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An Organic Reagent for the  
Volumetric Determination of Tin

Harold Boardman

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*Head of Department of Chemistry*

## Foreword

The chemist is often called upon to perform analyses which have interferences difficult to overcome by inorganic methods; the expanding field of the application of organic reagents to inorganic analysis promises to overcome many of these difficulties.

This work, intended to remove certain interferences in the analysis of tin, was done under the expert supervision of J. Allen Harris, Ph.D., to whom I wish to express my thanks.

H. Boardman

## TABLE OF CONTENTS

	Page
A. General Theory of Organic Reagents	1
B. Organic Reagents for Tin	2
C. Experimental Work	
(a) Preparation of the Reagent	6
(b) The Search for a Volumetric Procedure	8
1. The Permanganate Precipitate	9
2. The Dichromate Precipitate	12
3. Triphenyl naphthyl arsonium Chloride	15
4. The Thiosulphate Precipitate	16
(c) The Determination of Tin	19
D. Conclusions and Suggestionf for Further Work	20
E. Bibliography	22

## An Organic Reagent for the Volumetric Determination of Tin

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### General Theory of Organic Reagents

Organic reagents are extremely useful in the three fields of quantitative analysis - gravimetric, volumetric and colorimetric determinations - where their use supplants tedious or inaccurate inorganic methods.

Organic reagents which react with only one element are termed specific and reagents which react with a limited number of elements are termed selective. Often a selective reagent may be made specific for a given element in a mixture by inactivating other components by means of a masking reagent.

Feigl (1,2) has done much in clarifying the theory of the action of organic reagents. By far the largest group of organic reagents are those that form the so-called inner-complex compounds. The ability of these reagents to form inner-complex salts is due to ~~the~~ certain salt forming acidic atomic groupings which are largely: sulphonic ( $\text{SO}_3\text{H}$ ), sulfinic ( $\text{SO}_2\text{H}$ ), carboxyl, hydroxyl, sulfhydryl ( $\text{SH}$ ), Oxime ( $\text{NOH=}$ ), and imine ( $=\text{NH}$ ). The hydrogen atoms are replaceable by one equivalent of metal. The molecule must

be so constituted, however, that the metal may also coordinate with some other atom (thus saturating the secondary valences of the metal atom). This atom often is oxygen, nitrogen or sulphur. The ring thus formed contributes to the stability of the resulting compound.

The solubility of the compound is, of course, important in gravimetric and volumetric analysis. Solubility is often influenced by other atomic groupings present in the molecule. In general, the solubility is greater the more similar the molecules of the solute and solvent are. Thus the presence of hydroxyl groups in the molecule increases the solubility of a compound in water. The sulfonic acid group has also the ability to bind water and hence increase the solubility.

Another important point as regards solubility is the so-called "weighting effect". In general, the greater the molecular weight the less is the solubility. Evidently insolubility should be as great as possible since this increases the sensitivity.

### Organic Reagents for Tin

The experimental work consisted of a search for a volumetric method for tin that would be accurate, quite rapid, and applicable to the analysis of ores, etc. The existent methods for tin depend upon the oxidation from the stannous to the stannic condition. Controversy has centred around the

initial reduction of tin and the question of air oxidation. Various reducing agents have been used, among the latest being powdered antimony or aluminum. With powdered antimony it is usual to boil the solution, which has a high acid concentration, for forty-five minutes to ensure complete reduction. Air oxidation exercises a considerable effect on the titration. Apparatus has been devised for the exclusion of air by  $\text{CO}_2$  (3). Another method in use in many laboratories is to reduce the tin in a large Erlenmeyer, add solid  $\text{NaHCO}_3$ , to the acid solution, cork and cool. After the flask is cool the cork is removed and the solution is titrated as rapidly as possible with an iodine solution of suitable concentration. Blanks have to be run also. Discrepancies sometimes occur, which are undoubtedly due to the method of reduction or the effect of air oxidation. A method for determining tin in the stannic condition would be free of both these errors. There is no method for the volumetric determination of tin in the stannic condition by inorganic reagents.

Cupferron will precipitate tin (4). A 10% solution of cupferron is added; with vigorous stirring the precipitate becomes compact and brittle (30-45 min.). With it, tetravalent tin can be separated from arsenic and antimony in acid solution (6). Hillebrand and Lundell's book covers the uses of cupferron.

