

METHOD 7061A

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 ground water. Method 7061A 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 dissolution step prior to analysis. Spiked samples and relevant standard 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 (Step 7.1). Next, the arsenic in the digestate is reduced to the trivalent form with tin chloride. The trivalent arsenic is then converted to a volatile hydride using hydrogen produced from a zinc/hydrochloric acid 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 lamp 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 work-up can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of sulfur trioxide (SO₃) are observed.

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

4.0 APPARATUS AND MATERIALS

4.1 Beaker or equivalent - 100-mL.

4.2 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

4.3.1 Medicine dropper - Capable of fitting into a size "0" rubber stopper and delivering 1.5 mL.

4.3.2 Pear-shaped reaction flask - 50-mL, with two 14/20 necks (Scientific Glass JM-5835 or equivalent).

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

4.3.6 Flow meter - Capable of measuring 1 liter/min.

4.3.7 Class A volumetric flasks.

4.3.8 Graduated cylinder or equivalent.

4.4 Atomic absorption spectrophotometer - Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier 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 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interferent free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3 . Acid should be analyzed to determine levels of impurities. If a method blank is $< \text{MDL}$, the acid can be used.

5.4 Sulfuric acid (concentrated), H_2SO_4 . Acid should be analyzed to determine levels of impurities. If a method blank is $< MDL$, the acid can be used.

5.5 Hydrochloric acid (concentrated), HCl . Acid should be analyzed to determine levels of impurities. If a method blank is $< MDL$, the acid can be used.

5.6 Diluent - Add 100 mL 18N H_2SO_4 and 400 mL concentrated HCl to 400 mL water and dilute to a final volume of 1 liter with water.

5.7 Potassium iodide solution - Dissolve 20 g KI in 100 mL water.

5.8 Stannous chloride solution - Dissolve 100 g $SnCl_2$ in 100 mL concentrated HCl .

5.9 Arsenic solutions

5.9.1 Arsenic standard solution (1,000 mg/L) - Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide As_2O_3 in 100 mL of water containing 4 g $NaOH$. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.9.2 Intermediate arsenic solution - Pipet 1 mL stock arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO_3 /liter (1 mL = 10 ug As).

5.9.3 Standard arsenic solution - Pipet 10 mL intermediate arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO_3 /liter (1 mL = 1 ug 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 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 < 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-mL aliquot of digested 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 concentrated HNO_3 and 12 mL 18N 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 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 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 ug 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 of each of these standards into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each flask. Bring to volume with water containing 1.5 mL HCl/liter.

7.4 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with water containing 1.5 mL HCl/liter. This is the zero addition aliquot.

NOTE: The absorbance from the zero addition aliquot will be one-fifth that produced by the prepared sample. The absorbance from the spiked samples will be one-half that produced by the standards plus the contribution from one-fifth of the prepared sample. Keeping these absorbances in mind will assist in judging the correct dilutions to produce optimum absorbance.

7.5 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel and add 1 mL KI solution. Add 0.5 mL SnCl_2 solution. Allow at least 10 minutes 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; therefore, 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-fifth 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 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.3 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods For Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.
2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

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