

## VINYL ACETATE

1453



MW: 86.09

CAS: 108-05-4

RTECS: AK0875000

METHOD: 1453, Issue 2

EVALUATION: UNRATED

Issue 1: 15 August 1994

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**OSHA :** no PEL  
**NIOSH:** C 4 ppm/15 min  
**ACGIH:** 10 ppm; STEL 15 ppm  
 (1 ppm = 3.52 mg/m<sup>3</sup> @ NTP)

**PROPERTIES:** liquid; BP 72.7 °C; d 0.934 g/mL @ 20 °C;  
 VP 11.1 kPa (83 mm, Hg, 1.2%) @ 20 °C;  
 vapor density (air = 1) 3.0

**SYNONYMS:** acetic acid, vinyl ester; acetic acid, ethenyl ester; Vinyl A monomer; ethylene ethanoate; 1-acetoxyethylene; ethenyl acetate; vinyl acetate monomer; vinyl ethanoate

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	SOLID SORBENT TUBE (carbon molecular sieve; 160 mg/80 mg; ORBO-92 or equivalent)	<b>TECHNIQUE:</b>	GAS CHROMATOGRAPHY, FID
<b>FLOW RATE:</b>	0.1 to 0.2 L/min	<b>ANALYTE:</b>	vinyl acetate
<b>VOL-MIN:</b>	0.085 L @ 10 ppm	<b>DESORPTION:</b>	1.0 mL 95:5 methylene chloride: methanol
<b>-MAX:</b>	24 L	<b>INJECTION VOLUME:</b>	1 µL
<b>SHIPMENT:</b>	routine	<b>TEMPERATURE-INJECTION:</b>	210 °C
<b>SAMPLE STABILITY:</b>	at least 30 days @ 5 °C [1]	<b>-DETECTOR:</b>	260 °C
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>-COLUMN:</b>	35 °C, 5 min; 5 °C/min to 50 °C; hold 1 min
<b>ACCURACY</b>		<b>COLUMN:</b>	capillary, fused silica, 30 m x 0.32-mm, coated internally with 1.00-µm film 5% – (phenyl)-methylpolysiloxane, or equivalent
<b>RANGE STUDIED:</b>	7.8 to 29.6 mg/m <sup>3</sup> [2]	<b>CALIBRATION:</b>	standard solutions of vinyl acetate in 95:5 methylene chloride: methanol
<b>BIAS:</b>	not determined	<b>RANGE:</b>	3 to 8700 µg per sample [1]
<b>OVERALL PRECISION (S<sub>r</sub>):</b>	not determined	<b>ESTIMATED LOD:</b>	1 µg per sample [1]
<b>ACCURACY:</b>	not determined	<b>PRECISION (S<sub>r</sub>):</b>	0.018 [1]

**APPLICABILITY:** The working range is 0.085 to 247 ppm (0.3 to 870 mg/m<sup>3</sup>) for a 10-L air sample. The method is sensitive enough for ceiling measurements. [1,2]

**INTERFERENCES:** Vinyl acetate that is not stabilized or has been depleted of inhibitor can polymerize. Any substance collected with the vinyl acetate that is capable of reacting with it is a potential interference. Acids, bases, free radical initiators, etc., are capable of reacting with vinyl acetate during and after air sampling.

**OTHER METHODS:** This method is adapted from OSHA Method No. 51 [2] and replaces NIOSH method P&CAM 278 [3].

**REAGENTS:**

1. Vinyl acetate, practical grade, inhibited with 275 to 325 ppm diphenylamine.
2. Methanol, distilled in glass.
3. Methylene chloride\*, distilled in glass.
4. Eluent, 95:5 (v/v) methylene chloride:methanol.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.
8. Calibration stock solution, 74.7 mg/mL. Add 160  $\mu$ L vinyl acetate into 2-mL volumetric flask and dilute to volume with methanol.

