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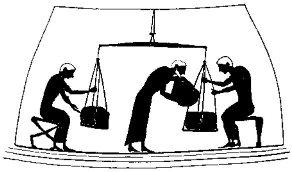

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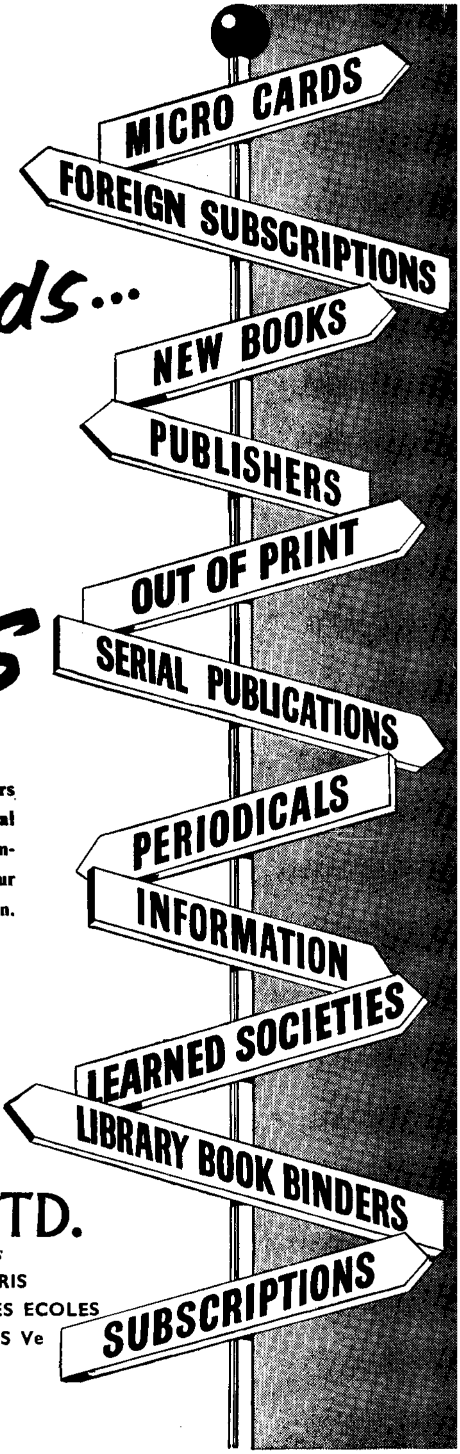
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# THE GRAVIMETRIC SEMI-MICRO DETERMINATION OF PHOSPHORUS, AS QUINOLINE PHOSPHOMOLYBDATE, IN ORGANIC COMPOUNDS

T. R. F. W. FENNELL and J. R. WEBB
Royal Aircraft Establishment, Farnborough, Hants, England

(*Received* 19 *September* 1958)

**Summary**—A gravimetric finish has been applied to the semi-micro determination of phosphorus in organic compounds after fusion with sodium peroxide. It has been shown that the precipitate of quinoline phosphomolybdate prepared from 3 mg of phosphorus has the theoretical composition and that, using a special weighing technique, very precise results can be obtained. Two other weighing techniques are described which give results satisfactory for semi-micro work.

IN a previous paper[1] a method was described for the semi-micro determination of phosphorus in organic compounds using a modified peroxide bomb fusion followed by precipitation of quinoline phosphomolybdate which was determined alkalimetrically.

Although Wilson[2] stated that the precipitate of quinoline phosphomolybdate could be used gravimetrically on the micro scale, no further interest in this method appears to have been shown. Brabson and Edwards[3] weighed the analogous oxine precipitate, but others using quinoline phosphomolybdate[4,5] have employed the volumetric finish. Wilson[2] claimed that the quinoline phosphomolybdate was of the correct composition when up to 1·75 mg of phosphorus were precipitated but found high and variable apparent molecular weights for precipitates obtained from 4·5 to 14 mg of phosphorus. The range required for semi-micro organic analysis is 2 to 3 mg. The gravimetric determination of phosphorus in this range has now been investigated. It was considered that a gravimetric finish would be preferable as difficulty was sometimes experienced with the titrimetric finish owing to atmospheric contamination.

## EXPERIMENTAL

*Oven-drying conditions:* Thermogravimetric examination of the precipitate previously dried at 110° established that no decomposition occurred below a temperature of 370°. It was found that 15 minutes oven drying at 160° was sufficient for routine purposes but for the highest possible accuracy a drying time of 30 minutes is recommended.

### *Molecular weight of the precipitate*

In this and subsequent work on standard phosphate solutions, a 0·01$M$ solution of potassium dihydrogen phosphate was used. Ten ml of this solution contain 3·098 mg of phosphorus. Crucibles were weighed on a semi-micro aperiodic balance.

As Wilson's observation[2] that the precipitate is slightly hygroscopic was confirmed, a weighing technique designed to minimise this effect was used to establish the molecular weight of the precipitate. Two matched sintered glass crucibles (porosity 4) were washed with water, dried at 160° for 30 minutes and cooled in a desiccator for 30 minutes. They were then transferred to the balance pans and weighed *immediately*—the lighter crucible acting as tare. Precipitated quinoline phosphomolybdate[1] was filtered by suction, washed with dilute (1 + 9) hydrochloric acid and then with water until free from acid. The two crucibles were then dried and weighed as described above. As this two-crucible procedure permitted weighing immediately after removing the crucibles from the desiccator, the necessity for conditioning in the balance case was obviated thereby minimising errors due to the hygroscopic nature of the precipitate. The apparent molecular weights shown in Table I were determined by multiplying the precipitate weight, in mg, by ten.

TABLE I. APPARENT MOLECULAR WEIGHT OF THE PRECIPITATE

| Test | Molecular weight found | Phosphorus found, *mg* | Error, *μg* |
|---|---|---|---|
| 1 | 2214·0 | 3·100 | +2 |
| 2 | 2212·0 | 3·097 | −1 |
| 3 | 2214·1 | 3·100 | +2 |
| 4 | 2212·0 | 3·097 | −1 |
| 5 | 2213·6 | 3·099 | +1 |
| 6 | 2211·5 | 3·096 | −2 |
| Mean | 2212·9 | 3·098 | |
| Theoretical | 2212·87 | 3·098 | |

It is apparent that, under the conditions employed, the precipitate has the theoretical composition and that the theoretical factor of 0·01400 can be used for calculating the phosphorus content.

*Effect of added sodium chloride and fluoride*

As it was desired to use the gravimetric finish for analysis of organic materials after decomposition with sodium peroxide, the effect of adding 1·5 g of sodium chloride (equivalent to the 1 g of sodium peroxide used for the fusion) was investigated. Since fluorinated materials were to be analysed, the effect of added sodium fluoride ($\equiv$ 20 mg $F^-$), complexed with boric acid,[1] was also examined.

A slight amount of contamination was indicated but even in the worst case the error was not significant for semi-micro analysis of organic materials.

*Analysis of organic materials*

The results obtained for the analysis of organic materials are shown in Table II. The preliminary fusion and precipitation procedure previously described[1] was employed.

An additional filtration, before precipitation of the phosphorus, was necessary during the analysis of the silver salt because of the necessity for removing all the silver chloride. This is not necessary when the volumetric finish is used. The first three compounds listed in Table II are standard materials and the last four were produced during research work.

*Alternative weighing procedures*

(*a*) *After oven-drying:* The two-crucible technique has the disadvantage that, for routine work, a large number of crucibles and desiccators are necessary. It was found that the error caused by the slightly hygroscopic nature of the precipitate did not unduly influence the result when only the working crucible was dried at 160° and weighed against a tare kept in the balance case.

(*b*) *Rapid procedure:* The oven-drying procedures take over an hour from the completion of filtration. A rapid procedure was found by which this time could be cut to about 15 minutes, approximately the same time as is required for the volumetric finish.

After completion of the aqueous washing of the precipitate, the filter-crucible was removed and its exterior wiped to remove excess of water. The crucible was replaced in the suction apparatus and the interior washed with three 2 ml portions of dioxan and three 2 ml portions of dry ether. Dry air was drawn through the crucible for 5 minutes. It was then wiped, transferred to the balance pan and weighed on the fifth minute against a tare kept in the balance case. The empty filter crucible had been weighed initially after similar treatment.

TABLE II. ANALYSIS OF ORGANIC MATERIALS

| Compound | Sample weight, *mg* | Phosphorus calc, *mg* | Phosphorus found, *mg* | Phosphorus calc, % | Phosphorus found, % | Absolute error, % |
|---|---|---|---|---|---|---|
| Triphenyl phosphine | 25·27 | 2·98 | 2·95 | 11·81 | 11·68 | −0·13 |
| | 25·17 | 2·97 | 2·94 | | 11·67 | −0·14 |
| | 28·19 | 3·33 | 3·29 | | 11·68 | −0·13 |
| Tri-*m*-cresyl phosphate | 24·09 | 2·03 | 2·01 | 8·41 | 8·36 | −0·05 |
| | 22·71 | 1·91 | 1·90 | | 8·38 | −0·03 |
| | 24·61 | 2·07 | 2·06 | | 8·37 | −0·04 |
| Tri-*n*-butyl phosphate | 24·27 | 2·82 | 2·82 | 11·63 | 11·63 | 0 |
| | 24·38 | 2·84 | 2·83 | | 11·60 | −0·03 |
| | 24·76 | 2·88 | 2·87 | | 11·60 | −0·03 |
| $C_6H_5{\cdot}O{\cdot}P(O)[O{\cdot}C_4H_9]_2$ | 24·57 | 2·66 | 2·65 | 10·82 | 10·80 | −0·02 |
| | 30·98 | 3·35 | 3·34 | | 10·79 | −0·03 |
| *$[CH_3{\cdot}O]_2P(O)C_6H_4{\cdot}NH_2$ | 19·45 | 3·00 | 2·97 | 15·40 | 15·28 | −0·12 |
| | 18·82 | 2·90 | 2·86 | | 15·17 | −0·23 |
| $[C_4H_9{\cdot}O]_2P(O)O{\cdot}Ag$ | 26·92 | 2·63 | 2·62 | 9·77 | 9·73 | −0·04 |
| | 24·70 | 2·41 | 2·39 | | 9·66 | −0·11 |
| $[C_3F_7{\cdot}CH_2{\cdot}O]_3PO$ | 54·47 | 2·62 | 2·62 | 4·81 | 4·81 | 0 |
| | 54·12 | 2·60 | 2·62 | | 4·84 | +0·03 |

* The preparation of this compound has not yet been described in the literature.

These precipitates were subsequently dried at 160° and weighed using the two-crucible technique in order to attempt to establish the composition of the solvent washed precipitate. The results obtained are shown in Table III.

TABLE III. RAPID DRYING PROCEDURE

| | | | | | | |
|---|---|---|---|---|---|---|
| Weight of precipitate, *mg* | 225·28 | 225·29 | 225·14 | 225·08 | 225·28 | 225·16 |
| Phosphorus found (factor 0·013757), *mg* | 3·099 | 3·099 | 3·097 | 3·096 | 3·099 | 3·097 |
| Phosphorus found (factor 0·013775), *mg* | 3·103 | 3·103 | 3·101 | 3·100 | 3·103 | 3·102 |
| Weight of precipitate after drying at 160°, *mg* | 221·25 | 221·33 | 221·35 | 221·18 | 221·27 | 221·22 |
| Phosphorus found, *mg* | 3·098 | 3·099 | 3·099 | 3·097 | 3·098 | 3·097 |
| Error, *μg* | 0 | +1 | +1 | −1 | 0 | −1 |

The oven-drying check shows that there is no loss of precipitate by the use of the organic solvents. The factor 0·013757 was derived from the average weight of precipitate which gave an apparent molecular weight of 2252·05; 0·013775 is the theoretical factor for quinoline phosphomolybdate dihydrate (molecular weight 2248·90).

## DISCUSSION

The results obtained by the two-crucible weighing technique indicate that, in spite of the hygroscopicity of the precipitate, very precise results may be obtained by using quinoline phosphomolybdate as a weighing form for the determination of phosphorus. It also appears that the theoretical factor can be used, although it was assumed that the potassium dihydrogen phosphate used to make the standard phosphate solution was pure. The fact that the results are so close to the theoretical indicates that this assumption was correct and it is considered that any other method of analysis to check the purity of the standard would be far less accurate than the method described.

For routine semi-micro determination of phosphorus, either of the alternative weighing procedures may be used. Of these, the rapid procedure seems to offer the greater advantage although the precipitate does not, under the conditions applied, have a stoicheiometric composition. It approximates closely to the dihydrate (*cf.* oxine phosphomolybdate[6]) and as can be seen in Table III, the theoretical factor for the dihydrate may be used to give results which are quite satisfactory for semi-micro analysis.

The two-crucible technique was used for the analysis of organic compounds and the results obtained were within the normally accepted limits. The preponderance of negative errors may be ascribed to slight impurity of the compounds or to losses during the procedure prior to precipitation. The reason for the consistently low results for the analysis of triphenyl phosphine is being investigated.

Although the method has been used only after mineralisation with sodium peroxide, it is considered that it should be equally satisfactory after decomposition by wet oxidation procedures or after the oxygen flask method.[7] The method has not been checked on the micro scale, the success of the semi-micro procedure being a good indication that Wilson's claim[2] for the utility of the gravimetric method for microanalysis is correct.

*Acknowledgements*—We thank Mr. E. J. P. Fear and Dr. I. M. White for provision of samples and Dr. R. Belcher for useful discussions.

**Zusammenfassung**—Nach Verschmelzung mit Natrium-hyperoxyd wird Phosphor in organischen Verbindungen durch eine Halb-mikrogravimetrische Methode bestimmt. Es wird gezeigt, dass der von 3 mg von Phosphor hergestellter Niederschlag von Chinolin-phosphormolybdänat die theoretische Zusammensetzung hat, und dass sehr präzise Resultate mittels einer besonderen Wägemethode erhalten werden. Zwei andere Wägemethoden werden beschrieben, die die Resultate fur Halbmikroarbeit befriedigend lieferten.

**Résumé**—Une fin gravimétrique à été appliquée à la détermination semi-micro du phosphore dans les composés organiques après fusion avec du peroxyde de sodium. On a montré que le précipité de phosphomolybdate de quinoléine, préparé à partir de 3 mg de phosphore, a la composition théorique et que, en utilisant une technique spéciale de pesée, on peut obtenir des résultats très précis. On décrit deux autres techniques de pesée qui donnent des résultats satisfaisants pour les travaux de semi-micro analyse.

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# DIRECT THERMOMETRIC TITRATION OF BORIC ACID

F. J. MILLER and P. F. THOMASON
Analytical Chemistry Division, Oak Ridge National Laboratory*
Oak Ridge, Tennessee, U.S.A.

(*Received* 19 *September* 1958)

**Summary**—Boric acid has been titrated directly with a standard solution of sodium hydroxide by the use of an automatic thermometric procedure. This titration was performed as one of a series of various types of titrations that could be made by an automatic thermometric procedure. Boric acid can be titrated either alone or in the presence of strong acids. Mannitol, if added to the solution of boric acid, sharpens the end-point by improving the shape of the titration curve; however, it is not necessary to add mannitol in order to obtain a good titration. Quantities of boric acid in the range of 0.3 meq. can be titrated by the automatic thermometric procedure with a relative standard deviation of 1%.

IT is customary in the determination of boron to acidify the solution that is obtained following its distillation as methyl borate, to titrate the acidified solution to the point of colour change of phenolphthalein, to add mannitol or glycerin, and then to titrate again to the phenolphthalein end point. The additional titer is taken as a measure of the boric acid that is present.

Hillebrand *et al.*[2] state: "An aqueous solution of boric acid cannot be titrated directly with a standard solution of sodium hydroxide, for no indicator is known that gives a sufficiently sharp colour change at the neutralization point, which occurs at approximately pH 11." The results that have been obtained in automatic thermometric titrations described herein indicate that boric acid can be titrated directly, either by itself or in the presence of a strong acid, with a standard solution of sodium hydroxide as the titrant.

The use of a thermometric procedure as an analytical tool dates back to Dutoit and Grobet.[1] Müller[6] suggested the use of a thermistor, a heat-sensitive device, as a replacement for the still-valuable Beckman thermometer. More recently Linde, Rogers, and Hume[4] published the results of their work on automatic thermometric titrations. Jordan and Alleman[3] have used a technique similar to that used by Linde, Rogers, and Hume to perform chelation titrations and to measure heats of chelation. Miller and Thomason[5] have used the thermometric titration as a means of determining free acid in the presence of certain hydrolyzable ions.

## EXPERIMENTAL DETAILS

### *Apparatus*

The equipment used in the titrations was very similar to that used by Linde, Rogers, and Hume[4] and by Jordan and Alleman.[3] The thermistor and bridge arrangement have been described by Jordan and Alleman.[3]

The stirring motor was a 115-v, a-c model, available from A. S. LaPine and Co. as Cat. Item No. 38286. The motor has two shafts, that is, an armature shaft turning at 1550 rpm and a slow speed

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* Operated for the U.S. Atomic Energy Commission by Union Carbide Nuclear Co., Division of Union Carbide and Carbon Corp.

shaft turning through an integral 5 : 1 geared speed reducer at 310 rpm. The motor was wrapped with a coil of 1/8 in.-dia. copper tubing through which water flowed at a slow rate. The cooling coil prevented an excessive rise in the temperature of the motor during long periods of operation. A glass stirrer was made by twisting a piece of flat glass into a spiral that was 1½ in. long and ½ in. wide and attaching it to a ¼-in. dia. glass rod.

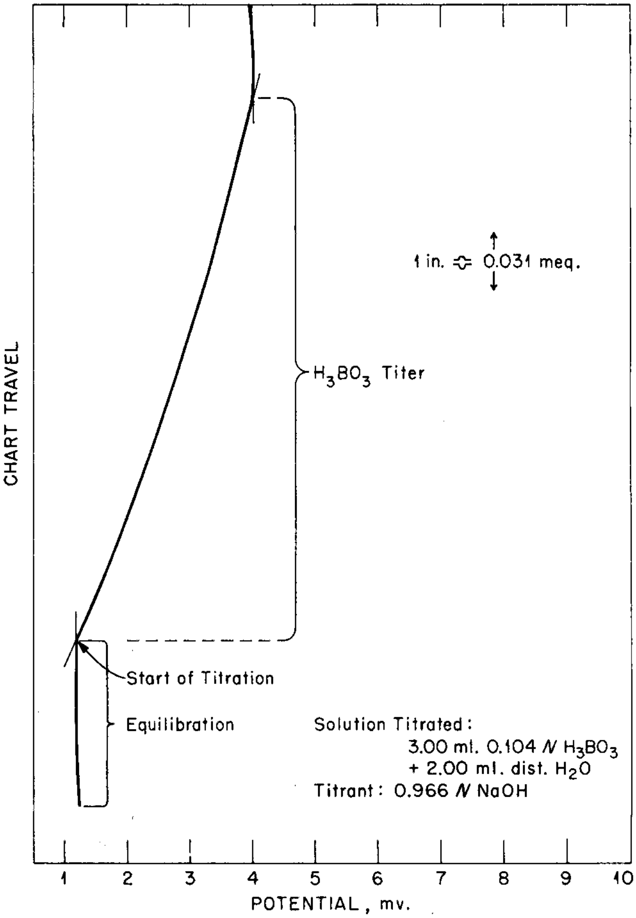

FIG. 1. Typical curve for the thermometric titration of boric acid with sodium hydroxide solution.

A Brown Electronik recorder, model No. Y153X17(VA)-X-30A3C2G, made by the Brown Instruments Division of the Minneapolis-Honeywell Regulator Co., Philadelphia, Pa., was used to record the potential across the bridge. This model recorder is convenient to use in experimental work since it has a variable span and variable zero suppression.

A Greiner, syringe-type microburette, which has a delivery capacity of 1 ml, was used in the investigation. It was fitted with a constant-speed, Bodine motor through a coupling gear so that delivery of titrant would be at a rate constant with time. A release mechanism makes possible the rapid refilling of the burette by manually turning a crank.

The titration was performed in a 20-ml, polyethylene beaker that was supported on a Styrofoam block; both the beaker and the support were contained in a 250-ml, wide-mouth, Dewar flask.

### *Reagents*

The solutions of boric acid were made up by weighing out reagent-grade, crystalline boric acid and dissolving it in water. Solutions of sulphuric acid and of hydrochloric acid were made by diluting reagent-grade acids.

*Procedure*

The test portion of a solution was pipetted into the polyethylene beaker. Sufficient distilled water was added to bring the total volume to 5.00 ml. The stirring motor, the thermistor bridge, and the recorder were turned on. The recorder was standarised, and the bridge was brought to a balance point. After a 5- to 10-minute equilibration period, the bridge was rebalanced, and the drive motor of the burette was turned on. The titration curve was recorded and the equipment shut down. The burette was refilled with the standard solution of sodium hydroxide, and the equipment was then ready for another titration.

A calibration factor was established to relate inches of chart travel to milliequivalents of sodium hydroxide delivered by the burette; this was done by titrating aliquots of a standard solution of hydrochloric acid with a standard solution of sodium hydroxide.

TABLE I. LINEARITY TEST DATA

*Solution Titrated:* indicated test portion of 0.104*N* $H_3BO_3$ + dist. $H_2O$ to make a total of 5.00 ml.

*Titrant:* 0.966*N* NaOH

*Calibration Factor:* 1.0 in. of chart travel $\Bumpeq$ 0.031 meq. $H_3BO_3$

| Test Portion of 0.104*N* Soln., *ml* | *meq* | Chart Travel, *in.* | NaOH, *meq* |
|---|---|---|---|
| 1.00 | 0.104 | 3.10 | 0.097 |
| 2.00 | 0.208 | 6.25 | 0.196 |
| 3.00 | 0.312 | 9.40 | 0.294 |
| 4.00 | 0.416 | 12.60 | 0.394 |
| 5.00 | 0.520 | 15.60 | 0.488 |

## RESULTS AND DISCUSSION

A series of titrations were performed to determine the feasibility of the thermometric titration of boric acid. Boric acid was titrated with sodium hydroxide solution both by itself and in the separate presence of mannitol, hydrochloric acid, and sulphuric acid. The results obtained with hydrochloric acid were so similar to those obtained with sulphuric acid that an extended series of titrations were made with only sulphuric acid. The addition of mannitol to the boric acid solution improves the shape of the titration curve; the starting point and the end-point are more distinct. The curve closely resembles the curve obtained in the titration of strong acids with sodium hydroxide solution. In a solution that contains both boric acid and sulphuric or hydrochloric acid, the strong acid is titrated first and then the boric acid is titrated.

The linearity of the results of the titration of boric acid with a standard solution of sodium hydroxide is illustrated by the data of Table I. A typical titration curve is shown in Figure 1. It is shown in Figure 2 how the addition of mannitol to the boric acid solution that is being titrated improves the shape of the curve.

The results obtained in the sequential titrations of constant amounts of boric acid and variable quantities of sulphuric acid in the presence of each other are given in Table II. The curve that results from the sequential titrations of these acids is shown in Figure 3.

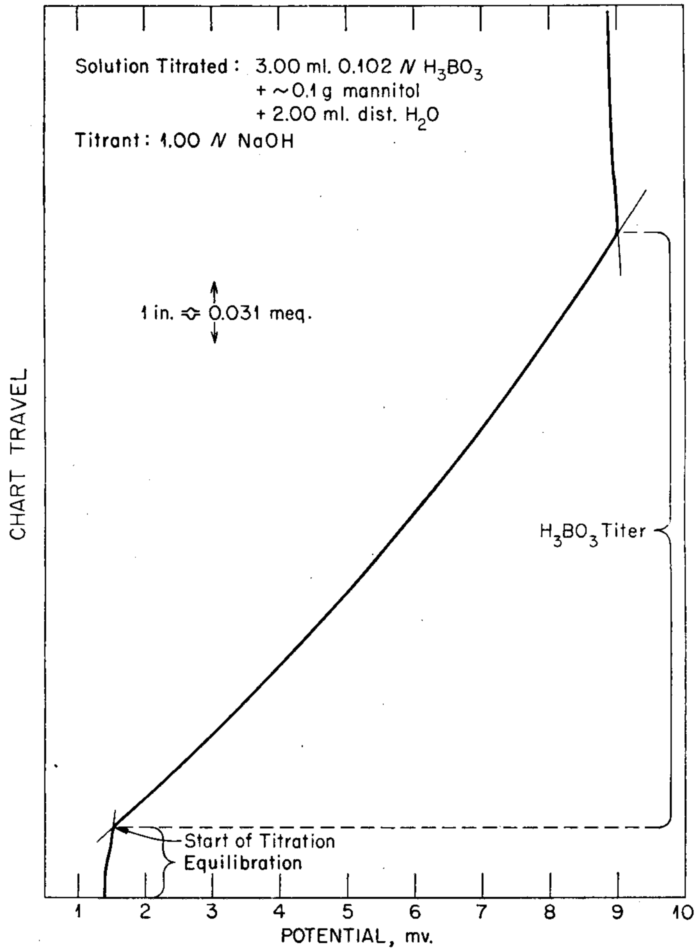

FIG. 2. Typical curve for the thermometric titration of boric acid with sodium hydroxide solution in the presence of mannitol.

TABLE II. SEQUENTIAL TITRATION OF SULPHURIC ACID AND BORIC ACID (CONSTANT AMOUNT OF BORIC ACID)

*Solution Titrated:* 1.00 ml of 0.102$N$ $H_3BO_3$ + indicated test portion of 0.908$N$ $H_2SO_4$ + dist. $H_2O$ to make 5.00 ml.

*Titrant:* 1.000$N$ NaOH

*Calibration Factor:* 1.0 in. of chart travel ≎ 0.031 meq.

| Test Portion of 0.908$N$ $H_2SO_4$, *ml* | NaOH Required, *meq* | |
|---|---|---|
| | $H_2SO_4$ Titer | $H_3BO_3$ Titer |
| — | — | 0.098 |
| 0.05 | 0.039 | 0.101 |
| 0.10 | 0.089 | 0.102 |
| 0.20 | 0.178 | 0.103 |
| 0.50 | 0.461 | 0.103 |

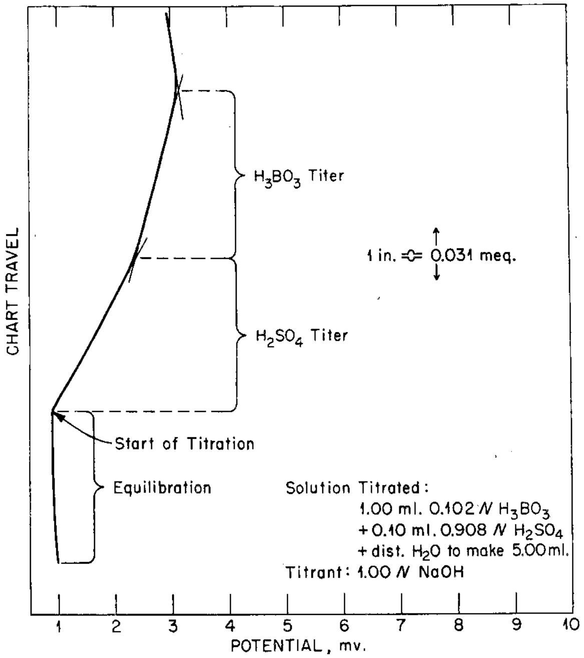

FIG. 3. Typical curve for the sequential thermometric titration of sulphuric acid and boric acid.

The results obtained in the sequential titrations of constant amounts of sulphuric acid and variable quantities of boric acid in the presence of each other are given in Table III.

The results of a study of the precision of the method indicate that in ten replicate titrations of 3 ml of 0.102*N* $H_3BO_3$ with 1.000N NaOH a standard deviation of 1.19% was obtained.

The data presented demonstrate that boric acid can be titrated directly with a standard solution of sodium hydroxide by thermometric means. The boric acid can

TABLE III. SEQUENTIAL TITRATION OF SULPHURIC ACID AND BORIC ACID (CONSTANT AMOUNT OF SULPHURIC ACID)

*Solution Titrated:* 0.10 ml of 0.908*N* $H_2SO_4$ + indicated test portion of 0.102*N* $H_3BO_3$ + dist. $H_2O$ to make 5.00 ml.

*Titrant:* 1.000*N* NaOH

*Calibration Factor:* 1.0 in. of chart travel ≙ 0.031 meq.

| Test Portion of 0.102*N* $H_3BO_3$, *ml.* | NaOH Required, *meq.* | |
|---|---|---|
| | $H_2SO_4$ Titer | $H_3BO_3$ Titer |
| 1.00 | — | 0.098 |
| — | 0.091 | — |
| 1.00 | 0.088 | 0.103 |
| 2.00 | 0.090 | 0.200 |
| 3.00 | 0.086 | 0.306 |
| 4.00 | 0.102 | 0.408 |
| 5.00 | 0.097 | 0.466 |

be determined in the presence of a strong acid, and the quantity of strong acid present can also be determined. The addition of mannitol to the boric acid solution improves the titration, but is not a requisite.

*Acknowledgement*—The authors are indebted to M. T. Kelley for his invaluable advice and to Harold C. Jones for the attachment of motor and gear system to the Greiner microburette.

**Zusammenfassung**—Borax-säure wird mit einer Standard-Lösung von Natrium-hydroxyd mittels eines automatischen thermometrischen Verfahrens direkt titriert. Man kann Borax-säure entweder allein oder in der Anwesenheit von starken Säuren titrieren. Wenn Mannit der Borax-säure-lösung hinzufügt wird, so wird der End-punkt durch Verbesserung der Form der Titrationskurve geschärft. Es ist jedenfalls nicht nötig, Mannit hinzufügen, um eine gute Titration zu erhalten. Borax säuremengen auf dem Gebiet von 0.3 milliäquivalent kann man durch das automatische thermometrische Verfahren mit einer relativen Standard-Abweichung von 1% titrieren.

**Résumé**—L'acide borique a été titré directement avec une solution étalon de soude en utilisant une technique thermométrique automatique. Le titrage était effectué comme l'un d'une série de types variés de titrages qui peuvent être faits par un tel procédé. On peut titrer l'acide borique soit seul, soit en présence d'acides forts. Le mannitol ajouté à la solution d'acide borique rend plus net le point équivalent en améliorant la forme de la courbe de titrage; cependant il n'est pas nécessaire d'ajouter du mannitol pour obtenir un bon titrage. On peut titrer des quantités d'acide borique de l'ordre de 0,3 milliéquivalents par ce procédé automatique thermométrique avec une déviation relative standard de 1%.

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# ACTIVATION ANALYSIS OF TUNGSTEN IN HIGH ALLOY STEELS

G. LELIAERT, J. HOSTE and Z. EECKHAUT
Laboratory of Analytical Chemistry, University of Ghent, Belgium

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**Summary**—Tungsten was determined by neutron activation analysis in high alloy steels. As the absorption cross-section of high alloy steels can be quite high, precautions are necessary to avoid errors due to self-shielding effects, if irradiated samples are large. Two procedures were developed namely with and without chemical separation of tungsten. Although the latter procedure is reliable in the absence of specified limiting amounts of Cu, As and Mo results are available only after 15 days. This disadvantage can be avoided by separating tungsten as tungstic acid. Both procedures were tested successfully on a number of N.B.S. standard steels. Accuracy and precision appear to be of the same order of magnitude as careful chemical analysis.

## INTRODUCTION

WHEN determining tungsten in high alloy steels it is difficult to achieve quantitative separation of small amounts of tungstic acid, when cinchonine or $\beta$-naphthoquinoline are used as precipitants. Furthermore, the precipitate is impure due to co-precipitation or adsorption of molybdenum, vanadium, tantalum, niobium, silica and other elements.

It is possible to avoid these difficulties when determining tungsten by neutron activation analysis, as the nuclear properties of this element are rather favourable. Although activation analysis is usually only used for the determination of trace elements, it appears that the method is also valuable for the analysis of minor constituents in complex materials, as shown previously in the activation analysis of vanadium in high alloy steels containing from 0·01 to 2% of this element.[1]

## NUCLEAR DATA

Natural tungsten consists of a number of isotopes which give rise to several radioactive species, whose properties are summarised in Table I.

TABLE I. PROPERTIES OF TUNGSTEN ISOTOPES

| Natural isotope | Abundance, $\theta$ | $\theta . \sigma_{act}$, *barns* | Radioisotope formed | $T_{\frac{1}{2}}$ | Radiation and energy, *MeV* |
|---|---|---|---|---|---|
| $^{180}W$ | 0·0014 | 0·028 | $^{181}W$ | 140 d | E.C.//$\gamma$0·136/0·152 |
| $^{182}W$ | 0·262 | — | $^{183}W$ | stable | — |
| $^{183}W$ | 0·143 | — | $^{184}W$ | stable | — |
| $^{184}W$ | 0·307 | 0·61 | $^{185}W$ | 74 d | $\beta^-$ 0·426/0·368//$\gamma$ 0·058 |
| $^{186}W$ | 0·284 | 9·7 | $^{187}W$ | 24 h | $\beta^-$ 0·408/0·627/1·318<br>$\gamma$ 0·68/0·645/0·478<br>0·133/0·072 |

As can be seen from Table I, the predominantly formed isotope is $^{187}W$, half life 24.0 h, whose decay scheme is given in Fig. 1.

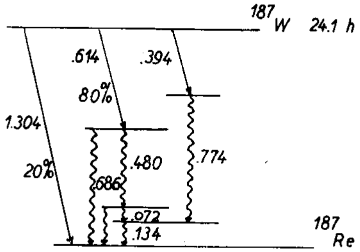

FIG. 1. Decay scheme of $^{187}W$(3).

## INTERFERING ACTIVITIES

When irradiating high alloy steels, several isotopes are produced from the steel constituents. The most important ones are represented in Table II.

