

C₁₀H₁₆

MW: 136.24

CAS: Table 1

RTECS: Table 1

METHOD: 1552, Issue 1

EVALUATION: PARTIAL

Issue 1: 15 May 1996

OSHA : no PEL

NIOSH: no REL

ACGIH: no TLV

(1 ppm = 5.57 mg/m³ @ NTP)

PROPERTIES: Table 1

NAMES AND SYNONYMS: (1) limonene, d-,l-: cinene
 (2) α-pinene: 2-pinene
 (3) β-pinene: nopinene, pseudopinene
 (4) 3-carene: isodiprene

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	ANALYTES:	limonene, α-pinene, β-pinene, 3-carene
VOL-MIN:	2 L @ 100 mg/m ³ [1,2]	DESORPTION:	1 mL CS ₂ , stand 30 min [4]
-MAX:	30 L @ 100 mg/m ³ [1,2]	INJECTION VOLUME:	1 μL
SHIPMENT:	routine	TEMPERATURE-INJECTION:	250 °C
SAMPLE STABILITY:	30 days @ 5 °C [3]	-DETECTOR:	300 °C
BLANKS:	2 to 10 field blanks per set	-COLUMN:	35 to 135 °C @ 10 °C/min
ACCURACY		CARRIER GAS:	He, 30 mL/min
RANGE STUDIED:	not studied	COLUMN:	Stabilwax, 30 m, 0.53-mm ID, 3-μm film
BIAS:	not determined	CALIBRATION:	standard solutions of terpenes in CS ₂
OVERALL PRECISION ($\hat{S}_{r,r}$):	not determined	RANGE:	2 to 840 μg/sample [1-3]
ACCURACY:	not determined	ESTIMATED LOD:	Table 2
		PRECISION ($\hat{S}_{r,r}$):	Table 2

APPLICABILITY:The working range is 0.02 to 36 ppm (0.13 to 200 mg/m³) for a 15-L sample. This method may be applicable to other monocyclic and dicyclic terpenes that exhibit acceptable stability on charcoal tubes and in carbon disulfide (desorption solvent).

INTERFERENCES:Other terpenes or compounds with similar retention times may interfere. There is also the possibility of interfering peaks from the decompositional rearrangement of some terpenes from prolonged storage on charcoal or in carbon disulfide [3,4].

OTHER METHODS: This is a new method for the determination of four terpenes. Other researchers have developed methods for individual terpene compounds [1, 2].

REAGENTS:

1. Carbon disulfide (CS₂), chromatographic grade.*
2. Limonene, reagent grade.*
3. α-Pinene, reagent grade.*
4. β-Pinene, reagent grade.*
5. 3-Carene, reagent grade.*
6. Helium, prepurified.
7. Hydrogen, purified.
8. Air, filtered, dry.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, 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.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph with flame ionization detector, integrator, and column (p. 1552-1).
4. Vials, 2-mL, glass, PTFE-lined crimp caps.
5. Syringes, 10- and 25-μL, readable to 0.1 μL.
6. Pipets, various sizes for standard preparation.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic, flammable, and explosive (flash point = -30 °C). Terpenes are flammable and are considered irritants. Perform all work 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 between 0.01 and 0.2 L/min for a total sample size of 2 to 30 L.
4. Cap the samplers with plastic caps and pack securely for shipment.
NOTE: Store samples at 5 °C. Analyze as soon as possible to reduce risk of analyte rearrangement (see EVALUATION OF METHOD).