\* 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 carbon molecular sieve, Carboxen-564 (front = 160 mg, back = 80 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 backsection. Pressure drop across the tube at 1 L/min airflow must be less than 25 mm/Hg. Tubes are commercially available (Supelco ORBO-92, or equivalent).
2. Personal sampling pump, 0.1 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph with an FID detector, recorder, integrator and column (page 1453-1).
4. Vials, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10- $\mu$ L and other sizes as needed.
6. Volumetric flasks, 2-mL.

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**SPECIAL PRECAUTIONS:** Vinyl acetate can irritate the eyes, nose, and throat. Methylene chloride is an irritant, can be absorbed through the skin, and is a suspect carcinogen [4]. Wear protective clothing. Prepare samples in a hood.

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**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 of 0.1 to 0.2 L/min for a total sample size of 0.75 to 24 L.
4. Cap the samplers. Pack securely for shipment.

**SAMPLE PREPARATION:**

5. Place the front sorbent section along with the glass wool plug in a separate vial from the back sorbent section of the sampler. Discard the foam plugs.
6. Add 1.0 mL of 95:5 methylene chloride:methanol to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

**CALIBRATION AND QUALITY CONTROL:**

8. Calibrate daily with at least six working standards in the range of interest.
  - a. Add known amounts of calibration stock to eluent in 2-mL volumetric flasks. Use serial dilutions as needed to obtain the desired concentration range.
  - b. Analyze with samples and blanks (steps 11 and 12).
  - c. Prepare calibration graph (area vs.  $\mu$ g/mL).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest (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 (2 to 20  $\mu$ L) of a standard mixture of vinyl acetate 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 with working standards (steps 11 and 12).

- e. Prepare a graph of DE vs.  $\mu\text{g}$  vinyl acetate recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

**MEASUREMENT:**

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1453-1. 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 an aliquot of the desorbed liquid with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

**CALCULATIONS:**

13. Determine the mass,  $\mu\text{g}$  (corrected for DE) of vinyl acetate 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 vinyl acetate in the air volume sampled,  $V$  (L):

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

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

**EVALUATION OF METHOD:**

This method was validated by the Organic Methods Development Branch, OSHA Technical Center, Salt Lake City, UT, over the range 187 to 710  $\mu\text{g}$  per sample. The recovery from samples stored 14 days at  $5^\circ\text{C}$  remained above 90% for the same levels. The pooled relative standard deviation ( $\bar{s}_r$ ) obtained from replicate determinations of analytical standards in this range was 0.0073 [2]. Breakthrough studies at 70% RH, sampling an atmosphere of 150  $\text{mg/m}^3$  at 0.19 L/min, indicated a tube capacity of approximately 9 mg of vinyl acetate [2]. In a recent study to update this method, the average desorption efficiency for samples from 2.8  $\mu\text{g}$  to 1120  $\mu\text{g}$  per sample was 98.5% with  $\bar{s}_r = 0.018$  [1]. Recoveries ranged from 96.8% to 102%. Samples stored from 7 to 30 days at  $5^\circ\text{C}$  had a recoveries above 93% [1].

**REFERENCES:**

- [1] Yoon YH, Perkins JB [1998]. Vinyl acetate by GC-FID back-up data report (unpublished). DataChem Laboratories, Salt Lake City, UT.
- [2] OSHA [1988]. OSHA Analytical Methods Manual, USDOL/OSHA Method No. 51, U.S. Occupational Safety and Health Administration, OSHA Analytical Laboratory, American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1988).
- [3] NIOSH [1978]. Vinyl acetate: Method P&CAM 278. In: Taylor DG, ed. NIOSH Manual of Analytical Methods, 2<sup>nd</sup> ed., Vol 4. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175.
- [4] NIOSH [1997]. NIOSH Pocket Guide to Chemical Hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Publ. (NIOSH) 97-140, available as GPO Stock No. 017-033-00483-8 from Superintendent of Documents, Washington, DC 20402.

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