TABLE II. PROPERTIES OF STEEL CONSTITUENTS, SUBJECT TO ACTIVATION BY THERMAL NEUTRONS

| Element | % in steel | Natural isotope | $\theta . \sigma_{act}$ | Isotope produced | $T_{\frac{1}{2}}$ | Radiation and energy |
|---|---|---|---|---|---|---|
| V | $\leqslant$2·5 | $V^{51}$ | 4·5 | $V^{52}$ | 3·75 m | $\beta^-$ 2·7// $\gamma$ . 1·46 |
| Cu | 0·1 | $Cu^{65}$ | 0·68 | $Cu^{66}$ | 5·1 m | $\beta^-$ 2·63/1·59// $\gamma$ 1·04 |
| Co | up to 45 | $Co^{59}$ | 17 | $Co^{60m}$ | 10·5 m | $\gamma$ 0·058 |
| Mo | seldom >2 | $Mo^{100}$ | 0·019 | $Mo^{101}$ | 14·6 m | $\beta^-$ 2·2/1·2// $\gamma$ 0·96/0·191 |
| Mn | 0·25–1·3 | $Mn^{55}$ | 13 | $Mn^{56}$ | 2·56 h | $\beta^-$ 2·86/1·05/0·75// $\gamma$ 1·77/0·82/2·06 |
| Ni | up to 40 | $Ni^{64}$ | 0·03 | $Ni^{65}$ | 2·59 h | $\beta^-$ 2·09// $\gamma$ 1·49/1·12 |
| Cu | 0·1 | $Cu^{63}$ | 2·97 | $Cu^{64}$ | 12·9 h | E.C./$\beta^+$/$\beta^-$// $\gamma$ 1·34 |
| As | 0·07 | $As^{75}$ | 4·3 | $As^{76}$ | 26·4 h | $\beta^-$ 0·4–2·98// $\gamma$ 0·55/0·64/1·2/1·4/1·7/2·05 |
| Mo | seldom >2 | $Mo^{98}$ | 0·03 | $Mo^{99}$ | 68 h | $\beta^-$ 1·23/0·45/0·2// $\gamma$ 0·74/0·18/0,14 /0·78/0·367 |
| Cr | up to 20 | $Cr^{50}$ | 0·73 | $Cr^{51}$ | 27 d | E.C.// $\gamma$ 0·32 |
| Fe | chief const. | $Fe^{58}$ | 0·0026 | $Fe^{59}$ | 45 d | $\beta^-$ 0·26/0·46// $\gamma$ 1·28/1·1/0·19 |
| Ta | 1.2 | $Ta^{181}$ | 21 | $Ta^{182}$ | 118 d | $\beta^-$ 0·53/1·1// $\gamma$ 0·05–1·2 |
| Co | up to 45 | $Co^{59}$ | 34 | $Co^{60}$ | 5·2 y | $\beta^-$ 0·309/1·48// $\gamma$ 1·17/1·33 |

If tungsten is not chemically separated before the activity measurements, a number of these isotopes are likely to interfere. Whereas $^{52}V$, $^{66}Cu$, $^{60m}Co$ and $^{101}Mo$ will decay completely within a few hours after the end of the bombardment, $^{56}Mn$ is still measurable after 24 h. Analysis of the decay curve allows us to correct for this activity as the half-life is sufficiently different from that of $^{187}W$. Activities due to the long lived species $^{51}Cr$, $^{59}Fe$, $^{182}Ta$ and $^{60}Co$ can also be easily distinguished from $^{187}W$ by analysis of the decay curve. The half lives of $^{64}Cu$, $^{76}As$ and $^{99}Mo$ are however similar to that of $^{187}W$ and are likely to cause serious interference if present in large amounts. Interferences as a function of time are represented in Fig. 2 for $^{64}Cu$, $^{76}As$ and $^{99}Mo$ to $^{187}W$ ratios of respectively 0.2, 0.01 and 5. Measurements were carried out with a Tracerlab P-20A well-type $\gamma$-detector after an activation run of 1 hour at a flux of approximately $10^7$ n/cm$^2$ sec. It is apparent that chemical separation will be necessary if these elements are present in larger amounts than those indicated above, although this will only occur exceptionally.

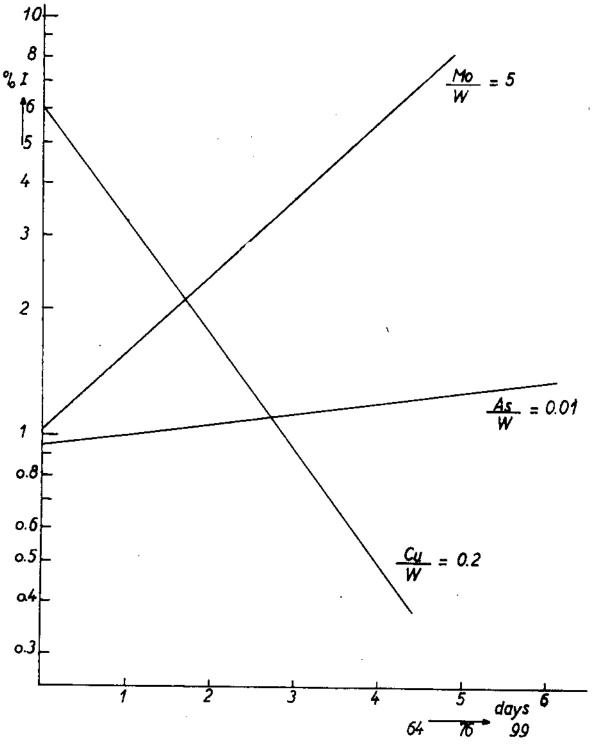

FIG. 2. Interfering activities of $^{64}$Cu,$^{76}$As,$^{99}$Mo.

## NEUTRON SELF-SHIELDING EFFECTS

As the cross-sections of the $WO_3$ used as reference standard and of some high alloy steel constituents are quite large, errors due to self-shielding effects are to be expected, especially when large samples are required as is the case at a flux of approximately $10^7$ n/cm$^2$ sec, available at the Louvain cyclotron. Fig. 3 gives a survey of the

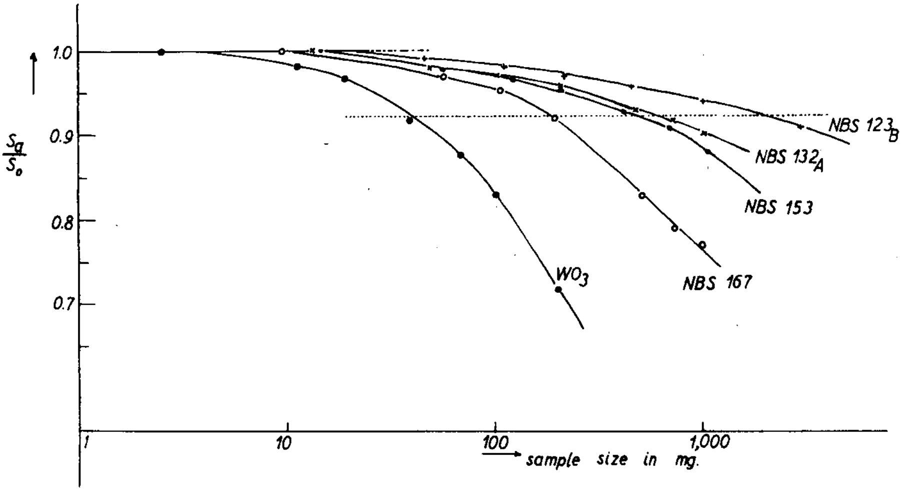

FIG. 3. Influence of sample size on the neutron self shielding.

influence of sample size on the specific activity of $WO_3$ and of the different steels under investigation.

As is apparent from Fig. 3, neutron self-shielding effects are quite important for $WO_3$ and steel NBS 167. These results are in agreement with the computed average absorption cross-section of the steel samples summarised in Table III.

TABLE III. MEAN NEUTRON ABSORPTION CROSS-SECTIONS AND COMPOSITION OF NBS HIGH ALLOY W STEELS

| % $i$ | % Fe | % Mn | % Ni | % Cr | % Co | % V | % Mo | % W | % Ta | $\frac{\sigma_i . \% i}{100}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\sigma_i$ | 2·4 | 13·3 | 4·6 | 3·1 | 37 | 2·5 | 4·9 | 18 | 22 | |
| NBS steel | | | | | | | | | | |
| $132_A$ | 81·0 | 0·268 | 0·137 | 4·21 | — | 1·94 | 4·51 | 6·20 | — | 3·5 |
| 153 | 73·9 | 0·219 | 0·107 | 4·14 | 8·45 | 2·04 | 8·39 | 1·58 | — | 5·4 |
| 155 | 96·6 | 1·24 | 0·100 | 0·485 | — | 0·014 | 0·039 | 0·517 | — | 2·6 |
| $123_B$ | 98·1 | — | — | — | — | 0·05 | 0·17 | 0·18 | 0·20 | 2·4$^5$ |
| 167 | 2·13 | 1·64 | 20·65 | 20·00 | 42·9 | 0·01 | 3·90 | 4·5 | 0·08 | 17·4 |

Three methods have been used, in order to avoid errors, due to self-shielding: at a high neutron flux of $10^{11}$ n/cm$^2$ sec, as available in the BR1 reactor, a sufficiently small sample size could be taken, so as to make self shielding effects negligible. When using a flux of $10^7$ n/cm$^2$ sec however, the sample size of the $WO_3$ reference standard and of the steel samples were adjusted to obtain a constant effect at a level illustrated in Fig. 3 (dotted line). In some other analyses errors due to self shielding were avoided by using an internal standard. This procedure has been described in detail elsewhere.[1,2]

## TUNGSTEN DETERMINATION WITHOUT CHEMICAL SEPARATION

As shown above, the activity due to $^{187}W$ in the presence of other species, activated in high alloy steels, can be computed from the graphical analysis of the decay curve if Cu, As and Mo do not exceed certain limits, as is the case with the investigated NBS steels.

### *Procedure*

Appropriate amounts of steel turnings and of $WO_3$ are weighed in polythene containers. When using the cyclotron as a neutron source, by 11·5 MeV deuteron bombardment on a beryllium target, sample size was adjusted so as to obtain a constant self-shielding effect.

At a 100 $\mu$A beam intensity, a neutron flux of approximately $10^7$ n/cm$^2$ sec was obtained in the paraffin block, used as moderator. This cylindrical block, provided with concentric irradiation holes, rotated near the cyclotron at 20 rpm. In these conditions an irradiation time of 1 hour gives an activity, large enough to allow accurate counting.

In the BRI reactor a flux of $10^{11}$ n/cm$^2$ sec was available, so that samples small enough to avoid self shielding were possible. An irradiation time of about 1 minute is convenient.

Activity measurements were carried out twice daily during 15 days by means of a Tracerlab P-20A well type Na(T1)I detector, coupled to a Tracerlab Superscaler. The sensitivity of the pre-amplifier was regulated so as to discriminate against weak gamma radiation to avoid self absorption effects.

A typical decay curve for steel $132_A$ and $123_B$ is represented in Fig. 4, and results are summarised in Table IV.

From Table IV it appears that the results are in good agreement with those of the NBS, the mean error on a number of determinations being of the same order of magnitude as those computed from the NBS certificates.

For steel samples 167 and 123B the internal standard method was also applied, allowing a direct correction of neutron self-shielding effects and possible neutron flux irregularities. In this case two steel samples were irradiated of respectively *a* and *b* mg, *c* mg pure $WO_3$ being homogeneously mixed with the latter. If $A_{tL}$ and $A'_{tL}$ are the respective activities of the long lived species at a time *t* after decay of $^{187}W$, the neutron correction factor will be given by

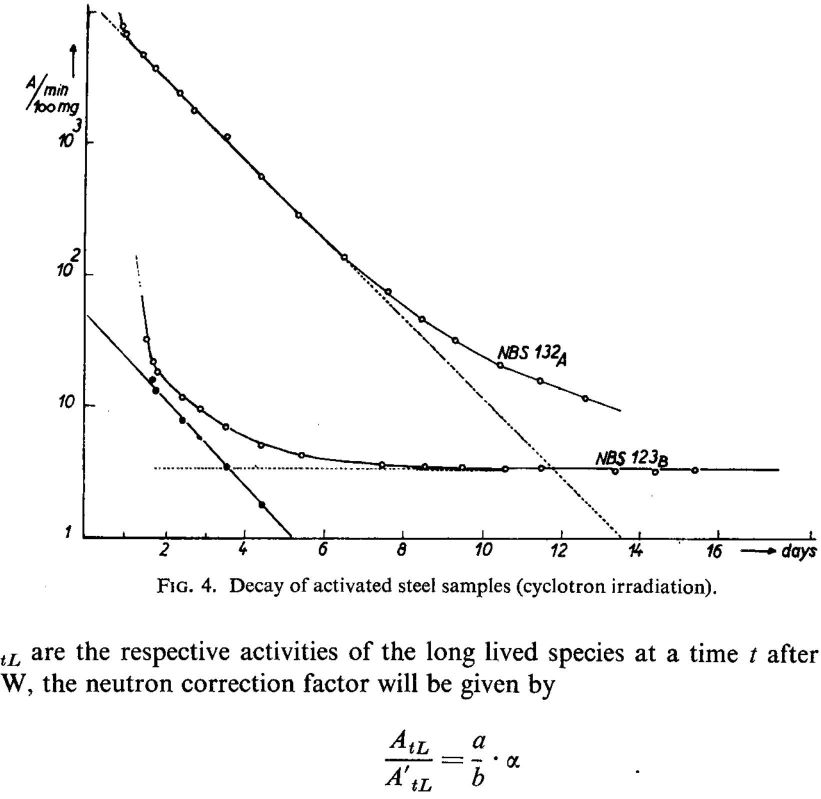

FIG. 4. Decay of activated steel samples (cyclotron irradiation).

$$\frac{A_{tL}}{A'_{tL}} = \frac{a}{b} \cdot \alpha \quad .$$

If $A_{t_0,w}$ and $A'_{t_0,w}$ are the computed tungsten activities at the time $t_0$, the specific activity in counts per mg of $^{187}W$ in the sample at this moment will be given by

$$S_{t_0,w} = \frac{1}{c}\left[A'_{t_0,w} \cdot \alpha - \frac{b}{a} \cdot A_{t_0,w}\right]$$

The tungsten content in per cent is then given by

$$\%W = \frac{A_{t_0,w} \cdot 100}{a \cdot S_{t_0,w}}$$

Decay curves corresponding to an analysis of steel 123B are represented in Fig. 5. Results are summarised in Table V and appear to be in good agreement with those of the NBS.

TABLE IV. ACTIVATION ANALYSIS FOR W WITHOUT CHEMICAL SEPARATION

| NBS Steel | NBS results | Mean error, $\bar{\Delta}$ | Sample size, *mg* | % W | Mean value | Mean error, $\bar{\Delta}$ |
|---|---|---|---|---|---|---|
| $132_A$ | 6·20 | 0·07 | 510·9<br>506·4<br>601·9<br>601·2<br>603·4<br>614·6 | 6·07<br>6·13<br>6·15<br>6·05<br>6·21<br>6·25 | 6·14* | 0·08 |
| | | | 22·272<br>22·484<br>18·363<br>17·748 | 6·24<br>6·25<br>6·20<br>6·11 | 6·20† | 0·045 |
| 167 | 4·5 | provis. certif. | 190·0<br>190·0 | 4·25<br>4·30 | 4·30* | 0·05 |
| | | | 11·082<br>14·174<br>13·230<br>20·284 | 4·39<br>4·41<br>4·42<br>4·37 | 4·40† | 0·02 |
| 153 | 1·58 | 0·027 | 506·4<br>501·2 | 1·58<br>1·59 | 1·59* | 0·01 |
| | | | 17·672<br>32·379<br>23·084<br>28·259 | 1·61<br>1·56<br>$1{\cdot}60_5$<br>1·62 | 1·60† | 0·02 |
| 155 | 0·517 | 0·006 | 1,055·9<br>1,092·9 | 0·516<br>0·512 | 0·514* | 0·01 |
| | | | 66·851<br>68·547<br>34·519 | 0·527<br>0·528<br>0·508<br>0·518 | 0·520† | 0·007 |
| $123_B$ | 0·18 | provis. certif. | 2,122·0<br>2,009·6 | 0·191<br>0·209 | 0·20* | 0·02 |

* Cyclotron activation
† BR1 reaction activation

## TUNGSTEN DETERMINATION WITH CHEMICAL SEPARATION

As pointed out before, chemical separation of tungsten becomes necessary as soon as the Cu, As and Mo to W ratios are higher than the respective values of 0·2, 0·01 and 5. Furthermore, results from the direct method do not become available until 15 days after the irradiation, as graphical analysis of the decay curves are necessary. It is possible to avoid these disadvantages by chemical separation of tungsten as tungstic acid.

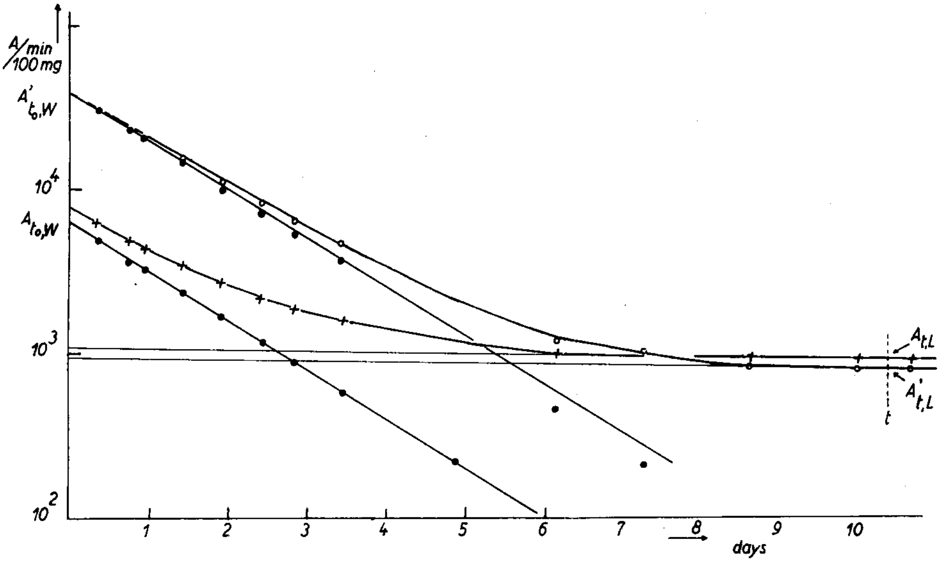

FIG. 5. Determination in NBS steel 123B by means of internal standard.

### *Procedure*

The irradiated steel samples are dissolved in 6 *N* HCl. After the reaction has subsided, concentrated $HNO_3$ is added dropwise, followed by 20 ml $HClO_4$ ($d = 1{\cdot}67$). The solution, containing the yellow tungstic acid precipitate is heated on a hot plate until HCl and $HNO_3$ are completely removed. After cooling, the solution is diluted with 50 ml water and 2 to 5 ml $H_2O_2$ (30%) are added to solubilize the tungstic acid as peroxytungstate. 3 ml 1% tungsten carrier (as $Na_2WO_4.2H_2O$) and 5 ml 1% vanadium (as $Na_3VO_4$) are added. The latter reduces molybdate adsorption on the tungstic acid precipitate to a considerable extent, as shown experimentally in separate tracer experiments.

The solution is heated on a hot plate, causing homogeneous precipitation of the tungstic acid by

TABLE V. ACTIVATION ANALYSIS WITH INTERNAL STANDARD

| NBS steel | NBS results | Means error, $\bar{\Delta}$ | Sample size, *mg* *a* | *b* | *c* | α | $A_{0}$,W | $A'_{0}$,W | % W | Mean | $\bar{\Delta}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 167 | 4·5 | provis. certif. | 397·7 | 381·5 | 126·6 | 0·997 | 6,980 | 53,420 | 4·77 | 4·53* | 0·23 |
| | | | 497·8 | 406·5 | 136·2 | 0·874 | 7,105 | 52,240 | 4·88 | | |
| | | | 610·6 | 451·6 | 126·7 | 1·112 | 9,650 | 49,660 | 4·35 | | |
| | | | 682·4 | 698·2 | 142·1 | 1·003 | 10,380 | 62,370 | 4·16 | | |
| | | | 499·8 | 508·8 | 127·6 | 0·775 | 12,150 | 61,820 | 4·50 | | |
| | | | 23·672 | 30·297 | 7·457 | 0·983 | 29,500 | 57,000 | 4·67 | 4·66† | 0·06 |
| | | | 27·736 | 29·537 | 8·753 | 0·991 | 29,400 | 63,500 | 4·74 | | |
| | | | 20·558 | 40·090 | 12·322 | 1·006 | 28,600 | 88,250 | 4·56 | | |
| 123B | 0,18 | provis. certif. | 1061·1 | 922·7 | 9·523 | 0·99 | 506 | 2,980 | 0·181 | 0·18$^2$† | 0·007 |
| | | | 770·8 | 917·6 | 17·270 | 1·076 | 325 | 3,810 | 0·196 | | |
| | | | 821·9 | 951·3 | 10·835 | 0·976 | 172 | 1,580 | 0·169 | | |

* Cyclotron activation
† BR1 reactor activation

decomposition of the peroxyacid. Disappearance of the wine red colour of peroxyvanadic acid serves as an indicator. Heating is continued for an additional 15 minutes, the precipitate filtered off on fine grained paper and washed with 3% $HNO_3$.

Tungstic acid adhering to the beaker wall is dissolved in a few drops 5% NaOH and 30% $H_2O_2$. The filtrate is transferred to this original beaker and the precipitation repeated after addition of a second 3 ml portion of tungsten carrier.

This procedure ensures a tungsten recovery better than 99·8%. The tungstic acid precipitates, together with the filter paper, are counted either separately or together in the counting equipment described above.

This procedure gives a sufficient radiochemical purification from most of the steel constituents as shown by decay measurements, gamma spectrometry and measurement of relative beta absorption according to Plumb and Lewis.[4]

In the presence of tantalum, this element is coprecipitated with tungsten and necessitates a graphical analysis of the decay curve. The presence of niobium or titanium causes no radiochemical interference.

Results are summarized in Table VI and appear to be in good agreement with the expected values.

Table VI. Activation analysis for W, with chemical separation

| NBS steel | NBS results | Mean error, $\bar{\Delta}$ | Sample size, *mg* | % W | Mean value, *m* | Mean error, $\bar{\Delta}$ |
|---|---|---|---|---|---|---|
| $132_A$ | 6·20 | 0·07 | 491·4<br>507·0<br>596·7<br>598·5 | 6·17<br>6·28<br>6·25<br>6·22 | 6·23* | 0·04 |
| 155 | 0·517 | 0·006 | 4008·1<br>1067·6 | 0·52$_1$<br>0·52$_3$ | 0·52$^2$* | 0·001 |
| 167 | 4·5 | provis. certif. | 190·5<br>190·0 | 4·17<br>4·25 | 4·21* | 0·04 |
| | | | 5·075<br>5·382<br>9·816 | 4·30<br>4·26<br>4·35 | 4·30† | 0·03 |
| 153 | 1·58 | 0·027 | 467·6<br>518·1 | 1·60<br>1·60 | 1·60* | 0·01 |
| $123_B$ | 0·18 | provis. certif. | 1967·8<br>2085·5 | 0·170<br>0·172 | 0·171* | 0·001 |

* Cyclotron irradiation
† BR1 reactor irradiation

*Acknowledgments*—Acknowledgments are due to the staff members of the cyclotron in Louvain and particularly to Dr. Képenne, as well as to Dr. de Dorlodot of the S. C. K. in Mol.

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**Zusammenfassung**—Wolfram wird durch Neutron-Aktivierungsanalyse in Hochlegierungsstahlen bestimmt. Da der Absorbierungsquerschnitt der Hochlegierungsstahlen gelegentlich ziemlich gross ist, sind Vorsichtsmassregeln nötig, um Fehler von selbstschirmenden Effekten zu vermeiden, wenn die gestrahlten Proben gross sind.

Zwei Verfahren, mit und ohne chemische Trennung von Wolfram, werden entwickelt. Obgleich das Verfahren zuverlässig ist, sind Resultate erst nach 15 Tagen vorhanden. Man kann diesen Nachteil durch Trennung von Wolfram als Wolframsäure vermeiden. Beide Verfahren werden mit einigen NBS Standard-Stahlen probiert. Genauigkeit und Präzision scheinen genau so gross zu sein wie bei sorgefältiger chemische Analyse.

**Résumé**—On a mis au point une méthode d'analyse par activation d'aciers hautement alliés à l'aide de neutrons thermiques. La section efficace de certains aciers étant assez grande, certaines précautions sont nécessaires afin d'éviter des effects de "self-shielding", surtout si les échantillons à irradier sont grands. Deux modes opératoires ont été développés: avec et sans séparation chimique.

Les résultats obtenus à l'aide des deux procédés sont valables, quoique dans le dernier cas ils ne sont disponibles qu'après 15 jours. Les deux méthodes ont été appliquées à un nombre d'aciers du N. B. S.

La précision et la reproductibilité sont du même ordre de grandeur que l'analyse chimique.

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# THE USE OF EDTA TO ELIMINATE INTERFERENCES IN THE ZINC-FERROCYANIDE TITRATION

DONALD G. DAVIS and HENRY T. MCLENDON
School of Chemistry, Georgia Institute of Technology, Atlanta 13, Georgia, U.S.A.

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**Summary**—The use of EDTA as a masking agent in the titration of zinc with potassium ferrocyanide has been investigated. If the pH is controlled at 2.0 to 2.1 and EDTA is added, accurate determination of zinc can be made in the presence of iron, nickel, lead and aluminium. However, the interference of copper, cobalt, cadmium and manganese could not be eliminated by this method.

THE determination of zinc by titration with standard potassium ferrocyanide solution has been extensively studied.[6] Lingane and Hartley[7] have noted the profound effect of pH on the composition of the zinc-ferrocyanide precipitate and other characteristics of the titration. Although they obtained accurate results over a pH range of 1 to 3, only samples of pure zinc were titrated. Because many metal ions form precipitates with ferrocyanide, its analytical usefulness is rather limited. This work was undertaken to make the ferrocyanide titration more generally useful in the presence of interfering metal ions. Cheng[3] has investigated the use of strong complexing agents, such as EDTA, for the elimination of interferences in the titration of manganese with ferrocyanide, Cheng was not able to determine zinc by the titration of ferrocyanide in the presence of EDTA at pH 2.5. In the present study a method has been developed for the titration of zinc in the presence of various metal ions whose interferences are eliminated by complexing them with EDTA. Optimum pH values have been established and various electrical methods of end-point detection have been discussed.

## REAGENTS AND APPARATUS

CP chemicals and distilled water were used to prepare all reagent solutions. The standard zinc solution was made by dissolving pure zinc in 1 : 1 hydrochloric or sulphuric acid with the appropriate amount of water.

A manual polarograph was used as an end-point detecting device in all the amperometric titrations. The electrodes used for two-electrode amperometry were prepared by sealing pieces of platinum wire in soft glass tubing. For one-electrode amperometry a Sargent Syncronous Rotator and a hook-type electrode (E. H. Sargent and Co., Chicago, Illinois) were used.

Potentiometric titrations at constant current were performed using the same electrode systems as used for two-electrode amperometry. The constant current was maintained by an apparatus similar to that of Bishop.[1] In this case, potentials were measured with a Leeds Northrup Student-type potentiometer.

## DISCUSSION

### *End-point detection*

Various electrical end-point detection methods for the titration of zinc with ferrocyanide have been proposed.[2,5,7,9] Of these, it was found that amperometric methods lead to easier and more accurate end-point detection. In general, the potentiometric methods were found to be somewhat slow in attaining stable potentials. This was especially true of classical potentiometry, but even true of potentiometric titrations at constant current using two indicator electrodes. Of the two amperometric methods, amperometry using two indicator electrodes has the advantage of simplicity since no reference electrode is necessary. However, greater sensitivity was found in the use of one-electrode amperometry. This is undoubtedly due to the fact that the indicator electrode is rotated and thus more effective stirring is achieved. One-electrode amperometry also has the advantage that no ferricyanide ion need be added as in the other end-point detecting methods. In this study two-electrode amperometry was generally used because of its simplicity except in those cases where the addition of ferricyanide was impossible due to side reactions, such as in the attempted determination of zinc-copper mixtures. A brief study indicated that a potential of 0·1 volt applied across the two indicator electrodes yielded satisfactory results when approximately ten drops of a 1% potassium ferricyanide solution (freshly prepared) were added per 100 ml of solution. The form of the titration curve has been discussed by Kies.[5] Ordinarily the curve need not be plotted as the end-point can easily be determined. Ideal curves were generally not obtained, but the end-point was always marked by a sharp increase in current when one drop of excess 0·1 *N* ferrocyanide solution was added. In some cases, a distinct dip in the indicator current was noticed just prior to the end point.

### *Effect of* pH *and* EDTA *concentration*

The effect of EDTA on the results of the zinc-ferrocyanide titration was studied at varying pH. The range of possible usefulness was between pH 1 and 3. Outside this range the composition of the zinc ferrocyanide precipitate tends to vary and useful results are not obtained. Ideally, a pH close to 3 would allow the optimum possibility for elimination of interferences. However, it was found that unless the pH was 2.1 or lower, the presence of EDTA would cause errors in the determination of zinc. This explains the difficulty Cheng[3] had, since his attempted titrations were performed from pH 2.3 to 2.5. Even at a pH of 2.1, only a certain concentration of EDTA could be tolerated before noticeable complexation of the zinc occurred. As indicated in Table I, the ratio of moles of excess EDTA per mole of zinc can be no higher than about 0.6. This, however, would allow reasonable leeway, especially in the determination of those samples whose approximate composition is known. It was found later that sufficient EDTA could be added to a sample solution to complex all of some interfering ions, such as nickel, and then the excess of 0.6 moles, with no ill effect.

### *The elimination of interferences*

The effectiveness of the masking power of EDTA on various interfering metals was tested by titrating synthetic mixtures containing zinc ion and various other metal ions. To an aliquot of zinc solution containing approximately 150 mg of zinc were added varying amounts of the metal ion whose interference was to be tested. The amounts of the various metals taken do not necessarily represent the maximum possible concentration, but were chosen on the basis of normal analytical situations. Sufficient 0.1 *M* solution of the tetra-sodium salt of EDTA was added to complex all of the interfering metal ion and an excess equivalent to approximately half of the zinc. The pH was adjusted to 2.1 ± 0.05 and ten drops of potassium ferricyanide solution were added. The solution was diluted to approximately 100 ml with water and titrated amperometrically with 0.1 *M* potassium ferrocyanide solution. Since a pH greater than 2.1 is generally assured by using the tetra-sodium salt of EDTA, the pH may easily be adjusted to 2.1 with dilute hydrochloric acid. The pH remained constant throughout the titration. Efficient stirring was provided by a magnetic stirrer.

Table I.

| Moles EDTA/Mole Zn | Zinc, *mg* | | Error, % |
|---|---|---|---|
| | Taken | Found | |
| 0 | 149.8 | 150.2 | +0.3 |
| 0.4 | | 149.5 | −0.2 |
| 0.4 | | 150.2 | +0.3 |
| 0.6 | | 149.4 | −0.3 |
| 0.6 | | 153.3 | +2.3 |
| 0.75 | | 143.2 | −4.4 |
| 0.75 | | 140.2 | −6.4 |
| 1.00 | | 121.2 | −19.1 |

The interference of nickel, iron, and lead were successfully eliminated by this method as indicated in Table II. In addition, it was found that aluminium, manganese, chloride and sulphate ions caused no errors in the titration of zinc whether or not EDTA was present. The interferences of copper, cadmium, and cobalt could not be eliminated by the addition of EDTA. This is what might be expected since the EDTA complexes of lead, nickel, and iron are stronger than that of zinc, but those of cadmium and cobalt are of equal strength.[8]

Table II.

| Metals added, *mg* | | Zinc, *mg* | | Error, % |
|---|---|---|---|---|
| | | Taken | Found | |
| $Fe^{III}$ | 28 | 163.4 | 163.4 | 0.0 |
| | 55 | | 161.9 | −0.9 |
| | 83 | | 161.9 | −0.9 |
| $Ni^{II}$ | 24 | 163.4 | 163.4 | 0.0 |
| | 48 | | 163.4 | 0.0 |
| | 72 | | 158.9 | +2.7 |
| $Pb^{II}$ | 104 | 170.3 | 169.8 | −0.3 |
| | 208 | | 169.8 | −0.3 |
| | 312 | | 170.8 | +0.3 |
| $Al^{III}$* | 23 | 170.3 | 170.1 | −0.1 |
| $Mg^{II}$* | 34 | 170.3 | 170.7 | +0.2 |

* No EDTA added.

A special effort was made to eliminate interferences of copper since copper–zinc alloys are of great commerical importance, and since the strength of the copper EDTA complex indicated that this might be possible. Copper has been effectively masked with thiosulphate ion in certain compleximetric titrations.[4] In the ferrocyanide titration, however, since the pH had to be maintained at a low value, thiosulphate ion decomposed rather rapidly and, although some success was achieved, erratic results were generally found. The addition of hydrazine sulphate was also tried as a method of eliminating the interference of copper. It was found that the hydrazine sulphate reduced the copper to cuprous ions which would not react with ferrocyanide. Complete reduction was achieved by removing the air from the solution to be titrated with purified nitrogen and the addition of 25 ml of saturated hydrazine sulphate solution. After the pH was adjusted to 2.1, the zinc was titrated using one-electrode amperometry as an end-point detecting device. An indicator electrode potential of $+0.25$ volt *vs.* S.C.E. was selected. Current–potential curves indicated that this potential would provide a maximum current from excess ferrocyanide ion with a minimum of interference from other oxidizable species in solution. The interference of cupric ion could effectively be eliminated by the addition of hydrazine sulphate, but in about 50% of the cases, excessively low results were obtained indicating that some of the zinc ion had been effectively removed from solution. In most cases some cuprous sulphate precipitated after the addition of hydrazine and when the amount of this precipitate was large a considerable amount of zinc was carried down with it. For this reason, the use of hydrazine sulphate to eliminate the interference of copper can only be recommended in those cases where the amount of copper is much smaller than the amount of zinc present. In the analysis of most samples, however, it would be convenient to remove and/or determine the copper by electrolysis and then determine the zinc by titration with ferrocyanide, eliminating the remaining interferences with EDTA.

