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√ *Anal. Chim. Acta*, Vol. 23, No. 1, p. 1—100, July 1960

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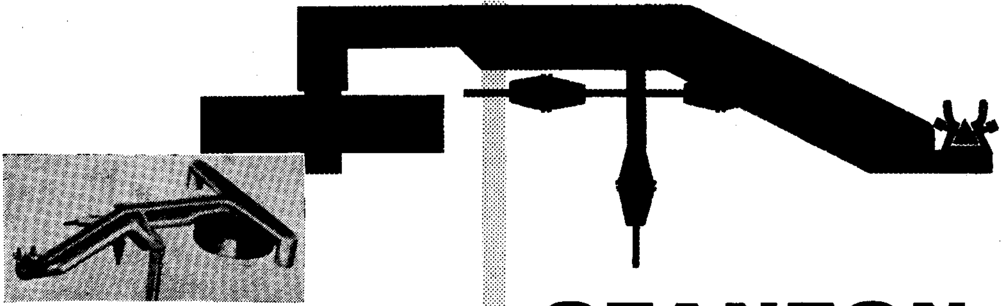

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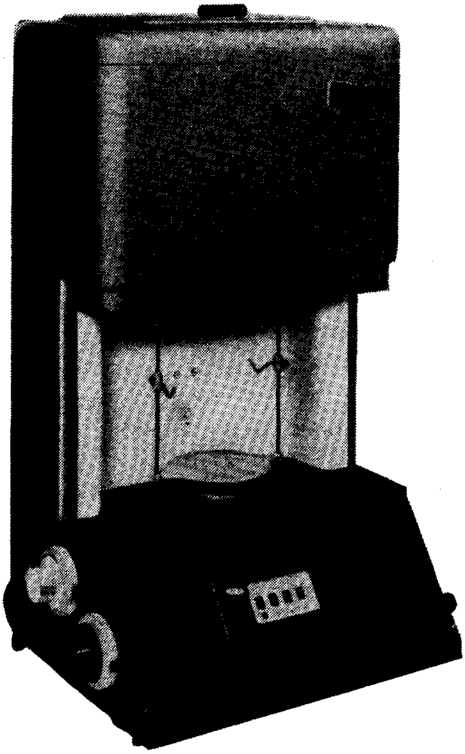

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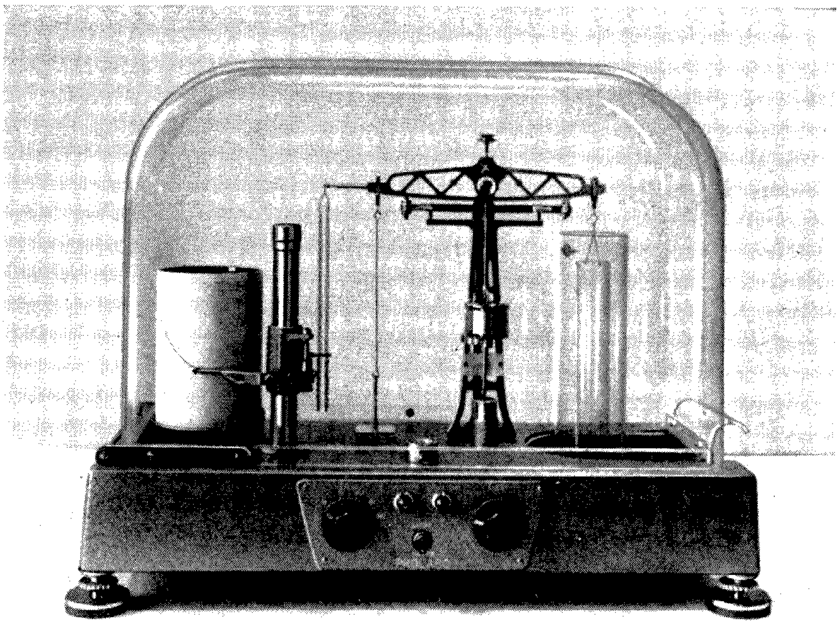

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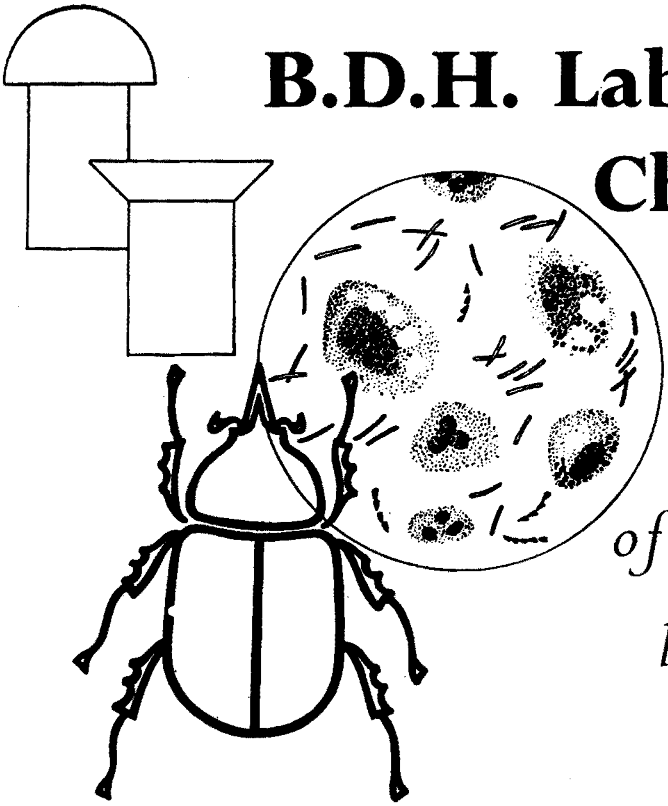

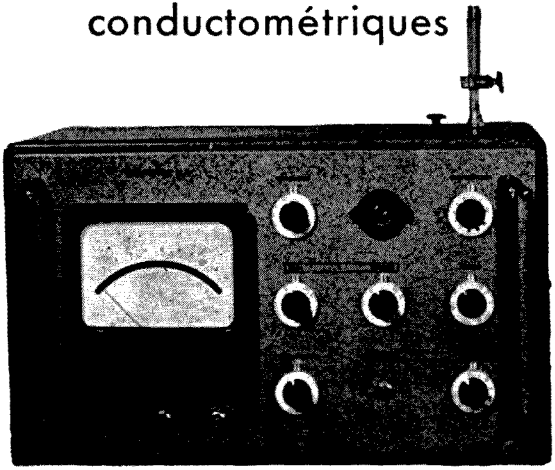

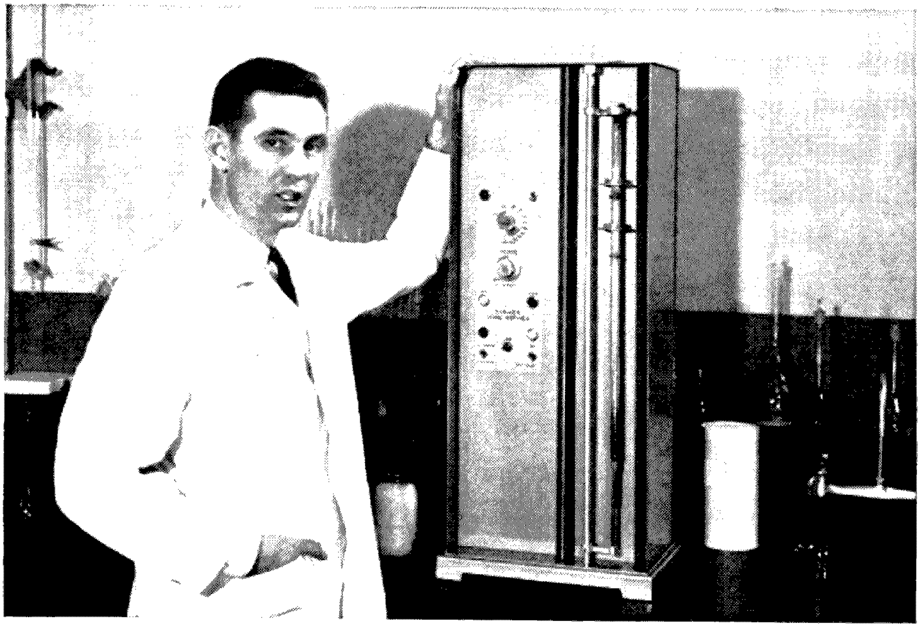

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Heterometry

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ANALYTICA CHIMICA ACTA

Vol. 23 (1960)

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Anal. Chim. Acta, Vol. 23 (1960)

Printed in The Netherlands by
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EFFECTS OF TEMPERATURE AND NON-AQUEOUS SOLVENT CHANGES ON SILVER DITHIZONATE EXTRACTIONS

F. F. DYER AND GEORGE K. SCHWEITZER

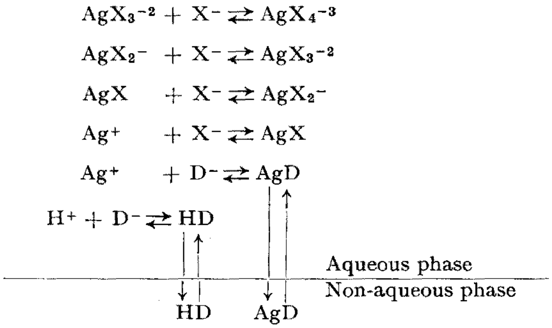
Department of Chemistry, University of Tennessee, Knoxville, Tenn. (U.S.A.)

(Received December 7th, 1959)

INTRODUCTION

Recently SCHWEITZER AND DYER[1] treated quite extensively the solvent extraction of silver dithizonate from aqueous solutions containing hydrogen ion and anions which mask the extraction of silver into chloroform and carbon tetrachloride. It was found possible to predict the effect of the masking agents, and predictions were made by calculating the pH of the aqueous phase at which 50% of the silver had extracted, $\text{pH}_{\frac{1}{2}}$.

The equation used to predict the $\text{pH}_{\frac{1}{2}}$ of these extractions was based on the following assumed equilibria:



$$AgX_3^{-2} + X^- \rightleftarrows AgX_4^{-3}$$
$$AgX_2^- + X^- \rightleftarrows AgX_3^{-2}$$
$$AgX + X^- \rightleftarrows AgX_2^-$$
$$Ag^+ + X^- \rightleftarrows AgX$$
$$Ag^+ + D^- \rightleftarrows AgD$$
$$H^+ + D^- \rightleftarrows HD$$

where X^- represents a specie in the aqueous phase which complexes with and masks the extraction of the silver ion, HD represents dithizone which ionizes in the aqueous phase to give the dithizonate ion D^- and hydrogen ion, and AgD represents the monobasic form of silver dithizonate. The complexes between Ag^+ and X^- were called the masking complexes by SCHWEITZER AND DYER[1]. The pH of the aqueous phase which gives 50% extraction was given[1] as

$$\text{pH}_{\frac{1}{2}} = -\log(\text{HD})_o - \log K + \log F \tag{1}$$

where $(\text{HD})_o$ is the molar concentration of dithizone in the non-aqueous phase, K is the extraction constant for the over-all extraction equilibrium, and F represents a summation term containing the stability constants of the masking complexes. The extraction constant is given by

$$K = \frac{(\mathrm{AgD})_o(\mathrm{H}^+)_w}{(\mathrm{Ag}^+)_w(\mathrm{HD})_o} \tag{2}$$

where the subscripts *o* and *w* refer to the non-aqueous and aqueous phases respectively. The summation term may may be written as

$$F = \sum_{i=0}^{i=4} K_i(\mathrm{X})_w^i \tag{3}$$

where K_i is the stability constant of the *i*th masking complex. K_o is taken as being unity. Equation (1) may be obtained as a special case from the more extensive relations developed by RYDBERG[2] and IRVING, ROSSOTTI AND WILLIAMS[3]. In the absence of masking agent the extraction constant may be written as

$$K = \frac{E(\mathrm{H}^+)_w}{(\mathrm{HD})_o} \tag{4}$$

where E is the extractability for the system defined as the ratio of the concentration of metal in the non-aqueous phase to the concentration of metal in the aqueous phase.

SCHWEITZER AND HONAKER[4] gave for non-masked extractions the equation

$$\frac{(\mathrm{H}^+)_w^n}{(\mathrm{H}^{+\prime})_w^n} = \frac{(S_r'/S_r)^n}{S_c'/S_c} \tag{5}$$

relating at equal extractabilities for two extractions into different non-aqueous solvents the hydrogen ion concentrations in the aqueous phase to the solubilities of the complexing agent and metal complex in the non-aqueous phase expressed as S_r and S_c respectively. The primed and unprimed quantities refer to different non-aqueous solvents, and the exponent n is used for cases in which a metal ion with a positive charge of n is extracted. Since the hydrogen ion concentration is related to the extraction constant, equation (5) may be modified to give

$$\frac{KS_r^n}{S_c} = \frac{K'S_r'^n}{S_c'} \tag{6}$$

It would appear then that for any number of extractions in which only the organic solvent is allowed to change the equation

$$\frac{KS_r^n}{S_c} = C \tag{7}$$

where C is a constant, should be valid. For extractions of silver dithizonate S_r and S_c represent the molar solubilities of dithizone and silver dithizonate respectively in the non-aqueous phase. In this report the constant C will be referred to as the solvent factor.

THE SYSTEM

For this research silver was chosen as the metal ion, dithizone as the complexing agent, and several non-aqueous solvents were used. The effects of two variables on the extraction were investigated. The variation of the extraction constant was studied as a function of temperature for extractions from aqueous solutions containing 1.0 M perchloric acid into chloroform and carbon tetrachloride containing dithizone. Extractions were made from 0.1 M potassium bromide solutions into the non-aqueous solvents dichloromethane, chloroform, carbon tetrachloride, benzene, chlorobenzene, bromobenzene, and toluene in order to calculate values of the extraction constant for these extractions. The consistancy of equation (7) was tested for some of the above named solvents from the values of the extraction constants and values for the solubility of dithizone and silver dithizonate in the solvents. In all extractions the concentration of silver ion in the original aqueous phase was approximately 10^{-7} M.

RESULTS AND INTERPRETATION

The effect of temperature

The results obtained for the effect of temperature change on extractions into chloroform and carbon tetrachloride are shown in Table I. Extractions into chloroform were carried out at intervals of 5° from 25° to 55°. Extractions into carbon tetrachloride were carried out at 30°, 35°, 45°, and 55°. In all except one of the extractions the concentration of dithizone in the non-aqueous phase was $1 \cdot 10^{-5}$ M. The concentration of perchloric acid in the aqueous phase was 1.0 M. Linear relations were found to exist between the logarithms of the extraction constants and the reciprocal of the absolute temperature. For extractions into chloroform the equation

$$\log K = 3.5 \times 10^{-3}\mathrm{T}^{-1} - 5.9 \qquad (8)$$

was obtained. For extractions into carbon tetrachloride the equation

$$\log K = 5.3 \times 10^{-3}\mathrm{T}^{-1} - 11.0 \qquad (9)$$

TABLE I

RESULTS OF TEMPERATURE CHANGES EXTRACTIONS[a]

Non-aqueous phase	*t°C*	*log K*
Chloroform	25	5.9
Chloroform	30	5.8
Chloroform	35	5.5
Chloroform	40	5.3
Chloroform	45	5.0
Chloroform	50	4.9
Chloroform	55	4.8
Carbon tetrachloride	30	6.5[b]
Carbon tetrachloride	35	6.3
Carbon tetrachloride	45	5.8
Carbon tetrachloride	55	5.3

[a] In all cases but one the initial concentration of dithizone in the non-aqueous phase was $1 \cdot 10^{-5}$ M.

[b] The value of log K for extractions into carbon tetrachloride and chloroform at 30° was reported by SCHWEITZER AND DYER[1].

was found to apply. Equations (8) and (9) are applicable between 25° and 55°. Presumably extrapolations could be made outside this temperature range using these relations. Equation (9) has been used to calculate a value for log K of 7.2 for extractions into carbon tetrachloride at 18°. This result compares well with the value of 7.6 which was obtained by TREMILLON[5].

From equations (8) and (9) it is possible to obtain values of the standard free energy, enthalpy and entropy for the extractions. For extractions into chloroform the values of the free energy, enthalpy and entropy were found to be —8.0 kcal/mole, —16 kcal/mole, and —30 e. u. respectively. Corresponding calculations for extractions into carbon tetrachloride gave —8.0 kcal/mole, —24 kcal/mole, and —50 e. u. for the free energy, enthalpy, and entropy respectively. These thermodynamic functions were found to be nearly constant over the temperature range investigated.

The effect of non-aqueous solvent

The results obtained for extractions into various non-aqueous solvents are shown in Table II. Equation (1) was used to calculate the extraction constant for these extractions. Extractions were made from 0.1 M potassium bromide solutions into non-aqueous solvents containing dithizone which was initially $5 \cdot 10^{-5}$ M. Values of the stability constants for the complexes formed between the silver ion and bromide ions were taken from the work of BERNE AND LEDEN[6]. These constants were used to calculate a value of F for use in equation (1). The solubilities of dithizone were taken from the work of SCHWEITZER AND HONAKER[4]. The solubilities of silver dithizonate were measured by a radio-tracer technique. The object of this part of the study was to test the consistancy of equation (7). Calculated values for the solvent factor, C, which are shown in Table II are seen to be fairly constant for the five solvents for which the solvent factor was calculated. Cyclohexane was tried as a non-aqueous solvent in one extraction. It was found that silver dithizonate is so insoluble in cyclohexane that it produced no coloration of the cyclohexane. Although silver dithizonate was found to be soluble in carbon disulfide little or no silver could be found in the aqueous or non-aqueous phases when extraction experiments were tried. The silver, probably in the form of silver dithizonate, appeared to be adsorbed on some interface in the system.

TABLE II

RESULTS OF NON-AQUEOUS SOLVENT CHANGES ON EXTRACTIONS[a]

Non-aqueous phase	$K \cdot 10^{-6}$	$C \cdot 10^{-6}$	*Solubility (moles/l)* $\cdot 10^2$	
			HD	*AgD*
Dichloromethane	1	4	4.9	1.2
Chloroform	0.6	3	7.9	1.6
Carbon tetrachloride	3	2	0.29	0.37
Benzene	2	3	1.4	0.82
Chlorobenzene	3	4	0.98	0.74
Bromobenzene	3			1.1
Toluene	2			0.46
Carbon disulfide				1.1

[a] All measurements were made at 30° from aqueous solutions containing potassium bromide at a concentration of 0.1 M into the non-aqueous solutions which were initially $5 \cdot 10^{-5}$ M with dithizone.

EXPERIMENTAL CONDITIONS

Extraction studies, chemicals, apparatus and technique

The chemicals, their preparation and purification, the apparatus used, and the techniques employed in the extraction studies were the same as used previously by SCHWEITZER AND DYER[1].

Solubility measurements, chemicals, apparatus and technique

The solubility of silver dithizonate in various non-aqueous solvents was measured by the use of radio-active silver dithizonate containing ^{110}Ag. More than enough silver dithizonate to saturate 5 ml of the non-aqueous solvent was placed in a 25-ml glass stoppered Erlenmeyer flask. Five ml of the non-aqueous solvent was added along with a magnetic stirring bar. The flasks were stoppered, placed in the constant temperature bath, and stirred for five hours. The solutions were then sampled by withdrawing a 0.1-ml sample through a cone of filter paper into a micropipette. The sample was placed on a planchet, allowed to dry, and counted with a Tracerlab 1000 Scaler using a G-M tube. By counting a 0.1-ml sample from a solution of the radio-active silver dithizonate of a known concentration, it was possible to obtain the unknown concentrations of the saturated solutions. The solution of known concentration was prepared by weighing a quantity of the silver dithizonate, placing it in a volumetric flask, and diluting with chloroform to the capacity of the flask.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to Union Carbide Nuclear Company for awarding to F. F. DYER in the school year 1956–57 the Union Carbide Nuclear Company Fellowship which is awarded annually to a graduate student in chemistry at the University of Tennessee.

SUMMARY

The extraction of 10^{-7} *M* silver ion from aqueous solutions into non-aqueous solvents containing dithizone has been investigated. The effects caused by changing the temperature and non-aqueous solvent were studied. Values of the extraction constant for extractions into chloroform and carbon tetrachloride were obtained as a function of temperature. Plots of the logarithm of the constants *versus* the reciprocal of the absolute temperature were straight lines. A linear relation was found between the extraction constant and the ratio of the solubilities of silver dithizonate and dithizone in the non-aqueous solvent. This relation was found to hold for extractions in which the non-aqueous phase was dichloromethane, chloroform, carbon tetrachloride, benzene and chlorobenzene.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction de l'argent dans des solvants non-aqueux renfermant de la dithizone. Ils ont examiné l'influence de la température et de divers solvants.

ZUSAMMENFASSUNG

Es wird eine Untersuchung beschrieben über die Extraktion von Silber mit nicht-wässrigen Lösungsmitteln in Gegenwart von Dithizon und der Einfluss von Temperaturänderungen und anderen Lösungsmittel geprüft.

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DETERMINATION OF METAL CYANIDE AND THIOCYANATE COMPLEXES BY KJELDAHL-GUNNING AND CARIUS SEALED TUBE DIGESTION METHODS

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(Received December 10th, 1959)

A variety of methods have been reported for the determination of the cyanide ion employing all of the general techniques of analytical chemistry as volumetric[1], spectrophotometric[2], and amperometric[3], to mention only a few. None of these methods are applicable to the determination of cyanides in the inert transition metal complexes. Many investigators have described the determination of metal cyanide complexes. Generally, each method is limited in its application to a specific compound and the iron cyanide complexes have been studied almost exclusively. Some other methods have been attempted for the determination of the cyanide complexes. Chief among these is the evolution method of RUBNER AND BACHKA as applied by BIEG[4]. Although this method is applicable to the inert transition metal complexes it requires much time and the handling of large amounts of distillate.

The chief limitation of the methods developed to date is that they may not be readily applied to the determination of the inert transition metal cyanide and thiocyanate complexes. Carbon analyses of these complexes are generally difficult. The same is true of the Dumas nitrogen determination.

This paper describes methods which are applicable to the determination of metal cyanide complexes using the classical Kjeldahl digestion or Carius combustion followed by a Kjeldahl type of distillation.

The use of the Kjeldahl apparatus has been reported by HORAN AND EPPIG[5] for the determination of ammonia in cobalt penta- and hexa-ammines. The Kjeldahl-Gunning method as described in A.S.T.M. has been used by JUNG AND COPELLO[6] for the analysis of blue pigments. The destruction of ferrocyanide in an autoclave at 130° employing ammonium polysulfide as the reducing agent has been reported by ADELSBERGER[7]. Also, the hydrolysis of cyanides in hydrochloric acid at 140° has been reported by GETTER AND GOLDBAUM[8], followed by a colorimetric determination of ammonia.

The modified Kjeldahl-Gunning method or the combined use of the Carius sealed tube digestion and Kjeldahl distillation enable the analysis of the metal cyanide, thiocyanate and mixed cyanodiphenanthroline complexes with greater ease and accuracy than provided by the existing methods. These procedures are especially applicable to micro analytical techniques and may be applied to for the analysis of metal cyanide, thiocyanate complexes.

EXPERIMENTAL

Reagents and apparatus

Reagent grade concentrated sulfuric acid, $d = 1.84$ was used for the digestion. Decomposition was catalysed by the reagent grade anhydrous mercuric sulfate and mercuric oxide mixture. The receiving flask contained 4% boric acid. Titration was carried out using approximately 0.015 N hydrochloric acid, the normality of which was checked against anhydrous sodium carbonate and ammonium sulfate using methyl red and methylene blue mixed indicator. 50% sodium hydroxide containing 5% thiosulfate was used to neutralize sulfuric acid in a distillation flask. Reagent grade sodium salt of ethylenediaminetetraacetic acid (EDTA) was added to break ammonia complexes of some of the transition metals.

Reagent grade potassium ferro- and ferricyanides, and mercuric thiocyanate were obtained from the Baker and Adamson Co.; potassium cobalticyanide was procured from the G. F. Smith Chemical Co. Sodium aquo-, amminopentacyanoferrates(II) and Reinecke's salt were prepared by the procedure described in the BRAUER's "Handbuch der Präparativen Anorganischen Chemie". Potassium salts of cyanide complexes of chromium(III), manganese(III), nickel(II) and molybdenum(IV) were obtained from G. ATKINSON, and dicyano-bis(1,10-phenanthroline)-iron(II) from A. SCHILT (both from our laboratories). All compounds were analysed for water of crystallization and metal contents.

Kjeldahl distillations were carried out using one piece micro Kjeldahl distillation apparatus.

PROCEDURE

Kjeldahl-Gunning method

The digestion of the transition metal cyanides was carried out essentially by the Kjeldahl-Gunning method. A sample weighing approximately 10 to 25 mg was placed directly from the charging tube into the micro Kjeldahl digestion flask. About 50 mg of mercuric sulfate and mercuric oxide mixture was then added to the digestion flask followed by the addition of 2.0 ml of concentrated sulfuric acid saturated with mercuric oxide. The contents were mixed slowly, and the flasks were placed on a low flame for about 10 min, then digestion was continued for an additional 80 min on full heat. Prolonged digestion caused poor reproducibility and low results. Throughout the digestion period flasks were rotated frequently to ensure complete mixing and to get all the spattered solid sulfates from the walls of the digestion flasks. At the end of the digestion the flasks were cooled. The contents were diluted with approximately 3–4 ml of water. The diluted digest was then transferred to the micro Kjeldahl distillation flask. About 150 mg of sodium salt of ethylenediaminetetraacetic acid (EDTA) was added. (The addition of EDTA was necessary with all the transition metal cations forming inert ammonia complexes). Six ml of 50% sodium hydroxide containing 5% thiosulfate was then added and the distillation was started. Samples were distilled for 7 min. The distillate was collected in 4% boric acid. The ammonia absorbed was titrated with a standard hydrochloric acid using methyl red and methylene blue mixed indicator.

Carius sealed tube method

An alternative Carius sealed tube digestion method was found to be superior (than the Kjeldahl-Gunning procedure). A micro sample was placed into the Carius combustion tube from the charging tube. Mercuric oxide and mercuric sulfate mixture and sulfuric acid were added as in the above procedure. The sealed tubes were placed in the Carius heating furnace. The samples were heated for 2 h at 315°. The tubes were cooled and they were opened taking regular precautions by releasing pressure first. The opened tubes were heated on the micro burner and they were boiled for about

TABLE I

ANALYSIS OF NITROGEN IN METAL CYANIDE AND THIOSULFATE COMPLEXES

Substance analyzed	*Method of*		*% calculated*[a]	*Ammonia found*	*Recovery of nitrogen %*	*Average deviation*[b] *p.p.t.*
	digestion	*distillation*				
Potassium ferrocyanide	Kjeld.-Gunn.	No EDTA	19.89	20.01	100.6	6
Potassium ferrocyanide	Carius	No EDTA	19.89	19.97	100.4	2
Potassium ferricyanide	Kjeld.-Gunn.	No EDTA	25.51	25.11	98.43	7
Potassium ferricyanide	Carius	No EDTA	25.51	25.34	99.33	5
Sodium ammonopentacyanoferrate(II)	Kjeld.-Gunn.	No EDTA	24.56	24.36	99.18	5
Sodium ammonopentacyanoferrate(II)	Carius	No EDTA	24.56	24.50	99.75	4
Sodium aquopentacyanoferrate(II)[c]	Kjeld.-Gunn.	No EDTA	21.41	21.63	101.0	9
Sodium aquopentacyanoferrate(II)[c]	Carius	No EDTA	21.41	21.52	100.5	5
Dicyano-bis(1,10-phenanthroline)-iron(II)	Kjeld.-Gunn.	No EDTA	5.98	11.30[d]	188.9	30
Dicyano-bis(1,10-phenanthroline)-iron(II)	Carius	No EDTA	5.98	6.03	100.8	5
Tetrapyridinodithiocyanato-iron(II)	Kjeld.-Gunn.	No EDTA	5.74	9.57[e]	166.7	100
Tetrapyridinodithiocyanato-iron(II)	Carius	No EDTA	5.74	8.32[e]	144.9	100
Potassium hexacyanochromate(III)	Kjeld.-Gunn.	EDTA added	24.46	24.58	100.5	11
Potassium hexacyanochromate(III)	Carius	EDTA added	24.46	24.42	99.83	4
Potassium hexacyanocobaltate(III)	Kjeld.-Gunn.	EDTA added	25.28	24.85	98.30	9
Potassium hexacyanocobaltate(III)	Carius	EDTA added	25.28	25.13	99.40	2
Potassium hexacyanomanganate(III)	Kjeld.-Gunn.	No EDTA	24.90	24.79	99.56	9
Potassium hexacyanomanganate(III)	Carius	No EDTA	24.90	24.97	100.3	4
Potassium octacyanomolybdate(IV)	Kjeld.-Gunn.	No EDTA	22.56	22.55	99.95	5
Potassium octacyanomolybdate(IV)	Carius	No EDTA	22.56	22.51	99.78	4
Potassium tetracyanonickelate(II)	Kjeld.-Gunn.	EDTA added	20.92	20.95	100.1	5
Potassium tetracyanonickelate(II)	Carius	EDTA added	20.92	20.95	100.1	5
Ammonium diammonotetrathiocyanatochromate(III)	Kjeld.-Gunn.	EDTA added	27.65	27.64	99.96	
Ammonium diammonotetrathiocyanatochromate(III)	Carius	EDTA added	27.65	27.63	99.93	3
Dithiocyanatomercury(II)	Kjeld.-Gunn.	No EDTA	8.84	8.77	99.20	5
Dithiocyanatomercury(II)	Carius	No EDTA	8.84	8.82	99.77	3

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[a] Calculated values are based on the results of the analyses rather than expected formula weights.

[b] Average deviation in p.p.t. is based at least on five determinations.

[c] Sodium aquopentacyanoferrate(II) contains sodium ferrocyanide and sodium nitroprusside as impurities.

[d] Some of the phenanthroline is decomposed during the digestion. Results depend on the digestion conditions.

[e] Some pyridine is distilled and the results vary with the time of distillation.

4 min until sulfur dioxide fumes were expelled. The digest was then diluted with water and the contents were transferred to the distillation flask.

RESULTS AND DISCUSSION

In concentrated sulfuric acid and in presence of mercuric ion as a catalyst conversion of metal cyanide complexes to ammonium sulfate proceeds rather rapidly. However, quantitative recovery of nitrogen as ammonia is greatly dependent upon the digestion conditions. Thus, Kjeldahl-Gunning and Carius sealed tube digestion methods have been investigated to a greater extent. The results of the analyses of metal cyanide, thiocyanate and ammonia complexes are summarized in Table I.

The phenanthroline–cyanide complexes yield high and irreproducible results when using the Kjeldahl-Gunning digestion method. Apparently, phenanthroline is decomposed somewhat under these conditions. In the Carius sealed tube digestion phenanthroline is not attacked and the cyanide is hydrolyzed to ammonia exclusively. The mixed complexes of pyridine–thiocyanate or cyanide cannot be analyzed by these methods. Pyridine is distilled with ammonia, and the results depend upon the time of distillation. The somewhat low results for the potassium ferricyanide are attributed to the absorption of water on the powdered sample.

Recovery of nitrogen as ammonia after the digestion by Kjeldahl-Gunning method is in the order of 99%. The results obtained are mostly low and there is a considerable scattering of the values. This is probably due to the loss of nitrogen during the digestion as has been observed by SELF[9] and CARPIAUX[10] when the final digest is a solid. Indeed, metal cyanide complexes during digestion yield insoluble sulfates. Reproducibility becomes poorer if the digestion has been extended over 3 h. In general, 90 min time of digestion is sufficient to decompose metal cyanide and thiocyanate complexes.

In the Carius sealed tube digestion method recoveries are better than 99% and the scattering of the results is less than in the Kjeldahl-Gunning method. The digestion temperature should be high enough to decompose cyanide and thiocyanate complexes and not too high to shatter the tubes. At 250° only about 90% of the cyanide is converted to ammonia; thiocyanates are not effected at this temperature. At 315° all of the metal cyanide and thiocyanate complexes studied are converted to ammonia quantitatively.

The conversion of cyanide to ammonia in the Kjeldahl-Gunning method is also greatly effected by the amount of water present in the original digest. The results are low by a few per cent and not reproducible if the sulfuric acid concentration falls below 15 M. At lower concentrations of sulfuric acid the recovery of ammonia becomes poorer. This is probably due to the loss of hydrocyanic acid. The evolution of cyanide as hydrocyanic acid has been used for the determination of cyanide by the Liebig method.

SUMMARY

Small amounts of metal cyanide and thiocyanate complexes can be determined using either the Kjeldahl-Gunning or Carius sealed tube digestion method. The results obtained by the Kjeldahl-Gunning method are somewhat low and the values are scattered. The Carius sealed tube digestion enables analysis not only of metal cyanide and thiocyanate but also of mixed phenanthroline–cyanide complexes. The results are reproducible and more accurate than in the Kjeldahl-Gunning method.

RÉSUMÉ

Les auteurs ont examiné le dosage des complexes métalliques cyanés et thiocyanés, soit par la méthode de Kjeldahl-Gunning, soit par la méthode en tube scellé de Carius. C'est cette dernière qui a donné les résultats les meilleurs. Elle permet en outre l'analyse de complexes mixtes phénanthroline–cyanure.

ZUSAMMENFASSUNG

Die Bestimmung von komplexen Metallcyaniden und thiocyanaten kann entweder nach der Kjeldahl-Gunning oder Carius Methode erfolgen. Die Kjeldahl-Gunning Methode ergibt etwas zu tiefe und streuende Werte. Die Carius Methode gibt bessere Werte und kann ausserdem auch für Phenanthrolin–Cyanid Komplexgemische angewandt werden.

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FURTHER APPLICATIONS OF ELECTRO-STATIC DISCHARGE CURRENT (ES. D.)

VII. A MOISTURE GAUGE FOR CHROMATOGRAPHS

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(Received December 7th, 1959)

The importance of moisture in determining the conductance of chromatograph zones which contain soluble compounds is well known. By placing the chromatograph in a "humidiser" prior to zone location the writer showed[1] that the conductivity of an otherwise almost undetectable zone or spot could be located and underlined automatically.

The correct length of exposure to moisture in the "humidiser" varies in accordance with the humidity of the atmosphere. Automatic underlining is possible over a comparatively wide range of humidity, from a degree where there is only just sufficient moisture to permit reliable operation to the point where the chromatograph becomes oversaturated.

The simple device described in the present paper is a gauge whereby the gradual conditioning of the chromatograph can be monitored until it reaches the most favourable condition.

The electrical circuit

As shown in Fig. 1, the circuit is virtually the same as that employed[2] in a previous paper except that the conductimetric tube is now replaced by the "humidity gauge" F. The latter consists of a strip of No. 1. Whatman's filter-paper which has been soaked in $N/1$ cobalt chloride or another hygroscopic solute. When dry it is mounted in front of back plate 'B', Fig. 2. To ensure good contact, that portion which is covered by the washers between which it is clamped, is coated with graphite.

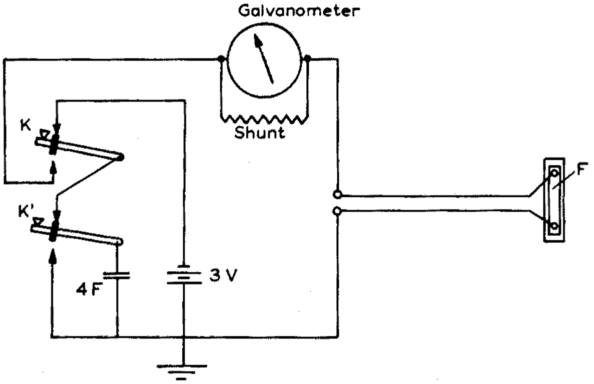

Fig. 1. The electrical circuit employed with BLAKE's humidity gauge.

There is an air space between the strip and the plate. The humidity gauge is then placed at the end of the humidiser and is shut in under its glass cover. From time to time key K* (Fig. 1) is depressed and galvanometer swings are recorded covering the humidity range within which automatic recording can be relied upon. A swing 'X' is found a short distance past the centre of this range and an indicator is attached to the galvanometer scale at that point.

