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DEVELOPMENT OF AIR SAMPLING AND ANALYTICAL METHODS FOR TOXIC CHLORINATED ORGANIC COMPOUNDS

Research Report for p-Chlorophenol

to

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service, Center for Disease Control
National Institute for Occupational Safety and Health
Cincinnati, Ohio 45226

Contract No. 210-78-0012

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Research Report for p-Chlorophenol

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Public Health Service
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Cincinnati, Ohio 45226

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ABSTRACT

This report describes the development of a sampling and analytical method for the determination of p-chlorophenol in air. The developed method is based on the collection of the compound from air with a solid sorbent, silica gel; the desorption of the compound with acetonitrile; and the analysis of the extract by high performance liquid chromatography with ultraviolet absorption spectrophotometric detection. The overall method was evaluated in the concentration range of 0.91 to 23 mg/m^3 in 3-L air samples. The average bias from an independent sampling method was -2% over the entire range of the method. The pooled relative standard deviation for the overall sampling and analytical method was 6.1%.

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AN AIR SAMPLING AND ANALYTICAL METHOD FOR p-CHLOROPHENOL

I. GENERAL CONSIDERATIONS

A. Background

The need for air sampling and analytical methods for toxic contaminants in the workplace arises from provisions of the Occupational Safety and Health Act of 1970 requiring that regulations be prescribed limiting the exposure of employees to substances or physical agents that may endanger their health or safety. To prescribe such regulations and to ensure compliance, it is necessary to have available sampling and analytical methods suitable for use by employers and by Government personnel.

The compound p-chlorophenol (p-CP) is potentially a highly toxic workplace contaminant. The available toxicity data have been compiled in a Material Safety Data Sheet presented as Appendix A of this report. Concern for the exposure of workers to this compound is heightened by its similarity in structure to other chlorophenols that have been selected by the Environmental Protection Agency for priority attention as point source water effluent discharge toxic pollutants [C2]. No OSHA standard has been set for p-CP; however, the threshold limit value (TLV) in the U.S.S.R. is 1 mg/m^3 [A3].

In anticipation of the need of a standard for worker exposure, NIOSH decided to develop and evaluate a method for the compound. This report describes the work that was performed under contract with NIOSH to carry out this task.

B. Research Approach

The general approach to the development of the method involved several steps. First, a literature search for information relating to air sampling and analytical methodology for the compound was performed. Second, an experimental protocol was devised for development of the method according to NIOSH guidelines; the protocol was reviewed by NIOSH and revised. A method was then developed and evaluated according to the revised protocol. Upon the completion of the evaluation of the method, a written description of the method and a sampling data sheet were submitted to NIOSH.

The information gathered in the literature search has been incorporated into an outline that classifies the material according to the following topics:

- Physical and chemical properties.
- Toxicity.
- Manufacture.
- Commercial uses.

- Analytical procedures.
- Air sampling and analytical procedures.
- Properties of candidate sorbent materials.
- Statistics.

The outline serves to annotate briefly the information and has been included as the bibliography (Section VII) of this report. Not all of the references listed in the bibliography are cited in the text of this report.

The protocol that was employed in the development and evaluation of the sampling and analytical method was comprised of the following tasks:

- Optimization of the analytical procedure.
- Calibration of the analytical method.
- Screening tests to select the best sorbents. These included the determination of desorption efficiencies of p-CP from solid sorbents by solvent extraction and the determination of the stability of the analyte spikes on solid sorbent materials.
- Selection of sorbent.
- Construction and evaluation of an analyte vapor generator and sampling system (see Appendix B).
- Determination of the capacity of the sorbent of choice for p-CP.
- Determination of the stability of p-CP collected from air with the sorbent of choice.
- Determination of the accuracy and precision of the analytical procedure including the extraction step.
- Determination of the accuracy and precision of the total sampling and analytical method.

The developed method was tested and modified until it was considered valid. The following criteria were employed for validation.

- The efficiency of the desorption of p-CP from the sorbent of choice with an appropriate solvent had to be at least 0.8.
- The bias of the method from a reliable independent method had to be no more than about ±10%.

- The relative standard deviation (RSD) of the overall sampling and analytical procedure had to be no greater than the value necessary to ensure that the average result was within ±25% of the "true" result. For a bias of ±10%, the RSD should be no greater than 8%; however, for a nonbiased method, the RSD should be no greater than about 10% [I1].
- The mean of the results obtained with freshly exposed sorbent tubes could not differ statistically at the 0.05 significance level from the mean of results obtained with exposed tubes that were stored for 7, 14, or 28 d.

One other specific task in the development and evaluation of the method was to find the lowest level of p-CP that could be extracted from the sampling medium with at least an efficiency of 0.8 and with an RSD of 10%. This level was to be called the lowest analytically quantifiable level (LAQL). The lower concentration limit of the method was then to be defined as the LAQL. in a 3-L air sample. As is discussed below, a value was assigned to the LAQL that gave a higher extraction efficiency and a lower RSD than required.

The details of the analytical method developed for p-CP are presented in this report in Appendix D (Method Description) and Appendix E (Sampling Data Sheet).

II. DEVELOPMENT AND EVALUATION OF THE ANALYTICAL METHOD

Two analytical techniques were chosen for investigation in the determination of p-CP. One involved gas chromatography with flame ionization detection (GC/FID); the other, high performance liquid chromatography with ultraviolet absorption spectrophotometric detection (HPLC/UV). Operating conditions that optimized the separation of several potential interferents were established for each technique. With the selected operating conditions, the two methods were calibrated with solutions of p-CP in appropriate solvents.

On the basis of the evaluation of both techniques, HPLC/UV was selected as the method of choice because the technique allowed the separation of m- and p-CP, whereas the GC/FID procedure did not and because the detection limit with respect to the p-CP solution concentration was lower for HPLC/UV (0.1 μg/mL) than for GC/FID (0.6 μg/ml). Details of the evaluations are given below.

A. GC/FID Analysis

1. Selection of appropriate operating conditions

The optimum procedure for determining p-CP by GC/FID was established in the presence of nine suspected interferents: o-chlorophenol; phenol; 2,3-dichlorophenol; 2,4-dichlorophenol; 2,5-dichlorophenol; 2,6-dichlorophenol; 3,5-dichlorophenol; 3,4-dichlorophenol; and m-chlorophenol.

The gas chromatograph employed was the Perkin-Elmer 3920 equipped with an FID. The GC column was 1% SP-1240DA on Supelcoport (100/120 mesh) in glass tubing (2 m by 2 mm i.d.). SP-1240DA is a polyester-type stationary phase, modified for use with acidic compounds. Two-microliter aliquots of a mixture containing each compound (including p-CP) at a concentration of about 1 mg/mL in methanol were injected into the GC. The operating conditions were adjusted to provide a reasonably sharp peak for p-CP while resolving the peak from those of the other compounds. The following operating conditions were found to be optimum:

- Carrier gas: helium, 30 mL/min.
- Injection port temperature: 200 °C.
- Column temperature: 140 °C for 4 min, then programmed to 190 °C at 32 °C/min.
- FID temperature: 220 °C.

A chromatogram of a methanol solution of the compounds, each at a concentration of about 1 mg/mL, is presented in Figure 1. This chromatogram illustrates that the resolution of p-CP from the potential interferents was adequate except for m-CP. Both m- and p-CP were eluted with the same retention time, and attempts to separate them by altering operating conditions were to no avail.

A variety of nitrophenols and cresols that are classified by the Environmental Protection Agency (EPA) as consent decree priority pollutants in water were also investigated as potential interferents in the GC/FID procedure. They are as follows: p-nitrophenol; o-nitrophenol; 2,4-dinitrophenol; 2,4-dimethylphenol; 4-chloro-m-cresol; 4,6-dinitro-o-cresol; 2,4,6-trichlorophenol; and pentachlorophenol.

A mixture containing p-CP and this second set of suspected interferents, each at a concentration of about 100 μg/mL (0.1 μg of each injected in 1-μL injection volumes) in methanol, was injected into the GC. The following operating conditions were found to be optimum:

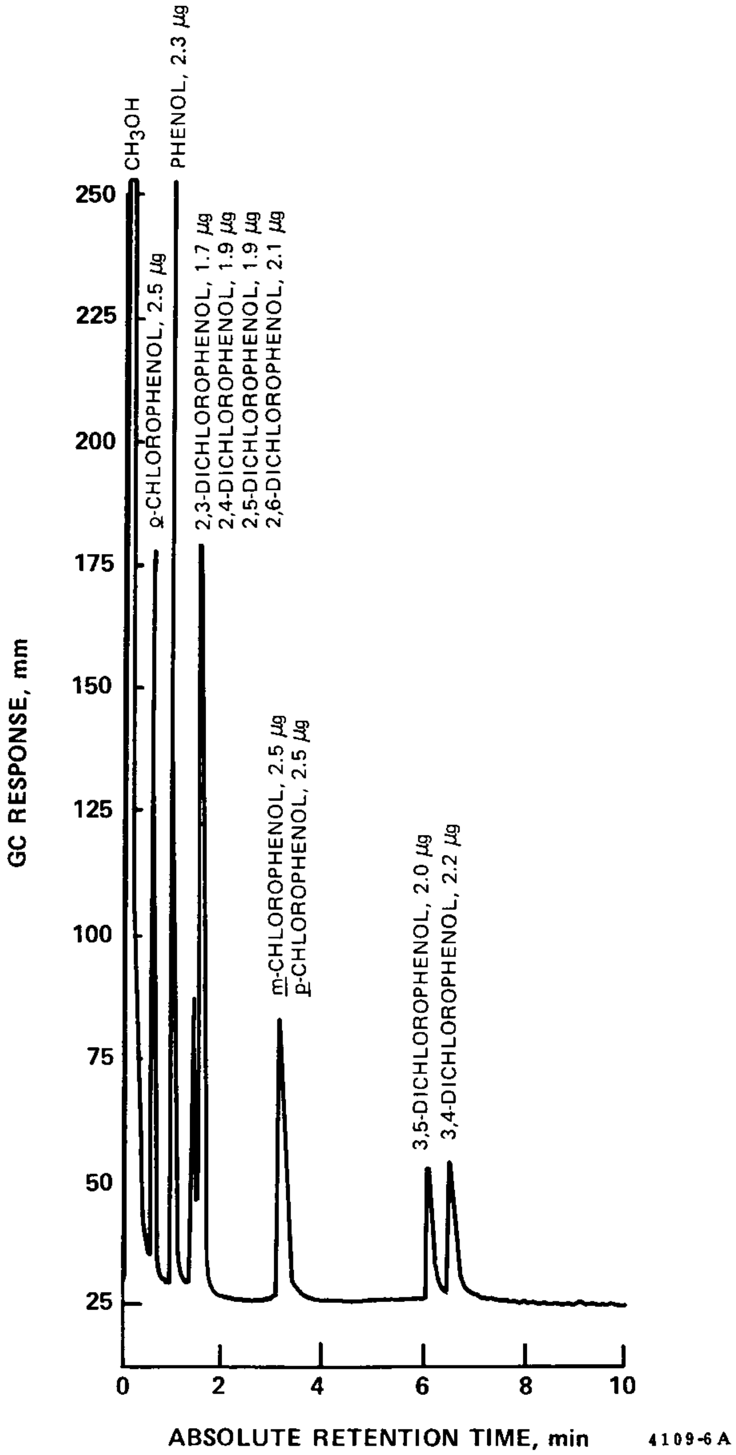

Figure 1. Gas chromatogram of p-chlorophenol and potential interferents.

