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ANALYTICAL METHODS EVALUATION AND VALIDATION FOR 1,2,4-TRICHLOROBENZENE; 1,2,4,5-TETRACHLOROBENZENE; PENTACHLOROBENZENE; AND POLYCHLORINATED TERPHENYLS

Contract No. 210-79-0102

Research Report for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; and Pentachlorobenzene

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The development of a personal sampling and analytical method for the determination of three chlorinated benzenes in the air, including 1,2,4-trichlorobenzene (120821), 1,2,4,5-tetrachlorobenzene (95943), and pentachlorobenzene (608935), are described. The selection of collection device and preliminary evaluation, an independent sampling method for the determination of the chlorinated benzenes, and evaluation of the total method are discussed. The personal air sampler consisted of a teflon filter in a stainless steel holder and a solid sorbent tube containing Amberlite XAD-s. The pooled relative standard deviations for the determinations of the compounds by the overall sampling and analytical method were 9.3 percent for 1,2,4-trichlorobenzene, 9.7 percent for 1,2,4,5-tetrachlorobenzene, and 9.8 percent for pentachlorobenzene.

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ABSTRACT

This report describes the development of a personal sampling and analytical method for the determination of three chlorinated benzenes in air: 1,2,4-trichlorobenzene; 1,2,4,5-tetrachlorobenzene; and pentachlorobenzene. The personal air sampler that was developed consists of a Teflon filter in a stainless steel holder in tandem with a solid sorbent tube containing Amberlite XAD-2. The sampler is compatible with a personal sampling pump capable of a flow rate of 0.2 L/min. The compounds are desorbed from the sampler with hexane, and the extracts are analyzed by gas chromatography with electron capture detection. The overall method was evaluated with 10-L test atmosphere samples over the following concentration ranges: 0.002 to 14 mg/m^3 of 1,2,4-trichlorobenzene, 0.003 to 31 mg/m^3 of 1,2,4,5-tetrachlorobenzene, and 0.008 to 22 mg/m^3 of pentachlorobenzene. For the three compounds, the average biases relative to an independent sampling method were as follows: -4% for 1,2,4-trichlorobenzene, 1% for 1,2,4,5-tetrachlorobenzene, and -3% for pentachlorobenzene. The pooled relative standard deviations for the determinations of the compounds by the overall sampling and analytical method were as follows: 9.3% for 1,2,4-trichlorobenzene, 9.7% for 1,2,4,5-tetrachlorobenzene, and 9.8% for pentachlorobenzene.

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Research Report for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; and Pentachlorobenzene

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SOUTHERN RESEARCH INSTITUTE
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RESEARCH REPORT FOR 1,2,4-TRICHLOROBENZENE; 1,2,4,5-TETRACHLOROBENZENE; AND PENTACHLOROBENZENE

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 Government personnel.

The three compounds—1,2,4-trichlorobenzene; 1,2,4,5-tetrachlorobenzene; and pentachlorobenzene—are recognized as potentially toxic workplace contaminants. The American Conference of Governmental Industrial Hygienists (ACGIH) has set a standard for 1,2,4-trichlorobenzene expressed as an 8-h, time-weighted average (TWA) of 40 mg/m^3 (5 ppm by volume) [C1]. Industrial Hygiene Guides have been set by Dow Chemical Company for the other two compounds [F19]. These self-imposed standards are also 8-h, time-weighted average limits and correspond to 3.5 mg/m^3 (0.4 ppm by volume) for 1,2,4,5-tetrachlorobenzene and 1.0 mg/m^3 (0.1 ppm by volume) for pentachlorobenzene.

All three compounds are known to accumulate in adipose tissue and may eventually cause changes in kidney and liver tissues [C10]. Of considerable concern is the experimental observation that the metabolites of the chlorinated benzenes are structurally related to the metabolites of the polycyclic aromatic hydrocarbons (PAHs) [C10]. Both the chlorinated benzenes and the PAHs are metabolized to arene oxides. Because the metabolically activated arene oxides of the PAHs are believed to be responsible for carcinogenic properties of the PAHs, the metabolites of the chlorinated benzenes are suspected of having the potential to cause cancer. Safety data sheets that include a summary of the toxicity information available for the three compounds are presented in Appendix A.

Because there was no validated air sampling and analytical method available for the determination in the workplace of these three potentially toxic polychlorinated benzenes, we developed and evaluated such a method under contract with NIOSH. This report describes our work.

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 compounds was performed. Second an experimental protocol was devised for the development of one single method for all three compounds according to NIOSH guidelines. The protocol presented an experimental plan for the development of a sampling device that would collect both aerosols and vapors because it was expected that 1,2,4,5-tetrachlorobenzene and pentachlorobenzene might occur in the solid or gaseous state in test atmospheres. The collected analytes were to be removed from the sampling device by solvent extraction, and the extracts were then to be analyzed for the three analytes by gas chromatography with electron capture detection (GC/ECD). The protocol was reviewed by NIOSH and revised, and subsequently a method was 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 materials 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 comprised the following tasks:

- Selection of the gas chromatographic operating conditions in the analytical procedure.
- Calibration of the analytical method.

- Screening tests to select the most promising sorbents, filter materials, and filter holders. The screening involved sorbent capacity, desorption efficiency, and storability tests. The affinities of the candidate filter and filter holder materials for the vapors of the analytes were also determined.
- Selection of sampling device (filter in tandem with sorbent material).
- Construction and evaluation of the test atmosphere generator and sampling system (see Appendix B).
- Determination of the stability of the analytes collected from air with the prototype sampling device.
- 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 each of the three analytes 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 given by the independent method. 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% [1].
- The mean of the results obtained with sampling devices that were exposed and stored for 1 d could not differ statistically at the 0.05 significance level from the mean of results obtained with exposed samplers that were stored for 7 or 14 d.

One other specific task in the development and evaluation of the method was to find the lowest level of each analyte 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 amount in an air volume corresponding to the minimum sampling volume. 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 the chlorinated benzenes are presented in this report in Appendix D (Method Description) and Appendix E (Sampling Data Sheet).

II. DEVELOPMENT AND EVALUATION OF THE ANALYTICAL METHOD

A. Selection of the Gas Chromatographic Operating Conditions

The first step undertaken in the laboratory was to define a suitable procedure for the simultaneous determination of all three of the chlorinated benzenes by gas chromatography with electron capture detection (GC/ECD). This task involved the selection of a column and the appropriate operating conditions for minimizing interferences from compounds that may occur with the analytes in workplace air. At least eight chlorinated benzenes coexist with the analytes in their manufacture. They are as follows: 1,2-, 1,3-, and 1,4-dichlorobenzene; 1,2,3- and 1,3,5-trichlorobenzene; 1,2,3,4- and 1,2,3,5-tetrachlorobenzene; and hexachlorobenzene. The three analytes are also likely to be found in environmental samples along with two pesticides—pentachlorophenol and pentachloronitrobenzene (PCNB)—and with two intermediates of PCNB—2,3,5,6- and 2,3,4,5-tetrachloronitrobenzene.

Solutions with concentrations near 15 μg/mL of each of these compounds and the analytes were prepared in hexane and were analyzed on a variety of packed GC columns. The columns are described in Table I. Among those tested were silicone oils (Columns Nos. 1 and 2), a mixture of a silicone oil and a fluorosilicone polymer (Column No. 3), polyglycols (Columns Nos. 4 and 5), a polyglycol with terephthalic acid (Column No. 6), a polyglycol with dinitroterephthalic acid (Columns Nos. 7 and 8), and a mixture of bentonite and a low polarity ester (Column No. 9). The supports for the liquid phases were diatomaceous earth. The columns were 1 to 2 m in length and 2 mm i.d. Most were of nickel; one was glass.

All of these columns, with the exception of those containing 10% FFAP and OV-225, separated the three analytes and generally yeilded satisfactory resolutions from all interferences except 1,2,3,5-tetrachlorobenzene. This compound was found to interfere with the determination of 1,2,4,5-tetrachlorobenzene with all columns tested regardless of the operating conditions. Since a variety of column types proved incapable of separating the two compounds, it seemed unlikely that the isomers could be resolved without a significant increase in column efficiency such as that obtainable with capillary chromatography.

The separate determination of 1,2,4,5- and 1,2,3,5-tetrachlorobenzene does not appear to be of primary importance, however, in the development of a method for the 1,2,4,5-isomer. It has been reported that the 1,2,3,5-isomer does not occur with the 1,2,4,5-isomer in significant quantities in environmental samples [F19]. This claim is apparently supported by the fact that the yield of the 1,2,3,5-isomer in the synethsis of chlorinated benzene compounds is a small percentage of the yield of the 1,2,4,5-isomer. It is possible that the two isomers may coexist in a workplace not involving the manufacture of chlorinated benzenes, but the possibility seems remote.

Table I. GC Columns Tested for the Determination of Polychlorobenzenes

Column No.	Liquid phase and loading	Support	Column length,[a] m
1	3% OV-17	μPartisorb (∿170 mesh)	2[b]
2	3% OV-225	Supelcoport (80/100 mesh)	2
3	1.5% OV-17 and 1.95% QF-1	Gas Chrom Q (80/100 mesh)	2
4	5% Carbowax 1500	Chromosorb W AW (80/100 mesh)	2
5	3% Carbowax 20M	Chromosorb W AW (80/100 mesh)	2
6	10% Carbowax 20M-TPA	Chromosorb W AW (80/100 mesh)	2
7	2% FFAP	Chromosorb W AW-DMCS (80/100 mesh)	1.5
8	10% FFAP	Chromosorb W AW (80/100 mesh)	1
9	5% Bentone 34 and 5% SP-1200	Supelcoport (100/120 mesh)	2

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a. Unless specified otherwise, column was nickel tubing (2 mm i.d., 3.1 mm o.d.).

b. Column was glass (2 mm i.d., 6.4 mm o.d.).

On the basis of the available information, we therefore decided to use in our method the packed column that performed most efficiently in our tests. Column No. 6 in Table I, the column containing Carbowax 20M-TPA, yielded the best resolution of the potential interferents and was therefore selected. The following operating conditions with the column were found to be optimum with a Perkin-Elmer 910 Gas Chromatograph equipped with a ^{63}Ni electron capture detector:

- Carrier gas: 30 mL/min N_2 (Linde, ultra high purity, 99.999%).

- Detector purge gas: 90 mL/min N_2 (Linde, ultra high purity, 99.999%).

- Temperatures:

  —injection port, 220 °C.
  —column, 160 °C.
  —detector, 300 °C.

A chromatogram of a mixture of hexane solutions of all fifteen organochlorine compounds is presented in Figure 1. The concentration of each was about 15 μg/mL; the injection volume was 1 μL. Not all of the interferents were resolved from each other but the three analytes were well resolved with the exception, of course, of two of the three tetrachlorobenzene isomers. Pentachlorophenol gave no response; this compound was presumably irreversibly sorbed by the GC column.

B. Calibration of the Analytical Procedure

In the calibration of the GC procedure, 2-μL aliquots of working standard solutions, each containing all three analytes, were injected into the Perkin-Elmer 910 gas chromatograph. The Carbowax 20M-TPA column was used with the operating conditions cited above. Multiple injections of each standard were performed by the solvent-flush technique. Concentrations of the analytes that were injected ranged from about 0.1 to 10,000 ng/mL (0.2 to 20,000 pg injected). The peak heights and peak areas were then measured and compared.

