PHENOL AND CRESOL

Method no.:	32
Matrix:	Air
Target concentration: (PEL)	19 mg/m^3 (5 ppm) for phenol 22 mg/m^3 (5 ppm) for cresol (all isomers)
Procedure:	The analytes are collected on an XAD-7 sampling tube and desorbed with methanol. The analysis is performed by HPLC with ultraviolet (UV) detection at 218 nm.
Recommended air volume and sampling rate:	24 L and 0.1 L/min
Reliable quantitation limit:	0.041 mg/m^3 (0.01 ppm) phenol 0.046 mg/m^3 (0.01 ppm) cresol
Standard error of estimate for ambient storage samples: (Figures 4.8.1, 4.8.3)	5.47% for phenol 5.41% for cresol
Status of method:	A sampling and analytical method which has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

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1. General Discussion

1.1 Background

1.1.1 History

The analysis of phenol and cresol, like many chemicals in use for a long period of time, has evolved from a number of nonspecific colorimetric methods to more selective separation techniques using gas chromatography (GC) or high performance liquid chromatography (HPLC) (Refs. 5.1-5.3). The analytical procedure presented in this method uses reverse phase HPLC with ultraviolet (UV) detection at 218 nm, since the unresolved cresol isomers respond equally at this wavelength. An alternate gas chromatographic method using flame ionization detection is also quite satisfactory. Although the GC method is less sensitive than the liquid chromatographic method, it does provide better resolution of the cresol isomers.

Air sampling and analytical methods for phenol and cresol developed by NIOSH have been in use for several years. The NIOSH phenol method uses an aqueous bubbler to collect vapors, whereas cresol vapors are collected on a silica gel tube. Both of these methods utilize gas chromatography with flame ionization detection for analysis (Refs. 5.3 and 5.4). Recently a very sensitive method for detecting phenol in air has been developed by Kuwata, et al. (Ref. 5.5). This method uses a 0.1 N NaOH bubbler solution to collect the phenol vapors followed by derivatization with p-nitrobenzenediazonium tetrafluoroborate and analysis by HPLC. Although the aqueous bubbler has been shown to be an effective sampling device for collecting phenol in air, in an effort to simplify procedures for the determination of both analytes, a combined sampling and analytical method using solid sorbent tubes was investigated. The results of breakthrough studies of a variety of sorbent materials indicated that a number of resins could potentially be used for monitoring worker exposure to phenol and cresol. XAD-7, a high surface area acrylic ester polymer, and the PoraPak R, S, and T resins all demonstrated high capacities for the analytes and large breakthrough air volumes. Lower breakthrough air volumes and capacities were observed for XAD-8, a lower surface area acrylic ester polymer, and for XAD-4, a high surface area styrene-divinylbenzene resin. Tenax and silica gel sampling tubes were the least effective sampling devices evaluated. All of these sorbent materials, with the possible exception of silica gel, exhibited a higher capacity for cresol than for phenol. XAD-7 was selected as the sampling medium for both of the analytes because of its effectiveness in sampling a combined atmosphere of phenol and cresol, and because it presents only minimal sampling and analytical problems.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy)

A number of cases of overexposure to phenol or cresol are reported in the literature. Both compounds are rapidly absorbed through the skin and can cause skin and eye burns upon contact. Comas, convulsions, cyanosis and death can result from overexposure to either compound. The ingestion of 15 g of phenol produced death in a 19 year old woman within 20 h. Internally, cresol and phenol affect the liver, kidneys, lungs, and vascular system. There is some indication that cresol may be more toxic than phenol when inhaled. Respiratory irritation in 8 of 10 human subjects exposed to 6 mg/m^3 of o-cresol vapor has been observed. Mice exposed to 22 to 76 mg/m^3 of o-cresol for 2 h/day, six days a week for a period of one month exhibited signs of lethargy and irritability. Central nervous system damage, lung hemorrhages, inflamed airways, and degeneration of myocardial fibers were observed upon autopsy. In contrast no pathological or clinical differences between controls and the study group were observed when monkeys, rats, and mice were exposed to 19 mg/m^3 of phenol for a month over an 8-h day, five days a week period. No evidence exists to indicate that either phenol or the cresols have any carcinogenic potential. Because of the adverse effects observed for inhaled cresol, NIOSH recommends lowering the time weighted average (TWA) standard to 10 mg/m^3. NIOSH recommends a 20-mg/m^3 TWA standard and a 15-min ceiling value of 60 mg/m^3 for phenol (Refs. 5.6 and 5.7).

1.1.3 Workplace exposure

Phenol is used to make phenolic resins, caprolactam, bisphenol A and alkyl phenols. In 1972, 1.23 million tons of phenol were produced in the U.S. primarily from synthetic processes. An estimated 10,000 employees are potentially exposed to phenol. This does not include possible worker exposure to products containing phenol (Ref. 5.6).

The majority of the cresols are derived from petroleum or coal tar acids. In 1975, 151 million tons of cresol and cresylic acids were produced in the U.S. Cresol is used to make phenolic resins, tricresyl phosphate, disinfectants, and antioxidants. o-Cresol is largely used to make the herbicides dinitro-o-cresol (DNOC) and 2-methyl-4-chloro-phenoxyacetic acid (MCPA). NIOSH estimates that 11,000 workers are potentially exposed to cresols. This estimate does not include intermittent exposures of workers to cresol containing products. (Refs. 5.1 and 5.7)

1.1.4 Physical properties (Refs. 5.6 and 5.7)

phenol

molecular weight:	94.11
melting point:	40 - 41°C
boiling point:	181.75°C
vapor pressure:	0.35 mm Hg (25°C)
specific gravity:	1.071 (25°C)
flash point:	85°C (open cup), 79°C (closed cup)
odor threshold:	3.8 mg/m^3

Soluble in water, ether, alcohol and benzene. Colorless to light pink solid.

cresol (ortho-, meta-, and para-isomers)

	o-cresol	m-cresol	p-cresol
MW:	108.13	108.13	108.13
mp:	30.9°C	12.0°C	34.8°C
bp:	191.0°C	202.7°C	201.9°C
vp(25°C):	0.25 mm Hg	0.15 mm Hg	0.11 mm Hg
sp gr(20°C):	1.048	1.034	1.35
flash pt: (closed cup)	81.1°C	86.1°C	86.1°C
odor threshold:	0.0028 mg/m^3	0.034 mg/m^3	0.0021 mg/m^3

Soluble in water, alcohol, ether, pet. ether and benzene.

1.2 Limit defining parameters (The analyte air concentrations listed throughout this method are based on an air volume of 24 L and a solvent desorption volume of 2 mL. Air concentrations listed in ppm are referenced to 25°C and 760 mm Hg.)

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 12 ng for phenol and 14 ng for cresol per injection. This is the amount of analyte which will give a peak whose height is 5 times the height of the baseline noise. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 0.97 µg per sample (0.041 mg/m^3 or 0.01 ppm) for phenol and 1.1 µg per sample (0.046 mg/m^3 or 0.01 ppm) for cresol. This is the amount of analyte spiked on the sampling device which allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure.(Section 4.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is 0.97 µg per sample (0.041 mg/m^3 or 0.01 ppm) for phenol and 1.1 µg per sample (0.046 mg/m^3 or 0.01 ppm) for cresol. This is the smallest amount of analyte which can be quantitated within the requirements of 75% recovery and 95% confidence limits of ±25%. (Section 4.3)

1.2.4 Sensitivity

The sensitivity of the analytical procedure over a concentration range representing 0.5 to 2 times the target concentration based on the recommended air volume is 14,777 area units/(µg/mL) for phenol and 13,756 area units/(µg/mL) for cresol. The sensitivity is determined from the slope of the calibration curve. The sensitivity may vary with instruments or instrumental conditions. (Section 4.5)

1.2.5 Recovery

The recovery of the analyte from the collection medium during storage must be 75% or greater. The recovery of phenol and cresol samples stored at ambient conditions for 15 days remained above 93% and 94% respectively. (Section 4.8)

1.2.6 Precision (analytical procedure)

The pooled coefficient of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the target concentration is 0.0044 for phenol and 0.0061 for cresol. (Section 4.4)

1.2.7 Precision (overall procedure)

The overall procedure must provide results at the target concentration that are ±25% or better at the 95% confidence level. The precision at the 95% confidence level for the 15-day storage test is ±10.7% for phenol and ±10.6% for the cresols. These values include an additional 5% for sampling error. (Figures 4.8.1 and 4.8.3)

1.3 Advantages

1.3.1 The solid sorbent sampling tube for phenol and cresol provides greater ease of sampling than an aqueous bubbler.

1.3.2 The analysis for phenol and cresols is rapid, sensitive, and precise.

2. Sampling Procedure

2.1 Apparatus

2.1.1 Use a personal sampling pump which can be calibrated to within ±5% of the recommended 0.1 L/min flow rate while the sampling tube is in line.

