PREPARATION OF MESOXALIC ACID

AND

ITS USE IN THE SEPARATION OF

ANTIMONY AND TIN

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ABSTRACT

Preparation of Mesoxalic Acid and its Use in the Separation of Antimony and Tin.

The more important part of the work consists of testing whether mesoxalic acid could be used as an agent for the separation of antimony and tin or not. Since the acid is not available, and a standard method of its preparation is not present in Chemical Reviews, the work had therefore to include its preparation. Following, is a brief summary of the main steps conducted for producing the acid, and applying it on the separation.

Malonic ester is readily oxidized by means of dry nitrous fumes into mesoxalic ester. The ester, after being distilled under reduced pressure, and after making several tedious trials, was finally hydrolyzed by water and a few drops of concentrated hydrochloric acid as a catalyst. The acid formed, was separated by suction, purified and dried.

Several trials were then performed which proved that when the required quantity of mesoxalic acid is added to mixtures containing varying quantities of antimonous and stannic ions, always stannic sulfide is precipitated and none of antimonous sulfide. The completeness of separation was confirmed quantitatively.
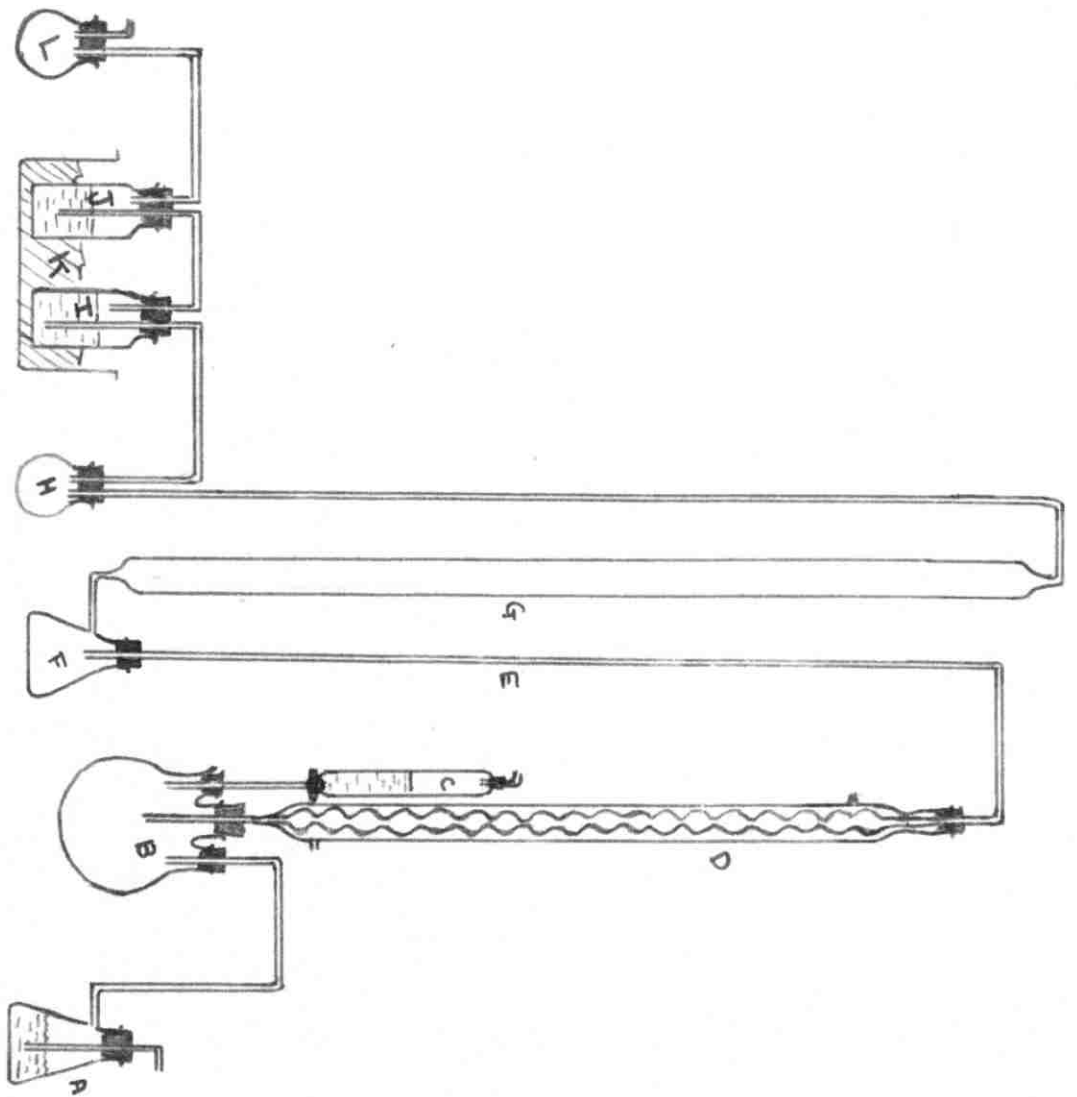
PREPARATION OF MESOXALIC ACID AND ITS USE IN THE
SEPARATION OF ANTIMONY AND TIN

