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1) *Chem. Eng. News*, 1960, **38** (**16**), 115.
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3) Hishta, C., *et al.*, *Anal. Chem.*, 1960, **32** (**7**), 880.

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1) Pollard, F. H., Hanson, P. and Geary, W. J., *Anal. Chim. Acta*, 1959, **20**, 26-31.
2) Wehber, P.. *Z. anal. Chem.*, 1959, **166**, 186-9.
3) Busev, A. I. and Kanaev, N. A., *C.A.*, 1959, **53**, 18747c.

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1) Billman, J. H., Janetos, N. S., and Chernin, R., *Anal. Chem.*, 1960, **32**, 1342-4.

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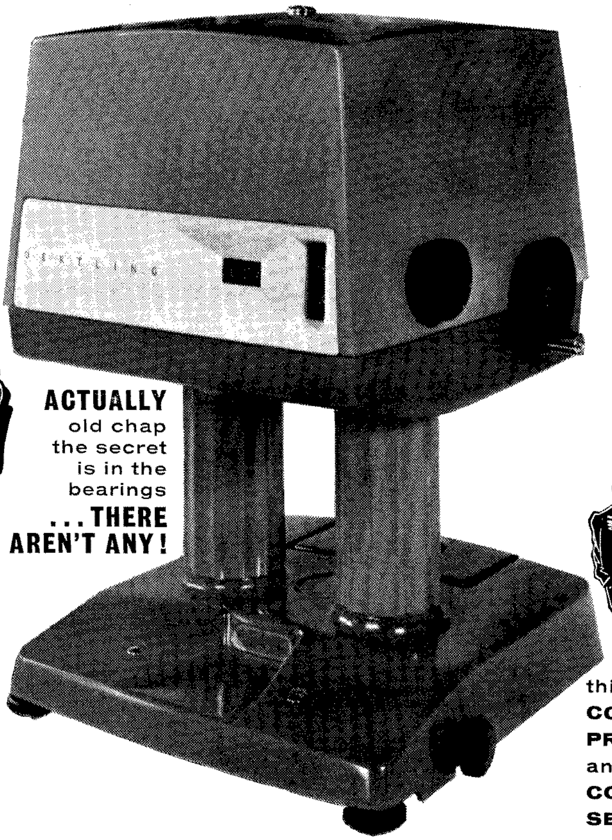

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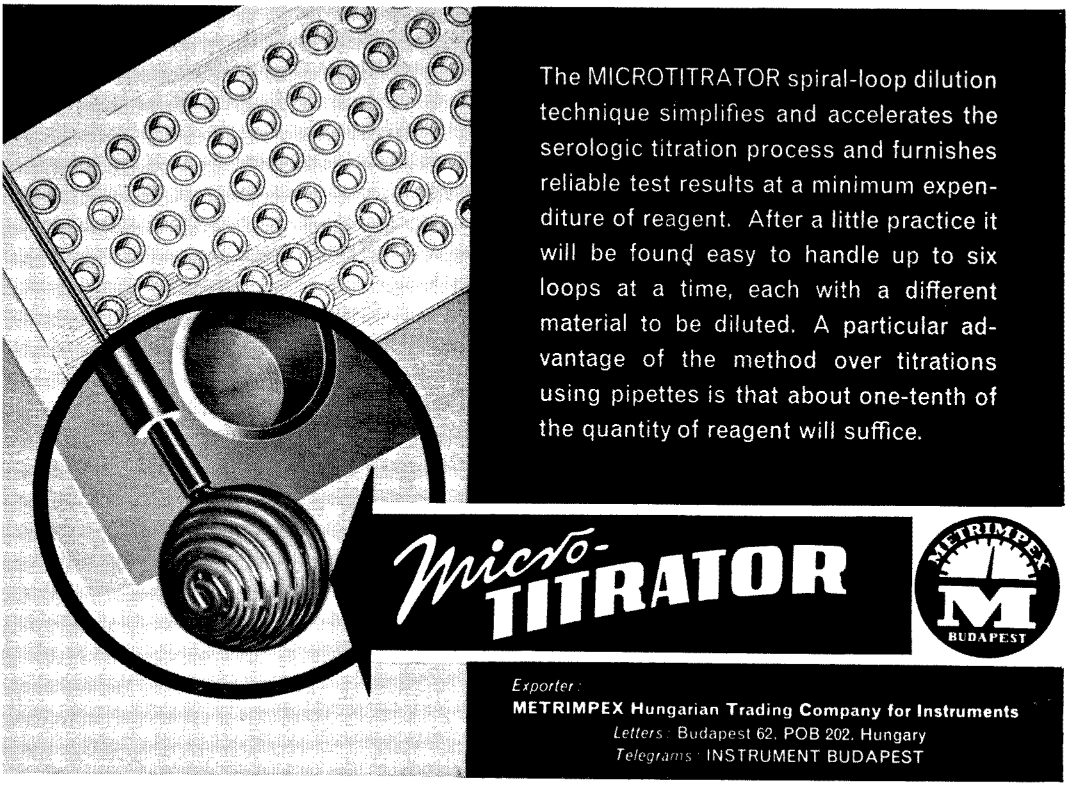

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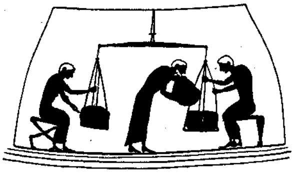

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[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.

[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.

[4] W. Jones, *Brit. Pat.* 654321, 1959.

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Preliminary communications

Short communications

Talanta, 1962, Vol. 9, pp. 473 to 481. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF ALKYL CELLULOSE ETHERS BY GAS CHROMATOGRAPHY

JOHN G. COBLER*, E. PAUL SAMSEL* and GARTH H. BEAVER†
The Dow Chemical Company, Midland Division, Midland, Michigan, U.S.A.

(*Received* 10 *October* 1961. *Accepted* 8 *November* 1961)

Summary—A gas chromatographic technique for the quantitative determination of mixed alkoxyl groups in cellulosics is presented. The procedure consists of reacting the alkoxyl constituents with hydriodic acid by a modified Zeisel method. The alkyl iodides thus formed are collected in a cold trap containing 2,2,5-trimethylhexane as a solvent. An aliquot of this solvent containing the alkyl iodides is subsequently analysed by gas chromatography. Known compounds containing methoxyl-, ethoxyl- and isopropoxyl groups are used as standards. Experimental and commercially available methylcellulose, ethylcellulose, ethylmethylcellulose, and hydroxypropylmethylcellulose have been analysed by this procedure. Results are compared with those obtained by other alkoxyl methods. The method provides a direct means for the simultaneous determination of mixed alkyl substituents in cellulose or related polysaccharides. Indirect methods requiring multiple determinations on the same sample and cumbersome fractional precipitation procedures are unnecessary.

DETERMINATION of the alkoxyl substituent of a cellulose compound commences with the classical hydriodic acid decomposition procedure of Zeisel.[1] The corresponding alkyl iodides thus formed are swept from the reaction mixture with nitrogen. Modifications or improvements of the Zeisel method may be divided into the following general areas: (1) gravimetric, (2) titrimetric, (3) differential solubility adaptations, and (4) instrumental adaptations including gas chromatography and infrared spectrometry.

There has been some interest in the absorption and combustion method of Friedrich[2] since it was first published in 1929. Hozumi[3] modified Friedrich's method by absorbing the distilled alkyl iodide on porous silver granules, then heating to decompose the alkyl iodide and absorption of the iodine on the silver. Fukuda[4] used the Zeisel method for decomposition, then subjected the alkyl iodide product to combustion over a platinum catalyst in an air stream to form iodine and carbon dioxide.

Samsel and McHard[5] modified the apparatus and technique of the Vieböck and Brecher[6] titrimetric method. Recently, Cundiff and Markunas[7] presented another titrimetric method for the determination of alkoxyl groups, whereby the alkyl iodide was absorbed in pyridine and titrated directly with tetrabutylammonium hydroxide. They extended their work so that it would also apply to the analysis of higher alkoxyl groups such as propoxyl or butoxyl.

Separations of mixed alkyl substituents have always been difficult. Classically, Willstätter and Utzinger[8] separated methyl iodide from ethyl iodide on the basis of the differential solubility in absolute alcohol of tetramethylammonium iodide and trimethylethylammonium iodide. Makens, Lothringer and Donia[9] also formed the trimethylethylammonium iodide and the tetramethylammonium iodide, but separated them by differences in their solubility in a trimethylamine-nitrobenzene solution.

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* Polymer Analysis Laboratory.
† Cellulose and Plastics Laboratory.

Sobue, Hatano and Arai[10] used a spectrophotometric technique to detect the presence of an alkyl iodide absorbed in pyridine. Anderson and Duncan[11] decomposed the alkoxyl-containing compounds by the Zeisel method, and used quantitative vapour phase infrared spectrometry to simultaneously determine the methoxyl or ethoxyl groups as the corresponding alkyl iodide.

With the developement of a practical instrumental gas chromatographic apparatus by Gohlke,[12] and the work of James and Martin,[13] which demonstrated that alkyl halides could be separated by gas chromatography, new improvements in the alkoxyl determination became possible.

Vertalier and Martin[14] decomposed the alkoxyl compound by the Zeisel technique, and used gas chromatography as a qualitative and semi-quantitative technique for alkoxyl determinations. They trapped the distilled alkyl iodide in a glass tube at dry ice temperature. Losses were reported at 25–50% of the theoretical value. However, their losses were constant as a function of the particular sample being decomposed. Kratzel and Gruber[15] separated alkyl halides by gas chromatography. They used the chromatograms for qualitative work, but felt that the condensation and subsequent vaporisation of the alkyl halides was unreliable for quantitative work. Kratzel and Gruber collected the individual alkyl iodides as they left the gas chromatographic column in the conventional bromine-glacial acetic acid-sodium acetate solution and titrated each fraction by the method of Vieböck and Brecher.[6]

Haslam, Hamilton and Jeffs[16] used gas chromatography to quantitatively determine acrylate esters which had been reduced to the alkyl iodide by the Zeisel technique. They incorporated known quantities of methyl chloride and ethylene dichloride with the mixture of trapped alkyl iodides, and used ratios of peak heights to quantitatively determine the alkyl iodides present.

In the present paper cellulosic- or polysaccharide-type compounds containing alkoxyl or mixed alkoxyl constituents are decomposed with hydriodic acid to form the corresponding alkyl iodides. The iodides are then removed from the reaction mixture by purging with nitrogen gas and are quantitatively absorbed in 2,2,5-trimethylhexane at a temperature of −80°. A portion of this solution containing the alkyl iodides is subsequently injected into a gas chromatographic apparatus. The areas under the various alkyl iodide peaks on the resulting chromatogram are compared with those obtained by the analysis of known compounds.

EXPERIMENTAL

Apparatus

Distillation apparatus (Fig. 1): This consists of a 50-ml side-arm flask, an air condenser with a scrubbing trap, an absorber trap, and an oil bath equipped with an electrical heating device so that the bath can be maintained at 150°.

Beckman gas chromatograph: GC-2A, with a 7-ft 1/4″ O.D. stainless steel tube column.

Absorbent: Di-2-ethylhexyl sebacate on firebrick (Absorbant No. 341-119, supplied by Burrell Corporation).

Microsyringe: 0·05-ml capacity.

Recorder.

Reagents

Methoxyl standard: *o*-Methoxybenzoic acid and/or *p*-methoxyphenol (Eastman Organic Chemicals).

Ethoxyl standard: *p*-Ethoxybenzoic acid (Eastman Organic Chemicals).

Propoxyl standard: 3-Isopropoxy-n-propylamine (American Cyanamid Co.).

2,2,5-Trimethylhexane: Pure grade (Phillips Petroleum Co.).
Phenol: Loose crystals, AnalaR.
Magnesium perchlorate: Anhydrous.
Helium gas.
Nitrogen gas.
Hydriodic acid: Constant boiling, reagent grade.

Conditions

The chromatographic apparatus is operated at 75°, using helium as the carrier gas at a flow rate of 68 ml/min. The recorder should have a range of 0–1 mV. The chart speed is 30 in. per hr. An attenuation of 50 is used for the methoxyl and /or ethoxyl determinations. When the simultaneous determination of methoxyl and hydroxypropoxyl substituents is performed, an attenuation of 50 is used for the methoxyl determination. After the methyl iodide peak has been recorded on the chromatogram, the attenuation should be changed to 2 for recording the isopropyl iodide peak. When large (60–80 mg) samples are analysed only for hydroxypropoxyl content, an attenuation of 5 is recommended.

Procedure

Place 3 ml of distilled water in the scrubbing trap (B) (see Fig. 1). Place a small amount of drying agent (magnesium perchlorate) into the inlet section of the absorber trap (E). With a hypodermic syringe, add 1 ml of 2,2,5-trimethylhexane to the outlet section of the absorber trap (E), and assemble the apparatus as shown in Fig. 1. Surround the trap (E) with a dry ice bath at −80°. To the reaction flask (C), add 2 g of phenol (loose crystals) and a few silicon carbide chips to prevent bumping. Add about 30 mg of sample, depending upon the alkoxyl content, and 6 ml of constant boiling hydriodic acid. Attach at once to the distillation apparatus, using a few drops of hydriodic acid to moisten the ground glass joint.

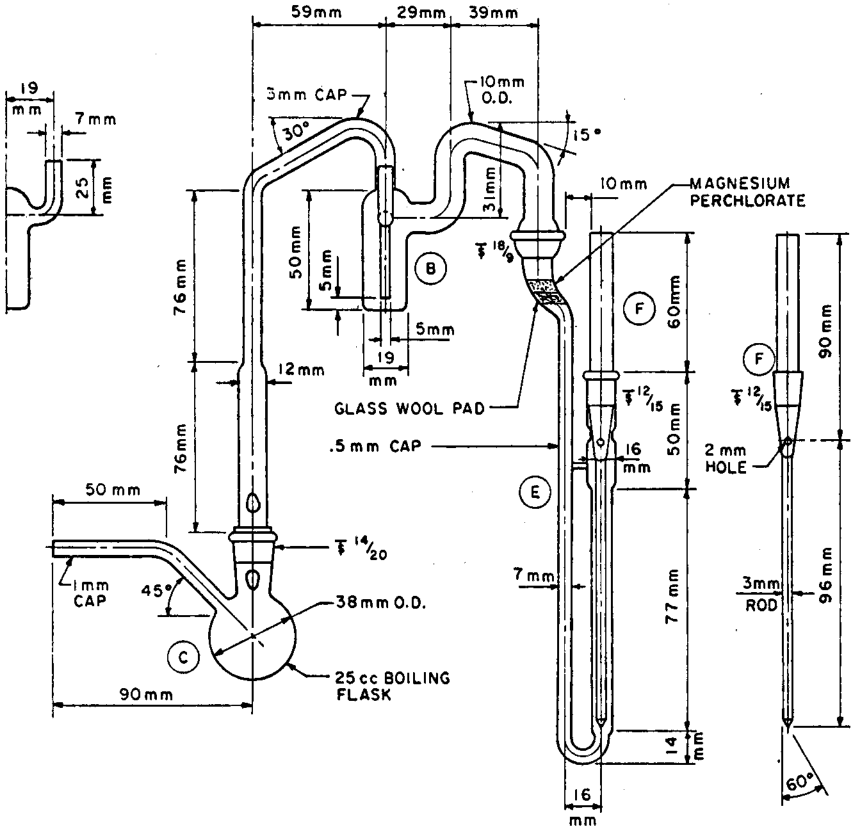

Fig. 1—Apparatus for alkyl iodide distillation and absorption.

Connect the side-arm to a source of nitrogen and pass the gas through the apparatus at the rate of 1–2 bubbles per sec. Immerse the reaction flask in an oil bath maintained at 150° and react for 1 hr. Upon completion of the hydrolysis, disconnect the absorber trap (E). By means of a microsyringe, immediately inject 0·05 ml of the 2,2,5-trimethylhexane solution containing the alkyl iodides into the gas chromatograph apparatus.

The concentration of the various alkyl iodides present in the 2,2,5-trimethylhexane will be recorded as the area under the corresponding peak on the chromatogram (Fig. 2). A blank determination on the apparatus and chromatograph column may be performed, although we have found the blank to be negligible.

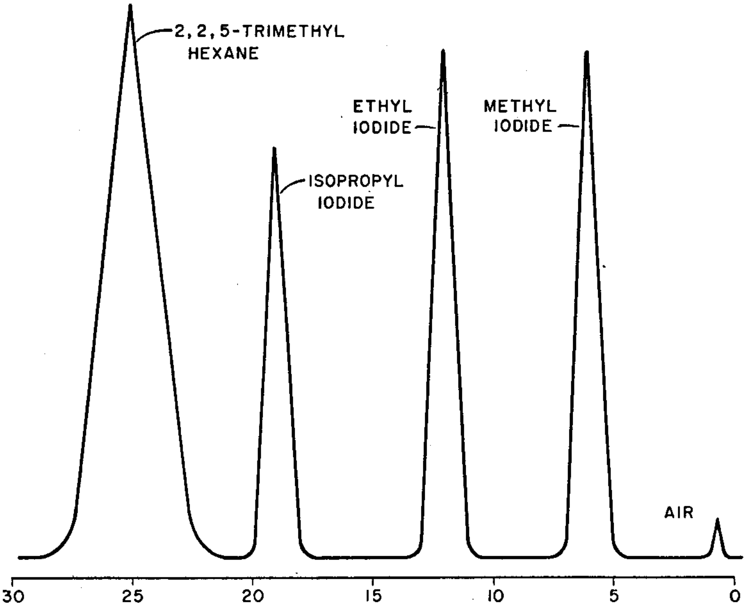

FIG. 2—Retention time in mins for alkyl iodides.
Column: 7ft, di-2-ethylhexyl sebacate
Flow rate: 68 ml of helium/min.
Temperature: 75°.
Current: 250 mA.
Chart speed: 30 in./hr.

Analysis of pure compounds should be performed by the method of Samsel and McHard,[5] and these results used to standardise the gas chromatographic method.

Once standardisation of the apparatus is accomplished by using various pure compounds, and a value obtained expressing mg of specific alkyl iodide per sq. cm. of chart area, this procedure may be used as a quantitative criterion.

Methoxyl analysis

o-Methoxybenzoic acid and *p*-methoxyphenol were used as methoxyl standards. A series of cellulose compounds containing methoxyl constituents was analysed as outlined under *Procedure.*

Ethoxyl analysis

p-Ethoxybenzoic acid was used as a standard. A series of ethoxyl-containing compounds was analysed by the procedure previously described.

Simultaneous methoxyl and ethoxyl analysis

Once chromatographic factors for methyl and ethyl iodide have been obtained, it is possible to simultaneously determine methyl and ethyl substituents in cellulose. A series of three mixed methylethylcelluloses was analysed using the previously described methoxyl and ethoxyl standards. In addition, a pure sample of β-methyltriethyl glucoside, prepared by A. W. Anderson of The Dow Chemical Company, was analysed.

Simultaneous methoxyl and hydroxypropoxyl analysis

3-Isopropoxy-n-propylamine was used as the isopropyl iodide standard. Analysis of this compound was performed by Samsel and McHard's method. A mass spectrographic analysis was also obtained on the halide decomposition products absorbed in the 2,2,5-trimethylhexane solvent. The previously discussed methoxyl standards were again used as methyl iodide reference materials. A series of commercially available mixed cellulose ethers containing methoxyl and hydroxypropoxyl substituents was analysed. An attenuation of 50 was used on the chromatograph recorder for the methyl iodide peak, while an attenuation of 2 was used for the isopropyl iodide peak.

DISCUSSION

Results for the determination of methoxyl substituents are presented in Table I. The methoxyl values obtained for both *o*-methoxybenzoic acid and *p*-methoxyphenol by the modified Zeisel method[5] agree with theoretical calculations. A series of cellulose compounds containing from 5% to 44·3% of methoxyl was analysed by the gas chromatographic method, and these results are in agreement with those obtained by the modified Zeisel method. In all cases but Sample D-3, results obtained by the gas chromatographic method agree to within 0·5% of the value obtained by the modified Zeisel method.

Table I—Determination of methoxyl substituents on cellulose

Compound	Methoxyl, %	
	By gas chromatography	By modified Zeisel
o-Methoxybenzoic acid	20·3[1]	20·3
p-Methoxyphenol	25·1[1]	24·9
Methycellulose A	4·9– 5.1	5·3
B	14·4–14·8	14·5
C	16·8–16·9	17·0
D-1	28·5–28·7	28·8
D-2	30·6–30·9	30·9
D-3	29·1–29·7	30·0
E	44·2–44·3	44·5

[1] Theoretical

Table II presents data on the determination of ethoxyl substituents. The value obtained for the standard *p*-ethoxybenzoic acid by the modified Zeisel method is the theoretical value. Here again, when the analyses of a series of ethylcellulose samples

Table II—Determination of ethoxyl substituents on cellulose

Compound	Ethoxyl, %	
	By gas chromatography	By modified Zeisel
p-Ethoxybenzoic acid	27·1[1]	27·0
Ethylcellulose A	33·2–33·5	33·5
B	36·1–36·5	36·6
C	37·1–37·4	36·8
D	45·8–46·3	46·1
E	48·4–48·6	48·8
F	48·5–48·7	48·8
G	51·1–51·4	51·3
H	52·9–53·3	53·8

[1] Theoretical

by the gas chromatographic method and the method of Samsel and McHard are compared, excellent correlation and agreement are obtained. An exception is ethylcellulose Sample H where a low result was obtained.

Results on the simultaneous determination of methoxyl and ethoxyl cosubstituents in polysaccharides are presented in Table III. The analysis of β-methyltriethyl glucoside obtained by the gas chromatographic method agrees with the theoretical values of the compound. The sample of Edifas "A" was supplied by Imperial Chemical Industries Ltd. (ICI), and their method of analysis is unknown. Results obtained by the gas chromatographic analysis of this sample agree closely with the reported values as to total alkoxyl substitution, although the value reported by gas chromatography is higher in the case of methoxyl content than that reported by ICI. Methylethylcellulose, Samples D and E, were prepared by Dr. G. D. Mercer of The Dow Chemical Company. Dr. Mercer ethylated methylcellulose having initial methoxyl contents of 30% and 16%, respectively. The "comparative method" value reported in Table III for the ethoxyl content of methylethylcellulose, Samples D and E, was obtained by performing a total alkoxyl determination by the modified Zeisel method of the finished polymer. Additional substitution present above the starting methoxyl content was calculated as newly substituted ethoxyl groups. Results obtained by gas chromatography for the ethoxyl content of these mixed ethers indicate more ethyl ether present than was calculated.

TABLE III—SIMULTANEOUS DETERMINATION OF METHOXYL AND ETHOXYL SUBSTITUENTS ON CELLULOSE

Compound	Methoxyl, %		Ethoxyl, %	
	Gas chromatography	Comparative method	Gas chromatography	Comparative method
β-Methyltriethyl glucoside	10·9–11·2	11·2[1]	48·1–48·5	48·6[1]
Edifas "A"	5·7– 6·0	5·6[2]	14·7–14·8	15·4[2]
Methylethylcellulose D	25·9–26·0	27·1[3]	17·0–17·4	15·0[3]
E	14·0–13·8	13·9[3]	23·3–23·7	21·5[3]

[1] Theoretical.
[2] Value reported by Imperial Chemical Industries Ltd.—method used unknown.
[3] By difference, based on total alkoxyl substitution.

Data on the simultaneous determination of methoxyl and hydroxypropoxyl substituents on cellulose are presented in Table IV. The standard, 3-isopropoxy-n-propylamine, had an isopropoxyl content of 49·7% by the modified Zeisel method, compared with a theoretical value of 50·2%. The (corrected) methoxyl content of the mixed ethers in Table IV was calculated by determining the total alkoxyl by the modified Zeisel method, then subtracting the value for hydroxypropoxyl content obtained by the chromic acid oxidation method of Lemieux and Purves.[17] The modified Zeisel method and the chromatographic method agree closely as regards total alkoxyl substitution. However, gas chromatographic analysis for hydroxypropoxyl substituents indicates a value of 80% of that value obtained by the chromic acid oxidation method. As a result, the methoxyl content, obtained by the modified Zeisel method, corrected by the chromic acid oxidation factor, is slightly lower than the gas chromatographic analysis for methoxyl content.

While isopropyl iodide is the alkyl iodide obtained by the hydriodic acid decomposition of 3-isopropoxy-n-propylamine, the analysis of the mixed cellulose ether is concerned with the determination of the hydroxypropoxyl substituent. A conversion factor was used to convert mg of isopropoxyl per sq. cm. of chart space to mg of hydroxypropoxyl per sq. cm. of chart space. This factor was 1·27.

