Particulate Antimony

Measurements Research Branch
Analytical Method

Analyte:	Particulate Antimony and compounds (as Sb)	Method No.:	P&CAM 261
Matrix:	Air	Range:	0.05 to 1.0 mg/m^3 for a 50-liter sample
Procedure:	Membrane Filter Collection, acid ash, graphite furnace AAS analysis		
Date Issued:	03/25/77	Precision:	3.8% (Analytical)
Date Revised:		Classification:	E (Proposed)

1. Synopsis

Particulate matter collected from air on membrane filters is wet ashed in a mixture of nitric, perchloric and sulfuric acids and the residue is diluted with distilled water. Aliquots are introduced into the graphite furnace and the absorbance measured at 217.6 nm.

2. Working Range, Sensitivity and Detection Limit

2.1 The analytical range is 0.05 to 1.0 mg Sb/m^3 (0.01 to 0.1 mg Sb/m^3 using a purge gas interrupt mode) for a 50 liter air sample (diluted to 50 ml following ashing and using a 25 µl aliquot for analysis). The range may be extended by using a smaller aliquot (10-20 µl) of sample in the furnace, and/or by diluting the digested sample to a volume other than 50 ml.

2.2 Sensitivity varies with different instruments and graphite tubes and may vary with different sample matrices. In this laboratory, sensitivity was determined to be 0.005 µg Sb/ml/1%A (125 pg 1%A) for a 25 µl aliquot.

2.3 The absolute detection limit of this method is 97 pg (25 µl of a 0.004 µg Sb/ml solution).

3. Interferences

3.1 Flameless atomic absorption is more prone to matrix effects than are flame methods. As a consequence, it is desirable to check for interferences by the method of standard addition.

3.2 For the determination of antimony in the presence of lead, the 231.2 nm resonance line should be used (lead may cause a spectral interference at 217.6 nm).

4. Precision and Accuracy

4.1 The pooled coefficient of variation for the analysis of five calibration solutions (10 determinations each) covering the range (0.05-1.0 µg/ml) was 0.038.

4.2 The recoveries of antimony from filters spiked with 5.0, 12.5 and 25.0 µg Sb/filter were 100 ± 3.9%, 99.3 ± 2.9% and 98.7 ± 3.2% respectively. The pooled coefficient of variation was 0.034.

5. Advantages and Disadvantages

5.1 A major advantage of the graphite furnace method is that it is approximately 100 times more sensitive than conventional flame atomic absorption, thereby allowing analysis of samples with lower concentrations of antimony. The graphite furnace method requires fewer sample handling steps and exhibits a lower coefficient of variation than hydride generation techniques.

5.2 A disadvantage is that matrix effects are more prevalent than in flame atomic absorption. Also, volatile antimony compounds, including stibine, are not collected by the sampling method.

6. Apparatus

6.1 Sampling Equipment

6.1.1 Cellulose ester membrane filters, 0.8-µm, 37-mm diameter, Millipore type AA, or equivalent.

6.1.2 Filter holder for 37-mm filter, Millipore MAWP 037 A0, or equivalent.

6.1.3 Personal sampling pump (1.5 - 2.5 lpm), capable of delivering a flow rate of 1.5 lpm to within ±5%, calibrated with a representative filter unit in the line.

6.1.4 Thermometer, manometer, and stopwatch.

6.2 Atomic Absorption Spectrophotometer

6.2.1 Atomic absorption spectrophotometer with graphite atomizer and deuterium or hydrogen continuum correction.

6.2.2 Hollow cathode or electrodeless discharge lamp for antimony (λ = 217.6 nm).

6.2.3 Argon, high purity, in a cylinder equipped with a two-stage pressure regulator and appropriate hose connections.

6.3 Glassware (borosilicate)

6.3.1 Phillips beakers with watchglass covers, (125 ml).

6.3.2 Volumetric flasks, (50 and 100 ml).

6.3.3 Volumetric pipets, (1, 5, and 10 ml).

6.3.4 Micro-pipettes, (10, 25, 50 and 100 µl).

6.3.5 Small test tubes (10 ml).

6.4 Variable temperature hotplate (capable of reaching 350°C).

6.5 Perchloric acid fume hood.

7. Reagents

Analytical reagent grade or equivalent. Water must be double distilled or deionized.