- Carrier gas: helium, 30 mL/min.
- Injection port temperature: 200 °C.
- Column temperature: 70 °C programmed to 185 °C at 8 °C/min, maintained at 185 °C for 8 min.
- FID temperature: 220 °C.

A chromatogram of the methanol solution of the compounds is represented in Figure 2. This chromatogram illustrates that the resolution of p-CP from all of these potential interferents was complete. Under the specified operating conditions, however, m- and p-CP were not found to be resolved as was also observed for the conditions employed in the investigation of the first set of potential interferents.

2. Calibration

A calibration curve for p-CP in carbon disulfide solutions was established to demonstrate the sensitivity and linear response range achievable with the GC/FID procedure under the second set of operating conditions detailed above. Carbon disulfide instead of methanol solutions were employed because the FID response to methanol interfered with the determination of p-CP at relatively low concentrations. Concentrations of p-CP in the range of 0.64 µg/mL (3 ng injected) to 127 µg/mL (635 ng injected) were measured.

A linear least-squares curve for peak height measurements is presented in Figure 3. The correlation coefficient (r) calculated from the peak-height data was 0.9979; the detection limit was estimated to be about 0.64 µg/mL, a concentration that gave a response that was about twice the noise level.

Standard solutions of p-CP in methanol and carbon disulfide (as well as other solvents investigated in additional work) were prepared as follows. First, a stock solution was prepared by accurately weighing about 500 mg of solid p-CP (Aldrich Chemical Co.), by dissolving the weighed amount in the solvent, and by then diluting the solution with the solvent to 25 mL in a volumetric flask. Serial dilutions were made with the solvent to obtain working standards. Solutions were found to be stable indefinitely while stored in airtight stoppered Pyrex flasks at about 25 °C. No attempt was made to shield the flasks from the light.

B. HPLC/UV Analysis

1. Selection of appropriate operating conditions

The following operating conditions were found to be optimum for the separation of potential interferents with the Hewlett-Packard 1084B Liquid Chromatograph:

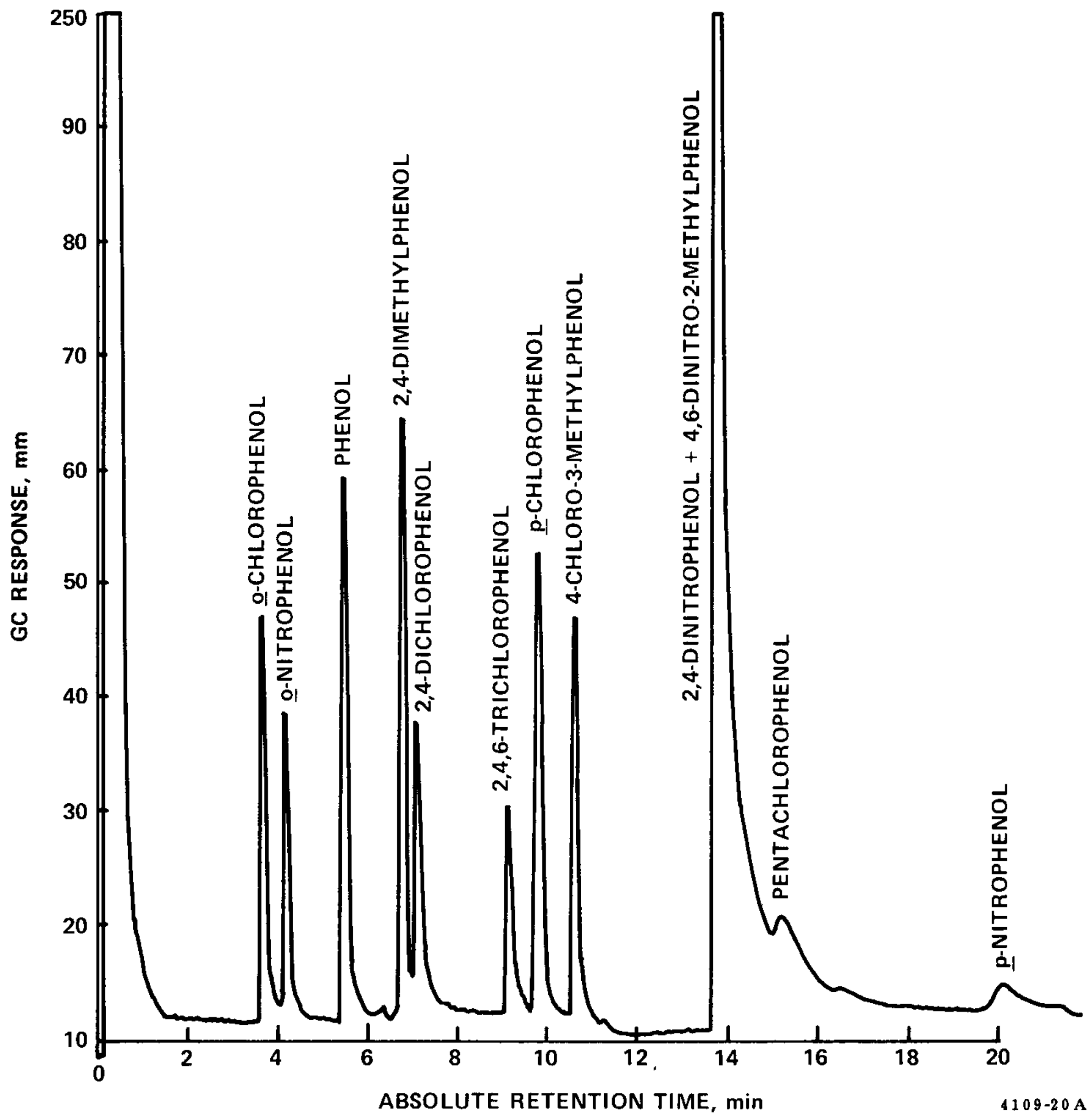

Figure 2. Gas chromatogram of 0.1-µg quantities of p-chlorophenol and Environmental Protection Agency's consent decree priority pollutant phenols.

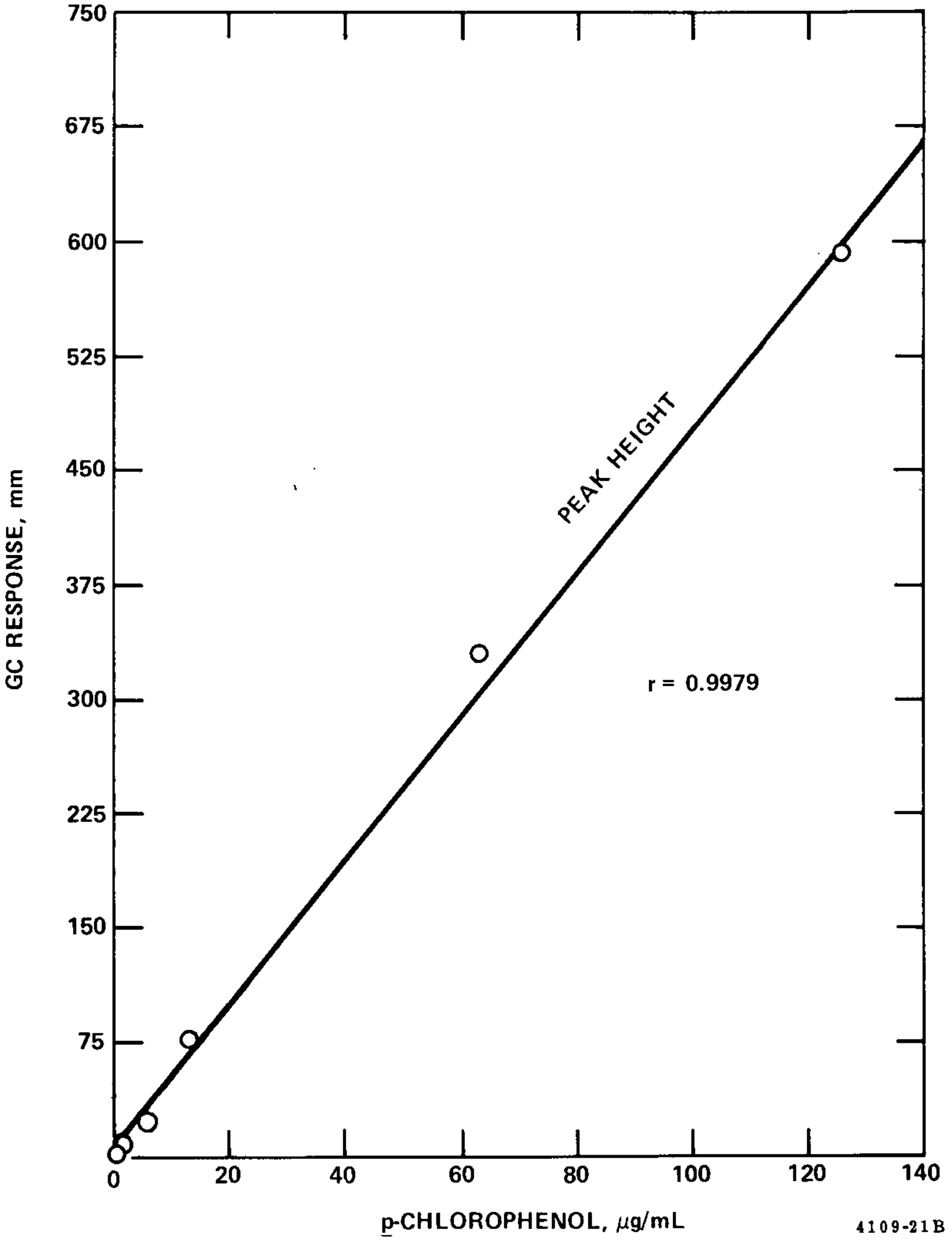

Figure 3. GC calibration curve for p-chlorophenol with 5-µL injection volumes.

- Column: MicroPak MCH-5, 5-μm particle size, 30 cm long by 4 mm i.d.
- Column temperature: 30 °C.
- Solvent A: Distilled, deionized water.
- Solvent B: Acetonitrile.
- Solvent program: 30% B to 80% B in 20 min.
- Solvent flow rate: 1 mL/min.
- UV detector: analytical wavelength, 280 nm; reference wavelength, 430 nm.
- Column cleanup procedure. At the end of each working day, the column was flushed with approximately 50 mL of acetonitrile (Solvent B) at a flow rate of 1 mL/min.

A chromatogram of a methanol solution containing p-CP and nine of the suspected interferents investigated in the GC/FID procedure, each at a concentration of about 1 mg/mL, is presented in Figure 4. Two-microliter injection volumes were employed. This chromatogram illustrates that the resolution of p-CP from comparable quantities of all of the compounds, including m-CP, was satisfactory. There was some overlap between the m- and p-CP peaks; however, the calculated resolution was 0.91.

A chromatogram of acetonitrile solutions of several of the other suspected interferents, each at a concentration of about 100 μg/mL, is presented in Figure 5. The resolution of p-CP from these compounds was complete.

2. Calibration

A calibration curve for p-CP in acetonitrile was determined to demonstrate the sensitivity and linear response range achievable with the HPLC/UV procedure. One-hundred-microliter injection volumes were employed. Concentrations of p-CP in the range of 0.118 μg/mL (12 ng injected) to 118 μg/mL (12 μg injected) were determined.