TABLE IV—SIMULTANEOUS DETERMINATION OF METHOXYL AND HYDROXYLPROPOXYL SUBSTITUENTS ON CELLULOSE

Compound	Methoxyl, %		Hydroxypropoxyl, %	
	By gas chromatography	By modified Zeisel (corrected)	By gas chromatography	By chromic acid oxidation[1]
3-Isopropoxy-n-propylamine	—	—	50·2[2]	49·7[3]
Mixed ether—A	24·2–23·8	25·3	5·6– 5·4	6·9
B	27·6–27·2	26·7	5·1– 5·0	6·4
C	29·5–28·9	27·8	7·6– 7·2	10·1
D	30·5–30·2	28·7	6·9– 6·7	9·1
E	28·5–27·6	28·3	8·2– 8·5	11·2
F	21·8–21·7	19·9	13·0–11·7	15·6

[1] Method of Lemieux and Purves.
[2] Isopropoxyl, theoretical.
[3] Isopropoxyl by modified Zeisel.

There has been considerable concern as to whether quantitative amounts of isopropyl iodide result when the mixed hydroxypropylmethylcellulose is decomposed with hydriodic acid, or whether some propylene is formed. It is a known fact that when ethylene glycol is decomposed with hydriodic acid, both ethylene and ethyl iodide are formed. It was felt that the hydroxypropoxyl group might react similarly and both propylene and isopropyl iodide could be reaction products. However, mass spectrographic results indicate the absence of propylene as a decomposition product of the hydriodic acid hydrolysis of methylhydroxypropylcellulose. This indicates that quantitative yields of isopropyl iodide are being obtained from the hydroxypropylmethylcellulose mixed ethers. Anderson and Duncan[18] have shown that when glycerol is subjected to the reaction conditions of the Zeisel method that isopropyl iodide is the only product. No propylene is formed.

The fact that hydroxypropoxyl analyses by the gas chromatographic method are consistently lower than those analyses obtained by the chromic acid oxidation method of Lemieux and Purves, suggested additional experiments. The same cellulose ether compounds were analysed by varying their sample weight to determine whether the quantity of isopropyl iodide formed was constant as a function of the total sample weight added to the reaction flask. Results of this experiment are presented in Table V, wherein 30- and 70-mg samples of three hydroxypropoxylmethylcelluloses were evaluated. A recorder attenuation of 5 was used for this analysis. Results were in excellent agreement and well within experimental error. They indicate that for our purposes all hydroxypropoxyl substituents in the cellulose ether have been transformed into isopropyl iodide and that this iodide is quantitatively determined in the gas chromatographic apparatus.

CONCLUSION

A method for the simultaneous determination of mixed alkyl substituents on cellulose has been presented. Both the methylethylcellulose and the methylhydroxypropylcellulose mixed ethers have been quantitatively analysed for their alkoxyl substituents in a single determination. This new method affords a 50% time saving over a present method of analysis.

TABLE V—DETERMINATION OF HYDROXYPROPOXYL CONTENT BY VARYING SAMPLE WEIGHT

Compound	Hydroxypropoxyl, %	
	30-mg sample	70-mg sample
IV—C	7·6	7·3
IV—D-1	6·9	6·8
IV—D-1	6·7	6·7

Availability of other hydroxypropoxyl standard compounds should enable complete resolution of the differences discussed concerning the results presented in Table IV. Particularly, a pure isopropoxybenzoic acid compound should assist in completely resolving any remaining discrepancy.

This method could be easily adapted to the analyses of other mixed ethers of cellulose, such as methylhydroxybutylcellulose. Compounds of this type are known in experimental quantities and are considered laboratory curiosities.

This method may find adaptation in the analysis of compounds such as hydroxyethylcellulose. Further research is suggested using, perhaps, hydrobromic acid to decompose the cellulose ether.

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Zusammenfassung—Eine gaschromatographische Methodik zur quantitativen Bestimmung gemischter Alkoxylgruppen in Zellulosen wird beschrieben. Die Alkoxylgruppen werden mit Jodwasserstoffsäure nach einer modifizierten Zeisel-Methode zur Reaktion gebracht. Die gebildeten Alkyljodide werden in einer Kühlfalle mit 2,2,5-Trimethylhexan als Solvent aufgefangen. Ein aliquoter Teil der Lösung wird in einen Gaschromatographen analysiert. Bekannte Verbindungen, die Methoxyl-, Äthoxyl- und Isopropoxylgruppen enthalten werden als Standards benutzt. Im Labor erzeugte und käufliche Zellulosen, die die oben genannten Gruppen einzel und im Gemisch enthielten, wurden analysiert und die Resultate mit denen nach anderen Alkoxylmethoden erhaltenen verglichen. Die Methode bietet eine Möglichkeit zur direkten Bestimmung der Alkoxyde in gemischt substituierter Zellulose und ähnlichen Polysacchariden. Indirekte Methoden benötigen Mehrfachbestimmungen und mühevolle fraktionierte Fällungsoperationen, die hier unnötig sind.

Résumé—Les auteurs présentent une méthode de dosage de mélanges de groupes alkoxyle dans les produits cellulosiques par chromatographie gazeuse. Le procédé consiste à faire réagir les constituants avec l'acide iodhydrique par une méthode de Zeisel modifiée. Les iodures d'alcoyle ainsi formés sont recueillis dans un piège froid contenant du 2,2,5-triméthylhexane comme solvant. Une partie aliquote de ce solvant contenant les iodures d'alcoyle est ensuite analysée par chromatographie gazeuse. Des composés connus contenant les groupements méthoxy, éthoxy et isopropoxy sont utilisés comme étalons. Les composés suivants préparés expérimentalement et disponibles dans le commerce sont analysés par cette méthode: méthylcellulose, éthylcellulose, éthyl-méthylcellulose et hydroxypropylméthylcellulose. Les résultats sont comparés avec ceux obtenus par d'autres procédés.

Cette méthode fournit un moyen direct de dosage simultané de mélanges de substituants alcoxyle dans la cellulose ou les polysaccharides qui s'y rattachent. Des méthodes indirectes nécessitant de multiples dosages sur le même échantillon et des procédés incommodes de précipitation fractionnée ne sont pas nécessaires.

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AN AUTOMATIC ANALYSER FOR HYPOPHOSPHITE WITH PARTICULAR REFERENCE TO ELECTROLESS* PLATING SOLUTIONS

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Summary—An apparatus is described for the continuous automatic determination of hypophosphite in a complex electroless nickel-plating solution. After catalytic oxidation of the hypophosphite, the evolved hydrogen is burned and the flame temperature used as a measure of the hydrogen and hence of the hypophosphite. The results are unaffected by changes in concentration of other ions present in the solution. Temperature variations in the range 20° to 70° produce only minor effects.

INTRODUCTION

IN response to a request for a continuous automatic analyser for the hypophosphite content of an electroless nickel-plating solution, a survey of the existing methods of analysis for hypophosphite was carried out.

Initially the plating solution contains sodium hypophosphite (the reducing agent), nickel sulphate (the source of nickel), various organic acids[1] (to buffer the pH), sodium hydroxide (to bring the pH to the optimum value) and also certain minor constituents. The effects on the plating of some of the minor constituents have been investigated by Brenner and Riddell.[2] As the bath ages the hypophosphite and nickel are consumed, phosphite is formed and the pH drops; it is necessary, therefore, to add sodium hydroxide, sodium hypophosphite and nickel sulphate as plating proceeds, thus producing with time a concentration gradient of sodium phosphite and sodium sulphate.

In view of the complex and changing nature of the plant liquor, especially the build-up of phosphite which occurs in operation of the plant, the normal titrimetric methods of analysis for hypophosphite were considered to be unsuitable for an automatic process. The colour of the nickel-organic acid complex present in the plating solution was a factor to be taken into account if colorimetric methods were to be considered.

Palladium black acts as a catalyst in the decomposition of hypophosphite and consequently the possibility of developing a method of analysis based on this reaction was examined.

The reaction which occurs is the dehydrogenation of the hypophosphite ions[3,4] with formation of phosphite ions and hydrogen gas:

$$H(H_2PO_2) \xrightarrow{\text{catalyst}} HPO_2 + H_2 \quad \text{(i)}$$

$$HPO_2 + H_2O \longrightarrow H_2(HPO_3) \quad \text{(ii)}$$

The method would be truly continuous and the hydrogen might be measured in a variety of ways: (a) detection with a katharometer, (b) detection with a Hersch-type

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* Electroless plating may be defined as an autocatalytic chemical reduction process for continuously plating a metal from a solution of the metal salt containing a reducing agent.

galvanic cell, (c) combustion of the hydrogen and measurement of the flame temperature with a thermocouple. Although methods (a) and (b) are both capable of very high sensitivities, method (c) can be much the simplest. For this reason it was chosen. The thermocouple was connected to a strip-chart recorder.

EXPERIMENTAL

The initial work on the development of this method was carried out using aqueous sodium hypophosphite solutions and a catalyst prepared by electroplating palladium on thin silver foil. However, when using plant liquor it was found that the rate of the reaction was greatly reduced thus necessitating the use of larger quantities of catalyst. The form of catalyst which was finally used was prepared by plating palladium on silver-plated copper gauze. The metals of Group VIII of the Periodic Table are catalytic at or near the boiling point of water. Palladium is an exception in that it is catalytic at room temperature. Most other metals will exchange with nickel in the plating bath, the deposited nickel being catalytic. It was found in practice that the palladium and the silver of the prepared catalyst both dissolved in the plating solution, depositing a form of nickel which was catalytic at room temperature. It was found that without the silver deposit on the copper, the palladium was not such an effective catalyst. No explanation of this fact could be discovered because neither copper nor silver alone would catalyse the reaction at room temperature. Once this deposit of nickel had formed, the activity of the catalyst remained constant.

In use, the activity of the catalyst fell off to near zero within a few hr but it could be revived by washing with ammonia solution, suggesting that the poisoning was caused by adsorption of the organic acid molecules on the active points of the catalyst. In order to prevent the catalyst from becoming poisoned, ammonium hydroxide solution (1N) was metered into the apparatus together with the plant liquor. The metering was accomplished in each case by a continuously variable micrometering pump. After approximately 9 months use the catalyst showed no signs of becoming poisoned under these conditions. Two pieces of catalyst are used in a U-shaped chamber and the analysis mixture flows down one limb and up the other, the evolved hydrogen being collected at the top and passed, via a spray trap, to the detector unit. The analysis mixture flows in and out of the catalyst chamber via U-tube seals to prevent loss of hydrogen. The inlet U-tube seal also acts as a mixing chamber for the ammonium hydroxide solution and the plant liquor.

The detection system consists of a copper-constantan thermocouple which is situated just above the flame. In an earlier apparatus a thermocouple with a very small junction was used in order to obtain maximum sensitivity. However, the trace was liable to occasional fluctuations of about 1% of the chart width in magnitude because of collapse of the foam which collected in the catalyst chamber. Since no way could be found to destroy the foam without introducing other difficulties, the junction of the thermocouple was made massive by soldering it to a piece of copper tubing, thus rendering the trace stable by increasing the thermal inertia of the couple. This resulted in a reduction of sensitivity by a factor of about one half. At the same time, by utilising the copper of a copper-to-glass seal it became possible to fix the position of the thermocouple quite accurately and rigidly in relation to the jet. The output from the thermocouple was fed directly into a 10-mV strip-chart recorder. A further improvement in the geometry of the detector unit was obtained by cutting to 2 mm in length the hypodermic needle used as the jet and arranging that the distance from the jet to the copper block housing the thermocouple was about 5 mm, greater distances resulting in a loss in sensitivity. In order to eliminate as far as possible the effects of incidental draughts the air inlet and flue gas outlets of the detector unit were fitted with baffles of stainless steel gauze discs; in use, these have proved to be adequate.

In the earlier experimental detector the flame was lit by dismantling the unit and applying a match. For operation on the plant this was obviously undesirable so that an ignition system was fitted in which a high voltage spark was caused to jump between two tungsten electrodes placed one on either side of the jet. There is an additional advantage in that this system can be operated from a remote point with no possibility of disturbing the geometry of the detector. The spark is generated by a 12-V car ignition coil, power being supplied by two 9-V grid bias batteries in series. A bell push completes the circuit. The spark jumps the gap when the primary circuit is broken. The catalyst chamber and detector system are shown in Fig. 1.

Preparation of the catalyst

A sheet of copper gauze (40 mesh, 8″ × 11″) was rolled into a tight cylinder and cleaned by immersion in nitric acid (3*N*), then washed with distilled water. The cylinder was silver plated in a cyanide bath (2% silver nitrate solution plus sufficient 10% potassium cyanide solution to redissolve the silver cyanide precipitate) using a platinum wire anode wound on the cylinder and insulated from it by porcelain leads. The silver coated gauze and anode assembly was then transferred to a 2%

w/v palladium^{II} chloride solution in 0·2N hydrochloric acid and electroplated using a potential of 4V. The electrolysis was continued until a heavy deposit of palladium had formed.

The gauze could not be plated and then rolled because the deposit was only loosely adherent and would have been removed in the rolling operation. After standing for a few hr in the plant liquor/ammonium hydroxide solution mixture the catalyst had become nickel plated and its activity was then constant.

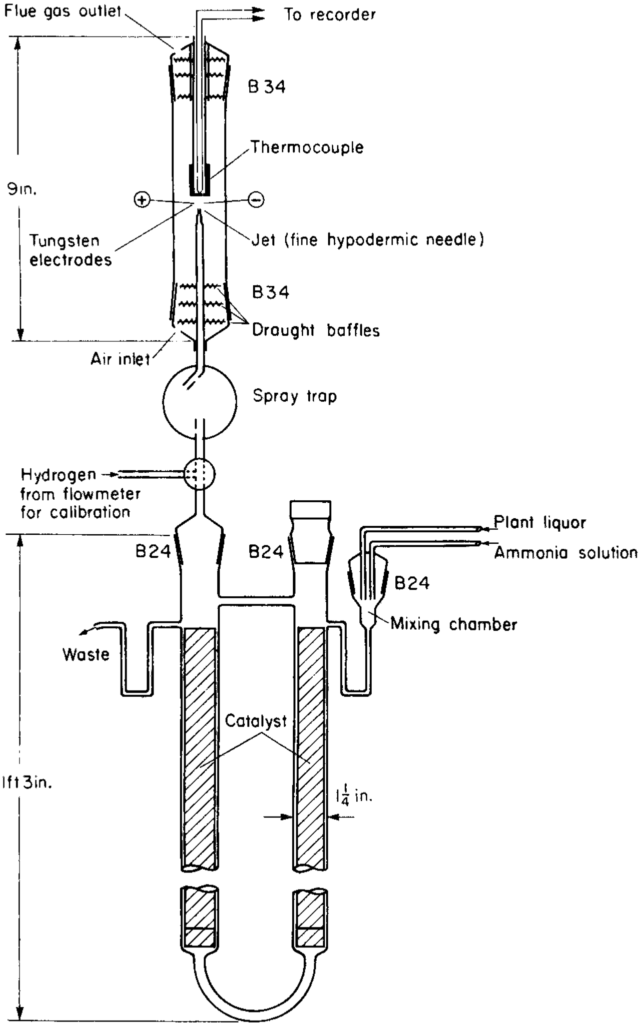

Fig. 1—Catalyst chamber and detector unit (not to scale).

RESULTS AND DISCUSSION

The apparatus described is capable of continuously analysing electroless nickel-plating solution for hypophosphite content. The most common concentration of hypophosphite is about 2%; the current calibration covers the range 1·5% to 3% but this can readily be altered, there being much latitude in the choice of flow rates, quantity of catalyst, and, for high concentrations, alteration in the sensitivity of the recorder. Where much lower concentrations of hypophosphite are concerned another detector, either of the Hersch-type or a katharometer, might be used. Fluctuations in the concentrations of the other constituents of the plant liquor are without effect on the results obtained.

Since the plant operates at about 95° the temperature of the liquor at the sample point may vary; however, this causes only minor variations in the results obtained, an increase of about 1·5% of the reading occurring for every 10° rise in temperature in the range 20° to 70°.

Since the catalyst is only about 75% efficient in the present arrangement, the apparatus must be standardised against synthetic plant liquors of known hypophosphite content. Experience indicates, however, that even for the most stringent plant control the standardisation need only be checked once per week.

Table I—Effects of variations of the flow rates of plant liquor and ammonium hydroxide solutions

Plant liquor flow rate, *ml. min*$^{-1}$	1·5	2·0	3·0	4·0	5·0	5·7	4·0	4·0	4·0
Ammonium hydroxide solution flow rate, *ml. min*$^{-1}$	5·0	5·0	5·0	5·0	5·0	5·0	5·0	2·0	5·0
Reading, *chart divisions*	0	38	51	59	61	62	57·5	58	58

The time taken to indicate an instantaneous change of 0·5% of sodium hypophosphite monohydrate is about 15 min, 45 min being required for attainment of the final steady reading which is approached in an asymptotic manner.

The effects of variation of flow rates of the plant liquor and ammonium hydroxide solution are shown in Table I.

From this table it can be seen that much latitude is permissible in the choice of flow rates for the two liquids; 4·0 ml. min^{-1} for the plant liquor and 5·0 ml. min^{-1} for the ammonium hydroxide solution were the values chosen for normal working.

Table II—Effects of variation of nickel sulphate concentration in a solution composed of 2% sodium hypophosphite monohydrate, sodium hydroxide, organic acids and minor constituents

$NiSO_4 \cdot 7H_2O$,%	1·5	2·0	2·5
Reading, *chart divisions*	35·5	36	35·5

Tables II and III show the results of variations in the concentrations of some of the constituents. Because sodium phosphite and sodium sulphate are formed in the plant at the same time their effects were determined together.

Calibration of the apparatus was carried out using synthetic plant solutions of known sodium hypophosphite content, the results being shown in Fig. 2. Also shown in Fig. 2 are the results of a calibration carried out using hydrogen gas from a cylinder. The gas was passed through a mixture of plant liquor and ammonium hydroxide

TABLE III—EFFECTS OF VARIATIONS OF SODIUM PHOSPHITE AND SODIUM SULPHATE CONCENTRATIONS IN A SOLUTION COMPOSED OF 2% SODIUM HYPOPHOSPHITE MONOHYDRATE, 2·5% NICKEL SULPHATE HEPTAHYDRATE, SODIUM HYDROXIDE, ORGANIC ACIDS AND MINOR CONSTITUENTS

$NaH_2PO_2 \cdot H_2O$, %	0	6·0	12·0	18·0
$Na_2SO_4 \cdot 10H_2O$, %	0	5·0	10·0	15·0
Reading, *chart divisions*	35·5	35	35	35

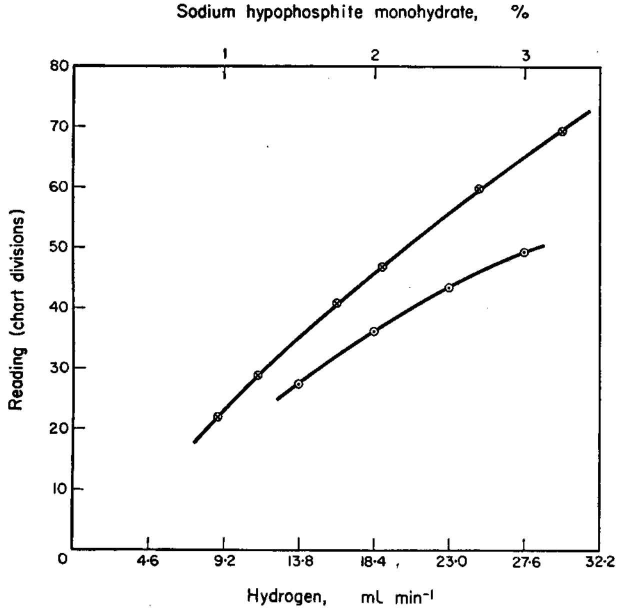

FIG. 2—Calibration graph (solution: 2% nickel sulphate heptahydrate, organic acids and minor constituents):
—○—○— calibration against sodium hypophosphite monohydrate,
—⊗—⊗— calibration against hydrogen.

TABLE IV—CATALYST EFFICIENCY

$NaH_2PO_2 \cdot H_2O$, %	1·5	2·0	2·5	3·0
Hydrogen (theoretical), *ml. min*$^{-1}$	13·8	18·4	23·0	27·5
Hydrogen (actual), *ml. min*$^{-1}$	10·7	14·2	17·1	19·7
Catalyst efficiency, %	78	77	75	72

solution flowing at the normal rates, then through a soap film flow meter and finally into the detector unit.

From the results shown in Fig. 2 the efficiency of the catalyst was calculated for several concentrations of hypophosphite (see Table IV).

Zusammenfassung—Ein Apparat zur kontinuierlichen, automatischen Bestimmung von Hypophosphit in einer Nickelplatierungslösung wird beschrieben. Nach katalitischer Oxydation des Hypophosphits wird der gebildete Wasserstoff verbrannt und die Flammtemperatur als Mass für den Gehalt gemessen. Die Ergebnisse werden durch Änderungen der Konzentration anderer anwesender Ionen nicht beeinflusst. Temperaturänderungen zwischen 20 und 70° haben nur geringen Einfluss.

Résumé—Les auteurs décrivent un appareil qui permet le dosage automatique continu des ions hypophosphite dans une solution complexe de revêtement de nickel non électrolytique. Après oxydation catalytique de l'hypophosphite, l'hydrogène dégagé est brulé; la températures de la flamme est utilisée comme mesure de la teneur en hydrogène. Les variations de concentrations des autres ions présents dans la solution n'influent pas sur les résultats. Des variations de températures dans le domaine de 20 à 70° n'ont pas d'effet important.

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INDIRECT DERIVATOGRAPHIC DETERMINATION OF CALCIUM, STRONTIUM AND BARIUM IONS IN THE PRESENCE OF ONE ANOTHER

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Summary—For the determination of calcium, strontium and barium in one sample, they are precipitated together in the form of the mixed oxalate hydrates. An aliquot of the precipitate is treated in a derivatograph fitted with a furnace that can be heated to 1150°. From the curves which result, the following values are obtained: precipitate weight, weight of carbon dioxide formed in the decomposition of calcium carbonate and weight of carbon dioxide formed in the decomposition of strontium carbonate. From these three values, the amounts of calcium, strontium and barium in the sample can be calculated. The values used for the calculations were chosen from five values after an evaluation of the possible errors.

IN a previous communication[1] we reported an indirect derivatographic determination of calcium, strontium and barium ions. The basis of the method is to precipitate these ions in the form of oxalates, and under thermal decomposition we measured the total weight of precipitates and the weights of water (of crystallisation) and carbon dioxide formed and removed during the process. More recent investigations have shown that the method can be improved if the derivatographic measurement is finished at a higher temperature, at about 1100°, and the weight of carbon dioxide, formed in the thermal decomposition of strontium carbonate, is also measured.

EXPERIMENTAL

Reagents

Calcium chloride, strontium chloride, barium chloride: 0·05 *M* solutions were prepared from analytically pure reagents. Their accurate concentrations were determined by the Winkler methods.[2,3,4]

Sodium oxalate: 2·5% solution.

Acetic acid: 1*M*.

Wash liquid: Ethyl alcohol.

Apparatus

The measurements were made by the derivatograph of Paulik, Paulik and Erdey.[5] We used a furnace that could be heated up to 1150°. The heating rate was controlled at 10° per min. The weights of precipitates used were about 400 mg.

Procedure

Neutralise 50–400 ml of solution containing 20–200 mg of calcium, 40–200 mg of strontium and 10–200 mg of barium to methyl orange, and add for each 100 ml 3 ml of 1*M* acetic acid. Boil the solution and add, dropwise, 2·5% sodium oxalate slowly in excess. (The solution should not contain ammonium salts because barium oxalate does not precipitate quantitatively in the presence of ammonium ions.) Let the precipitate stand overnight, and filter on a fine-porosity (G4) glass filter. Wash the precipitate first with several ml of cold water, then with 15 ml of ethyl alcohol, and finally dry by drawing air through the precipitate to constant weight. Weigh the dry precipitate. From the precipitate weigh a 0·2-g to 0·4-g aliquot accurately into the sample-holder crucible of the derivatograph. In calculating the results, the ratio of total precipitate weight: aliquot weight must be used as a multiplication factor. Use a 10°/min heating rate for the derivatographic measurement, and finish the procedure at 1140–1150°. From the developed derivatograms, results can be calculated on the basis of considerations described later.

DISCUSSION

In Fig. 1 a derivatogram obtained by the method is shown. The derivatograph marks the curves as a function of time. To achieve more comparable data, the derivatographic curves are re-drawn as a function of temperature. For simplicity the weights are calculated for 1 g of precipitate, although the precipitate weights used were about 0·2–0·4 g. Accurate calculation of the results can, of course, be made without any material alteration of the original derivatograms.