2.1.2 Use glass sampling tubes of approximately 4 to 5 cm in length (4-mm i.d. × 6-mm o.d.) which are packed with a 100-mg front section, and a 50-mg back section of 15/50 mesh XAD-7 resin (Rohm and Haas, Inc.). Empty glass sampling tubes, open on both ends with one of the tapered ends removed, are ideal for this purpose. Use small silanized glass wool plugs in the ends and in the middle of the tube to retain and separate the sorbent material. Prior to use in the sampling tube, the XAD-7 resin must first be rinsed with several small volumes of methanol to remove fine particles. The resin is then Soxhlet extracted with methanol for 48 h to remove trace impurities and finally dried by vacuum.

2.2 Reagents

None required

2.3 Technique

2.3.1 Label sampling tubes prior to sampling.

2.3.2 Attach the sampling tube to the pump using a section of flexible, plastic tubing. Do not place any tubing ahead of the sampling device. Attach the sampling device in the workers breathing zone in such a manner that it does not impede work performance.

2.3.3 After sampling for the appropriate time, remove the sampling device, and cap and seal the sampling tube with plastic caps.

2.3.4 Include at least one blank for each sampling set. The blank should be handled in the same manner as the samples with the exception that air is not drawn through it.

2.3.5 Any bulk samples submitted for analysis must be shipped in separate containers to avoid contamination of the air samples.

2.3.6 List any potential interferences on the sample data sheet.

2.4 Breakthrough

The volume of air containing 35.3 mg/m^3 phenol and 34.8 mg/m^3 cresols at 80% relative humidity which can be sampled at 0.2 L/min before 5% of the total analytes collected is detected on the backup section of the sampling tube is estimated to be 173 L for phenol and 216 L for cresol. These breakthrough volumes are based on two of three breakthrough studies using XAD-7 resin. These values reflect the calculated air volumes for a 100-mg front section of XAD-7 resin. The selection of XAD-7 resin as the sampling medium was based on an extensive evaluation of a variety of different solid sorbent materials. The methods used to evaluate these materials and the results of the evaluation are presented in Section 4.7.

2.5 Desorption efficiency

The desorption efficiency of the analytes from the collection medium must be 75% or greater. The average desorption efficiency over the range of 0.5 to 2 times the target concentration is 99.6% for phenol and 97.9% for cresol. (Section 4.6).

2.6 Recommended air volume and sampling rate

A 24-L air sample obtained by sampling at 0.1 L/min for 4 h is recommended for phenol and cresol. If necessary, the sensitivity of the analytical method will permit a sampling period as short as 15 min at 0.1 L/min for determination of the analytes at the target concentration.

2.7 Interferences

There are no known interferences to the sampling procedure.

2.8 Safety precautions

2.8.1 Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2 Follow all safety practices that apply to the work area being sampled.

3. Analytical Procedure

3.1 Apparatus

3.1.1 A high performance liquid chromatograph equipped with sample injector, analytical reverse-phase HPLC column, variable wavelength detector, chart recorder and all necessary hardware needed for the analysis. A Waters 6000A pump, a Waters WISP 710 auto sampler, a Perkin-Elmer LC-55 UV-Visible detector and a stainless steel column (25-cm length × 4.6-mm i.d.), slurry packed with spherical 8-µm Zorbax ODS packing material were used in this study.

3.1.2 An electronic integrator or other suitable means of measuring detector response is required. A Hewlett-Packard 3354 data system was used in this study.

3.1.3 Various sizes of volumetric glassware and pipettes are needed for sample and standard preparations.

3.1.4 Three-milliliter (or larger) screw-cap or crimp-type vials are needed for desorbing the XAD-7 sampling adsorbent. Four milliliter Waters WISP vials were used in this study.

3.1.5 Small brown glass bottles fitted with inert cap liners are needed to store standard solutions.

3.2 Reagents

3.2.1 HPLC grade methanol.

3.2.2 HPLC grade water. Our laboratory uses a commercially available water filtration system for the preparation of HPLC grade water.

3.2.3 Reagent grade phosphoric acid.

3.2.4 Reagent grade standards of phenol and the cresol isomers are required. The standards used in this study and their source are listed below:

Phenol, Chem. Service, (Lot 0-879), (West Chester, PA.); o-cresol 99+%, Matheson-Coleman-Bell (MCB), (Norwood, Ohio); m-cresol, (lot 4F22), MCB; p-cresol, (lot A7027), MCB.

3.3 Standard preparation

3.3.1 Prepare a stock solution of phenol by weighing approximately 120 mg of phenol into a 25-mL volumetric and diluting to volume with methanol. Prepare stock solutions of each of the cresol isomers by weighing approximately 35 mg of each isomer into separate 25-mL volumetrics and diluting to volume with methanol.

3.3.2 Prepare 1/50, 1/25, and 2/25 dilutions of phenol and of each of the cresol isomers into the appropriate volumes of methanol to yield standard mixtures of phenol and the cresol isomers which represent 0.5, 1, and 2 times the target concentration. Transfer the standards to dark brown glass bottles fitted with Teflon-lined caps for storage in the refrigerator.

3.4 Sample preparation

Transfer the front glass wool and sorbent section of the sampling tube to a 4-mL vial. Add 2 mL of methanol, immediately cap the vial, and shake it on a mechanical shaker for 15 min. Place the remaining backup section including both glass wool plugs into a separate 4-mL vial and desorb the sample in the same manner as the front sections.

3.5 Analysis

3.5.1 Prepare a high performance liquid chromatograph for sample analysis using the HPLC conditions listed below:

column:	(25 cm × 4.6-mm i.d.) stainless steel column packed with Zorbax 8-µm, ODS-bound, spherical, silica particles.
mobile phase:	59/41 (v/v) methanol/water, 0.1% H_3PO_4 (v/v)
flow rate:	1 mL/min
UV detector:	218 nm
injection volume:	25 µL
retention time:	phenol = 5.2 min cresol isomers = 6.9 min
chromatogram:	Figure 4.9

Insure that both the front and back sections of all sampling tubes are analyzed. Verify that all sample response values lie within the range of the responses observed for the standards.

3.5.2 The individual cresol isomers are not resolved by this method. A complete resolution of the three isomers in a tar acid mixture has been accomplished using normal phase HPLC methods although the analysis time is 30 to 40 min (Ref. 5.2). It is not necessary to resolve the cresol isomers in the analysis since the permissible exposure limit makes no distinction between isomers, and an equal response of the isomers is obtained at 218 nm. It must be recognized that analysis of a cresol sample at wavelengths other than 218 nm can produce erroneous results if the weight ratio of cresol isomers in a sample differs markedly from the ratio in an analytical standard. An equal weight ratio of ortho-, meta-, and para-cresol isomers was used in this study.

3.5.3 Analysis of phenol and cresol by gas chromatography (GC) with flame ionization detection provides a good alternate analytical method. Although somewhat less sensitive than UV detection, the GC analysis does provide a better separation of the cresol isomers (Figure 4.10).