A volumetric method for the determination of small amounts of tin in ores has been developed by Alimarin and S.M. Peuzner (5). This is based upon the reduction and

decomposition of methyl orange by tin in acid solution to sulfanilic acid and dimethyl-P-phenylenediamine. The tin in a 15-20% HCl solution is heated for 50-60 minutes in a CO<sub>2</sub> atmosphere and then titrated with 0.01 or 0.05% solution of methyl orange. Sb, As, Bi, Cu, Cd, Pb, Fe do not interfere. Ti, V, Mo, and W do.

A colorimetric method for determining tin has been worked on by R.E.D. Clark (7). The method uses substituted 1:2 dimercapto benzenes. The unknown solution is diluted after addition of a drop of thioglycollic acid until the concentration of tin lies between 1.5 and 6 p.p.m. A standard solution of tin containing about 10 p.p.m. together with about 0.2 g. of thioglycollic acid per liter is diluted in a measuring cylinder until a colour match is obtained in the following manner. Two test tubes containing identical volumes (5-10 ml.) of the two solutions are treated with 0.5 cc of HCl followed by an equal quantity of 4-chloro-1:2 dimercaptobenzene in a 2% solution of NaOH. This causes the precipitation of a white suspension of the mercaptan. The tubes are immersed in boiling water for 10 sec. by which time the pink colour has developed fully and the two colours are compared directly by reflected light. Accuracy = 10%. Salts of Fe may interfere at or above 2%. The preparation of the reagent is given (8).

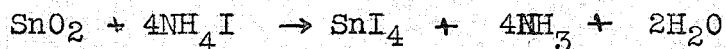
Another colorimetric method for tin is a modification of the molybdenum blue method recommended by Feigl (9). The method was developed by N. Strafford (10). The tin is

reduced to the stannous condition by boiling the acidified solution with a little aluminum in an atmosphere of  $\text{CO}_2$ . To the cooled solution is added an acid molybdate solution, and after standing a minute a measured amount of amyl alcohol (10 ml) is added; this extracts the whole of the blue coloured compounds. The amyl alcohol solution is separated; at this stage it is slightly turbid, but may be <sup>made</sup> quite bright by the addition of 1 ml of ethyl alcohol. The blue solution is then measured in the Lovibond Tintometer."

Cacotheline is used for the detection of tin only (11). The test solution is made alkaline with NaOH and reducing agents are removed. Then in acid solution cacotheline gives a purple colour which is easily destroyed by air oxidation.

A few other organic reagents for tin also exist.

In passing it might be well to mention a method for separating stannic oxide (the usual form in which tin occurs in ores) from various other oxides (12). An electric crucible furnace is required, the temperature of which can be controlled to within 5 degrees. Heating  $\text{SnO}_2$  with  $\text{NH}_4\text{I}$  at about  $425^\circ \text{C}$  affords a means of separating the  $\text{SnO}_2$  from the  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$  which are the common contaminants:



A method which promised a means of determining tin in the stannic condition with possible application to ores etc. was given by Willard and Smith (13). Tetraphenyl arsonium chloride is the reagent. This is an organic base similar to



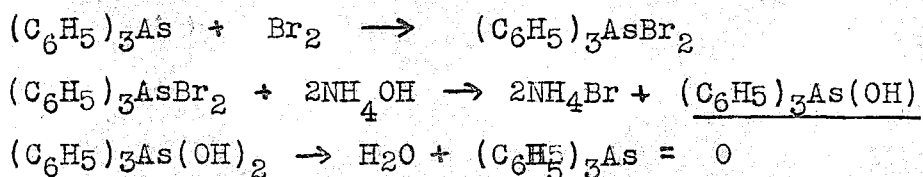
the organic ammonium bases such as tetraethyl ammonium hydroxide. The phenyl groups, of course, greatly weaken its basic properties, but it is quite soluble in water and will combine with the complex metallic acids of mercury, zinc, cadmium, bismuth and tin, as well as many other inorganic radicles. In other words, it is by no means a specific reagent but rather a reagent which is selective for certain acidic groups. Its application to the analysis of tin will depend upon the method of getting tin into solution whereby interfering elements are absent. The research in this laboratory was concerned with this reagent and another similar derivative that was prepared.