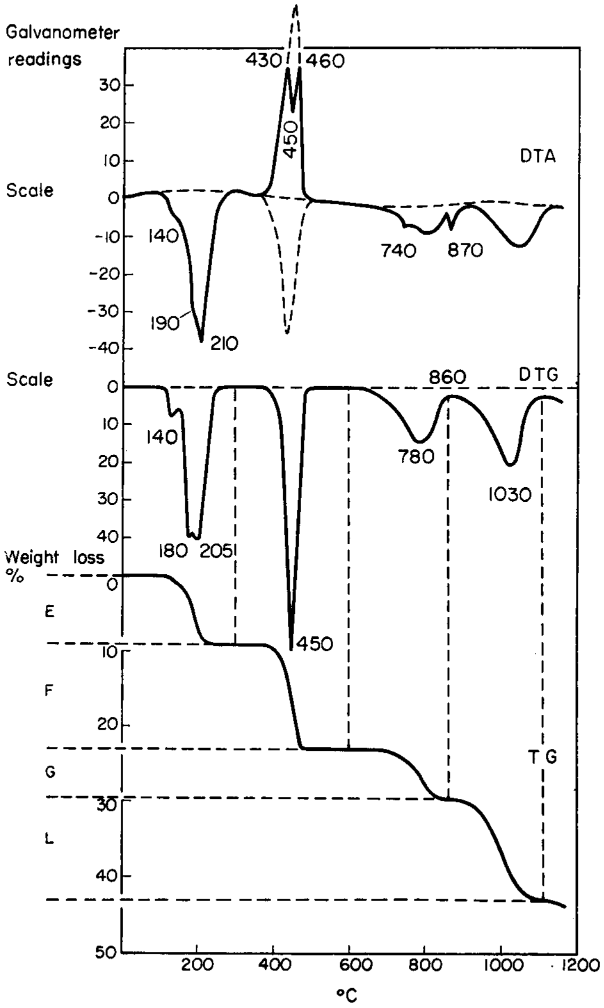

FIG. 1

From the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermoanalytical (DTA) curves, it can be seen that the decomposition processes are going on independently of one another. The precipitate showed no weight-losses up to 100°, *i.e.*, the air-dry precipitate contained no residual humidity. If, however, the precipitate contains moisture, the weight at 100° must be chosen as a "precipitate weight". Between 100 and 250° the water of crystallisation of the precipitates is being lost. In acetic acid medium, calcium and strontium oxalates each precipitate with 1 mole of water of crystallisation, while barium oxalate has 0·5 mole water of crystallisation. According to the curves the oxalate hydrates lose their water content in the order barium, strontium, calcium. Under these experimental conditions, only barium oxalate hydrate is decomposed separately (at 140°), and decomposition of strontium and calcium oxalates took place at nearly identical temperatures; double peaks (180 and 205°) and inflexion points show that the two decomposition processes took place in quick succession.

After the loss of water, the anhydrous oxalates had constant weights between 250° and 360°. Then the decomposition of all three anhydrous oxalates took place at the same time. The rate of decomposition is maximal at 450°. Under other experimental circumstances, however, decomposition of the single oxalates can be obtained separately in the order calcium, strontium, barium, that is in the reverse order to the oxalate hydrates.[6]

At the decomposition of the oxalate hydrates there is an exothermal peak on the DTA curve. Although the processes $M(COO)_2 \rightarrow MCO_3 + CO$ are endothermal, carbon monoxide, formed in the decomposition, partly burns in the furnace area, yielding the exothermal peak. As a result of these two opposing processes, curves of various shapes can be gained, because these processes may be shifted in time.[7] The probable shapes of the two opposing curves are added in dotted lines to the DTA curve.

The three carbonates formed have constant weights between 500° and 620°, and first calcium carbonate, then strontium carbonate decomposes with loss of carbon dioxide, the oxides being formed. Decomposition of calcium carbonate begins at 620° and under these experimental circumstances is finished at 860°. Within this temperature range the decomposition of strontium carbonate begins, and is complete at 1100°. Decomposition of barium carbonate only begins above 1100°. At 740° and 870° on the DTA curve the endothermal recrystallisation processes of strontium and barium carbonates respectively are indicated. If carbon dioxide is removed from the furnace space by suction, the partial pressure of carbon dioxide decreases and the reactions take place at lower temperatures. The decomposition temperatures are also shifted towards lower values if a smaller heating rate is used. If for example the heating rate is 2°/min, strontium carbonate is completely decomposed at 1000°.

CALCULATION OF THE RESULTS

From the TG curve, in conjunction with the DTG minima, the following data can be obtained: weight of dry precipitate (at 100°), *D*, weight of removed water of crystallisation, *E*, weight of carbon monoxide formed in the decomposition of the oxalates, *F*, weight of carbon dioxide formed in the decomposition of calcium carbonate, *G*, and weight of carbon dioxide formed at the decomposition of strontium carbonate, *L*. From these data the amounts of calcium, *C*, strontium, *S*, and barium, *B*, can be calculated. Of the five values (*D*, *E*, *F*, *G*, *L*) only three are needed for the calculation of the three unknown values (*C*, *S*, *B*). The three values used for the calculation must be so chosen, that the error should be as small as possible. Of the values *G* and *L* must be used in every case, because from these calcium and strontium can be determined directly (i.e., the error of the result is equal to the error of the measurement). The determination of barium however is made from three values, indirectly; the error of such measurements, as we have pointed out previously,[8] will be much greater than the errors of the individual measurements.

It is therefore necessary to choose one from among the D, E and F values. Errors were calculated using all possible combinations (G, L, D; G, L, E; G, L, F) as described previously.[1,8] It was assumed that the amounts of the single components were

Table I

$$C = S = B = 1$$

$$\frac{\Delta D}{D} = \frac{\Delta E}{E} = \frac{\Delta F}{F} = \frac{\Delta G}{G} = \frac{\Delta L}{L} = 0{\cdot}1\%$$

Values used for calculation	$\frac{\Delta C}{C}$, %	$\frac{\Delta S}{S}$, %	$\frac{\Delta B}{B}$, %	total error, %
D, G, L	0·1	0·1	0·78	0·98
E, G, L	0·1	0·1	1·64	1·84
F, G, L	0·1	0·1	1·76	1·96

Table 2

	Taken, *mg*	Found, *mg*	Difference	
			mg	%
C	22·7	22·7	0·0	0·0
S	42·5	42·8	+0·3	+0·7
B	39·3	37·4	−1·9	−4·8
C	22·7	22·5	−0·2	−0·9
S	42·5	42·7	+0·2	+0·5
B	39·3	39·1	−0·2	−0·5
C	45·5	45·2	−0·3	−0·7
S	42·5	42·3	−0·2	−0·5
B	39·3	38·2	−1·1	−2·8
C	45·5	44·9	−0·6	−1·3
S	42·5	42·9	+0·4	+0·9
B	39·3	38·7	−0·6	−1·5
C	22·7	22·4	−0·3	−1·3
S	85·0	85·6	+0·6	+0·7
B	39·3	40·0	+0·7	+1·8
C	22·7	22·5	−0·2	−0·9
S	85·0	85·8	+0·8	+0·9
B	39·3	39·9	+0·6	+1·5
C	22·7	22·6	−0·1	−0·4
S	42·5	42·1	−0·4	−0·9
B	80·8	80·9	+0·1	+0·1
C	22·7	22·8	+0·1	+0·4
S	42·5	42·9	+0·4	+0·9
B	80·8	79·9	−0·9	−1·1

unity and equal ($C = S = B = 1$), and that the relative error of the single measurements were in all cases 0·1% $\left(\frac{\Delta D}{D} = \frac{\Delta E}{E} = \frac{\Delta F}{F} = \frac{\Delta G}{G} = \frac{\Delta L}{L} = 0{\cdot}1\%\right)$. Since only comparable results were required, these assumptions could be justified. The errors $\frac{\Delta C}{C}, \frac{\Delta S}{S}, \frac{\Delta B}{B}$ obtained by the calculations are shown in Table I.

According to this, the least error occurs after calculations are made on the basis of the *D*, *L*, *G* values.

On the basis of simple stoichiometric considerations, the amounts of calcium, *C*, strontium, *S*, and barium, *B*, can be obtained from the precipitate weight, *D*, the weight of carbon dioxide formed in the decomposition of calcium carbonate, *G*, and the weight of carbon dioxide formed in the decomposition of strontium carbonate, *L*, by the following equations:

$$C = 0{,}91068 \,.\, G$$

$$S = 1{,}9911 \,.\, L$$

$$B = 0{,}58603 \,.\, D - 1{,}9457 \,.\, G - 2{,}5788 \,.\, L$$

The results are obtained in mg if the amounts of *D*, *L* and *G* are also in mg. The final results must be multiplied by the factor representing the ratio of total precipitate to the aliquot used.

The results of some determinations are shown in Table II.

Zusammenfassung—Zur Bestimmung von Ca, Sr und Ba in einer Probe muss man die Ionen zusammen als Oxalate fällen. Ein aliquoter Teil des Niederschlages wird in den Probetiegeln eines Derivatographen gewogen, der auf 1150°C heizbar ist. Ein Derivatogramm wird aufgenommen und aus ihm folgende Daten abgelesen: Gewicht des Niederschlages, Gewicht des Kohlendioxyds aus der Zersetzung des Calciumcarbonates und Gewicht des Kohlendioxydes aus der Zersetzung des Strontium carbonates. Mit diesen Daten können die Gehalte der drei Komponenten errechnet werden. Die Daten zur Berechnung wurden von 5 Bestimmungen genommen um eine Fehlerrechnung zu ermöglichen.

Résumé—Pour le dosage du calcium, du strontium et du baryum dans un échantillon, on les précipite ensemble sous forme d'hydrates et d'oxalates mixtes. Une partie aliquote du précipité doit être pesée dans le creuset support de l'échantillon; ce creuset fait partie d'un dérivatographe, ayant un four qui peut être chauffé à 1150°C. Une mesure dérivatographique est possible et les résultats suivants peuvent être obtenus d'après les courbes: poids du précipité, poids de l'anhydride carbonique formé par décomposition du carbonate de calcium et poids d'anhydride carbonique formé par décomposition du carbonate de strontium. D'après ces trois valeurs, les quantités de calcium, strontium et baryum dans l'échantillon peuvent être calculées. Les résultats, utilisés pour les calculs, sont choisis parmi cinq valeurs en se basant sur le calcul d'erreur.

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SEPARATION AND DETERMINATION OF CHROMIUM, TUNGSTEN, MOLYBDENUM AND VANADIUM BY PARTITION CHROMATOGRAPHY

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Summary—A method has been proposed for the separation and determination of microgram amounts of chromium, vanadium, tungsten and molybdenum, using the technique of partition chromatography. The solvent-mixture employed consisted of sym-collidine, 10 parts; iso-butanol, 38 parts, concentrated hydrochloric acid, 52 parts (v:v:v).

INTRODUCTION

VANADIUM of Group Vb of the Periodic Table, and chromium, tungsten and molybdenum of Group VIb show marked similarities in chemical properties and are, in the form of the metals, of considerable importance in alloy steels. In spite of their widespread use, however, methods for the separation and determination of microgram amounts of the four elements are not numerous. Several attempts have been made to separate mixtures of the elements by paper chromatography. Venturello and Ghe[1] used the radial paper chromatographic technique and a solvent-mixture composed of butanol, acetylacetic ester, and hydrochloric acid. Paper treated with perchlorate ion was employed by Murata[2] to separate the elements in the form of anions from each other and from sulphate ions. Aqueous solvents have also been used in an attempt to separate the elements,[3] but R_F values for chromate and molybdate are close, indicating overlap of the bands. Lacourt[4] obtained a more satisfactory separation by developing chromatograms with a mixture of acetone, chloroform and hydrochloric acid, after saturating the tank with the vapours of a mixture of equal parts of methylethylketone and chloroform. Many other solvent-mixtures have been tried, but in most cases there was either extensive tailing or the group of elements tended to migrate at the same rate.

This paper describes the investigations carried out and the results obtained with a solvent-mixture of the following composition: sym-collidine, 10 parts; iso-butanol, 38 parts; concentrated hydrochloric acid, 52 parts (v:v:v).

EXPERIMENTAL

Sym-collidine has been used in other circumstances as a constituent of solvent-mixtures in paper chromatography.[5] However, because of its high viscosity, it is necessary to dilute this solvent, if excessive periods of development are to be avoided. Because of its miscibility with alcohols, but low miscibility with water, a number of the former were examined and iso-butanol was ultimately selected. Because of the low basic strength of the anions, hydrochloric acid was chosen as a source of protons. To determine the optimal amount of collidine that should be present in the solvent-mixture, chromatograms were developed with solvent-mixtures containing varying proportion of collidine. The results are summarised in Table I.

It will be observed that satisfactory and consistent separations are achieved with solvent-mixtures containing 5 to 10% of sym-collidine. Further investigations indicated that the best combination was a solvent-mixture composed of 10 parts of sym-collidine, 38 parts of iso-butanol and 52 parts of concentrated hydrochloric acid.

Procedure

Solutions of sodium vanadate, molybdate, tungstate and chromate were prepared from AnalaR grade compounds, and mixtures containing varying proportions of the anions were obtained by mixing aliquots of these solutions. Using a micropipette, 0·01 ml of a mixture was applied to points 6 cm from the end of the strips of Whatman No. 1 filter paper, which were 40 cm long and 5 cm wide. The spots were allowed to dry in the air for 10 min, then the papers were transferred to a Shandon Chromatank previously saturated with the vapours of the developing agents (a beaker of solvent-mixture was placed in the tank at least 1 hr before introducing the strips). After insertion of the papers, the solvent reservoir was filled with the solvent-mixture, the tank was closed, and the chromatogram was allowed to develop by the descending technique for a period of 24 hr. During this time the solvent front advanced approximately 30 cm.

TABLE I.—EFFECT OF COLLIDINE CONCENTRATION ON R_F VALUES

* Collidine content of solvent mixture, *volume %*	R_F values			
	Cr	V	W	Mo
0	0·65	0·54	0·65	0·65
1	0·34	0·39	0·52	0·52
2	0·32	0·48	0·66	0·80
4	0·29	0·35	0·64	0·77
5	0·29	0·39	0·68	0·79
10	0·28	0·37	0·68	0·81
30	0·92	0·85	0·65	0·65 (elongated)

* All the above solvent mixtures contained, in addition to collidine 38% of isobutanol, the remainder being concentrated hydrochloric acid.

After development, the strips were removed from the tank, and were allowed to hang in the air for 1 hr. They were then dried in an oven at 60°.

TABLE II.—DETECTION OF THE ELEMENTS

No.	Cr		V		W		Mo	
	μg	R_F	μg	R_F	μg	R_F	μg	R_F
1	32	0·30	22	0·40	17	0·70	8	0·83
2	32	0·28	44	0·38	11	0·69	40	0·80
3	32	0·28	4	0·38	28	0·68	20	0·84
4	6	0·29	8	0·40	55	0·69	20	0·83
5	—	—	—	—	28	0·69	20	0·84
6	—	—	22	0·38	28	0·70	20	0·84
7	16	0·28	—	—	28	0·68	20	0·82
8	16	0·30	22	0·40	28	0·71	20	0·84
9	96	0·37	4	0·45	17	0·71	8	0·82
10	6	0·28	8	0·37	110	0·69	80	0·80
11	6	0·28	44	0·38	17	0·71	8	0·81

Detection of the elements

The components of the mixture were located by spraying the dry chromatogram with suitable detecting agents. One strip was sprayed with a mixture of 5% pyrogallol in alcohol and was then dried. The elements, if present, produce four bands as follows: green (Cr), blue (V), light brown (W), and bluish (Mo). A second strip was sprayed with 1% 8-hydroxyquinoline solution in a mixture of sodium acetate, acetic acid and water. With this reagent the elements produce bands which are yellow, excepting that of vanadium, which has a greenish tinge.

The R_F values were calculated for each ion, and the results are summarised in Table II.

It will be observed from the Table that less than 10 μg of each element can be separated from much higher concentrations of other elements and detected. It will also be observed that the R_F value of a particular species is only slightly influenced by the concentration of the other species present.

Determination of the elements

For the determination of the four elements, the procedure described above was used for separation, except that Whatman No. 40 paper was substituted for Whatman No. 1 paper. The former is acid washed paper, and was found to yield more compact bands after development.

To carry out the determination, four chromatograms of the same mixture were prepared in the same tank simultaneously. After drying, one of the chromatograms was sprayed with pyrogallol and other with 8-hydroxyquinoline reagent. By this means the bands of the individual components of the mixture were located. By comparison the position of the elements on the untreated chromatograms were located. A 3-cm square was cut around the region of the detected element. The paper removed in this way was boiled with 10 ml of $1N$ hydrochloric acid for 15 min to extract the metal ion. The extract was cooled, filtered and used for the determination of the element using the appropriate procedure, as indicated below.

(*a*) *Chromium:* The acid extract was carefully evaporated to dryness, and the residue was dissolved in water. By boiling with excess sodium peroxide until the excess was destroyed, all the chromium was oxidised to the sexavalent state. The quantity of chromium present was then determined photometrically using the diphenylcarbazide method.[6] Measurements were made at 540 mμ, and the chromium content was evaluated from a calibration curve.

(*b*) *Vanadium:* The hydrochloric acid extract was made alkaline with sodium hydroxide and was then boiled with sodium peroxide, to oxidise vanadium to the quinquevalent state. The solution was filtered into a 50-ml volumetric flask, and 5 ml of $4N$ H_2SO_4, 1 ml of 1:1 phosphoric acid and 0·5 ml of $0{\cdot}6M$ sodium tungstate were added. The mixture was shaken until the yellow colour of phosphotungstovanadic acid was formed. The solution was now boiled, cooled and made up to a standard volume. The extinction was measured at 400 mμ, and the vanadium content was determined from a calibration graph.

(*c*) *Tungsten:* The hydrochloric acid extract was transferred to a separating funnel together with 1 ml of $1N$ NaOH, 6 ml of 5% KCNS solution, and 10 ml of 10% $SnCl_2$ in concentrated hydrochloric acid. The solution was well shaken after the addition of each reagent. The mixture was allowed to stand for 1 hr, to permit the full development of the yellow colour. The thiocyanate complex was then extracted with two 10-ml portions of ethyl ether which had previously been shaken with potassium thiocyanate and stannous chloride solution.

The ether extract was transferred to a 25-ml volumetric flask and was diluted to standard volume with ether. The extinction of the solution was measured at 420 mμ,[6] and the tungsten content was determined by reference to a calibration curve similarly prepared.

(*d*) *Molybdenum:* The hydrochloric acid extract was transferred to a separating funnel, and 6 ml of 5% KCNS and 2 ml of 10% $SnCl_2$ in concentrated hydrochloric acid were added. After shaking, the amber-red colour formed was extracted into ether, as for tungsten. The extinction of this solution at 475 mμ[6] was measured, and the amount of molybdenum present was obtained by reference to a calibration graph.

Blanks were used in all the colorimetric determinations.

TABLE III.—ANALYSIS OF MIXTURES

Cr		Mo		W		V	
Given	Found	Given	Found	Given	Found	Given	Found
9	8·5	—	—	—	—	90	71
10	9	12	20	50	42	10	10
—	—	17	17	40	26	42	20
90	80	10	9	5	4·5	—	—
85	80	—	—	10	9	10	10

RESULTS

As a check on the procedure, a number of "unknown" mixtures were analysed by one of us (A. S. W.). The results are summarised in Table III. (All quantities in the Table are in micrograms.)

It will be observed from Table III that complete recovery of the individual elements was achieved in only three cases. In the others, recovery was 90% or more. In view of the small amount of material present, these results can be considered to be very satisfactory.

The low results may in part result from the following causes: firstly, the element may not be completely located in the "detected "spot on the chromatogram because of slight tailing from the starting point; secondly, extraction of the element from the paper may not have been complete; thirdly, there may have been errors or losses in the final evaluation stage of the analysis.

DISCUSSION

The use of an acid solvent-mixture for the paper separation of this group of anions requires a little explanation. The metals were placed on the paper in the form of their sodium salts, chromate, vanadate, tungstate and molybdate. The aqueous phase therefore contained the anions of group Vb and group VIb metals plus sodium ions, and hydroxonium ions are introduced by the mobile solvent. Under these conditions equilibria similar to the following arise:

$$4H^+ + CrO_4^= \rightleftharpoons 2H_2CrO_4 \rightleftharpoons H_2O + Cr_2O_7^=$$

Sym-collidine may also react with the acid introduced into the solvent, and become protonated at the basic nitrogen

$$\text{Collidine} + H^+ \rightleftharpoons [\text{Coll. H}]^+$$

The position of equilibrium in these reactions will be dependent on the acidity of the solvent mixture, since the concentration of hydrogen ions available in the aqueous phase will be controlled by partition of these ions from the mobile organic phase back into the water phase. Increasing the collidine content of the developing agent might therefore have several effects: (i) The increased concentration of protonated material can attract (by ion association) a larger proportion of anions into the mobile phase. This effect was exhibited by molybdenum (Table I); (*ii*) dissociation of protonated collidine can increase the acidity of the aqueous phase resulting in increased association in this phase and less solution in the mobile solvent. This effect was shown by chromium and vanadium; (*iii*) this reduced movement could be caused by partial reduction of these elements by the paper and chloride ions, since a large excess of collidine (*e.g.* 30%) resulted in enhanced movement (greater solution in the organic phase) of these two elements. The movement of tungstate did not appear to be significantly influenced by the presence of collidine in the solvent.

The complexity of the species that may be derived from the four elements studied in aqueous solution (*e.g.*, poly-salts) makes a complete explanation impossible, but in general terms, the separation of the anions can be explained by a mechanism based on the association of the anions with protonated collidine. The butanol in the solvent acts merely as a diluent for the collidine, and accelerates the rate of development of the chromatogram by reducing the viscosity of the solvent mixture.

Zusammenfassung—Eine verteilungschromatographische Methode zur Trennung und Bestimmung von Mikrogrammengen von Chrom, Vanadin, Wolfram und Molybdän wird vorgeschlagen. Die verwendete Lösungsmittelmischung ist sym.-Collidine:Isobutylalkohol:conc. Salzsäure = 10:38:52 (volumsteile).

Résumé—Les auteurs proposent une méthode de séparation et de dosage de microgrammes de chrome, vanadium, tungstène et molybdène, par chromatographie de partage. Le mélange de solvants utilisé comprend: 10 parties en volumes de collidine symmétrique, 38 parties d'isobutanol et 52 parties d'acide chlorhydrique concentré.

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STEPWISE DETERMINATION OF CADMIUM, MERCURY AND TELLURIUM

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Summary—Methods for the analysis of the tellurides of cadmium and mercury are described and discussed. In analysing mixtures of the two tellurides, cadmium and mercury can be determined by two stepwise EDTA titrations and tellurium is then determined by difference. Alternatively, tellurium and mercury can be directly determined gravimetrically in the presence of EDTA as tellurium dioxide and mercury-Bismuthiol II. For analysing small quantities, both cadmium and mercury are determined photometrically by dithizone methods at different acidities, and tellurium is determined photometrically by the Bismuthiol II method. The three elements may be determined in one solution, so that accurate results may be obtained on a small amount of sample. The methods are simple and rapid.

INTRODUCTION

FOR analysing either cadmium telluride or mercury telluride a similar method to that used for analysing lead telluride can be employed, *viz.* the tellurium is determined gravimetrically and the lead titrated complexometrically.[1] This method cannot, however, be directly applied to the analysis of mixtures of tellurides. Also, a limited sample size can often create an analytical problem because it requires the use of sensitive methods for the determination of the separate elements. The present paper reports methods suitable for determining cadmium, mercury and tellurium, both in limited and unlimited sample sizes; the analysis of three elements in one solution makes their determination possible for a minimum amount of sample. For unlimited samples cadmium and mercury are titrated together complexometrically; then, after precipitating the mercury from this solution as its Bismuthiol II complex,[2] mercury may be directly determined by weighing the precipitate or by titrating the EDTA liberated from the mercury-EDTA complex. Cadmium is obtained by difference. Tellurium is determined gravimetrically as tellurium dioxide,[1] or obtained by difference between the amount of sample taken and the sum of both mercury and cadmium found. For limited samples both cadmium and mercury are determined photometrically with dithizone[3] at different acidities, and tellurium is determined by the Bismuthiol II method.[4] The dithizone methods for cadmium and mercury are well known; however, without the two recently developed methods for tellurium the analysis of the tellurium mixture would not be easy, especially if the supply of sample is limited.

EXPERIMENTAL

Reagents

0·025*M EDTA solution;* Prepared from disodium ethylenediaminetetra-acetic acid and standardised by an appropriate method.

0·025*M standard zinc solution:* Prepared from pure zinc metal and hydrochloric acid.

Erio T indicator solution: Grind to a fine powder, 0·1 g of Eriochrome Black T with 10 g of sodium chloride.

pH 10 *buffer solution:* Dissolve 70 g of ammonium chloride in 570 ml of ammonium hydroxide (sp. gr. 0·9) and dilute to 1 litre with water.