To ensure reliable automatic operation the galvanometer swing must always reach the neighbourhood of the indicator.

Procedure for using the humidity gauge

Normally the gauge is suspended at some convenient place in proximity to the automatic zone locating apparatus. While it is still out in the open air and before it is placed in the humidiser a preliminary test is made. Key 'K' is depressed and a galvanometer swing is observed; if this comes well within the operational range *i.e.* close to point X on the scale, the chromatograph which also has been exposed to open air in the laboratory will not require any additional moisture and it can be run through the underlining apparatus as it is. However if the galvanometer swing falls short of the indicator on the scale, the chromatograph is too dry and the procedure is then as follows:

The gauge is placed inside the humidiser in the position indicated by A, Fig. 2. The chromatograph is then placed above it and along the groove in the usual manner. The humidiser is then sealed by its glass cover.

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* The functions of the two keys K and K' were described[2].

Key 'K' is then depressed every 15 sec or so until the required swing 'X' occurs. At this juncture the chromatograph is properly conditioned and underlining should be commenced.

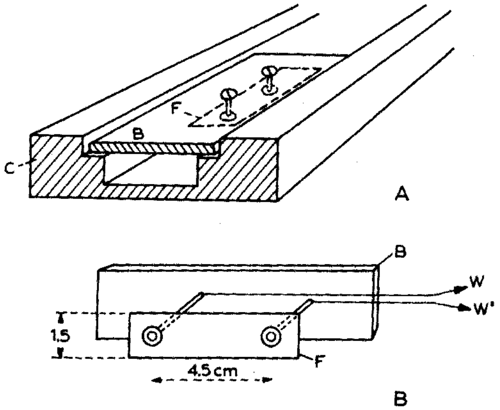

Fig. 2. A. This drawing shows the end-view of the "humidiser". The humidity gauge is seen in position where it rests along the top groove. B. This figure illustrates the general arrangement of the humidity gauge. F is the strip of filter-paper impregnated with cobalt chloride.

Originally the gauge was designed for use with the automatic apparatus; but it is of course equally applicable in the case of a hand operated locator.

An alternative scheme

Instead of impregnating the filter-paper strip with a hygroscopic substance, the writer has found that a similar strip of clean filter-paper (which itself is slightly hygroscopic) can be employed as a "humidity gauge" provided that the condenser is charged to a sufficiently high potential, 67.5 V gave satisfactory galvanometer swings.

SUMMARY

This paper describes a simple "humidity gauge" whereby the degree of humidity of a chromatograph is monitored both before and during its conditioning. Originally it was designed for use in conjunction with Blake's automatic zone locator. It can also be employed with a hand operated zone locator.

RÉSUMÉ

L'auteur décrit un dispositif permettant de contrôler le degré d'humidité d'un chromatographe, soit avant, soit au cours de son exécution.

ZUSAMMENFASSUNG

Es wird eine Einrichting beschrieben, die erlaubt, den Feuchtigkeitsgehalt in einer chromatographischen Kammer sowohl vor als auch während des Betriebes zu messen.

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A NEW GAS ABSORPTION DEVICE

ITS APPLICATION TO TITRIMETRIC AND CONDUCTOMETRIC MICRO DETERMINATIONS OF CARBON DIOXIDE IN AIR

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(Received December 7th, 1959)

The starting point for the present study was the widely used method for the titrimetric determination of carbon dioxide in atmospheric air developed by KROGH AND REHBERG[1] and slightly modified by FONSELIUS, KORELEFF AND BUCH[2]. In this method, a measured volume of atmospheric air (50 to 100 ml) is passed at a low flow rate (approximately 10 ml per minute) upwards through an oblique glass tube of diameter 0.4 to 0.5 cm and length about 15 cm. The bottom end of this tube is tapered and bent upwards, and the upper end is provided with a bulb with a diameter of about 1.5 cm (Fig. 1). In this tube is previously introduced 0.5 ml of a dilute solution of barium hydroxide. During the absorption the tilt of the tube should be adjusted so that droplets of the fluid separate the air bubbles of the ascending air stream until they reach the bulb where they break up, starting a counter stream of fluid flowing towards the bottom end of the tube in a layer wetting the inner surface of the tube. The liquid of the ascending droplets mixes with and stirs the descending liquid. The excess of hydroxide is finally titrated with hydrochloric acid.

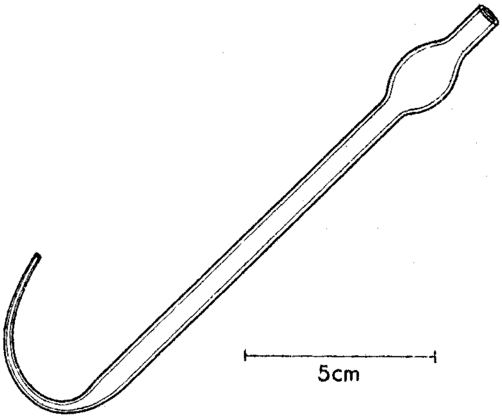

Fig. 1. The absorption tube of KROGH AND REHBERG.

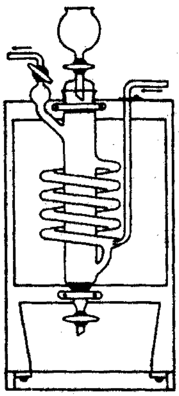

Fig. 2. The spiral absorber of WEAVER AND EDWARDS. With gas flowing at a rate of 100 ml per min the bubbles are stated to remain in the helix about 7 sec.

During an experimental study in which a great number of determinations of carbon dioxide in air had to be carried out, the writer considered the possibility of simplifying the procedure of KROGH AND REHBERG by carrying out the analyses as simple titrations of the barium hydroxide solution with air, thus avoiding the back titration of the surplus of hydroxide. In these experiments the absorption liquid was 0.5 ml of a 0.005 *N* barium hydroxide solution. Thymolphthalein, previously added to the barium hydroxide solution, was used as indicator.

It was found that the error involved in this technique corresponded to a loss of carbon dioxide which, for the same absorption tube and the same flow rate of the air, was quite accurately reproducible. Apparently, the error decreased with the flow rate. With air streams of 12, 7 and 2 ml per minute, the losses of carbon dioxide were found to be about 20, 8, and 4%, respectively. In consequence, more complete absorption of the carbon dioxide was attempted by increasing the length of the absorption tube. Experiments with a long tube of the same internal diameter, 0.42 cm, revealed that by very careful adjustment of the tilt of the tube, the ascending droplets of fluid could be made to travel about 60 cm before they broke up; they could travel only about 12 cm in the original KROGH AND REHBERG tube. By this arrangement, the area of contact between air and liquid and (for the same rate of flow) the duration of the contact are both increased by a factor of about five.

With air streams of 13, 5.5 and 2 ml per minute, the apparent escape of carbon dioxide was now found to be about 6 to 10, 1 to 4, and —3 to +1%, respectively. It was noticed that the colour change of the indicator in this modified tube, contrary to that in the original KROGH AND REHBERG tube, did not occur simultaneously in all the ascending droplets, but always started at the bottom end of the tube when about 85% of the air volume required to change the colour of the entire amount of hydroxide had passed. During the final period of the absorption, the colour change would gradually spread upwards through the entire volume of the absorbing liquid. This means that the absorbing area of contact between air and hydroxide towards the end of the absorption represented only a fraction of the total wetted inner surface of the tube.

From the above experiments it was concluded that more efficient absorption might be obtained if the recirculation of the absorption fluid from the top to the bottom of the tube could be improved. An absorption device was therefore made which combined the principal advantages of the above absorption tube (large absorbing surface and favourable ratio between the absorbing area and the volume of absorbing fluid) with the effective mixing and stirring of the absorption liquid offered by the so-called spiral absorbers originally described by WEAVER AND EDWARDS[3] (Fig. 2). These spiral absorbers also operate on the air lift principle. They have been used for many purposes including the collection of carbon dioxide from a stream of air with subsequent titrimetric determinations of the carbon dioxide absorbed (MARTIN AND GREEN[4], PIETERS[5], BLOM AND EDELHAUSEN[6]). They have also been adapted to conductometric determinations of carbon dioxide (DAILLY AND ELLIOT[7]).

However, the quantities of carbon dioxide required for analyses with the above spiral absorbers are much larger than those required by the KROGH AND REHBERG procedure, because 10 to 50 ml of absorption liquid are needed as against 0.5 ml in the KROGH AND REHBERG method. Furthermore, the ratio between the area of the absorbing surface and the volume of absorbing liquid in these spiral absorbers is less favourable, being of the order of 1 cm^2 per ml of liquid as against about 30 cm^2 per ml in the original Krogh and Rehberg tube, and more than 100 cm^2 per ml in the modified Krogh and Rehberg tube described above.

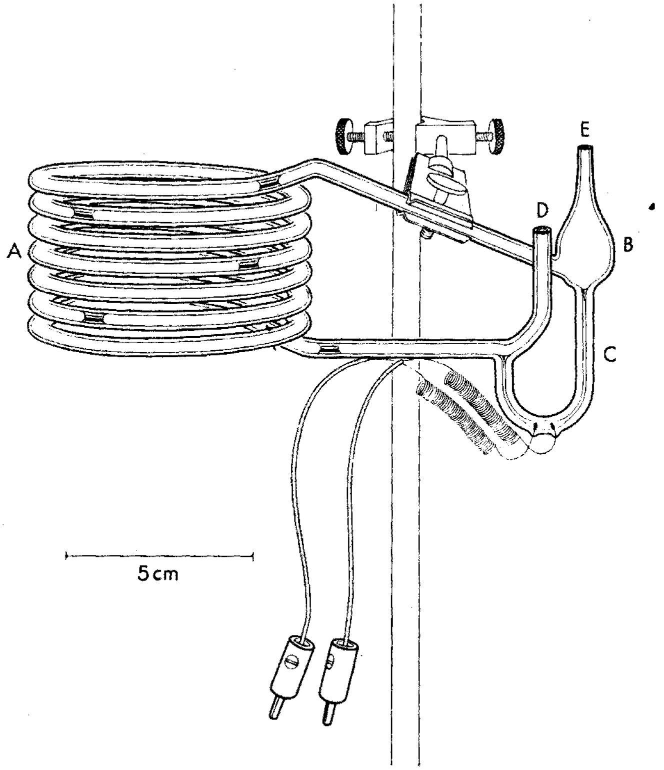

Fig. 3. The recommended spiral absorber with electrodes for conductivity measurements. For explanation, see text.

Fig. 3 shows the proposed absorption device in its final form which was reached after many experiments. Containing 0.5 ml of absorbing liquid, it gives a ratio between the area of the absorbing surface and the volume of the absorbing liquid of about 300 cm^2 per ml. The apparatus is made entirely of glass, "Pyrex" or "Jena Geräte". It consists of a spiral tube (A), the upper end of which ends in a flattened bulb (B), the bottom of which is connected to the lower end of the spiral through a capillary tube (C). The lower bend of (C) is provided with electrodes for conductivity measurements. D is the inlet tube for the air to be analyzed. E is the outlet tube.

Dimensions of apparatus

Spiral tube (A), length 160 cm, internal diameter 0.32 cm ± 0.02 cm; diameter of the helix (5 to) 7 cm; volume about 13 ml; internal surface area about 160 cm^2.

Bulb (B), horizontal outer diameters about 1.4 cm and 0.8 cm, respectively; volume about 1 ml.

Capillary tube (C), internal diameter 0.065 cm ± 0.005 cm. The difference between the levels of the upper and lower ends of this capillary tube is 1.9 cm ± 0.2 cm. At the lower bend the tube is slightly blown up to accommodate the platinum electrodes. The volume of the capillary tube is less than 0.05 ml.

Electrodes, consisting of platinum wires, 0.04 cm in diameter, are melted into the lower bend of the capillary tube. The ends protruding into the bore of the tube are flattened; the areas are a few mm^2. The distance between the electrodes is about 0.4 cm.

Inlet tube (D), internal diameter 0.32 cm. The part adjacent to the lower end of the capillary tube (C) is narrowed to a bore of about 0.26 cm.

Outlet tube (E), length about 1.2 cm; internal diameter about 0.2 cm.

The volume of air contained in the whole apparatus is about 15 ml.

Preparation of apparatus

Before the apparatus can be used for conductivity measurements the electrodes should be lightly covered with platinum black. This is done as follows: 0.1 ml of a solution containing chloroplatinic acid (3%) and lead acetate (0.02%) is placed in the apparatus and platinum black is deposited by connecting the electrodes through a resistance of about 1000 Ω to a 4-V source of direct current. The current is reversed every 15 sec. Three periods of 15 seconds in each direction are sufficient.

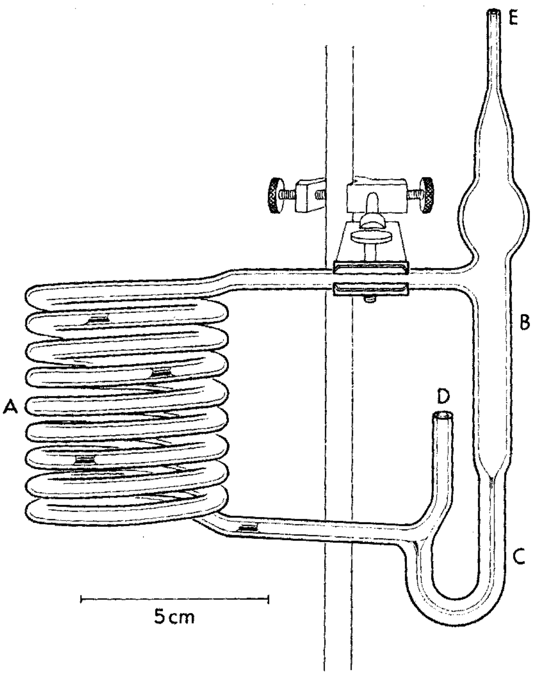

Fig. 4. A more primitive form of the proposed spiral absorber, without electrodes.

Fig. 4 shows a spiral absorber which may be preferred for certain purposes; a volume of absorption fluid up to about 2 ml can be circulated at a rate of up to about 20 ml per minute. It has a larger dead space than the absorber described above, and this is a disadvantage for many purposes.

The experiments discussed below were carried out with the spiral absorber shown in Fig. 3.

Before the apparatus is used for the first time, it is rinsed successively with approximately N hydrochloric acid, distilled water and alcohol. A water pump is connected to the outlet tube (E) and the washing fluid is introduced through the inlet tube (D). After the washing, the spiral is turned upside down and allowed to dry in the air stream before the suction pump is disconnected. The absorber is then ready for use.

The absorber is washed between each analysis with distilled water and alcohol only. The adhering precipitates of barium or strontium carbonate need only be removed occasionally by washing with hydrochloric acid.

Absorption solution

For both the visual titrimetric and conductometric analyses, the same solution is used for the absorption of carbon dioxide. Strontium hydroxide is preferred to barium hydroxide because strontium carbonate is less soluble than barium carbonate. For most purposes, 0.005 M strontium hydroxide, saturated with strontium carbonate and containing 10 ml of an alcoholic 0.1% thymolphthalein solution per litre was used. For precise analyses, this solution should be standardized by titration with standard hydrochloric acid at intervals of a few days.

By means of a KROGH syringe pipette 0.5 ml of the absorption solution is delivered into the inlet tube of the spiral absorber, which is immediately connected to the tubing delivering the air to be analyzed. The analysis is then carried out without delay.

End-point determination

The end-point of the visual titration is taken as the disappearance of the last traces of the blue colour of thymolphthalein.

The conductometric measurements are carried out with a very convenient and inexpensive commercial Wheatstone bridge, the Philips Measuring Bridge P.R. 9500. The measurements are performed with an alternating current of 1000 cycles per second from an oscillator incorporated in the bridge. The margin of error of this instrument is not significant to the present study and will not be discussed in this paper.

The electrodes of the spiral absorber can be calibrated with a freshly prepared 0.01 M potassium chloride solution, the specific conductivity of which at $t°$ can be taken as $\varkappa_t = [1333 + 27(t - 22)] \cdot 10^{-6}$ Ohms^{-1} cm^{-1}. The electrode constant K is then computed from the equation

$$\varkappa_t = \frac{K}{R_t}$$

where R_t is the resistance in Ohms measured at $t°$. For the electrodes of the spiral absorbers, K should not exceed 15. In most of the absorbers K was about 13. K is not sufficiently constant to allow the initial concentration of strontium hydroxide in the absorbing liquid to be checked accurately from measurements of the specific conductivity. However, K does not change measurably during the performance of a single analysis.

In the determinations of carbon dioxide, it was found convenient to express the results of the conductivity measurements as the ratio between the conductance measured and the initial conductance of the absorption liquid, which is equal to R_0/R, where R_0 is the initial resistance of the absorption liquid and R the resistance measured.

Testing the apparatus

Before the spiral absorbers are used for the analyses, it should be ascertained that the absorption fluid circulates properly. The outlet tube of the absorber to be tested is connected to a Mariotte bottle as described below and the rate of air flow adjusted to about 12–15 ml per minute. By means of a measuring syringe, the absorption liquid is introduced in quantities of 0.1 ml through the inlet tube while the circulation of the fluid is watched.

The first 0.1 ml of fluid should fill the capillary tube and also yield a drop of fluid which travels with the air stream through the spiral. This drop is gradually reduced in size as it leaves a layer of fluid adhering to the wall of the spiral, and after having passed less than one third up the spiral tube it breaks up. The second quantity of 0.1 ml should start a drop travelling about two-thirds of the spiral before it breaks. The third quantity of 0.1 ml should complete the circuit and separate from the air in the bulb without splashing into the outlet tube; the fluid should return to the lower end of the spiral through the capillary tube without catching air bubbles in this tube. The spiral absorber should be able to function with 0.3 ml of fluid but only one or two droplets of fluid then travel simultaneously in it. By the addition of further liquid, the number of circulating droplets should increase. In most of the spirals, more than 1 ml of fluid may circulate without the accumulation of appreciable quantities in bulb B.

The spiral absorber is then disconnected, washed and dried as described above and again connected to the Mariotte bottle.

In the next test, a quantity of 0.5 ml of the absorption solution is delivered into the inlet tube before the air stream is started. The whole quantity of fluid apart from a small fraction filling the capillary starts to travel through the spiral forming an unbroken string of fluid. When it reaches the bulb, it should again be noticed if the fluid separates from the air without spraying into the outlet tube. Owing to the retardation caused by the capillary tube, the fluid entering the spiral for the second circulation should separate into at least two single drops, and in subsequent circuits the number of droplets should be at least five.

If the above test is repeated with 0.7 or 1.0 ml of absorbing liquid, the number of circulating droplets is further increased. However, only a few spirals with the dimensions given above for the absorber shown in Fig. 3 can circulate as much as 1 ml of fluid at a rate corresponding to an air-flow of 15 ml per minute without the permanent accumulation of fluid in the bulb. In the analyses discussed below, no permanent accumulation of fluid in the bulb was allowed.

Among about twenty of these absorbers tested, only one had to be discarded because it, for some reason, constantly trapped air bubbles in the capillary tube, so that the recirculation of the fluid was blocked. In two absorbers, the same fault was overcome by decreasing the distance between the levels of the upper and lower end of the capillary tube by 0.2 cm.

The principal errors to be expected in carrying out determinations of carbon dioxide in air with this absorber may be grouped as follows:

1. Errors caused by the exchange of carbon dioxide through the wall of the flexible tubing leading the sample stream of air to the inlet tube of the absorber.

2. Errors caused by the liberation of substances from glass into the absorption liquid and by adsorption and sorption to the glass of ions from the liquid, as well as errors due to exchange of ions between liquid and glass.

3. A positive error due to the absorption of part of the carbon dioxide in the air initially present in the apparatus.

4. A negative error due to incomplete absorption of carbon dioxide from the sample air stream.

To elucidate the significance of these errors a number of experiments were carried out. Samples of air with different concentrations of carbon dioxide were used.

a. Carbon dioxide-free air was obtained by passing ordinary air at a constant rate (about 30 ml per minute) by means of a small membrane pump first through a tower filled with soda lime and then through a wash-bottle containing distilled water. The following measures sufficed to minimize any errors caused by diffusion of carbon dioxide through the walls of the flexible tubing joining the tower, the wash bottle and the spiral absorber (*cf.* the errors in group 1 above): (1) only "Tygun" tubing, which is known to be far less permeable to carbon dioxide than rubber tubing, was used; (2) one cm from the end of the tubing leading to the inlet of the absorber a T-glass joint was interposed, the side branch of which was fitted with 30 cm of flexible tubing for the escape of surplus air. In this way, the effect of diffusion of carbon dioxide through the flexible tubing on the carbon dioxide concentration of the air entering the absorber was made independent of the air-flow through the spiral; in all experiments this was less than 20 ml per minute. When carbon dioxide-free air was used to wash the absorber before an experiment, the tubing attached to the side branch of the T-tube was closed by a stopper.

b. Atmospheric air was sampled through a 2-m long "Tygun" tube from the outdoor atmosphere. A T-glass joint was again interposed 1 cm from the inlet of the absorber. The side-arm was connected to a suction pump for washing the tube with atmospheric air before the air was passed through the absorber. Continuous washing during the absorption procedure proved unnecessary.

c. Air containing carbon dioxide in different concentrations. In some experiments these mixtures were stored in a Douglas bag. Owing to the solubility of carbon dioxide in rubber, the carbon dioxide concentration of these samples changed continuously.

During the experiments carried out with these qualities of air, the sample air was drawn through the absorber at different rates. This was established by connecting the outlet tube (E) of the absorber to a Mariotte bottle, from which the water could be drained through different capillary tubes. The volume of air passed was taken to be equal to the volume of water delivered by the bottle.

In all experiments discussed below, the fluctuation of the temperature measured by a thermometer suspended adjacent to the spirals was less than ±0.2° during periods of 10 minutes, and less than ±0.4° in 30 minutes; no correction for the effect of temperature changes on the conductivity were made.

Errors caused by the liberation of substances from the glass, by adsorption and sorption to the glass, and by exchange of ions between liquid and glass were studied by the following experiments with carbon dioxide-free air.

A clean dry absorber was connected as described above to the apparatus delivering carbon dioxide-free air. The T-joint in this experiment was connected to the inlet tube of the absorber by 2 cm of rubber tubing. In order to avoid any back-diffusion of carbon dioxide from the ambient air, the outlet tube of the absorber was provided with a 30-cm length of "Tygun" tubing. After washing with the carbon dioxide-free air for 10 minutes the outlet tubing was connected to the Mariotte bottle; 0.5 ml of the standard strontium hydroxide solution was injected by means of a KROGH measuring syringe provided with a fine needle through the short rubber connection into the inlet tube of the absorber. The initial resistance of the absorption solution, R_0, was measured, and a stream of carbon dioxide-free air of about 10 ml per minute was started by opening the outflow tube of the Mariotte bottle. The resistance, R, between the electrodes was then measured at intervals over a period of several hours.

An initial, instantaneous decrease in conductivity of 3.5% was found and this was followed by a steady decrease in the conductivity of about 4% per hour. On repeated runs, the initial drop of conductivity was invariably found to be between 2.5 and 4%; it could not be reduced even when the period of washing with carbon dioxide-free air was extended to several hours. The same initial drop occurred when the experiment was repeated with different absorbers, of which some were made of "Pyrex" glass and others of "Jena Geräte" glass. The steady loss, however, varied between 2 and 6% per hour, apparently being higher in experiments with new absorbers than with those which had been used for days or weeks. This steady loss could not be reduced by interposing a scrubber with sodium hydroxide solution between the soda lime tower and the water-filled scrubber; moreover, the decrease per hour was independent of the rate of the air stream which was varied between 1 and about 15 ml per min. It was found, however, that raising the temperature of the absorber greatly increased the rate of the continuous decrement of the conductivity. At about 55°, the conductivity of the usual strontium hydroxide solution decreased by about 20% of the initial conductivity at 55° during the first hour. When the spiral was then cooled to room temperature (22°), the rate of the decrease returned to its usual magnitude of 4% of the initial conductivity at 22° during the following hour.

From these observations it was concluded that the changes in the conductivity of the absorption fluid were not caused by contamination of the so-called carbon dioxide-free air with carbon dioxide, but should be explained as the results of reactions between the absorption fluid and the glass.

The initial drop in the conductivity of the absorption liquid of 3.5% corresponds to the disappearance from the solution of $3.5/100 \times 2.5$ μmoles = approx. 0.09 μmoles of strontium hydroxide. If this quantity of strontium hydroxide were adsorbed on the glass surface, it would (on the assumption that it forms a monolayer of cubical, closely packed molecules) cover a surface of 80 cm^2, *i.e.* about 50% of the internal surface of the spiral. Therefore, it seems not unlikely that the initial drop in the conductivity of the strontium hydroxide solution may be caused by adsorption of strontium hydroxide on the surface of the glass spiral.

In view of the results of the above experiments, the continuous decrease in conductivity must also be ascribed to interactions between the strontium hydroxide solution and the glass, possibly a steady liberation of silica from the glass.

These experiments were supplemented by some in which three spiral absorbers were connected in series. "Tygun" tubing and glass tubes were used except for short lengths of 2 cm of rubber tubing adjacent to the inlet tubes of the spiral absorbers. After the clean and dry absorbers had been washed with carbon dioxide-free air, the usual quantity of strontium hydroxide solution was added to the inlet tubes of the first and the third absorber by injection through the rubber tubing. After about 1 hour, the same quantity of strontium hydroxide was injected into the inlet tube of the second spiral absorber. Immediately after the injections, the usual initial drop in conductivity invariably occurred in each absorber.

Similar experiments were carried out with more dilute solutions of strontium hydroxide prepared by exposing the above 0.005 *M* solution to atmospheric air. The strontium hydroxide concentrations of these solutions were determined by conductivity measurements. With these solutions, the initial drop in conductivity expressed as above, *i.e.*, as a percentage of the initial conductivity of the hydroxide solution used for the experiment, was larger; however, the decrement was found to be smaller than that corresponding to the disappearance of the same quantity of strontium hydroxide. The initial drop in the conductivity of 0.002 *M* strontium hydroxide solutions was found to be about 5%; thus the quantity of presumably adsorbed strontium hydroxide was only about two-thirds of that found with undiluted strontium hydroxide solution.

A still more dilute ($4 \cdot 10^{-4} M$) solution showed an initial decrement of conductivity of about 10%; *i.e.* the absorption was about one-fourth of the amount with the undiluted solution. With a 0.015 *M* strontium hydroxide solution, the initial drop in the conductivity was 1.3% of the initial conductivity of this solution; *i.e.* the same quantity of strontium hydroxide was absorbed as with the 0.005 *M* solution.

Any error arising from the absorption of part of the carbon dioxide present in the air contained in the apparatus at the beginning of the analysis was studied in similar experiments in which the spiral absorbers were washed with air with different concentrations of carbon dioxide before the introduction of the usual quantity of 0.005 *M* strontium hydroxide solution. Then carbon dioxide-free air was passed through the absorber and the initial drop in conductivity was determined. The difference between this drop and the above-mentioned initial drop of 3.5% (due to adsorption) was assumed to be caused by the absorption in the hydroxide of carbon dioxide from the air originally present in the spiral.

With fresh atmospheric air this difference amounted to about 1% of the initial conductivity of the usual strontium hydroxide solution; this corresponds to the carbon dioxide contained in about 2 ml of fresh atmospheric air, and this volume is about 13% of the total volume of air contained in the absorber. With air streams ranging from 2 to 15 ml per minute that part of the initial drop in conductivity caused by the absorption of carbon dioxide from the air originally present in the apparatus seemed to be independent of the flow rate. The quantity of carbon dioxide absorbed was further found to be roughly proportional to the square root of the concentration of carbon dioxide in the air originally contained in the apparatus.

With these experimental data, it is possible to consider experiments for elucidating the significance of the error caused by incomplete absorption of carbon dioxide under various experimental conditions.

In the first experiments to be discussed, carbon dioxide was liberated from a mixture of sulphuric acid and measured quantities of a very carefully prepared solution of 0.005 *M* sodium bicarbonate. By means of a stream of carbon dioxide-free air the carbon dioxide was carried through two successive spiral absorbers with strontium hydroxide; the conductivities were measured.

These experiments were carried out with three absorbers connected in series with short lengths of rubber tubing interposed in the connecting tubings adjacent to the inlet tubes of the absorbers as described on page 19. In the first absorber (No. 0), which had previously been rinsed with hydrochloric acid, washed and dried as described on page 16, was introduced 0.5 ml of 0.1 *N* sulphuric acid. After washing with a stream of carbon dioxide-free air, about 10 ml per minute, for 30 minutes, 0.5000 ml of the usual strontium hydroxide solution was injected through the walls of the rubber tubing into each of the other two absorbers (Nos. 1 and 2). After a further 30 to 120 min, a measured quantity of the sodium bicarbonate solution was injected into absorber No. 0.

The first experiments with this arrangement were carried out with 0.5000 ml of the bicarbonate solution. The quantity of carbon dioxide liberated, 2.50 μmoles, was equivalent to the absorption capacity of the strontium hydroxide present in each of the subsequent spiral absorbers; conductivity measurements showed that 88% was absorbed in No. 1 and 12% in No. 2. This poor result was assumed to be due to the very sudden transference of the carbon dioxide in a too concentrated mixture with air. Consequently, the experiment was repeated with a glass bulb (volume about 25 ml) interposed in the tubing between the absorber in which the carbon dioxide was liberated and the absorber containing strontium hydroxide.

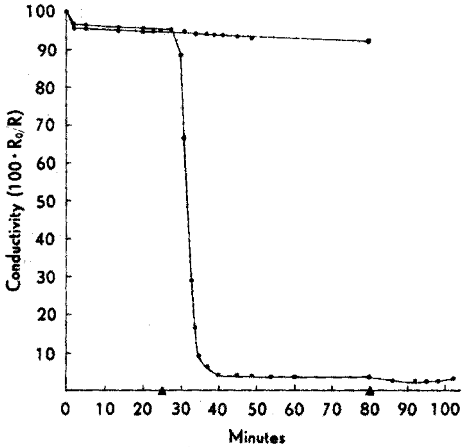

Fig. 5. The conductivities of the absorption liquids of two absorbers connected in series plotted against time; carbon dioxide equivalent to 97% of the capacity of the solution in absorber No. 1 was carried through the absorbers by means of carbon dioxide-free air. The carbon dioxide was liberated after 25 min. After 80 min the air stream was changed to fresh atmospheric air.

The results of this experiment are given in Fig. 5, in which the conductivities of the absorption fluids of the two spiral absorbers, expressed as percentages of the initial conductivities, are plotted against time, measured in minutes after the introduction of the hydroxide to the absorbers. The flow-rate of the carbon dioxide-free air was 8.33 ml per min. By titration, the concentration of strontium hydroxide in the absorbent was found to be 0.00515 *M*. Thus, the quantity of strontium hydroxide, 0.500 ml, in each spiral absorber was 3.0% in excess of the amount equivalent to the carbon dioxide liberated.

The conductivity curves exhibited the usual initial drop of about 3.5% (3.0% in absorber No. 1 and 4.0% in absorber No. 2). The subsequent continuous decrement of conductivity during a period of 25 min in which only carbon dioxide-free air was passed was 1.5% in both cases.

After the bicarbonate had been added to the sulphuric acid, the conductivity curve of the strontium hydroxide solution in absorber No. 2 was not affected; the conductivity of the liquid in absorber No. 1 dropped during less than 20 min to a level of 4.0%, and during the next 40 min steadily decreased to 3.5%. During this period the liquid still possessed a faint but clearly visible blue colour. When now fresh atmospheric air was admitted to absorber No. 1, the conductivity of the liquid in it rapidly passed its minimum value of 2.2% of the initial conductivity; at the same time the last traces of the blue colour disappeared. Then a slow but steady increase due to the uptake of carbon dioxide as bicarbonate took place. During the next 10 min the conductivity increased from 2.2 to 2.9%. This experiment was repeated several times with essentially the same results.

Under these experimental conditions there was no measurable escape of carbon dioxide from the solution in absorber No. 1. This means that even towards the end of the absorption process when only a very small surplus of hydroxide is present, the removal of carbon dioxide from a very dilute mixture with carbon dioxide-free air is still complete.

After the absorption of 2.50 μmoles of carbon dioxide in a quantity of strontium hydroxide equivalent to 103% of the carbon dioxide, and 1 hour after the strontium hydroxide had been placed in the absorber, there remained an excess of hydroxide of about 1.3%; this leaves 1.7% of the initial strontium hydroxide to have been removed by interaction with the glass. It is reasonable to assume that this 1.7% corresponds to the continuous drop of conductivity of the absorption liquid mentioned above; the initial drop of about 3.5% must be due to reversible processes, probably adsorption, (*cf.* page 20) and, consequently, cannot affect the amount of carbon dioxide which can be taken up by the hydroxide solution.

In further experiments the amount of strontium hydroxide placed in absorber No. 1 minus the amount corresponding to the continuous decrement of the conductivity before the delivery of the bicarbonate, was equivalent to the amount of bicarbonate placed in absorber No. 0; the escape of carbon dioxide from absorber No. 1 was then determined to be about 1% from conductivity measurements in absorber No. 2. In these experiments in which the absorption of the last few per cent of carbon dioxide took place from a very dilute air mixture, the rate of the air stream did not measurably influence the amount of carbon dioxide escaping absorption.

The next experiments were carried out with air streams, whose carbon dioxide concentrations were constant throughout each experiment. They were intended to correlate the quantity of carbon dioxide escaping absorption (1) to the rate of the air stream and (2) to the concentration of carbon dioxide in the sample air. These experiments were also carried out with three absorbers connected in series as described on page 19. After washing with carbon dioxide-free air as described above, 0.5 ml of the strontium hydroxide solution was injected in each absorber and carbon dioxide-free air at about 10 ml per min was passed for 30 to 120 minutes. The stream of the sample air was then turned on, and the conductivity was measured in each of the three absorbers at suitable intervals until the indicator had changed colour in all three spirals.

The results of a representative experiment carried out with a stream of atmospheric air of 8.33 ml per min are shown in Fig. 6. It can be seen that the conductivity of the absorption fluid in each of the first two absorbers had attained its minimum level before the conductivity measured in the subsequent absorber was affected by more than about 1%. However, it is not justifiable to conclude that there had been practically no escape of carbon dioxide from the absorbers during the last few minutes before the minimum conductivity was reached. The volume of air contained in each spiral plus the volume of the preceding interconnecting tubing was about 17 ml; as the rate of the air stream was 8.33 ml per min, the registration by the conductivity measurement of the carbon dioxide escaping from the preceding absorber must have been delayed by more than 2 min.

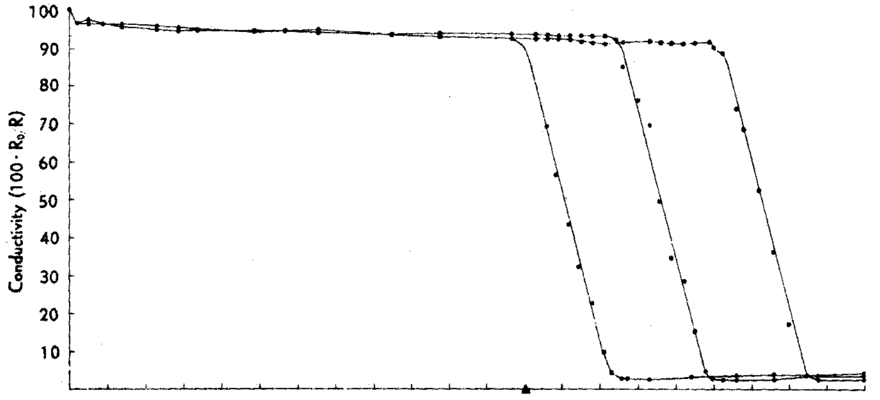

Fig. 6. The conductivities of the absorption liquids in three absorbers in series plotted against time. After 120 minutes the stream of carbon dioxide-free air was changed to atmospheric air at a rate of 8.3 ml per min.

