METHOD 7061

ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 Scope and Application

1.1 Method 7061 is an atomic absorption procedure for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and groundwater. Method 7061 is approved only for sample matrices that do not contain high concentrations of chromium, copper, mercury, nickel, silver, cobalt, and molybdenum. All samples must be subjected to an appropriate solution step prior to analysis. Spiked samples and relevant standard reference reference materials are employed 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/sulfuric acid digestion procedure described in this method. Next, the arsenic in the digestate is reduced to the trivalent form using tin chloride. The trivalent arsenic is then converted to a volatile hydride using hydrogen produced from a zinc/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the hollow cathode radiation is proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 0.002 mg/l.

3.0 Interferences

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample workup can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of SO_3 are observed.

3.3 Elemental arsenic and many of its compounds are volatile and therefore certain samples may be subject to losses of arsenic during sample preparation.

4.0 Apparatus and Materials

4.1 100-ml beaker.

4.2 Electric hot plate.

4.3 A commercially available zinc slurry/hydride generator or a generator constructed from the following materials (see Figure 1).

4.3.1 Medicine dropper that can be fitted into a size "0" rubber stopper and that is capable of delivering 1.5 ml.

4.3.2 50-ml pear-shaped reaction flask with two 14/20 necks (Scientific Glass JM-5835).

4.3.3 Gas inlet-outlet tube constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground glass joint.

4.3.4 Magnetic stirrer to homogenize the zinc slurry.

4.3.5 10-cm polyethylene drying tube filled with glass to prevent particulate matter from entering the burner.

4.3.6 Flow meter capable of measuring 1 liter/minute.

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 a strip chart recorder.

4.5 Burner recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Arsenic hollow cathode lamp or arsenic electrodeless discharge lamp.

4.7 Strip chart recorder.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Concentrated sulfuric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Concentrated hydrochloric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.5 Diluent: Add 100 ml 18 N H_2SO_4 and 400 ml concentrated HCl to 400 ml Type II water and dilute to a final volume of 1 liter with Ty water.

5.6 Potassium iodide solution: Dissolve 20 g KI in 100 ml Typ water.

5.7 Stannous chloride solution: Dissolve 100 g $SnCl_2$ in 100 m HCl.

5.8 Arsenic solutions

5.8.1 Arsenic standard solution (1,000 mg/l): Either prc certified aqueous standard from a supplier (Spex Industries, Alpha Products or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide As_2O_3 (analytical reagent grade) or equivalent in 100 ml of Type II water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter.

5.8.2 Intermediate arsenic solution: Pipet 1 ml stock arsenic solution into a 100-ml volumetric flask and bring to volume with deionized distilled water containing 1.5 ml concentrated HNO_3/liter (1 ml = 10 µg As).

5.8.3 Standard arsenic solution: Pipet 10 ml intermediate arsenic solution into a 100-ml volumetric flask and bring to volume with deionized distilled water containing 1.5 ml concentrated HNO_3/liter (1 ml = 1 µg 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 Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized 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 arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of less than 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 50-g sample (or, in the case of analysis of EP extracts, 50 ml) of the material to be analyzed in a 100-ml beaker. Add 10 ml conc.

HNO_3 and 12 ml 18 N H_2SO_4. Evaporate the sample in the hood on an electric hot plate until white SO_3 fumes are observed (a volume of about 20 ml). Do not let the sample char. If charring occurs, immediately turn off the heat, cool, and add an additional 3 ml of HNO_3. Continue to add additional HNO_3 in order to maintain an excess (as evidenced by the formation of brown fumes). Do not let the solution darken, because arsenic may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete. Cool the sample, add about 25 ml Type II water, and again evaporate until SO_3 fumes are produced in order to expel oxides of nitrogen. Cool. Transfer the digested sample to a 100-ml volumetric flask. Add 40 ml of concentrated HCl and bring to volume with Type II water.

7.2 Prepare working standards from the standard 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 As/liter.

7.3 If EP extracts are being analyzed or if a matrix interference is encountered, take the 15-, 20-, and 25-mg/liter standards and quantitatively transfer 25 ml from each of these standards into separate 50-ml volumetric flasks. Add 10 ml of the prepared sample to each flask. Bring to volume with Type II water containing 1.5 ml HNO_3/liter.

7.4 Add 10 ml of prepared sample to a 50-ml volumetric flask. Bring to volume with Type II water containing 1.5 ml HNO_3/liter. This is the blank.

NOTE: The absorbance from the blank will be one-fifth that produced by the prepared sample. The absorbance from the spiked standards will be one-half that produced by the standards plus the contribution from one-fifth of the prepared sample. Keeping these in mind, the correct dilutions to produce optimum absorbance can be judged.

7.5 Transfer a 25-ml portion of the digested sample or standard to the reaction vessel, and add 1 ml potassium iodide solution. Add 0.5 ml $SnCl_2$ solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 ml zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard solution. The metal hydride will produce a peak almost immediately. After the recorder pen begins to return to the base line, the reaction vessel can be removed. CAUTION: Arsine is very toxic. Precautions must be taken to avoid inhaling arsine gas.

7.6 Use the 193.7-nm wavelength and background correction for the analysis of arsenic.

7.7 Follow the manufacturer's instructions for operating an argon hydrogen flame. The argon-hydrogen flame is colorless, so it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.8 If the method of standard additions was employed, plot the absorbances of spiked samples and blank vs. the concentrations. The extrapolated value will be one-tenth the concentration of the original sample. 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 can be part of the calibration curve.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.