The detector response appeared to be linear below about 100 ng/mL (200 pg injected) for all three compounds. Typical plots for the linear range of the three calibration curves are presented in Figure 2. These curves are based on peak height measurements because they were found to be more precise than peak area measurements made with a mechanical integrator. As the data in Table II indicate, the correlation coefficient for peak heights was consistently higher than for peak areas in the 2- to 100-ng/mL range.

Table II. Comparison of Correlation Coefficients for Peak Height and Peak Area Measurements

Analyte	Correlation coefficient	
	Peak height	Peak area
1,2,4-Trichlorobenzene	0.9994	0.9975
1,2,4,5-Tetrachlorobenzene	0.9991	0.9983
Pentachlorobenzene	0.9990	0.9974

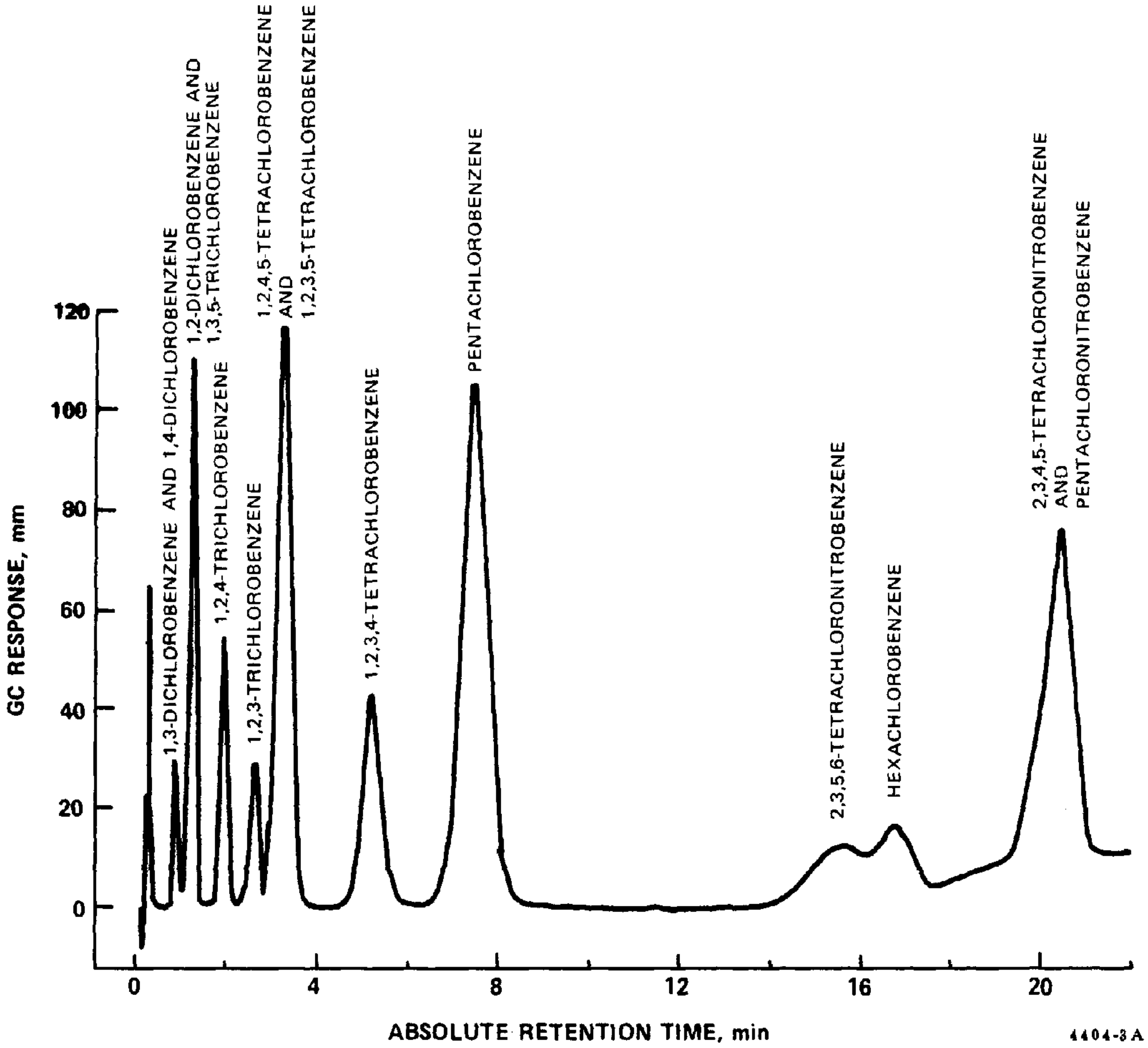

Figure 1. Chromatogram for a mixture of approximately 15-ng quantities (in a 1-μL injection volume) of the three analytes and twelve other organochlorine compounds illustrating the tetrachlorobenzene interference.

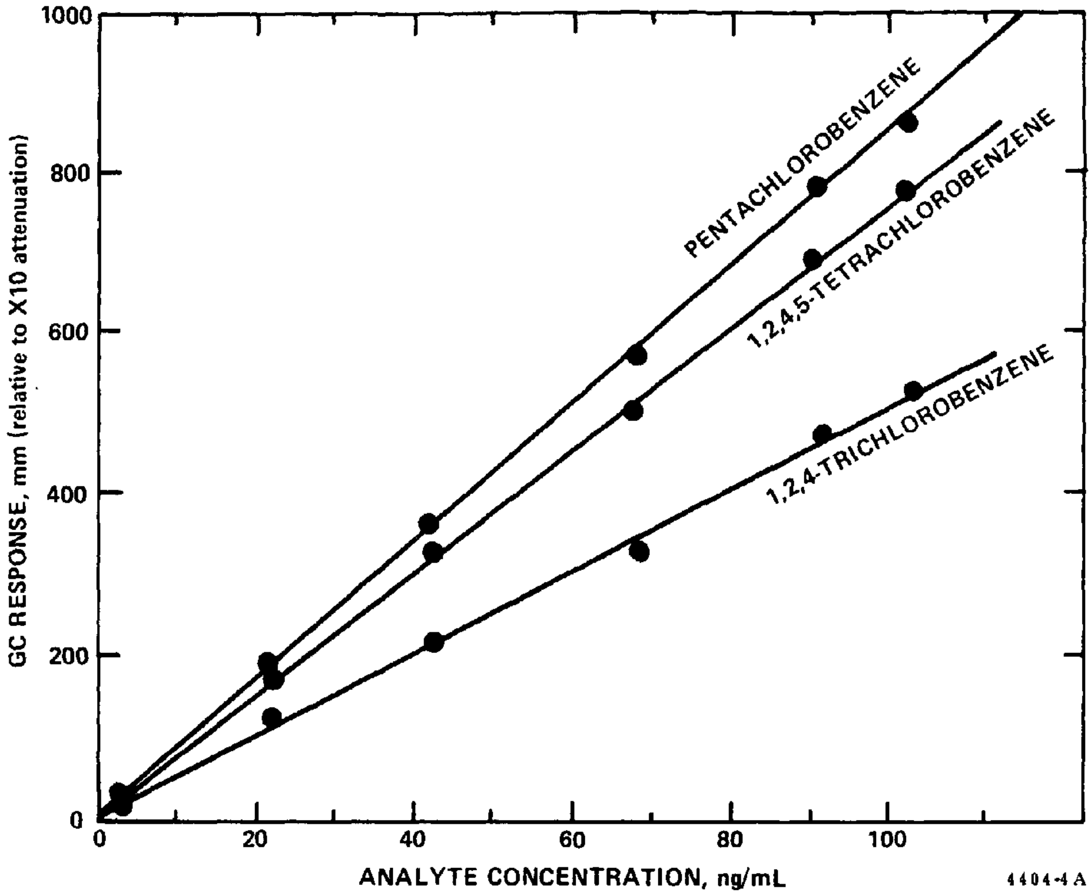

Figure 2. GC calibration curves for the three analytes with a 2-μL injection volume.

The detection limit (X) was found to be about 10 ng/mL (20 pg injected) for all three analytes. At this concentration level, a relative standard deviation of about 10% was obtained for replicate injections. The ratio of the peak height to the background noise was about 5:1. The ratio was about 2:1 at the concentration of 1 ng/mL (2 pg injected).

Although the ideal working range was found to be about 10 to 100 ng/mL, it appeared that satisfactory results could be obtained at concentratons up to about 500 ng/mL. At this concentration a slight flattening of the calibration curve occurred; however, unknown concentrations could be determined accurately by the use of standard solutions that would give responses near those of the unknown solutions.

III. SELECTION OF COLLECTION DEVICE AND PRELIMINARY EVALUATION

A. Choice of Candidate Sorbent and Filter Materials

The sorbent materials that were screened are as follows: coconut and petroleum-based charcoal (SKC, Inc.), a carbon molecular sieve (Carbosieve S), a synthetic magnesium silicate (Fluorisil PR), and several porous polymers (Amberlite XAD-2, Amberlite XAD-4, Porapak Q, and Porapak T). Some physical properties of these materials and their chemical compositions are presented in Table III. The charcoals were chosen for investigation primarily because their high specific surface areas were expected to result in large capacities for the chlorinated benzenes. Carbosieve S offered another advantage; it is a carbon molecular sieve that will selectively sorb compounds with molecular diameters below 10 to 12 Å [H1]. Because the calculated molecular diameters for the analytes range from 6 to 7 Å, these compounds were expected to be sorbed efficiently by Carbosieve S. Florisil PR, an inorganic sorbent with lower specific surface area, was selected for screening because of its extensive use in analytical methods for pesticide residues [H2]. Although porous polymers do have lower specific areas than many inorganic sorbents, they were expected to provide, in general, more stable sorption media for the analytes than most inorganic sorbents. Among the four porous polymers that were chosen for screening, Amberlite XAD-2, Amberlite XAD-4, and Porapak Q are relatively nonpolar materials while Porapak T is more polar [H5].

All candidate sorbent materials except the Amberlite XAD-2 obtained in commercial tubes from SKC, Inc., were cleaned before use. The cleaning procedure involved the Soxhlet extraction of bulk quantities of the materials with a 4:1 (v/v) mixture of acetone and methanol for 4 h followed by Soxhlet extraction with hexane for 4 h. (The solvents used were obtained from Burdick and Jackson Laboratories, Inc.) The washed materials were then dried overnight at 70 to 100 °C under vacuum.

Table III. Properties of Candidate Sorbents for Chlorinated Benzenes

Sorbent	Mesh size	Specific surface area, m^2/g	Average pore diameter, Å	Description	Lot No.	Supplier
Coconut charcoal, Cat. No. 226-01-01[a]	20/40	>1000	-	coconut charcoal	107	SKC, Inc.
Petroleum charcoal, Cat. No. 226-36-01[a]	20/40	>1000	-	petroleum-based charcoal	JXC	SKC, Inc.
Carbosieve S[b]	45/60	559	12	pyrolyzed Saran	Unknown	Supelco, Inc.
Florisil PR[c]	60/80[d]	300	-	coprecipitated mixture of silica gel and magnesium oxide	79-1	Analabs, Inc.
Amberlite XAD-2[e]	20/50	350	90	copolymer of styrene and divinylbenzene	1006	Supelco, Inc. and SKC, Inc.
Amberlite XAD-4[e]	20/40[f]	850	50	copolymer of styrene and divinylbenzene	2-6716	Supelco, Inc.
Porapak Q[e]	50/80	840	75	copolymer of ethylvinylbenzene and divinylbenzene	2072	Supelco, Inc.
Porapak T[e]	50/80	450	91	polymer of ethyleneglycoldimethylacrylate	1440	Supelco, Inc.