Least-squares curves for both peak height and peak area data are presented in Figure 6. The UV response was linear with respect to both peak height and peak area. The correlation coefficient calculated from the peak-height data was 0.9999 and from the peak-area data was 1.0000. The detection limit was estimated to be about 0.1 μg/mL, a concentration that gave a response that was about twice the noise level.

Although it was found that m- and p-CP could be separated with a resolution of 0.91, it was also observed that the peak area measurements for p-CP that were determined by the data system for the Hewlett-Packard

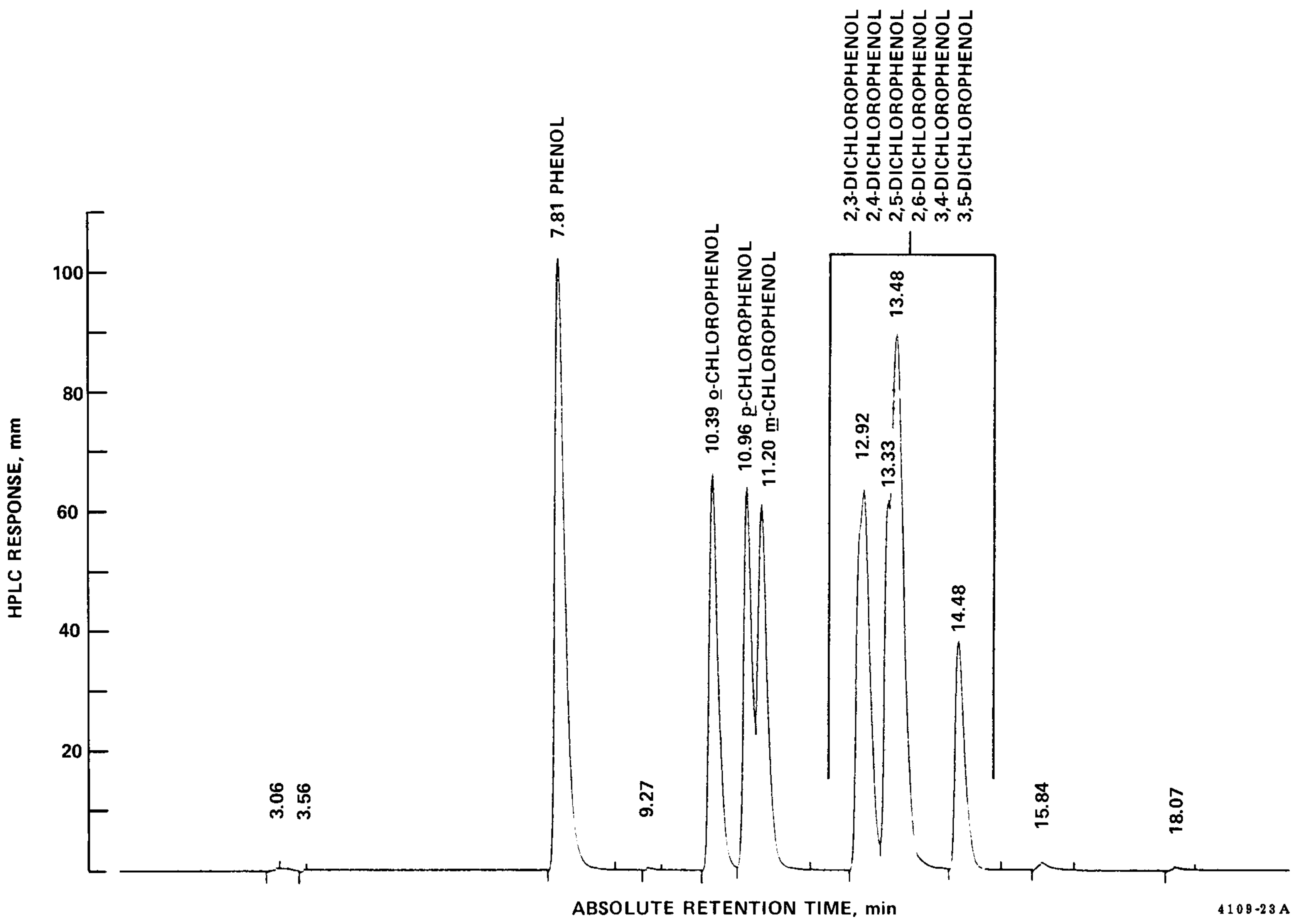

Figure 4. Chromatogram for HPLC determinations of 2-μg quantities of p-chlorophenol and potential interferents. (The numbers given above the peaks are absolute retention times.)

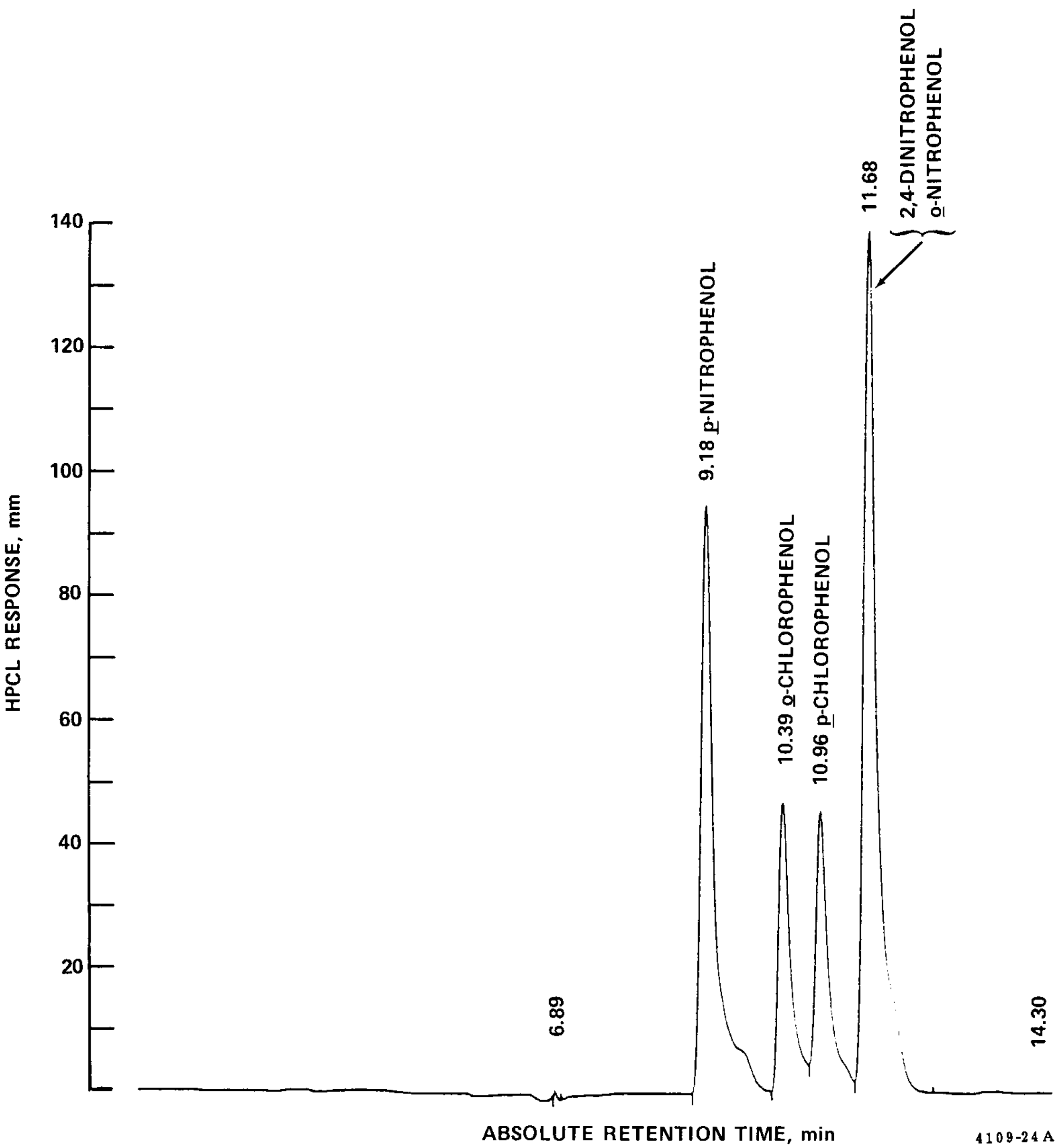

Figure 5. Chromatogram for HPLC determinations of 0.2-μg quantities of p-chlorophenol and several of the Environmental Protection Agency's constant decree priority pollutant phenols. (The numbers given above the peaks are absolute retention times.)

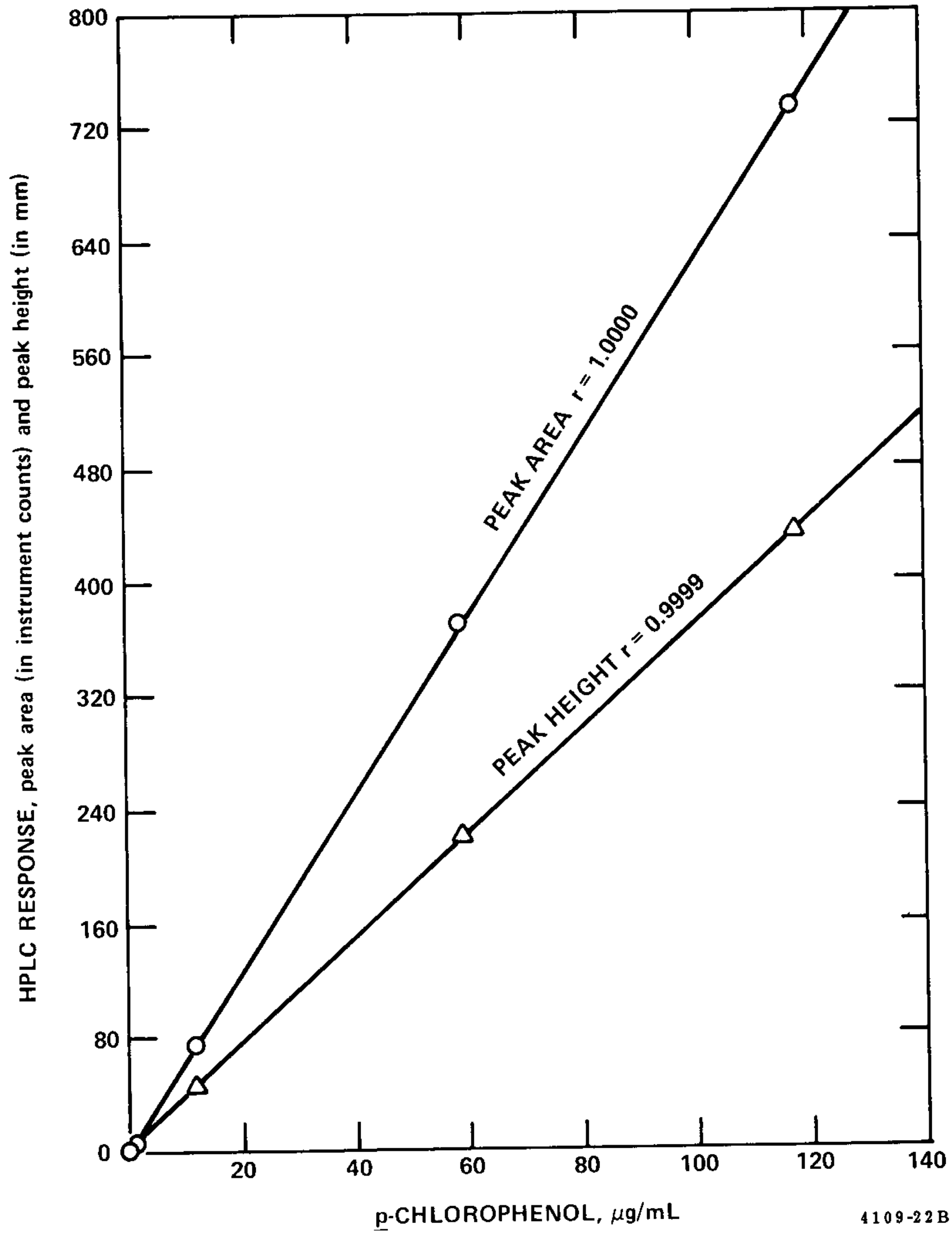

Figure 6. HPLC calibration curve for p-chlorophenol with 100-μL injection volumes.