**Zusammenfassung**—Die Anwendung von ÄDTA in der Rolle des maskierende Mittels während der Titration von Zink mit Kaliumeisencyanür wurde untersucht. In Anwesenheit von ÄDTA und pH von 2,0–2,1 ist eine genaue Bestimmung von Zink neben Fe, Ni, Pb, und Al, möglich. Man kann aber die störung von Cu, Co, Cd, Mn, nicht eliminieren.

**Résumé**—Les auteurs ont étudié l'utilisation de l'EDTA comme agent de dissimulation dans le dosage du zinc par le ferro-cyanure de potassium. Si le pH est fixé à une valeur de 2 ou 2,1 et si on ajoute de l'EDTA, on peut doser le zinc avec précision en présence de fer, nickel, plomb et aluminium. Cependant cette méthode ne pourrait pas éliminer l'interférence du cuivre, du cobalt, du cadmium et du manganèse.

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# NEW COLOUR TESTS FOR THE LARGER POLYNUCLEAR AROMATIC HYDROCARBONS

EUGENE SAWICKI and ROGER BARRY
Community Air Pollution Program
Robert A. Taft Sanitary Engineering Center, Public Health Service
U.S. Department of Health, Education, and Welfare
Cincinnati 26, Ohio

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**Summary**—An investigation of the reaction of the aromatic aldehyde-phosphorus pentachloride reagents with polynuclear aromatic hydrocarbons has shown that a number of aldehydes can be substituted for piperonal in this spectral test but only two were specific for the more basic aromatic compounds. The 9-anthraldehyde reagent gives intense bands in the 800–960 mμ spectral region with the larger hydrocarbons. The 3-nitro-4-dimethylaminobenzaldehyde reagent reacts readily in most cases with the benzene extract of air particulates. This procedure is ideal for the analysis of peri-condensed aromatic hydrocarbons.

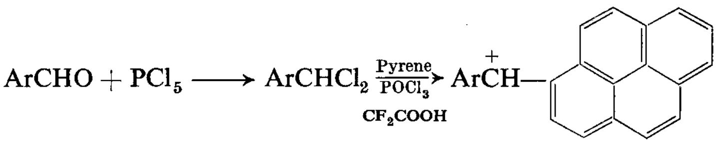
It was found that trifluoroacetic anhydride could be substituted for phosphorus pentachloride in the test reagent, but no particular advantage was incurred by this substitution.

## INTRODUCTION

UNTIL recently simple colorimetric methods for the analysis of polynuclear aromatic hydrocarbons have been practically non-existent in the literature. With the piperonal chloride test, intensely brilliant, stable colours can be formed with aromatic and hetero-aromatic compounds which are more basic than benzene under the conditions of the test, and which have their highest electron density at an aromatic carbon atom.[1,2] Of great interest are the reactions of this reagent with the strongly carcinogenic 2-acetylaminofluorene,[3] 2-trifluoroacetylaminofluorene,[3] and benzo(a)pyrene[1] to give brilliant stable colours susceptible to quantitative study. The reagent has also been applied to the study of aromatic compounds in air particulate matter.[2]

Although piperonal chloride is an excellent general reagent for aromatic compounds, sensitive reagents are needed which are specific for a smaller group of compounds or for individual hydrocarbons of air pollution interest. With the desire to obtain a reagent specific for the larger polynuclear hydrocarbons, among which are found the vast majority of potent hydrocarbon carcinogens,[4] many aldehydes have been investigated.

In these colour tests the following reactions take place, e.g. with pyrene:



The phosphorus oxychloride serves as a catalyst. Without the added extra amount the sensitivities are not as good. The trifluoroacetic acid is necessary as a strongly acidic solvent, as a proton donor, and as a reaction initiator. The evidence indicates the formation of a diarylmethane dye.[1]

## EXPERIMENTAL

### *Reagents and equipment*

Trifluoroacetic acid was obtained from the Minnesota Mining and Manufacturing Co. Furfural was obtained from the Fisher Scientific Co. Indole-3-aldehyde, 2-thenaldehyde, 2-naphthaldehyde, 9-anthraldehyde, benzo(a)pyrene and benzo(g, h, i)perylene were obtained from the Aldrich Chemical Co. Perylene was obtained from the K and K Laboratories; benzo(e)pyrene from Terra Chemicals Inc., 500 Fifth Ave, New York 36, N.Y.; acenaphthene, pyrene, anthracene, chrysene, fluoranthene and trifluoroacetic anhydride from Matheson, Coleman and Bell, Norwood, Ohio. Anthanthrene, m.p. 258°, was prepared by the reduction[5] of anthanthrone (Aldrich Chemical Co.).

3-Nitro-4-dimethylamino-benzaldehyde was prepared by the following procedure. To a stirred solution of 15 g of *p*-dimethylaminobenzaldehyde in 150 ml of concentrated sulphuric acid was added 6.6 ml of nitric acid (d. 1.42) dropwise at 0–5°. The mixture was then poured into ice water. Crystallization from methanol gave an 80–90% yield of yellow needles, m.p. 103–105°, Lit. m.p.[6] 103–105°.

A Cary recording quartz spectrophotometer Model 11, and a Beckman Model DU spectrophotometer were used for wave length maxima determinations.

### *Aldehyde*–$PCl_5$ *reagents*

*Furfural*: Fifty milligrams of furfural and 100 mg of phosphorus pentachloride were dissolved in 100 ml of chloroform with cooling.

2-*Thenaldehyde*: Fifty milligrams of this aldehyde and 100 mg of phosphorus pentachloride were boiled for 1 min in 20 ml of chloroform and then cooled. The solution was then diluted to 25 ml.

3-*Nitro*-4-*dimethylaminobenzaldehyde*: Fifty milligrams of the aldehyde and 500 mg of phosphorus pentachloride in approximately 20 ml of *o*-dichlorobenzene were heated at the boiling point until a clear solution was obtained. The solution was then cooled and diluted to 25 ml with *o*-dichlorobenzene.

9-*Anthraldehyde*: In a similar fashion 125 mg of the aldehyde and 250 mg of phosphorus pentachloride were boiled in approximately 20 ml of chloroform. The solution was cooled and diluted to 25 ml with chloroform.

*Indole*-3-*aldehyde*: Two hundred and fifty milligrams of the indole aldehyde was dissolved in 12 ml of *o*-dichlorobenzene by boiling the solution for 1 min; similarly 375 mg of phosphorus pentachloride was dissolved in 3 ml of *o*-dichlorobenzene. The cooled phosphorus pentachloride solution was added to the cooled solution of the aldehyde with stirring. The mixture was boiled for 1 min and then diluted to 25 ml with *o*-dichlorobenzene.

### *Procedure*

(*a*) To 1 ml of the chloroform test solution was added 1 ml of the aldehyde-phosphorus pentachloride solution, 0.5 ml of phosphorus oxychloride, and trifluoroacetic acid to a final volume of 10 ml. After each addition the mixture was shaken gently to ensure complete mixing. The absorption spectrum was then determined against a blank of the same solvent-reagent composition. Only the more intense long wave length bands have been reported.

(*b*) *Trifluoroacetic anhydride method*: To 1 ml of a 2% solution of 2-naphthaldehyde in chloroform was added 0.1 ml of trifluoroacetic anhydride followed by 1 ml of the chloroform test solution. After the mixture was allowed to stand for 5 min, 1 ml of phosphorus oxychloride was added and the solution was diluted to 10 ml with trifluoroacetic acid. The absorption spectrum was then determined against a blank.

## DISCUSSION OF RESULTS

Investigation of a large number of aldehydes has shown that in the test for aromatic compounds,[2] piperonal can be replaced by the following analogous aldehydes—anisaldehyde, veratraldehyde, *o*-methoxybenzaldehyde and 3:4:5-trimethoxybenzaldehyde with not too great a change in the sensitivity or wave length maxima.

TABLE I. 2-FURFURAL TEST FOR PERI CONDENSED AROMATIC HYDROCARBONS

| Compound | $\lambda_{\max}$, $m\mu$ | Sensitivity[a] |
|---|---|---|
| Pyrene | 535 | 0.04 |
| | 630 | 0.007 |
| | 670 | 0.005 |
| Benzo(e)pyrene | 573 | 0.007 |
| | 668 | 0.009 |
| Benzo(a)pyrene | 685 | 0.008 |
| | 743 | 0.007 |
| Benzo(g, h, i)perylene | 820 | 0.005 |
| Anthanthrene | 750s[b] | 0.006 |
| | 787 | 0.005 |
| Perylene | 820 | 0.005 |

[a] Micromoles in 3 ml of solution giving an absorbance of 0.1 in a 1-cm cell.
[b] s = shoulder.

In a previous publication[7] it was predicted that aromatic aldehydetrifluoroacetic anhydride condensation products would be capable of detecting aromatic compounds in appropriate acidic media. The prediction was verified, for the 2-naphthaldehyde-trifluoroacetic anhydride procedure gave a wave length maximum of 805–810 m$\mu$ with a sensitivity of 0.007 for perylene and a wave length maximum of 685 m$\mu$ with

TABLE II. 2-THENALDEHYDE STET

| Compound | $\lambda_{\max}$, $m\mu$ | Sensitivity[a] |
|---|---|---|
| Fluoranthene | 585 | 0.020 |
| Acenaphthene | 623 | 0.008 |
| Pyrene | 630s[b] | 0.006 |
| | 670 | 0.004 |
| Benzo(e)pyrene | 578 | 0.008 |
| | 684 | 0.008 |
| Benzo(a)pyrene | 705 | 0.006 |
| | 750 | 0.005 |
| Benzo(g, h, i)perylene | 760 | 0.007 |
| Anthanthrene | 560 | 0.014 |
| | 775 | 0.005 |
| Perylene | 825 | 0.005 |

[a] Micromoles in 3 ml of solution giving an absorbance of 0.1 in a 1-cm cell.
[b] s = shoulder.

approximately the same sensitivity for pyrene. Other aldehydes can be substituted in the test procedure, but this method does not appear to offer any particular advantage over the phosphorus pentachloride methods.

The simplest aldehydes found to react with polynuclear hydrocarbons under the conditions of the test are 2-furfural and 2-thenaldehyde. These reagents are not as powerful as piperonal in that they do not react with 2-acetylaminofluorene and analogous derivatives, while piperonal does.[3] On the other hand they do react with the peri condensed hydrocarbons and with some of the less basic ring systems such as fluoranthene and chrysene (Tables 1 and II). However, they do not have the necessary specificity under the conditions of the test.

TABLE III. INDOLE-3-ALDEHYDE TEST

| Compound | $\lambda_{max}$, $m\mu$ | Sensitivity[a] |
|---|---|---|
| 1-Methoxynaphthalene | 570 | 0.011 |
| 1-Naphthol | 575 | 0.09 |
| 9-Ethylcarbazole | 575 | 0.012 |
| 1-Anilinonaphthalene | 597 | 0.007 |
| Phenyl selenide | 616 | 0.016 |
| 1-Anthrol | 650 | 0.025 |
| Anthrone | 651 | 0.009 |
| Benzo(e)pyrene | 685 | 0.038 |
| Pyrene | 690 | 0.006 |
| Benzo(a)pyrene | 750 | 0.006 |
| Anthanthrene | 790 | 0.020 |
| Perylene | 830 | 0.006 |

[a] Micromoles in 3 ml of solution giving an absorbance of 0.1 in a 1-cm cell.

The indole-3-aldehyde reagent reacted readily with various types of aromatic compounds (Table III). This compound did not have the reactivity of piperonal or the required specificity. For indole-3-aldehyde as for all the other aldehydes, it is

TABLE IV. 9-ANTHRALDEHYDE TEST

| Compound | $\lambda_{max}$, $m\mu$ | Sensitivity[a] |
|---|---|---|
| Acenaphthene | 790 | 0.010 |
| Pyrene | 850 | 0.008 |
| Benzo(a)pyrene | 860 | 0.012 |
| Anthracene | 860 | 0.010 |
| Benzo(a)pyrene | 910 | 0.008 |
| Benzo(g, h, i)perylene | 910 | 0.004 |
| Anthanthrene | 955 | 0.006 |
| Perylene | 965 | 0.010 |

[a] Micromoles in 3 ml of solution giving an absorbance of 0.1 in a 1-cm cell.

possible that by a proper manipulation of conditions much greater sensitivities could be obtained.

With the 9-anthraldehyde reagent the peri condensed aromatic hydrocarbons gave dyes absorbing at extremely long wave length, (Table IV). In this area the wave length maxima and the sensitivities are considered to be approximations. Note should be taken of the extremely long wave lengths at which anthanthrene and perylene are analyzed. Benzene, toluene, xylene, biphenyl, fluorene, chrysene and fluoranthene were found to be essentially insensitive to this reagent. These results suggest that aromatic compounds weaker than, or of the same order of basicity as chrysene do not react with the reagent.

TABLE V. 3-NITRO-4-DIMETHYLAMINOBENZALDEHYDE TEST

| Compound | $\lambda_{max}$, mμ | Sensitivity[a] |
|---|---|---|
| Acenaphthene | 618 | 0.010 |
| Pyrene | 702 | 0.003 |
| Benzo(e)pyrene | 710 | 0.020 |
| 3-Methylcholanthrene | 743 | 0.016 |
| Anthracene | 748 | 0.013 |
| Benzo(a)pyrene | 770 | 0.005 |
| Benzo(g, h, i)perylene | 770 | 0.030 |
| Anthanthrene | 845 | 0.005 |
| Perylene | 860 | 0.006 |

[a] Micromoles in 3 ml of solution giving an absorbance of 0.1 in a 1-cm cell.

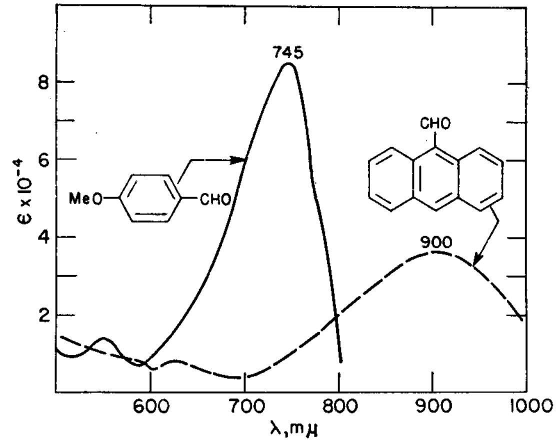


FIG. 1. Aromatic aldehyde-phosphorus pentachloride tests for benzo(a)pyrene. Anisaldehyde (——); Anthraldehyde(- - -).

Of all the aldehydes so far tested 3-nitro-4-dimethylaminobenzaldehyde appears to be the best for the polynuclear aromatic hydrocarbons, (Table V). It must be emphasized that the anthraldehyde and 3-nitro-4-dimethylaminobenzaldehyde tests are not in the strict sense colour tests, for the colours obtained in the analysis of the larger polynuclear aromatic hydrocarbons are not due to the main band but to weak secondary visible bands. The main band is out of the visible region of the spectrum, so the resultant "colour" due to this absorption band cannot be seen by the human eye. The 3-nitro-4-dimethylaminobenzaldehyde test was the most thoroughly investigated. It was found to give negative results with the following compounds: benzene, toluene, *m*-xylene, mesitylene, durene, biphenyl; *p*-terphenyl, fluorene, naphthalene, phenanthrene, fluoranthene, triphenylene, chrysene, picene, stilbene, phenol and anthrone. The vast majority of these compounds react with piperonal chloride. Like 9-anthraldehyde this reagent reacts with the more basic larger polynuclear aromatic hydrocarbons. With all of these aldehyde reagents, except 9-anthraldehyde, the carcinogenic benzo(a)pyrene reacts to give an intense band near 750 m$\mu$. With 9-anthraldehyde a fairly intense band at about 910 m$\mu$ is obtained. This latter test for benzo(a)pyrene is compared with the anisaldehyde method in Fig. 1.

When the benzene-soluble extract of a Cincinnati air particulates sample was reacted in the 3-nitro-4-dimethylaminobenzaldehyde test, a strong band was obtained near 790 m$\mu$. This indicates the predominance of the larger polynuclear aromatic hydrocarbons with ring systems containing 3 to 5 fused rings. Separation of the neutral aromatic fraction from this benzene soluble extract by standard procedure[8] and reaction of this fraction in the test gave a strong band at 850 m$\mu$. This indicates that of the large polynuclear aromatic hydrocarbons in the aromatic fraction the 5-, 6- and probably 7-membered fused ring structures predominate.

**Zusammenfassung**—Eine Untersuchung der Reaktion der aromatischen Aldehydphosphorpentachlorid-Reagens mit polykernaromatischen Kohlwasserstoffen hat gezeigt, dass manche Aldehyde den Piperonal in dieser Spektral-photometrischen Methode substitutieren können, aber nur zwei Aldehyde für die mehr-basischen aromatischen Verbindungen spezifisch sind. Das 9-Anthraldehyd-Reagens zeigt intensive Bänder bei 800–960 m$\mu$ mit Kohlenwasserstoffen von höheren C-Zahl. Das 3-Nitro-4-dimethylaminobenzaldehyd-Reagens reagiert glatt mit Benzol-Extraktion von Luft-Partikelchen. Dieses Verfahren ist wahrscheinlich die erste analytische in dem Infraroten-Bereich angewandte Methode. Man kann Trifluoro-essig-anhydrid für Phosphor-pentachlorid in Reagensmischung substitutieren. Es wurden jedoch dabei keine besondere Vorteile beobachtet.

**Résumé**—Une étude de réaction entre les réactifs du type aldéhyde aromatique-penta chlorure de phosphore et les hydrocarbures aromatiques polynucléaires, a montré qu'un certain nombre d'aldéhydes peuvent remplacer le piperonal dans ce test spectrophotométrique, mais seuls deux d'entre eux sont spécifiques pour les composés aromatiques les plus basiques. Le réactif au 9-anthraldehyde donne des bandes intenses dans la région spectrale 800–960 m$\mu$ avec les hydrocarbures supérieurs. Le réactif au nitro-3-diméthyl-4-aminobenzaldehyde réagit presque toujours facilement avec les composés que donnent les particules de poussière dans l'air par extraction avec le benzène.

Ce procédé est probablement la première méthode analytique utilisant des longueurs d'onde en dehors de la région visible du spectre dans le proche infra-rouge. On a trouvé que l'anhydride trifluoroacétique pouvait remplacer le penta chlorure de phosphore dans le réactif-test, mais il n'y a aucun avantage particulier à cette substitution.

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# AN ELECTROCHEMICAL SEPARATION PROCESS FOR USE IN POLAROGRAPHY*

R. L. Faircloth
U.K.A.E.A. Research Group, Atomic Energy Research Establishment,
Harwell, Berks, England

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**Summary**—A simple electrochemical method is described whereby metals which are soluble in mercury can be analysed polarographically for traces of more electronegative impurities. The technique was specifically developed for the analysis of bismuth using a square wave polarograph and full details, both experimental and theoretical, are given in this case. Other possible uses of the method in the analysis of mercury-soluble metals employing both conventional and square wave polarographs and also in the analysis of aqueous salt solutions are suggested.

## INTRODUCTION

It is well known that considerable difficulty is encountered in direct current polarography when attempting to estimate the concentration of a minor constituent of a mixture in the presence of a more readily reducible major constituent. This problem is frequently encountered in metallurgical analysis, where, for example, one might wish to estimate the amount of zinc present in a sample of cadmium[1,2,3] or lead[4]. Usually the major constituent must be removed from the mixture before the polarographic analysis can be carried out.

Because of the derivative form of polarograms obtained with alternating current polarographs a considerable improvement in mixture analysis is achieved. Loss of sensitivity, however, will result if the ratio of the concentration of the more readily reducible major constituent to that of the minor constituent becomes too large. This loss of performance may be caused by irregular motion of the surface of the mercury drop, by the wave arising from the electropositive substance becoming so large that it overlaps other waves and by the failure of the electronic circuits of the polarograph to handle the large direct current flowing. It may therefore still be desirable and even necessary to carry out some preliminary separation procedure in low level determinations of trace impurities in metals.

In this paper a simple separation procedure is described which is of particular value in the polarographic analysis of metals such as bismuth, lead and cadmium, that dissolve readily in mercury. The method was specifically developed for the analysis of bismuth using a square wave polarograph[5] and the experimental procedure used in this case is described later in some detail. Other possible applications in both a.c. and d.c. polarography are also outlined.

## ANALYSIS OF BISMUTH WITH A SQUARE WAVE POLAROGRAPH

### *Introduction*

The square wave polarograph can be used to estimate the concentration of a minor constituent in the presence of a $10^5$-fold excess of a more readily reducible

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* This paper was presented at a meeting of the Polarographic Society, held at Nobel Division, Imperial Chemical Industries Ltd., Stevenston, Ayrshire, on 26 September, 1958.

major constituent provided that the concentration of the latter constituent does not exceed $\sim 10^{-2}M$. This means, therefore, that in the analysis of bismuth by dissolution of the metal in acid and subsequent dilution to $10^{-2}M$ with respect to bismuth, it is possible to estimate electronegative impurities whose concentration in the final solution is $10^{-7}M$. Thus the concentration of these impurities in the original metal must not be less than $\sim$10 ppm if they are to be estimated with any degree of accuracy. In any case $10^{-7}M$ is close to the lower level of concentration of even a single substance to which the square wave polarograph can be applied qualitatively. Also, impurities which might be as high as $10^{-6}M$ may be introduced by the reagents and supporting electrolyte. Thus to determine the concentration of low level ($<$10 ppm) impurities in bismuth with the square wave polarograph, some preliminary separation process must be employed.

Methods which have been used in the past have involved the dissolution of the bismuth metal sample into a suitable medium, followed by the removal of almost all bismuth by precipitation, volatilisation or electro-deposition at controlled potential.[6] The first and second of these methods are subject to the possibility of losses during the separation stages. Also, the addition of the various reagents may complicate the polarographic analysis of the final solution. Although the electrodeposition method does not have either of these disadvantages it is rather tedious to perform experimentally.

It was with these points in mind that the following simple technique was developed. It is based on electrochemical principles and is much easier to carry out than the electrodeposition method mentioned above.

If pure bismuth is dissolved in mercury and the resulting amalgam contacted with, for example, *M* hydrochloric acid solution containing some $Bi^{3+}$ ions, the amalgam takes up a potential controlled by the relative concentrations of bismuth metal and bismuth ions in the amalgam and solution phases respectively. This potential will not be greatly affected when the bismuth contains trace impurities. If the standard potential of the electrode reaction $M(Hg) = M^{n+} + nE$ where M is some metallic impurity (originally in the bismuth but now dissolved in the amalgam), is more negative than the actual amalgam potential, the metal M will tend to pass from the amalgam to the aqueous phase. In this way separation of the electronegative impurities from the bismuth will be obtained and the aqueous phase can be examined polarographically. The concentration of bismuth in the aqueous phase can be controlled by the previous addition to the solution of a calculated quantity of mercurous chloride. The mercurous ion is reduced by the amalgam forming mercury metal which dissolves in the amalgam and an equivalent amount of bismuth is oxidised and passes into the solution.

## EXPERIMENTAL

10 ml of mercury were placed in a stoppered glass tube (1 cm diameter, 12·5 ml volume) and covered with 2 ml of *M* hydrochloric acid containing 0·4% mercurous chloride. One gram of bismuth, in small pieces was dropped through the acid layer into the mercury. Nitrogen was passed over the solution surface for some time and the tube was then quickly stoppered.* The tube was then gently shaken until the bismuth had completely dissolved in the mercury, the mercury being heated if necessary. The tube was then vigorously shaken for a further 15 minutes, and finally a known volume

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* Oxygen must be removed from the gas space above the aqueous phase to avoid oxidation of the bismuth amalgam and the concomitant formation of hydrogen peroxide.

of the acid layer was rapidly removed with a dry pipette and placed in a small polarographic cell. After deoxygenation square wave polarograms were recorded in the usual way, making standard additions to determine the concentrations of the various impurities.

Some typical square wave polarograms for the determination of lead in bismuth are shown in Figures 1 and 2. Figures 1(a) and (b) were both obtained at $\frac{1}{32}$ maximum sensitivity and refer respectively to bismuth samples taken before and after purification. The wave height of Figure 1(a) corresponds to ~3 ppm of lead in the original bismuth sample. Figure 2 is a polarogram from the same solution as in Figure 1(b) but at an increased sensitivity of $\frac{1}{4}$ maximum. The indicated concentration is here ~0·5 ppm and the height of this wave can be estimated with an accuracy of better than ±2%.

## *Discussion*

For the experimental conditions outlined above the concentration of bismuth in the amalgam phase is $\sim 0{\cdot}5M$ and in the aqueous phase $\sim 5 \times 10^{-3}M$. If the bismuth originally contains a metallic impurity at a level of 10 ppm and all this impurity is transferred to the aqueous phase, its concentration in the latter phase will be $\sim 2{\cdot}5 \times 10^{-5}M$. Compared therefore, with the case where the bismuth is dissolved directly and then diluted to $10^{-2}M$, the concentration of the impurity in the final solution has increased 250 times, whereas the bismuth concentration has gone down by a factor of 2. It would, on paper at least, appear to be possible to determine impurities down to 0·1 ppm with an accuracy of ±2% in a bismuth sample using this amalgamation technique in conjunction with a square wave polarograph. In very low level determinations it will, of course, be necessary to carry out a blank experiment in the absence of bismuth.

To discover which metallic impurities can be determined in bismuth by this method some information regarding the potential of the bismuth-mercury amalgam must be obtained. From the Nernst equation it follows that

$$E^A = E_0{}^A - \frac{RT}{3F} \ln \frac{C_A{}^{\text{Bi}}}{C_S{}^{\text{Bi}}} \text{volt} \tag{1}$$

where $E^A$ = amalgam potential,

$C_S{}^{\text{Bi}} C_A{}^{\text{Bi}}$ = concentration of bismuth in the solution and amalgam phases respectively,

and $E_0{}^A$ = standard potential of the reaction $\text{Bi(Hg)} = \text{Bi}^{3+} + 3E$.

Thus, since $C_A{}^{\text{Bi}} \doteqdot 0{\cdot}5M$ and $C_S{}^{\text{Bi}} \doteqdot 5 \times 10^{-3}M$

$$E^A \doteqdot E_0{}^A \doteqdot 0{\cdot}039 \text{ volt} \tag{2}$$

For $\geqslant 99{\cdot}5\%$ transfer at equilibrium of a metallic impurity M from the amalgam to the aqueous phase, when the volume of the amalgam is five times that of the solution the Nernst equation predicts that

$$E^A \geqslant E_0{}^M + \frac{3RT}{nF} \text{volt} \tag{3}$$

where $E_0{}^M$ = Standard potential of the electrode reaction $\text{M(Hg)} = \text{M}^{n+} + nE$. In the case where $n = 2$

$$E^A \geqslant E_0{}^M + 0{\cdot}088 \text{ volt} \tag{4}$$

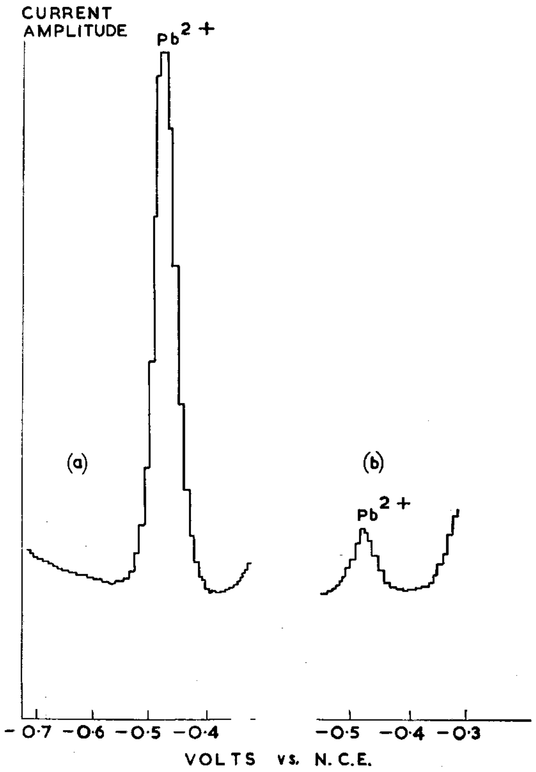

FIG. 1

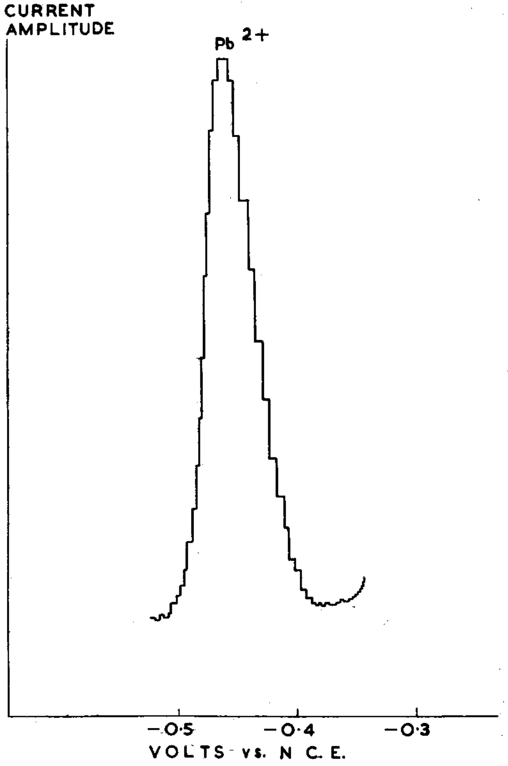

FIG. 2

FIGS. 1, 2. Square wave polarograms obtained in the analysis of bismuth for lead.

and therefore from equations (3) and (4)

$$E_0^M \leqslant E_0^A - 0{\cdot}127 \text{ volt} \tag{5}$$

It may be assumed for simplicity that for reversible electrode processes $E_0^M$ and $E_0^A$ are equal to the corresponding polarographic half wave potentials. Thus for 99·5% transfer of metal M to the aqueous phase the half-wave potential for $M^{2+}$ in the medium in question (in this case *M* hydrochloric acid) must be at least 0·13 volt more negative than the half-wave potential for the reduction of bismuth ions from the same medium. For impurities which form univalent ions (*i.e.* $n = 1$) the calculated potential difference for 99·5% extraction is slightly greater than 0·2 volt. This means that cadmium, indium, lead, thallium and zinc can all be estimated by the amalgamation method. Copper, however, which is somewhat more electropositive than bismuth, cannot be determined.

Different metals will be extracted from the amalgam simultaneously if the relevant electrode reactions are polarographically reversible as the rate of extraction of each metal is then diffusion controlled.

## OTHER APPLICATIONS

The analysis of cadmium for zinc has been carried out using the amalgamation technique and a square wave polarograph. The experimental procedure as outlined above was modified slightly as follows. One g of cadmium metal was dissolved in 10 ml of mercury and extracted with 5 ml of slightly acidified (pH = 2) *M* potassium chloride containing 0·25% calomel. A polarogram obtained in this way is shown in Figure 3(a), the sensitivity being ¼ maximum. The zinc wave indicates 0·5 ppm of zinc in the original cadmium metal. For comparison Figure 3(b) shows the polarogram obtained (¼ maximum sensitivity) for a solution ($10^{-2}M$ $Cd^{2+}$) prepared by dissolving a sample of the same cadmium metal in hydrochloric and nitric acids, evaporating to dryness several times with hydrochloric acid, and dissolving the residue in *M* KCl (pH 2). A blank experiment indicated that the small zinc wave in Figure 3(b) arose from impurities in the reagents used.

So far only the application of this separation technique to square-wave polarography has been investigated but there is little doubt that it could be used with advantage in conventional direct current polarography. As an example the analysis of bismuth containing 0·2% lead may be considered. By following the experimental procedure outlined above for bismuth a solution containing $5 \times 10^{-3}M$ bismuth and $5 \times 10^{-3}M$ lead would be obtained. If this solution were diluted 5 times with water and polarographed, the lead concentration could be accurately determined.

Other examples of metal analysis which could be treated similarly are the determination of cadmium and zinc in lead and of zinc in thallium. The method is, of course, not suitable for the analysis of metals which are insoluble or only slightly soluble in mercury, such as copper, iron and silver.

The technique can also be extended to the determinations of trace impurities in salt solutions. Suppose that 20 ml of a deoxygenated salt solution (for example, saturated sodium carbonate) are shaken vigorously with 10 ml of mercury containing $10^{-3}M$ zinc of "specpure" quality. This dilute zinc amalgam takes up a potential close to the zinc half-wave potential and all the more electropositive impurities (Cu, Pb, Cd, etc.) in the solution are reduced and pass into the amalgam phase. The amalgam is then separated from the solution and shaken with 2 ml of *M* hydrochloric acid containing somewhat more mercurous chloride than is required to oxidise all the zinc. The impurities in the amalgam are transferred, along with the zinc, to the acid which can be analysed polarographically. The zinc wave does not interfere with the waves obtained from the more electropositive elements. In this way the impurity concentrations are increased by a factor of 10 and they are also transferred to a more satisfactory supporting electrolyte.

