...VARIOUS METHODS...
VOLUMETRIC DETERMINATION
OF ANTIMONY

WAYNE V. PARKER
THE UNIVERSITY OF WICHITA

AN INVESTIGATION OF VARIOUS METHODS
FOR THE VOLUMETRIC
DETERMINATION OF ANTIMONY

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
IN CANDIDACY FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF CHEMISTRY

WICHITA, KANSAS
MAY 1932
The writer wishes to express his sincere appreciation and thanks to Dr. L. McKinley, Head of the Department of Chemistry of the University of Wichita, for his excellent advice and encouragement during the progress of this investigation.

Wayne V. Parker
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>II. The Permanganate Method</td>
<td>5</td>
</tr>
<tr>
<td>III. The Potassium Bromate Method</td>
<td>7</td>
</tr>
<tr>
<td>IV. The Iodine Method</td>
<td>9</td>
</tr>
<tr>
<td>V. The Potassium Iodide Method</td>
<td>11</td>
</tr>
<tr>
<td>VI. Tables</td>
<td>14</td>
</tr>
<tr>
<td>VII. Conclusion</td>
<td>18</td>
</tr>
<tr>
<td>Bibliography</td>
<td>19</td>
</tr>
<tr>
<td>Footnotes</td>
<td>20</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION

This investigation was prompted by the fact that a local industrial plant was unable to make satisfactory determinations of the antimony content of the low melting point alloys used in their products. The problem presented is of great practical importance and was thought to be worthy of a careful research.

A search for literature describing methods of analyzing substances for antimony content carried us through all the numbers of "Chemical Abstracts" together with numerous text books which described analytical procedures.

The decision was made to confine the laboratory work to four of the volumetric methods described in the literature which seemed to be the most practical. These are known as the permanganate method, bromate method, iodine method, and potassium iodide method. Briefly, the first three methods mentioned are based on the oxidation of the trivalent antimonous ion to the pentavalent antimononic ion. The fourth method is based on the liberation of iodine from potassium iodide by the pentavalent antimononic ion and a titration of the liberated iodine with standard sodium thiosulfate.

Precautions were taken to eliminate as much error as possible. Since the volumetric apparatus is calibrated
at 20°C. and the room temperature averaged about 25°C., we inclosed the buret with a pyrex glass cylinder filled with water at 20°C. All standard solutions whose volumes were to be measured were brought to a temperature of 20°C.

Sodium oxalate and arsenic trioxide of known purity were used to standardize the potassium permanganate and iodine solutions respectively. The potassium bromate salt being of excellent purity was recrystallized three times and made into a solution of definite strength without the necessity of standardizing against some other substance.

It was thought that the methods could be compared best by using them on antimony samples of known strength. A standard solution of antimony was accordingly made by slowly boiling about 10 grams of C. P. antimony powder with 500 cc. of concentrated hydrochloric acid and 50 cc. of a saturated solution of bromine in hydrochloric acid, adding more hydrochloric acid and bromine solution when necessary. When the antimony was all in solution the bromine was boiled off and the solution cooled and diluted to two liters with distilled water and sufficient concentrated hydrochloric acid to keep the acidity about twenty per cent by volume. This value was found by experiment, the method being to add water until a white
precipitate persisted after shaking the flask then adding acid until it disappeared, thus always keeping the acidity great enough to prevent hydrolysis. It was found that this stock solution was a mixture of the trichloride and the pentachloride consequently samples drawn for an oxidization reaction were reduced by boiling with sodium sulfite and those drawn for the reduction reaction by potassium iodide were oxidized by boiling with potassium chlorate.

Another method of preparing an antimony stock solution suggested itself which reduced the time to less than an hour and was less expensive in materials. This made use of the well known fact that antimony goes into solution rapidly with sulfuric acid. A weighed quantity of antimony powder was digested in concentrated sulfuric acid the amount of acid being in this case approximately 50 cc. for 2.5 grams of antimony. When the antimony was all in solution and liberated sulfur had disappeared the solution was cooled and carefully diluted with sufficient water to prevent any decomposition of the concentrated hydrochloric acid which was then added. The solution was then boiled ten minutes with 40 cc. of concentrated hydrochloric acid, cooled and diluted to 500 cc. by the addition of distilled water and sufficient hydrochloric acid to prevent hydrolysis. By this method no bromine is needed, less acid is used, and much time
is saved. Samples drawn from this stock solution were treated in a manner similar to those from the first described stock solution.