Bismuthiol II solution: A 1% aqueous solution of the potassium salt of mercaptophenylthiolthiadiazolone.

Standard cadmium solution: Dissolve 0·5000 g of pure cadmium in 10 ml of nitric acid (1:1) and dilute to 500 ml with water. Prepare a solution containing 1·0 μg of cadmium per ml by appropriate dilution.

Standard mercury solution: Dissolve 0·1354 g of mercury II chloride in 100 ml of 1*N* sulphuric acid (1 mg of mercury per ml). Prepare a solution containing 2·0 μg of mercury per ml by appropriate dilution.

Standard tellurium solution: Dissolve 0·1 g of pure tellurium in 5 ml of concentrated sulphuric acid by heating. Fume to evaporate off most of the acid. After cooling, carefully add 100 ml of water and dissolve the tellurous acid precipitate by adding a minimum amount of 4*M* potassium hydroxide solution, making to 1 litre. This solution contains 0·1 mg of tellurium per ml. Prepare a solution containing 5 μg of tellurium per ml by appropriate dilution.

Citric acid: 1*M*.

Ammonium sulphate solution: A 50% w/v aqueous solution adjusted to pH 2·2 with sulphuric acid.

Sulphuric acid: 5*N*.

Dithizone solution: A 0·01% w/v solution in chloroform. Store in a refrigerator. Prepare a fresh solution of 0·001% in chloroform from the stock solution every day.

Sodium hydroxide solution: A 50% solution obtained from J. T. Baker Chemical Company.

Apparatus

Beckman spectrophotometer Model DU and Beckman pH meter Model G or equivalent were used. Other chemicals used were reagent grade.

Procedures

1. *Dissolution of sample*

A. *For unlimited samples.* Weigh 0·1 g or more of sample into a 250-ml beaker. Add 2 ml of concentrated nitric acid and 1 ml of concentrated hydrochloric acid. If necessary, heat gently on a hot plate to speed up the reaction until solution is complete.

B. *For limited samples.* Add 1 ml of concentrated nitric acid and 1 or 2 drops of concentrated hydrochloric acid.

2. *Analysis of solution 1-A*

A. *Tellurium.* Add accurately a slight excess of EDTA and dilute to approximately 50 ml with water. Adjust to pH 10 with ammonium hydroxide solution. The solution should be clear and colourless. Add Erio T indicator (approximately 80 mg) and back titrate the excess EDTA with the standard zinc solution, the end-point being from blue to purplish red. This titration gives the sum of the cadmium and mercury contents, and the tellurium content is obtained by difference. If its direct determination is desired, readjust the pH to 4·5 with hydrochloric acid to precipitate tellurous acid. Cover the beaker with a watch glass, boil, cool to room temperature or below, and filter through a sintered glass crucible. Wash three times with a few-ml portions of 50% methanol. Dry at 132° to 140° until constant weight is obtained. Weigh as TeO_2, the gravimetric factor being 0·7995.

B. *Mercury.* Heat the filtrate from the tellurium determination to boiling and make ammoniacal; add a slight excess of Bismuthiol II and stir to precipitate the mercury complex. While hot, filter the solution through a sintered glass crucible. Wash three times with water. (If the gravimetric determination of mercury is desired, dry the precipitate at 105° until constant weight is obtained; the gravimetric factor is 0·3080.) To the filtrate add 5 ml of the pH 10 buffer solution, (Erio T indicator powder, if necessary) and back titrate the EDTA liberated from the mercury-EDTA complex with the standard zinc solution. This titration is for mercury. The titrimetric result may be compared with the gravimetric one.

C. *Cadmium.* The difference in the two EDTA titrations is for cadmium.

3. *Analysis of solution 1-B*

The solution is made to a suitable volume, 50 or 100 ml.

A. *Mercury.* To an aliquot containing not more than 20 μg of mercury, add suitable amounts of 5*N* sulphuric acid and water so that the final volume is approximately 25 ml and contains 25 milliequivalents of sulphuric acid. Add 10 ml of 0·001% dithizone in chloroform and shake vigorously for 1 min. Filter the extract through glass wool and measure the absorbance at 500 mμ against a reagent blank. Prepare similarly a calibration curve with known amounts (less than 20 μg) of mercury.

B. *Cadmium.* After the mercury determination, drain off practically all of the organic phase. Shake the aqueous phase with a few ml of chloroform to remove any dithizone remaining. Drain off the chloroform as completely as possible and discard it. Add 2 ml of 50% sodium hydroxide solution to raise the pH >12, and 4 drops of 20% hydroxylamine hydrochloride solution. Cool and extract for 1 min with 10 ml of 0·001% dithizone in chloroform (5 ml may be used if the amount of cadmium in the solution is less than 2 μg). Filter the extract through glass wool and measure the absorbance at 530 mμ against a reagent blank. Prepare similarly a calibration curve with known amounts (less than 10 μg) of cadmium.

C. *Tellurium.* After the cadmium determination, drain off practically all of the organic layer. Acidify the aqueous layer and remove any dithizone by extracting with chloroform. Separate the aqueous phase and adjust to pH 2·2 after adding 1 ml of 0·025*M* EDTA solution, 1 ml of 1*M* citric acid solution, and 6 ml of 50% ammonium sulphate solution. Add 3 ml of 1% Bismuthiol II solution and let stand for 20 min or longer. Again adjust to pH 6·5, transfer to a 125-ml separatory funnel, and extract with 10 ml of carbon tetrachloride for 1 min. Filter the extract through glass wool and measure the absorbance at 335 mμ against a reagent blank. Prepare similarly a calibration curve with known amounts (less than 50 μg) of tellurium.

DISCUSSION AND RESULTS

Since the tellurides are usually made of pure metals, it may be reasonably assumed that the samples contain negligible amounts of impurities. Cadmium telluride was easily decomposed in hot concentrated nitric acid but not in sulphuric acid; mercury telluride could be decomposed in hot sulphuric acid but not easily in nitric acid. An attempt was made to decompose the sample of tellurides of cadmium and mercury with concentrated nitric acid first and concentrated sulphuric acid later; incomplete decomposition resulted. This difficulty is overcome by the use of nitric acid and hydrochloric acid. After complete decomposition the solution, which is made ammoniacal in the presence of EDTA, should be colourless and clear. If the solution becomes dirty brown and turbid, this indicates incomplete decomposition. When chloride was present, mercury was lost upon fuming with sulphuric acid; however, no loss of mercury was noticed when the sample was heated with the mixture of nitric acid and hydrochloric acid at a temperature below 150°. Therefore, the mixture of nitric acid and hydrochloric acid seems to be the best for the decomposition of the sample; gentle heating may be necessary to speed up the reaction.

For analysing either cadmium telluride or mercury telluride, the methods for analysing lead telluride may be directly applied. For analysing a mixture of cadmium telluride and mercury telluride, other methods than the one discussed herein may be feasible for determining cadmium and mercury individually. For example, after separating tellurium as tellurous acid in the presence of EDTA, the combined amount of cadmium and mercury might be found by back titration of the filtrate with a standard magnesium solution. Then a slight excess of cyanide might be added to complex both mercury and cadmium, followed by the addition of formaldehyde to decompose free cyanide and the relatively weak cadmium cyanide complex. A further EDTA titration should give the amount of cadmium. The difference between the combined amount of cadmium and mercury and the amount of cadmium should give the amount of mercury.

When the values of cadmium and mercury are known through two stepwise EDTA titrations, tellurium may be determined by difference. A slightly higher result for mercury was often obtained by the gravimetric method for more than 100 mg of mercury. This may be attributed to the fact that a very small amount of water trapped in the large compact precipitate may be difficultly removed at 105°. Therefore, the EDTA titration is usually preferred. However, the gravimetric results may be used for comparison.

The proposed procedure is simple and accurate (see Table I). All three elements can be determined in one solution. By using EDTA as a masking agent, tellurium is precipitated in the presence of mercury and cadmium, then mercury is precipitated in the presence of cadmium by Bismuthiol II.[2] An examination of the precipitates of tellurium dioxide and of mercury-Bismuthiol II showed that they contained only traces of impurities.

For analysing limited samples of the telluride mixture, the dithizone methods are selective for cadmium and mercury.[3] It is known that mercury can be extracted by

TABLE I. GRAVIMETRIC AND TITRIMETRIC DETERMINATION OF CADMIUM, MERCURY AND TELLURIUM.

Element taken, *mmole*	Form	Found, *mmole*
0·178 Cd	Cd	0·179[b]
0·245 Hg	HgO	0·245[a]
0·470 Te	Te	0·469[c]
0·153 Cd	CdTe	0·150
0·153 Te	CdTe	0·151
0·416 Cd	CdTe	0·413
0·416 Te	CdTe	0·416
0·313 Hg	HgTe	0·318[a]
0·313 Te	HgTe	0·310
0·304 Hg	HgTe	0·302[b]
0·304 Te	HgTe	0·301
0·153 Cd	CdTe + HgTe	0·150[b]
0·313 Hg	CdTe + HgTe	0·316[a]
0·466 Te	CdTe + HgTe	0·461
0·125 Cd	CdTe + HgTe	0·124[b]
0·250 Hg	CdTe + HgTe	0·250[a]
0·375 Te	CdTe + HgTe	0·371

[a] By Bismuthiol II method[2]
[b] By EDTA titration[1]
[c] By gravimetric method as TeO_2[1]

TABLE II. PHOTOMETRIC DETERMINATION OF CADMIUM, MERCURY AND TELLURIUM.

Element taken, *μg*	Found, *μg*
8·0 Hg + 500 Cd	8·1 Hg
8·0 Hg + 500 Te	8·0 Hg
8·0 Hg + 500 Cd + 500 Te	8·0 Hg
2·0 Cd + 40 Hg	2·0 Cd[a]
2·0 Cd + 200 Te	2·0 Cd
2·0 Cd + 40 Hg + 200 Te	2·0 Cd[a]
30 Te + 5 Cd	30·1 Te
30 Te + 20 Hg	30·0 Te[a]
30 Te + 5 Cd + 20 Hg	30·0 Te[b]
20 Te + 10 Cd + 20 Hg	25·5 Te[c]
30 Te + 10 Cd + 20 Hg	29·8 Te[d]

[a] Mercury was removed by dithizone in 1*N* sulphuric acid.
[b] Both mercury and cadmium were removed by dithizone.
[c] Only mercury was removed, no EDTA was added.
[d] Only mercury was removed and 0·1 mmole of EDTA was added.

dithizone in the presence of many metals, including cadmium. It has been reported that tellurium is also extracted by dithizone at pH 1 and in $1N$ hydrochloric acid medium.[5] However, it was found that no noticeable tellurium was extracted in $1N$ sulphuric acid, as demonstrated in Table II. The dithizone extraction of cadmium at $pH > 12$ is selective; mercury is previously removed, and tellurium is not extractable by dithizone in an alkaline medium. Although the addition of cyanide makes the dithizone extraction for cadmium more selective, it may not be necessary for the pure materials studied. If the presence of significant amounts of interfering metals, *e.g.*, copper, is known, cyanide must be used. The subsequent tellurium determination with Bismuthiol II should be made after the cyanide has been removed either by vaporisation from the acid medium or by decomposition with formaldehyde. Alternatively, tellurium may be determined on a separate aliquot after removing mercury, if sufficient sample is available. By using EDTA as a masking agent, it was found that small amounts of cadmium did not affect the tellurium determination. Cheng's Bismuthiol II method for tellurium is the most sensitive chemical method known at present and should not be confused with other less sensitive methods employing the same reagent; for details the original paper should be consulted.[4] Nitrite and other oxidising agents interfere with the determination of tellurium with Bismuthiol II; therefore, any brown fumes formed during the dissolution of the sample with hydrochloric acid and nitric acid should be removed. If their presence is suspected, the solution may be evaporated to sulphuric acid fumes after separating the mercury and cadmium and then followed by the Bismuthiol II method for tellurium.

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Zusammenfassung—Methoden zur Analyse der Telluride von Cadmium und Quecksilber werden diskutiert. Cadmium und Quecksilber können stufenweise mit ÄDTE titriert werden und das Tellur wird aus der Differenz (Gewicht des Ausgangsmaterials) erhalten. Oder aber Tellur und Quecksilber können direkt gravimetrisch als TeO_2 in Gegenwart von ÄDTE und Quecksilber mit Bismuthiol II bestimmt werden. In kleinen Proben werden Cadmium und Quecksilber bei verschiedener Azidität nach der Dithizonmethode und Tellur mittels Bismuthiol II photometrisch bestimmt. Die drei Elemente können in einer Probelösung bestimmt werden, sodass genaue Ergebnisse auch bei kleinen Probemengen erhalten werden. Die Methoden sind rasch und einfach.

Résumé—L'auteur décrit et discute les méthodes d'analyse des tellurures de cadmium et de mercure. En analysant le produit de départ des mélanges des deux tellurures, le cadmium et le mercure peuvent être dosés par deux titrages successifs au moyen de l'EDTA et le tellure est ensuite déterminé par différence.

Le tellure et le mercure peuvent être dosés directement par gravimétrie en présence d'EDTA sous forme de TeO_2 et de bismuthiol II de mercure. Pour l'analyse de faibles quantités, le cadmium et le mercure sont dosés tous les deux par photométrie par les méthodes à la dithizone à différentes acidités, le tellure est titré par photométrie par la méthode au bismuthiol II. Les trois éléments peuvent être dosés sur une solution, de sorte que l'on peut obtenir des résultats précis sur une faible quantité d'échantillon. Les méthodes sont simples et rapides.

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THE APPLICATION OF AN IMPROVED STEAM DISTILLATION APPARATUS TO THE DETERMINATION OF FLUORIDE IN ROCKS AND MINERALS*

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Summary—The efficiency of the Willard and Winter steam distillation of fluoride can be improved by using sulphuric or phosphoric acid instead of perchloric acid solutions. However, sulphate and phosphate must be kept out of the distillate, for they interfere in many methods of determination, including the commonly-used thorium nitrate titration.

A newly-designed apparatus is described which permits close control of the distillation, and rapid and complete recovery of fluorine, free from significant amounts of sulphate or phosphate. Procedures are outlined whereby fluorine can be quantitatively recovered from silicate rocks and minerals and easily determined with precision and accuracy.

FLUORINE determinations are mostly accomplished after steam distillation according to Willard and Winter.[21] In silicate analysis, preliminary operations normally include an alkaline fusion followed by a Berzelius separation or some modification of it.[8] After steam distillation from acid solution, fluoride in the distillate is determined by one of a number of methods.[19]

The fusion and separation operation has been much simplified as a result of the work of Shell and Craig,[15] and of Grimaldi, Ingram, and Cuttitta,[6] who use a zinc oxide-sodium carbonate flux. Leaching of the melt with water results in the separation of fluorine from most of the silica and alumina in a single operation.

For the determination of fluorine in the distillate, thorium nitrate titration in 50% ethanol was used in this work because in our experience it is reliable and precise. The details of the procedure are due to Ellestad,[4] and are based on the work of Willard and Winter,[21] Hoskins and Ferris,[10] Armstrong,[1] and others. In this titration, phosphate must be absent, and sulphate in excess of about 0·5 mg cannot be tolerated. Undoubtedly other methods of determination are equally satisfactory. Xylenol Orange may prove an excellent reagent for fluorine.[20]

Since steam distillation was first proposed as a key step in the determination of fluorine in silicates, considerable attention has been given to the design of stills in attempts to reduce the time and supervision required,[5,11,12,14] prevent entrainment of the distilling acid,[13] and achieve quantitative recovery of the fluorine.[10] To date, spray traps,[17,18] special steam outlet tubes,[16] and control of distillation rate[9,11] have not been entirely successful. That incomplete recovery of fluorine remains a problem has been confirmed recently by Haff, Butler and Bisso.[7] A valuable study of factors involved in steam distillation of fluorine has been carried out by Dahle and Wichmann,[3] and the whole problem of determining small amounts of fluorine has been exhaustively reviewed by Valach.[19]

To minimise acid entrainment and improve fluorine recovery, a special still has

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been designed (Fig. 1). The essential feature of this apparatus is an internal splash trap which removes entrained acid from the steam without permitting condensation. The distillation from sulphuric acid solution containing a little perchloric acid normally requires about 1 hour, including the time required to bring the sample solution up to distilling temperature. Heating is done by means of a manually controlled flame, but may also be accomplished automatically.[5,12,14]

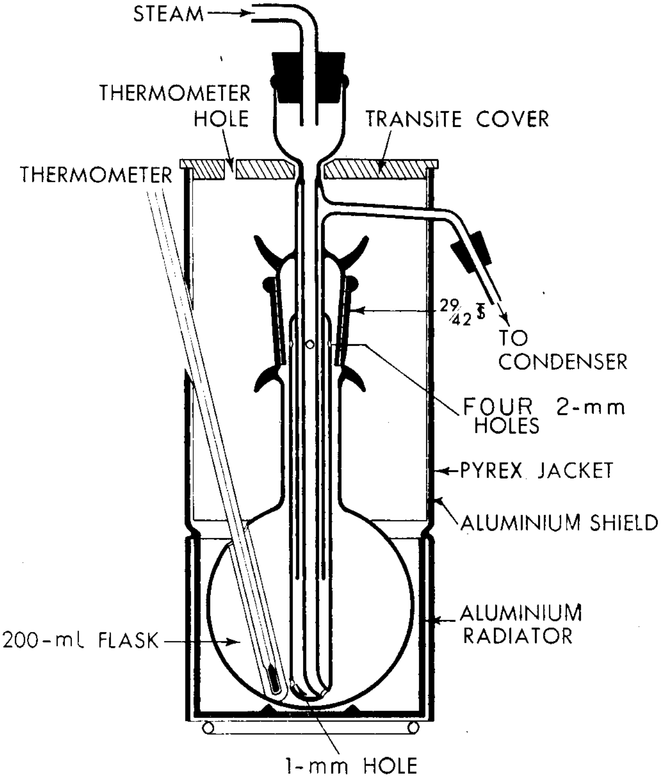

FIG. 1.—Special still for the steam distillation of fluorine.
Steam is generated in a 2000-ml flask by boiling water containing a little sodium hydroxide. A 200-mm coil type Graham condenser is convenient for use with this still.

An air bath consisting of a Pyrex jacket lined with bright aluminium sheet completely encloses the still. A window should be cut in the aluminium for observation purposes.

In operation, steam passes through the sample solution, rises between the neck of the flask and the trap, enters the latter through four 2-mm diameter holes within the 29/42$ stopper, passes downwards to the exit tube which surrounds the steam inlet, and then upwards to the outlet. A 1-mm hole which drains the trap should be located 90° from the thermometer well, rather than immediately opposite it as schematically indicated in the drawing: this avoids erratic thermometer readings.

The steam inlet should dip just below the surface of 30 ml of distilling acid, and the steam exit tube should reach within about 1·5 cm of the surface of the solution at its highest level—*i.e.*, before the distillation is started. If 30 ml of distilling acid are used, and the sample solution and washings do not exceed 25 ml, the end of the steam exit can be as low as the centre of the 200-ml flask. If too much liquid is used, some of it will, of course, be thrown over into the condenser as soon as distillation starts.

A cross-section of the flask and trap at the level of the four 2-mm holes (Fig. 2) gives the recommended tubing dimensions.

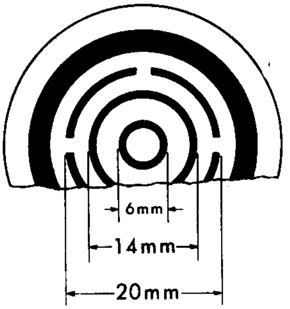

FIG. 2.—Cross section of still at the level of the four 2-mm holes which admit steam to the internal splash trap, showing the recommended tubing dimensions.

In setting up the still, it is advantageous to bolt the cast aluminium radiator to a supporting ring. The air bath may then be supported on the radiator by means of an annular constriction.

The entire still is made of Pyrex glass.

Perchloric acid was employed by Willard and Winter in their original procedure,[21] and has the advantage that moderate concentrations in the distillate are without sensible effect on the thorium nitrate titration. However, distillation of fluorine from perchloric acid is not as effective as from sulphuric or phosphoric acid,[3] because a lower temperature must be used. With the new still, it is possible to take full advantage of the higher temperatures attainable with sulphuric or phosphoric acids, without collecting harmful amounts in the distillate.

Recovery of fluorine from sulphuric acid solution is much improved if a little perchloric acid is also present. Some of this distils with the fluorine and presumably helps to prevent absorption on the glass surfaces within the still. In the recommended procedure, a small perchloric acid addition is made during the preparation of the solution. This addition improves the separation of alumina, and is conveniently used to rinse the fusion crucible, which may otherwise retain a little fluorine.

Shell and Craig[15] have pointed out that reasonably good results for fluorine in silicates can often be obtained without any separations before distillation from perchloric acid solution. In their rapid procedure, the sample is simply fused with sodium carbonate, transferred to the distilling flask with water, and distilled after the addition of perchloric acid. For phosphate rock, this is in fact the preferred procedure, since phosphate prevents complete recovery of fluorine in water leaching of alkali carbonate fusions.

To investigate the possibilities of direct distillation, 0·1 g and 0·2 g of several silicate samples were decomposed by sodium peroxide fusion and distilled directly with sulphuric or phosphoric acids. Experiments with sulphuric acid were not very successful because of the separation of large amounts of gelatinous silicic acid. With phosphoric acid, on the other hand, no difficulties were encountered: the water leach of the peroxide fusion dissolved almost completely, and relatively little silicic acid separated during distillation. The new still proved almost completely effective in preventing the collection of phosphate in the distillate, even when the distilling temperature was increased to 160°. A rapid procedure involving direct distillation from phosphoric acid after sodium peroxide fusion is presented, but should be used with caution: undoubtedly it cannot be used, for example, with samples containing much sulphur, unless a method of determination is available which is unaffected by sulphate.

The longer method given, involving mixed alkali carbonate-zinc oxide fusion and separation of silica and alumina before distillation, is quite generally applicable to silicate rocks and minerals.

EXPERIMENTAL

Reagents

Special flux: Grind together and mix thoroughly zinc oxide and anhydrous alkali carbonates in the ratio K_2CO_3:Na_2CO_3:ZnO: :9:7:3 (parts by weight). Run a blank determination to be sure that the flux does not contain fluorine.

Monochloracetate buffer: Dissolve 9·5 g of monochloracetic acid in water. Neutralise half the solution with carbonate-free sodium hydroxide, using phenolphthalein indicator. Combine and dilute to 50 ml. The buffer should be freshly prepared.

Alizarin Red S indicator: 0·05% aqueous solution.

Standard thorium nitrate: 0·005*M* in 0·04% nitric acid.

Standard fluoride solution: Heat reagent-grade sodium fluoride in a platinum crucible at low red heat (650°) for 1–2 hr. Cool, weigh exactly 0·1500 g, dissolve in water, and dilute to 200 ml. One ml of this solution contains 0·000339 g of fluoride, and is very approximately equivalent to 1 ml of the standard thorium nitrate solution (theoretically 1 ml of 0·005*M* $Th(NO_3)_4$ = 0·000380 g of F).

Procedure for silicate rocks and minerals

Grind somewhat more than 0·5 g of sample to an impalpable powder in an agate mortar, weigh 0·5000 g into a large (60-ml) nickel crucible, and add 6 g of special flux. Mix throughly, and heat, tightly covered, at the maximum temperature of a Meker burner for 35 min. Only the bottom half of the crucible should become heated to redness during the fusion. The crucible cover may be cooled by means of another containing water,[9] to be certain that there is no loss of fluorine.

Cool, add about 25 ml of water, and keep warm overnight. Because creeping sometimes occurs, the crucible should be placed on a clean cover glass and protected from the laboratory atmosphere, which may contain fluoride.

Transfer the contents of the crucible quantitatively to a 250-ml beaker, using about 80 ml of water. Rinse the crucible briefly with 10 ml of 1:10 perchloric acid, and pour this all at once into the beaker. Boil for 5 min, and filter into a 300-ml platinum or silver dish. Wash once or twice with hot water, sluice the residue back into the beaker, reboil and refilter. Wash with hot water, ignoring any peptisation which may occur.

Evaporate the filtrate (in silver or platinum, not in glass) to near dryness on the steam bath, and transfer to the special still through the steam inlet tube, using a minimum of water. Add about 20 mg of potters' flint. Put 30 ml of 24*N* sulphuric acid in the silver dish, and add it cautiously to the sample solution, dropwise at first to avoid mechanical loss. The liquid level in the still must be kept at least 1–1·5 cm below the end of the steam outlet in the splash trap.

