### ARSINE

**Formula:** AsH₃  
**MW:** 77.95  
**CAS:** 7784-42-1  
**RTECS:** CG6475000

**METHOD:** 6001, Issue 2  
**EVALUATION:** FULL  
**Issue 1:** 15 May 1985  
**Issue 2:** 15 August 1994

**OSHA:** 0.05 ppm  
**NIOSH:** C 0.002 mg/m³/15 min; carcinogen  
**ACGIH:** 0.05 ppm; carcinogen  

(1 ppm = 3.19 mg/m³ @ NTP)

**PROPERTIES:** gas; d 3.48 g/L @ 20 °C; BP -62.5 °C; MP -116.3 °C

**SYNONYMS:** hydrogen arsenide; arsenic trihydride.

### SAMPLING

**SAMPLER:** SOLID SORBENT TUBE  
(coconut shell charcoal, 100 mg/50 mg)  
**FLOW RATE:** 0.01 to 0.2 L/min  
**VOL-MIN:** 0.1 L @ 0.05 ppm  
**-MAX:** 10 L  
**SHIPMENT:** routine

**SAMPLE STABILITY:** at least 6 days @ 25 °C [1]

**BLANKS:** 2 to 10 field blanks per set

### MEASUREMENT

**TECHNIQUE:** ATOMIC ABSORPTION, GRAPHITE FURNACE

**ANALYTE:** arsenic

**DESORPTION:** 1 mL 0.01 M HNO₃; 30 min in ultrasonic bath

**MATRIX MODIFIER:** Ni²⁺, 1000 µg/mL

**WAVELENGTH:** 193.7 nm; D₂ or H₂ correction

**GRAPHITE FURNACE:** DRY: 40 sec @ 110 °C; CHAR: 15 sec @ 1200 °C; ATOMIZE 7 sec @ 2540 °C

**INJECTION:** 50 µL

**CALIBRATION:** As(III) in 0.01 M HNO₃ with 100 mg charcoal present

**RANGE:** 0.01 to 0.3 µg per sample [2]

**ESTIMATED LOD:** 0.004 µg per sample

**PRECISION (S̄):** 0.060 @ 0.012 to 0.11 µg per sample [2]

**ACCURACY:** ± 23.2%

**APPLICABILITY:** The working range is 0.0003 to 0.06 ppm (0.001 to 0.2 mg/m³) for a 10-L air sample. This is an elemental analysis and is not compound-specific.

**INTERFERENCES:** Use background correction to control molecular absorption. Other arsenic compounds (gases or aerosols) may be collected on the sampler and would be erroneously reported as arsine. A cellulose ester filter in front of the charcoal tube may be used to remove aerosols [3,4]. The effect of relative humidity on the capacity of charcoal for arsine has not been studied.

**OTHER METHODS:** This method combines and replaces P&CAM 265 [5] and S229 [6] for arsine.

REAGENTS:

1. Water, distilled or deionized.
2. Nitric acid, conc.*
3. Nitric acid, 0.01 M. Dilute 0.4 mL conc. HNO₃ to 1 L with water.
4. Nitric acid, 0.1 M. Dilute 4 mL conc. HNO₃ to 1 L with water.
5. Arsenic stock solution, 1000 µg As(III)/mL.* Commercial standard or dissolve 1.322 g dried, certified reagent As₂O₃ in 100 mL 0.1 M HNO₃; dilute to 1 L with 0.1 M HNO₃.
6. Calibration stock solution, 1.0 µg As(III)/mL.* Dilute 0.1 mL arsenic stock solution (1000 µg As/mL) to 100 mL with 0.01 M HNO₃. Prepare fresh daily.
7. Nickel nitrate solution, 1000 µg Ni/mL. Commercial nickel atomic absorption standard or dissolve 3.112 g dried reagent Ni(NO₃)₂ in 100 mL 0.1 M HNO₃; dilute to 1 L with water.
8. Argon, compressed.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.

NOTE: Use a cellulose ester membrane filter in front of the sampler if particulate arsenic is present [3,4].