### Experimental Work

#### Preparation of the Reagent

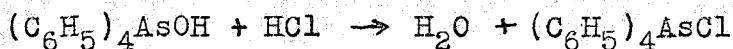
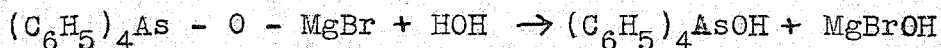
The method used for the preparation of the reagent was that of Blicke, Willard and Taras (14). Commercial triphenyl arsine was obtained from Eastman and from this triphenyl arsine oxide was made (15). The triphenyl arsine (20 g.) is dissolved in an excess of glacial acetic acid. Then bromine is added (14g.) slowly and with stirring. Concentrated  $\text{NH}_4\text{OH}$  is then added slowly in excess, until the triphenyl arsine hydroxide has precipitated. This is filtered on a Buchner funnel and washed with water; the precipitate is dissolved with warming in the smallest possible amount of ethyl alcohol and reprecipitated by adding an excess of water,

whereby fine white crystals of the hydroxide are obtained. These are dessicated in vacuo over concentrated sulphuric acid for several days whence water is lost, leaving triphenyl arsine oxide.



Then phenylmagnesium bromide is made from 15g of Mg, 68 cc. of bromobenzene and 300 cc. of dry ether in a liter flask equipped with a reflux condenser and stirrer. After reaction is complete (started by adding a little iodine and warming) 500 cc. of dry benzene is poured in and 60 g. of triphenylarsine oxide is added, a little at a time (over four hours) with stirring. Then stirring is continued for three more hours until all the oxide has disappeared.

The ether-benzene layer is decanted off from the viscous oil and 500 cc. of water is added slowly while the oil is stirred with a stirring rod. After thorough trituration about 150 cc. of conc. HCl are added until all the white solid that appears dissolves. The mixture is allowed to stand until the oil on the bottom has crystallized. This is filtered. The filtrate is neutralized with NaOH and a little NaCl is added to recover any tetraphenyl arsonium chloride in solution. The crude tetraphenyl arsonium chloride is purified by dissolving in 800 cc. of hot water and adding 150 g. NaCl, cooling and filtering.



In the later work a new derivative was prepared - triphenyl, naphthyl arsonium chloride. This was made in exactly the same manner - except that naphthyl magnesium bromide was used instead of phenylmagnesium bromide. (The same molar proportions were used.)

#### The Search for a Volumetric Procedure

Although tetraphenyl arsonium chloride precipitates with tin, some method of determining the reagent volumetrically is necessary. The reagent gives precipitates with iodine (in presence of KI), molybdate, dichromate, permanganate and other ions. Willard and Smith used iodine to determine the reagent, a potentiometric titration being employed. The precipitate is of a rusty brown colour, difficult to filter; its composition shows it to be the periodide:



"5 - 10 ml. of the water solution (0.01 - 0.03 M) are measured and diluted to nearly 100 cc. with water or saturated NaCl solution. The reference and indicator electrodes are immersed in this solution while standard iodine solution of about the same concentration containing 6 - 8 g. KI /l. is added slowly with constant stirring. As the iodine is added

the potential decreases to a min. value. When this minimum is reached the iodine is added dropwise and time allowed for the system to reach equilibrium. When an equivalent quantity of iodine has been added, there is a sudden increase in potential. Near the end point the solution must be completely saturated with salt before the titration is completed."

In a test of this titration the E.M.F. dropped to a minimum and stayed there. It was not very applicable to the determination of any range of reagent; this was the only method investigated for titrating the reagent. Three reactions were studied: with  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and  $\text{Na}_2\text{S}_2\text{O}_3$ .

#### The Permanganate Precipitate

Tetraphenyl arsonium permanganate is a dark red insoluble salt which removes any possibility of titrating the reagent with  $\text{KMnO}_4$  using an indicator. The precipitate forms in neutral or acid solutions, but not in basic solutions, possibly because of the formation of tetraphenyl arsonium hydroxide. The pure salt in water gives a Ph of <sup>2.7</sup>~~4.5~~ showing that hydrolysis takes place. Below is listed a table of the properties of the precipitate.

#### Properties of $(\text{C}_6\text{H}_5)_4\text{AsMnO}_4$

1. Ph of a saturated solution - ~~4.5~~<sup>2.7</sup>
2. Fairly soluble in a solution made acid with acetic.
3. Insoluble in above solution if  $\text{NH}_4\text{Cl}$  is present.
4. Insoluble in a solution made basic with  $\text{NH}_4\text{OH}$  (once formed).  
Decomposes upon boiling.
5. Sensitivity - will not precipitate with less than 3 ml. of

of 0.01 M. reagent in a volume of 60 ml.