In order to measure the escape of carbon dioxide towards the end of the titration in analyses carried out on atmospheric air the following procedure was adopted. Three spiral absorbers were connected in series as described above except that a three-way stopcock was interposed between the inlet tube of the first absorber and the tubings delivering atmospheric air and carbon dioxide-free air. By this arrangement it was possible to make instantaneous changes between the streams of the two airs. The spiral absorbers were washed with carbon dioxide-free air before the usual quantity of strontium hydroxide was placed in each absorber. Carbon dioxide-free air was then passed for about 30 min in order to establish the slope of the conductivity curves caused by the interactions between the absorption fluid and glass. The air stream was then changed to atmospheric air. As soon as the colour had changed in the first absorber, the air stream was changed to carbon dioxide-free air; the quantity of carbon dioxide which had passed through the first absorber, was determined from the drop of the conductivity curve of the fluid in the subsequent absorber during the passage of a further 50 ml of carbon dioxide-free air, allowance being made for the continuous decrement of the conductivity due to interaction between the absorption fluid and the glass. The steady slope of the conductivity curve of the solution in the third absorber was only used as an indicator of temperature constancy during the experiments.

The amount of carbon dioxide escaping absorption in the first absorber, expressed as a percentage of the amount absorbed in this absorber, may, with sufficient accuracy, be considered equal to the drop in the conductivity of the solution in the second absorber expressed as a percentage of the initial conductivity of this solution; this amount is denoted as Δ. The percentage of the total quantity of carbon dioxide absorbed in the first plus the second absorber that has escaped the first absorber is then $(100 \times \Delta)/(100 + \Delta)$.

The first experiments were carried out with atmospheric air. This air stream was changed to carbon dioxide-free air when the last traces of the blue colour of thymolphthalein had disappeared. With air streams of 15, 8.3 and 2.2 ml per min, Δ was found to be about 6 to 8, 4 to 6, and 1 to 2%, respectively.

The next experiments were carried out with air streams of 15 and 8.33 ml per min; these rates were changed to 2 ml per minute as soon as the blue colour of the absorption liquid began to fade. The escape of carbon dioxide (Δ) was then found to be 3 to 6 and 2 to 4%, respectively.

In further experiments it was found that the above escape of carbon dioxide could not be significantly decreased by reducing the rate of the air stream below 2 ml per min whenever the first fading of the blue colour was noticed. However, it appeared that the amount of carbon dioxide escaping from the first absorber towards the end of the titration could always be reduced to less than 3% of the absorption capacity of the 0.5 ml of 0.005 M strontium hydroxide in this absorber if, whenever the first fading of the colour of the absorbent occurred, the stream of air was changed to an alternating passage of 40 ml of carbon dioxide-free air and 2 ml of atmospheric air. (Compare the results obtained with carbon dioxide liberated from bicarbonate and acid described on pages 21–22; these show that absorption of very low concentrations of carbon dioxide from air is nearly complete even just before the end-point of the titration is reached.)

Concerning the above-mentioned findings it should be noted that the escape of carbon dioxide is caused not only by its incomplete absorption while the fluid is still more alkaline than corresponds to the disappearance of the last colour of thymolphthalein (pH = 9.4); it must also be partly due to the unavoidable introduction of a surplus of carbon dioxide with the air stream, when, towards the end of the titration, only a small quantity of alkali is left.

If the average pH of the absorption liquid is assumed to be 10.4 when the first drop of the absorbent fades, the concentration of strontium hydroxide is $1.25 \cdot 10^{-4}$ M, or 2.5% of its initial concentration. The quantity of carbon dioxide which can be taken up as carbonate by this solution corresponds to the carbon dioxide contained in less than 5 ml of atmospheric air; this is only one-third of the volume contained in the spiral absorber.

These experiments with atmospheric air were repeated with samples of air containing lower concentrations of carbon dioxide (about 0.01 and 0.003%). The escape of carbon dioxide towards the end of the titration was found to decrease with decreasing concentrations of carbon dioxide. With air containing 0.01% of carbon dioxide, the escape of carbon dioxide from air streams of up to 12 ml per min was always below 2%. If the rate of this air stream was reduced to less than 5 ml per min as soon as the colour of the indicator began to fade, the escape of carbon dioxide was only about 1%.

Repetition of these experiments with air containing carbon dioxide in considerably higher concentrations showed an appreciable increase in the amount of carbon dioxide escaping absorption. With a stream of air containing 0.15% of carbon dioxide, *i.e.* about 5 times the concentration in fresh atmospheric air, the escape, Δ, at a constant flow rate of 8.3 ml per minute was found to be about 45%; this corresponds to an escape of $(100 \times 45)/145 = 31\%$ of the carbon dioxide content of the air passed through the first absorber. At 2 ml per minute, Δ was found to be 8 to 10%. When the flow rate was changed from 8.3 to 2 ml per min as soon as the first drop of the absorption liquid began to fade, the escape was about 12%. If at the first fading of the colour, the stream of air was changed to an alternating passage of 40 ml of carbon dioxide-free air and 2 ml of atmospheric air, the absorption liquid could be titrated to the end-point indicated by the disappearance of the last trace of the blue colour; the escape of carbon dioxide was then only about 5%.

CONCLUSIONS AND SUGGESTIONS

It seems reasonable to conclude from all these results that the absorption device described is suitable for the determination of carbon dioxide. Probably the spiral absorber could also be used for the determination of other gaseous substances.

The procedures to be recommended for the analyses depend on the accuracy required and the laboratory facilities available. It is beyond the scope of this study to discuss in detail the numerous ways in which the apparatus described can be adapted to different requirements and various experimental conditions. Only a few examples of analytical procedures which have been tested by the writer are outlined here.

1. *Colorimetric titrations of carbon dioxide in air by titration against strontium hydroxide*

0.500 ml of the strontium hydroxide solution is delivered into the open inlet tube of the spiral absorber by means of a KROGH syringe pipette and titrated with a stream of the air to be analyzed to an end-point determined by the complete disappearance of the colour of the first two drops of the circulating absorbing liquid. From the volume of air used for the titration, an empirical correction which is taken to be equal to the volume of air passed in one minute is deducted. The resulting volume is then reduced to dry air at 0° and 760 mm Hg most conveniently by means of a reduction factor read from a thermobarometer. The concentration of carbon dioxide at NTP is calculated by dividing the amount of strontium hydroxide used (about 2.5 μmoles) by the air volume. The carbon dioxide concentration thus obtained is expressed as μmoles CO_2 per ml of air at NTP. Multiplication by 2.24 gives the carbon dioxide concentration in per cent.

Provided that the concentration of carbon dioxide is below 0.1%, the relative error involved in the above procedure does not exceed 5%. The accuracy of the visual titrations may be improved by carrying out the simultaneous analyses of the sample air and air containing a known carbon dioxide concentration. The carbon dioxide concentration of the unknown air sample can be taken to be equal to the ratio between the volumes of the known and the unknown air samples multiplied by the carbon dioxide concentration of the known air. When the difference between the carbon dioxide concentrations of the two samples is small, in practice below 20%, the error is approximately the same as that found when samples of the same air are repeatedly titrated. For atmospheric air, the reproducibility was found to be better than ±2%. This procedure offers the advantage that the exact titre of the strontium hydroxide solution need not be known.

2. *Conductometric methods*

For the analysis of atmospheric air, conductometric procedures do not give results that are essentially more accurate than ±2%. However, the conductometric methods are indispensable for certain purposes, particularly for checking the accuracy of the visual procedures. Furthermore, they can be used for analyses when the visual procedures are unsuitable. The following analyses may be mentioned as examples.

1. Determination of changes occurring in the carbon dioxide concentration in a continuous stream of air.

2. Determination of the carbon dioxide concentration of small samples of air. By means of a stream of carbon dioxide-free air, small air samples can be carried through the spiral absorber and the carbon dioxide determined by measuring the resulting decrease in conductivity. To ascertain that no carbon dioxide has escaped, a second absorber may be connected in series. In this way, accurate determinations of the carbon dioxide content of 1-ml samples of expired air and of carbon dioxide liberated from small volumes of biological fluids by means of sulphuric acid can be carried out. (For technical details, see the experiments described on page 22).

ACKNOWLEDGEMENTS

The writer wishes to thank Professor P. BRANDT REHBERG, University of Copenhagen, for reading the manuscript. He is indebted to Mr. CHORFITZ PETERSEN, glass blower at the University of Aarhus, who very skilfully made the spiral absorbers, and to Mr. PREBEN GROSS, the Zoological Museum, Aarhus, for drawing the figures.

The work was aided by a grant from King Christian X's Foundation.

SUMMARY

A gas absorption device is described which is capable of absorbing gases from a stream of air (up to 15 ml/min) in a small volume (about 0.5 ml) of absorbing fluid. The absorbing area of contact between air and liquid is about 150 cm^2. The apparatus is provided with electrodes for measuring the electrolytic conductivity of the absorbing liquid. It can be used in the determination of carbon dioxide in air by means of conductometric titrations; visual titrations with air by means of thymolphthalein are also possible. No back-titration of the strontium hydroxide absorbent is needed.

RÉSUMÉ

Un nouvel appareil est décrit pour l'absorption des gaz. Il est pouvu d'électrodes, permettant la mesure de la conductibilité électrolytique du liquide absorbant. Se basant sur des mesures de conductivité, cet appareil a pu être appliqué au dosage de l'anhydride carbonique dans l'air. Il est possible également d'effectuer une détermination colorimétrique, grâce au changement de coloration de la thymolphtaléine, se produisant au point final du titrage.

ZUSAMMENFASSUNG

Es wird ein Absorptionsapparat beschrieben, welcher die Gasen in einem Luftstrom (bis *ca.* 15 ml/min) in etwa 0.5 ml einer Absorptionsflüssigkeit absorbiert. Der Apparat ist mit Elektroden versehen, zur Messung der elektrolytischen Leitfähigkeit der Absorptionsflüssigkeit. Er findet Anwendung zur Bestimmung des Kohlendioxydgehaltes der Luft durch konduktometrische oder kolorimetrische Titration. Rücktitration der angewandten Hydroxide ist nicht erforderlich.

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A SPECTROPHOTOMETRIC METHOD WITH 1,1'-DIANTHRIMIDE FOR THE DETERMINATION OF STRENGTH OF CONCENTRATED SULPHURIC ACID

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(Received December 4th, 1959)

INTRODUCTION

The strength of concentrated sulphuric acid is usually determined volumetrically, thermometrically, conductometrically or by density measurement. The conductometric method is widely applied in industry for continuous production control purposes. Owing to the small and irregular variation of density with concentration in the range 90 to 100% sulphuric acid, the measurement of density is less satisfactory in this range.

A spectrophotometric method of determining the concentration of sulphuric acid was introduced by ZIMMERMAN AND BRANDT[1]. These authors plotted absorption curves of quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) dissolved in concentrated sulphuric acids of varying strength and found an isosbestic point at 585 mμ. By measuring the extinctions at certain wavelengths and calculating the ratio of extinction, the concentrations of sulphuric acids in the range 85 to 99% could be determined.

In the present paper 1,1'-dianthrimide is applied in a similar way, the difference being the measurement of extinction at a single wavelength and the use of a constant amount of reagent. The organic reagent 1,1'-dianthrimide is mainly used for spectrophotometric determination of boron, but other elements, such as germanium and tellurium may also be determined. The colour of these complexes is only developed by heating and will not interfere in the present determination.

The reagent was found to be slightly soluble in sulphuric acid of strength below about 65%, but in the range 65 to 100% acid and in fuming acids 1,1'-dianthrimide dissolves readily producing a green-coloured solution. 1,1'-Dianthrimide seemed to exist in at least two modifications. The concentration of the green-coloured modification utilized in this investigation was found to increase with the strength of acid. This observation offers the possibility of determining the strength of sulphuric acid by spectrophotometry, and a method has been worked out for the determination of acids in a concentration range of about 80 to 99%.

Instruments and reagents

Instruments: Extinction measurements were made with a Zeiss spectrophotometer PMQ II and matched 1.0-cm cells.

Reagents: 1,1'-Dianthrimide, concentrated (95–97%) and fuming (about 20% SO_3) sulphuric acid were of reagent grade quality. The 1,1'-dianthrimide was stored in a desiccator. The strength of the stock solution of sulphuric acid was determined volumetrically and found to be 96.12%.

Standard solutions: The reagent may be added either in the solid state or as a standard solution. The latter was prepared by dissolving 1.000 g of 1,1'-dianthrimide in 100 ml of 96.12% sulphuric acid.

A series of sulphuric acids of known concentration was prepared by adding either distilled water or fuming acid to 96.12% acid. The exact strength of the solutions was determined by titration.

EXPERIMENTAL

Absorption and standard curves

A 10^{-3} *M* solution of 1,1'-dianthrimide in concentrated sulphuric acid showed a broad absorption maximum at about 650 mμ. At wavelengths below 500 mμ the absorption curves rose steeply, and at wavelengths above 700 mμ the extinctions decreased to small values. At 650 mμ and at a constant concentration of 1,1'-dianthrimide the extinction was found to vary with the strength of acid.

In Fig. 1 extinctions are given for two series of acids containing 20 and 80 mg of reagent per 100 ml. The measurements were carried out at 650 mμ against 96.12% acid as blank solution.

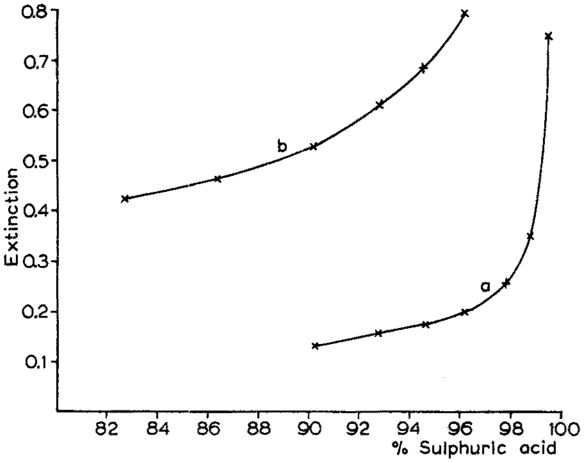

Fig. 1. Extinctions of two series of sulphuric acids containing 20 (Curve a) and 80 (Curve b) mg of 1,1'-dianthrimide standard solution per 100 ml. Wavelength 650 mμ.

From Fig. 1 it is seen that the extinction increased slowly and nearly linearly with the concentration of acid up to about 96%. At higher acid concentrations the extinction rose steeply to high values. The extinction of the solutions was measured immediately after preparation and was found to be constant for about one week, except for the 99.45% acid in which the extinction increased slowly with the time of standing.

In the present investigation a standard solution of 1,1'-dianthrimide in 96.12% sulphuric acid was used, 2 or 8 ml of this solution (corresponding to 20 or 80 mg of reagent) being pipetted into 100-ml volumetric flasks. The flasks were then filled up to volume with sulphuric acids, the strengths of which are given in Fig. 1. For the determination of acids in the range 80 to 96% the addition of 8 ml of standard solution (80 mg of 1,1′-dianthrimide) was found suitable. For acids in the concentration range 96 to about 99.5%, 2 ml of standard solution (20 mg of 1,1′-dianthrimide) were added.

Volumetric flasks with ground glass stoppers are recommended. The solutions should not be exposed to the atmosphere for any length of time. To prevent precipitation of 1,1′-dianthrimide by dilution with water, cells, pipettes etc., should first be cleaned with concentrated sulphuric acid and then with distilled water.

ACKNOWLEDGEMENT

The authors are indebted to Professor HAAKON HARALDSEN for his interest in this investigation and for the facilities placed at their disposal.

SUMMARY

The strength of sulphuric acids in the concentration range 80 to 99.5% can be determined spectrophotometrically at 650 mμ with 1,1′-dianthrimide. 1,1′-Dianthrimide dissolved in concentrated sulphuric acid seems to exist in two forms, the green form concentration increasing with the strength of acid.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour la détermination de la force d'un acide sulfurique (de 80 à 99.5%). On utilise la dianthrimide-1,1′ comme réactif.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung der Stärke von Schwefelsäure (80–99.5%). Zur Messung gelangt die mit einer bekannten Menge Dianthrimid-1,1′ erzeugte grüne Färbung.

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Anal. Chim. Acta, 23 (1960) 28–30

A NEW SCHEME OF ANALYSIS FOR THE COMMON ANIONS BASED ON PAPER CHROMATOGRAPHY

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(Received December 7th, 1959)

A scheme of analysis for the common cations based on paper chromatography has already been described; three solvent mixtures were needed and the technique was called the chromatogram comparison method[1].

A differential spraying method for the location, identification and confirmation of the common anions is now described. The method depends on the use of a single solvent mixture (ethanol–pyridine–ammonia). A general mixed spray of Laurents' acid, ammoniacal silver nitrate and fluorescein is used for the location and tentative confirmation of the anions; these are finally confirmed by specific sprays.

EXPERIMENTAL AND RESULTS

Dissolution of the powder

1. A solution is prepared by boiling about 0.2 g of the sample with 2 ml of distilled water. The solution is cooled and centrifuged to remove any precipitate; the clear supernatant solution is used for analysis.

2. Any insoluble salts present after centrifuging are tested for carbonates by the usual tests. They can then be brought into solution by fusion with "AnalaR" sodium carbonate; the fused mass is powdered and 0.2 g of the powder is boiled with 2 ml of distilled water. The solution is cooled and centrifuged, and only the clear supernatant liquid is chromatographed.

Preparation of the chromatograms

The apparatus consists of a glass trough supported in a glass tank, 50 × 25 × 15 cm, tightly covered with a glass plate. It is placed in an insulated cupboard at room temperature.

The best solvent for the separation of the common anions was found to be a mixture of 60 ml of absolute ethyl alcohol, 20 ml of purified pyridine, 16 ml of distilled water, and 4 ml of concentrated A.R. 0.880 ammonia. This homogeneous solvent gave the best separations and most concentrated spots for almost all anions under consideration (see Fig. 1). Some of the solvent is placed in the trough and some in a petri-dish at the bottom of the glass tank.

Filter paper sheets are cut into 5 × 40 cm strips and the trough height is adjusted so that the paper strips can hang from both sides of the trough with their top edges dipping into the solvent.

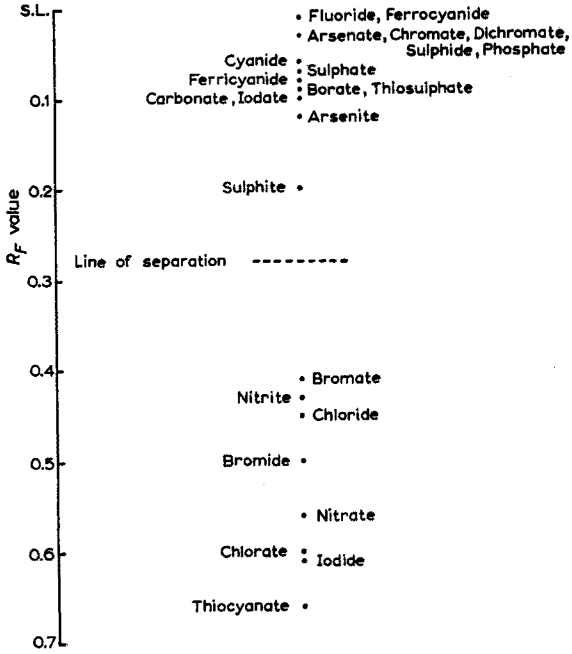

Fig. 1.

For every complete analysis twelve strips should be prepared on one or more tanks with the above solvent mixture. The solvent front should run at least 30 cm from the starting line; this usually takes about 10 hours.

The filter paper sheets must be of proper chromatographic quality. All reagents must be of AnalaR purity.

Analysis of the chromatograms

The strips are removed from the tanks and dried in a stream of hot air. One strip is used for treatment with a freshly prepared general spray consisting of 50 ml of ammoniacal silver nitrate solution, 50 ml of a saturated solution of Laurents' acid in distilled water, and 0.05 g of fluorescein. After spraying the strip is allowed to dry and viewed under U.V. light. In daylight some spots on the strip appear very clearly while others remain pale. The paper strip can be warmed very gently or preferably allowed to stand for one or two hours when the pale spots should appear very clearly in daylight. Table I shows the appearance of anions under U.V. light and in daylight, after treatment with the general spray.

Five strips are used for double spraying while six strips are used for single spraying. This is carried out as follows.

1. A pencilled line is drawn across the strips at an R_F value of 0.28. The upper zone contains fluoride, ferrocyanide, arsenate, chromate, dichromate, sulphide,

TABLE I

Anions	*Appearance in day light*	*Appearance under U.V. light*		
		Bright spots	*Dark spots*	*Colour*
Fluoride	Pale grey		—	Grey
Ferrocyanide	Bright yellow	++		Bright yellow
Arsenate	Green-yellow		—	Green-grey
Chromate	Brown		— —	Dark grey
Dichromate	Brown		—	Green-grey
Sulphide	Dirty green		— —	Dark green-grey
Phosphate	Yellow-green	+++		Bright green-yellow
Cyanide	Bright green-yellow	+++		Bright green-yellow
Sulphate	Bright yellow	+++		Bright yellow
Ferricyanide	Pink		— —	Dark red-violet
Borate	Pale grey		—	Blue
Thiosulphate	Brown		— —	Dark violet-grey
Carbonate	Pale green-yellow	+		Green-yellow
Iodate	Yellow	++		Bright yellow
Arsenite	Dirty yellow		— —	Dark green-grey
Sulphite	Pale brown		— —	Dark grey
Bromate	Yellow	+		Yellow
Nitrite	Pale yellow	+		Yellow
Chloride	Grey	++		Bright yellow
Bromide	Dark grey		— —	Dark grey
Nitrate	Yellow	+		Yellow
Chlorate	Pale yellow	+		Yellow
Iodide	Red		— —	Dark violet
Thiocyanate	Pink	++		Bright yellow

phosphate, cyanide, sulphate, ferricyanide, borate, thiosulphate, carbonate, iodate, arsenite and sulphite. The lower zone contains bromate, nitrite, chloride, bromide, nitrate, chlorate, iodide and thiocyanate.

2. A sheet of aluminium (about 20 × 20 cm) is used to mask one zone while the other is sprayed. During spraying the paper strip is kept taut by fixing "Bulldog" clips to its lower edge.

3. The presence of anions in the upper zone should be confirmed first, while the lower zone is masked. The anions in the lower zone can then be confirmed, after the paper strip has been dried. Double spraying is best carried out in the following order.

Strip 1: Fluoride then chlorate, bromate and nitrate. Strip 2: Arsenate then nitrite. Strip 3: Sulphate then chloride. Strip 4: Cyanide then bromide and thiocyanate. Strip 5: Borate then iodide.

4. Single spraying is carried out for each of the following anions in the upper zone:

Strip 1: Ferrocyanide and ferricyanide. Strip 2: Chromate and dichromate. Strip 3: Arsenite. Strip 4: Iodate. Strip 5: Sulphide, thiosulphate and phosphate. Strip 6: Sulphite and carbonate.

List of confirmatory sprays

Fluoride: R_F value 0.01. 10 ml of 1% zirconium nitrate in water mixed with 10 ml of 0.1% alizarin red S in dilute nitric acid. A bright yellowish-white spot appears against the red-purple back-ground.

Ferrocyanide: R_F value 0.01. 5 g of hydrated ferric chloride in 100 ml of water containing 2 ml of concentrated hydrochloric acid. A prussian blue spot appears[2].

Arsenate: R_F value 0.03. 10% potassium iodide in 2 *N* HCl. A stable dark brown colour appears on gentle warming.

Chromate: R_F value 0.03. 0.2 g of diphenylcarbazide in 100 ml of 2 *N* acetic acid. A deep violet-red colour is obtained.

Dichromate: R_F value 0.03. As for chromate. A deep violet-red colour appears.

Sulphide: R_F value 0.03. 5 g of ammonium molybdate in 100 ml of 2 *N* sulphuric acid. A violet-blue spot appears. The strip is dried and then sprayed with aqueous 5% sodium sulphite solution. A deep blue spot appears.

Phosphate: R_F value 0.03. Ammonium molybdate is prepared as for sulphide. A canary-yellow spot indicates phosphate. The strip is dried and sprayed with aqueous 5% sodium sulphite solution. A dull green spot appears which changes to blue-grey on gentle warming.

Cyanide: R_F value 0.06. 10 ml of 2% guaiacol in ethyl alcohol mixed with 1 ml of aqueous 0.1% copper sulphate. A permanent blue spot appears immediately.

N.B.: This test is given by carbonate only when cyanide is absent from the original solution (R_F value for carbonate = 0.1).

Sulphate: R_F value 0.07. 0.2 g of Laurents' acid in 100 ml of 50% ethanol. A violet spot appears under U.V. light.

Ferricyanide: R_F value 0.08. Ferric chloride solution as for ferrocyanide. A bright green colour appears.

Borate: R_F value 0.09. The strip is sprayed with 2 *N* HCl, allowed to dry, sprayed with a saturated solution of turmeric powder in distilled water, and dried by gentle warming. A pale red spot is obtained.

Thiosulphate: R_F value 0.09. Ammonium molybdate is prepared as for sulphide.

A violet-blue spot appears immediately. The strip is dried and sprayed with aqueous 5% sodium sulphite. A deep blue spot indicates thiosulphate.

Carbonate: R_F value 0.10. 0.1 g of kojic acid and 0.1 g of *o*-coumaric acid dissolved in 100 ml of ethanol. The strip is sprayed, dried, then sprayed with ammoniacal silver nitrate solution and allowed to dry. A dark-brown spot appears in daylight.

N.B.: This test is given by cyanide only when carbonate is absent from the original solution (R_F value for cyanide = 0.06).

Iodate: R_F value 0.10. 1 g of phenylhydrazine hydrochloride in 100 ml of 50% ethanol. A brownish-red spot appears on gentle warming.

Arsenite: R_F value 0.12. Ammoniacal silver nitrate solution. A bright canary-yellow spot appears.

Sulphite: R_F value 0.20. Kojic and *o*-coumaric acids as for carbonate. A medium grey spot appears under U.V. light. The strip is dried and sprayed with ammoniacal silver nitrate solution; a yellowish-white slightly fluorescent spot appears under U.V. light while the strip is still wet. When the strip is dry, a brown spot appears in daylight.

Bromate: R_F value 0.41. 0.02% solution of brucine in 2 *N* sulphuric acid. A deep red colour appears on gentle warming. When the strip is sprayed with 2 *N* sodium hydroxide solution, a deep blood-red colour appears immediately.

Nitrite: R_F value 0.43. 0.1 g of *o*-coumaric acid in 100 ml of ethanol. A dark green-grey spot appears under U.V. light.

Chloride: R_F value 0.45. The strip is sprayed with silver nitrate solution and washed immediately in distilled water. It is then dried and sprayed with colourless ammonium sulphide solution. A black spot at the given R_F value indicates chloride[3].

Bromide: R_F value 0.50. 5 g of ferric nitrate in 100 ml of 0.5 *N* nitric acid. A yellow colour appears on gentle warming.

Nitrate: R_F value 0.56. Brucine in sulphuric acid as for bromate. On gentle warming a red colour appears which changes to yellow. On spraying with 2 *N* sodium hydroxide solution, an orange-yellow colour develops immediately.

Chlorate: R_F value 0.60. Brucine in sulphuric acid as for bromate. The reddish-brown colour which appears on gentle warming changes to blood-red on spraying with 2 *N* sodium hydroxide.

Iodide: R_F value 0.61. The strip is sprayed with 5% potassium nitrite solution, dried and sprayed with a starch solution acidified with some drops of sulphuric acid. A deep blue colour appears.

Thiocyanate: R_F value 0.66. Ferric nitrate reagent as for bromide. A blood-red colour appears immediately.

It will be noticed from the above list that the following groups of anions require the same confirmatory spray.

1. Ferrocyanide and ferricyanide. 2. Chromate and dichromate. 3. Sulphide, phosphate and thiosulphate. 4. Carbonate and sulphite. 5. Bromate, nitrate and chlorate. 6. Bromide and thiocyanate.

DISCUSSION

Only 12 drops of test solution are required for the complete analysis of any mixture of the above-mentioned anions. The limit of detection of the method lies between 20 and 100 μg of each anion on the original spot. This corresponds to 0.2–1 g% of each anion in the original solution.

SUMMARY

A paper chromatographic method is described for the qualitative analysis of any mixture of common anions. A single solvent and differential spraying are used.

RÉSUMÉ

Les auteurs ont mis au point un schéma d'analyse qualitative des anions courants, en utilisant la chromatographie sur papier.

ZUSAMMENFASSUNG

Es wird ein qualitativer Analysengang für Anionen mit Hilfe der Papierchromatographie beschrieben.

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Anal. Chim. Acta, 23 (1960) 30–35

DETERMINATION OF METAL IONS IN SOLUTION BY MEANS OF TAA AND EDTA

I. GENERAL INTRODUCTION AND DETERMINATION OF ZINC

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(Received December 7th, 1959)

GENERAL INTRODUCTION

In many cases addition of an excess of EDTA to neutral or basic metal salt solutions considerably decreases the metal ion concentration[1]. Addition of calcium chloride to metal–EDTA complex solutions causes a shift of the metal–EDTA equilibrium, resulting in the formation of free metal ions[2].

Thioacetamide (TAA) decomposes slowly in acid and alkaline solutions to form hydrogen sulfide by hydrolysis[3]; this can be applied to the homogeneous precipitation of metal sulfides under well-defined conditions.

The combination of these three phenomena suggests many possibilities for the quantitative determination of metal ions in the hydrogen sulfide separation system. With the aid of TAA and EDTA, however, other subdivisions of the metal ions can be made, some improved separations are possible and precipitates with excellent filtration properties are obtained[4].

FLASCHKA[2] first described the behaviour of many metal ions in solution with TAA, both in absence and presence of EDTA and calcium ions but he did not mention any quantitative applications.

In Table I and II are summarised the observations made by FLASCHKA and our-

TABLE I

INFLUENCE OF EDTA AND CALCIUM CHLORIDE ON THE PRECIPITATION OF METAL IONS BY AMMONIA

Metal ion	NH_4OH	EDTA + NH_4OH	EDTA + NH_4OH + $CaCl_2$
Cu	—	—	—
Pb	+	—	—
Cd	—	—	—
Hg	+	—	—
Bi	+	—	—
As(III)	—	—	—
As(V)	—	—	—
Sb(III)	+	+	+
Sb(V)	+	+	+
Sn(II)	+	+	+
Sn(IV)	+	+	+
Zn	—	—	—
Fe(II)	+	—	+
Fe(III)	+	—	+
Co	±	—	—
Ni	—	—	—
Mn	±	—	+
Al	+	—	+
Cr	+	—	±

The symbols in the tables represent:
\+ = complete precipitation;
± = incomplete precipitation or precipitation depending on conditions such as concentration, etc.;
— = no precipitation.

selves on the behaviour of solutions containing many metal ions. Table I shows the influence of EDTA and calcium chloride on the precipitation of the metal ions by ammonia. The second column shows the effect of adding ammonia to acid solutions

TABLE II

INFLUENCE OF EDTA AND CALCIUM CHLORIDE ON THE PRECIPITATION OF METAL IONS WITH TAA

Metal ion	*Medium*			
	Acid	*Ammoniacal*		
		TAA	*EDTA + TAA*	*EDTA + TAA +* $CaCl_2$
Cu	+	+	+	+
Pb	±	+	+	+
Cd	±	+	±	+
Hg	+	+	+	+
Bi	+	+	+	+
As(III)	+	—	—	—
As(V)	+	—	—	—
Sb(III)	+	±	±	±
Sb(V)	+	±	±	±
Sn(II)	+	+	+	+
Sn(IV)	±	+	+	+
Zn	—	+	—	+
Fe(II)	—	+	—	+
Fe(III)	—	+	—	+
Co	—	+	—	±
Ni	—	+	—	±
Mn	—	+	—	+
Al	—	+	—	+
Cr	—	+	—	—

of the metal ions, the third the effect when the solution contains an excess of EDTA, and the fourth the effect of adding excess calcium chloride to the ammoniacal metal solutions containing EDTA.

Table II shows the influence of EDTA and calcium chloride on the precipitation of metal ions with TAA in ammoniacal solution. In the second column the behaviour of metal ions with TAA in acid medium is given since it slightly differs from that with hydrogen sulfide. In the other columns the action of TAA on ammoniacal metal ion solutions is described, as well as the influence of EDTA and calcium chloride on this action.

It is obvious that the familiar quantitative separations involving sulfides and hydroxides can be largely extended by introducing EDTA and calcium chloride as masking and demasking agents. In some cases it depends on the experimental conditions whether an element remains in solution or is precipitated as sulfide or hydroxide. This also increases the number of possible separations.

For quantitative determination, a metal ion need be separated only from those accompanying metals which interfere with the analytical method chosen. The selection of a suitable method of determination is therefore of the greatest importance. In some subsequent papers we will describe determinations of a few metal ions by means of these new possibilities, and show that rapid and simple determinations of small amounts of metals can be carried out with fair accuracy.

I. Determination of Zinc

INTRODUCTION

There is no good specific quantitative method for the determination of zinc in presence of group II and group III elements, hence zinc must be separated from these elements before its determination.

Sulfide separations of the elements of the second group from zinc by means of hydrogen sulfide are generally unsatisfactory; in strongly acid solutions precipitation of cadmium, lead and tin is incomplete, while in solutions of low acidity zinc is coprecipitated[5].

As has been pointed out above, the precipitates obtained with TAA are coarser than those obtained with hydrogen sulfide, relatively free from adhesion to glass walls, and are therefore more suitable for rapid quantitative filtration. Our experiments have shown that zinc can be separated from the group II elements much better by means of TAA than with hydrogen sulfide.

The difficult separation of zinc from the group III elements is also important. Hydroxide separations are usually incomplete. Zinc is normally precipitated at pH 2–3, but this has many disadvantages. The conditions must be carefully controlled and reprecipitation is necessary[5]. According to Tables I and II it should be possible to separate zinc from the other group III elements in two steps: first, zinc is separated from aluminium, manganese and iron by precipitation of the latter elements as hydroxides on addition of calcium chloride to an ammoniacal solution containing EDTA; secondly, zinc is precipitated in the filtrate as sulfide with TAA, while chromium remains in solution. As regards nickel and cobalt, the former can be kept in solution but cobalt is always coprecipitated with zinc.

After the precipitate of zinc sulfide has been dissolved, zinc can be determined by complexometric titration with EDTA, as described by SCHWARZENBACH[6].

In this paper the results of investigations on the determination of zinc in the presence of group III and group II elements are described.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade.

TAA, Merck, 2% and 6% solution in water; hydrochloric acid, 4 *N*; buffer solution, pH = 11 (NH_4OH – NH_4Cl); EDTA solution, 0.1 *M* and 0.25 *M*; $CaCl_2$ solution, 0.3 *M* and 0.75 *M*; NH_4Cl solution, 2%, slightly ammoniacal; NH_4Cl solution, 4 *M*; KOH solution, 20%.

Procedure

The determinations are carried out in 15-ml centrifuge tubes. To 5 ml of a slightly acid solution containing 0.6 – 6 mg of zinc, add 1 ml of hydrochloric acid and 1 ml of 2% TAA (or 1 ml of 6% TAA, when the solution contains a high concentration of group II elements). Heat for 20 min in a water bath at 90°. Centrifuge and separate the supernatant liquid from the precipitate by suction through a G4 glass filter stick into another centrifuge tube (see Fig. 1). Wash the precipitate three times with 1 ml of water and transfer the wash water into the second centrifuge tube in the same way. Reduce the volume of the filtrate to 5 ml and decompose the excess of TAA in a water bath at 95°.

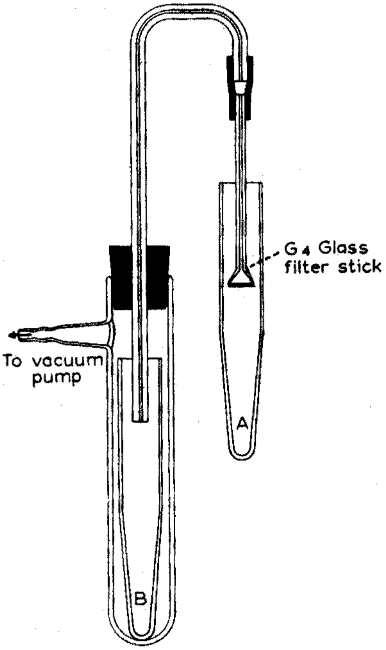

Fig. 1. The supernatant liquid is transferred from tube A to tube B, by raising tube A as the liquid level descends.

