ACETALDEHYDE by HPLC 3507

CH_3CHO MW: 44.05 CAS: 75-07-0 RTECS: AB1925000

METHOD: 3507, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA: 200 ppm
NIOSH: carcinogen; lowest feasible
ACGIH: C 25 ppm; suspect carcinogen
(1 ppm = 1.801 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.78 g/mL @ 20 °C; BP 20.4 °C; MP −123 °C; VP 100 kPa (750 mm Hg; 99% v/v) @ 20 °C; explosive range 4 to 60% in air

SYNONYMS: ethanal; acetic aldehyde

SAMPLING

SAMPLER: LIQUID IN BUBBLER
(midget bubbler containing 15 mL Girard T solution @ pH 4.5)

FLOW RATE: 0.1 to 0.5 L/min

VOL-MIN: 6 L @ 200 ppm
-MAX: 60 L

SHIPMENT: seal bubblers to prevent leakage before shipping; protect from light

SAMPLE STABILITY: 1 week @ 25 °C in dark [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 170 to 670 mg/m^3 [1] (60-L samples)

BIAS: 1.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.053 [1]

ACCURACY: ±14.4%

MEASUREMENT

TECHNIQUE: HPLC, UV

ANALYTE: Girard T derivative

SAMPLE PREPARATION: dilute 5 mL sample to 100 mL with HPLC mobile phase

INJECTION VOLUME: 50 µL

COLUMN: 50 cm × 2-mm ID SS, Zipax SCX

DETECTOR: UV @ 245 nm for acetaldehyde

MOBILE PHASE: Na_2HPO_4/NaH_2PO_4 buffer, 0.75 mL/min

CALIBRATION: standard solutions of acetaldehyde in Girard T reagent

RANGE: 2 to 60 mg per sample [1]

ESTIMATED LOD: 0.1 mg per sample [1]

PRECISION ($\bar{S}_r$): 0.024 @ 11 to 43 mg per sample [1]

APPLICABILITY: The working range is 18 to 372 ppm (33 to 670 mg/m^3) for a 60-L air sample. The method is sensitive enough for short-term exposure sampling and can be used to measure lower concentrations by diluting samples to less than the recommended 100 mL.

INTERFERENCES: Other volatile aldehydes and ketones (e.g., acetone, acrolein, benzaldehyde, formaldehyde, furfural, methyl ethyl ketone, and propionaldehyde) compete for the Girard T reagent which should be kept at a two-fold molar excess over aldehyde concentration. Chromatographic conditions may be adjusted to resolve acetaldehyde from other aldehydes [1].

OTHER METHODS: This revises S345 [2]. Method 2538 is an adaptation of OSHA Method 68, which uses solid sorbent collection and GC analysis. Other reported methods for acetaldehyde use collection in 2,4-dinitrophenylhydrazine solution [3,4].

REAGENTS:

1. Acetaldehyde.*
2. Citric acid.
3. Disodium hydrogen phosphate (Na_2HPO_4).
4. Girard T reagent [(carboxymethyl)-trimethylammonium chloride hydrazide] recrystallized from 95% ethanol.
5. Water, distilled, deionized (DD).
6. Ethanol, 95%.
7. Sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$).
8. Girard T solution: 5.39 g citric acid, 6.63 g Na_2HPO_4, and 16.77 g Girard T reagent diluted to 500 mL with DD water. Store in annealed flask in the dark. Use within two weeks.
9. HPLC mobile phase: 0.22 *M* $Na_2HPO_4 \cdot H_2O$, 0.019 *M* $NaH_2PO_4 \cdot H_2O$ in 20% ethanol. Dissolve and dilute 31.2 g Na_2HPO_4 and 26.2 g $NaH_2PO_4 \cdot H_2O$ to 1 L with DD water. Filter through 5-µm PTFE filter and degas prior to use. Bubble helium through the solution to prevent bacterial growth.
10. Calibration stock solution, 4.32 mg/mL acetaldehyde in 0.2 *M* Girard T solution. Weight 216 mg freshly-distilled acetaldehyde into 50-mL volumetric flask containing 49 mL Girard T solution. Make to volume with Girard T solution. Use within one day.
11. Helium.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: bubbler, glass, midget, with fritted glass stems, annealed,† with PTFE stoppers for shipping.
2. Personal sampling pump, 0.1 to 0.5 L/min, with trap made from midget bubbler with stem broken off and inert, flexible connecting tubing.
3. High pressure liquid chromatograph, with 245-nm UV detector, integrator, and column (page 3507-1) with 50-µL injection loop or autosampler.
4. Syringe, 2-mL, Luer-lock.
5. Distillation apparatus for preparation of high purity acetaldehyde.
6. Flasks, volumetric, 1-L; 10-,50-, and 100-mL; and 500-mL, annealed.†
7. Pipets, 0.02- to 1-mL; 5-, 10-, and 15-mL.
8. Marker, glass.
9. Cylinder, graduated, 250-mL.
10. Filter, 5-µm, PTFE, 37-mm, with holder for liquid filtration.
11. Balance, readable to 0.1 mg.

