ACETIC ACID

CH_3COOH MW: 60.05 CAS: 64-19-7 RTECS: AF1225000

METHOD: 1603, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 10 ppm
NIOSH: 10 ppm; STEL 15 ppm
ACGIH: 10 ppm; STEL 15 ppm
(1 ppm = 2.46 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.049 g/mL @ 25 °C;
BP 118 °C; MP 17 °C;
VP 1.5 kPa (11.4 mm Hg) @ 20 °C;
explosive range 5.4 to 16% v/v in air

SYNONYMS: glacial acetic acid; methane carboxylic acid; ethanoic acid

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 20 L @ 10 ppm
-MAX: 300 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 12.5 to 50 mg/m^3 [1] (173-L samples)

BIAS: 5.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.058 [1]

ACCURACY: ± 15.5%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: acetic acid

DESORPTION: 1 mL formic acid; stand 60 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 230 °C
-DETECTOR: 230 °C
-COLUMN: 130 to 180 °C, 10°/min or 100 °C isothermal

CARRIER GASES: N_2 or He, 60 mL/min

COLUMN: 1 m x 4-mm ID glass; Carbopack B 60/80 mesh/3% Carbowax 20M/0.5% H_3PO_4

CALIBRATION: standard solutions of acetic acid in 88 to 95% formic acid

RANGE: 0.5 to 10 mg per sample

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\hat{S}_r$): 0.007 @ 0.3 to 5 mg per sample [1,3]

APPLICABILITY: The working range is 2 to 40 ppm (5 to 100 mg/m^3) for a 100-L air sample. High (90% RH) humidity during sampling did not cause breakthrough at 39 mg/m^3 for 4.6 hrs [1].

INTERFERENCES: Formic acid contains a small amount of acetic acid which gives a significant blank value. High-purity formic acid must be used to achieve an acceptable detection limit. Alternate columns are 3-m glass, 2-mm ID, 0.3% SP-1000 + 0.3 % H_3PO_4 on Carbopack A and 2.4-m x 2-mm ID glass, 0.3% Carbowax 20M/0.1% H_3PO_4 on Carbopack C.

OTHER METHODS: This revises Method S169 [3].

REAGENTS:

1. Formic acid, aqueous 88% to 95%, high-purity (<0.02% acetic acid).*
   NOTE: The acetic acid content varies from lot to lot of formic acid. Test each lot before use.
2. Glacial acetic acid, reagent grade.*
3. Propionic acid, reagent grade.
4. Eluent: Formic acid, 88% to 95%, with 0.1% v/v propionic acid or other suitable internal standard.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube with plastic caps, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, 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 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (see page 1603-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 10-µL and other convenient sizes for preparing standards, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Care should be taken to avoid skin contact with formic acid and/or acetic acid. These reagents may cause severe burns.

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 1 L/min for a total sample size of 20 to 300 L.
4. Cap the samplers and 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.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 10 mg acetic acid per sample.
   a. Add known amounts of acetic acid to eluent 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 (ratio of peak area of analyte to peak area of internal standard vs. mg acetic acid).

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 acetic acid 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. mg acetic acid 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 1603-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with formic acid, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of acetic acid 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 acetic acid in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S169 was issued on May 13, 1977 [3], and validated over the range 12.5 to 50 mg/m^3 at 22 °C and 767 mm Hg using a 173-L sample [1,4]. Overall precision, $\hat{S}_{rT}$, was 0.058 with an average recovery of 105.4%, representing a non-significant bias. The concentration of acetic acid was independently verified by a total hydrogen analyzer. Desorption efficiency was 0.96 in the range 2.1 to 8.4 mg per sample. Breakthrough (5% on back section) was never achieved and testing was discontinued after 4.6 hrs when 10.4 mg of acetic acid was collected without breakthrough for a 269-L sample at 90% RH. A user check gave an estimated LOD of 0.01 mg per sample and a desorption efficiency of 1.01 in the range 0.3 to 5 mg per sample [2].

REFERENCES:

[1] Backup Data Report for Acetic Acid, prepared under NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods," Order No. PB 275-834 from NTIS, Springfield, VA 22161.
[2] User check, UBTL, NIOSH Sequence #4213-K (unpublished, January 31, 1984).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 4, S169, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

G. David Foley and Y. T. Gagnon, NIOSH/DPSE; S169 originally validated under NIOSH Contract CDC-210-76-0123.