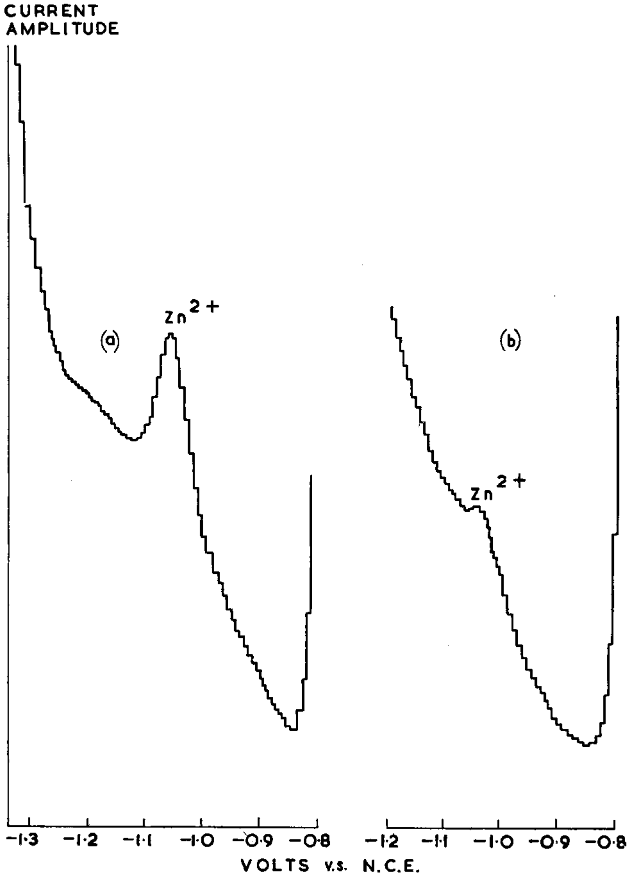

FIG. 3. Square wave polarograms obtained in the analysis of cadmium for zinc.

## CONCLUSION

Although as yet little use has been made of these simple techniques, they can clearly be used with any type of polarograph to obtain improved sensitivity and greater freedom from troubles associated with impurities in the reagents used in the preparation of solutions.

**Zusammenfassung**—Eine einfache elektrochemische Methode wurde beschrieben womit die in Quecksilber lösliche Metalle für Spuren-Verunreinigungen polarographisch analysiert werden können. Die Methode wurde zur Analyse von Wismuth mittels des "Square-Wave" Polarographs entwickelt, und die experimentelle und theoretische Grundlagen wurden erörtert. Die andere Anwendungen der Methode wurden beschrieben.

**Résumé**—Une méthode électrochimique simple est décrite permettant l'analyse polarographique de métaux solubles dans le mercure en présence de traces d'impuretés plus électronégatives. La technique a été développée spécifiquement pour le bismuth en utilisant un polarographe à tension carrée et de nombreux détails ont été donnés dans ce cas, aussi bien au point de vue expérimental qu'au point de vue théorique. Il est suggéré d'autres utilisations possibles de la méthode pour l'analyse de métaux solubles dans le mercure et de solutions salines aqueuses en employant soit le polarographe classique soit le polarographe à tension carrée.

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# THE PRECIPITATION OF NICKEL$^{II}$ SULPHIDE FROM ACID SOLUTIONS BY THIOACETAMIDE

DAVID F. BOWERSOX, DWIGHT M. SMITH and ERNEST H. SWIFT
California Institute of Technology, Pasadena, California, U.S.A.

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**Summary**—Rate measurements have shown that the precipitation of nickel$^{II}$ as sulphide by thioacetamide from solutions having hydrogen ion concentrations ranging from 0.3 to $1 \times 10^{-7}$ molal conforms to the expression

$$-\frac{d\,[\mathrm{Ni^{II}}]}{dt} = k\,[\mathrm{Ni^{II}}]\,[\mathrm{CH_3CSNH_2}]/[\mathrm{H^+}],^{\frac{1}{2}}$$

where $k$ is equal to $2.2 \times 10^{-4}$ litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ min$^{-1}$ at 90°. No hydrolysis controlled precipitation was observed. The energy of activation for the reaction, in the range 70°–90°, was calculated to be 20.8 kcal per mole. Precipitation conforming to this rate expression occurred at hydrogen ion concentrations at which precipitation by hydrogen sulphide was not obtained.

The effectiveness of the separation of lead$^{II}$ and cadmium$^{II}$ from nickel$^{II}$ by the use of thioacetamide in solutions of pH 1 and 2 and maintained at 90° was studied. The rate of formation of nickel sulphide conformed to the above rate expression and was independent of the quantity of metal sulphide present, and of the concentrations of lead$^{II}$, cadmium$^{II}$, and of hydrogen sulphide in the reaction solution. The amount of nickel sulphide precipitated with cadmium and lead sulphide by means of the direct reaction between nickel ion and thioacetamide exceeded that co-precipitated when cadmium and lead were precipitated by hydrogen sulphide. However, under properly controlled conditions effective separations can be made.

## INTRODUCTION

THE work reported in this paper is part of the general investigation being made in these laboratories of the use of thioacetamide as a precipitant for metal sulphides and as a means for effecting the precipitation of sulphides from homogeneous solutions. This type of precipitation may make it possible to improve certain existing sulphide separations and, especially in the case of nickel, to obtain sulphide precipitates which are more easily handled than those normally encountered.

Previous investigations of the reactions of thioacetamide and its products of hydrolysis with lead$^{II}$,[9] arsenic$^{III}$ and arsenic$^{V}$,[3] and cadmium$^{II}$,[2] have been made. The rate of precipitation of both cadmium$^{II}$ and lead$^{II}$ at hydrogen ion concentrations greater than $10^{-3}$ $M$ is controlled by the rate of hydrolysis of the thio group of the thioacetamide to give hydrogen sulphide and this rate is first order with respect to the thioacetamide and to the hydrogen ion concentrations. Precipitation by this means is designated as "hydrolysis controlled." The hydrolysis reaction has been assumed to consist of the attack of hydrogen ion upon the thioacetamide molecule and subsequent formation of hydrogen sulphide as the rate determining step. The reaction of the cation with the hydrogen sulphide to form a sulphide precipitate is apparently relatively rapid under the conditions studied.

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* Contribution No. 2427 from the Gates and Crellin Laboratories of Chemistry. Communications concerning this article should be addressed to E. H. Swift.

At lower hydrogen ion concentrations a precipitation reaction which is first order with respect to both the cation and the thioacetamide concentrations and inversely half-order with respect to the hydrogen ion concentration becomes predominant and rate controlling. The mechanism of this reaction is not yet understood. It is called the "direct reaction" to distinguish it from the "hydrolysis controlled" reaction.

No evidence for this direct reaction was found in studies of the precipitation of arsenic$^{III}$; the rate of precipitation of the sulphide appeared to be hydrolysis controlled even at pH 6. Arsenic$^{V}$ is reduced to arsenic$^{III}$ before precipitation of the sulphide by thioacetamide.

Although analytical studies[1,4] of the precipitation of nickel from ammoniacal solutions by thioacetamide have been made, there seems to have been no previous work on the precipitation of nickel by thioacetamide from acid solutions. This paper presents the results of a study of the precipitation of nickel sulphide by thioacetamide from acid solutions under various conditions and of the separation of cadmium and lead from nickel by the use of this reagent.

## EXPERIMENTAL

### *Reagents*

Reagent grade chemicals were used.

*Thioacetamide solutions*, 1.00 *VF* (volume formal, formula weights per litre), were prepared from Arapahoe Lot No. 1402 material. Although these solutions remained clear and colourless for longer times, they were freshly prepared at two-week intervals.

Solutions of *cadmium nitrate*, *lead nitrate* and *nickel*$^{II}$ *nitrate*, each 0.100 *VF*, were prepared by weight.

*Perchloric acid* and carbonate-free *sodium hydroxide* solutions were prepared and standardized by conventional methods.

A neutral 0.1 *VF* solution of *dimethylglyoxime* in ethanol was used.

The *hydrogen phthalate-phthalate buffer solutions* were prepared by adding calculated weights of potassium hydrogen phthalate to constant volumes of sodium hydroxide solution. These buffer solutions were diluted to a given volume in order to form the stock buffer solutions.

*Sodium nitrate*, 0.10 *VF*, was used to provide constancy of ionic strength, although later experiments revealed no significant ionic strength effect.

### *Apparatus*

The apparatus used for the quantitative study of the rate of precipitation of nickel sulphide was similar to that described by Swift and Butler.[9] Most of the rate measurements were made at 90 ± 1°.

The separations of cadmium and lead from nickel were carried out in 15 × 125-mm test tubes and 25-ml Erlenmeyer flasks placed in a water bath maintained at 90 ± 1°.

### *Procedure*

The more quantitative studies in the pH range 5–7 were made by mixing in a reaction tube measured volumes of the stock solutions of thioacetamide, nickel nitrate, and buffer. Enough sodium nitrate to attain an initial ionic strength of 0.40 was added and the solution diluted to 100 ml. The reaction tube was then placed in the constant temperature bath and 12-ml portions were removed at timed intervals. These portions were cooled in order to quench the reaction, centrifuged, and duplicate 5.00-ml samples of the clear centrifugate transferred to 15 × 125-mm test tubes.

An excess of 6 *VF* ammonium hydroxide was added to each sample, and the sample tubes were then placed in hot water in order to precipitate the nickel as sulphide. A coarse, easily separated precipitate was formed. The mixture was cooled and centrifuged. The centrifugate was drawn off and discarded.

The precipitate was first heated in a water bath with 1 ml of 9 *VF* perchloric acid and five drops of 6 *VF* nitric acid, then heated to fuming over a flame until all the precipitate had dissolved and any oxides of nitrogen were expelled. The solution was cooled and diluted to 2 ml with water. Five drops of 0.007 *VF* methyl red were added, and the solution adjusted to the transition colour by the alternate additions of 6 *VF* and 0.1 *VF* sodium hydroxide and 0.1 *VF* perchloric acid solutions. Comparison solutions were used in order to obtain this colour more exactly. An excess of 0.1 *VF* dimethylglyoxime solution was added, and the flocculent red precipitate centrifuged.

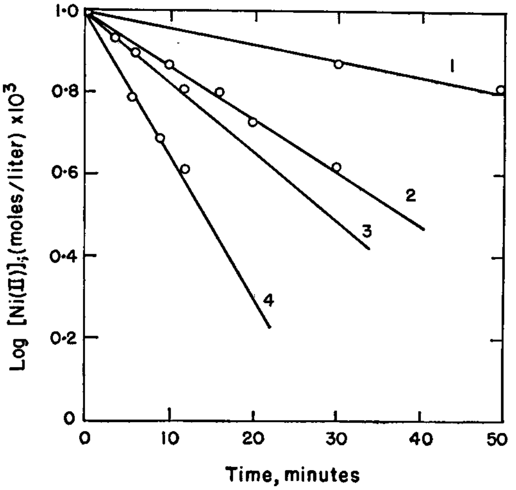

Fig. 1. Effect of nickel$^{II}$ concentration on the rate of nickel sulphide precipitation.
Initial thioacetamide: 0.10 *VF*; initial nickel$^{II}$: 0.010 *VF*; temperature: 90°.
1. pH 5.0 3. pH 6.5
2. pH 6.2 4. pH 7.1

If over two milligrams of nickel were judged to be present in the precipitate, a titration with 0.030 *VF* sodium hydroxide solution was made to the methyl red transition colour. The red precipitate interfered with the detection of this colour, particularly near the end-point, unless the mixture was centrifuged at intervals during the titration. This method of analysis was checked with known quantities of nickel$^{II}$ similar to those which were present in the precipitates, and the average deviation in the results was less than 1% provided comparison solutions were used.

When the quantity of nickel in the dimethylglyoxime precipitate was judged by visual inspection to be less than 2 mg, the estimation was made by comparing the volume of the centrifuged precipitate with known quantities of nickel precipitated under the same conditions. The accuracy of confirmatory estimations made with these quantities of nickel was within ±10% and was superior to the titrimetric method.

In the study of the rate of nickel precipitation and its separation from cadmium and lead at low pH values, 10 ml of reaction solution were prepared by mixing measured quantities of thioacetamide, metal nitrates and perchloric acid in each vessel. These vessels were then placed in a bath, at 90°, and removed at timed intervals. The reaction was quenched by cooling the reaction tube, and the precipitate separated by centrifuging the mixture. The clear centrifugate was discarded and the precipitates washed thoroughly by decantation. The precipitates were analyzed as described above. In those samples containing lead, however, the lead sulphate resulting from the dissolution step was removed by decanting the centrifugate before proceeding with the analysis.

## RESULTS AND DISCUSSION

### *The precipitation from acid solutions*

In preliminary qualitative experiments a very *slow* formation of nickel sulphide was observed at 90° in solutions 0.01 *VF* in nickel$^{II}$, and 0.10 *VF* in thioacetamide and in which the hydrogen ion concentration ranged from 0.3 *VM*–0.01 *VM*. In the same time interval similar solutions saturated with gaseous hydrogen sulphide, but containing no thioacetamide, gave *no* precipitate.

### *Rate measurements at* pH *values* 5–7

Measurements of the rate of precipitation were made in the pH range 5.0–7.1 and at 90°. In this pH range and at this temperature the precipitation took place at conveniently measurable rates and the results obtained could be readily compared with those found in previous studies.[2,3,9] The effects of the concentrations of nickel$^{II}$, thioacetamide, and hydrogen ion upon the rate of precipitation were evaluated in order to formulate a rate expression and to calculate a rate constant. These measurements were made in the presence of phthalate buffer systems. The agreement with those of subsequent measurements in perchloric acid solutions, described later, indicated that the phthalate buffer did not exert any significant effect on the rate of the direct reaction.

### *Effect of the nickel$^{II}$ concentration*

As is shown in Figure 1, plots of the logarithm of the nickel$^{II}$ concentration versus the reaction time at various hydrogen ion concentrations were linear; thus it appears that the precipitation reaction is first order with respect to the nickel$^{II}$ concentration at 90°.

TABLE I.—EFFECT OF THIOACETAMIDE ON THE RATE OF PRECIPITATION OF NICKEL SULPHIDE

Initial nickel$^{II}$: 0.010 *VF*, pH 6.4, $t = 90°$

| $(CH_3CSNH_2)$, *VM* | $k_1$[a] | $k_2 \times 10^4$ [b] (*litre*$^{\frac{1}{2}}$ *mole*$^{-\frac{1}{2}}$ *min*$^{-1}$) |
|---|---|---|
| 0.050 | 0.0177 | 2.25 |
| 0.100 | 0.0342 | 2.21 |
| 0.150 | 0.0553 | 2.31 |
| 0.200 | 0.0733 | 2.31 |
| 0.250[c] | 0.0774 | 2.19 |
| 0.300 | 0.1068 | 2.26 |

Average $(2.25 \pm 0.05) \times 10^{-4}$

[a] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = k_1[\mathrm{Ni^{II}}].$$

[b] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = k_2\frac{[\mathrm{Ni^{II}}]\,[CH_3CSNH_2]}{[H^+]^{\frac{1}{2}}}$$

[c] Measurements at pH 6.3.

### *Effect of the thioacetamide concentration*

Table I presents a tabulation of the rate constants calculated from a series of experiments made to determine the effect of the thioacetamide concentration upon the rate of precipitation. The constancy of these values shows that in the range of concentrations studied, 0.050 *VF* to 0.30 *VF* in thioacetamide, the rate of the reaction is first order with respect to the thioacetamide concentration.

### *Effect of the hydrogen ion concentration*

The effect of the hydrogen ion concentration on the rate of precipitation was studied over the range from 1 × $10^{-5}$ *VM* to $10^{-7}$ *VM*. Haring and Westfall[5] reported. that quantitative precipitation of nickel sulphide can be made in this range by means of hydrogen sulphide. Therefore, in some experiments, nitrogen was bubbled through the reaction solution in order to remove the hydrogen sulphide formed by the hydrolysis of the thioacetamide; in these experiments no significant change in the rate of precipitation was observed. The rate constants calculated from these measurements are given in Table II, and show that the reaction has an inverse half-order dependency upon the hydrogen ion concentration. In none of these experiments was there evidence of hydrolysis controlled precipitation. Some precipitation by the hydrogen sulphide resulting from the acid hydrolysis of thioacetamide is to be expected at pH values between approximately 5 and 2; however, rate measurements were not attempted in this pH range since the rate of this precipitation would not be likely to conform to the acid hydrolysis rate expression because of supersaturation effects.

TABLE II.—EFFECT OF HYDROGEN ION ON THE RATE OF PRECIPITATION OF NICKEL SULPHIDE BY THIOACETAMIDE

Initial nickel$^{II}$: 0.01 *VF*; initial thioacetamide: 0.10 *VF*, $t = 90°$

| pH | $k_1$[a] | $k_2 \times 10^4$ [b] |
|---|---|---|
| 7.1 | 0.078 | 2.21 |
| 6.5 | 0.039 | 2.23 |
| 6.4 | 0.034 | 2.21 |
| 6.2 | 0.029 | 2.30 |
| 5.0 | 0.006 | 2.14 |
| | | Average (2.22 ± 0.05) × $10^{-4}$ |

[a] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = k_1 [\mathrm{Ni^{II}}]$$

[b] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = k_2 \frac{[\mathrm{Ni^{II}}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}}$$

### *The rate expression.*

The data from the above measurements indicate that under the conditions of these experiments the precipitation of nickel sulphide by thioacetamide takes place by a direct reaction similar to those reported for lead[9] and cadmium.[2] The rate expression for this reaction is

$$-\frac{d[\mathrm{Ni^{2+}}]}{dt} = \frac{k\,[\mathrm{Ni^{2+}}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}} \tag{1}$$

and the calculated rate constant, $k$, is 2.2 × $10^{-4}$ litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ min$^{-1}$ at 90°.

### *The energy of activation*

In order to calculate the energy of activation the rates of this direct reaction were measured at 70° and 80° and the constants were calculated to be 8.95 × $10^{-5}$ and

$1.45 \times 10^{-4}$ litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ min$^{-1}$, respectively. From these values and that calculated at 90°, the energy of activation was calculated to be 20.8 ± 0.8 kcal per mole. This value is approximately the same as that calculated for the precipitation of cadmium sulphide.[2]

*The precipitation of nickel sulphide at* pH *values of* 1 *and* 2

Precipitations by direct reactions were not observed at pH 1 and 2 with lead[9] and cadmium[2] because such reactions would have been masked by the predominant hydrolysis controlled reaction. However, since no evidence of the hydrolysis controlled precipitation was observed with nickel in preliminary experiments, a check for precipitation by the direct reaction could be made at these hydrogen ion concentrations.

It was found that no precipitates were formed when solutions 0.040 *VF* in nickel$^{II}$ and having pH values of 1 and 2, established by means of perchloric acid, were saturated with hydrogen sulphide and maintained at 90° for one hour. In addition, solutions of the same composition were saturated with $H_2S$ and maintained for 70 hrs at room temperature without visible evidence of a nickel sulphide precipitate. However, when solutions 0.040 *VF* in nickel$^{II}$ and 0.40 *VF* in thioacetamide and having the same pH values were maintained at 90°, nickel sulphide was slowly formed. In other cases hydrogen sulphide was added to similar solutions but no change in the rate of precipitation of nickel sulphide was observed. The data given in Table III show that the amounts of nickel$^{II}$ found in the precipitates agree with those calculated by Expression 1 within the limits of the accuracy of the measurements. Experiments in which cadmium or lead sulphide precipitates were present showed that these did not alter the rate of nickel sulphide precipitation. Therefore, it was concluded that nickel sulphide is precipitated by the direct reaction at these hydrogen ion concentrations,

TABLE III.—EXPERIMENTAL VS. CALCULATED WEIGHTS OF NICKEL PRECIPITATED AS SULPHIDE BY THE DIRECT REACTION AT pH 1 AND 2

Initial $Ni(NO_3)_2$: 0.04 *VF*, initial $CH_3CSNH_2$: 0.40 *VF*, $t = 90°$

| Time, *min* | Nickel precipitated as NiS, *mg* | |
|---|---|---|
| | Found | Calculated[a] |
| pH 1 | | |
| 5 | 0.04 | 0.04 |
| 12 | 0.15 | 0.09 |
| pH 2 | | |
| 12 | 0.16 | 0.24 |
| 24 | 0.46 | 0.48 |
| 28 | 0.58 | 0.56 |
| 60 | 1.35 | 1.2 |
| 120 | 2.15 | 2.1 |

[a] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = 2.2 \times 10^{-4} \frac{[\mathrm{Ni^{II}}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}}$$

and that *it is possible to precipitate nickel sulphide by thioacetamide at higher hydrogen ion concentrations than precipitation can be obtained with hydrogen sulphide—at least in comparable times.*

Additional experiments were made with solutions initially 0.4 *VF* in nickel$^{II}$, 0.40 *VF* in thioacetamide, and 0.3 *VF* in perchloric acid to ascertain if the direct reaction would cause precipitation at this hydrogen ion concentration. Under these conditions the hydrolysis of the thioacetamide would cause its concentration to be decreased to 0.2 *VF* within ten minutes,[9] and the solution would be saturated with hydrogen sulphide. After twenty minutes the quantity of nickel precipitated as sulphide was seven mg; the quantity calculated from Expression 1 is five mg.

The precipitation of nickel sulphide by thioacetamide, and not by hydrogen sulphide, from acid solutions such as those described above, can be attributed to two possible causes. One of these would involve the assumption that the precipitation by thioacetamide resulted in an initial precipitate which was a less soluble form of nickel sulphide than that initially formed by hydrogen sulphide; the other would assume that the rate of the direct reaction was much faster than the rate of precipitation by hydrogen sulphide.

The above experiments with hydrogen sulphide and thioacetamide at pH 1 indicate that the precipitation by the direct reaction does not involve the formation of hydrogen sulphide. Also, Haring and Westfall[5] have reported, as was observed in this study, that nickel sulphide does not precipitate at a significant rate from solutions saturated with hydrogen sulphide at a pH of one or less. However, nickel sulphide once precipitated by hydrogen sulphide does not dissolve readily in cold 1 *VF* hydrochloric acid, and this effect is usually attributed to transformations between allotropic forms of nickel sulphide.[8]

Ringbom[7] reports that the solubility product constants of the $\alpha$, $\beta$ and $\gamma$ forms are $3 \times 10^{-19}$, $1 \times 10^{-24}$ and $2 \times 10^{-26}$ respectively. At equilibrium, calculations indicate that the first form would be soluble and the last would precipitate from a solution 0.040 *VF* in nickel$^{II}$ having a pH of 1 and saturated with hydrogen sulphide. It is possible that the $\gamma$ form of nickel sulphide is formed through the direct reaction of thioacetamide with hydrated nickel$^{II}$ and that, for this reason, precipitation was observed at a lower pH than previously reported with $H_2S$.

Middleton and Ward[6] suggest that the mechanism of precipitation of nickel sulphide by hydrogen sulphide involves, first, the precipitation of nickel monohydrogen sulphide, $Ni(HS)_2$, with subsequent conversion to a more insoluble nickel sulphide, NiS. If the precipitation involves a reaction between nickel$^{II}$ and monohydrogen sulphide ion, or sulphide ion, the relatively small concentrations of these ions existing in the solutions, compared with that of the thioacetamide, could be responsible for a much slower rate of precipitation by hydrogen sulphide than by thioacetamide.

It is of interest to note that the rate constants for the precipitation by the above direct reaction of the sulphides of nickel, cadmium,[2] and lead[9] are 2.2, 8.1 and $11.5 \times 10^{-4}$ litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ min$^{-1}$, respectively. The solubility product constants, as reported by Ringbom,[7] in the same order as above, are 20, 8 and $2.5 \times 10^{-27}$. Thus, for these elements the less soluble the sulphide, the more rapid is the rate of the direct reaction. More study will be needed before the validity or significance of any such correlation is established.

### *The separation of cadmium$^{II}$ and lead$^{II}$ from nickel$^{II}$ by the use of thioacetamide*

In conventional systems of qualitative analysis the Hydrogen Sulphide Group elements are separated from the remaining elements by precipitation from solutions which are saturated with hydrogen sulphide and which have hydrogen ion concentrations ranging from 0.1 to 0.3 volume molal. The sulphides of cadmium and lead are the most soluble of those precipitated and those of zinc and nickel are among the least soluble of those remaining in the solution. For this reason, and because sulphide precipitations are frequently used for quantitative separations of these elements, studies of the relative advantages of thioacetamide and hydrogen sulphide as the precipitant seemed warranted. The results from studies of the separation of cadmium and lead from nickel are presented below; the results from similar studies with zinc will be presented in a subsequent report.

Previous studies have shown that the rate of precipitation of lead[9] and cadmium[2] sulphides by thioacetamide in solutions having hydrogen ion concentrations above 0.01 is controlled by the rate of hydrolysis of the thioacetamide and that this rate is first order with respect to both the hydrogen ion and the thioacetamide concentrations. Since no evidence for the hydrolysis controlled precipitation of nickel was observed, it seemed at first that conditions were ideal for a homogeneous phase separation of lead and cadmium from nickel. However, preliminary experiments and subsequent calculations showed that there was significant precipitation of nickel by the direct reaction unless the time allowed for the precipitation and the concentrations of both thioacetamide and hydrogen ion were properly controlled.

Thus Table IV shows the data obtained from experiments with solutions at pH 2 which contained various initial quantities of nickel and of either cadmium or lead. After various times the sulphide precipitates were analyzed for nickel and the quantities found present are shown together with those calculated from the rate expression for the precipitation of nickel sulphide by the direct reaction (Expression 1). The agreement between the calculated and found quantities is in general within the accuracy of the analytical method regardless of the quantity of cadmium or lead present. This leads to the conclusion that the nickel *is not being co-precipitated but is being precipitated as sulphide by the direct reaction*, and that the rate of this reaction is not affected by the presence of lead or cadmium in the solution or of the sulphide precipitates of these elements.

A series of experiments was made to determine the extent to which under the same conditions nickel would be precipitated with cadmium and lead when hydrogen sulphide was the precipitant instead of thioacetamide. The data from these experiments are collected in Table V and they should be compared with those shown in Table IV. This comparison shows that in most cases the nickel co-precipitated by hydrogen sulphide is *relatively small* compared to that precipitated by thioacetamide under similar conditions as to pH, time, and quantity of other sulphide precipitated. These results again demonstrate the fallacy in the statement that thioacetamide can be substituted for hydrogen sulphide without change of experimental conditions.

In case one is interested in the separation of cadmium and lead from nickel by precipitation with thioacetamide it would be advantageous to work at a lower pH value than 2. Thus, since the precipitation of cadmium and lead is hydrolysis controlled, at a pH of 1 their rates of precipitation would be ten times faster than at a pH of 2 and their concentrations would be reduced to any desired concentration in one

TABLE IV.—NICKEL SULPHIDE FOUND WITH LEAD AND CADMIUM SULPHIDES PRECIPITATED AT pH 2 BY THIOACETAMIDE

Initial thioacetamide: 0.40 *VF*, Temperature: 90°, Solution volume: 10 ml.

| Time, *min* | Nickel (mg) calculated[a] and found with various amounts[b] of $Cd^{II}$ and $Pb^{II}$ | | | | |
|---|---|---|---|---|---|
| | Calc. | Found | | | |
| | | 11 mg Cd | 22 mg Cd | 21 mg Pb | 42 mg Pb |
| | | Initial $nickel^{II}$, 10 mg | | | |
| 4 | 0.04 | 0.04 | 0.04 | 0.06 | 0.06 |
| 8 | 0.08 | 0.06 | 0.07 | 0.10 | 0.08 |
| 12 | 0.12 | 0.12 | 0.10 | 0.12 | 0.10 |
| 16 | 0.16 | 0.15 | 0.13 | 0.18 | 0.16 |
| 20 | 0.20 | 0.19 | 0.16 | 0.23 | 0.21 |
| 24 | 0.24 | 0.23 | 0.19 | 0.26 | 0.25 |
| 28 | 0.28 | | 0.24 | 0.30 | 0.30 |
| | | Initial $nickel^{II}$, 20 mg | | | |
| 4 | 0.08 | 0.09 | | 0.09 | |
| 5 | 0.10 | 0.08 | | 0.09 | |
| 8 | 0.16 | 0.14 | | 0.16 | |
| 10 | 0.20 | 0.18 | | 0.18 | |
| 12 | 0.24 | 0.21 | | 0.25 | |
| 15 | 0.30 | 0.30 | | 0.30 | |
| 16 | 0.32 | 0.29 | | 0.31 | |
| 20 | 0.40 | 0.42 | | 0.39 | |
| 24 | 0.48 | 0.47 | | 0.47 | |
| 28 | 0.56 | 0.54 | | 0.60 | |
| 60 | 1.2 | 1.3 | | 1.1 | |
| 90 | 1.6 | 1.5 | | 1.5 | |
| 120 | 2.1 | 2.2 | | 2.0 | |

[a] Calculated from the expression

$$-\frac{d[Ni^{II}]}{dt} = 2.2 \times 10^{-4} \frac{[Ni^{II}]\,[CH_3CSNH_2]}{[H^+]^{\frac{1}{2}}}$$

[b] Hydrogen sulphide equivalent to 11 mg Cd or 21 mg Pb formed in 12 minutes; to 22 mg Cd or 42 mg Pb in 24 minutes.

tenth the time. In addition, the rate of precipitation of the nickel by the direct reaction would be one third as fast at pH 1 as at 2. As a result of these considerations experiments similar to those above were made at pH 1 and the data are shown in Table VI. The agreement of the quantities of nickel found in the precipitates with those calculated by Expression 1 is quite striking since some precipitation may have occurred during the heating of the solutions to 90° and no correction has been made for this, also a finite "induction" period during which no nickel sulphide precipitate was observed. The agreement between the quantities calculated and found is additional evidence that the nickel is not co-precipitated, but is precipitated by the direct reaction. It is to be noted in Table V that any co-precipitation of nickel with CdS and PbS at pH 1

TABLE V.—NICKEL FOUND WITH CADMIUM AND LEAD SULPHIDES PRECIPITATED AT pH 2 BY HYDROGEN SULPHIDE

Solution saturated with $H_2S$. Temperature 90°. Initial nickel: 20 mg.

| pH and mg Cd or Pb | Nickel, mg, found after various times | | | | |
|---|---|---|---|---|---|
| | 10 *min* | 12 *min* | 20 *min* | 60 *min* | 120 *min* |
| pH 2 | | | | | |
| 11 mg Cd | | 0.01 | | 0.02 | 0.06 |
| 22 mg Cd | | 0.01 | | 0.20 | 0.01 |
| 22 mg Cd + 42 mg Pb | | 0.10 | | | <0.01 |
| 21 mg Pb | | 0.01 | | | |
| 42 mg Pb | | <0.01 | | 0.04 | 0.02 |
| pH 1 | | | | | |
| 11 mg Cd | <0.01 | | <0.01 | | |
| 21 mg Pb | <0.01 | | <0.01 | | |
| 11 mg Cd + 21 mg Pb | <0.01 | | <0.01 | | |

TABLE VI.—NICKEL SULPHIDE FOUND WITH CADMIUM AND LEAD SULPHIDES PRECIPITATED AT pH 1 BY THIOACETAMIDE

Initial thioacetamide: 0.40 *VF*, Temperature: 90°, Initial nickel$^{II}$: 20 mg, Solution volume: 10 ml.

| Time, *min* | Nickel, mg, calculated[a] and found with various initial amounts of Cd$^{II}$ and Pb$^{II}$ [b] | | |
|---|---|---|---|
| | Calc.[a] | Found | |
| | | 11 mg Cd$^{II}$ | 21 mg Pb$^{II}$ |
| 2 | 0.01 | 0.02 | 0.02 |
| 4 | 0.03 | 0.03 | 0.05 |
| 5 | 0.03 | 0.04 | 0.04 |
| 6 | 0.04 | 0.05 | 0.08 |
| 8 | 0.05 | 0.07 | 0.11 |
| 10 | 0.07 | 0.07 | 0.07 |
| 12 | 0.09 | 0.14 | 0.15 |
| 15 | 0.10 | 0.11 | 0.11 |
| 20 | 0.13 | 0.15 | 0.15 |

[a] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = 2.2 \times 10^{-4} \frac{[\mathrm{Ni^{II}}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}}$$

[b] Hydrogen sulphide equivalent to 11 mg Cd$^{II}$ or 21 mg Pb$^{II}$ formed in 1.2 minutes.

is less than the limit of detection of the analytical method, which, under these conditions, was 0.01 mg of nickel.

### *Analytical considerations*

This investigation has shown that the hydrogen ion concentration and the time are both critical factors in the separation of cadmium$^{II}$ and lead$^{II}$, and also other elements of the Hydrogen Sulphide Group, from nickel$^{II}$ by sulphide precipitations from thioacetamide solutions. Calculations can be made which will permit predictions as to how effective such separations can be made. Thus if one assumes that he has 250 ml of a solution at 90° and initially 0.1 *VF* in thioacetamide and 0.10 *VM* in hydrogen ion, and containing 250 mg of cadmium$^{II}$ and nickel$^{II}$, one can calculate that sulphide equivalent to the cadmium$^{II}$ would be formed by hydrolysis of the thioacetamide within ten minutes; in this time one calculates that less than 0.25 mg of nickel sulphide would be precipitated by the direct reaction. However, the precipitation of nickel sulphide by the direct reaction will continue for as long as a significant concentration of thioacetamide remains in the solution, therefore as soon as quantitative precipitation of the cadmium sulphide is obtained one should remove the precipitate. This effect presents a serious source of trouble, especially when thioacetamide is used for analytical procedures intended for instructional purposes and where there may be intervals of days or more between periods.

A solution similar to the one above but having a pH of 2 would require almost one hundred minutes for quantitative precipitation of the cadmium$^{II}$. In this time over 6 mg of nickel$^{II}$ will precipitate. Therefore, in general, such separations should be carried out at the lowest permissible pH, and in the shortest time in order to obtain maximum effectiveness of separation.

It should be noted, however, that even at a pH of 1 the amount of nickel coprecipitated when cadmium and lead sulphides are precipitated by hydrogen sulphide is smaller than that precipitated with these sulphides in comparable periods of time by the direct reaction with thioacetamide; therefore a better separation is obtained by hydrogen sulphide at this pH value. It seems reasonable that by commencing the precipitation of cadmium and/or lead sulphide by thioacetamide at lower pH values (for example with the hydrogen ion concentration 1 volume molal), and then reducing the acidity to a pH of 1 to effect their complete precipitation, the precipitation of nickel sulphide by thioacetamide may be further diminished and a much more effective separation obtained.

The above discussion has completely neglected any complex ion effects and these can seriously affect both equilibrium and rate considerations. Thus unpublished experiments in these laboratories have shown that chloride ion can have a marked inhibiting effect on the rate of precipitation of both cadmium and lead by the direct reaction. In the course of this investigation an attempt was made to use a monochloracetic acid—monochloracetate buffer but it was found that an inhibition of the direct reaction between nickel$^{II}$ and thioacetamide resulted. This inhibition was shown not to be caused by chloride resulting from hydrolysis of the buffer.

This investigation has demonstrated the need for caution in the substitution of thioacetamide for hydrogen sulphide in analytical separations. It is hoped that further investigations will be made into other similar procedures.

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**Zusammenfassung**—Geschwindigkeit-messungen zeigen dass die Fällung von Nickel als Sulphid mit Thioacetamid in Lösungen von [H$^+$] Konzentration gleich 0,3 bis 1 × $10^{-7}$ *M*, mit der Gleichung

$$-\frac{d\,[\mathrm{Ni^{II}}]}{dt} = k\,[\mathrm{Ni^{II}}]\,[\mathrm{CH_3CSNH_2}]/[\mathrm{H^+}]^{\frac{1}{2}}$$

mit *k* gleich 2,2 × $10^{-4}\mathrm{L}^{\frac{1}{2}}$. $\mathrm{Mol}^{-\frac{1}{2}}$. $\mathrm{Min}^{-1}$ bei 90° beschrieben werden können. Die Aktivations-Energie wurde im Bereich 70° bis 90° auf 20.8 Kcal/Mol berechnet. Fällung fand in Ubereinstimmung mit dierer Geschwindigkeits-Gleichung bei [H$^+$] Konzentrationen statt, bei welchen Niederschlag mit Schweffelwasserstoffes erholten wurde. Die Wirksamkeit der Trennung von Blei(II) und Kadmium von Nickel mittels Thioacetamid in Lösungen von pH 1 bis 2 bei 90° wurde studiert. Die Bildungsgeschwindigkeit von Nickel-sulphid stimmt mit der Geschwindigkeits-Gleichung von der Konzentration von Blei, Kadmium und Schwefelwasserstoffen in der Lösung unabhängig. Die Menge von Nickel-sulphid gefällt mit Kadmium- und Blei-sulphid in Folge einer direkten Reaktion zwischen Nickel und Thioacetamid übertrifft die mitgefällte Menge im Falle der Kadmium und Blei-Fällung mit Schwefelwasserstoff. Unter optimalen Bedingungen sind aber Trennungen möglich.

**Résumé**—La précipitation du nickel$^{II}$ de ses solutions à l'état de sulfure par la thioacétamide dans un grand domaine de pH répond à une expression, dérivée de mesures de vitesse, qui n'implique pas une précipitation controlée par l'hydrolyse; cette précipitation a lieu à des concentrations d'ions hydrogènes auxquelles on n'obtient pas de précipitation par l'hydrogène sulfuré.

L'efficacité de la séparation du plomb$^{II}$ et du cadmium$^{II}$ d'une part et du nickel$^{II}$ d'autre part, par l'emploi de thioacétamide en solutions de pH 1 et 2 maintenues à 90°C a été étudiée. La vitesse de formation du sulfure de nickel est conforme à l'expression dérivée de la vitesse et est indépendante de la quantité de sulfure métallique présent ainsi que de lac oncentration du plomb$^{II}$, du cadmium$^{II}$ et de l'hydrogène sulfuré dans la solution. La quantité de sulfure de nickel précipitée avec les sulfures de cadmium et de plomb par réaction directe entre l'ion nickel et la thioacétamide dépasse celle ayant co-précipitée quand le cadmium et le plomb sont précipités par l'hydrogène sulfuré. Cependant dans des conditions correctement contrôlées on peut obtenir une séparation effective.

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# TITRIMETRIC DETERMINATION OF TETRAPHENYLBORON BY THALLIUM$^{I}$

BHARAT R. SANT and ANIL K. MUKHERJI
Coates Chemical Laboratories, Louisiana State University
Baton Rouge 3, La., U.S.A.

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**Summary**—A titrimetric procedure for the determination of sodium tetraphenylboron, based upon its precipitation by a known excess of thallium$^{I}$ and back-titration of the excess with standard potassium iodate, is described.

## INTRODUCTION

EARLIER work from these Laboratories[1] employing high-frequency technique for the detection of end-points has shown that thallium$^{I}$ and silver form sparingly soluble tetraphenylborates of the composition $Tl(C_6H_5)_4B$ and $Ag(C_6H_5)_4B$ respectively. Using these it was possible to determine small quantities of thallium, silver, or tetraphenylboron (TPB) in comparatively high dilutions.

Since its discovery by Wittig and co-workers[2] in 1949, sodium tetraphenylboron has been employed as a precipitating reagent for $K^+$, $Rb^+$, $Cs^+$, $Tl^+$, and $NH_4^+$ and several organic nitrogen compounds.[3] In all these procedures, excess of the reagent is always used and it is therefore not necessary to know the exact strength of NaTPB. While tetraphenylborates are usually analysed gravimetrically, titrimetric approaches, particularly for potassium, such as ignition of KTPB and titration of the resulting metaborate with standard acid[4,5] and argentometric titration of KTPB dissolved in acetone using an indicator[6] or amperometric[7] end-point, have also been described. The knowledge of exact strength of NaTPB is important when stoichiometric studies are made by a direct titration. This could be done by either weighing the sample of known purity or standardizing by a suitable method. Since little information is available in the literature, it was thought desirable to develop a rapid and reliable method for standardization. The present communication reports a titrimetric procedure, based on the quantitative precipitation of TPB ion by a known excess of thallium$^{1}$ solution and titrating the excess with standard potassium iodate.

## EXPERIMENTAL

An analytically pure sample (99.8% assay) of NaTPB, supplied by J. T. Baker Chemical Company, was used in the present work. The given assay is based on the procedure of Flaschka and co-workers originally developed for the determination of potassium.[8] Mercuric chloride is added to an acetone solution of TPB in presence of an excess of standard alkali and the excess is back-titrated with a standard acid.

A standard solution of $KIO_3$ was prepared by direct weighing of the pure sample after drying it at 160–180° for 2–3 hours. Thallium$^{I}$ nitrate solution was standardized by titration in 3*N*–4*N* hydrochloric acid solution with iodate to the iodine monochloride end point using chloroform as indicator. The following procedure was adopted for the determination of tetraphenylboron:

### *Procedure*

An aliquot portion of NaTPB solution was precipitated by a known excess of thallium$^{I}$ nitrate. After standing 4–6 hours, the precipitate was filtered through Whatman No. 42, washed 8–10 times with about 10 ml of water, and the unused thallium$^{I}$ in the filtrate was titrated with standard $KIO_3$ in presence of hydrochloric acid as described above. The difference in the two titers of iodate corresponds to the weight of NaTPB present originally:

$$NaTPB + TlNO_3 \rightarrow TlTPB + NaNO_3$$

$$2TlNO_3 + KIO_3 + 8HCl \rightarrow 2TlCl_3 + KCl + ICl + 2HNO_3 + 3H_2O$$

Thus 1 ml of 1 M–$KIO_3$ is equivalent to 0.68447 g of NaTPB. Results of a representative set of experiments are entered in Table I.

TABLE I. DETERMINATION OF TETRAPHENYLBORON BY THALLIUM$^{I}$

| NaTPB, *g* | | Difference, *g* |
|---|---|---|
| Calculated | Found | |
| 0.03480 | 0.03470 | 0.0001 |
| 0.06865 | 0.06852 | 0.00013 |
| 0.06960 | 0.06940 | 0.0002 |
| 0.1044 | 0.1041 | 0.0003 |
| 0.1392 | 0.1388 | 0.0004 |
| 0.1740 | 0.1735 | 0.0005 |

It will be seen from Table I that the weight of NaTPB obtained experimentally is in fair agreement with that taken actually. Besides, the present method is simple and rapid with the additional advantage of using $KIO_3$ as a primary standard. A series of experiments performed by the described method showed that the TPB content, corresponding to what may be termed as the "precipitating power," of a given NaTPB solution remains unaltered for a period of seven days if the solution is stored in refrigerator. At room temperature (30°) and in ordinary daylight, the solution decreases in its strength after about 48 hours.

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**Zusammenfassung**—Es wurde ein titrimetrisches Verfahren zur Bestimmung von Natrium-tetraphenylbor durch Fällung mit einem Überschuss von Thallium(I) und Ruck-titrieren des Überschusses mittels Standard-Kalium-jodat beschrieben.

**Résumé**—Les auteurs décrivent une méthode volumétrique pour le dosage du tétraphenylborure de sodium, basée sur sa précipitation par un excès connu de thallium$^{I}$ et le dosage en retour de l'excès par de l'iodate de potassium titré.

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# EARLY PREPARATION AND ANALYTICAL USE OF HYDROGEN SULPHIDE

F. SZABADVÁRY
Institute of General Chemistry, Technical University Budapest, Hungary

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**Summary**—Robert Boyle obtained hydrogen sulphide and applied it as an analytical reagent in 1685 for the detection of mercury, tin, lead and copper.

THE "sulphur-liver" test has been known for a long time. Treated with acids hydrogen sulphide is developed. Even the alchemists must have met this phenomenon but, having no knowledge about gases at that time, they probably paid no attention to it. According to Kopp[1] it was F. Hoffman[2] who first mentioned hydrogen sulphide, writing about a gas smelling of rotten eggs and obtained by the acidification of caustic sulphur solutions. Hydrogen sulphide was more fully studied by Rouelle[3] in 1774. It was stated by Bergman,[4] that hydrogen sulphide water gave precipitates of different colour with many metal-salt solutions. These reactions were fully studied by him. It is interesting that this great analyst did not think of the analytical utilization of these reactions. Until now it has been held in the literature that Fourcroy[5], and at the same time Hahnemann,[6] both recommended hydrogen sulphide as an analytical reagent for the detection of lead. Robert Boyle, however, long before that, obtained hydrogen sulphide and applied it as analytical reagent. This appears from his *Memoirs for a Natural History of Mineral Waters* published in 1685.

Dealing with the use of the long known metal-reagent, tincture of galls, he states that its use is not so certain as it is believed to be. Some of the metals in water, like arsenic or lead may not give a colour with it. "But, probably, the sulphureous spirit we shall presently describe, wou'd have shewn that water to be impregnated with a body of the nature of vitriol, but not the common sort. For the' galls give no very blackish colour to a solution of Sacharum Saturni, that is, the vitriol of lead, in distill'd or rain-water yet I found this volatile sulphur wou'd soon manifestly do it: which expedient I made use of, because I had not then at hand the ores of lead, copper, etc. For the same reason I contented myself with the solutions of the several metals in their proper menstrua; for 'tis probable, that the metalline parts of the ores, wou'd have afforded either the same, or similar solutions, in the same menstrua; which consisting of nitre, sea-salt, and vitriol, bodies that abound in several parts of the earth thro' which springs flow, their several impregnated waters might exhibit phenomena of the same kind. We made then, among others, a solution of fine gold in Aqua regis; another of common running mercury in Aqua fortis; and a clear one of tin, in a peculiar solvent that readily acts upon it, and keeps it permanently dissolv'd. To these solutions I put galls, without obtaining any blackish colour, except from that which contained gold; but with our sulphureous liquor, we obtained notable changes of colour, tho' 'twas dark in all of them, except one, or tending to blackness. And tho' for that reason a careless eye might judge them indifferently blackish, yet, since the degrees, or some other modification of the same dark colour, seemed plainly not to be the same in them all; 'tis possible, that a very careful view may discern some little differences between those obscure colours, from whence to form a conjecture, what metalline substance is contained, or at least predominates in the respective liquors. And I particularly remember, that the colour which arose from our sulphureous liquor, and the solution of tin, was manifestly distinguishable from those produced in any of the other solutions; being not black or blackish, nor so much as purple; but of a kind of brownish yellow."[7]

Later Boyle also describes the production of the "sulphureous spirit": ". . . take equal parts of pure salt of tartar ($K_2CO_3$), flowers of sulphur, and good sal-ammoniac ($NH_4Cl$), reduce the first and the last to powder separately, melt the sulphur, over a gentle fire, and, by degrees, put to it the salt of tartar; stirring them well, that they may incorporate and grow reddish; then put the mixture, pulverized, into a glass-retort, pour on it the sal-ammoniac dissolv'd in fair water; and closing well the junctures, distil all in sand, by degrees of a moderate fire; shifting the receiver once or twice, because the liquors will be differently ting'd and strong, and that which ascends last, may bring over but very little of the sulphur, whose volatile tincture is yet the chief thing we aim at in this operation."[8]

Repeating Boyle's experiment I have found that hydrogen sulphide is in fact developed.

Boyle also used his reagent for the detection of copper: ". . . yet common English vitriol, as also that of Dantzick, which is of the copper kind, will presently turn it of a black or very dark colour."[9]

But it is worth observing that he did not get any precipitate with arsenic: ". . . and to another portion of the same liquor (arsenic) we put some of our volatile sulphureous spirit, but no precipitation ensued."[10] The solution was probably alkaline.

**Zusammenfassung**—Robert Boyle erzeugte schon im Jahre 1685 Schwefelwasserstoff und benützte es bei Wasseranalysen zum Nachweis von Quecksilber, Zinn, Blei und Kupfer.

**Résumé**—Robert Boyle a préparé de l'acide sulfhydrique et l'a utilisé comme réactif analytique en 1685 pour la caractérisation du mercure, étain, plomb et cuivre.

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# POLAROGRAPHIC EXAMINATION OF THE CHELATING POWER OF EDTA AND SOME CLOSELY RELATED CHELATING AGENTS*

W. HOYLE and T. S. WEST
Chemistry Department, The University, Edgbaston, Birmingham 15, England

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A rapid polarographic method has been devised for assessing the chelating power of new reagents of the complexone type and for comparing such reagents with complexones of known stability. A standard chelate scale based on $Cu^{II}$ chelates has been set up. A linear relationship appears to exist between $\Delta E_{\frac{1}{2}}$ and Log $K$ for known complexones, but this may not hold for newer complexones which are considerably more powerful in their cation binding powers.

IN the course of an investigation into the properties of some homologues of ethylenediaminetetra-acetic acid (EDTA) and other aminopolycarboxylic acids it was found necessary to evolve a rapid method for estimating the chelating power of these reagents.

It is well known that the polarographic wave for the aquo-ion complex of simple metal cations is shifted towards more negative potentials when the ion enters into chelate formation. There are several methods available for relating the induced shift in the half-wave potential to the instability constant of the chelate thus formed. These have been reviewed recently by Rossotti.[1] The most attractive of these methods appeared to be that in which the half-wave potential of the chelate wave is measured in the presence of varying excesses of the reagent. It is then only necessary to know the dissociation constant of the chelating acid and its concentration in order to calculate the desired $\log_{10} K$ value. Unfortunately the aqueous solubility of EDTA and similar reagents is sufficiently low to preclude the use of this method and moreover the waves do not appear to be fully reversible. It was therefore decided to establish a standard curve relating experimentally observed $E_{\frac{1}{2}}$ values to the known chelation constants of a selected cation with various reagents and to use this as a means of estimating unknown $K$ values for new reagents.

This method has the advantage of extreme rapidity and simplicity and it requires very little material.

In setting up such a chelate scale several factors must be considered in selecting a suitable cation.

(1) A low pH must be used to decrease the stability of the chelate.

(2) The cation itself must have a low $E_{\frac{1}{2}}$ value in order to give as wide a working range as possible between $E_{\frac{1}{2}}$ for the unchelated cation and the hydrogen wave.

(3) The cation should preferably give only one wave.

(4) The cation should be such that it allows a reasonable movement of $E_{\frac{1}{2}}$ on chelation with a strong reagent without the wave merging with that of hydrogen.

(5) The chelate formed with the weaker chelating agents, *e.g.* iminodiacetic acid, must be sufficiently stable not to break down at the selected pH.

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* This paper was presented in part at a meeting of the Polarographic Society, held at Nobel Division, Imperial Chemical Industries Ltd., Stevenston, Ayrshire, on 26 September 1958.

Zinc, nickel and cobalt give no chelate waves with EDTA at pH > 2.7 (*i.e.* the waves lie beyond the $H_2$ wave); thallium,$^{I}$ arsenic$^{III}$ and molybdenum$^{VI}$ do not fulfil condition (4); chromium$^{III}$ and tin$^{II}$ are also not suitable (Condition 3)[2]. Of the remaining common cations copper$^{II}$ and cadmium were selected for further investigation.

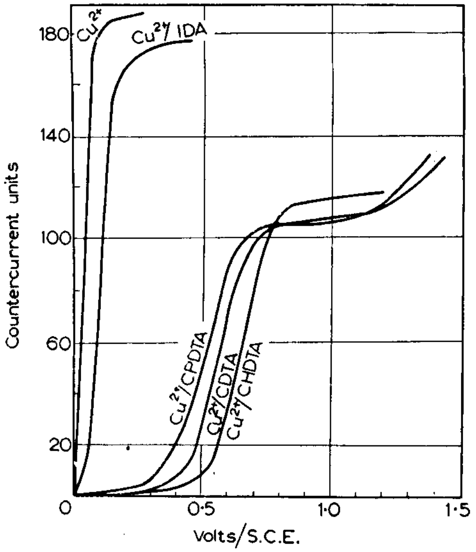

FIG. 1.

## INVESTIGATION OF CU$^{II}$ CHELATES

The half wave potential of the $Cu^{2+}$/EDTA chelate depends on several factors, *e.g.* pH, ionic strength, temperature, concentration of chelate, excess of chelating agent, concentration of buffer, etc. These variables all require control, but the most important single factor is the first mentioned.

At pH 4.6, weak chelating agents such as iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), etc., give a single chelate wave as do very strong chelating agents such as 1:2-diamino*cyclo*hexane-N:N:N′:N′-tetra-acetic acid (CDTA), *cf.* Fig. 1.* However, chelating agents of intermediate strength, *e.g.* EDTA give double waves and sometimes even more complex behaviour, *cf.* Fig. 2.

In 0.4*M* acetic acid all chelating agents examined were found to give a single wave which required the use of a maximum suppressing agent, *cf.* Fig. 3. Gelatin appeared to be the most effective of these. However, the concentration of gelatin has a considerable effect on the $E_{\frac{1}{2}}$ values for the chelate wave, *i.e.* $E_{\frac{1}{2}}$ is found to increase with gelatin concentration. Of other suppressing agents examined, only "Cetavalon" was successful, but it showed some disturbing effects on the relative order of chelation as related to $E_{\frac{1}{2}}$ values, and like gelatin, its concentration had a pronounced effect. The choice of maximum suppressing agent was therefore restricted to gelatin. It was noted that the greater the stability of the chelate, the lower the concentration of gelatin necessary to suppress the maximum. A final concentration of 0.025% was

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* The data in Figs. 1–3 were obtained in early experiments with a Cambridge manual polarograph.

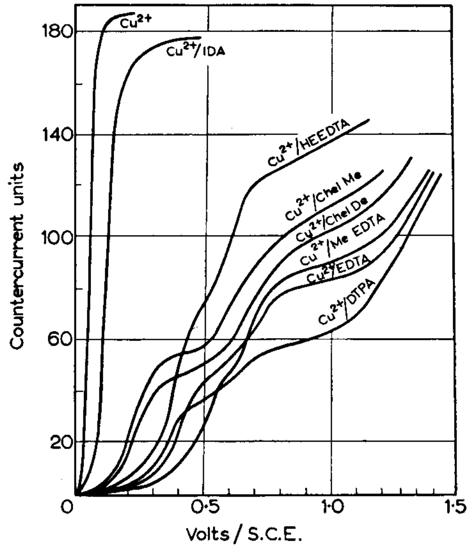

FIG. 2.

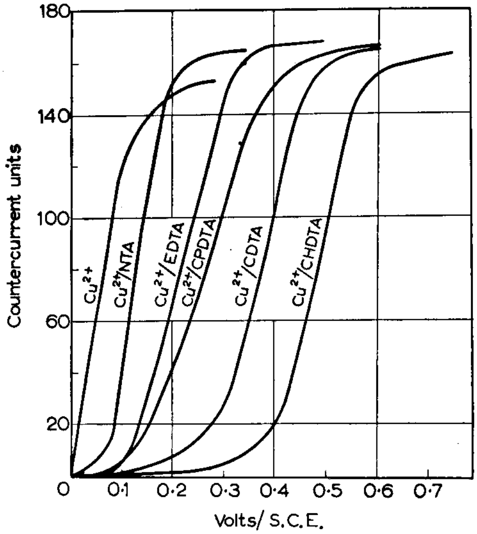

FIG. 3.

chosen as this was the minimum required for suppressing maxima obtained with the weaker reagents such as NTA.

When the optimum conditions for this and other factors had been established, the $E_{\frac{1}{2}}$ values were determined for a number of copper chelates of known stability. Since a stability constant cannot readily be assigned to the copper$^{II}$ aquo-ion complex, in an acetate medium, and since it is certainly not zero, the cupric chelate of di-(2 hydroxyethyl) glycine (DHEG) with $E_{\frac{1}{2}} = -0.02$ and $\log_{10} K = 8.1$ was chosen as arbitrary (zero) reference point, and a standard curve relating observed $\Delta E_{\frac{1}{2}}$ values* to known

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* $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}(\text{Chelate})} - E_{\frac{1}{2}(\text{DHEG})}$

Δ $\log_{10}$ K values[3] was established *cf.* Fig. 4. The curve was extrapolated beyond the plot for CDTA to enable us to assess the stability of new reagents which form more stable chelates than CDTA (previously the strongest known). The true shape of the curve beyond this point will become apparent when the instability constants for the new reagents have been determined.

About 20 aminopolycarboxylic acids of the "complexone" type were investigated in setting up this standard curve, *cf.* Table I. A list of estimated instability constants for some new chelating agents has been established as a result of this work, *cf.* Table II. Certain complexones, *e.g.* CHEL DE, which have extra co-ordinating centres do not fall on the curve. We presume that such reagents form protonated species for which data are not available.

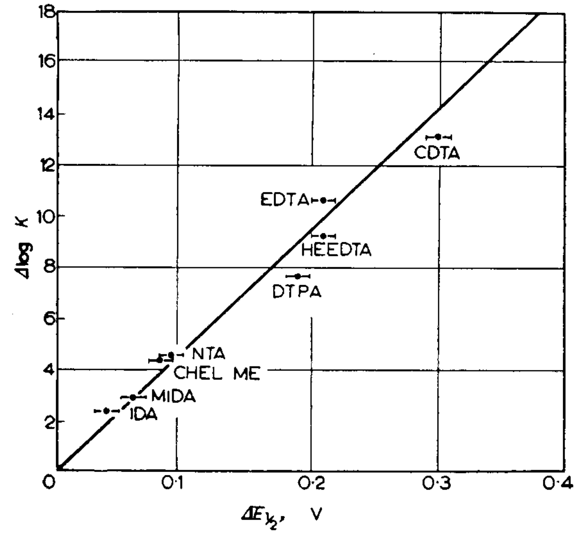

Fig. 4.

A number of chelating agents showed unusual "reversed current" behaviour at the dropping mercury electrode. During the early stages of reduction, *i.e.* before the $E_{\frac{1}{2}}$ point on the polarogram, these chelates behaved in such a way that the current was observed to decrease as the drop size increased and to increase immediately the drop fell off. However, at a more cathodic potential, but before the limiting current was reached, the normal pattern of behaviour was observed *viz* increase of current up to maximum drop size. The point of change over was indicated by a sharp kink in the polarogram, *cf.* Fig. 5.

This phenomenon is probably associated with the gelatin coverage of the surface of the mercury drop. Under certain circumstances the coverage of the mercury surface by gelatin is known to increase as the drop surface advances out into the liquid.[4] Consequently, during its life-time the mercury drop becomes increasingly protected against the phenomenon which causes the formation of maxima so that as the drop grows the current falls of to a minimum at maximum drop size and increases sharply as soon as the new drop begins to form. During the early stages of reduction, *i.e.* before the $E_{\frac{1}{2}}$ value for the polarogram has been attained, the electrode reaction is relatively slow and so this phenomenon is observed, but at more cathodic potentials

TABLE I. CATHODIC HALF-WAVE POTENTIALS FOR THE POLAROGRAMS OF VARIOUS CHELATES AT pH 2.5

| Chelate | $E_{\frac{1}{2}}$ | | Chelate | $E_{\frac{1}{2}}$ | |
|---|---|---|---|---|---|
| | $Cu^{2+}$ | $Cd^{2+}$ | | $Cu^{2+}$ | $Cd^{2+}$ |
| D.H.E.G. | 0.02 | | Chel. 138 | 0.16 | |
| I.D.A. | 0.06 | 0.60 | D.T.P.A. | 0.21 | |
| M.I.D.A. | 0.08 | | H.E.E.D.T.A. | 0.23 | |
| A.A.D.A. | 0.08 | | E.D.T.A. | 0.23 | 0.82 |
| Chel. ME. | 0.10 | | C.P.D.T.A. | 0.24 | 0.93 |
| Chel. DE. | 0.11 | | M.E.D.T.A. | 0.29 | 0.88 |
| D.P.T.A. | 0.11 | | C.D.T.A. | 0.32 | 1.04 |
| N.T.A. | 0.11 | 0.60 | 2 : 3 B.D.T.A. | 0.41 | 0.97 |
| U.D.A. | 0.16 | | C.H.D.T.A. | 0.42 | 1.08 |

*Abbreviations:*

M.I.D.A. Methyliminodiacetic acid.
A.A.D.A. *o*-Carboxyphenyliminodiacetic acid.
U.D.A. Uramil-N:N-diacetic acid.
M.E.D.T.A. 1:2-Propylenediamine-N:N:N′:N′-tetra-acetic acid.
* Chel. ME. 2:2′-Bis[di(carboxymethyl)amino]diethyl ether.
* Chel. DE. 1:2-Bis-[2-di(carboxymethyl)aminoethoxy] ethane
* D.P.T.A. 1:3 Diaminopropan-2-ol-N:N:N′:N′-tetra-acetic acid.
* Chel. 138 N:N′-Ethylene bis [2-(*o*-hydroxyphenyl)] glycine.
D.T.P.A. Diethylene triamine-N:N:N′:N″:N″-penta acetic acid.
* H.E.E.D.T.A. N-(2-Hydroxyethyl) ethylene diamine-N:N′:N′-tri acetic acid.
† C.P.D.T.A. *trans*-1:2-Diamino*cyclo*pentane-N:N:N′:N′-tetra-acetic acid.
† C.H.D.T.A. 1:2-Diamino*cyclo*heptane-N:N:N′:N′-tetra-acetic acid.
† 2:3 B.D.T.A. 2:3-Diaminobutane-N:N:N′:N′-tetra-acetic acid.

* Supplied by The Geigy Co. Ltd.
† Synthesised by the authors.[6]

TABLE II.—STABILITY OF CHELATES BY THE POLAROGRAPHIC METHOD

| $Cu^{2+}$ Chelate | Estimated log $K$ |
|---|---|
| U.D.A. | 15 |
| A.A.D.A. | 11 |
| C.P.D.T.A. | 19 |
| M.E.D.T.A. | 21 |
| 2 : 3 B.D.T.A. | >22 |
| C.H.D.T.A. | >22 |

the reduction process speeds up and the electrode reaction then becomes diffusion controlled so that the effect of the gelatin coverage of the drop surface is no longer observed. Where such polarograms were encountered, current measurements were made on the part of the curve corresponding to maximum *drop* size.

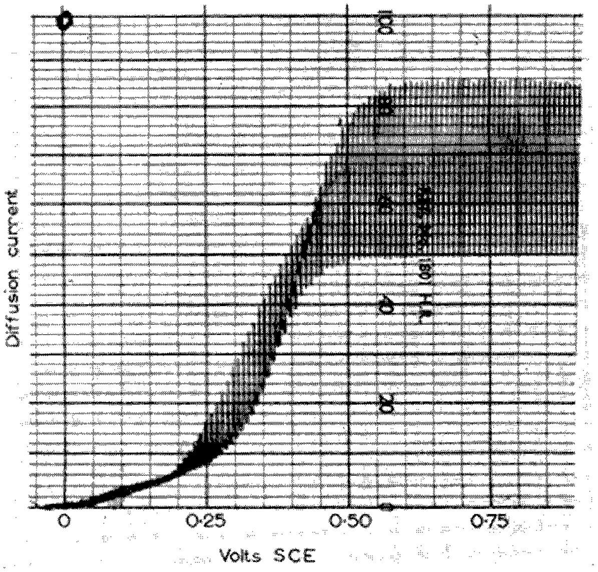

FIG. 5

## INVESTIGATION OF CADMIUM CHELATES

Cadmium is less satisfactory than copper for the purpose of setting up a chelate scale because of the lower stability of the chelates of this cation and the more cathodic value of the $E_{\frac{1}{2}}$ value for the unchelated ion. Thus weak chelating agents which yield quite satisfactory chelates waves with $Cu^{II}$ show no such wave with $Cd^{2+}$, whilst the polarogram for strong chelating agents is situated too close to the hydrogen wave to permit accurate measurements. The $Cd^{2+}$/EDTA polarogram (pH 2.5) shows two waves, the first of which corresponds to free cadmium ion and the second to the $Cd^{2+}$ chelate. Whilst this work was in progress a similar observation was reported by Schmid and Reilley[5] in the U.S.A.

We have determined the polarograms of a range of the more powerful chelating agents with cadmium in 0.4*M* acetic acid at pH 2.5 without the use of a maximum suppressing agent. Most of these polarograms show twin waves, but the more powerful the chelating agent the smaller was the wave due to free cadmium till eventually for reagents such as CDTA (and some of the yet more powerful chelating agents which we have devised) no free cadmium could be observed. At the same time, the half-wave potential of the second wave became more negative and for the more powerful reagents it eventually became difficult to determine $E_{\frac{1}{2}}$ because the diffusion current of the chelate merged with the start of the hydrogen wave.

A $Cd^{2+}$ chelate scale corresponding to the $Cu^{II}$ scale was not set up as sufficient data are not available. Only the relative strengths of the chelates were determined. These show some slight divergence from the order obtained with $Cu^{II}$, but this is not entirely unexpected.

## CONCLUSIONS

As a result of the evolution of this rapid method for the estimation of the chelating ability of new reagents on quite minute amounts of material, it was possible to obtain fairly precise data on the chelating power of new reagents in a matter of a few hours rather than the days it would have taken by more customary methods. Furthermore less precise data could sometimes be obtained on the reaction mixture itself without having recourse to the extremely tedious procedures which are usually necessary for the isolation of some of the aminopolycarboxylic acids.

## EXPERIMENTAL

### *Reagents*

*Copper sulphate solution*: 0.002*M* in 0.4*M* acetic acid containing 0.025% of gelatin, freshly prepared before use, pH 2.5.

*Complexones*: 0.1*M* aqueous solutions of the sodium salts.

*Cadmium sulphate solution*: 0.001*M* solution in 0.4*M* acetic acid, pH 2.5.

### *Apparatus*

Tinsley Recording Polarograph Mark 19, with dropping mercury electrode (drop time 5.2 sec, under an open head of mercury of 37 cm) and a saturated calomel electrode with a potassium chloride bridge as a reference electrode. E.I.L. Direct Reading pH Meter.

### *The polarographic determination of chelate stability*

To 10 ml of the copper sulphate solution in a 20-ml beaker, 0.3 ml of the complexone solution was added. The pH of the solution was measured, and adjusted where necessary to pH 2.5 with concentrated hydrochloric acid or sodium hydroxide solution. After the solution had been deoxygenated with hydrgoen an undamped polarogram was recorded using a sensitivity of 12 μA, no counter current, and a chart scale of 1 volt/4″. All the determinations were done at room temperature. The half-wave potentials were measured to within ±10 mV, from the curve drawn through the points given by the current at maximum drop size.

*The polarographic examination of some cadmium chelates*

To 10 ml of the cadmium sulphate solution, 0.2 ml of the complexone solution was added. The pH of the solution was checked to be 2.5, and a polarogram determined after deoxygenation at a sensitivity of 7.5 $\mu$A, with no damping, a counter current of 2 or 3, and a chart scale of 1 volt/4″. The determinations were done at room temperature. The half-wave potentials were measured as above.

*Acknowledgements*—We are grateful to The Geigy Co. Ltd. for the provision of a research grant to one of us in aid of this work, and to Dr. R. Belcher for his interest and helpful advice.

**Zusammenfassung**—Aus der polarographischen Untersuchung der Reihe von Kupfer- und Kadmium-Chelate mit grossen Anzahl der Komplexon-Art-Verbindungen wurde eine Methode zur raschen Bestimmung des Chelat-Vermögens eines neuen Reagens entwickelt.

**Résumé**—On a imaginé une méthode pour l'analyse rapide du pouvoir complexant d'un noveau réactif à partir d'une étude polarographique des complexes du cuivre et du cadmium, avec une large série de composés du type "complexon".

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# QUANTITATIVE EVALUATION OF CHROMATOGRAMS BY DOUBLE DECOMPOSITION WITH SIMPLE RADIOACTIVE REAGENTS—I

## THE USE OF $Ag^{131}I$ IN RADIOMETRIC ESTIMATION OF ORGANIC AND PHOSPHORIC ACIDS

Z. J. Zubrzycki, A. Z. Budzyński and I. G. Campbell
Departments of Radiobiology and Radiochemistry, Institute of Nuclear Research,
Warsaw 9, Poland

(*Received* 13 *November* 1958)

**Summary**—A method which it is proposed to call "double decomposition radiochromatography" has been developed for the radiometric estimation of saturated fatty acids, inorganic phosphates and glucose-1-phosphates on paper chromatograms, by forming insoluble silver salts on the paper strip, followed by decomposition of the salt with $^{131}I$-iodide, and radiometry of the $Ag^{131}I$ deposit. Integrated activities of spots are linearly related to spot content. The maximal (peak) spot activity is proportional to the logarithm of spot content for fatty acids and phosphates, but not for glucose-1-phosphate.

In a previous publication[1] the authors have shown that saturated fatty acids could be estimated after paper chromatographic separation, by forming insoluble silver soaps on the strip, followed by decomposition of the soaps with radioactive iodide to form localized precipitates of $Ag^{131}I$, corresponding in geometry to the fatty acid spots. In general it would seem that this method could be applied in all cases where the chromatographically separated substances can form insoluble local precipitates on the strip with a cation or anion, which in turn by double decomposition can form a second insoluble precipitate with an appropriate radioactive anion or cation. In this way, by using simple precipitation reactions, it might be possible to label chromatograms for quantitative radiometric estimation, with easily available active anions or cations, without the necessity for preparing specially labelled, more complex reagents for attaching the tracer to the chromatographed material.

In the case of silver soaps decomposed with $^{131}I^-$, it was shown that reproducible relationships could be established between spot content and such parameters as radiometrically defined spot length or peak spot activity. These relationships were adequate for estimating content of substance in the spot. Such parameters can be adequately estimated by means of radioactive labelling, even if the labelling agent is not stoichiometrically bound to the spot. This fact gives wider possibilities of application to the method which we propose to call "double decomposition radiochromatography".

Silver ion forms precipitates of sufficient degree of insolubility for localization on the chromatogram with a number of anions, and all these precipitates will in turn undergo double decomposition with $I^-$, in view of the exceptional insolubility of AgI. This paper deals with the use of $Ag^{131}I$ in the radiometrical analysis of chromatograms of organic acids, phosphoric acids, and an ester of phosphoric acid, all of which give adequately insoluble silver salts.

In all cases where the labelling isotope has a $\beta$-particle energy sufficiently high to render counting efficiency practically independent of fluctuations of paper thickness, radiometric methods for estimating chromatograms will be superior to the photometry of coloured spots on strip, which is liable to considerable error due to variation of strip thickness. Thus methods which simplify labelling of chromatograms could receive wide application.

## EXPERIMENTAL

The following compounds were chromatographed:

(a) lauric, myristic, palmitic and stearic acids as representatives of carboxylic acids,

(b) orthophosphate, pyrophosphate, trimetaphosphate and hypophosphate as representatives of phosphates,

(c) glucose-1-phosphate as representative of phosphoric acid esters.

The carboxylic acids were separated by reversed-phase chromatography on Schleicher and Schüll 598 L paper strips of 15 mm width and 280 mm length by a previously described method[2], using a mixture of synthetic hydrocarbons of very low bromine number (0·16), and boiling point 180–190° C., called 'Mepasine' (Polish product, Ciech, Warsaw), as stationary phase, and 90 per acetic acid saturated with 'Mepasine' as mobile phase in ascending reversed phase chromatography under nitrogen. 'Mepasine' is applied to the strips as a 20 per cent solution in freshly distilled ether free of peroxide, followed by evaporation of the ether. Phosphates and phosphate ester were chromatographed by the method of Ebel and Volmar[3] on Whatman No. 4 paper.

After chromatography the strips were dried in air and then immersed in narrow vessels made of paraffin wax of minimal volume to immerse the freely hanging strips fully, for subsequent operations. Fifteen ml of a saturated solution of silver acetate were poured into the vessels, and served to cover the chromatograms. After 15 minutes this solution was decanted and the chromatograms then washed three times for five minutes each with water. After decanting the final portion of water, there was added 15 ml of solution $0{\cdot}01M$ in potassium iodide, and containing about 3 $\mu$C $K^{131}I$ per ml. After 15 minutes immersion, the active solution was removed, and the chromatograms washed three times for five minutes with water, and then removed from the vessels, and allowed to dry in the dark at room temperature.

Activity measurements were made with a previously described apparatus[1] using a 2-mm slit width.

## RESULTS AND DISCUSSION

The results are shown in Figs. 1–6.

Figs. 1–3 show the relationship between spot content and integrated spot activity (as previously defined[1]). As can be seen, in all cases a linear relationship is obtained suitable for estimation of spot content within a useful range of amounts of chromatographed substance. In our hands average errors for determination of the organic acids lie in the range 4·6–7·1% for 50–400 $\mu$g of chromatographed substance, 4·9–11·2% for the phosphoric acid ions for 50–500 $\mu$g of chromatographed substance, and 1·9% for glucose-1-phosphate for 20–300 $\mu$g of chromatographed substance. These errors must be considered quite satisfactory for quantitative evaluation of radiochromatograms.

Figs. 4–6 show the relationship between spot content and maximal spot activity (as previously defined[1]). Figs. 4 and 5 show that for saturated fatty acids and phosphates a satisfactory linear relationship is obtained between maximum spot activity and logarithm of spot content. On the other hand an inverse relationship appears to prevail for glucose-1-phosphate, as shown in Fig. 6. where the logarithm of maximal activity seems rather to be proportional to spot content.

The average error for determination of the chromatographed substances using

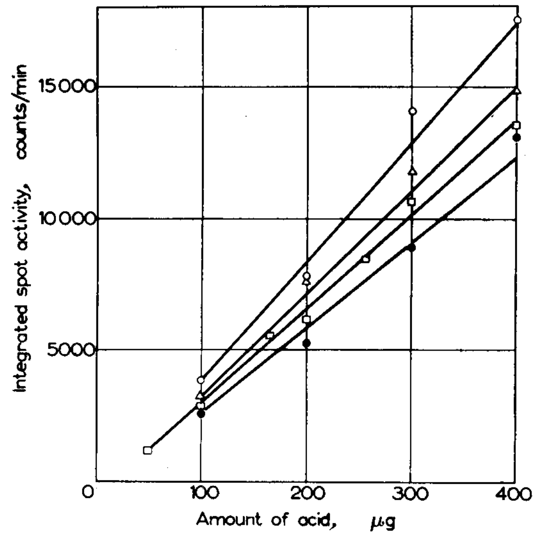

FIG. 1. Relationship between integrated spot activity and spot content for saturated fatty acids after decomposition of the silver soaps with $^{131}I^-$; ○ lauric acid, △ myristic acid, □ palmitic acid, ● stearic acid.

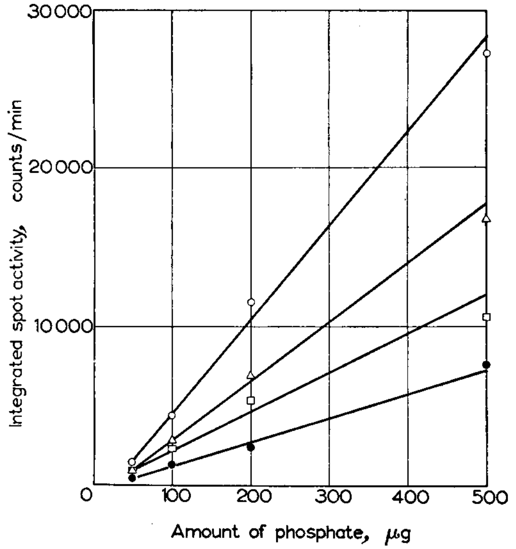

FIG. 2. Relationship between integrated spot activity and spot content for phosphates after decomposition of the silver salts with $^{131}I^-$; ○ $Na_2HPO_4$, △ $K_4P_2O_6$, □ $K_4P_2O_7$ ● $Na_3(PO_3)_3$.

the relationships between maximal spot activity and spot content as shown in Figs. 4–6, was less than 8·5% for all the substances examined. This error is also satisfactory for quantitative chromatographic analysis. Where the components of a mixture are well separated on a chromatogram it will be better to use the relationship between integrated spot activity and spot content for quantitation, but if peaks are crowded together and overlap it may sometimes be difficult to evaluate the peak

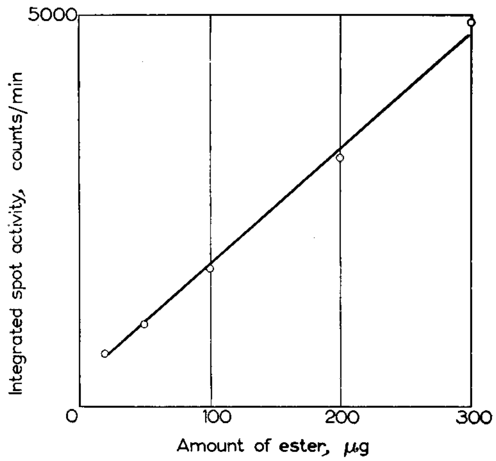

Fig. 3. Relationship between integrated spot activity and spot content for glucose-1-phosphate after decomposition of the silver salt with $^{131}I^-$.

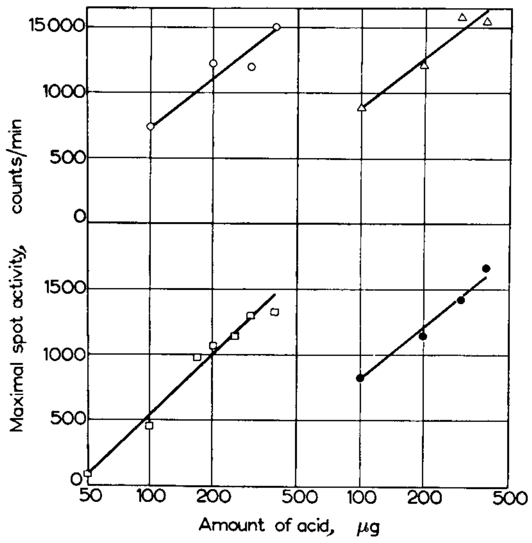

Fig. 4. Relationship between maximal spot activity and logarithm of spot content for saturated fatty acids after decomposition of the silver soaps with $^{131}I^-$; ○ lauric acid, △ myristic acid, ⊡ palmitic acid, ● stearic acid.

area, and in this case the relationship between maximal spot height and spot content can be very useful.

In all cases examined, except palmitic and stearic acids, no satisfactory linear or logarithmic relationship was found between spot content and radiometrically defined spot length, contrary to the situation found previously[4] with chromatograms of unsaturated fatty acids iodinated with $^{131}I$.

For purposes of quantitative estimation it is necessary to set up calibration curves based on chromatograms of known amounts of pure substances alongside the chromatogram of the mixture being analysed, to allow for given chromatographic conditions.

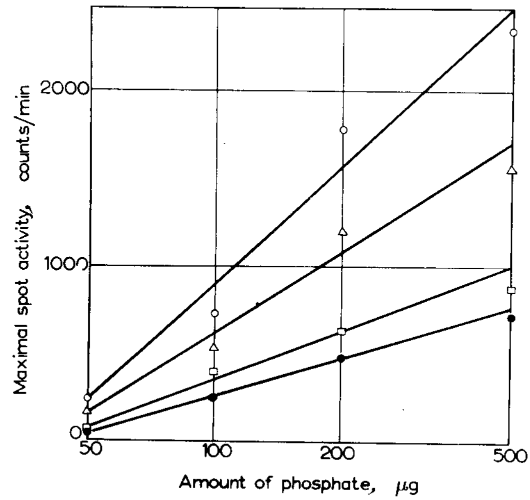

FIG. 5. Relationship between maximal spot activity and logarithm of spot content for phosphates after decomposition of the silver salts with $^{131}I^-$; ○ $Na_2HPO_4$, △ $K_4P_2O_6$, □ $K_4P_2O_7$, ● $Na_3(PO_3)_3$.

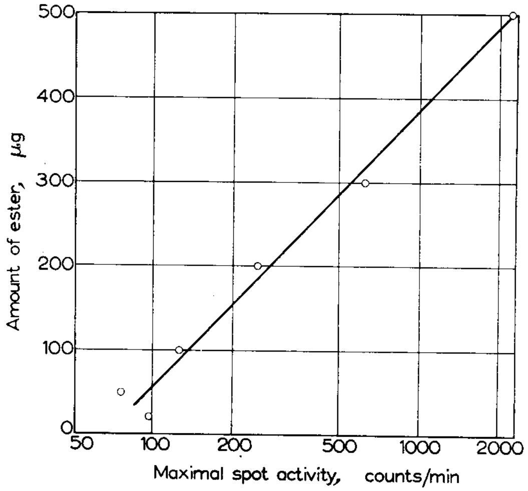

FIG. 6. Relationship between spot content and logarithm of maximal spot activity for glucose-1-phosphate after decomposition of the silver salt with $^{131}I^-$.

From the above results together with previous results[1] it can be seen that integrated spot activity is proportional to spot content after decomposition of silver salts with $^{131}I^-$ for fatty acids, phosphates and a phosphate ester. The maintenance of such a relationship for different substances suggests that in all examples studied, the silver salts are quantitatively formed on the chromatograms, and quantitatively decomposed by the $^{131}I^-$, without significant losses from the paper during washing.

In the case of the saturated fatty acids and phosphates, the linear relationship between maximum spot activity and logarithm of spot content previously found[4] for unsaturated fatty acids iodinated with $^{131}I$, is satisfactorily maintained. This suggests that such a logarithmic relationship between maximum thickness of spot and spot content may be widely applicable in paper chromatography, although the occurrence of an inverse relationship for glucose-1-phosphate shows that the phenomenon is not entirely general.

Failure to find a satisfactory linear relationship between radiometrically defined spot length and spot content for the substances here examined, indicates that the maintenance of such a relationship for unsaturated acids iodinated with $^{131}$I as previously reported[4] is probably of limited significance.

The present work shows that double decomposition radio-chromatography with Ag$^{131}$I can be used for estimation of chemically different substances capable of forming insoluble salts with silver on the chromatogram.

**Zusammenfassung**—Es wird eine Methode "Doppel-Zersetzung-Radiochromatographie" genant zur radiometrischen Bestimmung von gesättigen Fettsäuren, anorganischen Phosphaten und Glykose-1-phosphaten auf Papier-chromatogrammen durch Bildung von unlöslichen Silber-salze auf dem Papier, und dann Zersetzung des Salzes mittels radioaktiven Iodid und Radiometrie der Ag$^{131}$I-Restes entwickelt. Die maximale Aktivität ist mit dem Logarithmus des Flecken-Gehaltes fur Fettsäuren Phosphaten, aber micht für Glykose-1-phosphat, proportional.

**Résumé**—On décrit une méthode que l'on propose d'appeler double décomposition radiochromatographique et qui consiste en l'analyse radiométrique d'acides gras saturés, de phosphates minéraux et de phosphate de glucosyl à partir des chromatogrammes sur papier: le sel d'argent insoluble est formé sur la bande de papier puis décomposé par l'iodure 131, on mesure alors la radioactivité de IAg déposé. L'activité totale des taches est une fonction linéaire de la composition de la tache. Le maximum (pic) d'activité de la tache est proportionnel au logarithme de la composition de la tache pour les acides gras et les phosphates mais non pour le phosphate de glucosyl.

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# TITRIMETRIC DETERMINATION OF MANGANESE FOLLOWING NITRIC ACID OXIDATION IN THE PRESENCE OF PYROPHOSPHATE

C. OLIVER INGAMELLS
Rock Analysis Laboratory, University of Minnesota, Minneapolis, Minn., U.S.A.

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**Summary**—A new method for the determination of manganese is presented in which the element is oxidized to the tervalent state in strong phosphoric acid-pyrophosphate solution by means of nitric acid, and is then titrated with ferrous solution, using diphenylamine or diphenylamine sulphonate as an indicator. The method is applicable with little modification to a wide variety of materials, including steels, ores, and silicate minerals.

PRESENTLY available methods for the determination of manganese are in general fairly satisfactory. For small amounts, colorimetry or photometry based on the colour of the $MnO_4^-$ ion in solution is the usual technique, and for large amounts the bismuthate method and the newer pyrophosphate method of Lingane and Karplus[2] are widely applied. The chief disadvantages of the bismuthate method are procedural; close attention to detail is necessary for good results, and because of the valence change a large amount of standard reducing substance must be used. In the method of Lingane and Karplus, the end-point is determined electrometrically, and there is no possibility of repeating the titration on the same solution.

The method proposed here is believed to be a decided improvement over any existing for the determination of moderate amounts of manganese. It utilizes the same valence change (II–III) as the Lingane and Karplus method, but in reverse, the manganese being quantitatively oxidized to the tervalent state, and then reduced with standard ferrous solution, diphenylamine or diphenylamine sulphonate being used as the indicator. In most instances no preliminary separations are necessary. The sample may be dissolved in any suitable acid and treated directly by the procedure to be described.

In strong phosphoric acid solution, $Mn^{II}$ is oxidized to $Mn^{III}$ by nitric or perchloric acids on heating, and by chromic acid in the cold, giving a coloured solution which resembles permanganate, but which is much less intense for the same amount of manganese. It is possible to make a photometric determination, utilizing the $Mn^{III}$ colour, simply by adding to the $Mn^{II}$ solution 3–4 times its volume of 85% phosphoric acid and an excess of dichromate. After allowing the solution to stand at room temperature for a few minutes to be sure that the oxidation is complete, the resulting colour is read photometrically. The excess chromate and the $Cr^{III}$ formed in the reaction do not interfere, despite their intense colour, provided that the same amount of chromic acid is added to standards and unknowns. Perchloric, sulphuric, and nitric acids have no effect, but hydrochloric acid interferes. The spectrophotometry of $Mn^{III}$ in phosphate solution has been studied by Tomula and Aho[4] and by Purdy and Hume,[3] who used bromate as the oxidant.

For the titrimetric determination, the oxidation of the manganese is best done with nitric acid, although perchloric or chromic acids may be used if the solution is heated sufficiently to decompose the chromate (either added or originating in the sample). In phosphoric acid solution chromate decomposes rapidly above 250°, and this temperature is easily attained on an electric hot plate. Photometry may also follow nitric acid oxidation of the manganese if convenient, but the titration is so simple and precise over such a wide range of manganese concentrations that it is preferred. So far as the writer has been able to determine, vanadium is the only interfering element, and it is quantitatively oxidized by nitric acid and reduced to $V^{IV}$ by ferrous iron, so that it may be determined separately and a correction applied. It is possible that a potentiometric titration would permit the simultaneous determination of both elements.

## EXPERIMENTAL

### *Reagents*

*Standard ferrous ammonium sulphate*: 0.1 or 0.02*N* in 5% (v/v) sulphuric acid, preferably prepared fresh, with water which has been boiled to remove dissolved oxygen.

*Diphenylamine*: 0.2% aqueous solution of barium diphenylamine sulphonate, or a 1% solution of diphenylamine in concentrated sulphuric acid.

1 : 1 *nitric acid*: boiled to remove lower nitrogen oxides.

### *Procedure*

To the $Mn^{II}$ solution in a wide-mouth conical flask, which should preferably contain nitric acid as the only acid, and which should not have too large a volume, add 10 ml of 85% phosphoric acid plus an additional 15 ml for every 40 mg of MnO expected. Add 5 ml of nitric acid and evaporate on the hot plate, controlling the temperature so that evaporation takes place without boiling. Boiling phosphoric acid solutions is not recommended because of their extreme tendency to spatter. When the volume has been reduced to approximately that of the phosphoric acid used, add 5–6 g of sodium pyrophosphate for every 20 ml of phosphoric acid, and continue heating until the nitric acid is substantially all expelled, as indicated by the lack of condensation on the walls of the flask. Temperature is not a critical factor; the solution temperature will reach about 145° if the plate temperature is such that evaporation proceeds without boiling. Finally add 1 ml of 1 : 1 nitric acid (free from lower oxides of nitrogen) and continue heating for 10–15 minutes, during which time the nitric acid will reflux on the walls of the flask. Complete removal of nitric acid is undesirable.

Remove from the heat (before all the nitric acid is gone), cool until the flask can be handled, and add ¼ the volume of *cold* water. Mix and cool in running water. A larger addition of water at this stage may lead to slightly low results, particularly if the manganese concentration is near the maximum of approximately 2 mg of MnO per ml of phosphoric acid. The solution should not be allowed to cool completely before making the small addition of water, because it may become glassy and hard to dilute, When cold, dilute to about 20% in $H_3PO_4$, cool in running water, and titrate with standard ferrous solution, adding diphenylamine or diphenylamine sulphonate just before the end-point. It is best to delay the indicator addition until the pink colour of tervalent manganese is nearly discharged. The end point is extremely sharp, even with the 0.02*N* ferrous solution.

If a check on the titration is desired, add nitric acid and evaporate as before, and repeat the procedure.

Results obtained by the method on pure manganese solutions are given in Table I. For these titrations, a 0.1*N* ferrous solution in a 10-ml buret graduated to 0.02 ml was employed, and in each case 15 ml of 85% phosphoric acid was used. The ferrous solution was standardized against standard dichromate solution. The results indicate that with more than about 40 mg of MnO in this volume of phosphoric acid, it is difficult to oxidize the manganese completely. A safe limiting concentration is 2 mg of MnO per ml of phosphoric acid.

Many silicates may be decomposed by heating on the hot plate with phosphoric acid and sodium pyrophosphate, and this fact has been used to advantage in the determination of manganese in biotite, garnet, and other minerals. Chromite is decomposed only very slowly by the mixture, but dissolves reasonably quickly in perchloric acid.

The new method has been used successfully with little modification for the determination of manganese in tungsten steel, ferromanganese,[1] manganese minerals, and silicates. Some comparative results for various materials are given in Table II. In all cases, the ferrous solution was standardized against standard dichromate solution.

TABLE I. DETERMINATION OF MANGANESE IN PURE SOLUTIONS

| MnO taken, *mg* | MnO found, *mg* |
|---|---|
| 0.20 | 0.17 |
| 0.40 | 0.39 |
| 1.00 | 0.97 |
| 2.00 | 2.00 |
| 10.00 | 9.95 |
| 20.00 | 19.99 |
| 40.00 | 39.90 |
| 53.9 | 52.9 |

TABLE II. COMPARATIVE RESULTS

| Sample | MnO present | MnO found |
|---|---|---|
| Garnet* | 4.57 (gravimetric) | 4.56 |
| Garnet* | 10.70 (gravimetric) | 10.71 |
| Garnet* | 14.56 (gravimetric) | 14.55 |
| Garnet* | 8.70 (gravimetric) | 8.71 |
| Phosphate mineral* | 6.35 (gravimetric) | 6.27<br>6.30 |
| Biotite* | .89 (colorimetric) | .91 |
| Bauxite*† (U. S. Bureau of Standards Sample No. 69) | .55 | .54 |
| Nickel-chromium steel‡ (U. S. Bureau of Standards Sample No. 32c) | .752§ | .75§ |
| Iron ore** (U. S. Bureau of Standards Sample No. 28a) | .435§ | .45§ |
| Manganese ore** (Bureau of Standards Sample No. 25b) | 58.35§ | 58.54§ |

* Sample dissolved directly in phosphoric acid-sodium pyrophosphate on the hot plate.
† A large amount of material remained undissolved; result uncorrected for 0.03 $V_2O_3$.
‡ Sample dissolved in dilute nitric acid before adding phosphoric acid.
§ Reported as per cent Mn.
** Hydrochloric acid used to aid in solution of the sample.

## DISCUSSION

Omission of the sodium pyrophosphate addition makes very little difference in the results, particularly if manganese is low. However, when the MnO concentration approaches the limit of approximately 2 mg per ml of phosphoric acid, complete oxidation is more certain in the presence of added pyrophosphate. When silicates are to be decomposed directly, the sodium pyrophosphate prevents the precipitation of silicic acid and greatly facilitates solution.

The addition of 1 ml of 1:1 nitric acid in the final stages of the procedure may be omitted when less than about 5 mg of MnO is in question, With larger amounts, oxidation is not quite complete unless this step is included. If the titrant is standardized against a similar material carried through the procedure, the extra addition could in many cases be omitted in routine analysis, with little effect on accuracy.

TABLE III. RESULTS FROM REPEATED TITRATIONS

| Mineral | MnO found in first titration, *mg* | MnO found in second titration, *mg* | MnO present, *mg* |
|---|---|---|---|
| Tremolite | 1.82 | 1.82 | |
| Amphibole | 13.83 | 13.94 | 13.88* |
| Rhodonite | 44.96 | 45.18 | 45.15* |

* Determined by the pyrophosphate method of Lingane and Karplus.[8]

With 4.0, 10.0, and 20.0 mg of MnO, 3.92, 9.97, and 18.68 mg were found when the final addition of nitric acid was omitted. In another experiment, in which the oxidation of the manganese was done with perchloric acid, with the same amounts of added manganese, 3.98, 9.91, and 19.4 mg were found. Care must be taken that the nitric acid is free from lower oxides, for they either reduce $Mn^{III}$, or are incompletely removed during the 10–15 minute heating period.

The silicate minerals which were dissolved directly in the phosphoric acid–sodium pyrophosphate mixture were ground to pass a 115-mesh screen. One to two hours heating, during which the temperature of the mixture approached 200°, sufficed for the garnets; biotite required only about 15 minutes. Iron ore and manganese ore required the preliminary use of hydrochloric acid. Hydrochloric acid should be removed (by repeated evaporation with nitric acid, or by fuming with perchloric acid) before adding the phosphoric acid. Steels should be dissolved, when possible, in dilute nitric acid before adding the phosphoric acid; however other solution procedures are sometimes necessary—for instance tungsten steels are best treated with mixed phosphoric and perchloric acids directly.

Chloride or perchlorate in the presence of nitrate can lead to erroneous results.

When large amounts of chromium are present, and particularly if perchloric acid is used as the oxidant, sulphate should be absent, for on occasion an insoluble precipitate separates (presumably $Cr_2(SO_4)_3$). Results are always low when this happens, probably because the precipitate carries down manganese.

The ferrous ammonium sulphate solution used in the titration may be standardized by any of the usual methods, but it is best to prepare a standard solution from manganese metal of known purity. Aliquot parts of this solution may then be run through the procedure at the same time as the unknowns.

When silicate minerals are dissolved directly in the phosphoric acid-sodium pyrophosphate mixture, there is some difficulty in determining whether or not attack is complete. In such cases, it is always advisable to evaporate the solution after titration, add more acid, and repeat the procedure. To illustrate this point the figures resulting from three determinations are given in Table III.

*Acknowledgment*—The author wishes to acknowledge the advice and assistance of S. S. Goldich in this work. Thanks are also due to E. B. Sandell and R. B. Ellestad for reading and commentary on the manuscript. The investigation was made possible by a grant from the Geological Society of America to the Rock Analysis Laboratory in support of research in methods of silicate analysis.

**Zusammenfassung**—Eien neue Methode zur Bestimmung von Mangan wird angegeben. Das Element wird in konzentrierter Phosphorsäure-pyrophosphat Lösung zu drei-wertigem Zustand mittels Saltpetersäure oxydiert, und wird dann mittels Eisen (II)-Lösung mit Diphenylamin-sulphonat als Indikator titriert. Die Methode ist durch geringe Modifikation auf eine grosse Mannigfaltigkeit von Materialien anwendbar, u.a. Stahlen, Erze und Silikat-Materialien.

**Résumé**—Une nouvelle méthode pour la détermination du manganèse est proposée. Dans cette méthode l'élément est oxydé au degré d'oxydation III dans une solution concontrée d'acide phosphorique et de pyrophosphate au moyen d'acide nitrique et est alors titré par une solution ferreuse utilisant de la diphénylamine ou de la diphénylamine sulfonée comme indicateur. La méthode peut être étendue avec peu de modification à une grande variété de substances, comprenant les aciers, les alliages et les silicates.

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# THE SPECTROPHOTOMETRIC DETERMINATION OF CERIUM IN FLUORIDE SALTS

J. C. WHITE and R. F. APPLE
Analytical Chemistry Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee

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**Summary**—Cerium$^{III}$ in fluoride salt mixtures can be determined by measurement of its ultraviolet absorption peak at 253 m$\mu$ in 3*M* HCl. Over the range of 0 to 0.4 mg of Ce per millilitre, Beer's law is obeyed. The interfering ions, Fe$^{III}$, Cr$^{VI}$, and U$^{VI}$, are removed by extraction from a 7*M* HCl solution into a *cyclo*-hexane solution of tri-*n*-octylphosphine oxide. The method is rapid and precise and avoids difficulties which are encountered because of the instability of solutions which contain Ce$^{IV}$.

THE solubility of cerous fluoride in mixtures of fluoride salts such as $NaF–ZrF_4–UF_4$ (50–46–4 mole per cent) has been investigated by Ward, Strehlow, Grimes and Watson[11] who used $^{141}CeF_3$ as a tracer. In order to confirm their analytical data, chemical methods for the determination of cerium in fluoride salts were also investigated. The venerable oxalate precipitation method is not particularly applicable in this case, although, with sufficient care, reproducible and reliable numbers can be obtained. The titrimetric oxidation-reduction procedure is time-consuming and also requires considerable careful technique. For these reasons spectrophotometric methods were also considered. These are based either on the absorbance of a cerium$^{IV}$ perhydroxide complex in basic solution[3,7,8,10] or the absorbance of cerium$^{IV}$ in acidic media.[4,6] Neither of these absorbance measurements is entirely satisfactory because of turbidity problems encountered in basic solutions with cerium$^{IV}$ and the instability of dilute cerium$^{IV}$ solutions in acidic solutions.

Greenhaus, Feibush and Gordon[5] exploited the ultraviolet spectrum of cerium$^{III}$ in sulphuric acid solution to determine cerium. Their method depends on the absorbance of cerium$^{III}$ in 0.5*M* sulphuric acid at 253.6 m$\mu$. Both zirconium and uranium interfere strongly with their method. In this report, suitable modifications are described by which the ultraviolet spectrophotometric technique can be successfully applied to the determination of Ce in $NaF–ZrF_4–UF_4$ and other fluoride salt mixtures.

## REAGENTS AND APPARATUS

A concentrated stock solution of cerium$^{III}$ was prepared by dissolving 2.342 g of spectrographically pure cerous oxide (Research Chemicals, Inc., Burbank, California) in 25 ml of water to which 15 ml of concentrated hydrochloric acid and 10 ml of concentrated sulphuric acid were added. The solution was heated to heavy fumes of sulphur trioxide prior to dilution to volume with water.

Tri-*n*-octylphosphine oxide (TOPO) (Distillation Products Industries): A 0.05*M* solution was prepared by dissolving 3 g of reagent in 200 ml of *cyclo*hexane.

A Cary Model 14 recording spectrophotometer was used to obtain the spectra reported here. Matched fused 1-cm silica cells were used.

## RESULTS

### *Application to chloride solutions*

In his investigation Greenhaus discovered that chloride ion could be present in high concentrations without effect upon the absorbance of cerium$^{III}$ in 0.5$M$ sulphuric acid. Stewart and Kato[9] have also recently published the ultraviolet spectra of rare-earth chlorides in hydrochloric acid solution. As shown in Fig. 1, the ultraviolet spectra of cerium$^{III}$ in both sulphuric and hydrochloric acids are essentially identical. There are three absorption peaks, the maximum occurring at 253 m$\mu$. At this wavelength, an absorbance index of 755 was reported by Stewart and Kato. The value found in this laboratory, 775, is in quite good agreement. Using Greenhaus' data the value for cerium$^{III}$ in sulphuric acid is 694. The adherence to Beer's law at 253 m$\mu$ is excellent; the straight line function of absorbance to concentration extends to 0.4 mg per ml at an absorbance of two. This relationship is shown in Fig. 2.

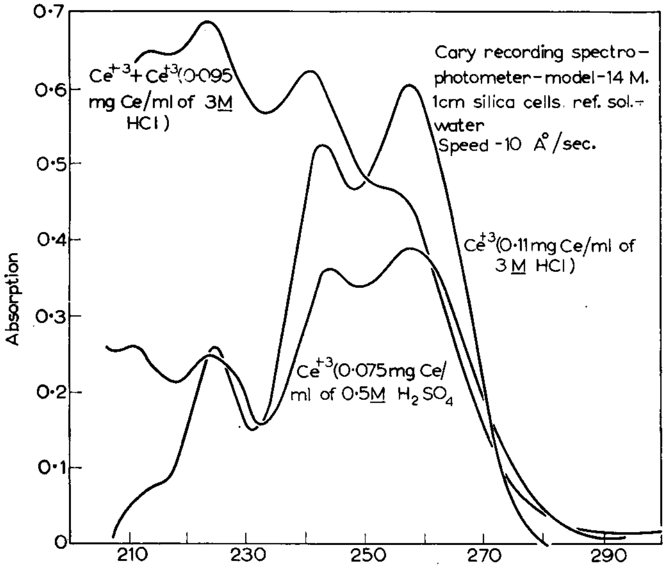

FIG. 1.

On the basis of these data, the ultraviolet absorbance technique is obviously applicable to chloride systems as well as sulphate solutions.

### *Effect of hydrochloric acid concentration*

Tests were conducted to determine the optimum acid concentration of the cerium$^{III}$ solution. Aliquots of the stock solution were diluted with hydrochloric acid of various concentrations from 0.1 to seven molar. The absorbance spectra of these solutions were recorded immediately thereafter. In each case the reference solution was water.

The spectra are identical, indicating that no appreciable formation of any cerium$^{III}$ chloride complexes occur under these conditions in solutions less concentrated than 7$M$ in HCl and that the cerium$^{III}$ ion is the light-absorbing species. Jorgensen[1] had reported some evidence for the formation of a cerium$^{III}$-chloride complex in solutions exceeding 5*M* HCl. This formation is not supported by the spectrophotometric data obtained in this investigation. In fact no change in absorbance spectra of cerium$^{\mathrm{III}}$ in 7*M* HCl was observed after 48 hours standing.

The absorbance of cerium$^{\mathrm{III}}$ is independent of acid concentration through 7*M* HCl. This independence from acid concentration is an important advantage in any spectrophotometric method because of the wide latitude that is available in establishing conditions for a working procedure.

