

ANALYTICA CHIMICA ACTA

International monthly dealing with every branch of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

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ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 24, No. 1, p. 1—100, January 1961

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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 24, No. 1, January 1961

PHYSICAL PROCEDURES FOR THE ANALYSIS OF MIXTURES OF POLYCHLOROETHANES

A mixture of seven polychloroethanes has been analysed by fractionation into binary mixtures using a combination of continuous fractionation and the technique of total reflux with intermittent take-off. The binary mixtures were analysed by refractive index measurements. The relationship between binary mixture refractive index and component mass fraction was found to be linear. The temperature dependence of the refractive indices of the polychloroethanes over the range, 15–35°, was also determined.

J. S. RATCLIFFE, *Anal. Chim. Acta*, 24 (1961) 2–4

A RAPID METHOD FOR THE DETERMINATION OF AMMONIA (COMBINED) AND PHOSPHATE IN THE SYSTEM OF DIAMMONIUM PHOSPHATE AND DIPOTASSIUM PHOSPHATE

In systems containing $(\text{NH}_4)_2\text{HPO}_4$ and K_2HPO_4 , it is possible to determine ammonium and phosphate ions by titrating 2 aliquots using methyl orange as the only indicator. Potassium can be calculated by difference. About 20 min are required for a single analysis.

B. PASCHKES AND B. BERNAS, *Anal. Chim. Acta*, 24 (1961) 5–10

DETERMINATION OF VERY SMALL QUANTITIES OF CARBON DIOXIDE AND ANALYTICAL APPLICATION OF THE METHOD (in German)

A volumetric method for the determination of very small quantities carbon dioxide is described. The procedure gives very satisfactory results and can be applied for the determination of carbon in organic compounds.

E. SCHULEK, J. TROMPLER, A. ENDRÖI-HAVAS AND I. REMPORT, *Anal. Chim. Acta*, 24 (1961) 11–19

THE ACCURATE DETERMINATION OF COBALT

II. GRAVIMETRIC METHODS AND IN PARTICULAR THE PHOSPHATE METHOD

Some gravimetric methods for determining cobalt have been examined in order to assess their value for the accurate determination of the metal. The electrolytic method was found to give high results (about 1.4%), and the anthranilate method slightly high results (0.2–0.3%). A modification of the phosphate method has been developed in which a former drawback, the solubility of $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, has been overcome using a rapid spectrophotometric determination of residual cobalt. The final procedure developed has been found to give accurate results ($\pm 0.1 - 0.2$) and its use is recommended where this degree of accuracy is required.

A. G. FOSTER AND W. J. WILLIAMS, *Anal. Chim. Acta*, 24 (1961) 20–32

GRAVIMETRIC DETERMINATION OF MOLYBDENUM AND ITS SEPARATION FROM OTHER METALS WITH N-BENZOYLPHENYLHYDROXYLAMINE

N-Benzoylphenylhydroxylamine is employed as a precipitant for the determination of molybdenum(VI). The precipitate can be weighed either directly or as molybdenum trioxide after ignition. Molybdenum can be determined in the presence of appreciable amounts of iron(III), cobalt(II), copper(II), chromium(VI) and vanadium(V).

S. K. SINHA AND S. C. SHOME, *Anal. Chim. Acta*, 24 (1961) 33-36

GRAVIMETRIC DETERMINATION OF BERYLLIUM WITH N-BENZOYLPHENYLHYDROXYLAMINE

N-Benzoylphenylhydroxylamine has been employed in the gravimetric determination of beryllium and in its separation from iron, aluminium and titanium. After suitable adjustment of pH iron, aluminium or titanium is precipitated quantitatively with the reagent; beryllium is subsequently precipitated after raising the pH of the filtrate. The metal may be determined by either igniting the precipitate to beryllium oxide or weighing it as $\text{Be}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})_2$.

J. DAS AND S. C. SHOME, *Anal. Chim. Acta*, 24 (1961) 37-40

IMPURITY DETERMINATION BY THERMAL ANALYSIS

II. THE MELTING CURVE OF A QUICKLY FROZEN SAMPLE

A temperature-heat content relation is derived for a homogeneous solid solution of a binary system showing a very restricted rate of diffusion in the solid. It is shown experimentally that quickly frozen samples behave like homogeneous solid solutions. According to the new theory the depressions determined on partly molten samples are usually small and depend on the conditions; thus purity determinations based on heating curves of quickly frozen samples are of dubious value. The theory shows that superheating of the solid may occur when a solid solution is melted; this is confirmed experimentally.

H. F. VAN WIJK AND W. M. SMIT, *Anal. Chim. Acta*, 24 (1961) 41-45

THE ASSAY OF SODIUM CITRATE AND SODIUM POTASSIUM TARTRATE BY CATION EXCHANGE AND NON-AQUEOUS TITRIMETRY

Sodium citrate and sodium potassium tartrate are assayed by passing aqueous solutions of the salts through cation exchange resin columns, concentrating the effluents from the columns, and then titrating the effluents with standard sodium hydroxide solution. Sodium citrate is assayed by titrating a solution of the salt in glacial acetic acid with standard acetous perchloric acid, the end-point being detected potentiometrically; sodium potassium tartrate is assayed by stirring the salt in excess standard acetous perchloric acid, and then back-titrating the excess acetous perchloric acid with standard acetous potassium acetate, the end-point being detected potentiometrically.

M. L. RICHARDSON, *Anal. Chim. Acta*, 24 (1961) 46-54

MICRODETERMINATION OF COBALT IN REACTOR-GRADE ZIRCONIUM (in French)

A method is described for the separation and determination of cobalt in 100 mg reactor-grade zirconium. Separation is effected by means of an ion-exchange resin. After elution, the cobalt is purified by extraction with dithizone and determined spectrophotometrically with the help of nitroso-R-salt. With this method a content of 0.0003% can be determined with an accuracy of $\pm 4\%$.

J. VOGEL, D. MONNIER AND W. HAERDI, *Anal. Chim. Acta*, 24 (1961) 55-60

DETERMINATION OF HIGHER MOLECULAR WEIGHT ALIPHATIC ALDEHYDES AND KETONES

The visible absorption spectra have been measured for the reaction products formed by aldehydes and ketones with *p*-nitrobenzenediazonium fluoborate in a phosphoric acid-2-methoxyethanol solvent medium. The absorption maxima for the reaction products of higher molecular weight aldehydes and ketones are much more intense than those formed by formaldehyde, acetaldehyde and acetone. This intensity effect has been used to analyze for propionaldehyde in mixtures also containing formaldehyde, acetaldehyde or acetone. The nature of the reaction products are considered.

A. P. ALTSHULLER AND I. R. COHEN, *Anal. Chim. Acta*, 24 (1961) 61-66

A METHOD FOR THE DETERMINATION OF STARCH IN WOOD

A rapid and simple method of estimating starch in wood is described which is suitable for carrying out large numbers of determinations.

F. R. HUMPHREYS AND J. KELLY, *Anal. Chim. Acta*, 24 (1961) 66-70

THE DETERMINATION OF LEAD IN COPPER-BASE ALLOYS AND STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

The principle of atomic absorption spectrophotometry has only recently been exploited as an analytical technique and details are given of the development of a procedure for determining lead in copper-base alloys and leaded steels. The recommended method is simple, rapid and provides results as accurate as those obtained by the more time-consuming alternative methods in current use.

W. T. ELWELL AND J. A. F. GIDLEY, *Anal. Chim. Acta*, 24 (1961) 71-78

CONDUCTOMETRIC TITRATION OF METAL ACETATES IN AQUEOUS MEDIUM

Fifteen metal acetates in aqueous medium have been conductometrically titrated with trichloroacetic acid. The method has been applied to the titration of mono- and bivalent metals and angles at the equivalence point are sharp enough to allow accurate results to be obtained. Metal salts of acids weaker than acetic can be determined following solution in an excess of acetic acid and titration, because the weaker acid which is displaced does not interfere.

F. GASLINI AND L. Z. NAHUM, *Anal. Chim. Acta*, 24 (1961) 79-82

AMPEROMETRIC ARGENTIMETRIC AND MERCURIMETRIC TITRATION OF SULFHYDRYL

I. ARGENTIMETRIC TITRATION

Results of amperometric argentimetric titrations at the rotated platinum wire electrode in ammonia buffers of cysteine, glutathione, thioglycolic acid and 2-mercaptoethanol are presented. The method gives satisfactory results with glutathione and 2-mercaptoethanol. Thioglycolic acid gives good results in the presence of sulfite but high results in its absence. Its disulfide can be titrated accurately in the presence of sulfite. In agreement with other workers it was found that cysteine yields high results. The error increases with increasing cysteine concentration and is reduced in the presence of 0.1 M sulfite. It becomes equal to zero at cysteine concentrations equal to or smaller than $5 \cdot 10^{-5}$ M.

I. M. KOLTHOFF AND J. EISENSTÄDTER, *Anal. Chim. Acta*, 24 (1961) 83-90

PRECISION NULL-POINT POTENTIOMETRY

DIRECT MICRODETERMINATION OF IODIDE IN SOLUTIONS WITH HIGH CHLORIDE CONCENTRATIONS

The determination of microamounts of iodide in the presence of large concentrations of chloride, such as found in brines or iodized salt, can be performed directly and rapidly by the precision null-point potentiometric method. The complete analysis time is about 3 min. Iodized salt samples containing 5-100 p.p.m. iodide were determined with an average deviation less than 0.3 p.p.m. and with relative errors of about 0.5% at 100 p.p.m. and about 5% at 10 p.p.m. iodide. The measured samples contained 1-20 μg of iodide in 20 ml of solution, and the sodium chloride to iodide weight ratio was as high as 200,000 to 1. Similar precision and accuracy were obtained for prepared brines containing 10-200 p.p.m. iodide and a wide range of chloride to iodide ratios.

H. V. MALMSTADT AND J. D. WINEFORDNER, *Anal. Chim. Acta*, 24 (1961) 91-96

COLORIMETRIC DETERMINATION OF STRONTIUM

(Short Communication; in German)

R. PALOUŠ AND S. MIZERA, *Anal. Chim. Acta*, 24 (1961) 96-97

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Printed in the Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

PUBLISHERS' NOTE

It is with regret that we announce the retirement of Professor P. E. WENGER as Editor of *Analytica Chimica Acta*. Professor WENGER was one of the founders of the journal and for fourteen years has rendered highly valuable service in his capacity as Editor. We are greatly indebted to him for his co-operation and devotion, and gladly take this opportunity to express to him our sincere thanks.

As from January 1, 1961, the duties of Editor will be shared by Professor PHILIP W. WEST, the former Regional Editor, and Dr. A. M. G. MACDONALD. To them we extend a cordial welcome and we trust that our association will be a long and fruitful one.

NOTE DE L'ÉDITEUR

Nous avons le regret d'annoncer la démission de Monsieur le Professeur P. E. WENGER comme Rédacteur de *Analytica Chimica Acta*. Le Professeur WENGER a été l'un des fondateurs de la revue et au cours de quatorze ans a rendu de précieux services en sa qualité de rédacteur. Les éditeurs lui sont redevables de sa coopération et de son dévouement; ils saisissent cette occasion pour lui exprimer leurs sincères remerciements.

A partir du 1er janvier 1961 la responsabilité de Rédacteur sera partagée entre le Professeur PHILIP W. WEST jusqu'à cette date "Regional Editor" et le Docteur A. M. G. MACDONALD. Nous leur souhaitons ici une cordiale bienvenue et nous sommes confiants que notre association sera longue et heureuse.

MITTEILUNG DES VERLEGERS

Mit Bedauern kündigen wir die Demission von Herrn Professor P. E. WENGER als Redakteur von *Analytica Chimica Acta* an. Professor WENGER war einer der Gründer der Zeitschrift und hat ihr im Laufe von vierzehn Jahren als Redakteur grosse Dienste erwiesen. Wir sind ihm für seine wertvolle Mitarbeit sehr verpflichtet und ergreifen gerne diese Gelegenheit um ihm unseren aufrichtigen Dank auszusprechen.

Ab 1. Januar 1961 wird die Verantwortung für die Schriftleitung von Professor PHILIP W. WEST, dem bisherigen "Regional Editor" und Dr. A. M. G. MACDONALD gemeinsam getragen werden. Wir heissen diese Mitarbeiter hier herzlichst willkommen und sind davon überzeugt, dass unsere Zusammenarbeit lang und ergebnisreich sein wird.

PHYSICAL PROCEDURES FOR THE ANALYSIS OF MIXTURES OF POLYCHLOROETHANES

J. S. RATCLIFFE

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(Received July 7th, 1960)

INTRODUCTION

A chlorination study required the analysis of mixtures of polychloroethanes. Such mixtures could contain seven constituents of similar chemical properties with relatively close boiling points. Most of the compounds exhibited a strong tendency to dehydrochlorinate and had to be stored in the absence of light. Variation in physical properties could be detected after several days. For this reason the compounds, which were prepared by classical methods, were given a number of water washes and fractionations immediately before use. Anhydrous magnesium sulphate was used for drying purposes.

Previous experience suggested that the analysis could be achieved by separation of the constituents into binary mixtures, with a minimum of thermal stress, followed by examination of such mixtures through refractive index measurements.

Separation into binary mixtures

The possible components of the polychloroethane mixtures were as follows (see Table I).

TABLE I

<i>Components</i>	<i>B.P. (760 mm)°C</i>
1,1-Dichloroethane	57
1,2-Dichloroethane	83.5
1,1,1-Trichloroethane	75
1,1,2-Trichloroethane	113
1,1,1,2-Tetrachloroethane	130
1,1,2,2-Tetrachloroethane	147
Pentachloroethane	92 (100 mm)
(decomposes before boiling at 760 mm)	

Fractionations of these mixtures using packed columns and reflux-ratio heads was discarded because of too much hold-up. A Vigreux column and sluice-head, with fine adjustment stop-cock, was substituted.

The technique of total reflux with intermittent take-off was rejected because of low recoveries (92%) due to thermal stress. Continuous fractionation gave similarly low recoveries and larger hold-up due to increased column length and higher reflux required. It did not establish satisfactorily the presence of small amounts (5%) of a

component where the study reaction-path was uncertain. Also, where recoveries and hold-up were controlled by shorter columns, sharpness of separation suffered. Discrepancies with test mixtures could be explained only by small amounts of ternary mixtures being produced near fraction turn-over points.

For these reasons, the two techniques were combined in the shorter column of the total reflux method. Continuous fractionation was used between possible component boiling points and total reflux with intermittent take-off, was used within $\pm 2-3^\circ$ of the boiling point. This increased recoveries to 98+ % by lowering thermal stress and hold-up. It was also effective in increasing sharpness of separation at the critical points, without the penalty of lower recoveries obtained when the total reflux technique was used throughout the fractionation. The procedure established the reaction path.

Analysis of binary mixtures

Nine binary mixtures could be produced by the fractionation procedure from mixtures of the seven compounds resulting from the chlorination study. Within each binary mixture, the relationship of mass fraction and refractive index was found to be linear within the limits of refractive index measurement. The latter was considered to be 0.0002 with the Abbé type, refractometer held to $\pm 0.1^\circ$. This was equivalent to a composition variation within a binary mixture, of less than 0.5%. Such a mixture constituted only a fraction of the sample for analysis.

The net effect of these procedures gave accuracies between 0.5-2.0% on test mixtures; reproducibility tending to the lower figure and accuracy toward the higher.

The presence of hexachloroethane in the distillation residue was usually in the form of a solid solution in pentachloroethane. After weighing, further pentachloroethane was added to produce an homogeneous liquid phase of less than 20% hexachloroethane. The refractive index of this mixture established the hexachloroethane content of the *residue* and the pentachloroethane in same by difference.

Temperature dependence of refractive index

In association with the analytical work, the refractive indices were determined at intervals of 4° in the range $15-35^\circ$. It was found that parallel straight lines could be drawn, respectively, through points for each component, within the reproducibility of 0.0002.

From this it was found that for this series of compounds, $dn/dt = -5.26 \cdot 10^{-4}$, whereas the average general value¹ is $-4.5 \cdot 10^{-4}$, where the relationship is linear.

The values at 20° (see Table II) are in agreement with other workers (temperatures shown in brackets) and the above relationship.

TABLE II

<i>Components</i>	<i>Refractive index</i>
1,1-Dichloroethane	1.4164 (20°) ²
1,2-Dichloroethane	1.4449 (20°) ^{3,4} , (15°) ⁵ (25°) ⁶
1,1,1-Trichloroethane	1.4379 (20°) ⁷
1,1,2-Trichloroethane	1.4706 (20°) ²
1,1,1,2-Tetrachloroethane	1.4828 (20°) ⁸
1,1,2,2-Tetrachloroethane	1.4942 (20°) ⁹ , (15°) ¹⁰
Pentachloroethane	1.5030 (20°) ¹¹ , (15°) ¹⁰
Hexachloroethane	1.5001 (30°) (20% in pentachloroethane)

SUMMARY

A mixture of seven polychloroethanes has been analysed by fractionation into binary mixtures using a combination of continuous fractionation and the technique of total reflux with intermittent take-off. The binary mixtures were analysed by refractive index measurements. The relationship between binary mixture refractive index and component mass fraction was found to be linear. The temperature dependence of the refractive indices of the polychloroethanes over the range, 15–35°, was also determined.

RÉSUMÉ

Des méthodes physiques sont proposées pour l'analyse de mélanges de polychloroéthanés, par fractionnement en mélanges binaires, et mesure des indices de réfraction de ces derniers.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Analyse eines Gemisches von Polychloräthanen durch Zerlegung (Destillation) in binäre Gemische und Messung deren Refraktionsindizes.

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A RAPID METHOD FOR THE DETERMINATION OF AMMONIA (COMBINED) AND PHOSPHATE IN THE SYSTEM OF DIAMMONIUM PHOSPHATE AND DIPOTASSIUM PHOSPHATE

B. PASCHKES AND B. BERNAS

Israel Mining Industries Laboratories, Haifa (Israel)

(Received June 10th, 1960)

INTRODUCTION

A simple titration method was required to determine phosphate and ammonium ions in the system $(\text{NH}_4)_2\text{HPO}_4$ and K_2HPO_4 which would be suitable for rapid routine control analysis without instrumental techniques.

When an excess of alkali is added to diammonium hydrogen phosphate, the ammonia can be quantitatively eliminated by boiling. Back titration of the excess alkali with $N/10$ hydrochloric acid followed by titration from $\text{HPO}_4^{-2} \rightarrow \text{H}_2\text{PO}_4^{-}$ yields titers which correspond to the ammonium and the phosphate. Methyl orange is the only indicator used. When dipotassium hydrogen phosphate is present, potassium can thus be calculated by difference.

EXPERIMENTAL PART

Standard solutions and reagents

Solution A. K_2HPO_4 aqueous solution containing 26.43 mg PO_4^{-3} per ml. *Solution B.* $(\text{NH}_4)_2\text{HPO}_4$ aqueous solution containing 12.47 mg NH_4^+ per ml and 33.02 mg PO_4^{-3} per ml. *Methyl orange (M.O.)* indicator, 0.05% aqueous. *Phenolphthalein (Ph)* indicator, 0.5% in 50% ethanol. *Mixed indicator (M.I.)* phenolphthalein + α -naphtholphthalein (2 parts 0.5% phenolphthalein in 50% ethanol and 1 part 0.1% α -naphtholphthalein in 50% ethanol¹). *Brilliant yellow indicator paper* obtained by soaking strips of filter paper with a 0.1% brilliant yellow aqueous solution and drying.

The first stage of the procedure where phosphate and ammonium ions are determined by a single titration with phenolphthalein and methyl orange indicator, or mixed indicator and methyl orange indicator, is presented in Table I. Throughout experiments No. 1-3 a synthetic sample was obtained by mixing aliquots of solution A and solution B as given in Table I. The volume was brought to approximately 100 ml with carbon dioxide-free distilled water; standard carbon dioxide-free $N/10$ sodium hydroxide in the amounts stated in column 3 of Table I was added to the sample and the solution was boiled till free of ammonia. The solution was cooled and titrated first to phenolphthalein and subsequently to the methyl orange end-point. In experiment No. 2 the solution was half saturated with sodium chloride to repress hydrolysis². In experiment No. 3 the mixed indicator was tested.

If the total theoretical alkalinity to methyl orange is calculated (column 6, Table I) we see that the total titer to methyl orange found is correct and reproducible (column 5, Table I), the maximum deviation being $\pm 0.75\%$ relative.

TABLE I
THE DETERMINATION OF AMMONIUM AND PHOSPHATE BY A SINGLE TITRATION USING PHENOLPHTHALEIN AND METHYL ORANGE OR MIXED INDICATOR AND METHYL ORANGE

Experi- ment No.	Taken ^a		Added		Titrated		Theoretically required			Found		Relative deviation	
	PO ₄ ⁻³ mg 1	NH ₄ ⁺ mg 2	N/10 NaOH (<i>f</i> = 1.034) ml 3	Indicator	N/10 HCl (<i>f</i> = 1.007) ml 5	Actually titrated N/10 HCl (<i>f</i> = 1.007) ml 6	N/10 HCl (<i>f</i> = 1.007) ml 6	PO ₄ ⁻³ mg 7	NH ₄ ⁺ mg 8	PO ₄ ⁻³ % 9	NH ₄ ⁺ % 10		
1	59.45	12.47	20.00	Ph	12.70	19.90 ^d	70.31	14.25	+18.08	+14.28			
				Ph → M.O.	7.35						20.05 ^b		
2	59.45	12.47	20.00	Ph	12.40	19.90	70.31	14.79	+18.08	+18.61			
				Ph → M.O.	7.35						19.75 ^b		
3	59.45	12.47	20.00	M.I.	12.90 - 13.30 ^c	19.90	67.44-63.60	13.87-13.15	+13.44	+11.23			
				M.I. → M.O.	7.05 - 6.65 ^c						19.95 ^b	+ 7.00	+ 5.45

^a 1.00 ml of solution A plus 1.00 ml of solution B were taken in each experiment.

^b Total titer to M.O.

^c The end-point was not clearly distinguished.

^d Calculation: 20.00 ml N/10 NaOH (column 3) corr. to 20.68 ml N/10 NaOH (*f* = 1.000). Alkali requirement for 12.47 mg NH₄⁺ (column 2) corr. to 6.91 ml N/10 NaOH (*f* = 1.000). 13.77 ml N/10 NaOH (*f* = 1.000) corresponding to excess NaOH in the solution = 13.68 ml N/10 HCl (*f* = 1.007). 59.45 mg PO₄⁻³ (column 1) corresponds to 6.22 ml N/10 HCl (*f* = 1.007) (HPO₄⁻² → H₂PO₄⁻²). 19.90 is the theoretically required total back titer N/10 HCl (*f* = 1.007).

Representing the reaction schematically (Fig. 1) we see that if ac (compare columns 5 and 6 in Table I) is exact, the interpretation of the point b is not correct at the end-point of the phenolphthalein or mixed indicator (column 5, Table I). A displacement of b gives a displacement of d in the same direction. In our case it was displaced to the right giving too high results (by 5–18% relative) for phosphate as well as for ammonium ion (see columns 1, 2, 7, 8, Table I).

The second stage of the experimental part, therefore, involves the actual determination of point b by a direct titration of bc .

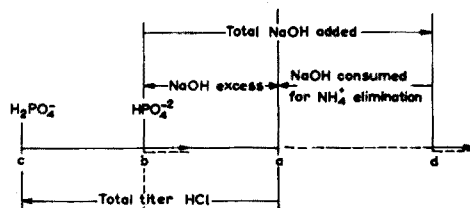


Fig. 1. Addition of NaOH (bd); elimination of NH_3 by boiling (da); back titration with HCl of excess NaOH to phenolphthalein or mixed indicator end-point (ab); titration $\text{HPO}_4^{-2} \rightarrow \text{H}_2\text{PO}_4^-$ from phenolphthalein or mixed indicator end-point to methyl orange (bc). Total titer HCl (ac).
 → displacement of b causes displacement of d .

DETERMINATION OF PHOSPHATE AND AMMONIUM BY TWO TITRATIONS USING METHYL ORANGE AS THE ONLY INDICATOR

When the sample is titrated directly with hydrochloric acid to methyl orange satisfactory values are obtained for $\text{HPO}_4^{-2} \rightarrow \text{H}_2\text{PO}_4^-$. If this titer is deducted from the total titer to methyl orange obtained in the first experimental part (column 5, Table I), the interference of the pH range of hydrolysis of the dibasic salt is avoided and stoichiometrically correct results are obtained.

Experiment No. 4

In this experiment an aliquot of the synthetic sample of $(\text{NH}_4)_2\text{HPO}_4$ and K_2HPO_4 (same composition as in experiments No. 1–3) was diluted to about 50 ml with distilled water and directly titrated with $N/10$ hydrochloric acid to methyl orange indicator. Amount of titrant used:

6.27 ml $N/10$ HCl ($f = 1.007$) to methyl orange = 59.98 mg PO_4^{-3} . This titer corresponds to bc , i.e. titration of $\text{HPO}_4^{-2} \rightarrow \text{H}_2\text{PO}_4^-$. The calculation of the NH_4^+ is therefore done in the following manner (see Fig. 2):

$$\begin{aligned} ac - bc &= ab \text{ (excess NaOH in the solution)} \\ db - ab &= (\text{total NaOH} - \text{excess NaOH}) = da \text{ (corresponds to } \text{NH}_4^+ \text{)}. \end{aligned}$$

For example: In experiment No. 3 the total titer was 19.95 ml $N/10$ HCl ($f = 1.007$) (column 5, Table I).

19.95 ml (ac)	<i>Net titer</i>	
−6.27 ml (bc)		20.68 ml $N/10$ NaOH added (db)*
13.68 ml $N/10$ HCl ($f = 1.007$)	→	−13.77 ml $N/10$ NaOH excess (ab)*
		6.91 ml (for NH_4^+) (da)
		6.91 · 1.804 = 12.47 mg NH_4^+

* calculated to $f = 1.000$

TABLE II
VALUES OBTAINED BY THE PROPOSED VOLUMETRIC DETERMINATION OF AMMONIUM AND PHOSPHATE

Experiment No.	Taken		Found				Relative deviation	
	Composition of aliquots ^a I and II	Containing PO ₄ ⁻³ mg NH ₄ ⁺ mg	N/10 NaOH (f = 1.004) added to aliquot II ml	N/10 HCl (f = 1.007) Titration of aliquots I ml II ml	PO ₄ ⁻³ mg NH ₄ ⁺ mg	PO ₄ ⁻³ % NH ₄ ⁺ %	PO ₄ ⁻³ % NH ₄ ⁺ %	
5	2.00 ml Solution A 0.50 ml Solution B Total	52.86 ml 16.51 6.235 69.37 6.235	20.00	7.32 23.91	70.01 6.096	+0.92	-2.23	
5a	As above		8.00	not done 12.00	N.D. ^c 6.01	—	-3.6	
6	0.50 ml Solution A 2.00 ml Solution B Total	13.22 ml 66.04 24.94 79.26 24.94	25.00	8.32 19.51	79.58 24.96	+0.4	+0.08	

^a In accordance with Fig. 2.

^b Calculated as in Experiment No. 4.

^c N.D. = Not determined.

If the total titer of $N/10$ hydrochloric acid is taken from Expts. No. 1 and 2 (column 5, Table I) the results are respectively: 12.27 mg NH_4^+ and 12.82 mg NH_4^+ (relative deviation = -1.6% ; $+2.8\%$).

These and the following results indicate that it is possible to determine the phosphate and ammonium content by two separate titrations in two aliquots of the sample using only methyl orange indicator.

Schematically the two titrations can be represented as follows:

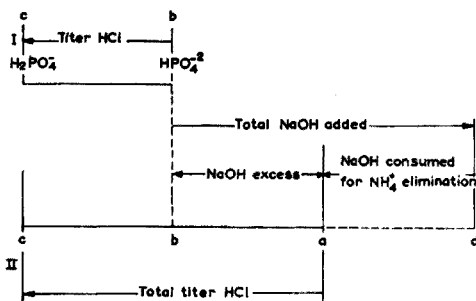


Fig. 2. Aliquot I. Direct titration with HCl to methyl orange end-point from HPO_4^{-2} to H_2PO_4^- (bc). Aliquot II. Addition of NaOH (bd); elimination of NH_3 by boiling (da); back titration with HCl of excess NaOH + $\text{HPO}_4^{-2} \rightarrow \text{H}_2\text{PO}_4^-$ (ac).

From the above it follows that titers ac and bc were proved to be correct; it follows therefore that point b must be correct and consequently also ab as well as ad are reliable.

The reproducible values as obtainable by the method are shown in Expts. No. 5 and 6.

CONDITIONS OF DETERMINATION

Aliquot I (Fig. 2): The aliquot taken was diluted to about 50 ml with distilled water and titrated to methyl orange indicator with $N/10$ hydrochloric acid.

Aliquot II (Fig. 2): Another aliquot of the same composition was diluted to about 100 ml; $N/10$ sodium hydroxide was added and the solution boiled until free of ammonia; after cooling it was titrated to methyl orange indicator with $N/10$ hydrochloric acid.

Details and results are summarized in Table II. When diammonium hydrogen phosphate is titrated directly with $N/10$ hydrochloric acid to methyl orange (titer A ml) (first titration Fig. 2) the ammonium ion will require the presence of $2A$ ml titer of $N/10$ sodium hydroxide, assuming that all the phosphate is present as the diammonium salt; then $2A + 5$ ml will be a sufficient excess to cover the total alkali requirement for the ammonia determination.

If the amount of the ammonium ion is known to be low the quantity of added alkali can be decreased. This is shown in experiment No. 5a (Table II).

METHOD

Procedure

1. Dilute an aliquot containing about 60 mg of phosphate with distilled water

to about 50 ml and titrate with $N/10$ hydrochloric acid to methyl orange (titer A).

2. Place another aliquot containing about 15 mg of ammonium ion in a 250-ml Erlenmeyer flask, add $N/10$ sodium hydroxide* in an excess of at least 5 ml, dilute to about 100 ml and boil till ammonia-free (about 15 min) testing the vapours with moist brilliant yellow paper. When the paper remains yellow no more free NH_3 is present in the solution. Cool and titrate with $N/10$ hydrochloric acid to methyl orange (titer B).

Calculation

1. Phosphate

$$\frac{\text{titer } A \cdot f(N/10 \text{ HCl}) \cdot 0.0095 \cdot 1000}{\text{aliquot ml}} = \text{PO}_4^{3-} \text{ in g/l}$$

2. Ammonium

$$\frac{\text{ml } N/10 \text{ NaOH corresponding to } \text{NH}_4^+ \cdot 0.001804 \cdot 1000}{\text{aliquot ml}} = \text{NH}_4^+ \text{ in g/l}$$

titer B — titer A = ml HCl corresponding to excess NaOH

Total $N/10$ NaOH added** — excess $N/10$ NaOH** = $N/10$ NaOH corresponding to NH_4^+ .

Note

The calculation is made on the basis of identical aliquots.

ACKNOWLEDGEMENTS

Thanks are due to Dr. A. ALON, Chief Analyst, Mr. D. ELROI and Mrs. V. VARSANYI for their help and constructive criticism and the Management of Israel Mining Industries for the kind permission to publish this work.

SUMMARY

In systems containing $(\text{NH}_4)_2\text{HPO}_4$ and K_2HPO_4 , it is possible to determine ammonium and phosphate ions by titrating 2 aliquots using methyl orange as the only indicator. Potassium can be calculated by difference. About 20 min are required for a single analysis.

RÉSUMÉ

Une méthode volumétrique est proposée pour le dosage de l'ammonium et de l'anion phosphorique dans un mélange de phosphate diammonique et de phosphate dipotassique. La teneur en potassium est calculée par différence.

ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung von Ammonium und Phosphat in einem Gemisch von Diammoniumphosphat und Dikaliumphosphat. Der Gehalt an Kalium wird durch Differenz berechnet.

REFERENCES

- ¹ A. VOGEL, *Quantitative Inorganic Analysis*, 2nd ed., Longmans, 1951, pp. 54, 64, 65, 66.
- ² I. M. KOLTHOFF AND E. B. SANDELL, *A Textbook of Quantitative Inorganic Analysis*, 3rd ed., MacMillan, 1952, p. 536.

* If the order of magnitude of NH_4^+ is unknown, add 2· A ml of $N/10$ NaOH + 5 ml excess.

** To be calculated to factor 1.000.

BESTIMMUNG SEHR KLEINER MENGEN KOHLENDIOXYDS UND DIE ANALYTISCHE ANWENDUNG DES VERFAHRENS

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(Eingegangen den 20. Juni, 1960)

Es wurden bisher zahlreiche titrimetrische Verfahren zur Bestimmung kleiner Mengen Kohlendioxyds ausgearbeitet, weiterentwickelt und hinsichtlich ihrer Zuverlässigkeit überprüft. Das Studium der in diesem Zusammenhang aufgeworfenen Probleme hat auch gegenwärtig nichts an Aktualität eingebüsst, was auch verständlich ist, wenn man bedenkt, dass die titrimetrische Verfahrenstechnik anderen Messmethoden gegenüber grosse Vorteile besitzt. Als gebräuchlichstes Reagenz der Kohlensäure wird $\text{Ba}(\text{OH})_2$ -Lösung gebraucht. Die nicht in Reaktion getretene $\text{Ba}(\text{OH})_2$ -Menge kann unter Anwendung eines entsprechenden Indikators, meistens ist dies Phenolphthalein, acidimetrisch gemessen werden. BELCHER, THOMPSON UND WEST¹ befassen sich in ihrer jüngst erschienenen Arbeit, unter Berücksichtigung der Feststellungen anderer Forscher, eingehend mit den Problemen dieser Messmethode und bringen ein Verfahren zur Kohlenstoffbestimmung organischer Substanzen in Vorschlag. Im Rahmen dieser Arbeit sollen unsere eigenen Erfahrungen, Methoden und Messergebnisse behandelt werden. Wir befassten uns mit folgenden Themen:

I. Bestimmung des chemisch gebundenen Kohlendioxyds².

II. Bestimmung des chemisch gebundenen, aber in Freiheit gesetzten Kohlendioxyds.

III. Bestimmung des Kohlenstoffgehaltes organischer Verbindungen.

Wir möchten vor der Behandlung dieser einzelnen Themen einige bedeutende Probleme verfahrenstechnischen Charakters herausheben und unsere diesbezüglichen Untersuchungsergebnisse kurz zusammenfassen. Es handelt sich um Fragen des Fernhaltens atmosphärischer Kohlensäure und der Anwendungsmöglichkeit von Phenolphthalein als Indikator.

