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METHOD 108A—DETERMINATION OF ARSENIC CONTENT IN ORE SAMPLES FROM NONFERROUS SMELTERS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of Method 12.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Arsenic compounds as arsenic (As)	7440-38-2	Lower limit 10 µg/ml or less.

1.2 Applicability. This method applies to the determination of inorganic As content of process ore and reverberatory matte samples from nonferrous smelters and other sources as specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Arsenic bound in ore samples is liberated by acid digestion and analyzed by flame atomic absorption spectrophotometry (AAS).

3.0 Definitions [Reserved]

4.0 Interferences

Analysis for As by flame AAS is sensitive to the chemical composition and to the physical properties (*e.g.*, viscosity, pH) of the sample. The analytical procedure includes a check for matrix effects (section 11.5).

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the

responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures that prevent chemical splashes are recommended. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.3 Hydrogen Peroxide (H₂O₂). Very harmful to eyes. 30% H₂O₂ can burn skin, nose, and lungs.

5.2.4 Nitric Acid (HNO₃). Highly corrosive to eyes, skin, nose, and lungs. Vapors are highly toxic and can cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.5 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

6.0 *Equipment and Supplies*

6.1 Sample Collection and Preparation. The following items are required for sample collection and preparation:

6.1.1 Parr Acid Digestion Bomb. Stainless steel with vapor-tight Teflon cup and cover.

6.1.2 Volumetric Pipets. 2- and 5-ml sizes.

6.1.3 Volumetric Flask. 50-ml polypropylene with screw caps, (one needed per standard).

6.1.4 Funnel. Polyethylene or polypropylene.

6.1.5 Oven. Capable of maintaining a temperature of approximately 105 °C (221 °F).

6.1.6 Analytical Balance. To measure to within 0.1 mg.

6.2 Analysis. The following items are required for analysis:

6.2.1 Spectrophotometer and Recorder. Equipped with an electrodeless discharge lamp and a background corrector to measure absorbance at 193.7 nm. For measuring samples having less than 10 µg As/ml, use a graphite furnace or vapor generator accessory. The recorder shall match the output of the spectrophotometer.

6.2.2 Volumetric Flasks. Class A, 50-ml (one needed per sample and blank), 500-ml, and 1-liter.

6.2.3 Volumetric Pipets. Class A, 1-, 5-, 10-, and 25-ml sizes.

7.0 Reagents and Standards.

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection and Preparation. The following reagents are required for sample collection and preparation:

7.1.1 Water. Deionized distilled to meet ASTM D 1193-77 or 91 Type 3 (incorporated by reference—See §61.18). When high concentrations of organic matter are not expected to be present, the KMnO_4 test for oxidizable organic matter may be omitted. Use in all dilutions requiring water.

7.1.2 Nitric Acid Concentrated.

7.1.3 Nitric Acid, 0.5 N. In a 1-liter volumetric flask containing water, add 32 ml of concentrated HNO_3 and dilute to volume with water.

7.1.4 Hydrofluoric Acid, Concentrated.

7.1.5 Potassium Chloride (KCl) Solution, 10 percent weight by volume (W/V). Dissolve 10 g KCl in water, add 3 ml concentrated HNO_3 , and dilute to 100 ml.

7.1.6 Filter. Teflon filters, 3-micron porosity, 47-mm size. (Available from Millipore Co., type FS, Catalog Number FSLW04700.)

7.1.7 Sodium Borohydride (NaBH_4), 5 Percent (W/V). Dissolve 50.0 g of NaBH_4 in about 500 ml of 0.1 N NaOH in a 1-liter volumetric flask. Then, dilute to exactly 1.0 liter with 0.1 N NaOH.

7.1.8 Nickel Nitrate, 5 Percent Ni (W/V). Dissolve 24.780 g of nickel nitrate hexahydrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] in water in a 100-ml volumetric flask, and dilute to 100 ml with water.

7.1.9 Nickel Nitrate, 1 Percent Ni (W/V). Pipet 20 ml of 5 percent nickel nitrate solution into a 100-ml volumetric flask, and dilute to 100 ml with water.

7.2 Analysis. The following reagents and standards are required for analysis:

7.2.2 Sodium Hydroxide, 0.1 N. Dissolve 2.00 g of NaOH in water in a 500-ml volumetric flask. Dilute to volume with water.

