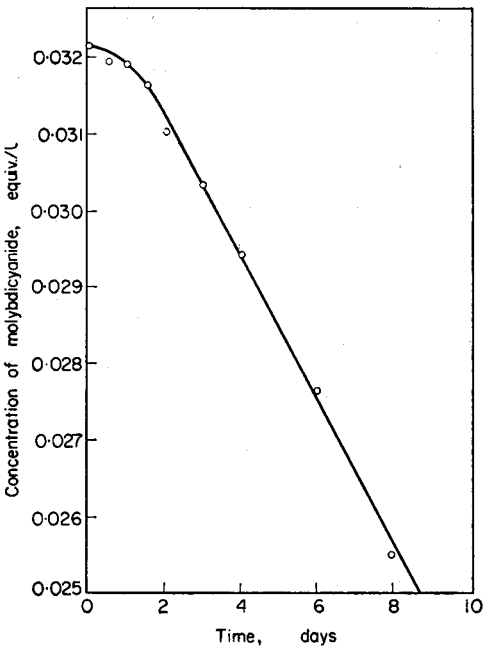

FIG. 1.—Change in concentration of a solution of potassium molybdicyanide in subdued light over a period of eight days

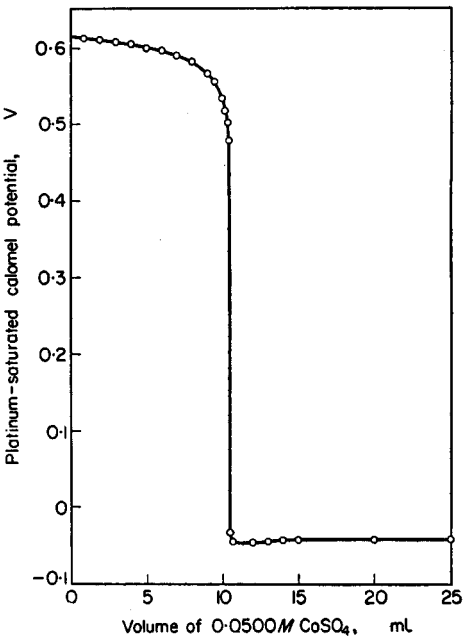

FIG. 2.—Titration of potassium molybdicyanide with cobalt^{II} sulphate in the presence of ammonia and ammomium citrate

only fluoride was found acceptable, for in the presence of fluoride manganese was oxidized quantitatively to the quadrivalent oxidation state and precipitated as manganese dioxide. Unfortunately, the fluoride complex of iron^{III} is not stable enough under the alkaline conditions of the titration to prevent the precipitation of ferric hydroxide, so that the simultaneous presence of iron and manganese could not be tolerated. Attempts to use mixtures of citrate or tartrate and fluoride were unsuccessful because potential readings were not stable. Results of some typical titrations are given in Table I.

Substitution of ethylenediamine for ammonia was also investigated. Upon addition of ethylenediamine to a solution of potassium molybdicyanide the potential drifted steadily downward from 0.72 volt to about 0 volt versus the saturated calomel. Attempts were made to titrate cobalt in the presence of ethylenediamine with molybdicyanide, but in the region of the equivalence-point the potentials drifted seriously, indicating probable attack of the amine by the oxidizing agent.

TABLE I. TITRATION OF COBALT^{II} AND MANGANESE^{II} WITH POTASSIUM MOLYBDICYANIDE

Metal ion titrated	Other metal ion present, *mg*	Complexing agent	Metal taken, *mg*	Metal found, *mg*
Co^{II}	None	Citrate	5.44	5.41, 5.41, 5.44; ave. 5.42
Co^{II}	None	Citrate	48.32	48.41, 48.24, 48.21, 48.28; ave. 48.29
Co^{II}	Fe^{III}, 54.1	Citrate	14.73	14.70
Co^{II}	Fe^{III}, 270.5	Citrate	14.73	14.65
Mn^{II}	None	Citrate[a]	4.91	4.68[b]
Mn^{II}	None	Fluoride	4.91	4.89[b]
Co^{II}	Fe^{III}, 54.1	Fluoride	16.11	14.37[c]

[a] Potential break not sharp
[b] Calculated on basis of oxidation of Mn^{II} to Mn^{IV}
[c] Precipitate of ferric oxide formed

Coulometric Method

Apparatus

A Hewlett-Packard Model 712A power supply was used as a potential source. A 1000-ohm, 100-watt dropping resistor and a calibrated precision resistor of either 2 or 20 ohms were connected in series with the cell. The exact amount of current being passed during each run was determined by measuring the potential drop across the precision resistor with a Leeds and Northrup student potentiometer, the potentiometer being checked frequently against a standard cell. The potential of the power supply was adjusted as required during each run to keep the current constant. Time measurements were made with a stop watch.

A 250-ml beaker was used as a titration vessel, with a circular platinum gauze electrode suspended in the beaker to act as an anode. The cathode, a platinum foil fused to a platinum wire, was placed in a glass tube approximately 1 cm in diameter and 10 cm long into one end of which was fused a fine fritted glass disc. This tube, filled with a catholyte of dilute sulphuric acid (1:1), was placed in the center of the titration vessel. A Beckman Model H-2 pH meter with a bright platinum-saturated calomel electrode system was employed to detect the end-point. Magnetic stirring was used.

Procedure

Into the titration vessel was placed 10 ml of a 25% solution of ammonium citrate and 15 ml of concentrated ammonia. Approximately 0.5 g of potassium molybdocyanide for each 30 mg of cobalt was added. Portions of a solution of cobalt^{II} sulphate, prepared by weight from primary-standard

cobalt sulphate, were then pipetted into the cell and the stop watch and current started simultaneously. When the potential of the solution just began to rise rapidly from that of the cobalt^{III}–cobalt^{II} system, the time was noted.

The amount of cobalt present, B, in millimoles, was calculated from the equation

$$B = \frac{It}{nF}$$

where

I = current in milliamperes
t = time in seconds
n = number of electrons per molecule involved in the oxidation
F = Faraday, 96,500 coulombs per equivalent

Results for a series of titrations are given in Table II.

TABLE II. DETERMINATION OF COBALT BY CONSTANT CURRENT COULOMETRY WITH POTASSIUM MOLYBDICYANIDE

Current, *mA*	Cobalt taken *mg*	Cobalt found *mg*
9.98	2.72	2.72, 2.69, 2.70, 2.73, 2.72, 2.72; ave. 2.71
19.96	5.44	5.48, 5.39, 5.46, 5.42, 5.45, 5.42; ave. 5.44
48.83	13.60	13.55, 13.66, 13.67, 13.62, 13.57, 13.54; ave. 13.60
97.66	27.19	27.26, 27.07, 26.91, 27.15, 27.36, 27.27; ave. 27.17

Manganese and iron both interfere in the determination of cobalt by the coulometric method Excessive amounts of current are required to oxidize manganese alone in either citrate or fluoride media, as a film of manganese dioxide coats the platinum anode. When iron^{III} is present the results for cobalt are invariably low by a small amount. It is necessary, therefore, that cobalt be separated from these elements before titration.

Zusammenfassung—Cobalt wurde in alkalischem Medium titrimetrisch und coulometrisch bestimmt durch Oxydation des zweiwertigen Ions mit Kaliummolybdicyanid, $K_3Mo(CN)_8$

Résumé—Les auteurs ont dosé le cobalt volumétriquement et coulométriquement par oxydation de l'ion divalent par le molybdicyanure de potassium, $K_3Mo(CN)_8$, en milieu ammoniacal. La variation du potentiel au point équivalent est d'environ 0,6 volt. Le manganèse n'est pas oxydé stoechiométriquement dans les milieux citrique, mais on peut obtenir la totalité du cobalt et du manganèse en présence de fluorure. Le fer est complexé par le fluorure, mais pas quand on utilise le citrate comme agent complexant. La méthode n'est donc pas directement applicable aux aciers quand le fer et le manganèse sont presénts à la fois.

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Talanta, 1960, Vol. 3, pp. 351 to 355. Pergamon Press Ltd. Printed in Northern Ireland

THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH AMMONIUM PYROPHOSPHATE

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(*Received* 2 *September* 1959)

Summary—A spectrophotometric procedure for determining copper is described, utilising the absorption at 650 mμ of the copper^{II}-ammonium pyrophosphate complex. Optimum conditions have been established and interferences studied. It is suggested that the procedure could be used for the determination of major amounts of copper in various alloys.

INTRODUCTION

IT is a well known fact that the pyrophosphate ion is capable of forming complexes with several metallic radicals[1–3] and the range of complexes formed by various ratios of copper^{II}, ammonium and pyrophosphate ions has been studied by Watters and his co-workers[4]. In the course of investigating a similar system[5] it was noticed that the deep blue colour formed between copper^{II} and ammonium pyrophosphate solutions possessed properties that suggested its use as a quantitative procedure for the colorimetric determination of copper.

This paper describes the work that was carried out in developing this idea into a workable procedure and it will be shown that ammonium pyrophosphate is not suitable for determining minute traces of copper. This, it is felt, is an advantage in some respects in that it would enable major amounts of copper to be determined in various alloys without resorting to the undesirable technique of excessive dilution of a small aliquot.

EXPERIMENTAL

Apparatus

All absorption measurements were carried out on a Unicam SP500 spectrophotometer using glass cells.

Reagents

Ammonium pyrophosphate: Dissolve 20 g of pyrophosphoric acid (B.D.H. Laboratory Reagent) in 100 ml of distilled water, filtering the solution if necessary. Whilst cooling this solution in running water, add slowly and with stirring, ammonia solution (s.g. 0·880) until a white precipitate forms. Allow to settle, filter through a Büchner funnel and wash two or three times with ammonia solution (s.g. 0·880). Finally, wash once with acetone, transfer the precipitate to a large clock glass and allow to dry at room temperature, occasionally turning over the precipitate with a spatula. When the precipitate no longer smells of acetone (there is always a faint smell of ammonia) transfer to a stoppered bottle.

Standard metal solutions: All the solutions were prepared from high purity metals (Johnson, Matthey and Sons Ltd., London). They had a final acid concentration of 1 % with respect to hydrochloric acid and in every instance 1 ml of standard solution $\equiv$ 1 mg metal.

Other reagents: All other reagents were of AnalaR quality and were used as received.

The absorption curve of the copper^{II}–ammonium pyrophosphate complex

In order to exclude the possible interference of any anions, the following technique was used[5]:

A small ion-exchange column, 10 cm long and 1 cm internal diameter, was charged with one or two g of Zeokarb 225 in the hydrogen form and a 0·1*M* solution of copper sulphate was passed through the column until there was complete conversion of the resin to the copper form. The column was washed with water until washings were copper-free, and the resin was then transferred to a small Büchner funnel and dried as much as possible by suction. It was finally transferred to an oven and dried overnight at 60°.