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a. See Reference H4.
b. See Reference H1.
c. See References I2 and I3.
d. Material of this mesh-size range was sieved from 60/100-mesh material obtained commercially.
e. See Reference H5.
f. Material of this mesh-size range was sieved from 16/50-mesh material obtained commercially.

Only the three filter materials that are described in Table IV were evaluated in the screening tests. Two compacted fiber filters—a quartz fiber mat and a Teflon fiber mat—and one membrane filter—a cellulose ester material—were tested. The fiber filters were chosen for evaluation because they present less resistance to airflow and are, therefore, more amenable to sampling with a personal sampling pump than other types. The cellulose ester membrane filter with a pore diameter of 0.8 μm was chosen primarily because of its extensive usage in the sampling of particulate material in air in the past; this type of filter does not exhibit prohibitive resistance to airflow at typical sampling rates for personal monitoring.

Tests with the candidate filters were performed in three types of filter holders: (1) a 13-mm polystyrene holder (Millipore Swinnex Disc Filter Holder, Catalog No. SX00 01300), (2) a 13-mm stainless steel holder (Millipore Swinny Stainless Disc Filter Holder, Catalog No. XX30 01200), and (3) a 37-mm polystyrene two-piece cassette (Gelman Field Monitor, Catalog No. 4338).

Table IV. Description of Particulate Filter Materials Tested

Filter type	Mean pore size, μm	Description	Lot No.
Gelman Micro-Quartz	-	quartz fiber mat	8229
Millipore Type AA	0.8	mixed cellulose acetate and nitrate membrane	C8K63731B
Millipore Type LS (Mitex)	5.0	Teflon fiber mat	C9A92194C

B. Screening Tests

Capacity, desorption efficiency, and stability tests were performed to determine the suitability of the candidate sorbent materials for the collection of the vapors of the analytes.

In the investigation of the candidate filter materials and, also, the filter holders, tests were performed to find the filter and holder with the least affinity for the vapors of the compounds.

1. Sorbent capacity tests

In the capacity tests, 100-mg quantities of the candidate sorbents in glass tubes (7 cm long by 6 mm [0.25 in.] o.d. by 4 mm i.d.) were challenged with test atmospheres containing the vapors of all three of the chlorinated benzenes in air (see Appendix B for a description of the generation and sampling system). The nominal sampling rate was 0.2 L/min.

The breakthrough of the most volatile of the three compounds—1,2,4-trichlorobenzene—was monitored by periodically sampling the effluent from a sorbent tube with a GC gas sampling loop and by then determining the compound in the loop sample by GC/ECD (see Section IV for a description of the sampling and analytical method based on the use of the GC loop).

Simultaneous with the determination of the capacity of each type of sorbent material with a single-section tube as described above, a second tube containing a 100-mg sorbing section and a 50-mg backup section of the same sorbent material was exposed, also at a sampling rate of 0.2 L/min.

The generator operating conditions were as follows: The temperature inside the sampling chamber was maintained at about 40 °C; the relative humidity was 80%. The target levels for the vapor concentrations of the three analytes were 40 mg/m^3 for 1,2,4-trichlorobenzene and 10 mg/m^3 for 1,2,4,5-tetrachlorobenzene and pentachlorobenzene. Because the concentrations tended to drift with time, the actual concentrations generated covered the following ranges: 8 to 69 mg/m^3 for 1,2,4-trichlorobenzene, 4 to 29 mg/m^3 for 1,2,4,5-tetrachlorobenzene, and 1 to 15 mg/m^3 for pentachlorobenzene.

After the air sampling was completed for each type of sorbent, the sorbent sections (one in the first tube and two in the second) were individually extracted with hexane and the extracts were analyzed for the three chlorobenzenes.

The results of the capacity tests are presented in Table V. The data indicate that all but one of the materials possesses a reasonable capacity for 1,2,4-trichlorobenzene. Because 100% breakthrough of the compound was experienced with 100 mg of Florisil PR after only 2 L of the test air was sampled, the capacity of this sorbent was considered to be unsatisfactory. The carbon materials exhibited the greatest capacity for 1,2,4-trichlorobenzene. Of the porous polymers, Amberlite XAD-4, Porapak Q, and Porapak T exhibited greater capacities than did Amberlite XAD-2, the candidate sorbent with the smallest surface area. The Amberlite XAD-2 obtained from Supelco, Inc., outperformed the Amberlite XAD-2 in sorbent tubes obtained from SKC, Inc. The difference was due in part to the fact that the sorbing layer in the SKC sorbent tube was 80 mg, whereas 100-mg quantities of the material from Supelco, Inc., were tested. Because the Supelco material was washed thoroughly in the laboratory prior to its use but the SKC material was used as obtained from the supplier, perhaps another factor contributing to the discrepancy was the possibility that the Supelco material was cleaner and, therefore, possessed a greater collection surface area.

Table V. Screening of Sorbent Capacities for 1,2,4-Trichlorobenzene

Sorbent material	Sample Set No.	Sorbent Sample No.	Calculated analyte concentrations,[a] mg/m^3			Capacity for 1,2,4-TCBz		
			1,2,4-TCBz	1,2,4,5-TCBz	PCBz	Breakthrough time,[b] h	breakthrough volume,[c] L	Weight capacity,[d] mg
SKC petroleum charcoal	1	1[e]	35	6	2	>20[f]	>230	>8
		2[g]	37	6	2			
Carbosieve S	1	1[e]	30	4	1	>25[f]	>300	>9
		2[g]	23	4	1			
Florisil PR	1	1[e]	8	18	6	<0.2[h]	<2	<0.1
		2[g]	16	29	5			
Amberlite XAD-2 (Supelco, Inc.)	1	1[e]	45	22	15	2.1	24	1.0
		2[g]	44	21	15			
Amberlite XAD-2 (SKC, Inc.)	1	1[i]	39	17	4	0.5	6	0.2
		2[j]	40	17	5			
	2	1[i]	40	17	5	0.6	6	0.2
		2[j]	36	15	4			
	3	1[i]	42	13	7	0.5	5	0.2
		2[j]	41	12	6			
	4	1[i]	35	6	7	0.5	6	0.2
		2[j]	34	6	6			
Amberlite XAD-4	1	1[e]	10	8	3	7.5	90	0.9
		2[g]	8	6	3			
	2	1[e]	25	4	1	>10[k]	>120	>3
		2[g]	39	6	2			
Porapak Q	1	1[e]	69	29	2	4	43	3.0
		2[g]	61	27	2			
Porapak T	1	1[e]	44	9	1	>4.5[f]	>49	>2.2
		2[g]	42	9	1			

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a. The levels shown were calculated from the quantities of the analytes recovered from the 100-mg sorbent sections in each tube and the volume of air sampled through each tube. The quantity of each analyte that slipped through the 100-mg section of each tube always represented <1% of the total amount recovered.

b. Unless specified otherwise, the values listed were obtained when the GC loop samples indicated that the concentration of 1,2,4-trichlorobenzene (1,2,4-TCBz) in the tube effluent was 5% of the test concentration.

c. Sampling rate (0.17 to 0.20 L/min) multiplied by the breakthrough time.

d. Based on the quantity of 1,2,4-trichlorobenzene recovered from the 100-mg sorbing section.

e. Tube with single 100-mg sorbing section in tandem with GC loop.

f. No breakthrough was observed after this time interval.

g. Tube with 100-mg sorbing section and 50-mg backup layer.

h. The concentration of 1,2,4-trichlorobenzene in the tube effluent was equal to the test concentration after this time interval.

i. Commercial sorbent tube (SKC Catalog No. 226-30) with 80-mg sorbing section and a 40-mg backup section. The 40-mg backup section was removed for this test.

j. Commercial sorbent tube (SKC Catalog No. 226-30) with 80-mg sorbing section and a 40-mg backup section.

k. The concentration of 1,2,4-trichlorobenzene in the tube effluent was less than 1% of the test concentration after this time interval.

2. Preliminary determination of the stability and desorption efficiencies of the sorbed analytes

As the next step in sorbent selection, the desorption efficiencies by solvent extraction of each of the three chlorinated benzenes from several candidate materials were determined. These materials included the types that had been tested in the capacity tests and, also, a coconut charcoal purchased from SKC, Inc. (Catalog No. 226-01-01). Amberlite XAD-2 from Supelco, Inc., was included in these tests but Amberlite XAD-2 from SKC, Inc., was not.

One-hundred-milligram portions of these materials were spiked with 100-ng amounts of each test compound by the following procedure: A 5-μL aliquot of a solution of all three compounds in hexane was completely vaporized from a glass wool plug above a 100-mg sorbent bed in a glass tube and was then flushed into the bed by a filtered airstream moving through the tube. The exposed sorbent samples were stored 1 or 3 d and then each was extracted in a sealed vial with 2 mL of hexane or acetone in an ultrasonic bath for 1 h. (Acetone was only evaluated with the carbons in an attempt to increase the desorption efficiency above that found with the hexane extraction of each of these materials.)

The results of this procedure are summarized in Table VI. Satisfactory desorption of the analytes was obtained with several materials. The recoveries with Amberlite XAD-2 and Florisil PR exceeded 90%; the recoveries with Porapak Q, Porapak T, and Amberlite XAD-4 were between 82 and 89%. Recoveries with the three carbons—the materials with the highest capacities for the analytes—were disappointingly low; the use of a more polar solvent, acetone, did not significantly improve the results with identical samples of the carbon substrates.

Table VI. Recovery of 100-ng Quantities of the Chlorinated Benzenes by the Solvent Extraction of Spiked Sorbent Materials after Storage for 1 Day or 3 Days

Sorbent material	Storage time, d	No. of samples	Average recovery, %		
			1,2,4-TCBz	1,2,4,5-TCBz	PCBz
SKC coconut charcoal[a]	1	2	<10	<10	<10
SKC petroluem charcoal[a]	1	2	<10	<10	<10
Carbosieve S[a]	1	2	<10	<10	<10
Florisil PR	1	2	92.1	92.5	90.3
Amberlite XAD-2 (Supelco, Inc.)	3	3	93.3	96.9	95.0
Amberlite XAD-4	1	2	85.7	84.2	88.0
Porapak Q	1	2	87.5	87.5	88.5
Porapak T	1	2	83.0	81.7	83.1

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a. Two identical samples of this material were also extracted with acetone; there was no significant improvement in the desorption efficiency.

Additional desorption efficiency tests and preliminary stability tests were conducted with Amberlite XAD-2 (Supelco, Inc.), Amberlite XAD-4, Porapak Q and Porapak T. The same spiking procedure as described above was followed. Six sorbent samples of each type were spiked with 100 ng of each of the three analytes. Three of the six samples were analyzed after storage for 1 d; the recoveries with these samples were a measure of desorption efficiencies. The remaining three samples of each sorbent material were analyzed after storage for 7 d; the recoveries with these samples were an indication, in part, of the stabilities of the sorbed analytes.

The results of this test are summarized in Table VII. The recoveries with Amberlite XAD-2 exceeded 90% with all three analytes even after 7 d; the recoveries with Amberlite XAD-4 and Porapak Q were as low as 85 to 87%; and the recoveries with Porapak T were as low as 81 to 83%.