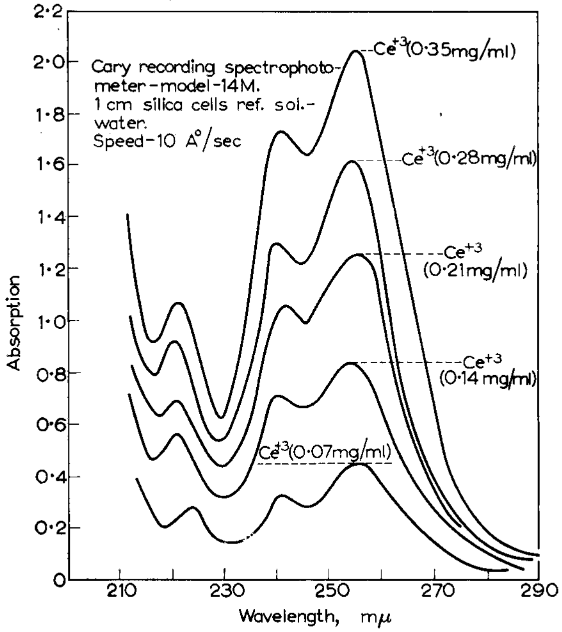

FIG. 2.

*Effect of oxidation state of cerium*

The presence of even trace amounts of cerium$^{\mathrm{IV}}$ in cerium$^{\mathrm{III}}$ could result in gross errors because the intensely yellow-coloured cerium$^{\mathrm{IV}}$ ion absorbs so strongly in the ultraviolet that it completely obliterates the absorbance peaks of cerium$^{\mathrm{III}}$ (see Fig. 3). Greenhaus found that in 0.5*M* $H_2SO_4$, as little as 1 μg per ml of cerium$^{\mathrm{IV}}$ caused an error of 3% in the determination of the cerium$^{\mathrm{III}}$ concentration.

In hydrochloric acid, however, the interference of cerium$^{\mathrm{IV}}$ is eliminated because of the oxidation-reduction reaction

$$\mathrm{Ce^{4+} + HCl \rightarrow Ce^{3+} + \tfrac{1}{2}Cl_2 + H^+}. \tag{1}$$

Hydrochloric acid in high concentrations drives this reaction to the right, as written, so that the concentration of cerium$^{\mathrm{IV}}$ in strong acid at equilibrium is indeed quite small. The reaction is quite dependent, however, on the concentration of HCl. This dependence is shown strikingly in Fig. 3. In 1*M* HCl, little reduction of cerium$^{\mathrm{IV}}$ occurs; the solution absorbs ultraviolet light so strongly that the cerium$^{\mathrm{III}}$ absorbance peak at 253 mμ is unobservable. The influence of HCl begins to become evident at 3*M* HCl, some cerium$^{\mathrm{III}}$ obviously being present. At 7*M* HCl the reduction is quantitative; the absorbance at 253 mμ is equivalent to that of pure cerium$^{III}$, which had been treated with hydroxylamine hydrochloride to insure complete reduction of any cerium$^{IV}$ to the tervalent state.

From the standpoint of effect of the oxidation state, strong hydrochloric acid media, therefore, have obvious advantages over sulphuric acid with respect to the interference of cerium$^{IV}$.

### *Effect of diverse elements*

Although the main interference, cerium$^{IV}$, is effectively eliminated through the use of strong hydrochloric acid media, knowledge of the effect of zirconium, uranium, beryllium and thorium on the ultraviolet spectrophotometric determination of cerium was required before the method could be applied to molten salt reactor fuels.

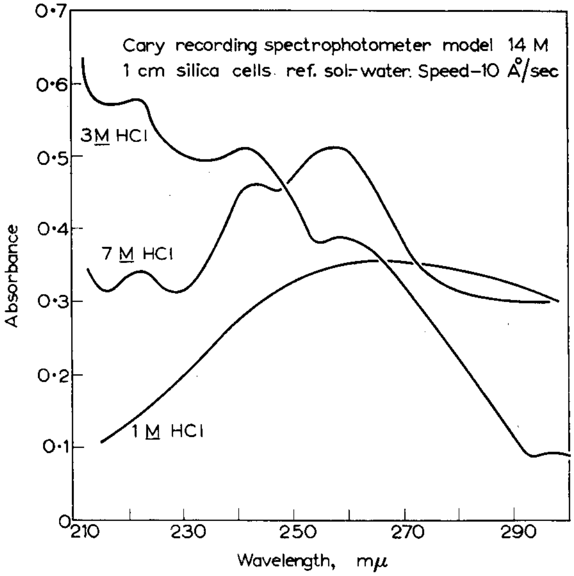

FIG. 3. Ce, 1 mg per ml.

Elements which are known to interfere with the ultraviolet spectrophotometric determination of cerium$^{III}$ are limited to those that have appreciable absorbance in the ultraviolet region.[2] Foremost of these are iron$^{III}$, titanium$^{IV}$, copper$^{II}$,uranium$^{VI}$, molybdenum$^{VI}$, zirconium$^{IV}$, hafnium$^{IV}$, and thorium$^{IV}$. Of the common anions, only nitrate presents much difficulty. Large amounts of either phosphate or perchlorate can be tolerated as long as no precipitation occurs.

In the application of this method to the analysis of fluoride salts and mixtures thereof, some of these interferences are eliminated by the procedure used for dissolving the fluoride salts. The fluoride salt is heated to strong fumes of sulphur trioxide, which removes fluoride and nitrate, if present, and converts the fluoride salt to the sulphate salt.

Copper and molybdenum do not commonly occur in these mixtures, and, if so, only in small concentration. They can be separated more or less completely from cerium by precipitation of the cerium with ammonia. In this precipitation zirconium, uranium, thorium and beryllium, which are major components of these solutions, also precipitate as insoluble hydrous oxides. Although this step ensures the completeness of the precipitation of cerium, copious amounts of elements that are known to interfere with this method must thus be removed in some manner.

White and Ross[12] in their studies of the extraction characteristics of tri-*n*-octylphosphine oxide (TOPO) have shown that this reagent is extremely effective in the extraction of zirconium, thorium, uranium, titanium, and iron from strong hydrochloric acid solution. They reported that cerium$^{III}$ did not extract under these acidic conditions. Since 7*M* HCl is the preferred medium for reducing any cerium$^{IV}$ that might be present, the separation of these metals from cerium by extraction with TOPO was tried.

Two weight ratios of interference to cerium were tested, the first, approximately 4 : 1 and the second, 10 : 1. The latter ratio is about the greatest difference in concentration that would ever likely be encountered in these fluoride salt mixtures. About 3 mg of cerium was used in each test and the 7*M* HCl solution was extracted with 10 ml of 0.2*M* tri-*n*-octylphosphine oxide in *cyclo*hexane.

Uranium, molybdenum, thorium, zirconium, beryllium, iron, and titanium did not interfere at either concentration level tested. This attests the efficiency of the extraction, since as little as 0.5 μg Fe per ml or 4 μg U per ml will increase the cerium result by 3%. As previously mentioned, copper and molybdenum are at least partially removed by the basic hydroxide precipitation. About 1 μg of either of these elements per ml will also produce a three per cent error in the cerium value.

TABLE I. EFFECT OF DIVERSE ELEMENTS ON THE METHOD AFTER EXTRACTION WITH TOPO

| Element | Weight ratio $\left(\frac{\text{element}}{\text{cerium}}\right)$ | Error, % |
|---|---|---|
| $Fe^{+3}$ | 10 | <1 |
| $Ti^{+4}$ | 10 | <1 |
| $Cu^{+2}$ | 10 | <1 |
| $UO_2^{+2}$ | 10 | <1 |
| $Mo^{+6}$ | 10 | <1 |
| $Zr^{+4}$ | 10 | <1 |
| $Cr^{+6}$ | 4 | +4 |
| $Cr^{+6}$ | 10 | +25 |

The only interference not eliminated by this extraction is chromium. Although hexavalent chromium is extracted by TOPO from hydrochloric acid solutions, in 7*M* HCl, hexavalent chromium is reduced to trivalent chromium, at which oxidation state chromium is not extracted. When present in a concentration three times that of cerium, chromium produces a 4% error. At the 10 : 1 level, the error is about 25%. Fortunately, chromium occurs in these fluoride salts as a corrosion product and rarely exceeds 1000 ppm. Chromium, therefore does not present too difficult a problem in this particular application. The effects of the diverse elements are summarized in Table 1.

### *Precision of the method*

The precision of the method was determined at three concentration levels of cerium, approximately 0.4 mg, 1, and 3 mg Ce. In all tests the zirconium and uranium concentrations were equivalent to those normally encountered, that is 10 to 30 times that of cerium. The overall coefficient of variation is 1%. There is no indication of a bias on the basis of these data.

TABLE II. PRECISION AND ACCURACY OF THE METHOD

| Cerium, *mg*, present | 0.336 | 1.13 | 3.00 |
|---|---|---|---|
| Number of determinations, N | 4 | 4 | 4 |
| Average, $\bar{x}$ | 0.336 | 1.14 | 3.01 |
| Coefficient of variation, % | 0.92 | 1.0 | 1.4 |

*Comparison with radio-tracer method*

Typical results for cerium as analyzed by the ultraviolet spectrophotometric method and the radio-tracer technique(11) are illustrated in Table III. The results are in excellent agreement over a wide range of cerium concentrations. The average difference is less than 2%.

TABLE III. TYPICAL RESULTS FOR THE COMPARISON OF THE SPECTROPHOTOMETRIC METHOD TO THE RADIO-TRACER DETERMINATION OF CERIUM

| Cerium, % | | Difference A - B |
|---|---|---|
| Spectrophotometric A | Radio-tracer B | |
| 0.40 | 0.37 | +0.03 |
| .64 | .59 | +0.05 |
| .88 | .83 | +0.05 |
| 1.15 | 1.14 | +0.01 |
| 1.91 | 1.97 | −0.06 |
| 2.27 | 2.35 | −0.08 |
| 2.41 | 2.34 | +0.07 |
| 3.88 | 3.78 | +0.10 |
| 7.62 | 7.53 | +0.09 |
| 8.00 | 8.16 | −0.16 |
| 8.67 | 8.72 | −0.05 |
| 8.90 | 8.88 | +0.02 |

| | |
|---|---|
| Average | 0.064 |
| Coefficient of variation, % | 4.08 |
| Overall agreement | 2% |

## RECOMMENDED PROCEDURE

Weigh a 2- to 5-g sample of fluoride salt to the nearest 10 mg and transfer to a platinum dish. Add about 1 g of boric acid and mix the solids. To the ultimate mixture add 5 ml of concentrated nitric acid, 20 ml of concentrated hydrochloric acid and 25 ml of concentrated sulphuric acid. Heat to strong fumes of sulphur trioxide and then dilute to 500 ml with water.

Transfer an aliquot, no larger than 10 ml, which contains preferably 0.5 to 5.0 mg of cerium, to a 15-ml centrifuge tube. Add concentrated ammonium hydroxide dropwise until the cerium is precipitated; then add about 2 ml excess and cool. Centrifuge the samples for two minutes. Decant the supernatant liquid and dissolve the precipitate in 10 ml of 7*M* hydrochloric acid. Transfer the solution to a 25-ml volumetric flask; then dilute to volume with 7*M* HCl. Transfer the solution to a 60-ml separatory funnel and add 5 ml of 0.05*M* TOPO in *cyclo*hexane; then shake the sample for two minutes. Allow the phases to separate and collect the aqueous phase in a 25-ml volumetric flask. Measure the absorbance at 253 mμ against water.

**Zusammenfassung**—Man kann Cer(III) in Fluorid-Salz-Mischungen durch Messung bei 253 mμ in 3*M* Salzsäure bestimmen. Im Bereich 0 bis 0,4 Milligrammen von Cer pro millilitre folgt die Lösung das Beer'schen Gesetz. Die störende Ionen, Fe(III), Cr(VI), und U(VI) werden durch Extraktion aus einer 7*M* Salzsäure Lösung in eine Cyclohexan-Lösung von Tri-*n*-octylphosphinoxyd entfernt. Die Methode ist rasch und präzis.

**Résumé**—On peut utiliser l'absorption maximale à 253 mμ en 3*M* HCl pour le dosage de Ce(III) en présence de fluorure. La loi de Beer est suivie quand la concentration de Ce est de 0 à 0,4 mg/ml. Les ions Fe(III), Cr(VI) et U(VI), qui gênent, sont extraits à l'aide de l'oxyde de tri-*n*-octylphosphine en milieu cyclohexane. Cette méthode, qui est rapide et précise, évite les difficultés produites par l'instabilité de solutions de Ce(IV).

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# SHORT COMMUNICATIONS

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## Ferrous iron-sulphuric acid reagent for the determination of pure œstrogens*

(*Received* 26 *August* 1958)

THE work of Wieland *et al.*[8] in 1929 established the fact that œstrone produces a green-gold colour with a blue-green fluorescence when treated with concentrated sulphuric acid. In 1930, Marrian,[7] described an orange colour with green fluorescence when œstriol was heated with concentrated sulphuric acid. In an investigation of these effects, Kober[6] in 1931 described a procedure for œstrogenic steroids which procedure now bears his name and covers a multitude of modifications and adaptations of the original method. In 1952, Brown[2] in a comprehensive study of the Kober reaction, found that reducing agents tended to induce a more intense colour reaction when used in the Kober test. Ferrous sulphate was reported as exerting the most pronounced effect.

Although the mechanism of the Kober reaction remains obscure and many reported conditions involving the colour reaction are seemingly contradictory, several salient facts reported in the recent literature concerning this process are of interest. Brown,[2] in his investigation of the Kober reaction, reported that the presence of a reducing agent in the first stage of the two stage process is necessary for full colour development. He also points out that the oxidizing agents such as ferric sulphate and hydrogen peroxide accelerate the red colour formation in the second stage but cause subsequent fading. Brown concludes that "... the reducing agents and their oxidized forms may poise" the reaction conditions so that the red colour can form by oxidation without simultaneous destruction by further oxidation.

The work reported by Haenni[5] would seem to lend credence to such a view even though reaction conditions were far different. Using ferric iron and phenol in sulphuric acid a stable and sensitive reaction resulted. The inference is again that a controlled oxidation took place.

The Kober colour can be formed through the mediation of other reactions. In a *p*-toluenesulphonic acid spot test[3] reported recently by the present authors, œstrogens when fused with the acid salt developed a red or orange colour with intense fluorescence. This coloured material when dissolved in concentrated phosphoric acid showed an absorption peak at 515 mμ (Coleman Universal). A similar reaction with methylenedisalicylic acid was reported by Feigl.[4] Further, one of the present authors has observed that œstrogen exposed to an atmosphere of sulphur trioxide (made by heating concentrated sulphuric acid in a closed vessel) develops a red colour. On the other hand, Axelrod[1] used fuming sulphuric acid with various steroids but did not report a colour absorbing in the vicinity of 510 mμ with œstrogens.

In all the aforementioned papers the procedure was carried out in two stages. In this study a ferrous ammonium sulphate-sulphuric acid reagent is used in a one-step procedure to estimate quantitatively œstradiol, œstrone and œstriol.

### APPARATUS AND REAGENTS

Chemicals were of reagent grade and all solutions were prepared in distilled water. The sulphuric acid used was the nine-pound per bottle variety.

*Ferrous ammonium sulphate, hexahydrate.*

*Œstrone:* purified crystals, m.p. 252–253°.

*Œstradiol* (œstradiol-17 β) purified crystals, m.p. 173–174°.

*Œstriol,* purified crystals, m.p. 272–273.5°. Œstrogens supplied by courtesy of Schering Corp.

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* Supported by Research Grant A–121–C from the Division of Research Grants and Fellowships of the National Institutes of Health.

*Sulphuric acid,* 52% (by volume).

*Sulphuric acid,* 70% (by volume).

*Œstradiol-œstrone acid reagent:* 290 mg of ferrous ammonium sulphate are mixed with 52% sulphuric acid (ferrous-acid reagent) to make 100 ml total volume. It remains stable for approximately three days if protected from air.

*Œstriol acid reagent:* 290 mg of ferrous ammonium sulphate are dissolved in 7.5 ml of distilled water and 70% sulphuric acid is added to make 100 ml total solution of 65% sulphuric acid at room temperature.

## COLOUR DEVELOPMENT

### *Œstrone:*

Measured amounts of œstrone solution are pipetted into Coleman Spectrophotometer 19 × 150 mm round cuvettes and the solvent is evaporated off in a water bath. Eight ml of 52% ferrous-acid reagent are delivered into each cuvette from a burette. The solutions are heated for 50 minutes in a boiling water bath. At the end of this period the tubes are cooled to room temperature and read at 505 mμ.

### *Œstradiol:*

In the same manner, measured amounts of œstradiol solution are heated with 52% ferrous-acid reagent in a boiling water bath for 30 minutes. The developed colours are read at room temperature at 505 mμ.

### *Œstriol*

Measured amounts of œstriol are heated with 65% ferrous-acid reagent for 50 minutes in a boiling water bath. After cooling, the developed colours are read at 500 mμ.

## RESULTS OF COLOUR REACTIONS WITH PURE ŒSTROGENS

As shown in Table I 4.3 μg of œstrone in 8 ml of solution (0.54 μg per ml) can be readily detected by this technique. The mean value at each concentration level is shown with the average deviation. Absorbance values for œstradiol and œstriol were obtained for similar numbers and weights of samples as described for œstrone. Weight of sample, mean absorbance and average deviation are given in Table I. Range of reproducibility values for œstrone was found to be 3–9%, usually 3–5%; for œstradiol, 5–8%; for œstriol, 1–5%.

## NOTES

1. Œstrone shows maximum absorbance in a range between 50–60% sulphuric acid. Œstradiol has a somewhat narrower range, namely 50–55%, while œstriol shows a peak absorbance in 65% sulphuric acid.

2. The time required to develop maximum colour for œstrone at 100° is 50 minutes. Œstradiol and œstriol require 30 minutes of heating, the latter showing no change in absorbance after 50 minutes.

3. A plateau of colour development is obtained with 20–56 mg of ferrous salt per 8 ml of volume.

4. Using a Beckman Du Spectrophotometer the absorption maxima for œstrone and œstradiol were found to be 512 mμ and that for œstriol 505 mμ. The $E^{1\%}_{1\,\mathrm{cm}}$ for œstrone, œstradiol and œstriol were 1350, 1362 and 1289 respectively.

5. The œstrone colour reaction obeys the Beer-Lambert law up to about 17.5 μg after which there is a perceptible curvature. This is due to the fact that this œstrogen, as well as œstradiol and œstriol, develops considerable fluorescence in sulphuric acid solution. At higher concentrations, under these conditions, the Beer-Lambert law does not hold.

The calibration curve for œstradiol is linear for about the same distance and shows the same curvature at concentrations greater than 20 μg. Œstriol presents a calibration curve similar to that of œstrone and œstradiol, remaining, however, linear to about 33 μg before deviations are noticed.

6. Colour formation tends to develop into the 520 mμ region in the case of sulphuric acid alone, but the curve is broad, presents no sharp absorption peak, and indicates less sensitivity than in the case of the ferrous-acid reagent. Using the latter reagent the absorption peak is sensitive, and well defined.

TABLE I. COLOUR REACTION OF ŒSTROGENS USING THE FERROUS-SULPHURIC ACID REAGENT

| | Micrograms of œstrone (52% sulphuric acid) | | | | |
|---|---|---|---|---|---|
| | 4.3 | 8.6 | 17.2 | 25.8 | 34.4 |
| Absorbance | 0.085 | 0.148 | 0.282 | 0.445 | 0.572 |
| | 0.087 | 0.150 | 0.326 | 0.378 | 0.570 |
| | 0.070 | 0.160 | 0.292 | 0.461 | 0.540 |
| | 0.068 | 0.149 | 0.298 | 0.425 | 0.595 |
| | 0.074 | 0.157 | 0.286 | 0.460 | |
| | | 0.160 | 0.325 | 0.447 | |
| | | 0.160 | 0.313 | 0.460 | |
| | | 0.152 | 0.320 | 0.430 | |
| | | 0.145 | 0.287 | | |
| | | 0.160 | 0.312 | | |
| | | 0.155 | | | |
| | | 0.150 | | | |
| | | 0.160 | | | |
| Mean absorbance | 0.077 | 0.155 | 0.304 | 0.438 | 0.569 |
| Average deviation | 0.007 | 0.005 | 0.016 | 0.021 | 0.015 |
| | Micrograms of œstradiol (52% sulphuric acid) | | | | |
| | 4.6 | 9.2 | 18.4 | 27.6 | 36.8 |
| Mean absorbance | 0.081 | 0.166 | 0.317 | 0.482 | 0.558 |
| Average deviation | 0.007 | 0.012 | 0.017 | 0.025 | 0.038 |
| | Micrograms of œstriol (65% sulphuric acid) | | | | |
| | 4.1 | 8.2 | 16.4 | 24.6 | 32.8 |
| Mean absorbance | 0.062 | 0.124 | 0.272 | 0.416 | 0.542 |
| Average deviation | 0.003 | 0.004 | 0.010 | 0.004 | 0.010 |

7. Ferric iron hastens colour production but promotes fading. It also lessens absorbance for œstrone and œstradiol despite the presence of ferrous iron. It appears to have no depressing effect on œstriol.

Emanuel Epstein*
William O. Maddock
A. J. Boyle

*Departments of Chemistry and Medicine,*
*Wayne State University,*
*Detroit* 2, *Michigan, U.S.A.*

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* Present address: St. Joseph Mercy Hospital, Pontiac, Michigan.

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# Determination of zirconium in high temperature alloys

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It is known that small amounts of boron and zirconium play an important role in improving the physical properties of nickel-base high-temperature alloys. There is need of a sensitive and selective method of determining the zirconium content in the high temperature alloys. A highly selective colour reaction for zirconium (and hafnium) with Xylenol Orange has been reported.[1] This short note describes a simple procedure of determining small amounts of zirconium in alloys, using Xylenol Orange.

*Procedure:* Dissolve by gentle heating one gram of alloy sample with 30 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid. Add 30 ml of 1:1 sulphuric acid, heat and fume a few minutes. Cool and dilute with water to approximately 100 ml. Separate nickel, cobalt, and other metals by mercury cathode (Dyna Cath) at 15 amperes until giving negative or very faint thiocyanate test for molybdenum. Precipitate zirconium and titanium by adding $10N$ sodium hydroxide and digest for 15 minutes on a hot-plate. Filter through a No. 42 Whatman filter paper and

Table I. Determination of zirconium in high temperature alloy

| Sample | Zirconium, % | |
|---|---|---|
| | Present† | Found |
| M-252* No. 2 | 0.035<br>0.039 | 0.038 |
| M-252 No. 6 | 0.122<br>0.130 | 0.129 |

* M-252 contains approximately 20% Cr, 10% Co, 10% Mo, 3% Ti, 1% Al, Ni base, and traces of B and Zr.

† Determined by the gravimetric phosphate method after the mercury cathode and cupferron separations.

wash three times with hot water. Dissolve the precipitates on the filter paper with hot 0.8*N* perchloric acid into a 250-ml volumetric flask. Cool and make to volume with 0.8*N* perchloric acid. Take a suitable aliquot for the colour development with Xylenol Orange as described elsewhere.[1]

The results shown in Table I are excellent. It is believed that this procedure would be suitable for determining small amounts of zirconium in other types of alloys.

K. L. CHENG

*Utica Metals Division*
*Kelsey-Hayes Company,*
*Utica, 4, New York, U.S.A.*

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# Studies on organic reagents for inorganic analysis—V
# *m*-Nitrophenylfluorone for the spectrophotometric determination of zirconium

(*Received* 18 *July* 1958)

FOR the determination of zirconium, phenylfluorone (abbreviation of 2:3:7-trihydroxy-9-phenylfluorone) method was recommended previously by the author and K. Kimura.[1] The reactions between phenylfluorone and several metals were also studied.[2,3] The method, which is about forty times more sensitive than the Alizarin Red S method,[4] is the most sensitive method hitherto reported for the colorimetric determination of zirconium, but the absorbance of the chelate decreases with increasing acidity in the solution. On the other hand, several derivatives of phenylfluorone were synthesized by the author, and the effect of the substituent on the utility of the derivatives as a spectrophotometric reagent was studied.[5,6] The results suggested that *m*-nitrophenylfluorone [abbreviation of 2:3:7-trihydroxy-9-(3′-nitrophenyl)fluorone] was one of the most excellent reagents for the pruopse in view of the sensitivity, stability, and other properties. In this paper, a detailed procedure for the spectrophotometric determination of zirconium using this reagent is described.

## EXPERIMENTAL AND RESULTS

### *Apparatus and reagents used*

The absorbance measurements were made with a UVISPEK spectrophotometer using 10-mm glass cell. The reference cell contained distilled water for all the measurements, except for the measurement of the absorption spectrum of the chelate, in which the blank solution was used as a reference solution.

*Ethanolic solution of* m-*nitrophenylfluorone*: *m*-Nitrophenylfluorone, was synthesized from hydroxyhydroquinone triacetate and *m*-nitrobenzaldehyde according to the method reported previously,[2,3] and 0.120 g of this reagent was dissolved in 150 ml of ethanol and 1 ml of 5*N* hydrochloric acid by warming. After being cooled, the solution was diluted to 200 ml with ethanol.

*Zirconyl chloride stock solution*: analytical grade zirconyl chloride octahydrate dissolved in 1*N* hydrochloric acid, and standardized gravimetrically using distilled ammonium hydroxide. This solution should contain 2.07 mg of zirconium per ml. A fresh working solution was prepared from the stock solution by dilution with dilute hydrochloric acid, for each experiment.

*Cyclohexanol*: Reagent grade *cyclo*hexanol without any purification.

*Ethanol*: Reagent grade 100% ethyl alcohol.

Spectral absorbance data for the reagent blank and 20.7 $\mu$g of zirconium (following the standard procedure mentioned later) are given in Fig. 1. The absorption maximum of the dye and the chelate was found at 475 m$\mu$ and 550 m$\mu$, respectively. The optimum wavelength was taken as 550 m$\mu$ because at this point the absorption given by the blank solution is small and that by zirconium *m*-nitrophenylfluoronate is maximum.

*Effect of cyclohexanol and ethanol concentration*

A precipitate of zirconium *m*-nitrophenylfluoronate forms after a time from solution containing no *cyclo*hexanol and less than 5 ml of ethanol. The coloured solution becomes stable with increasing amount of *cyclo*hexanol added, but a *cyclo*hexanol layer separates from the ethanolic water layer above a certain proportion of *cyclo*hexanol to the amount of ethanol added. The solution shows no difference in the position of the absorption maximum when the amount of *cyclo*hexanol or ethanol added is altered, although there is a slight difference in the detailed shape of the absorption curve.

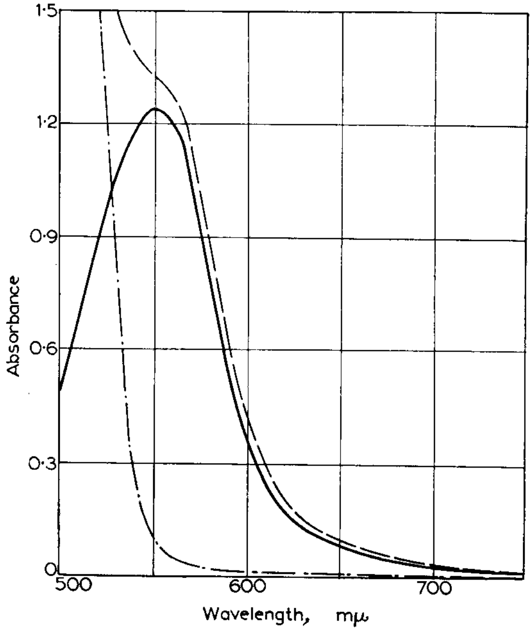

FIG. 1. Absorption curve. – · – blank solution (ref. solution, water); – – – – Zirconium-dye complex (ref. solution, blank solution); —— Zirconium-dye complex (ref. solution, blank solution).

From these results, 2.5 ml of *cyclo*hexanol, 5 ml of ethanol, and 5 ml of ethanolic solution of *m*-nitrophenylfluorone were optimum. In this condition, the solution gives no visible precipitate of *m*-nitrophenylfluoronate with a zirconium concentration below 3 μg per 25 ml if allowed to stand for a day or more.

*Effect of acidity*

In the acidity range higher than 1.5*N* hydrochloric acid concentration, the absorbances increase slowly with increasing digestion time. The absorbance is almost independent of hydrochloric acid concentration in the region below 0.1*N* whereas no plateau range is found above 0.05*N* acid concentration in the case of phenylfluoronate.

*Effect of digestion time*

In a solution containing more than 4 μg zirconium, a precipitate of zirconium *m*-nitrophenylfluoronate is obtained when the solution is allowed to stand for a day, but the stable suspension may be regenerated on short shaking by hand. The absorbance is nearly constant for forty minutes after the preparation.

*Standard procedure*

The following is recommended as an optimum procedure.

Transfer the sample solution (less than 10 ml) to a 25-ml volumetric flask. If the sample is known to contain more than 20 to 25 μg zirconium, an aliquot portion of the sample solution containing the desired amount of zirconium in a final volume is pipetted into a 25-ml volumetric flask. Additional acid will then be required to bring the acidity up to 0.10*N* hydrochloric acid used in the determination of zirconium with *m*-nitrophenylfluorone. Adjust the volume to about 10 to 12 ml with distilled water. Add 5 ml of ethanol, 2.5 ml of cyclohexanol, and 5 ml of ethanolic solution containing 3 mg of *m*-nitrophenylfluorone, in this order. Make the solution to the mark with distilled water, mix with shaking by hand, allow to stand for an hour, and obtain the absorbance of the solution in the spectrophotometer at 550 mμ using 10-mm glass cells and distilled water as a control solution. Determine the amount of zirconium by reference to the standard working curve prepared previously.

TABLE I.—INTERFERING IONS

| Ion | Amount added, *ppm* | Error, % | Permissible amount, *ppm* |
|---|---|---|---|
| $Fe^{II}$ | 2.0 | 2 | 3 |
| $Fe^{III}$ | 2.0 | 10 | 0.6 |
| $Ti^{IV}$ | 0.2 | 40 | 0.01 |
| $Ge^{IV}$ | 0.4 | 20 | 0.06 |
| $Sn^{IV}$ | 0.4 | 10 | 0.1 |
| $As^{III}$ | 10 | 2 | 15 |
| $As^{V}$ | 10 | 10 | 3 |
| $Sb^{III}$ | 2 | 10 | 0.6 |
| $Sb^{V}$ | 2 | 10 | 0.6 |
| $F^-$ | 2 | 25 | 0.2 |
| $C_2O_4^{2-}$ | 5 | 20 | 0.7 |
| $HPO_4^{2-}$ | 5 | 20 | 0.7 |

*Working curve*

A straightline relationship exists between absorbance and amount of zirconium up to 0.6 ppm. Solutions containing from 0.6 to 10 ppm deviate slightly from Beer's law but their absorbances are reproducible. The region from 0 to 0.10 ppm of zirconium was examined in detail for any deviation from the straight-line relationship, but none was found.

*Effect of diverse ions*

The effect of various ions was studied using 0.3 ppm of zirconium. The standard procedure was employed, except that the desired amount of the other ion was added to a volumetric flask before the addition of zirconium solution. The concentrations of zirconium and other ion are expressed on the basis of the final volume 25 ml. The change in absorbance was then measured at 550 mμ. Errors of less than 3% of the zirconium present were considered to be negligible. A negligible error was obtained with the following approximate maxima:

| | |
|---|---|
| 2000 ppm of: | sodium, potassium, ammonium, and magnesium ion. |
| 1000 ppm of: | calcium, barium, strontium, and mercuric ion. |
| 500 ppm of: | lanthanum, neodymium, cerrous, cadmium, zinc ion. |
| 100 ppm of: | aluminium, and thorium ion. |

Chloride, bromide, nitrate (2000 ppm) and sulphate (1000 ppm) ions do not interfere with the reaction.

Some elements interfere by increasing the colour intensity. Some elements quench the colour given by zirconium *m*-nitrophenylfluoronate. Table I lists the interfering ions and their effect.

Serious interference is given by the following ions: titanium, germanium, tin, iron, antimony, oxalate, phosphate and fluoride tested.

## DISCUSSION

The colour change resulting from the reaction of *m*-nitrophenylfluorone with zirconium closely resembles that with phenylfluorone, namely the shift of the absorption maximum caused by chelate formation is 75 m$\mu$ in *m*-nitrophenylfluorone, and 72 m$\mu$ in phenylfluorone,[2] whereas the differences of the absorption maximum between the phenylfluorone or its zirconium chelate and *m*-nitrophenylfluorone or its zirconium chelate are 7 and 10 m$\mu$, respectively. The trend in the effect of the acidity of the solution on the absorbance is, however, considerably different. In the *m*-nitrophenylfluorone method, recommended here, the constancy of the absorbance is obtained at the region of the acidity below 0.10*N* hydrochloric acid concentration, whereas there is no such constancy in phenylfluorone method. This may be caused by the effect of *m*-nitro group, in attracting the electron of the -OH group at the 3 position and increasing the electronegativity of the oxygen atom. Furthermore, the absorbance of *m*-nitrophenylfluoronate is greater than that of the corresponding phenylfluoronate. The sensitivity of this method, given by the slope of the working curve, is nearly fifty times that for the Alizarin Red S method,[4] about five times that for the quercetin method,[7] and about 1.2 times that for the phenylfluorone method.[1] In the region from zero to 0.15 ppm of zirconium the solution may be kept without any visible precipitation for three days or more. The method is therefore excellent for the determination of micro amounts of zirconium.

*Acknowledgement*—The author is indebted to Dr. Kenjiro Kimura, Professor Emeritus and Dr. Nobufusa Saito, Professor in this laboratory, for their encouragement to carry out this study. This work was supported partly by a grant from the Ministry of Education.

