

p-CHLOROPHENOL

2014

 C_6H_4ClOH

MW: 128.56

CAS: 106-48-9

RTECS: SK2800000

METHOD: 2014, Issue 2

EVALUATION: FULL

Issue 1: 19 September 1980

Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV
 (1 ppm = 5.26 mg/m³ @ NTP)

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		MEASUREMENT	
SAMPLER:	SORBENT TUBE (silica gel, 150 mg/75 mg)	TECHNIQUE:	HPLC/UV
FLOW RATE:	0.05 - 0.2 L/min	ANALYTE:	p-chlorophenol
VOL-MIN:	1.5 L @ 1 ppm	EXTRACTION:	1 mL acetonitrile
-MAX:	40 L	INJECTION VOLUME:	100 µL
SHIPMENT:	Routine	MOBILE PHASE:	30% acetonitrile, 70% water to 80% acetonitrile/20% water in 20 minutes, 1 mL/min
SAMPLE STABILITY:	7 days @ 25 °C at least 29 days @ 0 °C [1]	COLUMN:	C18. (5 µm particle size, 4-mm ID by 30-cm long stainless steel)
BLANKS:	2 to 10 field blanks per set	DETECTOR:	UV, 280 nm
ACCURACY		CALIBRATION:	p-chlorophenol in 30% (v/v) acetonitrile in water
RANGE STUDIED:	0.910 to 23.4 mg/m ³ [1] (3-L samples)	RANGE:	8 to 64 µg/sample [1]
BIAS:	none identified	ESTIMATED LOD:	2.5 µg/sample [1]
OVERALL PRECISION (\hat{S}_{rt}):	0.061 for range studied [1]	PRECISION (\hat{S}_r):	0.024 [1]
ACCURACY:	± 15% (12-28%)		

APPLICABILITY: The working range is 0.15 to 53 ppm (0.8 to 280 mg/m³) 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.
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. DE stock solution, 5 mg/mL. Dissolve 125 mg p-chlorophenol in hexane to make 25 mL solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Pyrex 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 sorbing section and a 75-mg backup section separated and held in place with glass wool plugs). Tubes are commercially available (SAC, Inc. 226-10 or equivalent.)
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 (Variant MicroPak MCH-5 or equivalent), 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):

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

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/m³ 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/m³, 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} , 2.4% for loadings of 2.54 - 48.0 µg of p-chlorophenol on 150-mg beds of sorbent material.

REFERENCES:

- [1] Dillon, H.K., Emory, M.B. Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds: Research Report for p-Chlorophenol. NIOSH Contract 210-78-0012, Southern Research Institute, Birmingham, Alabama (1980).

- [2] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 337, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).
- [3] Korhonen, I.O. "Separation of Chlorophenol Isomers on Quartz Columns." J. Chromatogr., 303 (1), 197-205 (1980).
- [4] Buisson et al., "Determination of Chlorinated Phenols by Capillary GC/ECD." J. Chromatogr. Sci., 22 (8), 399-42 (1984).
- [5] Lee, H.B. et al., "Determination of Chlorinated Phenolics in Pulp and Paper Effluents." J. Assoc. of Anal. Chem., 72 (6), 979-984 (1989).

METHOD REVISED BY:

Charles Neumeister, NIOSH/DPSE.