A stock solution of known antimony content was standardized by each of the four methods as will be described.
CHAPTER II

THE PERMANGANATE METHOD

The determination of antimony with potassium permanganate solution depends on the oxidation of the trivalent antimonous ion to the pentavent antimononic ion with a consequent reduction of the permanganate ion to bivalent manganeous ion. When titrating antimony trichloride solution the reaction is:

\[ 5\text{SbCl}_3 + 2\text{KMnO}_4 + 16\text{HCl} \rightarrow 5\text{SbCl}_5 + 2\text{KCl} + 2\text{MnCl}_2 + 8\text{H}_2\text{O} \]

The titration is done in acid solution, the amount of acidity being sufficient to prevent hydrolysis of the sample and sufficient also to allow the reaction to proceed normally. High acidity will destroy the color at the end point and low acidity may give low values for the determination.\(^1\) The end point may be made visible by adding three or four drops of methyl orange to sample and titrating very slowly. At the end point the chlorine liberated will bleach the methyl orange.\(^2\) However, we found this method of estimating antimony to be on the whole quite unsatisfactory as compared with the electrometric method.

The use of the electrometric titration apparatus eliminates the necessity of color end points since the substantial increase in voltage indicates the end of the reaction. Several samples were titrated electrometrically with no suggestion of a color end point.

Several experiments were made to determine the proper conditions for the oxidation of the antimony by the potassium
permanganate.

The stock solution as before mentioned was approximately twenty per cent acid. Fifty cubic centimeter samples were pipetted from the stock solution into separate Erlenmeyer flasks of 500 cc. capacity. To each sample 25 cc. of concentrated hydrochloric acid and one gram of sodium sulfite were added and the solution boiled down to half its former volume. The samples were then cooled somewhat, and 50 cc. of a ten per cent tartaric acid solution added to each and the boiling continued for about five minutes. The samples were cooled under the tap as much as possible and then transferred into a suitable beaker for titration, the flask being washed out with several portions of water from the wash bottle. The titrations were carried on rapidly at first and then more slowly as the end point was approached, the last half cubic centimeter being added a drop at a time then one-half drop at a time, readings being taken after each half drop.

The use of a preventive solution such as is used in the determination of iron by the permanganate method was tried with no beneficial results.
CHAPTER III

THE POTASSIUM BROMATE METHOD

This method makes use of the oxidizing property of potassium bromate and was originated by St. Gyory in 1893. Zintl and Wattenburg titrated antimony electrometrically by this method.

The reaction is:

\[ \text{KBrO}_3 + 3\text{SbCl}_3 + 6\text{HCl} \rightarrow 3\text{SbCl}_5 + \text{KBr} + 3\text{H}_2\text{O} \]

Determinations by this method are not difficult since the reaction, works well under a variation of conditions of acidity. According to various authors the acidity may be as low as 5 per cent or as high as 25 per cent. This research showed that the acidity should be nearer 15 per cent than 5 per cent by volume of concentrated hydrochloric acid to make sure that no hydrolysis occurred.

The procedure which was found to give good results when using samples from the stock solution was to add to each 50 cc. sample, 25 cc. of concentrated hydrochloric acid and approximately one gram of sodium sulfite and boil down to about 40 cc. volume. The sample was then carefully washed into a 250 cc. beaker and if hydrolysis occurred due to adding water, enough concentrated hydrochloric acid was added to eliminate the hydrolysis and make the acidity great enough to prevent its recurring when the additional water of the titrating solution was added. Since the reaction proceeds more rapidly at tem-

-7-
peratures above room temperature, the sample was next heated to 60°C., electrodes adjusted and solution titrated with standard potassium bromate with constant stirring. Within about 5 cc. of the end point three or four drops of methyl orange were added. As the end point was closely approached, the readings of both buret and potentiometer were taken. The last stages of titration were conducted one-half drop at a time. A perceptible fading of the indicator was accompanied by a marked change in the potentiometer reading. In fact the two end points, colorimetric and electrometric are in excellent agreement. Rapid titration is to be avoided since local excesses created, liberate chlorine which tends to bleach the indicator and oxidize the antimony. The reaction between potassium bromate and hydrochloric acid is:

\[ 2 \text{KBrO}_3 + 12 \text{HCl} = 2 \text{KCl} + \text{Br}_2 + 5 \text{Cl}_2 + 6 \text{H}_2\text{O}. \]

The potassium bromate first oxidizes the antimony and then the hydrochloric acid.
CHAPTER IV
THE IODINE METHOD

Free iodine will oxidize trivalent antimony to the pentavalent condition with the reduction of the iodine to hydrogen iodide. This offers a convenient method of determining antimony and was originated by Mohr.

If hydrogen iodide be present in sufficient quantity the reaction will tend to go in the opposite direction, hence sodium bicarbonate is added which buffers the solution keeping it about neutral. This is the proper condition for the oxidation to proceed to completion. In this investigation the antimony samples were reduced in the usual manner followed by the addition of 25 cc. of 20 per cent tartaric acid, a drop of phenolphthalein, and sufficient 20 per cent by weight sodium hydroxide to neutralize the excess acid.