Neutralise the solution with KOH (if a permanent precipitate is formed, add a drop of HCl) and add 1 ml of 0.1 *M* EDTA (1 ml of 0.25 *M* if the solution is very concentrated), 1 ml of buffer and 1 ml of 0.3 *M* $CaCl_2$ (1 ml of 0.75 *M* when 0.25 *M* EDTA is used). Heat for 30 min in a water bath at 95°. Centrifuge and separate the precipitate by decanting the liquid into another centrifuge tube. Wash the precipitate three times with a slightly ammoniacal solution of NH_4Cl and decant the wash liquid in the same way. Reduce the volume of the decanted solution to 5 ml by evaporation in a water bath at 95°.

Cool the solution and add 0.5 ml of buffer solution and 1 ml of 2% TAA. Allow to stand for 30 min and then heat for 30 min in a water bath at 80°. Centrifuge and remove the supernatant liquid by suction through a G4 glass filter stick. Take care to remove as little as possible of the precipitate from the tube into the glass filter. Wash the precipitate three times with 1 ml of slightly ammoniacal NH_4Cl solution and remove the wash liquid in the same way.

Dissolve the precipitate in the centrifuge tube and on the filter stick in a few drops of hydrochloric acid. Transfer the combined solutions to a titration beaker, boil to drive out hydrogen sulfide and titrate with EDTA according to the procedure given after the notes.

Notes

1. The procedure outlined above is suitable if Sn, Pb, Cd, Fe(II), Cr, Ni and Co are absent. It can be modified to deal with the presence of most of these elements.

a. The presence of tin should be avoided completely. If tin is present it precipitates as the hydrated oxide, together with iron, aluminium and manganese. This precipitate is very voluminous and coprecipitation of zinc always occurs. In the case of alloys tin does not interfere with the normal course of an analysis, since it is precipitated as $SnO_2 \cdot nH_2O$ during dissolution of the alloy in nitric acid.

b. In strongly acid solutions lead is incompletely precipitated by TAA. It can be separated from zinc as $PbSO_4$ before the zinc is precipitated and determined. It is also possible to precipitate zinc according to the above procedure, and to separate any lead accompanying the zinc as the sulfate.

c. The separation of zinc and cadmium has always been very difficult. In the above procedure, cadmium does not precipitate completely with the group II elements, and there is practically no coprecipitation of zinc with these elements. The residual cadmium precipitates with zinc and it is then possible to separate them completely. After the precipitate has been dissolved, the solution is made 0.3 *N* with respect to hydrochloric acid and 1 ml of 2% TAA is added. After heating for at least 20 and at most 30 min in a waterbath at 80°, there is no precipitation of zinc whilst the precipitation of cadmium is complete, except when there is much cadmium and little zinc; in this case reprecipitation should be carried out.

d. If Fe(II) is present, a few drops of bromine water are added to oxidise all the Fe(II) to Fe(III), before the solution is neutralized.

e. If chromium is present, the solution is heated for 15 minutes, directly after the neutralisation and the addition of EDTA and before the addition of buffer and of calcium chloride. Chromium gives a very stable complex on heating with EDTA and remains completely in solution when this procedure is followed.

f. If nickel is present, it can be separated from zinc, but the amount of zinc present must be known approximately. After separation of the hydroxides, 0.5 ml of buffer, 1 ml of 4 *M* NH_4Cl and not more than twice the required amount of TAA are added to the solution. Only zinc is precipitated and it can be separated before nickel precipitates.

g. If cobalt is present, it always precipitates with zinc and the two metals cannot be separated by the above procedure. Before the titration potassium cyanide is added to mask both cobalt and nickel. Addition of formaldehyde demasks zinc only, which can then be titrated[7].

2. The separation of zinc and aluminium is not complete. A small amount of aluminium remains in the solution; this can be masked by means of ammonium fluoride.

The titration

Reagents: EDTA solution, 0.001 *M* and 0.01 *M*; NaOH solution, 2 *N*; buffer, $NH_4OH - NH_4Cl$, pH = 10 (7 g of NH_4Cl and 57 ml of concentrated ammonia, diluted to 100 ml); Erio T, 100 mg ground with 10 g NaCl; methyl red, 0.1% in alcohol; NH_4F.

Procedure

a. *Titration with 0.001 M EDTA:* Heat the acid solution containing zinc to 40°. Add two drops of methyl red and neutralise with NaOH. To 25 ml of solution add 0.2 ml of buffer, 750 mg of NH_4F and some Erio T. Titrate till the colour changes from red to pure green;

b. *Titration with 0.01 M EDTA:* The same procedure can be used, but the solution need not be heated. To 25 ml solution 0.5 ml of buffer is added.

Notes

1. Some calcium is always present. Calcium and magnesium can be masked during the titration by means of ammonium fluoride.

2. When determinations are carried out with 0.001 *M* EDTA parallel determination of a known amount of zinc is recommended. The results of titrations with 0.001 *M* EDTA are slightly influenced by the amount of buffer and fluoride added. The amounts given above lead to the best results.

RESULTS

Typical results of the determination of zinc in presence of other elements are shown in Table III.

TABLE III

DETERMINATION OF ZINC IN PRESENCE OF GROUP II AND GROUP III ELEMENTS

Amounts of other elements in mg												*mg Zn present*	*mg Zn found*	*Error in %*
Cu	*Hg*	*Pb*	*Cd*	*As*	*Sb*	*Bi*	*Fe*	*Al*	*Mn*	*Cr*	*Ni*			
6	5	5	3	4	6	3						6.00	5.97	—0.5
0.6	0.5	1	0.6	0.4	0.6	0.7						0.600	0.602	+0.3
3	5			4	6	7						0.600	0.597	—0.5
6	5	10	3	4	6	7						0.600	0.591	—1.5
							3	1	2	3	2	6.00	5.98	—0.3
							3	1		3		6.00	5.97	—0.5
							6	3	6			6.00	6.01	+0.2
							0.6	0.3	0.5	0.6	0.5	0.600	0.606	+1.0
							3	1		3		0.600	0.595	—0.8
							3	1	2	3	2	0.600	0.588	—2.0

The procedure has also been applied to the analysis of an alloy of the National Bureau of Standards (164), containing 21.89% Zn, about 64% Cu, 6% Al, 5% Mn, 2.5% Fe, 1% Sn and traces of Pb, Ni and Si. The mean of 6 determinations was found to be 21.79% with a standard deviation of the mean of 0.02%. The small systematic error is probably due to a coprecipitation of traces of zinc with $SnO_2 \cdot nH_2O$ on dissolving the alloy in nitric acid.

DISCUSSION

The method described above gives correct results for small amounts of zinc in presence of large amounts of other elements present; the experimental technique and equipment are very simple.

The time required for the determination of zinc largely depends on the presence of other elements. Some of them require time-consuming separations (Cd and Pb), while in other cases rapid determinations are possible (Ni and Cr). In general, the time required for the analysis of zinc in mixed samples varies from one to three hours.

ACKNOWLEDGEMENT

The authors are indebted to Prof. Dr. W. VAN TONGEREN for his interest in this investigation and for many suggestions for the improvement of the manuscript.

SUMMARY

The behaviour of metal ions with EDTA and TAA in acid and alkaline solutions is discussed and a specific quantitative determination of zinc is described. The use of TAA instead of hydrogen sulfide provides a much better separation of zinc from the elements of group II. After addition of EDTA and ammonia, iron, aluminium and manganese are precipitated in the filtrate as hydroxides by addition of calcium chloride. Zinc is then precipitated as the sulfide with TAA, while nickel and chromium remain in solution. After the precipitate has been dissolved zinc is determined by chelatometric titration with EDTA. As little as 0.6 mg of zinc can be determined in presence of a large excess of other group II and group III elements.

RÉSUMÉ

Après une introduction générale sur le comportement des métaux en présence d'EDTA et de thioacétamide, les auteurs proposent un dosage spécifique du zinc. Après séparation des autres cations, le zinc est précipité comme sulfure et finalement titré par complexométrie au moyen de l'acide éthylènediaminotétracétique.

ZUSAMMENFASSUNG

Es wird über das Verhalten von Metall-Ionen in Gegenwart von EDTA und Thioacetamid berichtet und eine Bestimmung von Zink beschrieben. Nach Trennung von anderen Kationen wird das Zink als Sulfid gefällt und komplexometrisch mit EDTA bestimmt.

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THE MICRO-HETEROMETRIC DETERMINATION OF PLATINUM, PALLADIUM AND GOLD WITH PAPAVERINE

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(Received November 17th, 1959)

INTRODUCTION

In two previous reports on the reactions of the noble metal halides with phenanthroline[1], many final compounds (↓↓) of different composition were stoichiometrically and quantitatively obtained. In addition to this, many series of intermediate compounds (↓) were derived from the curves. Structural formulae for many of the compounds were also suggested. Many methods were given for the determination of platinum, palladium and gold in mixtures and for the determination of phenanthroline. With the exception of palladium, the sensitivities of these reactions were low.

It was suspected that the low sensitivities of the reactions were caused by the presence of two nitrogen atoms in the phenanthrene molecule. We were therefore interested to study heterometrically on a parallel basis the reaction of the noble metal chlorides with *papaverine*, which has only one pyridinic nitrogen atom in the complex molecule. We were surprised to establish that the reactions with the noble metals were 3–4 times as sensitive as when using phenanthroline.

On the other hand, with the exception of platinum iodide, in all reactions with the three metals only *one final* compound, ($MePv_2$↓↓) was always obtained; platinum iodide gave the compound $PtPv_4$↓↓. Nevertheless, the metal-halogeno-papaverine compounds obtained showed many specific properties, depending on the specific halogen used. This enabled us to determine the metals in a single titration. The errors in the determination of the final end-points fluctuated in most cases between zero and one per cent. A titration took 15–20 min, just as with phenanthroline. The longer titration time indicated that the papaverine had to be co-ordinated into the halogeno-complexes of the metals analysed.

The action of papaverine as a pure cation is less probable, for such a reaction would require less titration time. Moreover, we obtained the same molar ratio of [Me] : 2[Pv] with gold chloride as with the other metals, and in the case of platinum iodide we always found the final compound at a molar ratio of 1[Pt] : 4[Pv]. In spite of this, it is very reasonable to suppose that the sequences of *intermediate* compounds possess structures with a salt nature in which the papaverine is complexed with the cation only, while either the halide anion or the metal halogen anion acts as an anion of the salt complex obtained. It is therefore risky to present specific structures for the $MePv_2$↓↓, obtained under the different working conditions.

The differences in the behaviour of the apparently analogously composed final compounds ($MePv_2$↓↓) may be explained partly by differences in the structures and partly by the different solubilities of the various halogeno-compounds obtained.

In this report, parallel experiments were carried out in chloride, bromide, iodide and thiocyanate solutions at pH values of *ca.* 1 and *ca.* 7. The most interesting and successful results were obtained in the thiocyanate and the iodide solutions. In special cases iodide was even more sensitive than the thiocyanate.

In order to give an idea of the sensitivity in the presence of the latter anions, we may cite that *ca.* 0.5 mg of gold or platinum was necessary for the determination of these metals in thiocyanate solutions with papaverine. In the case of palladium, *ca.* 0.3 mg of the metal was sufficient. This is about 3–4 times less than in the corresponding titrations with phenanthroline. On the other hand, if gold or platinum was titrated with papaverine in iodide solution, half of the above amounts was quite sufficient for the same analysis. If both gold and platinum were present in the iodide solution, they could both be determined with precision from two critical points of a single titration curve.

EXPERIMENTAL

Reagents

Papaverine hydrochloricum, Roche DAB VI was used. 0.3758 g was dissolved in 100 ml of water to give a 0.01 *M* solution.

Platinum chloride, Johnson, Matthey & Co. ($H_2PtCl_6 \cdot xH_2O$) about 40% Pt. 1 g was dissolved in 250 ml of water (approx. 0.008 *M*).

Palladium chloride, Johnson, Matthey & Co. 1 g was dissolved in 250 ml of 0.2 *N* HCl. (approx. 0.022 *M* $PdCl_2$ in 0.2 *N* HCl).

Gold chloride (brown), B.D.H. Laboratory reagent. 1 g $HAuCl_4 \cdot 3H_2O$ and 25 ml *N* HCl were dissolved in water to give a volume of 250 ml (approx. 0.01 *M* $HAuCl_4$ in 0.1 *N* HCl).

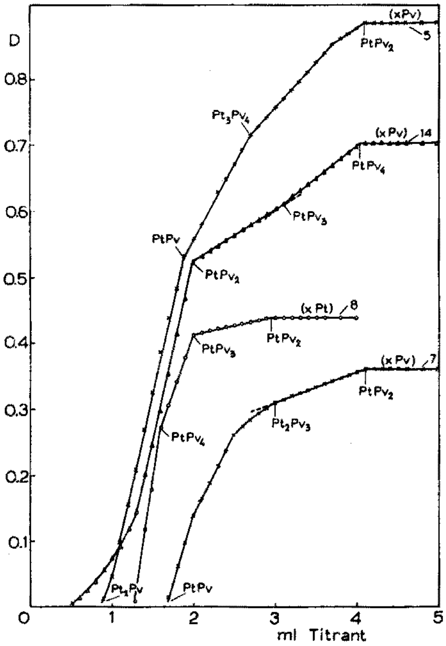

Fig. 1. Titrations of chloroplatinic acid with papaverine and the reverse (Table I).

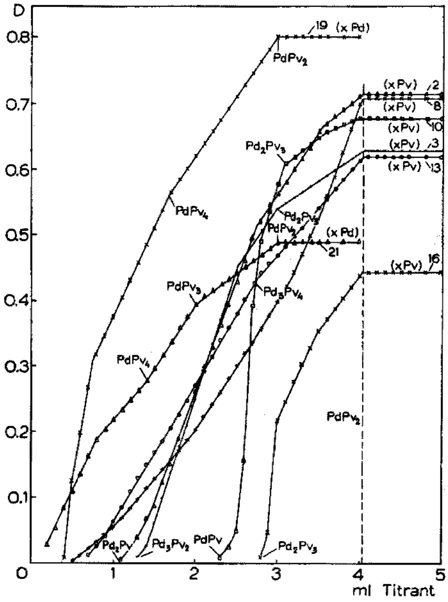

Fig. 2. Titrations of palladium chloride solutions with papaverine and the reverse (Table II).

TABLE I

General composition: a ml reagents

Expt. No.	*Solution titrated*	*Titrant*		*Titrati time i min*
		Name	*Molarity*	
1	6 ml 0.001 M H_2PtCl_6 + 2 ml M HNO_3 + 1 ml M NaCl	Pv	0.003	
2	6 ml 0.001 M H_2PtCl_6 + 2 ml M HNO_3 + 1 ml M KBr	Pv	0.003	
3	3 ml 0.001 M H_2PtCl_6 + 2 ml M HNO_3 + 2 ml 0.25 M KCNS	Pv	0.0015	17
4	3 ml 0.001 M H_2PtCl_6 + 2 ml M HNO_3 + 6 ml 0.25 M KCNS	Pv	0.0015	20
5	3 ml 0.001 M H_2PtCl_6 + 4 ml M HNO_3 + 2 ml 0.25 M KCNS	Pv	0.0015	18
6	3 ml 0.001 M H_2PtCl_6 + 4 ml M HNO_3 + 6 ml 0.25 M KCNS	Pv	0.0015	19
7	3 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COOH + 1 ml 0.1 M CH_3COONa + 2 ml 0.25 M KCNS	Pv	0.0015	25
8	3 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COOH + 1 ml 0.1 M CH_3COONa + 2 ml M KCNS	Pv	0.0015	26
9	3 ml 0.001 M H_2PtCl_6 + 1 ml M CH_3COOH + 1 ml M CH_3COONa + 2 ml M KCNS	Pv	0.0015	
10	3 ml 0.001 M H_2PtCl_6 + 1 ml M CH_3COONa + 3 ml 0.25 M KCNS	Pv	0.0015	
11	4 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COONa + 2 ml M KCNS	Pv	0.002	
12	3 ml 0.001 M H_2PtCl_6 + 3 ml M HNO_3 + 2 ml 0.25 M KCNS + 5 ml alc.	Pv	0.0015	
13	3 ml 0.001 M H_2PtCl_6 + 2 ml M HNO_3 + 1 ml 0.1 M KI	Pv	0.003	7
14	4 ml 0.0005 M H_2PtCl_6 + 2 ml M HNO_3 + 1 ml 0.1 M KI	Pv	0.002	15
15	6 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COONa + 1 ml M NaCl	Pv	0.003	
16	6 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COONa + 1 ml M KBr	Pv	0.003	
17	3 ml 0.001 M H_2PtCl_6 + 2 ml M CH_3COONa + 1 ml 0.1 M KI	Pv	0.003	7
18	4 ml 0.0015 M Pv + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	H_2PtCl_6	0.001	18
19	4 ml 0.0015 M Pv + 2 ml M CH_3COOH + 1 ml 0.1 M CH_3COONa + 2 ml 0.25 M KCNS	H_2PtCl_6	0.001	
20	4 ml 0.0015 M Pv + 1 ml M CH_3COONa + 2 ml 0.25 M KCNS	H_2PtCl_6	0.001	

Pv = papaverine; i = intersection point; c = contact point; h = horizontal maximum density line;

Technique

The same apparatus and technique were used as in previous heterometric investigations[2]. The reaction temperature was always 20°. In all experiments with iodide a red Corning filter 2412 was used.

RESULTS

1. *Reactions with chloroplatinic acid*

Table I presents the data on a selection of experiments carried out. The course of some titrations is shown in Fig. 1. The same numeration was used in the tables and in the corresponding curves. All the halides were tried. It can be seen that no precipitation whatsoever occurred in the presence of chloride or bromide either at pH *ca.* 1 or at pH *ca.* 7. (Expts. 1, 2, 15 and 16). In thiocyanate solutions the following results were obtained: at pH *ca.* 1, if 2 ml of M nitric acid were present, normal precipitation occurred, but the maximum density value was much higher if less thiocyanate was used (Expts. 3 and 4), although the final compound always had the same formal composition; but if more nitric acid was used, the influence of the thiocyanate concentration seemed to be annulled (Expts. 5 and 6). In acetic acid solution, at

— *a*) ml H_2O + *x* ml titrant, *T* = 20°

TABLE I

ml titrant used at the		*End-point (↓↓)*			*Calculated molar ratios [Pt]:[Pv]*
Init. ppt. oint (↑)	*Intermediate intersection points (↓)*	*at ml*	*Maximum density value*	*% error*	
>5			0.0		
>5			0.0		
0.7	c 2.0 ; 2.9	i 4.10 h	0.86	1.0	1 : 1↓ → 2 : 3↓ → 1 : 2↓↓
1.5	c 2.5 ; 3.0	i 4.10 h	0.41	1.0	4 : 3↑ → ~3 : 4↓ → 2 : 3↓ → 1 : 2↓↓
0.9	1.9 ; 2.7	i 4.10 h	0.88	1.0	2 : 1↑ → 1 : 1↓ → 3 : 4↓ → 1 : 2↓↓
1.1	2.85	i 4.07 h	0.90	0.5	2 : 1↑ → 2 : 3↓ → 1 : 2↓↓
1.8	2.5 ; 3.0	i 4.10 h	0.36	1.0	~1 : 1↑ → 2 : 3↓ → 1 : 2↓↓
2.0		i 4.05 h	0.24	0.0	1 : 1↑ → 1 : 2↓↓
>5			0.0		
>5			0.0		
>5			0.0		
>5			0.0		
0.1	2.0 ; 3.2	i 4.01 h	×1.05	1.0	1 : 2↓ → 1 : 3↓ → 1 : 4↓↓
0.5	1.97; 3.1	i 4.05 h	×0.70	0.0	1 : 2↓ → 1 : 3↓ → 1 : 4↓↓
>5			0.0		
>5			0.0		
>5			×0.02		
1.4	1.6 ; 2.0	i 2.90 h	0.44	2.0	1 : 4↑ → 1 : 3↓ → 1 : 2↓↓
>5			0.0		
>5			0.0		

= H_2PtCl_6; × = Red filter (Corning 2412).

pH *ca.* 3, if the same amount of platinum was titrated, the maximum optical density was already too low for a normal heterometric titration (Expts. 7 and 8). At pH *ca.* 5 and *ca.* 7 no more precipitation was obtained in the thiocyanate solution (Expts. 9–11); at pH *ca.* 1 in 25% alcohol medium the thiocyanate was dissolved (Expt. 12). At pH *ca.* 1, in the presence of iodide, the heterometrically very sensitive insoluble Pt_1Pv_4↓↓ was obtained (Expts. 13 and 14); but if the titration was carried out at pH *ca.* 7, no precipitation of the iodide occurred (Expt. 17). In the reverse titrations, in the thiocyanate solution, the same dependency on the pH of the solution was observed as before (Expts. 18–20).

Summing up, the results obtained with papaverine were qualitatively entirely analogous to those obtained with phenanthroline. The dependency of the solubility of the compounds on the pH value was also similar. This indicates that the chemistry in both cases is also similar.

2. *Reactions with palladium chloride*

Table II contains the data on a selection of experiments made. Fig. 2 (p. 43) shows

TABLE II

General composition: *a* ml reagen

Expt. No.	*Solution titrated*	*Titrant*		*Titration time in min*
		Name	*Molarity*	
1	3 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml M NaCl	Pv	0.0015	
2	3 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 3 ml 0.25 M KCNS	Pv	0.0015	15
3	3 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml M KCNS	Pv	0.0015	12
4	6 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml M NaCl	Pv	0.003	
5	3 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml 0.1 M KBr	Pv	0.0015	
6	3 ml 0.001 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml M KBr	Pv	0.0015	
7	3 ml 0.0005 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml 0.1 M KI	Pv	0.0015	
8	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COOH + 1 ml 0.1 M CH_3COONa + 1 ml 0.1 M KCNS	Pv	0.0015	20
9	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COOH + 1 ml 0. 1 M CH_3COONa + 1 ml M KCNS	Pv	0.0015	17
10	6 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml M NaCl	Pv	0.003	14
11	3 ml 0.001 M $PdCl_2$ + 1 ml M CH_3COONa	Pv	0.0015	
12	3 ml 0.001 M $PdCl_2$ + 1 ml M CH_3COONa + 1 ml 0.25 M KCNS	Pv	0.0015	25
13	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml 0.25 M KCNS	Pv	0.0015	18
14	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml M KCNS	Pv	0.0015	15
15	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml 0.1 M KBr	Pv	0.0015	39
16	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml M KBr	Pv	0.0015	38
17	3 ml 0.001 M $PdCl_2$ + 2 ml M CH_3COONa + 1 ml 0.1 M KI	Pv	0.003	
18	4 ml 0.0015 M Pv + 1 ml M HNO_3 + 1 ml 0.25 M KCNS	$PdCl_2$	0.001	19
19	4 ml 0.0015 M Pv + 2 ml M CH_3COOH + 1 ml 0.25 M KCNS	$PdCl_2$	0.001	18
20	4 ml 0.0015 M Pv + 1 ml M CH_3COOH + 1 ml M CH_3COONa + 1 ml 0.25 M KCNS	$PdCl_2$	0.001	19
21	4 ml 0.0015 M Pv + 1 ml M CH_3COONa + 1 ml 0.25 M KCNS	$PdCl_2$	0.001	22
22	4 ml 0.0015 M Pv + 5 ml 0.2 M Na_2HPO_4 + 1 ml 0.25 M KCNS	$PdCl_2$	0.001	50

Pd = $PdCl_2$. For other symbols, see Table I.

the courses of a few titrations. At pH *ca.* 1, no precipitation occurred in the chloride or the bromide solutions (Expts. 1, 4, 5 and 6), but at pH *ca.* 7 in both cases precipitation occurred (Expts. 10, 15 and 16), in contrast to the behaviour of phenanthroline. In the presence of iodide the following results were obtained: if the usual amount of palladium was taken, precipitation occurred at pH *ca.* 1 with the first drops of papaverine, but no regular heterometric titration could be carried out. However, if half of this amount of palladium was titrated (Expt. 7), no precipitation at all occurred. At pH *ca.* 7 the titration was just as unsuccessful (Expt. 17). The following results were obtained in the thiocyanate solution: the precipitation was equally successful whether the palladium was titrated with papaverine at pH *ca.* 1 or pH *ca.* 7 (Expts. 2, 3, 8, 9, 12, 13 and 14), but in almost all cases the maximum density values were lower with higher amounts of thiocyanate. In addition, at pH *ca.* 7 higher maximum densities were obtained if less sodium acetate was present (Expts. 12 and 13). In contrast to this, in the reverse titrations the maximum density values decreased with rise in the pH value of the solution (Expts. 19–22). Similar phenomena were observed when phenanthroline was used.

3. *Reactions with gold chloride*

Table III contains the data on a selection of experiments. Fig. 3 (p. 51) shows the course of a few experiments. The reaction of gold with papaverine in the presence of halides

+ (20 — a) ml H_2O + x ml titrant, T = 20°

TABLE II

ml titrant used at the		*End-point (↓↓)*			*Calculated molar ratios [Pd]:[Pv]*
Init. ppt. point (↑)	*Intermediate intersection points (↓)*	*at ml*	*Maximum density value*	*% error*	
		>5	0.0		
1.2		i 4.05 h	0.72	0.0	2 : 1↑ 1 : 2↓↓
1.4	i 3.0	i 4.04 h	0.63	0.2	~3 : 2↑ → 2 : 3↓ → 1 : 2↓↓
		>5	0.0		
		>5	0.09		
		>5	0.0		
			×0.0		
0.6		i 4.04 h	0.71	0.2	1 : 2↓↓
1.8	i 2.4	i 4.02 h	0.56	0.6	~1 : 1↑ → 1 : 2↓↓
2.4	3.05	3.98	0.68	1.2	~1 : 1↑ → 2 : 3↓↓ → 1 : 2↓↓
		>5	0.0		
0.6		i 4.10 h	0.80	1.0	1 : 2↓↓
0.7	2.7	4.03	0.62	0.4	3 : 4↓ → 1 : 2↓↓
1.3	i 2.5	i 4.04 h	0.44	0.2	3 : 2↑ → ~3 : 4↓ → 1 : 2↓↓
3.0		i 4.00 h	0.43	1.0	2 : 3↑ → 1 : 2↓↓
2.9		i 4.01 h	0.44	0.8	2 : 3↑ → 1 : 2↓↓
		0.2	×0.17		
0.3	c 1.1 ; c ~2.05	i 2.88 h	0.78	2.7	~1 : 6↓ → 1 : 3↓ → 1 : 2↓↓
0.5	0.75; 1.7	i 3.00 h	0.80	1.3	~1 : 4↓? → 1 : 2↓↓
0.4	c 1.3	i 3.00 h	0.66	1.3	~1 : 4↓ → 1 : 2↓↓
0.2	0.8 ; 1.4; 2.0	i 3.00 h	0.49	1.3	1 : 6↓ → 1 : 4↓ → 1 : 3↓ → 1 : 2↓↓
1.0	~1.5	i 2.90 h	0.19	2.0	1 : 6↑ → 1 : 4↓ → 1 : 2↓↓

showed some features not met before: the most sensitive reactions were those with the bromide or with the iodide. No precipitation was obtained with the chloride at pH *ca.* 1 even if the amount of gold was more than usual (Expt. 1). In all other cases, precipitation occurred. At pH *ca.* 1 in the presence of thiocyanate, precipitation occurred only if a higher amount of gold was present (Expts. 2, 3 and 4). The reaction was insensitive to the amount of thiocyanate or nitric acid in solution (Expts. 4 and 5).

At pH *ca.* 7 precipitation occurred in the presence of all the halides including the chloride (Expt. 10). The reaction with the bromide was more sensitive than that with the thiocyanate (Expts. 2, 3, 6 and 7). The reaction was most sensitive with the iodide (Expts. 8, 9 and 14). Probably the sensitivity at pH *ca.* 1 was even higher than at pH *ca.* 7 (Expts. 9 and 14).

GENERAL CONCLUSIONS

In Table IV are summarized all the results of the titrations of single metals with papaverine and vice versa. In each case, the approximate optimum value of the maximum optical density obtained is cited, so that all the results of titrations can be compared. In those experiments when the amount of analysed metal was more or less than usual, this is marked in the table; usual amounts of metal are not marked.

From Table IV, we can come to the following conclusions when a mixture of metal chlorides was analysed.

TABLE III

General composition: *a* ml reagents

Expt. No.	*Solution titrated*	*Titrant*		*Titratio time i min*
		Name	*Molarity*	
1	6 ml 0.001 *M* $HAuCl_4$ + 2 ml *M* HNO_3 + 1 ml *M* NaCl	Pv	0.003	
2	3 ml 0.001 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml 0.25 *M* KCNS	Pv	0.0015	
3	6 ml 0.001 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 2 ml 0.25 *M* KCNS	Pv	0.003	20
4	6 ml 0.001 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 6 ml 0.25 *M* KCNS	Pv	0.003	20
5	6 ml 0.001 *M* $HAuCl_4$ + 3 ml *M* HNO_3 + 2 ml 0.25 *M* KCNS	Pv	0.003	20
6	6 ml 0.001 *M* $HAuCl_4$ + 2 ml *M* HNO_3 + 1 ml *M* KBr	Pv	0.003	17
7	3 ml 0.001 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 4 ml *M* KBr	Pv	0.002	16
8	4 ml 0.001 *M* $HAuCl_4$ + 2 ml *M* HNO_3 + 1 ml 0.1 *M* KI	Pv	0.002	
9	3 ml 0.0005 *M* $HAuCl_4$ + 2 ml *M* HNO_3 + 1 ml 0.1 *M* KI	Pv	0.00075	16
10	6 ml 0.001 *M* $HAuCl_4$ + 2 ml *M* CH_3COONa + 1 ml *M* NaCl	Pv	0.003	20
11	6 ml 0.001 *M* $HAuCl_4$ + 2 ml *M* CH_3COONa + 1 ml 0.25 *M* KCNS	Pv	0.003	20
12	6 ml 0.001 *M* $HAuCl_4$ + 2 ml *M* CH_3COONa + 6 ml 0.25 *M* KCNS	Pv	0.003	19
13	6 ml 0.001 *M* $HAuCl_4$ + 2 ml *M* CH_3COONa + 1 ml *M* KBr	Pv	0.003	21
14	3 ml 0.0005 *M* $HAuCl_4$ + 2 ml *M* CH_3COONa + 1 ml 0.1 *M* KI	Pv	0.00075	17
15	4 ml 0.003 *M* Pv + 1 ml *M* HNO_3 + 2 ml 0.25 *M* KCNS	$HAuCl_4$	0.002	17
16	4 ml 0.003 *M* Pv + 1 ml *M* HNO_3 + 6 ml 0.25 *M* KCNS	$HAuCl_4$	0.002	19
17	4 ml 0.003 *M* Pv + 1 ml *M* CH_3COONa + 2 ml 0.25 *M* KCNS	$HAuCl_4$	0.002	18

Au = $HAuCl_4$; for other symbols see Table I.

No precipitation of platinum occurred in the chloride solution. Neither palladium nor gold gave a precipitation at pH *ca.* 1; the latter precipitated at pH *ca.* 7, but the results were not very promising.

No precipitation of platinum occurred in the bromide solution. Palladium did not precipitate at pH *ca.* 1, and gave a low density at pH *ca.* 7. Gold in bromide solution gave normal densities at all pH values.

In the presence of thiocyanate, platinum gave the highest density values at pH *ca.* 1, while at pH 5–7 no precipitation occurred. Palladium gave normal results at all pH values. At pH *ca.* 7, the densities were even somewhat higher. Gold gave normal density values only if higher amounts of the metal were present.

In the presence of iodide, platinum gave no precipitation at pH *ca.* 7; high density values were obtained at pH *ca.* 1. Small amounts of palladium gave no precipitation at pH *ca.* 1, and could not be titrated at pH *ca.* 7. High densities were obtained with gold at all pH values.

STRUCTURES

It would be risky to give one kind of structure only. Probably when the titrant is changed and different halides are used, the same empirical compound $MePv_2(\downarrow\downarrow)$ might be constructed differently.

If the sequences of intermediates were considered, the problem of the structure of $MePv_2$ would require an extended report. The first of the writers will discuss this later in connection with other coordinated nitrogen compounds. At the

– *a*) ml H_2O + *x* ml titrant, *T* = 20°

TABLE III

ml titrant used at the		*End-point (↓↓)*			*Calculated molar ratios [Au] : [Pv]*
Init. ppt. oint (↑)	*Intermediate intersection points (↓)*	*at ml*	*Maximum density value*	*% error*	
5			0.0		
5			0.0		
1.2	c 2.5 ; 3.1	i 4.10 h	0.67	1.0	~2 : 1↑ → 1 : 1↓? → 2 : 3↓ → 1 : 2↓↓
1.4	c 2.9	i 4.08 h	0.62	0.6	~3 : 2↑ → 2 : 3↓ → 1 : 2↓↓
1.2	~3.0	i 4.10 h	0.65	1.0	~2 : 1↑ → 2 : 3↓ → 1 : 2↓↓
0.1	c 1.7 ; 2.9	i 4.00 h	1.05	1.0	~1 : 1↓ → 2 : 3↓ → 1 : 2↓↓
0.4	(?) 1.3 ; 2.0; (?) 2.6	i 3.00 h	0.60	1.0	~1 : 1↓ → 3 : 4↓ → ~2 : 3↓ → 1 : 2↓↓
0.1			× > 1.1		
0.1	c 1.2 ; 2.0	i 4.00 h	× 0.79	1.0	3 : 2↓ → 1 : 1↓ → 1 : 2↓↓
0.1	i 2.1	i 4.07 h	0.59	0.4	1 : 1↓ → 1 : 2↓↓
1.6	c 2.7	i 4.06 h	0.61	0.2	4 : 1↑ → 3 : 4↓ → 1 : 2↓↓
2.0	i 2.9	i 4.02 h	0.49	0.6	1 : 1↑ → 2 : 3↓ → 1 : 2↓↓
0.1	i 2.2 ; i 3.1	i 4.02 h	0.60	0.6	~1 : 1↓ → 2 : 3↓ → 1 : 2↓↓
0.5	i 2.0 ; i 2.6; 3.17	i 4.00 h	× 0.55	1.0	1 : 1↓ → 3 : 4↓ → 2 : 3↓ → 1 : 2↓↓
0.6	c 2.0	i 3.00 h	1.08	1.0	1 : 3↓ → 1 : 2↓↓
0.6	2.25	i 3.00 h	1.13	1.0	~1 : 3↓ → 1 : 2↓↓
0.5		i 3.00 h	0.86	1.0	1 : 2↓↓

present moment, the following structures for the final compounds are suggested.

$$PtPv_2\text{:}\quad \underset{(1)}{[\underset{R_2}{\mathrm{PtPv_4}}]\,[\mathrm{PtR_6}]} \quad \text{or} \quad \underset{(2)}{\begin{bmatrix}\mathrm{PtPv_2}\\ \mathrm{R_4}\end{bmatrix}^{\circ}}$$

$$PtPv_4\text{:}\quad \underset{(3)}{\begin{bmatrix}\mathrm{PtPv_4}\\ \mathrm{I_2}\end{bmatrix}\mathrm{I_2}}$$

$$PdPv_2\text{:}\ \underset{(4)}{[\mathrm{PdPv_4}]\,[\mathrm{PdR_4}]} \quad \text{or} \quad \underset{(5)}{[\mathrm{PdPv_2R_2}]^{\circ}}$$

$$AuPv_2\text{:}\ \underset{(6)}{[\mathrm{AuPv_4}]\,[\overset{R_2}{\mathrm{AuR_4}}]} \quad \text{or} \quad \underset{(7)}{\begin{bmatrix}\mathrm{AuPv_2}\\ \mathrm{R_2}\end{bmatrix}\mathrm{R}}\ .$$

ANALYTICAL ASPECT

Table V contains a selection of titrations of mixtures of metal chlorides with papaverine at different pH values and in the presence of different anions. Fig. 4 contains the course of a few of these titrations. These experiments were intended to establish the best conditions for the determination of the metals. The critical points of the intermediates obtained are also cited in the table. When a critical point of an inter-

TABLE IV

H_2PtCl_6				*$PdCl_2$*				*$HAuCl_4$*			
Titrant	*pH*	*R^-*	*Approx. maximum density value*	*Titrant*	*pH*	*R^-*	*Approx. maximum density value*	*Titrant*	*pH*	*R^-*	*Approx. maximum density value*
Pv	~ 1	Cl^-	$>$ Pt 0.0	Pv	~ 1	Cl^-	$>$ Pd 0.0	Pv	~ 1	Cl^-	$>$ Au 0.0
Pv	~ 7	Cl^-	$>$ Pt 0.0	Pv	~ 7	Cl^-	$>$ Pd 0.7	Pv	~ 7	Cl^-	$>$ Au 0.6
Pv	~ 1	Br^-	$>$ Pt 0.0	Pv	~ 1	Br^-	0.0	Pv	~ 1	Br^-	0.6
Pv	~ 7	Br^-	$>$ Pt 0.0	Pv	~ 7	Br^-	0.4	Pv	~ 7	Br^-	$>$ Au 0.6
Pv	~ 1	CNS^-	0.8	Pv	~ 1	CNS^-	0.6	Pv	~ 1	CNS^-	$>$ Au 0.7
Pv	~ 3	CNS^-	0.4	Pv	~ 3	CNS^-	0.7	Pv	~ 7	CNS^-	$>$ Au 0.6
Pv	~ 5	CNS^-	0.0	Pv	~ 7	CNS^-	0.8	Pv	~ 1	I^-	1.1
Pv	~ 7	CNS^-	0.0	Pv	~ 1	I^-	$<$ Pd 0.0	Pv	~ 7	I^-	$<$ Au 0.6–08
Pv	~ 1	I^-	1.0	Pv	~ 7	I^-	0.2	$HAuCl_4$	~ 1	CNS^-	1.0
				$PdCl_2$	~ 1	CNS^-	0.8	$HAuCl_4$	~ 7	CNS^-	0.9
Pv	~ 7	I^-	0.0	$PdCl_2$	~ 3	CNS^-	0.8				
H_2PtCl_6	~ 1	CNS^-	0.4	$PdCl_2$	~ 5	CNS^-	0.7				
H_2PtCl_6	~ 3	CNS^-	0.0	$PdCl_2$	~ 7	CNS^-	0.5				
H_2PtCl_6	~ 7	CNS^-	0.0	$PdCl_2$	~ 9	CNS^-	0.2				

mediate served as an analytical end-point it is marked in the table as ↓↓. The errors cited in the table concern the first maximum density points.

