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 pp	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.

(1 ppm = 1.68 mg/m³ @ NTP)

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

- Sampler: glass tube, 10 cm, 6-mm ID, flamesealed 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-µL 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 μL ACN = 78.3 μg) 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. µg acetonitrile).
- 10. Determine the desorption efficiency (DE) ateast 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. a. Remove the back sorbent section of the sampler.
- b. Inject a known amount of calibration stock solution directly onto the front sorbent section of each charcoal tube.
- c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
- d. Desorb (steps 5 through 8) and analyze together with standards and blanks (steps 11 and 12).
- e. Prepare a graph of DE vs. µg acetonitrile recovered.

MEASUREMENT:

- 11. 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.
- 12. Measure peak areas.

CALCULATIONS:

- 13. Determine the mass, μg (corrected for DE), for acetonitrile found in the sample front (Wand back (W_b) sorbent sections, and in the average media blank front (B and back (B) sorbent sections. NOTE: If W_b > W_f/10, report breakthrough and possible sample loss.
- 14. Calculate concentration, C, of acetonitrile in the air volume sampled, V (L):

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

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

EVALUATION OF METHOD:

This method development was based upon NMAM user requests to update and improve problematic gas chromatographymethods. 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 μ g to 275 μ g. The average DE for acetonitrile was determined to be 1.019. The LOD was determined to be 0.8g per sample. The precision, as determined from the pooled relative standard deviation (\$, 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:

- [1] Pendergrass SM [1997]. Acetonitrile Backup Data Report, unpublished data, NIOSH/DPSE.
- [2] NIOSH [1977]. Documentation of the NIOSH Validation Tests, S165, U.S. Department of Health, Education, and Welfare (NIOSH) Publ. No. 77-185.
- [3] NIOSH [1981]. Health Hazard Evaluation Report, HHE 81-359-1058.
- [4] 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.

METHOD WRITTEN BY: Stephanie M. Pendergrass, NIOSH/DPSE