Der störende Einfluss der atmosphärischen Kohlensäure kann auf verschiedene Weise behoben werden. Meistens wird ein kohlendioxydfreier Gasstrom angewendet, dessen Unbequemlichkeit aber beim Arbeiten bekannt ist. TINSLEY, TAYLOR UND MOORE³ verwenden Petroläther als Schutzsubstanz. Unsere Untersuchungen² ergaben, dass Pentan besser als Petroläther, Propan und Butan enthaltendes Pentan aber besonders vorteilhaft angewendet werden kann. Die Vorzüge einer solchen Flüssigkeit ergeben sich erstens aus ihrer grossen Flüchtigkeit und zweitens aus der verhältnismässig hohen Dichte der gebildeten Dampfphase. Es war mit Recht zu erwarten, dass die Dämpfe die Luft und damit auch das Kohlendioxyd aus dem zur Anwendung gelangenden Absorptions- bzw. Titrierkolben rasch austreiben werden. Pentan löst

Kohlendioxyd in messbarer Menge nur dann, wenn ein verhältnismässig hoher Partialdruck des Gases aufrechterhalten wird. Ein mit CO_2 gesättigtes Pentan gibt infolge des oben Gesagten beim Stehen im offenen Gefäss das Kohlendioxyd sehr rasch an die Atmosphäre ab und kann vorteilhaft nicht nur in diesem Fall, sondern auch zum bequemen Fernhalten der Luft d.h. also besonders des oft unerwünschten Sauerstoffs herangezogen werden. Schmalhalsige Kolben und mit entsprechend verlängerten Hahnansatzkapillaren versehene Büretten (Abb. 2) sichern eine grosse Messgenauigkeit. Dies bezieht sich in erster Linie auf das Arbeiten mit 0.05 und 0.01 N $\text{Ba}(\text{OH})_2$ -Lösungen.

Zur Anwendung des Phenolphthaleins ($\text{pH} = 8.3-10$) als Indikator sollen einige kurze Bemerkungen gemacht werden. Es kann bei der Endpunktanzeige von Titrationen im Mikromassstab nur dann gute Dienste leisten, wenn die Kohlensäure der Atmosphäre, besonders aber die der Atemluft ferngehalten wird. Pentan eignet sich zu diesem Zweck besonders gut. Wenn eine 0.01 N HCl - oder Essigsäurelösung unter Anwendung von Phenolphthalein und auch Pentan mit 0.01 N NaOH -Lösung titriert wird, so erfolgt eine gut bemerkbare Entfärbung der im Endpunkt rosafarbenen Lösung erst nach 25 Sek. Ohne Pentan tritt dies bereits nach 1 Sek auf. Man sieht also, dass Pentan tatsächlich vorteilhaft angewendet werden kann. Untersuchungen ergaben, dass die Entfärbung der auch durch Pentan geschützten Lösungen nicht auf die Einwirkung der atmosphärischen Kohlensäure, sondern auf strukturelle Veränderungen des Phenolphthaleins zurückzuführen ist. Die Ursache dieses Verhaltens des Phenolphthaleins kann mit der bereits in schwach alkalischer Lösung stattfindenden Aufspaltung seiner Laktonbindung erklärt werden. Man muss diese langsam verlaufende Reaktion beim Titrieren von Basen unbedingt berücksichtigen und dementsprechend verfahren. Es ist zweckmässig, wenn zu Beginn der Titration nur 2 Tropfen Phenolphthalein-Lösung zugegeben werden. Der Rest, vorteilhaft noch 4 Tropfen, wird erst vor dem Endpunkt zugefügt.

I. BESTIMMUNG DES ANORGANISCH-CHEMISCH GEBUNDEN KOHLENDIOXYDS²

Die Versuche wurden unter Anwendung sorgfältig hergestellter und analytisch kontrollierter 0.1 N NaOH - und 0.1 N KHCO_3 -Stammlösungen durchgeführt. Als Reagenz wandten wir eine 40 Vol. % Äthanol enthaltende 0.05 N $\text{Ba}(\text{OH})_2$ -Lösung an, u. zw. deshalb, um die Hydrolyse des BaCO_3 zurückzudrängen. Aus dem gleichen Grunde wurde der mit $\text{Ba}(\text{OH})_2$ versetzten und durch Pentan geschützten Lösung auch $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ zugefügt. Betreffs Einzelheiten verweisen wir auf die bereits erwähnte, unter Druck befindliche Arbeit.

II. BESTIMMUNG DES CHEMISCH GEBUNDENEN, ABER IN FREIHEIT GESETZTEN KOHLENDIOXYDS

Die genaue Bestimmung des in der Gasphase befindlichen Kohlendioxyds hängt in erster Linie von der Zuverlässigkeit des angewandten Absorptionsverfahrens ab. Das ist verständlich, wenn man bedenkt, dass das Bariumhydroxyd nicht direkt mit dem in Lösung befindlichen Kohlendioxyd, sondern mit dessen Hydrolysenprodukt, mit der Kohlensäure reagiert. Es ist bekannt, dass im System Kohlendioxyd-Wasser die Hauptmenge des Kohlendioxyds als CO_2 und nicht als H_2CO_3 vorliegt, und dass die Hydrolyse im Gegensatz zur Neutralisationsreaktion, wenn Lauge zugegeben wird,

langsam verläuft⁶. Die experimentelle Tatsache, wonach eine 28%-ige KOH-Lösung CO₂ mit maximaler Geschwindigkeit zu absorbieren vermag⁷, beweist ebenfalls, dass zur quantitativen Bindung des Kohlendioxyds als Carbonat Zeit beansprucht wird. Bei der quantitativen Messung kleiner Kohlendioxydmengen nach dem Ba(OH)₂-Prinzip müssen demgemäß zwei wichtige Zeitfaktoren berücksichtigt werden. Erstens die Absorption, also der Übergang des CO₂ aus der Gas- in die Flüssigkeitsphase, und zweitens die Hydrolyse zu Kohlensäure. Die Anwendung eines kontinuierlichen Gasstromes kann aus diesem Grund unserer Meinung nach zu systematischen Fehlern führen. Dies bezieht sich besonders auf den Fall, wenn Ba(OH)₂ in wässrig-alkoholischer Lösung zur Anwendung gelangt.

Unter Berücksichtigung der erwähnten Vorbedingungen arbeiteten wir ein neues Messverfahren aus, das sowohl im Halbmikro-, als auch im Mikromassstab angewendet werden kann. Die Absorption des in der Gasphase befindlichen Kohlendioxyds erfolgt nicht im offenen System, d.h. unter Anwendung eines kontinuierlichen Gasstromes, sondern im geschlossenen. Die Überführung des Kohlendioxyds zur Ba(OH)₂-Lösung sicherten wir durch ein Druckgefälle zwischen Absorptionsgefäß und Aussenluft.

Beschreibung der Einrichtung

Auf Fig. 1 ist die von uns angewandte Einrichtung abgebildet. Der 250 ml fassende Rundkolben (A) wird als Absorptions- und Titriergefäß verwendet. Den Verschluss nach der Atmosphäre hin sichert der sorgfältig eingeschliffene gedrungene Glasstopfen und ein daran befindlicher Karlsruher Hahn (3). Der Hals des Kolbens ist knapp über dem Schliiff kelchartig erweitert. Der Kolben (A) kann über den Hahn (3), den Dreiweghahn (2) und ein Nadelventil (1) mit der Wasserstrahlluftpumpe verbunden werden. Zur Kontrolle des Vakuums dient ein einfaches Hg-Manometer (F). Durch entsprechendes Einstellen des Hahns (3) kann Kolben (A) auch mit dem eiförmigen Kolben (B) verbunden werden. Die am unteren Ende pfeifenartig nach aufwärts gebogene dickwandige Kapillare des Kolbens (B) mündet über Glashahn (4) in ein

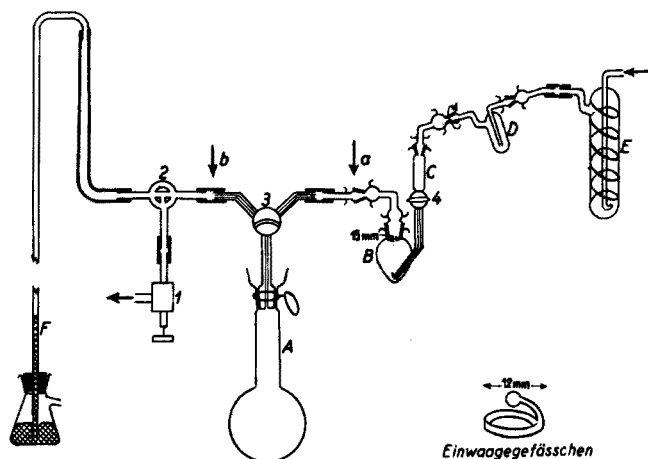


Fig. 1. A. Rundkolben zur Aufnahme der Ba(OH)₂-Lösung, B. Kolben zur Aufnahme der Untersuchungssubstanz, C. Trichterchen, D. Gaswaschgefäß, E. Gaswaschgefäß, F. Hg-Manometer, 1. Nadelventil, 2. Dreiweghahn, 3. Karlsruher Hahn, 4. Zweiweghahn.

10-ml Trichterchen (C). An letzteres sind die Gaswaschgefäße (D) und (E) angeschlossen u.zw. in der aus Fig. 1 ersichtlichen Anordnung. (E) ist ein Spiralgaswaschgefäß und dient zum Fernhalten der atmosphärischen Kohlensäure. Als Absorptionsmittel wurde etwa 28%-ige KOH-Lösung gewählt. Es ist sehr vorteilhaft, wenn Kolben (A), Dreiweghahn (2), Nadelventil (1) und Manometer (F) an ein Bunsen-Gestell befestigt werden. (Das Manometer kommt dabei auf die nach rückwärts geschwenkte Bodenplatte zu stehen). Ebenso verfährt man beim Befestigen der Geräteteile (B), (C), (D) und (E). Man erhält auf diese Weise zwei Geräte-Einheiten, die bequem auf der Tischplatte verschoben und mit Hilfe eines einzigen Glasschliffes (siehe Pfeil a auf Fig. 1) gasdicht verbunden werden können. Als Schmiermittel der Glasschliffe bewährte sich konzentrierte Schwefelsäure, noch besser aber dickflüssige Phosphorsäure.

Als Vorratsbürette wurde eine L. W. WINKLERSche⁴ benutzt, deren Hahnansatzkapillare auf etwa 15 cm verlängert wurde. Die Vorratsbürette wurde mit niederschlagsfreier $\text{Ba}(\text{OH})_2$ -Lösung folgendermassen aufgefüllt (siehe Fig. 2a). Die Hahn-

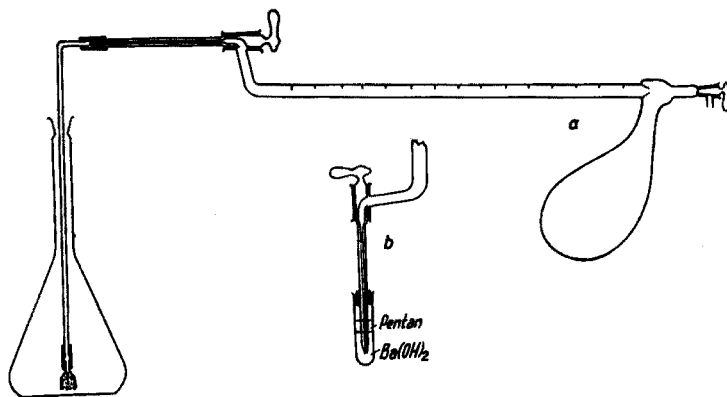


Fig. 2.

ansatzkapillare der Bürette wurde mit einer rechtwinklig gebogenen Glasröhre mit Hilfe eines Kautschukrohrstückchens, — an dessen Ende sich ein mit Baumwolle versehenes Trichterchen befand — angeschlossen und mit Hilfe der oben beschriebenen Vorrichtung mit Kohlendioxydfreier Luft gefüllt. Nun brachte man die Bürette in horizontale Lage (siehe Fig. 2a) und tauchte das Trichterchen in die vorbereitete und schon abgesetzte $\text{Ba}(\text{OH})_2$ -Lösung. Die Lösung wurde endlich in die Vorratsbürette mit Hilfe der Vorrichtung eingesaugt.

Um die Ausfällung von BaCO_3 an der Spitze der Hahnansatzkapillare zu vermeiden, wird diese, wie auf der Fig. 2b zu sehen ist, in ein mit der Masslösung beschicktes Probierröhrchen eingetaucht. Die in dem Probierröhrchen befindliche Masslösung ist mit einer Pentanschicht bedeckt, um das atmosphärische Kohlendioxyd fernzuhalten. Das Probierröhrchen ist mit Hilfe eines an der Seite eingeschnitzten Korkes an der Hahnansatzkapillare befestigt.

Mit Hilfe der beschriebenen Einrichtung bestimmten wir den Kohlendioxydgehalt des Calciumcarbonats (Calcit) und Kaliumhydrogencarbonats. Das Kohlendioxyd des ersteren wurde mittels 60%-iger Perchlorsäure, das des letzteren aber unter Anwendung 85%-iger Schwefelsäure in Freiheit gesetzt und durch eine 0.1 N $\text{Ba}(\text{OH})_2$ -

Lösung absorbiert. Die zur Einwaage gelangenden Substanzen waren Calcitstücke, bzw. nach dem Verfahren von WINKLER hergestelltes Kaliumhydrogencarbonat. Die Einwaage erfolgte unter Benützung des auf Fig. 1 abgebildeten Gefässchens. Zum Fernhalten der atmosphärischen Kohlensäure (beim Einfüllen und Titrieren des Bariumhydroxyds) diente Pentan, als Indikator wurde Phenolphthalein angewandt. Leerversuche zeigten, dass erstens das Pentan und zweitens die 25–28%-ige KOH-Lösung die atmosphärische Kohlensäure vom System fernhält. Gleichfalls musste kontrolliert werden, ob 60%-ige Perchlorsäure (E. Merck) und 85%-ige Schwefelsäure als Lösungsmittel bzw. als Kohlendioxyd in Freiheit setzende Reagenzien verwendet werden konnten. Wir wollen bereits an dieser Stelle darauf hinweisen, dass beide Säuren (in der angegebenen Konzentration) nicht bloss den halbmikro-, sondern auch den mikroanalytischen Anforderungen entsprachen.

Beschreibung des Verfahrens im 0.1 N Massstab

In das Gaswaschgefäss (E) wird 25–28%-ige KOH-Lösung, in (D) 3–5 ml 60%-ige Perchlorsäure oder 85%-ige Schwefelsäure gefüllt und die Einrichtung gemäss Fig. 1 zusammengestellt. Hähne und Schliche werden mit dickflüssiger Phosphorsäure gedichtet — der Glasstopfen des Kolbens (A) bleibt trocken! — und durch Gummiringe gesichert. Die Wasserstrahlluftpumpe wird nach Öffnen der Hähne (2, 3, 4) und Schliessen des Nadelventils (1) in Gang gesetzt. Durch entsprechendes Einstellen des letzteren (man beobachtet die in (E) aufsteigenden Luftblasen) kann das ganze System bequem durchspült werden. Das Gaswaschgefäss (D) wird in ein 50–60° warmes Wasserbad getaucht und auf diese Weise das in den konzentrierten Säuren gelöste Kohlendioxyd beschleunigt entfernt.

Inzwischen misst man die zu untersuchende Substanz, unter Anwendung des Gefässchens (siehe Fig. 1) und eines Uhrenglases als Unterlage, auf der Waage ab. Nadelventil (1) und Hahn (4) werden geschlossen und die Einrichtung beim Glasschliff (siehe Pfeil (a) auf Fig. 1) getrennt. Nach Entfernen des rechtwinkeligen Zwischenrohrstückes setzt man das Gefässchen mit Hilfe einer Pinzette auf den Boden bzw. auf die pfeifenartige Kapillarmündung des eiförmigen Kolbens (B). Die Geräteteile werden erneut aneinandergesetzt und Hahn (4), sowie Nadelventil (1) geöffnet. Während des nun fortgesetzten Durchspülens nimmt man Kolben (A) ab, giesst in diesen etwa 10 ml Pentan, wartet kurze Zeit und füllt 10.00 ml 0.1 N Ba(OH)₂-Lösung ein. (Die verlängerte, etwa 10 cm lange Hahnansatzkapillare der Vorratsbürette soll tief unten am Hals des Kolbens anliegen). Der Kolben wird an seine ursprüngliche Stelle gebracht, durch entsprechendes Einstellen des Hahnes (3) mit der Wasserstrahlluftpumpe verbunden und nach weiterem Öffnen des Nadelventils (1) evakuiert. Die Grösse und Konstanz des Vakuums kann am Hg-Manometer (F) kontrolliert werden. Hahn (4) wird geschlossen und die konzentrierte Säure durch Umschwenken des Gefässes (D) in das Trichterchen (C) übergeführt. (Das Wasserbad wird von (D) nach (B) versetzt). Anschliessend verbindet man über Hahn (3) die Kolben (A und B), öffnet vorsichtig Hahn (4) und lässt die konzentrierte Säure aus (C) nach (B) fliessen. Die im Einwaagegefässchen befindliche Carbonat-Probe gerät mit der Säure in Berührung und löst sich darin unter CO₂-Entwicklung rasch auf. Bis zum gänzlichen Auflösen muss der durch Hahn (4) regulierte Luftstrom stark gedrosselt werden. Wenn auch bei ganz geöffnetem Hahn (4) keine Luftblasen mehr aufsteigen, wird Hahn (3) und Hahn (4) geschlossen, die Rohrverbindungen bei Pfeil (a und b) gelöst und der

Kolben (A) vom Gestell abgenommen. (Es ist vorteilhaft, wenn der Stopfen des Kolbens durch eine Gummischleife fixiert wird). Den Kolben stellt man auf 15–20 Min beiseite und schüttelt dessen Inhalt öfters durch. Anschliessend wird in die kelchartige Erweiterung etwa 10 ml Pentan gegossen und erst dann der Stopfen aus dem Glasschliff herausgehoben. Der im Kolben sich sofort bildende Pentandampf verhindert das Eindringen atmosphärischer Kohlensäure und gestattet ein äusserst bequemes Messen des überschüssigen Bariumhydroxyds. — Als Masslösung wird 0.1 N Salz- oder Perchlorsäurelösung, als Indikator 6 Tropfen 1%-ige Phenolphthaleinlösung angewandt.

1 ml 0.1 N Ba(OH)₂-Lösung entspricht 2.2005 mg CO₂ (log 0.34252)

TABELLE I

Substanz	Einwaage		Verbraucht 0.1 N Ba(OH) ₂ - Lösung ml	Gefunden CO ₂ mg	Abweichung vom theoret. Wert %
	mg	entspricht theoretisch CO ₂ mg			
CaCO ₃ (Calcit)	21.8	9.61	4.38	9.63	+0.2
	27.9	12.28	5.56	12.24	—0.3
	14.6	6.42	2.94	6.46	+0.6
	19.4	8.53	3.85	8.47	—0.7
	28.0	12.32	5.57	12.27	—0.4
	18.1	7.96	3.62	7.92	+0.1
KHCO ₃	18.1	7.95	3.61	7.94	—0.1
	24.6	10.81	4.89	10.77	—0.4
	31.1	13.67	6.24	13.75	+0.6

TABELLE II

DOLOMIT

Einwaage mg	CO ₂ -Gehalt g/g %
18.6	47.63
20.9	47.68
19.4	47.48
27.2	47.22
24.4	47.23
23.6	47.18
16.5	47.40

Die Messergebnisse sind in Tabelle I zusammengestellt. Es ist daraus zu ersehen, dass wir etwa 10 mg Kohlendioxyd mit einer Genauigkeit von $\pm 0.5\%$ bestimmten, obzwar beide Substanzen, also das CaCO₃ und KHCO₃, bloss auf 0.1 mg genau abgewogen werden konnten. Unter Berücksichtigung dieses Umstandes muss das erhaltene Resultat als sehr zufriedenstellend bezeichnet werden. Die Analysenergebnisse einer Dolomit-Probe (siehe Tabelle II) bestätigen diese Feststellung ebenfalls.

Das beschriebene Verfahren konnte auch zur Bestimmung von etwa 1 mg CO₂ d.h. beim Arbeiten mit 0.01 N Ba(OH)₂-Lösung herangezogen werden. Als Untersuchungssubstanz diente Calcit. Da uns derzeit eine Mikrowaage nicht zur Verfügung stand, lösten wir das Problem der Einwaage folgendermassen. Sowohl das Calcit als auch das als Verdünnungssubstanz dienende Glas wurden im Achatmörser feinstens zerrieben, dann abgewogen und im gleichen Mörser vermengt. 10 mg Pulvergemisch enthielt 0.2283 mg CaCO₃.

Die 0.01 N Ba(OH)₂-Lösung wurde durch Verdünnung einer 0.1 N Lösung hergestellt und enthielt 50 g BaCl₂ · 2 H₂O im L. Zweck dieses Zusatzes war die Hydrolyse des gebildeten BaCO₃ zurückzudrängen. Um noch eine grössere Wirkung zu erzielen, wurde dem nach der Absorption des Kohlendioxyds erhaltenen Reaktionsgemisch 5 ml 96%-iges Äthanol zugesetzt. Phenolphthalein bewährte sich in diesem Fall nicht als Indikator und musste durch α -Naphtholphthalein (pH = 7.0–9.0) ersetzt werden. Das Umschlagsintervall dieses Indikators liegt zwar, was das Titrieren bei Anwesenheit von BaCO₃ betrifft, etwas ungünstiger, — dieser Nachteil wird aber durch andere Vorteile ausgeglichen. Erstens dadurch, dass der Farbumschlag auch beim Arbeiten mit 0.01 N Masslösungen sehr genau festgestellt werden kann und zweitens, dass die Nähe des Endpunktes angezeigt wird. Der Umschlag erfolgt nämlich von blau über grün nach gelb. Das zur Anwendung gelangende Äthanol musste zwecks Entfernung des gelösten Kohlendioxyds zuerst ausgekocht und nach Abkühlung auf den erwähnten Indikator (eben gelb) eingestellt werden.

Beschreibung des Verfahrens im 0.01 N Massstab

Die Handhabung der Apparatur ist die gleiche wie beim Arbeiten im Halbmikromassstab, Kolben (A) wird nach erfolgter Absorption des Kohlendioxyds unter Anwendung von Pentan geöffnet und mit einer Pipette 5.0 ml 96%-iges Äthanol zugegeben. (Zur Vorbereitung und Aufbewahrung des Äthanol nimmt man am zweckmässigsten einen mit Glasschliff versehenen 100-ml Messkolben). Nach Zufügen von 2 Tropfen 0.2%-iger alkoholischer α -Naphtholphthaleinlösung titriert man mit 0.01 N HCl- oder HClO₄-Lösung bis zum Farbumschlag von grün nach gelb. Die zur Kohlendioxydbindung angewandte gleiche Menge 0.01 N Ba(OH)₂-Lösung wird unter Anwendung von 5 ml Alkohol ebenfalls titriert. Aus der Differenz der beiden Messungen kann der CO₂-Gehalt der Untersuchungssubstanz berechnet werden.

1 ml 0.01 N Ba(OH)₂-Lösung entspricht 0.2200 mg CO₂ (log 0.34252)

TABELLE III

Einwaage		Verbraucht 0.01 N Ba(OH) ₂ - Lösung ml	Gefunden CO ₂ mg	Abweichung vom theoretischen Wert %
Calcit-Glas- Pulvergemisch* mg	entspricht theoretisch CO ₂ mg			
75.7	0.760	3.43	0.754	—0.8
73.6	0.739	3.32	0.731	—1.1
73.6	0.739	3.38	0.744	+0.6
73.5	0.738	3.33	0.733	—0.65

* 10 mg Pulvergemisch enthielt 0.2283 mg CaCO₃.

Tabelle III enthält die Messergebnisse des Calcit-Glas-Pulvergemisches. Aus den Angaben der Tabelle ist zu ersehen, dass auf diesem Wege noch etwa 0.7 mg CO₂ gemessen werden können. Wenn berücksichtigt wird, dass erstens mit 0.01 N Masslösungen gearbeitet wurde und dass zweitens ein Pulvergemisch, also keine einheitliche Substanz zur Einwaage gelangte, so muss die Bestimmungsgenauigkeit von $\pm 1\%$ als sehr zufriedenstellend bezeichnet werden.

III. BESTIMMUNG DES KOHLENSTOFFGEHALTES ORGANISCHER VERBINDUNGEN

Das ausgearbeitete titrimetrische Verfahren konnte bei der organischen Mikroelemen-

taranalyse mit sehr gutem Erfolg an Stelle der üblichen gewichtsanalytischen Methode angewandt werden. Es wurde sowohl mit 0.1 N als auch mit 0.01 N Masslösungen gearbeitet. Im ersten Fall kam ein 250-ml, in zweiten ein 125-ml Rundkolben als Absorptions- und Titriergefäß zur Anwendung. Die Verbrennung erfolgte nach der Methode von KÖRBL⁵. Das Mikroverbrennungsrohr nach KÖRBL wurde (bei Pfeil (a) der Fig. 1) über einen Kapillarglashahn an den Rundkolben (A) mit Hilfe von Vakuumgummischläuchen (Glas an Glas) angeschlossen. Der Kapillarglashahn diente zur Regulierung des Gasstromes, also der durch das Vakuum angesaugten Verbrennungsprodukte. Die Versuche bewiesen, dass das zur Verfügung stehende Kolbenvolumen zur Aufnahme und Einspülung des gebildeten Kohlendioxyds vollkommen ausreicht. Die optimale Strömungsgeschwindigkeit betrug im 0.1 N Masstab (beim 250-ml Kolben) etwa 8 ml/Min, im 0.01 N Masstab (beim 125-ml Kolben) etwa 20 ml/Min. Die Silberpermanganatfüllung des Verbrennungsrohres wurde auf 440–450° gehalten. Die übliche Anordnung der Sauerstoffgaszuführung wurde beibehalten (Blasenzähler, Manostat usw.). Die Rückdiffusion des gebildeten Kohlendioxyds konnte durch einen in das Verbrennungsrohr eingeschobenen Glasstab verhindert werden. Wir wollen auch an dieser Stelle erwähnen, dass sich die Pentan-Methode als eine äusserst elegante, einfache und zuverlässige erwies. Das titrimetrische Verfahren unterscheidet sich in nichts von dem bereits beschriebenen. Eine genaue Beschreibung des Verfahrens soll auch schon aus diesem Grunde fortbleiben.

TABELLE IV

Gravimetrisch nach Körbl			Titrimetrisch (0.1 N Masstab)		
% H	% C	Abweichung vom theoretischen Wert %	% C	Abweichung vom theoretischen Wert %	
4.22	60.31	—0.9	61.03	+0.3	
4.34	60.59	—0.5	61.19	+0.5	
4.44	60.92	+0.1	60.86	0.0	
4.43	60.73	—0.2	60.77	—0.1	
4.33	60.64	—0.4	60.77	—0.1	
4.36	60.68	—0.3	61.03	+0.3	
			60.53	—0.6	
			60.96	+0.1	
Mittelwert	4.35	60.64	—0.38	60.89	+0.05

Die Salicylsäure enthält theoretisch 4.38% H und 60.87% C.

Die Zuverlässigkeit und Genauigkeit des neuen Verfahrens wurde an Salicylsäure *p.a.* (Chinoin) als Untersuchungssubstanz geprüft. Tabelle IV enthält die mit der üblichen gewichtsanalytischen Methode, sowie die mit dem titrimetrischen Verfahren im 0.1 N Masstab erhaltenen Messergebnisse. Die Einwaage an Salicylsäure betrug in beiden Fällen 3–5 mg und erfolgte auf einer Sartorius Mikrowaage (Messgenauigkeit $\pm 2 \mu\text{g}$). Als Füllmittel der Absorptionsrohre diente Magnesiumperchlorat und Natronasbest. Aus den Angaben der Tabelle IV ist zu entnehmen, dass das titrimetrische Kohlendioxyd — bzw. Kohlenstoff-Bestimmungsverfahren zuverlässige und genaue Messergebnisse liefert. Die Genauigkeit des Verfahrens ändert sich kaum, wenn mit 0.01 N Masslösungen gearbeitet, d.h. bloss 0.8 mg Salicylsäure analysiert wird.

Tabelle V enthält unsere diesbezüglichen Messergebnisse. Wegen der Sicherung der Einwaagegenauigkeit mussten verhältnismässig grosse Salicylsäuremengen angewandt werden, obwohl das titrimetrische Verfahren auch die C-Bestimmung von

TABELLE V

Titrimetrisch (0.01 N Masstab)	
% C	Abweichung vom theoretischen Wert %
60.88	0.0
60.59	-0.5
60.73	-0.2
60.88	0.0
60.75	-0.2
60.67	-0.3
60.52	-0.6
60.82	-0.1
60.75	-0.2
60.67	-0.3
Mittelwert 60.72	-0.24

Die Salicylsäure enthält theoretisch 60.87% C.

0.3 mg Substanz gestatten würde. Die vorzügliche Übereinstimmung des experimentell bestimmten und theoretisch berechneten Kohlenstoffgehalts beweist eindeutig, dass das Verfahren auch im Mikromasstab mit grosser Genauigkeit angewandt werden kann.

ZUSAMMENFASSUNG

Die Verfasser beschäftigen sich mit Problemen des Fernhaltens der atmosphärischen Kohlensäure, bzw. der Anwendungsmöglichkeit von Phenolphthalein als Indikator und bringen ein titrimetrisches CO₂-Bestimmungsverfahren in Vorschlag. Das chemisch gebundene oder in Freiheit gesetzte Kohlendioxyd wird durch überschüssige 0.1 oder 0.01 N Ba(OH)₂-Lösung gefällt bzw. absorbiert. Das Kohlendioxyd der Atmosphäre und Atemluft kann unter Anwendung von Pentan auf sehr einfache Weise ferngehalten werden. Im 0.1 N Masstab wird Phenolphthalein, im 0.01 N hingegen α -Naphtholphthalein als Indikator empfohlen. Das Verfahren kann mit sehr gutem Erfolg auch bei der organischen Mikroelementaranalyse angewandt werden.

SUMMARY

A volumetric method for the determination of very small quantities carbon dioxide is described. The procedure gives very satisfactory results and can be applied for the determination of carbon in organic compounds.

RÉSUMÉ

Les auteurs proposent une méthode volumétrique permettant le dosage de très petites quantités d'anhydride carbonique. Ce procédé donne des résultats très satisfaisants et peut être appliqué au dosage du carbone dans les substances organiques.

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THE ACCURATE DETERMINATION OF COBALT II. GRAVIMETRIC METHODS AND IN PARTICULAR THE PHOSPHATE METHOD

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(Received January 14th, 1960)

INTRODUCTION

Gravimetric methods used in the determination of cobalt have been critically discussed¹. The precipitation of cobalt by α -nitroso- β -naphthol introduced by ILINSKI AND VON KNORRE² in 1885 was one of the first methods used for the determination of a metal with the aid of a selective organic reagent. In spite of its many defects, and the large number of other methods proposed, it remains, in modified form, one of the most frequently recommended methods for the determination of cobalt. No matter which modification is used, the method is open to much criticism. The precipitate itself is impure, due to the cobalt being in two valency states; the reagent also acts as an oxidant, itself becoming reduced to products which further contaminate the precipitate. Poisonous fumes are given off on heating, and the bulky nature of the precipitate and its tendency to stick to glassware make filtration difficult.

Ignition of the complex to the 'oxide' leads to further difficulty owing to its uncertain composition. Reduction of the 'oxide' by hydrogen to metallic cobalt for final weighing is the form of the method claimed to be most accurate. The important question here is whether the metallic residue contains traces of unreduced oxide. Also, in this form, weighing errors have the maximum effect. This, no doubt, is a reason why conversion of metallic cobalt to CoSO_4 for final weighing has also been recommended.

Reduction by hydrogen to the metal via " Co_3O_4 " of uncertain composition has been recommended as the final procedure in many methods of cobalt analysis.

Variation in composition of the precipitate or final weighing form is the major source of error in a number of cobalt gravimetric methods *e.g.* the phenylthiohydantoic acid and cobaltinitrite methods. Its effect on the sulphate method will be apparent from the examination of CoSO_4 as a possible reference standard¹.

Slight solubility of the precipitate is the major source of error in other cobalt methods, particularly the phosphate method.

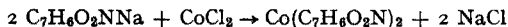
The aim of the present work was to examine experimentally a number of cobalt methods using a cobalt reference standard previously shown to be reliable¹. In selecting methods for detailed examination, consideration was given to relevant data already available *e.g.* thermogravimetric behaviour of precipitates involved. Those

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finally chosen for critical examination were the anthranilate, phosphate, and electrolytic methods, the last being included for convenience with gravimetric methods. Methods depending on final reduction to metallic cobalt, or ignition as CoSO_4 were rejected for reasons given above.

REVIEW OF METHODS

The anthranilate method introduced by FUNK AND DITT³ consists of adding excess of a 3% sodium anthranilate solution to a hot neutral or very slightly acid solution of cobalt.



The complex was dried at $105^\circ\text{--}110^\circ$. GOTO⁴ found the minimum pH for complete precipitation, and the maximum pH at which no precipitation took place to be 4.41 and 3.36 respectively. These values have been criticised and re-determined⁵. SHENNAN *et al.*⁶ investigated the precipitation of cobalt anthranilate in buffered solution.

Although accurate results were claimed in unbuffered solution, low results were found in the presence of acetates and tartrates.

The phosphate method is analogous to the corresponding methods for zinc and magnesium, but although much investigated, it has not received similar recognition. The overall reaction may be represented by the equation



Ignition of the ammonium phosphate yields the pyrophosphate, an alternative weighing form.