Before the different methods for the determination of the metals are detailed the results of Table V and the working principles should be discussed.

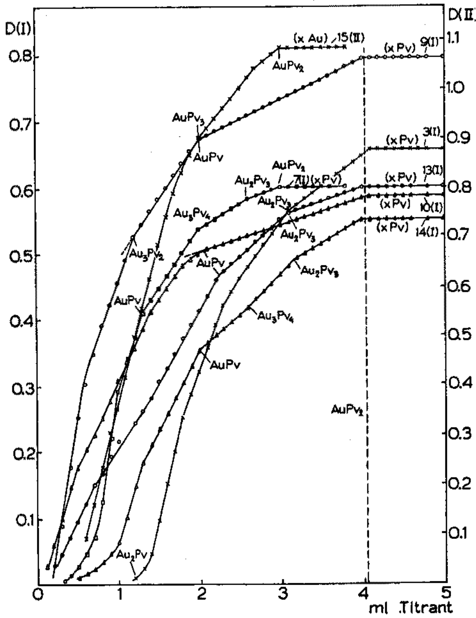

Fig. 3. Titrations of gold chloride solutions with papaverine and the reverse (Table III).

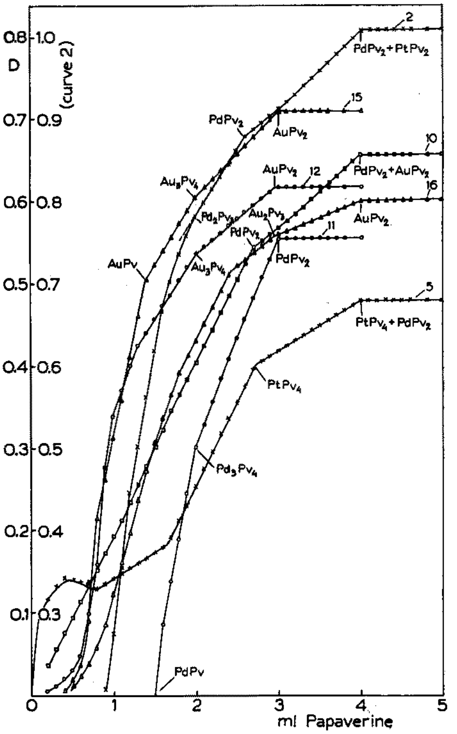

Fig. 4. Titrations of mixtures of platinum, palladium and gold halides with papaverine (Table V).

When mixtures of platinum and palladium were analysed, thiocyanate solution could be used at any pH value: at pH *ca.* 1 (Expts. 1 and 2), *ca.* 5 (Expt. 6) or *ca.* 7 (Expts. 7 and 8). In the last case, the platinum remained dissolved, and the palladium only was determined. At pH 1–5 both metals could be determined from one titration curve: the first end-point coincided with the quantitative formation of the last intermediates. This was either $PtPv_2$ (Expts. 1 and 6) or $PdPv_2$ (Expt. 2), depending on which of the two metals was in excess.

The titration of the mixture of metals could also be carried out in solutions of bromide at pH *ca.* 7; the platinum remained dissolved and the palladium only was determined as $PdPv_2$ (Expt. 11). Similar mixtures of these metals, but in a more dilute solution, could be determined at pH *ca.* 1 in a solution of iodide (Expts. 3–5). Both metals were determined in one titration; the platinum precipitated first.

Mixtures of palladium with gold could be determined at pH *ca.* 1 in solutions of iodide (Expts. 17 and 18). If the palladium was in excess, both metals could be deter-

TABLE V

General composition: *a* ml reagents

Expt. No.	*Composition*	*% / mg metal*			*Molarity of Pv*
		Pt	*Pd*	*Au*	
1	4 ml 0.001 *M* H_2PtCl_2 + 4 ml 0.0005 *M* $PdCl_2$ + 1 ml *M* HNO_3 + 2 ml 0.25 *M* KCNS	78.5% 0.7809	21.5% 0.2134		0.003
2	4 ml 0.0005 *M* H_2PtCl_6 + 4 ml 0.001 *M* $PdCl_2$ + 1 ml *M* HNO_3 + 2 ml 0.25 *M* KCNS	47.8% 0.3905	52.2% 0.4268		0.003
3	3 ml 0.0005 *M* H_2PtCl_6 + 3 ml 0.0005 *M* $PdCl_2$ + 1 ml *M* HNO_3 + 1 ml 0.1 *M* KI	64.7% 0.2928	35.3% 0.1600		0.003
4	4 ml 0.0005 *M* H_2PtCl_6 + 3 ml 0.0005 *M* $PdCl_2$ + 1 ml *M* HNO_3 + 1 ml 0.1 *M* KI	70.9% 0.3905	29.1% 0.1600		0.003
5	4 ml 0.0005 *M* H_2PtCl_6 + 4 ml 0.0005 *M* $PdCl_2$ + 1 ml *M* HNO_3 + 1 ml 0.1 *M* KI	64.7% 0.3905	35.3% 0.2134		0.003
6	6 ml 0.001 *M* H_2PtCl_6 + 3 ml 0.001 *M* $PdCl_2$ + 1 ml *M* CH_3COOH + 1 ml *M* CH_3COONa + 2 ml 0.25 *M* KCNS	78.5% 1.1714	21.5% 0.3201		0.004
7	6 ml 0.001 *M* H_2PtCl_6 + 3 ml 0.001 *M* $PdCl_2$ + 1 ml *M* CH_3COONa + 1 ml 0.25 *M* KCNS	78.5% 1.1714	21.5% 0.3201		0.002
8	6 ml 0.001 *M* H_2PtCl_6 + 3 ml 0.001 *M* $PdCl_2$ + 2 ml *M* CH_3COONa + 1 ml 0.25 *M* KCNS	78.5% 1.1714	21.5% 0.3201		0.002
9	6 ml 0.001 *M* H_2PtCl_6 + 3 ml 0.001 *M* $PdCl_2$ + 3 ml 0.001 *M* $HAuCl_4$ + 2 ml *M* CH_3COONa + 1 ml 0.25 *M* KCNS	56.2% 1.1714	15.4% 0.3201	28.4% 0.5916	0.003
10	6 ml 0.001 *M* H_2PtCl_6 + 4 ml 0.001 *M* $PdCl_2$ + 4 ml 0.0005 *M* $HAuCl_4$ + 2 ml *M* CH_3COONa + 1 ml 0.25 *M* KCNS	58.8% 1.1714	21.4% 0.4268	19.8% 0.3944	0.003
11	6 ml 0.001 *M* H_2PtCl_6 + 3 ml 0.001 *M* $PdCl_2$ + 2 ml *M* CH_3COONa + 1 ml *M* KBr	78.5% 1.1714	21.5% 0.3201		0.002
12	6 ml 0.001 *M* H_2PtCl_6 + 3 ml 0.001 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml *M* KBr	66.4% 1.1714		33.6% 0.5916	0.002
13	9 ml 0.001 *M* $PdCl_2$ + 3 ml 0.001 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml *M* KBr		61.9% 0.9603	38.1% 0.5916	0.002
14	9 ml 0.001 *M* $PdCl_2$ + 3 ml 0.001 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml *M* KBr		61.9% 0.9603	38.1% 0.5916	0.001
15	6 ml 0.001 *M* H_2PtCl_6 + 9 ml 0.001 *M* $PdCl_2$ + 3 ml 0.001 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml *M* KBr	43% 1.1714	35.3% 0.9603	21.7% 0.5916	0.002
16	4 ml 0.001 *M* H_2PtCl_6 + 4 ml 0.0005 *M* $HAuCl_4$ + 2 ml *M* CH_3COONa + 1 ml 0.1 *M* KI	66.4% 0.7809		33.6% 0.3944	0.001
17	3 ml 0.0005 *M* $PdCl_2$ + 3 ml 0.0005 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml 0.1 *M* KI		35.1% 0.1600	64.9% 0.2958	0.001
18	5 ml 0.0005 *M* $PdCl_2$ + 3 ml 0.0005 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml 0.1 *M* KI		47.4% 0.2668	52.6% 0.2958	0.002
19	4 ml 0.00025 *M* H_2PtCl_6 + 4 ml 0.00025 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml 0.1 *M* KI	49.7% 0.1952		50.3% 0.1972	0.001
20	4 ml 0.00025 *M* H_2PtCl_6 + 3 ml 0.00025 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml 0.1 *M* KI	56.8% 0.1952		43.2% 0.1479	0.001
21	3 ml 0.00025 *M* H_2PtCl_6 + 6 ml 0.00025 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml 0.1 *M* KI	33.1% 0.1464		66.9% 0.2958	0.001
22	4 ml 0.0005 *M* H_2PtCl_6 + 4 ml 0.001 *M* $HAuCl_4$ + 2 ml 0.25 *M* KCNS + 1 ml *M* HNO_3	33.1% 0.3905		66.9% 0.7888	0.003
23	3 ml 0.001 *M* H_2PtCl_6 + 3 ml 0.001 *M* $HAuCl_4$ + 2 ml 0.25 *M* KCNS + 1 ml *M* HNO_3	49.7% 0.5857		50.3% 0.5916	0.003

For symbols see Table I.

o — a) ml H_2O + x ml bM papaverine (Pv), $T = 20°$

TABLE V

Found								Titration time in min
Init. ppt.		Intermediates		End-point				
at Pv	compound	ml of Pv used	Compounds obtained	at ml Pv	Compounds obtained	Optical density value	% error	
0.4		c 1.61(?); i 2.7	$PtPv_2\downarrow\downarrow$	i 4.00 h	$PtPv_2\downarrow\downarrow + PdPv_2\downarrow\downarrow$	0.98	0.0	15
0.5		c 2.0 ; 2.6	c $Pd_2Pv_3\downarrow \rightarrow PdPv_2\downarrow\downarrow$	i 4.00 h	$PdPv_2\downarrow\downarrow + PtPv_2\downarrow\downarrow$	1.01	0.0	14
0.1		2.0	$PtPv_4\downarrow\downarrow$	i 3.00 h	$PtPv_4\downarrow\downarrow + PdPv_2\downarrow\downarrow$	×0.49	0.0	12
0.1		2.7	$PtPv_4\downarrow\downarrow$	i 3.70 h	$PtPv_4\downarrow\downarrow + PdPv_2\downarrow\downarrow$	×0.49	0.9	20
0.0		1.67 ; 2.7	$PtPv_4\downarrow\downarrow$	i 4.00 h	$PtPv_4\downarrow\downarrow + PdPv_2\downarrow\downarrow$	×0.48	0.0	12
0.5		1.53 ; 2.9	$PtPv\downarrow \rightarrow PtPv_2\downarrow\downarrow$	i 4.50 h	$PtPv_2\downarrow\downarrow + PdPv_2\downarrow\downarrow$	0.86	0.0	32
0.5		c 2.7		i 3.00 h	$PdPv_2\downarrow\downarrow$	0.57	0.0	18
0.3		2.1	$Pd_3Pv_4\downarrow$	i 3.03 h	$PdPv_2\downarrow\downarrow$	0.43	1.0	17
0.3		1.52 ; 2.94	$Au_2Pv_3\downarrow \rightarrow Pd_3Pv_4\downarrow \rightarrow$	i 4.00 h	$PdPv_2\downarrow\downarrow + AuPv_2\downarrow\downarrow$	0.59	0.0	13
0.2		2.70	$PdPv_2\downarrow\downarrow$	i 4.00 h	$PdPv_2\downarrow\downarrow + AuPv_2\downarrow\downarrow$	0.66	0.0	12
1.5	PdPv	2.0	$Pd_3Pv_4\downarrow$	i 3.01 h	$PdPv_2\downarrow\downarrow$	0.55	0.3	35
0.3		2.0	$Au_3Pv_4\downarrow$	i 2.97 h	$AuPv_2\downarrow\downarrow$	0.62	1.0	17
0.3		2.1	$Au_3Pv_4\downarrow$	i 3.00 h	$AuPv_2\downarrow\downarrow$	0.76	0.0	16
0.7		2.0 ; 2.75	$AuPv\downarrow \rightarrow \sim Au_3Pv_4\downarrow$	i 4.00 h	$AuPv_2\downarrow\downarrow$	0.66	0.0	18
0.5		1.4 ; 2.0	$AuPv\downarrow \rightarrow Au_3Pv_4\downarrow$	i 3.00 h	$AuPv_2\downarrow\downarrow$	0.70	0.0	16
0.5		2.4 (?); 3.0	$Au_2Pv_3\downarrow$	i 4.00 h	$AuPv_2\downarrow\downarrow$	×0.60	0.0	24
0.1		1.4 ; 2.5	$Au_2Pv_3\downarrow$?	i 4.00 h	$AuPv_2\downarrow\downarrow + PdPv_2\downarrow\downarrow$	×0.31	0.0	14
0.0		2.56	$PdPv_2\downarrow\downarrow$	i 4.00 h	$PdPv_2\downarrow\downarrow + AuPv_2\downarrow\downarrow$	×0.30	0.0	13
0.2		2.1 ; 2.7	$PtPv_3\downarrow \rightarrow PtPv_4\downarrow\downarrow$	i 4.00 h	$PtPv_4\downarrow\downarrow + AuPv_2\downarrow\downarrow$	×0.83	0.0	15
0.2		1.08 ; 1.9 ; 2.62	$Pt_2Pv_3\downarrow \rightarrow PtPv_3\downarrow \rightarrow PtPv_4\downarrow\downarrow$	i 3.68 h	$PtPv_4\downarrow\downarrow + AuPv_2\downarrow\downarrow$	×0.65	0.5	15
0.2		1.30 ; 2.05; 3.0	$PtPv_4\downarrow\downarrow \rightarrow AuPv\downarrow$	i 4.00 h	$PtPv_4\downarrow\downarrow + AuPv_2\downarrow\downarrow$	×0.92	0.0	15
0.9		c.i. 2.03 ; 2.85		i 4.00 h	$PtPv_2\downarrow\downarrow + AuPv_2\downarrow\downarrow$	0.52	0.0	15
0.5		1.75 ; 2.35; 3.06		i 4.00 h	$PtPv_2\downarrow\downarrow + AuPv_2\downarrow\downarrow$	0.76	0.0	14

mined in one titration (Expt. 18). The maximum density was low; probably more of the metal should have been used.

Mixtures of palladium and gold (Expts. 13 and 14) could also be titrated at pH *ca.* 1 in bromide solution; the palladium remained dissolved, and the gold was determined.

Mixtures of platinum and gold could be titrated at pH *ca.* 1 in bromide solution; the platinum remained dissolved and the gold was determined (Expt. 12). The sum of both metals could be determined at pH *ca.* 1 in thiocyanate solution (Expts. 22 and 23). Only gold was determined at pH *ca.* 7 in the iodide solution (Expt. 16). Both metals could be determined at pH *ca.* 1 in iodide solution in one titration, but the metal solution had to be more dilute (Expts. 19–21). The platinum always precipitated first.

METHODS

General remarks

1. In all the following determinations, the error at the first maximum density point was between zero and one per cent.
2. The intermediate end-point was always obtained from the intersection of the two adjacent lines (branches). The error at this point could be greatly reduced after experience had been gained in the method concerned.
3. In all titrations with iodide a red filter (Corning 2412) should be used.

1. *Determination of platinum*

Method A: Approximately 0.5 mg of platinum (as H_2PtCl_6) in 20 ml of aqueous solution, containing 4 ml of *M* nitric acid and 1–2 ml of 0.5 *M* potassium thiocyanate, was titrated with *ca.* 0.0015 *M* aqueous papaverine. The first maximum density point coincided with the quantitative formation of $PtPv_2\downarrow\downarrow$.

Method B: Approximately 0.4 mg of platinum (as H_2PtCl_6) in 20 ml of aqueous solution, containing 1 ml of 0.1 *M* potassium iodide and 2 ml of *M* nitric acid, was titrated with *ca.* 0.002 *M* aqueous papaverine. The first maximum density point coincided with the quantitative formation of $PtPv_4\downarrow\downarrow$.

2. *Determination of palladium*

Method A: Approximately 0.3 mg of palladium (as chloride) in 20 ml of aqueous solution, containing 1 ml of *M* nitric acid and 1–2 ml of 0.25 *M* potassium thiocyanate, was titrated with *ca.* 0.0015 *M* aqueous papaverine.

Method B: Approximately 0.3 mg of palladium (as chloride) in 20 ml of aqueous solution, containing 1 ml of *M* sodium acetate and 1 ml of 0.25 *M* thiocyanate, was titrated with *ca.* 0.0015 *M* aqueous papaverine

The first maximum density point in both methods A and B coincided with the quantitative formation of $PdPv_2\downarrow\downarrow$.

3. *Determination of gold*

Method A: Approximately 0.5 mg of gold (as chloride) in 20 ml of aqueous solution, containing 2 ml of *M* nitric acid and 1 ml of *M* potassium bromide, was titrated with *ca.* 0.002 *M* aqueous papaverine.

Method B: Approximately 0.3 mg of gold (as chloride) in 20 ml of aqueous solution, containing 2 ml of *M* nitric acid and 1 ml of 0.1 *M* potassium iodie, was titrated with *ca.* 0.00075 *M* aqueous papaverine.

Method C: Approximately 0.3 mg of gold (as chloride) in 20 ml of aqueous solution, containing 2 ml of *M* sodium acetate and 1 ml of 0.1 *M* potassium iodide, was titrated with *ca.* 0.00075 *M* aqueous papaverine.

The first maximum density point coincided with the quantitative formation of $AuPv_2\downarrow\downarrow$ in each of these three methods. Method B was preferable.

4. *Determination of palladium in platinum*

Method A: Proceed as in method 2 B.

Method B: Approximately 1.5 mg of the alloy, or of the metals as chlorides in 20 ml of aqueous solution, containing 2 ml of *M* sodium acetate and *ca.* 1 ml of *M* potassium bromide, was titrated with *ca.* 0.002 *M* aqueous papaverine. The first maximum density point occurred at quantitative formation of $PdPv_2\downarrow\downarrow$. Method A was preferable.

5. *Determination of gold in platinum*

Method A: Approximately 1.5 mg of the alloy or of the metals as chlorides in 20 ml of aqueous solution, was titrated according to method 3 A except that the amount of nitric acid added was reduced to 1 ml.

Method B: Approximately $\geqslant$ 1 mg of the alloy or the metals as chlorides was titrated according to method 3 C but with *ca.* 0.001 *M* aqueous papaverine.

6. *Determination of gold in palladium*

Proceed as in method 5 A but titrate with *ca.* 0.0015 *M* aqueous papaverine.

7. *Determination of gold in platinum and palladium*

$\geqslant$ 2 mg of alloy or metals as chlorides was titrated according to method 5 A.

8. *Determination of platinum and palladium*

Method A: Approximately 1 mg of the alloy or of the metals as chlorides in 20 ml of aqueous solution, containing 1 ml of *M* nitric acid and 2 ml of 0.25 *M* potassium thiocyanate, was titrated with *ca.* 0.003 *M* aqueous papaverine. Two critical points were obtained. The first point (the last intersection point) coincided with the quantitative formation of $PdPv_2$ ($\downarrow$) or of $PtPv_2$ ($\downarrow$). (The metal which was in excess precipitated at this point). The second point (the first maximum density point) coincided exactly with the quantitative formation of $PtPv_2\downarrow\downarrow + PdPv_2\downarrow\downarrow$.

Method B: Approximately 0.5 mg of the alloy or of the metals as chlorides in 20 ml of aqueous solution, containing *ca.* 1 ml of *M* nitric acid and 1 ml of 0.1 *M* potassium iodide, was titrated with *ca.* 0.003 *M* aqueous papaverine. Two critical points were obtained. The first point (the last intersection point) coincided with the quantitative formation of $PtPv_4$ ($\downarrow$). The second point (the first maximum density point) coincided exactly with the quantitative formation of $PtPv_4\downarrow\downarrow + PdPv_2\downarrow\downarrow$.

Method C: Approximately 1.5 mg of the alloy or of the metals as chlorides in 20 ml of aqueous solution, containing 1 ml of *N* acetic acid, 1 ml of *M* sodium acetate and 2 ml of 0.25 *M* potassium thiocyanate was titrated with *ca.* 0.004 *M* aqueous papaverine. Two critical points were obtained. The first point (the last intersection point) coincided with the quantitative formation of $PtPv_2\downarrow\downarrow$. The second point (the first maximum density point) coincided exactly with the quantitative formation of $PtPv_2\downarrow\downarrow + PdPv_2\downarrow\downarrow$.

9. *Determination of palladium and gold (in alloys of platinum, palladium and gold)*

Approximately 2 mg of the alloy or metals as chlorides in 20 ml of aqueous solution, containing 2 ml of *M* sodium acetate and 1 ml of 0.25 *M* potassium thiocyanate were titrated with *ca.* 0.003 *M* aqueous papaverine. Two critical points were obtained; the first point (the last intermediate point) coincided with the quantitative formation of $PdPv_2$ ($\downarrow\downarrow$). The second point (the first maximum density point) coincided exactly with the quantitative formation of $PdPv_2\downarrow\downarrow + AuPv_2\downarrow\downarrow$.

10. *Determination of platinum and gold*

Method A: Approximately 0.4 mg of the alloy or metals as chlorides was titrated according to method 8 B but with *ca.* 0.0015 *M* aqueous papaverine. Two critical points were obtained. The first point (the last intersection point) mostly coincided with the quantitative formation of $PtPv_4(\downarrow\downarrow)$, while the second point coincided exactly with that of $PtPv_4\downarrow\downarrow + AuPv_2\downarrow\downarrow$.

Method B: 1.2–1.5 mg of the alloy or the metals as chlorides was titrated according to method 8 A. The first maximum density point coincided exactly with the quantitative formation of $PtPv_2\downarrow\downarrow + AuPv_2\downarrow\downarrow$.

11. *Determination of papaverine*

Approximately 2 mg of papaverine in 20 ml of aqueous solution, containing 1 ml of *M* nitric acid and 1 ml of 0.25 *M* potassium thiocyanate, were titrated with aqueous *ca.* 0.001 *M* palladium chloride, or gold chloride.

The first maximum density point coincided with the quantitative formation of $MePv_2\downarrow\downarrow$.

SUMMARY

The reactions between papaverine and platinum(IV), palladium(II) or gold(III) in chloride, bromide, iodide and thiocyanate solutions, were studied heterometrically at pH values 1–9. The sequences and structures of intermediate and final compounds are discussed; the final compounds usually had the composition $MePv_2$. Methods are presented for the determination of the metals (0.3–0.5 mg) singly or in mixtures. In mixtures, all three metals could be determined directly from one or two titration curves.

RÉSUMÉ

Une étude hétérométrique a été effectuée sur les réactions se produisant entre la papavérine et le platine(IV), le palladium(II) et l'or(III) dans des solutions renfermant chlorure, bromure, iodure et thiocyanate. Plusieurs méthodes sont proposées pour le dosage de ces métaux (Pd, Au, Pt).

ZUSAMMENFASSUNG

Der Verlauf der Reaktionen zwischen Papaverin und Platin(IV), Palladium(II) und Gold(III) in Gegenwart von Chlorid, Bromid, Jodid und Thiocyanat wurde heterometrisch untersucht. Methoden zur Bestimmung dieser Metalle werden beschrieben.

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POLAROGRAPHIC DETERMINATION OF MANGANESE

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(Received December 12th, 1959)

INTRODUCTION

Although several polarographic methods for the determination of manganese have been devised, none is applicable to every kind of sample. VON STACKELBERG, KLINGER, KOCH AND KRATH[1] neutralized an acidic solution of the sample with barium carbonate to precipitate iron(III) and chromium, and measured the height of the cathode manganese(II) wave in the supernatant solution. Large amounts of nickel (and also of many other elements) or cobalt interfere with the measurement of the manganese diffusion current in this procedure, and necessitate a tedious preliminary separation of manganese as the dioxide. In addition, there would appear to be considerable danger of coprecipitation when traces of manganese are being determined.

VERDIER[2] recommended the use of a cyanide medium for the determination of manganese in the presence of chromium(III), copper, iron(II), and zinc, which were said to be polarographically inert in such a medium, and stated that cobalt was the only common interfering element. However, HUME AND KOLTHOFF[4] have since reported that nickel also yields a wave overlapping the manganese wave[3], and that chromium(III) will also interfere to the extent that it is present as $[Cr(CN)_6]^{-3}$.

VERDIER[5] also discovered an anodic wave corresponding to the oxidation of manganese(II) to manganese(III) in a strongly alkaline tartrate solution, and applied this to the determination of manganese in the presence of iron, nickel, and cobalt. Little information has been available concerning the effects of other elements that might be present.

A much more versatile method, developed by KOLTHOFF AND WATTERS[6], involves the measurement of the height of the cathodic manganese(III) wave in a moderately acidic pyrophosphate solution. Chloride, cerium, chromium, vanadium, and large amounts of iron interfere; although the metals can be removed by precipitation with pyridine, the chemical pretreatment required is rather lengthy. It is also disadvantageous that the manganese(III) complex is reduced at an appreciable rate by metallic mercury.

This paper describes a method employing the alkaline tartrate supporting electro-

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* Based on a thesis submitted by HENRY A. CATHERINO to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the B.S. in Chemistry degree, 1959.

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lyte devised by VERDIER[5]. Controlled 1/*n* potential electrolysis is used to remove interfering elements or render them innocuous, and also to ensure that no error can result from air-oxidation of the powerfully reducing manganese(II) complex prior to the polarographic measurement. The method is simple and accurate and is subject to no known interferences. It should be applicable to the determination of manganese in any kind of sample.

EXPERIMENTAL

Polarograms were obtained with a specially-designed recording polarograph which has been described elsewhere[7]. An H-cell[8] provided with a sintered-glass gas-dispersion cylinder for rapid deaeration[9] was used to obtain the data shown in Table I. A silver–silver chloride–saturated potassium chloride reference electrode was employed, but all half-wave potentials have been recalculated to refer to the more customary saturated calomel electrode. Frequent replacement of the agar bridge was necessary, apparently because of the fairly rapid diffusion of complex chloroargentous ions from the reference electrode compartment into the bridge, so that the agar deteriorated rapidly. Silver–silver chloride reference electrodes do not appear to be suitable for routine use with this type of cell.

Controlled-potential electrolyses were carried out with an Analytical Instruments, Inc. (Bristol, Conn.) potentiostat and a double-diaphragm cell with a conical working-electrode compartment[10]. Polarograms of the electrolyzed solutions were obtained without removing them from the cell by inserting a dropping electrode through a 10-mm i.d. vertical tube which was sealed to the horizontal cross-member of the cell and which provided access to the solution in the working electrode compartment. The cell was immersed in a water thermostat at 25.00 ± 0.02°. The silver–silver chloride reference electrode described by MEITES AND MOROS[11] was used without difficulty for both the electrolyses and the subsequent polarograms.

Reagent-grade chemicals were employed throughout. Mercury was purified by the procedure of MEITES AND MOROS[11]. Prepurified nitrogen was scrubbed with chromous chloride to ensure complete removal of oxygen.

DATA AND DISCUSSION

Data on the polarographic characteristics of 29 common metal ions in a supporting electrolyte containing 2.0 *F* sodium hydroxide and 0.25 *F* sodium tartrate are shown in Table I. The technique used in obtaining these data, and the precautions adopted to ensure their reliability, have been described elsewhere[12]. With a few exceptions which are probably due to the difference in supporting electrolyte compositions, these values are in generally good agreement with those obtained for a few of these ions in 0.1 *F* sodium hydroxide–0.5 *F* sodium tartrate by LINGANE[13].

From this information on the polarographic characteristics of manganese(II) and (III) in this medium, it is evident that any manganese(III) formed by air-oxidation during the preparation of the solution could be quantitatively re-reduced to manganese(II) by controlled-potential electrolysis even if the working electrode potential were maintained at a value as positive as —0.8 V *vs.* S.C.E. However, this is so near the foot of the manganese(III) wave that the reduction would proceed only very slowly, and it is therefore advantageous to employ a potential at least as negative

TABLE I

HALF-WAVE POTENTIALS OF METAL IONS IN 2.0 *F* SODIUM HYDROXIDE – 0.25 *F* SODIUM TARTRATE

Element and oxidation state	$E_{\frac{1}{2}}$ *(V) vs. S.C.E.*	*Oxidation state of product*	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ *(mV)*	*Notes*
As(III)	(—0.310)	V	+38	Very w.-d.
As(V)	NR			
Bi(III)	—0.961	0	—81	W.-d.
Cd(II)	—0.856	0	—26	Very w.-d.[a]
Ce(III)	(—0.30)	IV	+91	I.-d.
Ce(IV)	—0.3		—100	All very i.-d.
	—0.7		—100	
	—1.0		—100	
	—1.3	III[b]	—100	
Co(II)	—1.65	0	—80	I.-d.
Cr(III)	NR			
Cr(VI)	—0.913	III[b]	—92	W.-d.
Cu(II)	—0.52	0	—40	W.-d.
Fe(II)	(—1.00)	III	+58	W.-d.
	—1.38	0[c]	—135	I.-d.
Fe(III)	—1.00	II	—58	W.-d.
	—1.38	0[c]	—135	I.-d.
Mn(II)	(—0.46)	III	46	W.-d.
	—1.82	0	—40	I.-d.
Mn(III)[d]	—0.88	II	—80	Fairly i.-d.
	—1.82	0	—40	I.-d.
Mo(VI)	NR			
Ni(II)	NR			
Pb(II)	—0.827	0	—35	Very w.-d.
Sb(III)	(—0.389)	V	+45	W.-d.
	—1.332	0	—55	W.-d.
Sb(V)	NR			
Sn(II)[e]	(—1.01)	IV	+56	W.-d.
	—1.19	0	—62	W.-d.
Sn(IV)	NR			
Te(IV)	—1.39	0	—43	W.-d.
Te(VI)	NR			
Tl(I)[e]	—0.52	0	—59	W.-d.
U(VI)[f]	—0.87	?	—66	W.-d.
V(IV)	(—0.41)	V	+113	I.-d.
V(V)	—1.86	IV(?)	—100	I.-d.
W(VI)	NR			
Zn(II)[e]	—1.521	0	—51	W.-d.

[a] Maximum eliminated by 0.002% Triton X-100. [b] Confirmed by controlled-potential electrolysis. [c] The height of this wave is much less than twice that of the first wave, and prolonged controlled-potential electrolysis on its plateau yields Fe(II) as the only identifiable product. [d] Prepared by controlled-potential electrooxidation of Mn(II) in this medium. [e] With 0.002% Triton X-100. [f] Partial precipitation.

as —1.0 V *vs.* S.C.E. in order to achieve essentially complete reduction within a reasonable length of time. At the same time, there is no danger of reducing manganese to the metallic state unless the working electrode potential becomes more negative than about —1.65 V *vs.* S.C.E. In view of these considerations, a working electrode potential of —1.50 V *vs.* S.C.E. was selected for use in subsequent experiments.

The proportionality between the diffusion current of the anodic wave and the concentration of manganese was examined by the following procedure, in which controlled-potential electrolysis was employed to ensure that the manganese was entirely present in the +2 state prior to the polarographic measurement. Exactly 100 ml of 2.0 *F* sodium hydroxide–0.25 *F* sodium tartrate was pipetted into the working-electrode compartment of a controlled-potential electrolysis cell containing about 25 ml of pure mercury, and was deaerated briefly with a rapid stream of nitrogen. The central and auxiliary-electrode compartments of the cell had previously been filled with the supporting electrolyte solution in accordance with the standard procedure[10], and a few drops of saturated hydrazine dihydrochloride solution had been added to the auxiliary-electrode compartment to prevent anodic attack of the platinum wire used as the auxiliary electrode. A measured volume of a standard manganese(II) solution was then added. This usually resulted in the appearance of a yellow to brown color due to manganese(III) formed by reaction with the oxygen dissolved in the standard solution, but no precipitation was ever observed. The solution was then electrolyzed at a working-electrode potential of —1.50 V *vs.* S.C.E. for 45 min. This sufficed to decrease the electrolysis current, which was indicated by the counting rate of an Analytical Instruments, Inc., current integrator connected in series with the cell, to a value indistinguishable from the background current obtained when the supporting electrolyte alone was electrolyzed under the same conditions. In routine work it would, of course, suffice to electrolyze only until about 99.5% of the manganese had been reduced to the +2 state, which would require considerably less time than was used here, and a further saving of time could be achieved by using a smaller volume of solution.

When the electrolysis was complete, the potentiostat was turned off, the nitrogen stream was diverted over the surface of the solution, a dropping electrode was lowered into the solution, and the reference electrode was disconnected from the potentiostat and connected to the polarograph. A typical polarogram of manganese(II) obtained in this way is shown in Fig. 1.