2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with graphite furnace, non-pyrolytic tubes, background correction and electrodeless discharge (and power supply) or hollow cathode lamp for arsenic.
4. Volumetric flasks, 1-L and 100-mL.*
5. Micropipets, 5- to 500-µL.*
6. Centrifuge tubes, 10- or 15-mL.*
7. Ultrasonic bath.
8. Centrifuge.
9. Syringe, gas, 0.1-mL, readable to 1 µL.

*Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Arsenic is a human carcinogen [7]. Perform all concentrated acid handling in a fume hood. Arsine is extremely poisonous by inhalation. Handle in well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.

NOTE: Use a cellulose ester membrane prefilter if particulate arsenic compounds may be present [3,4].

3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.1 to 10 L.
4. Cap the sampler with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate centrifuge tubes. Discard the glass wool and foam plugs.

6. Add 1.0 mL 0.01 M HNO₃ to each tube. Cap each tube.
7. Agitate for 30 min in an ultrasonic bath.
8. Centrifuge each tube.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.004 to 0.3 µg arsenic per sample.
   a. Add known amounts of calibration stock solution and 0.01 M HNO₃ for a 1.0-mL final solution volume to centrifuge tubes containing 100 mg activated charcoal from a media blank sampler.
   b. Analyze standards together with samples and blanks (steps 12 and 13). Analyze a working standard for every five samples to check for instrument drift.
   c. Prepare a calibration graph (absorbance vs. µg arsenic).
10. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the range 0.004 to 2 µg arsenic per sample. Prepare three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount of pure arsine gas (or a certified gas mixture containing arsine) directly onto front sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze together with working standards (steps 12 and 13).
    e. Prepare a graph of DE vs. µg arsenic recovered.
11. Analyze three quality control spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set the spectrophotometer and furnace to manufacturer’s recommendations and to conditions given on page 6001-1.
13. Inject a 50-µL aliquot of sample or standard followed by a 50-µL aliquot of nickel nitrate solution prior to initiating the analysis program. Measure peak area.

   NOTE 1: If sample absorbance is above the linear range of the standards, dilute with 0.01 M HNO₃, reanalyze and apply the appropriate dilution factor in calculations.

   NOTE 2: Monitor the reproducibility of peak area for a working standard throughout the measurements. If erratic results occur, reoptimize instrumental parameters and replace the graphite tube.

CALCULATIONS:

14. Determine the mass, µg, of arsine found in the sample front (Wᵢ) and back (Wᵢ) sorbent sections, and in the average media blank front (Bᵢ) and back (Bᵢ) sorbent sections by multiplying the mass of arsenic found for each of these sections by 1.040 (M.W. of arsine/M.W. of arsenic).

   NOTE: If Wᵢ > Wᵢ/10, report breakthrough and possible sample loss.
15. Calculate concentration, C, of arsine in the air volume sampled, V (L):

\[ C = \frac{Wᵢ + Wᵢ - Bᵢ - Bᵢ}{V}, \text{ mg/m}^3. \]
EVALUATION OF METHOD:

Method S229 [6] was evaluated over the range 0.094 to 0.404 mg/m$^3$ using 10-L air samples collected on SKC Lot 105 activated coconut charcoal [1]. Breakthrough (onto the backup section) did not occur after 240 min of sampling at 0.227 L/min from an arsine concentration of 0.405 mg/m$^3$ (0.022 mg loading). The recovery was found to be 93.7%. Desorption efficiency was 0.90 at 1 µg arsine per sample and 1.00 at 2 and 4 µg arsine per sample.

Method P&CAM 265 [5] was evaluated over the range 0.001 to 0.01 mg/m$^3$ using 15-L air samples [2]. These samples were collected on SKC Lot 106 activated coconut charcoal at a sampling flow rate of 0.875 L/min for 15 min. At this flow rate, a collection efficiency of 89.1% was found [3]. The effect of high humidity on the sampler capacity was not studied. Desorption efficiency was 0.90 in the range 0.015 to 0.2 µg arsine per sample.

REFERENCES:


METHOD REVISED BY:

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