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## DEPARTMENT OF MINES AND TECHNICAL SURVEYS

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# AN INVESTIGATION OF THE CHEMICAL BEHAVIOUR OF ANTIMONY IN ACIDIC SOLUTIONS

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### AN INVESTIGATION OF THE CHEMICAL BEHAVIOUR OF ANTIMONY IN ACIDIC SOLUTIONS

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K.R. Wilson\* and C.H. McMaster\*\*

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#### SUMMARY OF RESULTS

The behaviour of antimony, in solutions of sulphuric, nitric, and hydrochloric acids, has been studied using procedures frequently encountered in the analytical chemistry laboratory.

The unreactive species that exists in sulphuric acid solutions is believed to be a hydrolyzed form of antimony (V). This species is not extracted with isopropyl ether, but can be converted to the extractable form by the addition of hydrochloric acid.

Antimony (III) can be lost by volatilization from hot hydrochloric acid solutions. The addition of nitric acid to the chloride solution reduces the loss due to volatilization, probably by oxidation of antimony to the less volatile pentavalent state.

Wet ashing procedures, using sulphuric and nitric acids, produce mixtures of antimony (III) and antimony (V).

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#### INTRODUCTION

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In aqueous solution the two stable oxidation states of antimony are: antimony (III), and antimony (V). Many of the common analytical procedures used for the determination of small amounts of antimony in various materials depend on the complete conversion of the element to one of these two states. The trivalent state can be obtained simply by dissolving the metal in hot sulphuric acid (1) or by reducing an aqueous solution of antimony with sulphite solution (2). Oxidation to the pentavalent state, however, is a rather difficult task, and only powerful oxidants such as cerium (IV) under certain conditions give complete conversion (3).

A major difficulty in obtaining antimony (V) is the formation of an "unreactive species" during treatment of a sample with various acids. This peculiar species of antimony, first observed by Maren (4), appears to be associated with neither the trivalent nor the pentavalent state. Maren found that this species is converted quantitatively to antimony (III) when treated with sulphite, yet resisted oxidation to antimony (V), even with cerium (IV). It was also noticed that the species formed in varying amounts following the digestion of biological tissue with sulphuric and nitric acids. A typical analysis of a digested sample yielded 20% antimony (V), 40% antimony (III), and 40% "unreactive species". The formation of the unreactive fraction was undesirable, since Maren had hoped to achieve quantitative oxidation to antimony (V), which was necessary for complete extraction into isopropyl ether and formation of an analytically important metal-dye complex with Rhodamine B. To this end he found that perchloric acid added to the digestive mixture prevented the unreactive species and effected complete oxidation to the pentavalent state.

The appearance and peculiar nature of the unreactive species remains of interest. It is noteworthy that Maren had temporarily labelled his unreactive portion, "antimony (IV)", such as found in the tetroxide,  $Sb_2O_4$ . Little evidence has been found in support of the existence of a stable tetravalent state in aqueous solution, although Maren's term "antimony (IV)" has been echoed by Ward and Lakin (5) in 1954, and by Lowe, et al. (6) as late as 1961. However, Kronopik and Zwiauer (7) concluded that  $Sb_2O_4$  in solution is actually antimonyl antimonate,  $Sb(SbO_4)$ , and not a form of antimony (IV).

The purpose of this report is to examine the behaviour of antimony under conditions commonly used in laboratory analyses, such as the dissolution of samples in combinations of sulphuric, nitric, and hydrochloric acids. The amount of trivalent and pentavalent antimony produced in various treatments in acidic media was determined using conventional procedures (8,9).

#### APPARATUS AND REAGENTS

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#### Polarograph:

Polarographic Cell:

Isopropyl Ether:

Sulphite Solution:

Leeds and Northrup Electrochemograph, Type E.

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A single compartment cell with a mercury pool anode and a dropping mercury cathode was used. The temperature of the cell was maintained at  $30 \pm 0.5$  °C.

C P grade. This reagent was stored over acidified ferrous sulphate solution.

Freshly prepared by saturating distilled water with sulphur dioxide.