Especially when the concentration of manganese is very small, it is essential to exercise considerable care in the measurement of the diffusion current. This is partly

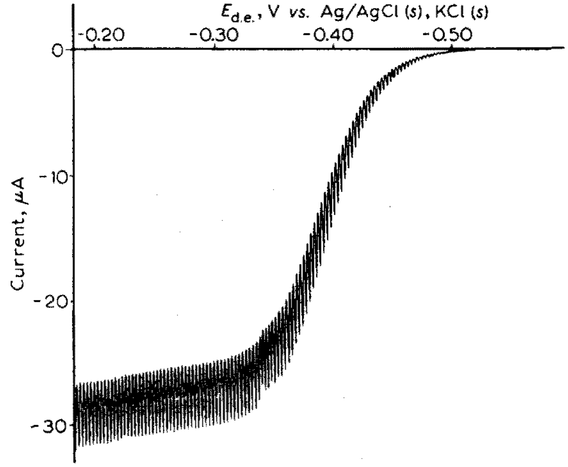

Fig. 1. Polarogram of 5.86 m*M* manganese(II) in 2.0 *F* sodium hydroxide – 0.25 *F* sodium tartrate, obtained after a controlled-potential electrolysis at —1.50 V *vs.* S.C.E. m = 2.93 mg/sec; t = 3.41 sec at $E_{d.e.}$ = —0.36 V *vs.* S.C.E.

due to the fact that the residual current curve is appreciably curved over the range of potentials corresponding to the plateau of the wave, so that the customary extrapolation procedures do not yield a sufficiently accurate estimate of the residual current correction. Another problem is due to the presence of traces of iron in the sodium tartrate employed in the supporting electrolyte. Iron is converted to the ferrous state by a controlled-potential electrolysis at -1.50 V *vs.* S.C.E. in this medium. As shown by the very negative half-wave potential of its anodic wave (-1.00 V *vs.* S.C.E.), ferrous iron is an extremely powerful reducing agent under these conditions, and it reacts rapidly with any traces of oxygen entering from the atmosphere. Hence the anodic diffusion current of ferrous iron decreases slowly on standing, and this, of course, causes the residual current at potentials on the manganese(II) wave to drift toward more positive values. The average magnitude of this effect was found to be about $5 \cdot 10^{-5}$ μA/min. It is thus negligible unless the concentration of manganese is very small. However, it is obviously desirable to record the polarogram as rapidly as possible after the completion of the electrolysis to minimize errors resulting from this cause.

The diffusion currents listed in Table II were obtained by the following procedure. The residual current portion of the polarogram, which begins at about -0.57 V *vs.* S.C.E., was extrapolated linearly toward less negative potentials, and the wave height was taken as the vertical distance between this extrapolated line and the midpoint of the oscillations on the plateau at the arbitrarily selected potential of -0.36 V *vs.* S.C.E., which is just barely on the plateau of the wave. This procedure tends to eliminate errors resulting from the slow air-oxidation of ferrous iron, which merely shifts the entire polarogram upward along the current axis, and is therefore preferable to a correction based on the measurement of the residual current in a separate experiment with the supporting electrolyte alone. Moreover, the use of as positive a potential as possible tends to minimize the effect of the curvature of the residual current curve.

The data shown in Table II demonstrate that the diffusion current thus measured is proportional to the concentration of manganese over at least a 100-fold range with

TABLE II

DIFFUSION CURRENT CONSTANT OF MANGANESE(II) IN 2.0 *F* SODIUM HYDROXIDE – 0.25 *F* SODIUM TARTRATE

c *mmoles/l*	i_d μA	i_d/c $\mu A/mmoles/l$
0.06225	-0.0893	-1.44_{6}
0.2042	-0.294_{3}	-1.43_{6}
0.4009	-0.576_{2}	-1.43_{7}
0.5900	-0.861_{2}	-1.45_{1}
0.7721	-1.137	-1.47_{2}
2.192	-3.162	-1.44_{2}
3.978	-5.68	-1.42_{7}
5.952	-8.58	-1.44_{1}
7.663	-10.92	-1.42_{5}
		Mean: $-1.44_{2} + 0.01_{0}$
		$i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}} = -0.95_{4} \pm 0.00_{7}$

The data were obtained with a capillary for which $m = 1.190$ mg/sec and $t = 5.93$ sec at $E_{d.e.} = -0.36$ V *vs.*S.C.E.

a mean error of only ±0.7%. The mean value of the diffusion current constant is in good agreement with that (—1.03) obtained by MEITES[14].

It was found that the diffusion current of manganese(II) in this medium is unusually sensitive to changes in supporting electrolyte concentration. In 1.75 *F* sodium hydroxide–0.22 *F* sodium tartrate, for example, the diffusion current is about 20% higher than in 2.0 *F* sodium hydroxide–0.25 *F* sodium tartrate under otherwise exactly the same conditions. The supporting electrolyte concentration must therefore be controlled to within about ±5%; variations equal to or smaller than this have no detectable effect on the diffusion current.

Care in cleaning the cell between analyses is essential to the success of this procedure. If it is merely washed with water, manganese compounds precipitate on its walls and in the pores of the sintered-glass disc and gas-dispersion cylinder, and remain there to contaminate the next sample. This is best eliminated by thorough washing with saturated oxalic acid or with dilute hydrochloric acid containing a little hydrogen peroxide.

The effects of other elements on the measurement of the anodic diffusion current of manganese(II) in this medium can easily be deduced from the data given in Table I. Arsenic(III), antimony(III), tin(II), and vanadium(IV) give rise to waves overlapping the manganese wave, and would therefore interfere seriously.

However, these potential interferences are easily eliminated by the simple expedient of employing an oxidizing attack in the preparation of the sample, because the higher oxidation state of each is polarographically inert in this supporting electrolyte. This inertness is shared by molybdenum, nickel, and tungsten.

When the solution of the sample is electrolyzed at —1.50 V *vs.* S.C.E. to ensure that the manganese is entirely present in the +2 state, a number of other elements will be reduced to the metallic state and removed from the solution. These include bismuth, cadmium, copper, lead, tellurium, and thallium. Cobalt and zinc can also be completely deposited, but only by a very prolonged electrolysis. However, both can be rapidly and completely removed by increasing the working electrode potential to about —1.65 V *vs.* S.C.E.; this may be useful in determining traces of manganese in the presence of a large amount of either of these elements, because it eliminates any effect they may have on the viscosity and tartrate concentration of the solution.

Electrolysis at —1.50 V *vs.* S.C.E. also converts chromium to the +3 state, which is inert, iron to the +2 state, and cerium to the +3 state. Iron(II) gives rise to an anodic wave whose half-wave potential is —1.00 V *vs.* S.C.E. This wave is so well-defined that no further treatment is necessary unless its height is so large as to interfere with the measurement of the height of the manganese wave. However, if the iron/manganese ratio is very large, which will very often be the case, it is necessary to re-oxidize most of the iron to the +3 state by a controlled-potential electrolysis at about —0.8 V *vs.* S.C.E. It suffices to carry out this second electrolysis until the concentration of iron(II) remaining unoxidized becomes roughly equal to the concentration of manganese.

Successive controlled-potential electrolyses at —1.50 V and at —0.8 V *vs.* S.C.E. therefore yield a solution of which cerium(III) is the only constituent that can give rise to a wave interfering with the measurement of the diffusion current of the anodic manganese(II) wave. Unless the cerium/manganese ratio is extremely high, which would be very unusual, the interference of cerium can be eliminated by the following additional steps. A polarogram of the solution is obtained at the end of the electrolysis at —0.8 V *vs.* S.C.E. (or, if the iron/manganese ratio is small enough to permit it, this electrolysis may be omitted and the polarogram may be obtained at the end of the electrolysis at —1.50 V *vs.* S.C.E.), and the diffusion current at —0.36 V *vs.* S.C.E. is obtained as described above. This will include a contribution from the oxidation of cerium(III). If copper is known or believed to be present in the sample, the electrolytic mercury is discarded and replaced by fresh mercury to avoid reoxidation of the previously deposited copper during the next step. This is necessary because copper(II) gives a wave in the range of potentials used to establish the residual current line in measuring the diffusion current in the next step. The potential of the working electrode is now adjusted to —0.44 V *vs.* S.C.E., and the solution is electrolyzed until the electrolysis current becomes constant. Manganese(II) is quantitatively reoxidized to manganese(III) by this electrolysis, but cerium(III) is unaffected. At the completion of this electrolysis a second polarogram is recorded. The diffusion current at —0.36 V *vs.* S.C.E. is measured from this polarogram and subtracted from that obtained from the first polarogram. The difference between these two values is equal to the diffusion current of manganese. By this procedure results accurate to within ±1% were obtained in analyses of samples containing equal concentrations of manganese and cerium.

The considerations just outlined were checked by analyses of synthetic samples containing known amounts of manganese together with various other elements, and were then combined to give the following procedure, which is recommended for use in practical work.

RECOMMENDED PROCEDURE

Weight about 0.5 g of the sample into a small flask and add first 20 ml of 6 *F* perchloric acid, then 10 ml of concentrated nitric acid. Evaporate to fumes of perchloric acid, cool, and transfer to a 100-ml volumetric flask, using 50 ml of 6.5 *F* sodium hydroxide–0.62 *F* sodium tartrate in several small portions for rinsing the flask in which the sample was dissolved. Dilute to the mark with water and mix.

Fill the central compartment of a clean double-diaphragm cell for controlled-potential electrolysis with 2.0 *F* sodium hydroxide–0.25 *F* sodium tartrate and insert the stopper. Into the auxiliary-electrode compartment of the cell pour enough of the same solution so that its level during the electrolysis will be just above that of the solution in the working-electrode compartment, and add a few drops of saturated hydrazine dihydrochloride solution to protect the platinum auxiliary electrode.

Pour about 50 ml of the solution of the sample into the working-electrode compartment, add about 30 ml of pure mercury, and pass a rapid stream of oxygen-free nitrogen into this solution. Adjust a potentiostat to maintain the potential of the working electrode at —1.50 V *vs.* S.C.E., and electrolyse until the current has decreased to a low and practically constant value.

If the percentage of iron in the sample is expected to be greater than about ten times the percentage of manganese, reset the potentiostat to maintain the working electrode potential at —0.8 V *vs.* S.C.E. and electrolyze at that potential until the concentration of iron(II) remaining unoxidized becomes too small to interfere with the measurement of the height of the manganese wave. The time required for this step will depend on the iron/manganese ratio; with optimum stirring in a cell of the type used in these experiments, the time (in minutes) needed can be estimated from the equation $t = 7 \log (\% \text{Fe}/\% \text{Mn})$.

Insert a dropping electrode into the electrolyzed solution, divert the nitrogen stream over the surface of the solution, turn off the potentiostat and the stirrer, and obtain the polarogram of the solution from 0.2 to —0.7 V *vs.* S.C.E. It is convenient to use a low-resistance reference electrode for both the electrolytic and polarographic steps in order to simplify the apparatus required.

Measure the diffusion current at —0.36 V *vs.* S.C.E., employing the modified extrapolation method described above. If cerium is known to be present in the sample, or if the presence of cerium is indicated by a considerable increase of the anodic diffusion current with increasing positive potential on the plateau of the wave, carry out another controlled-potential electrolysis at —0.44 V *vs.* S.C.E. This should be continued until the electrolysis current has become constant. At its conclusion, obtain a second polarogram in the same fashion, and find the diffusion current of manganese as described above.

The concentration of manganese in the prepared solution may be calculated from the equation $C_{\text{Mn}} = -i_d/0.954\, m^{2/3}t^{1/6}$.

Typical results obtained by this method are shown in Table III, in which the polarographic results are seen to agree with the National Bureau of Standards certificate values to well within the probable uncertainties of the latter.

TABLE III

DETERMINATION OF MANGANESE IN NATIONAL BUREAU OF STANDARD SAMPLES

Sample description and N.B.S. designation	*Certified composition*	*% Mn found*
62b	1.29% Mn; 57.4% Cu, 38.0% Zn, 1.0% Al, 1.0% Sn, 0.8% Fe, 0.3% Pb, 0.3% Ni, 0.05% Si, 0.005% As, 0.0005% Sb, 0.004% Ag	1.28_6
72d	0.537% Mn; 1.0% Cr, 0.31% C, 0.28% Si, 0.21% Mo, 0.13% Ni, 0.04% Cu, 0.02% P, 0.01% S, 0.005% V	0.531

SUMMARY

A method for the polarographic determination of manganese is described. It depends on the measurement of the diffusion current of the anodic wave of manganese(II) in a sodium hydroxide–sodium tartrate supporting electrolyte following controlled-potential electrolyses which serve to convert manganese quantitatively into the desired state and to remove other potentially interfering elements or render them innocuous. It is simple, accurate, and specific, and should be applicable to the determination of manganese in any type of sample.

RÉSUMÉ

Une méthode est décrite pour le dosage polarographique du manganèse. Elle est basée sur la mesure du courant de diffusion de la vague anodique du manganèse(II), en utilisant le mélange hydroxyde de sodium, tartrate de sodium comme électrolyte de base.

ZUSAMMENFASSUNG

Beschreibung einer polarographischen Methode zur Bestimmung von Mangan, die auf der Messung des Diffusionstromes der anodischen Welle von Mangan(II) beruht. Als Grundelektrolyt wird eine Mischung von Natriumhydroxyd und Natriumtartrat verwendet.

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SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH 1,4-DIPHENYLTHIOSEMICARBAZIDE WITH SPECIAL REFERENCE TO METEORITES

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(Received December 10th, 1959)

For the photometric determination of ruthenium in meteorites, a reagent is needed which will allow 0.5–15 μg Ru to be determined in a 1- or 2-g sample without separation of osmium. 2,4-Diphenylthiosemicarbazide appeared to be a promising possibility. Its use for the determination of 8–30 μg Ru has recently been described[1]. In addition to not reacting appreciably with osmium, it has the advantage of giving a chloroform-extractable ruthenium complex. Adequate sensitivity can thus be obtained by extracting ruthenium into a relatively small volume of chloroform after distillation of the tetroxide, in spite of the mediocre intrinsic sensitivity (0.010 μg Ru/cm^2 for A = 0.001 at 565 mμ).

A trial of 2,4-diphenylthiosemicarbazide for the determination of ruthenium following separation as the tetroxide showed the reagent to have some shortcomings. The color intensity was found to vary somewhat with the concentration of the sulfur dioxide or hydroxylammonium chloride solution in which ruthenium tetroxide is

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caught on distillation. Stannous chloride is not suitable as an absorbent because it decreases the color intensity. Moreover, the blank absorbance (sulfur dioxide–hydrochloric acid) fluctuates from 0.006 to 0.015 (5 ml chloroform, 1-cm cell).

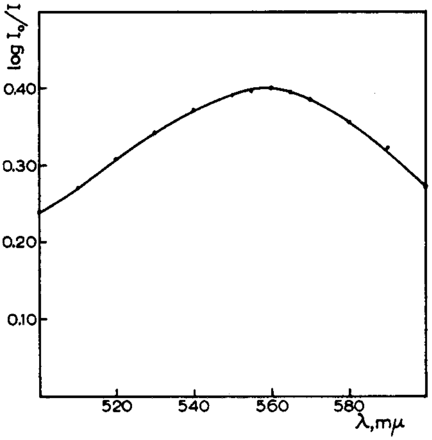

Fig. 1. Absorption curve of ruthenium 1,4-diphenylthiosemicarbazide complex in chloroform (20 μg Ru in 5 ml).

This variability makes 2,4-diphenylcarbazide unsuitable for determining less than 5–10 μg Ru.

We have found that 1,4-diphenylthiosemicarbazide is a more satisfactory reagent. This compound has been listed as a qualitative color reagent for ruthenium but has not been used quantitatively[2]. It gives a blank absorbance of zero under the conditions of the determination. Like the 2,4 isomer, it does not react with osmium and its red-violet ruthenium complex is extractable into chloroform. The sensitivity is 0.010

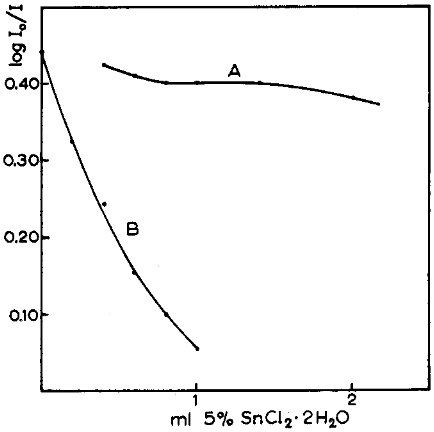

Fig. 2. Effect of stannous chloride concentration on color development with (*A*) 1,4-diphenylthiosemicarbazide, and (*B*) 2,4-diphenylthiosemicarbazide. Color developed in 80 ml 6 *N* hydrochloric acid; 5 ml chloroform for extraction; 20 μg Ru.

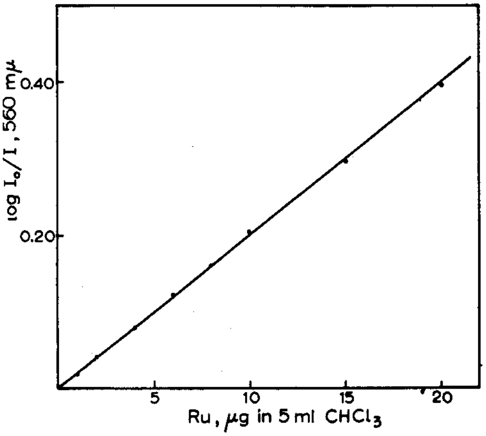

Fig. 3. Standard curve, Ru–1,4-diphenylthiosemicarbazide.

μg Ru/cm² in chloroform for A = 0.001 at 560 mμ. The absorbance curve is shown in Fig. 1.

Stannous chloride is a suitable absorbent for ruthenium tetroxide in the determination of ruthenium with the 1,4 reagent. The composition of the ruthenium complex (or complexes) has not been established. Ruthenium is probably present in the +3 oxidation state.

Factors affecting color intensity and stability

The principal factors are the acidity, time of heating, and the stannous chloride concentration. The color develops slowly at low hydrochloric acid concentrations, more rapidly at higher, but fading occurs if the acidity is too great. The optimum hydrochloric acid concentration is 5.5–6.5 *N*. Full color development is obtained on heating for 10–15 min at 100°. The concentration of stannous chloride must be regulated fairly closely. In the range 0.8 to 1.4 ml of 5% $SnCl_2 \cdot 2\,H_2O$ in 80 ml of 6 *N* hydrochloric acid solution the color intensity remains constant (Fig. 2).

The absorbance is proportional to the ruthenium concentration at least as high as 20 μg Ru in 5 ml of chloroform. The precision of the procedure may be judged from Fig. 3. The results in Table I (obtained without separating ruthenium by volatilization of the tetroxide) show that a tenfold quantity of osmium can be tolerated but that rhenium interferes by giving a coloration.

TABLE I

DETERMINATION OF RUTHENIUM IN THE PRESENCE OF OSMIUM AND RHENIUM

Addition	*μg Ru*	
	taken	*found*
100 μg Os[a]	0	0.0
100 μg Os	1.0	1.0
100 μg Os	2.0	2.0
100 μg Os	5.0	4.9
140 μg Os	10.0	9.6
140 μg Os	20.0	19.8
100 μg Re[b]	0	5.5
100 μg Re	2.0	7.4

[a] As K_2OsCl_6
[b] As $KReO_4$

Separation of ruthenium

Volatilization of ruthenium as tetroxide has been adopted for its separation from iron and other constituents of the sample. A combination of sodium bismuthate and potassium permanganate as oxidizing agents was found to give satisfactory recoveries of ruthenium*. The large amount of ferrous iron in solution after dissolving iron meteorites in a non-oxidizing acid can best be oxidized with permanganate. The excess of the latter must be controlled. An excess greater than about 0.01 g leads to slightly low recoveries in the subsequent distillation. For example, 0.2 g of potassium permanganate in excess gave 90% recovery of 5 μg Ru, compared to 99% recovery

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* Unexpectedly, recoveries of 1 μg Ru (added as $(NH_4)_2RuCl_6$) amounted to 85–88% when 0.5 or 1 g $NaBiO_3$ was used alone as oxidizing agent. With 5 μg Ru, the recovery was 95% with bismuthate alone.

with 0.01 g in excess (1 g sodium bismuthate also present in each). Oxidation of ferrous iron with excess chromic acid or cerium(IV), followed by addition of sodium bismuthate and distillation, gave poor recoveries of ruthenium; in the absence of ferrous iron initially, good recoveries could be obtained with either oxidizing agent in combination with bismuthate.

TABLE II

DETERMINATION OF RUTHENIUM AFTER DISTILLATION AS THE TETROXIDE

Addition	*μg Ru*	
	taken	*found*
1 g Fe(II)	0	0.0
1 g Fe(II)	1.0	1.0
1 g Fe(II)	2.0	1.85
1 g Fe(II)	5.0	4.8
1 g Fe(II)	20.0	19.8
1 g Fe(II), 0.4 g Ni	1.0	1.0
1 g Fe(II), 0.2 g Ni	5.0	5.0
1 g Fe(II), 100 μg Os, 100 μg Re	1.0	0.9
1 g Fe(II), 100 μg Os, 100 μg Re	2.0	1.9
1 g Fe(II), 100 μg Os, 100 μg Re	5.0	4.8
1 g Fe(II), 100 μg Os, 100 μg Re	8.0	8.0

Nitric acid, chlorine and other volatile strong oxidizing agents must not be present in the distillation mixture. They react with 1,4-diphenylthiosemicarbazide to give a yellow oxidation product. The meteorite sample is therefore treated with hydrochloric acid to dissolve the metal phase, chlorides are converted to sulfates by evaporation with sulfuric acid, and iron(II) is then oxidized with permanganate. Silicates and any other insoluble material are decomposed with sodium peroxide and the solution of the melt is combined with the acid portion.

Rhenium does not distil since its heptoxide is not appreciably volatile at the distillation temperature (~ 108°) of the procedure. Osmium will of course accompany ruthenium in the distillation, but this does not matter because of the tolerance of the reagent to this element.

The results in Table II demonstrate that satisfactory recoveries of microgram amounts of ruthenium can be obtained in the presence of much iron by the distillation method. A simulated determination of ruthenium in an iron meteorite, in which ruthenium was added to iron metal and the whole procedure carried through, gave recoveries of 95% (Table III). Further, the recovery of ruthenium from a stony meteorite was checked by adding 1.0 and 2.0 μg Ru to 2-g portions of the Ness County, Kansas, chondrite. Subtraction of the ruthenium present in the meteorite (1.44 μg in

TABLE III

DETERMINATION OF RUTHENIUM IN IRON[a]

μg Ru taken	1.0	2.0	5.0	8.0
μg Ru found	0.95	1.9	4.8	7.6

[a] Ru added as $(NH_4)_2RuCl_6$ to 1.0 g pure metallic iron which was dissolved in HCl. Chlorides were converted to sulfates by evaporating to fumes with sulfuric acid. Distillation of RuO_4 carried out as in procedure after oxidizing Fe(II) with slight excess of $KMnO_4 \cdot Na_2O_2$ fusion was made.

2 g) as determined by the proposed method, gave recoveries of 0.91 and 1.92 μg Ru, or 91 and 96%. From these results it appears that application of a +5% correction will bring the analytical values closer to the true value.

EXPERIMENTAL

Distillation apparatus

The apparatus described by BANKS AND O'LAUGHLIN[3] is suitable. This consists of a 125-ml Erlenmeyer flask connected to a vertical condenser, the lower end of which reaches almost to the bottom of a 125-ml Erlenmeyer receiving flask, to which is attached a bubbler tube. Connections are made by means of ground glass joints. An inlet tube extends to the bottom of the distillation flask so that air can be passed through the apparatus to facilitate the volatilization of ruthenium tetroxide. Absorbing solution is placed in both the receiver flask and the bubbler. Doubtless similar distillation apparatus can be used as well, with an increase in distillation time if need be.

Special solutions

1,4-Diphenylthiosemicarbazide, saturated solution at room temperature in methyl alcohol. The reagent may be synthesized as follows, essentially according to the procedure of WALTHER[4]. Heat 40 g of thiocarbanilide with 70 g of phenylhydrazine on the water bath. Stir until the mixture suddenly crystallizes to a paste. Add 150 ml of methyl alcohol and stir the warm mixture well. Cool to room temperature, filter off the solid on sintered glass, and wash with small portions of methyl alcohol until the washings are colorless. Dry the product in a vacuum desiccator protected from strong light. M.p. 176°.

Stannous chloride, 5.0 g of $SnCl_2 \cdot 2\,H_2O$ in 100 ml of 6.0 N hydrochloric acid. Filter if not clear. Prepare fresh every 3 days.

Potassium permanganate, 1% aqueous solution.

Standard ruthenium solution. Ammonium chlororuthenate(IV) furnishes a convenient source of ruthenium*. Prepare a stock solution containing approximately 250 p.p.m. Ru by dissolving 0.20 g of ammonium chlororuthenate in 250 ml 1 N sulfuric acid. Dilute this solution with water to obtain a standard solution containing approximately 10 p.p.m. Ru. Determine the ruthenium content of the ammonium chlororuthenate by ignition to the metal in a stream of hydrogen in the usual way.

PROCEDURE

Iron meteorites

Dissolve 1 g of sample in 40 ml of 1 : 3 hydrochloric acid in a beaker, warming to hasten solution. Cool to room temperature and add 10 ml of concentrated sulfuric acid. Evaporate to fumes and continue fuming for 20 min. Cool to room temperature and add 35 ml of water. Warm to dissolve ferrous sulfate.

Filter the solution through a small porous porcelain crucible, the bottom of which has been covered with about 50 mg of aluminum oxide powder. Wash with a little water and transfer filtrate and washings to the original beaker. Place this on a steam bath to reduce the volume of the solution.

Dry the crucible in an oven and transfer the aluminum oxide and any insoluble material to a nickel crucible. Add to the latter about 0.5 g of sodium peroxide, which first has been used to clean the porcelain crucible. Heat the nickel crucible to low redness for 20–30 min, occasionally swirling the contents. Cool the crucible and dissolve the melt in 10 ml of water. Transfer the solution to a small beaker and cool in ice water. Add a slight excess of dilute sulfuric acid (cessation of gas evolution). Combine this solution, together with the few drops of sulfuric acid used to clean the nickel crucible, with the main portion, and continue the evaporation to a volume of about 40 ml.

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* Chlorides or sulfates of Ru(III) or (IV) can also be used.

Transfer the solution to the distilling flask, using 10 ml of water for rinsing so that the total volume is near 50 ml. Cool the flask in ice water and oxidize ferrous iron with a slight excess of permanganate. This is best done by adding finely powdered potassium permanganate in small portions with good mixing until the major portion of the ferrous iron has been oxidized, and completing the oxidation by adding 1% potassium permanganate solution. Add an excess of 1 ml of the latter. If too large an excess of permanganate is added, it can of course be destroyed with ferrous ammonium sulfate and a new adjustment made.

Add 1 g of sodium bismuthate to the flask, avoiding getting any on the neck of the flask. The volume of the solution at this point should be 50–60 ml. Immediately connect the flask to the condenser, which has been attached to the receiver flask containing 40 ml of 0.1% stannous chloride solution (add 1.0 ml 5% stannous chloride to 50 ml of 6.0 *N* hydrochloric acid and place 40 ml of this solution in the receiver and 10 ml in the bubbler). Heat the distillation flask with a burner and pass air through the system at a rate of two bubbles per second. After the solution has begun to boil and the condensate has reached the upper part of the condenser, continue the distillation for 5 min.

Disassemble the apparatus and transfer the absorbing solution (including that in the bubbler) to a 150-ml Erlenmeyer flask. Rinse the condenser and receiver with 30 ml of 6.0 *N* hydrochloric acid and add the rinsings to the Erlenmeyer. Add 3.0 ml of 1,4-diphenylthiosemicarbazide solution, mix, and heat the flask in a water bath at 100° for 12 min. Cool, transfer the solution to a separatory funnel, and rinse the flask with 20 ml 6 *N* hydrochloric acid, so that the total volume is close to 100 ml. Add 5.0 ml of reagent-grade chloroform and shake for one min. Allow the phases to separate, and, if the chloroform layer is not entirely free from water droplets, filter it through a very small rapid filter paper. Measure the absorbance of the extract against chloroform in a 1-cm cell at 560 mμ.

Establish the standard curve by taking 0, 5, 10, 15 and 20 μg of Ru(IV) and proceeding as described in the preceding paragraph. Run a blank through the whole procedure.

Silicate meteorites

Treat 2–2.5 g of crushed, representative sample with hydrochloric acid and evaporate with sulfuric acid as described under iron meteorites. Filter off the insoluble material in a porous porcelain crucible, wash, dry and fuse with 5 g of sodium peroxide in a nickel crucible. Then continue as described under iron meteorites.

ACKNOWLEDGEMENT

This work was made possible by a DuPont postdoctoral grant.

SUMMARY

Ruthenium is determined in iron and silicate meteorites as the red-violet chloroform-extractable complex of 1,4-diphenylthiosemicarbazide, following volatilization as the tetroxide by oxidation with potassium permanganate and sodium bismuthate. Osmium need not be separated. From 0.5 to 15 p.p.m. (or more) of Ru can be determined in 1–2 g samples.

RÉSUMÉ

Les auteurs ont établi une méthode pour le dosage spectrophotométrique du ruthénium dans les météorites. Elle est basée sur la formation du complexe violet rouge, obtenu avec la diphényl-1,4-thiosemicarbazide. Le ruthénium est séparé au préalable par distillation de son tétroxyde (oxydation avec le permanganate de potassium et le bismuthate de sodium).

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur spektrophotometrischen Bestimmung von Ruthenium in Meteoriten. Sie beruht auf der Reaktion mit Diphenyl-1,4-thiosemicarbazid unter Bildung eines rotviolett gefärbten Komplexes. Zur Abtrennung wird Ruthenium zum Tetroxyd oxydiert und dieses abdestilliert.

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POLAROGRAPHIC DETERMINATION OF TRACES OF EUROPIUM IN MINERALS AND ORES*

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(Received October 16th, 1959)

INTRODUCTION

Among the rare earth elements with high capture cross-sections, europium is most likely to be used in reactor components such as control rods, etc. Europium is generally present in negligible amounts in minerals rich in rare earths[1,2]. In nature it usually occurs in the bivalent state and consequently does not accompany the other lanthanides which are trivalent; instead it becomes concentrated in other minerals. A survey of the analytical data for most minerals reveals that results for europium are rarely reported.

Various volumetric[3] and spectrophotometric[4,5] determinations of europium have been described but none of these is suitable for determination of trace amounts of europium in minerals and ores.

In the polarographic study of rare earth metals[6,7] it has been shown that europium gives a wave at —0.67 V *vs.*S.C.E. in 0.1 M ammonium chloride supporting electrolyte; this is convenient for analysis because it is well separated from the half-wave potentials of the only other two rare earth elements which give waves, *viz.* samarium and ytterbium at —1.80 and —1.17 V respectively. Among the rare earths only these three elements are reduced from the trivalent to the divalent state. The reduction of the others proceeds from the trivalent state to the metal, with half-wave potentials between —1.75 and —1.95 V *vs.* S.C.E.

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* Presented to the Indian Standards Convention held in December 1959.

HOLLECK[6] proposed an indirect polarographic determination of europium which involved additions of known concentration of zinc to the rare earth solution and the calculation of the europium content from the difference in the wave heights obtained for zinc. LAITINEN AND TAIBEL[7] suggested that "since europium occurs only in very small concentrations in natural rare earth minerals, the usual analytical problem involves its determination in rare earth mixtures in which the europium concentration has been greatly increased by partial separation", but they did not indicate which special procedure was to be followed. They did not determine europium in minerals but used a synthetic mixture of europium and ytterbium oxides and determined europium polarographically, the percentage of europium oxide in the mixture being as high as 55.0% and 54.7%.

A better sensitivity in the determination of europium and ytterbium was obtained by POMEROY *et al.*[8] who used differential polarography. They proposed a modification of the Cambridge polarograph for derivative polarography and repeated the work of LAITINEN AND TAIBEL on the derivative polarograph. It was again not clear whether any partial separation of europium was made and what were the lowest limits in their determinations.

In the method described in this paper europium is determined in the total rare earths obtained from minerals without any further concentration of the element. The measurements were made at —0.67 V *vs.* S.C.E. in a supporting electrolyte of 0.1 *M* ammonium chloride on a "Du Bellay" polarograph.

EXPERIMENTAL

Standardisation

A linear relationship was obtained with 25 to 200 μg of europium in 25 ml of the solution containing 2.5 ml of 1.0 *M* ammonium chloride as supporting electrolyte.

Determination in minerals

In the case of minerals and ores 0.5 to 2 g of the sample was decomposed and the total rare earths were separated by conventional analytical procedures. The rare earth oxides obtained by ignition at 600° were dissolved in the minimum amount of

TABLE I

STANDARD ADDITION OF EUROPIUM TO DIFFERENT ORES

No.	*Sample*	*Weight of the sample g*	*Eu added μg*	*Total Eu expected μg*	*Eu found μg*	*% Difference*
1	Monazite	0.5	0.0	—	80	—
1a	Monazite	0.5	25	105	100	—4.76
1b	Monazite	0.5	50	130	130	0.0
1c	Monazite	0.5	75	155	160	+3.2
2	Crude rare earth oxide	0.5	—	—	160	—
2a	Crude rare earth oxide	0.5	200	360	360	0.0
2b	Crude rare earth oxide	0.5	400	560	560	0.0
3	Samarskite	1.0	—	—	75	—
3a	Samarskite	1.0	100	175	181	+3.5

hydrochloric acid and the solution was evaporated on a water bath. The residue was taken up with water, 2.5 ml of 1 M ammonium chloride were added and the volume was diluted to 25 ml in a measuring flask. A polarogram was then recorded.

For the polarographic determination europium had to be in the trivalent state and large amounts of lead, if present, had to be removed; for lead in an ammonium chloride supporting electrolyte gives a wave, the half wave potential being —0.45 V (approx.) *vs.* S.C.E. which is not far from the half wave for europium. Lead was removed by fuming the sample solution with sulphuric acid and separating the lead before the rare earths were separated. Any residual lead did not interfere in the determination.

In order to test the recoveries of europium in the separation process and the accuracy of the determination, the method of standard addition was adopted. The europium was added when the sample was dissolved before the separation of total rare earths. The results obtained with monazite and samarskite and a sample of crude rare earth oxides are given in Table I.

As can be seen from the Table, the accuracy of the determination in the range studied was better than 5%; with a 2-g sample, it is possible to determine as little as 10 p.p.m. in the sample. The results on monazite and samarskite samples showed europium contents of 0.016% and 0.0075% respectively.

ACKNOWLEDGEMENT

Our thanks are due to SHRI M. M. TILLU for carrying out the preliminary separation of total rare earths from the samples studied.

SUMMARY

A method is described for the determination as little as 10–12 p.p.m. of europium in minerals and ores. After lead separation, the total rare earths are separated by conventional methods and the rare earth oxides are dissolved in hydrochloric acid. Europium gives a wave in 0.1 M ammonium chloride supporting electrolyte at —0.67 V *vs.* S.C.E. and there are no interferences. Europium is determined in monazite and samarskite.

RÉSUMÉ

Les auteurs ont mis au point une méthode polarographique pour le dosage de traces d'europium dans des minerais et en particulier en présence des autres terres rares (samarskite, monazite).

ZUSAMMENFASSUNG

Beschreibung einer polarographischen Methode zur Bestimmung von Europium in Mineralien (Monazit, Samarskit) in Gegenwart anderer seltener Erden.

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POLAROGRAPHIC DETERMINATION OF NICKEL, CHROMIUM AND TIN IN ZIRCALOY AND ZIRCONIUM METAL*

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(Received October 16th, 1959)

INTRODUCTION

Zirconium and its alloys are finding ever-increasing use in nuclear reactors. Certain alloys of zirconium have become standard because of their resistance to corrosion and high temperature. The composition of zircaloy 2 is as follows: tin 1.4–1.6%; chromium 0.08–0.12%; iron 0.1–0.15% and nickel 0.04–0.06%. In zircaloy 3, iron and tin are of the order of 0.25% each.

Recently, ELWELL[1] has surveyed all the methods for the determination of different elements and impurities in zircaloy and zirconium metal. As regards the determination of chromium, nickel and tin in zircaloy by polarography, only the polarographic determination of tin[2] has been reported. The purpose of this paper is to describe suitable polarographic methods for the determination of these elements in zircaloy as well as in high purity zirconium metal.

