ARSENIC, organo- 5022

(1) $CH_3AsO_3H_2$	MW: (1) 139.96	CAS: (1)124-58-3	RTECS: (1) PA1575000
(2) $(CH_3)_2AsO_2H$	(2) 137.99	(2)75-60-5	(2) CH7525000
(3) $H_2NC_6H_4AsO_3H$	(3) 217.07	(3) 98-50-0	(3) CF7875000

METHOD: 5022, Issue 3 **EVALUATION:** FULL **Issue 1:** 15 May 1985 **Issue 3:** 3 March 2016

OSHA: 0.5 mg/m³ (as As)
NIOSH: None

PROPERTIES: (1) Solid; MP 161 °C
(2) Solid; MP 195 °C
(3) Solid; MP 232 °C

SYNONYMS: (1) Methylarsonic acid: methanearsonic acid. (2) Dimethylarsinic acid: cacodylic acid; hydroxydimethyl arsine oxide. (3) *p*-Aminophenyl arsonic acid: *p*-arsanilic acid; atoxylic acid.

SAMPLING

SAMPLER: FILTER (1-µm PTFE)

FLOW RATE: 1 - 3 L/min

VOL-MIN: 50 L @ 0.1 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.005 to 0.2 mg/m³ [1,2]

BIAS: none significant

OVERALL PRECISION ($\hat{S}_{rT}$): 0.047 @ 0.02 mg/m³ [1]; 0.14 @ 0.005 mg/m³ [1]

ACCURACY: ± 20% @ 0.02 mg/m³

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY/HYDRIDE ATOMIC ABSORPTION

ANALYTE: anions (IC); AsH_3 (AAS)

EXTRACTION: borate-carbonate buffer, 25 mL

ION CHROMATOGRAPHY:
INJECTION LOOP VOLUME: 0.8 mL

COLUMNS: two, 3 x 150-mm anion

ELUENT: borate-carbonate buffer; 2.5 mL/min; 3450 kPa (500 psi); ambient temperature

AAS:
QUARTZ FURNANCE: 800 °C

WAVELENGTH: 193.7 nm (no D_2)

CALIBRATION: organoarsenicals in water

RANGE: 0.5 to 2 µg As per sample

ESTIMATED LOD: 0.2 µg As per sample [1]

PRECISION ($\bar{S}_r$): Table 1

APPLICABILITY: The working range is 0.005 to 10 mg/m³ (as As) for a 100-L air sample. The method is designed to quantitate particulate organo-arsenic compounds.

INTERFERENCES: Inorganic arsenic (III) co-elutes with dimethylarsenic acid using Eluent A but the two may be separated with Eluent B. Other ions at high concentrations in the sample can interfere with the chromatographic separation of the arsenicals. As_2O_3 is not efficiently sampled by this sampler; for quantitation of that compound see Method 7901.

OTHER METHODS: This is P&CAM 320 in revised format [2]. Method 7200 measures total As by hydride/AAS. Method 7901 measures As_2O_3, which can exist as a vapor and aerosol.

REAGENTS:

1. Deionized water.
2. Hydrochloric acid, conc.
3. Eluent A (2.4 mM HCO_3^-/1.9 mM CO_3^{2-}/1.0 mM $B_4O_7^{2-}$). Dissolve 0.8067 g $NaHCO_3$, 0.8055g Na_2CO_3, and 1.5257 g $Na_2B_4O_7 \cdot 10H_2O$ in 4 L deionized water.
4. Eluent B (5 mM $B_4O_7^{2-}$). Dissolve 7.6284 g $Na_2B_4O_7 \cdot 10\ H_2O$ in 4L deionized waster.
5. Potassium persulfate solution,* $K_2S_2O_8$, saturated in 15% (v/v) HCl.
6. Sodium borohydride, 1% $NaBH_4$ (w/v) in 0.2% KOH (w/v). Add 5 g $NaBH_4$ and 1 g KOH to deionized water; dilute to 500 mL. Prepare fresh weekly.
7. Stock standards, 1000 µg As/mL:
   a. Methylarsonic acid.* Dissolve 0.9341 g $CH_3AsO_3H_2$, in deionized water; dilute to 500 mL.
   b. Dimethylarsenic acid.* Dissolve 0.9210 g $(CH_3)_2AsO_2H$ in deionized water; dilute to 500 mL.
   c. *p*-Aminophenylarsonic acid.* Dissolve 1.4485 g *p*-$H_2NC_6H_4AsO_3H_2$ in 5 mL 1 N NaOH. Dilute to 500 mL with deionized water. Protect from light.
   d. Arsenic trioxide.* Dissolve 0.6602 g As_2O_3 in 5 mL 1 N NaOH. Dilute to 500 mL with deionized water.
   e. Arsenic pentoxide.* Dissolve 0.7669 g As_2O_5 in 5 mL 1 N NaOH. Dilute to 500 mL with deionized water.
8. Calibration stock solution, 1 µg/mL mixed analyte. Dilute 0.1 mL of each stock standard (REAGENTS, 7.) with Eluent A in a 100-mL volumetric flask. Prepare fresh daily.
9. Argon.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: PTFE polyethylene-backed membrane filter, 1-µm pore size, 37-mm diameter with backup pad; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Ion chromatograph with suppressor and detector bypassed. Route column effluent via PTFE tubing (0.3mm ID x 0.6mm OD) directly into arsine generator (Figure 1).
4. Syringes, plastic, 10-mL, with male luer lock style fittings.
5. Arsine generator: proportioning pump with flow-rated pump tubes and 1.5-mm ID x 3-mm OD manifold mixing coils, 5-turn and 20-turn, 1.5-mm ID x 3.5-mm OD glass "T" connectors; gas-liquid separator and expansion chamber (Figure 2); 1 m of 1/4" OD PTFE tubing; three PTFE 1/4" ID Swagelok fittings; and rotometer (100 to 900 mL/min).
6. Atomic absorption spectrophotometer (reciprocal linear UV dispersion 0.65 nm/mm); As electrodeless discharge lamp and power supply; and atomization cell (16-cm x 13-mm ID windowless quartz tube with 18-cm x 4-mm ID inlet tube fused in the center), wound with Nichrome wire (14 Ω/m, spaced 2 to 3 mm between turns and wrapped with heat resistant tape) (Figure 3). Temperature in the cell is measured by a thermocouple (800 °C). Mount the cell on top of a single-slot AAS burner head and align with burner alignment controls.
7. Beakers, 50-mL.**
8. Ultrasonic waterbath.
9. Volumetric flasks, 10-, 100- and 500-mL.**
10. Pipets, 25-µL and 0.1- to 1-mL.

**Soak all glassware in mild detergent, rinse with deionized water, 10% HNO_3, and deionized water.

SPECIAL PRECAUTIONS: Wear gloves, lab coat, and safety glasses while handling chemicals. All work should be performed in a fume hood. Potassium persulfate is a powerful oxidizing agent. Arsine gas is extremely toxic and can be fatal. The arsenic compounds used in the stock standards are poisonous [3].

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 volume of 50 to 1000 L.
3. Cap the cassettes and pack securely for shipment.

SAMPLE PREPARATION:

4. For each sample, pipet 25 mL Eluent A into a clean 50-mL beaker.
5. Open the cassette, remove the PTFE filter with clean forceps, and transfer it to the beaker. Place the exposed side of the filter in contact with the solution. Cover beaker.
6. Agitate contents of the beaker for 30 min in an ultrasonic water bath. If the extracts will not be analyzed immediately, store at ca. 4 °C until measurement.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.2 to 2 µg As per sample (0.008 to 0.08 µg As/mL).
   a. Add known amounts of calibration stock solution to Eluent A in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with the samples and blanks (steps 8 through 12).
   c. Prepare calibration graph for each arsenic species (peak area or height vs. µg As).

MEASUREMENT:

8. Set the ion chromatograph to the conditions given on page 5022-1. Allow the columns to equilibrate with eluent >1 h before connecting effluent to the arsine generator.
   NOTE: Eluent A allows the separation of methylarsonic acid (retention time (t_r) = 2 min), *p*-aminophenylarsonic acid (t_r = 4 min), and As(V) (t_r = 7.5 min); As(III) and dimethylarsenic acid (t_r = 1 min) are not resolved. If a signal is obtained at the approximate retention time of the latter two compounds, or if both compounds are known to be present in the sample, perform a second analysis using Eluent B (lower ionic strength). If either of the two compounds is known not to be present, Eluent A will effectively determine the remaining compounds. With Eluent B the other species have very long retention times and will accumulate on the column, tying up active resin sites. Therefore, flush the column with Eluent A after each 10 to 15 samples and reequilibrate with Eluent B before further analysis.
9. Connect the IC effluent to the arsine generator into which the following flow:
   Saturated $K_2S_2O_8$ solution: 0.8 mL/min
   $NaBH_4$ solution: 2.0 mL/min
   Ar carrier gas: 300 mL/min
   NOTE: The gaseous arsines formed in the arsine generator are first separated from liquid solution using the gas-liquid separator (Figure 2) and then transferred by argon carrier gas through PTFE tubing to the heated quartz furnace.
10. Set the AAS according to manufacturer's recommendations and to the conditions given on page 5022-1. Align the quartz cell in the optical path. Heat the quartz cell gradually to 800 °C using a variable transformer and thermocouple.
11. Using a syringe, inject a sample aliquot (ca. 2 to 3 mL) into the chromatograph, flushing the injection loop to avoid contamination from the previous injection. Rinse the syringe with deionized water and dry it between samples, or use disposable syringes.
12. Identify the component peaks. Measure peak height or area.

Calculations

13. From the calibration graphs, calculate the amount (µg) of arsenic for each species in the sample (W) and in the average media blank (B).
14. Calculate the arsenic concentrations, C, (mg/m^3) in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, mg/m^3$$

EVALUATION OF METHOD:

The measurement precision obtained under the conditions recommended in this procedure is presented in Table 1 [1]. The overall precision of the method was tested using filters loaded in a dynamic aerosol generation/sampling system with particulates of the three organoarsenical compounds. The concentration levels tested for each species were 5, 10, and 20 µg As/m^3 of air. Depending on the concentration and species, the relative standard deviation ranged from 14.4% at the lowest level to 4.7% at the highest level.

The collection efficiency of the method for organoarsenicals in the range of 5 to 20 µg/m^3 using a 300-L sample was found to be >99%. The collection efficiency of the method for inorganic arsenic was not determined.

The accuracy of the overall method was determined by analyzing additional aerosol samples from each set using Neutron Activation (NAA) and X-ray Fluorescence (XRF) analyses. Since NAA and XRF techniques provide only the total elemental arsenic, the total arsenic obtained from the IC-AAS analysis was used for comparison. The accuracy ranged from 90 to 120% of the values obtained by NAA and XRF.

REFERENCES:

[1] Colovos G, Hester N, Ricci GR, Shepard, LS. [1980]. Development of a method for the determination of organoarsenicals in air. NIOSH Contract #210-77-0134, NTIS No. PB83-180794.

[2] NIOSH [1980]. Particulate arsenicals: Method P&CAM 320. In: Taylor, DG, ed. NIOSH manual of analytical methods, 2nd ed. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 80-125.

[3] Budavari S, [1989]. Merck Index. 11th ed. Rahway, NJ: Merck & Co., Inc.

METHOD REVISED BY:

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P&CAM 320 originally developed under NIOSH Contract 210-77-0134.

TABLE 1. Sensitivity, detection limit and working range data for analysis of particulate arsenicals [1].

Arsenical	Sensitivity (ng/mL/ 1% Abs)	Detection limit (as As) for 300 L sample volume (µg/m³)	Detection limit (as As) for solution (ng/mL)	Range* for 300 L sample volume (µg/m³)	Range* for solution (ng/mL)	Measurement precision (% $\overline{S}_r$)
Dimethylarsenic acid	1.3	0.62	7	1.7-6.7	20-80	11.2
Arsenic (III)	2.1	0.71	8	1.7-6.7	20-80	11.2
Methylarsonic acid	2.1	0.72	9	1.7-6.7	20-80	8.1
p-Aminophenylarsonic acid	6.3	0.64	8	1.7-6.7	20-80	6.0
Arsenic (V)	13.0	0.46	6	1.7-6.7	20-80	10.8

*The upper limit of the range can be increased by using higher concentration standards which are injected via loops of smaller volume. Although not tested with air samples, the useful range can be extended from 5 µg/m³ down to 1.7 µg/m³ based upon the measurement range.

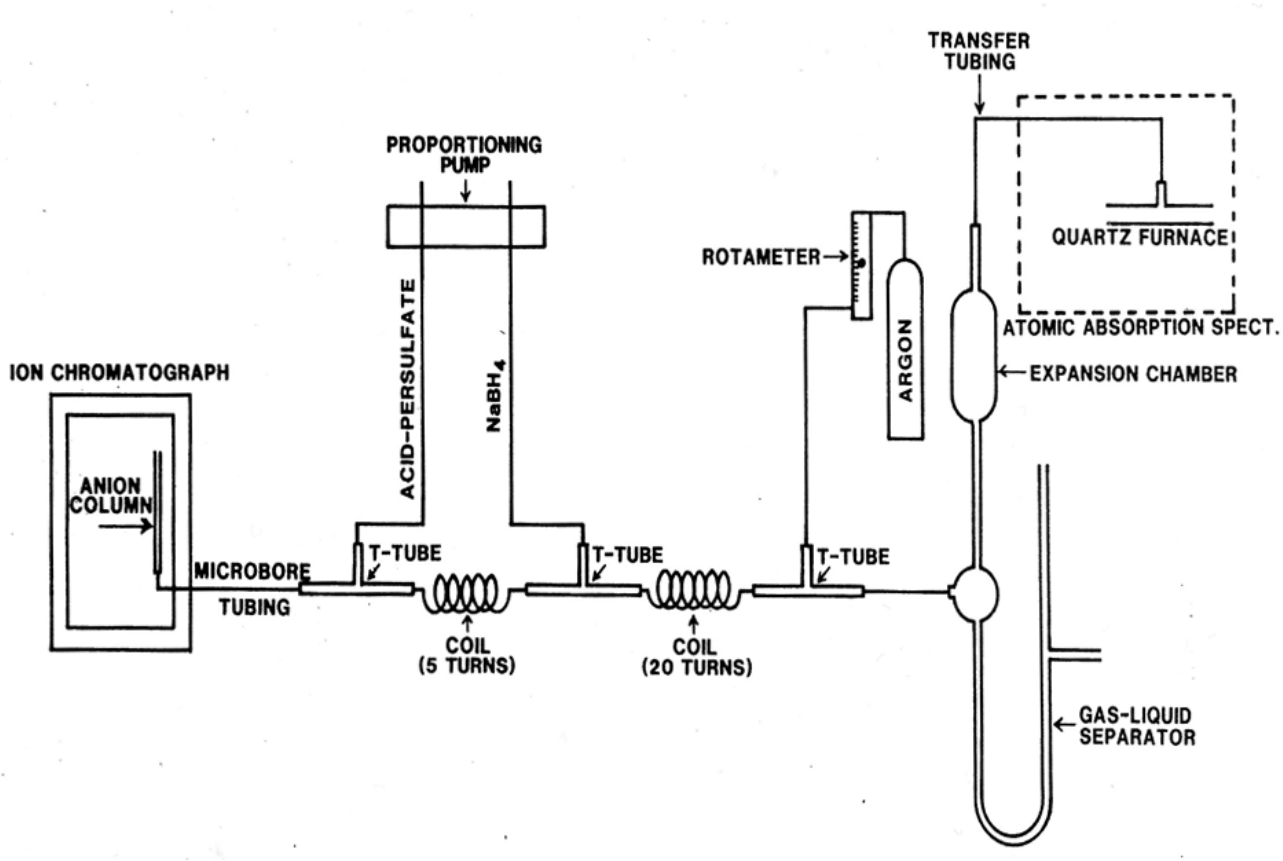

FIGURE 1. IC/AAS Analytical System.

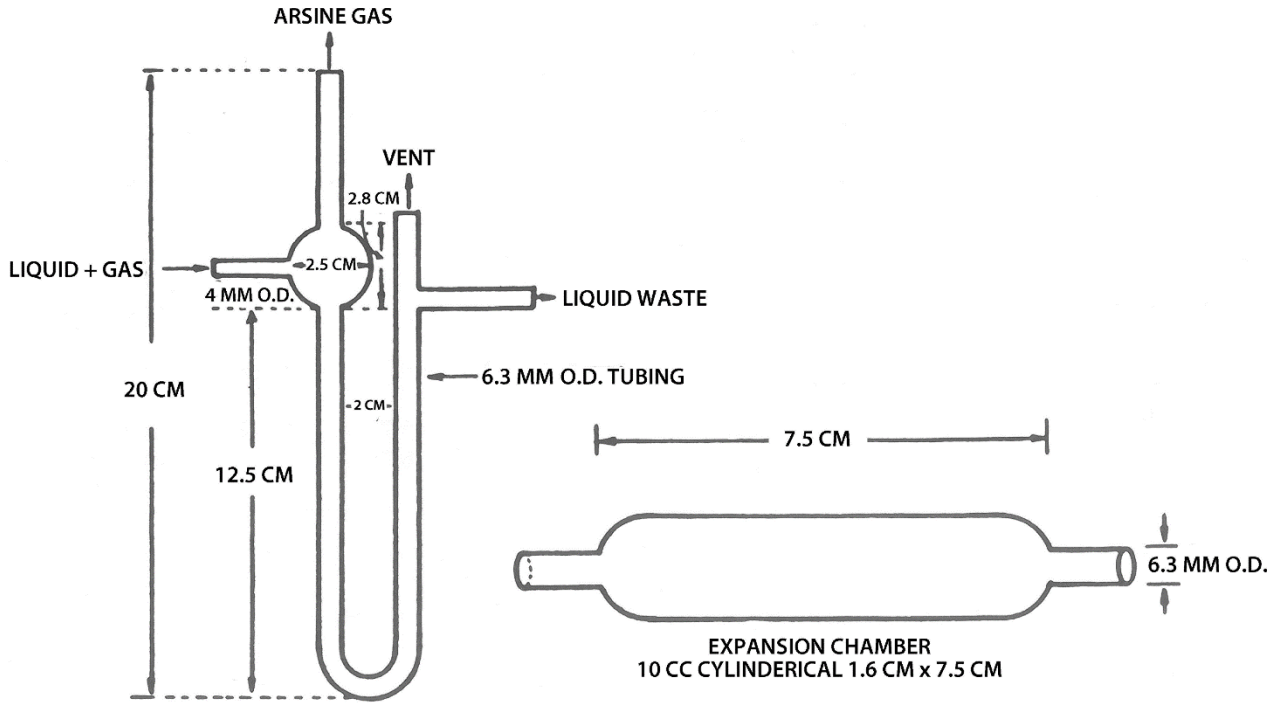

FIGURE 2. Gas-Liquid Separator and Expansion Chamber.

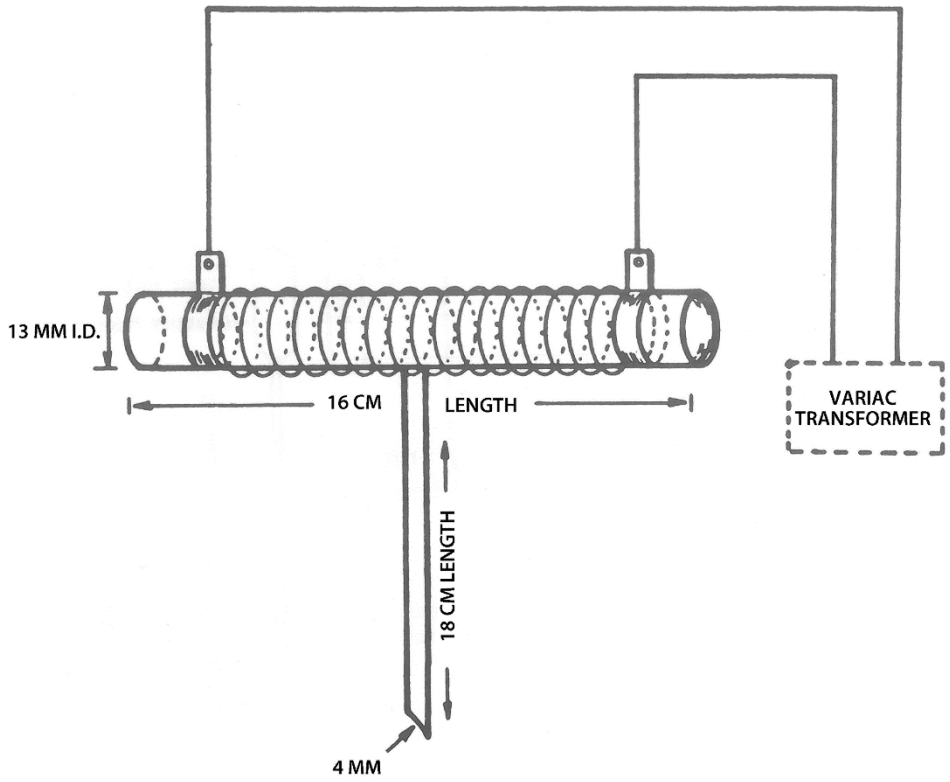

FIGURE 3. Quartz Furnace Atomization Cell.