

METHOD 7062

ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7062 is an atomic absorption procedure for determining 1 µg/L to 400 µg/L concentrations of antimony and arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7062 is approved for sample matrices that contain up to a total of 4000 mg/L concentrations of cobalt, copper, iron, mercury, or nickel. A solid sample can contain up to 40% by weight of the interferences before exceeding 4000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are used to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near dryness at the end of the digestion followed by degassing the samples upon addition of urea. L-cysteine is then added as a masking agent. Next, the antimony and arsenic in the digest are reduced to the trivalent forms with potassium iodide. The trivalent antimony and arsenic are then converted to volatile hydrides using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydrides are swept into, and decompose in, a heated quartz cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic or antimony concentration.

2.3 The typical detection limit for this method is 1.0 µg/L.

3.0 INTERFERENCES

3.1 Very high (>4000 mg/L) concentrations of cobalt, copper, iron, mercury, and nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near dryness followed by reaction with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

3.3 Even after acid digestion, organic compounds will remain in the sample. These flame gases and these organic compounds can absorb at the analytical wavelengths and background correction must be used.

4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min; and potassium iodide flow = 0.5 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of a fluorocarbon (PFA or TFM) and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater, if appropriate: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting and separating liquid and gaseous products (P.T. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier

gas with the hydrides is dried by passing the gasses through a small (< 25 mL) volume condensor coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter/Regulator: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17 cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with an appropriate recording device.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Antimony and arsenic hollow cathode lamps or antimony and arsenic electrodeless discharge lamps and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

5.0 REAGENTS

5.1 Reagent water: Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid (HNO₃): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide (H₂O₂): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

