

1,3-CYCLOPENTADIENE

2523

C₅H₆

MW: 66.10

CAS: 542-92-7

RTECS: GY1000000

METHOD: 2523, Issue 2

EVALUATION: FULL

Issue 1: 15 May 1985

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OSHA : 75 ppm
NIOSH: 75 ppm
ACGIH: TWA 75 ppm
 (1 ppm = 2.70 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.8021 g/mL @ 20 °C;
 BP 42 °C; MP - 85 °C; dimerizes to solid
 (MP 32.5 °C); VP not available

SYNONYMS: none

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (maleic anhydride on Chromosorb 104, 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.05 L/min	ANALYTE:	1,3-cyclopentadiene-maleic anhydride adduct (see REAGENTS, 1.)
VOL-MIN:	1 L @ 75 ppm	DESORPTION:	10 mL ethyl acetate; stand 15 min
-MAX:	5 L	INJECTION VOLUME:	5 µL
SHIPMENT:	routine	TEMPERATURE-INJECTION:	200 °C
SAMPLE STABILITY:	at least 1 week @ 25 °C [1]	-DETECTOR:	250 °C
BLANKS:	2 to 10 field blanks per set	-COLUMN:	155 °C
ACCURACY		CARRIER GAS:	N ₂ , 30 mL/min
RANGE STUDIED:	73 to 370 mg/m ³ [1]	COLUMN:	3 m x 3-mm OD stainless steel packed with 5% OV-17 on 100/120 mesh Chromosorb WHP
BIAS:	3.6% [1]	CALIBRATION:	analyte in ethyl acetate
OVERALL PRECISION ($\hat{S}_{r,t}$):	0.66 [1]	RANGE:	0.2 to 1.2 mg 1,3-cyclopentadiene per sample
ACCURACY:	± 16.5%	ESTIMATED LOD:	0.01 mg per sample [1]
		PRECISION ($\hat{S}_{\bar{S}}$):	0.031 @ 0.3 to 1.2 mg per sample [1]

APPLICABILITY: The working range is 25 to 150 ppm (67 to 400 mg/m³) for a 3-L air sample, based on sampler capacity at high relative humidity.

INTERFERENCES: None identified.

OTHER METHODS: This revises P&CAM 294 [2].

REAGENTS:

1. Analyte: 5-norbornene-2,3-dicarboxylic anhydride (Eastman Chemicals).
NOTE: This is the Diels-Alder adduct formed by reaction of 1,3-cyclopentadiene and maleic anhydride.* Both endo- and exo-forms are present.
2. Calibration stock solution, 50 mg/mL.
Dissolve 500 mg analyte in ethyl acetate* to make 10 mL solution.
3. Acetone.*
4. Ethyl acetate.*
5. Maleic anhydride.*
6. Sorbent: acrylonitrile-divinyl benzene copolymer, 60/80 mesh, with surface area 100 to 200 m²/g (Chromosorb 104, Johns-Manville).
7. Nitrogen, purified.
8. Hydrogen, prepurified.
9. Air filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 8.5 cm, 6-mm OD, 4-mm ID, with plastic caps, containing two sections of coated sorbent (front = 100 mg; back = 50 mg), held in place and separated with glass wool plugs. Prior to packing, rinse the empty tube with acetone and dry to eliminate static adhesion of sorbent onto the tube wall. Pressure drop across sampler \leq 2.5 kPa (25 cm water) at 0.05 L/min airflow.
NOTE: See APPENDIX for preparation of coated sorbent. Use the coated sorbent within 20 days of preparation. Tubes available by special order (SKC, Inc.).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph with FID, integrator, and column (page 2523-1).
4. Vials, 20-mL, with PTFE-lined caps.
5. Flask, round-bottom, 250-mL.
6. Rotary evaporator.
7. Vacuum oven.
8. Syringes, 10- μ L, readable to 0.1 μ L.
9. Pipet, volumetric, 10-mL, with pipet bulb.
10. Pipets, micro, 10- to 1000- μ L.