7.2.3 Nitric Acid, 0.5 N. Same as in Section 7.1.3.

7.2.4 Potassium Chloride Solution, 10 percent. Same as in Section 7.1.5.

7.2.5 Hydrochloric Acid, Concentrated.

7.2.6 Potassium Iodide (KI), 30 Percent (W/V). Dissolve 300 g of KI in about 500 ml of water in a 1-liter volumetric flask. Then, dilute to exactly 1.0 liter with water.

7.2.7 Hydrogen Peroxide, 3 Percent by Volume. Pipet 50 ml of 30 percent H₂O₂ into a 500-ml volumetric flask, and dilute to exactly 500 ml with water.

7.2.8 Stock Arsenic Standard, 1 mg As/ml. Dissolve 1.3203 g of primary grade As₂O₃ in 20 ml of 0.1 N NaOH. Slowly add 30 ml of concentrated HNO₃, and heat in an oven at 105 °C (221 °F) for 2 hours. Allow to cool, and dilute to 1 liter with deionized distilled water.

7.2.9 Nitrous Oxide. Suitable quality for AAS analysis.

7.2.10 Acetylene. Suitable quality for AAS analysis.

7.2.11 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA regional Office or from the responsible enforcement authority.

NOTE: The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

8.0 *Sample Collection, Preservation, Transport, and Storage*

8.1 Sample Collection. A sample that is representative of the ore lot to be tested must be taken prior to analysis. (A portion of the samples routinely collected for metals analysis may be used provided the sample is representative of the ore being tested.)

8.2 Sample Preparation. The sample must be ground into a finely pulverized state.

9.0 QUALITY CONTROL

Section	Quality control measure	Effect
10.2	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

11.5	Check for matrix effects	Eliminate matrix effects.
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10.0 Calibration and Standardizations

NOTE: Maintain a laboratory log of all calibrations.

10.1 Preparation of Standard Solutions. Pipet 1, 5, 10, and 25 ml of the stock As solution into separate 100-ml volumetric flasks. Add 10 ml KCl solution and dilute to the mark with 0.5 N HNO₃. This will give standard concentrations of 10, 50, 100, and 250 µg As/ml. For low-level arsenic samples that require the use of a graphite furnace or vapor generator, follow the procedures in Section 11.3:1. Dilute 10 ml of KCl solution to 100 ml with 0.5 N HNO₃ and use as a reagent blank.

10.2 Calibration Curve. Analyze the reagent blank and each standard solution according to the procedures outlined in Section 11.3. Repeat this procedure on each standard solution until two consecutive peaks agree within 3 percent of their average value. Subtract the average peak height (or peak area) of the blank—which must be less than 2 percent of recorder full scale—from the averaged peak heights of each standard solution. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is Hg contamination of a reagent or carry-over of As from a previous sample. Prepare the calibration curve by plotting the corrected peak height of each standard solution versus the corresponding final total As weight in the solution.

10.3 Spectrophotometer Calibration Quality Control. Calculate the least squares slope of the calibration curve. The line must pass through the origin or through a point no further from the origin than ±2 percent of the recorder full scale. Multiply the corrected peak height by the reciprocal of the least squares slope to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations must be less than 7 percent for all standards.

NOTE: For instruments equipped with direct concentration readout devices, preparation of a standard curve will not be necessary. In all cases, follow calibration and operational procedures in the manufacturer's instruction manual.

11.0 Analytical Procedure

11.1 Sample Preparation. Weigh 50 to 500 mg of finely pulverized sample to the nearest 0.1 mg. Transfer the sample into the Teflon cup of the digestion bomb, and add 2 ml each of concentrated HNO₃ and HF. Seal the bomb immediately to prevent the loss of any volatile arsenic compounds that may form. Heat in an oven at 105 °C (221 °F) for 2 hours. Remove the bomb from the oven and allow to cool. Using a Teflon filter, quantitatively filter the digested sample into a 50-ml polypropylene volumetric flask. Rinse the bomb three times with small portions of 0.5 N HNO₃, and filter the rinses into the flask. Add 5 ml of KCl solution to the flask, and dilute to 50 ml with 0.5 N HNO₃.

11.2 Spectrophotometer Preparation.

11.2.1 Turn on the power; set the wavelength, slit width, and lamp current. Adjust the background corrector as instructed by the manufacturer's manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.

