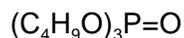


TRIBUTYL PHOSPHATE

5034



MW: 266.32

CAS: 126-73-8

RTECS: TC7700000

METHOD: 5034, Issue 1

EVALUATION: PARTIAL

Issue 1: 15 August 1994

OSHA : 0.5 ppm

NIOSH: 0.2 ppm

ACGIH: 0.2 ppm

(1 ppm = 10.9 mg/m³ @ NTP)

PROPERTIES: liquid; boiling point 293 °C; density 0.98 g/mL @ 20 °C; VP very low @ 20 °C; vapor density 9.2 (air=1); flash point 166 °C (closed cup)

SYNONYMS: phosphoric acid, tributyl ester; tri-n-butyl phosphate; TBP; Celluphos 4

APPLICABILITY: The working range is 0.006 to 1.4 ppm (0.06 to 15 mg/m³) for a 100-L air sample. This method may be adapted to other phosphates of relatively low volatility with appropriate changes in chromatographic conditions.

INTERFERENCES: Any phosphorus-containing compound that has the same retention time as the analyte is an interference. A non-polar capillary column may be used for better resolution.

OTHER METHODS: This revises Method S208 [2]. Analytical methods for tributyl phosphate (TBP) have been reviewed [3]. Another packed-column GC procedure has been described recently [4]. TBP has been determined in air by capillary-column GC/NPD preceded by sampling on a glass fiber filter or XAD-7 resin [5]. GC/MS [6], LC/MS [7], and LC/TID (thermionic detection) [8] have all been shown to be useful methods for the analysis of TBP in environmental samples. Finally, a continuous phosphorus gas analyzer has been used to monitor TBP in air [9].

REAGENTS:

1. Diethyl ether^{*}, anhydrous, reagent grade.
2. Tributyl phosphate^{*}, reagent grade.
3. Hydrogen, purified
4. Compressed air, prefiltered
5. Nitrogen, purified
6. Calibration stock solution, tributyl phosphate in diethyl ether

* See Special Precautions

EQUIPMENT:

1. Sampler: 37-mm mixed cellulose ester membrane filter (0.8- μ m pore size) supported by cellulose backup pad in three-piece filter holder.

NOTE: Backup filter unit is needed when sampling at temperatures above 23 °C.

2. Personal sampling pump, 1 to 3 L/min, with flexible polyethylene or PTFE tubing.
3. Gas chromatograph equipped with a flame photometric detector, phosphorus filter, and column (p. 5034-1).
4. Electronic integrator or some other suitable method for measuring peak areas.
5. Tweezers.
6. Jars: 2 oz ointment jars for sample extraction, squat form with aluminum-lined screw caps.
7. Syringes, 10- μ L and other convenient sizes.
8. Volumetric flasks, 10-mL and other convenient sizes.
9. Pipets, 10-mL and other convenient sizes.

SPECIAL PRECAUTIONS: Store diethyl ether away from heat, light, and sources of ignition in a well-ventilated area. Do not leave container open. Diethyl ether can oxidize in air to form explosive peroxides, a reaction accelerated by light. Distillation and evaporation can concentrate unstable peroxides in the residue, a potentially explosive condition [10].

Avoid inhalation of tributyl phosphate vapors and contact with eyes, skin, and clothing [11,12]. Handle only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with the representative filter cassettes in line.
2. Remove cassette plugs and connect cassette filter to the personal sampling pump with flexible tubing.
NOTE: If ambient temperature is above 23 °C, use two filter cassettes connected in series with a short piece of flexible tubing for sample collection. Some tributyl phosphate may exist as vapor above 23 °C.
3. Sample at an accurately known flow rate of 1 to 3 L/min for a total sample size of 2 to 100 L.
4. Separate front and backup filter cassettes (if two cassettes were used). Firmly seal collected sample cassettes with plugs, and pack securely for shipment.

SAMPLE PREPARATION:

5. Transfer the filter and backup pad to an ointment jar using tweezers.

6. Pipet 10.0 mL of diethyl ether into each jar. Seal the jar immediately to minimize evaporation.
7. Allow samples to stand for at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 2 to 1000 µg per sample.
 - a. Add known amounts of calibration stock solution to 10-mL volumetric flasks and dilute to volume with diethyl ether.
 - b. Analyze working standards together with samples and blanks (steps 11 and 12). This will minimize the effect of variations in FPD response with time.

NOTE 1: The FPD response is very sensitive to minor variations in hydrogen flow rate and, therefore, it is recommended that calibration standards be carefully interspersed with the samples.

NOTE 2: Use of an internal standard is recommended to minimize errors caused by sample solvent evaporation and FPD response variations.
 - c. Prepare a calibration graph of area vs. µg of tributyl phosphate per 10 mL of sample.
9. Determine recovery in the concentration range of interest for each lot of filters used for sampling. Prepare three filters at each of five levels plus three media blanks.
 - a. Spike aliquot of calibration solution onto each filter.
 - b. After air-drying, extract filters with 10 mL diethyl ether (steps 5 through 7).
 - c. Analyze together with working standards (steps 11 and 12).
 - d. Prepare graph of recovery vs. µg tributyl phosphate.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5034-1. Inject 5-µL sample aliquot using solvent flush technique or with autosampler.

NOTE: If peak area is above linear range of the calibration graph, dilute with diethyl ether, analyze, and apply appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine mass, µg (corrected for recovery), of tributyl phosphate found in the sample (W) and the average media blank (B).
14. Calculate concentration of tributyl phosphate in the actual air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was evaluated over the range 2.7 to 12.6 mg/m³ at 19 °C and pressure of 761 mm Hg with 100-L air samples [1]. Overall sampling and measurement precision, $\hat{S}_{(T)}$, was 0.076. The average collection efficiencies for test concentrations of 12.6 mg/m³ and 9.3 mg/m³ were 100.0% and 99.6%, respectively. The average recovery from filters spiked in the range 234 µg to 973 µg per filter was 100.4%. Therefore, there is no significant bias in the method. No tests of sample stability during storage were conducted.

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METHOD REVISED BY:

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