p-CHLOROPHENOL 2014

C_6H_4ClO MW: 128.56 CAS: 106-48-9 RTECS: SK2800000

METHOD: 2014, Issue 2 **EVALUATION:** FULL **Issue 1:** 19 September 1980
Issue 2: 25 February 2016

OSHA: None
NIOSH: None

PROPERTIES: crystals; d 1.224 g/mL @ 20 °C; MP 43.2-43.7 °C; BP 220 °C; VP 0.013 kPa (0.1 mm Hg) @ 20 °C; flash point 121 °C (closed cup)

SYNONYMS: 4-chlorophenol; 4-chloro-1-hydroxybenzene

SAMPLING

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

FLOW RATE: 0.05 - 0.2 L/min

VOL-MIN: 1.5 L @ 1 ppm
-MAX: 40 L

SHIPMENT: routine

SAMPLE STABILITY: 7 days @ 25 °C at least 29 days @ 0 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.910 to 23.4 mg/m^3 [1] (3-L samples)

BIAS: none identified

OVERALL PRECISION ($\hat{S}_{rT}$): 0.061 for range studied [1]

ACCURACY: ± 15% (12-28%)

MEASUREMENT

TECHNIQUE: HPLC/UV

ANALYTE: *p*-chlorophenol

EXTRACTION: 1 mL acetonitrile

MOBILE PHASE: 30% acetonitrile, 70% water to 80% acetonitrile/20% water in 20 minutes, 1 mL/min

COLUMN: C18 (5 µm particle size, 4-mm ID by 30-cm long, stainless steel)

DETECTOR: UV @ 280 nm

CALIBRATION: *p*-chlorophenol in 30% (v/v) acetonitrile in water

RANGE: 8 to 64 µg/sample [1]

ESTIMATED LOD: 2.5 µg/sample [1]

PRECISION ($\bar{S}_r$): 0.024 [1]

APPLICABILITY: The working range is 0.15 to 53 ppm (0.8 to 280 mg/m^3) for a 10-L air sample.

INTERFERENCES: None identified. The chromatographic conditions described will separate phenol; *o*-chlorophenol; 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5- dichlorophenol; *o*- and *p*-nitrophenol; 2,4-dimethylphenol; 2,4,5-trichlorophenol; 4-chloro-*o*-methylphenol; 2,4-dinitrophenol; 4,6-dinitro-2-methylphenol; and pentachlorophenol.

OTHER METHODS: This method replaces P&CAM 337 [2]. The other columns for the analysis of *p*-chlorophenol have been reported in the literature [3-5].

REAGENTS:

1. *p*-Chlorophenol 99%.*
2. Acetonitrile, distilled in glass.
3. Hexane, distilled in glass.
4. Water, HPLC quality distilled, deionized.
5. *p*-Chlorophenol stock solution, 20 mg/mL. Dissolve 500 mg *p*-chlorophenol in 30% (v/v) acetonitrile in water to make 25 mL solution. Stable at least 3 months in airtight container.
6. Desorption efficiency (DE) stock solution, 5 mg/mL. Dissolve 125 mg *p*-chlorophenol in hexane to make 25 mL solution.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: borosilicate glass tubes, 7 cm long with a 6-mm OD and a 4-mm ID, flame sealed at both ends. Each tube contains two sections of 20/40 mesh silica gel (a 150-mg sorbent section and a 75-mg backup section separated and held in place with glass wool plugs). Tubes are commercially available.
2. Personal sampling pump, calibrated, capable of operating 8 hours at 0.05 to 0.2 L/min with flexible connecting tubing.
3. HPLC with UV detector (280 nm), C18 column, injector, and electronic integrator.
4. Microliter syringes, various sizes.
5. Volumetric flasks, various sizes.
6. Centrifuge tubes, 12-mL, glass with screw caps.
7. Pipette, 1- and 2-mL, and convenient sizes for making dilutions.
8. Vials, 1-mL, with caps containing PTFE-lined silicone septa.
9. Ultrasonic bath.

SPECIAL PRECAUTIONS: *p*-Chlorophenol is toxic by skin absorption, inhalation, or ingestion. It also is a strong irritant to tissue and is combustible with a flash point of 121 °C.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break open the ends of the tube to provide openings that are at least 2-mm in diameter. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flowrate between 0.05 and 0.2 L/min for a total sample size of 1 to 40 liters.
4. Cap the tubes, record sample identity and all relevant sample data (duration, ambient temperature and pressure). Pack securely for shipment.
   NOTE: Refrigerate all samples at 0 °C when stored longer than 7 days.