SPECIAL PRECAUTIONS: Maleic anhydride is a powerful irritant and can cause burns and pulmonary edema. Avoid exposure to concentrated vapor. Avoid contact with skin, eyes and clothing. Acetone and ethyl acetate are serious fire risks.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Uncap 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 0.05 L/min for a total sample size of 1 to 5 L.
4. Cap the samplers. 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 plugs.
6. Add 10.0 mL ethyl acetate to each vial. Attach cap to each vial.
7. Allow to stand 15 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 1.2 mg 1,3-cyclopentadiene (0.03 to 3 mg analyte) per sample.
 - a. Add known amounts of calibration stock solution, or a dilution thereof, to ethyl acetate 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 (peak area vs. mg analyte).
9. Determine recovery at least once for each lot of coated sorbent 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 (1 to 20 μ L) of calibration stock solution, or a dilution thereof, directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. Allow to stand overnight.
 - d. Prepare (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
 - e. Prepare a graph of recovery vs. mg analyte 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 2523-1. Inject sample aliquot manually using solvent flush technique or with autosampler. $t_r = 6.5$ min under these conditions.
NOTE: If peak area is above the linear range of the working standards, dilute with ethyl acetate, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for recovery) of analyte 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 1,3-cyclopentadiene in the air volume sampled, V (L) applying the factor 0.403 (MW of 1,3-cyclopentadiene/MW of analyte) for conversion of adduct to 1,3-cyclopentadiene:

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 0.403 \cdot 10^3}{V} \text{ mg / m}^3$$

EVALUATION OF METHOD:

P&CAM 294 [2] was issued in 1978 and evaluated over the range 73.4 to 370 mg/m^3 [1,3]. The average recovery for 3-L air samples was 1.036 which represents a non-significant bias. Test atmospheres were generated using a syringe pump delivering 3a,4,7,7a-tetrahydro-4,7-methano-1H-indene (dicyclopentadiene) to a glass pyrolysis tube which thermally decomposed (375 $^{\circ}$ C) the dimer to monomer. The concentrations of 1,3-cyclopentadiene were confirmed by collecting samples

from the generator in bubblers containing 15 mL solution of 74 mg/mL maleic anhydride in ethyl acetate and analysis by GC/FID. Samples were stored at room temperature for one week and found to be stable. Recovery averaged 0.99 in the range 0.75 to 3 mg analyte (equivalent to 0.3 to 1.2 mg 1,3-cyclopentadiene) per sample. Breakthrough capacity exceeded 3.8 mg 1,3-cyclopentadiene when sampling with freshly prepared (four-day old) coated sorbent and was 1.6 mg with the same batch of coated sorbent 24 days after preparation under similar sampling conditions (360 mg/m³, 0.045 L/min, >80% RH).

REFERENCES:

- [1] Backup Data Report, P&CAM 294 (NIOSH, unpublished, October 13, 1978).
- [2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 294, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
- [3] 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).
- [4] Failure Report, S83 (NIOSH, unpublished, April 14, 1978).

METHOD WRITTEN (REVISED) BY:

Ardith Grote, NIOSH/DPSE; P&CAM 294 originally developed under NIOSH Contract 210-76-0123.

APPENDIX:

PREPARATION OF COATED SORBENT

1. Add 25 g of sorbent to a 250-mL round-bottom flask.
NOTE: This will make enough coated sorbent to pack about 150 tubes.
2. Add 100 mL acetone, swirl, and allow sorbent to settle. Decant the acetone. Repeat twice.
NOTE: This removes the fines and washes the sorbent.
3. Remove the remaining solvent in a rotary evaporator. Dry in a vacuum oven at 30 °C for 1 h.
4. Weigh the dry sorbent and place it in a 250-mL round-bottom flask.
5. Weigh an amount of maleic anhydride equivalent to 20% of the weight of the sorbent and dissolve it in 50 mL acetone.
6. Add the maleic anhydride solution to the sorbent, swirl, and remove the solvent in a rotary evaporator. Dry in a vacuum oven at 30 °C for 15 min. Use the coated sorbent within 20 days of preparation.
NOTE: Refrigeration in a sealed container may prolong shelf life [1,4].