A 0·2 g portion of the resin thus prepared was weighed into a small conical flask, 25 ml of approximately 0·2*M* (50 g per litre) ammonium pyrophosphate were added, the flask was stoppered and set aside for three days with occasional swirling. The resulting dark blue supernatant liquid was carefully

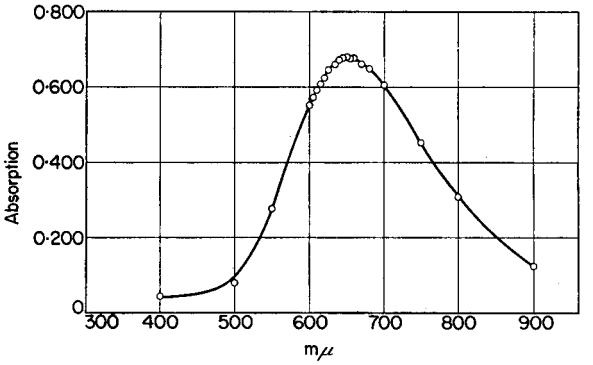

FIG. 1.—The absorption curve of the copper^{II}–ammonium pyrophosphate complex.

decanted into a 50-ml graduated flask and the solution was diluted to standard volume with 0·2*M* ammonium pyrophosphate. The absorption curve was plotted and the result is shown in Fig. 1. It shows a maximum absorption at 650 mμ and this wavelength was used for all readings. Chloride, nitrate, sulphate and perchlorate ions subsequently added as their sodium salts, caused no shift in the absorption maximum.

DISCUSSION

Effect of reagent concentration

In order to study the effect of excess reagent on the coloured complex, 1-ml aliquots of standard copper solution were added to five 25-ml graduated flasks. Ammonia solution (1 + 4) was added dropwise to each flask until the initial pale blue precipitate just redissolved and then the contents of the flasks were diluted to standard volume with 0·2, 0·3, 0·4, 0·5 and 0·6*M* ammonium pyrophosphate solutions respectively. The absorption readings of all these solutions at 650 mμ were identical within the range of experimental error.

Effect of pH

For successful colour development, the pH of the solution before adding the ammonium pyrophosphate reagent must not be less than 10. Adjustment of solutions to this pH value is made with dilute ammonia solution and checked with wide-range indicator papers.

Stability of the colour to time and temperature

Repeat absorption readings taken after standing for two days at room temperature agreed with the original figures to within the accuracy of the instrument. In addition, identical readings were obtained on the solutions at 35°.

Beer's law

To ascertain the adherence of the system to Beer's law a calibration graph was prepared in the following manner: To a series of 25-ml graduated flasks were added different volumes of standard copper solution, the pH was adjusted to between 10 and 11 by the dropwise addition of ammonia and the solutions were diluted to standard volume with approximately 0·2*M* ammonium pyrophosphate. The absorption of

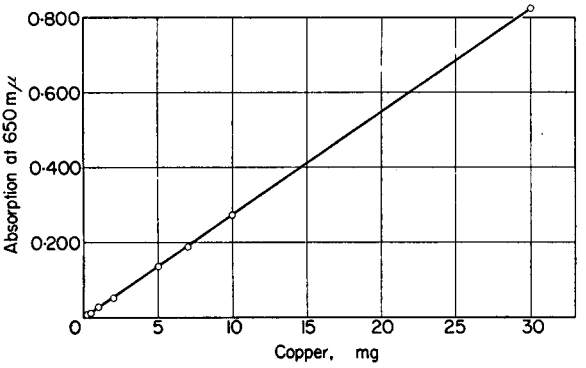

FIG. 2.—Adherence of the copper^{II}–ammonium pyrophosphate system to Beer's law.

each solution was measured at 650 mμ against a reagent blank of ammonium pyrophosphate solution. On plotting absorption against concentration (Fig. 2) it is seen that the system obeys Beer's law up to the maximum concentration tested, namely 1·2 mg copper per ml.

Precision and sensitivity of the method

The standard deviation was determined by transferring 10-ml portions of standard copper solution into each of five 25-ml graduated flasks, adjusting the pH to between

TABLE I.—STANDARD DEVIATION EXPERIMENTS

Test	Absorption at 650 mμ	Deviation
1	0·277	0·001
2	0·280	0·002
3	0·275	0·003
4	0·277	0·001
5	0·282	0·004
	Average 0·278	

10 and 11 with ammonia solution and then diluting to standard volume with 0·2*M* ammonium pyrophosphate. The results are given in Table I.

From these results it follows that the Standard Deviation is 0·002(5) units.

As can be seen from Fig. 2, the proposed reagent is not capable of determining minute amounts of copper. This fact would be useful in applying the method to determining copper as a major constituent in various alloys.

Optimum range and accuracy

The optimum range was determined by Ringbom's procedure[6] a curve being plotted with % absorption as the y axis and log concentration as the x axis. The graph, reproduced in Fig. 3, shows that the optimum range lies between 7 and 30 mg copper *i.e.* the section of the curve with steepest slope.

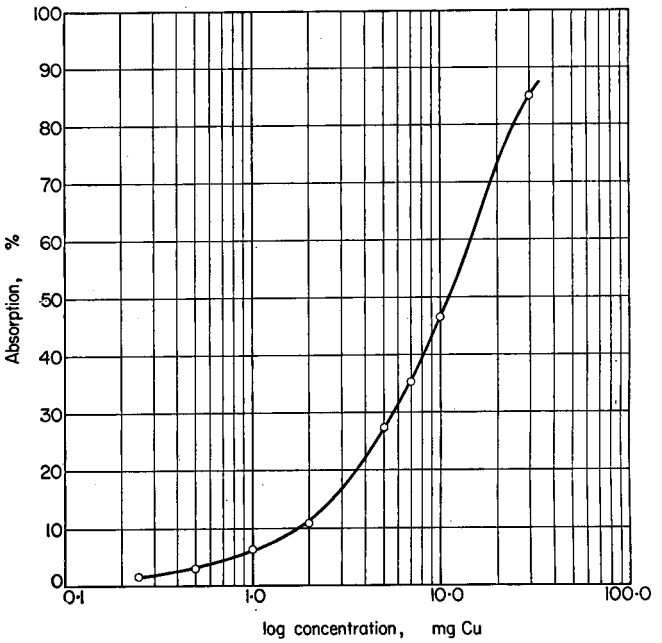

FIG. 3.—Ringbom's curve showing optimum range.

Applying the formula according to Ayres[7]:—

$$\frac{\%\text{ relative analysis error}}{1\%\text{ absolute photometric error}} = \frac{230}{\mathrm{dI/d}\log c}$$

for the range 7 to 30 mg copper, a relative analysis error of 2·9 % is obtained per 1 % absolute photometric error. This is in good agreement with the value of 2·7 % which is the minimum error attainable as imposed by Beer's law.

Interferences

As mentioned previously, common anions such as chloride, nitrate, sulphate and perchlorate do not interfere and in addition, $\mathrm{tin^{II}}$, zinc, cadmium and manganese have no harmful effect. On making the test solution ammoniacal before adding the ammonium pyrophosphate reagent, lead and bismuth form precipitates which can be removed either by filtering or centrifuging the suspension. Cobalt and nickel cause more serious interference and corrections must be made if these elements are present. At 650 mμ 5·0 mg of cobalt give an absorption equivalent to 0·6 mg of copper and 10·0 mg of cobalt are equivalent to 2·0 mg copper. Similarly, 5·0 mg of nickel correspond to 0·55 mg of copper whereas 10·0 mg are equivalent to 1·0 mg of copper.

Acknowledgements—The author records his grateful thanks to Dr. J. E. Salmon and Mr. J. A. R. Genge for helpful discussions and assistance in the preparation of this paper.

Zusammenfassung—Es wird eine spectrophotometrische Methode zur Bestimmung von Kupfer beschrieben, die von der Absorption des Kupfer (II)ammonium-pyrophosphates bei 650 mμ Gebrauch macht. Die optimalen Bedingungen wurden festgestellt und Störungen untersucht. Die Methode wird zur Bestimmung von grösseren Kupfermengen in Legierungen als geeignet erachtet.

Résumé—On décrit un procédé spectrophotométrique pour le dosage du cuivre en utilisant l'absorption du complexe Cu II-pyrophosphate d'ammonium à 650 mμ. On a établi les conditions optimum et étudié les interférences. On a suggéré l'emploi du procédé pour la détermination de grandes quantités de cuivre dans divers alliages.

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Talanta, 1960, Vol. 3, pp. 356 to 363. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF DEUTERIUM IN ORGANIC COMPOUNDS BY INFRARED SPECTROPHOTOMETRY*

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Summary—The Trenner–Arison–Walker method for the micro-analysis of deuterium in organic compounds involves oxidation of the compound with copper oxide in a sealed tube, collection of the water by vacuum distillation, and analysis of the water by infrared spectrophotometry. Experience in applying this technique to a variety of organic compounds in our laboratory has suggested a number of procedural modifications. These principally affect the methods of sample handling and water collection. Difficulties associated with temperature changes on the spectrophotometry of the deuterium-enriched water are overcome by differential analysis against natural-abundance water using a double-beam spectrophotometer.

AN infrared method for the determination of the deuterium content of water was first described by Thornton and Condon.[1] This method depends on the fact that HDO has an absorption band at 2520 cm^{-1} which can be observed through the overlapping spectrum of H_2O. At high isotopic dilution, where the concentration of D_2O is negligible, the intensity of the HDO band provides a direct measure of the total deuterium content of the water sample. This technique was developed by Trenner, Arison and Walker[2–5] for the determination of deuterium in organic compounds by assay of the water formed on combustion. In their earlier work[2] these investigators used the conventional Pregl micro-analytical type of combustion train for the oxidation of the organic compound, but subsequently[3] they replaced this by a static oxidation method in which the organic compound is heated with a large excess of copper oxide in a sealed quartz tube at 750–800°.

The object of this paper is to review our experience with this technique, which we have applied to deuterium-enriched organic compounds of various types; during this time a number of changes have been made in the apparatus and procedure. The principal modifications are concerned with the collection of the water sample and its transfer to the micro absorption cell. It has also been found that the determination of HDO is facilitated by differential analysis against natural-abundance water on a double-beam spectrometer in place of the single-beam cell-in/cell-out method used originally. The volatility and other physical characteristics of the compound critically determine the methods which must be used to obtain accurate dilution ratios, and they also influence the procedures to be followed for filling the combustion tube and subsequently evacuating and sealing it. This phase of the technique has not been discussed by previous investigators.

* Published as Contribution No. 5501 from the Laboratories of the National Research Council of Canada.

APPARATUS

The apparatus used for the collection and transfer of the water is shown in Figs. 1–3. The main difference from the distillation train used by Trenner and collaborators is the elimination of the vacuum-controlled capillary system for sample transfer from the collecting vessel to the absorption cell. This simplifies the apparatus and eliminates three of the stop-cocks. In our experience the water sample which finally collects at the bottom of the collecting vessel can be transferred to the micro-cell by withdrawal into a separate glass capillary tube after releasing the vacuum and detaching the collecting vessel at the ground-glass joint. This simplifies the manipulation and allows greater flexibility in collecting the water from the walls of the vessel above the cooling tip.