Introduction

The idea for the use of mesoxalic acid as an agent for the separation of the ions of antimony and tin was suggested by Dr. A.W.C. Menzies to my advisor Dr. W.A. West on a private conversation about the coordination compounds of tin. Dr. West suggested to me that the acid in question is a highly negative one due to the two hydroxyl groups which it holds on its alpha-carbon atom and because the chain of carbon atoms in this acid is not a long one. This being the case, the acid may give a good enough concentration of mesoxalate ions in solution, to form a complex ion with tin as the oxalate ion does. This would make the acid a useful agent in the separation of antimony and tin.

The acid being unavailable on commercial supply, it had to be prepared from commercially available products as malonic ester. This part of the work did not prove to be as easy as expected, and most of the time had to be devoted on it. When the acid was prepared, the second part of the work was smoothly run over with promising results obtained.

Preparation of Ethyl Oxo-Malonate

$$\underset{\substack{COOC_2H_5 \\ | \\ H-C-H \\ | \\ COOC_2H_5}}{} + \quad 2 N_2O_3 \quad \longrightarrow \quad \underset{\substack{COOC_2H_5 \\ | \\ C=O \\ | \\ COOC_2H_5}}{} + \quad H_2O \quad + \quad 4NO$$

The starting material for making mesoxalic acid is diethyl malonate. The preparation consists of two general steps:

1- Oxidation of malonic ester into mesoxalic ester, and

2- Hydrolysis of the ester obtained into the corresponding acid.

Apparatus

Set up the apparatus as indicated in the accompanying diagram.

A- is a 500 cc. pyrex filter flask.

B- is a 2 liter three-necked, round bottom flask.

C- is a 300 cc. dropping funnel.

D- is a 75 cm. water-cooled bulb condenser

E- is a large-bore glass tube.

F- is a 500 cc. filter flask.

G- is a drying tower.

H- is a 500 cc. round-bottomed "sight flask".

I and J- are 500 cc. absorption bottles.

K is a trough.

L- is a 500 cc. round-bottomed sight flask.

Chemicals

Before finally assembling the apparatus, the various units are charged as follows:-

A is one third filled with water to serve as a bubble counter.

Funnel C is filled with concentrated nitric acid. Generator B is about one quarter filled with dry powdered arsenious oxide. Drying tower G is filled with anhydrous calcium chloride. A wad of glass-wool is put in front of the entrance and exit tubes. In each of the two absorption bottles I and J, is placed 200 gms. (1.25 moles) of ethyl malonate. Dish K is filled with an ice-salt freezing mixture.

Procedure

When assembled as indicated, the apparatus is ready for operation. Flask A is connected to an air-compressing machine. The compressed air ensures an excess of oxygen, and thus complete oxidation. It is insufficient if any colorless gas, which turns brown on comming in contact with air, leaves the apparatus at L. Only a slow stream is found to be necessary, two to three bubbles per second.