1084B were significantly different from those determined in the absence of m-CP. For instance, with both m-and p-CP present at concentrations of 1.26 and 1.27 mg/mL, respectively, the measured peak areas for p-CP were only about 70% of those found with the same concentration of p-CP alone. However, p-CP peak height measurements in the same chromatograms only differed by about 5%, a difference that was attributed to experimental error alone. The larger discrepancy in area measurements appeared to be an artifact of the instrument integration process. (In these tests, 2-μL injection volumes were employed.)

C. Selection of Analytical Method of Choice

From the evaluation of the two analytical procedures, there resulted two significant advantages of the HPLC/UV technique over the GC/FID procedure. First, m- and p-CP were adequately separated by HPLC. Second, because larger injection volumes could be employed in the HPLC procedure than with the GC method, lower solution concentrations could be accurately determined than by the GC procedure. The HPLC procedure was, therefore, the method of choice for our method development.

III. SELECTION OF COLLECTION MEDIUM AND PRELIMINARY EVALUATION

A. Screening Tests

Screening tests were limited to the determination of the desorption efficiency in the solvent extraction of p-CP from various solid sorbents and the determination of the stability of p-CP on the sorbent materials. (Sorbents were not screened with respect to their capacities for p-CP because it was expected that most any sorbent material would exhibit an adequate breakthrough volume for p-CP vapor.) The term "desorption efficiency" was applied to the recovery of p-CP from spiked sorbent samples obtained after storage for only 1 d. For sorbent samples stored for more than 1 d, the recovery was then considered to be related not only to the "desorption efficiency" but also to the "stability" of the analyte on the sorbent.

The sorbent materials that were investigated are as follows: silica gel (20/40 mesh taken from tubes purchased from SKC, Inc., Catalog No. 226-10), alumina (20/40 mesh, Applied Sciences Laboratories, Inc.), Florisil (60/200 mesh, Analabs, Inc.), Porapak R (50/80 mesh, Supelco, Inc.), Porapak T (50/80 mesh, Supelco, Inc.), Amberlite XAD-2 (20/50 mesh, Supelco, Inc.), and Amberlite XAD-4 (20/40 mesh, Supelco, Inc.).

Prior to their usage, the porous polymers were cleaned by Soxhlet extraction with a 4:1 acetone/methanol solution for 4 h and then with hexane for 4 h. The materials were subsequently dried under vacuum at 50 to 100 °C overnight.

In the initial desorption efficiency and stability tests, 2.54-µg spikes were applied to 150-mg quantities of each of the candidate sorbents by the following procedure: Each sorbent sample was placed in a 4-mm i.d. Pyrex tube. The sorbent material was held in place with two glass wool plugs. A 5-µL aliquot of a 508-µg/mL solution of p-CP in hexane was deposited in one of the glass wool plugs while approximately 6 L of air free of p-CP was drawn at about 0.2 L/min through the tube. The p-CP was vaporized and transferred onto the sorbent material. The exposed tube was then sealed with plastic caps and stored for 1 to 6 d before extraction with an appropriate solvent and analysis of the extract.

The results are presented in Table I. With silica gel, extraction with 30% (v/v) acetonitrile in water gave adequate results (82 to 107% recovery) after the samples were stored for 6 d. The recovery after 1 d, however, ranged from 59 to 74%. The discrepancy between the results for the two storage periods was unexpected and no reason could be found for it. The extraction of exposed silica gel samples with methanol in water after storage for 6 d gave a much lower recovery than obtained with acetonitrile in water as the extractant. The results obtained with the alumina samples after extraction with either acetonitrile in water or methanol in water were low, also. Although the low recoveries may have been due to either inefficient extraction of the p-CP from the alumina or to loss of the compound from the sorbent during the 4-d storage period, the results were clearly unacceptable. The results with Florisil were also unacceptable. The low recoveries found for the porous polymer sorbents with the acetonitrile/water extractant mixtures were probably the result of insufficient "wetting" of the generally hydrophobic sorbents. The use of acetonitrile alone gave inconclusive results.

B. Additional Desorption Efficiency and Stability Tests with Silica Gel Leading to the Establishment of the LAQL

Because silica gel gave the most satisfactory results in the initial tests, additional experiments were performed with commercially available tubes (SKC Catalog No. 226-10), each containing a 150-mg sorbing section and a 75-mg backup section of 20/40 mesh silica gel. Twelve tubes were each spiked with 2.54 µg of p-CP and sealed with plastic caps. Six tubes were stored for 1 d at 25 °C under fluorescent lighting prior to extraction and analysis; the remaining six tubes were stored for 7 d under the same conditions. Because the results with silica gel in the earlier tests had been inconsistent, the extraction procedure was changed in an attempt to maintain a high desorption efficiency. Each sorbent sample was extracted ultrasonically for 30 min with 1 mL of acetonitrile. Then 2 mL of distilled, deionized water was added to the extract prior to analysis. The sorbing and backup sorbent sections were extracted separately.

The results are presented in Table II. The average recovery after 1 d was 91.5% and after 7 d was 94.7%. The RSD was less than 2.5% after both 1- and 7-d storage times. There was a statistical difference at the 0.05 significance level for a two-tailed t-test between the average result obtained

Table I. Recovery of p-CP from Candidate Sorbent Materials by Solvent Extraction after Various Storage Periods

Sorbent material[a]	Extraction solvent	Storage time, d	Recovery, %
Silica gel	30% CH_3CN in H_2O	1	71
			59
			74
		6	102
			82
			94
			107
			87
	30% CH_3OH in H_2O	6	57
			51
			72
			70
			70
			72
Alumina	30% CH_3CN in H_2O	4	68
	30% CH_3OH in H_2O	4	66
Florisil	30% CH_3CN in H_2O	1	58
		2	58
	100% CH_3CN	2	No data obtained[b]
Porapak R	30% CH_3CN in H_2O	1	21
		2	13
	100% CH_3CN	2	No data obtained[b]
Porapak T	30% CH_3CN in H_2O	1	39
		2	19
	100% CH_3CN	2	No data obtained[b]
Amberlite XAD-2	30% CH_3CN in H_2O	1	28
		2	25
	100% CH_3CN	2	No data obtained[b]
Amberlite XAD-4	30% CH_3CN in H_2O	1	48

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a. One-hundred-fifty-milligram portions were each spiked with 2.54-μg quantities of p-CP.

b. HPLC peaks were asymmetrical and nonreproducible.

Table II. Desorption Efficiency and Stability of 2.54-μg Quantities of *p*-CP on Silica Gel[a]

Storage time, d	*p*-CP found, μg	Recovery,[b] %	Average recovery, % (RSD)
1	2.29	89.9	91.8 (2.5%)
	2.34	92.0	
	2.40	94.3	
	2.40	94.3	
	2.30	90.5	
	2.26	88.9	
7	2.40	94.5	94.7 (1.0%)
	2.40	94.5	
	2.42	95.3	
	2.44	96.0	
	2.37	93.1	
	2.40	94.5	
$t_{(observed)}$	-2.955		
$t_{(critical)}$	-2.228		

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a. Commercially available tubes (SKC Catalog No. 226-10) containing a 150-mg sorbing section and a 75-mg backup section of 20/40-mesh silica gel were each spiked with 2.54 μg of *p*-CP and then after the appropriate time were extracted with 1 mL of acetonitrile.

b. Recovery was calculated from the level of *p*-CP recovered relative to the level added.

for samples stored for 7 d and the average result for samples stored for 1 d. This difference may be interpreted as an experimentally significant increase in recovery; however, no explanation can be offered for the increase. Both average values of recovery are much greater than the minimally acceptable value of 80%.

The 2.54-μg level was subsequently chosen as the LAQL although the desorption efficiency was greater than 80% and the RSD was less than 10%. It was felt that a desorption efficiency of at least 90% was more desirable as a criterion for selecting the quantity of *p*-CP corresponding to the lower limit of the analytical method.

C. Capacity Tests with Silica Gel Sorbent Tubes

Tests to determine the capacity of silica gel sorbent tubes for p-CP were performed as follows: Generator effluent* was sampled into SKC tubes (Cat. No. 226-10) for exposure periods of about 4, 5, or 6 h. For each of the sampling times, duplicate tubes were exposed at a sampling rate of about 0.2 L/min. The p-CP concentration in the generator effluent was about 73 mg/m^3 (as determined by impinger sampling) at a temperature of 43 °C and a relative humidity of about 80%. After sampling, the two sorbent sections of each tube were analyzed separately. The "weight breakthrough" was expressed as the fraction of the total amount of the p-CP recovered from a tube that was found on the backup sorbent section.

The results of these capacity tests are presented in Table III. The weight capacity when the "weight breakthrough" became about 5% was more than 4 mg of p-CP and the "weight-breakthrough" volume was greater than 60 L. The recovery of p-CP from the tubes averaged 107%. Because the capacity of the silica gel tube appeared to be acceptable (i.e., would allow a sampling period of greater than 2 h) under the rigorous test conditions employed, additional tests were considered unnecessary.

The "weight-breakthrough" volume for a nonreactive sorbent such as silica gel is expected to be larger than the "concentration-breakthrough" volume, which is defined as the volume of air that has been sampled through a sampling device when the concentration of the analyte in the effluent of the device becomes 5% of the test concentration. The "weight-breakthrough" volume, therefore, is a less conservative measure of breakthrough than the "concentration-breakthrough" volume. Consequently, the maximum allowable sampling volume for p-CP was recommended to be lower than 60 L or about 40 L.

D. Recommended Sampling Device for the Determination of p-CP Vapor

From the results of the desorption efficiency and stability tests and the capacity tests, commercially available silica gel sorbent tubes (SKC Catalog No. 226-10) were deemed appropriate for the determination of p-CP vapor in air. With 2.54-µg quantities of p-CP, the silica gel exhibited an acceptable desorption efficiency for the extraction of the p-CP with acetonitrile and proved to be an inert medium for storing the collected p-CP. At a p-CP concentration of 73 mg/m^3, a sampling time of about 5 h was found to be permissible at a sampling rate of about 0.2 L/min with a 150-mg sorbing bed.

The pressure drop across six separate sorbent tubes averaged 1.4 in. H_2O (350 kPa) at 25 °C at a sampling rate of 0.2 L/min. The RSD for the pressure drop measurements was 7.4%.