The corresponding method for magnesium has an extensive literature; a good account of the difficulties involved is given by KOLTHOFF AND SANDELL⁷.

Earlier work on the cobalt method took no account of residual cobalt in the filtrate which DUFTY⁸ and later SCHOELLER⁹ determined gravimetrically following precipitation as sulphide. DUFTY's results, which indicated that there was a significant amount of cobalt in the filtrate, were ignored by some later workers. In assessing the phosphate method WILLARD AND HALL¹⁰ invariably obtained high results.

More recently MATSUO¹¹ has investigated the effect of pH and ammonium ion concentration on the precipitation of cobalt ammonium phosphate. Precipitates produced under various conditions, were in each case ignited to the pyrophosphate and corrected for cobalt in solution, which was determined using α -nitroso- β -naphthol. Low results were obtained under all conditions, and the method was rejected.

The pyrolysis curve¹² for $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ indicates that the pyrophosphate, which appears at 580° , is a good weighing form. Much of the work done on the phosphate method has been concerned with separating nickel from cobalt as well as a means of determining the latter.

Little attention has been given to the best method of producing a precipitate of satisfactory composition. The conflicting results of WILLARD AND HALL¹⁰ and MATSUO¹¹ suggest variation in composition of the precipitate, although use of faulty reference standards may have been a contributory factor.

In its existing form, with the determination of cobalt in the filtrate by sulphide

precipitation followed by ignition to 'Co₃O₄', two gravimetric procedures are involved which detract considerably from the value of the method.

The electrolytic method has been recommended as the best for determinations involving large amounts of cobalt, and where high accuracy is desired. The method has been used to standardise cobalt stock solutions for use in assessing other methods of cobalt analysis. Electrolytic cobalt has been used by many workers as a reference standard.

Some of the unsatisfactory features are said to be: (a) incomplete deposition; (b) an occasional slight anode deposit in the absence of a reducing agent; (c) a contaminated deposit in the presence of a reducing agent; (d) a tendency for the platinum anode to dissolve during prolonged electrolysis.

The electrolytic method has been carried out with a greater diversity of procedure than any other method. Chemical composition of the electrolyte, time of electrolysis, current density, temperature, type of electrode, rate of stirring, and pH of the solution have been varied.

Various procedures have been evolved in an attempt to overcome the unsatisfactory features of the method. Treatment of the spent electrolyte with H₂S to determine residual cobalt via 'Co₃O₄' has been recommended¹³. KALLMAN¹⁴ determined sulphur in the electrodeposited cobalt (arising from the use of sodium bisulphite), as BaSO₄, and corrected the weight of deposit accordingly.

EXAMINATION OF METHODS

The Anthranilate Method

Aliquots of a standard solution of cobalt were analysed using this method. Previous examination of filtrates from the anthranilate method had indicated the presence of small amounts of cobalt. All filtrates and washings, therefore, were made up to 500 ml and analysed for cobalt using a Nitroso-R-salt method. Generally, the filtrates were analysed as soon as possible because light turns sodium anthranilate brown. Otherwise the filtrates were stored overnight in a dark place.

Recoveries of cobalt in the Nitroso-R-salt method were shown to be unaffected by the amount of sodium anthranilate present. Some representative results are given in Table I.

In carrying out the above procedure, a drawback was encountered which previous

TABLE I
ANTHRANILATE METHOD
Normal procedure

No.	Cobalt taken mg	Excess 3% anthranilate used %	Cobalt found as anthranilate mg	Filtrate cobalt mg	Total cobalt found mg	Error mg
1	120.3	10	120.6	0.1	120.7	+0.4
2	120.3	15	120.5	0.2	120.7	+0.4
3	120.3	20	120.2	0.5	120.7	+0.4
4	120.3	30	120.3	0.2	120.5	+0.2
5	120.3	30	120.3	0.2	120.5	+0.2
6	120.3	30	120.5	0.1	120.6	+0.3
7	120.3	30	120.5	0.1	120.6	+0.3
Mean error: +0.31 mg +0.26%						

workers do not appear to have mentioned. The precipitate is very light, and even on the most gentle boiling of the test solution spraying occurs, which results in particles of the precipitate being deposited on the walls of the beaker and the underside of the covering glass. Much care is required to remove this quantitatively.

In an attempt to overcome this difficulty, experiments were carried out to find whether heating the solution on a water bath could replace the five minutes' boiling. The results are shown in Table II.

TABLE II
ANTHRANILATE METHOD
Effect of heating on water bath rather than boiling

No.	Cobalt taken mg	Excess 3% anthranilate used %	Time heated on bath min	Cobalt found as anthranilate mg	Filtrate cobalt mg	Total cobalt found mg	Error mg
1	120.3	10	30	119.0	2.1	121.1	+0.8
2	120.3	15	30	120.1	1.1	121.2	+0.9
3	120.3	20	30	120.5	0.5	121.0	+0.7
4	120.3	30	30	120.5	0.3	120.8	+0.5
5	120.3	30	45	120.8	0.2	121.0	+0.7
6	120.3	40	45	121.2	0	121.2	+0.9
7	120.3	30	45	121.0	0.1	121.1	+0.8
Mean error: +0.76 mg +0.63%							

In his determination of the pH range for complete precipitation, GOTO⁴ used an acetate buffer. He did not detect the increased solubility of the precipitate in its presence, as SHENNAN, SMITH and WARD⁶ did in later work.

Owing to the ease with which cobalt in solution may be determined using Nitroso-R-salt, some determinations were made in acetate and tartrate buffers. The method was similar to the first method described above. The results are given in Table III.

Nitrate ions are alleged to interfere with some cobalt methods. The anthranilate method was therefore carried out in the presence of 1 g potassium nitrate, but the filtrate cobalt was normal and the total cobalt unaffected.

TABLE III
ANTHRANILATE METHOD
Effect of acetate and tartrate

No.	Cobalt taken mg	Excess 3% anthranilate used %	Buffer present	Cobalt found as anthranilate mg	Filtrate cobalt mg	Total cobalt found mg	Error mg
1	120.3	30	3 g sodium acetate	118.4	0.2	118.6	-1.7
2	120.3	30	3 g sodium acetate	118.4	0.3	118.7	-1.6
3	120.3	30	3 g sodium tartrate	113.0	6.4	119.4	-0.9

Experimental*

Reference standard: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was used. Stock solutions were prepared as described in Part I.

* General technique described in Part I (ref. 1).

Sodium anthranilate solution: Batches of 5–8 g ordinary grade anthranilic acid were boiled with water in the presence of animal charcoal, filtered, and left to re-crystallise. The product after three treatments was very faintly yellowish, m.p. 144° . It was dried over P_2O_5 .

Sodium anthranilate solution 3% was prepared in the following way. Slightly less than 7.5 g anthranilic acid was shaken up with 55 ml *N* NaOH diluted to 100 ml with water. One drop of phenolphthalein was added, and the solution made slightly acid by adding a saturated aqueous solution of anthranilic acid. The total volume was made up to 250 ml with water and the reagent stored in a dark bottle in a cool place.

Nitroso-R-salt solution: A 0.2% aqueous solution was prepared. It was found to be stable for several months if kept in a dark bottle and stored in a dark place.

Anthranilate method

The volume of the cobalt solution was adjusted to 200 ml, then 1.0 *N* sodium carbonate solution added until a slight cloudiness appeared. This was just cleared by addition of 1 : 200 (v/v) HCl. The solution was heated until it boiled, further additions of HCl being made to maintain a clear solution. An excess of 3% sodium anthranilate was slowly added, the solution being stirred. After five minutes of gentle boiling it was left to stand for one hour, filtered (X4 sintered glass filter), and washed with cold 0.15% solution followed by 5 ml alcohol. After drying for one hour at 115° it was cooled and weighed.

Results and discussion

The anthranilate method is difficult to apply because there is a tendency for the precipitate to splash. The results are all slightly high, probably due to contamination of the precipitate by the reagent itself. When heating is carried out on a water bath, the error is doubled, thus making this procedure inadmissible.

If a factor were employed, it would have to be based on the total cobalt, including cobalt recovered from the filtrate, on account of the latter not being constant. From the results shown in Table I, such a factor would have the value 0.997.

The determinations made in the presence of sodium acetate and sodium tartrate indicate that the behaviour is not simply a question of solubility of the precipitate as previously suggested. In the presence of acetate ions, cobalt in the filtrate is normal, but the total cobalt is low. In contrast, the presence of tartrate ions leads to an abnormally high amount of cobalt in the filtrate, but a lower negative error for total cobalt. The method cannot be used in the presence of these ions even when residual cobalt is determined in the filtrate.

The anthranilate method is not entirely satisfactory. Its only advantage appears to be the non-interference by nitrate ion.

The Phosphate Method

The first procedure tried was based on the standard zinc method¹⁵. This consisted of adding an excess of 10% di-ammonium phosphate solution to a hot neutral cobalt solution buffered with a mixture of ammonium chloride and sodium acetate. The precipitate of cobalt ammonium phosphate was subsequently filtered, washed with 1% di-ammonium phosphate solution followed by alcohol, and ignited at 730° to the pyrophosphate for weighing. It was the phosphate method I used in Part I (ref. 1).

Using $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ as reference standard, results were consistent but invariably high. The precipitate was rather fine, and easy to transfer, but had a tendency to make washing and filtering difficult by becoming tightly packed under suction.

In order to determine whether under different conditions of pH (*a*) the residual cobalt might be less or (*b*) the composition of the precipitate might be slightly different and give more accurate results, the pH values were adjusted before precipitation using 1.0 *N* NaOH or 1.0 *N* HCl, so that for the series the values were distributed between pH 6.0 and pH 8.5. The remaining procedure followed that of Phosphate method I.

After precipitation, the precipitate undergoes a series of colour changes, passing through a royal blue phase and ending in the violet form. It is essential for this sequence to be completed before filtration; in any of the intermediate forms the precipitate passes through the filter. In this series, the analyses at the higher pH values took about 3 h on the water bath to turn violet. The resulting loss of ammonia led to a large drop in pH, so that the final pH range for the series was narrow. The results indicated that the relative error was independent of pH for the procedure used.

MATSUO¹¹ in investigating the effect of pH on the precipitation of $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ adjusted the pH after precipitation. This work, with slight modification, was repeated. The results are shown in Table IV.

TABLE IV
EFFECT OF pH ON THE PRECIPITATION OF COBALT AMMONIUM PHOSPHATE

Cobalt taken mg	Cobalt found as $\text{Co}_2\text{P}_2\text{O}_7$ mg	Filtrate cobalt mg	Total cobalt mg	pH filtrate
99.5	100.6	0.6	101.2	8.36
99.5	100.3	0.5	100.8	8.04
99.5	100.0	0.6	100.6	7.92
99.5	99.8	0.8	100.6	7.09
99.5	99.6	0.8	100.4	6.74
99.5	99.3	1.0	100.3	6.40
99.5	99.2	0.9	100.1	6.28
99.5	98.8	1.2	100.0	5.63

The alternative method of precipitating $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ was then investigated. This consists of adding ammonia to an acid cobaltous solution containing di-ammonium phosphate. The method has been recommended by SCHOELLER⁹ who determined soluble cobalt gravimetrically as sulphide and corrected the major fraction as $\text{Co}_2\text{P}_2\text{O}_7$ accordingly. SCHOELLER's method, with filtrate cobalt determined by Nitroso-R-salt was found to be very reproducible. A modification of it was used (Phosphate method II) in Part I. Results on the basis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ are included in Series II, Part I. The mean relative error was 0.19%. The precipitate in this form of the method is more difficult to handle. It has a tendency to stick to glassware.

It was found that if an equivalent amount of H_2SO_4 was used instead of HCl, the final results were lower by 0.1–0.2%. As the mean error using HCl was +0.19%, use of H_2SO_4 would produce almost exact results. A large number of determinations has confirmed this.

The only disadvantage found in using H_2SO_4 rather than HCl was that the change

from the blue amorphous precipitate formed initially, to the final violet form took twice as long (30–40 min).

Further investigation of this form of the phosphate method was carried out, the influence of the following factors being determined:

(a) excess of di-ammonium phosphate used; (b) excess of 1 : 1 ammonia added to effect precipitation; (c) time interval before filtration. A series of analyses using Phosphate method II was carried out, the precipitates being filtered 10 min, 20 min, 1 h, 4 h and 6 h after changing into the violet form; (d) effect of washing the precipitate with water rather than 1% di-ammonium phosphate solution; (e) effect of weighing as $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ rather than $\text{Co}_2\text{P}_2\text{O}_7$. A series of determinations was carried out using Phosphate method II, in which the ammonium phosphate was weighed after drying at 100° and after ignition at 730°. The results are given in Table V.

TABLE V
PHOSPHATE METHOD
Effect of weighing as $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{Co}_2\text{P}_2\text{O}_7$

<i>Cobalt found as $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ (mg)</i>	<i>Cobalt found as $\text{Co}_2\text{P}_2\text{O}_7$ (mg)</i>
148.1	147.4
147.8	147.6
77.6	77.3
77.5	77.2
77.4	77.2
77.2	77.1
77.3	77.0
102.9	106.0
106.2	106.1

Samples of $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ produced by Phosphate method II were heated for 1 h at intervals of 5° above 100°, cooled and re-weighed.

A series of determinations using Phosphate method II was carried out in which the $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ was ignited at various temperatures between 650° and 900°.

Experimental

Experimental details of the two principal phosphate methods (Phosphate methods I and II) have been given in Part I.

Reference standard: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Effect of pH on the precipitation of $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$. Sufficient NH_4Cl was added to the cobalt solution to give, together with 25 ml of 10% (w/v) di-ammonium phosphate solution added later, a 1 : 50 Co^{+2} : NH_4^+ molar ratio. The total volume was adjusted to 100 ml. After heating on a water bath for a few minutes, 25 ml di-ammonium phosphate solution, 10% (w/v), was added, and the pH adjusted using 1.0 N NH_4OH . The precipitate was left to stand overnight. It was filtered, washed with water followed by a little alcohol, dried at 100° and ignited to the pyrophosphate. The pH of each filtrate was measured and the residual cobalt determined using Nitroso-R-salt.

Effect of excess di-ammonium phosphate. The procedure was identical with Phosphate method II except that 10 ml 1 : 2 H_2SO_4 (v/v) was used instead of HCl, the precipitate

was washed with water instead of 1% (w/v) di-ammonium phosphate, and the amount of di-ammonium phosphate used (as 10% w/v solution) was that indicated in Table VI which contains the results.

TABLE VI
PHOSPHATE METHOD
Effect of excess di-ammonium phosphate

Cobalt taken mg	Phosphate ion: Co ⁺² molar ratio	Total cobalt found mg
99.4	2.5	99.4
99.4	4.3	99.4
99.4	10.0	99.6
99.4	25.0	99.9
99.4	50.0	100.3

Effect of adding different amounts of 1 : 1 ammonia. In Phosphate method II additional 1 : 1 ammonia was added so that the precipitate formed, just dissolved. The solution was stirred vigorously; the precipitate slowly appeared and the analysis continued.

Results and discussion

The results given for Phosphate methods I and II in Part I of this series indicate that variation in procedure leads to different results. This must be due to slight variations in the composition of the precipitates. Some of the published results in the literature using methods similar to Phosphate method I have claimed good results in contrast to the high results found in the present work. This may be due to a compensation of errors. For example, DICK¹⁶ and KRAUS¹⁷ use similar methods, but both neglect residual cobalt. In all the phosphate determinations, some residual cobalt was found in the filtrate, the amount varying from 0.4 mg to 3.0 mg for a total cobalt of 100 mg. Procedures based on acidimetric titration of $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ¹⁸ would therefore lead to erroneous results. As the residual cobalt is not proportional to the total cobalt the use of a factor is not possible.

The results shown in Table IV support the trends shown in MATSUO's work¹¹, namely that the total cobalt is greater as the pH increases. However the actual values for total cobalt found, in relation to the amount taken, differs considerably, all the present results being high in contrast to those of MATSUO.

For example, at pH 8.0, for a $\text{NH}_4^+ : \text{Co}^{+2}$ molar ratio of 50 : 1 the result is 0.4% low whereas the present work indicates the total cobalt to be 1.4% high.

Washing the precipitate with water instead of 1% di-ammonium phosphate resulted in the amount of cobalt in the filtrate being increased by 50%. As the filtrate cobalt is determined in any case, there appears to be no advantage in using the ammonium phosphate.

Results on the basis of $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ dried at 100° and then ignited at 730° are shown in Table V.

In all cases except one weighing as $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ leads to high results. Heating the cobalt ammonium phosphate at increments of 5° above 100° produced erratic results. In the present work, 730° was used for ignition to the pyrophosphate. DUVAL's work¹² indicates that similar results could be expected over a wide range of temper-

ature. This was verified in a series ignited at various temperatures between 650° and 900°.

Table VI indicates that the final result in the Phosphate method is influenced by the quantity of di-ammonium phosphate added. Use of 10 ml of 10% di-ammonium phosphate represents a phosphate: cobalt molar ratio of 4.3. The results indicate that no appreciable error would result from a relatively large change in this ratio.

In determinations where just sufficient 1 : 1 ammonia had been added to dissolve the precipitate completely, the residual cobalt was much higher. As the Nitroso-R-salt method is only about 1% accurate, this procedure is liable to introduce a slight error, and could account for slightly less reproducible results being obtained.

A similar error is possible if the filtration is made too soon *e.g.* within 10 min of the precipitate having turned into the violet form. It was found that by filtering the hot solution over 10 mg cobalt was found in the filtrate. Furthermore, on cooling before making up to 500 ml for application of the Nitroso-R-salt procedure, there was a slight tendency for the $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ to reprecipitate.

On the basis of the above work, the following procedure is recommended for the accurate determination of cobalt.

Recommended procedure

To the cobalt solution, which should be about neutral add 10 ml 1 : 2 H_2SO_4 (v/v), and 10 ml 10% (w/v) di-ammonium phosphate solution. Adjust the volume to 150 ml.

Heat until boiling and then transfer to a water bath; add sufficient 1 : 1 (v/v) ammonia to cause the precipitate formed to turn slightly purple and partly dissolve (approx. 25 ml required). Remove the beaker from the bath when the precipitate is violet and stand it in a cool place for at least one hour.

Filter through a X4 sintered crucible, and wash with cold water followed by 5 ml 50% (v/v) alcohol. Dry the precipitate for 15 min at 100° and then ignite for one hour at 700°–800°. Cool and weigh as $\text{Co}_2\text{P}_2\text{O}_7$.

Dilute the filtrate and washings to 500 ml in a volumetric flask and transfer either a 10- or 25-ml aliquot to a beaker. Dilute to 40 ml, add one drop of phenolphthalein, and neutralise with 1 : 50 (v/v) HCl. Add a few ml excess of the acid, and boil gently on a hot plate. Add 4 ml 50% (w/v) sodium acetate solution, continue boiling, and then add 4 ml 0.2% (w/v) Nitroso-R-salt. Allow the colour to develop fully (about 2 min), add 2 ml conc. HNO_3 and boil for a further minute. Cool rapidly and make up to 100 ml. Treat a blank similarly. Measure the optical density using a 4-cm cell and a 545-m μ filter.

From a previously constructed calibration curve, determine the residual cobalt and add this to the cobalt found as pyrophosphate.

Table VII contains a typical series of results using the method.

TABLE VII

Cobalt taken mg	Cobalt found mg	Relative error %
241.0	240.9	0.0
241.0	241.3	+0.1
120.5	120.5	0.0
48.2	48.2	0.0
48.2	48.1	-0.2
24.2	24.2	0.0
24.2	24.2	0.0

The Electrolytic Method

The present work was mainly restricted to an examination and comparison of some existing procedures, and an assessment of electrolytic cobalt as a reference standard in the determination of cobalt.

After each test, the spent electrolyte and washings were examined for cobalt using Nitroso-R-salt. The usual assumption was made that all platinum lost from the anode would have been deposited on the cathode. Some representative results are given in Table VIII.

TABLE VIII
ELECTROLYTIC PROCEDURE UNDER VARIABLE CONDITIONS

No.	Composition of electrolyte	Cobalt taken* mg	Time electrolysed min	Current density	Temp. of electrolyte °C	Change in wt. anode mg	Total cobalt found mg	Relative error %
1	CoSO ₄ NH ₄ Cl NH ₄ OH NaHSO ₃	98.6	30	2A 3.25V	room	-0.5	99.9	+1.3
2	as in 1	99.0	45	2A 3.25V	room	-0.8	100.5	+1.5
3	as in 1 but without NaHSO ₃	98.6	30	2A 3.25V	room	-0.9	98.9	+0.3
4	as in 3	98.6	30	2A 3.50V	room	-0.5	99.1	+0.5
5	CoSO ₄ (NH ₄) ₂ ·SO ₄ NH ₄ OH Hydrazine SO ₄	98.7	45	3A 2.25V	room	-0.3	100.1	+1.4
6	as in 5	98.7	120	1.5A	room	0	100.3	+1.6
7	as in 5	98.7	45	3A 2.25V	60	-1.6	100.1	+1.4
8	as in 5	98.7	45	3A 2.25V	75	-1.0	100.3	+1.3

* For this series, cobalt stock solutions were standardised using the phosphate method; in all electrolyses a high rate of stirring was maintained and the NaHSO₃ used was ordinary grade.

TABLE IX
ELECTRODEPOSITION FROM BICARBONATE-PEROXIDE COMPLEX

No.	Cobalt* taken (mg)	Time electrolysed (min)	Current density	Change in wt. anode (mg)	Residual cobalt (mg)	Total cobalt found (mg)	Relative error %
1	98.7	120	1.5A 3.5V	0	0.4	100.3	+1.6
2	96.2	65	2.0A 4.5V	+0.2	0.1	97.8	+1.6
3	96.2	60	2.0A 4.5V	-0.5	0.5	97.1	+0.9

No. 1 was a sulphate solution; Nos. 2 and 3 were chloride solutions.

Attempts were made to deposit cobalt quantitatively from the bicarbonate-hydrogen peroxide complex. The results are given in Table IX.

The evidence suggesting that electrodeposited cobalt is contaminated is indirect. A typical electrolytic deposit was analysed by the phosphate method and shown to be impure.

In all the above work, the cathode deposit was weighed after drying at 100°. The effect of drying at higher temperatures indicated no change in weight up to 140°.

Experimental

Electrodeposition apparatus: A Griffin and Tatlock electrochemical analysis apparatus with provision for heating and stirring the electrolyte was used. Platinum gauze cylindrical electrodes were employed.

Reference standard: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

General procedure. The solution, containing about 100 mg cobalt was electrolysed for a known time, a high rate of stirring being maintained. The average current passing and the potential difference between the electrodes was noted.

At the end of the electrolysis, the beaker was lowered from the electrode with the current still passing, the electrodes being washed with water at the same time. The spent electrolyte and washings were made up to 500 ml and cobalt was determined in an aliquot by means of Nitroso-R-salt. Blank tests carried out on the reagents other than cobalt indicated no interference with the method.

The washed electrodes were dipped into ethyl alcohol, dried at 100° for 15 min, cooled and weighed.

Deposition from the cobalt bicarbonate-peroxide complex. Sodium bicarbonate, 10 g and 10 ml 30% H_2O_2 were added to an aliquot of the cobalt solution. When effervescence had ceased, the sides of the beaker were washed down with water and the solution electrolysed in the manner described above.

Analysis of electrolytic cobalt. 50 ml of the cobalt solution was analysed using the Phosphate method II but nitric acid was used instead of sulphuric acid (because the subsequent cobalt deposit was dissolved in nitric acid, and nitrate ion affects the phosphate method giving low results). Another 50 ml of the cobalt solution was electrolysed in the presence of ammonia, ammonium sulphate and hydrazine sulphate. The weighed deposit was dissolved in nitric acid, and the solution analysed for cobalt using the same phosphate method with a correction for the amount of cobalt in the filtrate. The quantity of nitric acid used to dissolve the deposit was similar to that used in the first analysis.

Results and discussion

Table VIII contains representative results using slight variations of some recommended procedures for the determination of cobalt by electrodeposition. Results of electrolyses of the bicarbonate-peroxide complex are given in Table IX.

In all cases cobalt remained in the spent electrolyte at the end of the determinations and it ranged from 0.2 to 5.3 mg. The total cobalt in every case was invariably high, indicating that the deposit was contaminated. Excluding those containing no reducing agent, the results in Table VIII are 1.4% high.

Analysis of a typical deposit using the phosphate method gave the following results:

	<i>Cobalt found</i>
Analysis of 50 ml cobalt stock solution by phosphate method	98.7 mg
Weight deposit from 50 ml same solution	100.1 mg
Residual cobalt in spent electrode	0.3 mg
Deposit should therefore contain 98.4 mg cobalt (98.7 — 0.3)	
Cobalt actually found in deposit by phosphate analysis	98.6 mg

In this particular case the deposit contained about 1.6% impurity.

As to the nature of the contamination, sulphur is almost certainly one substance present; in the absence of sulphur the positive error is lower. Some previous investigations have suggested that carbon is one of the contaminants. Some electrodepositions were made in the absence of both sulphur and carbon, the electrolyte containing NH_4Cl , NH_4OH , and a little hydrazine hydrochloride. The results were still 0.7% high. It is difficult to avoid the conclusions that the deposit is contaminated with oxide or hydroxide.

A recent study of the electrodeposition of cobalt has been made by SALYER AND SWEET¹⁹, who suggest, on the basis of another investigation²⁰, that the contamination might be due to the oxide, hydroxide, or water. The hypothesis is considered that below a cobalt concentration of about 0.005 *N* such compounds as $\text{CoSO}_4 \cdot 3\text{Co}(\text{OH})_2 \cdot \text{H}_2\text{O}$ are deposited, although their experimental results do not support this theory in its simplest form. DELTOMBE AND POURBAIX²¹ in a recent study of the equilibrium-pH study of the system $\text{Co}-\text{H}_2\text{O}$ have shown that in the absence of complexing substances, a deposit contaminated with oxide is possible above pH 6.3. Knowledge of the system $\text{Co}-\text{NH}_3-\text{H}_2\text{O}$ would be required to decide whether such contamination was possible in ammoniacal solution.

From the analytical standpoint, the results given by SALYER AND SWEET agree with the present work, the average error in their case being +2.2%.

In view of the contaminated deposits obtained using the various procedures, the electrolytic method is rejected for the accurate determination of cobalt.

CONCLUSIONS

Of the gravimetric methods examined for the accurate determination of cobalt, only a modification of the phosphate method is capable of giving accurate results. The electrolytic method gives very high results owing to a contaminated deposit.

ACKNOWLEDGEMENTS

We are indebted to the Ministry of Education for a maintenance award (W.J.W.) and to the Central Research Fund of the University of London for the purchase of a Spekker absorptiometer.

SUMMARY

Some gravimetric methods for determining cobalt have been examined in order to assess their value for the accurate determination of the metal. The electrolytic method was found to give high results (about 1.4%), and the anthranilate method slightly high results (0.2 - 0.3%). A modification of the phosphate method has been developed in which a former drawback, the solubility of $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, has been overcome using a rapid spectrophotometric determination of residual cobalt. The final procedure developed has been found to give accurate results ($\pm 0.1 - 0.2\%$) and its use is recommended where this degree of accuracy is required.

RÉSUMÉ

Quelques méthodes de dosage gravimétrique du cobalt ont été examinées. La méthode au phosphate a donné les résultats les plus précis.

ZUSAMMENFASSUNG

Beschreibung einer kritischen Untersuchung über einige gravimetrische Methoden zur Bestimmung von Kobalt. Die besten Ergebnisse wurden mit einer modifizierten Phosphatmethode in Verbindung mit einer spektrophotometrischen Bestimmung erzielt.

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GRAVIMETRIC DETERMINATION OF MOLYBDENUM AND ITS SEPARATION FROM OTHER METALS WITH N-BENZOYLPHENYLHYDROXYLAMINE

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(Received June 14th, 1960)

Some organic reagents have been used in the gravimetric determination of molybdenum¹⁻³, but the scope of application of these methods is limited. SHOME⁴ has studied various derivatives of phenylhydroxylamine, with a view to improve on cupferron (ammonium salt of nitrosophenylhydroxylamine) which has several defects, and introduced N-benzoylphenylhydroxylamine as an analytical reagent for various metals⁵. SINHA AND SHOME⁶ employed this reagent in the determination of nickel, cobalt, thorium and cerium. DAS AND SHOME⁷ described a method for the colorimetric estimation of iron and copper using benzoylphenylhydroxylamine. Other investigators have found the reagent suitable in the gravimetric determination of tin⁸, and niobium and tantalum⁹⁻¹¹, and also in the solvent extraction of thorium, lanthanum and uranium(VI)¹². Recently SHOME and co-workers used the reagent to precipitate uranium, gallium, indium and the results will be published shortly. In the present work the reactions between benzoylphenylhydroxylamine and molybdenum(VI) ions were studied and a new method was developed for the gravimetric determination of molybdenum and for its separation from other metals. A preliminary report of this investigation¹³ was published in 1957.

REACTIONS OF BENZOYLPHENYLHYDROXYLAMINE WITH MOLYBDENUM(VI) IONS

Benzoylphenylhydroxylamine formed a yellowish white precipitate with molybdenum(VI) ions. The precipitate was slightly soluble in hot water at or above 80°, in concentrated acids at lower temperatures, and in alcohol. Analysis of the pure molybdenum complex indicated its composition to be $\text{MoO}_2(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})_2$. It decomposed at 165°-166°.

SOLUTIONS USED IN THE DETERMINATION OF THE METAL

A standard solution of ammonium molybdate was prepared to contain 3.08 mg of molybdenum per ml. Separate standard solutions of ferric alum, potassium chromate, copper sulphate, nickel sulphate, cobalt sulphate and sodium metavanadate were used in the study of the effect of foreign ions on the precipitation of molybdenum. A solution of benzoylphenylhydroxylamine in 95% ethyl alcohol was employed for the precipitation of molybdenum. All the chemicals employed were of A.R. quality.

DETERMINATION OF MOLYBDENUM(VI) BY IGNITING
THE PRECIPITATE AND WEIGHING AS MOLYBDENUM TRIOXIDE

A known volume of the ammonium molybdate solution was diluted with distilled water, acidified with 10 *N* hydrochloric acid, and the alcoholic solution of benzoyl-phenylhydroxylamine (10–15 ml) was slowly added with constant stirring. The yellowish white precipitate of molybdenum appeared only slowly when the acid concentration was low. As the molybdenum complex was moderately soluble in alcohol, the final volume of the solution should not contain more than 5% of alcohol. The precipitate was stirred for about 15 min, allowed to settle for another 15 min, filtered and washed with 0.02 *N* hydrochloric acid solution. It was moistened with one or two drops of 6 *N* ammonium hydroxide solution to neutralise the free acid present, ignited at 500–525° and weighed as molybdenum trioxide.

TABLE I
DETERMINATION OF MOLYBDENUM(VI) BY WEIGHING AS MOLYBDENUM TRIOXIDE
Volume of solution = 300 ml

<i>Mo</i> taken g	Temperature of solution °C	Benzoyl- phenyl- hydroxylamine g	Acidity of solution <i>N</i>	Weight of <i>MoO</i> ₃ g	<i>Mo</i> found g	Error g
0.0770	30	0.20	0.03	0.0675	0.0450	—0.0320
0.0770	30	0.30	0.03	0.1014	0.0676	—0.0094
0.0770	30	0.35	0.03	0.1140	0.0760	—0.0010
0.0770	30	0.42	0.03	0.1155	0.0770	0.0000
0.0770	30	0.42	0.01	0.1150	0.0767	—0.0003
0.0770	30	0.42	0.60	0.1152	0.0768	—0.0002
0.0770	30	0.42	1.60	0.1160	0.0773	+0.0003
0.0770	30	0.42	2.50	0.1159	0.0773	+0.0003
0.0770	50	0.42	0.03	0.1156	0.0771	+0.0001
0.0770	75	0.42	0.03	0.1158	0.0772	+0.0002
0.0770	80	0.42	0.03	0.1129	0.0753	—0.0017

The effects of various factors such as temperature of solution, reagent concentration and acidity of the reaction medium on the precipitation of molybdenum were studied. The results (Table I) indicate that the precipitation of molybdenum(VI) is complete when the supernatant liquid contains 0.03% (w/v) of the organic reagent in excess at a temperature below 70° and the acidity of the solution ranges from 0.01 to 2.50 *N* hydrochloric acid.

Molybdenum(VI) was also determined (Table II) in the presence of chromium(VI), vanadium(V), iron(III), cobalt(II), nickel(II), and copper(II). The metal was separated from cobalt, nickel or copper by precipitating molybdenum(VI) ions with benzoylphenylhydroxylamine (0.44 g) in the presence of a sufficient amount of acid, and washing the precipitate with 0.2 *N* hydrochloric acid, followed by a 0.02 *N* solution of the same acid. In the other separations the precipitate was washed with 0.02 *N* hydrochloric acid only. The interference of iron(III) and vanadium(V) ions was masked by adding disodium ethylenediamine tetraacetate (1–2 g) which forms stable complexes with the two metal ions. When the vanadate was heated with EDTA, it was probably reduced to vanadyl ion before the complex formation¹⁴.

