

METHOD 108C
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 this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Method 108A.

1.0 Scope and Application.

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Arsenic compounds	as arsen ic (As) 7440-38-2	Lower limit 0.0002 percent As by weight

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 the molybdenum blue photometric procedure.

3.0 Definitions. [Reserved]

4.0 Interferences. [Reserved]

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 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.

5.2.4 Perchloric Acid (HClO₄). Corrosive to eyes, skin, nose, and throat. Provide ventilation to limit exposure. Very strong oxidizer. Keep separate from water and oxidizable materials to prevent vigorous evolution of heat, spontaneous combustion, or explosion. Heat solutions containing HClO₄ only in hoods specifically designed for HClO₄.

5.2.5 Sulfuric acid (H₂SO₄). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m³ will cause lung damage in uninitiated. 1 mg/m³ for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies.

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

6.1.1 Analytical Balance. To measure to within 0.1 mg. 6.1.2 Erlenmeyer Flask. 300-ml.

6.1.3 Hot Plate.

6.1.4 Distillation Apparatus. No. 6, in ASTM E 50-82, 86, or 90 (Reapproved 1995)(incorporated by reference - see § 61.18); detailed in Figure 108C-1.

6.1.5 Graduated Cylinder. 50-ml.

6.1.6 Perchloric Acid Fume Hood.

6.2 Analysis. The following items are required for analysis:

6.2.1 Spectrophotometer. Capable of measuring at 660 nm.

6.2.2 Volumetric Flasks. 50- and 100-ml.

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 Preparation. The following reagents are required for sample 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 Hydrofluoric Acid, Concentrated.

7.1.4 Sulfuric Acid, Concentrated.

7.1.5 Perchloric Acid, 70 Percent.

7.1.6 Hydrochloric Acid, Concentrated.

7.1.7 Dilute Hydrochloric Acid. Add one part concentrated HCl to nine parts water.

7.1.8 Hydrazine Sulfate $[(\text{NH}_2)_2\cdot\text{H}_2\text{SO}_4]$.

7.1.9 Potassium Bromide (KBr).

7.1.10 Bromine Water, Saturated.

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

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 Methyl Orange Solution, 1 g/liter.

7.2.3 Ammonium Molybdate Solution, 5 g/liter. Dissolve 0.5 g $(\text{NH}_4)\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in water in a 100-ml volumetric flask, and dilute to the mark. This solution must be freshly prepared.

7.2.4 Standard Arsenic Solution, 10 μg As/ml. Dissolve 0.13203 g of As_2O_3 in 100 ml HCl in a 1-liter volumetric flask. Add 200 ml of water, cool, dilute to the mark with water, and mix. Transfer 100 ml of this solution to a 1-liter volumetric flask, add 40 ml HCl, cool, dilute to the mark, and mix.

7.2.5 Hydrazine Sulfate Solution, 1 g/liter. Dissolve 0.1 g of $[(\text{NH}_2)_2\cdot\text{H}_2\text{SO}_4]$ in water, and dilute to 100 ml in a volumetric flask. This solution must be freshly prepared.

7.2.6 Potassium Bromate (KBrO_3) Solution, 0.03 Percent Weight by Volume (W/V). Dissolve 0.3 g KBrO_3 in water, and dilute to 1 liter with water.

7.2.7 Ammonium Hydroxide (NH_4OH), Concentrated.

7.2.8 Boiling Granules.

7.2.9 Hydrochloric Acid, 50 percent by volume. Dilute equal parts concentrated HCl with water.

7.2.10 Quality Assurance Audit Samples. Same as in Method 108A, Section 7.2.11.

8.0 Sample Collection, Preservation, Transport, and Storage.

Same as in Method 108A, Sections 8.1 and 8.2.

9.0 Quality Control.

Section	Quality Control Measure	Effect
10.2	Calibration curve preparation	Ensure linearity of spectrophotometric analysis of standards
11.3	Audit sample analysis	Evaluate analyst's technique and standards preparation

10.0 Calibration and Standardizations.

NOTE: Maintain a laboratory log of all calibrations.

10.1 Preparation of Standard Solutions. Transfer 1.0, 2.0, 4.0, 8.0, 12.0, 16.0, and 20.0 ml of standard arsenic solution (10 μ g/ml) to each of seven 50-ml volumetric flasks. Dilute to 20 ml with dilute HCl. Add one drop of methyl orange solution and neutralize to the yellow color with dropwise addition of NH_4OH . Just bring back to the red color by dropwise addition of dilute HCl, and add 10 ml in excess. Proceed with the color development as described in Section 11.2.

10.2 Calibration Curve. Plot the spectrophotometric readings of the calibration solutions against μ g As per 50 ml of solution. Use this curve to determine the As concentration of each sample.

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.