GC conditions

column:	(6 ft × 1/8 in.) stainless steel column packed with 0.1% SP1000 on 80/100 Carbopack C
injector:	225°C

detector temp.:	225°C
detector gases:	250 mL/min, air; 20 mL/min, H_2
oven:	210°C
N_2 carrier gas:	20 mL/min

3.6 Interferences

Any compound which has the same retention time as phenol or cresol is a potential interference. Comparisons of the peak height ratios of analyte response obtained at two wavelengths for both samples and standards is a valuable confirmatory technique in HPLC. This technique can be applied to the analysis of phenol but not to the unresolved cresol isomers since different isomeric mixtures of standard and sample will give different wavelength ratios. Analysis by GC offers an excellent means of sample confirmation for both phenol and the cresols. A comparison of the results of an analysis of Beechwood creosote by both methods is given below:

Table 3.6
Analysis of Baker Lot #11946
Beechwood Creosote

	HPLC analysis	GC analysis
% phenol	6.55%	6.91%
% cresol	19.3%	19.7%

3.7 Calculations

3.7.1 Prepare a standard calibration curve of area response versus concentration for both of the analytes. Calculate the analyte concentration in the samples using a least-squares fit equation for the line obtained from the data for the standards. Enter the response values for the samples into the equation and solve for sample concentration. A laboratory data system, or many small hand-held calculators, can be used to perform these calculations.

3.7.2 Include in the calculations the concentration of the analytes found on the backup section of a sampling tube. Express results in mg/m^3 using the following equation:

$mg/m^3 = (\mu g/mL)(2\ mL\ desorption)/(air\ volume\ in\ liters)$

To convert to ppm at 760 mm and 25°C:

$ppm = (mg/m^3)(24.46)/(MW\ of\ analyte)$

24.46 is the molar volume of an ideal gas at 760 mm Hg and 25°C

3.8 Safety precautions

3.8.1 Minimize exposure to phenol and cresol vapors by performing standard preparations in a well ventilated hood.

3.8.2 Avoid all skin contact with phenol and cresol.

3.8.3 Restrict the use of solvents to well ventilated hoods.

3.8.4 Wear safety glasses in laboratory areas at all times.

4. Backup Data

4.1 Detection limit for analytical procedure

The detection limit for the analytical procedure is 12 ng for phenol and 14 ng for cresol. This is based on a 25 µL injection of a 0.485 ng/µL phenol and 0.549 ng/µL cresol standard mixture. A chromatogram of the detection limits of the analytical procedure for phenol and cresol are given in Figure 4.1.

4.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 0.97 µg per sample (0.041 mg/m^3 or 0.01 ppm) for phenol and 1.1 µg per sample (0.046 mg/m^3 or 0.01 ppm) for cresol. This is based on the presence of 0.485 µg/mL of phenol and 0.549 µg/mL of cresol in 2 mL of desorbing solution.

4.3 Reliable quantitation limit

The reliable quantitation limit is the same as the detection limit of the overall procedure since the recovery at this concentration is at least 75% and the precision is ±25% or better at the 95% confidence level. The front section of four XAD-7 sampling tubes was spiked with 5 µL of 194.2 µg/mL phenol and 219.6 µg/mL cresol in methanol and then capped for storage over a weekend in a laboratory drawer. The results of the following desorption with 2 mL of methanol are reported below:

Table 4.3
Reliable Quantitation Limit Data

analyte	phenol	cresol
µg/sample	0.971	1.10
µg	0.750	0.824
recovered	0.988	0.824
	0.868	0.952
	0.868	1.06
$\overline{X}$(%)	0.868(89)	0.915(83)
SD (%)	0.097(11.2)	0.115(12.6)
1.96SD(%)	0.190(220	0.225(25)

4.4 Precision

The pooled coefficients of variation over a range of 0.5 to 2 times the target concentration for both phenol and cresol were obtained from multiple 25-µL injections of three standard mixtures in methanol containing 97.08/109.8, 194.2/219.6, and 405.1/439.3 µg/mL of phenol and cresol respectively. The results are listed in Table 4.4.1 and 4.4.2.

Table 4.4.1
Analytical Precision Data for Phenol

µg/mL	97.08	194.2	405.1
area	1.487	2.822	6.033
response	1.488	2.809	6.003
$\times 10^6$	1.466	2.801	6.004
	1.482	2.790	6.022
	1.486	2.798	5.985
	1.490	2.810	6.012
$\overline{X}$	1.483	2.805	6.010
SD	0.0088	0.0111	0.0166
CV	0.0059	0.0040	0.0028
$\overline{CV}$	0.0044		

Table 4.4.2
Analytical Precision Data for Cresol

µg/mL	109.8	219.6	439.3
area	1.558	3.013	6.113
response	1.563	2.990	6.043
$\times 10^6$	1.537	3.003	6.081
	1.545	2.979	6.098
	1.569	2.981	6.059
	1.568	3.008	6.070
$\overline{X}$	1.557	2.996	6.078
SD	0.013	0.014	0.025
CV	0.0084	0.0048	0.0041
$\overline{CV}$	0.0061		

4.5 Sensitivity

The slope of the calibration curve over the range of 0.5 to 2 times the target concentration for the analytes represents the sensitivity of the method. The sensitivities determined in this manner are 14,777 and 13,756 area units/(µg/mL) respectively for phenol and cresol. (Figures 4.5.1 and 4.5.2)

4.6 Desorption efficiency

The desorption efficiency from spiked samples over the range of 0.5 to 2 times the target concentration is 99.6% for phenol and 97.9% for cresol. A total of 18 XAD-7 sampling tubes were spiked with variable amounts of a mixture of phenol and cresol equivalent to 0.5, 1, and 2 times the target concentration of the analytes for a 4-h air sample at 0.1 L/min. Six samples each were spiked with 2.6, 5, or 9.6 microliters of a standard mixture of 92.98/ 105.2 (mg/mL) phenol and cresol in methanol. The tubes were capped and stored overnight in a laboratory drawer. The following day each sample was desorbed with 2 mL of methanol and analyzed. The results are reported in Tables 4.6.1- 4.6.2.

Table 4.6.1
Desorption Efficiency for Phenol

× target concn	0.5×	1×	2×
phenol, µg	242	465	893
DE, %	101	99.0	96.8
	101	100	100
	103	99.0	101
	98.0	100	99.6
	100	99.0	97.3
	101	99.1	96.9
$\overline{X}$	101	99.3	98.6

Table 4.6.2
Desorption Efficiency for Cresol

× target concn	0.5×	1×	2×
cresol, µg	273	526	1010
DE, %	95.8	97.1	98.4
	95.8	98.1	102
	96.5	98.1	103
	96.5	97.1	101
	95.1	96.1	98.7
	96.0	98.1	98.7
$\overline{X}$	96.1	97.4	100.3

4.7 Breakthrough

Commercially available Tenax, Silica gel, XAD-4, and PoraPak R, S, and T sampling tubes from SKC, Inc. (Eighty-Four, PA 15330); and XAD-7 and XAD-8 tubes which were packed in the laboratory were evaluated for breakthrough. These sorbent materials were selected for evaluation either because of their high capacity for similar compounds when used as gas chromatographic packings, or because of their widespread use as sampling media (Ref. 5.8). All of the above materials exhibited high desorption efficiencies with methanol when spiked with target concentrations of the analytes and analyzed 24 h later.

The retention efficiency, which is the ability to retain the analytes when humid air was drawn through a sampling tube, was determined for all of the sorbent materials except Tenax. These retention efficiencies were measured by drawing humid air (80% RH) at 0.1 L/min, for a minimum of 3 h, through sorbent tubes which were spiked with an amount of phenol and cresol equivalent to twice the target concentration. Silica gel was the only sorbent material which failed to adequately retain the analytes on the front adsorbent section of the sampling tube.

