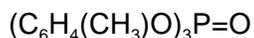


TRIORTHOCRESYL PHOSPHATE

5037



MW: 368.37

CAS: 78-30-8

RTECS: TD0350000

METHOD: 5037, Issue 1

EVALUATION: PARTIAL

Issue 1: 15 August 1994

OSHA : 0.1 mg/m³

NIOSH: 0.1 mg/m³ (skin)

ACGIH: 0.1 mg/m³ (skin)

PROPERTIES: liquid; melting point 11 °C; boiling point 410 °C 1.20 g/mL; VP very low at 20 °C; vapor density 12.7 (air=1); flash point 210 °C (closed cup)

SYNONYMS: phosphoric acid, tri-*o*-cresyl ester; phosphoric acid, tri-*o*-tolyl ester; phosphoric acid, tri(2-tolyl) ester; phosphoric acid, tris(2-methylphenyl) ester; *o*-cresyl phosphate; *o*-tolyl phosphate; tricresyl phosphate; tris(*o*-cresyl)phosphate; tris(*o*-tolyl)phosphate; tris(*o*-methylphenyl)phosphate; TOCP; TOTP; Phosflex 179-C

SAMPLING	MEASUREMENT
<p>SAMPLER: FILTER (0.8-μm MIXED CELLULOSE ESTER MEMBRANE)</p> <p>FLOW RATE: 1 to 3 L/min</p> <p>VOL-MIN: 2 L @ 0.1 mg/m³</p> <p>-MAX: 100 L</p> <p>SHIPMENT: routine</p> <p>SAMPLE STABILITY: not determined</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: GC, FPD in phosphorus mode</p> <p>ANALYTE: triorthocresyl phosphate</p> <p>EXTRACTION: 10 mL diethyl ether</p> <p>INJECTION VOLUME: 5 μL</p> <p>CARRIER GAS: N₂, 50 mL/min</p> <p>DETECTOR: H₂, 70 mL/min Air, 150 mL/min</p> <p>TEMPERATURES-INJECTION: 250 °C</p> <p>-DETECTOR: 250 °C</p> <p>-COLUMN: 220 °C</p>
ACCURACY	<p>COLUMN: 6-ft x $\frac{1}{8}$-in ID stainless steel, with 3% OV-101 on 100/120 mesh Supelcoport</p> <p>CALIBRATION: standard solutions of triorthocresyl phosphate in diethyl ether</p> <p>RANGE: 0.15 to 24 μg per sample</p> <p>ESTIMATED LOD: 0.05 μg per sample [1]</p> <p>PRECISION (\hat{S}_r): 0.0236 [1]</p>
<p>RANGE STUDIED: 29 to 170 μg/m³ (100-L samples) [1]</p> <p>BIAS: - 1.0%</p> <p>OVERALL PRECISION (\hat{S}_{rT}): 0.086 [1]</p> <p>ACCURACY: \pm 16.9%</p>	

APPLICABILITY: The working range of this method is 0.002 to 2 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. Triorthocresyl phosphate may be a minor component in a product containing numerous isomeric tricresyl phosphates. When dealing with such products, it must be verified that the chromatographic parameters employed result in separation of the triorthocresyl phosphate isomer from the other tricresyl phosphate isomers. A non-polar capillary column may be used for better resolution.

OTHER METHODS: This revises Method S209 [2]. The separation of aryl phosphate isomers by capillary-column GC has been investigated [3,4]. A GC/FID method has been reported that determines triorthocresyl phosphate (TOCP) in the presence of other isomeric tricresyl phosphates (TCPs) in edible oils [5]. GC/MS has been used to determine total TCP in water [6]. Reversed-phase (RP) LC/UV [7], RPLC/MS [8], and RPLC/TID (thermionic detection) [9] have been shown to be useful analytical methods for TOCP, but all were evaluated in the absence of other TCP isomers. Normal-phase (NP) LC/UV has been used to determine total TCP in edible oils [10]. NPLC has been used to quantify low levels of TOCP in commercial TCP products [11].

REAGENTS:

1. Diethyl ether^{*}, anhydrous, reagent grade.
2. Triorthocresyl phosphate^{*}, reagent grade.
3. Hydrogen, purified.
4. Compressed air, prefiltered.
5. Nitrogen, purified.
6. Calibration stock solution, triorthocresyl 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.
2. Personal sampling pump with flexible polyethylene or PTFE tubing.
3. Gas chromatograph equipped with a flame photometric detector, phosphorus filter, and column (p. 5037-1).
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 [12].

Triorthocresyl phosphate is more toxic than other tricresyl phosphate isomers and readily absorbed through the skin. Avoid contact of triorthocresyl phosphate with eyes, skin, and clothing [13,14]. Handle only in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with the representative filter cassette in line.
2. Remove cassette plugs and connect cassette filter to the personal sampling pump with flexible tubing.
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. Firmly seal collected sample cassettes with plugs. 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 0.05 to 24 μ g per sample.
 - a. Prepare a stock solution by weighing an appropriate quantity of triorthocresyl phosphate into a volumetric flask and diluting to volume with diethyl ether.

NOTE: Triorthocresyl phosphate is very viscous and thus difficult to measure with a microliter syringe.

- b. Add known amounts of calibration stock solution to 10-mL volumetric flasks and dilute to volume with diethyl ether.
- c. 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.

- d. Prepare a calibration graph of area vs. μg of triorthocresyl 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 triorthocresyl 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 5037-1. Inject 5- μL sample aliquot using solvent flush technique or with an autosampler.

NOTE: If peak area is above the 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 triorthocresyl phosphate found in the sample (W) and the average media blank (B).
14. Calculate concentration (C) of triorthocresyl 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 29 to 170 $\mu\text{g}/\text{m}^3$ at 19 °C and pressure of 761 mm Hg with 100-L air samples [1]. Overall sampling and measurement precision, \hat{S}_{rT} , was 0.086. The average collection efficiencies for test concentrations of 0.17, 0.19, and 3.8 mg/m^3 were 98.8%, 98.7%, and 99.5%, respectively. The average recovery from filters spiked in the range 5.85 μg to 23.4 μg per filter was 101.3%. Therefore, there is no significant bias in either the sampling or analytical method. No tests of sample stability during storage were conducted.

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METHOD REVISED BY:

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