Table VII. Recovery of 100-ng Quantities of the Chlorinated Benzenes by the Solvent Extraction of Spiked Sorbent Materials after Storage for 1 Day and 7 Days

Sorbent material	Average recovery,[a] %					
	1 Day			7 Days		
	1,2,4-TCBz	1,2,4,5-TCBz	PCBz	1,2,4-TCBz	1,2,4,5-TCBz	PCBz
Amberlite XAD-2	93.8	97.0	91.8	91.0	92.2	92.0
Amberlite XAD-4	90.0	94.0	91.0	84.5	85.5	86.3
Porapak Q	92.7	96.0	95.0	86.5	87.2	85.8
Porapak T	88.7	92.0	89.8	81.0	83.4	82.5

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a. Each number represents the average desorption efficiency for three identical samples. The individual values within each triplicate set differed from the average by no more than ±4% for Amberlite XAD-2 or Amberlite XAD-4 and no more than ±15% for Porapak Q or Porapak T.

Because Amberlite XAD-2 performed best in desorption efficiency tests and 7-d stability tests and also because Amberlite XAD-2 had demonstrated adequate capacity for the analytes in previous tests, this sorbent material was chosen for use in the method for chlorinated benzenes.

3. Screening of particulate filter materials and filter holders

Screening tests were conducted to evaluate the performance of the candidate filter materials—Gelman Micro-Quartz, Millipore Type AA, and Millipore Type LS—and the candidate filter holders—13-mm polypropylene and stainless steel holders and 37-mm polystyrene holders. Minimal retention of the vapors of the analytes by the materials was considered desirable.

In the initial screening tests, 13-mm discs of the candidate filter materials were mounted in the polypropylene holders. The holders were attached to Amberlite XAD-2 sorbent tubes to form sampling devices that would allow air to be drawn first through the filter holder and then through the sorbent tube.

After filter blanks had been extracted, analyzed, and found to be free of contaminants that might interfere with the analytical procedure, sampling devices were spiked according to the following procedure:

- Sampling devices were mounted vertically with their outlets (pointed downward) connected to a critical flow orifice and vacuum pump.
- While air was sampled at 0.2 L/min through the devices, 100 ng of each analyte in 5 μL of a hexane solution containing all three analytes was deposited on the surfaces of the filter device.
- Six liters of air was sampled through each sampling device to allow the evaporation of the solution aliquot from the filter discs.
- The spiked samples were immediately transferred to vials and extracted with hexane by agitation in an ultrasonic bath. (Filter and sorbent materials were extracted separately.)
- The extracts were then analyzed by the gas chromatographic procedure.

The results of this study, reported in Table VIII, indicate very little difference in the performance of the filter materials. Recoveries were somewhat inconsistent with several samples; but, in general, all three filter materials sorbed more 1,2,4-trichlorobenzene than the other analytes, and the recoveries were higher for this analyte than for the others. From additional work described below, it appears that the inconsistencies of the work described here may have been the result of the sorption of the analytes on the filter holders; however, the filter holders were not extracted in this work to determine the extent of sorption.

Table VIII. Recovery of 100-ng Spikes of Each of the Chlorinated Benzenes from Sampling Devices Consisting of 13-mm Filters in Polypropylene Filter Holders in Tandem with Amberlite XAD-2 Sorbent Tubes

Filter type	Sample No.[a]	Component of the sampling device	Recovery of specified analyte, %		
			1,2,4-TCBz	1,2,4,5-TCBz	PCBz
Gelman Micro-Quartz	1	filter	16.0	0.0	15.0
		tube	90.5	86.5	92.5
		total	106.5	86.5	107.5
Millipore Type AA	1	filter	17.0	0.0	4.0
		tube	87.0	85.0	74.0
		total	104.0	85.0	78.0
	2	filter	13.0	3.0	3.0
		tube	86.0	80.0	72.0
		total	99.0	83.0	75.0
Millipore Type LS	1	filter	15.0	0.0	2.0
		tube	106.5	104.0	89.0
		total	121.5	104.0	91.0
	2	filter	13.0	0.0	2.0
		tube	88.0	83.0	71.0
		total	101.0	83.0	73.0

---

a. Samples were extracted and analyzed immediately after spiking.

On the basis of the results of this test, it was difficult to select a filter material for use in the method. Of the materials tested, however, filter discs of Millipore Type LS were easier to work with and maintained their integrity better than the other materials both in the filter holder and during the extraction procedure. Furthermore, this material did appear to retain slightly less of the vapors of the analytes by sorption than did the other materials.

Additional spiking tests were performed at higher analyte levels with the Millipore Type LS Filters in the polypropylene holders. Six sampling devices were spiked with 500 ng of each analyte according to the procedure described earlier. The results of these spiking tests are reported in Table IX. They indicate that averages of about 45.2% of the pentachlorobenzene, 34.5% of the 1,2,4,5-tetrachlorobenzene, and 14.4% of the 1,2,4-trichlorobenzene were retained by the filter holders in these tests. The amount of the analytes sorbed by the filter holders was significant and varied from sample to sample.

Table IX. Recovery of 500-ng Spikes of Each of the Chlorinated Benzenes from Sampling Devices Consisting of 13-mm Millipore Type LS Filters in Polypropylene Filter Holders in Tandem with Amberlite XAD-2 Sorbent Tubes

Sample	Component of the	Recovery of specified analyte, %		
No.[a]	sampling device	1,2,4-TCBz	1,2,4,5-TCBz	PCBz
1	Filter	2.0	0.0	1.0
	Filter holder	16.5	38.0	51.0
	Tube	70.5	55.0	33.5
	Total	89.0	93.0	85.5
2	Filter	1.0	0.0	1.0
	Filter holder	19.0	35.0	52.0
	Tube	74.0	57.0	35.0
	Total	94.0	92.0	88.0
3	Filter	1.0	0.0	1.0
	Filter holder	13.5	32.0	46.0
	Tube	77.0	63.0	42.0
	Total	91.5	95.0	89.0
4	Filter	1.0	0.0	1.0
	Filter holder	10.0	24.0	34.0
	Tube	79.0	65.0	42.0
	Total	90.0	89.0	77.0
5	Filter	1.0	0.0	1.0
	Filter holder	11.0	41.0	38.0
	Tube	79.0	64.0	41.0
	Total	91.0	105.0	80.0
6	Filter	1.0	0.0	0.0
	Filter holder	16.5	37.0	50.0
	Tube	83.0	67.0	43.0
	Total	100.5	104.0	93.0
	Average	92.7	96.3	85.4
	RSD	4.5%	6.9%	7.0%

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a. Samples were extracted and analyzed immediately after spiking.

In an attempt to find a filter holder that would not sorb the analytes, filter holders made from stainless steel and polystyrene were evaluated in tests similar to those performed with polypropylene filter holders. In this evaluation, 13-mm discs of Millipore Type LS filter material were mounted in stainless steel holders (Millipore Swinny Stainless) and 37-mm discs of Schleicher and Schuell Teflon fiber filter material were mounted in polystyrene holders (Gelman Field Monitor). (Type LS material would have been used with the polystyrene holders but 37-mm discs of this material were not readily available for this exploratory study.) An Amberlite XAD-2 sorbent tube was attached to the outlet of each holder to form a complete sampling device. A 5-μL aliquot of a solution containing 500 ng of each analyte was deposited on the surface of each filter disc while air was sampled at a rate of 0.2 L/min through the filter and sorbent tube. (The total air volume sampled was about 6 L.) Each component of the sampling device was immediately extracted with hexane, and the extracts were analyzed.

The results of this study, reported in Table X, indicate that both holders performed satisfactorily; retention of the analytes by the holders appeared to be minimal. The Schleicher and Schuell Teflon filter material retained more of the vapors of the analytes than did the Millipore Type LS material. Perhaps the larger surface area of the 37-mm Schleicher and Schuell filters, about eight times that of the 13-mm filters, resulted in the sorption of larger amounts of the analytes.

The stainless steel holders appeared to be better suited than the polystyrene holders for personal sampling. The stainless steel holders were found to be more compact and convenient to use. The smaller diameter of the stainless steel holders may provide an additional advantage in the sampling of aerosols. Because the filter face velocity with a 13-mm holder is higher than that with a 37-mm holder at the same volume flow rate, the smaller holder will provide a higher collection efficiency for particles with diameters greater than about 0.3 μm at typical volume flow rates of 0.1 to 0.2 L/min [G5]. A significant fraction of the aerosols of interest (particles in the respirable size range) will possess diameters greater than 0.3 μm [G12].

C. Additional Desorption and Stability Tests Leading to the Determination of the LAQL

Additional desorption efficiency and stability tests were performed to verify the data collected in the screening tests and to determine the lowest analytically quantifiable level (LAQL).

The procedure followed was similar to that described in Section III.B.3. In the experiments described here, however, the tubes and filter holders were separated after their exposure to the analytes, sealed with plastic caps, and stored for approximately 1 to 7 d prior to extraction and analysis. Twenty-four sampling devices were spiked with either 20 or 500 ng of each analyte. Twelve were spiked with 20 ng and were stored for 3 or 7 d; the remaining twelve were spiked with 500 ng and stored for 1 or 7 d.

TABLE X. Recovery of 500-ng Spikes of Each of the Chlorinated Benzenes from Sampling Devices with Stainless Steel or Polystyrene Filter Holders

Sample No.[a]	Component of the sampling device[b]	Recovery of specified analyte from sampling devices with stainless steel filter holders,[c] %			Recovery of specified analyte from sampling devices with polystyrene filter holders,[d] %		
		1,2,4-TCBz	1,2,4,5-TCBz	PCBz	1,2,4-TCBz	1,2,4,5-TCBz	PCBz
1	Filter	0.0	0.0	3.0	4.0	17.0	38.0
	Filter holder	0.0	0.0	1.5	0.0	0.0	0.0
	Tube	94.0	93.0	87.5	92.0	78.0	53.0
	Total	94.0	93.0	92.0	96.0	95.0	91.0
2	Filter	0.0	0.0	3.5	5.0	20.0	44.0
	Filter holder	0.0	0.0	1.0	0.0	0.0	0.0
	Tube	96.0	95.0	89.0	95.0	79.0	49.0
	Total	96.0	95.0	93.5	100.0	99.0	93.0
3	Filter				5.0	18.0	40.0
	Filter holder				0.0	0.0	0.0
	Tube				97.0	82.0	56.0
					102.0	100.0	96.0

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a. Samples were extracted and analyzed immediately after the air was sampled.

b. Amberlite XAD-2 sorbent tubes were used.

c. Millipore Type LS filters were used.

d. Schleicher and Schuell Teflon fiber filters were used.

The test results are presented in Tables XI and XII. The recoveries of all three analytes at each of the storage times and for both analyte spiking levels were acceptable. In general, the results indicated that the analytes were quantitatively recoverable and were stable at levels as low as about 20 ng. The average recoveries were not statistically different at the 0.05 significance level when the 7-d results were compared to the 3-d or 1-d results with one exception. The recovery of approximately 20-ng spikes of pentachlorobenzene was about 10% higher after storage for 7 d than after storage for 3 d. No explanation was found for this discrepancy.