Further evaluations of a collection method for phenol and cresol were performed using a vapor generation system. A 1.00% aqueous solution of phenol and a 0.985% aqueous solution of an equal-weight mixture of the cresol isomers were metered into a 2 L/min airstream with separate 10-mL syringes at flow rates of 7.56 µL/min and 7.72 µL/min respectively. A constant 120°C temperature was maintained at the inlet to the vapor generation system by wrapping the inlet with heating tape to ensure rapid volatilization of the analytes. Based on the analysis of sampling tubes used to monitor the generated atmosphere, approximately 92% of the expected concentration of 37.8.0 mg/m^3 phenol and 38.0 mg/m^3 cresol was obtained with the system.

Attempts to monitor analyte breakthrough using either a total hydrocarbon analyzer, or a gas chromatograph equipped with a gas sampling valve mounted downstream from the sampling tube were unsuccessful. It is suspected that adsorption of the analytes onto the glass surfaces of the vapor generation system resulted in the long lag time observed between actual breakthrough and the time required for detection of breakthrough. Reliable measures of breakthrough were determined by analyzing both the front and back sections of solid sorbent sampling tubes placed in the vapor stream for various lengths of time. A maximum of six sampling tubes could be placed on the sampling manifold at one time. Critical flow orifices attached between the sampling tubes and the vacuum system were used to accurately sample the test atmosphere at 0.2 L/min. With only one exception, all breakthrough studies were performed at approximately 80% relative humidity. Breakthrough was measured by removing the sampling tubes from the vapor stream at various time intervals and then analyzing front and back sorbent sections including the glass wool plugs. The results for the various solid sorbents tested were compared by plotting the air volume sampled versus the percent of the total analyte found on the backup section. A least squares parabolic curve forced through zero was arbitrarily used to fit the data points. The air volumes necessary to give 5, 10, 15, and 20 percent breakthrough were determined from the equations for the curves. Representative breakthrough curves for XAD-7 (test 1) and for SKC, Inc. silica gel tubes are included. (Figures 4.7.1 - 4.7.4)

Due to the high analyte capacities observed for most of the sorbents tested, less than normal amounts of sorbent material were generally used in the breakthrough studies. Unless otherwise indicated, all of the breakthrough studies were performed with an accurately weighed 25-mg front portion of adsorbent and an approximate 50-mg back portion. Small silanized glass wool plugs were used to separate and retain the sections.

The results of breakthrough studies for all solid sorbents tested are presented in Tables 4.7.1 - 4.7.4. Breakthrough tests on XAD-7 were performed three times with the combined phenol and cresol atmosphere at 80% relative humidity and once at 50% relative humidity. Two tests of phenol breakthrough on XAD-7 in the absence of cresol, and one test of cresol on XAD-7 in the absence of phenol were also performed. Breakthrough tests were also conducted on PoraPak R, S, and T sorbents with the combined analyte atmosphere. Because of their greatly reduced capacities for phenol and cresol, the entire front sections of both silica gel and Tenax were tested for breakthrough. The breakthrough air volumes for silica gel listed in Tables 4.7.3 and 4.7.4 have been adjusted for the difference in the amount of sorbent used compared to the other sorbents.

An initial screening of SKC, Inc. Tenax (2,6-diphenyl-p-phenylene oxide polymer) tubes indicated that this material was not effective in trapping the analytes and further evaluations of breakthrough were not conducted. The sampling of 36 L of the phenol and cresol atmosphere at 0.2 L/min and at 80% relative humidity resulted in the retention (on the entire Tenax sampling tube) of only 22% of the total phenol and 56% of the total cresol present in the atmosphere.

The capacities of the various sorbents on a percent weight basis are reported in Tables 4.7.5 and 4.7.6. These values were determined from the breakthrough studies by dividing the amount of

analyte on the front section of the sampling tube at saturation by the weight of the solid sorbent used. With the possible exception of silica gel, all of the sorbents demonstrated a higher capacity for cresol than for phenol. These values are consistent with the differences in breakthrough air volumes observed for cresol and phenol. The low capacities measured for silica gel and Tenax are also reflected in low breakthrough air volumes for these adsorbents.

Examination of the breakthrough volume and the capacity data indicate that XAD-7, with the exception of one study, is a very effective solid sorbent for sampling phenol and cresol in air. Although the determination of breakthrough volumes was subject to some variation, it appears that the collection efficiency of either phenol or cresol on XAD-7 is not affected by the presence of the other analyte. Lowered humidity apparently does not have an effect on breakthrough air volumes or capacity. In only one study of XAD-7 were both reduced breakthrough volume and reduced capacities observed. The reason for the differences observed in this one study is not known.

The breakthrough volumes and the capacities determined for the PoraPak resins indicate that these sorbent materials are also quite effective in collecting the analytes. The SKC PoraPak sampling tubes were not selected for use because they presented some potential sampling and analytical problems. The fine mesh size of the PoraPak resins used in the SKC sampling tubes resulted in a large pressure drop of 5 inches of water across the sampling tube at a 0.1 L/min flow rate. This may affect sample pump performance during prolonged sampling periods. Some problems were also experienced with the analysis of the PoraPak sampling tubes. Difficulty in transferring the resins for methanol extraction was experienced, and extraneous UV-absorbing peaks extracted from the resins were observed upon analysis. All of the problems associated with the PoraPak resins might easily be overcome if properly sized and properly solvent-extracted resins are used in the sampling tubes.

Table 4.7.1
Parameters for Tests Listed in Table 4.7.2

	analyte	relative humidity (%)	amount of adsorbent (mg)
test 1	phenol/cresol	80	25
test 2	phenol/cresol	80	30*
test 3	phenol/cresol	80	25
test 4	phenol/cresol	50	25
test 5	phenol	80	25
test 6	phenol	80	25
test 7	cresol	80	25

* Air volumes of test 2 corrected by weight difference factor. (25 mg/30 mg) × air vol.

Table 4.7.2
Breakthrough (BT) Air Volumes (L) on XAD-7

%BT	1 phen/cres	2 phen/cres	3 phen/cres	4 phen/cres	5 phen	6 phen	7 cres
5	32.4/54.1	38.2/54.1	15.0/28.7	53.7/58.9	29.6	27.2	44.2
10	42.9/*	46.0/67.9	24.0/40.9	45.1/77.5	39.0	37.0	56.8
15	50.9/*	52.0/78.8	31.3/50.2	52.5/*	46.3	45.1	66.7
20	57.8/*	57.7/*	37.5/58.0	58.8/*	52.4	52.2	75.0

* No breakthrough data obtained at this level
test atmosphere concn: phenol - 37.8 mg/m^3, cresol - 38.0 mg/m^3

Table 4.7.3
Phenol Breakthrough (BT) Air Volume (L) for Solid Sorbents

% BT	PoraPak R	PoraPak S	PoraPak[1]T (30 mg)	PoraPak T	XAD-4	XAD-8	Silica Gel[1] (140 mg)
5	28.3	23.8	34.6	41.8	5.2	15	0.68
10	36.6	32.8	41.7	49.5	11.0	25.5	1.20
15	43.1	39.7	47.5	55.8	17.4	34.1	1.64
20	48.6	45.6	52.4	61.2	24.9	41.6	2.04

[1] Air volumes of test 2 corrected by weight difference factor (25 mg/30 mg used in test) × air vol

Table 4.7.4
Cresol Breakthrough (BT) Air Volume (L) for Solid Sorbents

% BT	PoraPak R	PoraPak S	PoraPak[1]T (30 mg)	PoraPak T	XAD-4	XAD-8
5	52.7	49.7	50.5	65.5	37.0	31.4
10	67.7	62.6	62.1	*	*	*
15	79.3	72.8	71.4	*	*	*
20	*	*	*	*	*	*

[1] Thirty milligrams used in test. Air volume corrected by weight difference factor. (25 mg/30 mg) × air vol
* No breakthrough data obtained at this concentration

Table 4.7.5
Capacity[1] of Phenol and Cresol on XAD-7

test	phenol	cresol
1	5.7	7.7
2 (30 mg)	5.2	7.3
3	4.8	6.8
4 (50% RH)	5.9	7.9
5 (phenol only)	5.6	
6 (phenol only)	5.8	
7 (cresol only)		7.8

