

ARSENIC TRIOXIDE, as As

7901



MW: 197.84

CAS: 1327-53-3

RTECS: CG3325000

METHOD: 7901, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984

Issue 2: 15 August 1994

OSHA : 0.01 mg/m³ (As)
NIOSH: C 0.002 mg/m³ (As)/15 min; carcinogen
ACGIH: 0.01 mg/m³; carcinogen

PROPERTIES: solid; MP 275 °C or 313 °C (sublimes);
 VP 0.0075 Pa (5.6 x 10⁻⁵ mm Hg; 0.45 µg
 As/m³) @ 25 °C

SYNONYMS: arsenous acid anhydride; arsenous sesquioxide; arsenolite; claudetite

SAMPLING	MEASUREMENT
<p>SAMPLER: FILTER (Na₂CO₃-impregnated, 0.8-µm cellulose ester membrane + backup pad)</p> <p>FLOW RATE: 1 to 3 L/min</p> <p>VOL-MIN: 30 L @ 0.01 mg/m³ -MAX: 1000 L</p> <p>SHIPMENT: routine</p> <p>SAMPLE STABILITY: stable</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE</p> <p>ANALYTE: arsenic</p> <p>ASHING: 15 mL HNO₃ + 6 mL H₂O₂; 150 °C</p> <p>FINAL SOLUTION: 10 mL 1% HNO₃, 0.1% Ni²⁺</p> <p>WAVELENGTH: 193.7 nm; D₂ or H₂ correction</p> <p>GRAPHITE TUBE: pyrolytic</p> <p>GRAPHITE FURNACE: DRY: 100 °C, 70 sec; CHAR: 1300 °C, 30 sec; ATOMIZE: 2700 °C, 10 sec</p> <p>INJECTION: 25 µL</p> <p>CALIBRATION: As in 1% HNO₃, 0.1% Ni²⁺</p> <p>RANGE: 0.3 to 13 µg per sample</p> <p>ESTIMATED LOD: 0.06 µg per sample</p> <p>PRECISION (\hat{S}_r): 0.029 [3,4]</p>
ACCURACY	
<p>RANGE STUDIED: 0.67 to 32 µg/m³ [1,2] (400-L samples)</p> <p>BIAS: - 0.55%</p> <p>OVERALL PRECISION ($\hat{S}_{r,T}$): 0.075 [1,2]</p> <p>ACCURACY: ± 11.9%</p>	

APPLICABILITY: The working range is 0.001 to 0.06 mg/m³ for a 200-L air sample. This method collects particulate arsenic compounds as well as arsenic trioxide vapor. **If only total particulate arsenic is of interest, the use of the treated filter and analysis of the backup pad is not required.** Arsine is not collected by this sampling method.

INTERFERENCES: Background absorption is overcome by the use of a deuterium background corrector. Matrix modification with Ni²⁺ solution allows the use of a higher char temperature in the graphite furnace. Other particulate arsenic compounds will interfere.

OTHER METHODS: This method combines and replaces P&CAM 346 [3], S309 [4], and P&CAM 286 [5]. Method 7300 (ICP-AES) and arsine generation (Method 7900 and the criteria document method [1]) are for particulate arsenic compounds. Other methods (P&CAM 173 [7], P&CAM 180 [8], and P&CAM 188 [9]) have not been revised because of interferences or poor sensitivity.

REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 1% (v/v). Dilute 10 mL conc. HNO₃ to 1 L with distilled or deionized water.
3. Hydrogen peroxide, 30% (w/w).
4. Ni²⁺ in 1% HNO₃, 1000 µg/mL. Dilute 4.95 g Ni(NO₃)₂ to 1 L with 1% HNO₃.
5. Calibration stock solution*, 1000 µg As/mL, commercially available, or dissolve 1.320 g primary standard As₂O₃ in 25 mL 20% (w/v) KOH. Neutralize with 20% (v/v) HNO₃ to a phenolphthalein endpoint. Dilute to 1 L with 1% HNO₃.
6. 1 M Na₂CO₃:glycerol solution, 20:1. Dissolve 9.5 g sodium carbonate in 100 mL distilled or deionized water. Add 5 mL pure glycerol.
7. Distilled or deionized water.
8. Argon.

