



VINYL ACETATE

1453

CH₃CO₂CHCH₂

MW: 86.09

CAS: 108-05-4

RTECS: AK0875000

METHOD: 1453, Issue 3

EVALUATION: FULL

Issue 1: 15 August 1994

Issue 3: 15 March 2013

OSHA: None
 MSHA: None
 NIOSH: Ceiling 4 ppm (15 min)
 OTHER OELs: [1,2]

PROPERTIES: Liquid; BP 72.7 °C; d 0.934 g/mL @ 20 °C;
 VP 11.8 kPa (89 mm Hg) @ 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	
SAMPLER:	SOLID SORBENT TUBE (carbon molecular sieve; 160 mg/80 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.05 to 0.2 L/min	ANALYTE:	Vinyl acetate
VOL-MIN:	1.5 L @ 4 ppm	DESORPTION:	1.0 mL 95:5% (v/v) methylene chloride/methanol
-MAX:	24 L	INJECTION VOLUME:	1 µL
SHIPMENT:	Routine	TEMPERATURE -INJECTION:	210 °C
SAMPLE STABILITY:	At least 30 days @ 5 °C	-DETECTOR:	260 °C
BLANKS:	2 to 10 field blanks per set	-COLUMN:	35 °C, 5 min; 5 °C/min to 50 °C; hold 1 min
ACCURACY		CARRIER GAS:	Helium, split flow 21.0 mL/min
RANGE STUDIED:	3.7 to 46 mg/m ³ (24-L sample) [3]	COLUMN:	Capillary, fused silica, 30 m x 0.32 mm, coated internally with 1 µm film (5% phenyl) methylpolysiloxane
BIAS:	-0.04	CALIBRATION:	Standard solutions of vinyl acetate in 95:5% (v/v) methylene chloride/methanol
OVERALL PRECISION ($\hat{S}_{r,T}$):	0.064	RANGE:	3 to 1120 µg per sample
ACCURACY:	14.1%	ESTIMATED LOD:	1 µg per sample
		PRECISION (\bar{S}_r):	0.040

APPLICABILITY: The working range is 0.02 to 13.1 ppm (0.07 to 46 mg/m³) for a 24-L air sample. The method is sensitive enough for ceiling measurements.

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 an update for NMAM 1453 first issued on August 15, 1994 [4]. This method is adapted from OSHA Method No. 51 [5] and NIOSH 1453 Issue 2 and replaces NIOSH method P&CAM 278 [6].

REAGENTS:

1. Vinyl acetate*, 99% purity, inhibited with 3 – 22 ppm hydroquinone.
2. Methanol*, distilled in glass.
3. Methylene chloride*, distilled in glass.
4. Desorption solvent, 95%/5% (v/v) methylene chloride/methanol.
5. Helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.
8. Calibration stock solution, 74.7 mg/mL. Add 400 μ L vinyl acetate into a 5-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, (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 back section. Pressure drop across the tube at 1 L/min airflow must be less than 25 mm/Hg. Tubes are commercially available.
2. Personal sampling pump, 0.1 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph with flame ionization detector (GC-FID), column (page 1453-1) and data collector.
4. Vials, 2-mL, with PTFE-lined caps.
5. Syringe, 10- μ L and other sizes as needed.
6. Volumetric flasks, 2- and 5-mL.

SPECIAL PRECAUTIONS: Methylene chloride is an irritant, can be absorbed through the skin, and is a potential occupational carcinogen [7]. Vinyl acetate can irritate the eyes, nose, and throat. Vinyl Acetate is flammable in air (percent by volume): lower, 2.6%; upper, 13.4% [8]. Vinyl acetate can become unstable if the polymerization inhibitor decreases to unsafe levels [8]. Methanol is flammable and a dangerous fire and explosion risk. It is moderately toxic by ingestion and inhalation. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

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 1.5 to 24 L.
NOTE: If high concentrations are expected, multiple samplers may need to be used to collect over an 8 hour period (collect two 4-hour samples for example) in order to not exceed the capacity of the sorbent tube
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% (v/v) 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.
 - a. Add 400 μ L vinyl acetate to methanol in a 5-mL volumetric flask and dilute to the mark. This is the stock calibration solution. 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. $\mu\text{g}/\text{mL}$).
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 μL) of a standard mixture of vinyl acetate directly onto front sorbent section with a microliter syringe.

NOTE: Inject no more than 20 μL onto the sorbent. Dilute stock solution as appropriate.
 - 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. μg 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 desorption solvent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure the peak area of the vinyl acetate signal.

CALCULATIONS:

13. Determine the mass, μg (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):

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

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

EVALUATION OF METHOD:

This method was validated originally by the Organic Methods Development Branch, OSHA Technical Center, Salt Lake City, UT, over the range 187 to 710 μg per sample using Amborsorb[®] XE-347 as sorbent. Breakthrough studies at 70% RH, sampling an atmosphere of 150 mg/m^3 at 0.19 L/min, indicated a tube capacity of approximately 9 mg of vinyl acetate [5].

This media is no longer available and is replaced with Carboxen[®] 564 carbon molecular sieve tubes (OrboTM-92 or equivalent tubes). Using OrboTM-92 media, the average desorption efficiency for samples in this range was 98.5%. Recoveries from samples stored for 30 days at 5 °C were 90 to 110% for samples spiked at 187 and 747 μg per sample. The pooled coefficient of variation obtained from replicate determinations of analytical standards in this range was 0.020 [3,9].

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METHOD REVISED BY:

3rd Issue (2013) Y. T. Gagnon and P. F. O'Connor, CDC/NIOSH, Cincinnati, Ohio.

2nd Issue (1998) Y. H. Yoon, Ph.D. and J. B. Perkins, DataChem Laboratories, Inc., Salt Lake City, Utah.

1st Issue (1994) A. A. Grote, CDC/NIOSH, Cincinnati, Ohio.

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