[1] percent by weight

Table 4.7.6
Capacity[1] of Other Sorbents

sorbent	phenol	cresol
PoraPak T	5.7	8.0
PoraPak T (30 mg)	5.0	7.3
PoraPak R	4.8	8.1
PoraPak S	5.0	7.9
XAD-4	4.2	6.4
Xad-8	4.4	5.4
silica gel	0.2	0.31
Tenax	0.5	1.5

[1] percent by weight

4.8 Storage data

No stability problems were observed upon storage of phenol and cresol on XAD-7 over a 15-day period. Samples for storage were generated using the same test atmosphere of phenol and cresols as was used for the breakthrough studies. The average concentration of the atmosphere, as determined from the analysis of all of the storage samples, was 35.3 mg/m^3 phenol and 34.8 mg/m^3 cresols. The storage samples were prepared from XAD-7 tubes containing both a front and a back section. Each sample was generated by sampling the test atmosphere at 80% relative humidity for 2 h with a 0.2 L/min flow rate. Three sets of six samples each were collected at two, three-day intervals, to give a total of 36 samples for storage. All of the samples generated on either of the two days were randomly assigned on an equal basis to a refrigerated or an ambient group for storage. Ambient samples were capped and stored in a laboratory drawer at room temperature. The refrigerated tubes were capped and stored in a refrigerator at 5°C. Six of the eighteen samples from the second group were randomly selected for analysis the same day as they were generated. These samples represent storage day zero. Six samples from the first group, three stored at ambient conditions, and three stored under refrigeration, were also analyzed at this time. These samples represent day three of storage. Similarly, over each of the next two six-day intervals, two groups of six samples were analyzed. These represent the storage samples for days 6 and 9, and for days 12 and 15 respectively. The average amount of phenol and cresol recovered from the six sampling tubes analyzed on day zero was used as the baseline to measure stability. Percent recovery of the remaining storage days is expressed relative to these averages. The results are presented in Tables 4.8.1 - 4.8.2 and Figures 4.8.1 - 4.8.4.

Table 4.8.1
Phenol Storage Test

storage time (days)	% recovery (ambient)			% recovery (refrigerated)		
0	97.9	103	97.3	99.8	102	99.6
3	99.8	99.2	98.2	97.6	96.9	98.3
6	99.4	96.7	96.0	98.2	96.9	93.8
9	99.2	97.9	95.9	97.3	97.2	97.8
12	97.0	102	93.8	103	95.2	97.7
15	96.9	99.5	99.5	98.7	101	98.0

Table 4.8.2
Cresol Storage Test

storage time (days)	% recovery (ambient)			% recovery (refrigerated)		
0	97.4	103	98.4	99.8	102	99.3
3	98.4	99.5	100	97.5	98.2	99.7
6	96.4	96.5	96.4	97.8	98.6	95.1
9	98.0	97.8	97.7	97.7	97.0	98.4
12	96.5	102	94.8	104	95.9	99.3
15	96.1	98.3	99.6	97.2	99.7	99.5

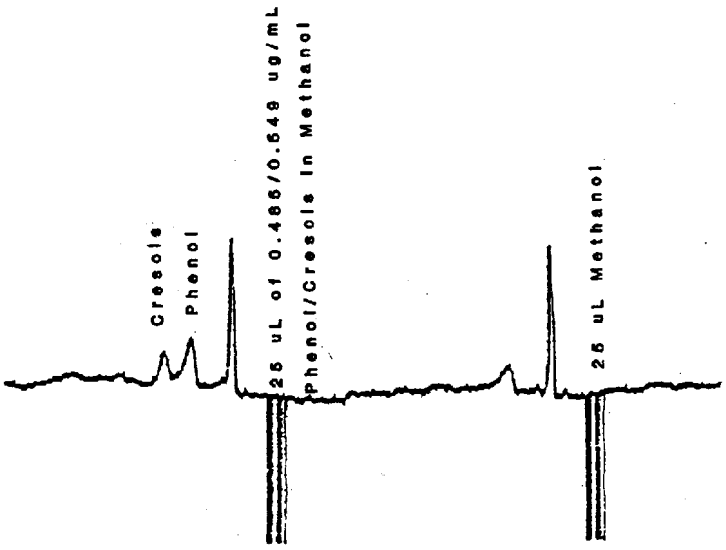

Figure 4.1. Detection limit for phenol and cresol.

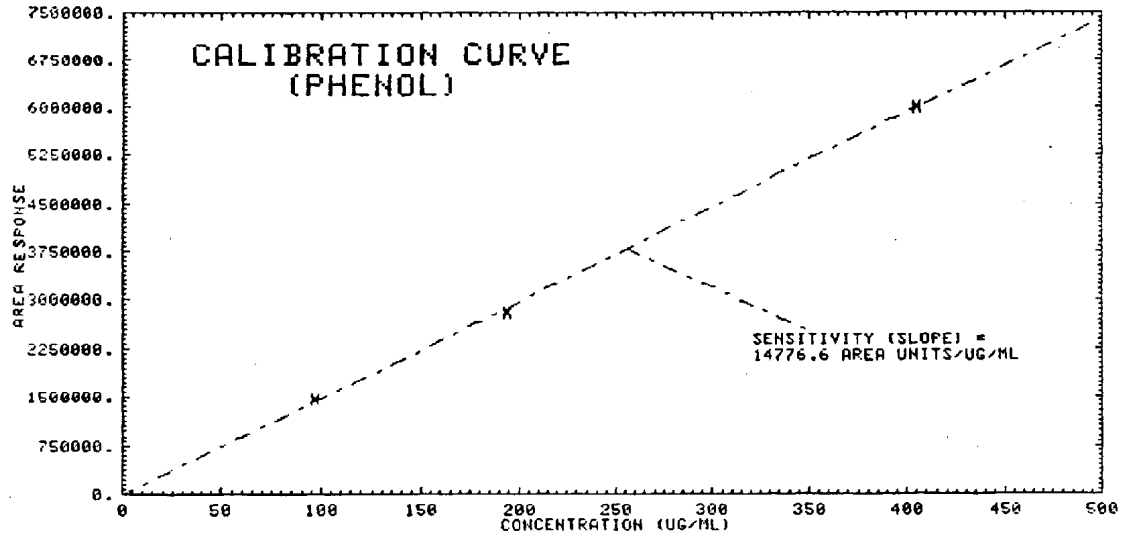

Figure 4.5.1. Calibration curve for phenol.

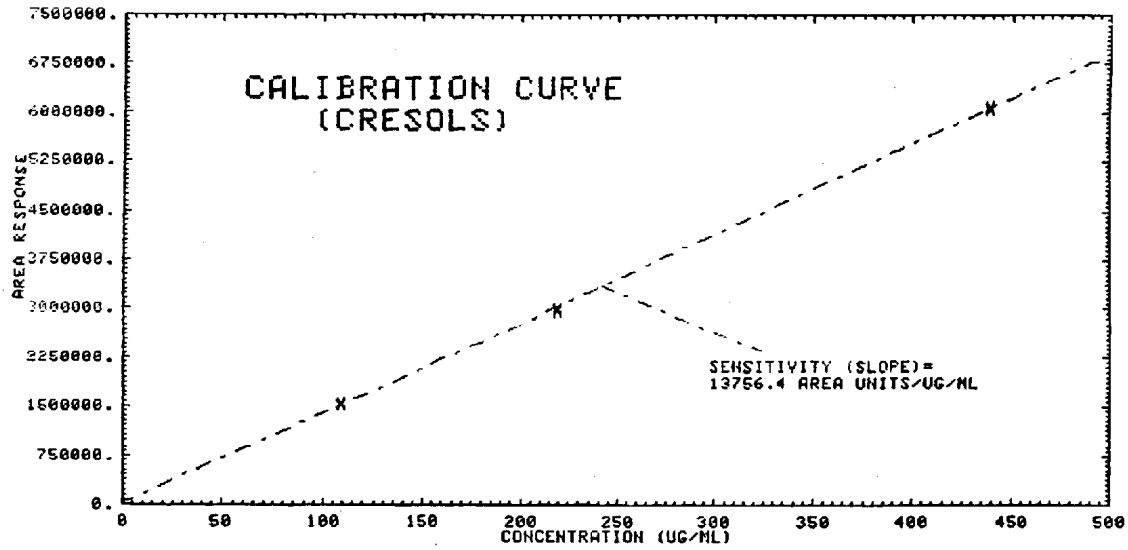

Figure 4.5.2. Calibration curve for cresols.