Antimony (III) Stock Solution: Weigh 200 mg of antimony metal and dissolve in 25 ml of hot, concentrated sulphuric acid. Dilute the solution to exactly 100 ml with water, remove a 50-ml aliquot and dilute with 9N sulphuric acid to exactly 500 ml. One ml of this stock solution contains 0.2 mg of antimony.

#### EXPERIMENTAL

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Experiments were designed to determine the extent of oxidation of antimony in sulphuric, nitric, and hydrochloric acids, and any loss due to conversion to an unreactive species or by volatilization. Known amounts of antimony metal or aliquots of the stock solution were treated with various combinations of the above-mentioned acids, and the resulting solutions were analysed for antimony (III), antimony (V), and total antimony.

#### Acid Treatments:

- 1. Dissolve 100 mg of antimony metal in 2 ml nitric acid and 5 ml hydrochloric acid with slight heating on a steam bath. Cool and dilute to exactly 100 ml with hydrochloric acid. Remove three 2-ml aliquots and analyse for antimony (III), antimony (V), and total antimony.
- 2. Dissolve 100 mg of antimony metal in 2 ml nitric acid and 5 ml hydrochloric acid. Add 5 ml sulphuric acid and heat on the steam bath for 1-2 hours to expel the nitric and hydrochloric acids. While the solution is still clear, dilute to exactly 100 ml with hydrochloric acid. Remove three 2-ml aliquots and analyse for antimony (III), antimony (V), and total antimony.
- 3. Dissolve 100 mg of antimony metal and expel the nitric and hydrochloric acids as in Treatment 2. Add 20 ml sulphuric acid and dilute to exactly 100 ml with water. This solution is 9 N in sulphuric acid. Remove three 2-ml aliquots and analyse for antimony (III), antimony (V), and total antimony.
- 4. Dissolve 100 mg of antimony metal in 2 ml nitric acid and 5 ml hydrochloric acid. Add 5 ml 18 N sulphuric acid and heat rapidly to fumes on a hot plate. Do not fume to dryness, but cool and dissolve the precipitate in hydrochloric acid, and dilute to exactly 100 ml with the same acid. Remove three 2-ml aliquots and analyse for antimony (III), antimony (V), and total antimony.
- 5. To each of two beakers add 10 ml of antimony stock solution, 2 ml nitric acid, and 5 ml hydrochloric acid. Expel the nitric and hydrochloric acids by heating on a steam bath. Analyse one of the samples for antimony (V), by rinsing it into an extraction mixture (consisting of 10 ml 6 N hydrochloric acid and 35 ml isopropyl ether) with 15 ml 6 N hydrochloric acid. Analyse the other sample for antimony (III).
- 6. To each of two beakers add 10 ml of stock solution, 2 ml nitric acid, 5 ml hydrochloric acid, and heat on the steam bath to expel the nitric and hydrochloric acids. Remove the beakers from the steam bath, place on a hot plate, and evaporate to dryness. Analyse one of the samples for antimony (V) by dissolving the residue in 12.5 ml hydrochloric acid and transferring it to an extraction mixture consisting of 12.5 ml water and 35 ml ether. Analyse the other sample for antimony (III).

7. To 10 ml of stock solution add 2 ml nitric acid and 5 ml hydrochloric acid. Cover and heat rapidly to fumes on a hot plate. Cool slightly, add another 2 ml nitric acid and 5 ml hydrochloric acid, and evaporate to dryness. Analyse for total antimony by reducing the entire sample with sulphite solution.