SAMPLE PREPARATION:

5. If refrigerated, allow tube to equilibrate to room temperature.
6. Transfer each section of silica gel in a sorbent tube to a separate 12-mL centrifuge tube. Combine the glass wool plug near the inlet with the front sorbent section. Combine the two urethane foam plugs with the back section.
7. Add 1 mL of acetonitrile, cap, and desorb in an ultrasonic bath for 30 minutes.
8. Add 2 mL of distilled, deionized water to each tube, cap, and mix the solutions.
9. Centrifuge the samples and transfer about 1 mL of the supernatant in each tube to a separate vial and seal with a PTFE-lined septum.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards in the range 2.5 to 64 µg per sample.
    a. Dilute aliquots of *p*-chlorophenol stock solution with 30% (v/v) acetonitrile in water in volumetric flasks to encompass the range of interest. Prepare fresh daily.
    b. Analyze working standards with samples and blanks steps.
    c. Prepare calibration graph (peak area or peak height vs. µg of *p*-chlorophenol per sample.
11. Determine desorption efficiency (DE) for each lot of silica gel used for sampling in the calibration range. Prepare three tubes at each of five levels.
    a. Remove backup section. Inject known amounts of DE stock solution (2 to 10 µL) onto the silica gel with a microliter syringe.
    b. Cap the tubes and allow to stand overnight.
    c. Desorb (steps 7 through 9) and analyze together with standards and blanks (steps 13 and 14).
    d. Prepare a graph DE vs. µg *p*-chlorophenol recovered.
12. Analyze three quality control spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

13. Set HPLC according to manufacturer's recommendations and to conditions on page 2014-1. Inject sample aliquot manually or with autosampler.
    NOTE: If peak is above the linear range of the working standards, dilute with 30% (v/v) acetonitrile in water, reanalyze, and apply the appropriate dilution factor.
14. Measure peak area or peak height.

CALCULATIONS:

15. Determine the mass, µg (corrected for DE), of analyte found on 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.
16. Calculate concentration of *p*-chlorophenol in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, mg/m^3$$

EVALUATION OF METHOD:

The overall method was evaluated by collecting 3-L samples of test atmospheres containing *p*-chlorophenol in the range of 0.91 - 23.4 mg/m^3 at 29 °C and a relative humidity of greater than 80%. The amounts collected ranged from 2.6 - 64 µg per 150-mg bed of silica gel. The breakthrough volume of the sorbent tube was found to be approximately 60 L with a sampling rate of 0.2 L/min at a *p*-chlorophenol concentration of about 70 mg/m^3, a sampling temperature of 43 °C, and a relative humidity of greater than 80%. Samples of *p*-chlorophenol on silica gel were found to be stable at 25 °C for 7 days and for 29 days if stored at 0 °C after the seventh day. Silica gel gave an average desorption efficiency of 96% with a $\bar{S}_r$ 2.4% for loadings of 2.54 - 48.0 µg of *p*-chlorophenol on 150-mg beds of sorbent material.

REFERENCES:

[1] Dillon HK, Emory MB [1980]. Development of air sampling and analytical methods for toxic chlorinated organic compounds: Research report for *p*-chlorophenol. NIOSH contract no. 210-78-0012. Birmingham, AL. Southern Research Institute.

[2] NIOSH [1981]. P-Chlorophenol: P&CAM 337. In: Taylor DG, ed. NIOSH manual of analytical methods. 2nd ed. Cincinnati, OH: U.S. Department of Health and Human Services, Center for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 82-100.

[3] Korhonen IO [1980]. Separation of chlorophenol isomers on quartz columns. J Chromatogr *303*(1):197-205.

[4] Buisson RSK, Kirk PWW, Lester JN [1984]. Determination of chlorinated phenols in water, wastewater and sludge by capillary GC/ECD. J Chromatogr Sci *22*(8):399-42.

[5] Lee HB, Hong-You RL, Fowlie PJ [1989]. Chemical derivatization analysis of phenols. Part VI. Determination of chlorinated phenolics in pulp and paper effluents. J Assoc Off Anal Chem *72*(6):979-984.

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