7.1 Nitric acid, concentrated, redistilled in glass.

7.2 Perchloric acid, 70%.

7.3 Sulfuric acid, 98%.

7.4 Ashing acid, (3:1:1, nitric:perchloric:sulfuric).

7.5 Antimony stock solution, 1000 µg Sb/ml. Prepared commercially or by dissolving 1.0000 g Sb metal granules in hot, concentrated sulfuric acid (30 ml) and diluting to one liter with distilled water.

7.6 Dilute standard "A" (100 µg Sb/ml). Transfer 10.0 ml of the 1000 µg/ml stock standard to a 100 ml volumetric flask, add 5 ml concentrated, H_2SO_4 and dilute to volume. Prepare fresh monthly.

7.7 Dilute standard "B" (10 µg Sb/ml). Transfer 1.0 ml of the 1000 µg/ml stock standard to a 100 ml volumetric flask, add 5 ml concentrated H_2SO_4 and dilute to volume. Prepare fresh monthly.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 All glassware should be cleaned before first use with a detergent solution followed by (in order) rinsing with water, rinsing with distilled water, soaking 30 minutes in concentrated nitric acid, and thorough rinsing with distilled water.

8.1.2 Glassware which has been cleaned once by this method (8.1.1) and subsequently used exclusively for antimony determination may be cleaned by soaking for 30 minutes in dilute (5% w/v) nitric acid and thoroughly rinsing with distilled water.

8.2 Collection and Shipping of Samples

8.2.1 With a filter in place, connect the filter holder to the sampling pump and sample the air at 1.5 lpm for 30 minutes (concentrations of 0.06 - 1.1 mg/m^3 may be determined with this sample volume). For suspected low or high antimony concentrations, adjust the sample volume accordingly. Since it is possible for the filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently and adjusted as needed. Accurately measure and record the date, flowrate, time, and/or volume.

8.2.2 Following sampling, replace the plastic plug on the inlet and outlet openings of the cassette and attach appropriate identification. At least one blank filter should be submitted with each group of samples; this filter is handled in the same way as the sample filters except that no air is drawn through it.

8.2.3 Measure and record the temperature and pressure of the atmosphere being sampled.

8.3 Analysis of Samples

8.3.1 Remove the filter blanks and filter samples from their containers and place in 125 ml Phillips beakers. Add 5 ml of ashing acid, cover with a watchglass, and heat at 140°C on a hotplate for 2 hours. Increase the temperature (to 200°C) and reduce the volume of solution to approximately 2 ml. If necessary to complete the ashing (a nearly colorless residual solution should result), additional small amounts (1 ml) of nitric acid may be added and evaporated before proceeding. Remove the watchglass and raise the temperature to 350°C to produce dense white fumes of sulfur trioxide. Reduce the volume to ~0.5 ml but do not allow the solution to evaporate to dryness. Cool, and add 1 ml H_2SO_4.

8.3.2 Transfer the solution quantitatively to a 50 ml volumetric flask and dilute to volume with distilled water.

8.3.3 Turn on the atomic absorption spectrophotometer, antimony lamp, continuum background correction, and recorder and allow at least 20 minutes for warmup. Follow the manufacturer's recommendations for operating conditions other

than the drying, charring and atomizing times and temperatures which are as follows: dry for 30 seconds at 110°C, char for 20 seconds at 700°C, and atomize for 8 seconds at 2700°C.

8.3.4 Pipet a 25 µl aliquot of the working standard (9.1.1) or sample (8.3.2) solution into the graphite furnace of the atomic absorption spectrophotometer, initiate the operation cycle and record the absorbance. Standard and sample solutions are run in triplicate with at least one standard analyzed for every three sample determinations.

8.4 In order to check for interferences a minimum of 2 samples and one blank from each set are analyzed by the method of standard additions and the results compared with those obtained in Section 10.1.

8.4.1 Three, 5 ml aliquots of the sample (or blank) solution are placed in small test tubes marked "I," "II" and "III." To tube "I" add an aliquot of antimony standard solution (A or B) sufficient to provide an amount of antimony equal to that estimated to be present in 5 ml of sample solution. Then add a volume of distilled water equal to volume of antimony solution just added. (For example, to 5 ml of sample containing about 0.2 µg/ml of antimony, add 10 µl of solution A and 10 µl of distilled water). To tube "II" add twice as much antimony standard solution as was added to tube "I." To tube "III" add a volume of water equal to the volume of antimony standard solution that was added to tube "II." Mix the solutions thoroughly.

8.4.2. Analyze at least three aliquots of each solution as described in Section 8.3.4.

9. Calibration and Standardization

9.1 Calibration Curve

9.1.1 Prepare working standard solutions for the analytical range of the method (~0.05 - 1.0 µg Sb/ml) by diluting 0.05 - 1.0 ml aliquots of standard solution A to 100 ml with distilled water plus 3 ml concentrated H_2SO_4. A minimum of 5 working standard solutions should be used in preparing the calibration curve. (Prepare fresh daily).

9.1.2 Absorbances, if any, recorded for an acid blank (3 ml H_2SO_4 diluted to 100 ml with distilled water) are subtracted from the absorbances recorded for the working standard solutions. A calibration curve is prepared by plotting absorbances vs. concentration (µg Sb/ml).

10. Calculations

10.1 Calibration Curve

From the peak absorbance of the samples, subtract the absorbance of the filter blank to determine the corrected sample absorbances. Compare the corrected sample absorbance with the calibration curve (9.1.2) to determine the amount of antimony, in µg/ml, in the sample solution. Convert to mg Sb/m^3 as described in Sections 10.3 and 10.4.

10.2 Method of Standard Additions

Plot the absorbance values for the sample solutions and the spiked sample solutions against an abscissa labeled "µg of Sb added/5ml." The abscissa to be plotted are the amounts (in µg/5ml) of antimony added to tubes "I," "II," and "III" (0.0 µg for tube "III"). Draw the best straight line through the three points. The intercept of this line on the negative abscissa (0.0 absorbance units) is read as the concentration in µg/5 ml of antimony in the sample solution (5 ml of sample solution was analyzed). The concentration is converted from µg/5 ml to µg/ml (e.g., x µg/5 ml = $(\frac{x}{5})$ µg/ml). Subtract the concentration, if any, in µg/ml for the blank from the samples. Convert to mg Sb/m^3 as described in Sections 10.3 and 10.4. If the result of this determination does not agree to within 10% of the values obtained with the procedures described in Section 10.1 an interference is indicated and standard additions techniques should be utilized for sample analysis.

10.3 For personal sampling pumps with rotameters only, the following correction for air volume sampled should be made:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sample flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.4 The concentration of antimony in air is calculated as follows:

$$C = \mu g\ Sb/ml \times \frac{V}{V_s}$$

where:

C = concentration of antimony (mg Sb/m^3)

$\mu g\ Sb/ml$ = concentration of antimony as determined in Section 10.1 or 10.2

V = volume of digested (8.3.2) solution (in ml)

V_s = volume of air sampled in liters

11. References

11.1 "Analytical Methods for Atomic Absorption Spectrophotometry," Perkin Elmer Corp., Norwalk, Conn. 1976.

11.2 "Analytical Methods for Atomic Absorption Spectrophotometry Using the Graphite Furnace," Perkin Elmer Corp., Norwalk, Conn. 1975.

11.3 NIOSH Technical Report, "Evaluation of Atomic Absorption Spectrophotometry Methods for Antimony," by R.D. Hull, May 1977.