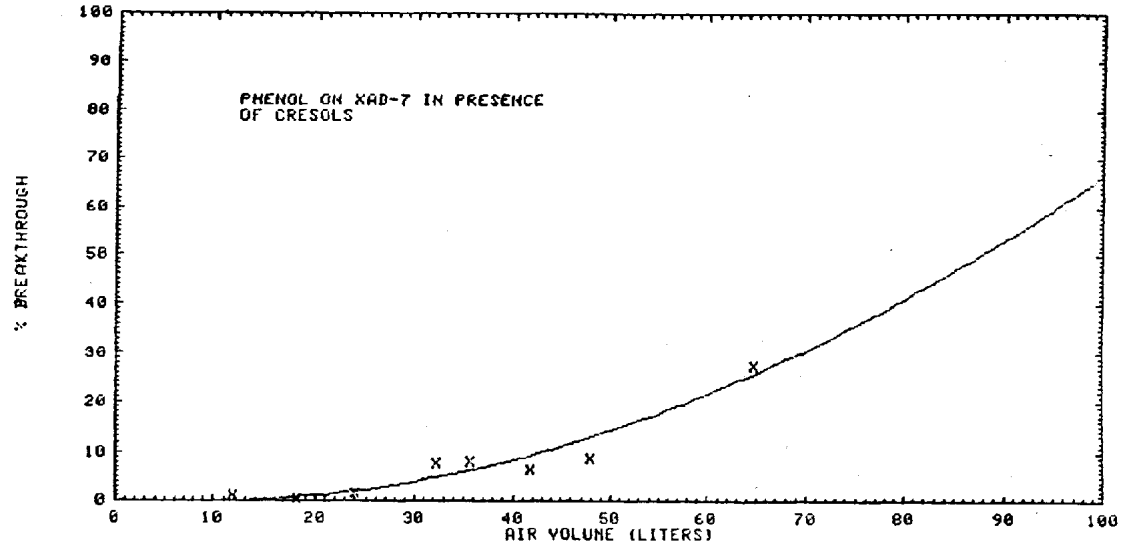

Figure 4.7.1. Breakthrough curve for phenol.

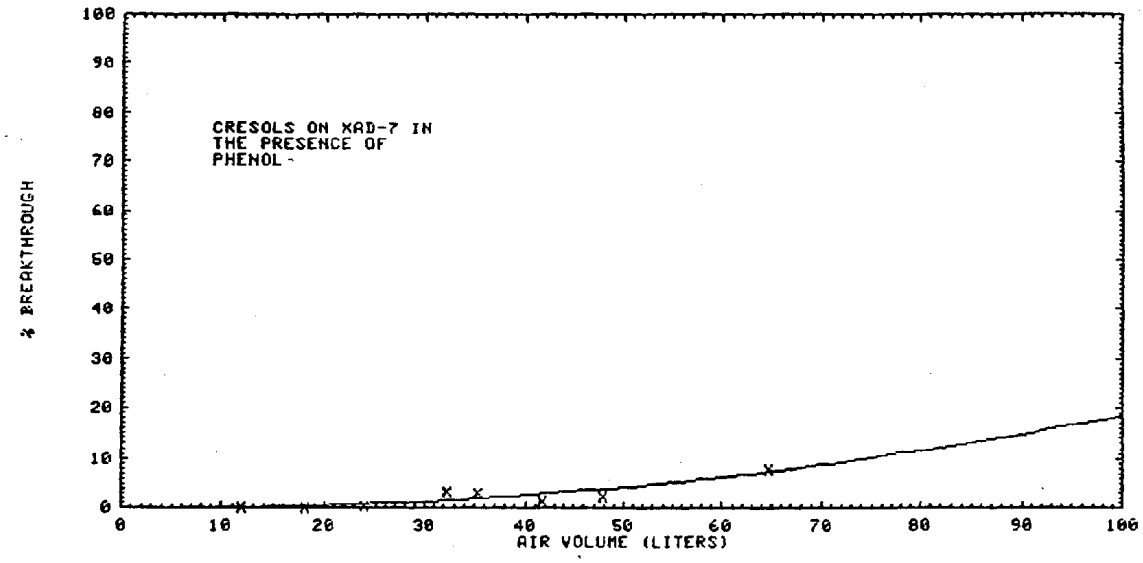

Figure 4.7.2 Breakthrough curve for cresols.

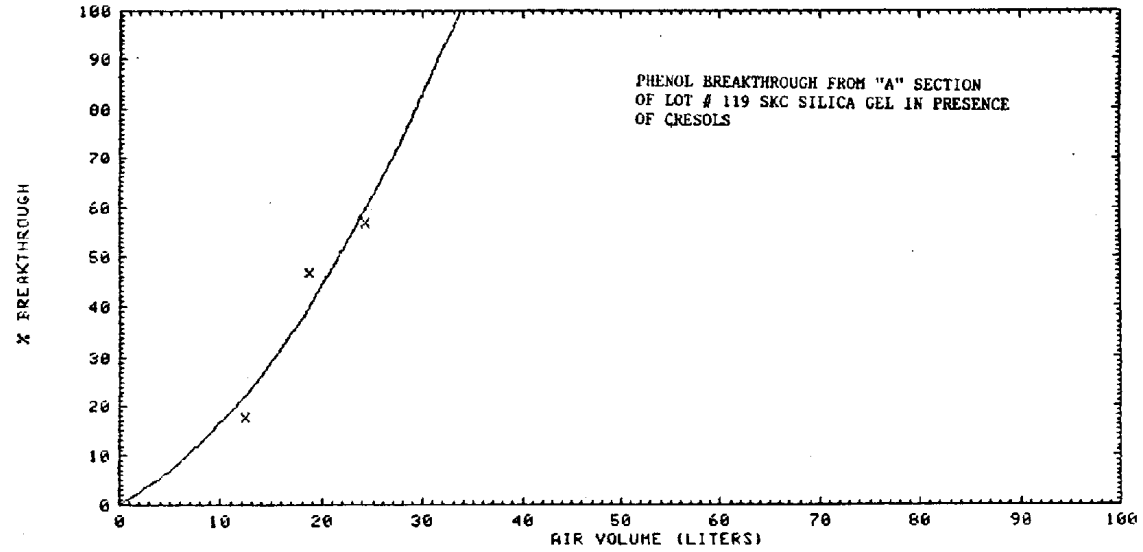

Figure 4.7.3. Breakthrough curve for phenol on silica gel.