The samples were then made just barely acid with tartaric acid and after adding ten grams of sodium bicarbonate were titrated with standard iodine. Near the end point 1 cc. of starch solution was added and the first permanent tinge of color whether blue or red was taken as the end point. As in the case of the potassium bromate method, the colorimetric end point was found to coincide essentially with the electrometric end point.
The reaction is:

\[ \text{Na}_3\text{SbO}_3 + 2\text{NaHCO}_3 + \text{I}_2 = \text{Na}_3\text{SbO}_4 + 2\text{NaI} + 2\text{CO}_2 + \text{H}_2\text{O}. \]

It is interesting to note that antimony trioxide like arsenic trioxide may be dissolved in sodium hydroxide of 20 per cent strength but must be heated for some time to effect complete solution. Neutralization must then be made with tartaric acid since the addition of hydrochloric acid would immediately precipitate the antimony oxychloride.
CHAPTER V

THE POTASSIUM IODIDE METHOD

The amount of iodine liberated from potassium iodide by pentavalent antimony is theoretically proportional to the amount of antimony present, consequently a sample of antimony in acid solution may be allowed to react with potassium iodide and the liberated iodine titrated with the sodium thiosulfate.

The reactions are:

\[ \text{SbCl}_5 + 2\text{KI} = \text{SbCl}_3 + 2\text{KCl} + \text{I}_2 \]
\[ 2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]

The reaction takes place in strong acid solution. As there are objections to using a very high acid concentration so are there objections to using a very low acid concentration. Scott recommends that the acid concentration shall be such that not more than one-fifth of the volume of the solution shall be hydrochloric acid (sp. gr. 1.16).\textsuperscript{5} Lower acid concentration than this he says, causes hydrolysis whereas higher concentration will result in the liberation of iodine by action of it on potassium iodide. In this investigation we found that the upper limit of acidity as specified by Scott, was not sufficient to prevent the formation of an amber colored compound \text{SbCl}_3.3\text{KI}.5\text{HCl}\textsuperscript{6} which seriously interfered with the titration and evidently caused low results. Only by working with a much higher acid concentration
could we realize a solution lighter in color. At this increased acid concentration, it was noted as predicted that iodine would be liberated by the action of acid only, on potassium iodide. This amount of excess iodine thus liberated, we were able to determine however and apply as a correction. There is also the possibility of a reaction between sodium thiosulfate and the acid which decomposes the thiosulfate liberating sulfur dioxide.

Difficulty was experienced in arriving at a suitable indicator. The use of carbon tetrachloride as recommended in Scott's procedure permitted us to realize no sharp end point, since it was difficult to determine when the last traces of pink color had faded. The ordinary procedure of choosing a few cc. of starch for indicator seemed out of the question since the color at once produced could be discharged only as a result of adding an enormous amount of excess sodium thiosulfate. It appeared as though minute particles of starch became surrounded by a protective film which caused the color to persist even in the presence of excess sodium thiosulfate.

The procedure which was finally adopted is as follows: A 50 cc. sample of the stock solution of antimony was oxidized by boiling with 25 cc. additional concentrated hydrochloric acid and 2 grams of potassium chlorate until all chlorine was expelled and the volume was reduced to
about 40 cc. To 50 cc. of a 10 per cent potassium iodide solution (when this quantity of potassium iodide is used the reaction is said to be practically instantaneous), was added 50 cc. of concentrated hydrochloric acid. This mixture was immediately added to the oxidized antimony solution which was next diluted by washing down the sides of the flask with 50 cc. of distilled water. The end point was found by alternately adding one drop of thiosulfate solution and stroking a slender glass rod wetted with starch solution through the solution being titrated. Previous to the end point the rod would leave a dark streak in the solution but at the end point would leave no color.

Table III

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Iodine Solution</th>
<th>Water (ml)</th>
<th>Total Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>40</td>
<td>42.5</td>
</tr>
<tr>
<td>2</td>
<td>2.6</td>
<td>40</td>
<td>42.6</td>
</tr>
<tr>
<td>3</td>
<td>2.7</td>
<td>40</td>
<td>42.7</td>
</tr>
<tr>
<td>4</td>
<td>2.8</td>
<td>40</td>
<td>42.8</td>
</tr>
<tr>
<td>5</td>
<td>2.9</td>
<td>40</td>
<td>42.9</td>
</tr>
</tbody>
</table>

Each measurement was done as a blank.

Note the small differences between the measurements.
CHAPTER VI

TABLES

Table I
Standardization of Potassium Permanganate Solution against Sodium Oxalate
Weight of Na₂C₂O₄ 99.63% pure 1.2532 g.
Cubic centimeters KMnO₄ vs. one-fifth of this sample.