TABLE II
DETERMINATION OF MOLYBDENUM(VI) BY WEIGHING AS MOLYBDENUM TRIOXIDE
Volume of solution = 300 ml

Mo taken g	Foreign ion added g	10 N HCl added ml	Weight of MoO ₃ g	M g	d	Error g
0.0770	0.128(Cu ⁺²)	10.0	0.1160	0.0773		+0.0003
0.0770	0.200(Ni ⁺²)	10.0	0.1161	0.0774		+0.0004
0.0770	0.107(Co ⁺²)	10.0	0.1152	0.0768		-0.0002
0.0770	0.004(Cr ⁺⁶)	1.0	0.1158	0.0772		+0.0002
0.0770	0.009(Cr ⁺⁶)	1.0	0.1160	0.0773		+0.0003
0.0770	0.056(Fe ⁺³)	0.3	0.1165	0.0777		+0.0007
0.0770	0.112(Fe ⁺³)	0.4	0.1163	0.0775		+0.0005
0.0770	0.003(V ⁺⁵)	0.8	0.1163	0.0775		+0.0005
0.0770	0.005(V ⁺⁵)	1.0	0.1165	0.0777		+0.0007

DETERMINATION OF MOLYBDENUM(VI) BY WEIGHING THE METAL COMPLEX DIRECTLY

An aliquot (10–25 ml) of the ammonium molybdate solution was diluted with distilled water, acidified with 10 N hydrochloric acid, heated to about 60° and molybdenum was precipitated by adding a solution of benzoylphenylhydroxylamine (0.25–0.44 g) in alcohol (10–15 ml). The molybdenum precipitate was heated at 60° for 30 min on a water-bath, filtered on a No. 3 glass-sintered crucible, washed with warm (60°) 0.02 N hydrochloric acid and finally with 10 ml of distilled water. The precipitate was dried at 110–115° for one hour and weighed. The molybdenum content was calculated on the basis that the precipitate contained 17.37% of the metal.

Molybdenum was also precipitated in the presence of other metallic ions as described before, but the precipitation and washings were carried out under warm conditions to prevent the contamination of the molybdenum complex with the precipitant.

TABLE III
DETERMINATION OF MOLYBDENUM(VI) BY WEIGHING THE PRECIPITATE DIRECTLY
Volume of solution = 300 ml

Mo taken g	Foreign ion added g	10 N HCl added ml	Disodium EDTA added g	Weight of ppt. g	Mo found g	Error g
0.03080	—	1.0	—	0.1777	0.03086	+0.00006
0.07700	—	1.0	—	0.4431	0.07695	-0.00005
0.03080	0.154(Ni ⁺²)	6.0	—	0.1769	0.03072	-0.00008
0.03080	0.107(Co ⁺²)	6.0	—	0.1780	0.03091	+0.00011
0.03080	0.051(Cu ⁺²)	6.0	—	0.1781	0.03092	+0.00012
0.03080	0.124(Cu ⁺²)	6.0	—	0.1767	0.03068	-0.00012
0.04620	0.384(Fe ⁺³)	0.4	3.0	0.2638	0.04581	-0.00039
0.04620	0.772(Fe ⁺³)	0.4	6.0	0.2641	0.04586	-0.00034
0.03080	0.004(V ⁺⁵)	0.8	2.0	0.1763	0.03061	-0.00019
0.03080	0.008(V ⁺⁵)	0.8	3.0	0.1758	0.03053	-0.00027

It can be seen from the results given in Table III that molybdenum(VI) can be determined by weighing as MoO₂(C₁₃H₁₀O₂N)₂ and this offers a simple method for the

separation of molybdenum from many other metal ions. Since chromium(VI) has a tendency to oxidise benzoylphenylhydroxylamine, especially in presence of hot acid, molybdenum(VI) cannot be determined in the presence of chromium(VI) by weighing the complex directly. Benzoylphenylhydroxylamine precipitates tungsten(VI) in acid medium, and it is not possible to separate molybdate from tungstate with the reagent.

ACKNOWLEDGEMENT

One of the authors (S. K. SINHA) is indebted to the Ministry of Scientific Research and Cultural Affairs, Government of India, for the grant of a scholarship.

SUMMARY

N-Benzoylphenylhydroxylamine is employed as a precipitant for the determination of molybdenum(VI). The precipitate can be weighed either directly or as molybdenum trioxide after ignition. Molybdenum can be determined in the presence of appreciable amounts of iron(III), cobalt(II), copper(II), chromium(VI) and vanadium(V).

RÉSUMÉ

La N-benzoylphénylhydroxylamine est proposée comme réactif pour le dosage gravimétrique du molybdène(VI). Ce dosage peut s'effectuer en présence de fer(III), de cobalt, de cuivre, de chrome(VI) et de vanadium.

ZUSAMMENFASSUNG

Zur gravimetrischen Bestimmung von Molybdän(VI) neben Eisen(III), Kobalt, Kupfer, Chrom(VI) und Vanadium kann N-Benzoylphenylhydroxylamin verwendet werden.

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GRAVIMETRIC DETERMINATION OF BERYLLIUM WITH N-BENZOYLPHENYLHYDROXYLAMINE

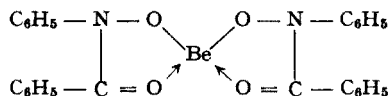
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(Received June 14th, 1960)

N-Benzoylphenylhydroxylamine has been recommended as a precipitant in the quantitative analysis of several metals by various authors¹. In the present investigation, it is employed in the gravimetric estimation of beryllium.

Stable complexes of beryllium are known to be formed with chelating agents which have oxygen as the electron donors. Benzoylphenylhydroxylamine provides such a favourable grouping and forms with beryllium a complex of composition $\text{Be}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})_2$. The complex is best represented as a chelate:



Since the precipitation of iron or aluminium with benzoylphenylhydroxylamine is complete at pH 4.0 whereas the precipitation of beryllium starts at pH 4.6, it is possible to precipitate iron or/and aluminium while beryllium remains in solution by a proper control of pH before adding the precipitant. Benzoylphenylhydroxylamine may also be used for precipitating titanium in the presence of beryllium at pH 1. Beryllium can be subsequently precipitated with the reagent after raising the pH of the filtrate. The precipitate may be either ignited to form beryllium oxide or weighed as $\text{Be}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})_2$.

SOLUTIONS USED IN THE DETERMINATION OF THE METAL

Standard beryllium solution

Beryllium hydroxide was precipitated from a solution of beryllium nitrate in presence of the disodium salt of ethylenediamine tetraacetic acid, washed with water, dissolved in nitric acid and diluted. The beryllium content of the solution was determined by the oxide method.

Foreign ions

Solutions of ferric nitrate, aluminium nitrate and titanium sulphate were employed when beryllium was precipitated in the presence of these metal ions.

Benzoylphenylhydroxylamine solution

A solution of the reagent in 95% ethyl alcohol was used for the precipitation of beryllium.

All the chemicals used were of A.R. quality.

PROPERTIES AND COMPOSITION OF THE BERYLLIUM COMPLEX

The beryllium complex of benzoylphenylhydroxylamine was obtained in the form of a white granular substance, insoluble in water up to a temperature of 70° and easily soluble in chloroform. The solubilities of the complex in carbon tetrachloride, acetone and 50% ethyl alcohol were comparatively low. It decomposed when treated with moderately concentrated mineral acids and melted with decomposition when heated to 220°. The pure complex was analysed for beryllium and nitrogen and the results indicated its composition as $\text{Be}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})_2$.

	Experimental, %	Theoretical, %
Be	2.06	2.08
N	6.41	6.46

DETERMINATION OF BERYLLIUM

A known quantity of the beryllium solution was diluted to 200 ml with distilled water, heated to 50–60° and the solution of benzoylphenylhydroxylamine (0.2–0.3 g in 10 ml of alcohol) was added slowly with constant stirring. Ammonium hydroxide (3 N) was then gradually added to adjust the pH of the solution to between 5.5 and 6.5. The precipitate was allowed to stand for a few minutes, filtered, washed and ignited to the oxide. The results recorded in Table I indicate that beryllium is quantitatively precipitated from aqueous solution by adding benzoylphenylhydroxylamine and can be determined by igniting the precipitate to beryllium oxide.

TABLE I
DETERMINATION OF BERYLLIUM BY WEIGHING AS OXIDE

<i>BeO taken (g)</i>	<i>BeO found (g)</i>	<i>Error (g)</i>
0.0077	0.0076	—0.0001
0.0077	0.0077	0.0000
0.0154	0.0153	—0.0001
0.0154	0.0152	—0.0002

In another series of experiments beryllium was precipitated as described above, the precipitate was heated at 50–60° for 15 min with occasional stirring, filtered on No. 3 sintered glass crucible, washed with warm water (50–60°) and dried at 110° to constant weight. The metal content was calculated on the above theoretical percentage (2.08%) of beryllium. The results are given in Table II.

TABLE II
DETERMINATION OF BERYLLIUM BY WEIGHING THE PRECIPITATE DIRECTLY

<i>Be taken (g)</i>	<i>Weight of ppt. (g)</i>	<i>Be found (g)</i>	<i>Error (g)</i>
0.00277	0.1328	0.00277	0.00000
0.00277	0.1339	0.00278	+0.00001
0.00139	0.0666	0.00138	—0.00001
0.00139	0.0660	0.00137	—0.00002
0.00083	0.0406	0.00084	+0.00001
0.00055	0.0270	0.00056	+0.00001
0.00055	0.0272	0.00056	+0.00001

Effect of concentration of benzoylphenylhydroxylamine

The precipitation of beryllium was carried out using different amounts of the reagent, the other conditions remaining the same. It was observed that the precipitation of the metal was complete when the supernatant solution contained 0.1% (w/v) of the reagent in excess at pH 6.0.

Effect of pH

When the solutions of beryllium were adjusted to different pH values with dilute ammonia (3 *N*) after adding benzoylphenylhydroxylamine (two and half times the theoretical quantity), it was found that the precipitation of the metal commenced at pH 4.6 and was complete between pH 5.0 and 8.0. The pH values were measured with the aid of a Cambridge pH meter (bench model).

SEPARATION OF BERYLLIUM FROM IRON AND ALUMINIUM

A mixture containing known amounts of beryllium nitrate and aluminium nitrate or/and ferric nitrate was diluted to 300 ml, acidified with a few drops of dilute sulphuric acid and a 10% (w/v) solution of sodium acetate was added to adjust the pH to 4.0. The solution was heated to about 65° and benzoylphenylhydroxylamine (0.4–0.9 g dissolved in 10–15 ml of alcohol) was added to precipitate iron or/and aluminium. The precipitate was heated on a boiling water-bath for 1–1½ h with occasional stirring, filtered and washed with hot water containing 0.1% (w/v) reagent and sufficient acid to adjust the pH to 4.0.

The filtrate and washings were concentrated to 200 ml and filtered if any organic matter appeared owing to prolonged heating of the reagent solution in air. Benzoylphenylhydroxylamine (0.1–0.15 g dissolved in 5 ml of alcohol) was then added to the beryllium solution and the metal was precipitated and weighed as $\text{Be}(\text{C}_{19}\text{H}_{10}\text{O}_2\text{N})_2$ as described above. The results given in Table III indicate that it is possible to separate beryllium quantitatively from iron or/and aluminium by the use of benzoylphenylhydroxylamine.

TABLE III

SEPARATION OF BERYLLIUM FROM IRON AND ALUMINIUM

<i>Be taken (g)</i>	<i>Foreign metal added (g)</i>		<i>Weight of ppt. (g)</i>	<i>Be found (g)</i>	<i>Error (g)</i>
	<i>Fe(III)</i>	<i>Al</i>			
0.00295	0.004	—	0.1425	0.00296	+0.00001
0.00295	0.008	—	0.1421	0.00295	0.00000
0.00295	0.019	—	0.1424	0.00296	+0.00001
0.00295	0.038	—	0.1410	0.00293	—0.00002
0.00295	0.038	—	0.1416	0.00294	—0.00001
0.00295	—	0.003	0.1423	0.00296	+0.00001
0.00295	—	0.007	0.1430	0.00297	+0.00002
0.00295	—	0.017	0.1416	0.00294	—0.00001
0.00295	—	0.034	0.1417	0.00294	—0.00001
0.00295	—	0.034	0.1412	0.00293	—0.00002
0.00295	0.004	0.003	0.1418	0.00294	—0.00001
0.00295	0.004	0.007	0.1426	0.00296	+0.00001
0.00295	0.008	0.007	0.1415	0.00293	—0.00002
0.00295	0.019	0.017	0.1415	0.00293	—0.00002

SEPARATION OF BERYLLIUM AND TITANIUM

Known volumes of beryllium nitrate and titanium sulphate solutions were taken, diluted to 300 ml, neutralised with 6 *N* ammonia and acidified with concentrated hydrochloric acid (3–4 ml). Titanium was precipitated by adding benzoylphenylhydroxylamine (0.4–0.7 g dissolved in 10 ml alcohol) with constant stirring. The titanium precipitate was allowed to stand for 45 min with occasional stirring, filtered and washed with dilute hydrochloric acid containing the organic reagent. The wash-liquid was prepared by adding 1 g of benzoylphenylhydroxylamine dissolved in 10 ml of alcohol to 1 l of warm distilled water, which was then cooled and mixed with 3 ml of concentrated hydrochloric acid. The filtrate and washings were concentrated, filtered and beryllium was determined as before. The results are shown in Table IV.

TABLE IV
SEPARATION OF BERYLLIUM FROM TITANIUM

<i>Be taken (g)</i>	<i>Ti added (g)</i>	<i>Weight of ppt. (g)</i>	<i>Be found (g)</i>	<i>Error (g)</i>
0.00295	0.002	0.1420	0.00295	0.00000
0.00295	0.003	0.1423	0.00296	+0.00001
0.00295	0.008	0.1418	0.00294	—0.00001
0.00295	0.017	0.1420	0.00295	0.00000
0.00295	0.017	0.1416	0.00294	—0.00001

Further work on the determination of beryllium in presence of other ions is in progress.

ACKNOWLEDGEMENT

The sample of benzoylphenylhydroxylamine was kindly supplied by E. Merck, Darmstadt, Germany.

SUMMARY

N-Benzoylphenylhydroxylamine has been employed in the gravimetric determination of beryllium and in its separation from iron, aluminium and titanium. After suitable adjustment of pH iron, aluminium or titanium is precipitated quantitatively with the reagent; beryllium is subsequently precipitated after raising the pH of the filtrate. The metal may be determined by either igniting the precipitate to beryllium oxide or weighing it as $\text{Be}(\text{C}_{12}\text{H}_{10}\text{O}_2\text{N})_2$.

RÉSUMÉ

La *N*-benzoylphénylhydroxylamine est proposée comme réactif pour le dosage gravimétrique du béryllium. Une séparation du béryllium est alors possible d'avec le fer, l'aluminium et le titane.

ZUSAMMENFASSUNG

Zur gravimetrischen Bestimmung von Beryllium und seine Trennung von Eisen, Aluminium und Titan kann *N*-Benzoylphenylhydroxylamin verwendet werden.

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Anal. Chim. Acta, 24 (1961) 37–40

IMPURITY DETERMINATION BY THERMAL ANALYSIS II. THE MELTING CURVE OF A QUICKLY FROZEN SAMPLE

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(Received June 24th, 1960)

INTRODUCTION

The heating curve of a gradually frozen sample was discussed in a previous paper¹. The melting curve of a sample obtained by quick freezing is now considered.

When a liquid sample is cooled rapidly to far below its freezing point, *total* equilibrium is excluded. It is hardly even likely that local equilibrium (in the sense of part I) is present. Sudden freezing of a sample often results in a homogeneous solid solution*. Intermediate stages between a build-up of the solid according to the local equilibrium theory (part I) and a homogeneous solid solution may occur, depending on the rate of cooling. These intermediate stages are likely to be badly reproducible and are not suitable for mathematical treatment. Therefore the present discussion is restricted to the melting curve of a homogeneous solid solution.

The melting curve of a homogeneous solid solution

The diffusion of the solid is assumed to be virtually restricted to a surface layer at the interface of solid and liquid. The liquid is assumed to be homogeneous. Little is known about the amount of substance contained in the surface layer. It can only be stated that it usually is maximal when melting starts and approaches zero when melting becomes complete. The concentration within the surface layer is a function of the distance from the interface. The surface layer is assumed to act in the same way as a solid fraction (*f*) of the sample which is in equilibrium with the liquid. The problem will be treated as if such a fraction *f*, having a concentration X_S is really present. Obviously *f* is a function of *y*.

Suppose a fraction *y* of the sample has melted. Since the surface layer is assumed to be in equilibrium with the liquid, the total fraction of the sample participating in the equilibrium may be represented by (*y* + *f*). According to the law of conservation of matter:

$$(y + f)X = yX_L + fX_S \quad (1)$$

where *X* is the concentration of the total sample and X_L the concentration in the liquid. When X_S and X_L are small, $X_S/X_L = k$ (constant) is valid. Thus

* Indications have been obtained that systems normally forming no solid solutions may form a supersaturated solid solution on quick freezing.

$$\left(\frac{y+f}{Y+kf}\right)X = X_L \quad (2)$$

Moreover when X_L is small: $X_L = k_L \Delta T$ is approximately valid. Consequently the following relation between ΔT and y may be considered as a fair approximation:

$$\Delta T = \frac{X}{k_L} \left(\frac{y+f}{y+kf}\right) \quad (3a)$$

or since X/k_L equals the depression of the final melting point (ΔT_m) of the sample:

$$\Delta T = \Delta T_m \left(\frac{y+f}{y+kf}\right) \quad (3b)$$

Discussion of the equations (3a) and (3b)

When no miscibility occurs in the solid, the whole solid has permanently the same concentration and may be considered to be in equilibrium with the liquid. Then f equals $(1-y)$. Since in that case $k = 0$, eqn. (3a) reduces to the well known White equation.

In order to avoid possible misunderstandings it should be noted that the following discussion is restricted to solid solutions. It has already been mentioned, that f is a function of y , being zero at $y = 1$. Little more is known about f . It can only be stated that f also depends on the shape and size of the crystals. When tiny crystals are formed the area of the interface of solid and liquid and thus f , may be large. The ultimate value of f equals $(1-y)$. Then eqn. (3a) becomes eqn. (9) of part I, which is valid for total equilibrium¹.

Especially when tiny or imperfect crystals are present f is also a function of time. For, as may be known, perfect and large crystals have a tendency to grow at the cost of small or imperfect crystals. When f is relatively small the temperature of the sample approaches its final melting point soon after melting has started (see eqn. 3b). Thus superheating of the bulk of the solid must occur, unless an additional interface is formed. Since the formation of new interface occurs by passing an energy barrier, the temperature of the sample may decrease suddenly when the new interface is formed. The formation of the new interface in the solid may be compared with the formation of a vapour bubble in a liquid. As is the case with superheating of liquids, the extent of superheating of solid solutions is unpredictable.

So f may change discontinuously to an unknown extent. It is thus clear that a quantitative experimental proof of eqns. (3a) and (3b) is impossible.

However, the foregoing permits a number of qualitative conclusions which can be checked by experiment:

The melting curve of a sample of solid solutions obtained by quick freezing may show the following features, *viz.*

(1) The temperatures observed will be higher than the corresponding temperatures of a curve calculated on the basis of total equilibrium (see ref.¹, eqn. 9) or at least be equal to these.

(2) The difference between the temperatures observed and those obtaining to a "total equilibrium curve" will be larger when the sample has been stored for a long time (preferably at elevated temperatures).

(3) After prolonged storage of the sample, its melting curve may resemble the curve of an extremely pure substance.

(4) Depending on the rate of formation of new interfaces, the melting curve of such a sample may show a maximum.

TABLE I

DEPRESSIONS FOUND AND CALCULATED ON A QUICKLY FROZEN SAMPLE OF DIPHENYL CONTAINING 0.181 mol% PHENANTHRENE

Fraction liquid	ΔT found			ΔT calculated according the total equilibrium theory
	without annealing	after 3 h annealing	after 10 days annealing	
0.1	0.13	0.11	0.10	0.22
0.2	0.09	0.08	0.08	0.18
0.3	0.08	0.08	0.08	0.14
0.4	0.08	0.08	0.08	0.12
0.5	0.08	0.08	0.08	0.10
0.6	0.08	0.08	0.08	0.09
0.7	0.08	0.08	0.08	0.08
1.0	0.07	0.08	0.08	0.07

TABLE II

DEPRESSIONS FOUND AND CALCULATED ON A QUICKLY FROZEN SAMPLE OF DIPHENYL CONTAINING 0.762 mol% OF PHENANTHRENE

Fraction liquid	ΔT found			ΔT calculated according the total equilibrium theory
	without annealing	after 3 h annealing	after 10 days annealing	
0.1	0.79	0.67	0.40	0.95
0.2	0.65	0.59	0.38	0.77
0.3	0.59	0.55	0.37	0.64
0.4	0.55	0.52	0.37	0.55
0.5	0.51	0.49	0.37	0.49
0.6	0.43	0.46	0.37	0.43
0.7	0.40	0.40	0.36	0.39
1.0	0.30	0.30	0.30	0.30

TABLE III

DEPRESSIONS FOUND AND CALCULATED ON A QUICKLY FROZEN SAMPLE OF TIN CONTAINING 0.300 mol% OF BISMUTH

Fraction liquid	ΔT found			ΔT calculated according the total equilibrium theory
	without annealing	after 3 h annealing	after 10 days annealing	
0.1	1.80	1.51	1.10	1.84
0.2	1.39	1.34	0.98	1.40
0.3	1.20	1.20	0.88	1.22
0.4	1.07	1.05	0.80	1.08
0.5	0.97	0.95	0.75	0.98
0.6	0.90	0.87	0.69	0.90
1.0	0.65	0.65	0.65	0.64

EXPERIMENTS

The samples used in the quick freezing experiments were the same samples as used during the experiments on gradual freezing (see part I). The heating curves were determined with the thin-film apparatus^{2,3}. The samples were melted in the measuring vessel and then frozen within 10–25 sec. After the sample had been stored for a definite time, its melting curve was determined. The experimental results, which are summarised in Tables I, II and III, illustrate the first three conclusions; see p. 42). Fig. 1 may be considered as an illustration of conclusion 4. The curve presented was obtained with a sample of tin containing 0.300 mol % of bismuth. The sample was quickly frozen and then stored for three hours at a temperature of 228°. Analogous curves were obtained on previous occasions with organic substances⁴.

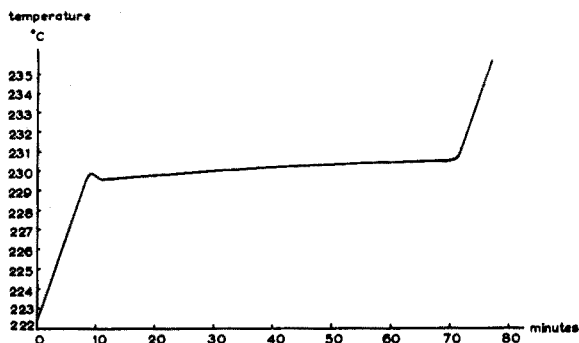


Fig. 1. Melting curve of a quickly frozen solution of 0.300 mol % bismuth in tin after three hours of annealing at 228°.

DISCUSSION

This discussion is restricted to solid solutions obtained by quick freezing.

Since so little is known about the function f , which is determined by the behaviour of the diffusion layer, it must be concluded that an impurity determination based on only one curve of a quickly frozen sample is of dubious value. As already mentioned it may happen that f equals $(1-y)$. This may occur when a complex of conditions is fulfilled, *viz.*

(a) the rate of diffusion in the solid is relatively high; the sample consists of a large number of tiny and imperfect crystals with only a small tendency to transform into large and perfect crystals;

(b) the melting curve is determined according to a quasi static method, the sample being kept under adiabatic conditions only to the extent required to obtain a constant temperature after addition of a certain amount of heat.

These conditions seem to have been met previously⁵ during the determination of the melting curve of a sample of diphenyl contaminated by phenanthrene. At least it appeared that the equation for total equilibrium was applicable in that case. However, in several other cases the conditions for attainment of total equilibrium seem to be absent. BADLEY⁶, for instance, investigated a number of quickly frozen samples of solid solutions and found his impurity determinations invariably low. In some cases only 6% of the amount of impurity added could be traced.

It may be useful to note here that the comparative method is applicable to quickly frozen samples, provided that the function f of the two samples to be compared is the same. Then, as can be shown easily, eqn. (12) of part I is valid¹.

Since it appears that the same equation of the comparative method is applicable to samples showing total equilibrium as well as to both gradually or quickly frozen samples, it is comprehensible that the comparative method yields acceptable results in so many cases.

The comparative method only demands the same pretreatment of both samples to be compared. Any special treatment is not required. Nevertheless it should be stressed that quick freezing is not recommended, even when the comparative method is applied. In addition to the risk of unforeseen variations in the behaviour of the quickly frozen sample, it should be remembered that quickly frozen mixtures show smaller depressions than any other mixture does.

ACKNOWLEDGEMENT

We wish to thank Mr. A. VAN KUYK for his accurate measurements.

SUMMARY

A temperature-heat content relation is derived for a homogeneous solid solution of a binary system showing a very restricted rate of diffusion in the solid. It is shown experimentally that quickly frozen samples behave like homogeneous solid solutions. According to the new theory the depressions determined on partly molten samples are usually small and depend on the conditions; thus purity determinations based on heating curves of quickly frozen samples are of dubious value. The theory shows that superheating of the solid may occur when a solid solution is melted; this is confirmed experimentally.

RÉSUMÉ

Lors de leur étude sur la détermination des impuretés par analyse thermique, les auteurs ont constaté que des échantillons refroidis rapidement se comportaient comme des solutions homogènes solides.

ZUSAMMENFASSUNG

Bei Bestimmungen des Reinheitsgrades durch thermische Analyse wurde gefunden, dass sich rasch abgekühlte Proben wie homogene feste Lösungen verhalten.

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THE ASSAY OF SODIUM CITRATE AND SODIUM POTASSIUM TARTRATE BY CATION EXCHANGE AND NON-AQUEOUS TITRIMETRY

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(Received May 9th, 1960)

INTRODUCTION

The official methods of the British Pharmacopoeia and of the B.P.C. for the assays of salts of organic acids, are time consuming and the burning and the transference stages require considerable care in order to avoid errors.

The B.P. assay gives a somewhat indirect measure of cation present by titrating the carbonate formed on carbonising the organic salt, whereas the cation exchange technique gives a direct measure of the anion, and non-aqueous titrimetry a direct measure of the cation.

(A) ASSAY BY CATION EXCHANGE RESINS

Investigation into suitability of conditions

Choice of indicator

For the titration of the liberated acids: Thymol blue was found to be the best indicator for citric acid and phenolphthalein for tartaric acid.

Column time

Experiments to determine the minimum time necessary for sodium citrate solution to pass through the column and also for minimum time for washing were carried out. As a result of these experiments a 20-min column time and a 20-min column wash time were found to be necessary, using the quantities of distilled water stated in *Method* below.

Column loading

In order to avoid the possibility of overloading the resin column it was concluded that not more than two assays should be carried out on the same resin column.

Method

Sodium citrate and sodium potassium tartrate assay by cation exchange resin, Amberlite I.R.120(H)

Principle. An ion exchange method employing Amberlite resin I.R.120(H), the effluent from the column containing the free acid is titrated with standard sodium hydroxide.

Apparatus. An all glass column 1.8 cm in diameter, with a 7.5-cm layer of resin supported on a sintered glass disc (porosity 1). When a fresh column is prepared it should be backwashed with distilled water to displace trapped air and also to wash away fine particles of dirt and resin.

Regeneration of (used and fresh) resin. Pass 300 ml of hydrochloric acid (4 *N*) through the column, this should take about 90 min. Follow this with a distilled water wash of about 2½ l, continue washing until the effluent no longer gives an acid reaction to methyl orange.

Reagents. Amberlite ion exchange resin I.R.120(H). Phenolphthalein indicator solution, 0.2% w/v in 60% v/v industrial methylated spirits. Methyl orange indicator solution, 0.04% w/v in 20% v/v industrial methylated spirits. Thymol blue indicator solution, dissolve 0.1 g thymol blue in 4.3 ml *N*/20 sodium hydroxide solution and 5 ml industrial methylated spirits with a little heat, dilute to 250 ml with 20% v/v industrial methylated spirits. 0.1 *N* sodium hydroxide, accurately standardised against potassium hydrogen phthalate. Hydrochloric acid, 4 *N*.

Procedure. Grind 5–6 g sample in a clean dry mortar to a fine powder. Accurately weigh 0.4 g in the case of sodium citrate and 0.6 g in the case of sodium potassium tartrate and quantitatively transfer to a 100-ml beaker, add 30 ml distilled water, warm to aid solution and when dissolved, transfer to a tap-funnel above the ion exchange column and dilute to about 75–80 ml. Allow the solution to run through the column. This should take about 20 min. The head of solution above the resin should be maintained at between 1.5 cm and 4.5 cm. Collect the effluent in a 400-ml conical beaker. Wash down the inside of the tap funnel and run a further 100 ml of distilled water through the column taking about 20 min and collecting the effluent in the same beaker. Wash the column through with a further quantity of 100 ml distilled water taking about 20 min for the water to go through the column and collect the effluent in another 400-ml beaker.

Evaporate the contents of both beakers down to about 15–20 ml, and allow to cool. Titrate with accurately standardised 0.1 *N* sodium hydroxide from a calibrated burette. In the case of sodium citrate use 5 drops of thymol blue indicator solution, and in the case of sodium potassium tartrate use 4 drops of phenolphthalein indicator solution.

The second beaker in each case should not require more than 0.1 ml 0.1 *N* sodium hydroxide. If the titration exceeds this amount, the assay should be repeated using freshly regenerated resin, as a larger titration in the second beaker is indicative of aged or poorly regenerated resin.

Calculation

If weight of sample = *S* g, and total titration = *A* ml, then

$$\begin{aligned} \text{assay} &= \frac{A}{S} \cdot 0.009804 \cdot 100\% \text{ sodium citrate } (\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}) \\ &= \frac{A}{S} \cdot 0.01411 \cdot 100\% \text{ sodium potassium tartrate } (\text{NaKC}_4\text{H}_6\text{O}_6 \cdot 4\text{H}_2\text{O}) \end{aligned}$$

Notes

1. The resin must be washed free from acid immediately prior to use.

2. On no account must resin as received be used — it must be regenerated first.
3. The resin must be regenerated after two determinations or freshly regenerated resin used.
4. The resin can be more conveniently regenerated in bulk.

(B) ASSAY BY NON-AQUEOUS TITRIMETRY

*(a) Sodium citrate assay, by titration with 0.1 N acetic perchloric acid**Investigation into the suitability of conditions**Choice of indicator*

The equivalent point — a purple coloration — with Oracet Blue B is much more easily detected than the equivalent point — a green coloration — with Crystal Violet. Quinaldine Red was also tried but no easily detectable end-point was observed.

Although the use of visual indicators (particularly Oracet Blue B) is fairly satisfactory, it has been found that the most reliable and accurate end-point detection is the potentiometric procedure as described under (b). The potentiometric method was used for the majority of this work.

Choice of primary standard

Potassium hydrogen phthalate was found to be most suitable because of the usual factors: high equivalent weight, high purity, non-hygroscopic salt, etc. The precipitate of potassium perchlorate formed during the titration can be safely ignored and has no adverse effect on the accuracy, particularly if the potentiometric method is used.

Choice of grade of acetic acid

The special grade of acetic acid "low water content acetic acid for non-aqueous titrations" is by far the best, but if the potentiometric method is used, "Laboratory Grade" has been found to be quite suitable. If "Laboratory grade" acetic acid is used, however, it is preferable to determine the water content by the Karl Fischer method and adjust the water content to 0.01 to 0.1% by means of acetic anhydride if necessary.

Effect of the presence of water

In the case of titration using Oracet Blue B as indicator, the end-point was found to be affected by the presence of water; increasing amounts of water giving increasing titrations and progressively more indistinct end-points. Addition of water at the end-point of the titration of 50 ml of the sodium citrate solution in glacial acetic acid gave the following results (Table I).

TABLE I

<i>ml water added</i>	<i>Additional titration required to the titration of 50 ml acetic sodium citrate solution (50 ml = 0.4 g) in order to reach the end-point on addition of the amounts of water shown (ml)</i>
0.2	0.15
0.5	0.40
1.0	0.90
2.0	1.81*

* end-point very indistinct

Method

Principle. Sodium citrate is dissolved in glacial acetic acid and its enhanced basicity titrated with acetous perchloric acid, detecting the end-point potentiometrically.

Apparatus. Magnetic stirrer. Direct reading pH meter, Pye model, Cat.No.111067. pH meter EMF "backing off" accessory, see (b). Glacial acetic acid reference electrode, E.I.L. Type RJ/24/5. Glass electrode, Pye Cat. No.11126.

Reagents. Glacial acetic acid. 0.1 N acetous perchloric acid, see Notes.

Procedure. Grind 5-6 g of sample to a fine powder and transfer 0.4 g, accurately weighed, to a 150-ml beaker, add 75 ml glacial acetic acid, warm to aid solution and allow to cool, under moisture-free conditions. Place the beaker on the magnetic stirrer, place the electrodes in position, switch the pH meter EMF 'Backing off' accessory on and switch the pH meter to 0-800-mV range. Adjust the meter reading to 700 mV using the variable resistance on the pH meter EMF' backing off' accessory and the set zero as fine control. Set the stirrer in motion and titrate with 0.1 N acetous perchloric acid until the meter registers 480 mV (*i.e.* the end-point) and read the burette.

Calculation

If weight of sample taken = S g, and corrected burette reading = V ml, then

$$\text{assay} = \frac{V}{S} \cdot 0.009804 \cdot 100\% \text{ sodium citrate } (\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O})$$

See also Appendix for temperature corrections.

Notes

The end-point is the point of inflexion in the curve obtained by plotting mV against ml titrant. A more accurate method of finding the end-point is to plot the first derivative against ml titrant; the maxima of the curve thus gives the end-point (See Figs. 2 and 3).

Preparation and standardisation of 0.1 N acetous perchloric acid

Transfer 1800 ml glacial acetic acid to a 2-l beaker, add very slowly with continuous stirring with the magnetic stirrer, 17.0 ml of perchloric acid (72%), followed by 60 ml of acetic anhydride. Transfer to a 2-l volumetric flask and dilute to 2 l with glacial acetic acid and allow to stand for 24 h. Standardise against 1.0 g (accurately weighed) potassium hydrogen phthalate using the above procedure.

(b) Sodium potassium tartrate assay by addition of an excess of 0.1 N acetous perchloric acid and back titration with 0.1 N acetous potassium acetate

Introduction

Sodium potassium tartrate is only slightly soluble in glacial acetic acid, due to the formation of potassium hydrogen tartrate. Hence a direct titration with acetous perchloric acid is very slow, taking about 15-20 min, but this has been found to give the correct result.