Concentrated nitric acid is run, in small portions, into generator B from dropping funnel C. After the action has started, the nitric acid has to be forced into flask B by connecting the top of funnel C to the air-compressing machine by means of a T-tube and then opening the stopcock. Later on, when the gas generation slackens, flask B is heated with a smoky flame. The evolution of gas is maintained at a steady rate by increasing the heat until finally all the arsenious oxide has dissolved and the frothing has ceased.

The moist oxides of nitrogen, in passing up through the condenser D, lose most of their moisture, and the gas on passing down trhough tube E should deposit very little water in trap F. The

gas is then thoroughly dried in the tower G. After passing
through the drying tower and through flask H, the gas is
absorbed by the cold ethyl malonate in vessels I and J. The
color of the liquid changes into dark green. Considerable gas
escapes from I and is taken up by J. When flask I has gained
200 gms. in weight it is disconnected and the reaction is
continued as before until J has also gained 200 gms. In about
three hours the reaction is completed.

By means of the depth of the color in flasks H and L, the
efficiency of absorption can be judged. The efficiency is best
if the color of the gas in flask L is much lighter than that in
flask H. Also flask H has the important function of catching any
liquid that might be sucked back from the absorption vessels.

Ethyl oxo-Malonate

The liquid is left in the freezing mixture for several hours,
then gradually allowed to come to room temperature. Red gases
are slowly evolved. After standing for two or more days at room
temperature, the liquid is transferred to a distilling flask
provided with a capillary air-intake, and the delivery tube
connected with a water-cooled condenser and receiver. The distil-
lation is performed under reduced pressure, by the use of water
pump. The receiver is a vacuum desiccator with two side openings.
In it is supported by a perforated disc holding several test
tubes for catching the different fractions. To one of its openings
is connected the water pump and a manometer for indicating the
pressure at which distillation is to take place.

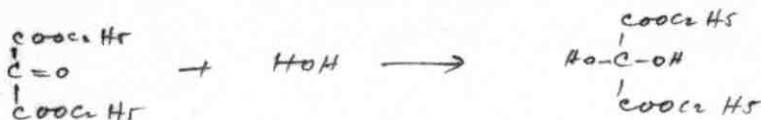When the apparatus is arranged in this way, the distilling

flask is heated gradually and the water pump is set into operation. Considerable nitric oxide is evolved before the pressure drops to 70 mm.

The first fraction consists mainly of water, and some ethyl oxomalonate which recombines with the water to form solid ethyl mesoxalate. When the pressure has dropped to 45 mm. and the temperature has risen to 110°C., the disc is moved. It is important to mention here that from this point on, the distillation must be conducted with extreme care. As soon as the ethyl oxomalonate has partly distilled over and the temperature has risen somewhat, some decomposition may take place and gases are liberated so rapidly that the thermometer and capillary or the cover of the desiccator may be blown out. If the manometer is watched closely, and at the first sign/liberation of gas, as shown by a sudden increase in pressure, a wet towel is placed around the flask, the reaction may be slowed down.

The main product, ethyl oxomalonate, now distills at 110° - 135°C. at 45 - 50 mm. pressure. If the oxidation has been complete very little residue is left. The distillate is golden yellow with a boiling point of 103 - 108°C., at 15 mm. pressure. The yield is about 70% of the theoretical.

Ethyl mesoxalate

Upon adding the calculated amount of water to ethyl oxomalonate decolorization takes place immediately with evolution of heat, and on cooling, a solid mass of plate-like crystals of ethyl mesoxalate results.

$$\begin{array}{ccc}
\begin{array}{l} COOC_2H_5 \\ | \\ C=O \\ | \\ COOC_2H_5 \end{array}
& + \quad HOH \longrightarrow &
\begin{array}{l} COOC_2H_5 \\ | \\ HO-C-OH \\ | \\ COOC_2H_5 \end{array}
\end{array}$$

Ethyl oxomalonate   **Ethyl mesoxalate**

The melting point of the product after recrystallization is 56 - 57°C.