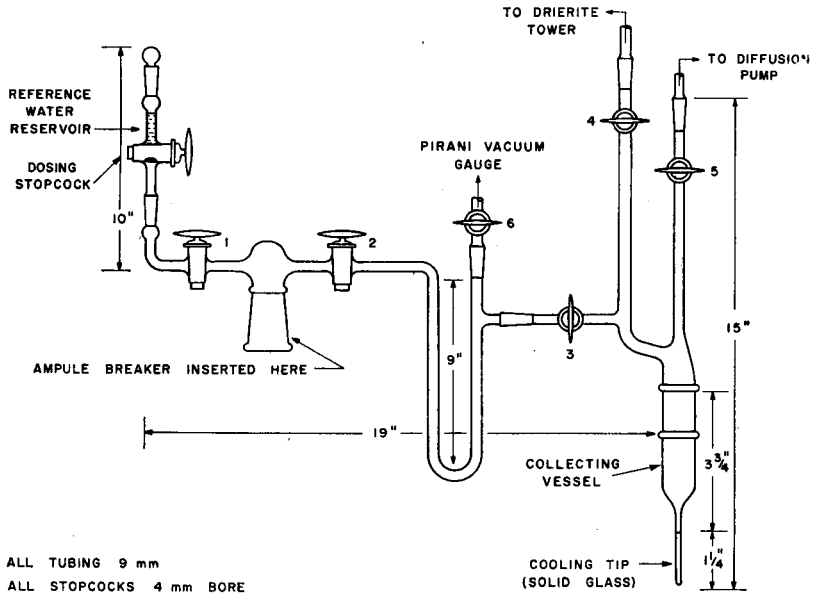


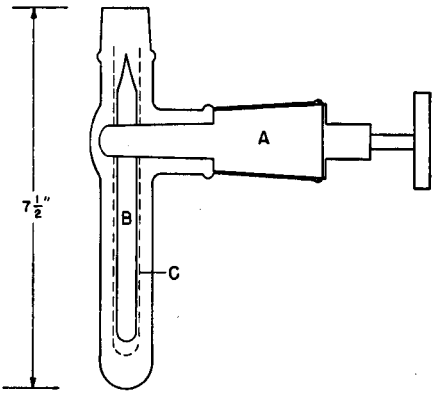
FIG. 1.

The ampule breaker, shown in Figs. 2 and 3, is based on designs kindly supplied to us by Dr. Trenner. The main part, including the standard tapered barrel, is constructed of aluminum, while the piston and plunger are made of brass. It should be noted that the piston, which is advanced by rotation of the screw-threaded plunger, is formed from a separate piece of brass rod, so that it does not rotate as the plunger is advanced. In normal operation the piston is only advanced far enough to break the ampule, and, after the water transfer is completed, it can be reset by means of a brass rod inserted down the breaker tube from the ground joint. A small hole in the anvil, in line with the axis of the screw thread, permits the insertion or removal of the piston without completely unscrewing the plunger. The vacuum seal in this unit is obtained by lubricating the screw thread with a grease formed by mixing hot Apiezon Wax (W-100) and Apiezon grease (T) in equal proportions.

SPECTROPHOTOMETRIC TECHNIQUE

The spectra are measured on a Perkin-Elmer Model 21 spectrophotometer using a sodium chloride prism. A standard Perkin-Elmer micro-cell of 0·2 mm thickness with calcium fluoride windows is used in the reference beam and a macro-cell of matched thickness in the sample beam. To reduce the parasitic volume of the micro-cell the filling tube is removed, as described by Trenner, Arison and Walker;[3] capillary attraction suffices to keep the water in the functional part of the cell over extended periods of time without evaporation or change in the deuterium content; no stoppers are required, and an analysis can be performed with 10 mg of water.

Since the transmission of a 0·2-mm layer of natural-abundance water at 2500 cm^{-1} is only about 5%, it is necessary to operate the spectrometer with wide slits (100–120 μ) to obtain sufficient energy.



AMPULE BREAKER ASSEMBLY

A - AMPULE BREAKER
B - AMPULE IN POSITION TO BE OPENED
C - WIRE GAUZE

FIG. 2.

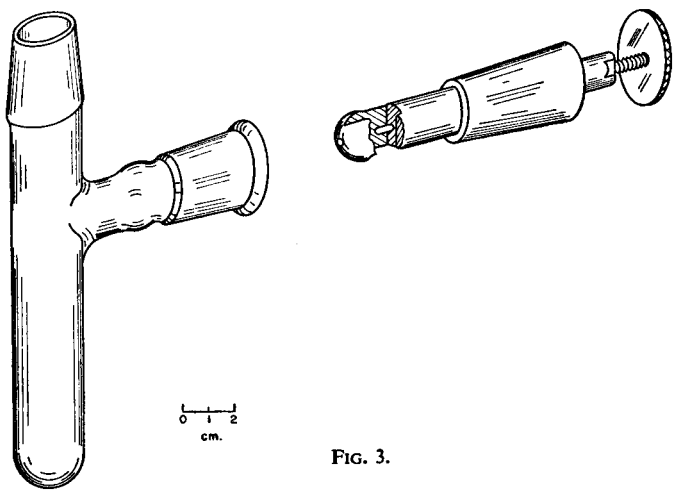


FIG. 3.

Reproducible operating conditions are obtained by first closing the sample beam, and, with no cell in the reference beam, recording the pen displacement produced by a test signal of 0·03 μ volt. This should correspond to an apparent absorption of 40–60% depending on the sensitivity of the spectrometer. The reference cell is next filled with repeatedly distilled natural-abundance water. With the reference cell in place, and no cell in the sample beam, the slit is now adjusted to produce a pen displacement equal to that of the 0·03 μ volt test signal. With natural-abundance water in both cells, the spectrometer is now set to 2500 cm^{-1} and the pen adjusted to read between 0·05 and 0·10 absorbance units, whereupon the background spectrum is recorded from 2800 to 2400 cm^{-1} (Curve A of Fig. 4). Both cells are then removed from the spectrometer, and the micro-cell is emptied, dried and refilled with the deuterium-enriched water. Both cells are next replaced simultaneously in the spectrometer and the spectrum is rescanned to record the HDO absorption peak (Curve B of Fig. 4). By following this procedure, adequate temperature equivalence is maintained in the two cells, and the need to thermostat the cells during measurement is avoided. If additional time is allowed for the cells to reach

thermal equilibrium with the spectrometer, a repeat measurement of the spectrum does not change the peak absorbance by more than 0·002 units.

The calibration curve, shown in Fig. 5, is plotted as total mole per cent deuterium oxide against peak absorbance, taking the natural abundance ratio H/D as 6400/1. The plot is linear at least up to 0·7% deuterium oxide and all measurements were made below this concentration. The curve has been checked periodically and has shown no deviation in three years. All standard deuterium-enriched water samples were obtained by dilution of a master standard prepared in turn by dilution of 99·8% deuterium oxide. Dilutions were made gravimetrically with repeatedly distilled natural-abundance water.

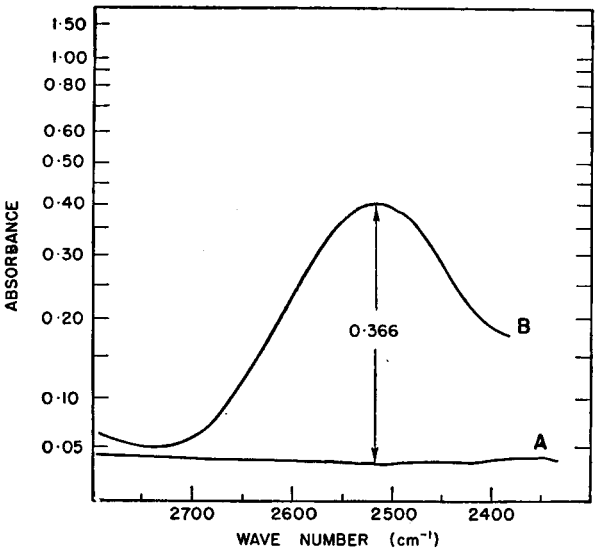


FIG. 4.

ANALYTICAL PROCEDURE

Dilution of the deuterium-enriched compound

Most of the compounds analysed contained between one and eight deuterium atoms per molecule, with molecular weights in the range 50–500. In all cases the deuterium-enriched compounds were diluted with the natural-abundance compound; the approximate deuterium contents of the compounds were known, and the dilution factors were adjusted to yield water samples containing 0·25–0·35% deuterium oxide. This required dilutions in the range 20 to 250.

The method of dilution depends on the physical characteristics of the substance. Crystalline solids are weighed on a micro-balance and then dissolved in a suitable volatile solvent, and the solvent is pumped off in vacuum. Non-viscous liquids are mixed directly, while viscous liquids are dissolved in a suitable solvent, the solvent is removed by distillation and the diluted compound is vacuum distilled.

Combustion

Oxidation is carried out in an ampule formed from a 15-cm length of Vycor quartz tubing. One end of the tube is sealed in an oxy-hydrogen flame, and the other end is attached through a graded seal to a male 14/35 Pyrex standard tapered joint for attachment to a vacuum line. Between 250 and 500 mg of copper oxide (Merck Reagent Grade) is introduced into the combustion tube, which is then evacuated at 105–110° for one hour. After cooling, the vacuum is released and the calculated amount of the diluted compound to yield 10–12 mg of water is added. This normally requires between 5 and 10 mg of compound. Solid compounds are introduced down the tube by means of a cylindrical glass scoop attached to the end of a glass rod, and liquids are added through a glass capillary. Quantitative

transfer, of course, is not necessary, but it is important to avoid contamination of the upper section of the Vycor tube. A capillary constriction of 1–2 mm internal diameter is next formed in the Vycor tube near the graded seal. The tube is then evacuated for approximately one hour and while still under vacuum, is sealed at the constriction, with an oxy-hydrogen flame. If the compound under analysis is volatile or heat sensitive, the lower end of the tube is kept cool with ice or solid carbon dioxide during the evacuation and sealing process.

