THE SEPARATION AND DETERMINATION

...OF...

TIN, ARSENIC AND ANTIMONY.

A THESIS

PRESENTED TO THE FACULTY OF THE COLLEGE OF SCIENCE

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...BY...

ERWIN HOWARD BERRY.

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As one glances over the science of chemistry, he is impressed by the amount of work to be done. In every branch he is almost lost. Yet one might suppose that in qualitative and quantitative analysis but little work would remain. There has been so much work done, and it is of such a practical nature that such a supposition is not to be wondered at. But when we come to consider all the different methods for determining the elements, we find that there is yet much work to be done.

Among the least satisfactory methods is that for the separation and determination of tin, arsenic, and antimony. The elements all of them give to their alloys with many of the other metals characteristic properties which tend to make them much used, and thus their determination becomes important. As is well known tin is much used in alloys, such as bronze composed of copper, tin and zinc, gun metal formed of tin and lead, and brittania metal made of antimony and tin. Antimony usually gives to its alloys a hardness and brittleness, also increasing its fusibility. Its most common alloy is with lead forming type metal. An alloy with lead is often used instead of bronze in taking casts of works of art. The presence of arsenic generally renders the alloy more brittle, more fusible, and brighter. It is not much used in technical chemistry except in making shot where it is alloyed with lead and gives to the alloy a property such that on
cooling the shot, it is kept rounded instead of becoming elongated. Thus one can see that although these metals are not used so much as many of the others, yet their use is quite extensive and sufficiently so to require a good method of separation and determination.

Among the methods at present employed for the separation of tin, arsenic and antimony may be mentioned the following:--

Clark's method (Chemical News, Vol. 39, page 257) based upon the fact that when oxalic acid is added to a boiling solution containing these elements and then hydrogen sulphide passed into the solution, antimony is precipitated along with arsenic if the latter be present, while tin remains in solution. After allowing the solution to stand in a warm place for about half an hour, it is filtered. Then the filtrate thus obtained is neutralized, the precipitate thus formed dissolved with yellow ammonium sulphide and the tin precipitated by the addition of acetic acid, and finally burned and weighed as the oxide. Another method is described by Carnot (Chemical News, August 20, 1886). Here instead of hydrogen sulphide, sodium hyposulphite is used to precipitate the antimony. The antimony is precipitated as \( \text{Sb}_2 \text{O}_3 \) along with considerable sulphur which is removed with carbon bisulphide. The antimony may then be converted into the persulphide by calcination in a dry current of carbon dioxide. The tin is precipitated
with ammonia, the sulfide salt decomposed with acetic acid and burned to the oxide. This method may also be used for the separation of all three elements. After the antimony has been removed as above the filtrate is made strongly acid with hydrochloric acid and then hydrogen sulfide passed through while the solution is almost boiling. Arsenic is precipitated while the tin remains in solution.

H. N. Warren (Chemical News, March 1888 page 125) dissolves the sulfides in aqua regia, evaporates nearly to dryness, dilutes with dilute hydrochloric acid and adds an excess of potassium ferro-cyanide. The tin is thus precipitated while the antimony remains in solution.

A method (Chemical News, October, 1890 page 217) somewhat similar to the first one mentioned consists in dissolving the sulfides of tin and antimony with sodium hydroxide and then dividing the filtrate into two equal parts. To one part oxalic acid is added, when the orange red precipitate of the sulfide is obtained and the antimony finally weighed as the oxide. From the other half of the solution tin and antimony sulfides are precipitated and the elements finally weighed as oxides and the tin determined by difference.

The mixed sulfides (Journal of the Society of Chemical Industry May 31, 1892, page 461) may be dissolved in ferric
chlorid solution containing hydrochloric acid. The arsenic is then distilled over, and weighed as arsenic sulphide. The antimony is then precipitated with hydrogen sulphide in the presence of oxalic acid while the tin remains in solution and may be determined in the usual manner.

Another method described ([Journal of the Society of Chemical Industry, March 30, 1895, page 302]) consists in dissolving the sulphides in yellow ammonium sulphide. The solution is acidified with hydrochloric acid and oxidised with potassium chlorate. After adding tartaric acid the solution is made ammoniacal, and the arsenic precipitated with magnesia mixture. After filtering, the filtrate is made acid and antimony and tin precipitated with hydrogen sulphide. The precipitate after being filtered from the solution is dissolved with freshly prepared sodium sulphide, and decomposed with sodium peroxide, added a little at a time, the solution cooled, alcohol added, and after standing for twenty four hours is filtered off and determined by any of the well known methods.