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* See Appendix B for a description of the vapor generator and sampling system.

Table III. Recovery of p-CP from Silica Gel in Sorbent Capacity Tests

Sampling set	Sorbent tube[a]	Tube section	Time of exposure, min	Volume sampled, L	Weight of p-CP recovered, µg	Weight breakthrough of p-CP,[b] %	Recovery of p-CP,[c] %
1	1	sorbing	240	49	3752	-	106
		backup	240	49	41	1	
	2	sorbing	240	53	4047	-	107
		backup	240	53	97	2	
2	1	sorbing	300	55	4322	-	111
		backup	300	55	123	3	
	2	sorbing	300	63	4663	-	105
		backup	300	63	174	4	
3	1	sorbing	365	75	5064	-	104
		backup	365	75	609	12	
	2	sorbing	365	73	5428	-	109
		backup	365	73	428	8	

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a. SKC, Inc., silica gel tubes (Cat. No. 226-10) were used.

b. Breakthrough was calculated from the weight of p-CP recovered from the backup section of the sorbent tube.

c. Recovery was calculated from the weight of p-CP recovered from both sections of the sorbent tubes relative to the calculated weight of p-CP to which the tubes were exposed based on impinger sampling during the exposure of each set of tubes.

IV. INDEPENDENT SAMPLING METHOD FOR THE DETERMINATION OF p-CP IN AIR

After attempts to employ a photoionization detector as an independent reference sampling and analytical method were unsuccessful (see below), it was decided to use impinger sampling as an independent sampling method for p-CP in the generator effluent with subsequent determination of the collected p-CP by HPLC/UV.

The impinger sampling procedure was as follows: Ten to twenty-five milliliters of 30% (v/v) acetonitrile in water was added to a standard midget impinger. The impinger was then attached to a generator sampling port (see Appendix B) with glass tubing and ground glass joints. In many tests, a second impinger was placed in series downstream from the first as a backup sampler. Generator effluent was then sampled through the impingers at about 0.2 L/min for periods ranging from 15 min to 6 h. The p-CP in the impinger solutions was determined by the HPLC/UV analysis procedure previously described.

The validity of the application of this sampling technique to the determination of p-CP was established as follows: First, it was found that the impinger was efficient in collecting p-CP vapor. In fact, in five sampling trials with front and backup impingers at p-CP concentrations in air ranging from 52 to 133 mg/m^3, not once did the fraction of p-CP found in the backup impinger amount to more than 1% of the total p-CP recovered. Second, it was determined that p-CP at concentrations as low as 0.85 $\mu g/mL$ was stable in 30% acetonitrile in water indefinitely at room temperature (about 25 °C).

As mentioned previously, attempts to use a photoionization detector as a monitor of p-CP concentrations in generator effluent did not achieve the desired result. The detector responded to phenol vapor in air (about 2000 mg/m^3) with the expected sensitivity; however, when exposed to p-CP vapor in air (about 70 mg/m^3), the detector gave a response that was much lower than expected. It appeared that much of the p-CP was sorbed by either the walls of the sampling probe or the sampling head. Heating the probe with a heat gun increased the response slightly but not enough to increase the sensitivity of the instrument significantly. After exposure to the generator effluent, the probe and head of the device smelled strongly of p-CP. It appeared that the response of the instrument for p-CP vapor could not be easily improved.

V. EVALUATION OF THE TOTAL METHOD

The purpose of this portion of the research was to validate the method developed in previous work for the determination of p-CP vapor in air. The accuracy and precision of the analytical procedure including the solvent desorption step were determined over a wide range of p-CP levels with p-CP/hexane solution spikes. The long-term storability of p-CP sorbed from a test atmosphere was then determined. Finally, the accuracy and precision of the total sampling and analytical method was assessed with test atmospheres over a wide range of concentrations of p-CP in air.

A. Accuracy and Precision of the Analytical Procedure

Tests were conducted for 2.54-, 12.00-, and 48.00-µg quantities of p-CP, which corresponded to the LAQL, about 5 x LAQL, and about 20 x LAQL. The spiking procedure was similar to that described above in Section III.A. A 5-µL aliquot of p-CP solution in hexane was injected into the glass wool plug preceding the 150-mg sorbing section of a prototype sampling tube while about 6 L of air free of p-CP was sampled through the tube. Exposed tubes were sealed with plastic caps and stored for 1 d under fluorescent lighting at about 25 °C. Each sorbent section was then extracted with 1 mL of acetonitrile in an ultrasonic bath for 30 min. To each extract was added 2 mL of distilled, deionized water and then the p-CP was determined by the HPLC/UV procedure.

The results are presented in Table IV. At the 2.54-µg level, results for the same samples were reported in Table II. The desorption efficiency averaged 0.960 over the range of solution spikes. The precision of results in the entire range was homogeneous by Bartlett's test (see Appendix C); the pooled RSD was 2.4%.

B. Stability of p-CP Collected with Silica Gel Tubes from Test Atmospheres

To test the stability of sorbed p-CP, 24 prototype silica gel tubes were exposed to generator effluent with a p-CP concentration that averaged 0.910 mg/m^3 over the exposure time. Approximately 3 L of test gas was sampled simultaneously through five tubes and one impinger at a time at a nominal rate of 0.2 L/min; this procedure was repeated for five experiments. About 2.5 µg of p-CP was collected by each tube.

The ends of the exposed tubes were wrapped with Teflon tape and sealed with plastic caps and stored at room temperature (25 to 28 °C). Six of the sorbent tubes were analyzed after 1 d. Six tubes were analyzed after storage for 6 d. The remaining 12 tubes were then refrigerated (0 °C) and stored for longer periods. Six of these tubes were analyzed after storage for a total of 14 d, and the remaining six tubes were analyzed after storage for 29 d.

Table IV. Desorption Efficiency of *p*-CP from SKC Silica Gel over the Range of 2.54 to 48.00 μg[a]

	Test level					
	2.54 μg		12.00 μg		48.00 μg	
	p-CP found, μg	DE[b]	*p*-CP found, μg	DE[b]	*p*-CP found, μg	DE[b]
	2.29	0.899	11.96	0.996	47.61	0.992
	2.34	0.920	12.30	1.025	48.07	1.002
	2.40	0.943	11.33	0.944	48.03	1.001
	2.40	0.943	11.72	0.977	46.85	0.976
	2.30	0.905	11.67	0.972	46.93	0.978
	2.26	0.889	11.75	0.979	45.62	0.950
Mean	2.33	0.918	11.79	0.982	47.19	0.983
Std dev	0.06	0.021	0.32	0.027	0.93	0.020
RSD, %	-	2.5	-	2.7	-	2.0

$\overline{DE}$[c] = 0.960

$\overline{RSD}_I$[d] = 2.4%

---

a. SKC, Inc., silica gel tubes (Cat. No. 226-10) were used.

b. Desorption efficiency was calculated from the level of *p*-CP recovered relative to the level added.

c. Average desorption efficiency.

d. Pooled precision.

The results of the storage tests are presented in Table V. The results reported have been corrected for desorption efficiency. There was no statistical difference at the 0.05 significance level for a two-tailed *t* test between the average recovery obtained for samples stored for 6 d and the recovery for tubes stored for 1 d. The same was found true for the 14-d results versus the 1-d results, and the 29-d versus the 1-d results.

C. Accuracy and Precision of the Overall Sampling and Analytical Method

The accuracy and precision of the total sampling and analytical method were determined with prototype silica gel tubes at three different concentration levels of *p*-CP in air: 0.910, 4.86, and 23.4 mg/m^3. The test at 0.910 mg/m^3 was actually part of the long-term stability test described previously and included the sample sorbent tubes

Table V. Long-Term Stability of p-CP Sorbed from a Test Atmosphere onto Silica Gel[a]

Sample set No.[b]	p-CP found, mg/m^3, after the indicated days of storage[c] 1 d	6 d	14 d	29 d
1	0.937 0.917	0.913	0.879	-[d]
2	0.912	0.916 0.950	0.908	0.910
3	0.843	0.853	0.861 0.933	0.895
4	0.901	0.887	0.827	0.844 0.903
5	0.944	0.871	0.941	0.804 0.976
Mean	0.909	0.898	0.892	0.883
Std dev	0.036	0.035	0.044	0.060
RSD, %	4.0	3.9	4.9	6.8
$\underline{t}$(observed)	-	0.537[e]	0.733[f]	0.910[g]
$\underline{t}$(critical)	-	2.228	2.228	2.228

---

a. The average p-CP concentration during the exposure of tubes was determined by impinger sampling in five separate determinations to be 0.910 mg/m^3 with an RSD of 10.4%.

b. Each sample set consisted of five prototype silica gel tubes (Catalog No. 226-10, SKC, Inc.). The air volume sampled was about 3 L.

c. No p-CP was found on any of the backup sorbent sections.

d. Sample was accidentally contaminated and subsequently discarded.

e. Comparison of means between the results of 1- and 6-d experiments by the Student's t-test at the 0.05 significance level.

f. Comparison of means between the results of 1- and 14-d experiments by the Student's t-test.

g. Comparison of means between the results of 1- and 29-d experiments by the Student's t-test.

that were stored for 1 d prior to analysis. Two sample sets were exposed at each of the other two concentration levels. Within each of these sample sets were two or three tubes and two or three impingers. Each impinger contained 10 mL of 30% (v/v) acetonitrile in water. All of the sampling devices were exposed to approximately 3 L of the test atmosphere at a nominal sampling rate of 0.2 L/min. The temperature of the test gas was about 29 °C; the relative humidity was 84%. The average amounts of p-CP sampled at the three different levels were 2.64, 14.3, and 63.6 μg, about 1, 5, and 25 times the LAQL. After storage for 1 d, the tubes were extracted and the extracts analyzed as usual.

The results for these tests are given in Tables VI, VII, and VIII. The RSD's for the results at the three concentration levels were found to be homogeneous by Bartlett's test ($\chi^2 = 2.84$) and were subsequently pooled to yield an RSD over the entire concentration range ($\overline{RSD_2}$) of 3.5%. The RSD for the total procedure ($\overline{RSD_T}$) was calculated to be 6.1% by the inclusion of $\overline{RSD_2}$ and two other sources of variability in the estimate of precision by the statistical formulas given in Appendix C. One of these other sources of variability was the error in air sampling that can be expected to be found when portable sampling pumps are employed in the field. This error was not reflected in the laboratory results because precise air sampling rates were obtained with critical flow orifices attached to vacuum pumps. Another source of error that had to be included in the calculation was the derived correction (see Appendix C) that estimated the error due to the use of the desorption efficiency factor in determining the quantities of p-CP collected during air sampling.

The average bias of the developed sampling and analytical method from the independent sampling method was -2% over the range 0.910 to 23.4 mg/m^3 of p-CP in humidified air.

VI. ACKNOWLEDGMENTS

Debra Y. Harton, Assistant Chemist, assisted in the laboratory work described in this report. Overall supervision of the project was the responsibility of Dr. William J. Barrett, Director, Applied Sciences Research, and Dr. Herbert C. Miller, Head, Analytical and Physical Chemistry Division. Other personnel of Southern Research Institute provided valuable advice. These include Ms. Ruby H. James, Head, Environmental Analytical Chemistry Section; Dr. Thomas P. Johnston, Head, Pharmaceutical Chemistry Division; and Dr. Edward B. Dismukes, Senior Research Adviser.