The assay, however, can be carried out by the following procedure, but the end-point is far from distinct using either Oracet Blue B or crystal violet indicators:

Transfer 0.6 g sample to a 150-ml B 24 neck flat-bottomed flask, add 50 ml 0.1 *N* acetous perchloric acid accurately, and stir the stoppered flask for at least 20 min. Then back titrate this solution with 0.1 *N* acetous sodium acetate or 0.1 *N* acetous potassium acetate.

Potentiometric procedure

A suitable electrode system consists of a glass electrode as indicator electrode with a saturated calomel half-cell of the 'sleeve' type as reference electrode. Care must be taken to prevent leakage of potassium chloride from the calomel electrode into the titration liquid, as this leads to vitiation of results due to the interaction of the potassium chloride with the perchloric acid titrant. (In view of this difficulty a specially constructed glacial acetic acid/mercurous acetate reference electrode was subsequently used).

The glass and reference electrodes are connected to a direct reading pH meter and the titration curve drawn by plotting the readings of either the mV- (or the pH scale) as ordinates, and the corresponding volumes as abscissae.

When a glass/calomel electrode system is immersed in an aqueous solution, the glass electrode usually assumes a negative potential with respect to the calomel electrode, but in glacial acetic acid, the glass electrode may assume a positive potential with respect to the calomel electrode, a phenomenon which may also occur in aqueous solution of low pH.

It is, therefore necessary to connect an auxilliary source of EMF in series with the electrodes in such a fashion as to "back off" a proportion of the electrode EMF. For routine titrations a 1.5-V dry cell in conjunction with a potential divider, is suitable, a convenient arrangement is shown in the diagram (Fig. 1).

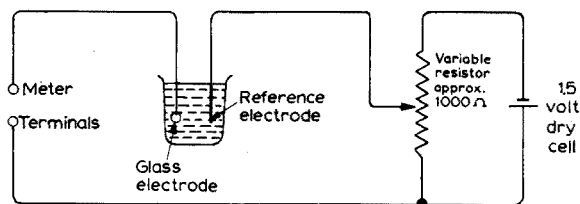


Fig. 1. EMF backing off accessory.

It is advisable to place the electrode system under a fume hood, as the vigorous stirring necessary to mix the solutions during a titration results in the dissipation of much acetic acid vapour. This is unpleasant for the operator and may cause corrosion and damage to the instrument.

The results may be represented either as a direct titration curve (Fig. 2) in which uncorrected meter readings are plotted as ordinates and the corresponding titration readings as abscissae, or as a differential curve $(\Delta mE)/\Delta V$ as ordinate and the corresponding titration reading as abscissae; where ΔmE is a small change in mV, and ΔV the corresponding change in volume of titrant (Fig. 3).

Time of stirring

The time for which the sodium potassium tartrate and 50 ml 0.1 *N* acetous per-

chloric acid is stirred is critical. A minimum period of 20 min was found to be necessary.

Choice of back titrant

From the titration curves of 0.1 *N* acetic sodium acetate titrated against standard 0.1 *N* acetic perchloric acid and 0.1 *N* acetic potassium acetate titrated against standard 0.1 *N* acetic perchloric acid it was found that acetic potassium acetate had the higher maxima on plotting the first derivative $(\Delta mE)/\Delta V$ against *V*. Hence acetic potassium acetate is preferred (see Figs. 2 and 3).

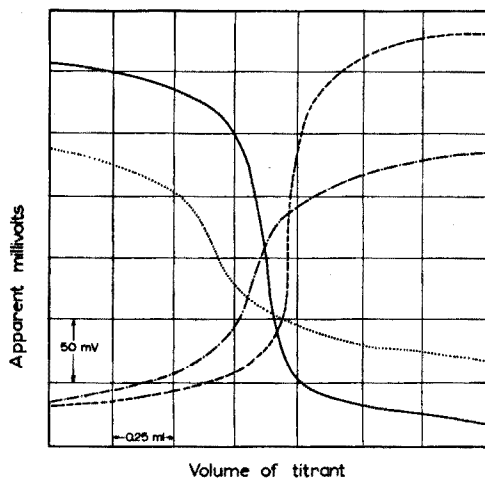


Fig. 2. Titration curves ——— Standardisation of acetic perchloric acid against potassium hydrogen phthalate; - - - Standardisation of acetic potassium acetate against acetic perchloric acid; Sodium citrate assay; · - · - Sodium potassium tartrate assay.

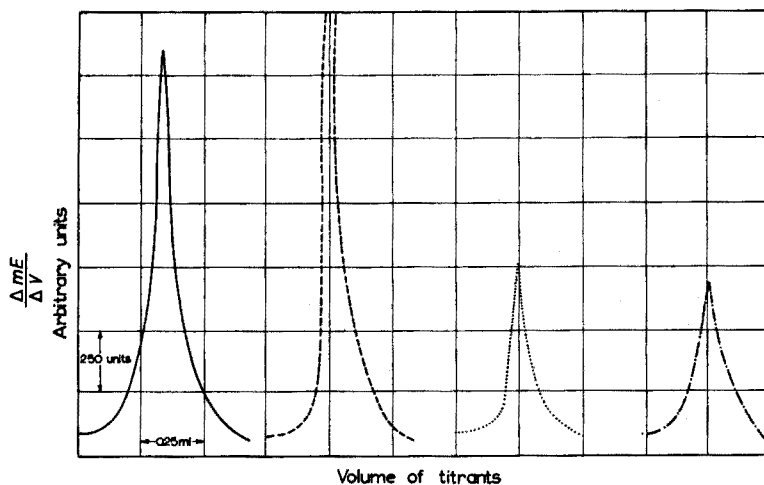


Fig. 3. First derivative curves. ——— Standardisation of acetic perchloric acid against potassium hydrogen phthalate; - - - Standardisation of acetic potassium acetate against acetic perchloric acid; Sodium citrate assay; · - · - Sodium potassium tartrate assay.

Method

Principle. The sodium potassium tartrate is stirred with excess standard acetous perchloric acid which reacts with the enhanced basicity of the salt. The excess of acetous perchloric acid is then back titrated with standard acetous potassium acetate, the end-point being determined potentiometrically. The precipitate of potassium perchlorate has no adverse effect on the titration.

Apparatus. Magnetic stirrer. Direct reading pH meter, Pye Model, Cat. No. 11067. pH meter EMF "backing off" accessory, as described above. Glacial acetic acid reference electrode, E.I.L. Type RJ24/5. Glass electrode, Pye Cat. No. 11126.

Reagents. Glacial acetic acid. 0.1 N acetous perchloric acid, standardised against potassium hydrogen phthalate. 0.1 N acetous potassium acetate, standardised against 0.1 N acetous perchloric acid.

Procedure. Grind 5–6 g of sample to a fine powder in a mortar, transfer 0.6 g accurately weighed to a 150-ml B.24 neck, flat bottomed flask, add 50 ml 0.1 N acetous perchloric acid from a burette, insert a 2.5-cm magnetic follower, stopper and stir the contents of the flask vigorously for 20 min using the magnetic stirrer. Transfer the contents of the flask to a 150-ml beaker, washing out the flask with a stream of glacial acetic acid. Place the beaker on the magnetic stirrer, place the electrodes in position, switch on the pH meter EMF "backing-off" accessory, switch the pH meter to the 0–800-mV range. Adjust the meter to 300 mV with the pH meter EMF "backing off" accessory and set zero as fine control. Set the stirrer in motion and titrate with 0.1 N acetous potassium acetate until the meter registers 470 mV (*i.e.* the end-point) and then read the burette.

Calculation

If weight of sample taken = S g, if corrected volume of 0.1 N acetous perchloric acid = V_1 ml, and corrected volume of 0.1 N acetous potassium acetate = V_2 ml, then

$$\text{assay} = \frac{(V_1 - V_2)}{S} \cdot 0.01411 \cdot 100\% \text{ sodium potassium tartrate (NaKC}_4\text{H}_6\text{O}_6 \cdot 4\text{H}_2\text{O)}$$

See the Appendix for temperature corrections.

Preparation and standardisation of acetous potassium acetate

Reagents. Glacial acetic acid. Potassium carbonate A.R.

Procedure. Dry about 20 g of potassium carbonate in a nickel dish in an electric oven at 150° for 2–3 h, and allow to cool in a desiccator. Accurately weigh out 6.91 g of the dried potassium carbonate, transfer to a 1-l beaker, add 200–300 ml glacial acetic acid and warm to aid solution, cool and transfer to a 1-l graduated flask and make up to the mark with glacial acetic acid.

Standardisation. Accurately transfer from a burette 45 ml of accurately standardised 0.1 N acetous perchloric acid to a 150-ml beaker, dilute to about 70–75 ml with glacial acetic acid. Place the beaker on the magnetic stirrer, place the electrodes in position, switch on the pH meter EMF "backing off" accessory, switch the pH meter to the 0–800 mV scale. Adjust the meter readings to 300 mV and titrate with the acetous potassium acetate until a meter reading of 480 is obtained, *i.e.* the end-point, and read the burette.

Calculation

Normality of acetous potassium acetate in terms of the normality of the 0.1 *N* acetous perchloric acid = A/B normal.

Where A = volume of 0.1 *N* acetous potassium acetate taken

B = volume of 0.1 *N* acetous potassium acetate required, and hence temperature or burette corrections are not required.

RESULTS

TABLE II

SODIUM CITRATE

Sample	Assay by		
	<i>B.P. method</i>	<i>Ion exchange</i>	<i>Non-aqueous</i>
1	99.8%	99.6%	99.7%
2	99.2%	99.3%	99.1%
3	99.7%	99.8%	99.7%
4	99.4%	99.5%	99.5%
5	99.5%	99.7%	99.7%
6	99.8%	99.8%	99.7%

TABLE III

SODIUM POTASSIUM TARTRATE

Sample	Assay by		
	<i>B.P. method</i>	<i>Ion exchange</i>	<i>Non-aqueous</i>
1	99.6%	99.5%	99.6%
2	99.9%	100.1%	100.0%
3	99.5%	99.6%	99.3%
4	100.0%	100.1%	100.0%
5	99.8%	99.7%	100.0%
6	99.3%	99.5%	99.4%

CONCLUSIONS

Hence it can be seen that both the cation exchange and non-aqueous titrimetry methods give very similar results to the *B.P.* method. The cation exchange method is unfortunately quite time consuming but gives a direct measure of the organic acid present, which cannot be conveniently or accurately carried out by any other method. It is, however, a convenient method for the determination of total anion content of acid salts.

The non-aqueous method, however, is much more rapid and less time consuming than the *B.P.* method.

Hence, in conclusion, the method of titration with perchloric acid in anhydrous acetic acid offers considerable advantages over the official methods used for the assays of salts of organic acids, because of its speed, simplicity and standardisation of procedure without any loss of accuracy. The major criticism of the method is the effect of the high coefficient of expansion of acetic acid solutions compared with aqueous solutions; but, however, a corrective factor can readily be applied — see Appendix.

APPENDIX

Temperature corrections

Multiply the volume of titrant by $1 - (t \cdot 0.001)$, if the titration is carried out at a

temperature above 20° or by $1 + (t \cdot 0.001)$, if the temperature is below 20°. (t = difference in ° from 20°).

ACKNOWLEDGEMENTS

The author wishes to thank the Directors of John & E. Sturge, Limited, for permission to publish this paper.

SUMMARY

Sodium citrate and sodium potassium tartrate are assayed by passing aqueous solutions of the salts through cation exchange resin columns, concentrating the effluents from the columns, and then titrating the effluents with standard sodium hydroxide solution. Sodium citrate is assayed by titrating a solution of the salt in glacial acetic acid with standard acetous perchloric acid, the end-point being detected potentiometrically; sodium potassium tartrate is assayed by stirring the salt in excess standard acetous perchloric acid, and then backtitrating the excess acetous perchloric acid with standard acetous potassium acetate, the end-point being detected potentiometrically.

RÉSUMÉ

Une méthode est proposée pour le dosage du citrate de sodium et du tartrate sodicopotassique par passage sur une résine, échangeur de cations, et titrage potentiométrique en milieu non-aqueux. Le citrate de sodium est titré, en solution dans l'acide acétique glacial, par une solution acétique d'acide perchlorique; le tartrate est traité par la solution acétique d'acide perchlorique et titré en retour par une solution étalon d'acétate de potassium.

ZUSAMMENFASSUNG

Natriumcitrat und Kalium-natriumtartrat können nach Behandlung mit einem Kationen-Austauscherharz im Eluat durch Titration mit Natriumhydroxydlösung bestimmt werden. Natriumcitrat, in Eisessig gelöst, kann mit Eisessig-Perchlorsäure titriert werden unter potentiometrischer Bestimmung des Endpunktes. Kalium-natriumtartrat wird mit einem Ueberschuss von Eisessig-Perchlorsäure versetzt und der Ueberschuss mit Kaliumacetat-Eisessiglösung zurücktitriert, wobei der Endpunkt ebenfalls potentiometrisch bestimmt wird.

MICRODOSAGE DU COBALT DANS LE „ZIRCONIUM REACTOR-GRADE”

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(Reçu le 20 juillet 1960)

Parmi les matériaux entrant dans la constitution des réacteurs atomiques, le zirconium et ses alliages occupent une place importante du fait de leur grande résistance à la corrosion par l'eau et les métaux fondus, de leur faible section efficace de capture des neutrons thermiques, de leur bonne conductibilité de la chaleur et de leur stabilité mécanique (absence de déformation sous l'influence du rayonnement). Ils conviennent particulièrement bien pour enrober les barreaux d'uranium.

Le contrôle de la pureté du métal et de ses alliages est un problème important car les tolérances admises, variables suivant la nature de l'impureté, sont souvent très faibles, notamment en ce qui concerne le cobalt.

Quelques méthodes de dosage du cobalt dans le zirconium ont été proposées dernièrement. Dans l'une¹, les auteurs déterminent le cobalt par spectrophotométrie de son complexe avec le nitroso-1-naphtol-2, après extraction de celui-ci par le chloroforme. On a fait également appel à une séparation électrolytique sur cathode de mercure²; après distillation de ce dernier, on dose le cobalt dans le résidu par spectrophotométrie en présence de nitroso-sel R. La prise est de 1 g dans chaque cas. La première méthode donne de bons résultats avec des quantités de cobalt comprises entre 0.5 et 30 μg par ml de solution finale. La seconde, plus sensible, va de 5 à 0.1 $\mu\text{g}/\text{ml}$. La détermination du cobalt à l'aide de nitroso-sel R a également été faite sans séparation préalable³, mais la présence de certains ions peut alors perturber le dosage.

Après l'étude que nous avons faite concernant la séparation et le dosage de traces de cobalt dans différents milieux minéraux et organiques⁴, nous avons constaté qu'il est avantageux de mettre à profit la grande sensibilité de la méthode spectrophotométrique utilisant le nitroso-sel R et la qualité des séparations obtenues en utilisant la résine Dowex 1-X8, pour effectuer des dosages sur des prises aussi faibles que possibles. On réduit ainsi la durée de la plupart des opérations telles que mise en solution, extraction, évaporation, etc. C'est pourquoi nous proposons une méthode permettant de doser le cobalt sur des prises de 100 mg de zirconium très pur (type RG.SG.101).

Principe de la méthode

Après solubilisation au moyen des acides nitrique, chlorhydrique et fluorhydrique, la solution obtenue est introduite dans une colonne échangeur d'ions contenant de la résine Dowex 1-X8. Le cobalt est séparé dans les conditions où l'on travaille. On purifie ensuite le cobalt élué par extraction à l'aide de dithizone, puis on minéralise

le dithizonate de cobalt et forme le complexe en présence de nitroso-sel R. On mesure la densité optique à 520 m μ par rapport à un blanc préparé dans les mêmes conditions. Lorsqu'on travaille sur des solutions contenant de très faibles quantités de cobalt, l'influence des pertes survenant au cours de l'analyse devient très importante, aussi avons nous utilisé du ^{60}Co comme traceur radioactif. Des mesures d'activité faites dans les mêmes conditions, au début et à la fin du dosage permettent de déterminer avec précision la valeur de ces pertes et de corriger les résultats en conséquence.

Les résultats proprement dits sont contrôlés d'autre part à l'aide de différents essais parallèles:

(a) Mesure spectrophotométrique (effectuée dans les mêmes conditions que l'analyse) d'une solution de cobalt pur dont la concentration, exactement connue, est voisine de celle de l'échantillon (étalon externe).

(b) Adjonction d'une quantité connue de cobalt dans la solution de l'échantillon (étalon interne). Après mesure et calcul du résultat d'après (a), on déduit la quantité de cobalt ajoutée. La valeur ainsi obtenue doit être égale à celle que donne un dosage fait sans adjonction de cobalt. De cette manière, on contrôle simultanément l'étalonnage (a) et l'absence d'effet gênant provenant de la solution (c).

(c) Adjonction d'une quantité connue de cobalt dans une fraction d'éluat recueillie immédiatement après le passage du cobalt de l'échantillon. L'étalon se trouve ainsi placé dans des conditions aussi voisines que possible de celles de l'analyse.

(d) Essais à blanc effectués dans les mêmes conditions que l'analyse.

Ces essais nous montrent une très bonne concordance entre les densités optiques obtenues dans ces différentes conditions. En pratique, les essais (a) et (b) sont à refaire avant chaque série d'analyses; l'essai (d) est à refaire lorsqu'on utilise de nouveaux réactifs.

Appareillage

Spectrophotomètre Beckman, modèle DU, avec photomultiplicateur permettant l'extention de la zone de lecture 90–100% sur toute la longueur de l'échelle.

Echelle décadique „Tracerlab”, type SC-33A „1000 Scaler”, avec sonde à scintillation P-20B équipée d'un cristal NaI(Tl) à puits.

Réactifs et solutions (Produits Merck pro anal.)

Acide chlorhydrique concentré et solutions 9 N, 4 N, 0.1 N et 0.01 N; acide nitrique concentré; acide perchlorique concentré; acide fluorhydrique 1/5; solution d'hydroxyde de sodium, concentrée (20 à 30%) et 1 N; solution de chlorure de sodium (ou KCl) 0.1 M; chlorure d'aluminium; citrate de sodium; éther; solution à 0.05% de dithizone dans l'éther; tampon acétique de pH 6 (solution d'acétate de sodium à 10% amenée au pH 6 par de l'acide acétique glacial); solution de nitroso-sel R à 0.05% dans l'eau (provenance Fluka); résine Dowex 1-X8 à anions $-\text{N}^+(\text{CH}_3)_3$ fortement basiques, de 100–200 mesh (provenance Fluka); solution de ^{60}Co ayant une activité de 0.025 $\mu\text{C}/\text{ml}$ et une concentration de 0.0035 $\mu\text{g}/\text{ml}$. Cette solution sert de traceur radioactif (provenance Harwell).

Mise en solution

Le zirconium est insoluble dans les acides, même à chaud. La littérature propose pour le dissoudre, soit l'eau régale, soit l'acide fluorhydrique. L'attaque du zirconium

par l'eau régale est trop lente pour que ce réactif puisse être retenu; l'acide fluorhydrique, par contre, dissout très rapidement ce métal, même à froid (la réaction est vive), mais l'emploi de cet acide présente de multiples inconvénients (attaque des récipients, vapeurs corrosives, élimination difficile, etc.). C'est pourquoi nous avons appliqué un autre processus de mise en solution. Il se trouve que l'acide fluorhydrique est non seulement un excellent oxydant du zirconium mais également un catalyseur d'oxydation et l'expérience montre que de petites quantités d'acide fluorhydrique, introduites dans l'eau régale, suffisent pour accélérer considérablement l'attaque, même à froid.

L'attaque à chaud se fait déjà lorsque le rapport HF/eau régale est égal à 1/2000. A une telle dilution, le verre n'est pas attaqué et il est facile de masquer le fluor restant.

Mode opératoire: On pèse 100 mg de zirconium sous forme de copeaux que l'on place dans un bécher Phillips de 100 ml en ajoutant 20 ml d'eau régale et 10 gouttes d'acide fluorhydrique 1/5. On ajoute 2 ml de la solution de ^{60}Co de marquage dont l'activité a été au préalable déterminée à l'aide du compteur à scintillation. On recouvre d'un verre de montre et porte à ébullition, en rajoutant si nécessaire, un peu d'eau régale de temps à autre jusqu'à dissolution. Lorsque celle-ci est complète, on ajoute environ 0.1 g de chlorure d'aluminium pour complexer les ions fluor, puis on évapore la plus grande partie de la solution. Il faut éviter une évaporation à sec qui favorise l'adsorption du cobalt sur les parois et rend difficile la remise en solution de la prise. Lorsqu'il ne reste que quelques ml de solution dans le bécher, on rajoute 10 ml d'acide chlorhydrique concentré et on évapore à nouveau presque complètement. On reprend finalement par 20 ml d'une solution de HCl 9 N, de manière à pouvoir ensuite effectuer directement le passage sur les colonnes échangeurs d'ions.

Séparation

Lorsque la solution 9 N, obtenue après attaque selon le processus décrit au paragraphe précédent, est introduite dans une colonne chromatographique contenant de la résine Dowex 1-X8, le cobalt (ainsi qu'un certain nombre d'autres cations tels que Fe, Cu, Zn, etc.) se fixe sous forme d'anions complexes. L'adjonction de HCl 4 N détruit le complexe du cobalt qui se trouve alors élué seul. La solution obtenue, pratiquement exempte de cations étrangers, contient cependant des traces de résine qui deviennent gênantes lorsqu'il s'agit de la détermination de très petites quantités de cobalt. On effectue alors une purification par extraction au moyen d'une solution éthérée de dithizone. Après minéralisation de l'extrait, le dosage du cobalt s'effectue dans les meilleures conditions possibles.

Mode opératoire: (a) On prépare les colonnes chromatographiques de la manière suivante: Laver plusieurs fois une quantité suffisante de résine Dowex avec HCl 0.01 N, en éliminant les particules trop fines par décantation. Placer cette résine dans des colonnes de 6 mm de diamètre intérieur, entre deux tampons de laine de verre, de manière à obtenir une hauteur de 120 mm environ, effectuer un lavage final en laissant écouler, à travers les colonnes, 30 ml de HCl 0.01 N. On sature ensuite par 5 ml de HCl 9 N. La vitesse de passage des solutions doit être de l'ordre de 1 ml par minute.

(b) On introduit dans une colonne la solution chlorhydrique 9 N contenant le zirconium. Après écoulement complet, on lave par 20 ml de HCl 9 N. On élue ensuite

le cobalt avec 25 ml de HCl 4 *N*. Les pertes de cobalt au cours de cette opération sont de l'ordre de 2 à 3%.

(c) On ajoute à la solution, du citrate de sodium afin que la concentration de celui-ci soit de 10% (soit 2.5 g pour un volume de 25 ml). On amène au pH d'environ 8.2 à l'aide d'une solution concentrée, puis d'hydroxyde de sodium 1 *N*. On transvase dans une ampoule à décanter de 100 ml et extrait par 5 ml d'une solution à 0.05% de dithizone dans l'éther en agitant énergiquement durant 2 min. On recommence cette dernière opération jusqu'à ce que la dithizone conserve sa couleur verte (deux extractions sont suffisantes dans le cas présent). On lave finalement la solution aqueuse avec 5 ml d'éther pur. Les solutions étherées renfermant le dithizonate de cobalt sont recueillies dans une ampoule à décanter, on élimine la solution aqueuse entraînée et on lave avec 2 ml de HCl 0.1 *N*. On laisse écouler la solution organique dans une capsule de pyrex et on évapore à sec.

(d) La minéralisation du dithizonate de cobalt doit être conduite avec soin car c'est elle qui peut être responsable des plus grandes pertes. On effectue une attaque préalable du résidu avec 1 ml d'acide nitrique et on évapore à sec au moyen d'une calotte chauffante. On ajoute ensuite 5 ml d'acide perchlorique, recouvre la capsule d'un verre de montre suffisamment creux contenant de l'eau pour favoriser la condensation des vapeurs d'acide et place le tout sur une plaque chauffante (à environ 250–280°) jusqu'à décoloration complète, ce qui nécessite environ 2 heures. On enlève alors le verre de montre et ajoute 2 ml de chlorure de sodium (ou KCl) 0.1 *M* (charge destinée à prévenir les adsorptions sur le verre), puis on évapore sous calotte chauffante. On reprend par 1 ml d'acide chlorhydrique concentré et évapore à nouveau pour détruire le perchlorate alcalin formé. On ajoute finalement 2 ou 3 ml d'eau bidistillée et évapore pour chasser les dernières traces d'acide. Le résidu final, qui doit être tout à fait blanc, est repris quantitativement par 2 ml d'eau bidistillée et transvasé dans une petite éprouvette; on en mesure l'activité à l'aide du compteur à scintillation.

Détermination spectrophotométrique

La solution contenant le cobalt (ainsi que le support ajouté au cours de la minéralisation) ne renferme pratiquement plus d'ions étrangers et la détermination spectrophotométrique peut être faite avec précision. On forme le complexe en présence de nitroso-sel R et mesure la densité optique à 520 μ . La méthode a été décrite en détails lors d'un article précédent⁵, aussi n'en donnerons nous qu'un bref résumé.

Mode opératoire: (a) La solution à analyser (2 ml) est transvasée dans un tube à centrifuger jaugeé de 5 ml en y ajoutant 2 ml de solution tampon acétique de pH 6. On introduit ensuite 0.5 ml de solution aqueuse de nitroso-sel R.

(b) On développe la coloration en chauffant durant 60 sec au bain-marie bouillant, puis on introduit 0.5 ml d'acide nitrique concentré et continue à chauffer durant 30 sec pour détruire l'excès de réactif.

(c) Après refroidissement sous un courant d'eau, on ajuste éventuellement au trait de jauge, puis on centrifuge durant 15 min à environ 3000 t/m pour éliminer toute trace de matière en suspension qui pourrait fausser la mesure spectrophotométrique.

(d) On introduit la solution dans une cuve colorimétrique de 10 mm et on mesure l'extinction à 520 μ par rapport à un essai témoin préparé dans les mêmes conditions.

On effectue dans les mêmes conditions une série de contrôle (voir page 56) afin d'éliminer tout risque d'erreur.

Interprétation des résultats

L'extinction ayant été déterminée, on se reportera aux essais témoins — (a), (b) et (c), page 56 ou à une courbe d'étalonnage⁵ — pour calculer la quantité de cobalt présente. On déduit de la valeur trouvée la quantité de cobalt introduite par les réactifs — (d), page 56 — et la solution de marquage et on effectue une correction pour tenir compte des pertes survenues en cours d'analyse. Ces pertes sont déterminées avec précision par le rapport des comptages initiaux (page 57) et finals (page 58). La stabilité du compteur à scintillation est contrôlée par une source étalon lors de chaque série de mesure.

Résultats du dosage du cobalt dans le zirconium RG.SG.101

Le dosage a été conduit selon la méthode décrite et les résultats trouvés sont donnés dans les Tableaux I et II.

TABLEAU I
DOSAGE SPECTROPHOTOMÉTRIQUE DU COBALT DANS LE ZIRCONIUM RG.SG.101
(volume lors de la détermination = 5 ml)

Prises (mg)	Marquage au ⁶⁰ Co			Densité optique	Co trouvé ^a (μg)	Teneur en cobalt (%)
	Initial (c.p.m.)	Final (c.p.m.)	Pertes (%)			
100	39827	31708	20.4	0.01255	0.314	0.00031
100	40243	35733	11.2	0.01402	0.315	0.00032
100	40988	34104	16.8	0.01157	0.277	0.00028
100	40438	35020	13.4	0.01260	0.290	0.00029
100	40339	33117	17.9	0.01309	0.318	0.00032
100	39405	35076	11.0	0.01348	0.302	0.00030
100	39875	29670	25.6	0.01162	0.312	0.00031
100	40134	36804	8.3	0.01260	0.273	0.00027

^a Compte tenu des pertes et déduction faite du cobalt de marquage (0.007 μg)

TABLEAU II
DOSAGE SPECTROPHOTOMÉTRIQUE DU COBALT DANS LE ZIRCONIUM RG.SG.101
AVEC CONTRÔLE PAR ADJONCTION D'UNE QUANTITÉ CONNUE DE COBALT (étalon interne)

Prises (mg)	Marquage au ⁶⁰ Co			Co ajouté (μg)	Densité optique	Co trouvé ^a (μg)	Teneur en Co (%)
	Initial (c.p.m.)	Final (c.p.m.)	Pertes (%)				
100	40211	34177	15.0	—	0.01407	0.331	0.00033
100	39120	33685	13.9	0.290	0.02564	0.600	0.00031
100	40314	33782	16.2	0.490	0.03358	0.810	0.00032

^a Compte tenu des pertes et déduction faite du cobalt de marquage (0.007 μg)

La valeur moyenne établie sur les 11 résultats précédents est de 0.000305%, l'écart standard étant de $\pm 0.0000058\%$. La limite de confiance calculée pour une probabilité de 95% est de $\pm 0.0000124\%$. La teneur en cobalt du zirconium RG.SG.101 est donc comprise entre 0.000293 et 0.000318%.

DISCUSSION

Le procédé de séparation et de dosage qui a été décrit peut être appliqué même si l'on ne dispose pas des instruments et des produits qui permettent le marquage par

isotopes radioactifs. Si l'on travaille dans les conditions indiquées, on constate que les pertes moyennes (contrôlées sur un grand nombre d'essais⁶) survenant en cours d'analyse sont de l'ordre de 15%. On devra donc multiplier les résultats obtenus par le facteur 1.176.

Mais si la méthode des traceurs est applicable avec le matériel de laboratoire dont on dispose, une simplification notable du processus général de séparation est possible. On procédera alors de la manière suivante:

Au cours de l'éluion du cobalt à l'aide d'acide chlorhydrique 4 N, on recueillera la solution par fractions successives de 2 ml environ. Une détermination rapide d'activité permettra alors de choisir 1 ou 2 fractions contenant la plus grande partie du cobalt. La portion d'éluat ainsi sélectionnée (2 à 4 ml au lieu de 25 ml) ne contient qu'extrêmement peu de résidus gênants provenant de la résine Dowex et une purification par extraction au moyen de dithizone devient inutile. Après avoir chassé l'acide chlorhydrique par évaporation, on reprend par 2 ml d'eau bidistillée et effectue la détermination spectrophotométrique de la manière habituelle (voir page 58).

La durée moyenne d'un dosage, qui est de 10 h environ en suivant la méthode décrite, se réduit à 6 h en suivant le processus de séparation simplifié.

REMERCIEMENTS

Nous remercions le Fonds National Suisse, Commission pour la Science Atomique, grâce auquel nous avons pu entreprendre ce travail.

RÉSUMÉ

Une étude a été faite concernant la séparation et le dosage du cobalt d'une prise de 100 mg de „zirconium reactor-grade". La séparation est faite à l'aide de résine Dowex 1-X8 et le cobalt, après éluion, est purifié par extraction par la dithizone. On dose le cobalt séparé par spectrophotométrie au moyen de nitroso-sel R. La méthode est contrôlée par l'emploi d'un traceur radioactif (⁶⁰Co). Une teneur de 0.0003% de Co est déterminée avec une précision de $\pm 4\%$.

SUMMARY

A method is described for the separation and determination of cobalt in 100 mg reactor-grade zirconium. Separation is effected by means of an ion-exchange resin. After elution, the cobalt is purified by extraction with dithizone and determined spectrophotometrically with the help of nitroso-R-salt. With this method a content of 0.0003% can be determined with an accuracy of $\pm 4\%$.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Abtrennung und Bestimmung von Kobalt in 100 mg Zirkonium-Reaktormaterial. Die Abtrennung erfolgt mit einem Austauschharz, die Reinigung über den Dithizonkomplex und die Bestimmung spektrophotometrisch mit Hilfe des Nitroso-R-Salzes. Ein Gehalt von 0.0003% kann nach dieser Methode mit einer Genauigkeit von $\pm 4\%$ erfasst werden.

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DETERMINATION OF HIGHER MOLECULAR WEIGHT ALIPHATIC ALDEHYDES AND KETONES

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(Received July 11th, 1960)

Several spectrophotometric methods have been developed for formaldehyde¹⁻⁵, for total aliphatic aldehydes and ketones⁵⁻⁷, total aliphatic aldehydes⁸⁻¹⁰ and ketones¹¹. In all of these methods the first members of the series, formaldehyde and acetone, have more intense absorption spectra than the remaining members of the series. The available data suggest that formaldehyde or acetone is the most prominent of the individual carbonyl compounds present in combustion gases^{12,13} or smog¹⁴. An analytical procedure capable of detecting and determining higher molecular weight aldehydes or ketones in the presence of formaldehyde or acetone would provide an additional means of studying the composition of carbonyl compounds in such mixtures.

In developing a new spectrophotometric method for diolefins¹⁵, it was found that formaldehyde, acetaldehyde and acetone were quite unreactive with the reagents used. However, propionaldehyde, acrolein, butanone and higher molecular weight aldehydes and ketones did react to form products with fairly intense absorption bands. In addition to absorption maxima in the 380 to 395 $m\mu$ range possessed by both the aldehydes and the ketones, the straight-chain aldehydes have absorption maxima or shoulders in the 440 to 465 $m\mu$ region. Most alkanediones react to form intense absorption maxima in the 380 to 390 $m\mu$ region.

EXPERIMENTAL PROCEDURE

The aldehyde or ketone is dissolved in 2-methoxyethanol containing 25% concentrated (85%) phosphoric acid. This solution is reacted in the ratio of 8 parts of sample solution to 2 parts of reagent, a 2% solution of *p*-nitrobenzenediazonium fluoroborate in 2-methoxyethanol. Since the reagent decomposes slowly on standing, it should be prepared on the day of use.

The sample and reagent are allowed to react for four hours at 35°. The spectra then are measured on a Cary Model 11 or equivalent spectrophotometer using cells that provide an optical path length of 1 cm.

RESULTS

Aldehydes and ketones

Some preliminary absorbance measurements were made on solutions containing 1.8% of the *p*-nitrobenzenediazonium reagent. However, this procedure results in lower

sensitivities, and the reagent blank is more highly colored and less stable than those resulting from use of solutions containing only 0.4% reagent. The solutions containing a 0.4% reagent concentration react for 4 h at 35° (Table I).