6. The precipitate dissolves to a clear solution when boiled with a solution of sodium oxalate acidified with  $\text{H}_2\text{SO}_4$ .

The last mentioned property can be used to determine the reagent provided adequate precautions are taken with respect to reaction of permanganate with  $\text{HCl}$  and organic matter.

To determine the composition of the precipitate an excess of standard  $\text{KMnO}_4$  solution was added to 5 ml. of reagent. The precipitate was filtered through a weighed gooch crucible and washed with water. The excess  $\text{KMnO}_4$  in the filtrate was determined with a standard sodium oxalate solution. Results are tabulated for duplicate samples.

Normality of  $\text{KMnO}_4 = 0.101$

" "  $\text{Na}_2\text{C}_2\text{O}_4 = 0.307$

Volume of reagent in each case was 5 ml. to which 10 ml. of  $\text{KMnO}_4$  were added. 5 ml. of  $\text{Na}_2\text{C}_2\text{O}_4$  solution was added to the filtrate and the excess  $\text{Na}_2\text{C}_2\text{O}_4$  back titrated with  $\text{KMnO}_4$ .

1.  $\text{KMnO}_4$  back titration = 9.4 ml.

Weight of precipitate = 0.0375 g.

2.  $\text{KMnO}_4$  back titration = 9.4 ml.

Weight of precipitate = 0.0365 g.

Assuming the composition of the precipitate to be  $(\text{C}_6\text{H}_5)_4\text{AsMnO}_4$ , weight of precipitate calculated = 0.0424 g.

Percentage error = 11.5%, probably arising from the experimental conditions. (Water was used for washing in which

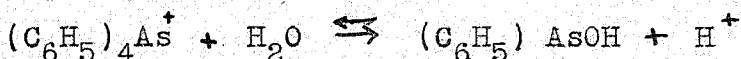
the precipitate is a little soluble due to hydrolysis.)

Since the sensitivity of the process is not very great it was abandoned.

Note that hydrolysis of the salt can take place because tetraphenyl arsonium hydroxide is a weak, and, in the presence of NaOH, a somewhat insoluble base. An attempt was made to find the approximate strength of the base:

$$K_B = \frac{[(C_6H_5)_4As^+][OH^-]}{[(C_6H_5)_4AsOH]}$$

In the hydrolysis of the chloride we have:



$$K_H = \frac{K_W}{K_B} = \frac{[(C_6H_5)_4AsOH][H^+]}{[(C_6H_5)_4As^+]}$$

$$K_H = \frac{Ch^2}{1-h}$$

where h = degree of hydrolysis

$Ch = [H^+] = [(C_6H_5)_4AsOH]$  which can be found by measuring the  $P_H$  of the solution.

$$K_H = \frac{[H^+]^2}{C - [H^+]}$$

0.3355 g. of pure tetraphenyl arsonium chloride was weighed and dissolved in exactly 80 ml. of water to make a 0.01 molal solution. The  $P_H$  of this solution was 2.65.

$$\therefore [H^+] = 2.24 \times 10^{-3}$$

$$K_H = \frac{5.02 \times 10^{-6}}{0.01 - 2.24 \times 10^{-3}} = 0.647 \times 10^{-3}$$

$$\therefore KB = \frac{10^{-14}}{0.647 \times 10^{-3}} = 1.6 \times 10^{-11}$$

### The Dichromate Precipitate

Tetra phenyl arsonium chloride gives a yellow flocculent precipitate with potassium dichromate in acid solution. The  $P_H$  of water containing the dichromate is 1.5 showing that considerable hydrolysis takes place. The precipitate is practically insoluble in acid solution at ordinary temperatures since the filtered solution that has been in contact with the solid for some time gives no precipitate with  $Pb^{+}$  in acetic acid solution. However, ferrous ammonium sulphate completely dissolves the precipitate in a solution acidified with HCl, showing that there are enough  $Cr_2O_7$  ions in solution to allow this reaction to go on. Furthermore, the precipitate is completely soluble at the temperature of boiling water.

