ARSINE 6001

AsH_3 MW: 77.95 CAS: 7784-42-1 RTECS: CG6475000

METHOD: 6001, Issue 2 **EVALUATION: FULL**

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OSHA :	0.05 ppm
NIOSH:	C 0.002 mg/m^3/15 min; carcinogen
ACGIH:	0.05 ppm; carcinogen (1 ppm = 3.19 mg/m^3 @ NTP)
PROPERTIES:	gas; d 3.484 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: **-MAX:**	0.1 L @ 0.05 ppm 10 L
SHIPMENT:	routine
SAMPLE STABILITY:	at least 6 days @ 25 °C [1]
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.09 to 0.4 mg/m^3 [1] (10-L samples); 0.001 to 0.01 mg/m^3 [2]
BIAS:	-6.13% at 0.01 to 0.2 L/min rates [1]; -11% @ 0.876 L/min [2]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.087 [2]
ACCURACY:	± 23.2%

MEASUREMENT

TECHNIQUE:	ATOMIC ABSORPTION, GRAPHITE FURNACE
ANALYTE:	arsenic
DESORPTION:	1 mL 0.01 <u>M</u> HNO_3; 30 min in ultrasonic bath
MATRIX MODIFIER:	Ni^{2+}, 1000 µg/mL
WAVELENGTH:	193.7 nm; D_2 or H_2 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 <u>M</u> HNO_3 with 100 mg charcoal present
RANGE:	0.01 to 0.3 µg per sample [2]
ESTIMATED LOD:	0.004 µg per sample
PRECISION ($\bar{S}_r$):	0.060 @ 0.012 to 0.11 µg per sample [2]

APPLICABILITY: The working range is 0.0003 to 0.06 ppm (0.001 to 0.2 mg/m ^{3}) 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. HNO_3 to 1 L with water.
4. Nitric acid, 0.1 M. Dilute 4 mL conc. HNO_3 to 1 L with water.
5. Arsenic stock solution, 1000 µg As(III)/mL.* Commercial standard or dissolve 1.322 g dried, certified reagent As_2O_3 in 100 mL 0.1 M HNO_3; dilute to 1 L with 0.1 M HNO_3.
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 HNO_3. Prepare fresh daily.
7. Nickel nitrate solution, 1000 µg Ni/mL. Commercial nickel atomic absorption standard or dissolve 3.112 g dried reagent $Ni(NO_3)_2$ in 100 mL 0.1 M HNO_3; dilute to 1 L with water.
8. Argon, compressed.
9. Arsine, *99%, or certified mixture in nitrogen.

* 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 HNO_3 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 HNO_3 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 HNO_3, 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 (M.W. of arsine/M.W. of arsenic).

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

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

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:

[1] Documentation of the NIOSH Validation Tests, S229, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), also available as Order No. PB 263959 from NTIS, Springfield, VA 22161 (1975).

[2] Evaluation and Refinement of Personal Sampling Method for Arsine, NIOSH Research Report, prepared under NIOSH Contract No. 210-76-0142 (NIOSH, unpublished, 1977).

[3] Costello, R. J., P. M. Eller and R. D. Hull. Measurement of Multiple Inorganic Arsenic Species, Am. Ind. Hyg. Assoc. J., 44(1), 21-28 (1983).

[4] Methods 7900 (Arsenic) and 7901 (Arsenic Trioxide), this Manual.

[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, P&CAM 265, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[6] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S229, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[7] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Arsenic, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-149 (1977).

METHOD REVISED BY:

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