TABLE I
ABSORPTION SPECTRA OF REACTION PRODUCTS FORMED BETWEEN *p*-NITROBENZEDIAZONIUM FLUOBORATE AND ALDEHYDE OR KETONES

Aldehyde or ketone	1.8% reagent concentration ^{a,b}		0.4% reagent concentration ^{a,c}	
	λ_{max} , $m\mu$	K_{spc} , $\mu g^{-1} ml cm^{-1}$ ^d	λ_{max} , $m\mu$	K_{spc} , $\mu g^{-1} ml cm^{-1}$ ^d
formaldehyde	470-480	0.000002	465	0.00005
acetaldehyde	420	0.0001	380	0.00089 ± 0.00013 ^e
	465	0.00008	450	0.00035 ± 0.00006
propionaldehyde	400	0.001	390	0.035 ± 0.007
	450	0.0015	440	0.024 ± 0.001
butanal	—	—	385	0.017 ± 0.001
			440 sh	0.012 ± 0.002
2-methyl-propanal	—	—	390	0.081 ± 0.005
pentanal	—	—	387	0.021 ± 0.003
3-methyl-butanal	—	—	395	0.021 ± 0.001
acrolein	—	—	387	0.03 ^f
2-butenal	450	0.003	390	0.016 ± 0.002
2-methyl-2-butenal	—	—	385	0.013 ± 0.003
			500 sh	0.002
acetone	400	0.0003	380	0.002
butanone	410	0.004	383	0.036 ± 0.003
3-pentanone	—	—	380	0.022 ± 0.003
3-methyl-2-butanone	—	—	392	0.051 ± 0.003
2,3-butanedione	—	—	390	0.0015
2,4-pentanedione	—	—	380	0.22 ± 0.04
1,2-cyclo-hexanedione	—	—	383	0.20

^a Reagent concentration in final solution after addition of reagent to sample solution.

^b 4-h reaction period at room temperature.

^c 4-h reaction period at 35°.

^d Specific absorption coefficient, absorbance per μg of aldehyde or ketone in each ml of initial sample solution.

^e Standard deviation.

^f At 20 μg , absorbance not linear with concentration.

All of the aldehydes and ketones except formaldehyde form products with absorption maxima in the 380-395 $m\mu$ range. However, the intensities of the products of the acetaldehyde, acetone, and 2,3-butanedione with *p*-nitrobenzenediazonium fluoborate are 0.1-0.01 of the products formed by the higher molecular weight aldehydes and ketones. The absorbances were found to be linear with concentration, at least in the 5 to 50 $\mu g/ml$ range, for the higher molecular weight compounds.

All of the straight-chain aldehydes used gave indications of a second absorption band in the 440-465 $m\mu$ region. The reaction product of the formaldehyde possesses only one band at 465 $m\mu$. In the acetaldehyde product this band intensifies somewhat and is shifted about 15 $m\mu$ towards the ultraviolet, while a second band appears at 380 $m\mu$. In the propionaldehyde product the higher wavelength band greatly increases in intensity and shifts another 10 $m\mu$ towards the ultraviolet. The overlap

between this higher wavelength band and the intensified lower wavelength band, now peaking at $390\text{ m}\mu$, is such as to make the $440\text{-m}\mu$ absorption appear as weak maximum or as a shoulder. The reaction product formed by the butanal also has a shoulder at about $440\text{ m}\mu$. The pentanal product shows only a slight inflection in the $430\text{--}440\text{ m}\mu$ region. Consequently, the higher wavelength absorption band becomes indistinguishable under the lower wavelength band as the molecular weight of straight-chain aldehyde increases. The intensities at $440\text{ m}\mu$ are linear with concentration in the $5\text{ to }50\text{ }\mu\text{g/ml}$ range for propionaldehyde, butanal and pentanal. The absorbance also is a linear function of concentration for acetaldehyde at $450\text{ m}\mu$ in the $500\text{ to }3000\text{ }\mu\text{g/ml}$ range.

The unsaturated straight-chain aldehydes, acrolein and crotonaldehyde, do not have a similar higher wavelength band appearing in the absorption spectra of their reaction products. The 2-methyl-2-butenal reaction product does show a shoulder at $500\text{ m}\mu$ in addition to the usual lower wavelength absorption band.

The substitution of an isopropyl group for an *n*-propyl group, or correspondingly, a methine for the methylene group alpha to the carbonyl group of an aldehyde or ketone, results in an appreciable increase in intensity and a small shift towards the visible of the absorption bands of the reaction products. This effect is clearly shown by comparing the absorption bands of the products formed by methylpropanal and 3-methyl-2-butanone with the corresponding bands of the products formed by butanal and 3-pentanone.

The presence in a ketone of two carbonyl groups either adjacent or separated by a methylene group also results in a large increase in intensity of the absorption bands of the reaction products. For example, the reaction product formed by 2,4-pentanedione has ten times as intense an absorption band as does 3-pentanone, and over one hundred times as intense a band as does butanedione.

Interferences

It has been reported elsewhere¹⁵ that some conjugated diolefins, and many phenols, couple with *p*-nitrobenzenediazonium fluoborate in phosphoric acid-2-methoxyethanol to form products absorbing in the $400\text{ m}\mu$ region. Phenol, *p*-cresol, almost all monoolefins, other classes of hydrocarbons and nitrogen oxides interfere only to a small or negligible extent¹⁵. Benzaldehyde reacts very slightly, if at all, with the diazonium salt.

Analysis of liquid mixtures

One of the applications suggested by the data given in Table I is the analysis of one or more higher aldehydes such as propionaldehyde in mixtures also containing formaldehyde, acetaldehyde or acetone. Formaldehyde, acetaldehyde and acetone have small or negligible absorption in the $440\text{--}460\text{ m}\mu$ range. Consequently, three liquid mixtures were analyzed. Two of these mixtures contained formaldehyde in large excess, acetaldehyde and propionaldehyde. The third mixture contained formaldehyde in large excess, acetone and propionaldehyde. All three of these mixtures reacted to produce absorption maxima at $456\text{ m}\mu$ and a second maximum at $375\text{--}380\text{ m}\mu$. Both of these types of maxima are shifted away from the positions of the wavelength maxima in reagent solutions containing only propionaldehyde (Table I). The composition of these mixtures and the calculated concentrations using both 440 and

456 $m\mu$ as the analytical wavelengths are given in Table II. The compositions are calculated from the absorptivities for propionaldehyde alone at 440 and 456 $m\mu$.

The calculated concentrations of propionaldehyde are in fair agreement with the actual concentrations. However, the concentration values obtained using 440 $m\mu$ as the analytical wavelength are 5% to 10% low, whereas the values obtained using 456 $m\mu$ as the analytical wavelength are 5% to 10% high. If 450 $m\mu$ were used as the analytical wavelength, the calculated and actual propionaldehyde concentrations would be in good agreement. However, the choice of 450 $m\mu$ is an arbitrary one and this wavelength might be less satisfactory for mixtures in a different concentration range or with other components present.

TABLE II

ANALYSIS OF LIQUID MIXTURES OF ALIPHATIC ALDEHYDES AND KETONES FOR PROPIONALDEHYDE

Mixture	Conc. $\mu\text{g/ml}$	Calculated conc. $\mu\text{g/ml}$ of propionaldehyde*	
		440 $m\mu$	456 $m\mu$
formaldehyde	945		
acetaldehyde	48	32	39
propionaldehyde	35.7		
formaldehyde	945		
acetaldehyde	48	44	49
propionaldehyde	45.4		
formaldehyde	945		
acetone	41	41	47
propionaldehyde	45.0		

* 4-h reaction period at 35°

DISCUSSION

The present method would appear to be applicable to the analysis of total straight-chain aldehydes in the three to five carbon atom range in mixtures also containing formaldehyde, acetaldehyde, and acetone. The reaction products formed by higher molecular weight branched-chain aldehydes and the four carbon and higher ketones also will absorb appreciably in the 440 to 460 $m\mu$ range. The specific absorptivities of the products in the 440 $m\mu$ region vary from about 0.005 $\mu\text{g}^{-1} \text{ml cm}^{-1}$ for 3-pentanone to 0.03 $\mu\text{g}^{-1} \text{ml cm}^{-1}$ for 2-methylpropanal. However, most of the absorptivities at 440 $m\mu$ are in the 0.01 to 0.02 $\mu\text{g}^{-1} \text{ml cm}^{-1}$ range. This wavelength region might be useful for a quantitative estimation of total higher molecular weight aldehydes and ketones in oxygenate mixtures.

The maxima in the 380- to 395- $m\mu$ region are most intense (Table I), but vary over a six-fold range (even excluding the diones). These maxima are more subject to interference by phenols and diolefins than are the absorption maxima in the 440- to 460- $m\mu$ range. Consequently, except for very simple mixtures, or possibly in mixtures containing appreciable quantities of 2,4-pentanedione or related diones, the 380- to 395- $m\mu$ region appears to be of limited analytical applicability.

The products formed by most of the higher molecular weight aldehydes and ketones do not appear to be *p*-nitrophenylhydrazones formed by direct attack of the diazo-

nium cation on the carbonyl group. Formaldehyde, acetaldehyde, acetone, 2,3-butanedione and benzaldehyde all form very weakly absorbing products. If the *p*-nitrophenylhydrazones of these carbonyl compounds are formed, the products should have about as intense absorption spectra as the other aldehydes and ketones. Consequently, the position of attack must be at the methylene or methine carbon atom alpha to the carbonyl group, and carbonyl compounds lacking such activated carbon-to-hydrogen bonds react only to a small extent with the diazonium compound.

The formation of the phenylhydrazones of triones have been reported when diazonium salts have been reacted with several diones including 2,4-pentanedione, 1,2-cyclopentanedione, 1,3-cyclohexanedione, etc.¹⁶. These may be the type of products formed by the 2,4-pentanedione and 1,2-cyclohexanedione in the solvent system used in the present investigation.

Aldehydes and ketones with activated carbon-to-hydrocarbon bonds also will react to form formazans with diazonium salts¹⁶. However, such reactions usually proceed readily in an alkaline rather than in acidic medium¹⁶. However, the formation of formazans from simple aldehydes and ketones recently have been reported in acidic media¹⁷ by reacting phenylhydrazines and an oxidant with the carbonyl compound or by reacting phenylhydrazines and a diazonium salt with the carbonyl compound. Propionaldehyde, butanone, acrolein and the higher molecular weight members of these series of oxygenated compounds also may be forming the corresponding formazans under the experimental conditions of this study.

The interpretation of the results reported here is somewhat complicated by the second absorption band formed in the reactions of straight-chain aldehydes. The presence of two band systems suggest that two types of reaction products may be formed from these compounds.

SUMMARY

The visible absorption spectra have been measured for the reaction products formed by aldehydes and ketones with *p*-nitrobenzenediazonium fluoborate in a phosphoric acid-2-methoxyethanol solvent medium. The absorption maxima for the reaction products of higher molecular weight aldehydes and ketones are much more intense than those formed by formaldehyde, acetaldehyde and acetone. This intensity effect has been used to analyze for propionaldehyde in mixtures also containing formaldehyde, acetaldehyde or acetone. The nature of the reaction products are considered.

RÉSUMÉ

Une méthode est proposée pour le dosage des aldéhydes et des cétones. Elle consiste à mesurer le spectre d'absorption de leur produit de réaction avec le fluoborate de *p*-nitrobenzènediazonium, en milieu acide phosphorique-méthoxyéthanol.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung höher molekularer Aldehyde und Ketone. Sie beruht auf der Messung der Absorptionsspektren der Reaktionsprodukte mit *p*-Nitrobenzoldiazonium-fluoborat in einem Gemisch von Phosphorsäure und 2-Methoxy-äthanol als Lösungsmittel.

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Anal. Chim. Acta, 24 (1961) 61-66

A METHOD FOR THE DETERMINATION OF STARCH IN WOOD

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(Received June 24th, 1960)

INTRODUCTION

In order to follow the process of starch resorption in fire-damaged and insect-defoliated eucalyptus trees it was necessary, as a first step, to devise a method of determining starch in large numbers of wood samples which was rapid, specific and sufficiently accurate to show starch variation in trees sampled at monthly intervals. The accurate determination of starch in wood has been a matter of some difficulty brought about mainly by the low concentration of starch normally present and the fact that it has common solubility properties with other polysaccharides occurring in wood. SCHORGER¹ reviewing work in this field found that the methods then in use involved either acid or enzyme hydrolysis and used dilute acid or hot water to isolate the starch. CAMPBELL² obtained results on English oak and Walnut wood by taka-diastase hydrolysis which were two to three times higher than were found on the same material by hot water extraction. GIBBS³ also used takadiastase with only moderate success to determine starch in the twigs of *Betula populifolia*. NIELSEN AND GLEASON⁴ used perchloric acid to disperse starch in small samples of fresh plant material and finally determined the starch by iodine spectrophotometry. This method, suitably modified, seemed most likely to provide useful results.

EXPERIMENTAL

Apparatus

All absorption measurements were made with a Unicam SP 500 Spectrophotometer using a tungsten filament lamp and 1-cm glass absorption cells.

Preparation of sample

The material for analysis was prepared by grinding the transverse cross-sectional face of a piece of sapwood with a disc-sander, passing the ground material through

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a 200-mesh sieve (B.S.S.) and drying it for three days in a desiccator over concentrated sulphuric acid. Experiments have shown that the transverse cross-sectional face is the best surface of the sample to use since it provides material, which is truly representative of the piece of wood being analysed, in a state which ensures that all the starch is dissolved. Material from tangential and radial faces contains some of the starch grains enclosed within cell walls which are not attacked by perchloric acid.

Procedure

Weigh approximately 0.4 g of material and transfer it to a 50-ml beaker. Add 4.7 ml of 7.2 *M* perchloric acid and allow to react for 10 min with occasional stirring. Transfer the contents of the beaker to a 50-ml volumetric flask and bring to volume. After centrifuging, place a 10-ml aliquot in a 50-ml volumetric flask together with a drop of phenolphthalein and make alkaline with 2 *N* sodium hydroxide. Add 2 *N* acetic acid until the colour is discharged and then add a further 2.5 ml followed by 0.5 ml 10% w/v potassium iodide and 5 ml 0.01 *N* potassium iodate. Allow the colour to develop for 15 min, bring to volume and measure the absorption at 650 m μ using a blank prepared without starch as zero. Repeat samples having more than 3% starch using smaller portions.

RESULTS AND DISCUSSION

Replicate analyses

Two series of six replications were carried out on one sample of 200-mesh wood to test the reproducibility of the method. A mean result of 3.25% was obtained with a standard deviation of 0.08%.

Effect of strength of perchloric acid

Equal weights of the same sample of ground wood were treated as above except that various strengths of perchloric acid were employed (Table I). 7.2 *M* perchloric acid was adopted for use in all subsequent analyses.

TABLE I

<i>Acid strength (M)</i>	<i>Optical density</i>	<i>Acid strength (M)</i>	<i>Optical density</i>
4.8	0.093	9.6	0.116
6.0	0.110	10.8	0.074
7.2	0.123	12.0	0.010
8.4	0.122		

Effect of time of contact with 7.2 M perchloric acid

Equal weights of ground wood were treated as above except that they were left in contact with the perchloric acid for varying periods (Table II).

TABLE II

<i>Time of contact (min)</i>	<i>Optical density</i>	<i>Time of contact (min)</i>	<i>Optical density</i>
5	0.272	20	0.288
10	0.293	25	0.272
15	0.287	30	0.277

It was decided that 10 min should be allowed for reaction between the starch and perchloric acid though it is evident that for up to 30 min the method is not very sensitive to this variable.

Size of aliquot in final solution

As its preparation is time consuming it was desirable to use as small a sample of wood as possible without sacrificing accuracy. For most samples it was found that 0.2 g wood did not provide a sufficient concentration of starch for a 5-ml aliquot to be used. Accordingly an experiment using a 25-ml aliquot was carried out. The results were very similar for both 5-ml and 25-ml aliquots though the greater dilution caused by the larger aliquot so retarded the reaction rate that the maximum optical density was not reached for several hours. Also, because of the necessity to restrict the volume to about 40 ml, strong alkali was needed in the neutralisation of the aliquot. Another experiment using 0.4 g of wood and 5- and 10-ml aliquots was carried out. From the results there was little to choose between them but because the larger aliquot gave a higher optical density it was decided that a sample of 0.4 g and an aliquot of 10 ml would be standardised upon. (Table III).

TABLE III

<i>Weight of sample g</i>	<i>Aliquot ml</i>	<i>Optical density</i>
0.4018	5	0.117
0.4018	10	0.262
0.4020	5	0.133
0.4020	10	0.254

Standard reference curve

A standard reference curve was set up using A.R. potato starch. Accurately weighed quantities of starch ranging from 0.0057 g to 0.04 g were weighed and treated according to the procedure given above*. The optical density was plotted against the weight of the starch corrected to zero moisture content. The moisture content was determined by heating a sample of the starch for 4 h at 105° and 25 mm Hg and measuring the loss of weight after cooling over phosphorus pentoxide in a desiccator⁶.

Because the method depends ultimately on the reaction of the amylose in the starch with iodine it was desirable to determine the amylose contained in the wood starch. This was done by comparing wood starch with A.R. potato starch, using both polarimetry and iodine-spectrophotometry. Three difficulties presented themselves in the polarimetric method when applied to the starch in wood.

(1) The calcium chloride solution is frequently so strongly coloured by tannins, etc. that optical rotation cannot be read.

(2) Other optically active water-soluble constituents may be present.

(3) Owing to the small amount of starch present the rotation is very low.

These difficulties were overcome by preparing a starch-enriched sample of wood in the following way: A large piece of the sapwood of a New Guinea species of *Crypto-*

5-ml aliquots were taken and diluted to 10 ml with water before the other reagents were added.

carya was reduced to sawdust and successive 200-g portions were stirred with about 2 to 3 l of water for 30 min each then filtered through a small pad of glass wool. The liquor volume was kept constant by the addition of more water as each new portion of sawdust was added to it. Next the liquor was left to stand and the supernatant solution removed. The residual material was washed through a 200-mesh sieve (B.S.S.) with cold water, centrifuged and dried under vacuum at room temperature. This process removed any optically active and colouring compounds present and provided a sample with a greater rotating power.

Known weights of this material and of A.R. potato starch were dispersed in CaCl_2 solutions and the starch content of each calculated from polarimeter measurements⁶. Since this measurement is independent of the amount of amylose in the starch it was taken as the actual starch content of the material.

Using the same solutions, the starch levels were then determined by the method given by KERR⁷. Aliquots of the potato starch solution were treated by the perchloric acid method. From the information obtained a reference curve was established (Fig. 1).

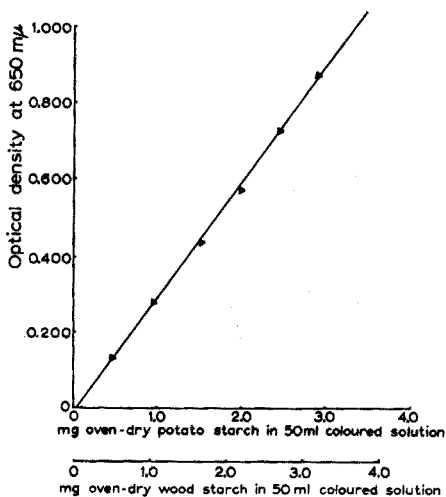


Fig. 1.

In order to calculate the amylose in wood starch from this data one final piece of information was required, namely, the amylose content of the potato starch. The figure chosen from among the many estimates made by various workers was 25.5% obtained by KERR AND TRUBELL⁸. BATES, FRENCH AND RUNDLE⁹ have stated that, judged on the basis of the fraction which takes up the most iodine "KERR's crystalline amylose is the best of the amylose fractions yet prepared" and "that it is also the amylose fraction which has been subject to the most careful refractionation, and the one showing the best crystalline properties".

Starch content of wood material by optical rotation = 21.2%

Starch content of wood material by iodine-spectrophotometry = 19.3%

Therefore amylose in wood starch = $\frac{19.3}{21.2} \cdot \frac{25.5}{1}$ = 23.2%

This value was used in all subsequent determinations of starch in wood. The data used for the reference curve together with the corresponding weights of wood starch obtained by application of a factor, 1.10 (25.5/23.2) are given in Table IV.

TABLE IV

Weight of moisture-free potato starch in 50 ml coloured solution mg	Optical density at 650 m μ (y)	Corresponding weight of moisture-free wood starch in 50 ml coloured solution (x) mg
0.00	0.000	0.00
0.46	0.130	0.51
0.95	0.279	1.05
1.50	0.433	1.65
1.97	0.575	2.17
2.44	0.728	2.68
2.89	0.870	3.18

$y = 0.2719x - 0.008$

Therefore if a 10-ml aliquot is taken from the original perchloric acid solution, starch in wood

$$= \left(\frac{1839(y + 0.008)}{\text{Moisture-free weight of sample in mg}} \right) \%$$

SUMMARY

A rapid and simple method of estimating starch in wood is described which is suitable for carrying out large numbers of determinations.

RÉSUMÉ

Une méthode rapide et simple est décrite pour le dosage de l'amidon dans le bois. Ce procédé convient à des analyses en série.

ZUSAMMENFASSUNG

Beschreibung einer für Serienbestimmungen geeigneten schnellen und einfachen Methode zur Bestimmung von Stärke in Holz.

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THE DETERMINATION OF LEAD IN COPPER-BASE ALLOYS AND STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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(Received August 22nd, 1960)

INTRODUCTION

There are at least three methods available for determining lead in copper-base alloys. One of these, a volumetric procedure based on precipitation of lead chromate by an excess of potassium dichromate and titration of the excess reagent with a standard ammonium ferrous sulphate solution, is rapid and is frequently used in routine control laboratories. The method is applicable to a wide range of samples but, unless very careful attention is given to detail, erroneous results are obtained.

A direct reading spectrometric method is available, using either a Hilger 3-m Polychromator or a Hilger direct reading attachment to a medium spectrograph¹. This procedure is also rapid but limited to samples available in a special form and regular calibration of the instrument, using similar samples of known lead content, is necessary.

These two procedures are in current use in industrial laboratories and there is also available, for referee work, a gravimetric method² based on an initial electrodeposition of lead peroxide and subsequent conversion of the recovered deposit to lead molybdate. This method is accurate but time-consuming; a single determination takes about a day to complete. It is permissible to weigh the lead peroxide (*i.e.* the increase in weight of the anode) and calculate the lead content of the sample using an empirical factor, but results obtained in this way are of doubtful accuracy, especially when the weight of deposit exceeds about 10 mg.

A rapid routine control procedure which is accurate and independent of sample form was, therefore, desirable and in view of our earlier successful work with atomic absorptiometric methods³, it was decided to investigate possible applications of this new analytical technique to the determination of lead in copper-base materials. This was the main objective of the experimental work subsequently described, but when this part of the work was completed it seemed that, with only simple modification, the procedure could be used for the direct determination of lead in steels and, through the courtesy of The British Iron and Steel Research Association, the samples referred to in Table VI were kindly supplied.

A method currently used for determining lead in steels⁴ is based on solution of the sample in hydrochloric acid, precipitation of lead as sulphide and subsequent conversion of the recovered lead precipitate to lead molybdate and weighing as such. This method is accurate but involves the use of hydrogen sulphide and a single determination takes at least 2 h to complete.

APPARATUS

The apparatus used was the same as that described by GIDLEY AND JONES³. A sealed-off hollow cathode lamp was made with a cathode machined from a solid piece of leaded brass containing about 3.5% of lead. The lamp consisted of a 250-ml round-bottom flask with a quartz window sealed across the neck with black wax. The electrodes were sealed into the lamp by using waxed cone and socket joints, for ease of replacement; the lamp was evacuated, filled with argon and processed in a manner similar to that described by JONES AND WALSH⁵. (A running life of at least 250 h has been achieved using this type of lamp). With this lamp it was possible to use a direct indication method for measuring intensity, which is simpler and more rapid than the integration method used earlier³.

EXPERIMENTAL

The most suitable line for absorption measurements was found to be Pb 2833.1 Å, but at low operating currents both the line intensity and line to background intensity ratio were low, resulting in negligible absorption when solutions containing 100 µg lead/ml were examined. Using higher currents both line intensity and line to background intensity ratios increased and corresponding absorptions also increased. Maximum absorption occurred when the lamp was operated at the maximum output current (50 mA) of the stabilised power supply but, under these conditions, the lamp became overheated and a compromise operating current (40 mA) was used for all subsequent work. Table I shows absorptions obtained with varying operating currents.

TABLE I
EFFECT OF HOLLOW CATHODE LAMP CURRENT ON ABSORPTION

Lamp current mA	Optical density due to 100 µg lead/ml
10	—
20	0.075
30	0.176
40	0.220
45	0.232
50	0.232

In order to reduce the effect due to continuous background radiation, a minimum monochromator slit width is necessary and, in addition, it is essential to use a narrow slit to separate the absorbed line (2833 Å) from two other emission lines at 2824 Å and 2840 Å which are not absorbed. Insufficient intensity was available to allow the narrowest available slit width to be used, and a width of 0.1 mm was shown to be the best compromise.

A calibration curve relating optical density and concentration, covering the range 0–200 µg lead/ml in an aqueous solution, showed a slight curvature towards the concentration axis. An optical density of 0.22 was obtained using a 100-µg lead/ml standard, with a limit of detection of 2 µg lead/ml, based on an arbitrary detection limit of an optical density of 0.005 (approximately 1% absorption).

Acids normally used for the dissolution of lead-bearing metallurgical samples were tested to establish their effect, if any, on absorption. Solutions (1 + 9) of nitric,

hydrochloric, perchloric and fluoboric acids were separately examined, each in the presence of 50 μg lead/ml, and very little interference was noted, as shown by results in Table II.

TABLE II
EFFECT OF ACIDS ON THE DETERMINATION OF LEAD
(50 μg lead/ml added)

<i>Acid*</i>	<i>μg lead/ml found</i>
Nitric	46.0
Hydrochloric	46.0
Perchloric	48.0
Fluoboric	46.0

* Normal laboratory reagent acids diluted (1 + 9)

The slight interference is probably due to the increased viscosity of the acid solution which reduces the rate at which the solution is atomised, with a consequent reduction in absorption. This, however, can be compensated for by adding the same volume of acid to the standard solution.

The effects of several elements, particularly those likely to be present in either alloying or trace amounts in non-ferrous materials normally analysed for lead, were examined separately for possible interferences. To a solution containing 50 μg lead/ml was added a solution containing 1000 μg /ml (a ratio of 20 : 1) of one of the following elements: sodium, calcium, copper, aluminium, magnesium, iron, nickel, tin, zinc, and silicon and, apart from the possible viscosity effect, none of these elements interfered (Table III).

TABLE III
EFFECT OF VARIOUS ELEMENTS ON THE DETERMINATION OF LEAD
(50 μg lead/ml in the presence of 1000 μg /ml of a second element)

<i>Element added</i>	<i>μg lead/ml found</i>
Sodium	49.5
Calcium	50.0
Copper	47.0
Aluminium	47.0
Magnesium	50.0
Iron	48.0
Nickel	50.0
Tin	48.3
Zinc	49.8
Silicon	50.0

It was expected that some elements which form refractory oxides, *e.g.* aluminium and silicon, might seriously interfere, but no such interference was observed.

Typical samples were analysed using a tentative procedure based on the experimental work so far described. A convenient weight of the sample, sufficient to give a final solution containing about 100 μg lead/ml, was dissolved in nitric acid containing

hydrochloric acid to inhibit precipitation of metastannic acid. The sample solution and a suitable standard solution were then atomised and optical densities were determined. The standard solution contained an *amount of copper* equivalent to the *weight of sample* in the test solution, to compensate for any viscosity effect caused by the presence of a high concentration of other elements.

The procedure was applied to several lead-bearing copper alloys, and results obtained (Table IV) compared very favourably with those obtained by the lead molybdate procedure².

TABLE IV
DETERMINATION OF LEAD IN COPPER ALLOYS

Sample	Lead (%)			
	Chemical		Atomic absorption	
B.C.S. Standard No. 183 Bronze A	1.83 ^a		1.81	1.81
B.C.S. Standard No. 179 Manganese Brass B	0.78 ^a		0.77	0.79
B.C.S. Standard No. 207 Bronze C	0.41 ^a		0.41	0.42
I.C.I. Reference Standard Brass No. 7	3.55		3.52	3.55
Leaded Brass XR.2	1.77	1.78	1.77	1.77
Leaded Brass XR.4	1.02	1.03	1.02	1.01
Leaded Brass XR.11	2.10	2.14	2.13	2.14
Leaded Brass XR.38	0.37	0.38	0.39	0.40
Leaded Brass XR.39	3.19	3.19	3.19	3.20

^a Certificate value

From a series of tests on leaded brass samples, it was established that the lead content of a single sample could be made available by one person within 20 min of receipt of the sample turnings, and two analysts could complete 50 similar samples in a normal working day of 8 h.

The method was also used for a routine check on results obtained on control samples of leaded brass, using the direct reading attachment¹. In these tests, involving more than 100 determinations, over the range 2.5–4.0% lead, the standard deviation of the differences between spectrometric and atomic absorption results was 0.06%. As the direct reading spectrometric method is only reproducible to 0.05%, this indicated that a high degree of calibration has been maintained for that instrument and a good accuracy for the atomic absorption procedure is implied.

Reproducibility of the method is controlled mainly by the uncertainty of the absorption measurement and, in a normal determination, the mean of from five to ten measurements is taken to improve the precision. From the range of individual measurements, an indication of reproducibility can be obtained. Based on a series of more than twenty determinations at the 100- μg lead/ml level, the reproducibility of measurement for a single test was calculated to be about 2%, expressed as a coefficient of variation.

To establish the accuracy of the proposed method for determining lead in complex copper alloys, British Chemical Standard No. 183/1, containing about 85% copper, 5% tin, 5% zinc and 3.5% lead, was analysed. A reference solution was also prepared containing, in about the same proportions, all the elements known to be present in

the standard; the amount of metallic lead used in preparing this solution was weighed accurately. Absorption due to lead, using the standard and sample solutions independently, was measured twenty times for each solution; the procedure was also repeated three times on independently weighed samples of the standard alloy. Results obtained are shown in Table V. When the lead values obtained by atomic absorption are compared with the reference solution, an accuracy of about 0.025%, expressed as a standard deviation, is indicated.

TABLE V
DETERMINATION OF LEAD IN B.C.S. NO. 183/1

<i>Proposed B.S.I. method*</i>	<i>Lead (%)</i>	
	<i>Atomic absorption</i>	
3.44	3.38	
3.46	3.39	
3.49	3.41	

* Preliminary separation of lead electrolytically, followed by conversion to, and weighing as, lead molybdate.

The possibility of determining lead in steels was not considered until after the method for copper-base alloys had been fully developed. It appeared, however, that only a few preliminary tests would be necessary in order to establish the validity of the method when applied to the examination of typical steels.

Six steel samples were kindly supplied, together with their established lead contents, by The British Iron and Steel Research Association. These samples had been extensively examined by the Pig Iron, Carbon and Low Alloy Steels Analysis Sub-Committee in the development of a referee gravimetric lead method⁴. Later, a further sample, 'X', was supplied by the Chairman of the same Sub-Committee (Mr. S. W. CRAVEN), following a request for a similar steel sample with an established lead content, to be disclosed to the authors only after the lead content had been determined by the proposed atomic absorption procedure. The samples were dissolved in hydrochloric acid, oxidised with nitric acid, atomised etc., and the lead contents evaluated from the relationship between optical densities resulting from test solutions and a

TABLE VI
DETERMINATION OF LEAD IN LEADED STEELS

<i>Sample</i>	<i>Lead (%)</i>	
	<i>Chemical*</i>	<i>Atomic absorption</i>
MGS/163	0.280	0.277 0.287
MGS/196A	0.175	0.182 0.185
MGS/257A	0.076	0.080 0.070
MGS/195	0.175	0.185
MGS/272	0.115	0.125
MGS/274	0.185	0.195
X	0.280 ^b	0.282 0.280

* Preliminary separation of lead as sulphide, followed by conversion to, and weighing as, lead molybdate.

^b Result supplied by Mr. S. W. CRAVEN; others (chemical) by B.I.S.R.A.

solution containing pure iron and pure lead. Results of these tests are shown in Table VI and all are in good agreement.

METHOD I. DETERMINATION OF LEAD IN COPPER-BASE ALLOYS

(0.05–5% Pb)

Equipment

Hilger atomic absorption attachment, H.909, to Uvispek spectrophotometer, H.700, fitted with photomultiplier detection.

Special solutions

Acid mixture: To about 300 ml of water add 300 ml of nitric acid ($d = 1.42$). Add 200 ml of hydrochloric acid ($d = 1.18$), cool and dilute to 1 l.

Standard lead solution: Weigh, as accurately as possible, 0.5 g of pure lead (e.g. British Chemical Standard No. 210b) and dissolve in the minimum volume of nitric acid (1 + 1). Cool and dilute to 1 l.

1 ml \equiv 0.5 mg lead.

Standard copper/lead solution A: Dissolve 10.00 g of high purity copper in 100 ml of the acid mixture. Cool, add 200.0 ml of the standard lead solution and dilute to 1 l.

1 ml \equiv 100 μ g lead.

Standard copper/lead solution B: Dissolve 5.00 g of high purity copper in 50 ml of the acid mixture. Cool, add 200.0 ml of the standard lead solution and dilute to 1 l.

1 ml \equiv 100 μ g lead.

Preparation of mean standard curve

To each of 5 100-ml calibrated flasks add, separately, 5.0, 10.0, 20.0, 30.0, and 40.0 ml of the standard lead solution and dilute each to the mark. These solutions contain 25, 50, 100, 150 and 200 μ g lead/ml respectively.

Instrument settings, using a leaded brass hollow cathode lamp, are as follows: lamp current, 40 mA; atomiser air pressure, 15 lb/sq.in.; wavelength, 2833 Å; photomultiplier voltage, 1100 V; slit width, 0.10 mm.

Switch on the hollow cathode lamp, light the burner and switch on the constant voltage supply to the photomultiplier tube. Allow 1 h for emission from the lamp to reach a constant value.

