CRESOL (all isomers) and PHENOL

$CH_3C_6H_4OH$	MW: 108.14	CAS: 1319-77-3	RTECS: GO5950000
C_6H_5OH	94.11	108-95-2	SJ3325000

METHOD: 2546, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : Table 1
NIOSH:
ACGIH:

PROPERTIES: Table 1

SYNONYMS: o-cresol: 2-methylphenol; CAS#95-48-7; m-cresol: 3-methylphenol; CAS#108-39-4; p-cresol: 4-methylphenol; CAS #106-44-5.
phenol: carbolic acid; hydroxybenzene

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-7, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.1 L/min

VOL-MIN: 1 L @ 5 ppm
-MAX: 24 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: cresol isomers/phenol

DESORPTION: 2 mL methanol; sonicate

INJECTION VOLUME: 1 µL (split 20:1)

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 160 - 225 °C (3 °C/min)

CARRIER GAS: He, 1 mL/min

COLUMN: Stabilwax DA fused silica capillary, 30 m, 0.32-mm ID, 0.25-mm film or equivalent

CALIBRATION: standard solutions of analytes in methanol

RANGE: 20 to 800 µg per sample

ESTIMATED LOD: 1 to 3 µg per sample

PRECISION ($\hat{S}_r$): 0.028 [1]

APPLICABILITY: The working range is 0.25 to 15 ppm (1 to 60 mg/m ^{3}) for cresols and phenol in a 20-L air sample.

INTERFERENCES: None identified. A DB-wax fused silica capillary column is an alternate column.

OTHER METHODS: This method uses a sampler similar to that of OSHA 32 [1] and replaces methods 2001 (Cresols) [2] and 3502 (Phenol) [3]. Analysis of the sample extracts can also be done by HPLC/UV [1,4].

REAGENTS:

1. Methanol, chromatographic quality.
2. n-Hexane.
3. Cresol (all isomers).* Dissolve 2 g o-cresol (solid), 3 g p-cresol (solid) in 4 g (4.13 mL) of m-cresol and mix.
4. Calibration stock solution, 10.4 mg/mL. Dilute 104 mg cresol isomer mixture (1.0 mL at 20 °C) to 10 mL with n-hexane.
5. Hydrogen, prepurified.
6. Nitrogen, purified.
7. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 11 cm long, 6-mm OD, 4- mm ID;two sections of 20/40 mesh XAD-7 separated by a 2-mm portion of silanized glass wool (front = 100 mg, back = 50 mg).
2. Personal sampling pump, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2001-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Pipet, 1.0-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.
8. Ultrasonic bath.

SPECIAL PRECAUTIONS: Cresol and phenol cause severe burns [5]. They are toxic if absorbed through skin, inhaled or ingested. All work with them should be performed in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.1 L/min for a total sample size of 5 to 24 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front sorbent section (together with the front glass wool plug) and back sorbent sections of the sampler tube in separate vials. Discard the other plugs.
6. Add 2.0 mL methanol to each vial. Attach crimp cap to each vial.
7. Ultrasonicate 30 min.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 1 to 800 µg cresol and phenol per sample.
   a. Add known amounts of calibration stock solution to methanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (total peak area vs. µg analyte).
9. Determine desorption efficiency (DE) at least once per year for each lot of sorbent used for sampling in the calibration range. Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2000-1. Inject 1-µL sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with methanol, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure total peak area of the two analyte peaks.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of cresols and phenol found in 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.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of cresols 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:

This is a modification of OSHA Method 32 (Phenol and Cresol) which uses the same sampling procedure [1]. Phenol and all cresol isomers were easily resolved by capillary GC using a split injection ratio of 20:1. The desorption efficiency (DE) results for all analytes were > 0.90. Analytes were stable for 30 days when refrigerated.

REFERENCES:

[1] Phenol and Cresol, Occupational Safety and Health Administration, OSHA Method 32, OSHA Analytical Laboratory, 1981.
[2] NIOSH Manual of Analytical Methods, 3rd ed., Vol. 2, Method 3502, U.S. Dept. of Health, Education, and Welfare, Publication #84-100 (NIOSH), 1984.
[3] Ibid, Method 2001.
[4] DataChem Laboratories Report, Seq. #7478-L (NIOSH, unpublished, May 8, 1992).
[5] NIOSH/OSHA, Occupational Health Guidelines for Chemical Hazards, USDHHS (NIOSH), Publ. 81-123 (1981).
[6] Pendergrass, S.M., An Improved Method for the Sampling and Analysis of Phenol and o-, m-, and p-Cresol by Capillary GC/FID, Amer. Ind. Hyg. Assoc. J. (accepted for publication, 1994).
[7] Gessner, H., Ed., Condensed Chemical Dictionary, 10th ed., Van Nostrand Reinhold, 1981.

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TABLE 1. PHYSICAL PROPERTIES [6].

Compound	BP (°C)	MP (°C)	Density @ 20 °C	Vapor Presssure 25 °C (Pa)	(mm Hg)	NIOSH REL*
o-cresol	190.95	30.9	1.047 g/mL	33	0.25	2.3 ppm
m-cresol	202.2	12.0	1.034	20	0.15	2.3 ppm
p-cresol	201.9	35.3	1.034	15	0.11	2.3 ppm
phenol	182.0	41.0	1.071 (25 °C)	47	0.35	5 ppm; C 15.6 ppm/15 min (skin)

* OSHA PEL and ACGIH TLV are 5 ppm (skin) for all the above compounds.
1 ppm = 4.42 mg/m ^{3} @ NTP for the cresols; 1 ppm = 3.85 mg/m ^{3} @ NTP for phenol.