The sealed ampule is next encased in a close-fitting but open-ended refractory jacket and heated in the furnace at 750–800° for 45–60 minutes. For this purpose a semi-micro Pregl-type electrical combustion furnace is used. The whole furnace is confined in a protective box made of $\frac{1}{16}$ inch sheet steel; openings are left in the rear of this box, which faces a blank wall, to allow for blast release in

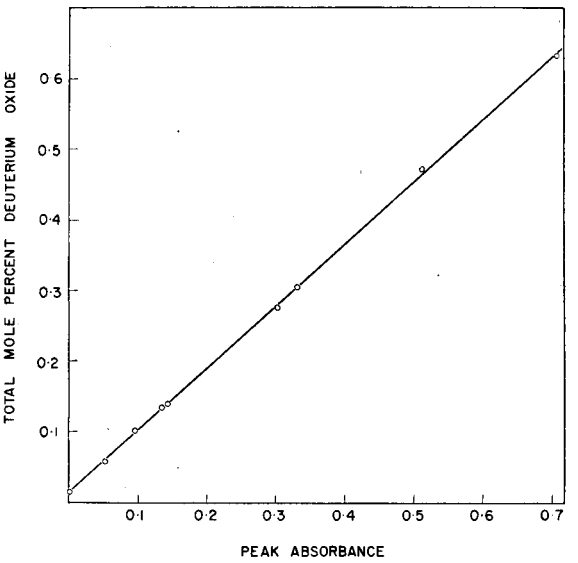


FIG. 5.

case of an explosion. The temperature during the combustion is monitored by a thermocouple in contact with the outer surface of the Vycor tube. Provided that the tube has been properly evacuated and sealed, explosions do not occur unless the temperature rises above 800°.

Distillation

After the combustion is completed the furnace is allowed to cool and the ampule is surrounded by a protective cylinder of wire mesh and inserted into the ampule breaker (Figs. 2, 3). This is next attached by the standard tapered joint to the thoroughly cleaned distillation apparatus. Particular care is necessary that the collecting vessel is free of any trace of grease and it must be washed each time before use with chromic anhydride cleaning solution and distilled water, followed by acetone and carbon tetrachloride. This is essential if the water sample is to form as a single, easily collectable drop.

With stop-cock 1 open, the distillation apparatus is next tested for vacuum tightness and pumped to 10^{-3} mm. The Pirani vacuum gauge is then disconnected from the system by closing stop-cock 6. Stop-cock 5 is also closed and a 10-mg dose of water containing about 0·3% deuterium oxide is introduced into the system from the water reservoir by means of the dosing stop-cock. Five minutes are allowed for isotopic equilibrium to be established in the system, after which stop-cock 5 is re-opened and the system is pumped for a further 45–60 minutes. Stop-cocks 1 and 5 are now closed, stop-cock 6 to the Pirani gauge is opened, and the system is checked again for vacuum tightness. For proper function of the Pirani gauge it is essential to isolate it when the vacuum system contains water vapor.

If the vacuum holds satisfactorily, stop-cocks 2, 3 and 6 are next closed and the ampule is broken by turning the breaker screw. The U-trap is immersed in liquid air, stop-cocks 2, 3 and 5 are opened in that sequence, and the system is pumped for about one minute. During this time the liberated water

collects at the bottom of the U-tube. Stop-cocks 2 and 5 are then closed again and the liquid air reservoir is transferred from the U-tube to the solid glass cooling tip on the bottom of the collecting vessel. Distillation then occurs from the U-tube to the collecting vessel and this can be accelerated by gently warming the U-tube with the palm of the hand. Provided that the apparatus has been properly cleaned, the water now collects as a single mass of ice crystals at the bottom of the collecting vessel. The system is next brought to atmospheric pressure by admitting air through stop-cock 4. As the collecting vessel warms to room temperature, the ice should melt into a single water drop. The collecting vessel is now detached at the ground-joint and the water is withdrawn into a vertically clamped capillary syringe, controlled by a micrometer screw head, and is subsequently discharged into the micro-absorption cell. Initial attempts to provide mechanical support for the micro-cell during this process were discontinued, as it was found that the manipulation could be made more delicately with the cell held in the hand. The water sample is then analysed as described in the section on spectrophotometric technique.

CALCULATIONS AND RESULTS

Although the spectrophotometric analysis requires that the deuterium be all present as HDO, it is more convenient, for purposes of computation, to consider the oxidation in terms of the general formula:—

$$C_aH_{(b-x)}D_xO_c + (2a + 0{\cdot}5b - c)\,CuO = (a){\cdot}CO_2 + 0{\cdot}5(b - x){\cdot}H_2O + 0{\cdot}5(x){\cdot}D_2O + (2a + 0{\cdot}5b - c){\cdot}Cu$$

where $C_aH_{b-x}D_xO_c$ represents the deuterium-enriched compound or undiluted isotopic mixture.

The combustion of w_1 mg of this material will yield $\frac{0{\cdot}5(b - x)}{(m + x)} \cdot w_1$ millimoles of H_2O and $\frac{0{\cdot}5x}{(m + x)} \cdot w_1$ millimoles of D_2O, where m is the molecular weight of $C_aH_bO_c$.

The addition of w_2 mg of diluent containing H/D in a ratio of 6400/1 will provide a further $\frac{0{\cdot}5b}{m} \cdot w_2$ millimoles of H_2O and $\frac{0{\cdot}5b}{(m + b)} \cdot w_2 \cdot \frac{1}{6400}$ millimoles of D_2O.

If D is the total mole per cent of deuterium oxide in the water collected,

$$D = \frac{\left[\frac{0{\cdot}5x}{(m + x)} \cdot w_1 + \frac{0{\cdot}5b}{(m + b)} \cdot w_2 \cdot \frac{1}{6400}\right] \times 100}{\left(\frac{0{\cdot}5x}{(m + x)} \cdot w_1\right) + \left(\frac{0{\cdot}5b}{(m + b)} \cdot w_2 \cdot \frac{1}{6400}\right) + \left(\frac{0{\cdot}5(b - x)}{(m + x)} \cdot w_1\right) + \left(\frac{0{\cdot}5b}{m} \cdot w_2\right)}$$

If the small term $\frac{0{\cdot}5b}{(m + b)} \cdot w_2 \cdot \frac{1}{6400}$ is neglected in the denominator, it follows algebraically that

$$x = \frac{Db(w_1 + w_2) - m\left(0{\cdot}0156\,\frac{bw_2}{(m + b)}\right)}{100w_1 - \frac{Db}{m} \cdot w_2 + \left(0{\cdot}0156\,\frac{bw_2}{(m + b)}\right)}$$

The results of some typical analyses are listed in Table I. The first four measurements are for deuterium-enriched steroids for which independent assays of the

TABLE I.—REPRESENTATIVE DEUTERIUM ANALYSES OF ORGANIC COMPOUNDS

Compound	*Deuterium Content (Atoms of D per molecule)*	
	Theoretical	*Found*
Cholesterol	0·414*	0·375, 0·372
Δ^4-Androstene-3:17-dione	0·475*	0·486, 0·464
Androstan-3-one	0·101*	0·100
Cholestan-3α-ol acetate	2·55*	2·58, 2·58
n-Dodecane-1-d_3	3	2·89, 2·92
n-Dodecane-1:12-d_6	6	5·81
Methyl laurate-12-d_3	3	2·86, 2·93
Methyl-d_3 laurate-2,2-d_2	5	5·12, 5·09
Methyl laurate-2:12-d_5	5	4·80, 4·45
Methyl-d_3 laurate-2:12-d_5	8	8·09, 8·06
n-Dodecyl-1-ol-1:12-d_5	5	5·10. 4·90
1-Bromo-*n*-dodecane-1:12-d_5	5	4·91, 4·78
Androstan-17-one-16-d_2	2	2·12, 2·09
Androstan-3-one-2:4-d_4	4	3·93, 4·29
Androstan-3:17-dione-2:4:16-d_6	6	5·79
3β-Acetoxy-d_3-androstan-17-one	3	3·25
3β-Acetoxy-androstan-17-one-16-d_2	2	2·18
3β-Acetoxy-d_3-androstan-17-one-16-d_2	5	5·16
17β-Acetoxy-d_3-androstan-3-one	3	3·16
17β-Acetoxy-androstan-3-one-2,4-d_4	4	3·71
17β-Acetoxy-d_3-androstan-3-one-2,4-d_4	7	6.72
3β-Hydroxy-androstan-17-one-16-d_2	2	1·94
17β-Hydroxy-androstan-3-one-2,4-d_4	4	3·65
Benzoic-2:4-d_2 acid	2	2·04, 2·08
Benzoic-2:6-d_2 acid	2	1·95, 1·93
Acetophenone-ω-d_3	3	2·53, 2·57
Acetophenone-2-*d*	1	0·90
Anthracene-9:10-d_2	2	1·70, 1·62
s-trans-(2-Phenyl)-2-*d*-*cyclo*hexylamine	1	0·93, 0·97

* Deuterium values determined by mass spectrometry.

deuterium content had been obtained by mass spectrometry. The satisfactory agreement between the two methods is evident.

Acknowledgements—We wish to acknowledge the helpful advice received from Dr. W. A. Patterson of Baird Associates Inc., and Dr. W. H. Stevens of Atomic Energy of Canada Ltd., in connection with the spectrophotometry. We are also grateful to Dr. N. R. Trenner of Merck and Co. Inc., who provided details of his ampule breaker, and to Dr. M. L. Eidinoff of the Sloan-Kettering Institute for Cancer Research who supplied the deuterium-enriched compounds which had been assayed by mass spectrometry.

Our thanks are also due to Mr. G. Ensell and Mr. A. Nadeau for assistance in the design and construction of the apparatus.

Zusämmenfassung—Die Trenner–Arison–Walker Methode zur Mikrobestimmung von Deuterium in organischen Verbindungen beruht auf Oxydation der Probe mit Kuperfoxyd in abgeschmolzener Röhre, Gewinnung des gebildeten Wassers durch Vakuumdestillation und Analyse desselben durch IR-Spektroskopie. Erfahrungen bei Verwendung dieser Methode zur Analyse verschiedener organischer Verbindungen legten einige Änderungen der Arbeitsvorschrift nahe. Diese betreffen in der Hauptsache die Behandlung des Probenmaterials und das Sammeln des Wassers. Schwierigkeiten, die durch Temperaturänderungen während der spektrophotometrischen Bestimmung des an Deuterium angereicherten Wassers auftreten, werden durch Verwendung einer differentialanalytischen Methode überwunden, indem es gegen natürliches Wasser in einem Doppelstrahlphotometer gemessen wird.

Résumé—La mèthode Trenner–Arison–Walker pour la microanalyse du deutérium dans les composés organiques nécessite l'oxydation du composé par l'oxyde de cuivre en tube scellé, la collection de l'eau par distillation sous vide et l'analyse de l'eau par spectrophotométrie infra-rouge. Pour l'application de cette technique à une variété de composés organiques l'expérience a suggéré un certain nombre de modifications du mode opératoire. Celles-ci affectent principalement les méthodes de manipulation de l'échantillon et de collection de l'eau. On surmonte les difficultés entraînées par les variations de température dans la spectrophotométrie de l'eau enrichie en deutérium en effectuant une analyse différentielle par rapport à une eau naturelle non enrichie en utilisant un spectrophotométre à double faisceau.

