



ARSINE

6001

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

METHOD: 6001, Issue 3

EVALUATION: FULL

Issue 1: 15 May 1985

Issue 3: 20 October 2015

OSHA: 0.05 ppm (0.2 mg/m³)
NIOSH: C 0.002 mg/m³ (15 min); carcinogen

PROPERTIES: Gas; d 3.484 g/L @ 20 °C; BP -62.5 °C; MP -116.3 °C

SYNONYMS: Hydrogen arsenide; arsenic trihydride

SAMPLING	MEASUREMENT
<p>SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)</p> <p>FLOW RATE: 0.01 L/min to 0.2 L/min</p> <p>VOL-MIN: 0.1 L @ 0.05 ppm -MAX: 10 L</p> <p>SHIPMENT: Routine</p> <p>SAMPLE STABILITY: At least 6 d @ 25 °C [1]</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE</p> <p>ANALYTE: Arsenic</p> <p>DESORPTION: 1 mL 0.01 mol/L nitric acid; 30 min in ultrasonic bath</p> <p>MATRIX MODIFIER: Nickel, 1000 µg/mL</p> <p>WAVELENGTH: 193.7 nm; deuterium or hydrogen correction</p>
ACCURACY	<p>GRAPHITE FURNACE: DRY: 40 s @ 110 °C; CHAR: 15 s @ 1200 °C; ATOMIZE: 7 s @ 2540 °C</p>
<p>RANGE STUDIED: 0.09 mg/m³ to 0.4 mg/m³ [1] (10 L samples); 0.001 mg/m³ to 0.01 mg/m³ [2]</p> <p>BIAS: -6.13% at 0.01 L/min to 0.2 L/min flow rates [1]; -11% @ 0.876 L/min [2]</p> <p>OVERALL PRECISION (\hat{S}_{pr}): 0.087 [2]</p> <p>ACCURACY: ±23.2%</p>	<p>INJECTION: 50 µL</p> <p>CALIBRATION: Arsenic in 0.01 mol/L nitric acid with 100 mg charcoal present</p> <p>RANGE: 0.01 µg to 0.3 µg per sample [2]</p> <p>ESTIMATED LOD: 0.004 µg per sample</p> <p>PRECISION (\bar{S}_r): 0.060 @ 0.012 µg to 0.11 µg per sample [2]</p>

APPLICABILITY: The working range is 0.0003 ppm to 0.06 ppm (0.001 mg/m³ 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 NIOSH methods P&CAM 265 [5] and S229 [6] for arsine.

REAGENTS:

1. Water, distilled or deionized.
2. Nitric acid, concentrated.*
3. Nitric acid, 0.01 mol/L. Dilute 0.4 mL concentrated nitric acid to 1 L with water.
4. Nitric acid, 0.1 mol/L. Dilute 4 mL concentrated nitric acid to 1 L with water.
5. Arsenic stock solution, 1000 µg/mL arsenic.* Commercial standard or dissolve 1.322 g dried, certified reagent arsenic trioxide in 100 mL of 0.1 mol/L nitric acid; dilute to 1 L with 0.1 mol/L nitric acid.
6. Calibration stock solution, 1.0 µg/mL arsenic.* Dilute 0.1 mL arsenic stock solution (1000 µg/mL arsenic) to 100 mL with 0.01 mol/L nitric acid. Prepare fresh daily.
7. Nickel nitrate solution, 1000 µg/mL nickel. Commercial nickel atomic absorption standard or dissolve 3.112 g dried reagent nickel nitrate in 100 mL of 0.1 mol/L nitric acid; dilute to 1 L with water.
8. Argon, compressed.*
9. Arsine,* 99%, or certified mixture in nitrogen.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Activated coconut shell charcoal (100 mg/50 mg sections, 20/40 mesh), in a glass tube, 7 cm long, 6 mm OD, 4 mm ID, with flame-sealed ends. A silylated glass wool plug precedes the front section and urethane foam plugs separate the sorbent sections and follow the back section.
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 L/min to 0.2 L/min, with flexible connecting tubing.
3. Graphite furnace atomic absorption spectrophotometer with 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 µL to 500 µL.[†]
6. Centrifuge tubes, 10 mL or 15 mL.[†]
7. Ultrasonic bath.
8. Centrifuge.
9. Syringe, gas, 0.1 mL, readable to 1 µL.

[†]Clean all glassware with concentrated nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Arsenic is a human carcinogen [7]. Wear gloves, lab coat, and safety glasses while handling acids. Perform all concentrated acid handling in a fume hood. Arsine is extremely poisonous by inhalation. Handle in well-ventilated hood and wear appropriate protective clothing and gloves. Users must be familiar with the proper use of flammable and nonflammable gases, cylinders, and regulators.

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 L/min and 0.2 L/min for a total sample size of 0.1 L 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 of 0.01 mol/L nitric acid 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 µg to 0.3 µg arsenic per sample.
 - a. Add known amounts of calibration stock solution and 0.01 mol/L nitric acid 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 µg 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, 6, 7, and 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 mol/L nitric acid, 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 (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections by multiplying the mass of arsenic found for each of these sections by 1.040 (MW of arsine/MW of arsenic).

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

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \mu\text{g/L or mg/m}^3.$$

EVALUATION OF METHOD:

NIOSH method S229 [6] was evaluated over the range 0.094 mg/m³ to 0.404 mg/m³ 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/m³ (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 µg and 4 µg arsine per sample.

NIOSH method P&CAM 265 [5] was evaluated over the range 0.001 mg/m³ to 0.01 mg/m³ 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 µg to 0.2 µg arsine per sample.

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