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- 8. To 10 ml of stock solution add 2 ml nitric acid and 5 ml hydrochloric acid. Cover, heat rapidly to fumes, and make a second addition of nitric and hydrochloric acids. Fume again and add 50 drops of hydrochloric acid without cooling. Continue heating to expel the hydrochloric acid, then add another 50 drops to the fuming solution. Repeat until five such additions have been made. Fume to dryness and analyse for total antimony.
- 9. To 10 ml of stock solution add 5 ml hydrochloric acid, cover the beaker and evaporate the solution to fumes. Add 50 drops of hydrochloric acid while fuming. Make a total of five additions of hydrochloric acid as in Treatment 8. Evaporate to dryness and analyse for total antimony.
- 10. To 10 ml of stock solution add 5 ml hydrochloric acid. Cover the beaker and heat on a steam bath for about three hours to expel the hydrochloric acid. Analyse for total antimony.
- 11. To each of three beakers add 10 ml of stock solution, a 12.5-cm circle of filter paper, and 15 ml nitric acid. Cover the beaker and heat strongly. If the sample chars add more nitric acid, and continue the additions of nitric acid until a clear solution is obtained. Evaporate to dryness and analyse one sample for antimony (III). Analyse a second sample for antimony (V) as in Treatment 6, and determine total antimony on the third sample.

#### Determination of Antimony:

1. Antimony (III)

If the sample is in solution form evaporate to dryness, using a steam bath for all samples containing hydrochloric acid. Dissolve the residue in 11.1 ml 18N sulphuric acid. Transfer to a 50-ml volumetric flask containing 0.5 ml triton X-100 as a maximum suppressor, and dilute to volume with water. Deaerate by bubbling nitrogen gas through the solution, and record the polarogram. The amount of antimony is obtained by comparing the height of the polarographic reduction step with a calibration curve constructed under identical conditions.

#### 2. Antimony (V)

In Treatments 1-4, add the 2-ml aliquot to a 125-ml separatory funnel containing 25 ml 6 N hydrochloric acid and 35 ml isopropyl ether. In Treatments 5, 6, and 11, follow the procedure described for each individual case.

Shake the solution in the separatory funnel for one minute. Discard the aqueous layer and transfer the ether layer to a beaker with an additional 5 ml ether. Allow the ether to evaporate using little or no heat. Dissolve the residue in 2 ml sulphuric acid and 5 ml nitric acid. Cover the beaker and heat strongly to fumes. Add another 5 ml nitric acid and evaporate to dryness. Dissolve the residue in 6 ml 18 N sulphuric acid. Add 12 ml water, 15 ml sulphite solution, and evaporate the solution to dryness.

Dissolve the residue in 11.1 ml 18 N sulphuric acid and prepare the solution for polarographic analysis as described under Antimony (III).

#### 3. Total Antimony

Evaporate the solution to dryness as described for Antimony (III). Dissolve the residue in 6 ml 18 N sulphuric acid. Add 12 ml water, 15 ml sulphite solution, and evaporate to dryness.

Dissolve the residue in 11.1 ml 18N sulphuric acid and prepare the solution for polarographic analysis as described under Antimony (III).

#### RESULTS

Table 1 shows the amounts of antimony recovered after the various acid treatments. Antimony (III) recoveries as high as 3-4% are shown as nil, because a blank determination on the supporting electrolyte gave a value equivalent to 2% antimony. Recoveries are shown to the nearest 5%.

The amounts of antimony (III) and antimony (V) recovered after the wet ash treatment were not reproducible. The antimony (III) recoveries ranged from nil to 20%, and the antimony (V) recoveries from 25-95%. The values shown in Table 1 are averages.