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Talanta, 1960, Vol. 3, pp. 364 to 369. Pergamon Press Ltd. Printed in Northern Ireland

A CRITICAL STUDY OF THE DETERMINATION OF PLATINUM WITH DIMETHYLPHENYLBENZYL-AMMONIUM CHLORIDE

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(*Received* 28 *September* 1959)

Summary—A study of the recorded method for the determination of platinum with dimethylphenylbenzylammonium chloride revealed defects which become serious for larger amounts. A revised procedure which yields accurate results for micro and semi-micro amounts is described. Samples which have been fumed in sulphuric acid solution may be handled with a slight modification of the recommended procedure.

THE more familiar methods for the gravimetric determination of platinum have been studied in recent years by Beamish and co-workers.[1,2] These investigations show that of the several precipitants which may be relied upon to provide satisfactory results with macro quantities, only zinc yields adequate precision and accuracy on the micro scale. A procedure which deserves to be regarded as the classical micro method was developed in the same laboratory. This utilizes thiophenol to precipitate platinum as a mercaptide.[3] These methods possess disadvantages, however. The former must be used with careful adherence to conditions and the latter involves a reagent which is unstable in air and possesses a disagreeable odour.

A variety of other organic precipitants for platinum have appeared recently in the literature. A review by Beamish[4] indicates their probable usefulness, but general acceptance of these methods should be preceded by careful re-investigations. We have found 4-phenylthiosemicarbazide[5] to be a convenient reagent but have been unable to avoid serious losses to the filtrate. There seems to be little hope of circumventing the trouble, as the reagent can be dissolved only in media in which its complex with platinum is slightly soluble.

Of the remaining reagents, dimethylphenylbenzylammonium chloride seemed the most attractive and worthy of further study.[6] This reagent precipitates bromoplatinate from hydrobromic acid solution and is thus analogous to ammonium chloride in the ammonium chloroplatinate method. Our initial attempts to make use of it met with little success, however. The sources of error discovered were: (*a*) failure to attain constant weight, (*b*) variable composition of the precipitate under certain conditions, and (*c*) prior fuming with sulphuric acid led frequently to low results. This last phenomenon was not unexpected, for many analytical procedures for platinum fail in the presence of sulphate. The handling of such solutions was considered of sufficient importance to warrant further attention.* These difficulties have been overcome and a modified procedure is described below.

* Fumed sulphuric acid solutions are frequently encountered in precious metals analysis: for example, see the classical isolation of platinum from the other members of the platinum group by hydrolytic precipitation.[7]

Apparatus and reagents

Weighings were performed on a Sartorius SM 10 balance with intercalibrated weights. The filtering crucibles used were manufactured by the Staatliche Porzellanwerke, Berlin, and were of A2 porosity, sizes M1 and M2.

Standard platinum solution: A stock solution was prepared from 1·9659 g of platinum supplied by Johnson, Matthey and Mallory, Ltd. This was dissolved in a small quantity of *aqua regia* and the solution evaporated to dryness. The residue was treated three times with conc. hydrochloric acid and evaporated each time to dryness. It was then taken up in water and filtered through a 7·0-cm Whatman No. 42 filter paper. The paper was ashed in a porcelain crucible and the residue treated with *aqua regia* and hydrochloric acid in the same fashion as before. The final residue was taken up in water and filtered. The two filtrates were combined and adjusted to 0·05*N* with hydrochloric acid in a 2·000 litre volume. The solution was standardized by means of the thiophenol method.[3] Found: 0·982 and 0·983 mg per ml; Taken: $0{\cdot}982_8$ mg per ml.

Dimethylphenylbenzylammoniumchloride: The compound was prepared as described by Ryan from Fisher Scientific Co. chemicals, Nos. A-746 and B-277. The 5% aqueous solution was filtered through a sintered-glass funnel. Although it was kept in a brown bottle, the solution became visibly oxidized (blue coloration) after two or three weeks. Weakly coloured solutions were used but more strongly coloured ones were discarded.

Hydrobromic acid: The concentrated acid supplied by Allied Chemical and Dye Corporation was distilled once and a colourless product obtained.

Dioxane and cyclohexane: Distillation Products Industries No. 2144 and Fisher Scientific Co. No. C-556, respectively, were filtered through a sintered-glass funnel.

Thermogravimetric study of the weighing form

It was found that precipitates prepared according to the procedure given by Ryan failed to attain constant weight. The losses on heating precipitates obtained from 10 mg of platinum in 100 ml of solution were generally small—of the order of 0·02 mg per hour. Precipitates obtained from 20-mg quantities experienced losses which were invariably serious. Typical weight-time curves for 20- and 40-mg samples are shown in Fig. 1.

Prolonged heating reduced the weight to very much less than the theoretical value and caused the complex to darken or even turn to tar. Drying at slightly lower temperatures in a well-controlled oven failed to improve the situation.

The reason for this apparent decrease in stability with increasing concentration of the original solution was evident when the precipitates were viewed under the microscope. Precipitates prepared from solutions containing 0·1 mg Pt per ml appeared under magnification to have the texture of blotting paper, whereas those formed from solutions containing 0·2 mg per ml or more appeared chalk-like indicating a much smaller particle size. It may be concluded that the decomposition upon heating, which takes place by evaporation of the organic portion of the complex, proceeds more readily when the surface to volume ratio is higher. Extremely slow addition of the reagent failed to produce coarser precipitates.

The solution to this problem consists in washing the precipitate with a highly volatile solvent and drying at a lower temperature. No single solvent was found to be suitable so the aqueous "holdup" was removed with dioxane and this in turn washed out with *cyclo*hexane. To estimate the magnitude of possible losses to the washings, 25-ml volumes of the organic wash liquids were passed through a large portion of the platinum complex and evaporated to dryness. The platinum content of these washings was determined colorimetrically. (See below under *Filtrate Tests.*) The

dioxane wash contained 5 μg of platinum and the *cyclo*hexane less than the detectable limit.

Composition of the precipitate

The nature of the precipitation reaction would suggest that the dimethylphenylbenzylammonium ion would be a suitable precipitant for platinum in the semi-micro range as well as the micro. It was found, however, that increasingly low values were obtained for increasing quantities of platinum precipitated from 100 ml of 2%

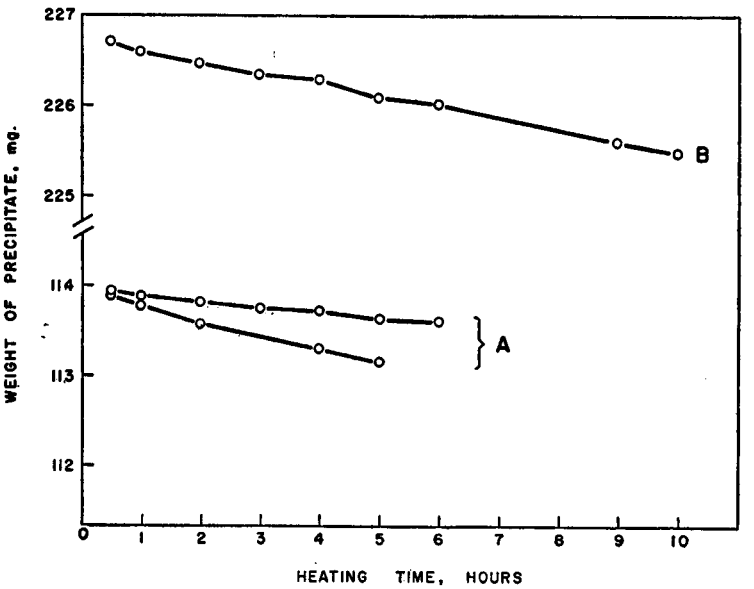

FIG. 1.—Loss of weight upon heating at 110°
A—10 mg of platinum taken
B—20 mg of platinum taken

hydrobromic acid solution. This was attributed to the formation of mixed precipitates. The average molecular weights of precipitates prepared from solutions of various concentrations are presented in Table I.

The most plausible explanation for the decrease in apparent molecular weight assumes that the equilibria:

$$PtBr_6^{2-} + H_2O \rightleftharpoons PtBr_5OH^{2-} + HBr$$

$$PtBr_5OH^{2-} + H_2O \rightleftharpoons PtBr_4(OH)_2^{2-} + HBr \qquad (1)$$

cause an appreciable concentration of the partially hydrolyzed species of lower molecular weight to appear at higher platinum concentrations. An alternative explanation might be based on the reaction:

$$PtBr_6^{2-} + Cl^- \rightleftharpoons PtBr_5Cl^{2-} + Br^- \qquad (2)$$

when large quantities of reagent are added. However, this latter possibility was seen to be at least not the major cause of the effect as essentially the same results were obtained with dimethylphenylbenzylammonium bromide as with the chloride reagent.

It follows that for higher platinum concentrations, the hydrobromic acid concentration must be increased accordingly.

During the course of experiments to determine optimum conditions, it was found that it is unnecessary to add as much reagent as was recommended by Ryan. We found that a final reagent concentration in the supernatant liquid of 0·25% is adequate. The required amount of washing depends upon the quantity of sodium bromide added. Very little washing is required for solutions containing little or no metal cation. When 5 g of sodium bromide had been added, it was necessary to wash large samples with about 50 ml of 0·1% dimethylphenylbenzylammonium chloride solution.

TABLE I.—AVERAGE MOLECULAR WEIGHTS OF PRECIPITATES FORMED FROM 2% HBr SOLUTION

No.	Wt. of Pt in precipitate, *mg*	Average molecular weight
1	31·55	1097·1
2	35·83	1094·8
3	42·69	1096·4
4	49·14	1088·9
5	53·63	1080·8
6	73·57	1077·5

The molecular weight of $(C_{15}H_{18}N)_2PtBr_6 = 1099{\cdot}4$.

In the light of our new knowledge of the precipitation of platinum with dimethylphenylbenzylammonium ion, the following procedure was arrived at.

Recommended procedure: A solution of bromoplatinate is prepared for precipitation by adjusting the acidity with hydrobromic acid. Four ml or more of the 48% acid are added for quantities of platinum of 10 mg or less. Approximately 4 ml of acid are added for each additional 10 mg of platinum. If the platinum concentration is entirely unknown, the acidity may be adjusted to as high as 30%. The sample is made up to approximately a 100-ml volume and a 5% solution of the precipitant is added slowly with stirring. A volume of 5 ml plus 1 ml for each 10 mg of platinum present is sufficient, but a large excess appears to be not detrimental. After allowing the precipitated sample to stand for 3 hours, it is filtered through a tared fritted crucible. The precipitate is washed with a 0·1% aqueous solution of the reagent, followed by 3 ml of dioxane and this in turn followed by 4 ml of *cyclo*hexane. The crucible is heated at 80° to constant weight which is attained in 0·5–1 hour.

