PHENYL ETHER-DIPHENYL MIXTURE

$(C_6H_5)_2O$ & $C_6H_5C_6H_5$ MW: 166 (average) CAS: 8004-13-5 RTECS: DV1500000

METHOD: 2013, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 1 ppm
NIOSH: 1 ppm
ACGIH: no TLV
(1 ppm = 6.79 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 257 °C; MP 12 °C; d = 1.06 g/mL @ 25°C; VP = 10 Pa (0.08 mm Hg) @ 25 °C; vapor density (air = 1) 5.7.; flammable limits in air 0.5 to 6.2% v/v

SYNONYMS: None. This is a liquid eutectic, prepared by dissolving 26.5 parts by weight solid diphenyl in 73.5 parts melted phenyl ether.

SAMPLING

SAMPLER: SORBENT TUBE (silica gel, 150/75 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 1 ppm
-MAX: 40 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required

ACCURACY

RANGE STUDIED: 3.86 to 15.7 mg/m^3 [1] (10-L samples)

BIAS: - 0.35%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.089 [1]

ACCURACY: ± 17.2%

MEASUREMENT

TECHNIQUE: gas chromatography, FID

ANALYTE: phenyl ether-diphenyl mixture

EXTRACTION: 0.5 mL benzene for 30 min

INJECTION VOLUME: 5 µL

CARRIER GAS: nitrogen, 50 mL/min

COLUMN: 10-ft x 1/8-in stainless steel column packed with 5% OV-17 on 80/100 mesh, acid washed DMCS Chromosorb W

DETECTOR: flame ionization detector

CALIBRATION: standard solutions of eutectic mixture in hexane

RANGE: 7 to 210 µg per sample [1]

ESTIMATED LOD: 4 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.073 @ 38 to 156.7 µg per sample [1]

APPLICABILITY: The working range is 0.1 to 10 ppm (0.7 to 70 mg/m^3) for a 10-L air sample. Better sensitivity may be achieved with a capillary column in place of a packed column; a DB-17 column (50% methyl, phenyl-50% dimethyl-polysiloxane) with appropriate instrumental conditions is recommended.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S73 [2] in fourth edition format.

REAGENTS:

1. Diphenyl*, reagent grade.
2. Phenyl ether*, reagent grade.
3. Phenyl ether-biphenyl mixture: dissolve 2.65 g solid diphenyl in 7.35 g melted phenyl ether (10 g mixture, liquid eutectic).
4. Benzene*, reagent grade.
5. Hexane, reagent grade.
6. Calibration stock solution, analyte mixture in hexane, 17.5 mg/mL.
7. Hydrogen, prepurified.
8. Air filtered, compressed.
9. Nitrogen, purified.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID; with plastic caps; containing two sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam (front = 150 mg; back = 75 mg). A silylated glass wool plug proceeds 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 0.20 L/min, with flexible polyethylene or PTFE tubing.
3. PTFE plugs and/or tubing.
4. Vials, glass, 1-mL with PTFE-lined crimp caps.
5. Gas chromatograph, flame ionization detector, recorder, integrator and column (page 2013-1).
6. Tweezers.
7. File.
8. Syringes, 5-, 50- and 100-µL, other sizes if needed.
9. Volumetric flasks, 10-mL.
10. Pipets, 0.5-, and 1.0-mL glass, delivery, graduated in 0.1-mL increments, with pipet bulb.
11. Graduated cylinders, glass, 10-mL.

SPECIAL PRECAUTIONS: Benzene is a carcinogen, toxic and is flammable. Phenyl ether is toxic by inhalation. Diphenyl is toxic. Work in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2-mm). 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 volume of 1 to 40 L.
4. After the sample is collected, cap each tube with plastic plugs and pack securely for shipment.
5. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

6. Place front and back sorbent sections of the sampler tube in separate vials. Discard the glass wood and foam plugs.
7. Add 0.5 mL benzene to each sample vial and attach the crimp cap.
8. Allow to stand for 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to 0.5 mL benzene.

b. Analyze with samples and blanks (steps 12 and 13).
c. Prepare calibration graph (peak area vs. µg phenyl ether-diphenyl mixture.

10. Determine desorption efficiency (DE) at least once for each lot of sorbent 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 of calibration stock solution directly onto front sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 6 through 8) and analyze with working standards (steps 12 and 13).
    e. Prepare a graph of DE vs. µg mixture recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2013-1. 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 an aliquot of the desorbed liquid with benzene, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area for each analyte peak and sum together for each sample or standard.

CALCULATIONS:

14. Determine the mass, µg (corrected for DE) of phenyl ether-diphenyl mixture 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.
15. Calculate concentration, C, of mixture 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:

This method was validated over the range 3.86 to 15.7 mg/m^3 using 10-L samples collected from dry air (0% RH) [2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.089, with average recovery of 100.1%, representing a non-significant bias. Recovery of analyte from silica gel tubes was 100.0% in the range 4.0 to 15.7 µg per sample after desorption efficiency correction. Desorption efficiency ranged from 89 to 101% over 7 to 102 µg/sample. No breakthrough was seen when a concentration of 14.9 mg/m^3 was collected at 0.18 L/min for 4 hours. Sample storage stability was not determined.

REFERENCES:

[1] Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
[2] NIOSH Manual of Analytical Methods, 2nd. ed. V. 2, S73, U. S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY:

Y.T. Gagnon, NIOSH/DPSE.