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Table VI. Accuracy and Precision of Sampling and Analysis at 0.910 mg/m³ of p-CP in Air

	Quantity found, μg[a]	Volume sampled, L	Calculated concn, mg/m³	Recovery,[b] %
	2.70	2.88	0.937	103
	2.58	2.81	0.917	101
	2.66	2.91	0.912	100
	2.64	2.93	0.901	99
	2.47	2.93	0.843	93
	2.77	2.93	0.944	104
Average	2.64	2.90	0.909	100
Std dev	-	-	0.036	3.9
RSD, %	-	-	-	3.9

---

a. The results reported have been corrected for desorption efficiency.

b. Relative to the concentration of 0.910 mg/m³ found by five impinger measurements; RSD = 10.4%.

Table VII. Accuracy and Precision of Sampling and Analysis at 4.86 mg/m^3 of p-CP in Air

	Quantity found, µg[a]	Volume sampled, L	Calculated concn, mg/m^3	Recovery,[b] %
	14.7	3.00	4.90	101
	14.5	2.93	4.95	102
	13.7	2.85	4.81	99
	15.0	3.00	5.00	103
	14.5	2.90	4.99	103
	13.4	2.78	4.82	99
Average	14.3	2.91	4.91	101
Std dev	-	-	0.083	1.8
RSD, %	-	-	-	1.8

---

a. The results reported have been corrected for desorption efficiency.

b. Relative to the concentration of 4.86 mg/m^3 found by four impinger measurements; RSD = 12.8%.

Table VIII. Accuracy and Precision of Sampling and Analysis at 23.4 mg/m³ of *p*-CP in Air

	Quantity found, µg[a]	Volume sampled, L	Calculated concn, mg/m³	Recovery,[b] %
	69.3	3.00	23.1	99
	58.3	2.81	20.7	89
	67.6	3.00	22.5	96
	63.1	2.91	21.7	93
	59.6	2.79	21.3	91
Average	63.6	2.90	21.9	94
Std dev	-	-	0.95	4.0
RSD, %	-	-	-	4.3

---

a. The results reported have been corrected for desorption efficiency.

b. Relative to the concentration of 23.4 mg/m³ found by six impinger measurements; RSD = 6.7%.

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APPENDIX A

MATERIAL SAFETY DATA SHEET

p-Chlorophenol

3	Highly toxic
1	Low flammability
2	Moderate reactivity

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME	Monsanto Industrial Chemicals Co.*	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.
ADDRESS		
FORMULA	C_6H_5OCl	
SYNONYMS	4-Chlorophenol, Parachlorophenol	

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%	HAZARD DATA
(homogeneous solid, 99+ % pure)		

III PHYSICAL DATA mol wt = 128.56

BOILING POINT, 760 mm Hg	217 °C	MELTING POINT	43 °C
SPECIFIC GRAVITY (H_2O = 1)	1.306 at 20 °C	VAPOR PRESSURE	0.25 torr at 20 °C
VAPOR DENSITY (AIR = 1)	4.4	SOLUBILITY IN H_2O, % BY WT	2.7 at 20 °C
% VOLATILES BY VOL.	-	EVAPORATION RATE (BUTYL ACETATE = 1)	-
APPEARANCE AND ODOR	Needle-like, white to straw colored crystals, unpleasant odor.		

* Numerous other manufacturers are listed in the "OPD Chemical Buyers Directory", 67th ed.; Schnell Publishing Co., Inc.: New York, N. Y., 1979.

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)	121 °C	AUTOIGNITION TEMPERATURE	None reported

FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER	None reported	UPPER	None reported.

EXTINGUISHING MEDIA	water, spray, mist, fog, foam, dry chemical
SPECIAL FIRE FIGHTING PROCEDURES	None reported
UNUSUAL FIRE AND EXPLOSION HAZARD	None reported

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA In U.S.S.R., TLV = 1 mg/m^3.

ROUTES OF EXPOSURE

INHALATION No data reported

SKIN CONTACT No data reported

SKIN ABSORPTION Subcutaneous, LD50 = 1030 mg/kg in rats.

EYE CONTACT No data reported

INGESTION Oral, LD50 = 500 mg/kg in rats; intraperitoneal, LD50 = 281 mg/kg in rats.

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE Irritation of skin, eyes, and respiratory tract.

CHRONIC OVEREXPOSURE None reported

EMERGENCY AND FIRST AID PROCEDURES*

EYES Irrigate immediately with water.

SKIN Flush with water immediately.

INHALATION Move to fresh air, perform artificial respiration if required.

INGESTION If the person is conscious, have him swallow large quantities of water. Try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

NOTES TO PHYSICIAN

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* By analogy to procedures for phenol.

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

None reported

INCOMPATIBILITY

Can react with oxidizing materials.

HAZARDOUS DECOMPOSITION PRODUCTS

When heated to decomposition, may emit toxic fumes of hydrogen chloride.

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

None reported

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED No specific procedure reported, but the following procedure is suggested: Sweep up as much as possible, collect in drums; dissolve the remainder in water, absorb solution with clay granules or sawdust, sweep up and collect in drums. Flush contaminated area with water; collect washings. Do not allow in sewers.

NEUTRALIZING CHEMICALS

None reported.

WASTE DISPOSAL METHOD

None reported, suggest incineration.

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

Effective hood or ventilation system.

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL) None reported; however, avoid breathing vapor.

EYE

None reported

GLOVES Wear rubber or plastic gloves to prevent skin contact with concentrated solutions or solid p-chlorophenol.

OTHER CLOTHING AND EQUIPMENT

Wear appropriate clothing or equipment to prevent repeated or prolonged skin contact.

IX SPECIAL PRECAUTIONS

PRECAUTIONARY STATEMENTS

Other chlorophenols with properties similar to those of *p*-chlorophenol have been selected for priority attention as point source water effluent discharge toxic pollutants.

OTHER HANDLING AND STORAGE REQUIREMENTS

Keep compound in a cool and well ventilated area. Do not breathe its vapor. Do not take the compound internally.

PREPARED BY H. Kenneth Dillon

ADDESSS Southern Research Institute
2000 Ninth Avenue South
Birmingham, Alabama 35255

DATE August, 1980

APPENDIX B

VAPOR GENERATION SYSTEM

VAPOR GENERATION SYSTEM

The generator was operated as follows: A reservoir for p-CP was maintained at a constant temperature to regulate the vapor pressure of the compound precisely. Nitrogen was flushed through a bed of p-CP crystals in the reservoir—a midget impinger—and became laden with the vapor of the compound. The nitrogen was then diluted with air to obtain the desired concentration. A schematic of the system is given in Figure 7.

Precautions were taken to ensure that contaminants were not introduced into the system in the air and nitrogen. To provide clean, dry dilution air for the generator prior to humidification to the desired level, house compressed air was treated in the following manner. The air was first passed through an oil trap and then dried with a Puregas Heatless Dryer obtained from Puregas Equipment Company, Capiague, New York. (The dryer contains beds of molecular sieve for removing water vapor.) The air was then passed sequentially through a bed of charcoal, a felt filter, and finally through a Gelman Acroflow membrane filter cartridge with an average pore diameter of 0.2 µm. (The filter membrane is a copolymer of acrylonitrile and vinyl chloride coated on a nylon web.) Ultrapure nitrogen (Matheson, 99.999%) was used for flushing the reservoir of p-CP.

The temperatures of the nitrogen gas and the impinger were regulated in the range of 0 to 50 °C in a constant temperature bath with a Haake E-12 temperature controller with a bath circulator. Ethylene glycol was used as a heat transfer medium.

The dilution air was humidified by metering part of the airstream through a heated Greenburg-Smith impinger containing distilled, deionized water. The humidified airstream and the residual dry airstream were combined and transferred to the mixing chamber of the system through heated Teflon tubing to avoid condensation of the water vapor.

The nitrogen laden with p-CP (4 to 250 mL/min) was mixed with the dilution air (6.1 L/min) in the cylindrical glass mixing and sampling chamber, a glass pipe 15 cm long by 10 cm o.d. with Teflon discs for end caps. The chamber was mounted vertically with the end caps at the top and bottom. The generator effluent entered through an opening in the bottom cap of the chamber. Seven sampling ports and a vent were located in the top cap. Sorbent tubes were mounted vertically through the ports so that the front (sorbing) sections of the tubes were inside the chamber during sampling. The test atmosphere was sampled at rates ranging from about 0.05 to 0.2 L/min through tubes and impingers with critical flow orifices connected to a vacuum pump.

The operation of the generator was determined to be satisfactory for the method development. Although no definitive study of the stability of the generator output with time was performed, concentrations of p-CP in generator

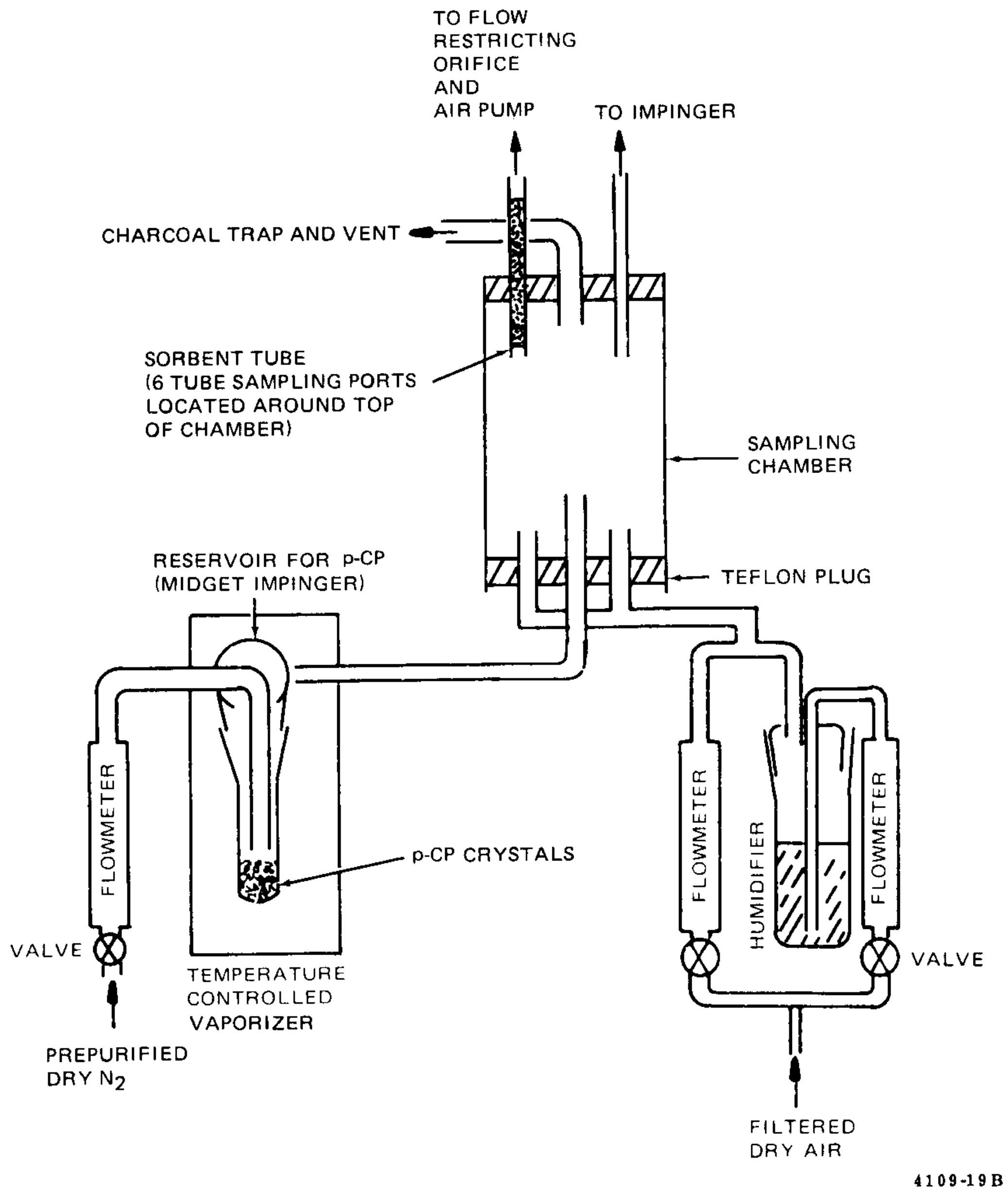

Figure 7. Schematic of vapor generator and sampling system.

effluent were found with impinger sampling to be generally constant for concentrations at a relative humidity of >80% and at a temperature of the sampling chamber of 29 °C.