Treatment of chloroplatinate solutions

Solutions to be precipitated probably should contain but little, if any, hydrochloric acid, otherwise interference from reaction (2) may be encountered. This condition was ensured by evaporating solutions of chloroplatinate to dryness in the presence of sodium bromide. A single evaporation in the presence of very little chloride was sufficient to effect 100% conversion to bromoplatinate. If much hydrochloric acid was present, it was deemed advisable to repeat the evaporation one or more times after moistening the dry residue with hydrobromic acid. It was frequently found that upon taking up the residue in dilute hydrobromic acid and filtering, a brown or black insoluble residue containing platinum and silica had been formed. This increased with the number of evaporations to which the sample was subjected. The formation

of this residue was kept to a minimum by using unetched beakers for the evaporation and a copious excess of sodium bromide.

Procedure: A sample containing relatively little hydrochloric acid is evaporated to dryness in the presence of 0·5 g of sodium bromide. The residue is dissolved in a little diluted hydrobromic acid and passed through a porous-bottom crucible. If any dark residue is found, this is leached with *aqua regia*. The leaching removes all but a yellow stain on the porous bottom. The leach solution is evaporated to dryness, the residue moistened three times with a few drops of hydrobromic acid and evaporated each time to dryness on the water bath. The final residue is taken up in water and filtered. No dark-coloured insoluble residue should be observed at this stage.

Aliquots of the stock solution were treated as described in the above procedures. The results of these determinations appear in Table II.

TABLE II.—RECOVERY OF PLATINUM FROM CHLOROPLATINATE SOLUTION

No.	Weight of Pt taken, *mg*	Weight of Pt recovered, *mg*	Filtrate loss, *μg*	Gravimetric error, *mg*
1	0·97	0·97	—	0·00
2	0·97	0·97	—	0·00
3	4·87	4·87	2	0·00
4	9·83	9·83	—	0·00
5	9·83	9·86	<2	+0·03
6	9·83	9·83	<2	0·00
7	9·83	9·82	2	−0·01
8	19·66	19·62	2	−0·04
9	19·66	19·67	<2	+0·01
10	34·42	34·43	<2	+0·01
11	49·15	49·17	8	+0·02
12	73·71	73·78	4	+0·07

Blanks were carried through the entire procedure. The weights obtained (not multiplied by the gravimetric factor, 0·1776) were 0·17, 0·14, 0·14, and 0·13 mg.

Treatment of solutions which have been fumed with sulphuric acid

The conversion to bromoplatinate when platinum has been complexed with sulphate is more difficult than the corresponding conversion to chloroplatinate. Whereas the latter may be effected by simple boiling with hydrochloric acid, the weights of precipitates obtained from sulphate solutions of platinum which had been boiled with hydrobromic acid were usually low. The conversion proceeds rapidly, however, at temperatures rather higher than the boiling point of hydrobromic acid. These can be attained if the chief constituent of the solution is sulphuric acid.

Procedure: A sample in sulphuric acid is fumed to about a 2-ml volume and allowed to cool. Approximately 1 ml of water and 10 drops of concentrated hydrobromic acid are added. The sample is heated until fumes of hydrobromic acid are evolved. It is cooled and the fuming repeated after adding a few more drops of hydrobromic acid. Heating must not proceed to a point when hydrobromic acid fumes cease to be evolved. The sample is filtered through a porous-bottom crucible. No insoluble platinum residue should be formed in the process.

Aliquot samples of the stock platinum solution were fumed strongly with 5 ml of concentrated sulphuric acid and treated as described in the preceding paragraph. Results of the gravimetric determinations appear in Table III.

TABLE III.—RECOVERY OF PLATINUM FROM FUMED SULPHURIC ACID SOLUTION

No.	Weight of Pt taken, *mg*	Weight of Pt recovered, *mg*	Filtrate loss, *μg*	Gravimetric error, *mg*
1	9·83	9·78	<2	−0·05
2	9·83	9.83	<2	0·00
3	9·83	9·82	<2	−0·01
4	19·66	19·62	5	−0·04
5	19·66	19·66	5	0·00

Filtrate tests

Filtrates and washings were evaporated to dryness and "wet-ashed" with sulphuric acid and 30% hydrogen peroxide. After treatment with boiling hydrochloric acid, platinum was determined in a 10-ml final volume with stannous chloride.[8]

Zusammenfassung—Die von Ryan veröffentlichte Methode zur gewichtsanalytischen Bestimmung von Platin mit Dimethylphenylbenzylammoniumchlorid wurde eingehender untersucht und die für grössere Platinmengen Fehlerquellen festgestellt. Eine modifizierte Methode, welche für den Mikro- sowie Halbmikro-bereich genaue Resultate erziehlt, wird beschrieben. Platinlösungen welche mit Schwefelsäure abgeraucht wurden, können mit kleinen Änderungen untersucht werden.

Résumé—La méthode de Ryan utilisant le chlorure de diméthyl phénylbenzylammonium pour le micro dosage du platine s'est révélée défectueuse et d'autant plus si les quantités sont grandes. Une modification de cette méthode fourni des résultats aussi précis à l'échelle micro que semi-micro. Même, si l'échantillon est digéré dans une solution sulfurique on peut le traiter en modifiant legérèment le processus opératoire.

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Talanta, 1960, Vol. 3, pp. 370 to 372. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

"Metalfluorechromic" indicators

Sir:

A new term, "metalfluorechromic indicators", has been recently proposed by Wilkins[1,2] for compounds called by Körbl and Vydra[3] "metallofluorescent indicators". In our opinion the term "metallofluorescent" expresses better both similarities and differences between these indicators and the metallochromic type. In the case of Fluorescein Complexone (Fluorexon, Calcein) it has been demonstrated[3] that metallofluorescent indicators change only the intensity of fluorescence; they do not in fact change colour, or the colour change is insignificant.

Two different types of reactions of Fluorescein Complexone have been observed[4] and an explanation of these has been offered[5], *viz.* those which result in quenching of the fluorescence (which take place at a lower pH), and those which, on the contrary, cause fluorescence (at a higher pH, *cf.*[6]). This explanation is consonant with the conception of similar colour phenomena with metallochromic indicators[7] but not with the explanation based on the presumed differences in the structure of the "normal" and "indicator reversal" complexes as proposed by Wilkins[6].

Our explanation is based on the known fact that the individual ligand atoms of a polydentate ligand generally are involved in the chelate successively, *i.e.* in the course of increasing pH, according to decreasing constants corresponding to the dissociation of protons from these atoms. Starting in the acidic range the cation bonding is effected first by carboxyl groups and nitrogen atoms; subsequently, but still in acidic medium, phenolic oxygen participates with the majority of cations. The phenolic oxygen bond is at the lower pH quite loose and of an ionic nature, and therefore the electronic structure of the chromophoric or fluorechromic system of the indicator molecule does not differ appreciably from the fully de-protonized anion. Bathochromic colour change of metallochromic indicators, or quenching of the fluorescence of the metallofluorescent indicator takes place. With increasing pH the phenolic oxygen bond is stabilized, whereas the stability of the bonds with the carboxyl groups is decreased. Consequently, the structure of the indicator chelate undergoes a change and the phenolic oxygen bond to the metal changes from ionic to covalent, in the limiting case with the same consequence for the colour or fluorescence properties as in the covalent association of the proton with the phenolic oxygen atom. With the metallochromic indicator a hypsochromic shift takes place; in metallofluorescent indicators fluorescence appears. These facts can be illustrated by the following model experiments:

1. The addition of a solution of Cu^{2+} to a solution of Phenol Complexone[8] in acidic solution produces the same blue colour as is formed with plain iminodiacetic acid. The phenolic hydroxyl does not take part. Only on increasing the pH to approximately 5 does the yellow colour appear which is characteristic for the extension of the chromophoric effect of Cu^{2+} over the ionically bonded phenolic oxygen to the benzene ring.

2. A similar reaction of Fe^{3+} with Phenol Complexone in strongly acidic medium again gives the same yellow colour as with the simple iminodiacetic acid. Approximately at pH 3 this colour changes to violet—the phenolate anion in its conducting form is involved. Finally in alkaline medium the solution again turns red and yellow—a non-conducting barrier of a covalent bond is formed between the chromophoric iron atom and the phenolic residue of the molecule.

In contrast to Wilkins' statement[6], both "normal" and "indicator reversal" reactions were noticed even with the same cation and the same indicator. Thus Ca^{2+} and Phenolphthalein Complexone at a lower pH (about 10) produce a red colour (normal reaction—ionic bond between the metal and phenolic oxygen); at a higher pH (13–14) the red colour of the indicator disappears (reversal reaction—covalent bond between the cation and the phenolic oxygen.)[9] This example demonstrates clearly that Wilkins' concept according to which structure *a* (fig. I, *cf.*[6]) should be assumed for the

lower pH and structure *b* for the higher pH, both with the same central atom (Ca), is not tenable. In that case a sign of

$$\overset{H^+}{\rightleftharpoons}$$

between the two structures could be justified though this would be in sharp contrast to the pH dependence of the existence of the two structures. Similar examples could be instanced for Cu^{2+} and Glycinethymol Blue[10] etc.

In this connection the consideration that the values K^{M}_{MHL} and K^{M}_{ML} can be close together[6] is so far incorrect that these constants cannot as such express to a mutually comparable degree the stability of the corresponding complexes for the given pH. In this case the pH-dependent constants should be compared, and these, of course, differ substantially for the pH ranges involved, because the actual concentrations of L and HL differ.

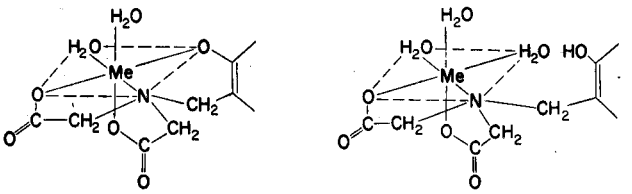

FIG. 1.

We conclude, therefore, that the only correct explanation of the fluorescent reaction of calcium with Fluorescein Complexone—and similarly also in other instances—is the assumption of the formation of a covalent bond (similar to the bond with hydrogen) between the phenolic oxygen and the calcium and not the assumption of the actual bonding of hydrogen to the Fluorescein Complexone anion.

