DIBUTYL PHOSPHATE 5017

$(C_4H_9O_2)(OH)P=O$ MW: 210.21 CAS: 107-66-4 RTECS: TB9605000

METHOD: 5017, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
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OSHA : 1 ppm
NIOSH: 1 ppm; STEL 2 ppm
ACGIH: 1 ppm; STEL 2 ppm
(1 ppm = 8.59 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.06 g/mL; decomposes @ 100 °C; VP unknown

SYNONYMS: phosphoric acid dibutyl ester

SAMPLING

SAMPLER: FILTER (1.0-µm PTFE)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 50 L @ 1 ppm
-MAX: 250 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days at room temperature [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.3 to 10 mg/m^3 [1] (180-L samples)

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1]

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOSPHORUS FPD

ANALYTE: dibutyl trimethylsilyl phosphate

DESORPTION: acetonitrile

DERIVATIZATION: N,O-bis(trimethylsilyl)tri fluoroacetamide (BSTFA)

INJECTION VOLUME: 1 µL

CARRIER GAS: He, 30 mL/min

TEMPERATURE-INJECTION: 220 °C
-DETECTOR: 210 °C
-COLUMN: 155 °C

COLUMN: glass; 1.2 m x 6-mm OD; 3% OV-101 on 100/120 mesh Chromosorb WHP

CALIBRATION: dibutyl phosphate in CH_3CN with internal standard

RANGE: 0.4 to 2 mg per sample

ESTIMATED LOD: 0.07 mg per sample [1]

PRECISION ($\hat{S}_r$): 0.017 [1]

APPLICABILITY: The working range is 0.2 to 1.2 ppm (2 to 10 mg/m^3) for a 200-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This method revises P&CAM 297 [2].

REAGENTS:

1. Dibutyl phosphate,* purified 99%, according to Ref. [3].
2. Eluent: Acetonitrile, reagent grade, containing 0.1% (v/v) tributyl phosphate internal standard.
3. Calibration stock solution, 45 mg/mL. Dissolve 0.45 g purified dibutyl phosphate in 10 mL acetonitrile.
4. N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), reagent grade.
5. Helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: PTFE membrane filter, 1-µm, (Millipore FA or equivalent), 37-mm diameter in a two-piece polystyrene cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Jars, squat-form, 60-mL, with PTFE film gaskets, and screw caps.
4. Vial, 2-mL, with PTFE-lined caps.
5. Gas chromatograph with phosphorus FPD, integrator, and column (page 5017-1).
6. Syringes, 5-, 10-, and 25-µL, for making standard solutions and GC injections.
7. Volumetric flasks, 10- and 100-mL.
8. Pipets, 1- and 5-mL.
9. Tweezers.

SPECIAL PRECAUTIONS: Dibutyl phosphate is toxic if inhaled or comes in contact with the eyes or skin [3]. Sample preparations should be conducted in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 50 to 250 L.

SAMPLE PREPARATION:

3. Using tweezers, carefully transfer the filter to a 60-mL jar.
4. Pipet 5.0 mL eluent into each jar. Cap the jar.
5. Allow to stand 30 min with occasional agitation.
6. Transfer 1.0 mL of the extract to a 2-mL vial. Add 100 µL BSTFA. Cap the vial, shake thoroughly, and let stand 30 min.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.1 to 2 mg dibutyl phosphate per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (ratio of peak area of dibutyl phosphate to peak area of internal standard vs. mg dibutyl phosphate).
8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

9. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5017-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
   NOTE 1: Under these conditions, approximate retention times are 4 min for dibutyl phosphate and 6 min for tributyl phosphate.
   NOTE 2: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
10. Measure peak area. Divide the peak area of dibutyl phosphate derivative by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

11. Determine the mass, mg of dibutyl phosphate found in the sample (W), and in the average media blank (B).
12. Calculate concentration, C (mg/m ^{3}), of dibutyl phosphate in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method P&CAM 297 was issued on November 8, 1978 [2]. The substance used to generate test atmospheres at 25 °C and 760 mm Hg in dry air was technical grade dibutyl phosphate containing ca. 55% dibutyl phosphate and 45% monobutyl phosphate [1,4]. The collection efficiencies and measurement recoveries were 1.00 in the range 0.5 to 5 mg per sample. Sample filters stored one week at ambient conditions gave recovery of 106 ± 5%. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.057. No independent method was available to estimate bias.

REFERENCES:

[1] Backup Data for P&CAM 297, prepared under NIOSH Contract 210-76-0123 (unpublished, November 8, 1978).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 297, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123, available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[4] 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).

METHOD REVISED BY:

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