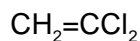


VINYLDENE CHLORIDE

1015



MW: 96.94

CAS: 75-35-4

RTECS: KV9275000

METHOD: 1015, Issue 2

EVALUATION: FULL

Issue 1: 15 August 1987

Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: lowest feasible; carcinogen
ACGIH: 5 ppm; STEL 20 ppm; carcinogen
 (1 ppm = 3.96 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.213 g/mL @ 20 °C;
 BP 31.7 °C; MP -122.5 °C; flammable

SYNONYMS: 1,1-dichloroethene; 1,1-dichloroethylene.

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	vinylidene chloride
VOL-MIN:	2.5 L @ 1 ppm	DESORPTION:	1 mL CS ₂ ; stand 30 min
-MAX:	7 L	INJECTION	
SHIPMENT:	routine	VOLUME:	5 µL
SAMPLE STABILITY:	7 days @ 25 °C 21 days @ 5 °C [2]	TEMPERATURE-INJECTION:	150 °C
BLANKS:	2 to 10 field blanks per set	-DETECTOR:	200 °C
		-COLUMN:	65 °C
		CARRIER GAS:	He or N ₂ , 30 mL/min
		COLUMN:	silanized glass, 3 m x 6-mm OD packed with Durapak OPN 100/120 mesh or equivalent
		CALIBRATION:	standard solutions of vinylidene chloride in CS ₂
		RANGE:	10 to 100 µg per sample
		ESTIMATED LOD:	7 µg per sample [2]
		PRECISION (\hat{S}_r):	0.048 @ 12 to 85 µg per sample [2]
ACCURACY			
RANGE STUDIED:	7.6 to 10 mg/m ³ [2]		
BIAS:	- 0.05		
OVERALL PRECISION (\hat{S}_{rT}):	0.069		
ACCURACY:	± 18.6%		

APPLICABILITY: The working range is 0.5 to 5 ppm (2 to 20 mg/m³) for a 5-L air sample. The capacity of charcoal for vinylidene chloride decreased rapidly with increasing relative humidity and was also found to be a function of concentration.

INTERFERENCES: The GC column will not separate vinyl chloride and carbon disulfide. Other GC packings that separate vinyl chloride and CS₂ may not separate vinylidene chloride and CS₂. If determination of both of these monomers is to be performed, a capillary column such as a 105 meter Rtx® 502.2 would be required.

OTHER METHODS: The revises P&CAM 266 [1].

REAGENTS:

1. Carbon disulfide (CS₂), chromatographic quality.*
2. Vinylidene chloride, 99%.*
3. Cyclohexane.
4. Calibration stock solution, 10 mg/mL. Dissolve 0.1 g vinylidene chloride in CS₂ to make 10 mL solution. Prepare in duplicate.
5. DE stock solution, 10 mg/mL. Dissolve 0.1 g vinylidene chloride in cyclohexane to make 10 mL solution. Prepare in duplicate.
6. Nitrogen or helium, purified.
7. Hydrogen, prepurified.
8. Air, filtered.

* 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 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 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1015-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipets, volumetric, 10- to 100-μL, and 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Vinylidene chloride is a suspect carcinogen [3]. Carbon disulfide and vinylidene chloride are toxic and severe fire and explosion hazards (flash point = -30 °C for CS₂ and -10 °C for vinylidene chloride). Work with both compounds only in a hood. Vinylidene chloride polymerizes above 0 °C, especially in the presence of oxygen or catalysts; explosive reaction products may result [4].

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 0.2 L/min for a total sample size of 2.5 to 7 L.
4. Cap the samplers. Pack securely for shipment.
NOTE: Refrigerated shipment will decrease migration of vinylidene chloride to back sorbent section.

SAMPLE PREPARATION:

5. Allow samples to equilibrate to room temperature before uncapping. Place the front and back sorbent sections of the sampler tube in separate vials.
6. Add 1.0 mL CS₂ to each vial. Cap vial immediately.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
 - a. Add known amounts of calibration stock solution to CS₂ in 10-mL volumetric flasks and dilute to the mark. Prepare working standards in the range 10 to 100 µg vinylidene chloride/mL.
 - b. Analyze with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph (peak area or peak height vs. µg vinylidene chloride).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the range of interest. 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 10 µL) of DE stock solution 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. µg vinylidene chloride recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 1015-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If response is above the linear range of the working standards, dilute with CS₂, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area or peak height.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of vinylidene chloride 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 vinylidene chloride in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method P&CAM 266 was issued on November 21, 1977 [1]. The method was tested with sample loadings between 13 and 85 µg vinylidene chloride per charcoal tube [2]. The samples were collected from atmospheres containing vinylidene chloride in the range 7.6 to 10.0 mg/m³ and having relative humidity in the range 10 to 95%. The pooled relative standard deviation of the measurement was 4.8% for the analysis of 36 samples over the range 12 to 85 µg vinylidene chloride per sample. Desorption efficiency was determined to be 80% for a loading of 7 µg vinylidene chloride at a vinylidene chloride concentration of 10 mg/m³ and high relative humidity; the breakthrough volume was 7.3 L when sampling at 0.2 L/min from this atmosphere. At 87% relative humidity, the breakthrough volume was 10% of the breakthrough volume at 10% relative humidity.

REFERENCES:

- [1] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 266, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
- [2] Foerst, D. "A Sampling and Analytical Method for Vinylidene Chloride in Air," Am. Ind. Hyg. Assoc. J., 40: 888-893 (1979).
- [3] NIOSH/OSHA Current Intelligence Bulletin 28, Vinyl Halides Carcinogenicity, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-102 (1978).
- [4] Merck Index, 11th ed., Merck & Co., Rahway, NJ (1989).

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