Mesoxalic acid

The usual methods of hydrolysis of esters were not found applicable for preparing this acid from its ester. The sodium and calcium salts of mesoxalic acid which are formed instantaneously upon the addition of solutions of NaOH and $CaCl_2$ to the ester, did not give any significant amount of the acid upon hydrolysing with hydrochloric and sulfuric acids respectively. Another procedure had to be adopted which proved to be successful.

The ester is put in a round-bottomed flask to which is connected an upward fractionating reflux condenser and thermometer. To the side of this condenser is connected a water cooled condenser and receiver. An equal volume of water is added to the ester and some drops of conc. HCl. The heating is done by immersing the flask in a steam bath. The temperature of steam keeps the water refluxing while it distills off the alcohol formed during hydrolysis. After heating in this way for about three hours, the ester lower layer gradually vanishes. The distilling flask with its contents is left to cool down overnight whereby solid mesoxalic acid separates out from the concentrated solution as needle-like crystals. After separating it from the mother liquor by suction, the acid is washed several times with chloroform, to ensure the separation from it of any residue of the

ester.   It is then put in a desiccator for a few days to dry
completely.   The melting point of the product is found to be
117 - 119°C.

Use of Mesoxalic Acid for the Separation of Antimony and Tin

Antimony and tin, together with arsenic appear in the B subgroup of group II in qualitative analysis. The sulfides of antimony and tin are soluble in concentrated HCl while that of arsenic is not. This makes it easy for the separation of arsenic. To separate antimony from tin for the sake of identifying each alone, there are several methods in use. It is worthy to mention briefly some of the more important ones.

1. Separation using oxalic acid

To a solution containing antimonous and stannic ions, excess oxalic acid is added. The latter reagent seems to react in some way with the stannic ion and not with the antimonous ion; such that when H_2S is passed into the solution, only orange Sb_2S_3 is precipitated and none of stannic sulfide. The theory involved in this separation is the complex ion formation between tin and oxalic acid.

Stannic chloride is a covalent compound, and tin being one of the heavy metals it has a coordination number of six. In other words it can form compounds in which it coordinates six pairs of electrons. Thus when stannic chloride is dissolved in Conc. HCl the following reaction takes place:

$$SnCl_4 + 2HCl \longrightarrow H_2SnCl_6$$
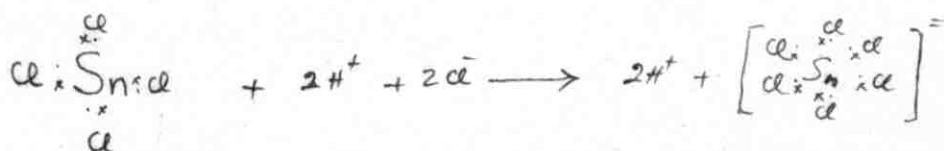
The chlorostannic acid formed in the first reaction
ionizes readily to form a large number of $SnCl_6^=$ ion and a few
Sn^{+4} stannic ions.

$$H_2SnCl_6 \rightleftharpoons 2H^+ + SnCl_6^=$$

$$SnCl_6^= \rightleftharpoons Sn^{+4} + 6Cl^-$$
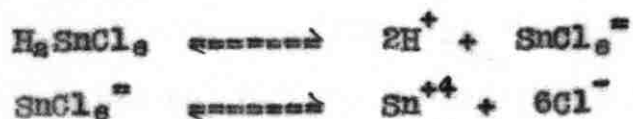
If the solution is too acidic in respect to HCl the stannic
ion concentration is diminished as is clear from the above
equilibria. Also the acidic medium decreases the sulfide ion
concentration when H_2S is passed into the solution. These two
facts will supplement each other in preventing the formation of
a precipitate of stannic sulfide in a highly acidic medium. At
the same time and for the same reason of low sulfide ion concentra-
tion, antimony is prevented from precipitation as antimony
sulfide in a highly acidic medium. This prevents the use of
hydrogen sulfide as a separating agent. On the other hand, when
the solution is slightly acidic there will be enough stannic ions
to ensure the precipitation of stannic sulfide. At the same time
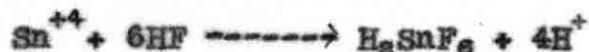antimony sulfide is also precipitated.