Stopper the steam inlet, and heat until the thermometer indicates a temperature of about 130°. Do not place the receiver under the condenser until the first signs of condensate appear in the exit tube of the still: otherwise, carbon dioxide collected therein will require excessive additions of alkali, which is undesirable. If there is any indication that some of the solution may have splashed over into the condenser, the first fraction should be returned to the still through the steam inlet, and redistilled.

Steam distil at a rate of about 2–3 ml per min, holding the temperature at a predetermined optimum (see below). Collect about 100 ml of distillate after this temperature has been reached. If the fluorine content of the sample is at all likely to be high—above 0·5–1·0%—a further 100 ml should be collected and treated separately. With most rocks, no fluorine will be found in the second 100 ml. With fluorine bearing minerals (*e.g.*, lepidolite), 300–500 ml should be collected, and the last 100 ml should be treated separately to provide assurance that the distillation is complete.

During the distillation, add just enough 0·1*N* sodium hydroxide to the distillate to keep it alkaline to phenolphthalein.

Evaporate the alkaline distillate to small volume, but not to dryness, in a silver or platinum dish, transfer to a 25- or 50-ml volumetric flask, and make up to volume. Make a preliminary determination on a 2- or 5-ml aliquot. Depending on the fluorine found, make a final titration, using either the balance of the solution (after re-evaporation to small volume), or a suitable aliquot chosen so that the titration will be 1–2 ml of standard thorium nitrate.

The titration is accomplished as follows: To the aliquot of the sample solution in a 50-ml beaker add 0·2N hydrochloric acid dropwise until the phenolphthalein is decolorised. Then add 3 drops of alizarin indicator, and continue the dropwise addition of dilute acid to a pure yellow colour. Do not add more than one drop of 0·2N acid in excess. Add 0·3 ml of monochloracetate buffer, and enough water to give a total of just 15 ml *at the end of the titration.* Add 15 ml of ethanol, and titrate from a 2- or 5-ml microburette with standard thorium nitrate.

Standardise the thorium nitrate against measured volumes of the standard sodium fluoride solution which have been distilled in exactly the same manner as sample solutions, *i.e.*, from 30 ml of 24N sulphuric acid containing 1 ml of perchloric acid, with the addition of potters' flint. With silicate rocks, which normally contain less than 0·5% of fluorine, a direct standardisation without distillation is adequate, once the satisfactory performance of the still has been established, for recovery of small amounts of fluorine is very close to 100%. Thus, in a typical standardisation 0·50, 1·00, and 2·00 ml of standard fluoride solution required 0·48, 0·98, and 1·90 ml of thorium nitrate after distillation, and 0·48, 0·95, and 1·95 ml directly.

It is quite necessary to have reference solutions to compare with the sample solution during titration, in order to detect the exact end-point. These are prepared by adding 0·00, 0·50, and 1·00 ml of 0·0001M thorium nitrate, freshly prepared by dilution of the 0·005M solution, to 50-ml beakers containing 14 ml of water, 15 ml of alcohol, 3 drops of indicator, and 0·3 ml of buffer. When high percentages of fluorine are determined, the unknown should be compared at the end-point with a titrated solution resulting from the distillation of a known weight of fluorine close to that contained in the sample, and an empirical standardisation of the thorium nitrate should be made. A sample of lepidolite which showed 7·88% F by this procedure, gave 7·56% when titrated and calculated in the usual way, using the thorium nitrate molarity obtained by direct titration of standard sodium fluoride.

Rapid determination of fluorine in silicate rocks

Fuse 0·200 g of rock powder with 2 g of sodium peroxide in an iron crucible. Leach the melt with 10–15 ml of water, and add 25 ml of phosphoric acid and 0·2 ml of perchloric acid. Transfer to the special still, stopper the steam inlet with a tube carrying a very slow current of air (1 bubble per sec) to prevent bumping, and heat to 135°. At this temperature start the steam flow, and allow the operating temperature to increase to 160–165° as registered on the thermometer. Collect about 125 ml adding 1% sodium hydroxide as necessary to keep the distillate alkaline to phenolphthalein. Determine fluorine as described above. With materials containing more than a few tenths of a per cent, a second 100 ml of distillate should be collected and treated separately.

A blank determination should be made, and the results corrected accordingly. A normal blank corresponds to about 0·02–0·03% F on a 0·2-g sample.

DISCUSSION

Experiment has shown that there is a rather narrow temperature range in which fluorine may be distilled completely and rapidly from sulphuric acid solution without appreciable volatilisation of the latter. This confirms the findings of Reynolds and Hill.[13] With the special still, the actual temperature of the sample solution is difficult to measure, because of the close proximity of the thermometer well to the trap drain and steam inlet, and heat losses within the well itself. An optimum temperature reading must be established for each still: only in this way can one be certain that harmful amounts of sulphate will not be contained in the distillates from actual samples. There is probably no satisfactory way of determining sulphate contamination in such distillates quantitatively, because of fluoride interference. Fluorine interferes, for example, in the chloranilic acid method of Bertolacini and Barney.[2]

The optimum operating temperature for each still is determined by passing steam through diluted sulphuric acid in the apparatus, exactly as in an actual determination except that no perchloric acid is added, collecting 10-ml fractions of distillate at gradually increasing temperature, and titrating them with 0·01N alkali. A typical set of results from this procedure is shown in Fig. 3. It is apparent that in this particular case, the safe maximum operating temperature is reached at a thermometer reading of about 140°. Above 145°, the amount of acid in the distillate increases rapidly. For three different stills, the best operating temperatures were determined to be 138°, 143°, and 140°. The actual temperature of the sample solution is estimated to be about 5–10° higher than that registered on the thermometer.

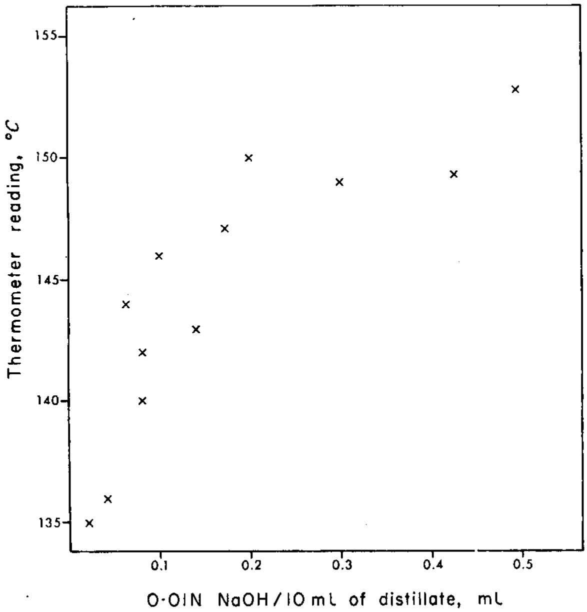

FIG. 3.—Determination of maximum operating temperature.
10-ml fractions of distillate from sulphuric acid were collected at gradually increasing temperature, and titrated with 0·01N alkali. Distillation rate, 3–4 ml per min.

Determining the lowest effective temperature is somewhat difficult. It appears to depend on incidental amounts of iron, aluminium, and other elements in the solution. With pure sodium fluoride distilled from 30 ml of 24N sulphuric acid containing 1 ml of perchloric acid, fluorine is quantitatively recovered in a relatively short time near the maximum permissible temperature, but incompletely in twice the time at temperatures only 5–10° lower (Fig. 4). The lower temperature does not result in appreciable lessening of the initial rate of recovery, but the last of the fluorine distils only slowly. This may arise from the presence of small amounts of complex fluorides which require the slightly higher temperature for their rapid dissociation, or it may be because fluoride absorption on the glass surfaces within the still is minimised by the passage of perchloric acid vapour with the steam. The former supposition is supported by the observation that filtrates derived from the treatment of rock samples vary widely in their behaviour when distilled at 130–135°, with incomplete recovery of fluorine as a rule, but at 140–145°, recovery is invariably rapid and complete. The more rapid recovery of fluorine when a little perchloric acid is present (as in the recommended procedure) supports the second supposition.

The temperature of the air bath during steam distillation is not critical, so long as condensation within the still is prevented. A thermometer suspended within the bath

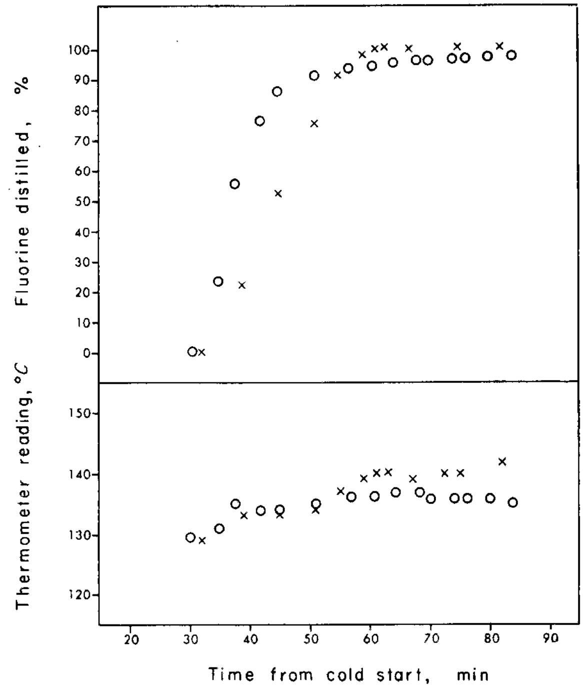

FIG. 4.—Effect of temperature on the steam distillation of fluorine.

Distillation of 3·39 mg of F from sulphuric acid containing a little perchloric acid: 10-ml fractions of distillate were collected and titrated with thorium nitrate as in the procedure, and the thermometer reading was recorded. A reading of 140° (corresponding to an estimated solution temperature of 150°) is required for rapid and complete recovery of fluorine.

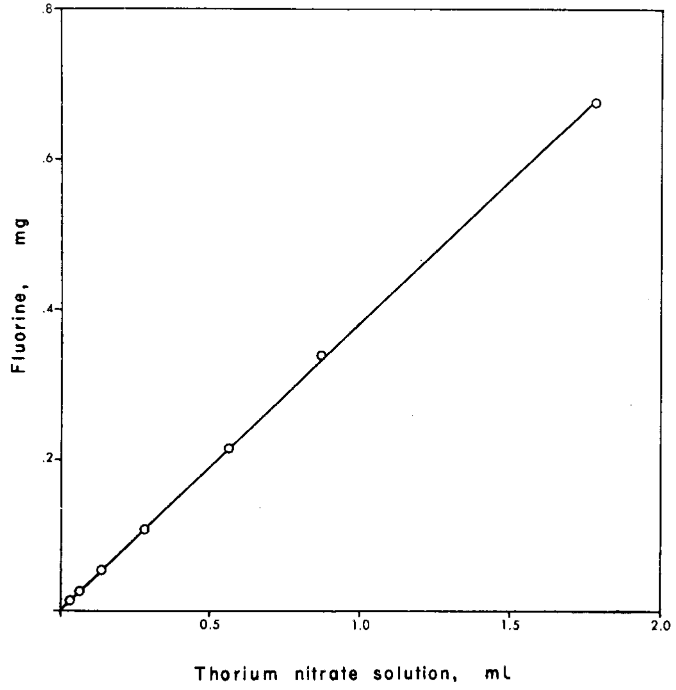

FIG. 5.—Titration curve in 50% ethanol solution.

The curve is essentially a straight line down to the limit of detection.

may register between about 85° and 105°, depending on the proximity of the bulb to the neck of the distilling flask.

Titration with thorium nitrate in 50 % alcohol is much superior to the aqueous titration, especially when small amounts of fluorine are involved. The titration curve (Fig. 5) is very nearly a straight line through the origin. Less than 5 μg of fluorine can be detected with certainty. Precision is best when the titration is between 1 and 2 ml of thorium nitrate solution, that is with about 0·5 mg of fluorine. This amount can be determined with a precision of about 2 % by the regular procedure, and 1 % if special precautions are taken, as suggested in the procedure for samples containing high percentages of fluorine.

TABLE I.—COMPARATIVE RESULTS
(Martha Bailey, analyst)

Sample	Description	F, %	
		Found	Accepted value
1 E/S 1	quartz monzonite	0·129	0·12[a]
2 F/MC 17	migmatite	0·109	0·09[a]
3 E/P 1	tourmaline granite	0·249 0·251 0·256	0·24[a]
4 S/T 1	tonalite	0·077 0·079 0·076	0·07[a]
5 G/G 1	nepheline syenite	0·062	0·05[a]
6 I/C 2	hornfels	0·064	0·06[a]
7 S/A 1	eucrite	0·000 0·002	0·01[a]
8 E/M 1	diabase	0·053 0·057	0·05[a]
9 E/H 1	marine shale	0·089 0·086 0·091	0·07[a]
10 I/C 1	semi-pelitic schist	0·096	0·08[a]
G–1	granite	0·074 0·073 0·069	0·073[b]
W–1	diabase	0·031 0·030	0·02[b]
	syenite[c]	0·168 0·167 0·170	

[a] Consensus mean of results reported by R. P. Hollingworth in a paper presented at the Annual Meeting of the Canadian Institute of Chemistry, Montreal, Canada, August, 1961.

[b] Recommended value, U.S. Geological Survey Bulletin 1113.

[c] Standard sample, Canadian Association for Applied Spectroscopy; other results not yet available. This sample contains zirconium, which may lead to low recoveries of fluorine.

An advantage of the microtitration in 50 % alcoholic solution, which is particularly evident when high percentages of fluorine are to be determined, is that only a small part of the distillate is used in the titration. This dilutes the small amount of sulphate present to the point where its effect is entirely negligible, and overcomes the difficulty, met with in some procedures, occasioned by the increasing interference of a given amount of sulphate with increasing fluorine content of the solution. In the recommended method, sulphate interference is at its worst when the whole of the distillate is used for the titration. It is for this reason that separate 100-ml portions of distillate should be collected with unknown samples, and titrated separately.

TABLE II.—DETERMINATION OF FLUORINE AFTER DIRECT DISTILLATION FROM PHOSPHORIC ACID
(C. O. Ingamells and Martha Bailey, analysts)

Sample	F, %	
	Found	Accepted value
1 E/S 1	0·12	0·12
2 F/MC 17	0·07	0·09
3 E/P 1	0·23 0·22	0·24
4 S/T 1	0·07	0·07
5 G/G 1	0·05	0·05
6 I/C 2	0·07	0·06
7 S/A 1	0·01	0·01
8 E/M 1	0·05	0·05
9 E/H 1	0·07	0·07
10 I/C 1	0·07	0·08
syenite	0·19	0·17[a]
lepidolite	7·78[b]	7·88[a,b]

[a] Determined by the general method presented in this paper.

[b] 400 ml of distillate collected: standardisation of the thorium nitrate made by titrating a similar volume of distillate from standard fluoride solution.

The general procedure given above has been used for several years with a still of conventional design, sulphate entrainment having been controlled by distilling very slowly (less than 1 ml per min). The new still has greatly improved the performance of the method and reduced the time required for a determination. The rapid procedure involving distillation from phosphoric acid has not yet been extensively tested, but preliminary experiments and the results summarised in Table II indicate that it may be of great value in routine work with samples which are known to be free from interfering elements such as sulphur. Results are not as precise as with the general method given above, because blanks are not as reproducible, and the very small amount of phosphate in the distillate affects the titration adversely. As the fluorine content of the sample increases, these factors become less serious.

Some comparative results obtained by the general method are given in Table I. The first given result for each of the samples (except G-1 and W-1) was obtained before any knowledge as to the nature of the sample or its fluorine content was available to the analyst.

Acknowledgements—The author wishes to acknowledge the invaluable assistance of R. P. Hollingworth in the preparation of the manuscript, and of Martha Bailey, who carried out most of the determinations reported herein.

Zusammenfassung—Der Wirkungsgrad der Fluoriddestillation nach Willard und Winter kann verbessert werden, wenn statt Perchlorsäure Schwefel- oder Phosphorsäure verwendet wird. Phosphat und Sulfat müssen jedoch vom Destillate fern gehalten werden, da sie viele Methoden (einschliesslich der üblichen Thoriumtitration) zur Bestimmung des Flourides stören. Ein Apparat wird beschrieben, der genaue Überwachung der Destillation gestattet und eine schnelle und vollständige Ansammlung des Fluorides in einem von Sulfat und Phosphat freien Destillat. Methoden werden mitgeteilt um Fluorid quantitativ aus Silikatgesteinen und Mineralen zu gewinnen und mit hoher Genauigkeit zu bestimmen.

Résumé—L'efficacité de l'entraînement à la vapeur du fluorure par la méthode de Willard et Winter peut être améliorée par l'utilisation de solutions d'acide sulfurique ou phosphorique au lieu de l'acide perchlorique. Cependant le sulfate et le phosphate ne doivent pas se trouver dans le distillat car ils gênent dans de nombreuses méthodes de dosage, y compris le titrage habituel au nitrate de thorium. On décrit un nouvel appareillage qui permet un contrôle efficace de la distillation et la récupération rapide et complète du fluor débarassé de quantités importantes de sulfate et de phosphate. On en tire des procèdés où les fluorures peuvent être extraits quantitativement des roches et minéraux siliciques et déterminés facilement avec exactitude et précision.

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CONTINUOUS DETERMINATION OF URANIUM IN IMPURE SOLUTIONS BY GAMMA SPECTROMETRY

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Summary—The non-destructive determination of uranium, by measurement of the 184-KeV gamma ray activity arising from the decay of uranium-235, has been extended to the continuous monitoring of impure plant solutions. Interference in the gamma spectrometric measurement at 184 KeV by the radioactive decay products of uranium is eliminated by means of an error signal. Measurement of the decay product gamma activity at higher energies is used to produce a signal which is injected, suitably proportioned and phased, into the measurement channel. An instrument is described which is suitable for the monitoring of uranium streams containing 5–30% w/v of natural uranium. Gross changes in the acidity and in the impurity content of the uranium stream have no appreciable effect on the indicated uranium concentration.

INTRODUCTION

THE operation of a uranium purification process requires that the concentration of uranium at various points should be known at any time. The delays unavoidably caused in the application of conventional analytical techniques may, in some instances, be an embarrassment in process control and point to the advantages to be gained from 'in line' automatic methods of analysis. In the ultimate such automatic analysers should be sufficiently rapid in response and should have an output in a form suitable for the operation of a servo mechanism capable of correcting for undesired changes as they occur.

The measurement of the gamma ray activity of uranium-235 has been used for its quantitative determination by gamma spectrometry.[1–11] This technique had been shown previously to offer a sufficiently precise and rapid method of non-destructive measurement to warrant further study as the basis for a continuous monitor. A comparison of the relative merits of gamma spectrometry with the more established technique of gamma absorptiometry[12–16] showed that, for impure solutions, the interference caused by gamma attenuation in the impurities would be smaller at the higher energies used in the gamma spectrometric measurement.[17]

The gamma spectrum of natural uranium comprises three main components. A gamma photopeak is observed at 90 KeV, which arises in the decay of uranium-238, uranium-235 and daughter activities. Two further photopeaks are observed at 143 KeV and 184 KeV arising from the decay of uranium-235 and, in addition, there is a continuum of activity to greater than 2 MeV. This is caused by Bremsstrahlung radiation arising from the interaction of decay product beta particles with the uranium.[18] The proportion of gamma activities at 90 KeV and in the continuum vary according to the extent of equilibrium of the uranium daughter products. The 184-KeV and 143-KeV photopeaks are influenced by the daughter product activities only to the extent of the small portion of the continuum included in them. Fig. 1 shows the gamma spectra of uranium in full equilibrium with daughter activities and of freshly purified uranium containing no daughter product activity. From these spectra it can be seen that a true measure of the uranium-235, and hence of the total uranium in the case of a fixed isotopic composition, as in natural uranium, can be obtained by measuring only the 184-KeV and 143-KeV photopeaks and correcting for the continuum.

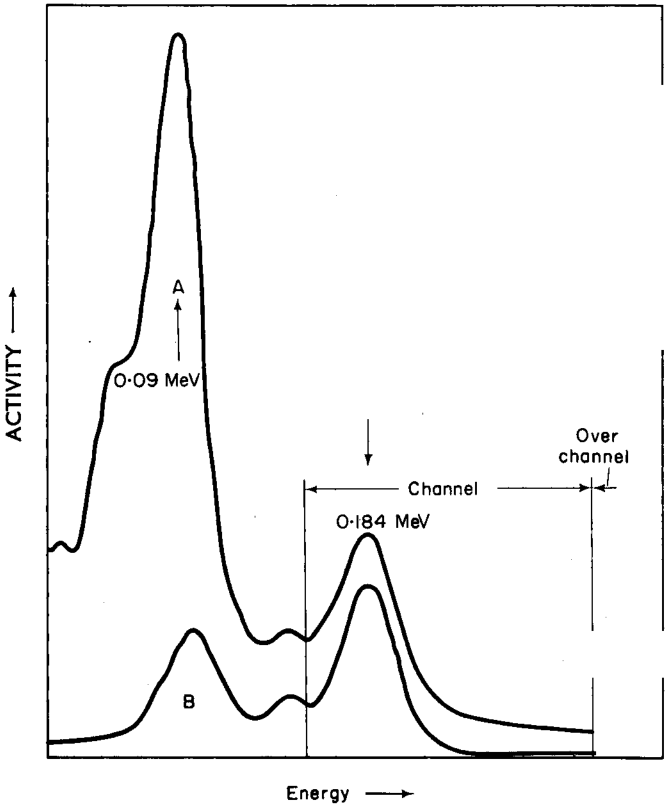


FIG. 1.—Gamma spectra of natural uranium:
A—equilibrium daughter activities,
B—no daughter activities.

The resolution of a good thallium activated sodium iodide crystal is adequate to differentiate between the 90 KeV and 184 KeV activities and it is, therefore, possible to measure the 184-KeV activity without interference from that at 90 KeV. This avoids the effects of the varying daughter product activity present in the 90-KeV photopeak.

The continuum of Bremsstrahlung radiation is present over the whole of the uranium spectrum and measurements in the energy region of the 184-KeV photopeak inevitably include a portion of the continuum. The continuum is, however, directly proportional to the decay product activity and measurement in any part of the spectrum away from the uranium photopeaks can be used to correct any other part, provided that the proportionality is known. A correction of this type had been used previously by making two measurements on a sample, one at 184 KeV to obtain the required uranium activity and another at 300 KeV to obtain the correction for daughter activity at 184 KeV. To do this continuously a two-channel gamma spectrometer measuring simultaneously at the two energy levels is required. The single channel instrument A.E.R.E. type 1168 does, however, have an auxiliary output giving an integrated measure of all activities greater than the channel being measured. If this could be used for measurement of the continuum considerable complication could be avoided.

A plot of uranium concentration versus gamma activity at 184 KeV gives a curve. The cause of the curvature is self absorption of the gamma rays in the uranium. Being predominantly caused by the photoelectric process, the absorption is proportional to atomic number to the fifth power $(Z^5)^{19}$ and hence falls off very rapidly for elements of lower atomic number. The effects of impurities on these gamma ray measurements would, therefore, be expected to be very small.

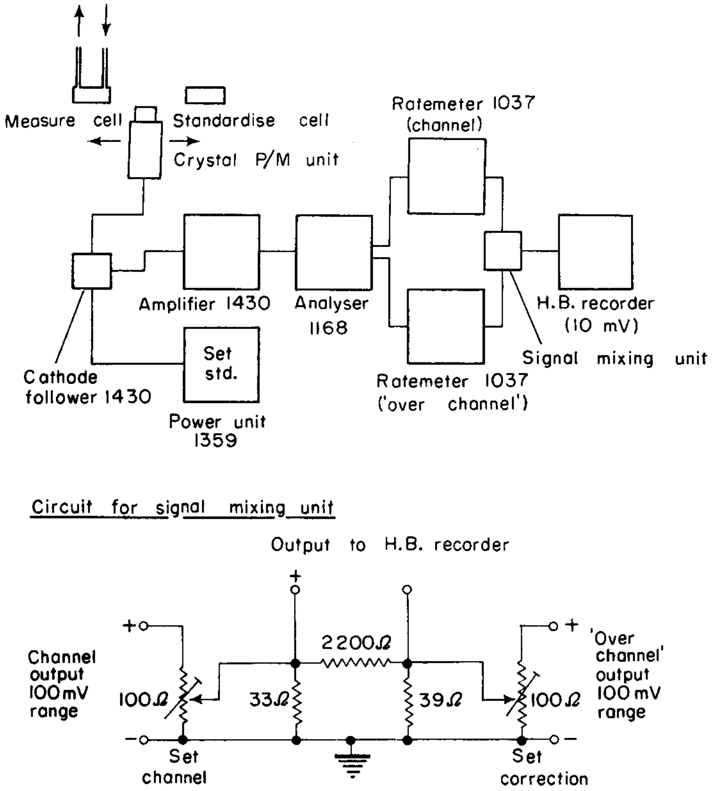


FIG. 2.—Layout of equipment and associated circuits.