The observed p-CP concentrations were approximately 10 to 30% of the theoretical values predicted from gas flow rates and the extrapolated volatility of p-CP as shown in Table IX.

Table IX. Theoretical *Versus* Actual Generator Output

N_2 flow rate through reservoir,[a] mL/min	Temp of dilution air, °C	Calculated p-CP concn, mg/m^3	Observed p-CP concn, mg/m^3
250	43	238	73
150	29	145	23.4
40	29	39.3	4.86
4	29	3.96	0.910

---

a. The p-CP reservoir temperature was 52 °C. The dilution air flow rate was maintained at 6.1 L/min. The relative humidity was >80% inside the sampling chamber.

APPENDIX C

SUMMARY OF
STATISTICAL TERMS AND FORMULAS

Summary of Statistical Terms and Formulas

The statistical terms and formulas employed in this report were adapted from those given in Appendix A of the "Documentation of the NIOSH Validation Tests" (11). The major deviation from the format given in that reference was that the relative standard deviation (RSD) instead of the coefficient of variation (CV) was used to express precision. The appropriate formulas were modified accordingly.

Mean - Arithmetic mean or average, defined as the sum of all the observations divided by the number of observations (n).

Standard deviation - Defined as the positive square root of the variance, which is defined as the sum of squares of the deviations of the observations from the mean ($\bar{x}$) divided by one less than the total number of observations (n-1).

$$\text{std dev} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}}$$

RSD - Relative standard deviation, defined as the standard deviation divided by the mean and multiplied by 100.

$$\text{RSD, \%} = \frac{\text{std dev}}{\text{mean}} \times 100$$

RSD_1^j - Relative standard deviation for the samples in the determination of the desorption efficiency at one of the spiking levels (the j^{th} level).

RSD_2^j - Relative standard deviation for the sorbent samples exposed to the test gas at one of the concentration levels (the j^{th} level).

$\overline{RSD}$ - Pooled relative standard deviation. The value is derived from the relative standard deviations obtained from the analysis of samples at each of the test levels. The mathematical equation is expressed as:

$$\overline{RSD} = \sqrt{\frac{\sum_{j=1}^{n} f_j \, (RSD^j)^2}{f}}$$

where: f_j = degrees of freedom, equal to number of observations minus one, at the j^{th} spike or concentration level.

RSD^j = Relative deviation of the observations at the j^{th} level.

$$f = \sum_{j=1}^{n} f_j$$

$\overline{RSD}_1$ - Pooled relative standard deviation calculated as above based on data for the determination of the desorption efficiency.

$\overline{RSD}_{A+\overline{DE}}$ - This is a derived correction to include error due to the use of the desorption efficiency factor which is an average of 6 values at each level.

$$\overline{RSD}_{A+\overline{DE}} = \overline{RSD}_1 \sqrt{7/6} = 1.0801 \, \overline{RSD}_1$$

$\overline{RSD}_2$ - Pooled relative standard deviation based on the data for all of the sorbent samples exposed to the test gas.

$\overline{RSD}_s$ - Pooled relative standard deviation in the sample collection procedure. The value is dependent on the data from the sorbent samples spiked with analyte and the sorbent samples exposed to the test gas.

$$\overline{RSD}_s = \sqrt{(\overline{RSD}_2)^2 - (\overline{RSD}_1)^2}$$

$\overline{RSD}_p$ - Relative standard deviation due to the pump error; assumed to be equal to 5%.

$\overline{RSD}_T$ - Relative standard deviation of the total procedure that consists of the composite variations in sampling and analysis, desorption efficiency, and the pump error.

$$\overline{RSD}_T = \sqrt{(\overline{RSD}_S)^2 + (\overline{RSD}_{A+\overline{DE}})^2 + (\overline{RSD}_P)^2}$$

or:

$$\overline{RSD}_T = \sqrt{(\overline{RSD}_2)^2 - (\overline{RSD}_1)^2 + 1.1667\,(\overline{RSD}_1)^2 + (5)^2}$$

Grubbs' Test for Rejection of an Observation

This test is applied in order to determine if one of the observations should be rejected as being an outlier. The following equation was used for the test:

$$B_1' = \frac{x - \bar{x}}{s} \text{ or } \frac{\bar{x} - x}{s}$$

where: x = observation being tested.

$\bar{x}$ = mean of all observations.

s = standard deviation based on n-1 degrees of freedom for n observations.

For any six observations, a value can be rejected if $B_1' \geq 1.944$. The B_1' limit is based on a 1% significance level (i.e., a B_1' value calculated from the data can be expected to exceed 1.944 only 1% of the time if the observation is a legitimate one conforming to the underlying theory.)

Bartlett's Test for Homogeneity

This test is applied in order to test the feasibility of "pooling" the relative standard deviations. The following equation for χ^2 with n-1 degrees of freedom was used:

$$\chi^2 = \frac{f \ln (\overline{RSD}_i)^2 - \sum_{j=1}^{n} f_j \ln (RSD_i^j)^2}{1 + \frac{1}{3(3-1)} \left[\left(\sum_{j=1}^{n} 1/f_j\right) - 1/f\right]}$$

where: i = 1 or 2. When i= 1, the precision of the desorption efficiency tests applies. When i = 2, the precision of the results with sorbent samples exposed to test atmospheres applies; thus:

$$\overline{RSD}_i = \overline{RSD}_1 \text{ or } \overline{RSD}_2$$

$\overline{RSD}_i^{\,j}$ = relative standard deviation at the j^{th} level for $i = 1$ or 2.

f_j = degrees of freedom associated with $(RSD_i^{\,j})^2$ and equal to the number of observations at the j^{th} level minus one (for $i = 1$ or 2).

$$f = \sum_{j=1}^{n} f_j$$

In order to pass Bartlett's test at the 1% significance level, χ^2 must be less than or equal to 9.21.

APPENDIX D

ANALYTICAL METHOD

p-CHLOROPHENOL

Analytical Method

Analyte:	*p*-Chlorophenol	Method No.:	P&CAM 337
Matrix:	Air	Range:	0.910 to 23.4 mg/m^3 in 3 L of air
Procedure:	Adsorption on silica gel, desorption with acetonitrile, high performance liquid chromatography	Precision:	0.06
Date Issued:	9/19/80		
Date Revised:		Classification:	B (ACCEPTED)

1. Synopsis

   1.1 A known volume of air is drawn through a silica gel tube to adsorb the *p*-chlorophenol vapor present.

   1.2 The silica gel in the tube is transferred to a small vial where the *p*-chlorophenol is desorbed with 1 mL of acetonitrile. Two milliliters of H_2O is added to the extract.

   1.3 An aliquot of the resulting solution is injected into a high performance liquid chromatograph.

   1.4 The area of the resulting peak for *p*-chlorophenol is determined and compared with the peak areas obtained from the injection of standards.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The overall method was evaluated by collecting 3-L samples of test atmospheres containing *p*-chlorophenol in the range of 0.910 to 23.4 mg/m^3 at 29 °C and a relative humidity of >80%. The amounts of *p*-chlorophenol collected ranged from 2.6 to 64 µg per 150-mg bed of silica gel. For the maximum allowable sampling volume of 40 L, the range is 0.064 to 1.6 mg/m^3.

   2.2 The slope of the analytical calibration curve was 62 area counts/ng of *p*-chlorophenol with an HP 1084B Liquid Chromatograph.

2.3 The lowest analytically quantifiable level for this method was determined to be about 2.5 µg of p-chlorophenol per sorbent sample extracted with 1.00 mL of acetonitrile and then diluted to 3.00 mL with 2.00 mL of distilled, deionized water. The instrumental detection limit was about 0.1 µg/mL, a concentration of p-chlorophenol in 30% acetonitrile in water that gave a response that was about twice the noise level under the operating conditions specified below.

2.4 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%.

3. Interferences

3.1 The chromatographic operating conditions described below 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; 2,4,6-trichlorophenol; 4-chloro-3-methylphenol; 2,4-dinitrophenol; 4,6-dinitro-2-methylphenol; and pentachlorophenol from p-chlorophenol. Partial separation of m- from p-chlorophenol can be achieved; with comparable concentrations of the two in solution, the resolution was found to be 0.91.

3.2 When two or more substances are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample because the substances may interfere with the determination of p-chlorophenol.

3.3 Any substance that has the same retention time as p-chlorophenol with the chromatographic operating conditions described in this method can interfere with the analysis. Therefore, retention time data cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, changing the separation conditions (column type or temperature, solvent flow rate, solvent programming rate, etc.) may circumvent the problem.

4. Precision and Accuracy

4.1 For the overall sampling and analytical method, the pooled relative standard deviation (RSD) for the replicate measurements was 6.1% over the range of 0.910 to 24.3 mg/m^3. The pooled RSD for the analytical method was 2.4% for 18 sorbent samples spiked with 2.54 to 48.0 µg of p-chlorophenol and stored for 24 h.

4.2 The concentration of p-chlorophenol in test atmospheres was determined in control experiments by impinger sampling. The determinations with sorbent sampling gave values that averaged 98% of those determined by impinger sampling.

4.3 Samples of p-chlorophenol on silica gel were found to be stable at 25 °C for 7 d and for 29 d if stored at 0 °C after the seventh day.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Many of the potential sources of interference are avoided by the analytical procedure. The samples are analyzed by means of a quick instrumental method.

5.2 One disadvantage is that the precision of the method is limited by the reproducibility of the pressure drop across the tubes. Variations in pressure drop will affect the flow rate. The reported sample volume will then be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal sampling pump capable of accurate performance (±5%) at 0.05 to 0.2 L/min and calibrated with a representative tube in the line.

6.2 Sorbent tubes: Pyrex tubes, 7 cm long with a 6 mm o.d. and a 4 mm i.d., 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. The sorbing section is preceded in the tube by a glass wool plug held in place with a metal spring. The sorbing section and backup section are separated with a polyurethane foam plug. There is also a foam plug placed near the outlet end of the tube to hold the backup sorbent section in place. The pressure drop across a typical tube is about 1.4 in. H_2O (350 kPa) at a sampling rate of 0.2 L/min. This type of tube is available from SKC, Inc. (Eighty Four, PA); its catalog number is 226-10.