The composition of the precipitate is  $[(C_6H_5)_4As]_2Cr_2O_7$  as shown by the following results. Some of the dichromate was prepared and washed thoroughly by decantation. The precipitate was dried and 0.1 g. weighed. This was dissolved in boiling water, acidified with acetic acid and treated with lead acetate.

Weight of  $PbCrO_4 = 0.0666$  g.

Theoretical weight of  $Cr_2O_7 = 0.1 \times \frac{216.02}{646.44} = 0.022$  g.

Experimental weight of  $Cr_2O_7 = 0.0666 \times \frac{216.02}{646.44} = 0.022$  g.

The dichromate is insoluble whereas the chromate is soluble at ordinary temperatures. Making the solution basic immediately dissolves the precipitate by forming the chromate ion and removing the tetraphenyl arsonium ion from solution as hydroxide.

To determine the reagent with potassium dichromate a direct titration or a determination of excess dichromate after filtering off the precipitate can be used. If possible, filtering is to be avoided. An attempt was made to develop a method for titrating the reagent directly. The indicator first selected consisted of one or two ml. of a 1% KI solution along with starch solution, the idea being that when an excess of  $\text{Cr}_2\text{O}_7^{=}$  ions were present these would set free  $\text{I}_2$  from the KI, thus giving the starch blue end point. The KI had to be a weak solution, otherwise  $\text{I}_2$  was set free before the end point and tetraphenyl arsonium periodide was precipitated. A saturated NaCl solution seemed to be necessary and accurate control of the acid concentration. The volume of the solution had to be kept down to a minimum. The following table shows some titration tests that were made. (Molality of reagent approx. 0.01).

Vol. of Reagent	$\text{K}_2\text{Cr}_2\text{O}_7$ titer	Vol. of Reagent	$\text{K}_2\text{Cr}_2\text{O}_7$ titer
1 ml	No precipitate	5 ml.	4.0 ml.
2 "	1.3 ml.	5 "	4.0 "
2 "	1.3 "	6 "	4.9 "
3 "	2.2 "	7 "	6.2 "
3 "	2.2 "	9 "	6.6 "
4 "	2.8 "	10 "	7.3 "



Although results are reproducible, the titration for higher volumes becomes higher showing that a blank would have to be subtracted; careful control of PH is also necessary. With higher volumes of reagent the yellow colour of the highly flocculent precipitate completely obscures the end point.

A redox indicator was tried - ortho phenanthroline and also diphenylamine. The same difficulty was found. Blank determinations were made with O-phenanthroline at different NaCl and HCl concentrations. The blank varies with both these concentrations from 0.3 to 2.6 ml. of dichromate solution. With these difficulties in view the process was abandoned.

Titration of excess  $K_2Cr_2O_7$  with ferrous ammonium sulphate could be used, but the filtration of the precipitate is tedious. Shown below are two standardizations of the reagent using this method. The precipitate is washed with water containing HCl.

$$1 \text{ ml. } FeSO_4 = .58 \text{ ml. } K_2Cr_2O_7$$

1. 5 ml. of reagent; 7.1 ml. of  $K_2Cr_2O_7$  added.

$$\text{Excess } K_2Cr_2O_7 = 4.7 \times .58 = 2.7 \text{ ml.}$$

2. 10 ml.  $\therefore$  4.3 ml. reacted.

2. 10 ml of reagent; 14.0 ml. of  $K_2Cr_2O_7$

$$\text{Excess } K_2Cr_2O_7 = 9.5 \times .58 = 5.5 \text{ ml.}$$

$\therefore$  8.5 ml. reacted.

The only practical application would be determining small amounts of dichromate gravimetrically. ~~Two~~ cases are cited to show the reproducibility of results. To 5 ml. of reagent in a volume of 60 ml. containing NaCl and HCl an excess of  $K_2Cr_2O_7$  was added <sup>and</sup> ~~with~~ the precipitate was filtered and washed.

1. Weight of precipitate = 0.0700 g.

2. Weight of precipitate = 0.0704 g.

### Triphenyl naphthyl arsonium chloride

At this stage of the research it was decided to try to prepare a reagent of different structure to see what effect it would have upon the precipitates mentioned. The preparation of this derivative has already been described.

