



Dicyclopentadiene

Method number: PV2098

Target Concentration: 5 ppm. There is no OSHA PEL for dicyclopentadiene. However, ACGIH has recommended a standard of 5 ppm. For the purpose of this study, the target concentration of 27 mg/m³ will be used (this is equivalent to 5 ppm assuming a 10-liter air volume).

Procedure: Samples are collected by drawing a known volume of air through a charcoal tube. Samples are desorbed with carbon disulfide and analyzed by gas chromatography using a flame ionization detector.

Air volume and sampling rate studied: 100 minutes at 0.1 L/min (10 L)

Status of method: Partially validated method. This method has been only partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of Procedure

The OSHA Analytical Laboratory recently received a set of field samples that required analysis for dicyclopentadiene. The air samples had been collected with isopropyl alcohol impingers. Due to the inconvenience of sampling with an impinger, we set out to find a solid sorbent tube to collect the dicyclopentadiene. Similar pentadiene compounds have been collected on solid sorbent tubes, desorbed with a suitable solvent, and analyzed by gas chromatography using a flame ionization detector. This procedure was tried for dicyclopentadiene using SKC Lot 120 charcoal tube and desorbing with carbon disulfide and was quite adequate.

1.1.2 Toxic effects. (This section is for information only and should not be taken as the basis of OSHA policy).

Dicyclopentadiene is classified as moderately toxic. The LD₅₀ for dicyclopentadiene given orally to rats is 353 mg/kg (Ref. 5.1).

1.1.3 Potential workplace exposure.

No workplace exposure level could be found in the literature but dicyclopentadiene is used as an intermediate for cyclodiene pesticides. It is also used as a fire retardant and as a curing agent for elastomers (Ref. 5.2).

1.1.4 Physical properties (Ref. 5.2)

Synonyms:	Bicyclopentadiene; 1,3-cyclopentadiene, dimer; DCPD
Molecular weight:	132.21
Boiling point:	64-65 °C at 14 mmHg
Melting point:	32 °C
Density:	0.9302 at 35 °C/4 °C
Flash point:	90 °F (OC)
Solubility:	Soluble in alcohol, acetic acid, carbon tetrachloride, and petroleum ether. Very soluble in ether. Insoluble in water at 20 °C
Description:	Colorless liquid, terpene-like odor
Molecular formula:	C ₁₀ H ₁₂

Structure:



1.2 Limit defining parameters

1.2.1 Detection limit

Detection limit of the analytical procedure is 2.1 ng/injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

1.2.2 Sensitivity

The sensitivity of the analytical procedure over a concentration range of 0.025 to 0.25 µg/mL is 532480 area units per µg/mL of dicyclopentadiene. The sensitivity is determined by the slope of the calibration curve (See Figure 3.5.3).

1.3 Advantages

- 1.3.1 The sampling procedure is convenient.
- 1.3.2 The analytical method is reproducible and sensitive.
- 1.3.3 Reanalysis of samples is possible.
- 1.3.4 It may be possible to analyze other compounds at the same time.
- 1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

None known.

2 Sampling procedure

2.1 Apparatus

- 2.1.1 A calibrated personal sampling pump whose flow can be determined within ±5% of the recommended flow with sample tube in line.
- 2.1.2 SKC Lot 120 charcoal tubes were used: glass tube with both ends flame sealed, 7-cm x 6-mm o.d. and 4-mm i.d., containing 2 sections of coconut shell charcoal separated by a 2-mm portion of urethane foam. The adsorbing section contains 100-mg of charcoal, the backup section 50-mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silanized glass wool is placed in front of the adsorbing section.

2.2 Reagents

None required.

2.3 Sampling technique

- 2.3.1 The ends of the charcoal tubes are opened immediately before sampling.
- 2.3.2 Connect the charcoal tube to the sampling pump with flexible tubing.
- 2.3.3 Tubes should be placed in a vertical position to minimize channeling, with the backup section of charcoal towards the pump.
- 2.3.4 Air being sampled should not pass through any hose or tubing before entering the charcoal tubes.
- 2.3.5 Seal the charcoal tubes with plastic caps immediately after sampling. Seal each sample lengthwise with a Form OSHA-21 seal.

- 2.3.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, and transport) except that no air is drawn through it.
- 2.3.7 Transport the samples (and corresponding paperwork) to the laboratory for analysis.
- 2.3.8 If bulk samples are submitted for analysis, they should be transported in glass containers with PTFE-lined caps. These samples must not be put in the same container used for the charcoal tubes.

2.4 Desorption efficiency

Six charcoal tubes each were spiked with dicyclopentadiene at $\frac{1}{2}x$, $1x$, and $2x$ the target concentration and refrigerated over night. The charcoal from each tube was placed in separate, 2-mL vials and desorbed with 1 mL carbon disulfide containing 1 μ L/mL ethyl benzene as the internal standard. The samples were then analyzed by gas chromatography with a flame ionization detector.

