

ACETONITRILE

1606

CH₃CN

MW: 41.06

CAS: 75-05-8

RTECS: AL7700000

METHOD: 1606, Issue 3

EVALUATION: FULL

Issue 1: 15 February 1984

Issue 3: 15 January 1998

OSHA: 40 ppm
 NIOSH: 20 ppm
 ACGIH: 40 ppm; STEL 60 ppm
 (1 ppm = 1.68 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.783 g/mL @ 20 °C; BP 82 °C;
 VP 12 kPa (89 mm Hg) @ 25 °C, explosive
 range 4.4 to 16% v/v in air

SYNONYMS: methyl cyanide, cyanomethane, ACN.

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (coconut shell charcoal, 400/200 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	acetonitrile
VOL-MIN:	1 L @ 40 ppm	DESORPTION:	2 mL methylene chloride/methanol (85:15); ultrasonic bath for 45 minutes.
-MAX:	25 L	INJECTION VOLUME:	1 µL
SHIPMENT:	keep cold; pack securely for shipment.	TEMPERATURE-INJECTION:	250 °C
SAMPLE STABILITY:	at least 30 days at 5 °C	-DETECTOR:	300 °C
BLANKS:	2 to 10 field blanks per set	-COLUMN:	35 °C, hold 4 min; 12 °C/min to 150 °C
ACCURACY		CARRIER GAS:	He, 2.4 mL/min
RANGE STUDIED:	39.2 to 275 mg/m ³ [1]	COLUMN:	capillary, fused silica, 30 m x 0.32-mm ID, 1- µm film, crossbonded PEG, Stabilwax® or equivalent
BIAS:	4.0%	CALIBRATION:	solutions of acetonitrile in methylene chloride/methanol (85:15)
OVERALL PRECISION (\hat{S}_{rr}):	0.071 [1,2]	RANGE:	2.6 to 2000 µg per sample [1, 2]
ACCURACY:	± 16.4%	ESTIMATED LOD:	0.8 µg per sample [1]
		PRECISION (\hat{S}_{r}):	0.015

APPLICABILITY: The working range is 0.06 to 7.4 ppm (0.1 to 12.5 mg/m³) for a 25-L air sample [1]. Large (400 mg/200 mg) charcoal tubes are required for analyte collection, since breakthrough volume is lower with smaller charcoal tubes [2]. Analyte capacity of the large charcoal tubes has not been determined under conditions of high relative humidity [3].

INTERFERENCES: Samples containing greater than 15% methanol or other alcohols.

OTHER METHODS: This method revises NMAM 1606 (dated 8/15/94) and is based on Method S165 [4]. In this method, a capillary GC column has replaced the original packed column. Improvements include but are not limited to the following: new and less hazardous desorption solvent, smaller volume of desorption solvent required, improved desorption efficiency (DE), and lower LOD/LOQ. A storage stability study was completed and was found acceptable at 98.5% after 30 days at 5 °C.

REAGENTS:

1. Acetonitrile (ACN), reagent grade (99.9+%)^{*}.
2. Methylene chloride, HPLC grade^{*}.
3. Methanol, HPLC grade^{*}.
4. Helium, purified.
5. Hydrogen, purified.
6. Air, prefiltered and purified.

^{*} See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 10 cm, 6-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated coconut shell charcoal (front = 400 mg, back = 200 mg), separated by a 3-mm section of polyurethane foam. A silanized glass wool plug precedes the front section and a 3-mm polyurethane plug follows the back section. Tubes are commercially available (SKC # 226-09, Supelco ORBO-32, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph, flame ionization detector (FID), integrator, and Stabilwax® fused silica capillary column, or equivalent (page 1606-1).
4. Vials, glass, 4-mL, PTFE-lined screw caps.
5. Syringes, 10- μ L to 1-mL.
6. Volumetric flasks, 10-mL.
7. Pipets, various sizes.
8. Refrigerant packs.

SPECIAL PRECAUTIONS: Acetonitrile is toxic and flammable. Methylene chloride is a potential carcinogen. Methanol is moderately toxic and flammable. Perform all work in a chemical hood and wear appropriate protective equipment.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sample tube in line.
2. Break open the ends of the sample tube immediately prior to sampling. Attach sample tube 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 1 to 25 L.
4. Cap both ends of the sample tubes with plastic caps and pack securely for shipment. Ship with refrigerant packs to keep samples cold.

SAMPLE PREPARATION:

5. Place the initial glass wool plug and front sorbent section of the sample tube in a 4-mL glass screw cap vial. Place the back sorbent section of the sample tube in separate 4-mL vial. Discard the polyurethane foam plugs.
6. Add 2.0 mL of methylene chloride/methanol (85:15) to each 4-mL vial and cap securely.
7. Place each vial in an ultrasonic bath for 45 minutes.
8. Transfer 1.0-mL aliquots of each sample to autosampler vials and analyze (steps 11 and 12).

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working calibration standards over the range of interest.
 - a. Add known amounts of calibration stock solution (prepare in concentration range of samples; 1 μ L ACN = 78.3 μ g) to methylene chloride/methanol (85:15) in 10-mL volumetric flasks and dilute to the mark.
 - b. Analyze together with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph (peak area vs. μ g acetonitrile).
10. Determine the desorption efficiency (DE) at least once for each batch of charcoal used for sampling

- in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
- Remove the back sorbent section of the sampler.
 - Inject a known amount of calibration stock solution directly onto the front sorbent section of each charcoal tube.
 - Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
 - Desorb (steps 5 through 8) and analyze together with standards and blanks (steps 11 and 12).
 - Prepare a graph of DE vs. μg acetonitrile recovered.

MEASUREMENT:

- Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1606-1. Inject a 1- μL sample aliquot manually using the solvent flush technique or with an autosampler. NOTE: If peak area is above the linear range of the working standards, dilute with methylene chloride/methanol (85:15), reanalyze and apply the appropriate dilution factor in the calculations.
- Measure peak areas.

CALCULATIONS:

- Determine the mass, μg (corrected for DE), for acetonitrile 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.
- Calculate concentration, C, of acetonitrile in the air volume sampled, V (L):

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

NOTE: $\mu\text{g/L} = \text{mg/m}^3$

EVALUATION OF METHOD:

This method development was based upon NMAM user requests to update and improve problematic gas chromatography methods. After determining that a methylene chloride/methanol (85:15) solution was the best desorption solvent (improved DE recovery and less hazardous than benzene), the desorption efficiency was determined for acetonitrile at 5 levels ranging from 39 μg to 275 μg . The average DE for acetonitrile was determined to be 1.019. The LOD was determined to be 0.8 μg per sample. The precision, as determined from the pooled relative standard deviation (S), was determined to be 0.015 [1]. Acetonitrile storage stability at 0.25 x REL and 5 °C, was acceptable after 30 days with an average recovery of 98.5%.

REFERENCES:

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- NIOSH [1981]. Health Hazard Evaluation Report, HHE 81-359-1058.
- NIOSH [1977]. Acetonitrile: Method S165. In: Taylor, DG, ed. NIOSH Manual of Analytical Methods, 2nd ed., V. 3, U.S. Department of Health, Education, and Welfare (NIOSH) Publication No. 77-157C.

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