When enough oxalic acid is added to a solution containing
Sn^{++} and $SnCl_6^=$ ions in equilibrium, three oxalate ions with two
pairs of electrons in each ready for sharing will be coordinated
with the stannic ion inorder that the coordination number of six
for tin is satisfied.
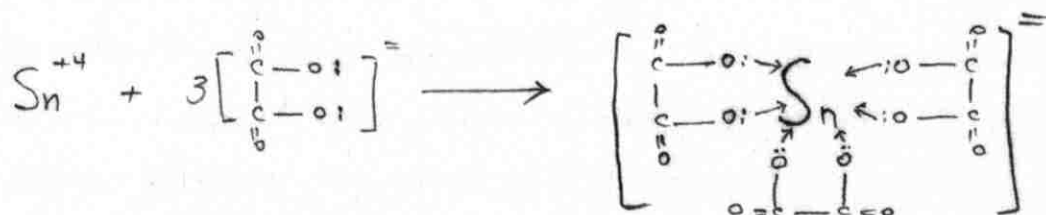
The resulting complex ion seems to be so stable that the few stannic ions formed from its ionization are not enough to saturate the solution with stannic sulfide when hydrogen sulfide is passed and so no precipitate of stannic sulfide is formed. At the same time the oxalate ion seems to be of no effect upon the antimonous ion so that antimony sulfide is precipitated under the same conditions.

2. Separation Using Hydrofluoric acid

Hydrofuloric acid reacts with the stannic ion in the same way as hydrochlorid acid reacts,

$$Sn^{+4} + 6HF \longrightarrow H_2SnF_6 + 4H^+$$

$$H_2SnF_6 \rightleftharpoons 2H^+ + SnF_6^=$$

$$SnF_6^= \rightleftharpoons Sn^{+4} + 6F^-$$

Employing HF as a reagent for the separation of antimony and tin works very well although the same reactions take place as with HCl. What seems to be different is that the ionization of the $SnF_6^=$ ion is so insignificant that only a few stannic ions are formed and so not enough to form a precipitate of stannic sulfide. Under the same conditions antimony sulfide is found to be precipitated.

3. Separation Using Phosphoric Acid

The following is a paragraph quoted from the Chemical Abstracts vol. 33 page 2839[2]:-

"To separate antimony from tin in a solution such as obtained by dissolving their sulfides in concentrated HCl and boiling off all H_2S, add sodium carbonate until neutral then an equal volume of H_3PO_4 (d. 1.3) and 1/5 volume of Conc. HCl. Under these conditions Sb_2S_3 will precipitate on introducing H_2S into the hot solution and tin will remain in solution".

A complex ion of the form $[Sn(PO_4)_2]^{=}$ seems to be formed in this case.

Separation Using Mesoxalic Acid

Mesoxalic acid has the formula

HO- $\begin{array}{l} COOH \\ C-OH \\ COOH \end{array}$ or $\begin{array}{l} COOH \\ C=O \\ COOH \end{array}$ the carbon

Atom in the middle holds two hydroxyl groups which might decompose under certain conditions to form a carbonyl group. Any how either formula is referred to as mesoxalic acid.

The substitut/ion of a negative group such as a chlorine atom or a hydroxyl group for a hydrogen on the alpha carbon atom of an acid will increase its acidity. This is true because the entering electronegative group being more negative than hydrogen will draw the binding electrons towards itself. This pair of electrons will therefore excercise a smaller repulsion on the other electrons of the carbon atom and so they move closer to the carbon atom. This results in a shift of the other electrons in the chain with the final result that the oxygen-hydrogen bond of the carboxyl group becomes more polar and hence ionizes more readily. As an example, chloroacetic acid is more acidic than acetic acid because the shift of electrons towards the point of substitution along the chain make the ionization of the substituted acid easier.

$$Cl \longleftarrow \overset{H}{\underset{H}{C}} \longleftarrow \overset{}{\underset{O}{C}} \longleftarrow O \longleftarrow H$$
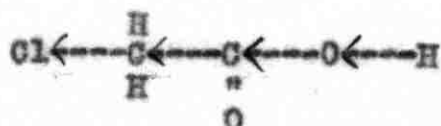
Dichloroacetic acid is still more acidic than the mono-substituent. Hydroxy acetic acid is more acidic than acetic acid for the same reason.