6.3 High performance liquid chromatograph, such as the Hewlett-Packard 1084B or equivalent, with ultraviolet absorption spectrophotometric detector.

6.4 Reverse-phase liquid chromatographic column, C_{18} bonded to silica, such as the Varian MicroPak MCH-5, 5-µm particle size, 4 mm i.d. by 30 cm long.

6.5 Centrifuge tubes, 12 mL, glass with screw caps.

6.6 Vials, 1 mL, with crimp-on caps containing Teflon-lined silicone rubber septa.

6.7 Pipets, 1.00- and 2.00-mL, and convenient sizes for making dilutions.

6.8 Ultrasonic bath.

6.9 Centrifuge for 12-mL tubes.

7. Reagents

7.1 p-Chlorophenol, 99+ % pure.

7.2 Acetonitrile, distilled in glass.

7.3 Water, distilled, deionized.

7.4 Hexane, distilled in glass.

8. Procedure

8.1 Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis should be thoroughly cleaned and rinsed with 50% nitric acid, tap water, and distilled water (in that order). The glassware should then be dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, break open the ends of the tube to provide openings that are at least 2 mm in diameter.

8.2.2 Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of silica gel is the backup layer and is positioned nearer the sampling pump.

8.2.3 Place the silica gel tube in a vertical position during sampling to prevent channeling through the tube.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the tube.

8.2.5 Sample the air at 0.05 to 0.2 L/min. Measure and report the flow rate and time or volume sampled. The maximum volume sampled should not exceed 40 L at 0.2 L/min.

8.2.6 Record the temperature and pressure of the air being sampled and measured.

8.2.7 Immediately after sampling, seal the ends of the tubes with Teflon tape and plastic caps.

8.2.8 To obtain a blank sample, process one unused silica gel tube in the same manner as the samples (break, seal, and transport) but do not sample air through this tube. Submit one blank sample tube for every ten samples with a minimum of three blank tubes.

8.2.9 If samples are shipped to a laboratory, pack them tightly to minimize tube breakage during shipping.

8.2.10 Ship nine to twelve unopened silica gel tubes so that desorption efficiency studies can be performed on the same type and lot of silica gel used for sampling.

8.2.11 Log samples as soon as they are received in the laboratory.

8.2.12 Refrigerate all samples stored longer than 7 d.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the silica gel tubes from the refrigerator and permit them to equilibrate to room temperature to prevent water condensation on the cold sorbent material. Transfer each section of silica gel in a sorbent tube to a separate 12-mL centrifuge tube. Add the glass wool plug near the sorbent tube inlet to the centrifuge tube containing the sorbing section; add the two urethane foam plugs to the centrifuge tube containing the backup section.

8.3.2 Desorption of Samples. After the two sections of a tube are transferred to centrifuge tubes, pipet 1.00 mL of acetonitrile into each tube. Cap each tube immediately after the acetonitrile has been added. Extract the sealed sorbent samples in an ultrasonic bath for 30 min at room temperature. Then add 2.00 mL of distilled, deionized water to each tube. Cap the tubes and mix the solutions well. Centrifuge the solutions for 10 min. Then transfer about 1 mL of the supernatant liquid in each tube to a separate 1-mL vial and seal the vial with a Teflon-lined septum.

8.3.3 Operating Conditions for the High Performance Liquid Chromatograph.

- Solvent flow rate: 1 mL/min.
- Solvent A: Distilled, deionized water.
- Solvent B: Acetonitrile.
- Solvent program: 30% B to 80% B in 20 min.
- Column temperature: 30 °C.
- UV detector: analytical wavelength, 280 nm; reference wavelength, 430 nm.

- Injection volume: 100 μL.
- Under these conditions, the analyte elutes in approximately 11 min.
- Column cleanup procedure. At the end of each working day, flush the column with approximately 50 mL of acetonitrile (Solvent B) at a flow rate of 1 mL/min.

8.3.4 Determination of Concentration. Determine the concentration of p-chlorophenol in the sample solution by comparing the peak area to the peak areas obtained with standard solutions as discussed in Section 9. Peak heights may also be used.

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound may vary between laboratories and batches of silica gel. Also, for a given batch of silica gel the desorption efficiency may vary with the weight of contaminant adsorbed. The silica gel used for the study of this method gave an average desorption efficiency of 0.960 with a pooled RSD of 2.4% for loadings of 2.54 to 48.0 μg of p-chlorophenol on 150-mg beds of sorbent material.

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third is an intermediate level. Dissolve p-chlorophenol in hexane to give stock solutions with concentrations such that 2.5 to 48 μg of p-chlorophenol will be injected onto the sorbent in no more than 5 μL of a stock solution. Inject an aliquot of the appropriate solution into the front sorbing section of a sorbent tube while sampling 6 L of analyte-free air through the tube at 0.2 L/min. Cap the tube and store it overnight at room temperature to ensure complete adsorption of the analyte onto the sorbent material. Prepare a standard at each level by injecting an identical amount of the corresponding stock solution into 3 mL of 30% (v/v) acetonitrile in water. Analyze the samples and standards as described in Section 8.3.

The desorption efficiency at each level is the ratio of the average amount found to the amount taken. A blank correction is not expected to be necessary but should be checked. The desorption efficiency curve is constructed by plotting the amount of p-chlorophenol found in a sample versus the desorption efficiency.

9. Calibration and Standardization

To make a stock solution, add 500 mg of p-chlorophenol to 25 mL of 30% (v/v) acetonitrile in water. By serial dilution with 30% CH_3CN/H_2O, prepare a series of working standards varying in concentration over the range of 0.5 to 100 µg/mL. Follow the dilution scheme presented below.

Initial concentration	Aliquot volume, mL	Final diluted volume, mL	Final concentration
20 mg/mL	1	10	2 mg/mL
2 mg/mL	5	10	1 mg/mL
1 mg/mL	1	10	100 µg/mL
100 µg/mL	5	10	50 µg/mL
100 µg/mL	1	10	10 µg/mL
10 µg/mL	1	10	1 µg/mL
1 µg/mL	5	10	0.5 µg/mL

Prepare fresh working standards daily; the same stock solution may be used indefinitely if stored in an airtight container. Analyze the five working standards under the same instrumental operating conditions and during the same time period as the samples. To establish a calibration curve, plot the concentration of the standards in µg/mL versus peak area.

10. Calculations

10.1 Determine the sample weight in micrograms from the standard curve.

10.2 Blank corrections are not expected to be necessary. If the analysis shows a blank correction is needed, make the correction as follows:

$$W_F = W_s - W_b$$

where: W_F = corrected amount (µg) on the front section of the silica gel tube

W_s = amount (µg) found on the front section of the silica gel tube

W_b = amount (µg) found on the front section of the blank silica gel tube

Follow a similar procedure for the backup section.

10.3 Make a correction for desorption efficiency as follows:

$$M_F = \frac{W_F}{D}$$

where: M_F = corrected amount (μg) in the front section

W_F = amount (μg) after blank correction

D = desorption efficiency corresponding to the weight W_F

10.4 Express the concentration, C, of p-chlorophenol in the air sampled in mg/m^3, which is numerically equal to μg/L.

$$C = \frac{M_F + M_B}{V}$$

where: M_F = corrected amount (μg) of p-chlorophenol found on front section

M_B = corrected amount (μg) of p-chlorophenol found on backup section

V = volume (L) of air sampled

10.5 If desired, the results may be expressed in ppm by volume at 25 °C (298 K) and 760 torr.

$$C(\text{ppm}) = C(\mu g/L) \times \frac{24.45}{128.56} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled

T = temperature (°C) of air sampled

24.45 = molecular volume (L/mol) at 25 °C and 760 torr

128.56 = molecular weight of p-chlorophenol

11. Reference

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; September, 1980.

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NIOSH Contract No. 210-78-0012

APPENDIX E

SAMPLING DATA SHEET

NIOSH SAMPLING DATA SHEET NO. 337 Class B

Substance

p-Chlorophenol.

Standard

A standard has not been established.

Analytical Method

A known volume of air is drawn through a silica gel tube to adsorb the p-chlorophenol vapor present. The analyte is desorbed from the sorbent with 1.00 mL of acetonitrile and the extract is diluted to 3.00 mL with distilled, deionized water. The p-chlorophenol in an aliquot of the solution is determined with a high performance liquid chromatograph. The front and rear sections of the sorbent tube are analyzed as individual samples. The rear section is used as a breakthrough indicator. The supporting analytical method has been evaluated for sample loadings between 2.54 and 48.0 µg per sorbent tube. The complete sampling and analytical method has been tested with air containing 0.910 to 23.4 mg/m^3 of p-chlorophenol at 29 °C and at a relative humidity of >80%. Details are provided in Reference Nos. 1 and 2.

Sampling Equipment

1. Personal sampling pump, capable of accurate flows (±5%) in the recommended range of sampling flow rates (0.05 to 0.2 L/min). The pump is calibrated at the recommended sampling flow rates with a representative sampling tube in the line.

2. Sorbent tubes: Pyrex tubes, 7 cm long with a 7 mm o.d. and a 4 mm i.d. 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. The sorbing section is preceded in the tube by a glass wool plug held in place with a metal spring. The sorbing section and backup section are separated with a polyurethane foam plug. There is also a foam plug placed near the outlet end of the tube to hold the backup sorbent section in place. The pressure drop across a typical tube is about 1.4 in. H_2O (350 kPa) at a sampling rate of 0.2 L/min. This type of tube is available from SKC, Inc. (Eighty Four, PA); its catalog number is 226-10.

Sample Size

The air sample volume should not exceed 40 L.

Sampling Procedure

1. Immediately before sampling, break open the ends of the tube to provide openings that are at least 2 mm in diameter.

2. Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of silica gel is the backup layer and is positioned nearer the sampling pump.

3. Place the sorbent tube in a vertical position during sampling to prevent channeling.

4. Air being sampled should not be passed through any hose or tubing before entering the tube.

5. Measure and report the flow rate and time or volume sampled. Sample at 0.05 to 0.2 L/min.

6. Measure and report the temperature and pressure of the air being sampled.

7. Immediately after sampling, seal the ends of the tube with Teflon tape and plastic caps.

8. To obtain a blank sample, process one unused silica gel tube in the same manner as the samples (break, seal, and transport) but do not sample air through this tube. Submit the one blank sample tube for every ten samples, with a minimum of three blank tubes.

9. If samples are shipped to a laboratory, pack them tightly to minimize tube breakage during shipping.

10. Ship six to twelve unopened tubes so that desorption efficiency studies can be performed on the same type and lot of silica gel used for sampling.

Special Considerations

1. Where two or more compounds are known or suspected to be present in the air, the identities of the substances should be transmitted with the sample.

2. The pump should not be operated more than 8 h continuously without recharging the battery.

Bulk Samples

If bulk samples of material containing p-chlorophenol are shipped to the laboratory, they should be submitted in precleaned* glass containers with Teflon-lined caps. Do not transport these samples in the same container with sorbent tubes.

Shipping Instructions

Capped sorbent tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Never transport, mail, or ship the bulk sample in the same container as the sample or blank tubes. When the samples are received by the laboratory, they should be stored under refrigeration to avoid any chance of loss of p-chlorophenol from the samples.

References

1. p-Chlorophenol, NIOSH Method No. P&CAM 337
2. 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; September, 1980.

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* See Reference No. 1 for cleaning procedure.