* See Special Precautions

EQUIPMENT:

1. Sampler: Cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter, and cellulose backup pad in cassette filter holder treated as follows:
 - a. Remove inlet plug from the loaded cassette.
 - b. Add 250 µL 20:1 Na₂CO₃:glycerol solution with a micropipet directly onto filter (wet entire surface).
 - c. Attach to vacuum source and draw 30 to 60 L clean air through the filter.
 - d. Let dry overnight or dry 8 h @ 120 °C. Replace the inlet plug.
 - e. Use within one week.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
NOTE: The treated filter has a high pressure drop; a personal sampling pump with flow rate control is required.
3. Atomic absorption spectrophotometer with graphite furnace atomizer, arsenic electrodeless discharge lamp, and background correction.
4. Regulator, two-stage for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.*
6. Volumetric flasks, 10-mL.*
7. Assorted volumetric pipets as needed.*
8. Hotplate, surface temperature to 150 °C.
9. Steambath.

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

SPECIAL PRECAUTIONS: Arsenic is a carcinogen [6]. Handle appropriately. Perform all digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 30 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Transfer both the treated filter and backup pad to a clean beaker.
4. Add 15 mL conc. HNO₃ and cover with a watchglass.
NOTE: Start reagent blanks at this step.
5. Heat on a 150 °C hotplate until the liquid volume is reduced to about 1 mL.

6. Carefully rinse the material on the bottom of the watchglass, and the sides of the beaker into the sample solution with distilled water. Add 6 mL 30% H₂O₂.
7. Evaporate just to dryness on the steambath.
8. Cool beakers. Add 10.0 mL 1000 µg/mL Ni²⁺ solution, cover, and mix for 30 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

9. Dilute the calibration stock solution 1:100 with 1000 µg/mL Ni⁺⁺ solution. This standard is 10.0 µg/mL As. Prepare fresh daily.
10. Prepare six working standards covering the range 0 to 1.25 µg/mL As.
 - a. Add aliquots of the 10.0 µg/mL As solution to 10-mL volumetric flasks and dilute to volume with 1000 µg/mL Ni²⁺ solution.
 - b. Analyze the working standards together with the samplers and blanks (steps 13 and 14).
 - c. Prepare calibration graph (absorbance vs. solution concentration, µg/mL). Inject a standard for every other sample to check instrument drift.
11. Check recoveries with at least two spiked media blanks per ten samples.
12. Use method of additions occasionally to check for interferences.

MEASUREMENT:

13. Set spectrophotometer according to manufacturer's recommendations to conditions on page 7901-1.
14. Inject standards and samples. Record absorbance (peak height) readings.
NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 1000 µg/mL Ni²⁺ solution, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

15. Record the actual solution volumes to which the sample, V_s (mL), and media blanks, V_b (mL) were diluted in step 8.
16. Calculate the solution concentration of arsenic in the sample, C_s (µg/mL), and average media blank, C_b (µg/mL), from the calibration graph.
17. Calculate the concentration of arsenic, C (mg/m³), in the air volume sampled, V(L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S309 [4] was issued on September 26, 1975, and validated with aerosols generated from As₂O₃ solutions in dilute NaOH [2]. Method P&CAM 346 was developed in August, 1981, over the range 0.67 to 32.2 µg/m³ for a 400-L air sample, corresponding to 0.268 to 12.8 µg As per sample [1]. Atmospheres were generated by passing air over heated As₂O₃. Collection efficiencies (CE) for As₂O₃ under these conditions were determined to be 0.42 and 0.67 for untreated 0.8-mm cellulose ester membrane filters, and cellulose backup pads, respectively. Under the same conditions, the Na₂CO₃-treated filter had CE = 0.93 [5]. This method was used in a lead-acid battery manufacturing plant in which vapor was found to be significant [10].

REFERENCES:

- [1] Carlin, L. M., G. Colovos, D. Garland, M. E. Jamin, M. Klenck, T. J. Long, and C. L. Nealy. Analytical Methods Evaluation and Validation - As, Ni, W, V, Talc, and Wood Dust, Rockwell International, Final Report on NIOSH Contract No. 210-79-0060; available as Order No. PB 83-155325 from NTIS, Springfield, VA 22161.
- [2] Documentation of the NIOSH Validation Tests, S309, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
- [3] Ibid, NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 346, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).
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- [5] Ibid, P&CAM 286.
- [6] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Arsenic, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-149 (1975).
- [7] Ibid, V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141-C (1979).
- [8] Ibid, V. 1, P&CAM 180, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
- [9] Ibid, P&CAM 188.
- [10] Costello, R. J., P. M. Eller, and R. D. Hull. Measurement of Multiple Inorganic Arsenic Species, Am. Ind. Hyg. Assoc. J., 44, 21-28 (1983).

METHOD REVISED BY:

M. Millson and P. M. Eller, Ph.D., NIOSH/DPSE; P&CAM 346 originally developed under NIOSH Contract 210-79-0060.