<table>
<thead>
<tr>
<th>Trial</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.05</td>
<td>37.03</td>
<td>37.03</td>
<td>37.04</td>
</tr>
</tbody>
</table>

Average value Sb titre = 0.006125 g.

Table II
Standard Potassium Bromate Solution
5.5705 grams pure salt diluted to 2 liters
Sb titre = 0.006092 g.

Table III
Standardization of Iodine Solution against Arsenic Trioxide
A. Weight of As₂O₃ 99.65% purity 1.0061 g.
Cubic centimeters iodine solution vs. 1/5 of this sample

<table>
<thead>
<tr>
<th>Trial</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
</table>

Sb titre = 0.006306 g.
B. Ten days later.

Weight of \( \text{As}_2\text{O}_3 \) 99.65% purity 1.0093 g.

Cubic centimeters iodine solution vs. 1/5 of this sample

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Av.</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.20</td>
<td>39.22</td>
<td>39.21</td>
</tr>
</tbody>
</table>

Sb titre = 0.006313 g.

Table IV

Standarization of Sodium Thiosulfate Solution against Standardized Iodine Solution. Sb titre 0.006313

Cubic centimeters \( \text{Na}_2\text{S}_2\text{O}_3 \) solution vs. 50.00 cc. \( \text{I}_2 \) solution.

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
<th>Av.</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.52</td>
<td>48.52</td>
<td>48.52</td>
<td>48.51</td>
<td>48.51</td>
</tr>
</tbody>
</table>

Sb titre = 0.006125 g.

Ten days later strength unchanged.

Table V

Standard Antimony Solution

Solution #1. 2.5038 g. of Mallinckrodt's C. P. antimony dissolved in sulfuric acid and diluted to 500 cc. with hydrochloric acid. 50 cc. sample contains 0.2503 g.

Solution #2. 10.0035 g. of Sb from same container as above dissolved by conc. HCl solution and bromine and diluted to 2000 cc. 50 cc. sample contains 0.2501 g. Sb.
Table VI
Titration of Antimony Solution

1. By potassium permanganate (0.006154 g. Sb titre).
   Cubic centimeters KMnO₄ solution vs. 50 cc. antimony solution #2 containing 0.2501 g. Sb.
   (Electrometric)
   | Trial 1 | Trial 2 | Trial 3 | Trial 4 | Av.   |
   | 41.06   | 41.02   | 41.05   | 41.02   | 41.04 |
   Calculated Sb 100.51%.

2. By potassium bromate (0.006092 g. Sb titre).
   Cubic centimeters KBrO₃ solution vs. 50 cc. antimony solution #1 containing 0.2503 g. Sb.
   (Electrometric)
   | Trial 1 | Trial 2 | Trial 3 | Trial 4 | Av.   |
   | 41.00   | 41.06   | 41.01   | 41.03   | 41.03 |
   Calculated Sb 99.86%.

3. By iodine solution (0.006313 g. Sb titre).
   Cubic centimeters iodine solution vs. 50 cc. antimony solution #2 containing 0.2501 g. Sb.
   | Trial 1 | Trial 2 | Trial 3 | Trial 4 | Av.   |
   Calculated Sb 99.00%.

4. By Na₂S₂O₃ (0.006125 g. Sb titre) KI method.
   Cubic centimeters Na₂S₂O₃ solution vs. 50 cc. antimony solution #2 containing 0.2501 g. Sb. Corrections shown.
Trial 1        Trial 2        Trial 3        Av.
40.98          40.98          41.01

.18            .18            .18

40.80          40.80          40.83          40.81

Calculated Sb 99.95%

Summary of Table VI

Comparison of Per Cents Sb by Various Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>KMnO₄</th>
<th>KBrO₃</th>
<th>I₂</th>
<th>KI (Na₂S₂O₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mallinckrodt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C. P. antimony</td>
<td>100.00%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

accepted purity  100.51%  99.86%  99.00%  99.95%
CHAPTER VII
CONCLUSION

The tables show the best results that could be obtained by the four volumetric methods described. Every precaution within reason was taken to insure the success of each operation and the deviations in results indicate that the methods are not developed to the state of perfection desired. The literature fails to be sufficiently detailed in its instructions to be of much value in overcoming many of the difficulties encountered.

When accuracy, cost of materials, ease of manipulation, and value of time are considered, the potassium bromate method for the determination of antimony is recommended as having the greatest possibilities.

Although excellent results were obtained by the potassium iodide method it is not as heartily recommended as the bromate method, because the proper conditions for its success are more difficult to realize.
BOOKS:


ARTICLES:

FOOTNOTES

1 Wilson H. Low, "Determination of Antimony in Tin and Babbitt, Type Metal or Other Alloys." Journal of the American Chemical Society, XXIX, (January, 1907), 66-74.