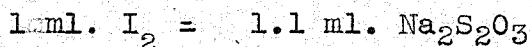
Triphenyl naphthyl arsonium chloride forms a precipitate with dichromate similar to the tetraphenyl derivative, except that once crystallized it is not readily soluble in basic solution, nor with ferrous ammonium sulphate in acid solution. It dissolves in boiling water. In water, the dichromate gives a PH of 3.2 as compared to 1.5 for the tetraphenyl derivative. Hence the naphthyl is less hydrolyzed. The permanganate precipitate of the naphthyl derivative is also similar to that of the tetraphenyl derivative. In water, it gives a PH of 4.5 as compared to 2.7 for the tetraphenyl derivative. Further work ~~was~~ carried out with the naphthyl derivative because of its greater sensitivity. The composition of this new reagent has not been determined; it is

just assumed that the structure is that given, because of the method of preparation.

### The Thiosulphate Precipitate

It had been observed that sodium thiosulphate completely dissolved tetraphenyl arsonium periodide leaving a white precipitate if excess thiosulphate was added. The thiosulphate precipitate of the new derivative was investigated. This is a white crystalline salt, formed in slightly acid solution but quite insoluble even in basic solution once formed. Half a ml. each of 0.005 M  $\text{Na}_2\text{S}_2\text{O}_3$  and reagent will give a precipitate in 60 ml. of solution. This will not dissolve even if the solution is boiled. Water that has been in contact with the salt for some time will not decolorize a little very weak iodine solution which confirms its complete insolubility. Also, in water this salt gives a PH of 7 showing that no hydrolysis takes place.

This led to an exact method for titrating the reagent. The idea was to add an excess of  $\text{Na}_2\text{S}_2\text{O}_3$  solution to a given volume of reagent and back titrate with an  $\text{I}_2$  solution, using starch as an indicator. Preliminary experiments gave the following results:



Total vol. of Soln.	Vol. of Reagent	Vol. of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	I <sub>2</sub> Titer	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Reacted
100 ml.	5 ml	5 ml	3.8 ml	0.8 ml
	10 ml	8 ml	5.6 ml	1.8 ml
	20 ml	5 ml	1.3 ml	3.6 ml
200 ml.	10 ml	5 ml	2.8 ml	1.9 ml
	20 ml	5 ml	1.0 ml	3.7 ml

The table shows the reproducibility of results and that the method is quite quantitative.

To investigate the conditions necessary for titration the potentiometer was used. It was found that when an excess of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added it took a little time for E to come to a steady value - corresponding to the time necessary for the completion of reaction. This took from ten to fifteen minutes usually. Then as the I<sub>2</sub> soln. is added the E drops slowly, until at the end point it drops quite rapidly. An example is given: 8 ml of thiosulphate were added to 5 ml of reagent and when E was steady the solution was titrated with I<sub>2</sub> soln. (automatically stirred).

Vol. of I <sub>2</sub>	E	Vol. of I <sub>2</sub>	E
0 ml	3.4	1.4 ml.	3.8
0.2 ml	3.7	1.5 "	3.72
0.5 "	3.8	1.7 "	3.62
0.7 "	3.85	1.8 "	3.60
0.8 "	3.90	1.9 "	3.55
1.0 "	3.90	2.2 "	2.9
1.2 "	3.85	2.3 "	drops rapidly

The titration was carried on fairly slowly in the above determination. Further titrations were made using the potentiometer and having the starch indicator in solution at the same time. The results are as follows:

1. 5 ml. of reagent, 8 ml. of thiosulphate

Indicator end point - 5.7 ml. thiosulphate reacted.

Potentiometer end point " " "

2. 6 ml. of reagent, 10 ml. of thiosulphate

Indicator end point - 7 ml. thiosulphate reacted

Potentiometer " " - 6.9 " " "

3. 10 ml. of reagent, 15 ml. of thiosulphate

Indicator end point - 11.4 ml. reacted

Potentiometer " " - " " "

The end point appears quickly but does not last very long, probably due to adsorption of  $I_2$  from solution by the precipitate; 0.1 ml. will restore the colour.

Further tests using 0.005 N solutions of  $Na_2S_2O_3$  and  $I_2$  showed that to get best results the thiosulphate must be added drop by drop with automatic stirring. Two or three ml. of HCl and a little NaCl must be present.

With larger volumes of reagent less thiosulphate appears to react with the reagent. This is probably because too large a volume of iodine is used because of adsorption. The fading end point would seem to confirm this; the analysis of tin solutions gives the same results (q.v.).

