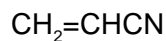


ACRYLONITRILE

1604



MW : 53.06

CAS: 107-13-1

RTECS: AT5250000

METHOD: 1604, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984

Issue 2: 15 August 1994

OSHA : 2 ppm; C 10 ppm (skin)
NIOSH: carcinogen; 1 ppm; C 10 ppm/15 min;
 Group I Pesticide (skin)
ACGIH: carcinogen; 2 ppm (skin)
 (1 ppm = 2.17 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.806 g/mL @ 20 °C;
 BP 77.2 °C; VP 11 kPa (83 mm Hg 11% v/v)
 @ 20 °C; explosive range 3 to 17% v/v in air

SYNONYMS: 2-propenenitrile; vinyl cyanide; AN.

APPLICABILITY: The working range is 0.7 to 46 ppm (1.5 to 100 mg/m³) for a 10-L air sample. This method is applicable to 15-minute ceiling measurements. NIOSH has sampled for acrylonitrile at acrylic and electric plants.

INTERFERENCES: None known. An alternate chromatographic column is a fused silica capillary, 30 m x 0.32-mm, coated with 0.5 µm DB-WAX or 1 µm DB-5.

OTHER METHODS: This revises NIOSH Method S156 [1,3] and Method 1604 (dated 2/15/84). P&CAM 202 has been dropped because of poor sensitivity (LOD 0.1 mg per sample) [4]. Marano et al. [5] have shown that the use of a nitrogen selective detector (NPD) increases the sensitivity and specificity of the analysis.

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Acetone, chromatographic quality.
3. Hexane, reagent grade.
4. Eluent: 2% acetone (v/v) in carbon disulfide.*
5. Acrylonitrile, stabilized.* Stable at least one month at 4 °C.
6. Acrylonitrile, freshly distilled.*
7. Calibration stock solution, 4 µg/µL.
Add 50 µL freshly distilled acrylonitrile to 10 mL hexane. Stable one week at 4 °C.
8. Helium, purified.
9. Hydrogen, prepurified.
10. Air, filtered.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, 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.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1604-1).
4. Micro-distillation apparatus for vacuum distillation of acrylonitrile.
5. Vials, 2-mL, PTFE-lined crimp caps.
6. Syringe, 10-µL and other sizes as needed, readable to 0.1 µL.
7. Volumetric flasks, 10-mL.
8. Pipets, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a severe fire and explosion hazard (flash point = -30 °C). Acrylonitrile is explosive, flammable, toxic, and a suspect carcinogen [3]. Work with these compounds only in a 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.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 3.5 to 20 L.
4. Cap the samplers pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
NOTE: An internal standard, e.g., 0.1% (v/v) benzene or n-hexane, may be added at this step.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 1 to 1000 µg acrylonitrile per sample.
 - a. Add known amounts of calibration stock solution, or a serial dilution thereof, to eluent in 10-mL volumetric flasks and dilute to the mark with eluent (2% acetone in CS₂).

- b. Analyze together with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph (peak area vs. μg acrylonitrile).
NOTE: Compare the peak areas of the working standards with a 0.1 mg/mL reference standard prepared from stabilized (undistilled) acrylonitrile in hexane. When the concentration of the working standards starts to decrease, prepare new working standards.
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). 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 calibration stock solution directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. Allow to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
 - e. Prepare a graph of DE vs. μg acrylonitrile recovered.
 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1604-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE 1: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
NOTE 2: Under these conditions t_r for acrylonitrile is ca. 8.5 min.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of acrylonitrile 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.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of acrylonitrile 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 S156 [2] was validated at levels of 0.48, 0.95, and 1.91 mg per sample, using samples of acrylonitrile prepared both by sampling standard atmospheres generated by calibrated syringe drive and by spiking standard solutions in hexane on to the charcoal [6].

After the OSHA standard for acrylonitrile was lowered to 2 ppm, the method was evaluated by NIOSH at levels of 8.6 and 16.6 μg per sample (desorption solvent 2% acetone in CS_2), using samples from gas bag atmospheres and by spiking the charcoal with standard solutions of acrylonitrile in hexane [1]. At the higher levels ($> 16 \mu\text{g}$), the recoveries of acrylonitrile averaged 94% and the \bar{S}_r was 0.06. At the lower level (8.6 μg), the recovery for the two sets of samples prepared from standard atmospheres averaged 79% with a \bar{S}_r of 0.14. The sample set prepared by spiking charcoal at the lower level had a recovery of 94%. The parity between the recoveries of samples obtained from test atmospheres and from liquid spikes at the lower level suggested a possible problem with accuracy at this level [1]. Samples were found to be stable for at least seven days at room temperature [1,6]. Several breakthrough studies have been reported. At 80% relative humidity, breakthrough occurred after 184 minutes (36.7 L) sampling 8 mg/m^3 at 0.2 L/min [7]. Breakthrough did not occur after sampling dry air at 92 mg/m^3 at 0.2 L/min for 4 hours [6].

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- [6] Documentation of the NIOSH Validation Tests, S156, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
- [7] OSHA Report, Acrylonitrile Method 37, Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, UT (May, 1982).

METHOD REVISED BY:

Y.T. Gagnon, NIOSH/DPSE; S156 originally validated under NIOSH Contract CDC-99-74-45.