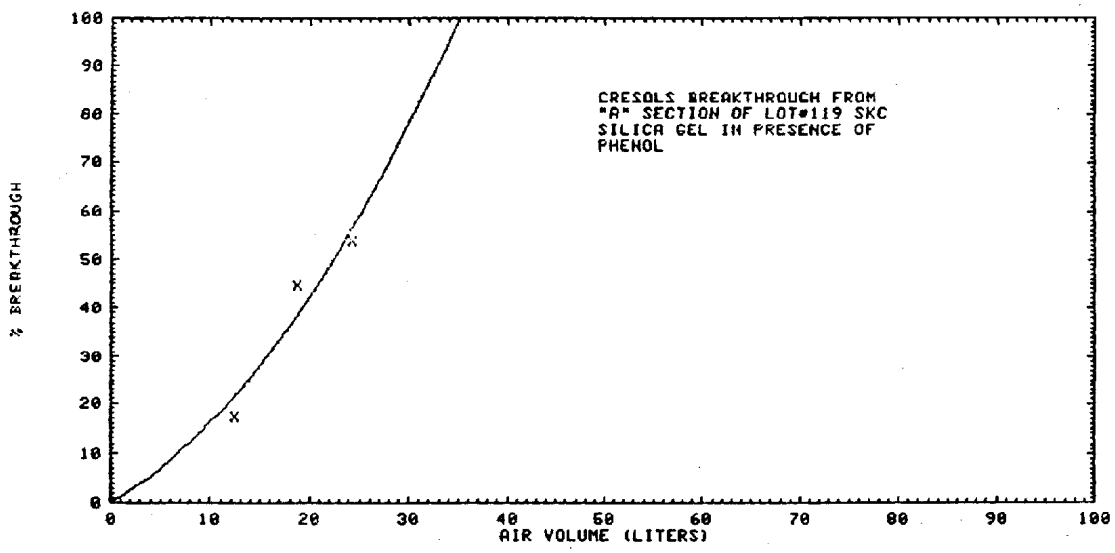

Figure 4.7.4. Breakthrough curve for cresols on silica gel.

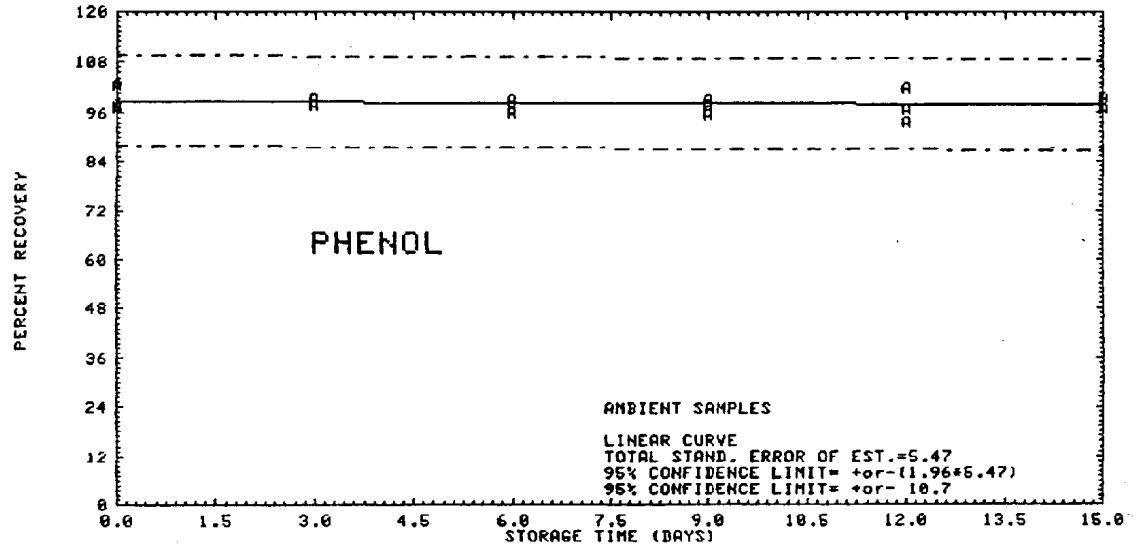

Figure 4.8.1. Ambient storage for phenol.

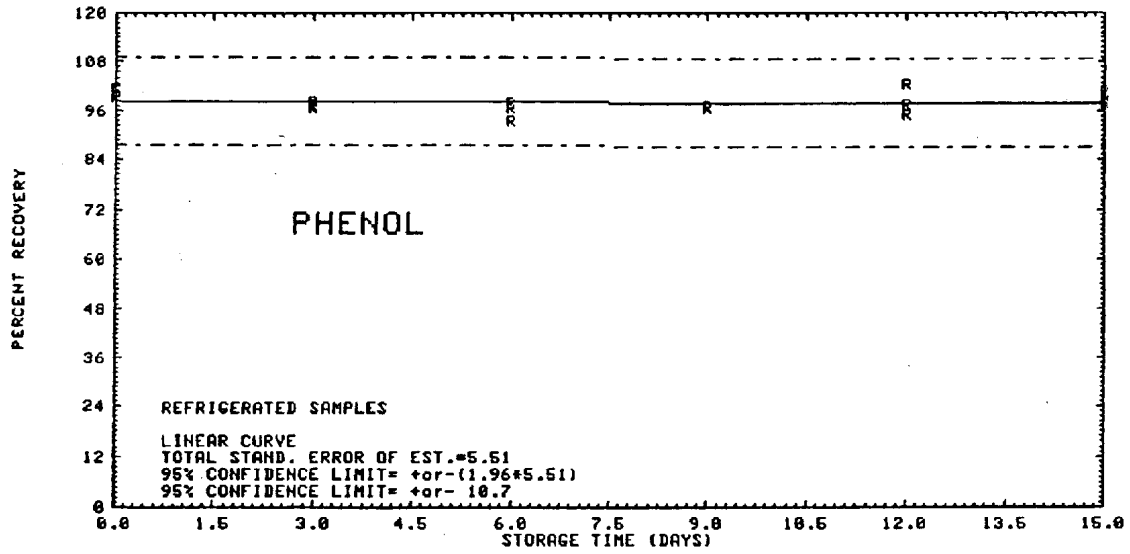

Figure 4.8.2. Refrigerated storage for phenol.

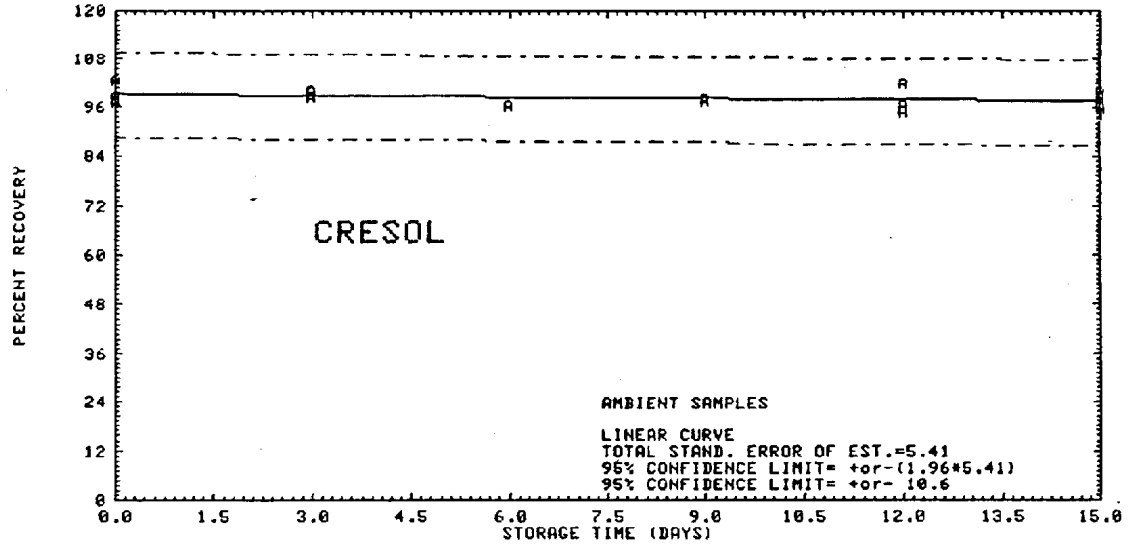

Figure 4.8.3. Ambient storage for cresols.