The results at the 20-ng level were better than those required to define the LAQL (i.e., >80% recovery and a RSD ≤10%). In fact, one must conclude that the LAQL for each analyte is below 20 ng. It was decided, however, not to conduct tests at levels below 20 ng and to choose the 20-ng level as a practical value of the LAQL with a RSD somewhat lower than 10% to allow for variations that were expected to be introduced later by the sampling procedure.

D. Recommended Sampling Device

From the screening tests and the additional desorption efficiency and stability tests, a suitable sampling device for the collection of the chlorinated benzenes seemed to be a sorbent tube containing 20/50-mesh Amberlite XAD-2 preceded by a 13-mm Millipore Type LS filter in a stainless steel holder (Millipore Swinny Stainless).

A sorbent tube (7 cm long by 6.4 mm [0.25 in.] o.d. by 4 mm i.d.) containing a 100-mg sorbing section and a 50-mg backup section of the porous polymer cleaned by the Soxhlet extraction procedure described in Section III.A. was considered to be more appropriate for use than the Amberlite XAD-2 tube available from SKC, Inc. The commercially available tube was less desirable because its capacity for 1,2,4-trichlorobenzene was found to be significantly lower than the capacity of the Amberlite XAD-2 tube prepared in the laboratory. With tubes packed in the laboratory, a breakthrough volume of 24 L was found with a test atmosphere at 40 °C and >80% relative humidity containing 45 mg/m^3 of 1,2,4-trichlorobenzene; 22 mg/m^3 of 1,2,4,5-tetrachlorobenzene; and 15 mg/m^3 of pentachlorobenzene. Desorption efficiencies greater than or equal to 90% were found with 20 to 500-ng solution spikes of the analyte on 100-mg samples of the sorbent; the analytes were also found to be stable on the porous polymer samples for at least 7 d when stored in sealed tubes at room temperature.

The Millipore Type LS filter (a Teflon fiber mat) was judged to be more appropriate than the other candidate filters primarily because the Teflon filter was easier to work with and it maintained its integrity better than the other materials during sampling and analysis. The affinities for all three analytes of all the candidate filters, including the Teflon fiber mat, quartz fiber, and cellulose acetate filters, were found to be comparable and reasonably low.

Table XI. Recovery of Approximately 20-ng Quantities of the Chlorinated Benzenes from Sampling Devices after Storage for 3 Days or 7 Days

Storage time, d	Component of the sampling device[b]	Quantity of the specified analyte recovered,[a] ng		
		1,2,4-TCBz	1,2,4,5-TCBz	PCBz
3	Filter	0.0	0.0	0.3
	Filter holder	0.0	0.0	0.0
	Tube	18.1	18.2	18.5
	Total	18.1	18.2	18.8
	Std. dev.	0.9	0.8	1.1
	Average Recovery, %	95.8	87.3	90.1
7	Filter	0.0	0.0	0.0
	Filter holder	0.0	0.0	0.0
	Tube	17.9	18.9	21.0
	Total	17.9	18.9	21.0
	Std. dev.	0.5	0.7	2.0
	Average Recovery, %	94.6	90.5	100.4
	t[c]	0.557	1.226	2.231

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a. Each value given represents the average of six samples. The spiking level was 18.9 ng of 1,2,4-TCBz, 20.9 ng of 1,2,4,5-TCBz, and 20.9 ng of PCBz.

b. A 13-mm Millipore Type LS filter/stainless steel filter holder/Amberlite XAD-2 sorbent tube.

c. Student's _t_ for a two-tailed test at the 0.05 significance level for 7-d versus 3-d results. The critical value of _t_ is 2.228.

Table XII. Recovery of 500-ng Spikes of the Chlorinated Benzenes from Sampling Devices after Storage for 1 Day or 7 Days

Storage time, d	Component of the sampling device[b]	Av. quantity of the specified analyte recovered,[a] ng		
		1,2,4-TCBz	1,2,4,5-TCBz	PCBz
1	Filter	0	2	13
	Filter holder	0	0	1
	Tube	444	448	418
	Total	444	450	432
	Std. dev.	21	24	33
	Average Recovery, %	88.9	90.0	86.4
7	Filter	0	0	0
	Filter holder	0	0	0
	Tube	446	445	439
	Total	446	445	439
	Std. dev.	10	9	10
	Average Recovery, %	89.2	89.0	87.8
	t^c	0.141	0.344	0.325

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a. Each value given represents the average of six samples.

b. A 13-mm Millipore Type LS filter/stainless steel filter holder/Amberlite XAD-2 sorbent tube.

c. Student's *t* for a two-tailed test at the 0.05 significance level for 7-d versus 3-d results. The critical value of *t* is 2.228.

Because of its low affinity for the analytes and its small size, the 13-mm stainless steel filter holder (Millipore Swinny Stainless) was judged to be more acceptable for personal sampling than the other two holders evaluated—the 13-mm polypropylene holder (Millipore Swinney) and the 37-mm polystyrene holder (Gelman Field Monitor). The polypropylene holder sorbed significant fractions of 500-ng analyte spikes and was, therefore, considered to be less satisfactory than the other two. The 37-mm polystyrene holder exhibited a low affinity for the analytes; however, its diameter would hinder the efficient collection of particulate material at typical sampling rates for personal samplers (0.2 L/min).

A schematic diagram of the recommended sampling device is presented in Figure 3. The sorbent tube (6.4 mm [0.25 in.] o.d.) is coupled to the stainless steel filter holder by means of a nylon 6.4 mm (0.25-in.) Swagelok union with Teflon ferrules. The ferrule for the outlet of the filter holder is a 6.4 mm (0.25 in.) o.d. reducing ferrule bored out from 0.125 in. to a diameter of 0.156 in. (4 mm). Plastic caps are employed to separately seal the filter holder and sorbent tube after the exposure of the sampling device.

The pressure drops across six assembled sampling devices averaged 4.0 in. H_2O (1 kPa) at 25 °C at a sampling rate of 0.2 L/min. The RSD for the pressure drop measurements was 6.1%.

Although the filter of the sampling device should provide an effective means of collecting particulate material in field sampling without sorbing vapors of the three chlorinated benzenes, the sorbent tube alone may serve to determine concentrations of the analytes to which personnel are exposed in many situations. This is true because the analytes, including tetra- and pentachlorobenzene, exist in the gaseous state at levels significantly above the recommended exposure levels, which are 40 mg/m^3 for 1,2,4-trichlorobenzene, 3.5 mg/m^3 for 1,2,4,5-tetrachlorobenzene, and 1 mg/m^3 for pentachlorobenzene [C1,F19]. The volatilities of the compounds at 25 °C, extrapolated from available vapor pressure data, are estimated to be 3000 mg/m^3 for 1,2,4-trichlorobenzene, 140 mg/m^3 for 1,2,4,5-tetrachlorobenzene, and 24 mg/m^3 for pentachlorobenzene [A3,B10].

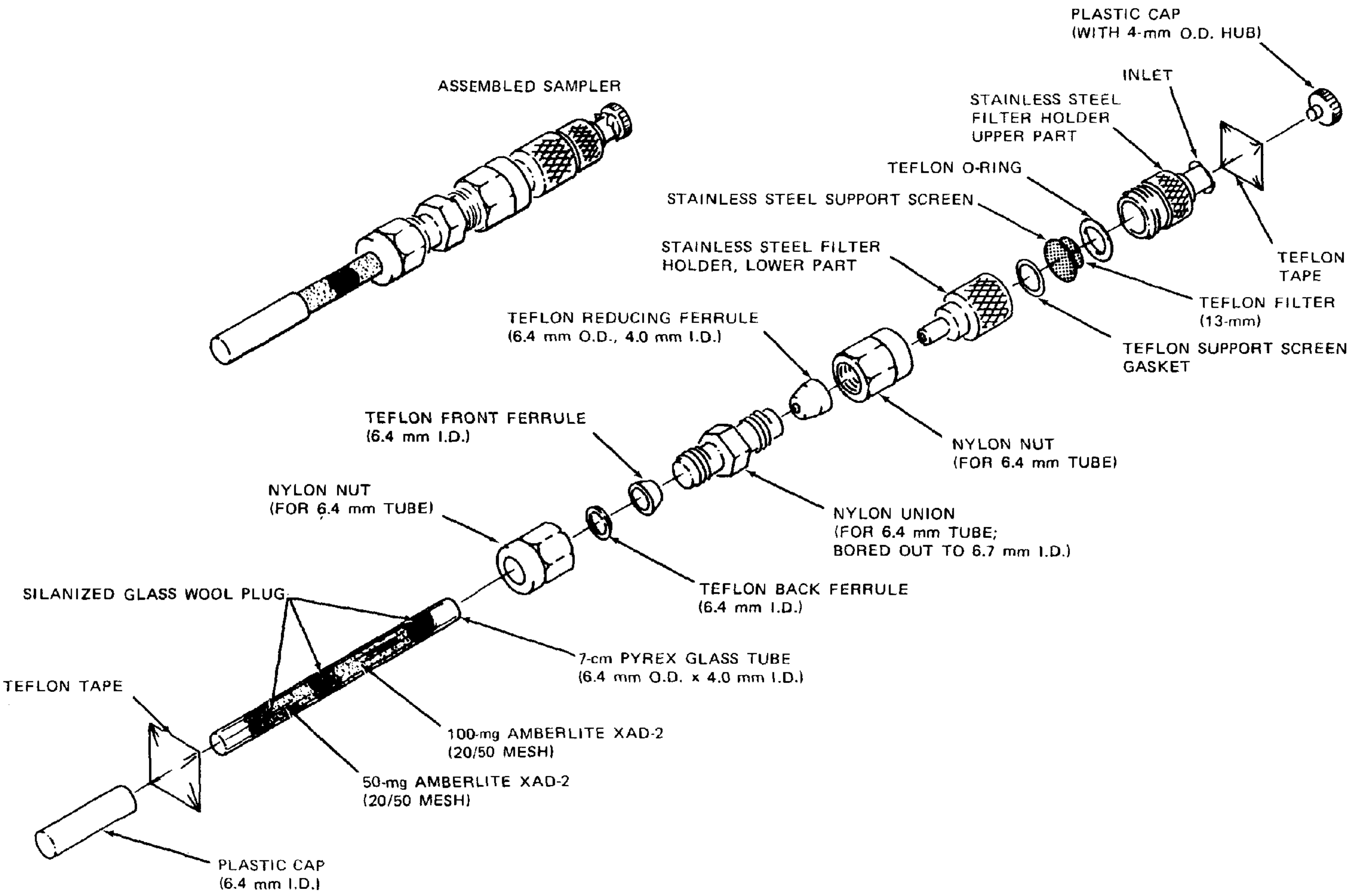

Figure 3. Schematic diagram of the two-stage sampler for the chlorinated benzenes.

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IV. INDEPENDENT SAMPLING METHOD FOR THE DETERMINATION OF THE CHLORINATED BENZENES

Two independent sampling methods were employed in the development and evaluation of a sampling and analytical method for the three chlorinated benzenes. These independent methods were employed to determine the concentrations of the analytes in test atmospheres of the compounds in air. (The test atmosphere generator is described in Appendix B.) A gas sampling loop attached to a gas chromatograph was employed in capacity screening tests. Later, when the developed method was evaluated at lower concentration levels where unsatisfactory results were obtained with the sampling loop, impinger sampling was utilized with both hexane and isooctane as absorbing solvents.

The method involving the GC gas sampling loop is described as follows: A gas sampling loop with a volume of 0.1 mL was attached to the GC/ECD system employed in the developed method and described in Section II. The loop was interfaced with the test atmosphere generator by means of a 5.5-ft long nickel tube (3.2 mm [0.125 in.] o.d. by 2 mm i.d.). The tube and loop were maintained at a temperature of about 100 °C to avoid the sorption of the analytes during sampling. Sample air was drawn at a rate of 0.1 L/min through the tube and loop by means of a critical flow orifice, which was maintained at room temperature. The orifice was attached to an electric vacuum pump. To determine the analytes in an air sample, the contents of the loop were injected onto the Carbowax 20M-TPA column under the operating conditions given in Section II.

The loop gave satisfactory results at analyte concentrations near or above 0.5 mg/m^3. The precision of replicate determinations of all three analytes simultaneously with the loop was good at levels of about 10 mg/m^3; the RSD was about 5% for each analyte. At levels below about 0.5 mg/m^3, the results were unsatisfactory. Difficulty was observed in the determination of the analytes because of interference from the response of the ECD system to oxygen. At low levels, a broad response to oxygen essentially masked the chlorinated benzene peaks, especially the peak for 1,2,4-trichlorobenzene.

At concentration levels near 0.5 mg/m^3 and above, the loop was calibrated as follows: Standard solutions of the three analytes in hexane were injected at known rates with a syringe pump into the heated transfer line leading from the dilution and sampling chamber to the gas sampling loop. The vaporized gases in the line were determined with the loop coupled to the GC/ECD. The actual rates of injection by the syringe pump ranged from about 0.1 to 2.0 µL/min, the flow rate through the transfer line was about 0.1 L/min, and the loop volume was about 0.1 mL. This yielded calculated analyte concentrations of about 0.5 to 12 mg/m^3 (50 to 1200 pg injected).

Typical plots for the resulting calibration curves are presented in Figures 4 and 5. As indicated in Figure 4, the GC/ECD response was found to be linear up to about 4 to 6 mg/m^3 (400 to 600 pg injected). Figure 5 illustrates the flattening of detector response beyond the linear

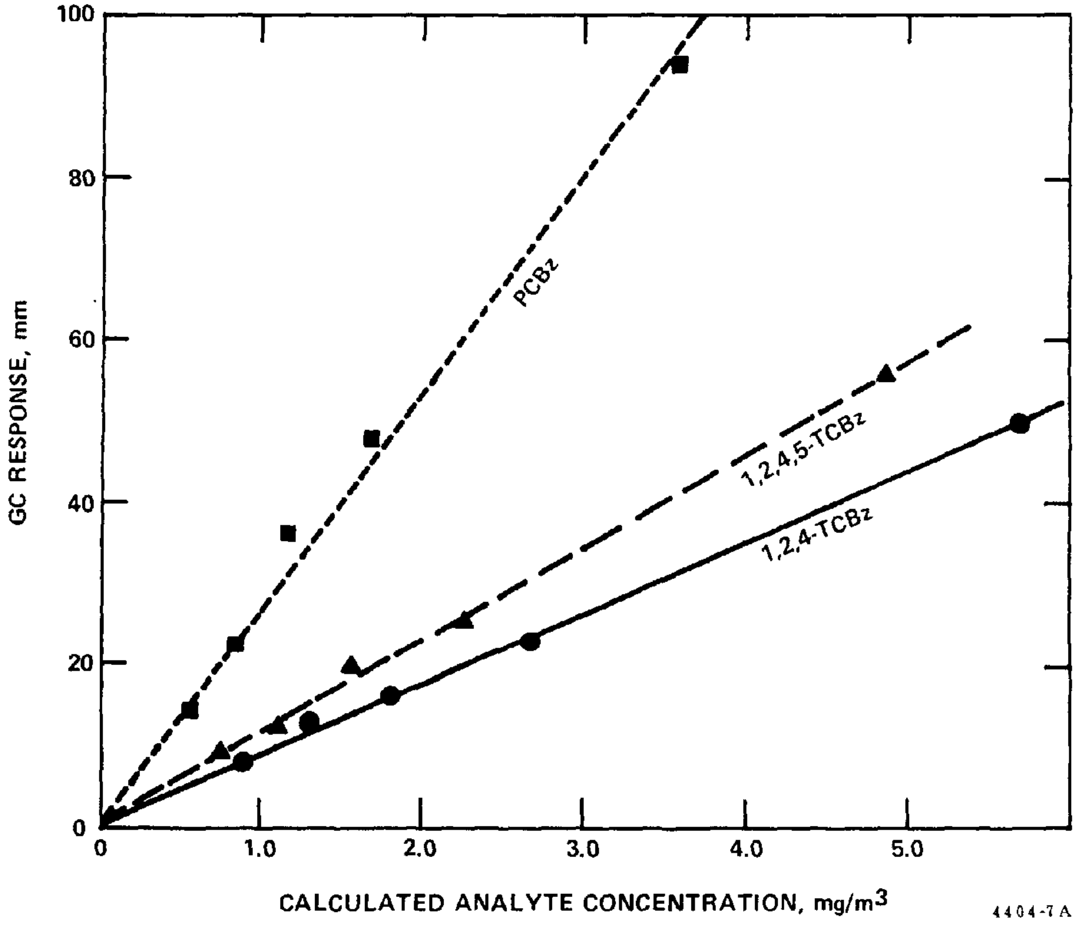

Figure 4. Calibration curves with the GC gas sampling loop for the three analytes.

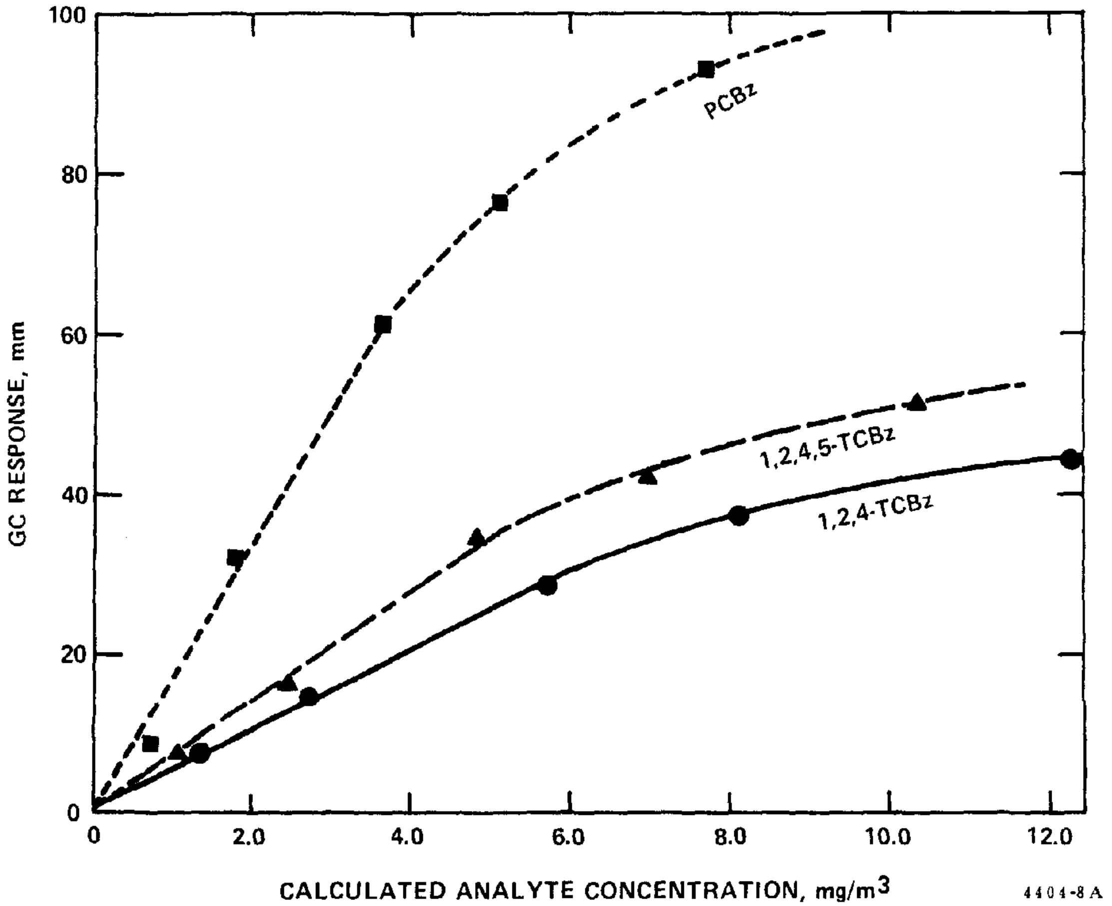

Figure 5. Calibration curves with the gas sampling loop for the three analytes extended beyond the linear range.

range. For accurate determinations above about 6 mg/m^3 for 1,2,4-trichlorobenzene, 5 mg/m^3 for 1,2,4,5-tetrachlorobenzene, and 4 mg/m^3 for pentachlorobenzene, calibration standards with concentrations corresponding to GC responses similar to that for the unknown analyte concentration were required.

An attempt was also made to calibrate the GC sampling loop by injecting gaseous standards of the analytes into the transfer line with the syringe pump. For 1,2,4-trichlorobenzene, the results of these determinations agreed well with those for liquid standards. The results for 1,2,4,5-tetrachlorobenzene and pentachlorobenzene were, however, unsatisfactorily low, apparently because of the adsorption of the analytes on the walls of the syringe and other glass containers employed for dilution.

The impinger sampling procedure was as follows: Ten to twenty-five milliliters of hexane or isooctane was added to a standard midget impinger. The impinger was then attached to a generator sampling port with glass tubing and ground glass joints. A second impinger, also containing hexane or isooctane, was placed in series downstream from the first as a backup sampler. Generator effluent was then sampled through the impingers at sampling rates ranging from about 0.1 to 0.5 L/min with critical flow orifices for periods ranging from 15 min to 6 h. The chlorinated benzenes in the impinger solutions were determined by the GC/ECD procedure given in Section II.

The validity of the application of this sampling technique to the determination of the analytes was established as follows: First, it was demonstrated that the impingers were efficient in collecting the vapors or the analytes. In several tests at concentrations of the analytes in air ranging from about 5 μg/m^3 to about 25 mg/m^3, the fraction of the analytes found in the backup impinger amounted to no more than 10% and seldom more than 1% of the total of the analytes recovered. This was true for hexane solutions although much of the hexane evaporated from the front bubbler during long-term sampling. Second, it was determined that concentrations as low as 10 ng/mL of the analytes in either hexane or isooctane solutions were stable at room temperature (about 25 °C).

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 the chlorinated benzenes in air. The accuracy and precision of the analytical procedure including the solvent desorption and determination steps were determined over a wide range of quantities of the analytes. The long-term storability of the compounds 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 the compounds in air.

A. Accuracy and Precision of the Analytical Procedure

To determine the accuracy and precision of the analytical procedure, additional desorption efficiency tests were required to supplement those described in Section III. The spiking and analysis procedure for these tests was similar to that employed for the earlier tests: An aliquot of a hexane solution of the three chlorinated benzenes was added to a filter in an assembled sampling device. Six liters of air free of the analytes was then drawn through the sampling device at a volume flow rate of 0.2 L/min. The filter holder and sorbent tube were then separated, individually sealed, and stored at room temperature in the dark for 1 d. The filter and each section of the sorbent tube were then individually extracted with hexane prior to the determination of the analytes by GC/ECD.