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24 *December* 1959

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AN APPEAL

SIR:

For more than twenty years it has been my practice to read, and frequently to test, methods published in journals devoted to analytical chemistry. I have to report not only that the presentation of the papers has not always pleased me but also that in few instances have the methods I tested been as good as the authors claimed. In some instances the methods have not worked at all, and letters addressed to the authors, although always acknowledged, have not given me answers to all my questions; and often those answers I did receive were vague in the extreme. I am forced, therefore, to conclude that many papers describing inferior and suspect methods are being printed. Owing to the apparently ready acceptance of papers by the editors of journals of analytical chemistry, many analysts are submitting for publication methods that are unsound, apparently under the impression that it is better for their prestige to get several inferior papers into print than one good one. Human nature being what it is, this practice will certainly continue unless referees make a more detailed examination of each paper they read and refuse to accept anything slipshod. Directions such as "transfer 0.1000 gm of sample and 0.5000 gm of *sodium peroxide* to the crucible . . . . "[1] indicate only cursory examination by the referee. Careful reading of the author's practical instructions usually throws a lot of light on the soundness of the method and if *any doubt* exists in the referee's mind the paper as it stands should be rejected. Even if such rigorous action reduces the size of the journal, the readers will realise they are getting quality if not quantity. I would like to see published in these journals only sound methods, or methods the shortcomings of which are described in detail. I am a regular reader of five journals of analytical chemistry and what strikes me most forcibly is the fact that no criticisms of previous papers are published except where they appear in papers claiming to carry out the estimation in a better manner. In order to discourage the submission of poor methods and slipshod papers I would suggest that provision be made in every journal for the publication of criticisms of methods already published; and in this connection I would like to point out that it is as important to praise a satisfactory method as it is to condemn one that is unsatisfactory. If this is done and editors take the view that no journal at all is better than one full of indifferent papers we should be able to look forward to the time when every method published is as good as the authors say it is.

A. A. Moss

Department of Mineralogy
British Museum (Natural History)
Cromwell Road, London, S.W.7

[1] *Analyst*, 1959.

Talanta, 1960, Vol. 3, pp. 373 to 374. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Treatise on Analytical Chemistry: A Comprehensive Account in Three Parts. Part I, Theory and Practice, Volume 1. Edited by I. M. KOLTHOFF and PHILIP J. ELVING, with the assistance of ERNEST B. SANDELL. pp. xxvi + 809. Interscience Publishers, New York, 1959. $17.50 (single), $15.00 (subscription).

THE stated object of Kolthoff and Elving's *Treatise*, of which this is the first volume to be published, is to present a "concise, critical, comprehensive, and systematic treatment of all aspects of classical and modern analytical chemistry." The rapid growth of analytical chemistry in recent years has created a need for some such unified treatment of the entire field; the magnitude of this need may be estimated from the bulk of this work, the first two of the projected three parts of which are expected to fill about nineteen volumes.

Part I of the *Treatise*, Theory and Practice, is composed of eight sections, two of which are contained in Volume 1. Each of the nineteen chapters of Volume 1 has been prepared by an expert in the field. The first four chapters, (Section A), deal with material more or less peculiar to analytical chemistry: the general analytical process (E. B. Sandell and P. J. Elving), errors (Sandell), statistics (W. J. Youden), and sampling (W. W. Walton and J. I. Hoffman). Section B, which comprises the bulk of Volume I, consists of fifteen chapters on basic principles of chemistry which are of significance in analysis. The first chapter of this section is a basic discussion of the elements and their compounds in quantum mechanical terms (J. I. Watters). This is followed by treatments of atomic weights (E. Wichers), chemical equilibrium and thermodynamics (T. S. Lee), equilibrium diagrams (L. G. Sillen), electrode potentials (R. G. Bates), pH (Bates), concepts of acids and bases (I. M. Kolthoff), aqueous acid-base equilibria (S. Bruckenstein and I. M. Kolthoff), nonaqueous acid-base equilibria (Kolthoff and Bruckenstein), complexation reactions (A. Ringbom), oxidation-reduction mechanisms (F. R. Duke), oxidation-reduction equilibria (Duke), solubility (D. L. Luessing), precipitates (M. L. Salutsky), and precipitation equilibria (J. F. Coetzee).

Volume 1 confines itself to the theory of analytical chemistry. Each topic is first discussed from a pure chemical point of view, and the ideas presented are then applied more or less specifically to analytical chemistry. Sufficient space has been alloted to permit ample discussion of each topic. Although really exhaustive treatments are not attempted, the presentations go far beyond statements and discussions of elementary principles. Topics have been treated in sufficient depth to make reference to specialized monographs unnecessary in most cases; however, each chapter contains a list of carefully selected specific references, and the important general references are also listed.

In view of the fact that seventeen authors have contributed to this volume, it is particularly notable that the approach to each topic and the quality of authorship are quite consistent, and consistently high. This gives to the work a degree of unity which is rather unusual in a book prepared by so many geographically separated contributors.

The high quality of the entire volume makes it difficult to point out any one chapter or group of chapters as especially praiseworthy; however, the finest feature of the book is probably the central core of chapters which deal rigorously and extensively with equilibria of all sorts. The use of figures is particularly admirable. They are employed only when necessary, they deal with real chemical entities, and they clearly demonstrate what they are intended to demonstrate. One cannot ask for more. Few criticisms can be made: the powerful Lewis concept of acids and bases could have been exploited more fully, and the topic of crystal growth could have been approached from a more modern point of view. These are, however, minor points, and are possibly a matter of taste.

The production of the book is excellent, and the text is nearly free of misprints.

Kolthoff and Elving's monumental *Treatise* is a major contribution to the science of analytical chemistry, and should prove to be an invaluable standard reference for chemists in all fields.

DAVID H. KLEIN

Contribution No. 2536.
Division of Chemistry and Chemical Engineering,
California Institute of Technology,
Pasadena, California, U.S.A.

Column Chromatography in Pharmaceutical Analysis. J. A. P. STROES. Thesis for the degree of Doctor of Philosophy. University of Groningen. 1959. (In Dutch.)

IN this thesis an enquiry has been made into the possibilities of applying chromatography—both ion exchange and partition—to the analysis of some unmixed organic drugs and their combinations as used in pharmacotherapy.

The eluates obtained in the chromatographic separation of mixtures were investigated spectrophotometrically, and this combination of column chromatography and UV-absorption spectrophotometry gave results which were better, more reproducible and more quickly obtained than with the classical methods.

Typical of the combinations investigated are

Acetylbromalum, Isopropylantipyrinum, Caffeinum, phenacetinum and papaverini hydrochloridum.

Acidum acetylsalicylicum, phenacetinum, caffeinum and aluminii hydroxydum colloidale. Barbitalum and apobarbitalum.

R. J. MAGEE

Electrophoresis. Theory, Methods and Applications. Edited by MILAN BIER. Pp. xx + 563, Academic Press Inc., New York, 1959.

THIS book is a collection of eleven articles by a number of authors, dealing with the principles and various aspects of electrophoresis. An Introduction by Tiseleus gives an excellent historical background to the subject. The intention is to provide an authoritative survey dealing with theory, methods and applications of electrophoresis and the emphasis has been placed upon the fundamental principles involved, the problems encountered and the means that must be adopted to solve them. All the chapters are of high standard but, as is unavoidable in such collaborative works, there is some unevenness in style and overlapping of material. Some re-arrangement in the order of the chapters might have been an improvement and, in certain cases, the title of the chapter is not an exact guide to the contents.

The book gives a very comprehensive picture of the various branches of the technique and the theory is well-presented with much detail. The descriptions of apparatus are complete and easily followed, the diagrams are excellent and the lists of references are large and valuable. The applications described, however, are very specialised, being mainly confined to proteins and related materials. There is an interesting chapter on the application of electrophoresis to viruses, bacteria and cells, which will be of great interest to those concerned with this field of study. A notable omission is that, although the subject of paper electrophoresis is treated at length, it is mainly confined to low voltage methods. A brief description of attempts to use high voltages is given, but no reference is made, in the relevant chapter, to the high voltage techniques now in fairly common use and only brief reference to them is made elsewhere.

This book must be welcomed as an important addition to the literature of the subject, which it greatly extends. It will be of great value to all workers in the subject, especially those concerned with proteins. In view of the highly mathematical treatment of some of the theory and the mass of specialised material it is not easy to read and beginners may find it confusing unless a selective study of its contents, under guidance, is made. Those with some knowledge of the subject will, however, find it a valuable work of reference and, as such, it is strongly recommended.

G. F. REYNOLDS
C. D'OYLY-WATKINS

Talanta, 1959, Vol. 3, pp. 375 to 376. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged:

Thursday 18 *February* 1960: **Society for Analytical Chemistry.** Symposium on *Food Analysis. Some Analytical Problems in the Dairy Industry:* K. A. HYDE, B.Sc., F.R.I.C. *Routine Control in the Brewery:* W. A. WHITLEY, M.I.Biol. *Control Tests in the Flour Milling Industry:* J. WILLIAMS, B.Sc., Ph.D., F.R.I.C. *Quality Control Analysis of Pre-packed Foods:* G. WALLEY, B.Sc., F.R.I.C. Council Chambers, Colmore Row, Birmingham, England. Afternoon session 2.30 p.m. Tea 5.00 p.m. Evening session 6.30 p.m.

Friday 19 *February* 1960: **Society for Analytical Chemistry,** Microchemistry Group. Annual General Meeting. Postgraduate Medical School, Ducane Road, London, W.12. 6.0 p.m.

Friday 19 *February* 1960: **Society for Analytical Chemistry,** Microchemistry Group and Biological Methods Group. *Microanalysis in Clinical Biochemistry:* Professor E. J. KING. *Completely Automatic Methods in Microanalysis:* Dr. I. D. P. WOOTTON. *Automatic Titration Apparatus:* Dr. RUTH HASLAM and Dr. I. D. P. WOOTTON. *Flame Photometric Analysis of Divalent Cations in Biological Materials:* Dr. IAN MACINTYRE. *Optical Rotatory Dispersion:* Dr. W. KLYNE. Postgraduate Medical School, Ducane Road, London, W.12. 7.0 p.m.

Wednesday 24 *February* 1960: **Society for Analytical Chemistry,** Midlands Section: **Royal Institute of Chemistry,** Birmingham and Midlands Section. *Some Analytical Aspects of Non-aqueous Reactions:* Professor V. GUTMANN. The University, Birmingham 15, England. 7.0 p.m.

Friday 26 *February* 1960: **Society for Analytical Chemistry,** Scottish Section. *Analytical Methods on the Hygienic Control of Industrial Atmospheres:* J. G. GAGE, B.Sc., F.R.I.C. *Analytical Problems in the Isolation and Measurement of Traces of Radioactivity in Foods:* Professor J. HAWTHORN, B.Sc., Ph.D., A.R.C.S.T., F.R.I.C. Central Hotel, Glasgow, C.1, Scotland, 7.15 p.m.

Wednesday 2 *March* 1960: **Society for Analytical Chemistry,** Annual General Meeting. Queen's Hotel, Birmingham, 2, England. 4.30 p.m.

Wednesday 2 *March* 1960: **Society for Analytical Chemistry.** *Bernard Dyer Memorial Lecture. The Contribution of Analytical Chemistry to Medical Progress:* Professor A. C. FRAZER. Queen's Hotel, Birmingham, 2, England. 5.0 p.m.

Wednesday 9 *March* 1960: **Society for Analytical Chemistry,** Midlands Section. *Plant Growth-promoting Substances—Some Analytical Aspects:* Professor R. L. WAIN. The University, Birmingham 3, England. 6.30 p.m.