EXPERIMENTAL

Instrument

A "DU Bellay" polarograph and an electronically operated thermostat were used. A mercury pool was used as anode and the temperature was kept constant at 30 ± 0.1°

Reagents

Stannic chloride solution (0.1 *M*) was prepared from E. Merck G. R. stannic chloride and was standardised volumetrically with iodine. 0.01 *M* Solutions of potassium chromate and nickel chloride were prepared from Merck's G.R. quality salts. The nickel solution was standardised with dimethylglyoxime. The solutions (100 μg/ml) of ferric chloride, manganese sulphate, lead nitrate, titanium sulphate, ammonium vanadate and aluminium chloride were also prepared from E. Merck G.R. quality salts.

Preparation of the synthetic sample for analysis

Zirconium metal (5 g) was dissolved by first treating it with a few ml of 40% hydrofluoric acid in a platinum dish and fuming it with concentrated sulphuric acid. The solution was diluted to 100 ml after addition of 10 ml of concentrated sulphuric acid to prevent subsequent hydrolysis.

To an appropriate aliquot of the zirconium solution, the requisite amounts of chromium, nickel and tin (in the form of solutions) were added in the ranges of their percentages in zircaloy and then taken through separate procedures for estimation of each element as described below.

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* Presented to the Indian Standards Convention held in December 1959.

Determination of nickel

Supporting electrolyte and separation of zirconium

Pyridine–pyridine sulphate was used as the supporting electrolyte; this is known to give a very good wave for nickel. In addition, pyridine effectively precipitates zirconium. Ammonia, ethanolamine and ethylenediamine were also tried, but the separation of zirconium resulted in gelatinous precipitates which were difficult to wash. Ammonia for separation of zirconium is not suitable: the original solution contains sulphuric acid which gives ammonium sulphate in the filtrate. When ammonium sulphate is present in the supporting electrolyte, the height of the nickel wave decreases with increasing amounts of ammonium sulphate. Amongst the supporting electrolytes mentioned above, the wave-height for nickel in pyridine–pyridine sulphate solution is the highest.

Standard curves

To obtain a standard curve, 20–500 μg of nickel as nickel chloride solution was taken in different 25-ml flasks; 7 ml of 13 *M* pyridine and 1–2 ml of concentrated sulphuric acid was added and the volume made up to 25 ml. The half-wave potential of nickel is at —0.925 V *vs.* S.C.E.

In the case of samples, an aliquot equivalent to 0.25 g (5 ml) of the sample (Zr-metal) was taken, 15 ml of water and 2–3 ml of concentrated sulphuric acid were added and zirconium was precipitated by addition of 14 ml of 13 *M* pyridine. The precipitate was filtered through No. 42 Whatman filter paper and washed with dilute pyridine solution (5% v/v). The filtrate and washings were collected in a 50-ml flask and the solution made up to the volume. Synthetic mixtures of zircaloy were prepared by adding the requisite amounts of elements present in the alloy. To one of the synthetic mixtures, the impurities generally present in zirconium metal were also added. Table I gives the results on synthetic samples.

TABLE I

DETERMINATION OF NICKEL IN SYNTHETIC SAMPLES

No.	*Wt. of sample as g of metal*	*Nickel added μg*	*Nickel found μg*	*Difference %*
1	0.25 alloy[a]	500	485	— 3
2	0.25 alloy[a]	200	188	— 6
3	0.2 alloy[a] with impurities[b]	200	188	— 6
4	0.5 metal[c]	20	17.5	—12.5
5	1.0 metal	75	71	— 5
6	1.0 metal	10	8.5	—15

[a] 0.25 g of synthetic alloy containing 0.104% chromium and 1.5% tin apart from zirconium.

[b] Iron (50 μg), aluminium (250 μg), titanium (25 μg) manganese (50 μg), lead (25 μg) were added as impurities to the synthetic alloy.

[c] The amount of nickel in the pure zirconium metal taken for analysis was 25 p.p.m. and was corrected for in calculating the results.

Determination of chromium

Advantage is taken of the fact that zirconium when treated with sodium peroxide is hydrolysed and precipitated. Chromium, if any, is oxidised to chromate which gives a good wave in a sodium hydroxide supporting electrolyte.

Standard curves for chromium were obtained as follows: 4 g of sodium peroxide were dissolved in water and the solution was boiled to remove excess of oxygen. It was then transferred to a 25-ml flask, measured quantities of chromate were added and the solution was made up to volume.

Synthetic samples containing appropriate aliquots of zirconium solution and varying amounts of chromium as indicated in Table II were used. To the solution (20 ml), 4 g of sodium peroxide were slowly added and the solution was boiled after addition of another 10–20 ml of water, cooled and then filtered. The precipitate of zirconium was washed thoroughly with dilute sodium hydroxide and the filtrate and washings were collected and concentrated to less than 25 ml. The solution was then transferred to a 25-ml flask and made up to volume. The polarogram was then recorded. Table II shows the results obtained for chromium on synthetic samples.

TABLE II

DETERMINATION OF CHROMIUM IN SYNTHETIC SAMPLES

No.	*Wt. of sample in g of metal*	*Cr added* µg	*Cr found* µg	*Difference* %
1	0.25 g alloy[a]	260	260	
2	0.25 g alloy[a]	130	126	—3
3	0.25 g alloy[a] with impurities[b]	130	130	
4	0.5 g metal[c]	20	20	
5	1.0 g metal	10	9	—10

[a] 0.25 g of synthetic alloy containing 0.08% nickel and 1.5% tin apart from zirconium.

[b] Impurities added are the same as in the case of nickel.

[c] The value of the chromium in the pure zirconium metal was 54 p.p.m. and was corrected for in calculating the results in Table II.

Determination of tin

The method of ALLSOPP AND DAMERALL[3] for the determination of tin in steels was applied. The method essentially consists of the precipitation of tin as stannic sulphide, ignition and subsequent fusion with bisulphate, leaching with 2 *N* hydrochloric acid, adding this solution to a 100-ml flask containing 21 g of ammonium chloride and 2 ml of 0.5% gelatin, making up to volume and recording the wave.

The earlier method of PORTER[2] for determination of tin in zircaloy by measuring the waves of stannous chloride without prior separation from the bulk of the solution was not used because of the difficulty of preventing oxidation of stannous chloride.

It is necessary to remove all oxygen from the reagents by passing nitrogen and to add iron powder to the solution to prevent oxidation of stannous tin. Although the method of ALLSOPP is rather lengthy no precautions are required and it is therefore more suitable for zircaloy.

The standard curves for tin were obtained by adding suitable quantities of tin to 100-ml volumetric flasks containing 21 g of ammonium chloride and 2 ml of 0.5% gelatin. Different quantities of tin were added to the synthetic sample and tin was determined by the above method. The results of this determination are shown in Table III.

A sample of zircaloy was analysed for nickel and chromium; the contents were found to be 0.063 and 0.12% respectively. The methods were also confirmed by additions of known amounts of nickel and chromium to the sample.

If the determination of tin in the range of 0.001% is required a 5-g sample of zirconium metal should be taken.

TABLE III

DETERMINATION OF TIN IN SYNTHETIC SAMPLES

No.	*Wt. of sample* g	% *tin added*	% *tin found*	*Difference* %
1	0.05 alloy[a]	1.74	1.68	—3.4
2	0.1 alloy[a]	1.74	1.68	—3.4
3	0.2 alloy[a]	0.50	0.47	—6.0
4	0.2 alloy[a]	0.25	0.275	+10.0
5	1.0 metal[b]	0.005	0.005	—

[a] The synthetic alloy sample contained 0.08% nickel and 0.104% chromium apart from zirconium.
[b] The tin content of the zirconium metal was less than 0.001% and has been corrected for.

SUMMARY

Polarographic methods are described for the determination of chromium, nickel and tin in zircaloy. The methods can be used to determine these three elements at the 10 p.p.m. level in pure zirconium metal.

RÉSUMÉ

Les auteurs ont mis au point une méthode polarographique pour le dosage du chrome, du nickel et de l'étain dans le zirconium et ses alliages.

ZUSAMMENFASSUNG

Es wird eine polarographische Methode beschrieben zur Bestimmung von Chrom, Nickel und Zinn in Zirkonium und dessen Legierungen.

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POLAROGRAPHY OF URANIUM IN THIOCYANATE MEDIUM

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(Received October 16th, 1959)

INTRODUCTION

The polarography of uranium in various media has been reported by numerous workers. This paper reports the polarography of uranium in thiocyanate medium.

EXPERIMENTAL

Apparatus

Current–voltage curves were determined on a manual set up[1]. A H-type cell[2] was used in which a saturated calomel electrode (S.C.E.) served as a reference electrode. Before making polarographic measurements, all solutions were made air-free by bubbling nitrogen for about forty-five minutes. All experiments were carried out at 30 ± 0.5°. The diffusion currents reported were corrected for the residual current. The capillary used in these measurements had the following characteristics: $m =$ 1.21 mg/sec and $t = 5.0$ sec in 0.1 N KCl (open circuit). A number of maximum suppressors was tried but only bromothymol blue (BTB) ($3 \cdot 10^{-3}\%$ in the final solution) was found satisfactory. All experiments were carried out at an ionic strength of 1.0 by the addition of requisite amounts of sodium perchlorate.

Chemicals

A stock solution of uranium perchlorate was obtained by fuming uranyl nitrate with perchloric acid and diluting to a known volume. The solution was standardized by the standard gravimetric method.

All chemicals used were AnalaR grade.

RESULTS

c–v curves

Fig. 1 gives the c–v curves for uranyl ion both in the presence and absence of thiocyanate. The acidity was 0.4 M in perchloric acid. Two waves were obtained in thiocyanate medium, the first corresponding to a 2-electron reduction of +6 to +4 uranium and the second to a 1-electron reduction of +4 to +3 as will be shown later.

In the text, $E'_{\frac{1}{2}}$ and $E''_{\frac{1}{2}}$ represent the half-wave potentials of the first and second wave respectively and i'_d and i''_d are the corresponding diffusion currents. i_t is the total diffusion current.

Half-wave potentials

The dependence of the half-wave potentials of the two waves on the hydrogen ion concentration was studied by varying the amounts of perchloric acid, the thiocyanate concentration being kept at 0.2 M. The results are given in Table I.

TABLE I

EFFECT OF ACID CONCENTRATION ON $E_{\frac{1}{2}}$

U = 1 mM, $NaClO_4 + HClO_4 = 0.8\ M$, $NH_4CNS = 0.2\ M$, BTB = $3 \cdot 10^{-3}\%$

Perchloric acid M	$E'_{\frac{1}{2}}$ *V vs. S.C.E.*	*Slope for first wave V*	$E''_{\frac{1}{2}}$ *V vs. S.C.E.*	*Slope for second wave V*
0.2	—0.146	0.034	—	—
0.3	—0.130	0.034	—0.892	0.062
0.4	—0.113	0.033	—0.892	0.064
0.46	—0.106	0.035	—0.894	0.068
0.5	—0.098	0.033	—0.890	0.065

According to HEYROVSKY-ILKOVIC[3], the potential at any point on the polarographic wave is given by

$$E_{d.e} = E_{\frac{1}{2}} - \frac{0.059}{n} \log \frac{i}{i_d - i} \qquad (1)$$

A plot of log $i/(i_d - i)$ *vs.* $E_{d.e}$ (Fig. 2) gave straight lines for the two waves. The slopes for the first and second wave were 34 mV and 65 mV indicating a 2-electron and 1-electron reduction respectively.

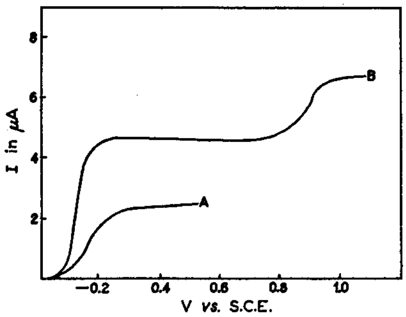

Fig. 1. Polarogram of uranyl ion in thiocyanate: U — 1 m*M*, $HClO_4$ — 0.4 *M*, $NaClO_4$ — 0.4 *M*, BTB — $3 \cdot 10^{-3}\%$, NH_4CNS — (A) 0 *M*, (B) 0.2 *M*.

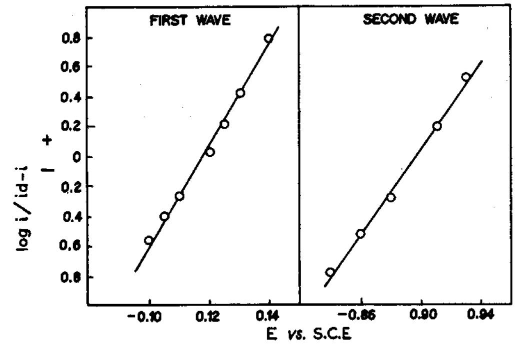

Fig. 2. Test of reversibility: log plot for equation (1).

Effect of thiocyanate concentration

Further experiments were carried out at an acid concentration of 0.4 *M*. Table II gives the effect of thiocyanate concentration on the two waves.

TABLE II

EFFECT OF THIOCYANATE CONCENTRATION

U = 1 m*M*, $HClO_4$ = 0.4 *M*, $NaClO_4 + NH_4CNS$ = 0.6 *M*, BTB = $3 \cdot 10^{-3}\%$

CNS⁻ concentration M	*First wave*			*Second wave*		
	$E'_{\frac{1}{2}}$ *V vs. S.C.E.*	*Slope V*	i_d' *at −0.5 V μA*	$E''_{\frac{1}{2}}$ *V vs. S.C.E.*	*Slope V*	i_t *at −0.98 V μA*
0	—	—	2.54	—	—	6.90
0.05	—0.111	0.034	4.49	—0.855	0.068	6.80
0.15	—0.112	—	4.61	—0.861	0.061	6.84
0.2	—0.113	0.033	4.61	—0.892	0.064	6.80
0.3	—0.117	0.031	4.64	—0.896	0.067	6.80
0.35	—0.118	0.030	4.66	—0.896	0.067	6.84
0.4	—0.115	0.035	4.61	—0.898	0.063	6.81

Effect of other factors:

(A) temperature

The temperature coefficient was determined by measuring the diffusion currents at different temperatures (Table III) and was found to be[4] of the order of +1.3%. The effect was also studied at a lower concentration of thiocyanate (0.01 *M*) where

i'_d had not reached the constant value of 4.62 µA; the temperature coefficient was found to be of the same order.

TABLE III

EFFECT OF TEMPERATURE ON THE DIFFUSION CURRENTS

U = 1 mM, $HClO_4$ = 0.4 M, $NaClO_4$ = 0.4 M, NH_4CNS = 0.2 M, BTB = $3 \cdot 10^{-3}$%

Temperature °C	*i_d' at −0.5 V vs. S.C.E. µA*	*i_t at −0.98 V vs. S.C.E. µA*	*Temperature coefficient % for*	
			i_d'	*i_t*
30	4.61	6.81	—	—
55	6.30	9.5	1.3	1.3
65	6.95	10.4	1.2	1.2

TABLE IV

EFFECT OF m AND t

U = 1 mM, $HClO_4$, $NaClO_4$ = 0.4 M each, NH_4CNS = 0.2 M, BTB = $3 \cdot 10^{-3}$%

$m^{2/3}t^{1/6}$ $mg^{2/3}sec^{-1/2}$	i_d' µA	$D_{UO_2^{+2}}$ $\times 10^5\ cm^2 sec^{-1}$	$\frac{i_d'}{cm^{2/3}t^{1/6}}$	i_d'' µA	$\frac{i_d''}{cm^{2/3}t^{1/6}}$
1.41	4.32	0.64	3.06	2.16	1.53
1.49	4.62	0.66	3.10	2.26	1.51
1.29	3.91	0.63	3.03	2.02	1.56

(B) m and t

The diffusion currents of the two waves were measured with different capillaries and the ratio of i_d to $cm^{2/3}t^{1/6}$ was found to be constant within the limit of experimental error (Table IV).

(C) Concentration of uranium

The diffusion currents of the two waves were measured at different concentration of uranium and were found to be proportional (Table V).

TABLE V

EFFECT OF CONCENTRATION OF URANIUM

Capillary characteristics: $m^{2/3}t^{1/6}$ = 1.41 $mg^{2/3}$ $sec^{-1/2}$, NH_4CNS = 0.2 M, $HClO_4$, $NaClO_4$ = 0.4 M each, BTB = $3 \cdot 10^{-3}$%

Concentration of uranium mM	*i_d' µA*	*i_t µA*	*i_d'' µA*	*i_d'/C*	*i_d''/C*
2.0	8.75	12.82	4.07	4.38	2.04
1.0	4.32	6.48	2.16	4.32	2.16
0.5	2.14	3.20	1.06	4.28	2.12
0.1	0.44	0.66	0.22	4.40	2.20

DISCUSSION

First wave

Uranyl ion in the presence of thiocyanate gave a polarogram (Fig. 1) consisting of two waves. The first wave gave a slope of 0.033 V for the log plot for equation (1) indicating a two-electron reduction (Tables I and II). The shift of $E_{1/2}$ to more positive potentials with increase in acid concentration (Table I) suggested the dependence of the first electrode reaction on hydrogen ion concentration. The reaction might be written as

$$UO_2^{+2} + 4\,H^+ + 2\,e \rightleftharpoons U^{+4} + 2\,H_2O \qquad (2)$$

Or in the presence of excess thiocyanate, the general form of the equation would be

$$UO_2(CNS)_p{}^{(2-p)+} + 4\,H^+ + 2\,e \rightleftharpoons UCNS_q{}^{(4-q)+} + (p-q)\,CNS^- \qquad (3)$$

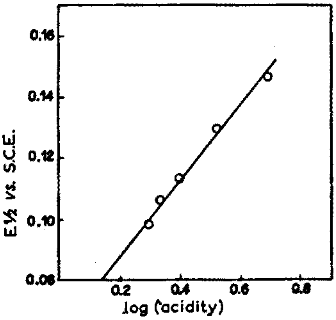

Fig. 3. First wave: log (acidity) *vs.* $E_{\frac{1}{2}}$.

The potential of the dropping electrode[3,5] at any point on the polarogram is expressed by

$$E_{d.e} = E^\circ + \frac{4RT}{nF} \ln a_{H^+} - \frac{RT}{nF} \ln \frac{i}{i_d - i} - \frac{(p-q)}{n} \frac{RT}{F} \ln a_{CNS^-} \qquad (4)$$

It follows that at a particular concentration of thiocyanate, a plot of $E_{\frac{1}{2}}$ *vs.* log (acidity) should give a straight line with slope equal to $4RT/nF$ (Fig. 3). A slope of 0.123 V was obtained against a theoretical slope of 0.12 V at 30°. The activity term was neglected.

$E'_{\frac{1}{2}}$ remained unaffected at —0.114 ± 0.003 V (*vs.* S.C.E.) with the change in concentration of thiocyanate (Table II). Hence, the value of $p - q$ was equal to zero. The dependence of the first wave on hydrogen ion concentration and the fact that the slope of the log plot of equation (6) was equal to the theoretical slope showed that under the conditions studied the first wave was due to the reduction of uranyl thiocyanate complex to U^{+4} ion. The $U^{+3} - U^{+4}$ couple was shown to be reversible at the dropping mercury electrode; the ionic species were U^{+3} and U^{+4} in acid solutions[6].

The first wave was found to be independent of the capillary characteristics (Table IV). The temperature coefficient (Table III) and the i'_d linearity with concentration of uranium (Table V) were also as expected.

For the diffusion currents obtained for a 1 m*M* solution of uranium with different capillaries and for a value of *n* equal to 2, the diffusion coefficient for UO_2^{+2} calculated from the ILKOVIC equation

$$i_d = 605\,n\,D^{\frac{1}{2}}\,c\,m^{\frac{2}{3}}t^{\frac{1}{6}} \qquad (5)$$

was 0.65 ± 0.02 · 10^{-5} cm² sec⁻¹. This was in fair agreement with the values reported[7–9] and was satisfactory evidence for a two-electron reduction.

Second wave

The half wave potential of the second wave remained unaffected with acid concentration at —0.89 V *vs.* S.C.E. (Table I). With 0.4 M perchloric acid, $E''_{\frac{1}{2}}$ remained constant with change in thiocyanate concentration. i'_d and $E''_{\frac{1}{2}}$ were constant above a thiocyanate concentration of 0.15 M. The total height of the two waves was constant at 6.86 μA; i'_d was 4.62 μA and i''_d was 2.26 μA. The ratio of 2 to 1 indicated a two- and one-electron reduction respectively. The slope for the log plot (Tables I and II) was 0.065 V indicating a one-electron reversible reduction.

The formal potential of the $U^{+3} - U^{+4}$ couple in this medium was calculated. In general, diffusion coefficients change little with changes in salt concentration and their ratios change even less; hence the correction for this effect was neglected. Since the activity coefficients f_{ox} and f_{red} of the two ions are not known with any accuracy, a formal electrode potential is defined by

$$E_f = E^\circ + 0.059 \log \frac{f_{ox}}{f_{red}} = E_{\frac{1}{2}} - \log \left(\frac{D_{red}}{D_{ox}} \right)^{\frac{1}{2}} \quad (6)$$

For the reaction

$$U^{+3} \rightleftharpoons U^{+4} + e \quad (7)$$

the half wave potential of the second wave was taken as —0.893 ± 0.003 V (*vs.* S.C.E.). The formal potential was +0.65 V. This value compared well with the values of +0.63 V in 1.0 M $HClO_4$,[6] +0.68 V[10] and +0.63 V previously reported[11].

ACKNOWLEDGEMENT

The authors wish to thank Dr. V. T. ATHAVALE, Head of the Analytical Division, Atomic Energy Establishment Trombay, for his kind interest and helpful suggestions.

SUMMARY

Uranyl ion in the presence of thiocyanate gave two polarographic waves, the first corresponding to a two-electron reduction of UO_2^{+2} to U^{+4} and the second corresponding to a one-electron reduction of U^{+4} to U^{+3}. The dependence of the two waves on acid concentration, temperature, etc., was studied.

RÉSUMÉ

Une étude a été effectuée sur le comportement polarographique de l'uranium (UO_2^{+2}) en présence de thiocyanate; on observe deux ondes dues à la réduction de UO_2^{+2} en U^{+4} et de U^{+4} en U^{+3}.

ZUSAMMENFASSUNG

Bei der polarographischen Bestimmung von Uranyl-Ion (UO_2^{+2}) in Gegenwart von Thiocyanat erhält man zwei Wellen, von denen die erste der Reduktion von UO_2^{+2} zu U^{+4} und die zweite der Reduktion von U^{+4} zu U^{+3} entspricht.

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PYROHYDROLYTIC SEPARATION OF FLUORIDES FROM CATALYSTS BY USE OF AN OXY-HYDROGEN BURNER

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(Received December 18th, 1959)

Coinciding with the rapid advancement of reforming technology within the petroleum industry, there has been a correspondingly intensified interest in catalyst composition and structure. This has emphasized the need for rapid catalyst analyses not only for adequate refinery process control, but also in research activity where many process variables are studied. Fluoride determination has heretofore been one of the major obstacles to rapid catalyst evaluation because of the nature of the chemical bonds and the geometry of the crystalline structure of catalytic materials.

The concept of pyrohydrolysis is not new, the essential technique having been reported by FREMY[1] in 1856. Early activities, which have been reviewed by WARF *et al.*[2], while concerned almost exclusively with qualitative observations and thermodynamic data, clearly indicated the analytical potentialities of the technique. However, it was not until the advent of atomic research and the preparation of large quantities of inorganic fluorides that these potentialities were exploited[2,3].

WARF[3] and later WARF, CLINE AND TEVEBAUGH[2] used a steam generator in conjunction with a resistance furnace and platinum combustion reactor and boat to obtain the fluoride content of many inorganic materials. Addition of accelerators was necessary in many instances to produce quantitative results in reasonably short periods of time. Of secondary interest was the pyrohydrolysis of inorganic chlorides and bromides. An all-metal refinement of the apparatus was introduced by SUSANO, WHITE AND LEE[4], and later modified by GAHLER AND PORTER[5] for the pyrohydrolytic determination of chlorides in titanium sponge. Radioactive samples were studied by LEE, EDGERTON AND KELLY[6] in an apparatus designed specifically for the purpose. The precision of the pyrohydrolytic technique applied to uranyl fluoride and uranium tetrafluoride was studied by HIBBITS[7]. Elimination of the somewhat cumbersome steam generator was reported by POWELL AND MENIS[8] who used a continuous flow of oxygen containing traces of moisture.

GAMBLE, PRICE AND JONES[9] adapted the basic method of WARF to the somewhat more difficult problem of determination of fluorides in silica-alumina catalysts. A major departure from previously employed apparatus was reported by CONRAD, EVANS AND GAYLOR[10] who employed a high frequency induction furnace, using silica as an accelerator.

Investigations carried out in this laboratory indicate that procedures using resistance furnaces in conjunction with steam or moist oxygen are not competitive with the technique involving a basic fusion followed by distillation according to Willard and Winter[11] when applied to commercial type silica–alumina catalysts. Although comparable results may be obtained, time cycles are usually prohibitive in the absence of added accelerators. Using the reported high frequency induction furnace method[10], quantitative results could not be obtained on typical petroleum catalysts.

All of the reported pyrohydrolytic techniques have certain disadvantages when employed for routine use on catalytic materials. The steam generator–resistance furnace combination is cumbersome. Use of platinum and special all-metal apparatus requires substantial monetary outlays and elaborate fabrication facilities. When steam is used, careful manipulation and control is required to prevent back diffusion of hydrogen fluoride into the generator. Addition of accelerators is somewhat tedious and time consuming.

The Wickbold type oxy–hydrogen burner[12] is now commercially available at relatively low cost[13]. It provides an excellent means of utilizing the inherent advantages of the pyrohydrolytic technique while simultaneously eliminating many disadvantages of other methods. The burner provides a combined source of heat and water vapor in the presence of excess oxygen. Investigation of these potentialities resulted in the development of a new pyrohydrolytic separation technique, adaptable to the separation of fluoride from catalysts and which is suitable for routine use by technicians.

APPARATUS

The Wickbold apparatus[12] was modified by insertion of a special quartz combustion tube as indicated in Fig. 1. The Wickbold suction burner and water-jacketed combus-

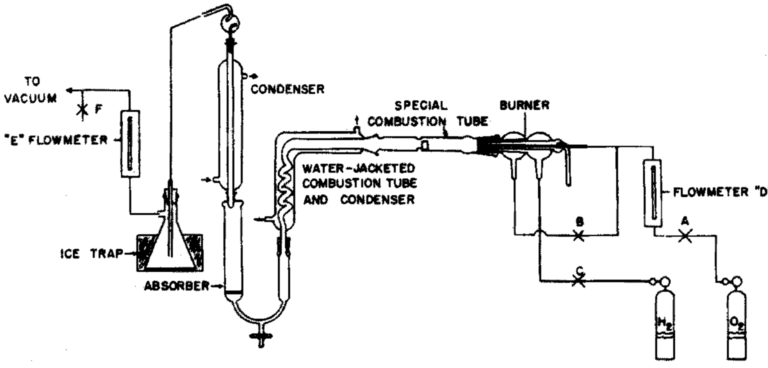

Fig. 1. Diagram of pyrohydrolysis apparatus.

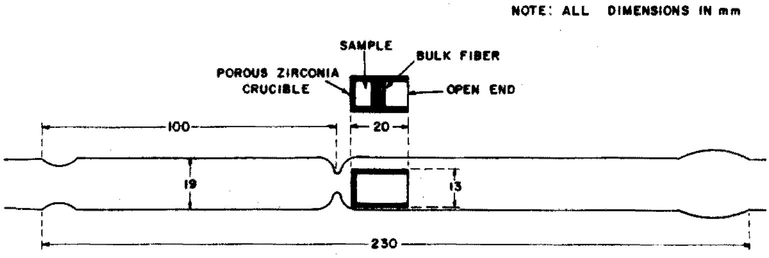

Fig. 2. Special combustion tube and sample holder.

tion tube with condenser, both fabricated from clear fused quartz, were purchased from the Amersil Company, Hillside, New Jersey.

A special quartz combustion tube and a zirconia sample holder are required and are illustrated in Fig. 2. The porous sample holder, which permits free flow of superheated oxygen and water vapor from the flame, was designed specifically for this application and fabricated by the Laboratory Equipment Corporation, St. Joseph, Michigan.

The sample was held firmly in position by the use of F-100 Refrasil bulk fiber which was purchased from the H. I. Thompson Fiber Glass Company, Los Angeles, California. The absorber used in an ASTM lamp combustion procedure[14] was modified to fit the apparatus, and a bottom stopcock inserted for convenient withdrawal of the solution. Oxygen and hydrogen were used from cylinders, without purification. Lines were equipped with flowmeters and valves as indicated in Fig. 1.

PROCEDURE

The sample, equivalent to at least 1 mg of fluoride, was charged to the sample holder followed by a layer of the bulk fiber. The combustion tube, with the sample container located as shown in Fig. 2, was inserted into the assembly. The absorber, containing about 15 ml of approximately 0.1 *N* sodium hydroxide solution, was placed in position. Prior to inserting the burner in the assembly, vacuum was applied to the system and regulated to permit a flow rate of 20 l per min through flowmeter E. With valves A and C closed, the reducing valves on the oxygen and hydrogen cylinders were regulated to 4 psig. The hydrogen valve C, was opened slightly and the burner ignited. With valve B fully open, valve A was adjusted to permit a flow of about 16.7 l of oxygen per min through flowmeter D. Final adjustment of oxygen flow, at this rate, was made while simultaneously adjusting the hydrogen flow rate to produce a flame about 1 cm in length. The burner was then inserted into the special combustion tube, and the hydrogen flow increased to produce a flame 4-5 cm in length. By means of valve B, the excess oxygen passing through the burner was decreased causing more oxygen to jet through the center orifice of the burner. The resultant long narrow flame heats the sample to an intense white heat. The reduced oxygen flow during actual operation was estimated at approximately 11 l per min. After five minutes, the hydrogen valve was closed, the burner removed from the assembly, and the oxygen valve closed. The vacuum was disconnected and the contents of the absorber filtered through Whatman No. 41 filter paper. Fluorides were determined spectrophotometrically, using the method of MEGREGIAN[15] without prior distillation.

DISCUSSION

A review of the various methods for elimination of interferences and ultimate fluoride analysis is considered beyond the scope of this paper. In order to evaluate the new pyrohydrolytic technique, however, it was necessary to select a referee method which would eliminate any probable interferences and provide an independent means of sample preparation. Basic fusion is considered standard technique for obtaining dissolution of alumina and silica base catalyst materials, and was used in conjunction with the distillation method of WILLARD AND WINTER[11], which has been accepted almost universally as an ideal means of eliminating interferences in the subsequent fluoride analysis. Furthermore, a background consisting of years of experience with experimental and commercial catalysts using the fusion–distillation technique was available. Fluorides were determined spectrophotometrically[15] regardless of whether the fusion–distillation or pyrohydrolytic technique was used.

TABLE I

COMPARISON OF PYROHYDROLYSIS AND FUSION–DISTILLATION ON EXPERIMENTAL CATALYSTS

Catalyst type	*Fluorine found*	
	Distillation fusion	*Pyrohydrolysis*
Fresh reforming—Al_2O_3	0.55	0.55; 0.55
Fresh cracking—Al_2O_3–SiO_2 base	2.87	3.02; 3.03
Spent cracking—Al_2O_3–SiO_2 base	0.35	0.32; 0.37
Fresh cracking—SiO_2–MgO base	1.75	1.79; 1.80
Fresh hydrogenation—Al_2O_3 base	1.51	1.52; 1.56
Spent hydrogenation—Al_2O_3–SiO_2 base	1.29	1.45; 1.46
Spent hydrogenation—Al_2O_3–SiO_2 base	0.91	1.00; 0.94

Results from the pyrohydrolysis of various experimental petroleum catalysts are shown in Table I. Comparison of the values with the fusion–distillation technique indicates slightly higher recovery by pyrohydrolysis in most instances. For purposes of confirming the higher values, several absorber solutions were divided in two parts; one portion was subjected directly to the photometric finish and the other portion distilled prior to the photometric finish. In no instance was any difference in fluoride values observed before and after the distillation. The slightly higher values obtained by pyrohydrolysis confirms the belief that, in some samples, the fusion–distillation technique was not quantitatively liberating all of the fluorides. The order of magnitude of the discrepancy, however, is not usually considered to be of practical significance.

The general agreement of values obtained by the two methods indicates no appreciable interference from any of the catalyst bases nor from platinum, magnesium, cobalt, molybdenum, chlorine, sulfur, and various other metals commonly used in the form of supported catalysts. The method was also found to be equally applicable to both fresh catalysts and spent catalysts containing carbonaceous material. No blank could be obtained on the gas streams. Over a range of fluoride concentration of 0.3 to 3% and covering several hundred analyses, a standard deviation of about 0.04% has been estimated for the new method.

Inasmuch as materials of interest usually contain Al–F bonds, it was logical to expect that the method should be applicable to aluminum fluoride. Analysis of a sample of aluminum fluoride by the pyrohydrolytic and fusion–distillation techniques indicated an assay of 88.7% and 88.0% respectively, calculated as $Al_2F_6 \cdot 7H_2O$. Although the aluminum fluoride was of reagent grade quality, semi-quantitative x-ray diffraction studies indicated quantities of $Al_2O_3 \cdot 3H_2O$ present in the material in amounts sufficient to account for the difference.

Reports by WARF and others on the difficulty of pyrohydrolyzing calcium fluoride in the absence of accelerators promoted a brief investigation. Two samples obtained from the National Bureau of Standards—"fluorspar" certified to contain 94.83% calcium fluoride and "opal glass" certified to contain 10.48% calcium oxide and 5.72% fluoride—were subjected to a 15-min period of pyrohydrolysis with virtually quantitative recovery of fluoride. Inasmuch as calcium fluoride is not of primary interest in reforming catalyst technology, detailed studies on this phase were not conducted. It was obvious, however, that the procedure could be adapted for materials of this type.

TABLE II

TIME REQUIREMENTS FOR VARIOUS CATALYST TYPES

Heating time, min	*Fluorine found, %*		
	Alumina	*Silica–magnesia*	*Experimental silica–alumina*
1	0.48	1.61	2.82
2	0.56	1.81	2.90
4	0.58	1.72	2.98
8	0.59	1.80	2.97
15	0.59	1.86	3.01

A brief study of time requirements for the pyrohydrolysis of four types of catalytic materials was conducted (Table II). The recovery of fluorine does not appear to be significantly affected until the heating period is reduced to one minute. Unfortunately, the absence of a convenient means of measuring the sample temperature complicates any thermodynamic calculations which could be applied to this system. It appears, however, that the recovery of fluorides is primarily a function of temperature rather than time. The temperature of the oxy–hydrogen flame has been estimated to be 2690° and 2810° by two investigators[16,17]. From the appearance of the Refrasil bulk fiber in conjunction with measurements on an optical pyrometer, it is estimated that under the conditions cited, a sample temperature of approximately 1400° is attained.

Several types of sample holders were evaluated. A boat with an open top, although covered with the bulk fibers, was unsatisfactory because of mechanical loss of sample resulting from the flow of excess oxygen. Sample containers fabricated from quartz are satisfactory, but care must be taken to avoid overheating and subsequent melting. A later refinement involved the use of the recommended zirconia sample holder. If holders fabricated from quartz are employed, it is advantageous to use an auxiliary burner (Bunsen type) placed below the sample holder. In this case, the size of the oxy–hydrogen flame may be diminished slightly and the life of the holder extended.

The time required to prepare a sample for the final measurement of fluoride is of the order of only ten minutes. This, when compared to about three hours for a fusion–distillation procedure, simplifies many problems associated with process research and control.

The extreme simplicity of the new pyrohydrolytic technique makes it readily adaptable to routine use at the technician level. The operation is quite safe when the usual precautions regarding the use of hydrogen are observed. The use of an antiflash back device in the hydrogen line, a safety shield, and a reliable source of vacuum is recommended.

Other potential applications of pyrohydrolysis using the oxygen–hydrogen flame, currently being explored, include pyrohydrolysis of the other halides. Techniques other than hydrolysis, such as volatilization of certain components in solid substances are also being considered.