Table 2.4
Desorption Efficiency

sample #	% recovered		
	$\frac{1}{2}x$ target 116.3 μ g	$1x$ target 232.6 μ g	$2x$ target 465.2 μ g
1	87.1	98.3	91.4
2	93.0	94.6	92.3
3	92.7	98.1	94.9
4	90.9	97.5	90.8
5	89.9	94.7	91.5
6	93.6	96.6	90.4
average	91.7%	96.6%	91.9%

2.5 Retention efficiency

Six charcoal tubes were spiked with 465.2 μ g of dicyclopentadiene. Ten liters of humid air (about 85% relative humidity) were drawn through each tube at 0.1 L/min. The tubes were desorbed with 1 mL of carbon disulfide containing 1 μ L/mL ethyl benzene internal standard and then analyzed by gas chromatography with a flame ionization detector.

Table 2.5
Retention Efficiency

sample #	% recovered
1	94.0
2	94.0
3	95.7
4	93.4
5	94.1
6	93.7
average	94.2%

2.6 Sample storage

Twelve charcoal tubes were spiked with 232.6 μ g of dicyclopentadiene. Six tubes were stored in a refrigerator for ten days and the other six tubes were stored at ambient temperature for ten days. The tubes were then opened, desorbed and analyzed.

Table 2.6
Storage Study

days stored	% recovered	
	refrigerated	ambient
10	94.5	92.5
10	94.6	92.6
10	94.0	93.2
10	94.6	92.9
10	95.0	93.4
10	94.2	94.1
average	94.5%	93.1%

2.7 Air volume and sampling rate studied.

2.7.1 The air volume was 10.0 liters.

2.7.2 The sampling rate was 0.1 liters per minute.

2.8 Interferences

It is important to be aware of other components in the atmosphere which may interfere with the collection of the analyte.

2.9 Safety precautions

2.9.1 Care must be taken when opening the sealed ends of the charcoal tubes to avoid serious cuts to the hands.

2.9.2 Safety glasses should be worn when opening the sealed ends of the charcoal tubes to avoid injury to the eyes from glass splinters.

2.9.3 Attach the sampling equipment to the worker in such a manner that it will not interfere with the work performance or safety of the employee.

2.9.4 Follow all safety practices that apply to the work area being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame ionization detector.

3.1.2 GC column capable of separating the analyte and an internal standard from any interference. The column used was a 12-ft × 1/8-in. stainless steel column packed with 10% FFAP on 80/100 Chromosorb WAW.

3.1.3 An electronic integrator or some other suitable method for measuring peak areas.

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 A 1- μ L syringe for sample injection.

3.1.6 Pipettes for dispensing the desorbing solution. The Glenco 1-mL dispenser was used in this method.

3.1.7 Volumetric flasks, 5 mL, and other convenient sizes for preparing standards.

3.1.8 Pipettes of a convenient size for standard preparation.

3.2 Reagents

3.2.1 Carbon disulfide, chromatographic grade.

3.2.2 Dicyclopentadiene, reagent grade.

3.2.3 An internal standard, such as ethyl benzene, reagent grade.

3.2.4 Purified GC grade nitrogen or helium, hydrogen, and air.

3.2.5 Desorbing reagent - 1 µL internal standard/1 mL carbon disulfide.

3.3 Standard preparation

3.3.1 Standards are prepared by diluting a known quantity of the analyte in the desorbing solution.

3.3.2 A concentration of 0.25 µL/mL of the analyte in the desorbing solution is equivalent to 4.45 ppm for a 10.0 liter air volume, using the desorption efficiency of 96.6%.

3.3.3 At least two separate standards should be made.

3.4 Sample preparation

3.4.1 Sample tubes are opened and the front and back sections of each tube are placed in a separate 2-mL vial.

3.4.2 Each section is desorbed with 1 mL of the desorbing reagent.

3.4.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.5 Analysis

3.5.1 GC conditions

<u>Flow Rates</u>	<u>(mL/min)</u>	<u>Temperature</u>	<u>(°C)</u>
Nitrogen:	20	Injector:	200
Hydrogen:	22	Detector:	250
Air:	240	Column:	120
<u>Injection:</u>	0.9 µL		
<u>Elution time:</u>	5.7 minutes		

Chromatogram:

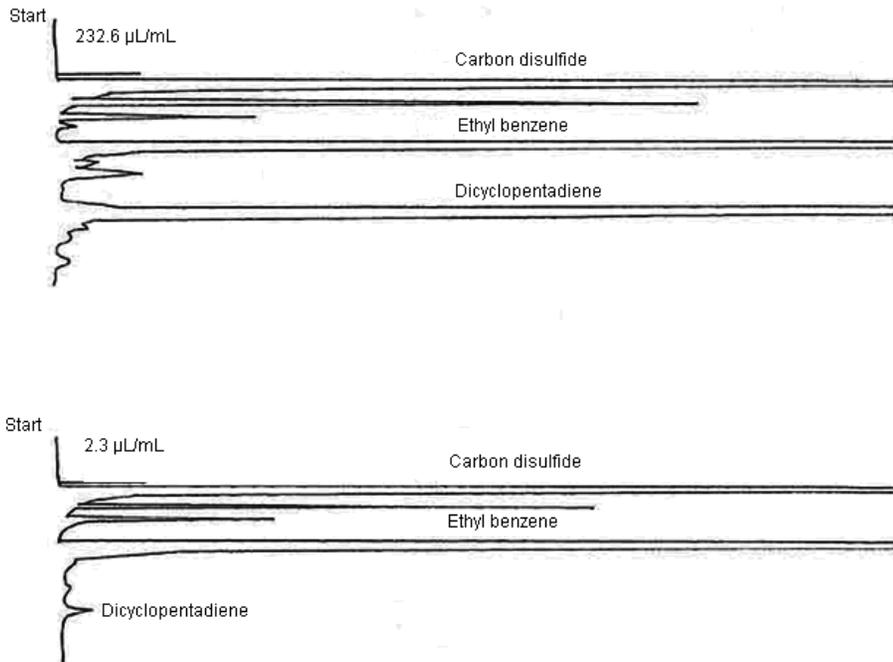
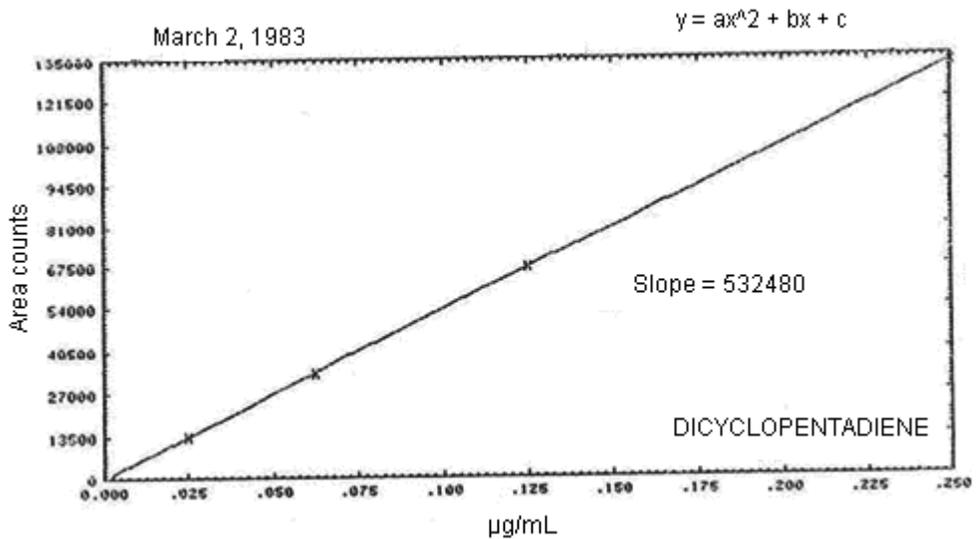


Figure 3.5.1. Chromatogram of Dicyclopentadiene at the Target Concentration and Detection Limit.

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.5.3 An internal standard procedure is used. The integrator is calibrated to report ppm based on the concentration of the analytical standards, a 10.0 liter air volume, and the desorption efficiency. A plot of dicyclopentadiene at different concentrations shows it to be very linear.



3.6 Interferences (analytical)

- 3.6.1 Any compound having the general retention time of the analyte or the internal standard used is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted, if necessary, so these interferences will pose no problems.
- 3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the PEL should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

- 3.7.1 To calculate the ppm of analyte in standards based on 10-liter air sample, and 1 mL desorbing solution.

$$\text{mass of analyte, } \mu\text{g} = \frac{(\mu\text{g} / \text{mL})(\text{desorption volume, mL})}{(\text{desorption efficiency, decimal})}$$

$$\text{moles of analyte} = \frac{(\text{mass of analyte, } \mu\text{g})(1\text{g})}{(\text{molecular weight})(10^6 \mu\text{g})}$$

$$\text{volume of analyte} = (\text{moles of analyte})(\text{molar volume})$$

$$\text{ppm} = \frac{(\text{volume of analyte})(10^6)^*}{(\text{air volume, L})}$$

* All units must cancel.

- 3.7.3 The above equations can be combined to give the following formula for calculating the concentration of dicyclopentadiene in the sample.

$$\text{ppm} = \frac{(\mu\text{g} / \text{mL})(\text{DV})(24.46)}{(\text{L})(\text{DE})(\text{MW})}$$

Where:

$\mu\text{g}/\text{mL}$ = concentration of analyte in sample
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
MW = Molecular weight (g/mole)
DV = Desorption volume, mL
10 L = Air volume, L
DE = Desorption efficiency, decimal

- 3.7.3 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

- 3.8.1 All handling of solvents should be done in a hood.
- 3.8.2 Avoid skin contact with all solvents.
- 3.8.3 Wear safety glasses, gloves, and lab coat at all times in laboratory areas.

4 Recommendations for further study

Further work should be done to fully validate this method.

5 References

- 5.1 Cysewski, S.J. et al, "Archive of Environmental Contamination Toxicology," 10(5); 605-15, (1981).
- 5.2 "Toxicology Data Bank," (online computerized database), National Library of Medicine.