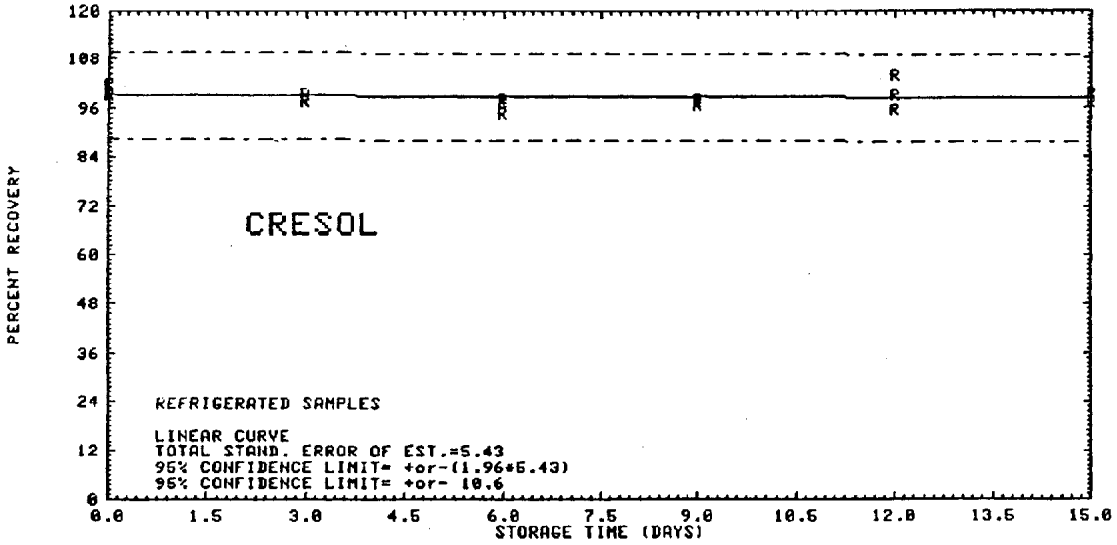

Figure 4.8.4. Refrigerated storage for cresols.

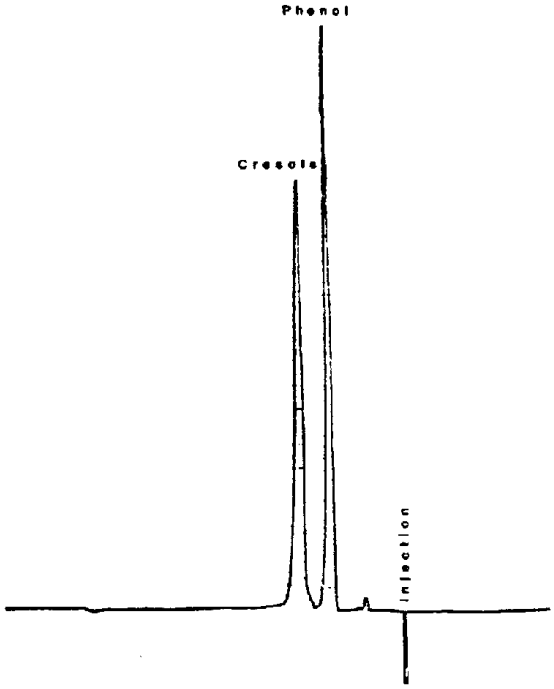

Figure 4.9. Chromatogram of phenol and cresols.

5. References

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Method 32 Appendix A

Introduction

With the advent of capillary columns, detection limits by gas chromatography are as low as with liquid chromatography for phenol and cresols, typically 1 µg/sample. Analysis of samples by liquid chromatography creates hazardous wastes, which do not occur with gas chromatography. The precision of capillary gas chromatography, with an internal standard, is typically as good or better than liquid chromatography. For these reasons the SLTC began analyzing phenol and cresol samples by capillary gas chromatography with a flame ionization detector (GC-FID). An internal standard of dimethyl formamide was used at a concentration of 1 µL/mL in the methanol. The method precision can be considered unchanged by the use of capillary GC-FID.

Experimental

Instrument:	HP5890 gas chromatograph with a flame ionization detector
Column:	60-m × 0.32-mm i.d. capillary coated with a 1.0-µm df DB-1 (J&W Scientific, Folsom, CA)
Injection size:	1 µL (19:1 split)
zone temperatures:	100°C (column), hold 4 min, ramp at 5°C/min to 160°C, hold 4 min 210°C (injector) 225°C (detector)
run time:	18 min
column gas flow:	2.9 mL/min (hydrogen)
septum purge:	1.9 mL/min (hydrogen)
retention times:	3.17 min (methyl alcohol) 6.22 min (DMF) 11.58 min (phenol) 14.20 min (o-cresol) 14.85 min (*m*- and *p*-cresol)
FID conditions:	
hydrogen flow:	38 mL/min
air flow:	450 mL/min
makeup flow:	30 mL/min (nitrogen)

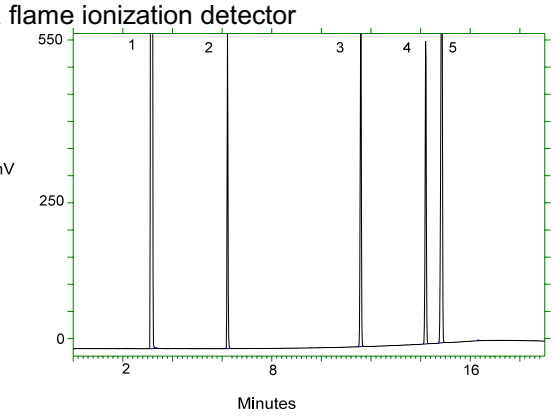

Figure A. A chromatogram of an analytical standard at the concentration of 379 µg/mL phenol, 452 µg/mL *o*-cresol, 517 µg/mL *m*-cresol, and 531 µg/mL *p*-cresol. The peaks are identified in the chromatogram as: 1 methanol, 2 DMF, 3 phenol, 4 *o*-cresol, and 5 *m*- and *p*-cresol.

Results

The desorption studies were performed by spiking XAD-7 tubes at concentrations of 379, 190, and 37.9 µg phenol; 452, 226, and 45.2 µg *o*-cresol; 517, 259, and 51.7 µg *m*-cresol; and 531, 266, and 53.1 µg *p*-cresol. The samples were allowed to equilibrate overnight at room temperature. They were opened, each section placed into a separate 2-mL vial, and desorbed with 1 mL of the desorbing solvent of 1 µL/mL DMF in methanol. The samples were placed on a shaker for ½ hour, and then analyzed by GC-FID. The average desorption efficiencies were phenol 98.4%, *o*-cresol 96.3%, *m*-cresol 96.8%, and *p*-cresol 97.5%. Quality control samples spiked with phenol, analyzed by GC-FID, over the period of 10/1/92 thru 10/1/97 had an average of 0.9601 for found/theoretical amounts.

Desorption Efficiency of Phenol

µg/sample	37.9	190	379
DE (%)	101	96.5	99.8
	96.5	98.9	97.5
	100	98.8	98.6
	99.1	98.9	97.7
	99.5	96.1	98.4
	99.7	97.1	97.0
$\overline{X}$	99.3	97.7	98.2

Desorption Efficiency of *o*-Cresol

µg/sample	45.2	226	452
DE (%)	98.3	96.8	97.2
	95.1	95.7	96.2
	97.0	96.1	96.8
	96.1	94.9	95.7
	96.5	95.0	96.8
	96.7	95.4	96.5
$\overline{X}$	96.6	95.7	96.5

Desorption Efficiency of *m*-Cresol

µg/sample	51.7	259	517
DE (%)	96.9	97.9	98.6
	94.3	97.0	97.8
	98.0	97.4	98.2
	95.1	94.0	97.4
	96.0	95.4	97.6
	95.3	98.6	97.5
$\overline{X}$	95.9	96.7	97.9

Desorption Efficiency of *p*-Cresol

µg/sample	53.1	266	531
DE (%)	99.4	97.4	97.9
	98.8	97.0	97.0
	99.0	97.4	98.2
	96.4	95.0	97.0
	96.6	96.1	97.0
	98.5	97.8	97.8
$\overline{X}$	98.1	96.8	97.5

Conclusion

Samples collected on XAD-7 tubes, requesting analysis for phenol and cresols, may be analyzed by either gas chromatography or liquid chromatography, to obtain the same results. To eliminate the hazardous wastes created by analysis with liquid chromatography, GC-FID may be the preferable means of analysis.