A solution ([Journal of the London Chemical Society, August, 1896, page 501]) containing tin, antimony and arsenic is distilled with hydrochloric acid and potassium bromide. Arsenic distilled over tin dissolves while the antimony remains undissolved. The author finds that a little of the antimony
dissolves so that he uses potassium iodide instead of potassium bromide. Each element is then determined by any of the known methods.

Another method (Journal London Chemical Society, Vol. 66, page 94) for separating tin and antimony in alloys consists in digesting the alloy in nitric acid. This converts the elements into their oxides which are weighed as such. The oxides are then mixed with a ball of tin and dilute hydrochloric acid and heated. The reduced antimony is collected on a filter, the tin going into solution, washed and weighed. The tin is then determined by difference.

If a solution (American Chemical Journal, Vol. 7, page 133) of the three elements in sodium sulphide be boiled with copper oxide, they will be converted into sodium stannate, sodium antimonate and sodium arsenate. The cuprous sulphide which is formed is removed by filtration and alcohol added to the filtrate. The antimony will be precipitated. After filtering off the antimony, the alcohol is evaporated off and ammonium chloride added. A milky precipitate indicates tin. Arsenic is precipitated with magnesia mixture. This method is merely qualitative.

Another method (Journal of the London Chemical Society, Vol. 62) is one based upon the fact from a solution containing arsenic and antimony, if potassium iodide be added and a current
of hydrochloric acid passed through the arsenic may be distilled over and determined in the distillate. The antimony remains in the residue and is determined by a volumetric method. It is first reduced with sulphurous acid, then the excess of this sulphurous acid is taken up by the addition of iodine. Tartaric acid is then added, the solution nearly made neutral with sodium hydroxide, sodium acid carbonate added to alkalinity and antimony determined by titration with tenth normal iodine. In the School of Mines Quarterly Vol. 15 Györy says the end reaction with the iodine titration is slow. He proposes using a solution acidified with hydrochloric acid containing potassium bromide. He then adds methyl orange and titratic with potassium bromate, the end reaction being when the solution becomes colorless.

Another method well recommended (Analyst, February, 1898) for determining antimony volumetrically consists in treating the sulphide of antimony with ferric sulphate. Then after diluting and adding strong sulphuric acid, the ferrous sulphate thus formed is titrated with permanganate solution.

These numerous methods are well recommended for accuracy. Yet they all allow much for errors. Thus the method which involves the weighing of either arsenic or antimony as sulphide is far from accurate owing to the difficulty of removing the free sulphur. It is almost impossible to remove it with carbon
bisulphide. Where the antimony is weighed as the oxide, there is no surety that the precipitate consists of a single oxide. On the other hand it more than likely consists of a mixture of different oxides. If the oxide is obtained from the sulphide, when there is free sulphur present during the ignition it tends to reduce the oxide and cause the antimony to volatilize. In the methods where the arsenic is distilled over from a strongly acid solution, there is danger that some of the arsenic will remain in the residue, while a little antimony may be carried over. In most of these methods, yellow ammonium sulphide is used, and any method involving its use is at best hard to operate as there is bound to be free sulphur, both in precipitates and in the filtrates. All of these methods are long and tedious and difficult of operation. Then there is no good volumetric method for antimony, which is very desirable owing to the variableness of its oxide.

Thus it can be seen how much need there is of other better and more accurate methods for the separation and determination of these elements. The common method in use for the separation of these elements from the other members of the second group is by the use of ammonium sulphide. But in the use of this substance there always comes the difficulty of getting rid of the free sulphur which comes from its use. To rid ourselves of this we first tried to find a substitute. Our attention was first
turned to sodium hydroxide. Now as is well known sodium hydroxide at first dissolves the tin precipitate and then reprecipitates it as tin hydroxide. It readily dissolves the sulphides of antimony and arsenic, which remain in solution. Our first thought was that if a dilute solution of sodium hydroxide would dissolve the sulphides in full, there would be no trouble from its reprecipitating tin. So we tried the solubility of the sulphides in different strengths of sodium hydroxide. We found all the sulphides very soluble with the single exception of stannous chloride, which took such a strength of sodium hydroxide solution to dissolve it that the tin would be precipitated again. Thus our plans were foiled and we were compelled to try something else. The following are the solubilities obtained with the exception of stannous sulphides. The results obtained for this were lost.