11.0 Analytical Procedure.

11.1 Sample Preparation.

11.1.1 Weigh 1.0 g of finely pulverized sample to the nearest 0.1 mg. Transfer the sample to a 300 ml Erlenmeyer flask and add 15 ml of HNO_3 , 4 ml HCl, 2 ml HF, 3 ml HClO_4 , and 15 ml H_2SO_4 , in the order listed. In a HClO_4 fume hood, heat on a hot plate to decompose the sample. Then heat while swirling over an open flame until dense white fumes evolve. Cool, add 15 ml of water, swirl to hydrate the H_2SO_4 completely, and add several boiling granules. Cool to room temperature.

11.1.2 Add 1 g of KBr, 1 g hydrazine sulfate, and 50 ml HCl. Immediately attach the distillation head with thermometer and dip the side arm into a 50-ml graduated cylinder containing 25 ml of water and 2 ml of bromine water. Keep the graduated cylinder immersed in a beaker of cold water during distillation. Distill until the temperature of the vapor in the flask reaches 107 $^\circ\text{C}$ (225 $^\circ\text{F}$). When distillation is complete, remove the flask from the hot plate, and simultaneously wash down the side arm with water as it is removed from the cylinder.

11.1.3 If the expected arsenic content is in the range of 0.0020 to 0.10 percent, dilute the distillate to the 50-ml mark of the cylinder with water, stopper, and mix. Transfer a 5.0-ml aliquot to a 50-ml volumetric

flask. Add 10 ml of water and a boiling granule. Place the flask on a hot plate, and heat gently until the bromine is expelled and the color of methyl orange indicator persists upon the addition of 1 to 2 drops. Cool the flask to room temperature. Neutralize just to the yellow color of the indicator with dropwise additions of NH_4OH . Bring back to the red color by dropwise addition of dilute HCl, and add 10 ml excess. Proceed with the molybdenum blue color development as described in Section 11.2.

11.1.4 If the expected arsenic content is in the range of 0.0002 to 0.0010 percent As, transfer either the entire initial distillate or the measured remaining distillate from Section 11.1.2 to a 250-ml beaker. Wash the cylinder with two successive portions of concentrated HNO_3 , adding each portion to the distillate in the beaker. Add 4 ml of concentrated HClO_4 , a boiling granule, and cover with a flat watch glass placed slightly to one side. Boil gently on a hot plate until the volume is reduced to approximately 10 ml. Add 3 ml of HNO_3 , and continue the evaporation until HClO_4 is refluxing on the beaker cover. Cool briefly, rinse the underside of the watch glass and the inside of the beaker with about 3-5 ml of water, cover, and continue the evaporation to expel all but 2 ml of the HClO_4 .

NOTE: If the solution appears cloudy due to a small amount of antimony distilling over, add 4 ml of 50 percent HCl and 5 ml of water, cover, and warm gently until clear. If cloudiness persists, add 5 ml of HNO_3 and 2 ml H_2SO_4 . Continue the evaporation of volatile acids to solubilize the antimony until dense white fumes of H_2SO_4 appear. Retain at least 1 ml of the H_2SO_4 .

11.1.5 To the 2 ml of HClO_4 solution or 1 ml of H_2SO_4 solution, add 15 ml of water, boil gently for 2 minutes, and then cool. Proceed with the molybdenum blue color development by neutralizing the solution directly in the beaker just to the yellow indicator color by dropwise addition of NH_4OH . Obtain the red color by dropwise addition of dilute HCl. Transfer the solution to a 50-ml volumetric flask. Rinse the beaker successively with 10 ml of dilute HCl, followed by several small portions of water. At this point the volume of solution in the flask should be no more than 40 ml. Continue with the color development as described in Section 11.2.

11.2 Analysis.

11.2.1 Add 1 ml of KBrO_3 solution to the flask and heat on a low-temperature hot plate to about 50 °C (122 °F) to oxidize the arsenic and methyl orange. Add 5.0 ml of ammonium molybdate solution to the warm solution and mix. Add 2.0 ml of hydrazine sulfate solution, dilute until the solution comes within the neck of the flask, and mix. Place the flask in a 400 ml beaker, 80 percent full of boiling water, for 10 minutes. Enough heat must be supplied to prevent the water bath from cooling much below the boiling point upon inserting the volumetric flask. Remove the flask, cool to room temperature, dilute to the mark, and mix.

11.2.2 Transfer a suitable portion of the reference solution to an absorption cell, and adjust the spectrophotometer to the initial setting using a light band centered at 660 nm. While maintaining this spectrophotometer adjustment, take the readings of the calibration solutions followed by the samples.

11.3 Audit Sample Analysis. Same as in Method 108A, Section 11.6.

12.0 Data Analysis and Calculations.

Same as in Method 108A, Section 12.0.

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References.

1. Ringwald, D. Arsenic Determination on Process Materials from ASARCO's Copper Smelter in Tacoma, Washington. Unpublished Report. Prepared for the Emission Measurement Branch, Technical Support Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. August 1980. 35 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data.