Four spiking levels were investigated in these tests: 100 ng, 400 ng, 25 μg, and 500 μg. For each spiking level, each of six prototype samplers were spiked with the specified quantity of each of the three analytes.

The results are given in Tables XIII and XIV. The results were acceptable; the desorption efficiencies were greater than 0.8 and the values of the RSD were <10%. As expected, significant portions of the 500-μg spikes of 1,2,4,5-tetrachlorobenzene (about 50%) and pentachlorobenzene (about 70%) were found on the filters and filter holders presumably because the volume of air sampled through the spiked filters was not large enough to evaporate the compounds entirely. Smaller fractions of the 100 and 400-ng spikes and of the 25-μg spikes of pentachlorobenzene were also found on the filters and filter holders.

The average desorption efficiencies at the 100- and 400-ng levels and the 25- and 500-μg levels were combined with previously reported desorption efficiencies at the 20 and 500-ng levels* to yield an overall average

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* The previously reported values are expressed as percent recoveries; the values were divided by 100 to yield the desorption efficiencies as fractions.

TABLE XIII. Recovery of Approximately 100- and 400-ng Quantities of the Chlorinated Benzenes from Sampling Devices

∿100 ng Spikes				∿400 ng Spikes			
Component of the sampling device[a]	Av. quantity of the specified analyte recovered,[b] ng			Component of the sampling device[a]	Av. quantity of the specified analyte recovered,[b] ng		
	1,2,4-TCBz	1,2,4,5-TCBz	PCBz		1,2,4-TCBz	1,2,4,5-TCBz	PCBz
Filter	0.0	0.0	1.4	Filter	0.0	0.0	38.5
Filter holder	0.0	0.0	1.1	Filter holder	0.0	0.0	32.4
Tube	87.2	95.4	91.3	Tube	341.0	372.1	366.4
Total	87.2	95.4	93.8	Total	341.0	372.1	437.3
Std. dev.	2.6	3.6	5.5	Std. dev.	19.4	14.8	26.9
Exact quantity added	94.4	104.4	104.4	Exact quantity added	377.5	417.5	417.5
Av. D.E.[c]	0.924	0.914	0.898	Av. D.E.[c]	0.903	0.891	1.047

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a. A 13-mm Millipore Type LS filter/stainless steel filter holder/Amberlite XAD-2 sorbent tube.

b. Each value given represents the average of six samples.

c. Average desorption efficiency: average quantity recovered divided by the quantity added.

TABLE XIV. Recovery of Approximately 25- and 500 μg Quantities of the Chlorinated Benzenes from Sampling Devices

	∿25 μg		
Component of the sampling device[a]	Av. quantity of the specified analyte recovered,[b] μg		
	1,2,4-TCBz	1,2,4,5-TCBz	PCBz
Filter	0.0	0.0	0.7
Filter holder	0.0	0.0	0.3
Tube	23.5	22.5	20.5
Total	23.5	22.5	21.5
Std. dev.	0.9	0.9	1.1
Exact quantity added, μg	25.1	25.3	25.6
Av. D.E.[c]	0.935	0.887	0.839

	∿500 μg		
Component of the sampling device[a]	Av. quantity of the specified analyte recovered,[b] μg		
	1,2,4-TCBz	1,2,4,5-TCBz	PCBz
Filter	15.1	115.4	155.8
Filter holder	16.4	147.6	177.3
Tube	408.3	213.7	157.6
Total	439.8	476.7	490.7
Std. dev.	13.2	14.7	14.1
Exact quantity added, μg	502.0	505.5	513.0
Av. D.E.[c]	0.876	0.943	0.957

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a. A 13-mm Millipore Type LS filter/stainless steel filter holder/Amberlite XAD-2 sorbent tube.

b. Each value given represents the average of six samples.

c. Average desorption efficiency: average quantity recovered divided by the quantity added.

desorption efficiency for each analyte. (The results at the 20- and 500-ng levels for samples stored for 7 d were not included in this calculation.) Also, the RSDs were pooled because the precision was homogeneous throughout the range of levels. The average desorption efficiencies and pooled RSDs are given in Table XV.

Table XV. Accuracy and Precision of the Analytical Methods over the Range of 20 ng to 500 µg[a]

	Chlorinated benzene compounds		
	1,2,4-TCBz	1,2,4,5-TCBz	PCBz
Average desorption efficiency[b]	0.908	0.901	0.917
Pooled RSD, %	4.4	4.2	5.7
χ^{2}[c]	3.50	1.30	3.89

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a. Six sampling devices were spiked with each chlorinated benzene at levels of 20 ng to 500 µg.

b. Recovery averaged over the test levels.

c. χ^2 critical = 13.28 for four degrees of freedom at the 0.01 significance level.

B. Determination of the Stabilities of the Sorbed Analytes after Collection from Air with Prototype Samplers

The stability of each of the three chlorinated benzenes collected from air was determined at low levels of each analyte according to the procedure given in the protocol. The test atmosphere concentrations were set at 14.1 µg/m^3 for 1,2,4-trichlorobenzene, 25.3 µg/m^3 for 1,2,4,5-tetrachlorobenzene, and 17.3 µg/m^3 for pentachlorobenzene at a relative humidity of about 80% and at a temperature of 33 °C.

Twenty-five test samplers (filters in tandem with sorbent tubes) were exposed at a sampling rate of about 0.2 L/min to approximately 2.5 L of the test atmosphere in five sampling sets with five devices included in each set. The air was sampled by means of critical flow orifices attached to a vacuum pump. On the average, the samplers were exposed to 35.3 ng of 1,2,4-trichlorobenzene, 63.1 ng of 1,2,4,5-tetrachlorobenzene, and 43.3 ng of pentachlorobenzene. During the exposures of each sampling set, the generator effluent was also sampled with three sets of two midget impingers in series containing hexane. After exposure, the filter holder and sorbent tubes of each test sampler were separated and sealed with Teflon tape and plastic caps. At least one sampler from each sampling set and two samplers from some sets were stored for 1, 7, 13, or 14 d. The 1-, 7-, and 13-d samples were stored at room temperature, while the 14-d samples were stored at room temperature for 7 d and 0 °C the remaining 7 d. After storage, the filter disc, filter holder, and the sorbent sections of each sampler were extracted with hexane separately, and the extracts were analyzed.

The apparent concentrations of the analytes in each air sample taken were determined by correcting the quantities of the analytes recovered for the desorption efficiencies determined previously and by then dividing the corrected amounts by the air sample volume.

The values for the recovery of each analyte within each sampling set were computed relative to the calculated actual quantities of the analytes drawn into the samplers. These quantities were computed by multiplying the air volume sampled by the average concentration of the analytes found with the three sets of impingers exposed with the prototype samplers.

The results of the stability test are given in Table XVI. The average recoveries of 1,2,4-trichlorobenzene and 1,2,4,5-tetrachlorobenzene were within 10% of the results obtained by impinger sampling; however, the recoveries of pentachlorobenzene after 1, 13, or 14 d of storage were 111 to 113% of the result obtained by impinger sampling. Nevertheless, the analytes were stable during storage. Although the average recovery of 1,2,4-trichlorobenzene after 7 d of storage was 8% lower than the average recovery after 1 d, the average recovery after about 2 wk of storage—either at room temperature or refrigerated for the last week—was not statistically different at the 0.05 significance level from the recovery after 1 d. Similar results were observed for pentachlorobenzene. For 1,2,4,5-tetrachlorobenzene, there was no statistical difference between the average result obtained after 7, 13, or 14 d of storage and the average result obtained after storage for 1 d.

C. Determination of the Accuracy and Precision of the Total Sampling and Analytical Method

The accuracy and precision of the total sampling and analytical method were determined for the three chlorinated benzenes in two sets of tests. In the first set, impinger sampling with hexane as the sorbing solution was employed as the independent sampling method. We obtained greater variability in the results with the hexane impingers than was desired, however. We surmised that the volatility of hexane may have contributed to uncertainties in the measurement of the air volumes sampled through the impingers even though the impinger sampling train (i.e., two impingers in series, critical flow orifice, and vacuum pump) was calibrated with a wet test meter situated upstream from the impingers. Consequently, a second set of samplers was exposed with a less volatile solvent, isooctane, as the sorbing solution in the impingers.

Table XVI. Storage Stability of the Chlorinated Benzenes Sampled from a Test Atmosphere Containing 14.1 $\mu g/m^3$ of 1,2,4-Trichlorobenzene, 25.3 $\mu g/m^3$ of 1,2,4,5-Tetrachlorobenzene, and 17.3 $\mu g/m^3$ of Pentachlorobenzene

Component of the sampling device	Av. concn. of the indicated compd. determined after the specified storage time,[a] $\mu g/m^3$											
	1,2,4-TCBz				1,2,4,5-TCBz				PCBz			
	1 d[b]	7 d[b]	13 d[b]	14 d[c]	1 d[b]	7 d[b]	13 d[b]	14 d[c]	1 d[b]	7 d[b]	13 d[b]	14 d[c]
Filter and holder[d]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
Section 1	14.9[f]	13.8[f]	14.2	15.0	24.7[f]	24.4[f]	23.4	24.8	19.1[f]	17.5[f]	17.8	19.1
Section 2			0.4	0.1			0.0	0.2			1.4	0.4
Total	14.9	13.8	14.6	15.1	24.7	24.4	23.4	25.0	19.3	17.5	19.2	19.5
Std. dev.	0.4	0.8	1.0	1.0	1.0	2.3	1.6	2.4	1.2	0.7	2.0	2.3
RSD, %	2.6	6.1	6.6	6.7	4.0	9.3	6.8	9.8	6.3	4.0	10.2	12.0
Mean recovery,%	106	98	104	106	98	96	92	99	111	101	111	113
_t_ (observed)[h]	-	3.01	0.68	0.23	-	0.29	1.69	0.28	-	2.95	0.11	0.18
_t_ (critical)	-	2.23	2.23	2.20	-	2.23	2.23	2.20	-	2.23	2.23	2.20

a. The average quantity of each analyte that was sampled in 2.5 L of air was 35.3 ng of 1,2,4-trichlorobenzene, 63.1 ng of 1,2,4,5-tetrachlorobenzene, and 43.3 ng of pentachlorobenzene.

b. Six samples were stored in the dark at room temperature. One of the samples stored for 7 d gave a pentachlorobenzene concentration (22.6 $\mu g/m^3$) that was found to be a statistical outlier by the Grubb's test. This result was consequently rejected.

c. Seven samples were stored in the dark at room temperature for 7 d and at 0 °C for the remaining 7 d.

d. Millipore Type LS filter and stainless steel holder.

e. Front section of sorbent tube, 100 mg of Amberlite XAD-2.

f. The contents of the sorbent tube were analyzed as a single sample.

g. Backup section of sorbent tube, 50 mg of Amberlite XAD-2.

h. Comparison of mean for 7-, 13-, or 14-d storage test to the mean for 1-d storage test by Student's t for a two-tailed test at the 0.05 significance level.