These considerations led to the conclusion that a single-channel gamma spectrometer could form the basis of a relatively simple and sufficiently precise automatic analyser for uranium. The curvature in the response to uranium must be kept within reasonable limits and other gamma activities must not be present in the parts of the spectrum used in the measurement of the 184-KeV photopeak and the continuum.

EXPERIMENTAL

Electronic equipment

The proposed layout of the electronic equipment shown in Fig. 2 was based entirely on standard A.E.R.E. type units. For the experimental work in assessing the technique, the two ratemeters were replaced by scaling units to enable more precise measurements to be made. The photomultiplier anode load was made 100 KΩ and the amplifier integrating and differentiating time constants were both set at 0·32 μsec. This combination had previously been shown to give the optimum pulse size consistent with short paralysis time ($<$ 10 μsec overall) for counting uranium gamma activity.

Selection of counting conditions

With the amplifier attenuation at zero, the high tension supply to the photomultiplier was increased until the uranium spectrum from a sample of natural uranium appeared at the pulse analyser, with the 184-KeV photopeak in the centre of the analyser base line.

For the instrument to fulfill the requirements for uranium determination, a number of conditions had to be satisfied:

(1) The channel used in measuring the 184-KeV peak must not contain any contribution from the 90-KeV peak.

(2) The integrated output measuring the continuum must not contain any contribution from the 184-KeV peak.

(3) The channel used in measuring the 184-KeV peak must be as wide as possible to obtain the highest possible counting rate and hence the best precision of measurement.

(4) The integrated output measuring the continuum for correction purposes must have a sufficiently high output to avoid seriously affecting the precision of the corrected channel output.

Condition (4) must be met by a suitable choice of detector crystal when using the integrated output of a single channel analyser unit, as there is no means of varying the channel width used for measurement of the continuum. In practice the 1″ thick by 1·5″ diameter crystal used was found to give an adequate output at the higher gamma energies. The other conditions were arrived at by studying the gamma spectra for uranium in equilibrium with, and after the separation of, daughter activities. Condition (1) was readily arrived at by setting the lower bias at 150 KeV in the valley between the 143-KeV and 184-KeV photopeaks. Conditions (2) and (3) then required only that the channel width was set such that the upper bias represented an energy well clear of the 184-KeV peak, a point at 300 KeV was selected for this as shown in Fig. 1.

A gamma spectrometer is inherently an unstable device, small changes in photomultiplier gain, overall amplification, photomultiplier high tension supply, *etc.*, giving rise to a lateral displacement of the observed spectrum up or down the energy scale. These effects are minimised by careful stabilisation of the electronic circuits but nevertheless they still exist. It is, therefore, necessary to choose conditions which will minimise the effects of electronic or other changes on the measurements if good stability of operation is to be attained. The measuring conditions chosen are seen to represent the best compromise in this respect. Drift of the upper bias point adds or subtracts only a minor contribution to the channel or over channel outputs. Drift of the lower bias point has a negligible effect on the over channel output but a more serious effect on the channel output, because of the relatively high activity in this part of the spectrum. The effect of drift on the channel output is, however, a minimum for the point selected in the valley between the 143-KeV and 184-KeV peaks.

Measuring cell

Lengths of stainless steel and glass tubing of various sizes were filled with uranium solutions of different concentrations and the gamma activities measured. The results showed that for uranium concentrations greater than 10% w/v self-absorption effects were prohibitive; below 10% w/v, the counting rates were too low to be of value.

Replacement of the tubing with a flat cell of the same diameter as the crystal (1·5″) showed a very considerable increase in counting rates and indicated that the self-absorption effects, and hence non-linearity, could be kept sufficiently small provided that the thickness of the cell was limited.

A series of experiments was undertaken to verify this, using uranium solutions of different concentrations, both in equilibrium and after removal of daughter products. Measurements were made on various thicknesses of each solution. The results of these measurements are shown in Fig. 3, and led to the following conclusions:

(1) Selection of a suitable cell thickness would enable a range of 5–30% w/v uranium to be covered (using a 1″ × 1·5″ crystal) with a non-linearity of less than 10%.

(2) Non-linearity was slightly worse in the measurement of uranium containing no decay product activities.

(3) Differences between the net counting rates for equilibrium and freshly extracted uranium were proportional to the counting rate of the 'over channel' integrated output for the uranium in equilibrium. This showed that the counting rate obtained for the continuum could be used in correcting for daughter activity interference.

Measuring cell assembly for 'in line' monitoring

For the 'in line' monitoring of uranium a flow-through measuring cell is required having a 'window' essentially transparent to the gamma rays. A cell was constructed in welded polythene and tested to 50 psi water pressure. This cell was designed from the data obtained previously for a range of 5–30% w/v uranium, the dimensions being shown in Fig. 4.

The cell was inserted in one side of the lead shielded assembly shown in Fig. 4 with a polythene cell of similar but arbitrary size in the opposite side. The crystal-photomultiplier was mounted on a swinging arm with locating stops such that the crystal could be brought accurately beneath either cell.

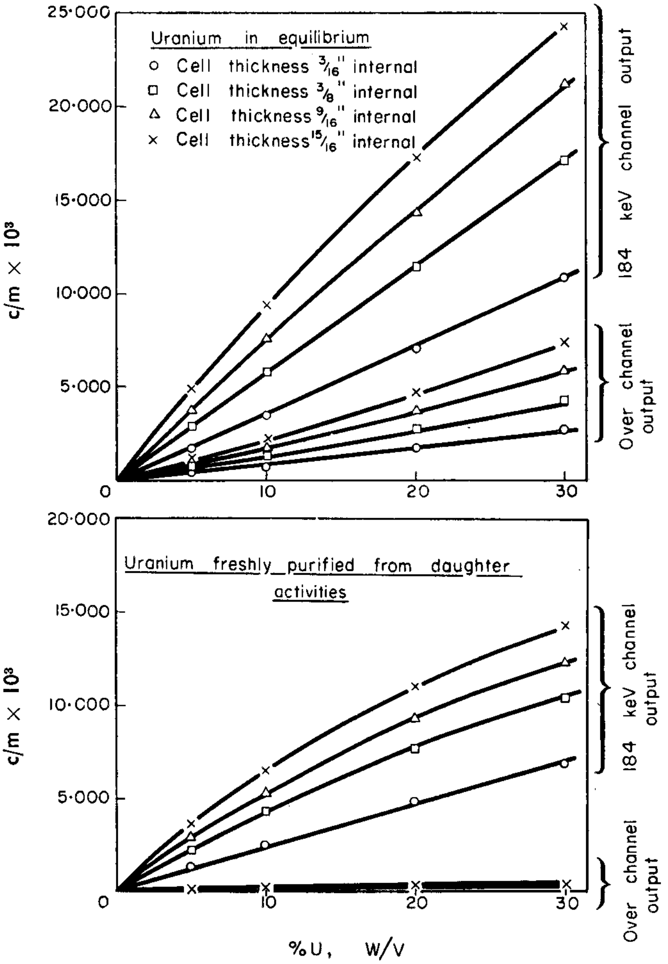


FIG. 3.—Effect of cell thickness on calibration.
(The lowest thick curve represents four separate curves.)

Uranium solution was then added to the second cell until the counting rate was the same as that obtained from the measuring cell when filled with a 20% w/v uranium solution. The second cell was then sealed and became a permanent standard, equivalent to 20% w/v uranium in the measuring cell. This procedure was adopted to avoid the difficulties in making two exactly matching cells for measurement and standardisation.

Daughter product activity correction ratio

Solutions of uranium at a concentration of 20% w/v, one in equilibrium with daughter products and the other freshly-extracted, were admitted to the measuring cell and their activities measured.

The following data was obtained:

Background with cell empty, channel output = 164 cpm
Background with cell empty, 'over channel' output = 282 cpm
20% w/v uranium in equilibrium, channel output = 6488 cpm
20% w/v uranium in equilibrium, 'over channel' output = 1695 cpm
20% w/v uranium freshly extracted, channel output = 4486 cpm
20% w/v uranium freshly extracted, 'over channel' ouptut = 325 cpm .

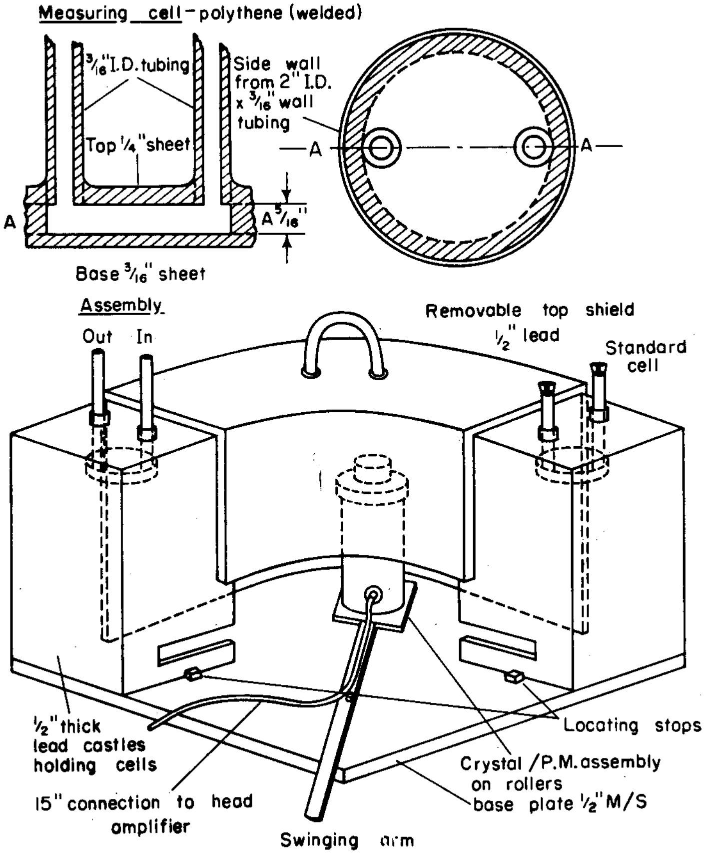


FIG. 4.—Measuring cell and cell assembly.

If the true reading for the uranium activity is y cpm and the ratio by which the "over channel" output must be increased to give the required correction is x, then for equilibrium uranium

$$6488 - 1695x = y \tag{1}$$

and for extracted uranium

$$4486 - 325x = y \tag{2}$$

Subtracting

$$1370x = 2002$$

and $x = 1{\cdot}46$ (background effects cancel).
Substituting in (1):

$$y = 6488 - 2478 = 4010.$$

For the output of the monitor to read 20%, the output from the channel must give a reading of

$$\frac{20 \times 6488}{4010} = 32{\cdot}4\% \text{ for an equilibrium } 20\% \text{ uranium solution.}$$

This reading then requires reduction to 20·0% by the signal from the 'over channel' output.

Correction circuit

The scaling units were replaced by the two ratemeters, one measuring the channel output and the other the 'over channel' output. The output from the ratemeters were connected in opposition using the circuit shown in Fig. 2. This enabled a varied output to be obtained from each with the strip chart recorder measuring the difference between the two. The instrument was then set to measure the 20% w/v equilibrium standard in the standardise cell and, with the 'over channel' output control at zero, the channel output was increased to give a reading of 32·4 on the recorder. The 'over channel' output was then increased until the recorder reading was reduced to 20·0. The two ratemeter output controls were then locked in these positions.

Statistical variations

The statistical variation in a ratemeter output is given by:

$$\sigma = \pm \frac{100}{\sqrt{2nT}} \tag{20}$$

where n is the mean pulse rate/sec and T is the integrating time in sec.
A 20% uranium solution in equilibrium gives

channel output = 108 cps
'over channel' output = 28 cps,

and at 30%

channel output = 162 cps
'over channel' output = 42 cps.

The longest time constant available on the ratemeter used (A.E.R.E. type 1037C) on the X 1000 range is 40 sec. This gives rise to rather wide statistical variations at these counting rates and was therefore increased, by increasing the integrating resistance of the ratemeter, to 160 sec.

For the combined output where the over channel output is increased by 1·46 before applying it as the correction:

$$\text{At } 20\%,\ \sigma = \pm\sqrt{\left(\frac{100}{\sqrt{2} \times 108 \times 160}\right)^2 + 1{\cdot}46 \times \left(\frac{100}{\sqrt{2} \times 28 \times 160}\right)^2}\ \%$$

$$= \pm \sqrt{0{\cdot}28 + 1{\cdot}64}\%$$

$$= \pm 1{\cdot}38\%$$

$$\therefore 3\sigma = \pm 4{\cdot}14\% \equiv \pm 0{\cdot}8\% \text{ uranium.}$$

$$\text{At } 30\%,\ \sigma = \pm\sqrt{\left(\frac{100}{\sqrt{2} \times 162 \times 160}\right)^2 + 1{\cdot}46 \left(\frac{100}{\sqrt{2} \times 42 \times 160}\right)^2}\ \%$$

$$= \pm \sqrt{0{\cdot}193 + 1{\cdot}09}\%$$

$$= 1{\cdot}13\%$$

$$\therefore 3\sigma = \pm 3{\cdot}39\% \equiv \pm 1{\cdot}0\% \text{ uranium.}$$

For solutions containing no decay product activity, the second term of the expression becomes negligible when the precisions (3σ) become 0·3 and 0·4% uranium at 20% and 30% uranium, respectively.

Further improvement in the precision of measurement could be obtained in two ways, either by further increasing the time constant, or by the use of a larger diameter crystal and measuring cell giving an increased counting rate. Further increase in the time constant would make the instrument response too sluggish, for the 160 sec used a 99% response is attained in about 4 C.R. or approximately 10 min and it was not felt desirable to increase this any further. Larger crystals were not available at the time.

Laboratory trials of the complete monitor

The following trials were carried out in the laboratory:

(1) Long term stability.
(2) Uranium calibration.
(3) Effect of varying the amount of daughter product activity present in the uranium.
(4) Effect of impurities.

The results of these trials are shown in Table I and Fig. 7(a) and (b).

TABLE I.—Laboratory trials of the complete monitor.

Solution measured	Object	Reading obtained U w/v	Observation
10% w/v U Equilibrium UXI	Calibration	10·2%	Within expected error
20% w/v U Equilibrium UXI	Calibration	19·8%	Within expected error
30% w/v U Equilibrium UXI	Calibration	30·0%	Within expected error
40% w/v U Equilibrium UXI	Calibration	37·3%	Low, due to self absorption
20% w/v U Equilibrium UXI	Stability check	20·0 ± 0·5%	20-hr run within expected error
30% w/v U Equilibrium UXI	Stability check	29·5 ± 0·75%	16-hr run within expected error
30% w/v U Equilibrium UXI	Stability check	29·8 ± 0·75%	20-hr run within expected error
20% w/v U No UXI	Stability and effect of UXI	20·0 ± 0·3%	16-hr run within expected error. Daughter product correction satisfactory.
25% w/v U Equilibrium UXI No free acid	Effect of acidity	24·8%	
25% w/v U Equilibrium UXI in 10*N* HNO_3	Effect of acidity	24·5%	No effect from HNO_3
25% w/v U containing 50% Fe on U basis	Effect of impurities	25·75	Slight positive error

The measuring cell thickness of 5/16″ had been chosen to work over a range of up to 30% w/v. uranium and, therefore, the self absorption effect observed at 40% w/v was expected. The reading obtained in the presence of iron is considered to be satisfactory in view of the high impurity content simulated. The reason for the error, in the presence of impurities, being in the positive direction is not fully understood but is believed to arise from the same effect which produces the difference in linearity between equilibrium and freshly extracted uranium apparent from Fig. 3.

PLANT-SCALE TRIAL OF THE MONITOR

The monitor was assembled on the plant with the measuring cell in parallel with the line feeding from a crude uranyl nitrate stock tank to the solvent purification system. Flow through the cell was controlled by a stopcock and was set at approximately 2 litres/min. A general view of the installation is shown in Fig. 5.

Several 24-hr runs were made in the standardise position, *i.e.* continuously measuring the 20% w/v uranium (equivalent) solution in the standardising cell. These showed that the stability on the plant, where temperature fluctuations and mains voltage variations were more likely to occur than in the laboratory, was as good as had been obtained in the laboratory. This indicated that the monitor would not require standardising more frequently than once each day.

The line was then monitored for a period of 10 days, the instrument being standardised each day. Standardisation entailed moving the crystal assembly to the standardise position, allowing the reading to settle, and then adjusting the high tension supply to the photomultiplier if the reading was outside the range 20 ± 0.5%. Adjustment was only required on three occasions during the 10 days and on these the reading was within 20 ± 1.0%.

Samples were taken from the line every 8 hr during the 10 days and analysed

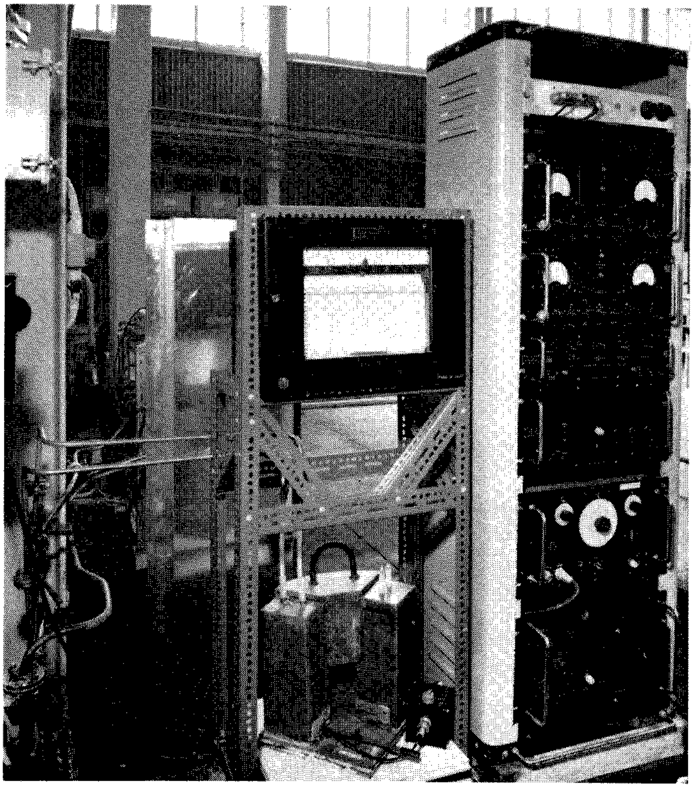
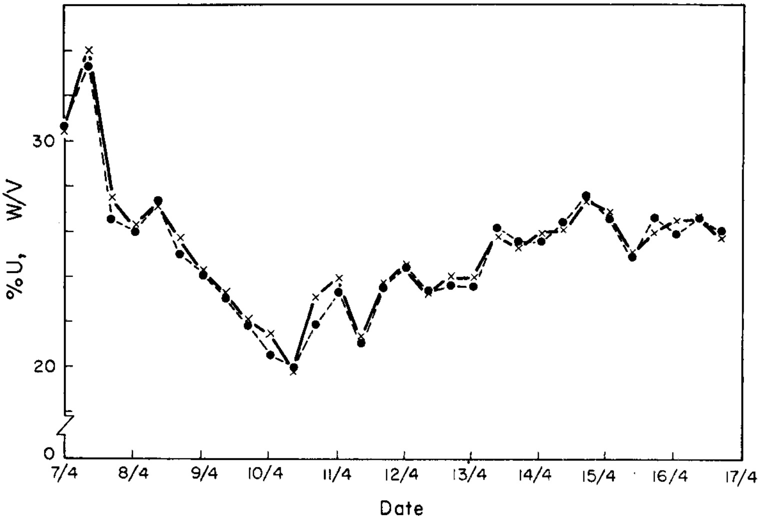


FIG. 5.—General view of installation.

chemically for uranium content by a gravimetric procedure. The comparison between the results read from the monitor strip chart and the chemical analyses are shown in Fig. 6. A record of the output from the recorder during 24 hr continuous operation is reproduced in Fig. 7(c).



Date	Time	%U, W/V	
		γSpec.	Chem.
7/4	0730	30·7	30·5
7/4	1530	33·3	34·0
7/4	2330	26·5	27·3
8/4	0730	26·0	26·1
8/4	1530	27·3	27·3
8/4	2330	25·0	25·7
9/4	0730	24·0	24·2
9/4	1530	23·0	23·2
9/4	2330	21·8	22·0
10/4	0730	20·5	21·5
10/4	1530	20·0	19·8
10/4	2330	21·8	23·1
11/4	0730	23·3	23·9
11/4	1530	21·0	21·2
11/4	2330	23·5	23·6

Date	Time	%U, W/V	
		γ Spec.	Chem.
12/4	0730	24·3	24·3
12/4	1530	23·3	23·2
12/4	2330	23·5	23·9
13/4	0730	23·5	23·8
13/4	1530	26·0	25·7
13/4	2330	25·5	25·3
14/4	0730	25·5	25·8
14/4	1530	26·3	26·1
14/4	2330	27·5	27·3
15/4	0730	26·5	26·8
15/4	1530	24·8	24·8
15/4	2330	26·5	25·9
16/4	0730	25·8	26·4
16/4	1530	26·5	26·4
16/4	2330	26·0	25·6

FIG. 6.—Uranium content—crude uranyl nitrate stock tank:
—X—X—chemical analysis.
– –O– –O– –gamma spectrometer.

APPLICATIONS

The gamma spectrometer has been applied here to the monitoring of impure solutions, arising from the dissolution of uranium concentrate in nitric acid, over a concentration range of 5–30% of natural uranium. Suitable measuring cell design and measuring crystal size would extend this range, but for natural uranium, the instrument is essentially a high concentration measuring device. It is doubtful whether a concentration of natural uranium much below 1% w/v could be usefully measured.

In measuring enriched uranium concentration, the sensitivity increases in proportion to the enrichment and the range of the instrument could be extended

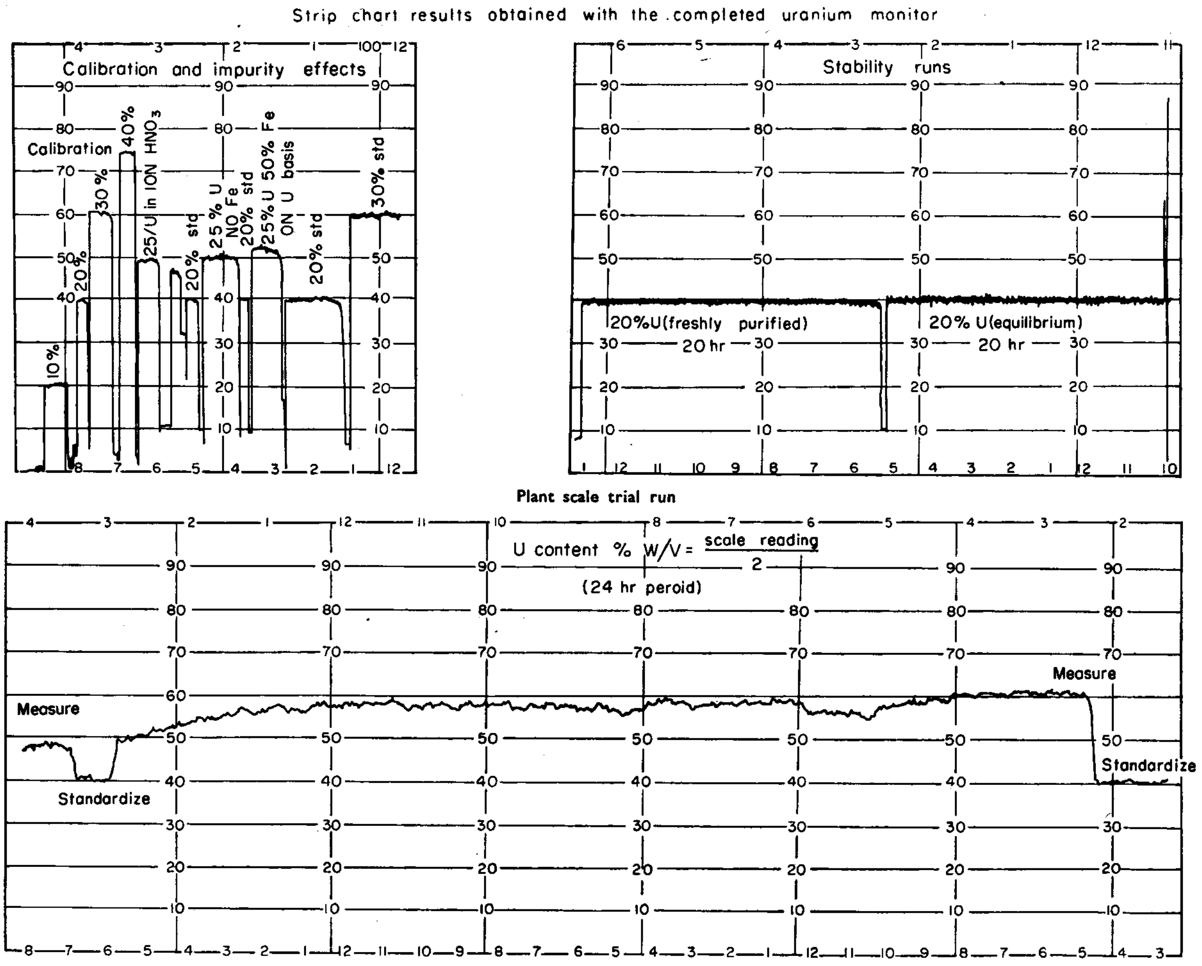


FIG. 7.—(a) Calibration and impurity effects. (b) Stability runs. (c) Plant-scale trial run.

considerably, down to the ppm. ranges. A number of enriched uranium residues are, however, known to contain other radioactive isotopes arising from thorium-228 and daughters as well as, in some cases, disproportionately high uranium daughter activity concentrations. A careful study of the effect of these would, therefore, be required.