SUMMARY

A new pyrohydrolytic technique has been developed. The procedure utilizes an oxy–hydrogen burner as a combined source of heat and water vapor for high temperature hydrolysis of fluorides in catalytic materials. Fluorides in typical petroleum catalysts are quantitatively liberated in less than 5 min, without the use of added accelerators and without resorting to fusion or distillation. Results obtained are comparable to the fusion–distillation technique with a standard deviation of not more than 0.04 % over the range of concentration investigated: 0.3 to 3%. Indications are that materials of much higher fluoride content may also be handled in the same manner.

RÉSUMÉ

Une nouvelle technique pyrohydrolytique a été élaborée. Elle peut être utilisée, dans l'industrie, du pétrole, pour la séparation des fluorures dans des substances de catalyse.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Abtrennung von Fluorid aus Katalysatoren durch Pyrohydrolyse. Die Substanz wird der Atmosphäre einer Knallgasflamme ausgesetzt und das Fluorid anschliessend spektrophotometrisch bestimmt. Weitere Anwendungsmöglichkeiten dieser Methode werden untersucht.

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THE DETERMINATION OF SULFHYDRYL GROUPS IN REDUCED HAIR KERATIN

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(Received December 18th, 1959)

INTRODUCTION

One of the distinguishing characteristics of the keratins is the presence of the reducible disulfide bond, and considerable activity in such fields as wool processing and hair chemistry has been directed to analytical means for estimating the disulfide and sulfhydryl groups. Because of the interest in these laboratories in the reduction of hair with mercaptans such as thioglycollic acid, the need for a rapid and precise method for determination of the sulfhydryl content of hair, preferably using intact, that is, nonhydrolyzed samples, is evident.

Earlier studies concerned with the determination of the disulfide and sulfhydryl groups in keratin involved a hydrolytic procedure for the liberation of the individual amino acids and a subsequent colorimetric measurement[1-6]. However, there is much controversy with respect to the specificity and quantitative nature of methods utilizing such an approach[7,8]. Other means of analysis have been proposed but they are not conveniently applicable. For example, the use of 1-(4-chloromercuriphenylazo)-naphthol-2[9-11] requires that the keratin be pulverized and reacted with the reagent for more than a day. Another reagent, iodosobenzoic acid, has been used to estimate the sulfhydryl content of denatured albumin and ovalbumin[12], but the technique was not applied to intact keratin samples. More recently, N-ethylmaleimide[13] and *p*-chloromercuribenzoic acid[8] have been used to estimate the sulfhydryl content of intact wool fibers. However, there is evidence presented that in both of these procedures these compounds are absorbed by the wool to some extent. Since the methods utilizing these chemicals, as well as the two mentioned previously, are indirect and are based on the decrease in concentration of reagent as a measure of sulfhydryl, loss of reagent by either absorption, adsorption, or in any other manner, could give rise to serious error.

BENESCH AND BENESCH[14] have used iodoacetamide for the quantitative determination of sulfhydryl groups in the soluble compounds cysteine, cysteinylglycine, and glutathione. Their method was based on the reaction

$$RSH + ICH_2CONH_2 \rightarrow RSCH_2CONH_2 + HI \qquad (1)$$

The analysis was completed by titrating the acid generated with standard base. Amounts of the order of 0.02 to 0.10 mequivs of material were determined. Since this procedure provides a direct measurement of the sulfhydryl content, an investigation was instituted to determine whether iodoacetamide could serve as a reagent for the determination of the sulfhydryl level of reduced human hair.

A direct application of the BENESCH method to hair was not considered practical for several reasons. It was almost certain that the reaction conditions suitable for the analysis of simple thiol-containing compounds would not be drastic enough to insure completeness of reaction between mercaptan groups in the insoluble protein and iodoacetamide. In addition, it was doubtful whether an acid–base titration could be conveniently applied to the desired low concentrations of interest, of the order of 0.0005 mequivs, particularly with buffering groups of the keratin protein being present.

It will be noted in reaction (1) above that iodide as well as hydrogen ion is liberated. The determination of sulfhydryl content via some quantitative measurement of iodide ion appeared to offer a better chance for the successful estimation in the microequivalent range. Potentiometric titrations of iodide ion with silver ion can be performed with good accuracy at low concentrations[15]. Therefore, this method of assay was chosen as the means of determining the amount of iodide ion liberated as a result of the iodoacetamide-reduced hair reaction.

To obtain samples of different sulfhydryl content, human hair was immersed in basic thioglycolate solutions of varied normality for different lengths of time. Such a treatment is known to convert the disulfide bond in keratin to thiol groups[16,17]. The use of thioglycolate reduction introduced the problem of the complete removal of the treatment solution since any reducing agent remaining on the hair would react readily with iodoacetamide and lead to erroneously high results. In addition to determining the conditions necessary to remove all of the thioglycolate, the following factors were considered:

(a) The time required for completion of the reaction between iodoacetamide and the mercaptan group in the reduced keratin;

(b) The reproducibility of the results for a given hair sample at different weight levels; and

(c) The stabilization of sulfhydryl groups in a sample so that reoxidation to the disulfide would not occur and consistent results for a given hair sample would be obtained over a period of time.

DEVELOPMENT OF METHOD

Preliminary

Preliminary experiments were made to determine the stability of iodoacetamide in basic solution for a time ranging from five minutes to several hours, an interval anticipated to be sufficient for complete reaction between reduced hair and iodoacetamide. For this purpose, 10.0-mg portions of iodoacetamide obtained from the Eastern Chemical Corporation, Newark, New Jersey, were placed into each of three 10-ml volumetric flasks. Clark and Lubs pH 10 borate buffer, containing potassium nitrate instead of potassium chloride, was added to the mark. The contents of the flask were shaken and, after five minutes, one hour, and two hours, a 5.00-ml aliquot was withdrawn by pipette and was transferred into a 50-ml beaker. The pH of the system was adjusted to approximately 7.5 by addition of three drops of 6 *N* nitric acid and solid sodium bicarbonate. The solution was then titrated with silver nitrate solution delivered from a 10-ml semimicro burette reading directly to 0.02 ml. The progress of the titration was followed potentiometrically, utilizing a Beckman Model G pH meter to measure the potentials. The electrodes employed were a Beckman silver indicator electrode and an isolated saturated calomel reference electrode. Contact between the two was made by means of a 1 *M* ammonium nitrate – 4% agar salt bridge. The silver solution used was 10^{-3} *N*, prepared daily as required by a 1 : 10 volumetric dilution of a standard 10^{-2} *N* solution. A blank value corresponding to approximately $1.8 \cdot 10^{-4}$ mequivs of silver ion was indicated for the one- and two-hour reaction times, whereas, $1.5 \cdot 10^{-4}$ mequivs of silver ion was required to titrate the sample which had reacted for five minutes. These results demonstrated that iodoacetamide could be used at pH 10 for at least two hours without appreciable hydrolysis. The iodide ion which was titrated could be accounted for by an appropriate blank value, slightly dependent upon the time of reaction at pH 10.

A similar experiment was carried out using iodoacetamide recrystallized from water. With this material, no iodide ion at all was found in solution after two hours in a pH 10 solution.

Reaction time study

Since the time required for the reaction between the sulfhydryl groups in hair and iodoacetamide to go to completion was not known, the amount of iodide ion liberated by a given hair sample as a function of reaction time was studied. For this experiment, a sample of human hair obtained from DeMeo Brothers, New York, was immersed for 30 min in 0.61 *N* ammonium thioglycolate solution which had been adjusted to pH 9.2 with ammonia and the excess thioglycolate was removed from the hair by three successive washings in hot glacial acetic acid. The sample was then cut into 1/8″ lengths and dried in a vacuum oven at 110° for one hour. An appropriate weight was then placed into a 10-ml volumetric flask, 10.0 mg of iodoacetamide were introduced and pH 10 buffer solution was added to the mark. The contents of the flask were shaken, and after a given time interval, a 5.00-ml aliquot was transferred from the flask by means of a pipette. After pH adjustment, the solution was titrated with standard 10^{-3} *N* silver nitrate solution as previously described. The results of the experiment are shown in Table I. The data show that 15 min is insufficient time for the reaction to go to completion but that essentially constant results can be obtained if the reaction time is 30 to 120 min.

TABLE I

EFFECT OF REACTION TIME ON THE RESULTS FOR SULFHYDRYL LEVEL

High SH-level

Weight of hair *mg*	*Reaction time* *min*	*SH-level* *mequivs/g*
20.0	15	0.651
20.0	30	0.779
20.0	60	0.776
20.2	120	0.782

To determine whether a 30- to 60-min reaction time is sufficient for samples of low sulfhydryl content, for hair which is much less reduced and thus, less susceptible to the penetration of iodoacetamide, the above experiment was repeated with hair reduced for six minutes in 0.30 *N* ammonium thioglycolate. These samples were then extracted with glacial acetic acid for two hours in a Soxhlet extractor, dried, and treated as before. In this particular series, reaction times of 5, 30, 60, 90, and 120 min were used. These results are shown in Table II.

TABLE II

EFFECT OF REACTION TIME ON THE RESULTS FOR SULFHYDRYL LEVEL

Low SH-level

Weight of hair *mg*	*Reaction time* *min*	*SH-level* *mequivs/g*
26.9	5	0.084
25.6	30	0.138
24.4	60	0.134
28.1	90	0.138
28.4	120	0.138

Since these results agree with the others, in that essentially constant values are obtained after 30 min, a reaction time of 45 min was used in all subsequent experiments.

Thioglycolate removal

To obtain a true value for the sulfhydryl content of a thioglycolate-reduced hair sample, it was necessary that all of the treatment solution be removed from the fibers. The procedure used in the first part of the above experiment, washing with three portions of hot glacial acetic acid, may not have removed the last traces of thioglycolate and, what is more important, some oxidation of the keratin sulfhydryl may have occurred during the rinsings. In an attempt to minimize or eliminate oxidation, and still accomplish the complete removal of thioglycolate solution, samples were extracted with glacial acetic acid in a Soxhlet extractor. In this experiment, three portions, each approximately 100 mg, of a given hair sample were each placed into a 1 × 5 cm extraction thimble, and the thimble was then set into a micro Soxhlet apparatus. The first sample was analyzed after one hour of extraction, the second after two hours, and the last one after three hours. Highly reduced hair was used in this experiment because it was thought that the greatest amount of residual thioglycolate would be present in this case. As a control, the behavior of hair containing a low sulfhydryl level was also observed.

The data obtained in the above experiments are shown in Table III. It is apparent that the extractions of one and two hours yielded essentially the same results, whereas, lower values were obtained when three-hour extractions were utilized. The reason for the difference could be due to some reoxidation of keratin sulfhydryl

TABLE III

EFFECT OF SOXHLET EXTRACTION WITH GLACIAL ACETIC ACID ON THE SULFHYDRYL LEVEL OF REDUCED HAIR

Extraction time *h*	*SH-level*[a] *mequivs/g*	*SH-level*[b] *mequivs/g*
1	1.030	0.094
2	1.030	0.091
3	0.980	0.085

[a] Hair reduced with 0.61 *N* thioglycolate, pH 9.2, for 30 min.
[b] Hair reduced with 0.30 *N* thioglycolate, pH 9.1, for 5 min.

during the longer treatment period, and for this reason an extraction time of two hours was chosen for thioglycolate removal.

Weight level study

The method developed was tested for reliability with different sample weights. Samples were prepared by immersion in 0.61 N ammonium thioglycolate solution for 20 min, followed by an isopropyl alcohol rinse and acetic acid extraction. Portions weighing from 10 to 40 mg were reacted with 10 mg iodoacetamide for 45 min, the pH was adjusted to 7.5, and an aliquot was titrated with 0.001 N silver nitrate solution. The results obtained are shown in Table IV. The data indicate that in the range between 4 and 15 μequivs, the results are not a function of the weight of sample taken.

TABLE IV

EFFECT OF SAMPLE WEIGHT ON THE RESULT FOR SULFHYDRYL LEVEL

Weight of hair mg	*SH-found microequiv.*	*SH-level mequivs/g*
10.0	3.86	0.772
20.1	7.86	0.782
30.1	11.71	0.760
40.1	15.40	0.768

Stability of sulfhydryl groups in reduced hair keratin

It was observed that the sulfhydryl level of a given hair sample would slowly decrease when it was allowed to remain in contact with the atmosphere for any appreciable length of time. Since meaningful results in an analysis could be obtained only if all of the mercaptan groups originally present in the sample were ultimately determined, it was mandatory that the sulfhydryl level be stabilized until the material was analyzed.

Storing the samples under nitrogen was found to be a convenient means for the stabilization. Samples from which all thioglycolate had been removed were merely placed in a desiccator; high purity dry nitrogen was flushed through the container for five minutes, and the desiccator was then closed. The results for two samples, over a period of 17 days, showed conclusively that samples stored under nitrogen maintain their original sulfhydryl content. These data are listed in Table V.

TABLE V

STABILITY OF HAIR KERATIN SULFHYDRYL WHEN STORED UNDER NITROGEN

Time of analysis after sample preparation, days	*SH-level*[a] *mequivs/g*	*SH-level*[b] *mequivs/g*
1	0.193	0.511
7	0.187	0.511
10	0.183	0.515
15	0.188	0.508
17	0.192	0.507

[a] Sample prepared by immersing hair in 0.30 N ammonium thioglycolate, pH 9.2, for 10 min.

[b] Sample prepared by immersing hair in 0.47 N ammonium thioglycolate, pH 9.1, for 15 min.

Recommended procedure

A detailed description of the method for the determination of the sulfhydryl content of reduced hair utilizing iodoacetamide is given below:

The sample is washed well with isopropyl alcohol and blotted dry. Approximately 75 mg of 1/8″ lengths are placed into a small extraction thimble and treated with glacial acetic acid in a micro Soxhlet extraction apparatus for two hours, then the sample is rinsed with isopropyl alcohol and blotted dry. Approximately 20 mg of the material are placed in a tared test tube and dried for one hour at 110° in a vacuum oven. After the tube has cooled to room temperature in a nitrogen-filled desiccator, it is reweighed to ascertain the exact amount of hair which it contains. Between 9.8 and 10.2 mg of iodoacetamide and 10.0 ml of pH 10 buffer are added to the tube. The contents are stirred with a glass rod at 15-min intervals and, when 45 min have elapsed, a 5-ml aliquot is withdrawn by means of a pipette and transferred to a 50-ml beaker. Enough 6 N nitric acid is added to the beaker (usually 3 drops) so that the solution pH drops below 7, and then solid sodium bicarbonate is introduced until a new addition results in no visible carbon dioxide evolution; the pH of such a solution is between 7 and 8.

A silver electrode and one end of a 1 M ammonium nitrate – 4% agar salt bridge are placed into the beaker, the other end of the bridge being placed into another beaker containing 1 M ammonium nitrate solution and a Beckman fiber-type calomel electrode. The leads of the two electrodes are connected to a Beckman Model G pH meter, the lead from the silver electrode being placed into the upper receptacle.

Standard 10^{-3} N silver nitrate solution is delivered into the beaker from a 10-ml semimicro burette. Near the end-point, 0.060-ml increments are added; because of the drifting of the readings, approximately one minute is required to reach potential equilibrium near equivalence. The end-point of the titration is determined by a double-derivative method. The sulfhydryl level of the sample is calculated from the relationship:

$$\text{SH-level, mequivs/g} = \frac{N\ \text{AgNO}_3 \times \text{volume in ml} \times 2}{\text{Weight sample in g}}$$

A typical titration curve is shown in Fig. 1.

Estimate of standard error of method

An estimate of the standard error of the procedure was obtained by preparing a series of hair samples, ranging from very low to high sulfhydryl content, and analyzing duplicate samples. The desired levels of reduction were attained by immersing hair in various ammonium thioglycolate solutions, 0.26 N to 0.71 N, each adjusted to pH 9.0–9.2 with ammonia, for five, ten, and twenty minutes. The recommended method of analysis was followed.

The data obtained are shown in Table VI.

DISCUSSION

As was anticipated, the time required for the complete reaction between hair keratin sulfhydryl and iodoacetamide was substantially longer than the time needed to complete the reaction with soluble thiol compounds (two minutes)[14]. This fact, however, is not too surprising inasmuch as the iodoacetamide molecule must first diffuse into the interior of the hair fiber, and the iodide ion liberated must then diffuse from the hair fiber into the bulk of the solution before the reaction can be considered completed for the purposes of the analysis.

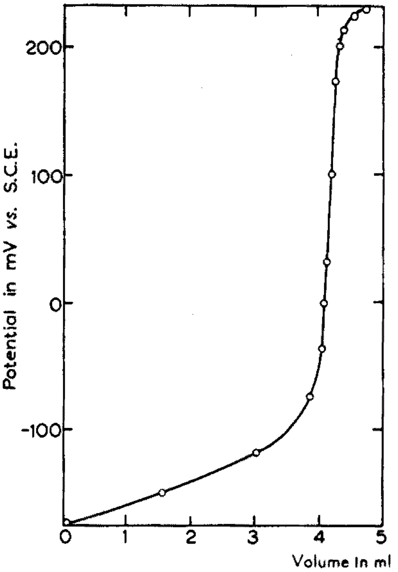

Fig. 1. Potentiometric titration of iodide ion with 10^{-3} N silver nitrate.

TABLE VI

DUPLICATE DETERMINATIONS OF THE SULFHYDRYL LEVEL OF HAIR REDUCED TO VARYING EXTENTS

Sample No.	*Sulfhydryl level, mequivs SH/g hair*	
1	0.001[a]	0.008[a]
2	0.083	0.082
3	0.097	0.105
4	0.120	0.122
5	0.167	0.160
6	0.201	0.207
7	0.224	0.216
8	0.227	0.223
9	0.311	0.312
10	0.320	0.336
11	0.346	0.351
12	0.399	0.400
13	0.411	0.408
14	0.503	0.506
15	0.509	0.548
16	0.637	0.644
17	0.783	0.778
18	0.850	0.831
19	0.840	0.876

[a] These values were obtained for an untreated hair sample.

It is apparent from the very low results obtained for the sulfhydryl content of the untreated sample, as reported in Table VI, that iodoacetamide reacts very slowly or not at all with side chains in the hair other than thiol groups. In addition to these particular results, other analyses of nonreduced hair were performed with this method and, in every case, a result below 0.010 mequivs SH/g hair was obtained. This fact is gratifying because the possibility of a side reaction with free amino groups exists[18] but apparently does not occur when the recommended procedure is followed.

The acetic acid extraction utilized for the removal of thioglycolate ion from the hair fibers proved to be satisfactory. However, a different system for the separation might be required if another reducing agent were employed. The exact conditions needed would be determined by the particular means of sulfhydryl group generation utilized; because of the success of the acetic acid extraction, it was not deemed necessary to examine other separation methods for the purposes of this investigation.

A regression analysis of the data in Table IV reveals that the estimate of the standard deviation of a single measurement is 0.074 μequiv. The value of "t" for the intercept is 1.00, so that there is insufficient evidence to maintain that the intercept differs from zero. In other words, there is no indication of a constant bias in the method.

The stabilization of the sulfhydryl level of a given hair sample was considered a prerequisite for the method since it is not always convenient to perform an analysis at the time the sulfhydryl groups are generated. The desired effect can be realized simply by storing the material in an inert atmosphere; samples kept in a nitrogen-filled desiccator in this laboratory were found to contain their original sulfhydryl content even after two months.

Some pH control of the iodide-containing solution being titrated with silver ion is necessary. If the pH is much above 8, hydroxide ion will begin competing for silver ion and will limit the "top" of the potentiometric titration curve. Below pH 7, the aerial oxidation of iodide ion becomes an important factor, especially in such dilute solutions. The means utilized in this work for pH adjustment, namely, the "breaking" of the pH 10 buffer with nitric acid and the subsequent addition of solid sodium bicarbonate until carbon dioxide evolution ceases, is a most convenient means whereby a suitable hydrogen ion concentration is assured.

The estimate of standard error of a single measurement in the 19 sets of duplicate results listed in Table VI is 0.010 mequivs SH/g hair. When this value is divided by the average result for mequiv. SH/g hair, 0.372, the estimate of average standard per cent error is found to be 2.7%. These values are perhaps not completely realistic because of the particular distribution of error. An examination of the data reveals that the largest discrepancies, by far, occurred in the samples of high sulfhydryl content. The major reason for this is probably that irregular reoxidation took place in these highly reduced samples, leading to a somewhat larger spread of results. Minimizing the sample's contact with atmospheric oxygen would undoubtedly decrease this source of variation.

The procedure developed should be applicable with little modification to the determination of sulfhydryl groups in other keratinous materials such as wool and callus. The simplicity and rapidity of the method and, especially, the fact that only those groups capable of reacting with iodoacetamide to produce iodide ions are determined, are particularly advantageous.

ACKNOWLEDGEMENTS

The authors wish to thank I. M. KLOTZ of Northwestern University and EDWARD M. CARR and HERMAN BOGATY of The Toni Company for their helpful comments and suggestions. The authors thank The Toni Company and The Gillette Company for permission to publish.

SUMMARY

A method for the determination of the mercaptan groups in intact, that is, nonhydrolyzed, human hair has been developed. The procedure is based upon the titration with silver nitrate of the iodide ion generated in the reaction between the sulfhydryl groups in the hair and iodoacetamide. The standard error of the method is of the order of 0.010 mequivs mercaptan/g hair.

RÉSUMÉ

Une méthode est proposée pour le dosage des groupes mercaptans dans les cheveux. Ce procédé est basé sur le titrage, au moyen de nitrate d'argent, de l'ion iodure formé lors de la réaction entre les groupes sulfhydriles du cheveu et l'iodoacétamide.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung der Mercaptogruppen in Menschenhaar. Sie beruht auf der Reaktion der Sulfhydrylgruppen mit Jodoacetamid und Titration des gebildeten Jods.

Anal. Chim. Acta, 23 (1960) 89–97

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BUCHBESPRECHUNGEN

Ionenaustauscher, Band I, *Grundlagen. Struktur-Herstellung-Theorie*, von F. Helfferich, Verlag Chemie, G.m.b.H., Weinheim/Bergstr. 1959.

Wie so oft im Bereich der Chemie ist auch bei den Ionenaustauschern die Entwicklung der praktischen Anwendungen dem theoretischen Verständnis der ablaufenden Vorgänge weit voraus geeilt. Auch heute noch wird bei technischer, präparativer aber auch analytischer Anwendung der Ionenaustauscher überwiegend unter empirisch ermittelten Versuchsbedingungen gearbeitet. Wenn in den letzten Jahren vielfach theoretische Betrachtungen zum Thema "Ionenaustausch" angestellt worden sind, so sind diese doch unter derart verschiedenen Gesichtspunkten angesetzt worden, dass es demjenigen, der sich nicht speziell mit diesem Problem befaßt, schwer fällt, eine Übersicht zu erlangen zumal der Umfang des Stoffes groß ist. So wird vielleicht zu selten von den häufig recht nützlichen Ansätzen Gebrauch gemacht, die es gestatten, Manches über optimale Arbeitsbedingungen vorauszusagen oder näherungsweise zu berechnen, wenn bestimmte, das Material eines Ionenaustauschers charakterisierende Grössen bekannt sind oder gemessen werden. Es ist das besondere Verdienst des Autors, in dem hier vorgelegten Buch das weit verstreute, oft heterogene Material kritisch auswählend unter übergeordneten Gesichtspunkten zusammengefasst zu haben.

Entsprechend ihrer überragenden praktischen Bedeutung nimmt die Behandlung der Harz-Austauscher den bei weitem grössten Raum ein. Nach einleitenden Bemerkungen über Struktur und Wirkungsweise der Austauscher werden die verschiedenen Austauschertypen, auch anorganische und solche auf Kohle-Basis, nach Aufbau und Eigenschaften besprochen. Es folgen Kapitel über Herstellungsprinzipien und die Kapazität von Harz-Austauschern. Besonders ausführlich und den theoretisch interessierten Leser besonders ansprechend sind die Kapitel über Gleichgewichte und Kinetik an Ionenaustauschern, Probleme zu denen der Autor in eigenen Arbeiten Bemerkenswertes beigetragen hat sowie über elektrochemische Eigenschaften. In den Kapiteln Ionenaustauschermembranen und Ionenaustauscherpackungen wird der Praktiker auch unmittelbar nützliche Hinweise finden, z.B. Ansätze für die Berechnung von Säulenabmessungen und für die rechnerische Behandlung von Nichtgleichgewichtszuständen. Die abschliessenden Kapitel über das Verhalten von Austauschern in nicht wässrigen oder gemischten Lösungsmitteln, über Ionenaustauscher als Katalysatoren sowie Elektronen- und Redox-Ionen-Austauscher sind entsprechend ihrer spezielleren und meist geringeren Bedeutung kürzer gehalten aber doch mit einer für das Verständnis ausreichenden Ausführlichkeit behandelt worden. Mit dem mehr als 1000 Literaturzitaten, die dem Text beigegeben sind, dürften die wichtigeren Arbeiten bis etwa zum Jahre 1957 hin nahezu vollständig erfasst sein.

Niemand wird erwarten, dasz bei der Fülle des Materials auf alle möglichen Betrachtungsweisen eingegangen wurde. Der gröszte Teil der Leser wird eine einheitliche Darstellung der Grundlagen und der Theorie in einer Weise wünschen, wie sie nach heutiger Anschauung den tatsächlichen Verhältnissen am nächsten kommt. So hat der Verfasser unter Verzicht auf historisch interessante oder vielleicht aussichtsreiche aber schwer zu übersehende oder abstrakte Ansätze solchen Betrachtungsweisen den Vorzug gegeben, die eine sachlich begründete einheitliche Darstellung erlauben und bei guter Anschaulichkeit ein möglichst hohes Mass an Aussagen gestatten. Es ist ihm dabei ein Werk aus einem Guss gelungen, das dem Wunsch nach Anschaulichkeit, Exaktheit und Geschlossenheit der Darstellung in bemerkenswerter Weise Rechnung trägt. Ein flüssiger, durchsichtiger Stil und Prägnanz im Ausdruck machen das Buch leicht lesbar auch für Jemanden, für den Deutsch Fremdsprache ist. Hervorzuheben sind ferner die Konsequenz in der Anwendung von Symbolik und Nomenklatur, die klare Gliederung des Textes, die instruktiven, geschickt ausgewählten Zeichnungen sowie eine sehr gute drucktechnische Gestaltung und Ausstattung.

Das Buch wird, da es einem ausgesprochenen Bedürfnis entgegenkommt, von allen am Ionenaustausch Interessierten freudig begrüsst werden.

H. BODE (Hannover)

Anal. Chim. Acta, 23 (1960) 97–98

Gmelins *Handbuch der anorganischen Chemie*, 8. Auflage, Verlag Chemie, G.m.b.H., Weinheim/Bergstr. *Magnetische Werkstoffe*, 2. Ergänzungsband zu Eisen, Teil D, 1959, xxxviii, 580 Seiten, 380 Fig., Kartoniert DM 321,—, Ganzleinen DM 326,—.

Dieser Ergänzungsband ist zugleich zugehörig zu den Systemnummern 52 (Chrom), 56 (Mangan), 57 (Nickel), und 58 (Kobalt). Nach einer Behandlung der Theorie des Ferromagnetismus (34 S.) erfolgt die Beschreibung der ferromagnetischen Elemente und Legierungen: Eisen (26 S.) und seine Legierungen (121 S.), Kobalt (11 S.) und Legierungen (13 S.), Nickel (63 S.) und Legierungen (42 S.), Legierungen des Mangans (22 S.), Legierungen des Chroms (2 S.), Ferromagnetische Halbleiter (121 S.). Sehr ausführlich behandelt sind neben den ferromagnetischen Elementen und den Systemen Fe-Co, Fe-Ni und Co-Ni vor allem das System Fe-Ni-Al und andere Systeme auf dieser Basis sowie das System Fe-Si. Bei den in den letzten Jahren besonders wichtig gewordenen Ferriten wurde die Literatur bis 1955 miterfasst. Auf Grund der technischen Bedeutung der magnetischen Werkstoffe wurde die Patentliteratur besonders beachtet und, nach sachlichen Gesichtspunkten geordnet, in einem besonderen Abschnitt „Patentschriften" (66 S.) angeführt. Wie alle neueren Gmelin-bände enthält auch dieser Band ein zweisprachiges Sachregister (deutsch und englisch) sowie Marginalien in englischer Sprache.

Der Inhalt dieses Sonderbandes steht auf gleich hohem Niveau wie die übrigen Gmelin-bände, obwohl er weniger den Chemiker als vor allem den Physiker und Ingenieur der Nachrichtentechnik interessieren wird.

K. EDER (Genf)

Anal. Chim. Acta, 23 (1960) 98

Gmelins *Handbuch der anorganischen Chemie*, 8. Auflage, Verlag Chemie, G.m.b.H., Weinheim/Bergstr. *Cadmium* (Ergänzungsband), System Nr. 33, 1959, iv, xciv, 802 Seiten, 218 Fig., Kartoniert DM 508,—, Ganzleinen DM 513,—.

Dieser Ergänzungsband zu dem 1925 erschienenen Band Cadmium umfasst die Forschungsergebnisse der Periode 1924 bis Ende 1949, wobei jedoch bei der Behandlung des Cadmium–Nickel Akkumulators die Literatur bis etwa 1958 berücksichtigt wurde.

Die Einteilung folgt dem üblichen Schema: Vorkommen (19 S.), Darstellung (24 S.) und physikalische Eigenschaften (140 S.), elektrochemisches Verhalten (127 S.), chemisches Verhalten (21 S.) und physiologische Eigenschaften (3 S.), Legierungen (60 S.) und Verbindungen (300 S.). Besondere Beachtung wurde der technischen Gewinnung des Elementes sowie seiner Bedeutung im Cadmium–Nickel Akkumulator zuteil. Bei den Verbindungen wurden die Additions- und Komplexverbin-

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dungen mit anorganischen und organischen neutralen Liganden (Ammoniak, Aminen und aminartigen Verbindungen) ausführlich behandelt.

Der Ergänzungsband enthält ein deutsch–englisches Inhaltsverzeichnis sowie englische Marginalien im Textteil.

K. EDER (Genf)

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Gmelins *Handbuch der anorganischen Chemie*, 8. Auflage, Verlag Chemie, G.m.b.H., Weinheim/Bergstr. *Silicium*, Teil B, (System Nr. 15): *Das Element und die anorganischen Verbindungen des Siliciums*. Deutsch-englisches Inhaltsverzeichnis und englische Marginalien im Textteil, 1959, iv, lix, 923 Seiten, 154 Fig., Kartoniert DM 570,—, Ganzleinen DM 575,—.

Dieser Band behandelt die Chemie und Physik des elementaren Siliciums sowie der anorganischen Si-Verbindungen: Hydride (Silane), Oxyde, Siloxane, Silanole, Siloxene, ferner die N-, Halogen-, Se-, Te-, B-, und C-Verbindungen des Siliciums.

Nach einer Beschreibung der verschiedenen Darstellungsmethoden im Laboratorium und in der Technik werden die physikalischen und chemischen Eigenschaften des Elementes behandelt, wobei besonders seine Eigenschaften als Halbleiter berücksichtigt wurden. Es folgt dann eine Zusammenstellung von spezifischen Nachweis- und Bestimmungsmethoden (*ca.* 100 S.) in den verschiedensten Materialien wie z.B. Metallen, Mineralien, Düngemittel, Farben und organischen Stoffen (Papier, Kohlen, Waschmittel, Drogen, Nahrungsmittel, usw.).

Unter den Verbindungen werden zunächst die Hydride (32 S.) und dann im grössten Teil des Bandes die Sauerstoffverbindungen (376 S.) behandelt. Während über das Monoxyd (11 S.) wenig Literatur vorliegt, ist sie über das Dioxyd und seinen Hydraten in deren verschiedenen Formen, Eigenschaften und Anwendungen umso umfangreicher. Im Anschluss an das Dioxyd werden die polymerisierbaren Siloxane, Silanole und Siloxene beschrieben.

Von den übrigen Siliciumverbindungen sind den Halogeniden, die teilweise als Ausgangsprodukte für die Herstellung der Silikone dienen, sowie dem Carbid, wegen seiner technischen Bedeutung, grössere Kapitel gewidmet.

Der Schluss des Bandes befasst sich mit der Glaselektrode (56 S.), deren Formen, Verhalten und Anwendungen.

Es braucht nicht hervorgehoben zu werden, dass auch dieser Band dem hohen Niveau entspricht, das dem Gmelin zuerkannt werden muss.

K. EDER (Genf)

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Lehrgang für das anorganisch-chemische Praktikum von Prof. Dr. G. SCHWARZENBACH, Juris-Verlag, Zürich, 1959, 197 Seiten, 18 Abb., Kartoniert SFr 25,—.

Dieses kleine Werk ist vor allem als Einführung in das Chemiestudium gedacht und skizziert den Lehrgang, der sich an der ETH Zürich seit Jahren bewährt hat.

Die Gliederung des Stoffes ist so vorgenommen, dass dem Anfänger zunächst nützliche Ratschläge, die den Arbeitsplatz betreffen, gegeben werden, wozu auch eine Anleitung zum Glasblasen und Angaben über die verschiedenen Glassorten gehören. An Hand von kurz, aber präzis beschriebenen Versuchen wird der Anfänger dann mit den wichtigsten chemischen Operationen wie Filtration, Kristallisation, Destillation, usw. vertraut gemacht. Hierbei wird bereits auf die Vorteile der Arbeit mit kleinen Substanzmengen hingewiesen. Es folgen dann die Beschreibung der wichtigsten Elemente und deren Verbindungen an Hand typischer Vertreter. Die weiteren Kapitel behandeln Stöchiometrie, Reaktionsgleichungen, wässrige Lösungen, Protonenübertragung in wässriger Lösung, Metallkomplexbildung (inkl. Komplexometrie), Fällungsreaktionen und Redoxreaktionen. Der Schluss des Bandes (etwa 1/3) beschreibt die Nachweisreaktionen für Kationen und Anionen sowie Trennungsgänge.

Das Buch enthält viele praktische Hinweise, die auch dem erfahrenen Chemiker oft von grossem Nutzen sein können. Sehr zu begrüssen ist die knappe, aber dafür sehr präzise und klare Fassung des Textes der theoretischen Erklärungen und Versuche, wodurch es möglich wurde, ein grosses Stoffgebiet auf verhältnismässig wenig Seiten unterzubringen. Durch die einseitige Bedruckung (Photodruckverfahren) hat das Buch allerdings das Doppelte des notwendigen Umfanges erhalten. Seines Inhalts wegen kann der Lehrgang bestens empfohlen werden.

K. EDER (Genf)

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BOOK REVIEW

The Analysis of Titanium and its Alloys, 3rd Ed., Imperial Chemical Industries Ltd., The Kynoch Press, Birmingham 1959, Pp. 119. Price 21 s. (see also *Anal. Chim. Acta*, 22 (1960) 499.)

In the review reference is made to the procedure on page 85 of the publication, for the determination of phosphorus in samples of titanium 'containing more than 3% manganese'. The reviewer has incorrectly concluded that this statement contains a typographical error, and I wish to point out that the instruction as it appears in our publication is correct.

In the examination of titanium samples containing small amounts of manganese, oxidation of phosphorus to ortho phosphate is achieved by oxidation with permanganate. Samples containing relatively large amounts of manganese cannot be oxidised effectively in this way, because manganous salts catalyse the reduction of permanganate and hence oxidation of phosphorus is less efficient. For this reason, a manganous salt is added when samples already contain an appreciable amount of manganese, then permanganate is formed, as recommended in the procedure, by oxidation with potassium periodate. In this way, complete oxidation of phosphorus is achieved.

Imperial Chemical Industries Ltd.,
Metals Division, Birmingham
(Great Britain)

W. T. ELWELL

Anal. Chim. Acta, 23 (1960) 100

ERRATUM

Anal. Chim. Acta, 21 (1959) 570, unter ERGEBNISSE: sind die Werte für 100 R_e folgendermassen zu verbessern:

Ba	38 - 44
Sr	54 - 60
Ca	64 - 72
Mg	81 - 85

VOL. 23 NO. 1 ANALYTICA CHIMICA ACTA JULY 1960

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ELSEVIER PUBLISHING COMPANY, AMSTERDAM
Printed in The Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH