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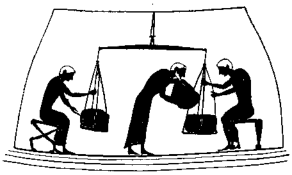

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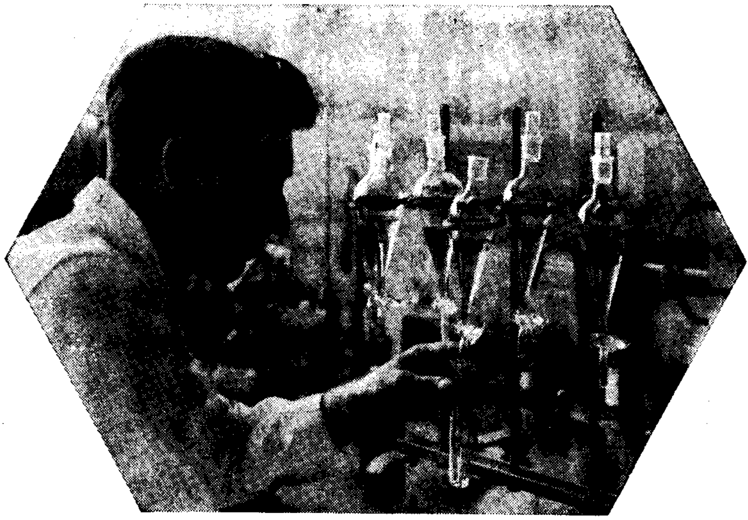

*Items of interest from our laboratory notebooks*

- Most analysts know about 1:10-phenanthroline and many use it for iron determinations. Not so many people seem to know that **4:7-diphenyl-1:10-phenanthroline** is twice as sensitive as 1:10-phenanthroline in the colorimetric determination of iron. There are several papers on the subject but the latest is *Analyst*, 1958, **83**, 80. The reagent is also called **Bathophenanthroline**, and we make it.
- Then, again the substitution of methyl groups in the 2:9 positions has the interesting effect of making the reagent insensitive to iron and we then have a selective and sensitive reagent for copper (see *Anal. Chem.*, 1956, **28**, 1158). Hopkin & Williams make **2:9-dimethyl-1:10-phenanthroline** (sometimes called **Neocuproin**).
- One does not think of sulphate as a radical one can determine absorptiometrically, but this is now possible for low concentrations. **Barium chloranilate** is the reagent and there are two papers on the subject—*Anal. Chem.*, 1957, **29**, 281 and *Anal. Chem.*, 1958, **30**, 202. Hopkin & Williams make it.
- Hopkin & Williams Ltd. were also early off the mark with supplies of the remarkable new colour-producing reagent for fluoride ions, **3-aminomethylalizarin-NN-diacetic acid**, described by Belcher, Leonard and West (*Talanta*, 1959, **2**, 92.) This important reagent is already available from stock.

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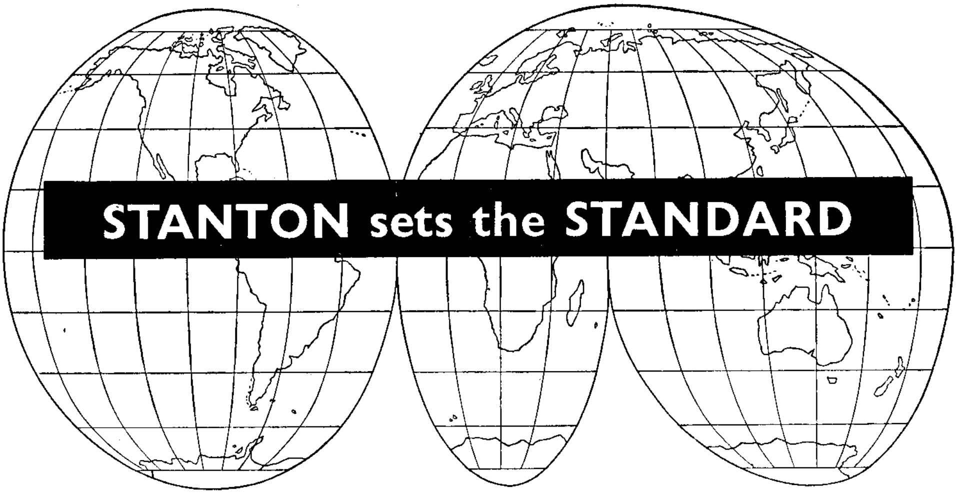

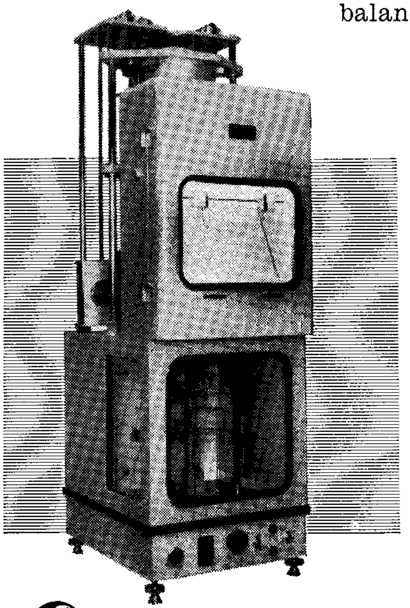

Talanta, 1960, Vol. 3, pp. 219 to 231. Pergamon Press Ltd. Printed in Northern Ireland

# A CRITICAL STUDY OF THE PRECIPITATION OF AMMONIUM PHOSPHO-12-MOLYBDATE

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(*Received* 29 *May* 1959: *Revised paper received* 13 *October* 1959)

**Summary**—The precipitation of yellow ammonium phospho-12-molybdate is used as a quantitative measure as well as a separative procedure for phosphorus. The procedure is subject to a number of errors. This paper describes the history of the recognition of some of them, and reports critical experiments involving some chemical variables not previously investigated. The precipitation is discussed with respect to the physico-chemical properties of molybdic oxide and phosphomolybdic acid, and a set of best conditions for the determination of phosphorus are described. The precipitation is not regarded as suitable for the most precise work, but may be used as a preliminary separation before weighing a substance of greater chemical integrity.

## INTRODUCTION

AMMONIUM phosphomolybdate is a material which has been of considerable interest to chemists since the time of Berzelius. It, its parent acid, and its related arsenic derivative have possessed importance in analytical chemistry for over a century, with regard to the precipitation of phosphates and arsenates. Although the precipitation and weighing of phosphorus as magnesium pyrophosphate is widely regarded as the best procedure available, it is not always thought attractive, and precipitation of phosphate in the form of phosphomolybdate is used in the interest of greater speed. This latter method is fraught with error: this paper attempts to review sources of such error, and to describe experimental evidence for conditions under which many of them may be eliminated.

When solutions containing alkali molybdates or alkali tungstates are mixed with solutions containing alkali phosphates or alkali arsenates, and the solutions are acidified, numerous substances may be crystallised out which have the general composition $wR_2O \cdot xP_2O_5 \cdot yXO_3 \cdot zH_2O$, where R represents an equivalent of a base and X is either a molybdenum or a tungsten atom. A large number of such substances has been reported, and it is noteworthy that the ratio of *e.g.* P : Mo in these materials never falls below 1 : 12.[1] However, the stability of many of these materials in solution has not been investigated; indeed, some are incapable of recrystallisation. Since such substances have frequently been formed by the mixing of the components in the right quantities and crystallising, it seems unlikely that the great majority of these reported substances represent compounds. On the other hand, those salts and acids in which the ratio P : Mo is 1 : 9 or 1 : 12 are capable of recrystallisation, and of repeated extraction with organic solvents without change in composition, and here there is definite evidence for complex formation.[2] Further, even when the actual ratio of P : Mo in solution is less than 1 : 12, the substances which separate after the addition of acid contain phosphorus and molybdenum in the ratio 1 : 12 or greater.

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The well-known yellow precipitate which is formed when phosphate is tested for with ammonium molybdate solution has, according to Hundeshagen,[3] the composition $(NH_4)_3 \cdot PO_4 \cdot 12MoO_3$, but this has recently been disputed by Thistlethwaite,[4] who described conditions under which yellow precipitates of like appearance but of varying composition may be obtained. The composition of this precipitate has been studied by a number of workers, but the remarkable fact remains that only Hundeshagen[3] and Thistlethwaite[4] have attempted a fully systematic study of the effect of varying the conditions of formation upon the composition. The other workers have concerned themselves with individual facets of the problem, particularly from the standpoint of the quantitative removal of phosphorus from solution, as an analytical method. The above formula represents the composition of the precipitate obtained under certain rigorously controlled conditions; this has been confirmed by Riegler[5] and also by Clarens,[6] both of whom also noted that although the ratio P : Mo in the solid remains constant at 1 : 12, the content of the base may vary, depending upon the conditions, from zero to three equivalents per phosphorus atom. On the other hand, Lagers[7] and Hissinck and van der Wearden[8] quoted formulae which contained a little more molybdic oxide, namely $(NH_4)_3PO_4 \cdot 12{\cdot}65MoO_3$. Richardson[9] supported Hundeshagen's original formula, with miscellaneous errors up to 1·2%, as also did Thistlethwaite.[4] Recently Stockdale[10] has given the formula of the fresh precipitate as $(NH_4)_2PO_4 \cdot 12MoO_3 \cdot H_2O$. The results obtained by workers in earlier days before the 1 : 12 ratio for the P : Mo ratio in the compound was accepted are shown in Table I.

From the above reports, it can be seen that a number of variables affect the composition. If the temperature at which precipitation is carried out is too high, it will cause some precipitation of molybdic oxide with the yellow precipitate, creating a higher ratio of P : Mo than is required by the Hundeshagen formula. This, incidentally, would destroy the efficiency of the use of the titrimetric method for the determination of phosphorus, which depends on a constancy of the composition of the yellow precipitate. The temperature range 40°–60° for the precipitation is recommended in order to avoid this error by Baxter,[11] Kilgore,[12] Baxter and Griffin,[13] Chesneau,[14] Hissinck and van der Waerden,[8] Artman,[15] Lagers[7] and Taylor and Miller.[16]

Frey[17] states that if precipitation is carried out below 65°, an ammonium phospho-9-molybdate is precipitated, whereas if the temperature is higher than 65°, ammonium phospho-12-molybdate is formed. He suggested dissolution and reprecipitation to obtain more consistent results. Thistlethwaite[4] has studied the effect of changing the temperature at which precipitation is effected, and the influence of the concentrations of the reactants upon the composition of the precipitate. Unfortunately, he did not always analyse weighed portions of the precipitate, apparently because of the hygroscopic nature of his preparation. His analyses are therefore restricted to the determination of the molar ratios of the components; the mean value of the ratios he obtained for $NH_4$ : P : Mo was 1 : 1 : 12, and he therefore gave ammonium phosphomolybdate the formula $(NH_4)H_2PO_4 \cdot 12MoO_3$. It is particularly evident from his work that physical variables such as time and the rate of stirring have an important effect on the composition of the precipitate; other workers have noted this type of effect, and many have given specific times for stirring.

It is also evident that the chemical conditions laid down for the precipitation of ammonium phosphomolybdate are very largely empirical. Thus, if a considerable excess of molybdenum and strong mineral acid is present in the reaction mixture, substances of approximate composition "1 : 12" are always obtained, but if weak acids such as acetic acid are used, then substances with a higher ratio of phosphorus to molybdenum are formed, which have a different colour. These may be other heteropoly acids, and may also have suffered some reduction. It is almost certainly true that the 1 : 12 compound cannot be formed under these conditions, since its precursors are not present at the high pH due to acetic acid.[2] Sulphuric acid is rarely used in this preparation, since it has a peculiar action on molybdic acid, alleged by Falk and Suguira[18] to be due to the formation of a sulphomolybdate. This is supposed by them to be precipitated with the yellow precipitate, thus leading to large positive errors in analysis, as noted by Gregersen,[19] Wardlaw,[20] Neumann,[21] Hissinck and van der Waerden,[8] Richardson[9] and Artman.[15] Stockdale[10] notes the same error, but ascribes it to co-precipitated $MoO_3$. However, a reagent containing sulphate has been recommended[22] and has enjoyed some popularity. Hydrochloric acid may be used, but there is the danger of dissolution of the molybdic oxide[23] as well as the slight chance of

TABLE I.—THE DEVELOPMENT OF THE PRESENT ACCEPTED FORMULA FOR AMMONIUM PHOSPHOMOLYBDATE

| Author | Reference | Formula and analytical data | | | | |
|---|---|---|---|---|---|---|
| | | $\%MoO_3$ | $\%P_2O_5$ | $\%NH_4$ | $\%H_2O$ | Notes |
| Sonnenschein | *J. prakt Chem.*, **53**, 342 | 85·42 | 3·12 | 11·40 | | (dried at 120°C) |
| | | 86·70 | 3·20 | 11·23 | | |
| | | 86·11 | 2·93 | 10·91 | | |
| Seligsohn | *J. prakt. Chem.*, **67**, 470 | 90·74 | 3·14 | 3·57 | 2·55 | (dried at 100°C) |
| Eggertz | *J. prakt. Chem.*, **79**, 496 | 91·28 | 3·74 | 3·31 | 1·32 | |
| Debray | *Compt. Rend.* **66**, 704 | Formula given as $20MoO_3 \cdot P_2O_5 \cdot 3(NH_4)_2O \cdot 3H_2O$; no figures | | | | |
| Rammelsberg | *Monatsber. der Akad.* 1877, 573 | $22MoO_3 \cdot P_2O_5 \cdot 3(NH_4)_2O \cdot 12H_2O$ | | | | |
| | | (calc.) 86·04 | 3·86 | 4·24 | 5·86 | |
| | | (obs.) 86·70 | 3·91 | | 5·63 | (dried at room temperature) |
| | | 86·21 | 3·86 | 4·25 | 5·91 | |
| | | 86·68 | 3·92 | | 5·77 | |
| Finkener | *Ber.*, 1883, **11**, 1638 | Gives ratio of Mo : P as 12 : 1, with 2–3 molecules of $NH_3$ per "$PO_4 \cdot 12MoO_3$" radical | | | | |
| Gibbs | *Amer. Chem. J.*, **3**, 317, 402 | 89·00 | 3·75 | 3·39 | 3·86 | |
| | | 87·21 | 3·86 | 8·93 | | |
| | | 89·21 | 4·25 | 4·12 | 2·54 | |
| Hundeshagen | *Z. analyt. Chem.*, 1883, **28**, 141 | Formula given as $(NH_4)_3 \cdot PO_4 \cdot 12MoO_3 \cdot H_2O$ or as $(NH_4)_3 \cdot PO_4 \cdot 12MoO_3 \cdot 2HCl \cdot H_2O$; no figures | | | | |

Where suitable data were recorded in these papers, the original results were recomputed using modern atomic weights.

reduction of the oxide. For these reasons, nitric acid is generally used for the acidification, but too great an excess must not be present, since, as Hundeshagen[3] observed, it will prevent the complete precipitation. With regard to the question of mineral acid-molybdic oxide interactions, Cannon[23] has recently shown that the solubility of molybdic oxide in nitric acid first increases with nitric acid concentration, and then drops to zero. This effect is very important in the present case, where a small excess of nitric acid (greater than $0{\cdot}1N$) will upset the quantitative nature of the precipitation unless a neutral salt be present. Ammonium nitrate is used for this purpose, and in order to promote the formation of an easily filtrable precipitate, but if too much be present, the precipitate dissolves in the solution of the salt and molybdic oxide is precipitated from the reagent solution. Stockdale[10] has minimized this effect in his commentary, with respect to added ammonium nitrate, but it is evident from his data that an increase of free acid in the mixture must be accompanied by an increase in the amount of precipitant (which contains free ammonia) in order to maintain complete precipitation.

The order of mixing the reagents is important, since if the molybdate solution be added to the acidified phosphate solution, the precipitate is (in the present work) formed as very small particles, and is rather hygroscopic after heating in the oven. This effect, which may be due to the occlusion of phosphate ions within the precipitate, or to a simple surface-area effect, may largely be avoided by adding the phosphate solution to the molybdate.

In addition to the highly critical conditions of formation, the manipulation and analysis of the solid obtained are also likely to introduce errors into the empirical formula. Firstly, the precipitate must be freed of its mother liquor. This cannot be accomplished using either water or dilute nitric acid solution alone, since the substance has a small but definite solubility,[14] and is in addition hydrolytically unstable.

A slightly acid, dilute solution of ammonium nitrate (0·8 % $NH_4NO_3$ in 0·8 % $HNO_3$ according to Thistlethwaite[4]) is preferred for this washing; if this solution is used, then the last traces of ammonium nitrate must be removed by heating. In this heating the water and nitric acid which were alleged by Hundeshagen[3] to be present in the air-dried substances are lost, producing a more or less hygroscopic body which is difficult to weigh. Stockdale[10] has proposed the use of a 2% nitric acid solution saturated with ammonium phosphomolybdate. Von Endredy[24] avoided this difficulty by washing the precipitate with anhydrous acetone, and then drying it in an air stream. Under these conditions, however, he found that the composition was not expressed by the formula $(NH_4)_3PO_4{\cdot}12MoO_3$, but that the solid still contained a little water. Drying under vacuum appears to have the same effect as heating, but it does not remove the water as quickly.[3]

For the determination of phosphorus, as a complete alternative to weighing the precipitate, the precipitate may be dissolved in a known amount of sodium hydroxide solution and the excess back-titrated with hydrochloric acid. This technique was used by a number of workers, among them Thilo,[25] and Pemberton Jr.,[26] all of whom standardised the method with a sample containing a known quantity of phosphorus. There is a complication here in that if phenolphthalein be used to indicate the end-point of the titration, the quantity of ammonia present (which has previously been noted to be variable) effects the end-point. Workers who subsequently recognised this difficulty and attempted to remove the ammonia, were Neumann,[21] who evaporated the alkaline solution, and Bang,[27] who used formaldehyde to form hexamine with the ammonia. Stockdale[10] has suggested a similar technique with a parallel titration of paramolybdate, but he did not consider the complicating effect of the phosphorus, which causes a "delay"[2] in the titration curve due to re-formation of the complex phosphomolybdate.

In spite of the established use of the formation of the yellow precipitate in the determination of phosphorus, there exist unresolved differences in individual reports. The differences in the formulae ascribed to the substance from time to time are most certainly partly due to improvements in analytical technique (compare the earlier results in Table I) but there is the need for systematic investigation of the formation of ammonium phosphomolybdate under various conditions, leading to the possible establishment of analytical methods which are exact and rapid, and which are based on a technique of some chemical integrity. Accordingly, an attempt has been made here to ascertain the conditions under which a precipitate of constant composition might be obtained. The principal conditions studied were:

(*a*) the effect of the concentration of nitric acid.

(*b*) the effect of temperature.

(*c*) the effect of the concentration of ammonium nitrate.

(*d*) the effect of the time for which the precipitate was allowed to stand before being removed from the solution.

(*e*) the relative values of various methods for drying the substance.

The effect of the time and rate of stirring was eliminated in this work, by not stirring the solution at all, and relying on convection currents in the mixture to effect mixing. This was thought justifiable in view of the great difficulties in defining what is meant by stirring *e.g.* with an unspecified glass rod for a given period of time.

## EXPERIMENTAL

### (*i*) *Chemicals and apparatus*

All chemicals used were of analytical reagent quality, particular care and attention being paid to procuring reagents which were free of arsenic and spurious phosphorus.

It was found necessary to use new hard glass apparatus for all the precipitations. This was pretreated by steaming out for several hours. Attempts to perform successive precipitations in the same glassware led to erroneous results, apparently due to the formation of sites of easy attack on the glass by the acid molybdate reagent.

Weighings were performed on a specially adjusted undamped Stanton Instruments balance with a seventy-second period, using weights calibrated against a National Physical Laboratory Class A master set.

### (*ii*) *The quantitative precipitation*

In the introduction it was seen that although the precipitation of ammonium phosphomolybdate might be used for the determination of phosphorus, the results were not always consistent, the variations in them being due either to incomplete precipitation or to the formation of a precipitate of inconstant composition, depending on the conditions under which the precipitation was carried out.

In order to gain first-hand knowledge of the accuracy of the determination, precipitations were carried out in accordance with the conditions set out by Hillebrand and Lundell,[28] by Scott and Furman[29] and by Mellor.[30] The cited method of preparation of the molybdate reagent solution was in each case examined to determine the excess hydrogen ion and neutral salt concentrations. It was thus determined that the condition of the reagent was essentially that of a supersaturated solution of molybdic oxide in nitric acid.[31] The concentrations of the various components of the precipitating systems are set out in Table II, together with the weights of precipitate obtained from the same quantity of phosphorus. The variations in the weight of precipitate obtained made it necessary to analyze the prepared samples for their various components. When this was done, and the precise contents of Mo, P and $NH_3$ known, it was apparent that all three techniques resulted in the formation of precipitates of so nearly equivalent a composition that the difference in weights could not be accounted for on the basis of differences in composition (the analysis for Mo was done gravimetrically using oxine,[4] for phosphorus using the magnesium pyrophosphate technique, and for ammonia by a conductometric titration).

TABLE II.—RESULTS OBTAINED IN THE PRECIPITATION OF AMMONIUM PHOSPHOMOLYBDATE, BY THE PROCEDURES OUTLINED BELOW

(The solution from which the precipitate was obtained was in each case 200 ml in volume.)

| Source | Procedures | Concentrations (*g.mols./l.*) | | | | Weight of ppt., *g* |
|---|---|---|---|---|---|---|
| | | $KH_2PO_4$ | $MoO_3$ | $HNO_3$ | $NH_4NO_3$ | |
| Hillebrand and Lundell[28] | 1. Molybdic acid soln, added to phosphate soln. at 45°.<br>2. Maintained at 45° for 1 hr., then 12 hrs. at 20°.<br>3. Washed with:<br>a. 0·1*M* $NH_4NO_3$ + 0·13*M* $HNO_3$<br>b. 0·15*M* $HNO_3$<br>4. Dried for 2 hrs. at 110°, with additional drying to constant weight for this work | ·007348 | 1·4<br>−2·3 | ·50<br>1·1 | 1·0 | 2·6604<br>2·7139<br>2·7134<br>2·7115<br>2·6810<br>mean 2·6960<br>99·4% of calc. wt. |
| Scott and Furman[29] | 1. Molybdic acid soln. added to phosphate soln. at 45°<br>2. Maintained at 45° for 1 hr.<br>3. as 3. above<br>4. Dried for 2 hrs. at 100°. | ·007348 | ·23 | 0·8 | 0·4 | 2·3640<br>2·3834<br>2·3952<br>2·5364<br>2·3652<br>2·3672<br>mean 2·3734<br>87·5% of calc. wt. |
| Mellor[30] ("alternative procedure") | 1. Molybdic acid soln. added to phosphate soln. at 20°.<br>2. Mixture brought to 60° and allowed to cool for 12 hrs.<br>3. as 3. above<br>4. as 4., Hillebrand and Lundell. | ·007348 | ·05 | 0·8 | 0·2 | 2·5230<br>2·3036<br>2·4876<br>2·6013<br>mean 2·4789<br>91·4% of calc. wt. |

The weight of yellow precipitate which would be obtained from 200 ml 0·007348*M* $KH_2PO_4$ solution were the formula of the yellow precipitate, $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3$, is 2·713 gms.

*(iii) The precipitation of ammonium phosphomolybdate under various conditions*

The method used for the preparation of ammonium phosphomolybdate samples under various conditions was as follows: 50 ml of a molybdate solution were placed in a beaker, and the required amount of excess nitric acid added. The volume was made up to 100 ml, the required amount of excess ammonium nitrate solid added, and the mixture brought to the required temperature on a water-bath. Fifty ml of a solution of potassium dihydrogen phosphate of known concentration were then added from a burette over a period of fifteen minutes. The mixture was maintained at the required temperature for a definite time (usually one hour) and allowed to cool before filtering the suspension through a weighed sintered glass crucible, porosity no. 4 ("fine"). The residue was washed on the filter with an acid ammonium nitrate solution, 0·15$M$ $NH_4NO_3$ and 0·10$M$ $HNO_3$, and finally with 0·13$M$ ammonium nitrate solution at 0°. The crucible and its contents were then dried at 130° to constant weight. The stock molybdate reagent solution was an acid solution of ammonium heptamolybdate in nitric acid, 35 g of ammonium heptamolybdate being dissolved in a mixture of 50 ml of water and 50 ml of ammonia solution, S.G.O. 880, this solution then being poured into 350 ml of a solution containing 168 ml of nitric acid, S.G. 1·42. The mixture was made up to 800 ml and filtered before use.

TABLE III.

| Conditions | Final wt. as a percentage of that calculated for the formula $(NH_4)_3PO_4 \cdot 12MoO_3$. |
|---|---|
| At room temperature in a desiccator containing $CaCl_2$ and KOH, for one month | 101·2<br>102·1 |
| 130° for 15 hrs. | 99·8<br>100·8 |

Ammonium phosphomolybdate samples prepared at 60°, from such a solution 1·8$M$ with respect to nitric acid and 0·1$M$ with respect to ammonium nitrate were dried under different conditions. Twenty-four hours were allowed for the solution to cool and the precipitation to complete itself. The results are presented in Table III.

The general influence of temperature upon the extent of precipitation was studied with a set of solutions containing the following concentrations of reactants: 0·083$M$ $MoO_3$, 0·15$M$ $NH_4NO_3$, 1·54$M$ $HNO_3$, ·001471$M$ $KH_2PO_4$. The precipitate weights and the molybdenum content of the various preparations are shown in Fig. 1 as a function of temperature. The results show a trend which agrees with that observed by Thistlethwaite,[4] but the effect of temperature on precipitate weight was much more marked in the present case.

It was found in this work that there was a strong correlation between the ratio Mo : P in solution and the final weight of the precipitate, even when the ratio Mo : P was very large (in excess of 30 : 1). Since this is one of the major results of Thistlethwaite's study,[4] there is little point in recording the present experimental observations. It is however worthwhile to note that the extreme effect of changing the ratio Mo : P from 56 : 1 (as above) to 63 : 1, and maintaining all other conditions constant, leads to a statistically significant (eight replicates) decrease in precipitate weight, from 102·3% of theoretical to 100·6%, at 60°.

The effects of changes in the nitric acid and ammonium nitrate concentration upon the precipitation are shown on Figs. 2 and 3. In these experiments, the solution was brought to 40° for one hour and allowed to stand 24 hr before filtering. The concentration of nitric acid present in the precipitating solutions had a profound effect on the observed weight of the precipitate. It was found that precipitation was not nearly quantitative with respect to the phosphate present if the concentration of the nitric acid was greater than 2·7$M$. However, when the filtrates from these latter experiments were diluted with neutral ammonium nitrate to bring the nitric acid concentration to 1$M$, and heated for one hour at 45°, a further precipitate of ammonium phosphomolybdate appeared, the weights of the combined precipitates being within 1% of that calculated on the basis of the formula $(NH_4)_3PO_4 \cdot 12MoO_3$.

The effect of length of time of standing on precipitate weight is shown in Table IV.

### (iv) *Analysis of the precipitate for its components*

The molybdenum contents of the preparations were determined by the oxine method,[4] which proved to be entirely satisfactory. It was found to be possible to determine ammonia by the hypobromite reagent, but it is necessary to distil the ammonia from the precipitate before its determination,

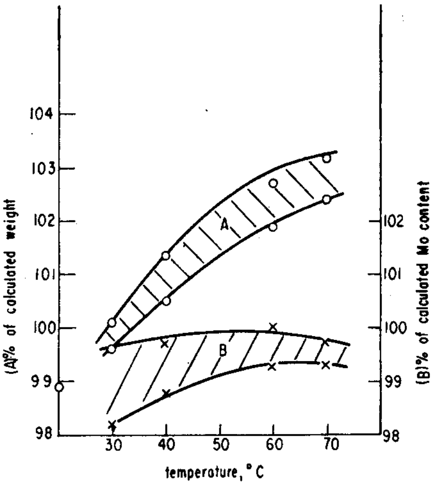

FIG. 1.—Effect of temperature upon the weight of precipitate recovered from a mixture of solutions 0·083$M$ $MoO_3$ 0·15$M$ $NH_4NO_3$, 1·54$M$ $HNO_3$ and 0·001471$M$ $KH_2PO_4$.

The precipitating medium was held at a temperature of x° for one hour, and then set aside for 24 hours at room temperature (*ca* 16°). The calculated weight is 100% for a quantitative yield of $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3$ with respect to the phosphorus in the system. The Mo content according to this formula is 61·36%.

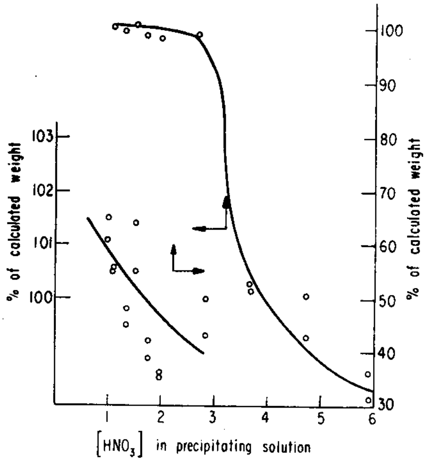

FIG. 2.—Effect of nitric acid concentration upon the weight of precipitate recovered from a mixture of solutions 0·083$M$ $MoO_3$, 0·12$M$ $NM_4NO_3$, ·001471$M$ $KH_2PO_4$ and x$M$ $HNO_3$.

Precipitation conditions: 40° for one hour, then set aside for 24 hours at room temperature (*ca.* 16°). The calculated weight is 100% for quantitative yield of $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3$ with respect to the phosphorus in the system.

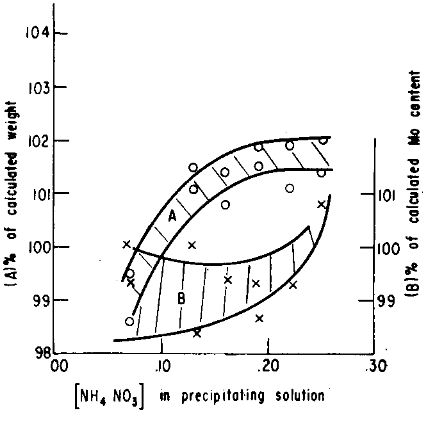

FIG. 3.—Effect of ammonium nitrate concentration upon the weight of precipitate recovered from a mixture of solutions 0·083$M$ $MoO_3$, 1·00$M$ $HNO_3$, ·001471$M$ $KH_2PO_4$ and x$M$ $NH_4NO_3$.

Precipitation conditions: 40° for one hour, then set aside for 24 hours at room temperature (*ca.* 16°). The calculated weight is 100% for a quantitative yield of $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3$ with respect to the phosphorus in the system. The Mo content according to this formula is 61·36%.

in order to use this technique, and consequently a direct conductometric titration method was developed. This was accomplished by back titration with acid of a solution of the precipitate in $CO_2$-free alkali. No exact systematic variation in the ammonia content of the precipitate was discovered, though smaller values were more frequently detected in the precipitates formed from highly acid media. The range of values found was between 0·03% and 3·73%: the most frequently occurring values were between 1·80% and 2·00%, corresponding approximately with the formula $(NH_4)_2HPO_4 \cdot 12MoO_3$, in agreement with Stockdale.[10] The average value was 2·42%.

In all the experiments, save those performed in solutions containing a large concentration of nitric acid, there was found to be no phosphate remaining in solution, after precipitation had taken place. The precise amount of phosphate present in the precipitate was in most cases in these experiments therefore taken to be the amount initially introduced into the precipitating solution.

TABLE IV.—THE VARIATION IN THE WEIGHT OF THE PRECIPITATE AND THE MOLYBDENUM CONTENT OF THE PRECIPITATE WITH THE LENGTH OF TIME THE MIXTURE WAS ALLOWED TO STAND BEFORE FILTRATION.

| Time, *hrs.* | % calculated wt. | %Mo |
|---|---|---|
| 1 | 92·4<br>96·1 | 59·8 |
| 24 | 98·9<br>99·5 | 59·8 |
| 72 | 99·2<br>100·0 | 60·5 |

(These precipitations were performed at 50°. The percentage of molybdenum according to the formula $(NH_4)_3 \cdot PO_4 \cdot 12MoO_3$, is 61·36. The per cent calculated weight is based on a quantitative recovery of precipitate of the above composition with respect to the phosphorus present).

### (*v*) *Back titration of solutions of ammonium phosphomolybdate in alkali*

This technique is fairly commonly employed as an alternative to weighing the precipitate. It is subject to errors introduced by varying the concentration of molybdenum in the system, and by the loss of ammonia to the atmosphere.

In this investigation, care was taken to reduce ammonia loss to a minimum by avoiding procedures such as boiling with alkali to effect dissolution of the precipitate, and the solutions which were prepared contained only small concentrations of ammonia (of the order 0·01*M*). The precipitate itself was dissolved in sodium hydroxide solution in such a manner that the pH of the solution was never higher than 11·4. Stirring was effected by a stream of purified nitrogen, and the precipitate was completely dissolved in ten minutes. In a blank experiment in which nitrogen was passed through a solution of 0·015*M* ammonium chloride, to which had been added sufficient sodium hydroxide to bring the pH of the solution to 11·4, it was found that a loss of 1·5% of the ammonia initially present occurred in ten minutes. By using a lower concentration of ammonium salt, a still lower loss would be observed. In spite of these precautions, and even when the back titrations were done potentiometrically and the results plotted differentially, it was found that the inflexions in the curves were so indistinct, at the low concentrations necessary to avoid the confusing effects due to neutral salt formation,[31] that the technique gave results which were useless for determining phosphorus to within ±10%. It is thus unlikely that this technique is of any great utility for precise work unless an arbitrary conversion factor is used.

## DISCUSSION

### (*i*) *Standard methods*

The somewhat elaborate directions cited in the literature and in texts for the preparation of the molybdate reagent appear to be designed to avoid spurious precipitation of molybdic oxide during the precipitation process. Depending on the molarity of the solution with respect to nitric acid, the molybdenum is present either as a polymolybdate[31] or a basic molybdenyl nitrate.[23] Whichever of these cases obtains in the present situation, the reagent is such that it is supersaturated with respect to molybdic oxide, since it will on standing spontaneously deposit the yellow dihydrate of molybdic oxide. Bearing this in mind and remembering the importance of the neutral salt and free acid concentrations to the precipitation, it might be quite reasonable to regard the precipitation basically as a salting-out process. It certainly is not directly comparable with any normal metathetical reaction.

The cited standard procedures give rather different results, but a trend towards a more reproducible, quantitative precipitation is seen with an increase in the Mo : P ratio in the initial system. The presence of a large excess of ammonium nitrate appears to aid the reproducibility of the precipitation, as measured by the weight of the dried precipitate. It appears that the best method is that which combines the longest time of heating, the longest time of standing, the largest excess of molybdate and ammonium nitrate in solution.

### *(ii) Experiments under deliberately varied conditions*

The effect of high nitric acid concentration in inhibiting complete precipitation appears to be due to the solubility of the precipitate in that acid. Thus, it was shown that on diluting the filtrate from highly acid precipitation media, more precipitation occurred, proceeding quantitatively to the limit of the earlier observed deficiency. The fact that the precipitate from highly acid systems is of a slightly variable composition with respect to molybdic oxide is explicable on the basis of a certain enhancement of the basic function of molybdic oxide in nitric acid.

The overall effect of an increase in the concentration of ammonium nitrate was to cause an increase in the total quantity of molybdenum associated with the precipitate, although the actual molybdenum content did not increase all the time. The precipitate was found to contain traces of nitrate when precipitated from solution containing $0{\cdot}25M$ $NH_4NO_3$.

If the precipitation functions by some salting-out mechanism, it is not surprising that the length of time which the precipitate is allowed to stand in contact with its mother liquor has an effect on the observed weight of the precipitate. In Table IV, it was shown that there is a certain minimum time for which the precipitate must be allowed to stand, if the precipitation is to be quantitative with respect to the phosphate present; if, however, the mixture is allowed to stand indefinitely, the molybdate reagent itself deposits molybdic oxide, and thereby upsets the accuracy of any analysis based on the precipitation. The general effect of temperature also involves the question of the stability of the reagent, which is also subject to ageing. However, the temperature must be maintained at least at 40°, since the precipitation will not be quantitative with respect to the phosphate present within a reasonable length of time at lower temperatures. Increase in the temperature appears to produce a slightly greater quantity of the precipitate under otherwise constant conditions, and associated with this increase, there is an increase in the molybdenum content of the precipitate, which may be due to the presence of molybdic oxide.

### *(iii) The properties of phospho-*12*-molybdic acid and the precipitation of ammonium phosphomolybdate*

Phosphomolybdates are formed when solutions containing phosphates and molybdates are acidified, or via the direct reaction between phosphoric acid and molybdic acid. By both methods, solutions are obtained which will furnish crystals of phospho-12-molybdic acid. This substance is readily extracted from cold, acidified solutions, by the use of ether, and this in itself demonstrates that the ratio 1 : 12 for phosphate : molybdate in this material marks a definite extent of combination.

It might be expected that since this substance contains a large proportion of molybdic oxide, the basic function of molybdic oxide would be manifested in strongly acid solutions of phospho-12-molybdic acid. This is not quite the case, since phospho-12-molybdic acid is not completely soluble, even in the most concentrated hydrochloric acid. It was also found that the addition of a quantity of similarly concentrated nitric acid to a saturated aqueous solution of phospho-12-molybdic acid produced a small precipitate, which analysed as the hydrated phospho-12-molybdic acid. This is important, since the conditions under which ammonium phospho-12-molybdate is formed are such that molybdic oxide is at its greatest solubility in nitric acid, whereas the solubility of phospho-12-molybdic acid has been substantially reduced. The addition of ammonium nitrate to such a solution of phospho-12-molybdic acid in nitric acid may then be expected to cause the salting-out of the sparingly soluble ammonium phospho-12-molybdate, as is indeed the case. The quantitative formation of ammonium phospho-12-molybdate then depends on the behaviour of phospho-12-molybdic acid itself, but is complicated by the presence of a necessary excess of molybdic oxide which may separate spontaneously.

The variation of the ammonia content of the precipitate may be due to either of two causes; the co-precipitation of phospho-12-molybdic acid with ammonium phospho-12-molybdate may occur (providing the hydrogen ion concentration of the solution is sufficient to prevent the degradation of the complex, but not sufficiently great to favor the formation of basic molybdenyl salts), or the base-exchange properties if the precipitate, mentioned by Thistlethwaite,[4] may be in evidence.

### (*iv*) *A recommended procedure*

From the results, it appears that the best conditions that can be observed for the quantitative precipitation of phosphate are that the solution should be about $0{\cdot}0015M$ with respect of phosphate, and also contain the following concentrations of reagents: $0{\cdot}08M$ $MoO_3$, $0{\cdot}1M$ $NH_4NO_3$, and $1{\cdot}5M$ $HNO_3$. The stabilized molybdate reagent should be prepared as described in the present experimental section. Precipitation should be performed in hard glass vessels at 40° for one hour, and the mixture allowed to stand 24 hours before filtering. Washing should be performed using acid ammonium nitrate ($0{\cdot}15M$ $NH_4NO_3$ $0{\cdot}1M$ $HNO_3$, followed by $0{\cdot}1M$ $HNO_3$ at 0°). In order to avoid difficulties with the hygroscopic nature of the oven-dried material, it has been found experimentally that if the phosphate solution is added to the molybdate solution, the precipitate is much less hygroscopic than if the reagents had been mixed in the reverse order. The precipitate should be dried at 130° for at least two hours, and preferably longer. The procedure should always be checked with a phosphate sample of known concentration, in order to make any allowance necessary for the deposition of molybdic oxide from the reagent. If no such allowance is thought necessary, the precipitate formed under the above conditions may be weighed as $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3$ with a standard deviation of less than 0·3 %.

This recommended procedure involves an elapsed time in excess of one day to obtain only semi-exact results, judging from the standard deviation observed. It is appreciated that this prolongs what is normally used as a rapid method, but it could be confined to occasions where the more exact result is required. For the most precise work, it is apparent that this precipitation should only be used as a separative procedure before weighing phosphorus as pyrophosphate.

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**Zusammenfassung**—Die Fällung des gelben Ammoniumphosphomolybdates wird sowohl zur Abtrennung als auch zur Bestimmung von Phosphor verwendet, Die Methode hat einige Fehlerquellen. Die vorliegende Arbeit teilt Geschichte der Entdeckung dieser Fehlermöglichkeiten mit und beschreibt einige kritische Experimente welche Abänderungen betreffen, die bisher nicht in Betracht gezogen wurden. Die Fällung selbst wird von physikalisch-chemischem Standpunkte aus diskutiert soweit es die Eigenschaften der Molybdän- und Phosphomolybdän-säure betrifft. Die bestmöglichen Bedingungen werden beschrieben. Die Fällung wird nicht als bestgeignet erachtet, wenn es sich um höchste Genauigkeit handelt, kann jedoch als Abtrennungsschritt verwendet werden bevor die endgültige Wägung einer günstigeren Wägeform erfolgt.

**Résumé**—La précipitation du phospho-12-molybdate d'ammonium jaune est utilisée comme mesure quantitative aussi bien que comme méthode de séparation pour le phosphore. La méthode est sujette à un grand nombre d'erreurs. Ce papier décrit l'historique de la mise en évidence de certaines d'entre elles et rend compte d'expériences critiques relatives à certaines variables chimiques qui n'avaient pas été étudiées jusqu'à présent. On discute les conditions de précipitation compte tenu des propriétés physico-chimiques de l'acide molybdique et phospho-molybdique et on décrit les conditions les meilleures pour le dosage du phosphore. On ne considère pas la précipitation comme adaptée à un travail très précis, mais elle peut convenir comme séparation préliminaire avant la pesée d'une substance de composition chimique mieux définie.

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# DOSAGE COLORIMETRIQUE DU SOUFRE EN FAIBLES TENEURS DANS LES ACIERS, LES FERS ET COBALTS PURS*

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**Résumé**—La méthode proposée consiste à dégager le soufre sous forme d'acide sulfhydrique et à le faire entrer alors dans la synthèse du bleu de méthylène à partir de diméthyl-para-amino-phénylènediamine. Le bleu de méthylène possède une coloration très intense et relativement stable. Différents modes d'attaque sont proposés suivant la nature du métal. Dans le cas des fers et aciers, on forme d'abord de l'acide sulfhydrique à partir des sulfures par attaque chlorhydrique. On peut alors réduire les formes oxydées du soufre par l'emploi du mélange réducteur des acides iodhydrique et hypophosphoreux. Dans le cas du cobalt, on met en solution dans l'acide nitrique concentré de façon à oxyder en sulfate tout le soufre présent. On en dégage alors $H_2S$ au moyen du mélange réducteur signalé.

## INTRODUCTION

AUCUNE des méthodes classiques de dosage du soufre dans les métaux (combustion et dosage iodométrique, gravimétrie, évolution classique) ne s'est révélée bien adéquate pour la détermination de teneurs de l'ordre de 0,010% dans le cobalt métallique.

C'est dans le cas de ce matériau que la méthode que nous proposons a été mise au point. Sa sensibilité la rend particulièrement intéressante pour le dosage de teneurs de 0,001 à 0,010% S.

Son applicabilité aux aciers et fers purs a été établie par quelques modifications de mode opératoire qui la rendent plus simple et plus rapide encore.

Cette méthode est basée sur la formation de bleu de méthylène à partir de diméthyl p-aminophénylène diamine et d'hydrogène sulfuré, ainsi que l'avaient proposé divers auteurs.[1,2,3]

Ceux-ci préconisent divers milieux absorbants de l'hydrogène sulfuré: soit l'acétate de zinc en milieu acide[1]—soit un mélange d'acétates de zinc et de sodium[2] soit une solution d'hydroxyde de cadmium[3]. Nous avons constaté que les résultats étaient plus exacts lorsqu'on utilise une solution alcaline d'acétate de zinc.

Précisons que le principe de l'attaque réductrice par le mélange $HI + H_3PO_2$ aux fins de libérer $H_2S$ après une mise en solution oxydante rapide a été proposé par Sands[8] et par Heineman et Rahn[9].

## I. DANS LES ACIERS ET FERS PURS

### A. *Principe de la méthode*

Le métal est attaqué par l'acide chlorhydrique concentré et le soufre est ainsi dégagé des sulfures sous forme d'acide sulfhydrique. Celui-ci est fixé dans une solution d'acétate de zinc en milieu sodique.

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Le soufre ainsi fixé entre dans la synthèse du bleu de méthylène à partir de diméthyl para-aminophénylène diamine.[1–3]

On effectue la colorimétrie du bleu de méthylène en milieu acide, à la longueur d'onde de 650 $m\mu$.

Après la fin de la dissolution chlorhydrique, on traite la liqueur d'attaque par un mélange réducteur d'acide iodhydrique et d'acide hypophosphoreux qui libère l'acide sulfhydrique à partir des combinaisons oxydées du soufre.[8,9] Cet acide sulfhydrique peut être recueilli séparément dans une solution absorbante identique à celle citée ci-dessus et entrer à son tour dans la formation de bleu de méthylène.

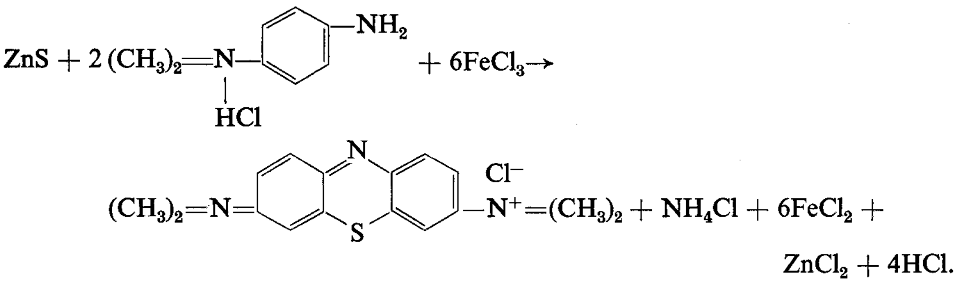
Le principe de la détermination répond aux équations suivantes:

$$MeS + 2HCl \rightarrow MeCl_2 + H_2S \nearrow$$

$$H_2S + Zn(C_2H_3O_2)_2 \rightarrow ZnS + 2C_2H_4O_2$$

$$MeSO_4 + 10HI \rightarrow MeI_2 + 4I_2 + 4H_2O + H_2S \nearrow$$

$$2I_2 + H_3PO_2 + 2H_2O \rightarrow 4HI + H_3PO_4$$



B. *Echantillon*

La sensibilité de la méthode étant telle que la prise d'essai, pour des teneurs habituelles, est de l'ordre de quelques décigrammes, seulement certaines précautions particulières sont à prendre pour l'échantillonnage.

Il est notamment requis de réduire les copaux à une granulométrie telle que la prise d'essai soit représentative du métal analysé. (Nos échantillons passaient entièrement au tarnis No. 35.)

C. *Appareillage*

Les différentes parties de l'appareil sont reliées entre elles par des rôdages normalisés, soit côniques, soit hémisphériques.

L'appareil comprend:

(1) un débitmètre à niveau
(2) un dispositif d'épuration du courant gazeux entraîneur. Celui-ci est composé de deux flacons laveurs, à plaque frittée, munis de 40 cc d'une solution de NaOH à 15%.
(3) un ballon d'attaque (fond plat) à deux tubulures
(4) un dispositif d'introduction sous pression des solutions d'attaque
(5) un réfrigérant à reflux
(6) un flacon laveur rempli de la solution (4); celle-ci est remplacée après chaque utilisation.

Nous avons préféré utiliser comme laveur une solution acide afin d'y réduire la solubilité de $H_2S$. L'acide iodhydrique y maintient un caractère réducteur car on sait que $H_2S$ s'oxyde facilement.

Ces deux dernières parties sont destinées à empêcher la distillation des acides iodhydrique et chlorhydrique jusqu'à l'absorbeur. Sinon, des colorations parasites se produiraient lors de l'addition du réactif organique.

(7) un absorbeur original à grande surface de contact.

La figure 1 représente schématiquement l'appareil.

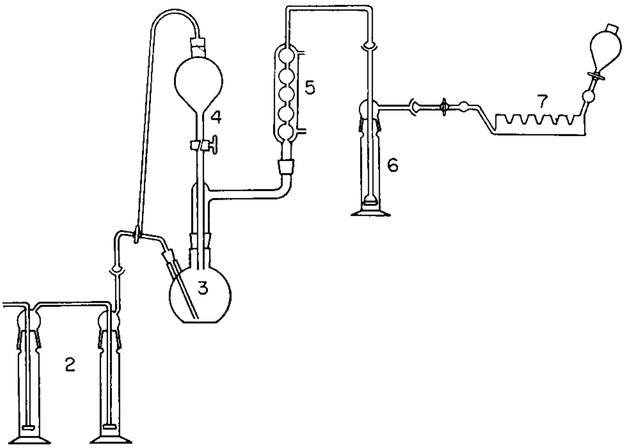


FIG. 1.—Schéma de l'appareil de distillation d'$H_2S$.

D. *Réactifs*

(1) *HCl* densité: 1,19

(2) *Acide formique* (*HCOOH*) 98 %

(3) *Mélange réducteur:* HI densité: 1,70 (56–57 %); $H_3PO_2$ densité: 1,274 (50 %); On mélange 100 cc HI et 25 cc $H_3PO_2$; on fait bouillir ce mélange pendant trois minutes et on garde en flacon bouché, à l'abri de la lumière.

(4) *Solution de lavage:* HCl 0,2 N et HI 0,1 %

(5) *Diméthyl para amino phénylène diamine. 2 HCl:* Dissoudre 0,5 gr dans de l'eau distillée. Ajouter 230 cc d'HCl concentré et amener à 500 cc par de l'eau distillée.

(6) *Solution de chlorure ferrique:* 0,6 à 0,7 gr de $FeCl_3 \cdot 6H_2O$ sont dissous dans 10 cc d'HCl concentré et cette solution est complétée au volume de 100 cc par de l'eau distillée.

(7) *Acétate de zinc* à 1 %: $Zn(C_2H_3O_2)_2$, $2H_2O$: Aciduler par 2 à 3 gouttes d'acide acétique par litre de solution afin d'empêcher le dépôt d'hydroxyde au cours de la conservation

(8) *NaOH:* solution aqueuse à 12 %

(9) *Sulfate de potassium* pour l'étalonnage: dissoudre 271,75 mgr dans 100 cc; reprendre 10 cc et amener à 500 cc par de l'eau distillée (1 cc = 10 $\mu$g S).

*Remarque:* Du fait de la grande sensibilité de la méthode, la pureté des réactifs a une grande influence sur la valeur de l'essai à blanc.

E. *Essai à blanc*

Les mêmes volumes de solution d'attaque et de solution absorbante sont mis en jeu en suivant exactement le même mode opératoire que celui décrit ci-après.

F. *Mode opératoire*

La prise d'essai est choisie de manière à mettre en jeu moins de 120 $\mu$g de S.* Cette prise d'essai est introduite dans le ballon d'attaque. Celui-ci est adapté sur l'appareil de distillation que l'on a préparé de la manière suivante:

Le laveur est rempli de 15 cm³ de la solution (4). L'absorbeur reçoit 2 cm³ de la solution (8) et 50 cm³ de la solution d'absorption (7). On sèche la tubulure d'entrée à l'aide d'une bandelette de papier filtre. Tous les rôdages sont graissés légèrement au moyen de graisse silicone Edwards. On balaye tout l'appareillage par un courant d'azote ou d'hydrogène pendant deux minutes environ. On introduit alors 15 cm³ d'HCl concentré dans l'entonnoir supérieur. On tourne le robinet à trois voies de façon à dériver le courant gazeux par la voie supérieure et on ouvre le robinet mettant en communication l'entonnoir et le ballon d'attaque.

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* Il est naturellement possible, en utilisant des cuvettes plus minces ou en opérant par dilution, de prolonger l'échelle de mesure dans le domaine des quantités de soufre plus importantes. Cependant, la loi de Beer n'étant pas respectée, il serait alors nécessaire de refaire un étalonnage dans les conditions choisies.

Dès que l'acide est complètement écoulé dans le ballon, on rétablit le courant d'azote par la voie normale* et on commence à chauffer le ballon de distillation. Le chauffage est réglé de façon à obtenir une ébullition douce après cinq minutes. Après une demi-heure, on observe, en général, une dissolution complète lorsque la prise d'essai n'est pas supérieure à 0,5 gr et que la granulométrie est suffisamment fine.

On isole alors le barbotteur au moyen de ses deux robinets et on le déconnecte. On y crée une légère dépression au moyen d'une trompe à eau en prenant garde de ne pas laisser aspirer de solution absorbante. Grâce au vide ainsi créé, les diverses solutions de rinçage et d'addition peuvent être introduites très rapidement dans l'absorbeur et sans risque de laisser échapper de l'hydrogène sulfuré.

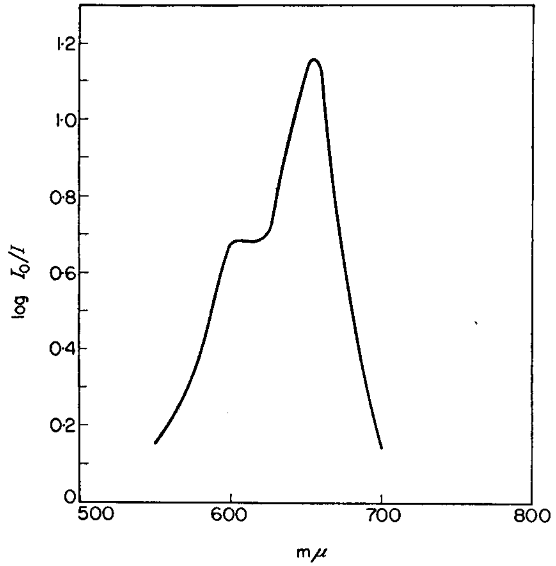

Fig. 2.—Courbe d'absorption du bleu de méthylène de 500 à 700 m$\mu$: Concentration correspondant à 120 $\mu$g de soufre/100 cc. 50 cm$^3$ acétate de zinc à 1 %—2 cm$^3$ NaOH à 12 %—10 cm$^3$ du réactif (5)—2 cm$^3$ de la solution (6).

On introduit, par l'ampoule, 10 cm$^3$ du réactif (5), puis on rince à l'eau distillée la tubulure d'entrée de l'absorbeur. On agite l'absorbeur bien fermé pendant environ une minute puis on y ajoute, par l'ampoule, 2 cm$^3$ de chlorure ferrique, réactif (6). La coloration bleue apparaît assez rapidement et on continue à agiter vigoureusement pendant quelques minutes. L'addition du réactif (5) en solution chlorhydrique a, en effet, redégagé de l'acide sulfhydrique et il faut favoriser par l'agitation le contact entre la solution et la phase gazeuse.

Après une dizaine de minutes, le contenu de l'absorbeur est transféré dans un ballon jaugé de 100 cm$^3$. Les eaux de rinçage de l'absorbeur sont ajoutées et l'ensemble est complété au volume par de l'eau distillée. Il est recommandé de mesurer la densité optique de cette solution dans un délai d'un quart d'heure à une heure après sa formation.

Nous avons effectué la colorimétrie en cuvettes de 2 cm d'épaisseur en utilisant un photomètre Spekker avec le filtre 608 ou en cuvettes d'un cm d'épaisseur avec un spectrophotomètre Beckman B.

La longueur d'onde du maximum d'absorption est assez controversée. G. Patterson Jr.[4] donne ce maximum à 745 m$\mu$ tandis que Roth[6] ainsi que Pomeroy[5] indiquent 670 m$\mu$. La courbe d'absorption que nous avons relevée de 500 à 700 m$\mu$ est donnée dans la figure 2 (120 $\mu$g S/100 cc).

Après la fin de la dissolution chlorhydrique, lorsqu'on enlève l'absorbeur, on peut le remplacer par un second dispositif d'absorption contenant une solution identique.

On ajoute alors, par petites portions, 15 cm$^3$ du mélange réducteur (3) à la liqueur d'attaque tout

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* Le courant entraîneur doit être suffisamment rapide pour obtenir un bon balayage de l'acide sulfhydrique, mais assez lent pour n'occasionner aucun entraînement mécanique important vers l'absorbeur. Pour l'appareil que nous avons utilisé (volume intérieur: environ 300 cm$^3$), un débit de 7 litres/heure s'est révélé satisfaisant.

en maintenant le courant gazeux et le chauffage. On distille pendant 25 à 30 minutes l'acide sulfhydrique formé par réduction des formes oxydées du soufre[8,9] puis on isole le second absorbeur et on y développe la coloration du bleu de méthylène comme plus haut.

## REMARQUES

(a) Lorsque l'appareil est resté quelques heures sans fonctionner, on apercoit, dans le réfrigérant et dans le tube qui le relie au laveur intermédiaire, des gouttelettes brunes provenant de l'oxydation de l'acide iodhydrique condensé sur les parois. Il est nécessaire d'éliminer ces gouttelettes, soit par un rinçage à l'eau, ou mieux en faisant distiller de l'acide iodhydrique pendant quelques minutes, réfrigérant coupé.

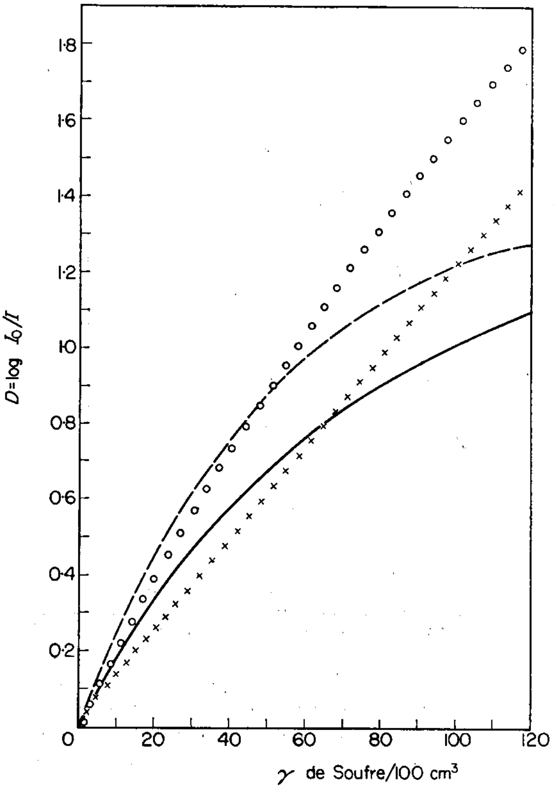

FIG. 3.—Densité optique des solutions de bleu de méthylène en fonction des quantités de soufre mises en oeuvre (en $\mu$g de S/100 cc).

—— bleu de méthylène produit à partir de $H_2S$ distillé
– – – bleu de méthylène pesé et dissous dans l'acétate de zinc et HCl
} courbes d'étalonnage obtenues à l'absorptiomètre Spekker

+ + bleu de méthylène produit à partir de $H_2S$ distillé
○ ○ bleu de méthylène pesé et dissous dans dans l'acétate de zinc et HCl
} courbes d'étalonnage obtenues au spectrophotomètre Beckman B ($\lambda = 655$ m$\mu$)

En effet, le résultat de la première distillation d'une série s'est toujours révélé trop bas et ceci est dû très probablement à l'oxydation de $H_2S$ par l'iode.

(b) Il est signalé dans la littérature[7] que le bleu de méthylène n'obéit pas à la loi de Beer Lambert. La courbe dans la Fig. 3 représente la variation de la densité optique mesurée au spectrophotomètre en utilisant des fentes très étroites ($\simeq$ 2 m$\mu$). La loi de Beer est respectée jusqu'à des concentrations d'environ 100 $\mu$g de soufre/100 cc. Au-delà de cette concentration on observe des écarts relativement importants qui sont dus à des réactions secondaires avec le solvant, réactions qui varient donc avec la dilution.

Cependant, la Fig. 3 montre également que la densité optique des solutions de bleu de méthylène produit à partir de $H_2S$ distillé est inférieure à celle des solutions de bleu de méthylène pesé et dissous dans le même milieu. Ceci provient de ce que la réaction de production du bleu de méthylène à partir de $H_2S$ est limitée à un équilibre. (Après un quart d'heure d'agitation, lorsqu'on ouvre l'absorbeur, on sent encore l'odeur de $H_2S$, si les teneurs en S se situent dans la partie supérieure de l'échelle de mesure.) Il est d'autre part intéressant de noter l'influence vraiment importante du polychromatisme sur l'obéissance à la loi de Beer.

Pour le cas du Spekker, on se trouve ici dans des conditions peu favorables. Le filtre 608 présente une bande passante très large (350 m$\mu$ à D = 2; 80 m$\mu$ à D = 0,1) alors que le pic d'absorption du bleu de méthylène est relativement étroit. Au fur et à mesure que la concentration croît, les radiations peu absorbées prennent la prépondérance et il en résulte une densité optique apparente inférieure à la densité optique réelle en lumière monochromatique et qui s'en écarte de plus en plus.

### G. *Etalonnage*

Les solutions de sulfures étant très instables et que les prises d'essai étaient trop faibles pour pouvoir utiliser directement des quantités pesées, nous avons préféré recourir à des solutions de sulfate potassique, (9).

Des quantités comprises entre 0 et 12 cm³ de la solution à 10 $\mu$g/cm³ ont été traitées dans le ballon d'attaque par 15 cm³ du mélange réducteur (3) pendant 25 à 30 minutes. Toutes les opérations ont été réalisées en respectant exactement le mode opératoire décrit ci-dessus et la courbe d'étalonnage est reprise a la Fig. 3.

### H. *Résultats*

| | Méthode proposée | | S total dosé par gravimétrie % | S total dosé par combustion et iodométrie % | S évolution (sans coeff. de correction par échant. type) % |
|---|---|---|---|---|---|
| | S à l'état de sulfures % | S oxydé % | | | |
| Fer pur VN12 | 0,0047 | 0,0003 | | 0,004 (Woestoff) | |
| | 0,0046 | 0,0004 | | 0,012 | |
| | 0,0040 | 0,0004 | | | |
| Acier 4 | 0,0106<br>0,012 | 0,0014<br>0,0007 | 0,018 | 0,015–0,015 | 0,014–0,0145 |
| Acier 5 | 0,014 | 0,0022 | 0,018 | 0,016–0,016 | 0,016–0,016 |
| Acier 6 | 0,025 | 0,0022 | 0,029 | 0,032–0,032 | 0,027–0,027 |

## II. DANS LE COBALT

*Mode opératoire*

Le cobalt s'attaquant beaucoup plus lentement dans l'acide chlorhydrique que les alliages ferreux, nous avons trouvé préférable de procéder de la façon suivante: 10 gr de cobalt sont attaqués par 40 cc d'acide nitrique concentré (d : 1,40). Celui-ci doit être ajouté par petites portions afin d'empêcher que la réaction ne s'emballe. Il est parfois nécessaire de refroidir le récipient d'attaque. Vers la fin de l'attaque, on commence à chauffer et on laisse bouillir 1 ou 2 minutes après la fin de la dissolution. On amène alors cette liqueur au volume de 200 cc et on l'homogénéise vigoureusement. On en prélève à la pipette 10–15 ou 20 cc que l'on introduit dans le ballon de l'appareil de distillation. On évapore cette solution jusqu'à ce que le volume soit réduit à environ 2 cc puis on ajoute 5 cc HCl. Une grande partie de l'acide nitrique s'élimine puis on ajoute 20 cc HCl et trois fois 0,5 cc d'acide formique au cours de l'évaporation qui suit.

On va jusqu'à un peu plus près de la siccité que la première fois, puis on ajoute à nouveau 10 cc HCl et 0,5 cc d'acide formique. On réédite exactement cette opération encore une fois, puis on évapore de nouveau jusqu'au même stade de siccité avant d'ajouter les dix derniers cc de HCl.

On évapore cette solution finale jusqu'à un volume d'environ 3–4 cc et on transfère le ballon sur l'appareil à distiller.

On procède alors à la distillation telle qu'elle est décrite pour le dosage du soufre oxydé dans les fers et les aciers.

L'étalonnage et l'essai à blanc sont réalisés conformément à ce dernier mode d'attaque.*

*Résultats*

Le tableau suivant montre la reproductibilité obtenue dans le cas de divers echantillons de cobalt métalliques de qualité commerciale.

| Repères | Teneurs |
|---|---|
| N° 1 | 0,013—0,009 |
| 2 | 0,011—0,013 |
| 3 | 0,0115—0,0105—0,012—0,010 |
| 4 | 0,013—0,0125—0,0135 |
| 5 | 0,008—0,009 |
| 6 | 0,0085—0,009—0,009 |
| 7 | 0,010—0,011 |
| 8 | 0,016—0,013 |
| 9 | 0,018—0,0145—0,015 |
| 10 | 0,016—0,020—0,016 |
| 11 | 0,015—0,0135 |
| 12 | 0,012—0,0145 |
| 13 | 0,0135—0,0125 |
| 14 | 0,010—0,0105—0,011—0,0115 |
| 15 | 0,0095—0,010 |
| 16 | 0,0085—0,0095 |
| 17 | 0,008—0,0095 |
| 18 | 0,006—0,006—0,006—0,0065—0,006—0,006 |
| 19 | 0,010—0,0085 |
| 20 | 0,0125—0,015 |

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* Pour réduire la valeur de l'essai à blanc, il est recommandé de faire bouillir tous les acides avant leur utilisation. (Essai à blanc moins de 10 $\mu$g S.)

## CONCLUSIONS GÉNÉRALES

La méthode proposée présente une grande sensibilité et est vraiment adaptée aux teneurs inférieures à 0,020%. En utilisant des prises d'essai d'environ un gramme, elle permet de doser des traces de l'ordre du millième de %.

Par ailleurs cette méthode ne requiert pas les précautions très sévères qui sont habituelles dans ces gammes de teneurs mais peut occasionnellement fournir des résultats erratiques. D'après Pomeroy, ceux-ci seraient dus à une élimination incomplète des nitrates.[5]

Dans le cas d'une attaque oxydante suivie de la réduction du soufre total, le dosage complèt dans une série dure 45 à 50 minutes. Dans le cas du dosage séparé du soufre "sulfures" et du soufre oxydé, la durée des deux analyses est d'environ 70 à 75 minutes. Dans le cas des aciers, nous pensons, de plus, que le dosage séparé du soufre "sulfures" et du soufre oxydé fournit au métallurgiste une donnée supplémentaire perfois très intéressante.

**Summary**—A method is proposed for the determination of small amounts of sulphur in steels, and in iron and cobalt, which involves conversion of the sulphur to hydrogen sulphide, and then conversion of this to methylene blue, using dimethyl-*p*-aminophenylenediamine. The methylene blue has an intense and relatively stable colour.

Various procedures have been proposed depending on the nature of the metal. For irons and steels sulphides are converted hydrochloric acid attack, and any oxidized forms of sulphur are reduced by a mixture of hydriodic and hypophosphorus acids. Cobalt is dissolved in nitric acid, thus converting all the sulphur to sulphate, which is subsequently converted by means of the same reducing mixture to hydrogen sulphide.

**Zusammenfassung**—Die zur Bestimmung von Schwefel in Metallen vorgeschlagene Methode beruht auf der Überführung des Schwefels in Schwefelwasserstoff und dessen Reaktion mit Dimethyl-*p*-aminophenylendiamin unter Bildung von Methylenblau, Die Farbe des Methylenblaus ist intensiv und relativ stabil.

Verschiedene Methoden wurden vorgeschlagen, abhängig vom Metall in dem der Schwefelgehalt bestimmt werden soll. Für Eisen und Stähle wird Salzsäure als Lösungsmittel verwendet und Oxyde des Schwefels werden mit einer Mischung von Jodwasserstoff und hypophosphoriger Säure reduziert. Cobalt wird in Salpetersäure gelöst wobei der gesamte Schwefel in Sulfat übergeführt wird, welch letzteres durch die obige Mischung zu Sulfid reduziert wird.

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# A COMPARISON OF THE ALKALI METHOXIDES IN THE HIGH-FREQUENCY TITRATION OF ACIDS IN DIMETHYLFORMAMIDE*

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**Summary**—The five alkali-methoxides were prepared and standardized in 9 : 1 benzene-methanol solution. The strengths of these bases were compared by means of *HF* response and conductance curves and by means of the titration of a selected series of acids dissolved in dimethylformamide. The caesium and rubidium methoxides were the strongest bases. However the difference in basicity of these two methoxides as compared to potassium and sodium methoxide does not warrant their preferred use. Lithium methoxide acted as a very weak base in the 9 : 1 benzene-methanol solvent but became more dissociated as the concentration of the methanol was increased.

There was a small but definite drift of the Oscillometer as the concentration of the methoxide ion was increased. This was shown to be due to the slight reaction of the methoxide ion with the dimethylformamide.

Traces of acidic impurities in the dimethylformamide caused salicylic acid to behave as a weak acid while in very pure dimethylformamide it acted as a medium strong acid.

## INTRODUCTION

MOST of the high-frequency titrations recorded by the early workers were in aqueous solutions. Since then a few investigators have studied certain titrations in a few non-aqueous solvents. The solvents used chiefly for weak bases have been glacial acetic acid and benzene-methanol solutions.

Ishidate and Masui[4] titrated some weak organic acids with sodium methoxide using a benzene-methanol solution as the solvent. Phenols and phenolic mixtures dissolved in benzene-methanol solutions were titrated with potassium methoxide by Karrman and Johansson.[5] Young[10] titrated some alkali halides in pyridine. Dean and Cain[1] titrated a number of organic acids in dimethylformamide with sodium methoxide.

The purpose of this investigation was to study the response and titration curves of a series of acids in dimethylformamide with the five alkali methoxides obtained by the high-frequency and conductance methods.

## EQUIPMENT AND REAGENTS

Sargent Chemical Oscillometer Model V equipped with cell compensator, standard condenser type cell, and a Sola voltage transformer. Protect the instrument from drafts to avoid thermal drift.

Leeds and Northrup Campbell-Shackelton Shielded Ratio Box with accessories and No. 4920 dip cell. Store this cell in dimethylformamide when not in use.

Perkin-Elmer Model 154-C Vapor Fractometer with column K at 80°, flow rate of helium 55 mm/min and column pressure 15 psi.

*Dimethylformamide:* Brothers Chemical Co. No. 1943 and Du Pont technical grade. To purify further and to reclaim solvent, distil over solid potassium hydroxide and calcium hydride. Store the purified solvent as well as solutions under dry nitrogen.

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* Supported by the United States Atomic Energy Commission.

*Benzene:* A.C.S. grade. Shake with Drierite and distil over phosphorous pentoxide.

*Methanol:* A.C.S. grade. Reflux with magnesium turnings and distil.

*Lithium, sodium, and potassium methoxides:* Dissolve approximately 0.025 gram equivalents of the metal in 25 ml of cold methanol then dilute to 200–250 ml with 9 : 1 benzene-methanol solution. Standardize against benzoic acid, using thymol blue indicator according to the procedure described by Fritz.[3] Then prepare the standard 0.01*N* alkali methoxides by the proper dilution of a portion of the above known solutions.

*Rubidium and caesium methoxides:* In contrast to the rather elaborate apparatus used by Thomas[9] to prepare caesium methoxide, a simple procedure was used. Partly immerse a 50 mm × 400 mm Pyrex test tube containing 25 ml of dry methanol in a large Dewar flask containing an acetone-dry ice slush. Pass argon into the test tube throughout the procedure. Scratch the glass vial containing the metal, then break into the opening of the tube under the argon and immediately drop. At the temperature of the acetone-dry ice mixture the reaction proceeds quite slowly.

Store all methoxides under nitrogen for additional protection from carbon dioxide and moisture.

Dissolve the acids in dimethylformamide then dilute to 0.01*N*. Standardize the dichloroacetic acid against standard sodium methoxide.

All the methoxides dissolved readily in the 9 : 1 benzene-methanol solution at approximately 0.1*N* concentration. This 9 : 1 ratio was greater than was expected to be possible for sodium methoxide[3] and appeared to be about the upper limit for lithium methoxide.

## EXPERIMENTAL PROCEDURE

Since dimethylformamide and other basic solvents absorb carbon dioxide rather rapidly the dry oscillometer and conductance cells were flooded with dry nitrogen before adding the solvent. Also nitrogen covered the solution during the titration and response curve procedures. The titration vessels were fitted with special Lucite covers.

All volumetric ware was dried and the air expelled with dry nitrogen. The burette was protected with drying tubes containing a desiccant and Ascarite. The flasks containing solutions were also kept in large desiccators charged with soda lime and phosphorous pentoxide or Ascarite.

As a special precaution all transfers of solutions were made with no or only minute contact with air or any moisture.

For the high-frequency measurements, after the instrument had been balanced to resonance, 100 ml of dimethylformamide and 5 ml (about 0.05 milliequivalent) of the sample were adedd to the cell. The titrant was added in 0.5-ml increments. Owing to the considerable drift of the Oscillometer after 8–10 ml of the titrant had been added, instrument readings were made precisely one half minute after the addition of each increment of titrant. The high-frequency response curves were obtained by adding 10 ml of 0.01*N* solution to 100 ml of dimethylformamide in 0.5-ml increments.

For the conductance vs. concentration curves and the conductometric titrations 170 ml of dimethylformamide were used in a 250-ml electrolytic beaker. Twenty ml of 0.01*N* methoxide and about 0.1 milliequivalent of acid were used.

## DISCUSSION

The instrument response curves for acids represent the concentration of the protonated dimethylformamide ion which has large capacitance effect and also represent the degree of dissociation of the acidic substances. The response curves for the acidic substances (Fig. 1), and the similar slopes obtained by conductance, indicate that the $NH_4^+$ ion is quite acidic in dimethylformamide and that benzoic acid has a very low degree ionization.

The slopes of the response curves (Fig. 2), as well as the similar slopes obtained by conductance, for the alkali methoxides indicate that these methoxides, except lithium methoxide, appear as strong bases in the 9 : 1 benzene-methanol solution. The slopes obtained by conductance were similar. These slopes decrease as $CsOCH_3 > RbOCH_3 > KOCH_3 > NaOCH_3 > LiOCH_3$ which is parallel with the decrease in ionic size of the alkali metals. This is according to Fajan's rule[8] that covalent linkage is favoured by the small cation; the lithium methoxide is the most covalent compound while the caesium methoxide is the most ionic compound and is the strongest base of the alkali methoxides.

The instrument response curves (Fig. 3) indicate that the degree of ionization of the lithium methoxide increases as the ratio of the methanol is increased. Methanol is more polar and its concentration apparently controls the degree of dissociation of the lithium methoxide. Since the response curve for the 9 : 1 benzene-methanol solution is very near to that for the lithium methoxide in this solvent the degree of dissociation is very low. In solvents with relatively low dielectric constants, as that of dimethylformamide or below,[6,7] the lithium methoxide due to ion association may be in the form of ion-pairs which will not contribute to the capacitance or conductance of the solution. Then as the solution becomes more concentrated, triple ions may form which bear a charge and can contribute to the capacitance or conductance of the solution. An increase in the conductance of the lithium methoxide in the 9 : 1 benzene-methanol ratio was not observed in the very dilute solutions but was detected when the solution became about $7 \times 10^{-4}M$.

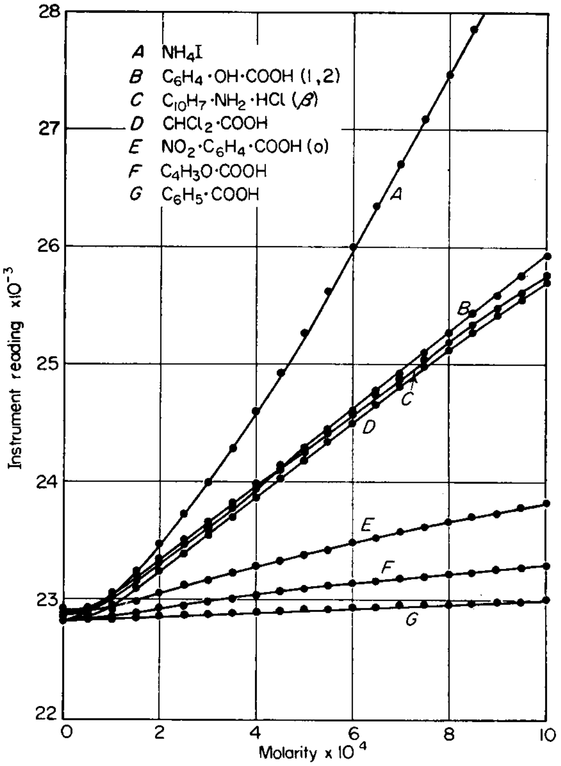


FIG. 1.—H-F response curves for acids and salts.

Increasing the ratio of methanol in the benzene-methanol solution had little effect on the other alkali methoxides. Thus the larger cations are more likely to be present in ionic form even though they are in a solvent of low dielectric value.[6]

When determining the response curves (Fig. 2), after a few millilitres of the alkali methoxide had been added to the dimethylformamide the drift of the Oscillometer became noticeable, as well as after the end-points during the titrations. It was observed that the magnitude of this drift increased with an increase in concentration of methoxide ion. The drift of the Oscillometer was negligible when operating under optimum conditions, *e.g.*, constant temperature, no draughts, and adequate warm up time. As expected, with an atmosphere of nitrogen or argon over the dimethylformamide there was no drift and the addition of pure benzene or methanol to the dimethylformamide produced no drift.

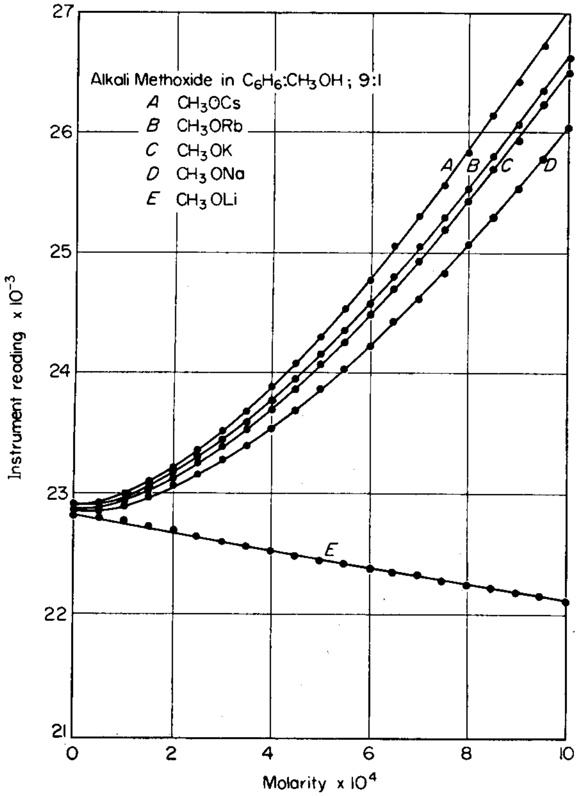
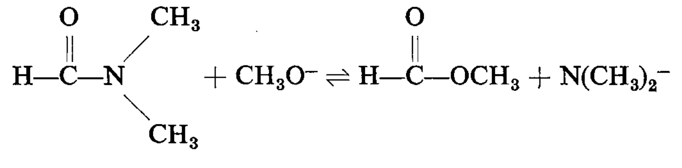


FIG. 2.—H-F response curves for the alkali methoxides.

With lithium methoxide in the 9 : 1 benzene-methanol solution there was a very small drift which increased greatly when potassium methoxide in 9 : 1 benzene-methanol solution or lithium methoxide in methanol was added. An increase in concentration of the methoxide ion also produced an increase in the magnitude of the drift, Fig. 4. Readings were recorded starting one minute after the addition of the initial quantity of the substance. The change in drift with respect to time indicates that the following equilibrium



$$\mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N(CH_3)_2} + \mathrm{CH_3O^-} \rightleftharpoons \mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_3} + \mathrm{N(CH_3)_2^-} \qquad (1)$$

is being shifted slightly to the right due to the mass action effect of the methoxide ion though the dimethylamide ion is the much stronger base. The dimethylamide ion will protonate according to

$$H_3COH + N(CH_3)_2^- \rightleftharpoons H_3CO^- + HN(CH_3)_2 \qquad (2)$$

By the use of vapour phase chromotography the dimethylaminde and methylformate were both identified as being present. Due to the very small quantities present, the reaction mixture was swept with dry nitrogen and the vapours condensed in a cold trap immersed in an acetone-dry ice slush.

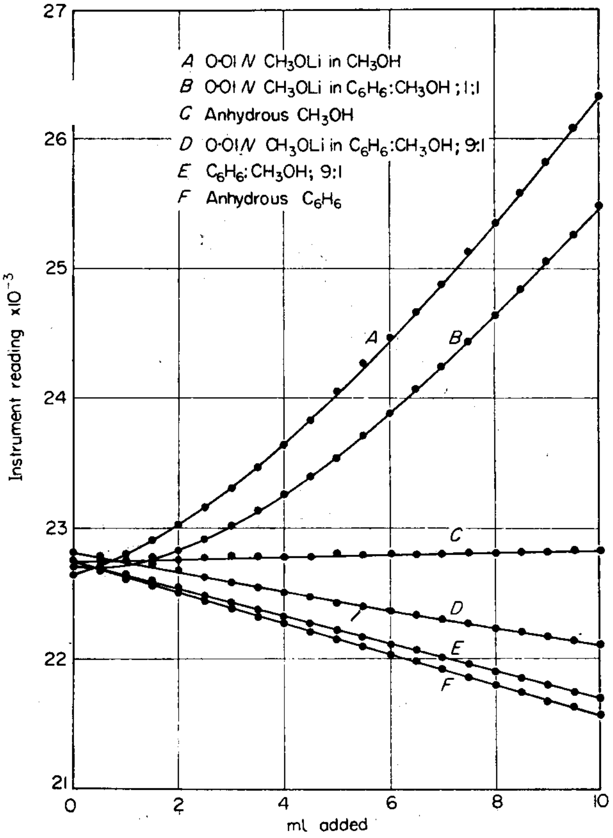
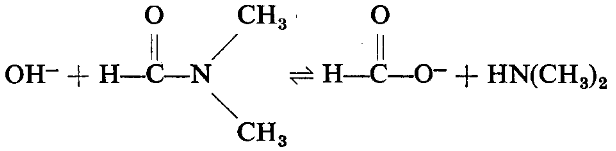


FIG. 3.—H-F response curves for $LiOCH_3$ and solvents.

The presence of water caused a rapid drift with an increase in capacitance (Fig. 4) due to the following:

$$CH_3O^- + H_2O \rightleftharpoons CH_3OH + OH^- \qquad (3)$$



$$OH^- + H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N\!\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array} \rightleftharpoons H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^- + HN(CH_3)_2 \qquad (4)$$

The effect of 0.2% water added to the dimethylformamide before the methoxide is shown by curve C. For curve D, Fig. 4, the dimethylformamide had been exposed to air for some time.

The dimethylformamide acts as a "non-levelling solvent" in the presence of the alkali methoxides. The dimethylamide ion, in Eq. 1, is a much stronger base than the methoxide ion consequently there is no levelling effect. If the concentration of the methoxide ion is increased by the use of caesium methoxide instead of lithium methoxide the equilibrium will shift slightly to the right and caesium methoxide acts as the stronger base.

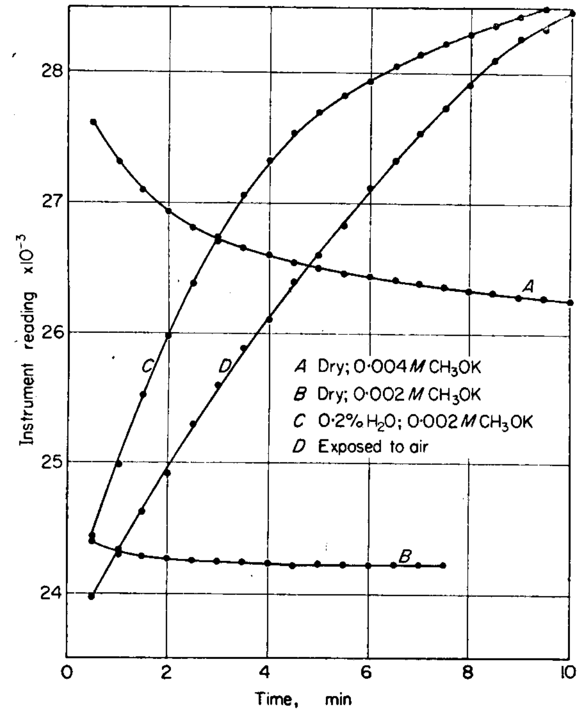


FIG. 4.—Drift of oscillometer; potassium methoxide in dimethylformamide.

The purity of the dimethylformamide may affect the shape of the response and titration curves. In this work using distilled dimethylformamide the response curves for the alkali methoxide and salicylic acid did not pass through a minimum, and salicylic acid did not behave as a slightly dissociated acid in concentrations above 0.0005*M* as reported by Dean and Cain.[1] In distilled dimethylformamide the titration curve for salicylic acid was characteristic of a medium strong acid (Fig. 5A) but in technical grade dimethylformamide (acid impurities neutralized to the thymol blue end-point with sodium methoxide) the titration curve was characteristic of a weak acid (Fig. 5B) and was similar in shape to the titration curve shown by Dean and Cain.[1] When the technical grade dimethylformamide was distilled as described for this work, salicylic acid reproduced the response and titration curves as observed with other distilled or redistilled solvent. This effect was not observed for any of the other acids reported in this work (Fig. 5) or for *p*-hydroxybenzoic acid. This behaviour of a solution of salicylic acid may be due to a tautomeric equilibrium between the classical and the chelate structures[2] and the impurities in the solvent shift the equilibrium to make the weak acid the predominant form.

The titration of the acids in dimethylformamide with the alkali methoxides is represented in Fig. 6. The differences in the angles at the end-point for the $NH_4^+$ ion and the different alkali methoxides are shown in Fig. 7. The high-frequency and conductance titration curves were very similar in shape.

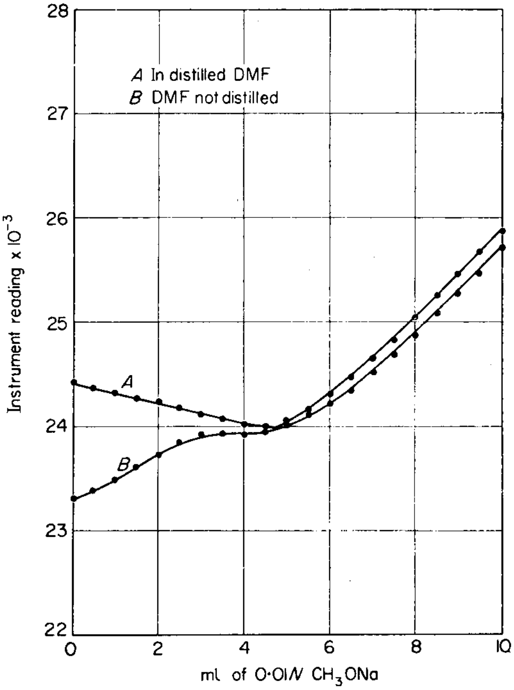


Fig. 5.—Titration of salicylic acid in distilled and non-distilled dimethylformamide.

Caesium methoxide and rubidium methoxide are the strongest bases of the alkali methoxides while lithium methoxide is the weakest in the 9 : 1 benzene-methanol solution. The strongest bases do produce slightly more acute end point angles as shown in Fig. 7; however the difference in basicity as compared to the potassium or sodium methoxide was not great enough to titrate successfully such very weak acids as phenol and do not justify their use due to the extra cost and care in handling, for ordinary use.

The end-points of the instrumental titration curves were in good agreement with the theoretical amount of acid when the strong methoxides were used as the titrant and in good agreement with the thymol blue end-points for those acids with a $pK_a$ of 3 or less. The high-frequency method was more convenient to use than the conductometric method due to the greater ease of handling the cells in an inert atmosphere, since no solution was in contact with the electrodes. Also, the high-frequency method is useful for titrations if a coloured impurity is present and if the compound is coloured or changes colour during the titration. However this method offers no advantage when the proper indicators are available.

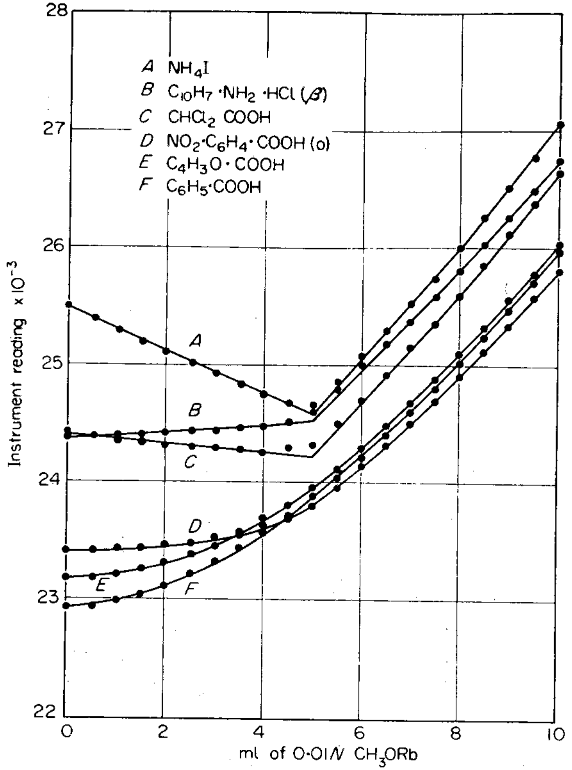


FIG. 6.—H-F titration curves of acids with rubidium methoxide.

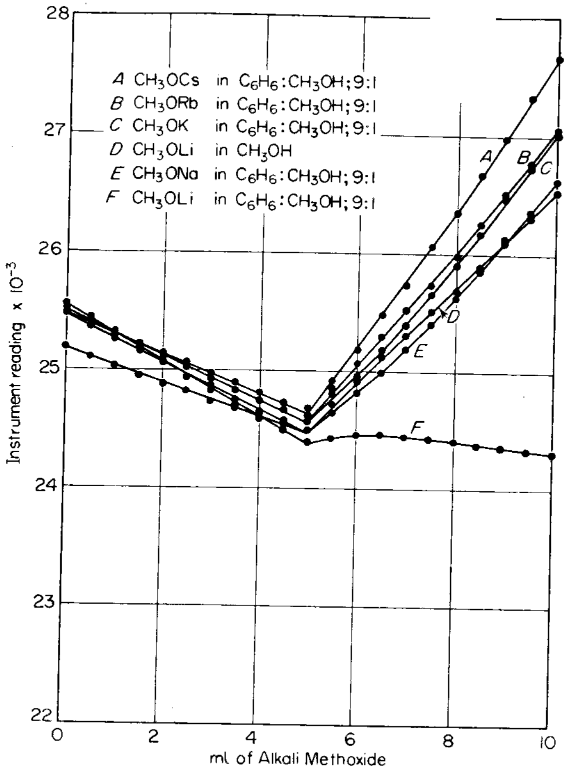


FIG. 7.—Comparison of the H-F titration curves for ammonium iodide with the alkali methoxides.

The high-frequency titration of the weak acids with lithium methoxide in the 9 : 1 benzene-methanol solution produced only a very small change of slope. This change in slope was after the stoichiometric end-point to the extent of about 10%. In the conductometric titrations this break appeared about 10% late or not at all.

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**Zusammenfassung**—Die fünf Alkalimethoxyde wurden hergestellt und in Benzol-Methanol (9 : 1) Lösung titriert. Die Stärke der Basen wurde durch Hochfrequenz- und Leitfähigkeitstitration ermittelt wobei verschiedene Säuren in Dimethylformamid gelöst als Titrationsmittel dienten. Caesium und Rubidum-methoxyd waren die stärksten Basen. Die Stärke ist jedoch keineswegs so beträchtlich höher, dass diese beiden Methoxyde denen des Natriums und Kaliums vorgezogen werden sollten. Litheummethoxyd war in 9 : 1 Benzol-Methanolmischung nur schwach basisch, doch nahm die Basizität zu, wenn der Methanolgehalt der Mischung gesteigert wurde.

Ein geringfügiges aber merkliches Wandern der Oscillometernadel konnte festgestellt werden, wenn die Konzentration des Methoxydions gesteigert wurde. Es konnte gezeigt werden, dass dies auf einer geringfügigen Reaktion des Methoxydions mit Diemthylformamid zurückzuführen ist. Spuren von sauren Verunreinigungen im Dimethylformamide bewirkten dass Salizylsäure als schwache Säure reagierte, während ihr Verhalten in völlig reinem Dimethylformamid das einer mittelstarken Säure war.

**Résumé**—Les cinq sels alcalins du methanol ont été préparés et étalonnés en solution benzène-méthanol (9 : 1). La force de ces bases a été comparée par des déterminations en haute fréquence et des courbes de conductivité et également par titrage d'une série sélectionnée d'acide dissous dans la dimethylformamide. Les méthanolates de cesium et de rubidium sont les bases les plus fortes. Cependant la différence entre la basicité de ces deux bases, et celle des méthanolates de sodium et de potassium, ne justifie pas leur emploi préférentiel. Le méthanolate de lithium se comporte comme une base très faible dans le mélange benzène-methanol (9 : 1) utilisé comme solvant, mais se dissocie davantage lorsque la concentration du méthanol augmente.

On observe sur l'oscillateur une faible mais nette dérive lorsque la concentration du méthanolate augmente. On montre que celà est produit par une légère action du méthanolate sur la diméthylformamide.

En présence d'impuretés acides dans la dimethylformamide, l'acide salicylique se comporte comme un acide faible alors qu'il réagit dans la dimethylformamide très pure comme un acide fort.

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# TITRATION OF METAL OXINATES IN ETHYLENEDIAMINE WITH POTASSIUM METHOXIDE

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**Summary**—Several metal oxinates can be titrated with potassium methoxide in ethylenediamine solution, using conductometric end-point detection. The reliability of the method has been established using aluminium oxinate samples representing about 2–13 mg of aluminium. Errors are generally under 1%. Evidence is presented for a simple interpretation of the behaviour of the oxinates as weak acids in ethylenediamine solution.

BECAUSE important analytical chelate compounds such as the metal 8-quinolinolates (oxinates) would be expected to exhibit weak acidic and basic properties, it was of interest to investigate whether they could be determined by nonaqueous titrimetry. One could then combine the selectivity of such reagents to effect separations, with the advantage of direct titrimetry to conclude the determinations. Titrations of certain oxinates, notably aluminium, with perchloric acid in glacial acetic acid solution were described recently,[1,2,3] but it was found that most of the oxinates could not feasibly be titrated in this way. It was reasonable then to see whether their acidic properties could be utilized in titrations with a very strong base like potassium methoxide. Such titrations in solvents like ethylenediamine and dimethylformamide have been reported many times and are now commonplace,[4] but their application to important analytical precipitates appears to be new.

For an oxinate like that of aluminium in an ethylenediamine system, one might formulate the following equilibria using the simple Bronsted ideas but substituting an aluminium ion for a proton:

$$\begin{array}{c} Al(Ox)_3 + 3en = (Alen_3)^{3+} + 3Ox^- \\ (Alen_3)^{3+} + 3CH_3O^- = Al(CH_3O)_3 + 3en \\ \hline Al(Ox)_3 + 3CH_3O^- = Al(CH_3O)_3 + 3Ox^- \end{array}$$

where $Ox^-$ represents an oxinate anion and en represents ethylenediamine. The titration process is then seen as a competition of three bases, oxinate, ethylenediamine, and methoxide, for the acidic aluminium ion. One might predict that the titration reaction would go well to completion because methoxide ion is obviously the strongest base, although it must be remembered that we are comparing bases with regard to their reaction with aluminium ion and not with the usual standard, namely hydrogen ion. In any case, the results show that the titration is feasible, not only for aluminium but for a number of other metal oxinates. Ultraviolet absorption spectra, mentioned below, support the above formulation.

Oxinate solutions in ethylenediamine are highly coloured, and it is not possible to perform the titrations visually. Conductometric end-point detection is emphasized in this paper, although potentiometric titrations with platinum or glass indicator electrodes and a calomel reference electrode can be performed as noted below. Conductivity measurements give stable and reproducible values, while electrode potentials in the systems studied are much more erratic. Photometric end-point detection would be possible in some cases, but precipitates which would interfere with the measurements form during the titrations with other oxinates.

The oxinates studied may be grouped into three classes: (1) Oxinates which give good to excellent end-points are those of aluminium, zinc, scandium, thorium, molybdenum, tungsten, vanadium, and magnesium. (2) Oxinates which give end-points that are fair to poor include uranium, copper, and manganese. (3) Oxinates of nickel, lanthanum, iron, and thallium yield no useful end-points at all. This grouping is naturally very rough; manganese, for example, is nearly as good as magnesium. Oxine itself gives a very good end-point.

Dimethylformamide was investigated briefly because in many ways it is a more convenient solvent with which to work than ethylenediamine, but the end-points were found to be much sharper in the latter solvent.

## EXPERIMENTAL

### *Apparatus and reagents*

The conductometric titration cell was a 150-ml beaker fitted with a rubber stopper which has holes for the electrodes, the burette, and the nitrogen inlet tube. Nitrogen simply escaped through the opening for the burette. The electrodes were platinized platinum foil, each 1 $cm^2$, tap-welded to short lengths of platinum wire which were sealed into soft glass tubing. The cell constant for the set-up used for most of the titrations was 0.28 $cm^{-1}$, as determined by measuring the resistance of a 0.100*M* aqueous potassium chloride solution at 25°. Measurements were performed with a Model RC-1B conductivity bridge from Industrial Instruments Inc. The burette was a 10-ml micro-burette graduated at intervals of 0.02-ml. A magnetic stirrer with a Teflon-coated stirring bar was employed. The titration cell was placed in a large pan of water at room temperature to minimize the effect of temperature changes upon the conductance values during the titrations. Potentiometric titrations were performed in a similar cell with Beckman glass-calomel or platinum-calomel electrode systems, using a Beckman "Zeromatic" pH meter. Ultraviolet absorption spectra were measured in 1-cm quartz cells with a Beckman Model DU spectrophotometer equipped with a hydrogen discharge tube.

The nitrogen used to blanket the solution in the titration cell was passed through a tube packed with Ascarite and silica gel. Ethylenediamine solvent was Eastman "white label", 98%. In the beginning, this was distilled from sodium and activated alumina, and collected under nitrogen, but later it was found to be suitable for use directly, provided a blank titration was run. The blank, generally less than 0.1-ml of 0.1*N* titrant for a 75-ml portion of the solvent, could be determined conductometrically or visually using azo violet indicator. Fresh bottles of ethylenediamine were transferred under nitrogen to all-glass siphon bottles protected by silica gel and Ascarite and provided with stopcocks for easy dispensing. Of a number of greases tested for these stopcocks, the best was Sisco 300 (from the Swedish Iron and Steel Co., Westfield, N.J.) as Katz and Glenn had found previously.[5] This grease was also more resistant than most to the titrant solution, although it was necessary to regrease the burette stopcock each day.

The titrant was 0.1*N* potassium methoxide in benzene-methanol, prepared according to the directions of Fritz and Keen.[6] It was stored in a siphon bottle protected from the air, and was delivered to the burette through a Teflon stopcock. This solution was standardized against aluminium oxinate by conductometric titration as described below. Sodium methoxide can be used as the titrant, but the end-points are slightly sharper with potassium.

The metal oxinates were prepared by various methods which are summarized in Hollingshead's monograph.[7] It is realized that there are doubts regarding the exact compositions of some of these compounds. In particular, there is often disagreement about the effect of drying temperature upon composition. Most of the quantitative work reported here was done with aluminium oxinate, about whose composition there seems to be no controversy. Actually, the titration method suggested here might be useful in studying the compositions of some of the uncertain oxinates.

### *Titration procedure*

A weighed quantity of the metal oxinate was placed in a 150-ml beaker, and the stopper bearing the electrodes and nitrogen inlet tube was inserted. 75-ml of ethylenediamine was then introduced through the hole for the burette; nitrogen flow over the solution was started as soon as sufficient ethylenediamine had been added to prevent dry particles of oxinate from blowing away. The solution was then placed in the pan of water over the magnetic stirrer, the burette was inserted with its tip in the liquid, and the titration was begun. After each addition of desired increments of titrant, the stirrer was stopped, and the resistance of the solution was measured. Because the titration curves are generally not strictly linear except fairly near the end-point (within, say, 1 to 2-ml), it was best to get a number of points near the end-point and not rely upon too extreme an extrapolation. Conductance values were corrected for dilution, and then the results were plotted for graphical determination of the end-point. The scale was blown up considerably so that the graphical process itself did not limit the obtainable accuracy.

So long as the numbers are consistent, the conductance units chosen for the plotting are obviously unimportant. In the figures in this paper, the conductances are in arbitrary units, but the units are the same for all the curves shown. To give an idea of the actual conductance values, it is mentioned that the number 100 on the figure ordinates represents an actual specific conductance of about $2.8 \times 10^{-6}$ ohm$^{-1}$cm$^{-1}$.

The benzene-methanol titrant, compared with water, has a fairly large coefficient of thermal expansion. Thus all volumes of titrant read from the graphs were corrected to a standard temperature of 22° using the equation

$$V_{22} = V_t\left(\frac{1 + 22\alpha}{1 + t\alpha}\right)$$

which is obtained from the usual equation

$$V_t = V_0(1 + \alpha t + \beta t^2 + \alpha t^3)$$

by dropping the negligible higher-order terms and eliminating $V_0$ between the two temperatures involved. A weighted mol fraction mean value, based upon the ratio of methanol to benzene in the titrant solution, was used for $\alpha$.

Aluminium oxinate dissolves rather slowly in ethylenediamine at room temperature. Rather than warming to effect complete solution, it was convenient to start the titration even though some suspended material remained. The solution cleared early during the titration, and the important points near the end-point were not jeopardized.

## RESULTS

### *Titrations of various oxinates*

Fig. 1 shows potentiometric titration curves for zinc oxinate using glass-calomel and platinum-calomel electrode systems. Successful potentiometric titrations of aluminium oxinate have also been carried out. But such titrations were generally frustrating. The electrodes equilibrated very slowly with the solutions, as much as an hour sometimes being required to complete a titration. Occasionally no electrode response whatsoever was obtained during a titration. And sometimes sudden emf changes of several hundred millivolts occurred for no apparent reason. These problems might have been overcome with experience, but the potentiometric titrations were abandoned when it was found that conductometric titrations worked very well.

Fig. 2–5 show conductometric titration curves for a number of oxinates. Most of these resemble typical weak acid-strong base titration curves as seen in the more familiar aqueous system. Aluminium oxinate was chosen for a more detailed study because it is probably the best known, most thoroughly studied, and most widely used of the metal oxinates.

*Titrations of aluminium oxinate*

Table I shows the results of a number of titrations of aluminium oxinate samples ranging from about 29 to 228 mg. The table is formulated on the basis of the corresponding quantities of aluminium (about 1.7 to 13.4 mg), which are perhaps of more interest. The average absolute error is 0.062 mg, which represents an average relative error of 0.9 %. If one omits the 5 worst results (numbers 1, 6, 7, 9, and 10), the relative error drops to 0.6 %, but all the results are retained in the table to indicate what may be expected in practice. Four of the worst 5 results are too high, suggesting that inadvertent admission of carbon dioxide (which is a strong acid in this system) to either the titrant or the ethylenediamine solution may have been the source of most of the occasional large errors, despite the exercise of reasonable care. It is felt that the results reported here are the best obtainable consistent with speed and convenience; unusual precautions could probably increase the accuracy slightly.

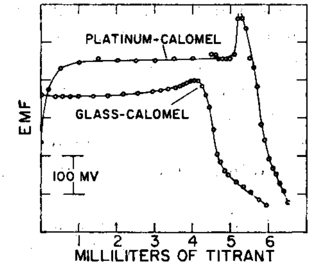

FIG. 1.—Potentiometric titration curves for zinc oxinate.

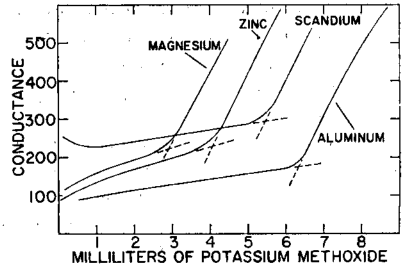

FIG. 2.—Conductometric titration curves for metal oxinates

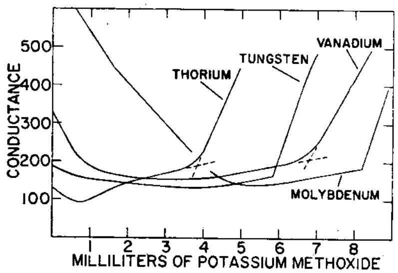

FIG. 3.—Conductometric titration curves for metal oxinates

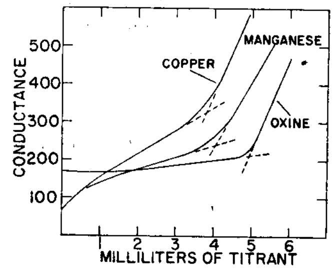

FIG. 4.—Conductometric titration curves for metal oxinates.

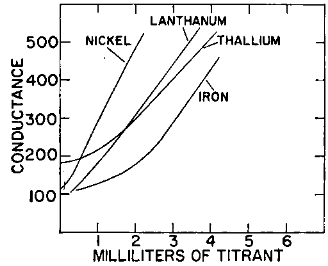

FIG. 5.—Conductometric titration curves for metal oxinates.

TABLE I.—RESULTS OF CONDUCTOMETRIC TITRATIONS OF ALUMINIUM OXINATE

| No. | Al taken, *mg* | Al found, *mg* | error, *mg* | relative error, % |
|---|---|---|---|---|
| 1 | 1.721 | 1.750 | 0.029 | 1.7 |
| 2 | 3.095 | 3.082 | 0.013 | 0.4 |
| 3 | 3.494 | 3.485 | 0.009 | 0.3 |
| 4 | 5.010 | 4.975 | 0.035 | 0.7 |
| 5 | 6.037 | 5.969 | 0.068 | 1.1 |
| 6 | 6.096 | 6.224 | 0.128 | 2.1 |
| 7 | 6.120 | 5.991 | 0.129 | 2.1 |
| 8 | 6.272 | 6.335 | 0.063 | 1.0 |
| 9 | 6.372 | 6.521 | 0.149 | 2.3 |
| 10 | 6.595 | 6.725 | 0.130 | 2.0 |
| 11 | 6.813 | 6.825 | 0.012 | 0.2 |
| 12 | 6.960 | 6.917 | 0.043 | 0.6 |
| 13 | 7.018 | 7.050 | 0.032 | 0.5 |
| 14 | 7.165 | 7.145 | 0.020 | 0.3 |
| 15 | 7.294 | 7.320 | 0.020 | 0.3 |
| 16 | 7.899 | 7.927 | 0.028 | 0.4 |
| 17 | 9.403 | 9.399 | 0.004 | 0.0 |
| 18 | 11.206 | 11.072 | 0.134 | 1.2 |
| 19 | 13.437 | 13.313 | 0.124 | 0.9 |
| | | | average: 0.062 | 0.9 |

## *Effect of water on the titration of aluminium oxinate*

Because in practice one might wish to titrate aluminium oxinate precipitated from aqueous solution, it was desirable to study the effect of water on the titration to see if it would be necessary to dry the precipitate. Fig. 6 shows that up to only

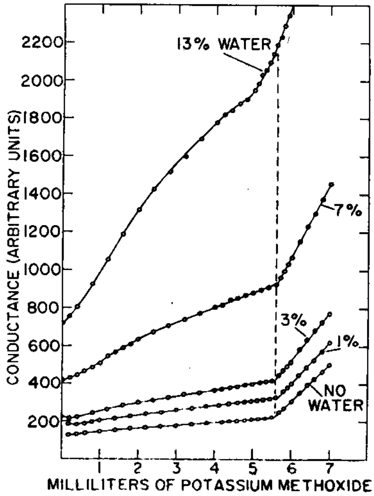

FIG. 6.—Effect of water on the titration of 100 mg of aluminium oxinate.

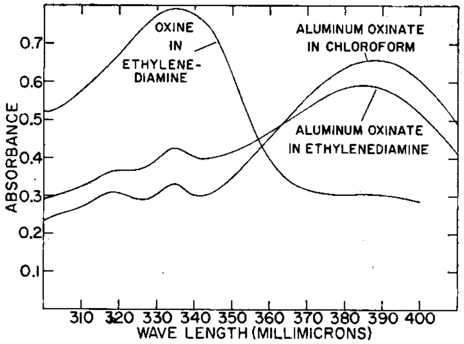

FIG. 7.—Ultraviolet absorption spectra of oxine and aluminium oxinate: all solutions 3 × $10^{-4}M$ in chromophore.

slightly more than 7% of water in the ethylenediamine solvent is well tolerated. (Percentages of water shown in the figure are approximate volume percentages based upon volumes taken and neglecting the slight volume change which occurs when water and ethylenediamine are mixed.) It is apparent that in handling fresh aluminium oxinate precipitates, suction filtrations or centrifugations would remove enough of the water to permit titration, and special drying would be unnecessary.

### *Absorption spectra*

Fig. 7 shows ultraviolet absorption spectra which are pertinent to the consideration of the dissociation of aluminium oxinate in ethylenediamine solution. Oxine itself exhibits an absorption maximum at about 335 m$\mu$ in ethylenediamine (in carbon tetrachloride, an inert solvent, the peak occurs at about 320 m$\mu$). Aluminium oxinate in chloroform exhibits a small peak in this same region, and a larger one at about 385 m$\mu$ which is not shown by oxine itself. But when aluminium oxinate is dissolved in ethylenediamine, the absorbance at the peak near 335 m$\mu$ increases, while that at 385 m$\mu$ decreases. As the figure shows, this shift in the aluminium oxinate spectrum toward that of oxine itself in ethylenediamine solution is far from complete, but it is appreciable, and it supports the dissociation picture presented earlier in this paper. Because copper ions generally have a much stronger affinity for nitrogen ligands than do aluminium ions, one might predict a much more pronounced spectral shift for copper oxinate in ethylenediamine, indicating greater dissociation than in the aluminium case. This is found to be true, although to save space the spectra are not shown here. The poorer titration curve for copper oxinate as compared with the less dissociated aluminium oxinate might then be interpreted as indicating that the titrant was not sufficiently more basic than the solvent to give equally good results, the term "basic" referring here to the tendency to accept copper ions.

**Zusammenfassung**—Mehrere Metalloxinate wurden in Äthylendiaminlösung mit Kaliummethoxyd konduktometrisch titriert. Die Zuverlässigkeit der Methode wurde an Hand von Analysen von Aluminiumoxinatproben (entsprechend 2–13 mg Al) gezeigt. Der Fehler ist im allgemeinen kleiner als 1%. Eine einfache Deutung des Verhaltens des Oxinates als schwache Säure in Äthylendiaminlosungen wird mitgeteilt.

**Résumé**—Plusieurs oxinates métalliques ont pu être titrés par le méthanolate de potassium en solution dans l'éthylène-diamine le point équivalent étant déterminé par conductimétrie. La méthode a été testée sur des échantillons d'oxinate d'aluminium correspondant à 2 à 13 mg d'aluminium. Les erreurs sont en général inférieures à 1%. Il est présenté une interprétation simple montrant que les oxinates se comportent comme des acides faibles dans des solutions d'éthylénediamine.

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# ACTIVATION-ANALYSIS OF TRACE COBALT IN TISSUE USING 10.5-MINUTE 60m-COBALT

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**Summary**—Microgram amounts of cobalt from vitamin $B_{12}$ have been analyzed by rapid activation-analysis in rat kidney tissue as well as in vitamin preparations. A 15-minute radiochemical separation procedure coupled with gamma-ray spectrometry permitted utilization of the 10.5-min $^{60m}$Co radioisotope. With this procedure the lower limit of detection at a thermal neutron flux of $10^{12}$ n/cm$^2$ sec was about $5 \times 10^{-8}$ grams of cobalt.

## INTRODUCTION

SINCE the advent of vitamin $B_{12}$ as a medicinal for the treatment of certain hæmatological disorders, considerable attention has been focused on the determination of cobalt in biological systems. Saltzman and Keenan[1] have presented a review of the methods used for the microdetermination of cobalt in biological materials. Determination of this element by conventional wet chemical procedures coupled with spectroscopy or sensitive colour reactions frequently lacks sensitivity or is complicated by trace contamination from the reagents. In many cases, however, the use of radioisotopes can offer a rapid and sensitive procedure to assist in this analysis.

Until now much effort has gone into using radioactive tracers of cobalt, or labelled vitamin $B_{12}$, in exploring the distribution of this element in biological systems. Several procedures have been described for the production of vitamin $B_{12}$ labelled with $^{60}$Co either by a biosynthetic route[2,3] or by direct slow neutron irradiation.[4] This labelled vitamin is available routinely[5] for tracer studies of pernicious anæmia in humans and is used in an isotope-dilution method for the assay of vitamin $B_{12}$ as described in the U.S. Pharmacopoeia.[6]

Published studies of tracer distributions include work with injected $^{60}$Co in polycythemic rats,[7] metabolism of $^{60}$Co-labelled vitamin $B_{12}$ by the rat,[8] and the distribution of orally administered $^{56}$Co-labelled vitamin $B_{12}$.[9]

Another method for determining the distribution of trace amounts of cobalt in a system is to analyse directly for this element but for many systems the sensitivities required eliminate most standard analytical techniques. Activation-analyses for trace amounts of cobalt have, however, been made on many types of samples using the long-lived $^{60}$Co. Smales, Mapper and Wood[10] have given an excellent discussion of the procedures used in the analysis of rocks and marine sediments by this technique. They checked the accuracy of their methods by analysing standard steel samples and report working sensitivities for cobalt of about $10^{-8}$ grams. The disadvantage of this method is that the 5.2-year $^{60}$Co formed requires a long activation to attain these sensitivities and many days may elapse between the time that an analysis is started (the beginning of the irradiation) and the time that the results can be obtained.

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We have been using the facilities of the Ford Nuclear Reactor at the University of Michigan to explore the use of short-lived radio-isotopes in activation-analysis. These rapid activation and measurement facilities have been coupled with a fast radiochemical separation to determine cobalt (by the 10.5-min $^{60m}$Co) in the kidneys of rats that had been given unlabelled vitamin $B_{12}$.

## EXPERIMENTAL

### *Apparatus*

Samples were irradiated in polyethylene snap-type "rabbits" in the pneumatic tube system of the Ford Nuclear Reactor of the University of Michigan. This system permits irradiations at thermal neutron fluxes of about $10^{12}$ n/cm$^2$ sec (when the reactor is operating at full power of 1 megawatt) and delivery to a hood in the neighbouring Michigan Memorial Phoenix Laboratory within 3 seconds after the end of irradiation. Samples were then worked up chemically and were measured by a 3″ × 3″ NaI(Tl) crystal coupled with a special 100-channel pulse-height analyzer with duplicate memories. This equipment has been described in detail elsewhere.[11–13]

### *Preparation of animals and tissue*

Holtzman* albino male rats weighing between 275 and 350 g were used in this study. They were maintained on Rockland Rat Diet† and had free access to drinking water. With the exception of animals No. 1 and 2, intraperitoneal injections of vitamin $B_{12}$‡ containing 45 micrograms§ of Co were administered 10 to 12 hours before sacrificing. Animal No. 1 received three 45 microgram doses 24 hours apart while animal No. 2 received two doses 24 hours apart. Both the kidneys and the liver tissue were surgically removed for analysis; however, the kidneys were found to be more readily adaptable to the chemical procedure.

The weighed tissues were allowed to air dry at room temperature for 24 hours and then re-weighed. They were placed in envelopes prepared from 4 mil thick polyethylene film, which were closed by heat sealing. The sealed sample was then irradiated in the "rabbit" along with suitable monitoring foils for a period of 30 minutes at full power.

### *Radiochemical separation*

While the sample was being irradiated a nickel crucible was prepared containing 10 mg of Co carrier solution plus a known amount of 5.2-year $^{60}$Co tracer. Three sodium hydroxide pellets were added and the solution heated almost to dryness. Two minutes before the end of the irradiation 10 g of sodium peroxide were added to the crucible and melted.

The irradiated sample was then fused in this melt for 1 minute. (CAUTION: A cover must be used on the crucible since the reaction may be quite violent.) The outside of the crucible was then cooled by dipping it into a beaker of cold water and the melt made to solidify in a thin, readily dissolved coating by manipulation of the crucible. The melt was then dissolved by immersion in 50 ml of distilled water, and 50–70 ml of liquid nitrogen were added to cool the solution to room temperature. Fifteen to twenty ml of glacial acetic acid were then added slowly and the solution was again cooled with liquid nitrogen.

This mixture at a pH of 5–6 was then transferred to a 150-ml separatory funnel containing 25 ml of 8-hydroxyquinoline solution (3% solution in chloroform) and shaken for 1 minute. Ten ml of 9*M* HCl were used to re-extract the cobalt from the organic layer. Co was then precipitated as the oxide from the HCl solution by addition of $Na_2O_2$. This precipitate was collected on a filter chimney,¶ was washed with water, and mounted for measurement on the spectrometer. The entire procedure could be completed in about 15 minutes with an average recovery of about 40% of the cobalt.

* Holtzman Company, Madison 4, Wisconsin.

† A product of Rockland Farms, New City, N.Y.; Manufactured by A. E. Staley Mfg. Co., Chicago 27, Illinois.

‡ Injection Vitamin $B_{12}$, (1000 micrograms/ml.), University Hospital Control No. 1104580, Ann Arbor, Michigan.

§ Based on the value of 4.5% as the amount of Co in Vitamin $B_{12}$ N. G. Brink, *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 1854.

¶ If foaming occurs add 10–15 ml of 0.1*M* HCl.

### *Activity determination*

Linearity of the measurement system was established by the use of $^{137}$Cs, $^{60}$Co, $^{203}$Hg, $^{75}$Se, and $^{113}$Sn standards. Spectra were obtained in the energy ranges of about 0–0.25 and 0–2.0 MeV as shown in Fig. 1. The amount of $^{60m}$Co was determined from the area under the 0.059 MeV photopeak while correction for chemical yield was made by measuring the recovery of the long lived tracer $^{60}$Co utilizing the 1.17 and 1.33 MeV photopeaks.

### *Monitoring procedures*

Gold foils weighing between 0.5 and 1.0 mg were wrapped in plastic envelopes and scotch taped to the inside of the cap of the "rabbit." Following irradiation the foils were dissolved in 4 ml of *aqua regia* and diluted to 10 ml with distilled water. An aliquot of this solution was placed on a filter paper and mounted for measurement of the 411 keV gamma ray of $^{198}$Au on the spectrometer. Comparison with other measurements made with calibrated gold foils permitted normalization of all irradiations to a neutron flux of $1 \times 10^{12}$.

## RESULTS AND DISCUSSION

Preliminary experiments were carried out using this procedure without the chemical separation on pure materials. Aliquots of the Vitamin $B_{12}$ injection were sealed in polyethylene tubing and irradiated in the same manner as described for the kidney samples. Spectral determinations in the 0–0.25 MeV range permitted the measurement of peak areas for the 0.059 MeV gamma ray emitted during the decay of the $^{60m}$Co. Successive spectra, taken at several-minute intervals, showed that the peak decayed with the 10.5-minute half life of this isomer. Analysis of decreasing concentrations of Vitamin $B_{12}$ showed the lower practical limit of detection to be about $5 \times 10^{-8}$ g of cobalt. The same procedure was performed on cobalt nitrate solutions with similar results.

Preliminary studies to determine the level of naturally occurring Co in normal rat kidney tissues indicated that it was less than $10^{-8}$ g, or below the limits of detection for this method at a flux of $10^{12}$. Thus experiments were conducted to determine the tissue level of Co after administration to the rat of a Co-containing pharmaceutical (Vitamin $B_{12}$).

Determinations made on tissues from ten different rats show that this method is readily applicable to $\mu$g amounts of Co in biological systems. The results, summarized in Table I, indicate that under the conditions of these experiments 1–3 $\mu$g of Co are found in rat kidney tissue 10–12 hours after the intraperitoneal administration of 45 $\mu$g of Co as Vitamin $B_{12}$. This does not indicate that the Co is present as Vitamin $B_{12}$ in the kidney but rather that the Co portion of the molecule is excreted via the kidney.

The chemical procedure went smoothly although Cu and Mn were found to be interfering elements. These elements are present in considerably greater quantities than Co in the kidney and this particular rapid procedure did not separate them completely. Half-life studies and energy determinations with the gamma spectrometer indicated that the 12.8-hour $^{64}$Cu and 2.6-hour $^{56}$Mn were responsible for the contamination. Attempts to reduce this contamination by extractions with EDTA, dithizone, and $NH_4CNS$ resulted in a significant decrease in the per cent recovery of the Co. Since for our work we were able to separate and determine the Co radiations by gamma spectrometry in the presence of the Cu and Mn, no further refinement of the chemical procedure was attempted at this time.

It should be pointed out that somewhat higher sensitivities can be obtained in

TABLE I.—ACTIVATION ANALYSIS FOR COBALT IN RAT KIDNEY TISSUE USING $^{60m}$Co

| Animal number | Live weight (gms.) | Co administered as vitamin $B_{12}$ ($\mu$g) | Fresh kidney weight (gms.) | Yield of separation procedure (%) | Co found in kidneys ($\mu$g)* |
|---|---|---|---|---|---|
| 1 | 335.7 | 135 | 2.47 | 39.4 | 8.85 |
| 2 | 323.4 | 90 | 2.02 | 40.3 | 6.60 |
| 3 | 315.3 | 45 | 2.38 | 23.8 | 3.02 |
| 4 | 268.1 | 45 | 1.87 | 38.8 | 1.80 |
| 5 | 287.2 | 45 | 2.12 | 49.5 | 3.37 |
| 6 | 363.0 | 45 | 2.19 | 50.4 | 2.18 |
| 7 | 374.0 | 45 | 2.28 | 44.3 | 1.60 |
| 8 | 349.3 | 45 | 2.27 | 53.8 | 2.56 |
| 9 | 259.2 | 45 | 1.98 | 35.7 | 1.25 |
| 10 | 363.5 | 45 | 2.10 | 36.9 | 1.94 |

* Corrected to neutron flux of 1 × $10^{12}$ n/cm$^2$ sec.

activation-analysis when gross gamma counting is used instead of spectrometry. Thus an improvement in the specificity of the Co separation to reduce the Cu and Mn to a point where the $^{60m}$Co activity is the primary activity present would permit

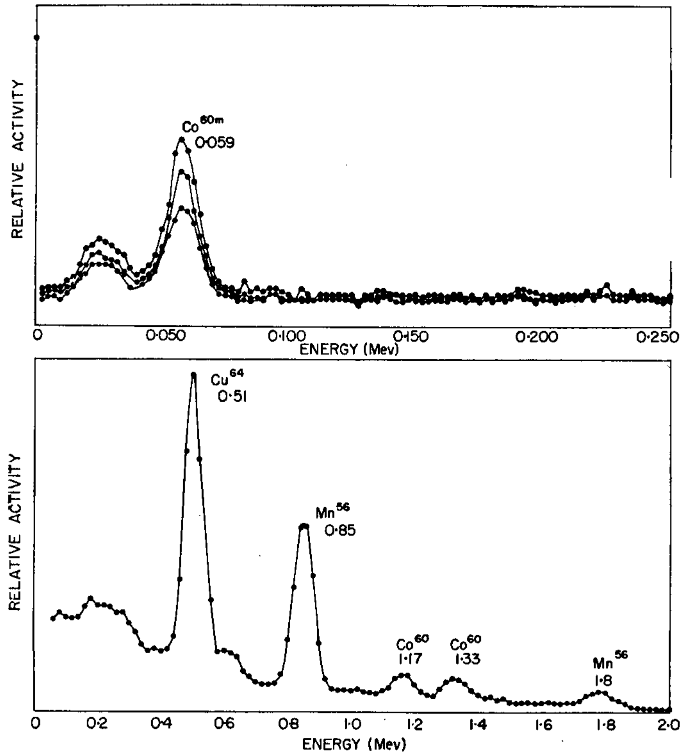

FIG. 1.—Gamma-ray spectra of cobalt fraction separated from rat kidney tissue. Spectra in top curve taken at four-minute intervals. Bottom curve taken after short-lived $^{60m}$Co has decayed out.

utilization of this method without elaborate spectrometry equipment and in addition would probably increase the sensitivity by a factor of 2–5.

The variability of individual rats does not permit an exact evaluation of this method such as is possible using standard samples of alloys, etc. The results of Table I do, however, show the right order of magnitude for the relative values. The overall reproducibility of the method for tissue samples was shown to be around 10% at these microgram levels by several runs in which known amounts of cobalt were added to rat liver before the analysis.

Preliminary investigations have also shown that this procedure may be readily adapted to the analysis of Co-containing vitamin capsules such as Myadec.* Single gelatin capsules were irradiated and subjected to the previously described chemical separation. Since Cu and Mn were also separated with this procedure a simultaneous determination of these elements could be performed using gamma spectrometry. The spectra obtained for this type of sample are quite similar to those shown in Fig. 1.

## CONCLUSION

Thermal neutron activation analysis has definite advantages over tracer studies for the determination of pharmaceutical localization. For medicinals amenable to this type of procedure the advantages are (1) the biological system is not exposed to radiation during the course of the experiment, (2) utilization of short-lived radioisotopes reduces the possibility of prolonged contamination, and (3) there is no problem of disposal of contaminated animal wastes such as carcasses or excreta. In addition, analysis by activation eliminates the problem of reagent blanks, so common to other analytical techniques.

Furthermore, the use of 10.5-min $^{60m}$Co in activation-analysis has been shown to be feasible and permits completion of analyses of this sort within a period of an hour or so rather than of days or weeks.

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**Zusammenfassung**—Microgrammengen von Cobalt aus Vitamin $B_{12}$ wurden im Gewebe von Rattennieren und auch in Vitaminpräparaten bestimmt. Es wurde eine Schnellaktivierungsmethode verwendet. Eine 15-Minuten radiochemische Trennungsmethode in Verbindung mit Gammstrahlen-spectrometrie gestattete die Verwendung des 10.5 Min. $^{60m}$Co-Isotopes. Bei der Methode lag die untere Grenze der Bestimmbarkeit bei einem von einem Thermal-Neutronen Strom von $10^{12}$ n/cm$^2$ sec bei etwa $5 \times 10^{-8}$ gram Cobalt.

**Résumé**—On dose quelques microgrammes de cobalt provenant de vitamine $B_{12}$, issue de tissus de rein de rat aussi bien que de préparations de vitamine, par une analyse par activation rapide. Une méthode de séparation radio-chimique de 15 minutes associée à une spectrometrie gamma permet l'utilisation de radioisotope 10,5 min $^{60m}$Co. Par ce procédé la limite inférieure de détection pour un flux de neutrons thermiques de $10^{12}$ n/cm$^2$ sec. est d'environ $5 \times 10^{-8}$ gramme de cobalt.

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# QUANTITATIVE OXIDATIONS BY POTASSIUM FERRICYANIDE

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**Summary**—Titrimetric methods using potassium ferricyanide as an oxidant for the estimation of various inorganic and organic substances are reviewed. An attempt has been made to evaluate the importance of these methods. Although the emphasis is on the literature that appeared in the past five years, some older procedures are included because of their significance.

IN contrast to commonly employed oxidants such as permanganate, cerate, halogens and several others, the use of potassium ferricyanide is relatively limited. Much of the work reported in this field is fragmentary and no extensive review or summary is available on potassium ferricyanide as an oxidizing agent in quantitative analysis. Thyagarajan[1] reviewed oxidations by ferricyanide from the standpoint of synthesis and reaction kinetics of organic compounds. Kolthoff and Belcher[2] in their third volume on *Volumetric Analysis* have devoted a small section to potassium ferricyanide. As the literature on potassium ferricyanide has built up considerably, especially in the last few years, it was thought useful to compile systematically the applications of potassium ferricyanide as an oxidizing agent. In the present review, methods of practical significance are described in some detail while relatively unimportant methods are either not included or cited only by references. Although the emphasis is on the literature that appeared in the last five years, some classical procedures are described because of their significance.

Potassium ferricyanide belongs to the class of oxidizing agents in which the oxidizing species is a complex-abstracting ion.

$$\mathrm{Fe(CN)_6{}^{3-} + e \rightleftarrows Fe(CN)_6{}^{4-}} \qquad E_0 = +0.3560\ \mathrm{V} \quad \text{at} \quad 25^\circ\mathrm{C}^3$$

The change of potential in a very dilute solution with increasing ionic strength is greater than that calculated on the basis of simple Debye–Hückel expression because of the incomplete dissociation of the alkali and the alkaline earth metal ferrocyanides. The value of $E_0'$ at pH 7 and at 30° is +0.43 volt, while the rH value is + 28.4.[4] The ferricyanide/ferrocyanide is one of the unique systems, the redox potential of which is

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unaffected by pH (except in strongly acidic solutions). The redox potentials in different acid media are given here:

| | Acid concentration, molar | | | |
|---|---|---|---|---|
| | 0.01 | 0.1 | 1 | 3 |
| HCl | +0.48*v* | +0.56*v* | +0.71*v* | — (5) |
| $H_2SO_4$ | — | +0.57*v* | +0.72*v* | +0.77*v* (5) |
| | | | +0.69*v* | (6) |
| $HClO_4$ | — | — | +0.72*v* | — (5) |

From the redox potential and rH values it is clear that ferricyanide ion is rather a weak oxidizing agent. This, and the fact that the reactions in many cases proceed slowly, precluded the extensive use of potassium ferricyanide as an oxidimetric reagent. In a few cases where oxidation did proceed reasonably rapidly, lack of suitable indicators for end-point detection in a titration naturally restricted its use. A few indicators have been suggested in specific instances: diphenylamine ($E_0 = 0.75$ volt)[7], ferrous dimethylglyoxime ($E_0'$ at pH 9.4 = 1.25 volts)[8], methylene blue ($E_0 = 0.53$ volt)[4], and thionine ($E_0 = 0.56$ volt)[4]. In certain instances, zinc sulphate is added initially, which helps in end-point detection through the formation of a white precipitate of zinc potassium ferrocyanide.[9] Potentiometric indication is possible in practically every case. Many reactions employing ferricyanide as an oxidant take place at elevated or boiling temperatures. Because of the inconvenience accompanied with the use of salt bridges at higher temperature, the potentiometric method is not very attractive. The derivative polarographic titration technique should be preferred for this purpose.[10,11]

In spite of the above demerits, potassium ferricyanide possesses distinct features as a titrimetric oxidant. The compound is obtainable in a high state of purity, is non-hygroscopic, has a large equivalent weight (329.26) and can serve as its own standard. Aqueous solutions of potassium ferricyanide are stable on long storage if properly protected from light.* The oxidizing capacity of ferricyanide is more particularly superior in alkaline than in acidic medium. Oxidations which are incomplete or slow under ordinary experimental conditions can be made to proceed quantitatively and rapidly by effecting them in presence of a catalyst and/or at elevated temperatures. Osmic acid is generally used as a catalyst in ferricyanide oxidations.[12] Alkaline solutions of ferricyanide are stable at elevated temperatures. The oxidizing capacity of potassium ferricyanide can also be enhanced by removing the ferrocyanide formed for instance, as the sparingly soluble zinc potassium ferrocyanide.

## METHODS USING FERRICYANIDE

The titrimetric approaches that have been made in determining reducing substances are: I. Oxidation of the substance using an excess of ferricyanide, and II. Direct titration. These procedures are discussed here with their applications.

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* 0.1*N* solution of potassium ferricyanide did not alter in strength for a period of 5 weeks.

## I. *Oxidation by Excess Ferricyanide*

Generally, two methods are practised in the estimation of a reducing substance by excess ferricyanide: (*i*) titration of the ferrocyanide formed against standard ceric sulphate and (*ii*) determination of the excess ferricyanide. The cerimetric titration of ferrocyanide can be performed either potentiometrically[13] or by using ferroïn or ferric chloride as indicator.[14]

$$Fe(CN)_6^{3-} + Ce^{4+} \rightarrow Fe(CN)_6^{4-} + Ce^{3+}$$

The stability of ceric sulphate solutions and its large equivalent weight are the chief advantages in this titration.[15] In addition, this approach eliminates the necessity of standardizing ferricyanide. In the latter method, the excess of ferricyanide is usually determined iodometrically.[2] The recommended procedure for this is the addition of 2 ml of 4*N* hydrochloric or sulphuric acid, 10 ml of *N* potassium iodide and 10 ml of 25% zinc sulphate solution to 25 ml of ferricyanide and after a minute, titrating the liberated iodine with standard thiosulphate adding starch towards the end. At the end-point the solution is colourless and a pure white precipitate is formed if all the reagents used are iron free.

$$2\,Fe(CN)_6^{3-} + 2I^- \rightleftharpoons 2\,Fe(CN)_6^{4-} + I_2$$

Zinc sulphate is added to shift the equilibrium from left to right.

### *Determination of metals having variable valency*

Quantitative oxidation of such metals as arsenic$^{III}$,[16] antimony$^{III}$,[16,17] cerium$^{III}$,[18] chromium$^{III}$,[16,19] manganese$^{II}$,[19] thallium$^{I}$,[18] tin$^{II}$,[16] and uranium$^{IV}$,[20] has been reported from time to time, but in view of existing superior and simpler methods, the ferricyanide oxidation for these metals is of little importance.

In contrast to other methods, the ferricyanide procedure for vanadyl ion appears more dependable.[21] The oxidation of vanadyl ion is effected by ferricyanide in 1*N*–2*N* alkali and after 0.5 hr the ferrocyanide formed is titrated with standard ceric sulphate in presence of sulphuric or hydrochloric acid using ferroïn or ferric chloride as indicator.

### *Hydrazine and hydroxylamine*

The reaction between hydrazine and ferricyanide has been a subject of numerous investigations.[22] Ray and Sen[23] were the first to employ this reaction for a gasometric analysis wherein the nitrogen evolved was measured.

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

Later, titrimetric methods were described based upon the estimation of either the resulting ferrocyanide[24] or the excess of ferricyanide.[25] The addition of too large an excess of ferricyanide obscures observation of the end-point in the ferrocyanide-cerimetric titration. Direct-titration methods for hydrazine estimation by ferricyanide have also been reported and these are described in a later section.

Sant[26] in a study of the reaction between hydroxylamine and ferricyanide showed that although in a strongly alkaline medium hydroxylamine is oxidized to various products, it is converted quantitatively to nitrogen if the pH of the medium is maintained at 8–10.

$$2NH_2OH + [O] \rightarrow N_2 + 3H_2O$$

*Sulphur compounds*

In a short communication, Solymosi[27] has shown that inorganic sulphur compounds such as sulphite, bisulphite, pyrosulphite, sulphide, dithionate, thiosulphate and tetrathionate are all oxidized to sulphate by ferricyanide in 4*N*–5*N* alkali, at 50°–60° and in presence of osmium tetroxide as catalyst. At room temperature and in 0.2*N*–1*N* alkali, dithionate is oxidized only to sulphite. It is not clear if the above sulphur compounds can be analyzed when present together.

*Thiourea:* Joshi[28] outlined a method for the quantitative oxidation of thiourea to sulphate and urea by alkaline ferricyanide:

$$CS(NH_2)_2 + 8Fe(CN)_6{}^{3-} + 10OH^- \rightarrow CO(NH_2)_2 + 8Fe(CN)_6{}^{4-} + SO_4{}^{2-} + 5H_2O$$

The experimental conditions are so restricted that a slight deviation from them tends to give erroneous results owing to the nonstoichiometric conversion of thiourea to products other than sulphate and urea.

*Thiocyanate:* The complete oxidation of thiocyanate to sulphate and cyanate by alkaline ferricyanide in presence of osmic acid to initiate and catalyze the reaction appears to be an excellent method for the determination of thiocyanate.[29]

$$SCN^- + 8Fe(CN)_6{}^{3-} + 10OH^- \rightarrow SO_4{}^{2-} + CNO^- + 8Fe(CN)_6{}^{4-} + 5H_2O$$

Besides the cerimetric and the iodometric finish, it has been shown that the excess ferricyanide can also be titrated conveniently with standard arsenite solution employing a potentiometric end-point.[30] The large equivalent is the chief advantage in analyzing very small quantities of thiocyanate. As this oxidation of thiocyanate takes place only in presence of osmic acid as catalyst, it should be useful in determining thiocyanate in presence of other readily oxidizable substances.

*Reducing sugars*

Potassium ferricyanide as an oxidant for aldoses and ketoses was reported by Gentele[31] a hundred years ago. The method, since then, has undergone several modifications. In concluding their critical study on methods of estimating reducing sugars, Blom and Rosted[32] consider that the cupric method is superior to the ferricyanide, because the latter oxidizes many non-sugar substances which copper does not attack at all. The ferricyanide method, although it lacks specificity and is empirical, has been immensely useful in biochemistry and is by far the most reliable method for evaluating true glucose, rather than total reducing substances, in blood.[33] Hagedorn and Jensen[34] laid down optimum conditions for such an analysis. In principle, a known excess of alkaline ferricyanide is added and the excess oxidant is determined iodometrically with standard thiosulphate. The Association of Official Agricultural Chemists[35] recommend the ferricyanide method for the determination of reducing and nonreducing sugars in flour and of the diastatic power of beverages, etc.

Milton[36] proposed a sensitive colorimetric analysis based upon the spectrophotometric determination of the ferrocyanide formed as brown uranyl ferrocyanide. Great precautions have to be taken to avoid interferences due to other reducing substances. According to Pinxteren[37] the ferrocyanide formed by the reduction of ferricyanide can be titrated potentiometrically with standard zinc sulphate solution.

### *Certain quaternary compounds*

Quaternary ammonium salts, such as, alkyldimethylbenzylammonium chloride, can be oxidized by ferricyanide in a sodium acetate-acetic acid buffered medium.[35] The excess ferricyanide is determined iodometrically. The method is applicable to commercial preservatives. Tomíček and Šimon[38] found that direct titration of ferricyanide with quaternary salt (obtained from quina alkaloids) is also possible. The titration is performed in 2–3 % potassium hydroxide and at 50°–60°, potentiometrically or visual. One mole of the salt requires 2 moles of ferricyanide. As the salt is slightly soluble in water, it is dissolved in a mixture of alcohol and water.

## II. *Direct Titration Methods*

In the majority of the cases, the reducing substance is used as the titrant. An electrometric end-point, in general, is possible in almost every instance. Indicators are suggested in a few cases. Titrations in the presence of zinc sulphate, where no indicator is needed, are also reported. Ferricyanide may be used as the titrant in a few instances.

### *Ascorbic acid (vitamin C)*

Erdey and Svehle[39] reported the titration of ferricyanide with ascorbic acid at pH 5–6.

$$C_6H_8O_6 + 4Fe(CN)_6^{3-} + 4OH^- \rightarrow C_6H_6O_6 + 4Fe(CN)_6^{4-} + 2H_2O$$

2:6-Dichlorophenolindophenol was suggested as an indicator. Near the end-point the greenish color changes to an azure-blue which disappears suddenly at the end-point. A potentiometric end-point is also possible. Sant[40] developed a simple method for the determination of ascorbic acid based upon its oxidation to dehydroascorbic acid by ferricyanide in presence of zinc acetate. The latter maintained the necessary pH and at the same time removed the ferrocyanide ion by precipitation. Potassium iodide-starch served as an internal indicator. This method was successfully applied for the determination of ascorbic acid in fruit juices.

### *Vanadyl sulphate*

Fresno and Mairlot[41] carried out potentiometric titrations, and Willard and Manalo[42] studied several diphenylamine derivatives as indicators in the titration of alkaline ferricyanide with vanadyl sulphate and found 2-carboxy-2-methoxy diphenylamine to be the most suitable. The method served as an indirect means for estimating arsenic$^{III}$, antimony$^{III}$, chromium$^{III}$, hydrazine and hydrogen peroxide. The procedure is only of academic interest.

### *Thallium$^{I}$*

Fresno and Valdes[43] first studied the potentiometric titration of thallium$^{I}$ with potassium ferricyanide in alkaline solution but obtained results which were 1 % low. Miura[44] claimed accurate results when the titration was performed in a strongly alkaline solution and at 60°. Recently Hartley and Lingane[45] studied this reaction coulometrically using electrogenerated ferricyanide, obtained through the anodic oxidation of ferrocyanide, as a source for the oxidation of univalent thallium. The equivalence point was located potentiometrically or amperometrically. These titrations could be performed in comparatively low alkali concentrations and at room temperature. The interference due to light and dissolved oxygen was easily avoided. Milligram quantities of thallium can be determined by the above procedure within an error of $\pm 0.2\%$.

The ferricyanide-ferrocyanide couple possesses very favourable characteristics and is applicable to both redox reactions and precipitation titration of various metal ions. Because of the intermediate formal potential (ranging from *ca.* +0.4 to +0.7 V *vs* N.H.E. depending upon acidity and other conditions) of this reversible couple, it is relatively easy to generate either ferricyanide or ferrocyanide ion at a platinum electrode with 100% efficiency over a wide range of solution conditions.

### *Mercury$^{\mathrm{I}}$*

In the presence of iodide[46] or thiocyanate,[47] ferricyanide can be titrated in controlled pH conditions (3–7) at about 15° with mercury$^{\mathrm{I}}$ perchlorate. The end-point is determined potentiometrically or by using diphenylamine sulphonate as indicator. The stability of mercurous perchlorate reagent on storage is noteworthy.

### *Cerium$^{\mathrm{III}}$*

The potentiometric method for the determination of cerium$^{\mathrm{III}}$ by ferricyanide in concentrated solution of potassium carbonate, though reliable and precise, gives poor inflection points when the ceric/cerous ratio is large. Leonard *et al.*[49] overcame this difficulty by adopting an amperometric end-point. The titrations were carried out using a rotating platinum electrode at an applied potential of 0.0 V *vs* the S.C.E. Good results were obtained in the presence of a 100-fold excess of ceric ion. In order to avoid air oxidation of cerium$^{\mathrm{III}}$, it is necessary to perform the titration in an atmosphere of nitrogen. Cerous impurity in solid ceric salts could be determined by the above method.

### *Cobalt*

The general principle involved in this method is the oxidation of cobalt$^{\mathrm{II}}$ in ammonium hydroxide-ammonium citrate medium by ferricyanide.[50] Cobalt sulphate is used as the titrant. The method is extensively applied in the determination of cobalt present in non-ferrous mining and metallurgical products,[51] irons and steels,[52] and cemented carbides.[53,54] The only common interfering element is manganese but this can be removed by a nitrochlorate separation. The following elements do not interfere: Hg$^{\mathrm{II}}$, Pb,Fe, Ni, Cu, Bi, Cd, As$^{\mathrm{V}}$, Sb, Sn$^{\mathrm{IV}}$, Se, Te, Mo, Be, Al, Zn, Ti, W, U, Zr, vanadate and chromate. By using ethylenediamine instead of ammonium hydroxide Diehl and Butler[55] obtained sharper end-points and carried out the successive determination of cobalt and manganese. The cobalt$^{\mathrm{II}}$-ethylenediamine complex is a stronger reducing agent than the corresponding ammonia complex by about 0.5 volt. However, dissolved oxygen now becomes an interfering factor and must be removed. Recently Kopanica and Doležal[56] described a direct titration of cobalt with standard potassium ferricyanide in presence of glycine. The latter forms a more stable complex with cobalt than either ammonia or ethylenediamine and no inert atmosphere is needed during the titration.

### *Arsenic*$^{\text{III}}$

Fresno and Valdes[43] studied the potentiometric titration of arsenic$^{\text{III}}$ with potassium ferricyanide as a titrant. These titrations were carried out at 70° in presence of 40 ml of 50% potassium hydroxide per 10 ml of the solution.

$$AsO_2^- + 2Fe(CN)_6^{3-} + 4OH^- \rightarrow AsO_4^{3-} + 2Fe(CN)_6^{4-} + 2H_2O$$

Solymosi[57] performed reverse titrations but with little advantage. Sant[58] worked out a simpler and more rapid method in which titrations were carried out in the presence of osmic acid as catalyst, in as low an alkalinity as 1*N* and at room temperature. An indirect method for the estimation of thiocyanate was developed, based on the back-titration of excess ferricyanide with a standard solution of sodium arsenite. The chief advantage, besides accuracy, of this method is that the two oxidation processes, *viz.*, of thiocyanate and arsenite take place under identical experimental conditions.

### *Glucose*

Britton and Phillips[59] studied the direct titration of ferricyanide with glucose in sodium carbonate medium and at 90° employing a potentiometric end-point. They also suggested methylene blue as a suitable internal indicator. The course and velocity of the glucose-ferricyanide reaction are dependent upon pH, the length of the oxidation period, temperature and the ionic strength of the medium. Adams *et al.*[11] re-investigated this reaction and recommended the derivative polarographic end-point. If a pair of platinum electrodes are polarized by a small constant current (*ca.* 2 $\mu$A), the electrode will give continuous e.m.f. readings corresponding to the slope of a polarographic curve at the zero current axis. The derivative voltage is measured with a Beckman Model G pH meter. The apparatus assembly is simple and the readings rapidly become steady. The end-points, which are sharper than in potentiometry, can be detected easily without plotting. As the reference half-cell and hence the salt bridge is eliminated, this method is ideally suited at high temperatures. As little as 20 $\mu$g of glucose could be estimated in a titration volume of 5 ml with an accuracy of $\pm 5\%$. A slight manipulation of ionic strength of the system is needed when analyzing unknown samples because of the dependence of the reduction equivalent of ferricyanide on the ionic strength.

### *Sulphide and hydrosulphite*

Charlot[60] found that in an ammonium chloride–ammonia buffer (pH = 9.4) sulphide is oxidized to sulphur by ferricyanide.

$$S^{2-} + 2Fe(CN)_6^{3-} \rightarrow S + 2Fe(CN)_6^{4-}$$

Ferrous dimethylglyoxime is used as an internal indicator. At the end-point the red colour of the ferrous complex disappears. As oxygen interferes in this method a hydrogen atmosphere has to be maintained. Sulphite, if present, is first removed by precipitation with barium chloride. The same procedure can be applied to the determination of hydrosulphite.[61]

$$S_2O_4^{2-} + 2Fe(CN)_6^{3-} + 4OH^- \rightarrow 2SO_3^{2-} + 2Fe(CN)_6^{4+} + 2H_2O$$

Scagliarini[62] suggested a potentiometric end-point in the titration of sulphide with ferricyanide. Recently, Kiboku[63] described the use of sodium nitroprusside as an indicator in the sulphide-ferricyanide titration. It is claimed that sulphite and thiosulphate will not interfere. No mention is made of interference due to atmospheric oxidation.

### *Hydrazine*

Vulterin and Zýka[64] reported that hydrazine, hydroxylamine and *iso*nicotinoyl hydrazide can be determined by direct potentiometric titration with potassium ferricyanide in 10–25% potassium hydroxide solution. In the presence of alkali the above compounds will exist as free bases, which are susceptible to air-oxidation and decomposition, and therefore the above method cannot be recommended. The same authors later reported reverse titration at an alkali concentration of 2.5–5% and at 70–80°. Sant[58] developed a simple procedure for the determination of hydrazine depending upon the potentiometric titration of alkaline ferricyanide with hydrazine sulphate at room temperature using osmic acid as a catalyst. In the presence of this catalyst the reduction of ferricyanide by hydrazine takes place very rapidly and therefore during the titration there is little chance for hydrazine to undergo atmospheric oxidation.

### *Cysteine*

Recently Waddill and Gorin[65] described an amperometric method for the determination of semimicro amounts of cysteine with standard potassium ferricyanide in a phosphate buffer of pH 7.

$$\begin{aligned} &2HSCH_2CH(NH_3^+)COO^- + 2Fe(CN)_6^{3-} \rightarrow \\ &\qquad [-SCH_2CH(NH_3^+)COO^-]_2 + 2Fe(CN)_6^{4-} + 2H^+ \end{aligned}$$

Copper sulphate is used to catalyze the reaction. The precision is within 1% and common amino-acids do not interfere. This method appears superior to other methods investigated heretofore.[66–69]

### *Titration of ferricyanide in presence of zinc sulphate*

The oxidation potential of the ferricyanide ion can be increased by removing the ferrocyanide formed as sparingly soluble zinc potassium ferrocyanide. Based on this principle, ferricyanide can be titrated with a reducing substance. The titrations are usually performed in boiling solution in a suitable pH environment, using the reducing substance in question as the titrant. The principal advantage of this titrimetric method is that no indicator is needed. During the titration there is a distinct yellow-orange precipitate of zinc ferricyanide. At the end-point a pure white precipitate of zinc potassium ferrocyanide is formed and the supernatant liquid is colourless. The first application of this titration was made by Bhukarov and Podlubnya[9] for the estimation of glucose.

Recently Sant studied the determination of hydrazine,[70] hydroxylamine[71] and nitrite[72] by the above method. In the hydrazine reaction, titration was performed in an almost neutral or slightly acidic solution. Beyond 0.8*N* alkali concentration the results were faulty and the end-point was difficult to discern. The corresponding nitrite-ferricyanide reaction, where nitrate is the oxidation product, takes place in an almost neutral medium (pH = 6–7). The oxidation of nitrite does not proceed rapidly at alkali concentrations beyond 0.3*N*. Large excess of nitrate has no adverse effect on the determination of nitrite. An important application of ferricyanide titration in the presence of zinc sulphate is in the analysis of a mixture of hydrazine and hydroxylamine. Very few rapid and accurate methods are available for such an analysis. In the presence of zinc sulphate, hydrazine and hydroxylamine are oxidized to nitrogen and nitric acid respectively, but in a weakly alkaline medium excess of ferricyanide oxidizes both to nitrogen. Oxidation of a mixture of hydrazine and hydroxylamine under two sets of conditions would give a measure of the individual components. The determination of hydroxylamine by the ferricyanide-zinc sulphate method is particularly useful for small quantities of hydroxylamine.

### *Miscellaneous*

Methods have also been described for the direct titration of the following with potassium ferricyanide: antimony$^{\text{III}}$,[43] hydrogen peroxide[73,74], quinol,[75] selenite,[76] titanium$^{\text{III}}$,[77–79] tin$^{\text{II}}$,[7,80,81] uranium$^{\text{IV}}$,[82] chromium$^{\text{III}}$,[83] chromium$^{\text{II}}$,[84] molybdenum,[84] tungsten$^{\text{IV}}$,[84] tungsten$^{\text{V}}$,[85] and iron$^{\text{II}}$.[86]

**Zusammenfassung**—Es wird eine Übersicht übert itrische Methoden unter Verwendung von Kaliumferricyanid als Oxydens gegeben. Es wurde versucht die Wichtigkeit der Methoden zu bewerten. Wenn auch in der Hauptsache die Literatur der letzten fünf Jahre besprochen wurde, so sind doch einige ältere Methoden wegen ihrer grossen Bedeutung mit einbezogen.

**Résumé**—On présente une mise au point des méthodes titrimétriques utilisant le ferricyanure de potassium comme oxydant pour le dosage de nombreuses substances inorganiques et organiques. Les auteurs ont tenté d'évaluer l'importance de ces méthodes. Bien que l'accent soit mis sur ce qui a paru durant ces cinq dernières années dans la littérature, quelques méthodes plus anciennes sont introduites en égard à leur importance.

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# SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM IN STEEL WITH 3:3′:4′:5:7-PENTAHYDROXYFLAVANONE

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**Summary**—Studies on the organic reagent 3:3′:4′:5:7-pentahydroxyflavanone (dihydroquercetin) have led to the development of a colorimetric method for molybdenum in steel. By an extraction process all interfering metals are removed except tungsten. The method is applicable to the determination of molybdenum in all substances which do not contain tungsten. Known methods of separating molybdenum from tungsten will permit its use when tungsten is present.

## INTRODUCTION

THE colorimetric or spectrophotometric method of analysis is a rapid and accurate means of determining low concentrations and traces of metals in alloys, ores and biological materials. In our study of the development of superior procedures for the accurate analysis of the special alloying metals used in high-temperature-resistant and high-strength alloys, colorimetry was found applicable in certain instances.

In our continuous screening of possible reagents for application to the solution to our problem, the naturally occurring material 3:3′:4′:5:7-pentahydroxyflavanone showed promise of being a suitable reagent for certain metals, one of these being molybdenum, which, under suitable conditions gave a yellow-coloured solution with this reagent. This reagent has the common name of dihydroquercetin and the symbol DHQ will be used hereafter in designating it in this report.

The history of DHQ and its preparation from the cork of Douglas fir bark[8] have been reported elsewhere[1,3,4,7,10,11]. Reagent quality DHQ, necessary for this study, was prepared by passing a diethyl ether solution of DHQ through a column of 1 : 3 activated carbon and celite. The colorless eluate, which appears first, was heated gently to remove the ether and obtain the pure product. The yellowish eluate was discarded. Recrystallize once from water which yields long colorless needles with 2–1/2 moles of water; m.p. 241–2°; solubility in boiling water 9.3 g/100 ml; optical rotation $[\alpha]_D^{25} + 39°$ (4 g in 100 ml of equal volumes of acetone and water).

## APPARATUS AND REAGENTS

Beckman DU Spectrophotometer.

Benzoin-α-oxime: 0.1% weight/volume in chloroform.

DHQ: 0.300 g dissolved in 100 ml absolute ethanol.

Molybdenum solution: appropriate quantities of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, Merck, were dissolved in water to give stock solutions containing 0.1, 0.2, 0.5 and 1.0 mg molybdenum per millilitre.

Acetate buffer, pH5: 0.67 mole sodium acetate plus 1.33 moles acetic acid per litre.

Other chemicals used were of reagent quality.

## PROCEDURE

### *Dissolution of the sample*

The steel sample of suitable size (containing approximately 1 to 2 mg molybdenum) was placed in 15 ml of 50% hydrochloric acid in a 30- or 50-ml beaker with a cover glass on a low temperature hot plate. When hydrogen evolution had ceased the mixture was cooled, sufficient concentrated nitric acid (1 ml or less) was added, and the beaker was returned to the hot plate. This dissolves any carbides and oxidizes, free carbon and the iron to $Fe^{III}$. A little more hydrochloric acid was added to insure that an excess was present and then the solution was evaporated to a small volume. If chromium or vanadium are present they will remain as $Cr^{III}$ and $V^{IV}$. Tungsten will be oxidized to $W^{VI}$ and will precipitate, carrying with it some of the molybdenum.

### *Extraction*

The extraction procedure of Goldstein[2] was used as follows: The steel sample solution was rinsed into an 125-ml separatory funnel with 5% hydrochloric acid to a final volume of about 50 ml. If the sample of steel taken contained more than 2 mg of molybdenum, it was transferred to a 50-ml volumetric flask and made up to volume with 5% hydrochloric acid, and an aliquot was taken for the extraction. The molybdenum was then extracted with 0.1% benzoin-α-oxime in reagent-grade chloroform using 10-,10-,10-,10-,5-ml portions. The combined extracts in another 125-ml separatory funnel were washed with 20 ml of 5% hydrochloric acid, and the chloroform layer was transferred to a 100-ml volumetric flask. The aqueous layer was washed with 5 ml of chloroform, which collects any droplets of extract clinging to the glass, and this chloroform was added to the main extract. A liberal portion of absolute ethanol was added, and then 1 ml of 5% sodium hydroxide in methanol. This mixture was agitated for a minute or two which caused the flocculent material in the extract to dissolve, forming a clear solution. The solution was then made up to volume with absolute ethanol.

### *Preparation of the solution for the spectrophotometric determination*

*To a 10-ml volumetric flask, using analytical pipettes, was added 0.5 ml of pH 5 acetate buffer* and 3 ml of 0.3% DHQ ethanol solution. To this was added with agitation 5 ml of the extract solution and 0.5 ml of water. The solution was then diluted to volume with absolute ethanol and thoroughly mixed. The maximum colour intensity is reached in 10 minutes and is stable for at least 24 hours.

### *Preparation of the spectrophotometric reference curve for molybdenum*

To conserve reagents, 10-ml volumetric flasks were used for preparation of all solutions for spectrophotometric observations. Place in the flask 0.5 ml of pH 5 sodium acetate-acetic acid buffer solution, 3 ml of 0.3% DHQ reagent solution and 3 ml of chloroform, and mix; add the aqueous molybdenum solution; add sufficient water to bring the total water present to 1 ml, and mix; dilute to volume with ethanol and mix. The order of addition of the reagents is important. A series of solutions containing 10 to 100 micrograms of molybdenum was prepared, and a reference solution containing all of the reagents, but no molybdenum. The colour intensity was read against the reference solution after 10 minutes at 410 millimicrons on the Beckman DU spectrophotometer. The absorption intensity follows Beer's law.

## DISCUSSION

### *Development of the procedure*

Preliminary studies on the colour reactions of DHQ with aqueous solutions of metals revealed that molybdenum gave a characteristic yellow colour. A spectrophotometric study showed that maximum absorption occurred at a wave length of 410 millimicrons. The colour reaches a maximum intensity at pH 5 and is appreciably less intense at 3.5 and 7.0. In aqueous solution buffered at pH 5 with sodium acetate-acetic acid buffer the absorbance follows Beer's law provided sufficient excess DHQ is present with 5 to 100 micrograms of molybdenum in 10 ml of solution. By use of the Slope Ratio Method of Harvey[5] the complex was found to contain two moles of DHQ to one gram atom of molybdenum. The molar extinction coefficient at 410 millimicrons is about 5000.

*Removal of molybdenum from steel for colorimetric determination*

It was early learned that DHQ forms an appreciable colour with iron, which yields a bluish-black precipitate upon standing. This interferes with the molybdenum determination and requires prior separation of the molybdenum from iron.

At first, removal of molybdenum from the steel solution was accomplished by precipitating with the specific reagent benzoin-α-oxime from hydrochloric acid solution.[6] Ashing this precipitate, dissolving the resulting molybdic oxide in ammonium hydroxide, evaporating gently to dryness, and taking the residue up with water yielded a solution of pH 5, free from iron, which with DHQ gave the characteristic colour. However, no matter how carefully the procedure was carried out, recovery of molybdenum in amounts of the order of a milligram or less was not quantitative.

The recovery of molybdenum from steel solutions was much more satisfactory with this same reagent, benzoin-α-oxime, by an extraction method.[2] Recovery of 99% of the molybdenum by this method (see procedure) was routine.

In order to obtain the molybdenum in a form to put into aqueous solution, an aliquot of the chloroform extract was very gently evaporated. The residue was ashed with sulphuric, sulphuric plus nitric or perchloric acid, and the acid removed on the hot plate. The carbonaceous ash was ignited in an electric muffle at 350°. Owing to the spreading of the residue by wet ashing and low-temperature of ignition over the inside of the small beaker used in this process, it was difficult to obtain quantitative results repeatedly for the molybdenum content of steel samples.

The chloroform extract of the molybdenum-benzoin-α-oxime is a suspension. Aliquoting this suspension leaves reason for doubt, and it was believed that variations in replicate assays were due at least in part to this inadequate aliquoting.

Upon addition of a secondary amine to the extract, the mixture became a homogeneous solution. Sometimes, however, too much water had been brought over in the extraction process and this water remained as a droplet which could very readily contain appreciable amine and molybdenum.

A dilute solution of sodium hydroxide in methanol was substituted for the amine, and the extract was made up to volume with ethanol giving a clear solution, which could then be aliquoted without error.

To avoid bringing the molybdenum into aqueous solution for the colorimetric determination, studies were made on the use of non-aqueous solvents for the colour development. By use of an ethanol solution of DHQ and an aliquot of the chloroform-ethanol-sodium hydroxide extract, a very faint yellow colour was obtained. On occasion this solution was alkaline and required to be brought to pH 5.

The addition of water alone greatly intensifies the colour, and by the addition of the aqueous pH 5 acetate buffer uniformity was obtained in colour development.

The colours of reference standards are stable for at least 24 hours. Steel solutions tend to drop in intensity by 1–2% in 24 hours.

## RESULTS

By the procedure developed, satisfactory results were obtained on synthetic steel samples, and on Bureau of Standards steel samples. Table I shows the results obtained.

TABLE I.—DETERMINATION OF MOLYBDENUM IN BUREAU OF STANDARDS STEEL SAMPLES

| Sample | Weight sample | Aliquot extracted | Molybdenum | | |
|---|---|---|---|---|---|
| | | | Present % | Found % | Error % |
| 30d | 0.8005 | all | 0.035 | 0.0340 | −0.0010 |
| | | | | 0.0341 | −0.0009 |
| | | | | 0.0341 | −0.0009 |
| | 1.2522 | all | | 0.0333 | −0.0017 |
| | | | | 0.0332 | −0.0018 |
| | 1.1658 | all | | 0.0337 | −0.0013 |
| 36 | 0.3960 | 0.20 | 1.01 | 1.042 | +0.032 |
| | | | | 1.026 | +0.016 |
| | | | | 1.016 | +0.006 |
| | | | | 1.030 | +0.020 |
| | 0.3960 | 0.20 | | 1.018 | +0.008 |
| | | | | 1.015 | +0.005 |
| | 0.3095 | 0.40 | | 0.986 | −0.024 |
| | | | | 0.986 | −0.024 |
| | 0.2249 | 0.40 | | 1.013 | +0.003 |
| | | | | 1.002 | −0.008 |

Note: 5 ml of the 100-ml extract was used in each of these determinations.

### *Interferences*

Tungstate, chromate and vanadate ions are partially extracted by the benzoin-α-oxime chloroform solution. No method of preventing the extraction of some tungsten could be found. However, the procedure for preparation of the steel sample solution for extraction purposes kept the vanadium as the vanadyl ion and the chromium in the tervalent state and these caused no interference.

Tungsten also forms a complex with DHQ which is colourless unless considerable tungsten is present, when the solution is tinged with yellow. A spectrophotometric study revealed that the maximum absorption peak of the tungsten complex is at wave length 365 millimicrons whereas the peak for the molybdenum complex is at 410 millimicrons.

It is theoretically possible to determine both molybdenum and tungsten in the same solution by taking measurements at these two wave lengths. Of course there is some absorption of the one metal complex at the absorption peak of the other metal complex. Considerable effort was expended to obtain the conditions for additiveness at these two wave lengths with these two metals, but without success.

The problem is further complicated by the fact that in the extraction process benzoin-α-oxime chloroform solution extracts up to 80% of any tungsten in the acid steel solution by the multiple extraction procedure. Since most of the tungsten in a steel sample, *e.g.*, Bureau of Standards No. 134, is precipitated by the solution procedure, both tungsten and molybdenum are lost in this process. By digesting the steel solution with sodium hydroxide, pH 10–11, acidifying and extracting, up to 80%

of the tungsten is recovered in the extract. If now the residual acid solution is again made alkaline, acidified and extracted, more tungsten is removed. A third treatment permits recovery of 98% of the tungsten as determined by use of radioactive tracer tungsten. Even though this procedure was followed, spectrophotometric analyses were low for both tungsten and molybdenum. Therefore this method is not applicable in its present form for the determination of molybdenum in steel samples containing tungsten.

By use of the hydrogen sulphide method of precipitating molybdenum free from tungsten, the method could be applied to steels which also contain tungsten.

**Zusammenfassung**—Studien am organischen Reagenz 3,3′,4′,5,7-Pentaoxyflavanon, (Dihydroquercetin) führten zu einer photometrischen Bestimmung von Molybdàn in Stahl. Mittels eines Extraktionsprozesses werden alle störenden Metalle ausser Wolfram entfernt. Die Methode ist anwendbar zur Bestimmung von Molybdän in allen Substanzen die frei von Wolfram sind. Bekannte Verfahren zur Trennung von Molybdän und Wolfram sollten die Anwendung auch auf wolframhältige Materialien erweitern.

**Résumé**—Une étude sur le réactif organique 3,3′,4′,5,7 pentahydroxyflavanone, "dihydroquercetine", a conduit au développement d'une méthode colorimétrique de dosage du molybdène dans l'acier. Par un procédé d'extraction on sépare tous les métaux gênants sauf le tungstène. La méthode est applicable au dosage du molybdène dans toutes les substances qui ne contiennent pas de tungstène. Des méthodes connues de séparation du molybdène et du tungstène permettront son utilisation quand le tungstène est présent.

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# THE PREPARATION OF IRIDIUM SOLUTIONS BY AN ACID ATTACK OF TIN–IRIDIUM ALLOYS*

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**Summary**—Iridium metal is alloyed with a large excess of tin, and the alloy is dissolved in a mixture of hydrochloric acid and hydrogen peroxide. The bulk of the tin is distilled from the solution as a mixed halide after the addition of a mixture of hydrochloric and hydrobromic acids. Residual tin is then separated from the iridium solution by precipitation with ammonium hydroxide.

## INTRODUCTION

A PROGRAMME has been undertaken at the Mines Branch laboratories to determine the suitability of tin as a collector for the platinum metals in fire assaying. During the course of this work radiochemical experiments involving the use of $^{192}$iridium were performed to study the behaviour of iridium during the crucible fusion process in which tin is used as the collector.

The radioactive iridium was obtained in the form of compact metal pellets weighing approximately 20 mg each. Because it was desired to add the $^{192}$iridium to the test samples in the form of a solution, a suitable method for dissolving the pellets had to be selected. The published methods for converting iridium metal or its native alloys to soluble forms[1,2] are time-consuming, and require special apparatus and rather exacting techniques; therefore, a simpler method was desired.

It is known that tin forms intermetallic compounds with all the precious metals with the possible exception of osmium;[3,4] however, little use of tin has been made as a collecting or working medium for the platinum metals. Pollard[4] developed a micro-titrimetric method for determining the iridium content of solutions prepared by dissolving tin–iridium alloys in a mixture of concentrated sulphuric acid and an alkali sulphate at temperatures over 300° C. The method is not, however, suitable for the preparation of pure solutions of iridium because the iridium is still associated with large quantities of tin and alkali sulphate in the final solution.

The present report describes a new and simple method for preparing iridium solutions from the metal.

## APPARATUS AND REAGENTS

*Preset time scaler:* Model SC15CST, Electronic Associates Ltd., Toronto, Canada.

*Glass envelope immersion-type Geiger–Müller tube*, Type B6, manufactured by 20th Century Electronics, Croydon, Surrey, England. The tube was fitted with a glass collar and a cell capable of holding a 5 ml sample when fitted around the tube.

*Vycor melting tube*, internal diameter 2·2 cm, height 10 cm.

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## GENERAL EXPERIMENTAL PROCEDURE

### *Preparation of alloys*

(a) *Tin-iridium master alloy* (0·1 ± 0·005% iridium): was prepared by alloying a 20 mg pellet of iridium containing approximately 2 mc of $^{192}$iridium with 20 grams of pure tin according to the procedure given below. To determine the homogeneity of the alloy, weighed portions were dissolved and the resulting solutions were assayed radiometrically for iridium as described below.

(b) *Test alloys:* Each test sample was prepared by placing a weighed quantity of the master tin-$^{192}$iridium alloy (0·5–1·0 gram), pure tin (3·0–3·5 grams), and in certain cases, iridium sponge, into the Vycor melting tube. Air was purged from the tube by nitrogen gas delivered through a 1 × 15-cm Vycor tube placed directly over the materials to be alloyed. The melting tube was then held in an open flame until the tin had melted. While a stream of nitrogen was played over the melt, the tube was vigorously swirled until the bed of iridium sponge at the bottom of the tube was taken up and alloyed with the molten tin. The nitrogen delivery tube was then removed from the melting vessel and the molten alloy was quickly poured into approximately 1 litre of cold water contained in a 2-litre beaker.

After decanting the water, the beaker was placed on the cool part of the hot-plate until the spongy tin-iridium alloy was thoroughly dry. Any alloy which had frozen on the upper walls of the melting tube during pouring was scraped off with a steel spatula, and combined with the main portion of the alloy in the beaker.

In each test the dried alloy particles were thoroughly mixed and two separate weighed samples (each representing approximately 10–15% of the total alloy) were removed for use as radiochemical standards as described below. The remainder of the test sample was brushed out of the beaker, weighed and transferred to a 300-ml tall-form beaker.

### *Dissolution of alloys*

Approximately 40 ml of concentrated hydrochloric acid was added, followed immediately and cautiously by 30% hydrogen peroxide. Further additions of hydrogen peroxide were made during the vigorous dissolution of the alloy, until an excess was present (as judged by the persistence of the colour of chloroiridate ion). The mixture was then heated and from time to time further dropwise additions of hydrogen peroxide were made until the alloy appeared to be completely dissolved and the solution was clear. (In several tests a few shiny metallic flakes remained at this stage but were dissolved in subsequent steps.) The solution was then evaporated to approximately 5 ml.

### *Volatilization of tin*

Next 10–20 mg of sodium chloride and 10 ml of a 7 : 2 mixture of hydrochloric and hydrobromic acids were added and the beaker was swirled over an open flame to volatilize tin. After evaporating to approximately 1 ml, a further addition of the mixed acids was made and the evaporation was repeated as before. To remove as much tin as possible, the volatilization step was repeated six times. The solution was then treated with 10 ml of a 1 : 1 mixture of hydrochloric acid and hydrogen peroxide to re-dissolve any iridium which might have separated out by thermal decomposition of the chloro-iridate. The solution was then evaporated to approximately 2 ml, diluted with water and filtered through a No. 42 Whatman filter paper into a 100 ml volumetric flask, and was finally diluted to the mark with water.

The $^{192}$iridium content of an aliquot of the solution was then determined radiometrically with the immersion Geiger–Müller tube and scaler.

Radiochemical standards were prepared by dissolving each of the portions removed from the main alloy sample in a mixture of hydrochloric acid and hydrogen peroxide as described above. The resulting solutions were each diluted to 100 ml in volumetric flasks without filtration and their $^{192}$iridium activities were determined radiometrically.

The amount of iridium present in the test solutions was calculated by comparing their activities with those of the standard reference solutions prepared in each test.

Self-absorption corrections were not needed for the activity figures of the test and standard solutions.

## RESULTS AND DISCUSSION

### *Effectiveness of acid attack on tin–iridium alloys*

A series of tests was done to determine the effectiveness of the acid attack on tin–iridium alloys. In each test 3·0–3·5 grams of tin, 0·5–1·0 gram of the master tin–$^{192}$iridium alloy and a weighed quantity of iridium sponge were alloyed and treated according to the procedure given above. Table I gives the results of these tests.

TABLE I.—EFFECTIVENESS OF ACID ATTACK IN PREPARING SOLUTIONS OF IRIDIUM TIN–IRIDIUM ALLOYS

| Test No. | Wt Ir in alloy, *mg* | Wt Sn in alloy, *grams* | Percent Ir in alloy | Percent of added Ir found in solution |
|---|---|---|---|---|
| 1 | 0·3* | 2·75 | 0·01 | 100·1 |
| 2 | 1·2 | 3·16 | 0·04 | 100·2 |
| 3 | 3·6 | 3·06 | 0·1 | 98·0 |
| 4 | 7·2 | 2·63 | 0·3 | 99·5 |
| 5 | 11·7 | 2·68 | 0·4 | 98·9 |
| 6 | 20·8 | 2·78 | 0·7 | 97·2 |
| 7 | 40·0 | 2·80 | 1·4 | Only partial dissolution of intermetallics |
| | | | | Average 98·9 |

* Iridium sponge not used in Test 1.

The results in Table I show that iridium in a tin–iridium alloy containing less than 0·7% iridium can be quantitatively dissolved in a mixture of hydrochloric acid and 30% hydrogen peroxide. With alloys containing more than 0·7% iridium, there is a tendency for large flakes of tin–iridium intermetallics to separate out. Although these particles can be dissolved in the hydrochloric–peroxide mixture, the time required is excessive.

### *Removal of residual tin by precipitation with ammonium hydroxide*

Because the presence of milligram quantities of tin in the iridium solutions would be undesirable in many cases, it was necessary to determine the effectiveness of the tin volatilization step described in the experimental procedure. After determining their $^{192}$iridium contents, certain of the test solutions were split into two 50-ml portions and the tin content of one portion from each test solution was determined polarographically[5] (Table II). Iridium did not interfere with this determination. Because the residual tin content of these solutions was found to be appreciable, the second 50-ml portion of each test solution was treated with an excess of ammonium hydroxide to precipitate the tin. After the stannic hydroxide had coagulated, it was filtered off on a No. 42 Whatman filter paper with the aid of pulp, and washed well with a dilute ammonium chloride–ammonium hydroxide solution. The stannic hydroxide was then dissolved from the paper with warm dilute hydrochloric acid and diluted to 50 ml in a volumetric flask. The $^{192}$iridium content of the tin solution was then measured radiometrically to determine the extent of co-precipitation and/or occlusion of iridium. The results of these experiments are given in Table II.

TABLE II.—EFFECTIVENESS OF SEPARATION OF IRIDIUM FROM RESIDUAL TIN

| Test No. | Weight Sn remaining in test solution (100 ml) after volatilization step, *mg* | Percent of added Ir retained by $Sn(OH)_4$ precipitate |
|---|---|---|
| 1 | 11·6 | 0·03 |
| 3 | 9·6 | 0·25 |
| 4 | 5·4 | 0·12 |
| 5 | 9·4 | 0·21 |

The results in Table II show that even after repeated evaporations with the hydrochloric–hydrobromic acid mixture, milligram quantities of tin remain in the iridium solution. However, the residual tin can be conveniently removed by precipitation with ammonium hydroxide, negligible quantities of iridium being retained in the stannic hydroxide precipitate. During the treatment of microgram quantities of iridium, it is probable that the degree of co-precipitation or occlusion would be significantly greater.

On addition of excess ammonium hydroxide, the iridium solutions gradually become decolorized, probably due to the formation of an ammine complex. This complex was destroyed when the solutions were evaporated to a small volume and then treated with a few millilitres of concentrated nitric acid. This also served to destroy the ammonium salts which were present in the solution. The iridium was converted back to chloro-iridate by repeated evaporations of the nitric acid solution with hydrochloric acid.

### *Chemical determination of effectiveness of acid attack on tin–iridium alloys*

Although visual observation indicated that the inactive iridium sponge used in the above tests was completely alloyed with the tin and behaved chemically in an identical fashion to the $^{192}$iridium derived from the master alloy, the radiometric results alone could not substantiate this observation. Therefore, a series of tests was performed in which weighed quantities of iridium sponge and pure tin were alloyed, dissolved, and the resultant solution freed of tin according to the procedures described

TABLE III.—CHEMICAL DETERMINATION OF COMPLETENESS OF SOLUTION OF IRIDIUM SPONGE

| Weight Ir taken, *mg* | Weight Sn in alloy, *grams* | Weight Ir found in final solution, *mg* |
|---|---|---|
| 6·18 | 3·73 | 6·16 |
| 9·27 | 3·84 | 9·10 |
| 8·76 | 3·90 | 8·90 |

above. The quantity of iridium present in each of the final solutions was determined by the Gilchrist method of bromate hydrolysis.[6] The results of these tests are given in Table III.

From the results given in Table III it can be concluded that the radiometric results of the tests described above are valid for the inactive iridium sponge as well as for the $^{192}$iridium added as the master alloy.

## CONCLUSIONS

It is considered that the method presented in this paper offers a new approach to the problem of converting iridium metal into a soluble form. It is more rapid than existing methods, it does not require special equipment and it is suitable for treating any quantity of iridium metal in either sponge or compact form. The method also makes it possible to prepare solutions of iridium which do not contain foreign cations.

**Zusammenfassung**—Iridiummetall wird mit grossem Überschuss von Zinn legiert und die Legierung in einer Mischung von Salzsäure und Wasserstoffperoxyd gelöst. Die Hauptmenge des Zinns wird als gemischtes Halogensalz nach Zugabe einer Mischung von Salz und Bromwasserstoffsäure abdestilliert. Das restliche Zinn wird vom Iridium durch Fällung mit Ammoniumhydroxyd abgetrennt.

**Résumé**—On fait un alliage avec l'irridium métal et un grand excès d'étain. L'alliage est alors dissous dans un mélange d'acide chlorhydrique et d'eau oxygénée. La majeure partie de l'étain est distillée à partir de la solution à l'état d'halogénures mixtes après addition d'acide chlorhydrique et bromhydrique. L'étain restant est alors séparé de l'iridium en solution par précipitation par l'ammoniaque.

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# THE PRECIPITATION OF ZINC SULPHIDE FROM ACID SOLUTIONS BY THIOACETAMIDE

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**Summary**—The rate of precipitation of zinc sulphide by thioacetamide from solutions having pH values less than 2.5 is controlled by the rate of hydrolysis of thioacetamide to give hydrogen sulphide; significant supersaturation may occur initially. This reaction is first order with respect to the hydrogen ion and the thioacetamide concentrations. In solutions having pH values between 4.5 and 6.3 the precipitation occurs by a direct reaction which conforms to the expression

$$-\frac{d\,[\mathrm{Zn(II)}]}{dt} = k_d\frac{[\mathrm{Zn(II)}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}}$$

The rate constant, $k_d$, is $4.2 \times 10^{-4}$ litre$^{1/2}$ mole$^{1/2}$ min$^{-1}$ at 90° and the energy of activation 19 ± 2 kcal per mole in the 70°–90° region.

Precipitation conforming to this rate expression occurred at hydrogen ion concentrations higher than those at which precipitation by hydrogen sulphide could be obtained. Studies of the relative effectiveness of thioacetamide and hydrogen sulphide for the separation of lead as sulphide from zinc by precipitation from solutions approximately 0.3 *VF* in hydrochloric acid showed that more zinc was precipitated by thioacetamide than by hydrogen sulphide; this precipitation is attributed to the above direct reaction. By modification of procedure and proper control of time and hydrogen ion concentration an effective separation can be made with thioacetamide.

Similarly, more nickel was precipitated with zinc sulphide from solutions of approximately pH 2 when thioacetamide was the precipitant.

Spectral studies have given no evidence of the formation of zinc thioacetamide complexes in neutral solutions.

## INTRODUCTION

This investigation was undertaken as part of the general study of the precipitation of metal sulphides by thioacetamide being carried out in these laboratories. The hydrolysis of thioacetamide in acid[4,18] and in alkaline solutions[4] and its reactions in certain buffer systems[14] have been the subjects of previous studies; the reactions involved in the precipitation of lead$^{\mathrm{II}}$,[18] arsenic$^{\mathrm{III}}$ and $^{\mathrm{V}}$,[3] cadmium,[1] and nickel[2] have also been investigated.

These investigations have shown that in solutions of hydrogen ion concentration greater than about $10^{-3}M$, the rates of precipitation of lead$^{\mathrm{II}}$ [18] and cadmium[1] are hydrolysis-controlled, that is they quantitatively follow the rate of hydrolysis of thioacetamide, which is first order with respect to both the thioacetamide and hydrogen ion concentrations. At hydrogen ion concentrations between about $10^{-3}M$ and $10^{-6}M$, lead$^{\mathrm{II}}$ and cadmium sulphides precipitate by what appears to be a direct reaction between the metal ion and thioacetamide. The rate of this precipitation is first order with respect to both the thioacetamide and metal ion concentrations and inversely half order with respect to the hydrogen ion concentration.

The precipitation of nickel sulphide by the hydrolysis-controlled reaction was not observed in solutions having pH values of 2 or less.[2] This is in accordance with the observations[2,7] that nickel sulphide does not precipitate in solutions saturated with hydrogen sulphide under similar conditions. However, precipitation of nickel sulphide by the direct reaction was observed in solutions 0.3–$10^{-7}M$ in hydrogen ion[2].

Equal contributions of the hydrolysis-controlled and direct reactions to the overall rate of precipitation have been shown to occur at approximately pH 3 in solutions 0.01 *V F* (volume formal) in lead$^{II}$ or cadmium and 0.10 *V F* in thioacetamide at 90°. That is, under these conditions, in solutions more acid than $10^{-3}M$ the hydrolysis reaction is predominant, and in solutions having hydrogen ion concentrations lower than $10^{-3}M$ the direct reaction is predominant.

Since the pH range of 2 to 3 has been reported to be most favourable for the quantitative precipitation of zinc sulphide by hydrogen sulphide there seems justification for a study of the mechanisms by which zinc sulphide is precipitated in acid solutions by thioacetamide and of the application of this reagent to the quantitative precipitation and separation of zinc from other elements.

## EXPERIMENTAL

### *Reagents*

Reagent grade chemicals were used throughout the investigation.

Arapahoe thioacetamide (Lots No. 1402 and 1651) was used to prepare 1.00 *VF* stock solutions by weight. These solutions were clear, colourless, and had approximately the pH of the distilled water that was used in their preparation.

Stock solutions of 0.10 *VF* zinc nitrate, 0.10 *VF* lead nitrate, and 3.0 *VF* ammonium chloride were prepared by weight, as were solutions of zinc, lead, and nickel nitrates containing 20 milligrams of metal per millilitre.

Hydrochloric acid solutions, 3.0 *VF* and 6 *VF*, and perchloric acid solutions, 1.0 *VF* and 0.10 *VF*, were prepared from the commercial acids.

Standard 0.05 *VF* potassium iodate solution was prepared by weight. Sodium thiosulphate solutions, approximately 0.05 *VF*, were standardized against the potassium iodate solution.

Stock carbon tetrachloride dithizone solutions, $3.9 \times 10^{-4}$ *VF*, were prepared as needed; $3.9 \times 10^{-5}$ *VF* solutions were prepared by dilution.

A 0.5 *VF* sodium acetate solution was prepared by weight and heavy metal traces removed by extraction with small portions of $2 \times 10^{-4}$ *VF* dithizone solution.

An acetic acid-acetate buffer solution of pH 4·8 was made by mixing appropriate volumes of 2 *VF* sodium acetate and 2 *VF* acetic acid.

A 1 *VF* sodium thiosulphate solution was prepared by weight.

Standard zinc solutions, 2.5 micrograms per ml., were prepared by dilution of previously standardized stock 0.10 *VF* zinc nitrate.

A sulphate-hydrogen sulphate buffer solution having a $HSO_4^-/SO_3^=$ ratio of 1 : 3 was prepared from the sodium salts; the total formal concentration of sulphate was 1.5. This solution was diluted by a ratio of 9 : 40 in the reaction solutions and under these conditions gave a pH of 1.7 at 25°.

A 0·1 *VF* solution of dimethylglyoxime in ethanol was used.

For the study of the rate of precipitation of zinc sulphide in the pH range 3–7, sodium formate-formic acid buffer solutions were prepared from sodium hydroxide and 90% formic acid solutions. These buffer solutions, which contained a constant sodium formate concentration, were prepared by mixing various quantities of formic acid with constant volumes of a 6 *VF* sodium hydroxide solution and then diluting each solution to the same final volume.

### *Apparatus*

The apparatus used for the rate studies was essentially that described by Swift and Butler[18]. In the separation study 50-ml centrifuge tubes were used as the reaction vessels.

### *Procedures*

The rate measurements and the separation studies were made by separate procedures as described below.

*Rate measurements.* In the measurements of the rate of precipitation of zinc sulphide, measured volumes of the stock zinc nitrate solution and either hydrochloric, perchloric, or sodium formate-formic acid buffer solutions were mixed in the reaction vessel, thioacetamide solution was added, and the solution was diluted to 100 ml. The solutions were heated to approximately 90° before mixing. The tube was then placed in the constant temperature bath.

At timed intervals, and after temperature equilibration, 12 ml of solution were removed from the reaction tube, immediately cooled to quench the reaction, and the zinc sulphide centrifuged. The precipitate was granular and easily separated. Duplicate 5.00-ml portions of the centrifugate were pipetted into 15 × 125-mm test tubes.

An excess of ammonium hydroxide was added to each test tube, and the solutions were placed in a bath of hot water in order to obtain rapid precipitation of the zinc sulphide. The mixtures were cooled, centrifuged and the centrifugate drawn off and discarded. The precipitate was washed with 2-ml portions of a formate-formic acid buffer having a pH of 5.4 until the wash solution was free of sulphide. The precipitate was washed into a 100-ml conical flask; then potassium iodide, standard potassium iodate solution, and 6 *VF* hydrochloric acid were added in the order listed. The solution was titrated with standard sodium thiosulphate solution. The average deviation in confirmatory analyses by this procedure was less than one part per hundred.

*Separation studies.* A colorimetric method was used to determine the quantity of zinc that precipitated with the lead sulphide when either thioacetamide or hydrogen sulphide was used to separate lead$^{II}$ from zinc. Reaction solutions were prepared by mixing measured quantities of zinc, lead$^{II}$, hydrochloric acid, and ammonium chloride solutions in 50-ml centrifuge tubes. Either distilled water and hydrogen sulphide gas or thioacetamide solution was added to each solution. In all cases, the solutions were heated quickly to about 90° over a flame and immediately placed in a bath at 90° ± 1°. The reaction solutions and thioacetamide were heated separately and mixed in the constant temperature bath. When hydrogen sulphide was used as the precipitating agent, the gas was slowly bubbled through the solution to insure saturation. The precipitations were carried out for timed intervals and then the vessels were cooled in a bath of ice-water. After centrifugation, the precipitates were washed with 10-ml portions of the formic acid-formate buffer until the washed solutions gave no dithizone test for zinc. To the precipitates were added 1 ml of 9 *VF* perchloric acid and 5 drops of 6 *VF* nitric, the tubes placed first in boiling water, then finally heated over a flame until all of the precipitate had dissolved and oxides of nitrogen were expelled. The solutions were neutralized to a pH of about 4.8 by the addition of purified 0.5 *VF* sodium acetate solution, diluted to 100.0 ml in a volumetric flask and aliquots of 1.00 ml or 5.00 ml taken for the colorimetric analysis.[16] The aliquot was diluted to 20 ml in a separatory funnel; 10 ml of acetate buffer, 2.00 ml of sodium thiosulphate solution, and 10.0 ml of dithizone reagent were added. The solutions were shaken for 2 minutes, portions of the carbon tetrachloride phases delivered into matched 1-cm Corex cells and the absorbancies of the solutions at 535 m$\mu$ determined by means of a Beckman Model DU Quartz Spectrophotometer. A calibration curve for this instrument was prepared with solutions containing known quantities of zinc and lead$^{II}$.

The effectiveness of the separation of zinc and nickel was studied by a similar procedure. Reaction solutions were prepared by mixing measured quantities of nickel, zinc, and sulphate-hydrogen sulphate buffer solution in 50-ml centrifuge tubes. The subsequent procedure for precipitation, washing, and dissolving of precipitates was exactly that described above for the separation study of zinc and lead$^{II}$.

The quantities of nickel precipitated were determined by the precipitation of nickel dimethylglyoxime and a comparison of the volume of the precipitate with precipitates from standard solutions of nickel. The procedure followed was essentially that described by Bowersox, Smith, and Swift[2], the only difference being the neutralization with, and addition of, excess ammonium hydroxide before the precipitation of nickel with dimethylglyoxime. Under the conditions employed here, the limit of detection of nickel was found to be 0.02 mg.

## RESULTS AND DISCUSSION

Flaschka[5] observed that only a small amount of zinc sulphide precipitated when neutral or slightly acidic solutions of thioacetamide and zinc salts were boiled, but that zinc sulphide was precipitated from ammoniacal solutions.

Preliminary qualitative experiments showed that the initial rate of formation of zinc sulphide from acid thioacetamide solutions having pH values less than 6 increased with increasing pH. However, in solutions at pH 1 and 2 the rate of zinc sulphide formation at 90° increased rapidly after six to eight minutes, indicating that supersaturation effects were involved.

Quantitative rate measurements were then made in solutions having pH values ranging from 2–6.3. The reactions were carried out at 90° in order to obtain a rate of precipitation which could be easily measured.

### *Precipitation by the direct reaction*

Qualitative experiments indicated that a direct reaction similar to that observed with lead$^{II}$,[18] cadmium,[1] and nickel$^{II}$[2] occurred between zinc and thioacetamide. Therefore formic acid-sodium formate buffer solutions were used to control the hydrogen ion concentration in the pH range 6.3–4.5 and measurements were made to determine the effects of the hydrogen ion, zinc ion, and thioacetamide concentrations on the rate of the precipitation.

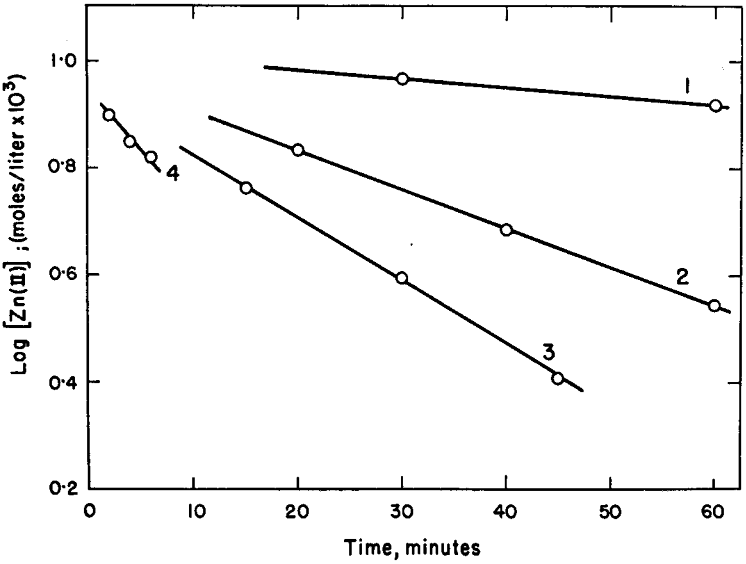

Fig. 1.—The effect of zinc and hydrogen ion concentrations on the rate of precipitation of zinc sulphide by thioacetamide.
Initial zinc, 0·04*VF*; thioacetamide, 0.10*VF*; 90°. 1, pH 4.56; 2, pH 5.40; 3, pH 5.70; 4, pH 6·31 .

### *Effect of zinc concentration*

As is shown by Fig. 1, plots of the logarithms of the zinc concentrations versus times for the pH region 6.3–4.5 are essentially linear; therefore one concludes that the reaction is first order with respect to the zinc concentration. The plots do not extrapolate back to exactly the same initial zinc concentration because of the method used in this rate study. Since temperature equilibration at the outset of the reaction was difficult, an initial point was taken when the reaction mixture achieved a constant 90° and after some reaction had taken place.

### *Effect of thioacetamide concentration*

At a pH of 5.7 the effect of the thioacetamide concentration was investigated over the range 0.05–0.3 *VF*. Rate constants calculated from the data are presented in Table I and show that the rate of precipitation is dependent upon the first power of the thioacetamide concentration.

TABLE 1.—EFFECT OF THIOACETAMIDE CONCENTRATION UPON THE RATE OF PRECIPITATION OF ZINC SULPHIDE

Initial zinc, 0.011 *VF*; hydrogen ion, $2.0 \times 10^{-6}$ M; 90°

| ($CH_3CSNH_2$) *Moles/liter* | $k_1 \times 10^{8}$ [a] | $k_2 \times 10^{7}$ [b] |
|---|---|---|
| 0.050 | 2.9 | 5.8 |
| 0.100 | 5.9 | 5.8 |
| 0.200 | 11.8 | 5.8 |
| 0.300 | 18.4 | 6.1 |

[a] Calculated from the expression $$-\frac{d[\mathrm{Zn(II)}]}{dt} = k_1[\mathrm{Zn(II)}]$$

[b] Calculated from the expression $$-\frac{d[\mathrm{Zn(II)}]}{dt} = k_2[\mathrm{Zn(II)}][\mathrm{CH_3CSNH_2}]$$

TABLE II.—EFFECT OF HYDROGEN ION CONCENTRATION UPON THE RATE OF PRECIPITATION OF ZINC SULPHIDE

Initial zinc, 0.011 *VF*; thioacetamide, 0.10 *VF*; 90°

| $[H^+]$ | $k_1 \times 10^{9}$ [a] | $k_2 \times 10^{4}$ [b] |
|---|---|---|
| $2.8 \times 10^{-5}$ | 21 | 4.0 |
| $4.0 \times 10^{-6}$ | 8 | 4.3 |
| $2.0 \times 10^{-6}$ | 6 | 4.2 |
| $5.0 \times 10^{-7}$ | 3 | 4.2 |
| | | Average $(4.2 \pm 0.1) \times 10^{-4}$ |

[a] Calculated from the expression $$-\frac{d[\mathrm{Zn(II)}]}{dt} = k_1\frac{[\mathrm{Zn(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]}$$

[b] Calculated from the expression $$-\frac{d[\mathrm{Zn(II)}]}{dt} = k_2\frac{[\mathrm{Zn(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}}$$

### *Effect of hydrogen ion concentration*

Rate measurements were made in which the hydrogen ion concentration was varied from $2.8 \times 10^{-5}$–$5 \times 10^{-7}$ *VM*; the initial thioacetamide and zinc ion concentrations were held constant. The rate constants calculated from these data are shown in Table II and show that the rate of precipitation is dependent on the inverse half power of the hydrogen ion concentration. This dependency upon hydrogen ion is the same as that found in the previous investigations of cadmium,[1] lead$^{\mathrm{II}}$,[18] and nickel.[2] No mechanism to explain this effect has been formulated.

### *The rate expression*

The results presented above indicate that the precipitation of zinc by thioacetamide at pH values greater than 4.5 is predominantly controlled by a direct reaction similar to that reported for the precipitation of cadmium, lead$^{II}$, and nickel. The rate expression has the form

$$-\frac{d\,[\mathrm{Zn(II)}]}{dt} = k_d \frac{[\mathrm{Zn(II)}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}} \tag{1}$$

and $k_d$, the direct reaction rate constant, is calculated to be $(4.2 \pm 0.1) \times 10^{-4}$ litre$^{1/2}$ mole$^{-1/2}$ min$^{-1}$ at 90°.

### *The direct reaction at higher hydrogen ion concentrations*

Rate measurements in solutions having pH values of 2.4 were made while nitrogen was bubbled through the reaction solution to prevent any reaction of zinc with the hydrogen sulphide formed by hydrolysis of thioacetamide at this pH. The rate constant for expression (1) above, obtained from these measurements, was $4.3 \times 10^{-4}$ litre$^{1/2}$ mole$^{-1/2}$ min$^{-1}$ at 90°. This agreement indicates that the precipitation at this pH is taking place by the direct reaction. Similar qualitative experiments at pH 1 indicated that precipitation by the same reaction occurred; no supersaturation was observed.

### *Effect of buffer concentration on direct reaction*

Rate measurements were made to determine whether the concentration of formate in the buffer solution affected the rate of the direct reaction. The calculated rate constants are shown in Table III. It is evident from the agreement of these values that the formate does not affect the rate significantly over the concentration range studied; the rate of the reaction was the same within the limits of experimental error. This indicates that only a very weak zinc-formate complex, if any, is formed under these conditions, or—as appears unlikely—that complex formation does not affect the rate.

TABLE III.—EFFECT OF BUFFER CONCENTRATION AND TEMPERATURE ON THE RATE OF PRECIPITATION OF ZINC SULPHIDE.

pH 5.70; initial zinc, 0.011 *VF*
initial thioacetamide, 0.10 *VF*

| Temp., °C | Formate concentration | $[\mathrm{HCOO^-}]/[\mathrm{Zn^{++}}]$ | $k_d \times 10^4$ [a] |
|---|---|---|---|
| 90 | 0.30 | 30 | 4 ± 1 |
| 90 | 0.15 | 15 | 4.1 ± 0.1 |
| 90 | 0.60 | 60 | 4.2 |
| 80 | 0.60 | 60 | 2.2 ± 0.1 |
| 70 | 0.60 | 60 | 0.92 ± 0.05 |

[a] Calculated from the expression

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = k_d \frac{[\mathrm{Zn(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}}$$

### *Temperature effect on the direct reaction*

The rates of the direct reaction between zinc and thioacetamide in solutions initially 0.011 *VF* in zinc nitrate and 0.10 *VF* in thioacetamide at pH 5.70 were determined at 70°, 80°, and 90°. Since it had been demonstrated that the rate of the direct reaction is the same in buffer solutions containing either 0.15*F*, 0.3*F*, or 0.6*F* formate, these measurements were made in the most concentrated buffer in order to obtain a higher buffer capacity. The rate constants obtained were $(9.2 \pm 0.5) \times 10^{-5}$, $(2.2 \pm 0.1) \times 10^{-4}$, and $4.2 \times 10^{-4}$, respectively (Table III). From a plot of log $k_d$ versus $1/T$ the energy of activation for this reaction over the temperature range from 70 to 90° was determined as 19 ± 2 kilocalories per mole. These data demonstrate the potentialities which exist for controlling the rate of precipitation of zinc sulphide by thioacetamide by varying the solution temperature.

### *Evidence for the non-existence of a zinc-thioacetamide complex*

The rate values presented above indicate the absence of any stable zinc-thioacetamide complex. However, since metal-thioacetamide complexes have been observed by various investigators,[8,11,12] a spectrophotometric investigation of zinc-thioacetamide solutions was made to determine if evidence for a complex could be observed.

TABLE IV.—ULTRAVIOLET ABSORPTION OF ZINC AND THIOACETAMIDE SOLUTIONS.

| | |
|---|---|
| Beckman DU spectrophotometer | 1-cm quartz cells |
| 25°C | $H_2O$ reference |
| | Zinc, $1.2 \times 10^{-4}$ *VF* |
| | Thioacetamide, $1.0 \times 10^{-5}$ *VF* |

| Wavelength, $m\mu$ | Absorbancy, *As* | | |
|---|---|---|---|
| | $ZnSO_4$ | TAA | $ZnSO_4$ + TAA |
| 220 | 0.002 | 0.076 | 0.082 |
| 230 | 0.000 | 0.048 | 0.056 |
| 240 | 0.000 | 0.087 | 0.089 |
| 250 | 0.000 | 0.164 | 0.165 |
| 255 | 0.000 | 0.201 | 0.203 |
| 260 | 0.000 | 0.223 | 0.223 |
| 265 | 0.000 | 0.214 | 0.214 |
| 270 | 0.000 | 0.170 | 0.170 |
| 280 | 0.004 | 0.055 | 0.055 |

Thioacetamide has a wavelength of maximum absorption in the 261–263 m$\mu$ region.[4,15] Zinc sulphate was used in this study rather than the nitrate since nitrate ion absorbs significantly in the 220–290 m$\mu$ region and sulphate has no appreciable absorption in this region. The spectra of $1.2 \times 10^{-4}$ *VF* zinc sulphate, of $1 \times 10^{-5}$ *VF* thioacetamide, and of a solution containing both $1.2 \times 10^{-4}$ *VF* zinc sulphate and $1 \times 10^{-5}$ *VF* thioacetamide, all in neutral solution, were measured in the 220–400 m$\mu$ region by means of a Beckman DU Spectrophotometer and matched 1-cm quartz cells. The pertinent results are presented in Table IV.

Since the spectra of the thioacetamide and zinc-thioacetamide solutions are essentially identical there is no evidence for the presence of a zinc-thioacetamide complex. A 12-fold excess of zinc over thioacetamide was used and no change in the spectrum of thioacetamide was observed. In order for a zinc-thioacetamide complex to exist and give these results, the absorbancy index of the complex at all wavelengths in this region would have to be of a magnitude such as to exactly compensate for the loss of thioacetamide by complexation. Thus it was concluded that there is no significant zinc-thioacetamide complex formation under these conditions.

### *The hydrolysis-controlled precipitation*

Measurements of the rate of precipitation were made in solutions having pH values of 2 and 2.5 where the rate of the direct reaction would be small compared to the rate of the acid hydrolysis of thioacetamide. These measurements were complicated by the fact that there was an initial period during which no zinc sulphide precipitate formed. Consequently measurements were made after six to eight minutes, when visible precipitation commenced.

In order to obtain evidence that zinc sulphide was precipitated by the hydrolysis mechanism at high acidity, semi-quantitative measurements were carried out at pH 2. Essentially the same procedure as was used for the direct reaction rate measurement was followed, except that the volumes of zinc sulphide precipitated were compared with those precipitated from standard solutions under the same conditions. Calculations showed that under the conditions prevailing the rate of precipitation of zinc sulphide by the hydrolysis-controlled reaction should have been 2.7 mg of zinc per 5 minutes. The quantities of zinc precipitated as zinc sulphide, once the precipitation began, were found to be 2–3 mg per 5 minutes. This indicates that the precipitation is predominantly hydrolysis-controlled.

Since the rate constant for the direct reaction had been previously determined at lower hydrogen ion concentrations and checked at pH 2 by bubbling nitrogen through the system, the contribution of this reaction to the total rate of precipitation could be calculated. The total rate of precipitation of zinc sulphide at pH 2.5, after initial precipitation began, conformed to the expression

$$-\frac{d[\mathrm{Zn^{++}}]}{dt} = k_h\,[\mathrm{H^+}]\,[\mathrm{CH_3CSNH_2}] + 4.2 \times 10^{-4}\,\frac{[\mathrm{Zn^{++}}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}} \qquad (2)$$

where $k_h$ was calculated to be 0.23 ± 0.08. The previously determined value[18] for $k_h$ is 0.21 ± 0.02.

### *Direct reaction rate constant correlations*

A rough correlation between the rate constants for the direct reactions of lead$^{\mathrm{II}}$, cadmium$^{\mathrm{II}}$, nickel$^{\mathrm{II}}$, and zinc$^{\mathrm{II}}$ with thioacetamide and the solubility products of the metal sulphides has been observed. Numerous conflicting values for the solubility products of these sulphides are to be found in the literature so only one source[19] was used in the comparison.

Waggoner[19] has evaluated the solubility product constants of the metal sulphides by means of the best available thermodynamic data. A comparison of the direct reaction constants observed so far with the solubility product constants of Waggoner (Table V) points out that, in general, the less soluble the precipitated sulphide, the faster is the rate of the direct reaction.

It is to be pointed out that these rate constants were obtained at 90° and the solubility products reported for 25°. In addition, the solubility product values certainly are not quantitatively applicable to solutions containing high concentrations of foreign electrolytes. For these reasons, no quantitative correlation between the rate constants and solubility products has been attempted.

Also, a correlation between the direct reaction rate constants of the above mentioned elements and the ionic radii of those elements has been observed. This correlation would seem to lend substantiation to the claim that the reactions of lead, cadmium, nickel, and zinc ions to form sulphides in the pH 3–6 region is a direct reaction between the metal ion and thioacetamide.

TABLE V.—CORRELATION OF DIRECT REACTION RATE CONSTANTS WITH SOLUBILITY PRODUCTS OF METAL SULPHIDES

| Metal | $k_d \times 10^4$ (90° C) | $k_{SP}$ (25° C) |
|---|---|---|
| $Ni^{II}$ | 2.2 | $1.8 \times 10^{-21}$ |
| $Zn^{II}$ | 4.2 | $8.8 \times 10^{-25}$ |
| $Cd^{II}$ | 8.1 | $7.8 \times 10^{-27}$ |
| $Pb^{II}$ | 11.3 | $8.4 \times 10^{-28}$ |

If the dielectric constant of the medium and the charge of the ion are kept constant, it can be shown that the logarithm of the rate constant should exhibit a linear relationship with the reciprocal of the square of the radius of the ion, for an ion-dipole interaction. The logarithms of the experimentally determined direct reaction rate constants for lead,[18] cadmium,[1] nickel,[2] and the zinc were plotted versus the reciprocal of the square of the crystal radii of these ions as given by Pauling[13]. A surprisingly linear relation was obtained for the cadmium, nickel, and zinc ions, with the slope of this plot in the theoretically predicted direction. The point for lead fell somewhat off this straight line in the direction which would be predicted from the knowledge that lead forms a formate complex of some stability under the conditions of the reaction carried out by Swift and Butler[18].

### *Analytical considerations*

Plots of the calculated rates of precipitation of zinc sulphide by thioacetamide at various pH values as a result of the hydrolysis and of the direct reactions are shown in Figure 2. The calculated rates are on the basis of solutions 0.01 *VF* in zinc and 0.10 *VF* in thioacetamide and at 90°. This graph is similar to those which have been shown for lead[18] and cadmium.[1] The effects on these rates of varying the thioacetamide, hydrogen ion, and zinc ion concentrations can be predicted from the rate expressions.

If one assumes solutions having the composition stated above, the following calculations can be made: $R_h = R_d$ at pH 3.1, where $R_d$ and $R_h$ are the rates of the direct and hydrolysis controlled reactions; $R_h = 1.6 \times 10^3 R_d$ at pH 1; and $R_d = 630 R_h$ at pH 5. The minimum rate of precipitation of zinc sulphide will occur at pH 3.3.

It is apparent from Figure 2 and the above calculations that in solutions having pH values of 2 or less the hydrolysis-controlled reaction predominates and at pH values of 4 or greater the direct reaction controls the precipitation rate. It should be kept in mind that the foregoing discussion neglects any supersaturation effects such as were observed in the hydrolysis-controlled region, and also neglects any effect which a complex-forming ligand might have on the rate of the direct reaction.

*Sulphide separations by the use of thioacetamide.* Some of the pitfalls involved in the substitution of thioacetamide for hydrogen sulphide as a means for effecting separations have been discussed in previous papers from these laboratories.[1,2,18] In order to ascertain if similar liabilities exist with sulphide separations involving zinc,

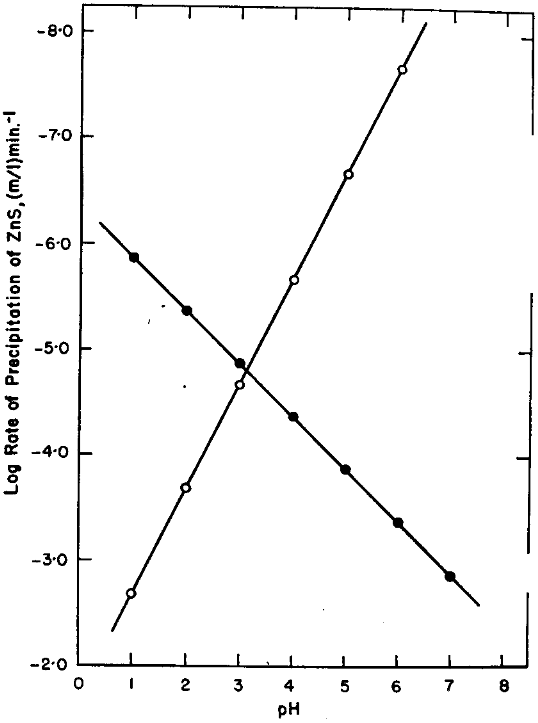

FIG. 2.—Calculated rates of zinc sulphide precipitation at various pH values by the hydrolysis and by the direct reactions.
Temperature: 90°.
0.01 *VF* $Zn(NO_3)_2$
0.10 *VF* $CH_3CSNH_2$
○ Hydrolysis of thioacetamide
● Direct reaction

the effectiveness of thioacetamide and hydrogen sulphide as precipitants for the separation of lead from zinc and of zinc from nickel were compared. A rigorous quantitative study of all variables was not the intent, but simply the gathering of adequate data to provide a basis for comparing the effectiveness of the two reagents under identical conditions.

*Separation of lead from zinc.* A hydrogen ion concentration of 0.3*VF* and a chloride concentration of 0.6*VF* are frequently recommended for the separation of the conventional Hydrogen Sulphide Group elements (lead, bismuth, copper, cadmium, mercury, arsenic, antimony, and tin) from zinc and the other common elements remaining in the solution. Since similar conditions are used for quantitative separations of these elements from zinc, a study was made of the relative effectiveness of thioacetamide and hydrogen sulphide for the separation of lead from zinc.

Preliminary qualitative experiments, summarized in Table VI, were carried out with solutions containing only zinc in order to obtain information on the effect of the concentrations of various acids and of the time allowed for the precipitation. The findings confirmed the expectation that the direct reaction between zinc and thioacetamide, even at high acidity, can proceed at such a rate as to cause more zinc to precipitate with lead than does hydrogen sulphide, at least without modification of procedure.

TABLE VI.—QUALITATIVE OBSERVATIONS ON THE PRECIPITATION OF ZINC SULPHIDE FROM ACID SOLUTION UNDER VARIOUS CONDITIONS

6 mg $Zn^{2+}$/ml 50-ml solution 0.40 *VF* $CH_3CSNH_2$
90° or saturated with $H_2S$

| Conditions | Precipitant | Time, *min* | ZnS precipitated, *mg* |
|---|---|---|---|
| 0.3 *VF* $HClO_4$ | $CH_3CSNH_2$ | 15 | > 100 |
| 0.3 *VF* $HClO_4$ | $H_2S$ | 10 | > 100 |
| 0.3 *VF* HCl | $CH_3CSNH_2$ | 20 | 1–2 |
| | | 65 | > 2 |
| 0.3 *VF* HCl | $H_2S$ | 65 | Slight turbidity |
| 1 *VF* $HClO_4$ | $CH_3CSNH_2$ | 25 | ~ 1 |
| 1 *VF* $HClO_4$ | $H_2S$ | 130 | Clear solution |
| 1 *VF* HCl | $CH_3CSNH_2$ | 60 | Slight turbidity |

The qualitative results showed that thioacetamide precipitated zinc in solution where hydrogen sulphide did not; presumably the precipitation was a result of the direct reaction. The only experiment shown in Table VI in which a significant amount of zinc sulphide was not produced by thioacetamide after one hour was that in which the solution was 1 *VF* in hydrochloric acid.

In order to evaluate quantitatively the relative effectiveness of hydrogen sulphide and thioacetamide, separations of lead from zinc by each precipitant were carried out in solutions 0.3 *VF* in hydrogen ion and 0.6 *VF* in chloride. Under the experimental conditions prevailing over one half of the thioacetamide should have hydrolyzed after 10 minutes; however, detailed calculations show that with 50, 100, and 200 mg of zinc initially present 0.3, 0.6, and 1.2 mg respectively should be precipitated from 40 ml of solution by the direct reaction in 60 minutes. Because of supersaturation effects, these calculations are subject to some uncertainty and the experimental results shown in Table VII are evidence of this. It is obvious, however, that the direct reaction causes a larger amount of zinc to precipitate with the lead than is the case with hydrogen sulphide. This is in accord with the observations of Lehrman and Schneider[10], who substituted thioacetamide for hydrogen sulphide as a precipitant for the Hydrogen Sulphide Group elements. Schweitzer and Correll[17] found less post-precipitation of zinc sulphide with copper sulphide when thioacetamide was used as the precipitant but these results are not easily comparable because of the different conditions involved.

The amount of zinc precipitated by means of the direct reaction can be minimized by proper control of hydrogen ion concentration and time of precipitation. Thus if the precipitation were begun at a higher hydrogen ion concentration and after an appropriate period this concentration decreased to the required value, precipitation by the direct reaction will be decreased. In addition, if the time of the precipitation is decreased the contribution of the direct reaction is minimized. This time effect is illustrated in Table VII in those experiments in which the time was limited to 15 min.

This study shows that before thioacetamide can be used with confidence as a substitute for hydrogen sulphide for this separation the above factors should be thoroughly studied.

*Separation of zinc from nickel.* Jeffreys and Swift[9] have outlined the optimum conditions for the separation of zinc from nickel by the precipitation of zinc sulphide with hydrogen sulphide. They recommend the use of a sulphate-hydrogen sulphate buffer of pH 1.8 with a total sulphate concentration of 0.35 *VF*. The effectiveness of thioacetamide as compared with hydrogen sulphide as a precipitant under these conditions was studied.

TABLE VII.—COMPARATIVE EFFECTIVENESS OF THIOACETAMIDE AND HYDROGEN SULPHIDE FOR THE SEPARATION OF LEAD FROM ZINC

| | |
|---|---|
| 90° C | Hydrogen ion, 0.3 *VM* |
| 40 ml of solution | Chloride, 0.6 *VF* |
| 100 mg lead initially | 0.40 *VF* thioacetamide[1] or saturated with hydrogen sulphide |

Zn estimated with Beckman DU spectrophotometer

| Zinc initially, *mg* | Precipitant | Time, *min* | Zinc precipitated, *mg* |
|---|---|---|---|
| 50 | $CH_3CSNH_2$ | 15 | 0.001 |
| 50 | $CH_3CSNH_2$ | 30 | 0.002 |
| 50 | $CH_3CSNH_2$ | 60 | 0.067 |
| 100 | $CH_3CSNH_2$ | 15 | 0.013 |
| 100 | $CH_3CSNH_2$ | 30 | 0.037 |
| 100 | $CH_3CSNH_2$ | 60 | 1.5 |
| 100 | $H_2S$ | 15 | 0.002 |
| 200 | $CH_3CSNH_2$ | 15 | 0.029 |
| 200 | $CH_3CSNH_2$ | 30 | 0.18 |
| 200 | $CH_3CSNH_2$ | 60 | 4.8 |
| 200 | $H_2S$ | 15 | 0.024 |
| 200 | $H_2S$ | 60 | 0.089 |

[1] Hydrogen sulphide equivalent to the lead should have been produced from the thioacetamide after 1 min.

Under the conditions shown in Table VIII one can calculate that at pH 1.7 about 25 minutes is required for the hydrolysis of thioacetamide to give a quantity of hydrogen sulphide equivalent to 100 mg of zinc. However, Bowersox, Smith, and Swift[2] have shown that in this time interval a significant amount of nickel sulphide would be produced by the direct reaction and the data in Table VIII show this effect. Again, these results are not in quantitative agreement with calculated values, but the pattern is as expected. Contamination of the zinc sulphide precipitate exceeded that found when hydrogen sulphide was the precipitant. The observations of Hahn and Shellington[6] that thioacetamide was less effective than hydrogen sulphide for the quantitative separation of zinc from cobalt suggest that cobalt sulphide, like nickel sulphide, may be precipitated by a direct reaction.

TABLE VIII.—COMPARATIVE EFFECTIVENESS OF THIOACETAMIDE AND HYDROGEN SULPHIDE FOR THE SEPARATION OF ZINC FROM NICKEL

90° pH = 1.7 (25°); 0.3*F* $HSO_4^-$–$SO_4^=$ buffer
40 ml of solution 0.38 *VF* thioacetamide[1] or saturated in
100 mg zinc initially[1] hydrogen sulphide

| Nickel initially, *mg* | Precipitant | Time,[1] *min* | Nickel precipitated, *mg* |
|---|---|---|---|
| 100 | $CH_3CSNH_2$ | 15 | $< 0.02$ |
| 100 | $CH_3CSNH_2$ | 30 | $< 0.02$ |
| 100 | $CH_3CSNH_2$ | 60 | 0.06 |
| 100 | $CH_3CSNH_2$ | 120 | 1 |
| 100 | $H_2S$ | 15 | $< 0.02$ |
| 100 | $H_2S$ | 120 | $< 0.02$ |
| 200 | $CH_3CSNH_2$ | 15 | $< 0.02$ |
| 200 | $CH_3CSNH_2$ | 30 | $< 0.02$ |
| 200 | $CH_3CSNH_2$ | 60 | 0.08 |
| 200 | $CH_3CSNH_2$ | 120 | 1.4 |
| 200 | $H_2S$ | 15 | 0.02 |
| 200 | $H_2S$ | 120 | 0.06 |

Hydrogen sulphide equivalent to 100 milligrams of zinc formed from thioacetamide after 25 min under these conditions.

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**Zusammenfassung**—Die Geschwindigkeit der Fällung von Zinksulfid durch Thioacetamid in Lösungen mit pH kleiner als 2·5 ist durch die Geschwindigkeit der Hydrolyse des Thioacetamid zu Schwefel wasserstoff kontrolliert. Ubersättigungserscheinungen treten am Beginne der Fällung auf. Die Reaktion ist erster Ordnung in Bezug auf die Konzentration von $H^+$-Ion und Thioacetamid. In Lösungen mit pH-Werten zwischen 4·5 und 6·3 verläuft die Fällung direkt nach der Geschwindigkeitgleichung

$$-\frac{d[Zn^{+2}]}{dt} = k_d\,\frac{[Zn^{+2}][CH_3CSNH_2]}{[H^+]^{1/2}}$$

Die Geschwindigkeitskonstante, $K_d$, ist 4·2 × $10^{-4}$ $Liter^{1/2}$ × $Mole^{-1/2}$ × $Min.^{-1}$ bei 90°C. Die Aktivierungsenergie ist 19 ± 2 kcal pro Mol im Gebiete 70–90°C.

Fällungen nach dieser Geschwindigkeitsgleichung traten auf bei Wasserstoffionenkonzentrationen die höher sind als jene, bei denen Zinksulfid durch Schwefelwasserstoff niedergeschlagen wird. Studien über die relative Wirksamkeit von Thioacetamid und Schwefelwasserstoff bei der Trennung von Blei und Zink durch Sulfidfällung aus ca. 0·3 m salzsaurer Lösung ergaben, dass durch Thioacetamid mehr Zink gefällt wird als durch Schwefelwasserstoff. Dies wird durch die obige, direkte Reaktion erklärt. Durch geeignete Modifikation der Methode, richtige Zeitkontrolle and korrekte Wasserstoffionenkonzentration ist eine völlige Trennung mittels Thioacetamide möglich.

In ähnlicher Weise wurde mehr Nickel mit Zink niedergeschlagen, wenn Thioacetamid als Fällungsmittel bei pH 2 verwendet wurde. Spectrophotometrische Studien gaben keine Evidenz für die Bildung von Zink-Thioacetamidkomplexen in neutraler Lösung.

**Résumé**—La vitesse de précipitation du sulfure de zinc par la thioacétamide à partir de solutions ayant des pH inférieurs à 2,5 est contrôlée par la vitesse d'hydrolyse de la thioacétamide en hydrogène sulfuré; il peut y avoir initialement une sursaturation importante. La réaction est du premier ordre par rapport aux concentrations en ion hydrogène et en thioacétamide. Dans des solutions ayant des

pH compris entre 4,5 et 6,3 la précipitation a lieu par une réaction directe conforme à l'expression

$$-\frac{d[\mathrm{Zn(II)}]}{dt}=k_a\frac{[\mathrm{Zn(II)}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}}$$

La constante de vitesse $k_a$ est égale à 4, $2 \cdot 10^{-4}$ litre$^{1/2}$ mole$^{-1/2}$ min$^{-1}$ à 90°C et l'énergie d'activation à 19 ± 2 kcal par mole dans le domaine 70–90°C.

La précipitation conforme à l'expression de la vitesse avait lieu pour des concentrations en ion hydrogène plus élevées que celles pour lesquelles on pouvait obtenir la précipitation par l'hydrogène sulfuré. Des études sur l'efficacité relative de la thioacétamide et de l'hydrogène sulfuré pour séparer le plomb à l'état de sulfure du zinc par précipitation à partir de solutions approximativement 0,3 *VF* en acide chlorhydrique ont montré que l'on précipitait plus de zinc par la thioacétamide que par l'hydrogène sulfuré; la précipitation est attribuée à la réaction directe ci-dessus. Par une modification du procédé et un contrôle convenable du temps et de la concentration en ions hydrogène on peut faire une séparation efficace avec la thioacétamide.

D'une manière analogue, on précipitait plus de nickel avec le sulfure de zinc à partir de solutions de pH environ 2 quand la thioacétamide était le réactif precéipitant.

Des études spectrales n'ont pas donné la preuve de la formation de complexes zinc-thioacétamide dans les solutions neutres.

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# PRELIMINARY COMMUNICATION

## The reactions of certain metals with thioacetamide

(*Received* 17 *December* 1959)

DURING the past several years a programme of investigations has been in progress in these laboratories on the reactions involved in the precipitation of metal sulphides from aqueous solutions by thioacetamide. Because of the present interest in this general topic we have decided to publish certain preliminary results which have been obtained, since in some cases it seems unlikely that the investigations can be completed within the near future. Other investigators wishing to concern themselves with these phenomena should feel free to do so.

Preliminary experiments by C. B. Moore have established that in acid solutions the rate of the precipitation of silver sulphide by thioacetamide (TAA) is controlled by the hydrolysis of the TAA at pH values less than 2, and by a direct reaction between the TAA and silver ion when the pH is greater than 3. Under the conditions prevailing, the rate of precipitation by the direct reaction was decreased by an increase in the concentration of TAA and the inhibition effect was observed to be third order. The kinetic evidence indicated the formation of a silver-TAA complex, and preliminary potentiometric studies by J. D. Lamb have established that in solutions of pH 2 to 3, in which the concentration of TAA is 5 to 10 times the silver concentration, a complex of the type $Ag(TAA)_4$ exists. The stability of this or similar complexes is such that precipitates of silver sulphide can be dissolved by concentrated TAA solutions.

Silver is the first metal for which the rate of precipitation of the sulphide by the direct reaction has been observed to be inhibited by TAA. Subsequent experiments by D. M. Smith and D. V. Owens have established a similar inhibition in the precipitation of mercury$^{II}$ sulphide by TAA from acetate buffer solutions having a pH of 4.

Frank Booth has observed that in ammoniacal solutions of copper$^{II}$ and TAA there is a rapid reaction to form a brown-black precipitate, presumably a sulphide, which appears to be complete in less than a minute at room temperature. In solutions having pH values of 1 or less, and with an initial ratio of TAA to copper$^{II}$ of 10 or greater, there is a very rapid, apparently quantitative, reduction of copper$^{II}$ to copper$^{I}$ accompanied by the formation of finely divided sulphur. A single determination of the amount of sulphur precipitated agreed within 5% with the stoichiometric value.

It appears that the resulting copper$^{I}$ is strongly complexed by the TAA, since passage of hydrogen sulphide through the solutions after the reduction produced no noticeable effect. In addition, solutions resulting from the reduction could be left standing in the cold for up to 36 hours without precipitate formation. If these solutions were heated to 50° or higher, brown-black precipitates quickly formed. Visual comparisons of sulphur precipitates indicated that the rate of formation of sulphur is first order with respect to the hydrogen ion, the TAA, and the copper$^{II}$ concentrations.

When the initial ratio of TAA to copper$^{II}$ was increased to 50 and the pH was approximately 3, the rate of the reduction appeared to be slower, but sulphide formation took place within a relatively short time after the reduction appeared to be quantitative. At higher pH values sulphide formation began before the reduction of the cupric copper appeared complete.

Experiments by Glenn Crabbs indicated that it is possible to obtain quantitative precipitation of approximately 1 millimole of tin$^{IV}$ by about 6 millimoles of TAA from 100 millilitres of $0{\cdot}3F$–$0{\cdot}6F$ hydrochloric acid solutions in 10–15 minutes at approximately 90°. No rate measurements were made.

Experiments by M. J. Kallerud indicated that precipitation of a sulphide from molybdenum$^{IV}$ solutions by TAA appears to take place through both the hydrolysis of the TAA and a direct reaction.

The direct reaction predominates at pH values of 4 and greater. The rate of the reduction of molybdenum$^{IV}$ appeared to decrease as the pH was increased.

Experiments by F. C. Anson have shown that the addition of hydrazine to acid solutions of TAA accelerates sulphide formation. This acceleration was most obvious at pH values between 4 and 7, where the acid hydrolysis is inconveniently slow for analytical purposes. Thus, sulphide formation is increased by approximately 16,000-fold when a solution buffered by an acetic acid-acetate buffer to a pH of 5 and with a TAA concentration of 0·03 *VF* is also made 0·08 *VF* in hydrazine. Because of the obvious analytical implications of this effect a study of the reactions involved is in progress.

*Contribution No.* 2539
*Division of Chemistry and Chemical Engineering*
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ERNEST H. SWIFT
FRED C. ANSON

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# SHORT COMMUNICATION

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## Radiochemical separations by amalgam exchange

(*Received* 23 *November* 1959)

A RAPID and selective radiochemical separation procedure has been developed using the techniques of amalgam exchange. Separation of the radio-isotope takes place by virtue of the rapid exchange occurring between an element present in a dilute amalgam and its ions in solution. If there are many more inactive atoms of the element in the amalgam than there are of its radio-isotope in solution, amalgam exchange will result in almost all of the activity being incorporated in the amalgam. (In this it is somewhat similar to the isotopic exchange separation of silver.[1]) Selectivity is obtained since ions of other elements in solution will not exchange with the desired element in the amalgam. In the case of cadmium, thallium, lead and bismuth, amalgam exchange has been reported to be exceedingly rapid,[2,3] thus the method can be useful for the separation of short-lived isotopes. In this preliminary survey of the method it appears that amalgam exchange can give satisfactory yields in short periods of time for a number of radio-elements.

### EXPERIMENTAL

#### *Apparatus and reagents*

A 50-ml round-bottom centrifuge tube was used for all extractions. The aqueous and mercury layers were vigorously agitated by a glass stirring rod rotated at 1500 to 2000 r.p.m. by an electric stirrer. All aqueous solutions were made with distilled water from salts of analytical reagent purity. Mercury and other solid metals used to make the amalgams were of analytical reagent purity, and in some cases of spectroscopic standard purity.

#### *Preparation of amalgams*

Amalgams of bismuth, cadmium, gallium, indium, lead, tin, thallium, and zinc were prepared by direct combination (with heating) of metal with the mercury. The strontium amalgam was prepared by reducing a solution of strontium nitrate with sodium amalgam. All amalgams were made to contain 2% by weight of the element to be exchanged.

#### *Procedure*

To test the method 2 ml of a solution containing a particular electrolyte and tracers of the element to be exchanged were added to the centrifuge tube. One half gram of the amalgam was added to the solution with a calibrated micro pipette and the solution stirred for five minutes. An aliquot of the solution was then measured for activity.

In all of the experiments a volume ratio of 40 : 1 was maintained between the aqueous solution and the amalgam.

### RESULTS AND CONCLUSIONS

A short summary of typical yield results for several different electrolytes is shown in Table I. Individual amalgams containing milligram amounts of cadmium, thallium, bismuth, strontium, zinc, indium, or lead have been found to remove trace amounts ($\mu$gm or smaller) of their respective radioactive isotopes from dilute acid or salt solution with a yield of at least 50% in five minutes of stirring. Tin and gallium did not exchange.

One problem arises in that these amalgams have a reducing power comparable to the reducing power of the pure metal of which the amalgam is made.[4] These contaminants as well as other oxidizing agents ($MnO_4^-$, $Cr_2O_7^{2-}$, etc.) can cause a considerable reduction in the yield of the desired

TABLE I. EXCHANGE OF AN ELEMENT WITH ITS AMALGAM
(Five minute stirring time)

| Isotope and amount | Solution | Exchange % |
|---|---|---|
| $^{212}$Bi (*) | 5*M* HCl | 49 |
| $^{115m}$Cd (24 $\mu$g) | 0.5*M* $NaClO_4$ | 94 |
| | 0.5*M* $Na_2C_2O_4$ | 94 |
| | 0.5*M* $NaNO_3$ | 94 |
| | 5*M* $HClO_4$ | 94 |
| $^{72}$Ga (1 mg) | 0.5*M* $NaNO_3$ | none |
| | sat'd NaCl | none |
| | 2*M* $HClO_4$ | none |
| | 2*M* $HNO_3$ | none |
| $^{114}$In (1 mg) | 5*M* HCl | 50 |
| $^{212}$Pb (*) | 0.5*M* $NaNO_3$ | 90 |
| $^{113}$Sn (1 mg) | 0.5*M* $NaNO_3$ | none |
| | sat'd NaCl | none |
| $^{90}$Sr (*) | 0.5*M* $NaNO_3$ | 50–60 |
| $^{204}$Tl (21 $\mu$g) | 0.5*M* $NaNO_3$† | 85 |
| $^{65}$Zn (40 $\mu$g) | 0.5*M* $NaNO_3$ | 90 |

* Carrier free.
† This value is taken at two minutes stirring.

metal. This potential source of contamination in the separation might be avoided, however, by bringing the solution into contact with an amalgam made of an element (scavenger) which is just below the desired element in the electromotive series. This separation would then be followed by contact with a larger amount of amalgam of the desired element.

The potentialities of this method can be shown in the separation of cadmium from zinc. This usually difficult separation was accomplished in three minutes with a decontamination factor for zinc of $10^4$ by agitation of the cadmium amalgam with a solution of the cadmium and zinc.

At the end of the separation the desired activity is in the amalgam. Direct gamma-ray counting of the amalgam may be possible without too large an error caused by absorption losses, although $\beta$ counting might prove more troublesome. In any case it may be possible to strip the element selectively from the mercury, either by a wash with an oxidant or by electrolytic stripping.

A detailed evaluation of this method for elements which demonstrate the exchange is being made by measuring the purity of activity separated from solutions containing many representative tracers. Problems of the accurate assay of the activity separated by this amalgam method are also being studied.

*Acknowledgement*—This work was supported in part by the U.S. Atomic Energy Commission.

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# JAROSLAV HEYROVSKÝ

## *Nobel Prizewinner in Chemistry* 1959

THE recent announcement of the award of the Nobel Prize in Chemistry for 1959 to Professor Jaroslav Heyrovský is one that will be received with acclaim, the world over. All chemistry is based essentially on good analysis and it is therefore fitting that the prize should once more be awarded for the evolution of an analytical technique.

The polarographic method of analysis first formulated by Heyrovský in a paper to *Chemické Listy* in 1922 has found application in all fields of chemistry. It has been used for purposes as diverse as measuring *in situ* the oxygen content of blood within the heart and the direct analysis of trace metals in fused salt media. Extensive applications have been found in inorganic, physical and organic chemistry where the method may be applied with equal facility to the determination of traces of metals, the study of reaction kinetics, the analysis of antibiotics, etc.

In the early stages the adoption of polarography as a standard method was curiously slow. During the 1930's some momentum was gained, but the war years brought recognition when dust-covers were removed from many instruments that had lain idle since the first flush of enthusiasm which led to their purchase. The high sensitivity and discrimination of polarography even with simple inexpensive equipment, and its toleration of high concentrations of indifferent electrolyte, ensured its speedy application when the need arose. Now the popularity of the method has burgeoned forth to such an extent that few institutions in industry or academic life can function properly without a polarograph. No longer does one hear references to "the polarographer's art"; the method has come of age and is accepted universally with respect.

And this, apart from the inherent merit of the method itself, is largely due to Heyrovský the man. In his laboratories and latterly his world-famous institute, like another Nobel prizewinner beloved of microanalysts, he has *taught* chemists of all nations with consummate skill and fired them with his own burning enthusiasm. (The enthusiasm of polarographers is well known.) No one who has met this quiet, gentle, unassuming Czech can fail to be impressed or to cherish the memory. It is difficult to decide which is the greatest: Heyrovský the scientist, the teacher or the man.

Heyrovský was born in Prague on December 20th, 1890, the son of Leopold Heyrovský, Professor of Roman Law at the Czech University. His chemical studies began there in 1909 and were continued at University College, London, where he took his B.Sc. in 1913, under the professorship of Sir William Ramsay. Whilst holding the post of University demonstrator there, his interest in electrochemistry was aroused by Professor F. G. Donnan.

After the war, Heyrovský, now at Charles University, Prague, and still interested primarily in electrochemistry, accepted a suggestion by Professor G. Kucera that he should investigate some mysterious inflections which the latter had observed in the electrocapillary curve for mercury when a dropping mercury electrode was used in a solution containing reducible ions. This eventually led to the "discovery" of polarography in 1922. The first polarograph was described by Heyrovský and his Japanese co-worker Shikata in 1925, and the mathematical theory was worked out by the Czech physicist D. Ilkovič in 1934. In 1922 Heyrovský was appointed Associate Professor at Charles University and in 1926 he became its first full Professor of physical chemistry. From that date the development and teaching of polarography proceeded hand in hand.

In 1950 Heyrovský was appointed director of the newly formed Polarographic Institute and in 1951 his country honoured him with the national laureateship. In 1952 the Polarographic Institute was incorporated in the Czechoslovak Academy of Sciences and in 1955 he was awarded the Order of the Czechoslovak Republic. He holds several honorary degrees and is an honorary member of nine foreign chemical societies. He has travelled extensively on lecture tours throughout Europe and the far East, and is a well known figure to many outside his own country.

His influence on the course of chemistry in Czechoslovakia and in the world generally has been most marked and it is indeed fitting that he should have been awarded the highest international scientific honour in this year of his sixty-ninth birthday.

T. S. WEST

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# BOOK REVIEWS

**Comprehensive Analytical Chemistry, Volume 1A: Classical Analysis.** Edited by CECIL L. WILSON and DAVID W. WILSON. Elsevier Publishing Company, Amsterdam: D. Van Nostrand Company, Ltd., London: D. Van Nostrand Company, Inc., New York. 1959. Pp. xix + 577. 105s.

THE announcement of the project of a new comprehensive work on analytical chemistry was received by analysts with great interest, and it is fair to say that all who heard of it were filled with curiosity to see how the Editors would tackle their task, and how comprehensive the result would turn out to be. It was clear from the advance advertisements that the work would be of great calibre, and this expectation was if anything enhanced by the eminence of the collaborators engaged on the text.

It is not long since emphasis was laid on the desiderata of textbooks on analytical chemistry in articles that appeared on both sides of the Atlantic; and the view was expressed with firmness in the United States of America that one could no longer expect a single specialist to master the whole subject. On the other hand, it was thought that each chemist might tend to think too much in terms of his own special group of methods, and so be unable to command the whole field of the subject. And it has to be recognised that this field becomes daily wider. What was needed, it was said, was an integration of such groups of methods into the whole scheme of analytical chemistry. "Unfortunately", it is written in *Analytical Chemistry*, "we do not find the climate of our Universities conducive to such growth... We trust that some editor-in-chief... may in his more mature years have gained sufficient wisdom, knowledge and inspiration to write a definitive work on how the various techniques should be integrated in solution of analytical problems so that the answer is obtained quickly. This is a challenging task, but we believe it is not impossible if the writer thinks in terms of analytical chemistry and not as a specialist."

These words have been quoted before, but no apology is needed for their re-appearance; they are surely fundamental to the matter of any new book on the subject under review. For not only are up-to-date descriptions of the newer techniques required in all parts of the work, but it is their assimilation into a comprehensive whole that must be achieved as well if the work is to reach its objective of presenting its subject as a living, vibrant whole.

And what subject could prove more fascinating to any craftsman? It is true that analysts are scientists, but the practising analyst must also be a craftsman, and one of a very high order of skill. The first volume of this work deals with *Classical Analysis*, a subject that has rudely been defined as beaker and filter work, but nevertheless one that offers the finest opportunities for the application of skill that are to be found. If, indeed, it tends sometimes to seem out-of-date and cumbersome to those newly entering the practice of analytical chemistry, one would advise them to see how closely they can match the more famous determinations, perhaps of atomic weights, in accuracy or precision of result.

This test is a severe one, and likely to be undertaken only by those who have already a feeling of pleasure in things well done for their own sake. Let us not, however, think that it is only classical analysis that can command such feelings. Some of the newer techniques lose in accuracy while having been made simpler to operate, and some "push-button" instruments are obviously not so accurate as the longer and more difficult methods they replace; but on the other hand many others of the newer methods of approach to analysis gain in delicacy from their mechanisation; and in skilful hands give information that could never have been derived by the more massive chemical separations. Often it is purely physical methods that give the extra delicacy of separation, but not always. Not a few of today's advances come from a refining of the already highly polished methods of yesterday. Compare, as this volume, does, the analytical balance of yesterday and today with the micro-balance and the ultra-micro balance; and the advance made in a decade or two is at once plain. Apply the study of Statistics to analytical work, and see how it will bring certainty, even if only certainty of how large is the uncertainty of one's work, to chemical analysis. Consider the need for accuracy in sampling, today an advanced subject, and see how much one relied on chance for accurate replication of results in the past, and how much more precise thay may be made now.

But this is to mention a very few of the branches of the subject that are dealt with in this first volume. It is right to mention all the headings: After a general introduction by the Editors, there is a chapter dealing with the *Materials* used for analytical vessels (G. H. Wyatt), *Sampling* (R. C. Tomlinson), *Statistics* (E. C. Wood), *Weighing* (G. F. Hodsman), *Measurement of Volume* (R. Goulden), *Solvent Extraction* (G. H. Morrison and H. Freiser), and *Organic Reagents in Inorganic Analysis* (F. Holmes).

*Gas Analysis* is described in the third chapter by A. E. Heron and H. N. Wilson. P. W. West, H. Weisz and A. O. Parks deal with *Inorganic Qualitative Analysis*, and A. McGookin with *Organic Qualitative Analysis*. The sixth and final chapter is on *Inorganic Gravimetric Analysis;* it is introduced by Professor C. L. Wilson, and written by F. E. Beamish and W. A. E. McBryde and L. Gordon. This last chapter discusses the preparation of precipitates, their filtration and washing, and subsequent weighing; the purity of reagents, the use of organic reagents, and practical and theoretical considerations; filtering media, crucibles, heating devices, desiccators and miscellaneous apparatus; and finally precipitation from homogeneous solution of hydroxides and various anions. Generally speaking this chapter may be said to review the subject of gravimetric inorganic analysis pretty thoroughly in the course of rather more than 100 pages; but the reader will not find in it the specialised directions for the determinations of each cation and anion that would have appeared in most of the older textbooks on analysis, except in a few instances.

The Editors have rather been at pains to achieve what has been looked for of late, and to review the whole subject covered by their title page. Emphatically they have not produced just another cookery-book.

It is too early to foresee just how the remaining volumes of this great work will turn out. A study of the first section leaves one full of respect for the Editors and authors and of pleasure at what they have already achieved. Let us hope that all concerned will go from strength to strength, and that the completed work will fully justify the promise of its start.

K. A. WILLIAMS

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**Laboratory Glassblowing.** L. M. PARR and C. A. HENDLEY. George Newnes Ltd., London, 1956. Pp. vii + 160. 21s.

VERBAL or written instructions of the technique of glassblowing can become extremely involved and detailed, but remain, at the same time, completely inadequate. The authors have avoided many of the usual faults of this type of book and have presented adequate details of most glassblowing techniques in a simple and lucid manner: in particular, their many diagrams are extremely clear and accurate. Two unusual aspects of this book deserve comment: first, for certain articles the authors give methods of construction which give satisfactory results but which are not necessarily employed by professional glassblower (indeed, he would probably be horrified with some of the details); second, as well as those for standard glassblowing exercises, details are given for the making of stopcocks, metal-to-glass seals and calibrated apparatus which the reader would not expect to find in such a small volume. The book is well-indexed, and contains appendices which list important data such as standard joint and tap specifications and sources of supply of glassblowing equipment.

The book is very readable, so much so that the text could be described as "gripping" in that it is difficult to put down the book until the job in hand is successfully completed. The book is also written with some gentle humour, not all of which is intentional; the legend "no sudden construction" at the end of an arrow pointing to the centre of a diagram of the requirements of a stopcock is wholly accurate for a beginner, if not wholly proof-read!

Because of the nature of glassblowing it is doubtful whether a complete novice would soon become a highly competent glassblower with the aid of this book alone. However, a worker with a little knowledge of the technique will become a much more accomplished glassblower in a much shorter time if he has this book at his side.

D. A. PANTONY

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# NOTICES

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## The following meetings have been arranged:

*Tuesday* 12 *January* 1960: **Society for Analytical Chemistry,** Midlands Section and Microchemistry Group. *Micro Gas Analysis:* G. J. MINKOFF, D.Sc., D.I.C. Mason Theatre, The University, Edmund Street, Birmingham, 3, England. 6.30 p.m.

*Wednesday* 20 *January* 1960: **Society for Analytical Chemistry,** Biological Methods Group. *Antibiotic Assay in Body Fluids:* Professor L. GARROD, M.A., M.D., F.R.C.P. Burlington House, London, W.1. 7.0 p.m.

*Monday–Thursday* 25–28 *January* 1960: Thirteenth Annual Symposium on *Modern Methods of Analytical Chemistry.* Louisiana State University, Baton Rouge, Louisiana, U.S.A. The speakers will include Dr. ROGER BATES, Dr. T. S. BURKHALTER, Dr. JAMES FRITZ, Dr. RUSSELL KEIRS, Dr. I. M. KOLTHOFF, Dr. HERBERT LAITINEN, Dr. SEAN McGLYNN, Dr. G. W. C. MILNER, Dr. ROBERT MITCHELL and Dr. JAMES W. ROBINSON.

*Wednesday* 27 *January* 1960: **Society for Analytical Chemistry,** Microchemistry Group. London Discussion Meeting. "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m.

*Friday* 29 *January* 1960: **Society for Analytical Chemistry,** Scottish Section. Annual General Meeting followed by an address by D. W. KENT-JONES, B.Sc., Ph.D., F.R.I.C. Glasgow, Scotland. 1.30 p.m.

*Saturday* 30 *January* 1960: **Society for Analytical Chemistry,** North of England Section. Annual General Meeting followed by *Analytical Methods in Clinical Biochemistry:* H. VARLEY, M.Sc., F.R.I.C. Nag's Head Hotel, Lloyd Street, Manchester, England. 2.15 p.m.

*Wednesday* 3 *February* 1960: **Society for Analytical Chemistry.** Organised by the Physical Methods Group in conjunction with the **Society of Chemical Industry,** Oils and Fats Group. *Spectroscopic Investigation of Fats.* Burlington House, London, W.1. 7 p.m.

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Registration forms for the Third Gas Chromatography Symposium, of which a preliminary notice appeared in our issue for August 1959, are now available. They may be obtained from Miss P. E. HUTCHINSON, Assistant Secretary, The Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1., or Mr. L. BREALEY, Standards Department, Boots Pure Drug Co., Ltd., Station Street, Nottingham, England, or Mr. D. H. DESTY, British Petroleum Co., Ltd., Research Station, Chertsey Road, Sunbury-on-Thames, Middlesex, England.

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The fifteenth Annual General Meeting of the Physical Methods Group of the Society for Analytical Chemistry was held on Tuesday 24 November 1959 in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the Chairman of the Group, Mr. R. A. C. ISBELL, A.Inst.P. The following Officers were elected for the forthcoming year:

| | |
|---|---|
| *Chairman:* | Dr. G. W. C. MILNER, F.R.I.C., A.Inst.P. |
| *Vice-Chairman:* | Dr. W. CULE DAVIES, F.R.I.C. |
| *Hon. Secretary and Treasurer:* | Dr. T. L. PARKINSON. B.Sc., F.R.I.C., Product Research Division, Beecham Foods Ltd., Beecham House, Great West Road, Brentford, Middlesex, England. |

The Annual General Meeting was followed by the 69th Ordinary Meeting of the Group. Dr. MILNER was in the Chair, and the retiring Chairman gave a lecture on *The Design of Optical Instruments for Chemical Analysis.*

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

*B.S.* 3145, 1959: *Laboratory potentiometric pH meters.* This specifies input current, details of calibration, stability, sensitivity, temperature compensation, auxiliary pH control, electrode-connexion and screening. (Price 3s.)

The following Standards have been revised:

*B.S.* 1016: *Methods for the Analysis and testing of coal and coke*, Part 8, 1959: *Chlorine in coal.* This deals with the determination of chlorine in coal by the Eschka and high temperature methods. (Price 4s. 6d.) Part 12: 1959: *Caking and swelling properties of coal.* This deals with the determination of the crucible swelling number and of the Gray-King coke type of coal. (Price 6s.)

*B.S.* 1309: 1959: *Methods of sampling and analysis of vegetable-tanned and chrome-tanned leathers.* In this, instructions for sampling are given, together with diagrams. Methods for the determination of volatile matter, total ash and *p*-nitrophenol in both vegetable-tanned and chrome-tanned leathers, water-soluble matter, sulphated total ash, sulphated ash of water-soluble matter, insoluble ash, oils and fats, nitrogen and hide substance, degree of tannage, sugars, magnesium salts, pH of aqueous extract and acid figure in vegetable-tanned oils and grease, and uncombined sulphur and chromium in chrome-tanned oils are provided. (Price 8s. 6d.)

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The Optical Society of America announces a translation, *Optics and Spectroscopy*, of the Russian Journal *Optika i Spektroscopiya.* This monthly Journal of the USSR Academy of Sciences commenced publication in 1956 and publishes the work of leading Russian scientists in all branches of optics and spectroscopy, including X-ray, ultra-violet, visible, infra-red, and micro-wave; thin layer optics, filters, detectors, diffraction gratings, electroluminescence thermal radiation backgrounds, infra-red polarizers, and their many other applications in science and industry. The English translation, which is being published with a grant-in-aid from the National Science Foundation, starts from Volume 6, January 1959, and it is the aim of the Society that *Optics and Spectroscopy* will appear within four months of the Russian original.

Further information may be obtained from Professor MARY WARGA, Executive Secretary, Optical Society of America, Executive Office, 1155 Sixteenth Street, N.W., Washington, 6, D.C., U.S.A.

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### *Developments in Analytical Chemistry*

The Birmingham and Midlands Section of the Royal Institute of Chemistry has arranged a Spring Lecture Course on *Developments in Analytical Chemistry* at the College of Advanced Technology, Birmingham, on the mornings of the Saturdays in March, 1960.

Registration forms and further particulars may be obtained from Dr. M. WILLIAMS, Hon. Asst. Secretary, B.M.S., R.I.C., 24, Conchar Road, Sutton Coldfield, Warwickshire.

Talanta, 1960, Vol. 3, p. 306. Pergamon Press Ltd. Printed in Northern Ireland

# PAPERS RECEIVED

**The analysis of beryllium and beryllium oxide—I: The determination of iron.** J. O. HIBBITS, W. F. DAVIS and M. R. MENKE. (23 *November* 1959).

**The analysis of beryllium and beryllium oxide—II: The determination of copper.** J. O. HIBBITS, W. F. DAVIS and M. R. MENKE. (23 *November* 1959).

**The analysis of beryllium and beryllium oxide—III: The determination of molybdenum.** J. O. HIBBITS, W. F. DAVIS, M. R. MENKE and S. KALLMANN. (23 *November* 1959).

**Spectrophotometric determination of zirconium in uranium alloys of the fission elements.** R. P. LARSEN, L. E. ROSS and GWENDOLYN KESSER. (23 *November* 1959).

**Spectrophotometric determination of fluoride using lanthanum chloride.** KIYOKO HAYASHI, TAEKO DANZUKA and KEIHEI UENO. (23 *November* 1959).

**Radiochemical separations by amalgam exchange.** JAMES R. DEVOE, CHONG K. KIM and W. WAYNE MEINKE. (23 *November* 1959).

**The minimum ignition temperature of aluminium oxide precipitates.** OSCAR I. MILNER and LOUIS GORDON. (23 *November* 1959).

**A new method for the determination of the actual content of acid chloride in the chlorides of carboxylic acids.** K. BURGER and E. SCHULEK. (30 *November* 1959).

**The chromatography of sugars.** R. W. BAILEY and J. B. PRIDHAM. (30 *November* 1959).

**The separation of carrier-free $^{234}$thorium ($UX_1$) from uranium by anion-exchange.** S. S. BERMAN, LORNA MCKINNEY and M. E. BEDNAS. (1 *December* 1959).

**Utilization of ternary and ion-association complexes in chemical analysis—II: Polarographic determination of indium.** M. KOPANICA and R. PŘIBIL. (8 *December* 1959).

**The determination of tantalum in rocks by neutron-activation analysis.** D. F. C. MORRIS and A. OLYA. (9 *December* 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.

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

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

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

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

## 2. Script Requirements

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

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

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

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

**△** △ ⊡ □ ● ○ ◬ ⊙ ⊕ ⊖ ⏻ ⊗

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

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

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

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

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

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

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## CONTENTS

Preliminary Communication:

Short Communication:

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