It should therefore be concluded that the mesoxalic acid with

two hydroxyl groups on the same alpha carbon atom should be much more acidic than malonic acid and probably it might be more acidic than oxalic acid itself.

Bearing in mind the fact that mesoxalic acid is highly acidic and that the mesoxalic ion could form readily in aqueous solution; trials were made to see whether mesoxalic acid could be used as oxalic acid for the separation of antimony and tin and to see whether it is of any more benifit. The results of such investigations proved that mesoxalic acid could be used as well to separate antimony from tin. This confirms the prediction that mesoxalic acid is a highly negative acid and so could be put into uses requiring this property.

The following are the trials put in tabular form:-

Trials	Molarity of SnCl$_4$ solution in a volume of 10 cc.	Molarity of HCl	Time of Boiling	Wt. of mesoxalic acid	result
I	0.1 M	0.5 M	2 min	1/2 gm.	a ppt. of SnS$_2$ is formed.
	0.05	0.5	2	1/2	"
	0.025	0.5	2	1/2	no ppt. is formed.
II	0.025	0.1	2	1/2	"
	0.025	0.2	2	1/2	"
	0.025	0.3	2	1/2	"
	0.025	0.4	2	1/2	"
	0.025	0.5	2	1/2	"
III	0.025	0.5	cold	1/2	"
	0.025	0.5	hot	1/2	"
IV	0.025	0.5	2	1/4	a ppt. of SnS$_2$ is formed in one minute.
	0.025	0.5	2	1/2	no ppt. was formed in five minutes.
	0.025	0.5	2	1	"

The results given above show that the acidity of the
solution and the time of boiling, within certain limits are
not factors of primary importance; and that to prevent SnS_2 from
precipitation in a solution whose volume is 10 cc. and is 0.025 M
in respect to $SnCl_4$, half a gram of mesoxalic acid is the
minimum amount required.

Here again it seems that mesoxalic acid forms a complex ion
with the stannic ion similar to that formed with oxalic acid, so,
preventing it from precipitation with H_2S reagent.
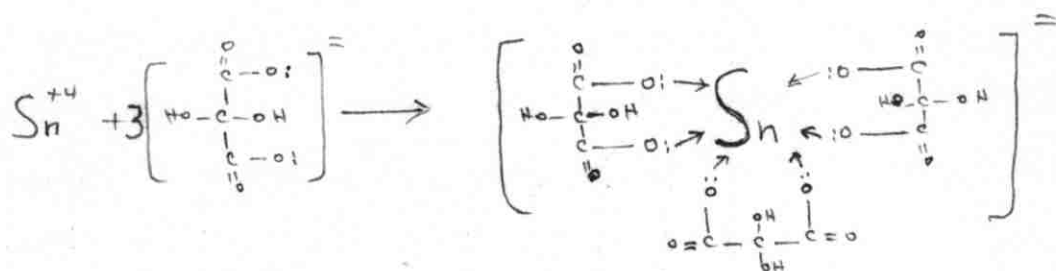
When similar trials were made with solutions containing the
antimonous ion, a ppt. of Sb_2S_3 was formed under all conditions.
again experiments were done upon solutions containing varying
quantities of stannic and antimonous ions and in all cases it was
found that if the necessary amount of mesoxalic acid is added,
namely half a gram for each 10 cc. of 0.025 M $SnCl_4$, only an oran-
ge precipitate of Sb_2S_3 is obtained.

Finally one quantitative determination was done to see whether
all the antimony is precipitated or not.

Quantitative Determination

Take 40 cc. of 0.025 M $SnCl_4$ solution. To this add an
exactly weighed quantity of $SbCl_3$.

Wt. of bottle + $SbCl_3$ = 12.2806 gms.