11.2.2 Develop a spectrophotometer calibration curve as outlined in Sections 10.2 and 10.3.

11.3 Arsenic Determination. Analyze an appropriately sized aliquot of each diluted sample (from Section 11.1) until two consecutive peak heights agree within 3 percent of their average value. If applicable, follow the procedures outlined in Section 11.3.1. If the sample concentration falls outside the range of the calibration curve, make an appropriate dilution with 0.5 N HNO₃ so that the final concentration falls within the range of the curve. Using the calibration curve, determine the As concentration in each sample.

NOTE: Because instruments vary between manufacturers, no detailed operating instructions will be given here. Instead, the instrument manufacturer's detailed operating instructions should be followed.

11.3.1 Arsenic Determination at Low Concentration. The lower limit of flame AAS is 10 µg As/ml. If the arsenic concentration of any sample is at a lower level, use the vapor generator or graphite furnace which is available as an accessory component. Flame, graphite furnace, or vapor generators may be used for samples whose concentrations are between 10 and 30 µg/ml. Follow the manufacturer's instructions in the use of such equipment.

11.3.1.1 Vapor Generator Procedure. Place a sample containing between 0 and 5 µg of arsenic in the reaction tube, and dilute to 15 ml with water. Since there is some trial and error involved in this procedure, it may be necessary to screen the samples by conventional AAS until an approximate concentration is determined. After determining the approximate concentration, adjust the volume of the sample accordingly. Pipet 15 ml of concentrated HCl into each tube. Add 1 ml of 30 percent KI solution. Place the reaction tube into a 50 °C (120 °F) water bath for 5 minutes. Cool to room temperature. Connect the reaction tube to the vapor generator assembly. When the instrument response has returned to baseline, inject 5.0 ml of 5 percent NaBH₄ and integrate the resulting spectrophotometer signal over a 30-second time period.

11.3.1.2 Graphite Furnace Procedure. Pipet 5 ml of the digested solution into a 10-ml volumetric flask. Add 1 ml of the 1 percent nickel nitrate solution, 0.5 ml of 50 percent HNO₃, and 1 ml of the 3 percent H₂O₂, and dilute to 10 ml with water. The sample is now ready to inject in the furnace for analysis.

11.4 Run a blank and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the origin than ±2 percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected average peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.5 Mandatory Check for Matrix Effects on the Arsenic Results. Same as Method 12, Section 11.5.

12.0 Data Analysis and Calculations

12.1 Calculate the percent arsenic in the ore sample as follows:

$$\% \text{ As} = \frac{5C_a F_d}{W} \quad \text{Eq. 108A-1}$$

Where:

C_a = Concentration of As as read from the standard curve, $\mu\text{g/ml}$.

F_d = Dilution factor (equals to 1 if the sample has not been diluted).

W = Weight of ore sample analyzed, mg.

5 = (50 ml sample " 100)/(10³ $\mu\text{g/mg}$).

13.0 Method Performance

13.1 Sensitivity. The lower limit of flame AAS is 10 $\mu\text{g As/ml}$. The analytical procedure includes provisions for the use of a graphite furnace or vapor generator for samples with a lower arsenic concentration.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures

16.1 Alternative Analyzer. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) may be used as an alternative to atomic absorption analysis provided the following conditions are met:

16.1.1 Sample collection, sample preparation, and analytical preparation procedures are as defined in the method except as necessary for the ICP-AES application.

16.1.2 Quality Assurance/Quality Control procedures, including audit material analysis, are conducted as prescribed in the method. The QA acceptance conditions must be met.

16.1.3 The limit of quantitation for the ICP-AES must be demonstrated and the sample concentrations reported should be no less than two times the limit of quantitation. The limit of quantitation is defined as ten times the standard deviation of the blank value. The standard deviation of the blank value is determined from the analysis of seven blanks. It has been reported that for mercury and those elements that form hydrides, a continuous-flow generator coupled to an ICP-AES offers detection limits comparable to cold vapor atomic absorption.

17.0 References

Same as References 1 through 9 of Section 17.0 of Method 5, with the addition of the following:

1. Perkin Elmer Corporation. Analytical Methods of Atomic Absorption Spectrophotometry. 303-0152. Norwalk, Connecticut. September 1976. pp 5-6.
2. Ringwald, D. Arsenic Determination on Process Materials from ASARCO's Copper Smelter in Tacoma, Washington. Unpublished Report. Prepared for Emission Measurement Branch, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. August 1980. 35 pp.
3. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

18.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]