No consideration has been given here to the effect of fission products on the principle of correction used in the monitor. There is no reason why the uranium daughter activity correction should not include a correction for the Compton scattering from fission product activity provided it is not too high. Gamma activity from fission products with an energy in the region of 184 KeV would, however, not be corrected for and could be the cause of considerable error in uranium measurements.

There is no evidence in the decay schemes for plutonium isotopes that these would cause direct interference. Previous work had shown that thorium in concentrations up to 2% on a uranium basis has no significant effect on gamma ray measurements as used in the monitor.

The continuous measurement of uranium should be possible in a number of different fields in uranium processing using the modified gamma spectrometer described. In particular, freedom from the effects of impurities, changes in acidity or uranium solvent, together with the stability of the instrument and its comparative simplicity make it compare favourably with other methods of continuous uranium measurement. A direct electrical signal representing uranium concentration is obtained for servo control should this be contemplated. The full response time of the monitor described is approximately 10 min. Whether this is sufficiently rapid for automatic plant control would require special consideration in the application to a particular plant.

The monitor was installed to give a continuous record of the uranium concentration on one plant line. There is no reason why one monitor should not be used to give an intermittent record on a number of plant lines. The liquor from each line could be fed to a simple valve system connected to the measuring cell and each line switched in as desired. The economic advantages of a system of this type are obvious, although some consideration would have to be given to the transit time if the feed lines to the monitor were unduly long.

Acknowledgement—The authors wish to thank Mr. J. C. C. Stewart, Managing Director of Production Group, U.K.A.E.A., for permission to publish this paper.

Zusammenfassung—Die nichtdestruktive Bestimmung von Uran (durch Messung der 184 KeV Aktivität des Zerfalls von 235 Isotopen) wurde ausgedehnt um die kontinuierliche Regelung von Lösungen im Fabriksbetriebe zu erzielen. Störung der gammaspektrometrischen Messung bei 184 KeV durch radioaktive Zerfallsprodukte des Urans wird mittels eines Fehlersihnals ausgeschaltet. Messung der Gammaaktivität der Zerfallsprodukte bei höherer Energie wird benutzt um ein Signal von geeigneter Grösse und Phase im Messkanal zu induzieren. Ein Instrument zu automatischen Strömungsregelung von Uranlösungen mit 5-30% (Gewicht/Volum) an natürlichem Uran wird beschrieben. Änderungen im Gehalt an Säure und Verunreinigungen haben keinen merkbaren Einfluss auf die Anzeige der Urankonzentration.

Résumé—Le dosage non destructif de l'uranium, par mesure de l'activité du rayonnement gamma de 184 KeV provenant de la dégradation de l'isotope 235, a été étendu au contrôle continu de solution de plante impure. Dans la mesure spectrométrique gamma à 184 KeV, l'interférence des produits de dégradation radioactifs de l'uranium est éliminée au moyen d'un signal d'erreur. La mesure de l'activité gamma du produit de dégradation aux très hautes énergies est utilisée pour produire un

signal qui est injecté dans le canal de mesure, en proportion convenable et en phase. Les auteurs décrivent un instrument qui convient au contrôle de courants d'uranium contenant de 5 à 30% (poids/volume) d'uranium naturel. De grandes variations d'acidité et de teneur en impureté du courant d'uranium n'ont pas d'effet appréciable sur la concentration d'uranium indiquée.

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PRELIMINARY COMMUNICATIONS

The use of oxycellulose for the collection of traces of metals: Qualitative investigations

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In previous work[1] the metal-binding capacity of cotton wool was investigated. The cotton wool was suitable for the collection of heavy metal ions which were contaminants of different solutions. Some experiments showed that oxycellulose was better for this purpose, therefore in our later work oxycellulose was used for the collection of such metals as Ag^+, Al^{3+}, Ba^{2+}, Bi^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from very dilute solutions.

TABLE I—QUALITATIVE INVESTIGATION OF OVERNIGHT COLLECTION OF METAL IONS ON OXYCELLULOSE FIBRILS.

Ion	Amount of ion collected (μg) from 1000 ml of distilled water or 10^{-4}% salt solutions* using 3 mg of oxycellulose	Spot tests used
Ag^+	10	*p*-Dimethylamino-benzylidenerhodanine[3]
Al^{3+}	1	Alizarin S[3]
Ba^{2+}	10	Sodium rhodizonate[3]
Bi^{3+}	5	Cinchonine and potassium iodide[3,4]
Cd^{2+}	10	Hydrogen sulphide
Co^{2+}	1	Ammonium thiocyanate in acetone[4]
Cu^{2+}	1	Rubeanic acid[3]
Fe^{2+}	1	α:α'-Bipyridyl[3]
Fe^{3+}	1	Potassium ferrocyanide[3,4]
Mn^{2+}	1	3:3'-Dimethylnaphthidine[3,4]
Ni^{2+}	1 5†	Dimethylglyoxime[3,4]
Pb^{2+}	1	Sodium rhodizonate[4]
Zn^{2+}	1	Mercury thiocyanate[4]

* $NaCl$, $NaNO_3$, NH_4Cl, NH_4NO_3
† from 5000 ml distilled water

Oxidised cellulose was prepared by alkaline hypobromite treatment of cotton wool, as described previously.[1] The pure oxidised cellulose, called oxycellulose, could be dispersed in distilled water to fibrils of 0·5–1 mm by shaking. These fibrils, suspended in 100, 1000, 5000 and in some cases in 10,000 ml of distilled water or very dilute inorganic salt solutions (10^{-4}%) at pH 5–6, gathered the metal ion contaminants of the solution on their surface. Even 1 μg of the above mentioned metal ions from 1000 ml distilled water, *i.e.* when the limit of the dilution was $1:10^9$, could be collected on 3 mg of oxycellulose. For qualitative purposes it was sufficient to shake the solutions, containing oxycellulose fibrils, on a shaking machine for 1 hr or put them aside overnight (see Table I). The reaction occurring between the metal ions and the carboxyl groups on the surface of the oxycellulose at pH 5–6 is called ion exchange according to the literature.[2] For the present we prefer to leave open the question as to whether the mechanism of the metal-binding is ion exchange or adsorption.

A simple and fast method was worked out for the filtration of the suspended oxycellulose fibrils. A sintered-glass filter stick, 5 mm in diameter, was dipped into the solution and the fibrils were collected on the filter by means of a water pump. The fibrils of the 3 mg of oxycellulose gathered on the filter and looked like a little disc. The disc was taken off the filter, placed on a spot plate and on this little disc the metals were identified by sensitive spot tests.[3] If there were several metal contaminants in the solution, we identified them by placing the disc in the middle of a filter paper on the Weisz ring oven,[4] where the metals were eluted, separated and tested. By the simple method described above, the dilution limits of the reactions were greatly increased, namely to pD 9.

Copper, nickel and zinc, bound as cyanide complexes in very dilute solutions, could not be identified by direct sensitive spot tests. By placing oxycellulose fibrils into the solutions and subsequent filtration, the testing of the copper, nickel and zinc ions could be successfully achieved on the oxycellulose disc.

Future work will be concerned with the quantitative collection of traces of metals, including radioactive isotopes, contaminants of water and extremely dilute solutions, some problems of complex stability and theoretical questions concerning the processes on the surface of the oxycellulose.

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Summary—For the collection and filtration of traces of several metal ions from extremely dilute solutions, a simple and fast method has been worked out using oxycellulose fibrils as a collector. pD 9 can be reached. Even metals bound in complexes can be filtered out.

Zusammenfassung—Es wurde ein Verfahren zur Anreicherung von Metallspuren aus extrem verdünnten wässrigen Lösungen ($1:10^9$) ausgearbeitet. Als Kollektor wurden Oxycellulose Fädchen verwendet: etwa 3 mg Oxycellulose für 1 1 Lösung. Es konnten sogar die Metallkomponenten weniger stabiler Komplexverbindungen aus extrem verdünnten Lösungen mit dem Verfahren isoliert werden.

Résumé—Les auteurs suggèrent une méthode simple et rapide pour recueillir et filtrer des traces de métaux lourds, à partir de solutions extrêmenent diluées, en utilisant l'oxycellulose comme collecteur.

On peut atteindre pD = 9. Même les métaux complexés peuvent être séparés par filtration.

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Determination of fluothane and its isomer by means of infrared spectrophotometry

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FLUOTHANE (Halothane), 1,1,1-trifluoro-2-bromo-2-chloroethane (I), a modern inhalation anaesthetic with outstanding properties,[1] is normally produced in one of three ways: by high-temperature bromination of 1,1,1-trifluoro-2-chloroethane,[2,3] by high-temperature chlorination of 1,1,1-trifluoro-2-bromoethane,[2,3] or by addition of hydrogen bromide to trifluorochloroethylene[4,5] and rearrangement of the 1,1,2-trifluoro-1-bromo-2-chloroethane (II) thus formed by means of aluminium chloride.[6]

$CF_3CHClBr$	$CF_2BrCHClF$
Fluothane	"Isomer"
I	II

The last of these methods for the production of fluothane calls for the accurate estimation of both fluothane and its isomer, and especially for the determination of small amounts of the isomer in fluothane.

The analytical separation and determination of fluothane and its isomer are very difficult. Their boiling points lie very close together (50° and 52°, respectively), and other physical properties correspond very closely. Gas-liquid chromatography, using kieselguhr impregnated with silicone oil, or Celite impregnated with dinonyl phthalate, failed entirely.[7] The retention times of the pure compounds differ only very slightly, and a mixture of the two isomers gives only a single peak.

It therefore seemed desirable to investigate the infrared characteristics of both compounds. The infrared spectra of fluothane[8] and its isomer[5] have been measured using sodium chloride optics. But as far as we can determine, no attempts have been made to record the infrared spectra at lower frequencies. Using potassium bromide optics the spectra of both compounds were recorded in the 400–700 cm^{-1} region and were found to show considerable differences, fluothane having maxima at frequencies at which its isomer does not absorb.

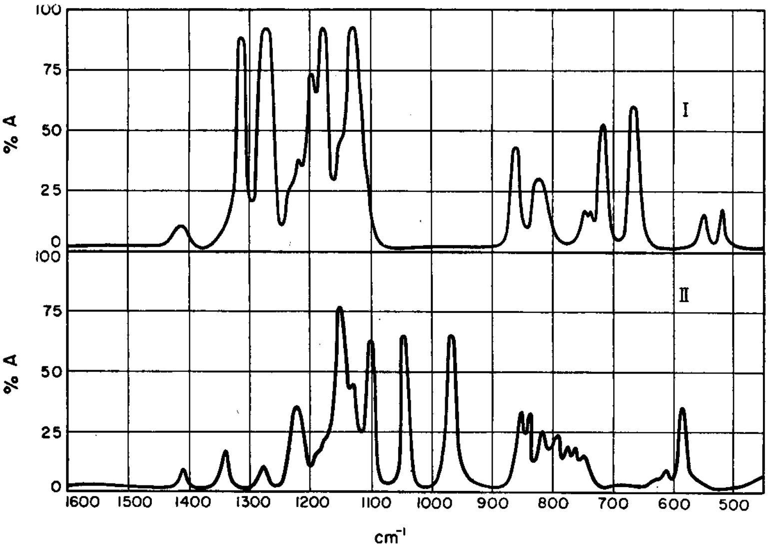

FIG. 1. Infrared spectra of fluothane and its isomer in tetrachloromethane solutions.
Curve I: Fluothane (1,1,1-trifluoro-2-bromo-2-chloroethane) (I); potassium bromide cell, c = 1 %, l = 0·4 mm.
Curve II: The isomer (1,1,2-trifluoro-1-bromo-2-chloroethane) (II); potassium bromide cell, c = 0·3 %, l = 0·4 mm.

TABLE I. EXTINCTION COEFFICIENTS OF FLUOTHANE AND ITS ISOMER

Fluothane		Isomer	
Frequency, *cm*$^{-1}$	Extinction coeff., *k*	Frequency, *cm*$^{-1}$	Extinction coeff., *k*
520	18·0	587	81·3
552	13·0	966	218·0
665	87·0	1043	218·0
715	60·0		

$$k = \frac{\mathrm{A}}{\mathrm{c(ml/10ml)\,.\,d(cm)}}$$

EXPERIMENTAL

The spectra were measured on a Zeiss UR-10 Infrared Spectrophotometer. Potassium bromide optics were used for measurements in the 400–700 cm^{-1} region, and sodium chloride optics for measurements at higher frequencies. Determinations were carried out in tetrachloromethane solutions in 0·04-cm potassium bromide cells. The tetrachloromethane used was of standard grade for infrared spectroscopy. The evaluation of the extinctions was carried out by the base line method.

(a) *Determination of the purity of fluothane*

The spectrum of a sample of fluothane in tetrachloromethane is recorded over the range 500–800 cm^{-1} with pure tetrachloromethane inserted in the reference beam. At 520, 552, 665, and 715 cm^{-1} extinctions are measured, and the corresponding concentrations of fluothane are read from a calibration curve constructed from measurements on fluothane solutions of known concentrations. The final value found can be taken as the arithmetic mean of the values obtained from the four frequencies.

(b) *Determination of the purity of the isomer*

The spectrum is recorded from 500 cm^{-1} to 1100 cm^{-1}. Concentrations are read from the corresponding calibration curves constructed from measurements of the absorptions at 587, 966, and 1043 cm^{-1} given by solutions of known concentrations of the isomer. The final value is taken as the arithmetic mean of the values obtained from the three independent frequencies.

(c) *Determination of the isomer in fluothane*

The crude product obtained on rearrangement of the isomer to fluothane does not, as a rule, contain more than 10% of the isomer, and usually less than 2%. The spectrum of such a sample is registered over the range 480–1100 cm^{-1}. The calculation may be based on the calibration curve of the pure isomer, or on a calibration curve constructed for mixtures of fluothane and its isomer. The latter gives more accurate results, especially when the content of the isomer in fluothane is lower than 1%. In this way it is possible to determine the content of the isomer in fluothane down to 0·1% with acceptable accuracy. By using 1·0-mm cells the sensitivity of this method could be further increased.

The accuracy of the method was checked on a series of mixtures prepared from known quantities of fluothane and its isomer. The results are given in Table II.

TABLE II. DETERMINATION OF THE AMOUNT OF THE ISOMER IN MIXTURES WITH FLUOTHANE

Concentration of the isomer in the mixture, %	Found*, %
10·0	10·06
5·0	5·02
2·0	2·07
1·0	0·98
0·5	0·52
0·2	0·22
0·1	0·11

* Average of 5 determinations.

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Summary—A new method for the determination of the purity of fluothane and its isomer, 1,1,2-trifluoro-1-bromo-2-chloroethane, is based on the evaluation of infrared spectra of both compounds. The method is particularly applicable to the determination of small amounts of the isomer in crude fluothane prepared by the rearrangement of the isomer. Using the conditions specified, the determination of as little as 0·1% of the isomer in fluothane is possible with a maximum relative error of 10%. This simple and rapid method is suitable for routine analyses.

Zusammenfassung—Eine neue analytische Methode zur Bestimmung der Reinheit von Fluothane und seinem Isomer, 1,1,2-Trifluor-1-brom-2-chloräthans, beruht auf der Verwertung von Infrarotspektren der beiden Verbindungen. Die Methode kann auch zur Bestimmung von kleinen Mengen des Isomers in rohem Fluothane, das durch Umlagerung seines Isomers bereitet wird, verwendet werden. Unter den beschriebenen Umständen ist es möglich, auch noch 0·1% des Isomers in Fluothane mit dem relativen Fehler von 10% zu bestimmen. Die Methode ist sehr einfach und wegen ihrer Schnellheit für Serienanalysen besonders zweckmässig.

Résumé—Une nouvelle méthode pour le dosage quantitatif du fluothane et son isomère, 1,1,2-trifluoro-1-bromo-2-chloroethane, utilise des spectres ultra-rouges de tous les deux composés. La méthode est aussi applicable pour détermination des petites quantités d'isomère dans fluothane, obtenu par le

rearrangement intramoléculaire de son isomère. Sous conditions décrites, des quantités si petites que 0·1% d'isomère dans fluothane peuvent être estimées avec une déviation maximale de 10% rélatif. La méthode est très simple, et pour sa rapidité, très convenable pour des analyses de routine.

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The determination of nitrate in water

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In searching for a simple and reliable method suitable for the routine determination of nitrate in water, a number of colorimetric reagents including brucine and phenol disulphonic acid were investigated, but these were, in general, found to be lacking in sensitivity. Methods in which nitrate is reduced to ammonia were also investigated. Among the reagents recommended for this purpose are ferrous hydroxide and other ferrous salts, titanous chloride and Devarda's alloy. All these were tested, but in no instance could reagents be obtained which gave sufficiently low blank tests. Ferrous salts gave blank values too high to measure colorimetrically. Three samples of titanous chloride from different sources gave blanks of 0·98, 1·16 and 1·20 ppm of N. Devarda's alloy gave a blank of 0·98 ppm of N. The chromous chloride blank is usually 0·04 ppm of N.

Chromous chloride, prepared as described by Buehrer and Schupp,[1] by the reduction of potassium dichromate with zinc, was tested, and this proved to be a very effective and reliable reducing agent. The reagent as first prepared, contained a rather excessive amount of ammonia, the source of which was found to be the zinc used to prepare the reagent. The ammonia presumably comes from nitride present on the surface of the zinc, as it was found that if the zinc was boiled for a short time with hydrochloric acid and washed with water before use, a reagent could be prepared which contained only a trace of ammonia.

Distillation of a reduced water with sodium carbonate did not liberate all the ammonia formed, but good recoveries were obtained using caustic soda.

EXPERIMENTAL

Reagents

(1) *Zinc:* Granulated zinc is washed by boiling for a few minutes with hydrochloric acid diluted with an equal volume of distilled water. It is then thoroughly rinsed with distilled water.

(2) *Chromous chloride:* Boil 2 g of AnalaR potassium dichromate in a 125-ml Erlenmeyer flask with 10 ml of conc. hydrochloric acid, 5 ml of distilled water, and a large excess of purified zinc, until the colour of the solution becomes a pale blue. This takes one or two minutes. Cool the flask immediately, and cover the solution with a layer of petroleum ether (B.P. 100-120°) to inhibit oxidation. Chromous chloride reacts readily with atmospheric oxygen and the reagent must be prepared immediately before use.

(3) *Caustic Soda Solution:* Dissolve 200 g of AnalaR sodium hydroxide in distilled water and adjust the volume to 1 litre. Heat this to boiling in a Pyrex flask and add an excess of chromous chloride solution (10 ml to 20 ml may be required). Boil the solution for about 30 min, cool, filter through a Whatman No. 54 filter and adjust the volume to 1 litre.

(4) *Standard ammonium chloride solution:* Dissolve 3·8190 grams of AnalaR ammonium chloride in distilled water and adjust the volume to 1 litre. Dilute 10 ml of this solution to 1 litre to provide the working standard. One ml of the working standard is equivalent to 0·00001 g N.

Experimental details

Pipette 50 ml of water sample into a litre flask and add 200 ml of ammonia-free distilled water. Connect the flask to a distillation apparatus fitted with a dropping funnel. Heat the solution to boiling until steam emerges from the end of the condenser (the cooling water being turned off). Turn on the condenser water and collect 50 ml of distillate, test this to ensure absence of ammonia, and discard it.

Pipette 1 ml of the chromous chloride reagent into the flask and boil the solution for about 15 sec to allow thorough mixing. Add 2 ml of the 20% caustic soda solution and heat the flask until two 50-ml portions of distillate have been collected in Nessler tubes. Estimate the ammonia present colorimetrically by comparison with standard ammonium chloride solutions, using Nessler's reagent. Carry out a "blank" test as above using 250 ml of ammonia-free distilled water, 1 ml of chromous chloride and 2 ml of caustic soda solutions.

Recovery of ammonia from standard nitrate solutions

Results obtained for the analysis of forty standard nitrate solutions are shown in Table I. On the average about 2% loss has occurred.

TABLE I.—RECOVERY OF NITRATE FROM STANDARD SOLUTIONS (RESULTS EXPRESSED IN PARTS OF $N/10^6$)

Nitrate added	Nitrate found	Recovery %	Nitrate added	Nitrate found	Recovery %
0·80	·73	91	1·18	1·22	103
0·80	·73	91	1·18	1·11	94
0·80	·78	98	1·18	1·18	100
0·80	·80	100	1·18	1·24	105
0·80	·76	95	1·18	1·18	100
0·80	·76	95	1·18	1·18	100
0·80	·78	98	1·18	1·26	107
0·80	·80	100	1·18	1·09	92
0·80	·73	91	1·18	1·11	94
0·89	·89	100	1·18	1·11	94
0·89	·91	102	1·18	1·18	100
0·89	·84	94	1·58	1·49	95
0·89	·84	94	1·58	1·44	91
0·89	·87	98	1·58	1·49	95
0·89	·84	94	1·58	1·71	108
0·89	·87	98	1·58	1·64	104
0·89	·87	98	1·58	1·60	101
0·89	·87	98	1·58	1·49	95
1·11	1·11	100	1·58	1·56	99
1·18	1·29	109	1·58	1·56	99

Interference

A possible source of interference in water is albuminoid matter, but the conditions of the test are not sufficiently alkaline to cause decomposition to ammonia in any waters examined. The method, as described, does not differentiate between nitrate and nitrite in water, and if the latter is present it must be determined separately, and due allowance made in calculating the true nitrate content.

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Zusammenfassung—Eine zuverlässige und schnelle Methode zur Bestimmung von Nitrat in Wasser wird beschrieben. Nitrat wird zu Ammoniak reduziert (Chrom-II-chlorid), letzteres abdestilliert und nach Nessler kolcrimetriert.

Résumé—L'auteur décrit une méthode rapide et sûre de dosage du nitrate dans l'eau. Le nitrate est reduit en ammoniac à l'aide d'une solution de chlorure chromeux l'ammoniac produit est chassé par distillation, puis dosé par colorimétrie avec le réactif de Nessler.

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SHORT COMMUNICATIONS

Rate of hydrolysis of thiolacetic acid in basic solutions*

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INTRODUCTION

THIOACETAMIDE has been used as a reagent for the precipitation of metal sulphides. Recently, there has been a great deal of interest in the reaction rates and reaction mechanisms of many metal ions with this reagent.[1-6] Hydrolysis of thioacetamide in acid and in alkaline solutions as well as in buffer systems[1,7-9] has been investigated.

Butler, Peters and Swift[8] noted that in alkaline solution, thioacetamide hydrolyses rapidly to yield the thiolacetate ion and ammonia, and that the subsequent conversion of the thiolacetate ion to produce the sulphide ion proceeds much more slowly. The rate of the latter was determined indirectly using thioacetamide as the starting material.

Rosenthal and Taylor[9] found supporting evidence that thiolacetic acid is an intermediate in the hydrolysis of thioacetamide in both acid and alkaline solutions.

The reactions of thiolacetic acid with some metal ions are known. Danziger[10] suggested that a compound is formed with cobalt, and Gutzeit[11] has shown that ammonium thiolacetate reacts with lead in cold hydrochloric acid solution to give a red precipitate of the sulphochloride which is transformed on heating into lead sulphide. Heap *et al.* obtained plumbous thiolacetate by heating tetraethyl lead and thiolacetic acid in the presence of silica gel.[12] Schiff and Tarugi recommend the use of a slightly ammoniacal solution of ammonium thiolacetate for precipitation of metal sulphide.[13] In this laboratory, preliminary investigations have shown that complex formation occurs between thiolacetic acid and salts of lead and tin. These compounds are the subject of investigations now in progress.

It was felt that before clarifying the role played by thiolacetic acid as an intermediate in the reactions of thioacetamide with metal ions, a more complete study of the properties of thiolacetic acid was necessary. Swift's value for the rate of hydrolysis of thiolacetic acid, obtained by an indirect method, is subject to question because of the assumptions made. Therefore, the rate of hydrolysis of thiolacetic acid was determined directly.