"   "   "   empty   = 12.2346 "

"   " $SbCl_3$ =   0.0460 "

This quantity of $SbCl_3$ (0.0460 gms) makes the solution 0.0050407 M in terms of $SbCl_3$ i.e. about one fifth the molarity of $SnCl_4$.

Wt. of Sb in 0.0460 gms of $SbCl_3$ = $\frac{121.76}{228.14}$ x 0.460

                                                = 0.02455 gms.

To this solution add Conc. HCl drop by drop until the $SbCl_3$ is dissolved. Heat, add two grams of mesoxalic acid and pass H_2S. Antimony sulfide will precipitate alone. Separate the precipitate by filtration, wash several times with water and then dissolve the precipitated Sb_2S_3 by adding conc. HCl. Make the solution formed 20% by volume in respect to conc. HCl. Boil to drive off the H_2S. Filter the suspended sulfur, heat the solution to 70°C. and add one or two drops of methyl orange indicator. Titrate with a 0.1N $KBrO_3$ solution which is previously prepared by dissolving exactly 2.784 gr. of it in one liter of water in a volumetric flask.

$$KBrO_3 + 3SbCl_3 + 6HCl \longrightarrow KBr + 3SbCl_5 + 3H_2O$$

Towards the end of the titration add the $KBrO_3$ a drop every two seconds till the pink color is discharged.

Calculation

Lower reading of burette   = 5.9

Upper   "   "   "   = 1.8

Vol. of $KBrO_3$ used   = 4.1 cc.

1 ml. of 1N KBrO$_3$ =   0.06088 gms of Sb

1 " " 0.1N "   =   0.006088 "   "   "

Wt. of antimony as determined = 0.006088 x 4.1

                                    = 0.0249608 gms.

Actual wt. of antimony   = 0.02455 gms.

Difference   = 0.0004108 gms.

This experiment shows that practically all the antimony is precipitated. Although it does not prove that a small amount of SnS$_2$ might have precipitated, since KBrO$_3$ is not effective on the stannic ion; yet the previous experiments done on samples of the same concentration of stannic ion with no sings of precipitate exclude the probability that any stannic sulfide is formed together with the antimony sulfide. This fact therefore makes it unnecessary to go through a quantitative determination of tin in solution.

Conclusion

At this point a brief comparison of the methods used for the separation of antimony and tin is worthy of mention.

The method that is most usually adopted is that by using oxalic acid. It is the preferred one, since the acid is quite available and there are no difficulties arising from using it. On the other hand it is well known that the acid is never completely effective in the separation, and that large quantities are required to ensure a maximum separation. These two facts are limitations which need to be taken into consideration when accuracy and economy are to be counted.

The other reagent, hydrofluoric acid is never adopted by

authors of qualitative analysis books since its use is limited by the fact that the acid attacks glass. This limitation necessitates a supply of other equipment made up by either platinum or quartz, the use of which is impractical. It is worthy to mention that as a sparating agent hydrofuloric acid is a very effective one.

Finally, the new reagent, mesoxalic acid seems from the previous experiments to be a better separating agent from the point of view that it is more effective, and definitely a smaller quantity of the acid is required to make the same separation. That a smaller quantity is needed could probably be due to the fact that for the smae number of molecules of the acids added, mesoxalic acid gives a greater number of mesoxalate ions ready for coordination. Anyhow this is just a prediction which needs clarification by a thorough study of the behaviour of this acid in aqueous solution as compared with that of oxalic acid; then one could be definitely sure of which is the better separating agant. With the few experiments I have performed, and at least with passion I expect mesoxalic acid to be the better and more effective one. As regards to its availability, the acid is not yet on the market, and even if it becomes so in the future, I believe it would be more expensive than oxalic acid. This of course would limit its use.

The use of the three acids I previously mentioned is becoming limited in qualitative analysis, due to the fact that newly dis-covered organic reagents are in use for detecting antimony and tin in the presence of each other without taking the labour of separa-ting them. On the other hand, when quantitative determinations are required the use of these acids and other separating agents cannot be escaped.