ca. $C_{10}H_{16}$ (e.g., pinene, dipentene, and other terpenes) MW: ca. 136 CAS: 8006-64-2 RTECS: YO8400000

METHOD: 1551, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 100 ppm
NIOSH: 100 ppm; Group III Pesticide
ACGIH: 100 ppm
(1 ppm = 5.60 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.860 to 0.875 g/mL @ 15 °C; BP 150 to 180 °C; VP 0.67 kPa (5 mm Hg; 6580 ppm) @ 20 °C; lower explosive limit 0.8% v/v in air

SYNONYMS: gumspirits, wood turpentine; oil of turpentine.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required, 1 to 10 mL

ACCURACY

RANGE STUDIED: 264 to 1107 mg/m^3 [1] (10-L samples)

BIAS: - 1.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.055 [1]

ACCURACY: ± 11.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: turpentine (all components)

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 1 to 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 50 to 250 °C @ 8°/min

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 6-mm, 10% SP-2100 on 80/100 mesh Supelcoport or 30 m x 0.32 mm ID fused silica capillary coated with DB-1

CALIBRATION: standard solutions of bulk turpentine in CS_2

RANGE: 0.5 to 20 mg per sample

ESTIMATED LOD: 0.1 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.013 [1]

APPLICABILITY: The working range is 9 to 360 ppm (50 to 2000 mg/m^3) for a 10-L air sample. Turpentine is widely used as a solvent in paints, varnishes and lacquers.

INTERFERENCES: The chief constituents of turpentine are pinene isomers, diterpene and other $C_{10}H_{16}$ terpenes. Naphtha mixtures containing C_9-C_{11} alkanes or alkyl-substituted benzenes could cause interferences with the turpentine mixture. GC column and conditions should then be optimized for maximum resolution.

OTHER METHODS: This is Method S88 [3] in a revised format.

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality, containing 0.8% v/v undecane, 0.1% v/v octane or other suitable internal standard.
2. Turpentine, bulk sample.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

* 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. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available. (SKC ST226-01, Supelco ORBO-32, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1551-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipet, volumetric, 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a 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 1 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and 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 and foam plugs.
   NOTE: Retain the glass wool plug if an estimate of aerosol is needed.
6. Add 1.0 mL eluent 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 0.1 to 20 mg turpentine per sample.
   a. Add known amounts of the turpentine bulk sample to eluent 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 (ratio of sum of peak areas of turpentine to peak area of internal standard).
9. Determine desorption efficiency (DE) at least once for each lot 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 amounts of the turpentine bulk sample 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 (steps 11 and 12).
e. Prepare a graph of DE vs. mg turpentine recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure 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 1551-1. 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 with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.
    NOTE: Compare chromatograms of the air samples and the turpentine bulk sample for evidence of qualitative differences and possible interferences.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of turpentine 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 turpentine in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method S88 [3] was issued on March 14, 1975, and validated over the range 264 to 1107 mg/m^3 at 24 °C and 766 mm Hg using 10-L air samples [1]. Turpentine oil, double rectified (Fisher Scientific Co.; BP 150 to 170 °C; d 0.868 g/mL) in a calibrated syringe drive was used to generate turpentine atmospheres in dry air. Overall precision, $\hat{S}_{rT}$, was 0.055 with average recovery of 99%, representing a non-significant bias. Desorption efficiency was 0.95 in the range 2.8 to 11.3 mg per sample. The chromatographic column used was 6 ft x 1/8 in stainless steel packed with 1.5% OV-101 on 100/120 mesh Chromosorb W. Breakthrough (5% on back section) occurred at 126 min when sampling an atmosphere containing 1107 mg/m^3 turpentine at 0.19 L/min at 0% RH.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S88, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #4121-O,P (unpublished, December 2, 1983).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., S88, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

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