With no light entering the monochromator, adjust the galvanometer to zero. With light from the lamp entering the monochromator, adjust the wavelength control until a peak intensity is indicated by the galvanometer.

Spray water through the atomiser, bring the galvanometer to zero, by means of the voltage dividing potentiometer, and take the reading (R_0), which is proportional to the light intensity falling on the photomultiplier. Spray each of the standard lead solutions, taking the reading (R) at the zero point each time. Repeat the series of tests five times. Prepare two more calibration curves in the same manner.

Calculate the optical density for each standard solution (optical density = $\log R_0/R$). Scale each curve to an optical density of 0.220 for 100 μ g lead/ml. Take the average readings for each of the three curves and plot these as the final mean standard curve.

TABLE VII
RECOMMENDED SAMPLE WEIGHT AND VOLUME OF ACID MIXTURE

Lead content (%)	Sample (g)	Acid mixture (ml)
0.1-1.0	1.0	10
1.0-3.5	0.5	5

Procedure

Dissolve the recommended weight of sample in the appropriate volume of acid mixture, boil, to expel nitrous fumes, cool and dilute to 100 ml in a calibrated flask.

Determine the optical density of the sample solution as described under *Preparation of mean standard curve*. Determine the optical density of the appropriate standard copper/lead solution in conjunction with each batch of samples, *i.e.* solution A for 1-g samples and solution B for 0.5-g samples (Note).

Scale the optical density of the standard solution to 0.220 and correct optical densities of sample solutions proportionally. Read off the amount of lead in the sample solution by reference to the mean standard curve and calculate the percentage of lead in the sample.

Note

The appropriate standard solution corresponding to the sample weight must be used to compensate for any variation in viscosity of the solutions. The use of distilled water in all dilutions is implied throughout.

METHOD 2. DETERMINATION OF LEAD IN STEELS (0.05-0.5% Pb)

Equipment

See Method 1.

Special solutions

Standard lead solution: 1 ml \equiv 0.5 mg lead. See Method 1.

Standard iron solution: Dissolve 2.00 g of high purity iron (*e.g.* H.H.P. iron) in 20 ml of hydrochloric acid ($d = 1.18$) and oxidise with 1-2 ml of nitric acid ($d = 1.42$). Cool and dilute to 100 ml.

Standard iron/lead solution: Dissolve 2.00 g of high purity iron in 20 ml of hydrochloric acid ($d = 1.18$) and oxidise with 1-2 ml of nitric acid ($d = 1.42$). Add 10 ml of standard lead solution and dilute to 100 ml.

1 ml \equiv 50 μ g lead (0.25% lead in iron).

Procedure

Dissolve 2.00 g of the sample in 20 ml of hydrochloric acid ($d = 1.18$) and oxidise with 1-2 ml of nitric acid ($d = 1.42$). Dilute and filter off any precipitated silica, wash the filter thoroughly with warm water and dilute the cooled filtrate to 100 ml.

Use the same instrument settings and setting up procedure as described under *Preparation of mean standard curve* in Method 1 and determine the optical density of the standard and sample solutions. Draw a calibration curve through the points

obtained for the two standard iron solutions, read off the amount of lead in the sample solution by reference to this curve and calculate the percentage of lead in the sample.

CONCLUSION

Atomic absorption spectrophotometry provides a simple, rapid and accurate procedure for determining lead in copper-base alloys and leaded steels. Because of its freedom from inter-element interference, there is no reason to doubt that the method could be applied to the determination of lead in other materials, e.g. highly alloyed steels.

ACKNOWLEDGEMENTS

Acknowledgements are made to The British Iron and Steel Research Association for supplying the steel samples and for permission to quote the results obtained by the Methods of Analysis Sub-Committee, and to Messrs. J. M. JACOBS and A. NICHOLLS for their helpful suggestions and experimental work in connection with the development of these procedures.

SUMMARY

The principle of atomic absorption spectrophotometry has only recently been exploited as an analytical technique and details are given of the development of a procedure for determining lead in copper-base alloys and leaded steels. The recommended method is simple, rapid and provides results as accurate as those obtained by the more time-consuming alternative methods in current use.

RÉSUMÉ

Une méthode est proposée pour le dosage du plomb dans des alliages à base de cuivre et dans des aciers, au moyen de la nouvelle technique de spectrophotométrie par absorption atomique. Le procédé recommandé est simple, rapide et donne des résultats aussi précis que ceux obtenus avec les méthodes habituelles.

ZUSAMMENFASSUNG

Beschreibung einer einfachen, raschen und genauen Methode zur Bestimmung von Blei in Kupferlegierungen und Stählen. Sie beruht auf der neuen Technik der Spektrophotometrie durch atomare Absorption.

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CONDUCTOMETRIC TITRATION OF METAL ACETATES
IN AQUEOUS MEDIUM

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(Received June 27th, 1960)

Methods for acid-base potentiometric titrations of metal acetates in nonaqueous medium have been recently reported. CASEY AND STARKE¹ titrated 18 metal acetates in glacial acetic acid using perchloric acid as a titrant; this method was unsuccessful for the acetates of copper, tin, antimony, bismuth and uranium which were not dissociated in that solvent. CUNDIFF AND MARKUNAS² titrated the acetates of copper, nickel and uranium by an indirect method which involved acidification of the salt with an excess of sulphuric acid, addition of a nonaqueous solvent and differential potentiometric titration; obviously this procedure gives the amount of the acetate ion, while the cation amount can be deduced only if there is a stoichiometric ratio between them. DAS AND PALIT³ titrated the acetates of calcium, cadmium, magnesium, zinc, lead and mercury using perchloric and hydrochloric acids as titrants.

Conductometric analysis has found wide application in the precipitation titrations of metal salts, while replacement titration with acids seems to have been applied only to alkali metals; thus sodium acetate titration with hydrochloric acid has been reported⁴, while titrations of less electro-positive metal acetates are not known.

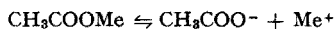
A recent finding in these laboratories has shown that weak organic bases, having ionization constants down to 10^{-12} , could be conductometrically titrated with trichloroacetic acid, following solution in an excess of aqueous acetic acid⁵. As this procedure is equivalent to the titration of an organic base acetate in the presence of an excess of acetic acid, we took into consideration the possibility of applying this method to the titration of metal acetates in aqueous medium.

The graph relating to the conductometric titration with a strong acid of a metal acetate, shows a first straight line corresponding to the conductance variation due to the replacement of the anion CH_3COO^- by the titrant anion; the former combines with the hydrogen ion of the titrant. After the equivalence point the conductance increases sharply as a consequence of the rapid increment of free hydrogen ions. Therefore in the titration curve of a given acetate, the sharpness of the equivalence point angle depends on the values of the ionization constant and of the anionic mobility of the titrant.

Trichloroacetic acid, being a strong acid ($K_A = 2 \cdot 10^{-1}$) and having an anionic mobility ($\lambda_{25}^\circ = 35.0$) lower than that of the acetic acid ($\lambda_{25}^\circ = 40.9$), seemed particularly suitable as titrant. The equilibrium



existing with the equilibrium



contributes to the curvature near the equivalence point without shifting it. Therefore it is possible to use an excess of acetic acid when this increases the salt solubility; this excess, which in the case of titrations of organic bases improves the sharpness of the end-point angle, in the case of the metal acetates exerts a practically negligible influence on the slope of the first straight line.

This method can also be applied to the titration of metal salts of acids weaker than acetic (*e.g.* carbonates) by dissolving them in an excess of aqueous acetic acid, as well as to salts of acids stronger than acetic if they can be transformed into acetates (*e.g.* nitrates).

EXPERIMENTAL

Apparatus

Resistance measurements were carried out using two alternating current Wheatstone bridges. The first bridge was as previously described⁶. The second one, which was constructed in our laboratories, was supplied by a very low distortion sinusoidal generator through an insulation transformer. Balance point zero readings were made on a cathode-ray tube through a tuned amplifier. Its operative characteristics were frequency 1000 hertz; bridge supply 0.5 V r.m.s.; sensitivity 0.1 %/100. It was equipped with an oil bath maintained at the working temperature $\pm 0.01^\circ$.

A modified Jones and Bollinger cell⁶ was used. The electrodes consisted of two discs of platinized platinum (diameter 2.3 cm) facing each other at a distance of 16.2 cm.

The automatic-filling microburet had a capacity of 5 ml with 0.01-ml graduations.

Reagents and procedure

Metal acetates were of C.P., or better, grade and were titrated as received, with the exception of sodium and potassium acetates which were previously dried.

A 2-N solution of trichloroacetic acid was obtained by dissolving chromatography grade trichloroacetic acid in distilled water and standardizing the solution conductometrically against anhydrous sodium acetate. Alternatively the acid was standardized with sodium carbonate using bromophenol blue as indicator.

Samples of acetates corresponding to 2–6 mmoles were dissolved in 40–50 ml of water or 50% water–ethanol mixtures. The titrations were carried out in a nitrogen atmosphere at about 22°. The measured resistance values were between 800 and 20000 ohms. The reciprocals of the measured resistance values were corrected for volume variations.

Analyses

The accuracy of the method was checked by analysis of each salt by conventional quantitative techniques. The acetates of sodium and potassium used were of AnalaR standard and therefore only required to be dried at 120° for 2 h.

The analytical method used: (a) Ammonium bicarbonate was treated with a strong base to liberate ammonia which was absorbed by an excess of acid. (b) Lithium, strontium and barium were determined as sulphates. (c) Calcium as oxide. (d) Magnesium, manganese and zinc as pyrophosphates. (e) Cadmium as the 2-(*o*-hydroxy-

phenyl)-benzoxazole complex. (f) Cobalt as the pyridine thiocyanate complex. (g) Silver as chloride. (h) Copper as thiocyanate. (i) Nickel as the dimethylglyoxime complex. (j) Uranium as the hydroxyquinoline complex.

RESULTS AND DISCUSSION

The titration curve of a metal acetate shows a rounding in the vicinity of the equivalence point, due to the trichloroacetate hydrolysis. This does not affect the intersection point location when the acetate of a monovalent metal is titrated (Fig. 1), but in the case of a bivalent metal this rounding hinders the location of the straight line corresponding to the weakest stage, and the end-points are not well defined.

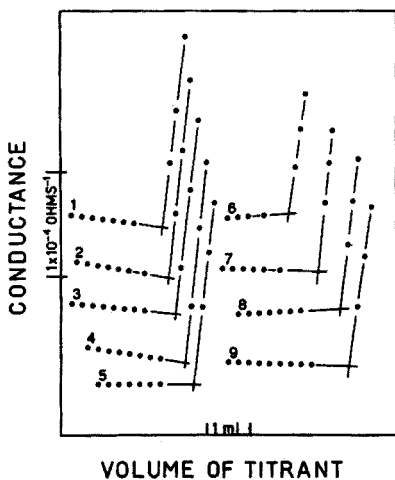


Fig. 1. Conductometric titration of metal acetates in aqueous medium with 2 *N* trichloroacetic acid. 1. Sodium; 2. Potassium; 3. Lithium; 4. Ammonium*; 5. Magnesium; 6. Silver; 7. Strontium; 8. Calcium; 9. Barium.

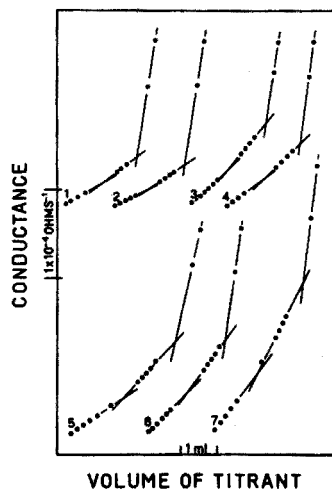


Fig. 2. Conductometric titration of metal acetates in 50% water-ethyl alcohol with 2 *N* trichloroacetic acid. 1. Nickel; 2. Manganese; 3. Cadmium; 4. Cobalt; 5. Uranium; 6. Zinc; 7. Copper.

This difficulty can be overcome by using as solvent a 50% water-ethanol mixture. Ethanol decreases hydrolysis enabling the second straight line to be obtained, but also decreases dissociation of the salt, which results in more obtuse end-point angles.

In Fig. 2 the curves show very obtuse angles at the first equivalence point. At the second end-point, they are more obtuse than those obtained in absence of ethanol (Fig. 1), but are sharp enough to allow a good accuracy.

Acetates of lithium, sodium, potassium, magnesium, calcium, strontium, barium, copper, silver, zinc, cadmium, uranium, manganese, cobalt and nickel were examined by the proposed method and all recoveries were in close agreement with the purity established by alternative analytical methods.

Ammonium bicarbonate was titrated following solution of the sample in an excess of aqueous acetic acid.

The acetates of iron, mercury and aluminium could not be titrated because their

* 0.4 g of ammonium bicarbonate dissolved in 40 ml of water containing 0.35 g acetic acid.

hydroxides or basic salts precipitated by hydrolysis were insoluble even in the presence of an excess of acetic acid. Chromium acetate gave a completely curved titration line. Lead acetate did not give a straight neutralization line, although it is a salt of a relatively strong base ($pK_B = 7.3$), probably owing to its small dissociation. Silver acetate was completely dissolved after a small addition of titrant.

For each compound examined, from two to four conductometric determinations were carried out. From the values obtained by this method a standard deviation of 0.3% was calculated. The value of the systematic error is negligible when compared with its standard deviation (Systematic error = $-0.13 \pm 0.64\%$).

SUMMARY

Fifteen metal acetates in aqueous medium have been conductometrically titrated with trichloroacetic acid. The method has been applied to the titration of mono- and bivalent metals and angles at the equivalence point are sharp enough to allow accurate results to be obtained. Metal salts of acids weaker than acetic can be determined following solution in an excess of acetic acid and titration, because the weaker acid which is displaced does not interfere.

RÉSUMÉ

Une méthode est proposée pour le titrage conductométrique d'acétates métalliques, au moyen de l'acide trichloracétique. Les sels d'acides plus faibles que l'acide acétique peuvent être également titrés, après dissolution dans l'acide acétique en excès.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von ein- und zweiwertigen Metallen durch konduktometrische Titration der Acetate mit Trichloressigsäure. Salze von schwächeren Säuren als Essigsäure können durch Zusatz von Essigsäure ebenfalls titriert werden.

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Anal. Chim. Acta, 24 (1961) 79-82

AMPEROMETRIC ARGENTIMETRIC AND MERCURIMETRIC
TITRATION OF SULFHYDRYL

I. ARGENTIMETRIC TITRATION

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(Received July 11th, 1960)

The amperometric argentimetric titration of sulfhydryl in unsubstituted mercaptans was introduced by KOLTHOFF AND HARRIS¹ using a rotating platinum wire electrode (R.Pt.W.E.) as indicator electrode. Titrations were carried out in 60–70% alcohol in ammonia buffers, to make chloride harmless. The accuracy of the method was reported to be 0.3% with amounts of 2 mg mercaptan sulfur per 100 ml and 1–2% with amounts of 0.2 mg mercaptan sulfur. The above procedure was applied without essential change by BENESCH AND BENESCH² to the determination of sulfhydryl groups in amino acids and proteins. Generally they used solutions of high alcohol content (90%). Results were reported: for thioglycolic acid, $98 \pm 4\%$ (0.09–0.46 mg/30 ml), for cysteine HCl, $102.5 \pm 1.2\%$ (0.162 mg/30 ml) and for glutathione (reduced), $97.7 \pm 2.7\%$. Working in 93% ethanol and using an ammonia buffer of pH 10.4, SARKER AND SIVARAMAN³ claim that 2–4 mg of cysteine could be determined with an accuracy of 0.4%.

The argentimetric determination of cysteine and cystine in aqueous solutions with ammonia buffer (0.2–0.3 M in NH_4NO_3 , 0.1 M in NH_3 was studied by KOLTHOFF AND STRICKS⁴. They found that silver cysteinat (RSAg) can react with an excess of silver; this reaction is slow and they recommend that the titrations be carried out very rapidly. It was also noticed that close to the equivalence point RAg is measurably dissociated into silver ions. This, combined with the fact that RAg can react with an excess of silver (*vide infra*), may be the reason why several authors observed that a considerable excess of silver is present at the graphically located amperometric end-point. Thus, STAIB AND TURBA⁵ report that at the end-point the molar ratio of cysteine and silver is 1 : 1.35. SLUYTERMAN⁶ carried out titrations in an ammonia buffer of pH 9.1 and also in a "tris" buffer of pH 7.7. This buffer, which is composed of tris(hydroxymethyl)aminoethane and its salt was introduced by BENESCH *et al.*⁷ for the titration of sulfhydryl in proteins. SLUYTERMAN reported the following results in an ammonia buffer of pH 9.1 (a) and in a tris buffer of pH 7.7 (b): cysteine, $133 \pm 3\%$ (a) and $155 \pm 3\%$ (b); glutathione, $92 \pm 2\%$ (a) and $98 \pm 1\%$ (b); cysteine ethyl ester, $108 \pm 2\%$ (a) and $143 \pm 4\%$ (b); thioglycolic acid, $132 \pm 3\%$ (a) and $136 \pm 3\%$ (b). In Table I are compared the results obtained by BURTON⁸ with those by other authors in the titration of cysteine (RSH) and glutathione (GSH).

The large errors obtained in the titration of cysteine must be attributed to the fact that the reaction between RSH and silver can give rise to the formation of a host of

TABLE I
RESULTS BY VARIOUS AUTHORS OBTAINED WITH CYSTEINE (RSH) AND GLUTATHIONE (GSH)
Results refer to 100% pure products

Compound	Author	Medium	Buffer	pH	End-point %	End-point % (Burton ⁸)
RSH	BENESCH AND BENESCH ²	alcohol	ammonia	10.0	102.5	145
RSH	SARKER AND SIVARAMAN ³	alcohol	ammonia	10.4	99.7	119
RSH	SLUYTERMAN ⁶	water	ammonia	9.1	133	142
RSH	SLUYTERMAN ⁶	water	tris	7.7	155	146
GSH	BENESCH AND BENESCH ²	alcohol	ammonia	10.0	95-100.4	90
GSH	SLUYTERMAN ⁶	water	ammonia	9.1	92	100
GSH	INGRAM ⁹	water	ammonia	9.2	≈100	100
GSH	BENESCH <i>et al.</i> ⁷	water	tris	7.4	98	130

complexes as was shown by KOLTHOFF AND STRICKS in unpublished work¹⁰. Argentimetric potentiometric titration curves of cysteine¹⁰ also indicate that RSAg reacts with excess of silver. The titrations were carried out with different initial concentrations of cysteine (in ammonia buffers of varying pH) using a silver electrode as indicator electrode. From the large number of results it appeared that at pH smaller than 8.4 the formation of RSAg is favored, while at higher pH several other complexes were formed. Dependent on the specific conditions under which the potentiometric titrations were carried out end-points were found where the excess of silver varied between 10 and 50%. Evidence for the formation of the following complexes, $(\text{RSAg})_{10}\text{Ag}^+$, $(\text{RSAg})_4\text{Ag}^+$ and $(\text{RSAg})_2\text{Ag}^+$, respectively was presented. Also in the potentiometric titration of thioglycolic acid silver complexes of varying composition were found. The above conclusions were substantiated by extensive polarographic studies with the dropping mercury electrode. When the ratio of RSH to Ag^+ was greater than one, a complex $\text{RSAg} \cdot \text{RSH}$ (or $[\text{Ag}(\text{RS})_2]^-$) was found. The anodic cysteine wave became equal to zero before the attainment of the equivalence point (RSAg). After this point the diffusion current of the silver ammine ion was found to be less than corresponds to the stoichiometric excess of silver, the amount of silver bound by RSAg could be calculated from this difference.

Solubility measurements¹⁰ of RSAg in a borax buffer in the presence of varying concentrations of silver nitrate showed that one silver ion combines with 4 RSAg when the concentration of silver nitrate is less than $10^{-3} M$ and with 3 RSAg when this concentration is greater than $10^{-3} M$. The saturated solution of RSAg was colorless but became yellow with an excess of silver. Altogether it appeared that the system $\text{RSAg}-\text{Ag}^+$ is quite complex.

CECIL AND MCPHEE¹¹ studied the potentiometric titration of cysteine and glutathione at various pH. In the pH range between 2.5 and 7.5 they found at the end-point 17% more silver bound than corresponds to RSAg . At pH less than 1.7 glutathione bound an amount of silver about 30% in excess to GSAg .

From this review it appears that the results of an amperometric argentimetric titration of a substituted mercaptan may be considerably in error. It appeared desirable to investigate this titration under different conditions with some substituted mercaptans in order to find which group or groups are responsible for the error in the titration and to find means to reduce the error. In a subsequent paper ampero-

metric titrations with mercuric chloride and nitrate respectively are described. Mercury mercaptides are much more stable than the silver mercaptides.

EXPERIMENTAL

Materials used

Silver nitrate was a Mallinckrodt analytical reagent. A 0.1-*M* stock solution of silver nitrate was standardized against pure sodium chloride. The stock solution was kept in a dark bottle and dilutions were prepared daily.

Sodium sulfite was a Mallinckrodt A.R. product. A 1-*M* oxygen-free stock solution was kept in a refrigerator. The titer was determined iodometrically. Diluted sulfite solutions were prepared daily under air-free conditions.

Cystine was a Merck reagent grade product which had been recrystallized and dried in vacuo at 70°. A stock solution was prepared which was 0.01 *M* in cystine and 0.1 *M* in nitric acid.

Cysteine was a Mann product. An air-free 0.1-*M* stock solution of cysteine in 0.2 *N* nitric acid was prepared and kept in a refrigerator. The titer was checked frequently by titrations with ferricyanide¹⁴. During a period of two months no change in the titer was found.

Cysteine hydrochloride: two products were used, one from Merck, which contained 2% water and the other from Brother, which contained 9.24% water. The sulfhydryl content was determined by LAVINE's iodometric procedure¹² and by the ferricyanide method¹⁴. Amperometric mercurimetric titrations to be described in a subsequent paper gave results which agreed within 1% with those obtained by the ferricyanide procedure, while the iodometric procedure gave results which were 2% high.

Glutathione (GSH) was an Eastman product which had been dried in vacuo at 70°. A 0.01-*M* stock solution was prepared under air-free conditions.

Pure thioglycolic acid (TSH) was obtained by distillation at reduced pressure (in nitrogen atmosphere) of an Eastman product. The stock solution was prepared from the fraction boiling between 95–100° at about 6 mm Hg.

Pure colorless 2-mercaptoethanol (ESH) was obtained by double distillation in vacuo of a technical product from Union Carbon Co. Dilute solutions of ESH and TSH were prepared daily from 0.1-*M* stock solutions and kept at ice temperature.

All other reagents were of reagent grade. Conductivity water has been used throughout.

Experimental methods

Current-potential curves were determined and amperometric titrations carried out using a manual apparatus¹³. The platinum wire electrode was rotated at a constant speed of 1800 r.p.m. Potentials are reported *vs.* the saturated calomel electrode (S.C.E.). A saturated KCl–agar salt bridge was used in experiments carried out in the presence of chloride and a saturated KNO₃–agar salt bridge in the absence of chloride. Most of the titrations were carried out with 50 ml deaerated solution in a 100-ml beaker. The nitrogen used was a Linde product which was bubbled through two wash bottles containing a chromium(II) solution and water respectively. For the deaeration of solutions buffered with ammonia buffers the nitrogen was then passed through two wash bottles containing the same buffer. Reagent was added from a 1-ml Guilmont type microburette. Titrations of cysteine were carried out with a silver-

coated platinum electrode. The electrode was daily cleaned with hot nitric acid (1 : 1) and coated with silver at -0.3 V for 10 min at a current of about $20 \mu\text{A}$ in an ammonia buffer of pH about 9. Between titrations the electrode was wiped between two fingers and washed with a stream of water. The titrations of other mercaptans were carried out using an uncoated platinum electrode which was cleaned after each experiment with concentrated nitric acid.

RESULTS

Titration of cysteine in ammonia and tris buffers

Titrations were carried out in an ammonia buffer of pH 9.05 or in 0.133 M tris buffer acidified with nitric acid to give a pH 7.4. Current-potential curves obtained in mixtures of 10^{-4} M RSH and varying excess of silver showed that the diffusion current of the excess of silver is not proportional to the concentration of the silver ammine ions in excess over RSAg. After addition of 30% excess of silver only a very small diffusion current was observed. On further addition of silver the diffusion current of the silver ammine ions increased rapidly. The results of amperometric titrations with solutions which were $2.5 \cdot 10^{-5}$ M to $4 \cdot 10^{-4}$ M in RSH at an applied potential of -0.3 V vs. SCE are reported in Table II. At cysteine concentrations less than 10^{-4} M

TABLE II

TITRATION OF CYSTEINE WITH AgNO_3 IN 50 ml 0.1 M AMMONIUM NITRATE-AMMONIA BUFFER
pH 9.05. $E_{\text{applied}} = -0.3$ V

Molarity of RSH	AgNO_3 used		mg RSH		Error %	Alcohol %
	ml	Molarity	Taken	Found		
$2.5 \cdot 10^{-5}$	0.665	$2.5 \cdot 10^{-3}$	0.152	0.201	+33	—
$5 \cdot 10^{-5}$	0.670	$5 \cdot 10^{-3}$	0.303	0.406	+34	—
$7.5 \cdot 10^{-5}$	1.010	$5 \cdot 10^{-3}$	0.454	0.611	+35	—
10^{-4}	1.35	$5 \cdot 10^{-3}$	0.606	0.832	+35	—
$2 \cdot 10^{-4}$	0.720	$2 \cdot 10^{-2}$	1.211	1.745	+44	—
$4 \cdot 10^{-4}$	0.600	$5 \cdot 10^{-2}$	2.423	3.63	+50	—
$6 \cdot 10^{-5}$	0.385	10^{-2}	0.364	0.468	+28	70
$9 \cdot 10^{-5}$	0.585	10^{-2}	0.546	0.710	+30	70
$1.6 \cdot 10^{-4}$	1.125	10^{-2}	0.971	1.363	+41	70
$2.4 \cdot 10^{-4}$	0.865	$2 \cdot 10^{-2}$	1.455	2.10	+44	70
$6 \cdot 10^{-5}$	0.365	10^{-2}	0.364	0.444	+22	86
$9 \cdot 10^{-5}$	0.550	10^{-2}	0.546	0.668	+23	86
$1.6 \cdot 10^{-4}$	1.040	10^{-2}	0.971	1.262	+30	86
$2.4 \cdot 10^{-4}$	0.830	$2 \cdot 10^{-2}$	1.455	2.013	+38	86

the error was constant and equal to +34% in aqueous medium, +30% in 70% alcohol and +23% in 86% alcohol. The error was found to increase at higher cysteine concentrations. Similar results were found in titrations of cystine after quantitative reduction with sodium amalgam. From a few examples of titration lines given in Fig. 1 it is clear that part of the silver added after the equivalence point (RSAg) is bound until about 30% after the end-point, when the excess reagent line is found. The error is reduced when the titrations are carried out in an ammonia buffer in the presence of 0.1 M sodium sulfite. For example in the titration of 2.5 , 5 , 10 and $20 \cdot 10^{-5}$ M

cysteine (or cystine) the errors were -2% , 0% , $+15\%$ and 20% respectively. In the presence of sulfite part of the ammino silver ions are transformed into complex sulfite ions which seem to be less reactive toward $RSAg$ than the ammino silver ions are.

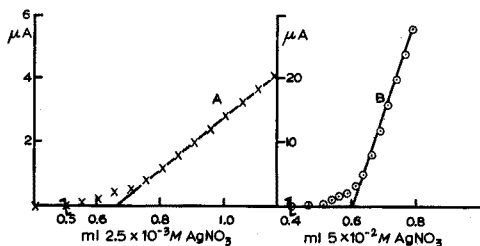


Fig. 1. Titration lines of cysteine in ammonia buffer, pH 9.05 at -0.3 V vs. SCE. A. $2.5 \cdot 10^{-5} M$ RSH; B. $4 \cdot 10^{-4} M$ RSH. \wedge indicates equivalence point [RSAg].

TABLE III
TITRATIONS IN TRIS BUFFER AT THE R.Pt.W.E.
Applied potential: -0.1 V

Molarity of RSH	$AgNO_3$ used		mg RSH		Error %	Alcohol %
	ml	Molarity	Taken	Found		
$4 \cdot 10^{-5}$	0.27	10^{-2}	0.242	0.327	+35	—
$8 \cdot 10^{-5}$	0.57	10^{-2}	0.485	0.690	+42	—
$1.6 \cdot 10^{-4}$	1.14	10^{-2}	0.971	1.380	+42	—
$4 \cdot 10^{-5}$	0.315	10^{-2}	0.242	0.380	+57	70
$8 \cdot 10^{-5}$	0.625	10^{-2}	0.485	0.757	+56	70

Titration carried out in buffer solutions which were $0.133 M$ in tris (pH 7.4) gave higher results than those obtained in ammoniacal buffers containing the same amount of cysteine. Some results are given in Table III. While in ammonia buffers the error decreased in the presence of 70% alcohol, the opposite effect was observed in the tris buffers where the error increased markedly. For example in the titration of $4 \cdot 10^{-5} M$ cysteine in aqueous medium the error was $+35\%$ as compared to 57% in 70% alcoholic medium.

Titration of glutathione (GSH)

As is evident from Table IV good results are obtained in this titration over the wide concentration range between $5 \cdot 10^{-5} M$ to $2 \cdot 10^{-3} M$ glutathione. Sulfite has no effect and the titration is very suitable for the determination of oxidized glutathione.

Thioglycolic acid (TSH)

Thioglycolic acid behaves toward silver similarly to cysteine. Current-potential curves in solutions $2 \cdot 10^{-4} M$ in TSH, $0.25 M$ in ammonium nitrate and $0.1 M$ in ammonia, containing various amounts of silver nitrate, showed that part of the silver in excess over $TSAg$ is bound. Titrations carried out with solutions $2 \cdot 10^{-4} M$ to $2 \cdot 10^{-3} M$ in TSH yielded end-points which were 20–34% higher than corresponds to

TABLE IV

TITRATION OF GLUTATHIONE IN AMMONIA BUFFER 0.25 *M* IN AMMONIUM NITRATE AND 0.1 *M* IN AMMONIA

$$E_{\text{applied}} = -0.3 \text{ V}$$

Molarity of GSH	AgNO ₃ used		mg GSH		Error %	Addition
	ml	Molarity	Taken	Found		
5 · 10 ⁻⁵	0.245	10 ⁻²	0.768	0.783	-2.0	
10 ⁻⁴	0.250	2 · 10 ⁻²	1.536	1.536	0.0	
2 · 10 ⁻⁴	0.495	2 · 10 ⁻²	3.073	3.104	-1.0	
4 · 10 ⁻⁴	1.00	2 · 10 ⁻²	6.146	6.146	0.0	
10 ⁻³	0.490	10 ⁻¹	15.366	15.673	-2.0	
2 · 10 ⁻³	1.010	10 ⁻¹	30.732	31.039	+1.0	
2 · 10 ⁻⁴	0.490	2 · 10 ⁻²	3.073	3.134	-2.0	0.1 <i>M</i> Na ₂ SO ₃
4 · 10 ⁻⁴	0.985	2 · 10 ⁻²	6.146	6.238	-1.5	0.1 <i>M</i> Na ₂ SO ₃

TSAg. As was found with cysteine more silver is bound at the end-point with increasing concentration of TSH (Table V). The error is decreased markedly in the presence of 0.1 *M* sulfite and is less than 2% at TSH concentrations smaller than 5 · 10⁻⁴ *M*. Thus the amperometric titration with silver in the presence of sulfite is suitable for the determination of small concentrations of thioglycolic acid and also of its disulfide.

TABLE V

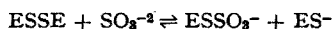
TITRATION OF THIOGLYCOLIC ACID IN 0.25 *M* AMMONIUM NITRATE 0.1 *M* AMMONIA BUFFER

$$E_{\text{applied}} = -0.3 \text{ V}$$

Molarity of TSH	AgNO ₃ used		mg TSH		Error %	Addition
	ml	Molarity	Taken	Found		
2 · 10 ⁻⁴	0.60	2 · 10 ⁻²	0.9212	1.105	+20	
4 · 10 ⁻⁴	1.20	2 · 10 ⁻²	1.8424	2.211	+20	
10 ⁻³	0.665	10 ⁻¹	4.606	6.12	+33	
2 · 10 ⁻³	1.34	10 ⁻¹	9.212	12.345	+34	
2 · 10 ⁻⁴	0.51	2 · 10 ⁻²	0.921	0.939	+2.0	0.1 <i>M</i> Na ₂ SO ₃
5 · 10 ⁻⁴	1.27	2 · 10 ⁻²	2.303	2.34	+1.6	0.1 <i>M</i> Na ₂ SO ₃
10 ⁻³	1.04	5 · 10 ⁻²	4.606	4.785	+4.0	0.1 <i>M</i> Na ₂ SO ₃

2-Mercaptoethanol (ESH)

As may be seen from Table VI solutions with a concentration varying between 5 · 10⁻⁵ and 1.2 · 10⁻³ *M* ESH can be titrated with an accuracy and precision within 2.5%. Neither 0.1 *M* sulfite nor 0.1 *M* chloride interfere. The method can be used for the determination of the disulfide ESSE in an ammonia buffer in the presence of 0.1 *M* sulfite:



Near the end-point the establishment of this equilibrium was relatively slow when there is some unreacted ESSE left and it was necessary to wait from one to two minutes after addition of silver before a constant current reading was found. With excess of silver a steady current was found immediately after addition of reagent. Solutions which were 1.6 · 10⁻⁴ and 3.2 · 10⁻⁴ *M* in ESSE, 0.1 *M* in Na₂SO₃, 0.2 *M* in NH₄NO₃ and 0.1 *M* in NH₃ were titrated with an error of ±1%.