# TABLE 1

# Recovery of Antimony After Acid Treatment

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| Treat-<br>ment<br>No. | Antimony (III) Antimony (V) Total Antimony<br>Summary of Treatment Recovered Recovered Recovered<br>% % |
|-----------------------|---|
| 1                     | Dissolve Sb metal in HNO <sub>3</sub> - 5 95 100<br>HCl, dilute with HCl.                               |
| 2                     | Dissolve Sb metal in HNO <sub>3</sub> - nil 100 100<br>HCl, convert to sulphate,<br>dilute with HCl.    |
| 3                     | Dissolve Sb metal in $HNO_3$ - nil 65<br>HCl, convert to sulphate,<br>dilute with $H_2SO_4$ .           |
| 4                     | Dissolve Sb metal in $HNO_3$ - nil 45 100<br>HCl, fume with $H_2SO_4$ ,<br>dissolve ppt in $H_2SO_4$ .  |
| 5                     | Treat Sb(III) solution with nil 40 100<br>HNO <sub>3</sub> -HCl, evaporate to<br>fumes.                 |
| 6                     | Treat Sb(III) solution with nil $50 - 100$<br>HNO <sub>3</sub> -HCl <sub>2</sub> evaporate to dryness.  |
| 7                     | Evaporate Sb(III) solution - $100$<br>with $H_2SO_4$ -HNO <sub>3</sub> -HCl to<br>fumes.                |
| 8                     | Evaporate Sb(V) solution $-$ 45<br>with $H_2SO_4$ -HCl to fumes.  |
| 9                     | Evaporate Sb(III) solution - $-5$<br>with $H_2SO_4$ -HCl to fumes.                                      |
| 10                    | Evaporate Sb(III) solution 90<br>with $H_2SO_4$ -HCl on steam<br>bath.                                  |
| . 11                  | Wet ash treatment with $10$ $60$ $100$ $H_2SO_4$ -HNO <sub>3</sub> .                                    |

#### DISCUSSION

Table 1 shows that, following all treatments except those involving sulphuric-hydrochloric acid mixtures, all of the antimony can be successfully recovered by reduction to the trivalent state with sulphite ion. Thus, during the course of such treatments, the antimony may change in form or in oxidation state, but none is lost by volatilization, even at fuming sulphuric acid temperatures.

In some treatments there appears to be an "unreactive" fraction which escapes analysis as either antimony (III) or antimony (V). This unreactive species is evident not only in the wet ash treatment, as Maren witnessed, but also in treatments which yield a sulphuric acid solution of antimony, and in treatments in which the antimony at some stage is allowed to precipitate from sulphuric acid solution. There is no unreactive fraction in solutions of antimony which are diluted directly with concentrated hydrochloric acid.

The fact that this unreactive species is reduced easily and, according to Maren, not oxidized at all, introduces the possibility that the species is already in the pentavalent state, but in a form which cannot be determined by the antimony (V) analysis employed.

This explanation is substantiated by Bonner and Goishi (10), who investigated the effects of the hydrolysis of antimony (V) in hydrochloric acid on its extractability into isopropyl ether. They found that excellent extraction is exhibited by the unhydrolysed form of antimony (V), which occurs quantitatively in concentrated hydrochloric acid. If this species is suddenly injected into 6 N hydrochloric acid, it converts slowly and almost completely to a hydrolysed form, which extracts poorly when shaken with isopropyl ether. However, if the ether is present when the unhydrolysed form is added, extraction takes place before any hydrolysis occurs (11). This explains why no unreactive species is observed in Treatments 1 and 2, where the oxidized antimony is stored in concentrated hydrochloric acid.

However, if an aliquot containing antimony (V) dissolved in sulphuric acid is added to the same extraction mixture of 6 N hydrochloric acid and isopropyl ether, the highly extracting unhydrolysed species cannot form, since this occurs only at higher hydrochloric acid concentrations. Instead, the antimony (V) converts at best to the poorly extracting hydrolysed form. This could well have occurred when the antimony (V) in Treatments 3 and 5 was determined. From this discussion it might appear that the unreactive species in sulphuric acid can be converted to the desired unhydrolysed form by evaporating the solution and dissolving the precipitate in concentrated hydrochloric acid. However, the low results obtained by Treatments 4, 6, and 11, in which precipitates formed, are evidence that the extractable form cannot be attained by this procedure.

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Incomplete recoveries of antimony are obtained after treatment with sulphuric and hydrochloric acids. Under these conditions losses can be attributed to volatilization of antimony chloride. At fuming sulphuric acid temperature only 5% antimony (III) remained after several additions of hydrochloric acid. The presence of nitric acid appears to reduce the tendency of the chloride to volatilize. This is probably due to the formation of antimony (V) which is less volatile than antimony (III) (12).

After wet ashing with sulphuric and nitric acids, variable amounts of antimony (III) and antimony (V) are produced. Similar results were obtained by Maren.

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