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS₂ to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range from 0.2 to 1000 μg per sample.
 - a. Add known amounts of analyte to CS₂ in 10-mL volumetric flasks and dilute to the mark.
 - b. Analyze together with samples and blanks (steps 11 and 12).
 - c. Prepare a calibration graph for each analyte (peak area or peak height vs. μg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal 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 of analyte 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 together with working standards and blanks (steps 11 and 12).
 - e. Prepare graph of DE vs. μg analyte recovered for each analyte.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration and DE graphs are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1552-1. Inject 1- μ L sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μ g (corrected for DE) 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 analyte 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:

Sampling and analytical conditions for each terpene were derived from independent methods [1-3]. Recovery was determined by spiking coconut shell charcoal tubes with known amounts of each analyte in CS₂ solution. Six samplers were spiked at each of three levels (20-, 60-, and 100- μ g) for each terpene (18 samples for each analyte). Recovery, LOD, and stability data are listed in Table 2. Mean recoveries ranged from 93.4% to 97.6% with precisions, as calculated from the pooled relative standard deviations (\bar{S}_r), of <2% for each analyte. The LODs ranged from 0.3 to 0.6 μ g per sample. Samples stored at 5 °C were stable for 30 days.

During the development of this method for terpenes, it was found that some terpenes (e.g., camphene, myrcene, γ -terpinene), upon exposure to activated charcoal and CS₂ exhibit rearrangement or decomposition to other terpenes or related compounds. Because γ -terpinene exhibited an acceptable recovery, it was selected for a study to determine the degree of decomposition/rearrangement. The difference between standards aged 21 days and freshly prepared standards was not significant. However, spiked charcoal tubes desorbed with and allowed to stand in CS₂ for 1 day gave a recovery of γ -terpinene of 77.4% with remainder converting to 1-methyl-3-methylethyl benzene. Spiked charcoal tubes aged for 30 days and then desorbed in CS₂ gave a γ -terpinene recovery of 12.4% with 87.6% converting to 1-methyl-3-methylethyl benzene [3].

REFERENCES:

- [1] Searle E [1989]. Determination of airborne limonene vapour by charcoal tube sampling and gas-liquid chromatographic analysis. *Analyst* 114:113-114.
- [2] Konttinen S, Kurttio P, Raunemaa T, Kalliokoski P [1989]. Comparison of methods for analyzing occupational monoterpene exposures. *Chemosphere* 19:1483-1488.
- [3] Pendergrass SM [1992]. Terpene method development. Unpublished report, NIOSH, DPSE, MRSB.
- [4] Stromvall M, Petersson G [1992]. Protection of terpenes against oxidative and acid decomposition on adsorbent cartridges. *J Chromatogr* 589:385-389.

[5] Kauppinen T[1986]. Occupational exposure to chemical agents in the plywood industry. *Ann Occup Hyg* 30:19-29.

METHOD WRITTEN BY:

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TABLE 1. TERPENES GENERAL INFORMATION

Analyte	CAS #	RTECS #	Properties
limonene (d- & l-)	138-86-3	OS8100000	liquid; d 0.84 g/mL @ 20 °C; BP 175 to 178 °C; FP -95.5 °C; RI 1.474 @ 20 °C; vp 0.280 kPa (2.1 mm Hg) @ 20 °C; vapor density (air=1) 4.7
α-pinene	80-56-8	DT7000000	liquid; d 0.8592 g/mL @ 20 °C; BP 156 to 160 °C; FP -40 °C; RI 1.4663 @ 20 °C
β-pinene	127-91-3	DT5077000	liquid; d 0.8654 g/mL @ 20 °C; BP 164 to 166 °C; RI 1.4739 @ 21 °C
3-carene	13466-78-9	FH8400000	liquid; d 0.8668 g/mL @ 15 °C; BP 168 to 169 °C; RI 1.4723 @ 20 °C

TABLE 2. TERPENE DATA FROM SPIKED SAMPLES

Analyte	n	Recovery (%)	Precision (\bar{S}_r) ^a	LOD (µg/sample)	Stability - 30 Day storage (% Recovery)	(\bar{S}) ^b
limonene	18	94.9	0.019	0.4	93.2	0.029
3-carene	18	95.4	0.015	0.3	89.0	0.031
α-pinene	18	93.4	0.016	0.6	92.2	0.093
β-pinene	18	97.6	0.019	0.4	95.4	0.045

^a Pooled relative standard deviation for 6 samples at each of 3 concentration levels.

^b Relative standard deviation for 6 samples.