### The Tin Precipitate

Both derivatives used give a white crystalline precipitate with tin, providing the solution is saturated with NaCl and contains a little HCl. The purpose of the NaCl is to form sodium chlorostannate and keep the resulting tetraphenyl arsonium chlorostannate (or triphenyl naphthyl

arsonium chlorostannate) insoluble. The purpose of the HCl is to prevent hydrolysis. The precipitates slowly dissolve in water.

#### Tin Determination

Willard and Smith give the directions for precipitating tetraphenyl arsonium chlorostannate as: "2 cc. of HCl and enough NaCl are added to give a 2.5 to 3.0 M concentration of NaCl in a final volume of 60 ml." It was found that the tetraphenyl arsonium chloride would not give a precipitate with 1 mg. of tin under these conditions but that the new derivative did. Furthermore the solution must be saturated with NaCl and in washing the precipitate a saturated solution of NaCl must also be used.

A tin solution was made by dissolving tin in HCl and complete oxidation to the stannic condition was ensured. This was standardized with an iodine solution and found to contain 9 mg. of tin per 10 ml. A given volume of the tin solution was measured, one or two ml. of HCl added and the solution was made up to 60 ml. and saturated with NaCl. The solutions tested below were allowed to stand for an hour or two, after addition of an excess of reagent, then filtered through number 40 Whatman and washed with saturated NaCl until free of reagent, (testing filtrate with  $I_2$  soln.). The precipitate was washed with a stream of water from a wash bottle into a 150 ml. beaker. A few ml. of HCl and a little NaCl were added then a measured volume of  $Na_2S_2O_3$  was added drop by drop, with stirring. The excess  $Na_2S_2O_3$  was then back titrated with

### Suggestions for further work

The composition of the thiosulphate precipitate and new derivative must be known for certain.

The conditions necessary for determining larger quantities of reagent (and therefore of tin) must be more fully investigated.

The properties of a higher derivative could be compared with the others. Eg. trinaphthyl arsine can be made (17); it may be possible to prepare trinaphthyl phenyl arsonium chloride or tetranaphthyl arsonium chloride. The arsonium compounds could also be compared to the stibonium, phosphonium and ammonium compounds. To this end triphenyl stibine was obtained but time has not permitted an investigation along these lines.

The reagent reacts with the thiocyanate complexes of cobalt and iron. It may be possible to use it for cobalt if the interference of iron could be removed. Apparently iron gives a great deal of trouble in determining Co in ores with a - nitroso B - naphthol.

The reagent also precipitates gold and platinum in presence of HCl, probably the chloroaurate and chloroplatinate being precipitated. It may be possible to use this property in qualitative analysis.

an  $I_2$  solution.

Normality of  $Na_2S_2O_3$  sol'n. - 0.0052

1 ml. of  $I_2$  - 0.96 ml. of  $Na_2S_2O_3$

Vol. of Sn soln.	$Na_2S_2O_3$ added	$I_2$ titer	$Na_2S_2O_3$ Reacted	Tin Found	Error
1. 2 ml.	5.1 ml.	2.4 ml.	2.8 ml.	1.7 ml.	-0.1 mg.
2. 4 ml.	10.5 ml.	4.8 ml.	5.9 ml.	3.6 ml.	0.0 mg.
3. 5 ml.	13.4 ml.	7.2 ml.	6.5 ml.	4.1 ml.	-0.4 mg.
4. 7 ml.	13.5 ml.	3.7 ml.	10.0 ml.	6.2 ml.	-0.1 mg.
5. 8 ml.	16.0 ml.	4.4 ml.	11.8 ml.	7.3 ml.	+0.1 mg.
6. 10ml.	18.3 ml.	6.1 ml.	12.4 ml.	7.7 ml.	-1.3 mg.

It can not be emphasized too much that a saturated solution of NaCl must be used. Saturation must always be tested by adding a little HCl to the NaCl solution whence some solid salt will precipitate.

When higher volumes of tin were used, results were low: thus for 12.6 mg. of tin, only 10.3 mg. were found.

### Conclusions

1. A method has been described for determining small amounts of tin in the stannic condition: this may be applied to larger amounts of tin if adsorption effects can be overcome. (thus, 10 ml of conc. HCl prevents a fading end-point.)

2. The error due to atmospheric oxidation of stannous tin is thus removed.

3. The time required for analysis is shortened by stirring.



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