TABLE VI
 TITRATION OF ESH IN 0.25 M AMMONIUM NITRATE-0.1 M AMMONIA BUFFER

$$E_{\text{applied}} = -0.3 \text{ V}$$

Molarity of ESH	AgNO ₃ used		mg ESH		Error %	Addition
	ml	Molarity	Taken	Found		
5.07 · 10 ⁻⁵	0.248	10 ⁻²	0.198	0.194	-2.0	
1.014 · 10 ⁻⁴	0.495	10 ⁻²	0.396	0.387	-2.6	
1.52 · 10 ⁻⁴	0.760	10 ⁻²	0.594	0.593	-0.2	
2.028 · 10 ⁻⁴	1.035	10 ⁻²	0.792	0.808	+2.0	
4.056 · 10 ⁻⁴	0.832	2.5 · 10 ⁻²	1.584	1.623	+2.4	
6.084 · 10 ⁻⁴	1.230	2.5 · 10 ⁻²	2.376	2.406	+1.3	
10.14 · 10 ⁻⁴	0.520	10 ⁻¹	3.961	4.06	+2.5	
5 · 10 ⁻⁵	0.240	10 ⁻²	0.195	0.187	-4.0	0.1 M Na ₂ SO ₃
10 ⁻⁴	0.490	10 ⁻²	0.391	0.383	-2.0	0.1 M Na ₂ SO ₃
2 · 10 ⁻⁴	0.995	10 ⁻²	0.781	0.777	-0.5	0.1 M Na ₂ SO ₃
4 · 10 ⁻⁴	0.512	4 · 10 ⁻²	1.563	1.60	+2.4	0.1 M Na ₂ SO ₃
8 · 10 ⁻⁴	0.987	4 · 10 ⁻²	3.126	3.084	-1.3	0.1 M Na ₂ SO ₃
1.2 · 10 ⁻³	1.520	4 · 10 ⁻²	4.689	4.63	-1.3	0.1 M Na ₂ SO ₃
2 · 10 ⁻⁴	0.395	2.5 · 10 ⁻²	0.781	0.790	-1.2	0.1 M NaCl
4 · 10 ⁻⁴	0.812	2.5 · 10 ⁻²	1.563	1.585	+1.5	0.1 M NaCl
10 ⁻³	2.012	2.5 · 10 ⁻²	3.91	3.933	+0.6	0.1 M NaCl

DISCUSSION

Our results with cysteine agree with those of SLUYTERMAN⁶ and of BURTON⁸. SLUYTERMAN reports 8% low results with reduced glutathione but in agreement with BURTON AND INGRAM⁹ we obtained theoretical results. With thioglycolic acid the positive error is about one half of that found with cysteine. As suggested by SLUYTERMAN both the carboxylate and the amino group in cysteine seem to be responsible for the binding of silver by RSAg, while the smaller error in thioglycolic acid is due to the carboxylate group. The fact that SLUYTERMAN found 8% high results with the ethyl ester of cysteine tends to show that the amino group contributes some to the binding of silver by RSAg. In the absence of silver binding groups (unsubstituted mercaptans, mercaptoethanol) the end-point is found at a molar ratio of sulfhydryl to silver 1 : 1. With the peptide (reduced) glutathione (GSH) and also with serum albumin¹⁵ the end-point is also found at the stoichiometric ratio. However, in acid medium (pH 2

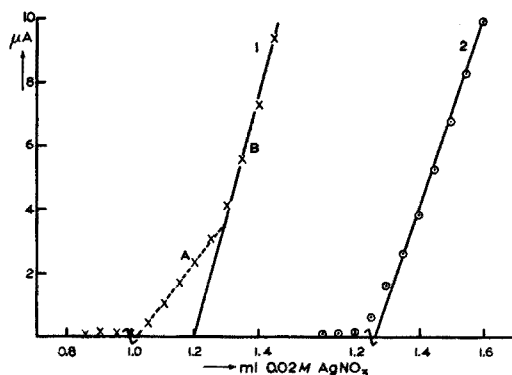


Fig. 2. Titration of thioglycolic acid in buffer 0.25 M in ammonium nitrate and 0.1 M in ammonia. $E_{\text{applied}} = -0.3 \text{ V}$ (1) $4 \cdot 10^{-4} \text{ M TSH}$; (2) $5 \cdot 10^{-4} \text{ M TSH}$ in presence of 0.1 M sulfite. \checkmark indicates equivalence point [TSAg].

to 5.2) GSH and silver react to give insoluble GSAg which reacts with a second equivalent of silver to form a soluble complex.

It is interesting to note that the error obtained with thioglycolic acid is reduced to zero in the presence of 0.1 *M* sulfite, while under these conditions the error of the cysteine titration is reduced to zero only when the RSH concentration is equal to or less than $5 \cdot 10^{-5}$ *M*. The error becomes one half of that observed in the absence of sulfite at concentrations greater than 10^{-5} *M*. It may be of interest to further study the effect of relatively mild complex formers with silver on the titration of thiol compounds with other reactive groups. The striking effect of sulfite on the TSH titration is illustrated in Fig. 2. In the absence of sulfite the first excess of reagent line (A in Fig. 2) is almost straight. In the example in Fig. 2 it intersects with the abscissa at a point corresponding to an error of +2.0%, while reagent line (B) indicates an end-point which is 20% high. The improvement of the situation by 0.1 *M* sulfite is clear from a comparison of titration lines 1 and 2.

ACKNOWLEDGEMENT

Acknowledgement is made to the U. S. Public Health Service for financial support of this research

SUMMARY

Results of amperometric argentimetric titrations at the rotated platinum wire electrode in ammonia buffers of cysteine, glutathione, thioglycolic acid and 2-mercaptoethanol are presented. The method gives satisfactory results with glutathione and 2-mercaptoethanol. Thioglycolic acid gives good results in the presence of sulfite but high results in its absence. Its disulfide can be titrated accurately in the presence of sulfite. In agreement with other workers it was found that cysteine yields high results. The error increases with increasing cysteine concentration and is reduced in the presence of 0.1 *M* sulfite. It becomes equal to zero at cysteine concentrations equal to or smaller than $5 \cdot 10^{-5}$ *M*.

RÉSUMÉ

Les auteurs ont effectué une étude du dosage ampérométrique de cystéine, glutathione, acide thioglycolique et mercaptoéthanol, par titrage argentimétrique.

ZUSAMMENFASSUNG

Beschreibung einer amperometrischen Methode zur Bestimmung von Cystein, Glutathion, Thio-glycolsäure und 2-Mercapto-äthanol durch argentometrische Titration.

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PRECISION NULL-POINT POTENTIOMETRY
DIRECT MICRODETERMINATION OF IODIDE IN SOLUTIONS WITH
HIGH CHLORIDE CONCENTRATIONS

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(Received July 11th, 1960)

Recently precision null-point potentiometric techniques were developed which provided high sensitivity, speed, simplicity and accuracy for the micro determination of chloride in water samples¹, blood serum², and solutions obtained by decomposing organic fractions containing chlorinated compounds³; and the general principles of the measurement method were presented^{4,5}. The same general technique is now described for the direct determination of iodide in the presence of large amounts of chloride, as found in brines or iodized salt. In iodized salt the sodium chloride weight usually exceeds the iodide by a factor of 10,000 to 200,000, and in brines the chloride weight exceeds the iodide by hundreds to thousands of times.

The determination of iodide in brines, iodized salt or similar samples is generally performed by separation of the iodide after oxidation and subsequent measurement by titration⁶⁻⁸. The separation is often necessary because the high ratio of chloride to iodide invalidates the measurement method. However, it is shown that a separation of iodide from chloride is not necessary by the precision null-point potentiometric technique. Since the measurement is also rapid it is possible to perform a complete analysis in about 3 min, including weighing the sample, addition of reagents, measurement, and calculation of results.

THE IODIDE MEASUREMENT METHOD

The null-point method is based on rapidly changing the iodide concentration of a prepared unknown sample until it is the same concentration as a constant reference iodide solution, using a potentiometric system to indicate the null-point. The requirements of the method include specific electrodes for iodide, electrical contact between the reference and unknown solutions without significant mixing of the two, and the absence of junction potentials or polarization of electrodes.

A pair of silver-silver iodide electrodes are sensitive to iodide concentration and can be readily prepared. The electrical contact is provided by an asbestos fiber sealed in the small reference-solution tube which is bathed in the beaker of unknown solution. The junction potential is made negligible by preparing the reference and unknown solutions and added reagents to have nearly the same ionic strength. This is done by adding a large amount of electrolyte to all solutions and by diluting the

brines or salt samples 100 to 1. Therefore, the electrolyte contribution by the sample is quite small in comparison with the contribution by the reagents. A high input-impedance measuring system prevents polarization of electrodes.

For speed of analysis it is desirable to have continuous indication on the null meter and continuous mixing and addition of reagent until the solutions are of equal concentration. An efficient stirring and measurement system and an arrangement so both solutions reach the same temperature rapidly have been described^{1,2}.

APPARATUS

Although the general type of equipment for the precision null-point potentiometric determination of iodide was the same for iodide as previously used for chloride determinations^{1,2}, there were the following specific differences:

Electrodes

The Ag-AgI electrodes were prepared by iodizing a pair of silver-plated platinum electrodes sealed in glass. The platinum electrodes were made by connecting approximately 3×10 mm platinum plates to platinum wires by flash welding and sealing the top edge of the platinum plate into 4-mm O.D. soft glass tubing. After thoroughly cleaning the platinum plates in boiling nitric acid and washing in demineralized or distilled water, the electrode pair was plated for 3 h at 2 mA/cm² in a solution of KAg(CN)₂ (about 10 g KAg(CN)₂/l) which was stirred during the plating process. The electrodes were then washed for 4 h in running tap water and finally for 2 h in running demineralized water.

The electrodes were iodized in an iodide solution (1 drop of concentrated HI per 100 ml of 0.05 M KI solution) for 12 min at 2 mA/cm². Immediately after preparation the electrodes were washed in demineralized water for about 5 min, placed in a beaker containing reference solution, and kept in the dark until used.

Because the Ag-AgI electrodes are sensitive to light, it is best to prevent exposure of the electrodes to continuous room light, either during use or storage. In the present work, the room lights were turned off at night or the window shades pulled during the day so that the only light striking the electrodes came through adjoining doors to the room and from around the window shades. A closed titration compartment such as available with the Sargent Spectro-Electro titrator⁹ eliminates the need for a room with subdued light.

Mixing in reference compartment

In order to be more certain of good stability during the null-point measurements it was found advantageous to vibrate the electrode continuously in the reference compartment by means of attaching the electrode to an alligator clip mounted so that a piece of spring steel, also attached to the clip, pressed firmly against the top knurled nut of the stirrer chuck on the electrode stand⁹. As the stirrer turned it caused a small vibration of the reference electrode which improved the stability of the measured voltage.

Null detector

A high input impedance Sargent comparator (E. H. Sargent Co., Chicago 30, Ill.) was used as the null detector.

REAGENTS

The null, sample, and concentration variation solutions are all prepared to contain 40,000 p.p.m. sodium acetate and 25,000 p.p.m. acetic acid. These readily available reagents usually contain negligible iodide and also buffer the solutions to provide stability of the iodide. Sodium chloride is also added to the reagent solutions when analyzing brines and iodized salt. The sodium chloride concentration is nearly the same in all samples of iodized salt so the reagents can be prepared to have the same concentration as the samples. However, the chloride concentration in brines may vary over a large range so the reagents are prepared to have a concentration of sodium chloride which is intermediate in the usual range. Although the range of chloride is large and other salts are present the over-all differences in ionic strength of sample and reagents is not large when solutions are properly prepared.

Stock solutions

KI solution. Several l of 10 mg I⁻/l were prepared by weighing out reagent grade potassium iodide and diluting to volume with deionized water.

NaCl solution. 1.000 l of 1.000 N NaOH was added to 1.000 l of 1.000 N HCl. Sodium chloride was prepared in this manner rather than using reagent grade sodium chloride because of the relatively large concentration (about 0.002%) of impurity iodide in the salts available.

Electrolyte solution. Each l contained 80.0 g reagent grade sodium acetate and 50.0 ml reagent grade acetic acid diluted to volume with deionized water. If several hundred samples are to be run it is best to prepare 10 l or more of this reagent.

Standard solutions for brine-type samples

Null reference solution A (1.000 mg I⁻/l). For each l, 500 ml of stock electrolyte, 10 ml stock NaCl, and 100.0 ml of stock KI solutions were mixed and diluted to volume with deionized water.

Standard dilution reagent B. It is prepared the same as the null reference solution A except with no stock KI added.

Standard addition reagent C. It is prepared the same as reagent A except that 200.0 ml of stock KI are added for each l.

Standard solutions for iodized salt

Null reference solution D (0.500 mg I⁻/l). For each l 500 ml of stock electrolyte, 200 ml stock NaCl, and 50.0 ml of stock KI solutions were mixed and diluted to volume with deionized water.

Standard dilution reagent E. It is prepared the same as reagent D except that no stock KI is added.

Standard addition reagent F. It is prepared the same as reagent D except that 100.0 ml of stock KI is added per l.

PROCEDURES

Preparation of samples for analysis

If brine samples have 10–200 p.p.m. iodide or iodized salt samples have 5–100 p.p.m. iodide, weigh 1.000 g and transfer into a 100-ml volumetric flask, add 50.0 ml of stock

electrolyte solution, dilute to volume with deionized water, and mix. If brine or salt has more or less iodide than in the given ranges, a smaller or larger sample could be taken and the same procedures used.

Establishment of the null point

At the beginning of each day the isolation compartment is emptied and filled to at least a few ml above the top of the Ag-AgI electrode with null reference solution A or D, depending on sample type. The method of establishing the nullpoint is the same as for chloride determinations.

Measurement of iodide concentration

After setting the nullpoint, the reference solution in the beaker is removed, and a beaker containing 20.00 ml of prepared sample is placed into position, the stirrer started and, depending on the direction of deflection of the null meter, either addition or dilution reagent is added from the appropriate buret (at a delivery rate of about 15 ml/min or less) until the nullpoint is nearly reached, at which time delivery of reagent is stopped. Small increments of reagent are then added by rapid rotation of the stopcock until the nullpoint is reached, the buret reading recorded to obtain V_a , and the iodide concentration calculated using equation (2) for brines and equation (3) for iodized salt.

CALCULATIONS

The concentration of iodide in p.p.m. is expressed by the general equation (1).

$$\text{p.p.m. iodide} = \frac{C_R}{W_s} (V_o \pm V_a) \quad (1)$$

where W_s is the weight in g of the sample actually measured, C_R is the iodide concentration of the null reference solution in mg/l or $\mu\text{g/ml}$, V_o is the volume in ml of prepared solution taken for measurement (20.00 ml in the given procedure) and V_a is the volume of standard addition or dilution reagent added in reaching the nullpoint. If addition reagent is delivered, then V_a is subtracted from V_o , and if dilution reagent is delivered V_a is added to V_o .

Equation (1) reduces to equation (2) for brines using a 1.000-g original sample (0.2000 g measured sample), null solution A, and reagent B or C.

$$\text{p.p.m. iodide} = 5 (20.00 \pm V_a) \quad (2)$$

Equation (1) reduces to equation (3) for iodized salt using a 1.000-g original sample, null solution D, and reagent E or F.

$$\text{p.p.m. iodide} = 2.5 (20.00 \pm V_a) \quad (3)$$

RESULTS

The results presented in Table I illustrate the precision and accuracy for iodide determination in samples containing a wide range of chloride, typical of brine samples. Two samples contain 10,000 p.p.m. each of calcium chloride, magnesium chloride, and sodium sulfate in addition to the sodium chloride. The sodium chloride concentration

TABLE I
DETERMINATION OF IODIDE IN 0.2000 g OF BRINE-TYPE SAMPLES
BY PRECISION NULL-POINT POTENTIOMETRIC METHOD

Quantity of iodide ^a , μg	Concentration of iodide in sample, p.p.m.		Weight ratio of chloride to iodide
	known	found ^b	
40.12	200.0	200.6 \pm 0.6	0
40.00	200.0	200.0 \pm 0.3	175
39.80	200.0	199.0 \pm 0.5	300 ^c
40.00	200.0	200.0 \pm 0.6	350
39.76	200.0	198.8 \pm 0.3	500
10.00	50.0	50.0 \pm 0.2	0
9.96	50.0	49.8 \pm 0.2	1000 ^c
10.12	50.0	50.6 \pm 0.3	1400
3.94	20.0	19.7 \pm 0.3	1800
1.90	10.0	9.5 \pm 0.3	3500

^a Average amount of iodide actually measured in 5 20-ml aliquots of prepared solutions containing 0.2000 g of sample.

^b Reproducibility is given as standard deviation for 5 samples.

^c Samples contained about 10,000 p.p.m. each of CaCl_2 , MgCl_2 and Na_2SO_4 as well as the large amount of NaCl .

TABLE II
DETERMINATION OF IODIDE IN 0.2000 g OF IODIZED SALT BY
PRECISION NULL-POINT POTENTIOMETRY

Quantity of iodide measured, μg	Concentration of iodide in samples, p.p.m.	
	known	found ^a
20.00	100.0	100.0 \pm 0.4
6.16	30.0	30.8 \pm 0.4
3.98	20.0	19.9 \pm 0.2
1.92	10.0	9.6 \pm 0.3
1.28	6.7	6.4 \pm 0.1
0.88	5.0	4.4 \pm 0.2

^a Reproducibility is given as standard deviation for 5 measured samples.

varies from 10,000–200,000 p.p.m. in the original sample, before the 100 to 1 dilution for measurement of iodide.

The samples presented in Table II have a larger chloride to iodide ratio as would occur in iodized salt samples. With these samples there is some lag in the response of the electrodes, but reagent can still be added at about 15 ml/min. If the null point should accidentally be overshoot, it can be approached from the opposite side by delivering appropriate reagent and subtracting this volume from that previously added. It is necessary to check the nullpoint after every 2–3 determinations because of a small drifting of the electrodes.

SUMMARY

The determination of micro amounts of iodide in the presence of large concentrations of chloride, such as found in brines or iodized salt, can be performed directly and rapidly by the precision

null-point potentiometric method. The complete analysis time is about 3 min. Iodized salt samples containing 5–100 p.p.m. iodide were determined with an average deviation less than 0.3 p.p.m. and with relative errors of about 0.5% at 100 p.p.m. and about 5% at 10 p.p.m. iodide. The measured samples contained 1–20 μg of iodide in 20 ml of solution, and the sodium chloride to iodide weight ratio was as high as 200,000 to 1. Similar precision and accuracy were obtained for prepared brines containing 10–200 p.p.m. iodide and a wide range of chloride to iodide ratios.

RÉSUMÉ

Une méthode potentiométrique est proposée pour le microdosage des iodures, en présence de fortes concentrations en chlorures. Ce procédé est précis et très rapide.

ZUSAMMENFASSUNG

Beschreibung einer potentiometrischen Bestimmung von sehr kleinen Mengen Jod in Gegenwart von grossen Mengen Chlorid.

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Short Communication

Colorimetrische Bestimmung von Strontium

Zur colorimetrischen Bestimmung von Strontium schlugen LUCCHESI *et al.*¹ die Chloranilsäure (2,5-Dichloro-3,6-dihydrochinon) vor. Diese Methode hat einige Nachteile; z.B. ist es notwendig, das Reaktionsgemisch 3 Stunden bei 0° stehen zu lassen, damit die Reaktion quantitativ verläuft.

Andere Reagentien zur colorimetrischen Bestimmung von Strontium sind noch nicht vorgeschlagen worden. Auch die Möglichkeit der Verwendung der Dilitursäure (5-Nitrobarbitursäure, 5-Nitro-2,4,6-trioxohexahydropyrimidin), die mit Strontium bereits bei Zimmertemperatur ein unlösliches Diliturat liefert (Löslichkeit² in Wasser bei 25°: 1.7 Mmol/1000 ml) wurde bis jetzt noch nicht untersucht. Anwendungen der Dilitursäure sind nur bekannt für die gravimetrische³, volumetrische⁴ und colorimetrische^{5,6} Bestimmung von Kalium und Magnesium⁸.

Die Herstellung der Dilitursäure erfolgte durch Nitrieren von Barbitursäure⁷. Das zweimal umkristallisierte Produkt wurde durch den Schmelzpunkt identifiziert. Für die Versuche wurde eine 0.05 N Lösung von Dilitursäure verwendet; zur Verminderung des infolge der geringen Löslichkeit von Strontiumdiliturat entstehenden Fehlers wurde die Lösung mit Strontiumdiliturat gesättigt. Die Titerstellung erfolgte durch Titration mit 0.1 N Natronlauge und Phenolphthalein als Indikator.

Die Konzentration des Strontiums betrug 0.0 bis 2.0 mg Sr/ml. Die Mischung der

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Probe mit dem Reagens (1 : 1) wurde nach 15 min filtriert und die Extinktion des Filtrates bei der Wellenlänge $420 \text{ m}\mu^6$ gemessen. Die photometrischen Messungen wurden mit einem Zeiss-Universalspektrophotometer (Cäsium-Antimon-Photozelle MSVB mit Messungsbereich 200–650 $\text{m}\mu$, 2-ml Küvetten mit Schichtdicke 0.498 cm) durchgeführt.

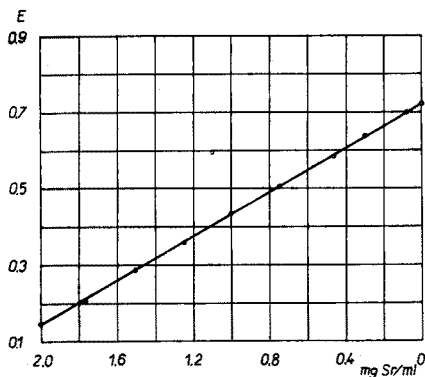


Fig. 1. Kalibrationskurve.

Der beobachtete Maximalfehler betrug $+ 0.02 \text{ mg Sr/ml}$ (relativer Fehler 2.5%); der durchschnittliche Fehler bei 2 Messungen derselben Probe betrug $\pm 0.006 \text{ mg Sr/ml}$.

In Übereinstimmung mit früher gemachten Beobachtungen bei colorimetrischen Bestimmungen mit Dilitursäure wurden die folgenden Ionen als störend festgestellt: NH_4 , K, Sn, Fe(II), Fe(III), Cr, Cd, Cu, Mn, Ca, Ba, Zn, Co, Ni, Hg(I), Ag und Pb; ferner die farbigen Anionen CrO_4^{-2} , $\text{Cr}_2\text{O}_7^{-2}$, MnO_4^- und $\text{Fe}(\text{CN})_6^{-4}$. Ohne Einfluss sind: NO_3^- , SO_4^{-2} , SO_3^{-2} , PO_4^{-3} , Cl^- , Br^- und I^- .

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¹ P. J. LUCCHESI, S. Z. LEWIN UND J. E. VANCE, *Anal. Chem.*, 26 (1954) 521.

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Eingegangen den 2. September, 1960

BOOK REVIEWS

National Academy of Sciences, National Research Council, Nuclear Science Series

- NAS-NS 3001, *The Radiochemistry of Cadmium*, by J. R. DEVOE, 57 pp., \$0.75.
NAS-NS 3002, *The Radiochemistry of Arsenic*, by H. C. BEARD, 27 pp., \$0.50.
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NAS-NS 3011, *The Radiochemistry of Zirconium and Hafnium*, by ELLIS P. STEINBERG, 48 pp., \$0.50.
NAS-NS 3014, *The Radiochemistry of Indium*, by D. N. SUNDERMAN AND C. W. TOWNLEY, 42 pp., \$0.50.

Available from the Office of Technical Services, Department of Commerce, Washington 25, D.C.

The Subcommittee on Radiochemistry of the Committee on Nuclear Science, National Academy of Sciences, National Research Council, with the aid of the U.S. Atomic Energy Commission is undertaking a laudable program of bringing out authoritative monographs on the radiochemistry of the various elements. Recognizing the need for an up-to-date compilation of radiochemical information and particularly laboratory procedures, the committee plans a series of monographs, each written by an expert on the element in question and designed to be of maximum usefulness to the worker at the laboratory bench.

A more or less standard format is followed, deviations occurring where it would otherwise be inappropriate to the element in question, and the sequence in the monograph on cadmium may be taken as typical. First, there is a section giving a general review of the inorganic and analytical chemistry of the element. This is followed by a survey of its radiochemical behavior and a table of isotopes. Next is a brief summary of the chemical properties having particular interest for radiochemists, including such characteristics as oxidation states, complexes, insoluble compounds, and extractability. A section is usually devoted to dissolution of samples and another to counting techniques. Finally, there is a collection of radiochemical procedures given in detail for direct laboratory application.

As in any such undertaking, the quality of the effort varies with the individual

author. One could wish that some of the authors had prepared their material with more attention to detail: there are minor annoyances such as author's names misspelled in literature references, misprints, and the inclusion in the tables of equilibrium constants of some numerical values which do not stand up under critical examination. Much more care appears to have been devoted to the radiochemical procedures, and it is in these that the real value of the series will lie. The monographs can be recommended as useful for the purpose for which they were written and should be of interest not only to radiochemists but also to workers in geochemistry, activation analysis, biochemistry, nuclear engineering, and other fields in which there is occasion to use radiochemical techniques.

Massachusetts, Institute of Technology

DAVID N. HUME

Anal. Chim. Acta, 24 (1961) 98-99

Radiometric Trace Analysis of Lead par P. C. VAN ERKELENS, Drukkerij Smits, Oudegracht 231, Utrecht, 1960, 104 pp.

À l'encontre de ce que laisse supposer le titre, ce livre n'a pas pour objet une étude bibliographique complète du dosage radiométrique du plomb. L'auteur a recours aux études déjà effectuées dans ce domaine mais il expose surtout ses propres travaux, les essais préliminaires comme les résultats positifs et négatifs qu'il a obtenus.

En fait, toutes les méthodes radiochimiques n'ont pas été mises à l'épreuve ainsi que l'indique le titre de l'ouvrage; il n'est pas question, par exemple, des méthodes par activation aux neutrons, qui ne présentent sans doute pas assez de sensibilité pour les applications que l'auteur veut en faire.

Les méthodes utilisant un réactif radioactif (R.R.) et celle qui est basée sur les échanges (R.E.) ont par contre été très minutieusement examinées. La lecture de cet ouvrage sera très profitable à tous et plus spécialement à ceux, trop nombreux encore, qui utilisent les méthodes de dosage de traces avec une rare désinvolture: le choix des réactifs, la détermination, la pureté de ceux-ci, les pertes et contaminations, le comportement des ions étrangers, l'étude minutieuse des diverses opérations analytiques, tous ces problèmes font l'objet d'examen approfondis et montrent que de tels dosages ne s'improvisant pas.

L'auteur arrive aux conclusions suivantes: deux méthodes se prêtent particulièrement bien à ce dosage: l'analyse R.R. avec le phosphate marqué au phosphore 32, qui permet de doser 1 μg de plomb; elle est relativement simple, mais plusieurs ions étrangers gênent, une liste en est donnée avec les quantités limites. L'analyse R.E. mise au point par l'auteur basée sur une extraction doublée d'un échange entre le plomb et le thallium et une mesure finale de l'activité du Tl 204. La déviation standard est de 11% pour 0.1 μg de plomb.

Ouvrage remarquable par la précision des techniques décrites.

D. MONNIER (Genève)

Anal. Chim. Acta, 24 (1961) 99

Gas Chromatography Abstracts 1959, edited by C. E. H. KNAPMAN, Assistant editor: C. G. SCOTT, Butterworths, London, 1960, Prix 42s.

Ce volume d'abstracts est la suite de celui publié l'année dernière (*Gas Chromatography Abstracts*, 1958) et recensé dans cette revue.

Le „Gas Chromatography Discussion Group” a estimé qu'il était nécessaire de poursuivre l'effort commencé, d'autant plus que le nombre de travaux effectués dans ce domaine ne cesse de croître et qu'il est impossible même aux spécialistes de se tenir au courant de tous les articles qui paraissent. Les auteurs ont répertorié 717 articles. De chacun d'eux, ils donnent le titre, le nom du ou des auteurs, celui du périodique avec la page, le numéro et l'année, puis un bref compte rendu de 3 à 6 lignes.

En fin d'ouvrage, une table alphabétique des auteurs et une table des sujets permettent de retrouver facilement l'article recherché.

D. MONNIER (Genève)

Anal. Chim. Acta, 24 (1961) 100

Physical Methods in Chemical Analysis, Edited by WALTER G. BERL, Vol. I, 2nd revised edition, xiv + 686 pp., Academic Press, New York and London, 1960, Prix 19\$.

La première édition du premier volume de cet ouvrage est de 1950, elle a été présentée par N. STRAFFORD dans cette revue (*Anal. Chim. Acta*, 5 (1951) 334).

Les têtes de chapitres n'ont pas été modifiées; quelques collaborateurs ont été adjoints ou changés. C'est ainsi que l'exposé sur la diffraction des rayons X appliquée aux fibres est l'oeuvre de J. A. HOWSOM ET N.M. WALTER, que le chapitre traitant de la spectrophotométrie est présenté par W. R. BRODE ET M. E. CORNING, que la microscopie électronique a été confiée à R. D. HEIDENREICH ET C. J. CALBRICK et la spectrométrie de masse à C. F. ROBINSON. Quant à la polarométrie, elle ne fait plus partie de ce volume.

La bibliographie a été complétée, elle va jusqu'en 1959. Elle n'est pas très étendue car les auteurs n'ont retenu que les articles et les livres les plus importants.

Chaque méthode est présentée avec soin, les principes fondamentaux en sont exposés de façon claire et logique. Les auteurs auraient peut-être pu s'étendre davantage sur les problèmes purement analytiques tels que: possibilités des divers processus, sensibilité, précision, applications au dosage des traces. Tel qu'il est, ce traité a déjà rendu et rendra encore de signalés services à tous ceux qui ont recours aux méthodes physicochimiques d'analyse.

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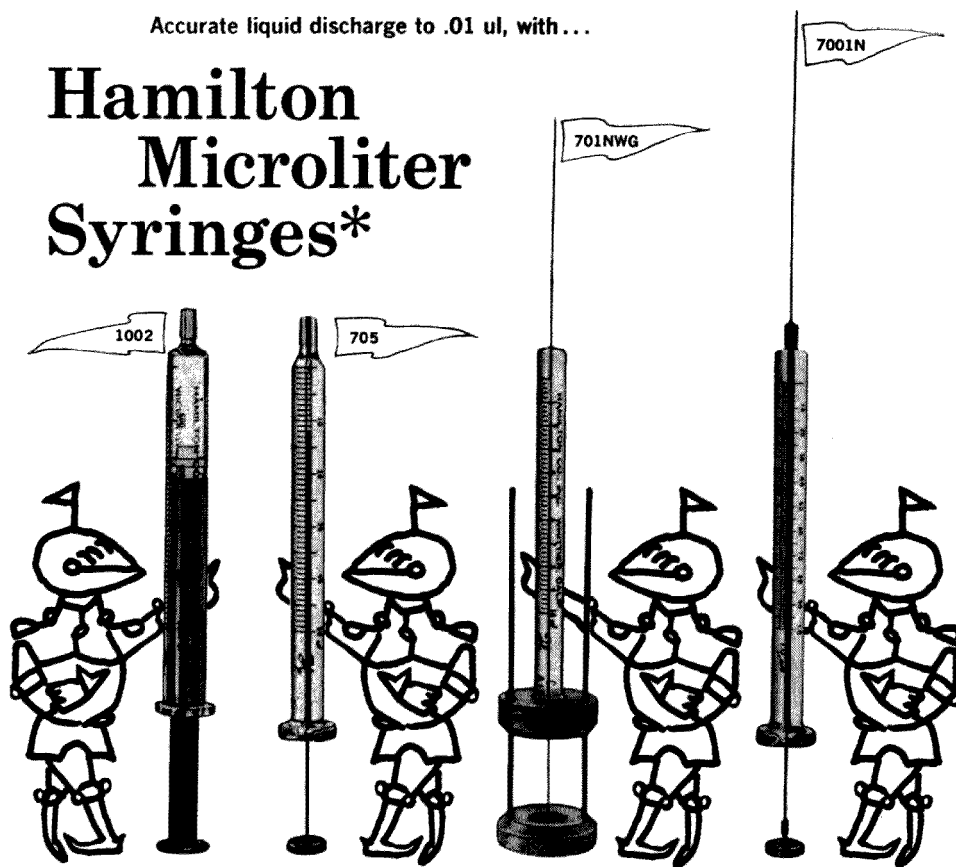
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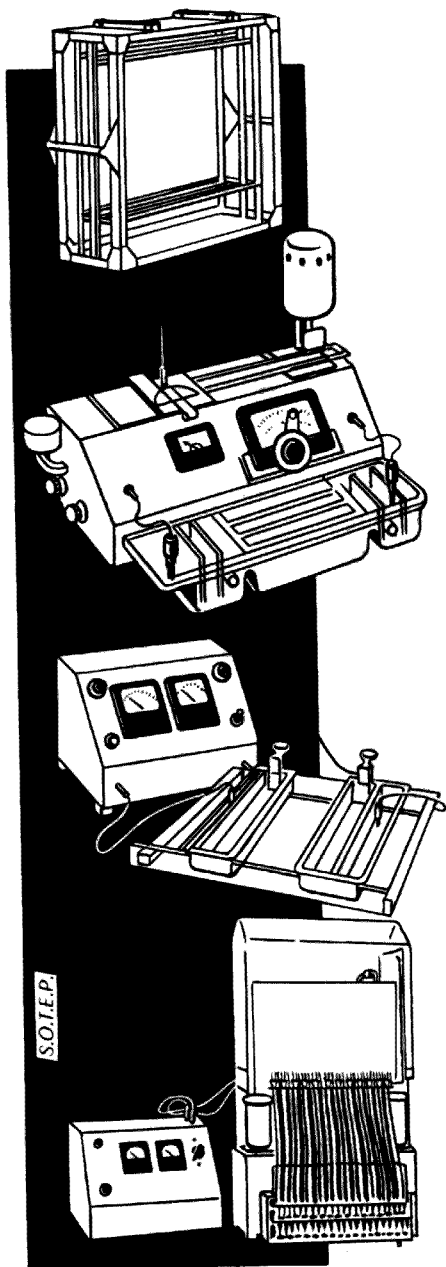
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