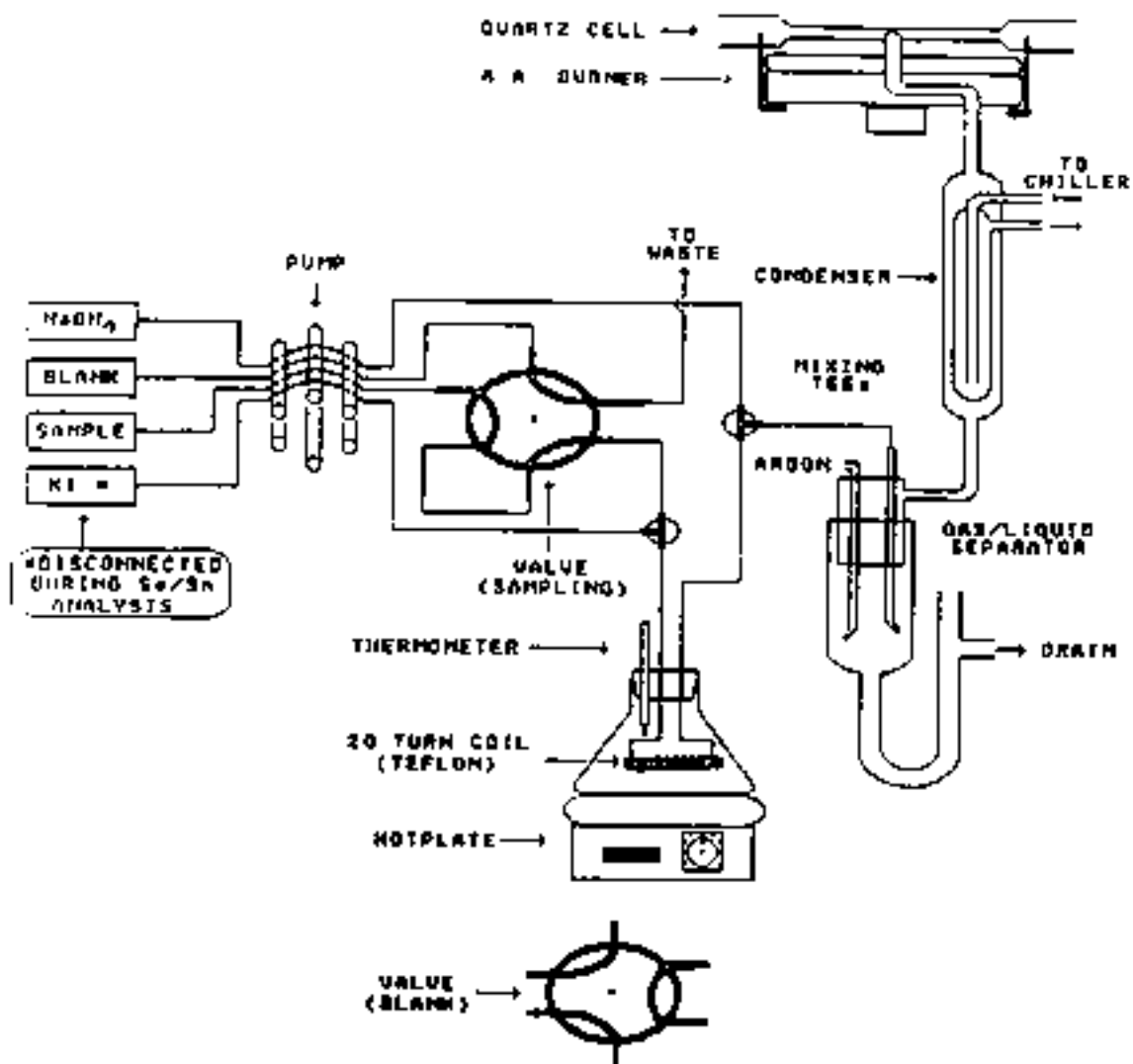


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus set-up and an AAS sample introduction system.

5.6 Urea (H_2NCONH_2): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

5.7 L-cysteine ($\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$): A 1.00-g portion of reagent grade L-cystine must be added to a 25-mL aliquot of each sample for masking the effects of suppressing transition metals (see Section 7.2).

5.8 20% Potassium iodide (KI): A 20% KI solution (20 g reagent-grade KI dissolved and brought to volume in 100 mL reagent water) must be prepared for reduction of antimony and arsenic to their +3 valence states.

5.9 4% Sodium borohydride (NaBH_4): A 4% sodium borohydride solution (20 g reagent-grade NaBH_4 plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the antimony and arsenic to their hydrides.

5.10 Analyte solutions:

5.10.1 **Antimony and arsenic stock standard solution (1,000 mg/L):** Either procure certified aqueous standards from a supplier and verify by comparison with a second standard, or dissolve 1.197 g of antimony trioxide Sb_2O_3 and 1.320 g of arsenic trioxide As_2O_3 in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.10.2 **Intermediate antimony and arsenic solution:** Pipet 1 mL stock antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3 /liter (1 mL = 10 μg each of Sb and As).

5.10.3 **Standard antimony and arsenic solution:** Pipet 10 mL intermediate antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3 /liter (1 mL = 1 μg each of Sb and As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile antimony and arsenic compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in antimony recovery; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if analytes are known to exceed 400 µg/L or if interferences are expected to exceed 4000 mg/L in the digestate.

Note: For solid digestions, the volume reduction stage is critical to obtain accurate data, especially for arsenic. Close monitoring of each sample is necessary when this critical stage is reached.

7.2 Prepare samples for hydride analysis by adding 5.00 g urea, 1.00 g L-cysteine, and 20 mL concentrated HCl to a 25-mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath until the L-cysteine has dissolved and effervescence has subsided (At least 30 minutes is suggested. If effervescence is still seen, repeat step 7.1 with more volume reduction.). Bring flask to volume with reagent water before analyzing. A 1:1 dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard antimony and arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 µg Sb and As/liter.

7.4 If EP extracts (Method 1310) are being analyzed for arsenic, the method of standard additions must be used. Spike appropriate amounts of intermediate or standard antimony and arsenic solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, the borohydride flow around 2.1 mL/min, and the potassium iodide flow around 0.5 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA, use the 217.6-nm wavelength and 0.7-nm slit width (or manufacturer's recommended slit-width) without background correction if analyzing for antimony. Use the 193.7-nm wavelength and 0.7-nm slit width (or manufacturer's recommended slit-width) with background correction for the analysis of arsenic. Begin all flows and allow 10 minutes for warm-up.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder or output meter. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. If a heating coil is not being used, KI must be added to the samples and heated for thirty minutes to ensure reduction.

CAUTION: The hydrides of antimony and arsenic are very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

8.0 QUALITY CONTROL

8.1 See section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The relative standard deviations obtained by a single laboratory for 7 replicates of a contaminated soil were 18% for antimony at 9.1 ug/L in solution and 4.6% for arsenic at 68 ug/L in solution. The average percent recovery of the analysis of an 8 µg/L spike on ten different samples is 103.7% for arsenic and 95.6% for antimony.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.
2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.

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