5 c.c. of \( \frac{1}{5} \% \) sol. NaOH 1 c.c. of \( \frac{1}{3} \% \) sol. NaOH

<table>
<thead>
<tr>
<th>Sulphide</th>
<th>5 c.c. ( \frac{1}{5} % ) sol. NaOH</th>
<th>1 c.c. ( \frac{1}{3} % ) sol. NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(_2)S(_3)</td>
<td>2.73 m.g.</td>
<td>2.00 m.g.</td>
</tr>
<tr>
<td>Sn(_2)S(_3)</td>
<td>5.143 &quot;</td>
<td>3.086 &quot;</td>
</tr>
<tr>
<td>Sb(_2)S(_3)</td>
<td>1.40 &quot;</td>
<td>2.8 &quot;</td>
</tr>
</tbody>
</table>

We took up yellow ammonium sulphide again. As above stated the objection to the use of this substance was the fact that all further manipulations are hampered by the presence of free sulphur. It was found that when yellow ammonium sulphide is boiled with hydrogen peroxide in the presence of ammonium
hydroxide, the sulphide is oxidised to the sulphate. It is evident that at first a more complex ammonium sulphide is found, as at first the solution becomes more deeply colored, then upon boiling a little the color begins to disappear and if enough hydrogen peroxide is added the solution becomes entirely colorless. We found that this worked all right when tin, antimony and arsenic have been dissolved in the yellow ammonium sulphide, and at the same time the tin is precipitated probably as the hydroxide. Then here is a method by which we get rid of the sulphide and at the same time precipitated the tin. The tin precipitated and out of the way, then how to precipitate the antimony? It was first thought that the antimony would precipitate upon making the solution acid. In fact part of it is precipitated. Then sodium peroxide was tried. This reagent was added to the boiling solution, strongly ammoniacal, a little at a time until there was no smell of ammonia, then the solution cooled and alcohol added, about equal volume to the solution. A white precipitate immediately formed. After standing over night it was found that, after filtration no antimony remained in the solution.

Here then was a method by which the antimony could be separated from the arsenic, which remained in solution. A gravimetric method was impracticable as the sodium pyro-antimonate consisted of a very fine precipitate, difficultly removed from
the beaker in which it was precipitated. If some method for reducing it could be found it could be found titrated with iodine solution. Many methods have been suggested by different ones for its reduction. Hydrogen peroxide was first tried. The antimony precipitate was first dissolved in hydrochloric acid and tartaric acid and then boiled with hydrogen peroxide. Then the solution was cooled, made nearly alkaline with sodium acid carbonate, starch added and a titration attempted with tenth normal iodine. The color appeared immediately. There could be no reduction. Great trouble was experienced in keeping the antimony in solution upon adding the sodium bi-carbonate.

The next method tried was by adding potassium iodide to the hydrochloric acid solution. Thus hydriodic acid was formed, a strong reducing agent. After boiling until the free iodine was removed the solution was made alkaline and titrated with tenth normal iodine. It was found that a considerable reduction took place but all determinations came very low. Whether the reduction was incomplete or whether some iodine from the hydriodic acid remained in the solution it was impossible to tell. Next a ferrous sulphate solution which had been standardized against a potassium permanganate solution was tried. After two or three attempts at titration of the excess of ferrous sulphate solution, it was remembered that tartaric acid also reduced potassium
permanganate, so that we were compelled to give up this method. As a last resort stannous chloride was tried. An excess of stannous chloride was added to the antimony solution and boiled from five to ten minutes. Now in acid solution stannous chloride is oxidized to stannic salt with iodine while the antimonous compound is not affected. So the iodine solution was added to coloration with starch solution, then the solution made alkaline with sodium hydroxide and acid sodium carbonate added and the antimony titrated with iodine solution. The following are some of the results obtained using this method, that is the reduction of the sodium pyro-antimonate with stannous chloride and final titration with iodine solution. For comparison metallic antimony was weighed out and dissolved in hydrochloric acid and tartaric acid using a few drops of nitric acid, then the antimony precipitated and determined as above.