†Heat in an oxidizing atmosphere at 580 °C.

SPECIAL PRECAUTIONS: Acetaldehyde is extremely volatile and a fire hazard. Cool containers of acetaldehyde to ice bath temperature to reduce pressure buildup and open in an exhaust hood only.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler and trap in line.
2. Add exactly 15 mL Girard T solution to each bubbler using a 15-mL pipet. Mark the initial liquid level in the bubbler with a glass marker. Make impinger-to-trap and trap-to-sampling pump connections with flexible inert tubing.
3. Sample at an accurately known flow rate between 0.1 and 0.5 L/min for a total sample size of 6 to 60 L.

   NOTE: Higher flow rates will cause frothing of the collection medium. If amount of liquid condensed in the trap is greater than 1 mL, collection efficiency of bubbler may be reduced and sample may be invalid.

SAMPLE PREPARATION:

4. Tap bubbler stem lightly against bubbler body to drain contents into the body. If necessary, bring samples up to the 15-mL mark with distilled water. Swirl bubbler to mix contents well. Do not add solution collected in the trap to the sample.
5. Transfer a 5-mL aliquot to a 100-mL flask and bring to volume with HPLC mobile phase.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 0.007 to 4 mg acetaldehyde per mL (0.1 to 60 mg acetaldehyde per sample).
   a. Add known amounts of calibration stock solution to Girard T solution in 10-mL volumetric flasks and dilute to the mark. Dilute 5 mL of each of these solutions to 100 mL with HPLC mobile phase. Prepare at least two blanks in the same manner.
   b. Analyze together with samples and blanks (steps 8 and 9).
   c. Prepare calibration graph (peak area vs. mg acetaldehyde per sample).
7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

8. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 2507-1. Inject 50-µL sample aliquot with injection loop or autosampler.
   NOTE: If peak area is above the linear range of the working standards, dilute with HPLC mobile phase, reanalyze, and apply the appropriate dilution factor in calculations.
9. Measure peak area.

CALCULATIONS:

10. Determine the mass, mg of acetaldehyde found in the sample (*W*), and in the average media blank (*B*).
11. Calculate concentration, *C*, of acetaldehyde in the air volume sampled, *V* (L):

$$C = \frac{(W - B) \times 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S345 was issued on March 16, 1979 [2], and validated over the range 170 to 670 mg/m³ at 21 °C and 756 mm Hg using a 60-L sample [1,5]. Overall precision, $\hat{S}_{rT}$, was 0.053 with an average recovery of 101.2% representing a non-significant bias. The concentration of acetaldehyde was independently verified by calibrated gas chromatograph. Collection efficiency of a single bubbler was determined to be >0.998 when 61-L air samples were taken at 0.5 L/min in atmospheres containing 670 mg/m³ acetaldehyde.

REFERENCES:

[1] Backup Data Report, S345, Acetaldehyde, prepared under NIOSH Contract 210-76-0123 (unpublished).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, S345, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] Kuwata, K., M. Uebori and Y. Yamasaki. *J. Chromatog. Sci.*, *17*, 264–268 (1979).
[4] Lipari, F. and S.J. Swarin. *J. Chromatog.*, *247*, 297–306 (1982).

[5] 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:

Eugene R. Kennedy, Ph.D., NIOSH/DPSE; Method S345 was validated under NIOSH Contract 210-76-0123.