Friday 11 *March* 1960: **Society for Analytical Chemistry,** Western Section: **Royal Institute of Chemistry,** South Wales Section: *Advantages and Disadvantages of Visual Colorimetry:* G. J. CHAMBERLAIN. Swansea, South Wales.

Saturday 12 *March* 1960: **Society for Analytical Chemistry,** North of England Section. *The Analysis of Non-soapy Detergent Products:* G. F. LONGMAN, B.Sc., F.R.I.C. Manchester, England. 2.15 p.m.

Wednesday 16 *March* 1960: **Society for Analytical Chemistry,** Microchemistry Group: London Discussion Meeting. "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m.

Friday 18 *March* 1960: **Society for Analytical Chemistry: Society for Chemical Industry,** Fine Chemicals Group. *Techniques of Automatic Analysis.* London. 6.30 p.m.

Wednesday 23 *March* 1960: **Society for Analytical Chemistry,** Midlands Section. Annual General Meeting. Nottingham and District Technical College, Burton Street, Nottingham, England. 7.0 p.m.

Friday 25 *March* 1960: **Society for Analytical Chemistry,** Scottish Section. *Volumetric Determination of Nitrogen as Nitrate:* A. F. WILLIAMS, B.Sc., F.R.I.C. *Control of Quality in Synthetic Foodstuff Colours:* H. E. STAGG, B.Sc. Royal Society of Edinburgh, 22, George Street, Edinburgh, 2, Scotland. 7.15 p.m.

Monday–Thursday 11–14 *April* 1960: **American Chemical Society,** Division of Analytical Chemistry. *Fisher Award Symposium* Honouring PHILIP J. ELVING. Programme Chairman, I. ROSENTHAL, Rohm and Haas Co., Philadelphia, Penna. *Gas Chromatography:* Programme Chairman, ROBERT A.

DINERSTEIN, Standard Oil Company, Whiting, Ind. *The Analysis of Fluoro-Containing Compounds:* Programme Chairman, A. STEYERMARK, Hoffman-LaRoche Company, Nutley 10, N.J. *Thermal Methods of Analysis*, (a) *Thermogravimetry*, (b) *Differential Thermal Analysis*, (c) *Zone Refining:* Programme Chairman, E. L. SIMONS, General Electric Company, Schenectady, N.Y. Cleveland, Ohio, U.S.A.

Thursday–Friday 14–15 *July* 1960: **Society for Analytical Chemistry,** Midlands Section. Symposium on *Analytical Methods in the Service of Agriculture. Determination of pesticide residues:* Dr. J. T. MARTIN. *Determination of Metals in Soils and Plants:* Dr. R. L. MITCHELL. *Analytical Aspects of Dairy-farming:* Dr. J. A. F. ROOK. *Determination of Systemic Insecticides:* K. GARDNER: *Analysis of Herbicides.* L. A. HADDOCK. *The Protection of the Consumer against Harmful Effects of Pesticide Residues:* Dr. E. J. MILLER. *Determination of Additives in Feeding Stuffs (with special reference to Prophylactics):* Dr. R. F. PHIPERS. The programme will also include a visit to a horticultural or agricultural research station, Nottingham University, Nottingham, England.

The fee for the Symposium will be £3–3s. An informal dinner at a cost of about £1–1s will be held on Thursday 14 July, and hostel accommodation will be available at Nottingham University.

Registration forms may be obtained, together with further information, from C. A. JOHNSON, B.Sc., B.Pharm., F.P.S., A.R.I.C., Standards Department, Boots Pure Drug Co., Ltd., Station Street, Nottingham, England.

The fifteenth Annual General Meeting of the Biological Methods Group of the Society for Analytical Chemistry was held on Wednesday 9 December 1959 in the Meeting Room of the Chemical Society Burlington House, Piccadilly, London, W.1. The Chairman of the Group, Dr. J. I. M JONES, F.R.I.C. presided.

The following were elected Officers of the Group for the forthcoming year.

Chairman:	Dr. J. I. M. JONES
Vice-Chairman:	Mr. J. S. SIMPSON
Hon. Secretary and Treasurer:	Mr. K. L. SMITH, Standards Department, Boots Pure Drug Co., Ltd., Nottingham, England.

American Chemical Society, Division of Analytical Chemistry. The following Officers have been elected for 1960:

Chairman:	H. A. LIEBHAFSKY
Chairman-elect:	CHARLES N. REILLEY
Secretary–Treasurer:	L. B. ROGERS, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, 39, Mass., U.S.A.

The *B.S.I. News* announces, among others, the following new British Standard:

B.S. 3156, 1959. *Methods for the sampling and analysis of fuel gases.* This describes methods of sampling and analysis applicable to coal gas, water gas, carburetted water gas, producer gas, methane, sewage gases, blast-furnace gases, Mond gas, Tully gas and oil gas. The constant-volume method and the soap-film method are given as alternatives for the determination of carbon dioxide, oxygen, saturated hydrocarbons, hydrogen, carbon monoxide, saturated hydrocarbons and nitrogen: the Metro method for nitrogen is also described. Methods for determining sulphur compounds, condensable vapours, nitrogenous gum, tar fog, ammonia, naphthalene, water vapour, hydrogen cyanide, iron carbonyl, specific gravity, calorific value and various arbitrary characteristics are given. (Price 25s.)

The following Standard has been revised:

B.S. 1428. *Microchemical apparatus,* Group A, *Combustion trains for the determination of elements.* Part A 2: 1959. *Nitrogen combustion train (micro-Dumas).* This specifies the components with dimensional drawings and an assembly drawing of the whole train. It describes a carbon dioxide generator using solid carbon dioxide as an alternative to the Tucker type. It refers to B.S. 1428, Part D 3 for the micro-nitrometer, and to B.S. 1428, Part A 1 for components common to both types of train. (Price 4s. 6d.)

Talanta, 1960, Vol. 3, p. 377. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Dalzin (diallyl dithiocarbamido-hydrazide) as a micro reagent—I: Estimation and separation of copper and nickel. N. K. DUTT and A. DUTTA AHMED. (11 *December* 1959).

Acid chlorides of substituted succinic and glutaric acids as hydrolytic agents for the determination of water. R. BELCHER, L. OTTENDORFER and T. S. WEST. (14 *December* 1959).

Determination of ultramicro amounts of sulphate as methylene blue—I: The colour reaction. LILLY GUSTAFSSON. (14 *December* 1959).

Determination of ultramicro amounts of sulphate as methylene blue—II: The reduction. LILLY GUSTAFSSON. (14 *December* 1959).

Comments on fluorechromic indicators. J. KÖRBL and V. SVOBODA. (24 *December* 1959).

The reactions of certain metals with thioacetamide. ERNEST H. SWIFT and FRED C. ANSON. (24 *December* 1959).

Analytical chemistry of α-benzoinoxime complexes of molybdenum, tungsten, vanadium and chromium. HENRY J. HOENES and K. G. STONE. (31 *December* 1959).

New methods of analysis for glyoxal. EUGENE SAWICKI and WALTER ELBERT. (11 *January* 1960).

A derivatographic study of potassium hydrogen phthalate. R. BELCHER, L. ERDEY, F. PAULIK and G. LIPTAY. (11 *January* 1960).

Separations involving sulphides—XIII: Separation of quinquevalent antimony from alkaline earths G. B. S. SALARIA. (19 *January* 1960).

Thiourea complexes of some noble metals: A polarographic determination of rhodium. FRANCESCO PANTANI and PIER GIORGIO DESIDERI. (20 *January* 1960).

Calcein Blue: A new metalfluorechromic indicator for chelometric titration. DONALD H. WILKINS. (28 *January* 1960).

Talanta, 1960, Vol. 3, p. 378. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Actas do XV Congresse Internacional de Química Pura e Aplicada (Quimica Analitica), Volume II. Lisboa, 1958, Communications presented in Sections IV, V and VI. Pp. 1046.

Trace Techniques Using the K1000 Cathode Ray Polarograph, Vol. I. J. HETMAN. Southern Instruments Limited, Camberley, Surrey, 1959. Pp. 49. 25s.

Optics and Spectroscopy, January 1959, Vol. VI, No. 1. Translated from the Russian on the initiative of the Optical Society of America, Inc. Distributed with the Journal of the Optical Society of America. Pp. 84.

The following publications have been received and are available from the Office of Technical Services, Department of Commerce, Washington, 25,/D.C., U.S.A.

Neutron and Gamma Effects in Dilute Aqueous Solutions: JAMES R. BARCUS. SCTM 22-59 (16) *March* 1959. Pp. 22. $0.75.

Solution of Multistage Separation Problems by Using Digital Computers: JOHN H. DUFFIN. UCRL 8787. *August* 1959. Pp. 267. $4.00.

Dissolution of Thorium in Mixtures of HNO_3 and HF: D. G. KARRAKER. DP-399. *September* 1959. Pp. 15. $0.50.

Reactor Technology, Report No. 10—Chemistry. KAPL-200-7. *September* 1959. Pp. ix + 62. $2.00.

Effect of Dissolved Stainless Steel Components on Vapour-Liquid Equilibria in Aqua-regia: B. E. PAIGE. IDO-14483. *October* 1959. Pp. 23. $0.75.

Spectrophotometric Determination of Cobalt in Sodium Metal: LOUIS SILVERMAN and RACHEL L. SEITZ. NAA-SR-4005. *October* 1959. Pp. 10. $0.50.

Sulfex Process: Depassivisation of Stainless Steel: T. A. GENS. ORNL-2785. *November* 1959. Pp. 14. $0.50.

Solubility Relations among Rare-Earth Fluorides in Selected Molten Fluoride Solvents: W. T. WARD, R. A. STREHLOW, W. R. GRIMES and G. M. WATSON. ORNL-2749. *November* 1959. Pp. 14, $0.75.

ERRATUM

Volume 3, page 50, Table I, last three column headings, replace mV by V.

TALANTA

An International Journal of Analytical Chemistry

VOLUME 3 1959–60

PERGAMON PRESS LONDON · NEW YORK · PARIS · LOS ANGELES

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AUTHOR INDEX

(Names of authors of books reviewed are in italics)

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

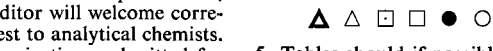
2. Script Requirements

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced. Where possible, research papers should follow the pattern: *Introduction, Discussion, Conclusion, Experimental* (or such of these headings as apply).

3. Summaries will not be required for short or preliminary communications. For other contributions the essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

4. Illustrations should be separated from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The lettering should be sufficiently large and bold to permit this reduction. The following standard symbols should be used on line drawings, since they are easily available to the printers:



5. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, e.g., standard deviation. The same information should not be reproduced in both tables and figures.

6. References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[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.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

7. Except in the case of preliminary communications, proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, when the amount of alteration makes it advisable.

8. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units.

FEBRUARY 1960 VOLUME 3 NUMBER 4

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PERGAMON PRESS LTD.

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Printed in Northern Ireland at The Universities Press, Belfast