<table>
<thead>
<tr>
<th>Antimony taken (m.g.)</th>
<th>Antimony found (m.g.)</th>
<th>Per cent found</th>
</tr>
</thead>
<tbody>
<tr>
<td>101.3</td>
<td>99.8</td>
<td>98.50</td>
</tr>
<tr>
<td>100.6</td>
<td>98.1</td>
<td>97.51</td>
</tr>
<tr>
<td>104.7</td>
<td>97.86</td>
<td>95.37</td>
</tr>
<tr>
<td>105.2</td>
<td>99.78</td>
<td>95.31</td>
</tr>
<tr>
<td>103.6</td>
<td>88.38</td>
<td>85.32</td>
</tr>
<tr>
<td>102.0</td>
<td>90.24</td>
<td>88.47</td>
</tr>
<tr>
<td>105.2</td>
<td>89.1</td>
<td>84.69</td>
</tr>
<tr>
<td>103.8</td>
<td>101.4</td>
<td>97.68</td>
</tr>
<tr>
<td>104.4</td>
<td>97.26</td>
<td>95.00</td>
</tr>
<tr>
<td>97.1</td>
<td>89.7</td>
<td>90.53</td>
</tr>
<tr>
<td>102.3</td>
<td>96.36</td>
<td>94.19</td>
</tr>
</tbody>
</table>

As can be seen these determinations do not come out
anywhere near satisfactory. Upon making a test for foreign sub-
substances in the metallic antimony, it was found that there was
lead in it. It is quite likely that the lead was not evenly
distributed through the antimony and that this fact accounts for
the wide variations in the results. Tartar emetic was then used
as a source of antimony.


<table>
<thead>
<tr>
<th>Tartar emetic taken</th>
<th>Metallic antimony</th>
<th>Found</th>
<th>Per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>299.6 m.g.</td>
<td>105.4 m.g.</td>
<td>104.4 m.g.</td>
<td>99.11</td>
</tr>
<tr>
<td>299.9 &quot;</td>
<td>105.5 &quot;</td>
<td>106.2 &quot;</td>
<td>100.66</td>
</tr>
</tbody>
</table>

It was desired to obtain a check on these determinations
so a solution was made up and the antimony determined, following
Furman. The method consists in obtaining the sulphides, removing
the sulphur with carbon bisulphide, then separating the
precipitate from the filter paper, oxidizing the filter paper with
nitric acid in a weighed crucible on a water-bath, then adding
the remainder of the precipitate to that in the crucible and
oxidizing that to the oxide with nitric acid and finally weighing
as the oxide. Two determinations were also made using the titra-
tion method by which the above results were obtained. The
following were the results obtained.

Antimony taken. Antimony obtained. Per cent.

<table>
<thead>
<tr>
<th>Antimony taken</th>
<th>Antimony obtained</th>
<th>Per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>105.5 m.g.</td>
<td>109.2 m.g.</td>
<td>97.53</td>
</tr>
<tr>
<td>105.5 &quot;</td>
<td>106.6 &quot;</td>
<td>101.04</td>
</tr>
</tbody>
</table>
Titration Method.

Antimony taken. Antimony obtained. Per cent.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>105.5 m.g.</td>
<td>104.1 m.g.</td>
<td>98.67</td>
</tr>
<tr>
<td>105.5 &quot;</td>
<td>105.0 &quot;</td>
<td>99.52</td>
</tr>
</tbody>
</table>

Thus it seems that the method is more accurate than most other methods used.

As stated before the arsenic is left in solution after the removal of the antimony and it may be determined from this by any of the well known methods.

When dissolving the sulphides in yellow ammonium sulphide it is well to have the latter strongly ammoniacal as then not so much is required to bring the sulphides into solution. The hydrogen peroxide should be added very slowly, as it decomposes so rapidly that upon adding large amounts much is lost. It is best added a drop at a time.

The greatest objection to this method is the use of so much hydrogen peroxide which is rather expensive, but if the above precautions are followed with regard to its use and that of the ammonium sulphide not very much is required. Otherwise the method is fairly accurate, and not difficult to run.
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