HIROTOSHI SANO

*Department of Chemistry,*
*Faculty of Science,*
*The University of Tokyo,*
*Hongo, Tokyo, Japan*

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# The use of the pool cathode in polarography

(*Received* 1 *September* 1958)

## INTRODUCTION

POLAROGRAPHY using a mercury pool as cathode instead of the conventional dropping mercury electrode (DME) has been described previously,[1-3] and increased sensitivity over the DME has been claimed for conventional polarographs. The main difficulty in the design of such cells is ensuring a closely reproducible pool size, as the cell current is directly proportional to the pool area. This is overcome in the cell used in the work described below by using a glass cup as the pool container, and filling the cup to overflowing every time a pool is used. This cell was designed by Mrs. B. Lamb of Tinsley Industrial Instruments Limited, and supplied by them. The cell is of the conventional H type, using a saturated calomel anode, with connection to the cathode compartment via an agar plug. The cell is shown in Fig. 1.

## CONVENTIONAL POLAROGRAPHY

When this cell is used with a conventional polarograph, a peaked polargram similar to those normally obtained with the cathode ray polarograph is obtained, in which peak height is proportional to concentration; sensitivity is increased by a factor of about 20. This is in agreement with the findings of earlier workers.[1–3]

There are, however, severe drawbacks to the use of the pool cathode cell with this type of instrument, namely:

1. Each cell must be calibrated independently, as cell current varies with pool area. This is much more inconvenient than calibrating a single capillary which can then be used with any number of cells. In practice, it is easier to use the same cell for all determinations, which takes much longer than the usual procedure.

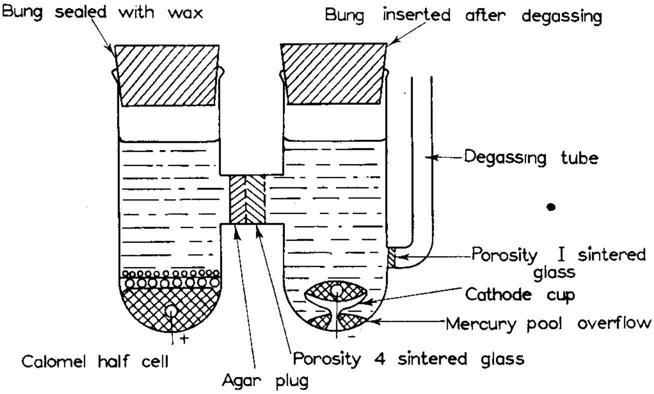

FIG. 1

2. Owing to the increased sensitivity of the electrode, the problem of residual oxygen becomes much more acute, as even after prolonged passage of hydrogen or nitrogen there is always an appreciable oxygen peak. This will often be very much higher than that due to the element being determined. This difficulty can be overcome to some extent by using a derivative circuit and is rendered easier by the absence of any drop wave, which also makes it less serious.

3. Again due to increased sensitivity, the sloping base line due to condenser current and the long drawn out hydrogen peroxide peak cause considerable difficulty in measuring heights at high sensitivity settings.

4. It was found that if a repeat polarogram was run immediately, the peak height had decreased by 10%–20% and further polarograms showed that this effect continued. This was at first attributed to depletion of the solution by deposition into the pool, but on allowing a solution to stand for 30 minutes with no applied potential it was found that the peak height returned very nearly to its original value. It is suggested that the effect may be due to the formation of a very thin layer of amalgam on the surface of the pool; on standing diffusion would take place in the pool and the original conditions would be restored.

## CATHODE RAY POLAROGRAPHY

This instrument presents repeat polarograms with each drop using the DME, or every 7 seconds using a pool or solid electrode. With the DME it is necessary to synchronise the voltage sweep and drop time in order to obtain reproducible polarograms. With a pool or solid electrode, this condition no longer applies and reproducible curves are obtained immediately. The preliminary results obtained showed promise, and a comparison of DME and pool cathode was made on this instrument.

The CRP represents a considerable advance over the conventional polarograph, but suffers from some disadvantages when attempts are made to use it with the DME at the limits of its performance.

These disadvantages are as follows:

1. The steep slope to the base line obtained at potentials more negative than about −0·6 volts, due to condenser current and the hydrogen peroxide peak.

2. The large, rounded rise in current obtained at about —0·4 volts. This has been attributed to the increase in diffusion layer capacity near the electrocapillary maximum.[4]

3. The hum on the trace, which is usually of the order of 5 mm–10 mm at maximum sensitivity, and resembles a sine wave at about 10 c.p.s.–20 c.p.s. This applies to the instrument in our laboratory, and will no doubt vary with the conditions of use. It is not electronic hum, and it is difficult to attribute it to capillary response when only one drop is concerned. The most likely source is vibration, either of the pool anode or the hanging drop, and it is significant that when the electrode stand was mounted directly on a laboratory bench this vibration problem was very much worse. It is possible that the mounting now employed is not completely efficient.

4. The fact that the derivative circuit, which will effectively compensate the steep slope referred to in (1) above, and minimise the effect of the electrocapillary maximum referred to in (2), causes the instrument to lose sensitivity. For most reactions with our instrument this loss in sensitivity is by a factor of about 100, which cannot easily be nullified by further amplification as the hum level is about the same as with the direct circuit.

5. The loss in sensitivity incurred when slow electrode reactions are examined. This loss is often attributed to the irreversibility of the reaction concerned, but in our experience is related in part, at least, to the reaction rate. For example, the reduction of Solochrome Violet RS, a 4-electron irreversible reaction, is one of the most sensitive on the CRP, while the reduction of niobium from EDTA solution at pH 3·05, reported by Ferrett and Milner[5] to be reversible, is a slow reaction and is insensitive.

## EXPERIMENTAL

It was hoped that the pool cathode cell would help to overcome some of these difficulties, and in order to assess it against the DME both electrodes were used with 3 reactions. These were:

(i) Cadmium in 0·1*N* KCl, a fast reversible reaction.
(ii) The aluminium complex of Solochrome Violet RS, a fast irreversible reaction.
(iii) Nickel in 0·1*N* KCl, a slow irreversible reaction.

In all cases, a strong solution was used at the beginning, and diluted with distilled water tenfold for the next tests at higher sensitivities, with suitable additions of base electrolyte.

The results obtained are shown in Tables I–III.

TABLE I. CADMIUM IN 0.1*N* KCl

| Cd, *ppm* | Peak height, $\mu A$ | | Remarks |
|---|---|---|---|
| DME | | | |
| 10 | †1·6 | | Smooth, ideal polarogram |
| 1·0 | 0·16 | | Smooth, ideal polarogram |
| 0·1 | 0·016* | | Marked hum, latter part of trace slopes steeply. Height varied 0·013–0·019 but 0·016 reproduced most often when hum low. |
| 0·01 | N.D.* | | Peak should be about ½″ in height but lost in ½″ hum on trace. |
| POOL | Direct | Derivative | |
| 10 | 100 | 2·1 | Smooth ideal polarogram |
| 1·0 | 10·0 | 0·21 | Smooth ideal polarogram |
| 0·1 | 1·1 | 0·022 | Smooth ideal polarogram but $O_2$ wave present became difficult to compensate |
| 0·01 | N.D. | N.D. | Direct wave lost because of steep base line. Derivative wave lost in hum. |

* Using maximum sensitivity; full scale = 0·020 $\mu$A.
† Derivative wave height 0·0064 using maximum sensitivity.

TABLE II. ALUMINIUM COMPLEX OF SOLOCHROME VIOLET RS

| *ppm Al* | Wave height, $\mu A$ | | Remarks |
|---|---|---|---|
| | Direct | Derivative | |
| DME | | | |
| 1·0 | 2·94 | 0·044 | Smooth ideal polarograms |
| 0·1 | 0·57 | *0·0096 | Smooth ideal polarograms |
| 0·01 | 0·075 | *0·002 | Smooth ideal polarograms |
| 0·001 | *N.D. | *N.D. | Direct wave lost "in electrocapillary maximum" followed by steep slope. |
| POOL | | | |
| 1·0 | 24·6 | 0·29 | Smooth ideal polarograms |
| 0·1 | 4·4 | 0·065 | Smooth ideal polarograms |
| 0·01 | 1·0 | 0·023 | Smooth ideal polarograms but $O_2$ wave difficult to compensate. |
| 0·001 | 0·10 | *0·003 | Good shape, clean wave on direct. Steeply sloping base line. |
| 0·0001 | N.D. | *N.D. | Direct wave lost in steeply sloping base line. |

* Using maximum sensitivity.

TABLE III. NICKEL IN 0·1*N* KCl

| *ppm Ni* | Wave height, $\mu A$ | | Remarks |
|---|---|---|---|
| | Direct | Derivative | |
| DME | | | |
| 10 | 3·0 | 0·028 | Smooth, unpeaked polarogram |
| 1·0 | 0·29 | *0·002 approx. | Unpeaked polarogram on sloping base line |
| 0·1 | 0·025 approx. | *N.D. | Unpeaked polarogram on very steeply sloping base line |
| POOL | | | |
| 10 | 62·5 | 0·40 | Smooth, peaked polarogram |
| 1·0 | N.D. | 0·040 | Direct wave merges into Zn wave from KCl |
| 0·1 (0·01 *N* KCl) | N.D. | *0·004 | Direct wave merges into Zn wave from KCl<br>Very steeply sloping base line |

* Using maximum sensitivity.

## REPRODUCIBILITY

The CRP produces polarograms every 7 seconds with a pool cathode. The peak height appears to be reproducible for at least 20–30 sweeps, which is ample time to measure the height. (2–3 sweeps are sufficient.) On standing, however, the peak height changed, and after 1 hour of sweeping every 7 seconds, the height *increased* by about 100%–200%. This is not considered a serious disadvantage, as only the first 2 or 3 sweeps are used for analytical purposes. It is suggested that the reason for this increase as opposed to the decrease obtained with the conventional polarograph is that the pool does not become contaminated to the same extent, as the potential does not remain high for more than about 1 second in every 7. Instead, electromigration slowly takes place, and a more concentrated solution is formed around the cathode. Increasing the concentration of base electrolyte decreases the rate at which the peak current increases, which would appear to lend some support to this theory.

The reproducibility of the cell was checked by measuring the peak heights obtained when several portions of the same lead solution (1 ppm in KCl) were examined, using a new pool each time. 10 results were obtained. The mean value was 4·02 $\mu$A; maximum deviations were $+0\cdot13$ $\mu$A and $-0\cdot17$ $\mu$A. Standard deviation was 0·103 $\mu$A, = 2·5%.

## CONCLUSIONS

### (*a*) *Conventional polarography*

The effective gain in sensitivity is by a factor of about 20. The fact that it is not possible to run a repeat polarogram is regarded as a very severe drawback, however, and for this reason alone the use of pool cathode is not recommended with this type of instrument.

### (*b*) *Cathode ray polarography*

The pool cathode appears to show some advantages over the DME with this instrument.

The increase in sensitivity, given by the ratio of cell current using the pool to that using the DME is 62·5 for Cd, 8·5 for Al Solochrome and 21 for Ni. No explanation is offered for this discrepancy. The effective gain in sensitivity is not as high as this, however, because the very steeply sloping base line obtained precludes the use of the direct circuit at the highest sensitivities. The derivative circuit benefits most from the use of the pool cathode, as the maximum sensitivity of the instrument can be used, and in many cases the derivative circuit sensitivity becomes as high as the maximum useable direct sensitivity with the DME.

The greatest advantage of the pool cathode cell with the direct circuit is the fact that small concentrations of reducible species can be determined using instrument conditions where the hum level is very low, instead of high sensitivities where the hum is appreciable. In addition, waves occurring at potentials where the base line slope is high can be measured on the derivative circuit without appreciable loss of sensitivity over the direct circuit DME combination. This has the further advantage that close waves can be resolved.

Ultimate usable sensitivity is also increased by a factor of about 10, or slightly more in favourable cases. This may well be nullified by the fact that the CRP in its original form is quite often so sensitive that it is reagent blanks rather than instrument sensitivity that provide the bottom limit of determination.

The disadvantages which remain are the fact that the cells must be individually calibrated, or the same cell used. This is not so serious using the CRP, as the measurements can be made much more quickly than with a conventional instrument.

The CRP will tolerate larger preceding waves than a conventional polarograph, so that the residual oxygen wave is of less importance; the derivative circuit is even better, and will tolerate preceding waves over 500 times as high as the wave being measured.

There is no improvement as regards the absolute value of the hum, but the ionic concentration at which it begins to interfere is lowered. Similarly, there is no improvement in measuring slow reactions other than the overall increase in sensitivity. In spite of these remaining disadvantages, it is felt that the pool cathode cell can offer some advance over the DME when used with the CRP.

*Acknowledgement*—The author wishes to thank the Director and Council of the British Cast Iron Research Association for permission to publish this work.

R. C. Rooney

*British Cast Iron Research Association*
*Bordesley Hall*
*Alvechurch*
*Birmingham, England*

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Talanta, 1959, Vol. 2, pp. 195 to 196. Pergamon Press Ltd. Printed in Northern Ireland

# BOOK REVIEWS

**A Manual of Paper Chromatography and Paper Electrophoresis.** R. J. BLOCK, E. L. DURRUM and G. ZWEIG. Academic Press, Inc., New York: Academic Books Ltd., London. Second edition, 1958. Pp. xi + 710. $12.80.

The object of this book, as stated by the authors, is to present some of the results of the numerous investigations on paper chromatography and paper electrophoresis so that the student may have a sufficient idea of past studies in order to allow him to choose the method which appears to be most promising for the solution of his particular problem. The authors have succeeded in organizing the large amount of material in a convenient manner and the descriptions of methods are readable and explicit.

As in the first edition (1955), this book is divided into two parts. The first part, written by R. J. Block and G. Zweig, is a practical manual on paper chromatography. The second and shorter part by E. L. Durrum is devoted to the practical aspects of paper electrophoresis.

The section of paper chromatography (483 pp.) includes a short chapter on theory, two chapters on general and quantitative methods, ten chapters on specific procedures for various classes of organic compounds, and one chapter on inorganic separations. These procedures include solvent systems for separations, methods of detection of compounds on paper, and other pertinent information.

The section on paper electrophoresis (185 pp.) includes general theory, general and quantitative methods, two-dimensional techniques and continuous flow methods.

The major change from the first edition has been an expansion of the methods to include material published up through 1956 (almost a three-fold increase in references). In view of the rapid growth of these separation techniques in recent years, particularly in the organic and biochemical fields, this new edition serves as an up to date comprehensive manual of methods. As in the past, the authors give the reader the benefit of their judgment and experience by pointing out in some instances those procedures which are recommended.

This book continues to be a valuable addition to any laboratory employing these paper chromatographic or electrophoretic methods.

GEORGE H. MORRISON

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**An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry.** A. E. GILLAM and E. S. STERN; with a foreword by E. R. H. JONES, F.R.S. Second Edition, Edward Arnold (Publishers) Ltd., London, 1958. pp. xi + 326. 50s.

THIS is not intended to be a text-book for the analyst, and half of its sixteen chapters are concerned with the relations between the structures and light absorption of organic molecules. It gives, however, spectra or spectral data in the ultraviolet and visible regions for some 800 compounds, which may well be of interest to the organic analyst. For the specialist within this field there is a chapter on the detection and identification of carotenoids, anthocyanins, dyes and industrial colours, blood pigments and a number of miscellaneous colourless, but ultraviolet absorbing, substances. Quantitative analysis is considered in two chapters which give examples of various techniques for determining single substances and mixtures, and also in a chapter on miscellaneous applications, where the determination of some physical constants is described. Differential methods are only mentioned.

Where the analyst who uses ultraviolet and visible absorption spectra can well find the book useful is in the more general chapters where the theory and measurement of absorption spectra are clearly and concisely presented. Many such analysts should certainly study the sections on the reliability of photoelectric instruments and the accuracy of quantitative determinations.

There are over 500 references to the literature, amplified by an appendix giving a bibliography of general and absorption spectroscopy. Other appendices give useful information on the absorption characteristics of common solvents and the influence of temperature on absorption measurements of organic compounds. The diagrams are clear and the book is well produced.

DAVID W. WILSON

**Modern Manufacturing Formulary.** EMIL J. BELANGER. Chemical Publishing Co., Inc., New York. Pp. 399. $10.00.

FOR many of us the word "goldmine" arouses a strong, if somewhat juvenile interest, and this book is described on the dust cover as being a "goldmine of practical formulae and recipes for professional and amateur chemists . . . " It is attractively produced, the formulae being in separate sections devoted to food products, flavourings, practical household formulae, cosmetics, medicinal preparations, veterinary remedies, beverages, and miscellaneous. The appendix gives some account of Food and Drug Regulations (U.S.A.), and there is a classified directory of sources of supply (U.S.A.) and a fairly complete index.

The formulae vary from the familiar older type including some "omnibus" mixtures which would defy any analyst, to such things as polystyrene long-wear nylon spray and home-permanent-wave lotions. Very many of the more modern type formulae use materials having trade names, and these names are not distinguished in any way in the text from commonly accepted names. It is rather surprising to find absent, in a "modern" formulary, products such as rust inhibitors, selective weed killers, plant-cutting hormone mixtures, and even antifreeze.

The sources directory, although a fairly full one, would, in places, certainly confuse the amateur. Thus there are headings for boracic acid and borax (different suppliers), but under the heading "boric acid" one is referred to borax. Another heading is "dextrose (cane sugar)".

It is possible that the analyst might find this book of some value in examining a commercial product, although its value, especially outside the U.S.A., is greatly reduced by the extensive use of trade names. One would be interested to know what active constituents one might be expected to encounter in a cough mixture containing "ground life everlasting" as one of the materials from which an infusion is prepared!

A. B. ANGUS

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**Instrumental Methods of Analysis.** H. H. WILLARD, L. L. MERRITT JR. and J. A. DEAN. D. Van Nostrand Co. Ltd., New York and London. Third edition, 1958. Pp. vi + 626. 56s. 6d.

Most analysts interested in instrumental methods will be familiar with the earlier editions of this work in their unusual and rather unwieldy format and they will consequently welcome this third edition, excellently produced in more conventional style and size with a good index.

Each instrumental technique dealt with is first discussed theoretically, generally briefly but nevertheless adequately, so that a proper appreciation of the basic principles involved is gained; then follows a description of typical instruments and principal techniques of application, step by step laboratory instructions for experimental operation, a few questions and problems and finally some selected references.

In addition to the wide range of techniques dealt with in the previous editions, space has now very properly been found for useful introductions to some of the newer methods such as gas chromatography, nuclear magnetic resonance and X-ray fluorescence. In covering the large, heterogeneous and expanding field of analytical instrumentation it is by no means easy to maintain balance and in this volume one feels, that from the students point of view at least, there is some lack of proportion in the very full treatment accorded to, say, flame photometry (40 pages) compared with all other emission spectrographic methods (some 33 pages).

The references selected for further reading are for the most part very judicious but perhaps the European reader may wish to augment the recommendations in a few cases; Courteney Phillips' useful introduction to gas chromatography is referred to in the text (page 349) but the promise that it will be "listed at the end of the chapter" is unfulfilled.

The book has well over 300 illustrations which are generally excellent although the instructional value of some of those depicting little more than instrument consoles may be doubted.

As one of the few texts which attempts to deal with the whole field of instrumental methods of analysis, this reasonably priced, up-to-date volume is definitely to be recommended, although it must be borne in mind that in the instrument description sections, quite naturally, American instruments figure predominantly.

F. J. WOODMAN

Talanta, 1959, Vol. 2, pp. 197 to 200. Pergamon Press Ltd. Printed in Northern Ireland

# NOTICES

## The Society for Analytical Chemistry

The eighty-fifth Annual General Meeting of the Society was held on Friday 6 March, 1959, in The Meeting Room of the Royal Society, Burlington House, London, W.1, with the President, Dr. J. H. Hamence, M.Sc., F.R.I.C., in the Chair.

The following Officers and Members of Council were elected for the forthcoming year:—

*President:* R. C. Chirnside;
*Past Presidents serving on the Council:* J. H. Hamence, D. W. Kent-Jones, J. R. Nicholls, K. A. Williams;
*Vice-Presidents:* D. C. Garratt, Magnus A. Pyke, J. G. Sherratt;
*Honorary Treasurer:* A. J. Amos;
*Honorary Secretary:* R. E. Stuckey;
*Honorary Assistant Secretaries:* L. Brealey (Programmes Secretary), S. A. Price.
*Other Members of Council:* N. L. Allport, H. E. Brookes, R. A. Chalmers, W. T. Elwell, C. H. R. Gentry, J. Haslam, E. I. Johnson, G. W. C. Milner, R. F. Milton, F. C. J. Poulton, T. S. West and C. Whalley.
*Ex-officio Members:* J. R. Edisbury (Chairman of the North of England Section), A. N. Harrow (Chairman of the Scottish Section), S. Dixon (Chairman of the Western Section), S. H. Jenkins (Chairman of the Midlands Section), F. Holmes (Chairman of the Microchemistry Group), R. A. C. Isbell (Chairman of the Physical Methods Group) and J. I. M. Jones (Chairman of the Biological Methods Group).

After the Annual General Meeting, Mr Chirnside took the Chair and Dr. Hamence delivered his Presidential Address.

Dr. Hamence devoted the major part of his address to the developments that had taken place over the past two years, and devoted the latter part of the address to a limited number of observations on the future course of analytical chemistry.

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The fourth Annual General Meeting of the Midlands Section of the Society was held on Tuesday 3 March, 1959, in the Mason Theatre, The University, Edmund Street, Birmingham 3. The Chairman of the Section, Dr. R. Belcher, F.R.I.C., F.Inst.F., presided.

The following were elected Officers of the Section for the forthcoming year:—

*Chairman:* Dr. S. H. Jenkins
*Vice-Chairman:* Dr. H. C. Smith
*Hon. Secretary:* Mr. G. W. Cherry, 48 George Frederick Road, Sutton Coldfield, Warwickshire.
*Hon. Treasurer:* Mr. F. C. J. Poulton
*Hon. Assistant Secretary:* Mr. R. Adkins

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The Fifteenth Annual General Meeting of the Microchemistry Group of the Society was held at 6.45 p.m. on Friday 20 February, 1959, at the School of Pharmacy, Brunswick Square, London, W.C.1. By permission of the Dean, the meeting was preceded by visits to the laboratories of the School of Pharmacy.

The Chairman of the Group, D. F. Phillips, F.R.I.C., presided. The Officers and Members of Committee for 1959 are as follows:—

*Chairman:* Mr. F. Holmes

*Vice-Chairman:* Mr. C. Whalley

*Hon. Secretary:* Mr. D. W. Wilson, Department of Chemistry, Sir John Cass College, Jewry Street, London, E.C.3.

*Hon Treasurer:* Mr. G. Ingram.

*Members of Committee:* Miss M. Corner, Mr. E. Bishop, Mr. J. A. Hunter, Mr C. A. Johnson, Dr. R. J. Magee and Mr. D. F. Phillips.

The *Hon. Auditors*, Mr. H. Childs and Dr. L. H. N. Cooper, were re-appointed.

The Annual General Meeting was followed by an Ordinary Meeting of the Group, at which Mr. D. F. Phillips gave the Retiring Chairman's Address.

## The following meetings have been arranged:

*Monday–Tuesday* 6–7 *April* 1959: **Chemical Institute of Canada,** Analytical Chemistry Division, Eighth Regional Conference. Symposium: *Instrumental Methods of Analysis.* Information from J. D. Sands, Polymer Corporation, Ltd., Sarnia, Ontario, Canada.

*Monday–Saturday* 6–11 *April* 1959: **International Union of Pure and Applied Chemistry:** International Conference on *Coordination Chemistry.* Information from The Chemical Society, Burlington House, Piccadilly, London, W.1, England.

*Wednesday* 8 *April* 1959: **Royal Institute of Chemistry,** Mid Southern Counties Section: **Society for Analytical Chemistry,** Western Section. Visit to works of Tintometer Ltd. *Advantages and Disadvantages of Visual Colorimetry:* G. J. Chamberlin. Cathedral Hotel, Salisbury, Wilts, England. 7.45 p.m. (Works visit 5.30 p.m.)

*Wednesday* 8 *April* 1959: **Society for Analytical Chemistry,** Microchemistry Group. Review Discussion Group, "The Feathers", Tudor Street, Bouverie Street, Fleet Street, London, E.C.4, England. 6.30 p.m.

*Thursday* 9 *April* 1959: **Society for Analytical Chemistry,** Midlands Section: *Analytical Chemistry in Glass Manufacture:* J. Davies, The University, Birmingham, 3, England. 6.30 p.m.

*Saturday* 11 *April* 1959: **Society for Analytical Chemistry,** North of England Section: *The Training of Analytical Chemists:* G. F. Longman, B.Sc., F.R.I.C. City Laboratories, Mount Pleasant, Liverpool, England. 2.15 p.m.

*Wednesday* 15 *April* 1959: **Society for Analytical Chemistry,** Scottish Section: *The Analytical Chemistry of Some of the Lower Phosphorus Oxyacids:* Dr. D. S. Payne. A.R.C.S., A.R.I.C. *Qualitative Analysis by Solvent Extraction Methods:* Dr. R. A. Chalmers and D. M. Dick, B.Sc. Central Hotel, Glasgow, Scotland. 7.15 p.m.

*Thursday* 16 *April* 1959: **Society for Analytical Chemistry,** Biological Methods Group: *Problems of Recording and Communicating Technical Information in a Commercial Research Organisation:* Pamela D. Waterhouse. "The Feathers", Tudor Street, Bouverie Street, Fleet Street, London, E.C.4. 6.30 p.m.

*Thursday* 30 *April* 1959: **Society for Analytical Chemistry,** Midlands Section: Works Visit and Lecture: *Quality Control in a Pharmaceutical Organisation:* Dr. D. C. Garratt, F.R.I.C. Boots Pure Drug Co., Ltd., Nottingham, England. 12.30 p.m.

*Friday* 8 *May* 1959: **Royal Institute of Chemistry,** South Wales Section: **Society for Analytical Chemistry,** Western Section and Microchemistry Group: *Rock and Mineral Analysis and Geochemical Prospecting.* Swansea, South Wales.

*Monday–Wednesday* 18–20 *May* 1959: **Instrument Society of America:** Fifth National Symposium on *Instrumental Methods of Analysis.* Houston, Texas, U.S.A. Information from M. D. Weiss, Union Carbide Olefins Co., South Charleston, W. Va., U.S.A.

*Monday–Thursday* 1–4 *June* 1959: **American Association of Spectrographers:** Tenth Annual Symposium on Spectroscopy. Conrad Hilton Hotel, Chicago, Ill. Information from H. M. Wilson, Continental Can Co., 7622 So. Racine Ave., Chicago, 20, Ill., U.S.A.

*Wednesday–Friday* 10–12 *June* 1959: **American Chemical Society,** Division of Analytical Chemistry, and *Analytical Chemistry:* 1959 Summer Symposium: *Complex Reactions in Analytical Chemistry.* University of Illinois. Information from G. L. CLARK, University of Illinois, Urbana, Ill., U.S.A.

*Wednesday–Friday* 10–12 *June* 1959: **Instrument Society of America:** Second International Symposium on *Gas Chromatography.* East Lansing, Michigan. Information from H. S. KINDLER, ISA, 313 Sixth Avenue, Pittsburgh, 22, Pa., U.S.A.

*Tuesday–Tuesday* 1–8 *September* 1959: **Czechoslovak Chemical Society of the Czechoslovak Academy of Sciences:** Third International Conference on Analytical Chemistry, Prague. Review and discussion of *The Current State of Analytical Chemistry.* For the participants, and especially for foreign visitors, visits to university laboratories and industrial research centres, and cultural programmes will be arranged. From *Tuesday* 8 *September* to *Friday* 11 *September* an International Pharmaceutical Congress will take place in Karlovy Vary (Czechoslovakia) so that participants in the Analytical Conference could also take part in this.

Information from Dr. JAROSLAV ZÝKA, Department of Analytical Chemistry, Charles University, Praha, II, Albertov 2030, Czechoslovakia.

Revised British Standards have been published as follows:

**B.S. 903:** *Methods of testing vulcanised rubber.* **Part B19: 1958:** *Preparation and examination of water extract* (replacing **Part 12** in **B.S. 903: 1950**) Price 3s.

This covers the preparation of the water extract and the following tests: Total water soluble material, electrical resistivity, free acid or free alkali, pH value, chloride, sulphate, ammonium salts.

**B.S. 1016:** *Methods for the analysis and testing of coal and coke:* **Part 6: 1958.** *Ultimate analysis of coal.* Price 10s.

This deals with the determination of carbon, hydrogen, nitrogen and sulphur in coal.

British Standards Institution Publications may be obtained from the B.S.I. Sales Branch, 2 Park Street, London, W.1, England.

# BOOKS RECEIVED

**Colorimetric Intermination of Traces of Metals,** 3rd ed. E. B. SANDELL. Interscience Publishers Inc. New York, $24.00.

**Precipitation from Homogeneous Solutions.** L. GORDON, M. L. SALUTSKY and H. H .WILLARD. John Wiley & Sons Inc., New York, 1959. Pp. viii + 187.

**Gas Chromatographie.** A. I. M. KEULEMANS, transl. E. CREMER. Verlag Chemie, Weinheim, 1959. Pp. xvi + 208. DM. 24.

**Tables of Constants and Numerical Data, Vol. 8. Selected Constants: Oxidation-Reduction Potentials.** G. CHARLOT. Pergamon Press, London, New York, Paris, 1958. Pp. vi + 41. 30s.

**Chemistry of the Co-ordinate Compounds.** International Series of Monographs on Inorganic Chemistry, Vol. I. Edited by H. TAUBE and A. G. MADDOCK. Rome Symposium, 15–21 September, 1957. Pergamon Press, London, New York, Paris, 1958. Pp. 638. L5.

**EDTA Titrations: An Introduction to the Theory and Practice.** H. FLASCHKA. Pergamon Press, London, New York, Paris, 1959. Pp. 138. 42s.

# PAPERS RECEIVED

**Argentometrische Titrationen mit Redoxindikation—II. Bestimmung von Ammoniak, Ammonium. Ionen und stickstoffhaltigen organischen Substanzen.** L. ERDEY, K. VIGH and L. POLOS. (1 *January* 1959.)

**Argentometric Titrations with Redox Indicators—III. Determination of Nitrate Ions and Nitro Compounds.** L. ERDEY, L. POLOS and Z. GREGOROWICZ. (2 *January* 1959.)

**Untersuchung von als Redoxindicatoren Anwendbaren Variaminblauderivaten.** L. ERDEY, E. BANYAI und E. B.-GERE. (2 *January* 1959.)

**Analytical Applications of Xylenol Orange—II. Spectrometric Study of the Zirconium Xylenol Orange Complex.** K. L. CHENG. (17 *January* 1959.)

**Studies on Oxygen Determination in Organic Microanalysis—I. A Modified Purification Method for Nitrogen Gas.** SATOSHI MIZUKAMI, TADAYOSHI IEKI and KAZUE NUMOTO. (26 *January* 1959.)

**Studies on Oxygen Determination in Organic Microanalysis—II. The Microanalysis of Oxygen by the Decrease in the Quantity of Anhydroiodic Acid.** SATOSHI MIZUKAMI and TADAYOSHI IEKI. (26 *January* 1959.)

**Direkte komplexometrische Eisenbestimmung mit Xylenolorange als Indikator.** F. VYDRA, R. PŘIBIL und J. KORBL. (27 *January* 1959.)

**Metalfluorechromic Indicators.** D. H. WILKINS. (28 *January* 1959.)

**The Determination of Conductivities using Unconventional Electrode Systems.** V. S. GRIFFITHS. (27 *January* 1959.)

**On the Heterolytic and Homolytic Dissociation of Bromine Chloride and on the Determination of the Bromine Formed during Homolytic Dissociation.** E. SCHULEK and K. BURGER. (9 *February* 1959.)

**The Detection of Carbon in Spot Test Analysis.** ALCIDES CALDAS and VICENTE GENTIL. (18 *February* 1959.)

**The Determination of vic-Dioximes.** CHARLES V. BANKS and JOHN J. RICHARD. (25 *February* 1959.)

**The Effect of Absorbancy upon Raman Intensities in Solution.** FREDERICK VRATNY and ROBERT B. FISCHER. (4 *March* 1959.)

**Spectrophotometric Determination of Palladium with Thiomalic Acid.** VERNON L. WAGNER, Jr. and JOHN H. YOE. (27 *February* 1959.)

**Benzidine and Derivatives in Analytical Chemistry.** S. J. LYLE. (5 *March* 1959.)

**Spectrophotometric Determination of Ruthenium with N:N′-bis-(3-Dimethylaminopropyl)-dithiooxamide.** WILLIAM D. JACOBS and JOHN H. YOE. (10 *March* 1959.)

**Spectrophotometric Determination of Rhodium with Thiomalic Acid and the Simultaneous Determination of Rhodium and Palladium.** VERNON L. WAGNER, Jr. and JOHN H. YOE. (12 *March* 1959.)

**A Transistorised Drop-Counter for Chromatographic Use.** G. GEERINCK and J. HOSTE. (13 *March* 1959.)

**Le Séparation Niobium-Tantale en Milieu Chloro-Oxalique sur Echangeur D'Anions.** A. SPEESKE and J. HOSTE. (13 *March* 1959).

**Direct-Reading Current Integrator for Coulometric Analysis.** SHIGEKI HANAMURA. (13 *March* 1959.)

**A Critical Evaluation of Spectrographic, Fluorescent X-Ray and Polarographic Methods for the Determination of the Platinum Metals.** F. E. BEAMISH. (13 *March* 1959.)

**Co-ordination of the NO Group in Hexa-co-ordinated Iron Compounds.** D. J. MORGAN. (18 *March* 1959.)

**Rapid Method for Coulometric Analysis using an I-Q Recorder.** SHIGEKI HANAMURA. (19 *March* 1959.)

# NOTES FOR CONTRIBUTORS

## 1. General

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

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

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

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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

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

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