EXPERIMENTAL

Reagents

Thiolacetic acid: Eastman (practical grade), was distilled at 87-88°, and infrared spectra run at periodic intervals showed that the acid was stable for reasonable periods of time. Solutions (0·1*M*) were prepared from freshly distilled material.

Sodium hydroxide solutions: Standardised with potassium acid phthalate.

Sodium perchlorate solutions: Standardised gravimetrically with potassium chloride.

Reagent grade chemicals were used in the preparation of all solutions. For the infrared studies of thiolacetic acid, spectral grade *carbon tetrachloride* was employed as the solvent.

Apparatus

Infrared measurements were made with a Perkin-Elmer, Model 21, double beam spectrophotometer equipped with sodium chloride optics.

The ultraviolet spectrum was initially determined on a Perkin-Elmer Spectracord, Model 4000. A Beckman, Model DU, quartz spectrophotometer with a hydrogen discharge lamp and 1-cm quartz cells was also used.

The reaction vessel for the rate studies was a 38- × 200-mm test-tube with a two-hole rubber stopper.

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* This investigation was supported by a U.S. Atomic Energy Commission Grant, Contract No. AT(30-1)906.

Procedure

Spectrophotometry: Solutions of thiolacetic acid, 10^{-4} *M*, were prepared, and each was adjusted with sodium hydroxide or hydrochloric acid to give a pH in the range 4·5-11·0. The ultraviolet spectrum of each solution was obtained, and the relationship between concentration of the acid and optical density was determined at 243 mμ. For the infrared spectrum, a 5% (by weight) solution of thiolacetic acid in carbon tetrachloride was found to be satisfactory.

Rate measurements: Solutions for each experiment were prepared from distilled water and standard stock solutions of sodium hydroxide and sodium perchlorate. Each solution was preheated in the reaction tube to a temperature of 90° ± 1° and the thiolacetic acid solution was then pipetted into the vessel.

At timed intervals, ranging from 10-160 min after initiating reaction, samples of the solution were removed from the reaction tube and transferred to 50-ml volumetric flasks. After dilution, the thiolacetic acid concentration was determined spectrophotometrically.

RESULTS AND DISCUSSION

Spectrophotometry

The infrared spectrum for a solution of thiolacetic acid in carbon tetrachloride is shown in Table I and is compared with the values and assignments of Sheppard[14] for thiolacetic acid as a vapour. The results are essentially identical.

TABLE I.—INFRARED ANALYSIS OF THIOLACETIC ACID

Assignment*		Literature values*(vapour)		Observed (liquid)	
CH_3	Stretch	2920 cm^{-1}	(m)		
SH	Stretch	2550	(m)	2550 cm^{-1}	(m)
C=O	Stretch	1696	(vs)	1690	(vs)
CH_3	Asymm. deform.	1415	(m)	1410	(m)
CH_3	Symm. deform.	1352	(s)	1350	(s)
CH_3	In-plane wag	1126	(s)	1120	(s)
C—C	Stretch	993	(s)	990	(s)
SH	Deform.	838	(m)	830	(m)

* Sheppard[14]

Crouch[15] attributes the absence of bands at 3400 cm^{-1} and 960 cm^{-1} to the absence of OH and C=S groups respectively, indicating that the acid has the thiol structure, $CH_3.CO.SH$, rather than the thio structure, $CH_3.CS.OH$. It is also worthy of note that thiolacetic acid, upon standing for several days does not show any change in the infrared spectrum.

In the ultraviolet region Rosenthal and Taylor[9] observed a shift in the maximum for very acidic or very basic thiolacetic acid solutions. However, for the pH range 4·5-11·0, the maximum absorbance remained at 243 mμ.

Rate measurements

Experiments were conducted with various initial thiolacetic acid and sodium hydroxide concentrations. These concentrations were chosen in order to obtain information on conditions comparable to those described in the literature[8] for the rate of hydrolysis of thiolacetic acid using thioacetamide as the starting material. The results are shown in Table II.

TABLE II.—SECOND-ORDER RATE CONSTANT FOR THE HYDROLYSIS OF THIOLACETIC ACID IN ALKALINE SOLUTION AT 90°.

Series	Init. conc., *mole/litre* NaOH	CH_3COSH	No. of detns.	k′, *litre/mole/min*
1	0·10	0.03	20	0·011
2	0·10	0·02	3	0·011
3	0·08	0·02	3	0·010
4	0·30	0·02	3	0·010
			Weighted Average	0·010 ± ·0015

The ionic strength for all experiments was 0·30; all initial concentrations are for 25°.

Order of reaction and calculation of velocity constant

For the reaction

$$A + B \ldots \xrightarrow{k'} \text{products}$$

the second-order rate constant was calculated from the integrated form of the rate equation[16]:

$$\ln \frac{C_A}{C_B} = (C_{A_0} - C_B)\,k't + \ln \frac{C_{A_0}}{C_B}$$

when A represents thiolacetic acid and B is the hydroxyl ion. C_{A_0} and C_{B_0} are initial concentrations of thiolacetic acid and hydroxyl ion respectively at time, t = 0.

The logarithmic plot of the ratio $\frac{C_A}{C_B}$ versus time gives a straight line whose slope is equal to $[C_{A_0} - C_{B_0}]\,k'$. The value of k′ was calculated from this expression and the second-order velocity constant is found to be 0·010 ± 0·0015 litre mole^{-1} min.^{-1} at 90°.

Temperature dependence of hydrolysis of thiolacetate

A series of experiments was performed to determine the change in the rate of hydrolysis of thiolacetate over the range 70°-90°. The reaction solutions were initially 0·03*M* in thiolacetate and 0.010*M* in sodium hydroxide; the ionic strength of the solution was adjusted to 0·030 with sodium perchlorate. In Table III are shown the values of the second-order velocity constant, k′, obtained for the temperatures stated. The energy of activation was calculated from a plot of $-\log k'$ *vs* $\frac{1}{T}$ and was found to be 23 ± 2 kcal per mole.

TABLE III.—VARIATION WITH TEMPERATURE OF SECOND-ORDER RATE CONSTANT FOR HYDROLYSIS OF THIOLACETIC ACID IN ALKALINE SOLUTIONS

Temperature, *°C*	Second-order rate constant, k′, *litre mole⁻¹ min⁻¹*
70	0·0020
80	0·0044
90	0·010

The values for the second-order rate constants are about one-half those reported by Butler[8] while the activation energy was found to be approximately the same. Butler used thioacetamide as the starting material and although the similarity in activation energies indicates that the same reaction may be involved in both cases, the rate constants are sufficiently different to warrant consideration.

Analytical considerations

These experiments show that thiolacetic acid hydrolysis is slower than previously thought. Further considerations of this discrepancy in reacton rates must be made and incorporated into any proposed mechanism of thioacetamide reaction. If one assumes that the rate of hydrolysis is slower, this suggests that there might be sufficient thiolacetic acid present as the result of the breakdown of thioacetamide to be significant in forming intermediates with metal ions. Apparently the reaction of thioacetamide with different metals does not show any significant trends which could result from the fact that complex formation between thiolacetic acid and metal ions has been neglected.

Preliminary investigations in this laboratory have shown that lead and tin complex-formation occurs with thiolacetic acid. The complexes have been isolated and studied, and the work has been expanded to include various cations.

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Summary—The infrared spectrum obtained for thiolacetic acid dissolved in carbon tetrachloride has been found to be similar to that of the vapour phase. The ultraviolet spectrum had been determined in solutions of varying pH (4·5-11·0) and it has been found that the spectral curve as a function of acidity remains unchanged. The molar extinction coefficient at 243 mμ for thiolacetic acid has been calculated to be 6666 litre mole^{-1}cm^{-1}. The rate of hydrolysis of thiolacetic acid in alkaline solutions is found to be first-order with respect to the thiolacetate and hydroxyl ion concentrations. The second-order rate constant is 0·010 ± 0·0015 litre mole^{-1} min^{-1} at 90°. The energy of activation has been calculated to be 23 ± 2 kcal per mole from 70° to 90°.

Zusammenfassung—Das Infrarotspektrum von in Tetrachlorkohlenstoff gelöster Thioessigsäure wird als ähnlich dem der Gasphase gefunden. Das UV-Spektrum in Lösungen verschiedenen pH-Wertes (4·5-11·0) wurde studiert und es wurde gefunden, dass die Kurven unabhängig vom Säuregrad sind. Der molare Extinktionskoeffizient bei 243 mμ wurde zu 6666 l.mol^{-1}.cm^{-1} berechnet. Die Geschwindigkeit der Hydrolyse wurde bestimmt. Es wurde gefunden, dass die Reaktion in Bezug auf Thioessigsäure und Hydroxylionen erster Ordnung ist. Die Geschwindigkeitskonstante der Reaktion zweiter Ordnung ist 0·01 ± 0·0015 l.mol^{-1}.min^{-1} bei 90°C. Die Altivierungsenergie wurde zu 23 ± 2 kcal per Mol (70 – 90°C) berechnet.

Résumé—Le spectre infra-rouge obtenu pour l'acide thiolacétique dissous dans le tétrachlorure de carbone est trouvé semblable à celui de la phase vapeur.

Le spectre ultra-violet a été déterminé dans des solutions de différents pH(4, 5-11,0); les auteurs ont trouvé que la courbe spectrale en fonction de l'acidité restait inchangée. Le coefficient d'extinction molaire à 243 mμ pour l'acide thiolacétique a été calculé : 6666 litres molé$^{-1}$ cm^{-1}.

La vitesse d'hydrolyse de l'acide thiolacétique en solution alcaline a été déterminée : elle est du premier ordre par rapport aux concentrations du thiolacétate et de l'ion hydroxyle. La constante de vitesse du deuxieme ordre est 0,010 ± 0,0015 litre molé$^{-1}$min^{-1}. à 90°C. L'énergie d'activation calculée est 23 ± 2 kcal. par mole de 70 à 90°C.

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Spot test for bi- and quadrivalent sulphur in organic compounds based on reduction with Raney alloy*

(*Received* 25 *January* 1962. *Accepted* 22 *February* 1962)

In a previous paper[1] it has been reported that Raney alloy and caustic alkali is a much more reactive reductant than Devarda alloy. For instance, if alkaline solutions of aromatic sulphonic acids or pyridine (or pyridinesulphonic acids) are heated with these alloys, reductive separation of the SO_3H group or hydrogenation to piperidine is accomplished only by the Raney alloy. The latter consists

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* Translated by Ralph E. Oesper, University of Cincinnati, Ohio, U.S.A.

of 50% Ni and 50% Al. Tests for aromatic sulphonic acids and their derivatives, and also a test for pyridine (and pyridinesulphonic acids) have been based on this finding.[2] The reason that reductions which fail with Devarda alloy can be accomplished in alkaline media through Raney alloy is that the hydrogen liberated during the formation of the alkali aluminate is partly retained by metallic nickel as hydride, so that so-called Raney nickel results. Accordingly, metallic nickel or, more correctly, the formation of nickel hydride, catalytically hastens reductions in alkaline media. It seemed logical to assume that solution of Raney alloy in hydrochloric acid with initial production of aluminium chloride and hydrogen would likewise result in the formation of nickel hydride through union of the hydrogen with the slightly soluble metallic nickel. If this were the case, it should be possible to accomplish reductions which do not succeed with the hydrogen obtained from Devarda alloy and acid. A necessary condition would be that the speed of formation of the hydride and of reduction are greater than the solution velocity of the Raney alloy and the Raney nickel formed from this alloy. This is the case with methylene blue, as shown by the following experiment. If equal parts of a 5% hydrochloric acid solution of the dyestuff are treated with several cg of (a) Raney alloy, or (b) Devarda alloy, hydrogen sulphide is produced only by the Raney alloy, as revealed by the blackening of lead acetate paper. This effect may be observed even with very dilute solutions of the dyestuff.

Since it is well known that methylene blue is very quickly reduced to the leuco compound by hydrogen, the production of hydrogen sulphide on warming with Raney alloy demonstrates that nickel hydride in acid media can bring about a reductive cleavage of the bivalent sulphur from the leuco compound. This is in conformity with the additional finding that open and cyclic thioethers, as well as aliphatic and aromatic disulphides, behave in this same manner when they are warmed with Raney alloy and acid. This production of hydrogen sulphide leads to a means of detecting compounds of these types hitherto lacking. It should be noted that thiols and thioketones are reductively cleaved by "nascent" hydrogen (hence by Devarda alloy and acid) with production of hydrogen sulphide. Similarly, sulphoxides and sulphinic acids yield hydrogen sulphide when warmed with Raney alloy and acid, whereas sulphonic acids and their derivatives, as well as sulphones, *i.e.*, compounds containing sexavalent sulphur, remain unaltered. Accordingly, reduction with Raney alloy provides a reliable preliminary test for bi- and quadrivalent sulphur in organic compounds, even in the presence of sexavalent sulphur.

The reductive cleavage of organic sulphides by Raney alloy in hydrochloric acid solution, with participation of nickel hydride (Raney nickel) as hydrogen donor, can be formulated

$$[\mathrm{R(Ar)}]_2\mathrm{S} + 4\mathrm{NiH} + 8\mathrm{HCl} \rightarrow 2\mathrm{R(Ar)H} + \mathrm{H_2S} + 4\mathrm{NiCl_2} + 8\mathrm{H}^0$$

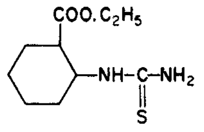
Analogous equations can be written for disulphides and other aliphatic and aromatic compounds containing bi- and quadrivalent sulphur.

The test described here provides a means of detecting sulphur dyes, *e.g.*, thiazine dyes in the presence of dyes which contain sulphonic groups, *i.e.*, sexavalent sulphur. This test may also be applied in the differentiation of sulpha compounds (sulpha drugs) since only those which contain bivalent sulphur react with Raney alloy and acid to yield hydrogen sulphide. Such dyestuffs and sulpha compounds were among the compounds tested by us.

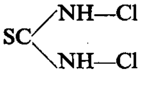
Procedure: The test is conducted in a micro test-tube. A little of the solid test material, or 1 drop of its solution, is treated with several cg of Raney alloy and 1–2 drops of concentrated hydrochloric acid. After the vigorous evolution of hydrogen has subsided, the open end of the test-tube is covered with a piece of lead acetate paper. The test-tube is then placed in a water bath at 80° and then at 100°. A positive response is shown by the development of a brown or black stain on the reagent paper.

Limits of identification:

2·5 μg *o*-carboxyphenylthiourea ethyl ester,

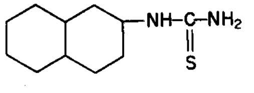


2·5 μg dichlorothiourea,



$$\mathrm{SC}\begin{cases}\mathrm{NH{-}Cl}\\ \mathrm{NH{-}Cl}\end{cases}$$

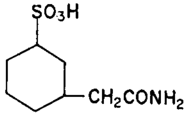
2·5 μg 1-naphthylthiourea,



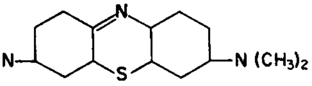
5 μg 4,4′-bis(dimethylamino)thiobenzophenone, $[(\mathrm{CH_3})_2\mathrm{NC_6H_5}]_2\mathrm{CS}$

2·5 μg thiocarbanilide, $C_6H_5—NH—CS—NH—C_6H_5$

2·5 μg 3-acetamino-4-methoxy-benzolsulphinic acid,

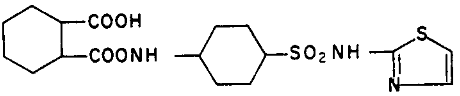


2·5 μg methylene blue,



2·5 μg 1-cystine, $[—SCH_2CH(NH_2)COOH]_2$

3 μg phthalyl sulphathiazole,



5 μg dithio-oxamide, $NH_2CSCSNH_2$

1 μg benzene sulphinic acid, sodium salt, $C_6H_5SO_2Na$

5 μg *p*-toluene sulphinic acid, sodium salt, $CH_3C_6H_4SO_2Na$

Acknowledgement—We gratefully acknowledge the financial support provided by the Conselho Nacional de pesquisas.

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Summary—Organic compounds containing bi- or quadrivalent sulphur are cleaved when warmed with Raney alloy and hydrochloric acid, and yield hydrogen sulphide. This has been made the basis of a preliminary test for compounds of this kind. Identification limits from 1–5 μg are obtained in spot test analyses.

Zusammenfassung—Organische Verbindungen die 2-oder 4-wertigen Schwefel enthalten, spalten bei Erwärmung mit Raney Legierung und Salzsäure Schwefelwasserstoff ab. Darauf lässt sich ein Vorprobe auf hierhergehörige Verbindungen begründen. In der Arbeitsweise der Tüpfelanalyse werden Erfassungsgrenzen vom 1-5 ug erhalten.

Résumé—Les composés organiques contenant du soufre aux degrés d'oxydation +2 ou +4 sont clivés lorsqu'ils sont chauffés avec l'alliage Raney et de l'acide chlorhydrique, et forment de l'acide sulfhydrique. Cette découverte est la base d'une recherche préliminaire des composés de cette espèce. Des limites d'identification de 1–5 μg ont été obtenues au moyen de la technique d'essai par touches.

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Talanta, 1962, Vol. 9, p. 543. Pergamon Press Ltd. Printed in Northern Ireland

EDITORIAL NOTES

1. Starting in January, 1963, all books submitted to TALANTA will be listed under the heading of "Publications Received". The number of actual book reviews published will, however, be substantially reduced.

2. The attention of contributors is drawn to the fact that papers submitted for publication in TALANTA should essentially be new publications. The submission of a paper to the Editor-in-Chief is held to imply that it has not previously been published in any major language, that it is not under consideration for publication elsewhere and that, if accepted for publication, it will not be published elsewhere in the same form in any major language without the written consent of the Editor-in-Chief.

3. In response to request from subscribers, the volume indexes for TALANTA in future years will be included as a separate inset and not bound in with the issue in which they appear.

Talanta, 1962, Vol. 9, pp. 545 to 546. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

AUSTRALIA

February 1963: **First Australian Conference on Electrochemistry:** *Royal Australian Chemical Institute, University of Tasmania and University of N.S.W.* Sydney and Hobart.

The following topics are among those to be discussed: thermodynamics of electrolytes, electroanalytical methods, electrode processes, fused salts and non-aqueous electrochemistry.

Further details are available from Dr. F. Gutmann, Department of Physical Chemistry, University of N.S.W., P.O. Box 1, Kensington, N.S.W., Australia.

CZECHOSLOVAKIA

Monday-Tuesday 30–31 *July* 1962: **Meeting of I.U.P.A.C. Division for Oils and Fats.** Prague.

UNITED KINGDOM

Thursday–Friday 28–29 *June* 1962: Symposium on **Instrument Techniques in Industry and Research:** *Society for Analytical Chemistry, Scottish and North of England Sections.* Queen's University of Belfast, N. Ireland.

The following papers are among those to be presented:

Analytical Uses of the Flame Emission Spectra of Lead and Titanium.	C. L. Chakrabarti, R. J. Magee and C. L. Wilson
Quantitative Gas-Liquid Chromatography in the Routine and Research Laboratory.	A. F. Williams
Applications of Vapour Phase Infrared Spectroscopy to the Functional Group Analysis of Propoxy- and Butoxy-Compounds by Modified Zeisel Reactions.	D. M. W. Anderson

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Thursday–Friday 5–6 *July* 1962: Symposium on **Spectroscopy in the Metallurgical Industry:** *Institute of Physics and Physical Society, Spectroscopy Group* and *British Non-Ferrous Metals Research Association* and *British Iron and Steel Research Association.* Buxton, Derbyshire.

Further details may be obtained from the Administration Assistant, Institute of Physics and Physical Society, 47, Belgrave Square, London, S.W.1

Thursday–Saturday 20–22 *September* 1962: Joint Symposium on **Standardisation in Non-Destructive Testing:** *Non-Destructive Testing Society of Great Britain* and *Institution of Production Engineering. Old Swan Hotel,* Harrogate.

Further details may be obtained from the Secretary, Institution of Production Engineering, 10, Chesterfield Street, Mayfair, London, W.1.

Wednesday–Friday 3–5 *April* 1963: Symposium on **Soil Analysis and Its Relation to Plant Composition and Growth:** *Society of Chemical Industry, Agriculture Group:* Bristol.

Further details may be obtained from the Assistant Secretary, Society of Chemical Industry, 14, Belgrave Square, London, S.W.1.

13–17 *April* 1964: **Second International Fermentation Symposium:** Society of Chemical Industry. London.

The subjects to be discussed are classified under the following broad groups:

Instrumentation.
Antibiotics and Other Products of Fermentation.
Biochemical Engineering.
Culture Maintenance and Genetics.
Continuous Culture.
Tissue Culture and Vaccines.

Further details may be obtained from the Hon. Secretary, Second International Fermentation Symposium, Society of Chemical Industry, 14, Belgrave Square, London, W.1.

The following *New British Standard* is announced by **British Standards Institution:**

B.S. 3477: 1962: Method for the determination of oils, fats and waxes in cotton. This describes a method for the removal and determination of oil, fat or fatty acid, in raw, scoured, and bleached cotton, and in cotton containing a stated variety of ingredients added as size or finish. Certain materials containing oxidised unsaturated oils, waterproofing or softening preparations, rot-proofing agents and synthetic resins are excluded. (Price 3s.)

The following *Revised British Standard* is announced:

B.S. 846: 1962: Burettes and bulb burettes. This specifies in Part 1, 10 sizes of burette from 1 to 100-ml capacity and in Part 2 bulb burettes of 45, 65, 85 and 105-ml capacity. It includes dimensions, tolerances on capacity, delivery times, and requirements for material, construction and graduation (Price 7s. 6d.)

The following *Amendment Slips* are announced:

B.S. 1728: Methods for the analysis of aluminium and aluminium alloys: Part 4: 1952: Zinc (polarographic method). Amendment No. 2: PD 4521.

B.S. 2728: Methods of testing plastics: Part 4: 1958: Analytical methods and viscosity in solution. Amendment No. 8: Methods 401: PD 4467.

UNITED STATES OF AMERICA

Tuesday–Friday 17–20 *July* 1962: **Second International Symposium on Fluorine Chemistry:** *American Chemical Society*, *Division of Industrial and Engineering Chemistry* and *Air Force Materials Central* and *University of Denver*. The Stanley Hotel, Estes Park, Colo.

The lecture programme contains the following paper of interest to analytical chemists:

Null-Point Potentiometric Determination of Fluoride. T. A. O'Donnell

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Monday–Tuesday 6–7 *August* 1962: **Fifth Annual Rocky Mountain Spectroscopy Conference:** *Society for Applied Spectroscopy, Rocky Mountain Section.* Olin Hotel, Denver, Colo.

The conference will feature symposia on:

Medical and Biochemical Materials
Applications of the Vacuum Ultraviolet Region
Trace Analysis
Mineralogical Analysis.

Further details may be obtained from Francis S. Bonomo, Denver Research Institute, University of Denver, Denver 10, Colo.

Monday 29 *October* 1962: Third Informal Symposium on **Vacuum Microbalance Techniques.** Statler Hilton Hotel, Los Angeles, California.

Further details may be obtained from Dr. Klaus Behrndt, Dept. 592-50, General Dynamics/Astronautics, P.O. Box 166, San Diego 12, Calif.

ERRATA—Volume 9

Page 225: the author in reference 4 should read J. S. Hetman.

Page 405, line 12: for 1933 read 1923.

Talanta, 1962, Vol. 9, p 547. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

The determination of thallium in urine: M. Ariel and D. Bach. (2 *April* 1962)

Quantitative treatment of exchange equilibria involving complexans—I: General consideration and scope of applications in analytical chemistry: Genkichi Nadagawa and Motoharu Tanaka. (3 *April* 1962)

Photometric determination of uranium in calcium fluoride with 1-(2-pyridylazo)-2-naphthol (pan) using 1,2-diaminocyclohexane-tetra-acetic acid as masking agent: K. L. Cheng. (6 *April* 1962).

Thermogravimetry of some uranium^{VI} 8-hydroxyquinolates: Jon Bordner and Louis Gordon. (6 *April* 1962)

Identification of polyatomic anions by infrared spectroscopy: F. R. Haba and C. L. Wilson. (27 *April* 1962)

Sub-micro determination of iron in organic materials: T. R. F. W. Fennell and J. R. Webb. (27 *April* 1962)

The separation and determination of microgram or sub-microgram quantities of gold in copper: The use of mercury as a collector: Atsushi Mizuike. (27 *April* 1962)

Quantitative treatment of exchange equilibria involving complexans—II: Polarographic determination of calcium in the presence of magnesium: Genkichi Nakagawa and Motoharu Tanaka. (27 *April* 1962)

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