The general experimental procedure for the accuracy and precision tests was as follows: The test atmosphere concentration of each of the three analytes was adjusted to the desired level inside the sampling chamber. The relative humidity inside the chamber was maintained at about 80% and the temperature between 26 and 32 °C. The test atmosphere, which contained all three analytes, was sampled through prototype samplers at nominal volume flow rates of 0.2 L/min with critical flow orifices attached to a vacuum pump. Approximately 10 L of air was sampled through each sampler. Three sets of two standard midget impingers, each containing either hexane or isooctane, were exposed along with each set of six prototype samplers. After sampling, the filter holder and sorbent tube of each test sampler were separated, sealed with plastic caps and Teflon tape, and stored overnight at room temperature. After storage, the filter disc, the filter holder, and the sorbent sections were extracted with hexane separately and the extracts were analyzed.

1. Results for tests with hexane impingers as the independent sampling device

Three tests were performed. The test levels as determined by impinger sampling and the test results are presented in Table XVII. The results, in general, are satisfactory. Although, in some tests, the absolute difference between the average concentration determined with impingers and the average concentration determined with prototype samplers is greater than 10%, it is not true that the bias is statistically greater than 10% at the 95% confidence level. With only one exception, there is no statistical difference for a two-tailed test at the 0.05 significance level between the average result obtained with prototype samplers and the average result obtained with impingers. Even for the exceptional case (Test 2—1,2,4-TCBz concentration), the average result for the prototype samplers is not statistically different from 0.9 times the average result found with impinger samples. The values of the RSD for prototype samplers are below 10% with two exceptions. In Test 1, carried out at relatively low analyte concentrations, the RSD for the determinations of 1,2,4-trichlorobenzene is 11.5% and for pentachlorobenzene is 10.4%. One prototype sampler in Test 3 gave anomalously low results; apparently the volume of test air that was sampled was less than 10 L. The variability of the determinations with impingers is higher than desired for Test 3.

No significant quantity of particulate material was generated in Tests 1, 2, or 3. Even in Test 3 where the pentachlorobenzene concentration was 6.64 mg/m^3, the filter catch of the compound represented only about 1% of the total amount recovered.

2. Results of tests with the isooctane impingers as the independent sampling device

Accuracy and precision tests were repeated with the use of isooctane impingers in the reference sampling procedure at three different concentrations of each analyte. Although the concentrations again covered a broad range, they were chosen not to correspond closely to the test atmosphere concentrations investigated in the previous tests. The results and test levels are presented in Table XVIII. The pentachlorobenzene concentration was lower than could be reliably measured by impinger sampling over

Table XVII. Accuracy and Precision of the Total Sampling and Analytical Method for the Chlorinated Benzenes with the Use of Hexane Impingers in the Independent Sampling Method

	Av. concentrations determined with prototype samplers[a]								
	Test 1			Test 2			Test 3		
Component of the sampling device	1,2,4-TCBz, $\mu g/m^3$	1,2,4,5-TCBz, $\mu g/m^3$	PCBz, $\mu g/m^3$	1,2,4-TCBz, $\mu g/m^3$	1,2,4,5-TCBz, $\mu g/m^3$	PCBz, $\mu g/m^3$	1,2,4-TCBz, mg/m^3	1,2,4,5-TCBz, mg/m^3	PCBz, mg/m^3
Filter and holder[b]	0.00	0.00	0.00	1	0.3	1.6	0.0	0.00	0.06
Section 1[c]	2.25	6.30	7.61	303	102.0	68.9	14.7	6.91	6.73
Section 2[d]	0.00	0.00	0.02	0	0.0	0.0	0.0	0.00	0.00
Total	2.25	6.30	7.63	304	102.3	70.5	14.7	6.91	6.79
Std. dev.	0.26	0.62	0.80	18	7.8	5.4	0.9	0.63	0.46
RSD, %	11.5	9.8	10.4	5.8	7.6	7.6	6.4	9.1	6.8
Test level[e]	2.20	6.25	8.01	357[f]	91.8[f]	80.6[f]	14.0	6.16	6.64
(RSD, %)	(5.0)	(10.8)	(2.1)	(5.3)	(5.6)	(5.0)	(14.3)	(17.8)	(12.2)
Average recovery,[g] %	102.3	100.8	95.4	85.2	111.4	87.5	105.0	112.2	102.3
t (observed)[h]	0.31	0.11	0.77	3.57	1.73	2.38	0.70	1.50	0.34
t* (observed)[i]	-	-	-	1.17	-	-	-	-	-
t (critical)	2.36	2.36	2.36	2.45	2.45	2.45	2.36	2.36	2.36

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a. Ten-liter test atmosphere samples were taken at a rate of about 0.2 L/min. The average concentrations found in Tests 1 and 2 were based on six replicate samples. In Test 3, one sample was found to yield concentrations of the analytes that were statistical outliers of the Grubb's test; these results were rejected. Consequently, the values given for Test 3 are each the average of five replicate sample results.

b. Millipore Type LS 13-mm filter and stainless steel filter holder.

c. Front section of sorbent tube, 100 mg of Amberlite XAD-2.

d. Backup section of sorbent tube, 50 mg of Amberlite XAD-2.

e. The test level was determined by impinger sampling with hexane as the solvent and with subsequent determinations of the analytes in the impinger solution by GC/ECD. The relative standard deviation of the impinger results is given in parentheses.

f. This value is based on only two impinger samples; the value for the third was not considered because the critical orifice attached to the impinger became clogged during sampling.

g. Relative to impinger sampling.

h. Comparison of mean obtained with prototype samplers to mean obtained with impingers by Student's t for a two-tailed test at the 0.05 significance level.

i. Comparison of mean obtained with prototype samplers to 0.9X mean obtained with impingers by Student's t for a two-tailed test at the 0.05 significance level.

Table XVIII. Accuracy and Precision of the Total Sampling and Analytical Method for the Chlorinated Benzenes with the Use of Isooctane Impingers in the Independent Sampling Method

Component of the sampling device	Av. concentrations determined with prototype samplers[a]								
	Test 4			Test 5			Test 6		
	1,2,4-TCBz, $\mu g/m^3$	1,2,4,5-TCBz, $\mu g/m^3$	PCBz,[b] $\mu g/m^3$	1,2,4-TCBz, $\mu g/m^3$	1,2,4,5-TCBz, $\mu g/m^3$	PCBz, $\mu g/m^3$	1,2,4-TCBz, mg/m^3	1,2,4,5-TCBz, mg/m^3	PCBz, mg/m^3
Filter and holder[c]	0.00	0.00	0.00	0	0	0	0.0	0.0	0.2
Section 1[d]	4.07	2.76	4.65	158	650	460	11.6	28.0	22.9
Section 2[e]	0.00	0.00	0.00	0	0	0	0.0	0.0	0.0
Total	4.07	2.76	4.65	158	650	460	11.6	28.0	23.1
Std. dev.	0.40	0.25	0.33	8	35	26	0.6	1.9	1.8
RSD, %	9.8	9.1	7.1	5.0	5.3	5.6	4.8	6.9	7.8
Test level[f]	4.27	2.62[g]	-[h]	177	745	493	13.4	30.6	22.2
Std. dev.	(0.49)	(0.16)	-	(17)	(74)	(6)	(1.1)	(2.3)	(1.7)
Average recovery,[i] %	95.3	105.3	-	89.3	87.2	93.3	86.6	91.5	104.1
t (observed)[j]	0.66	0.72	-	2.37	2.72	2.10	3.28	1.82	0.32
t* (observed)[k]	-	-	-	0.12	0.60	-	0.91	-	-
t (critical)	2.36	2.36	-	2.36	2.36	2.36	2.36	2.36	2.36

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a. Ten-liter test atmosphere samples were taken at a rate of about 0.2 L/min. Unless specified otherwise, each average result is based on six replicate samples.

b. Two unidentified contaminants produced an anomalous positive bias in the GC determination of pentachlorobenzene in three of the samples. These results were, therefore, rejected. The statistical analysis of the data was consequently based on only three samples.

c. Millipore Type LS 13-mm filter and stainless steel filter holder.

d. Front section of sorbent tube, 100 mg of Amberlite XAD-2.

e. Backup section of sorbent tube, 50 mg of Amberlite XAD-2.

f. The test level was determined by impinger sampling with isooctane as the solvent and with the subsequent determination of the analytes in the impinger solutions by GC/ECD. Three sets of impingers (front and backup) were usually employed. The standard deviation of the impinger results in given in parentheses.

g. This value is based on only two impinger samples; the value for the third set was not considered because a contaminant in the impinger solution interfered with the peak for 1,2,4,5-tetrachlorobenzene.

h. The test level could not be accurately determined because the pentachlorobenzene concentration in the impinger solutions gave ECD responses about twice the size of the instrument's noise level. Twice the noise level corresponded to a concentration of pentachlorobenzene in a 10-L air sample of about 5 $\mu g/m^3$.

i. Relative to impinger sampling.

j. Comparison of mean obtained with prototype samples to mean obtained with impingers by Student's t for a two-tailed test at the 0.05 significance level.

k. Comparison of mean obtained with prototype samplers to 0.9X mean obtained with impingers by Student's t for a two-tailed test at the 0.05 significance level.

the test sampling period (about 50 min); the concentration was apparently about 4.5 $\mu g/m^3$ according to results obtained with the prototype samplers. The precision of results with the prototype samplers and also with the isooctane impingers is slightly better than was found earlier with hexane impingers. The absolute difference between the average results obtained with prototype samplers and the average result obtained with impingers is, in some tests, greater than 10%; however, by the same argument given above in Section V.C.1 based on statistical significance tests at the 0.05 significance level, it cannot be concluded that the bias is greater than 10%. In Test 4, three of the prototype samplers were contaminated with two compounds of unknown identity that were unresolved from pentachlorobenzene in the GC analysis of sampler extracts. Thus, anomalously high results were obtained for those samples.

Once again, no significant concentration of pentachlorobenzene was generated as particulate material even at a concentration of 22 to 23 mg/m^3.

In one additional test, the accuracy and precision of the total sampling and analytical method was ascertained when the method was applied to the determination of a 1,2,4-trichlorobenzene concentration of about 100 mg/m^3. This test was performed to extend the applicability of the method to 1,2,4-trichlorobenzene concentration values greater than the ACGIH TWA of about 40 mg/m^3.

The test procedure was similar to that in previous experiments except that only the XAD-2 sorbent tube of the sampling device was employed; the filter, the filter holder, and the nylon connector were not used. Six sorbent tubes (100-mg front section; two 50-mg backup sections*) were exposed to the test atmosphere concurrently with the exposure of three sets of two standard midget impingers, each containing 25 mL of isooctane. The sampling rate for the tubes and the impingers was nominally 0.2 L/min. Approximately 12 L of test air was sampled. The test atmosphere was maintained at a temperature of 37 °C and at a relative humidity of about 80%. The impinger solutions were analyzed for 1,2,4-trichlorobenzene the same day that the exposure tests were performed. The exposed tubes were sealed with Teflon tape and plastic caps and stored overnight prior to extraction and analysis. After storage, each sorbent section of each tube was extracted with 2 mL of hexane in an ultrasonic bath for 30 min. The extracts were then analyzed for 1,2,4-trichlorobenzene.

The average concentration found with the sorbent tubes was 107 mg/m^3 with a standard deviation of 7 mg/m^3. With the impingers, an average value of 102 mg/m^3 was found with a standard deviation of 5 mg/m^3. For a two-tailed test, at the 0.05 significance level, there was no statistical difference between the average result obtained with tubes and the average result obtained with impingers (t [observed] = 0.91; t [critical] = 1.90). The test results also revealed that there was no breakthrough of the compound into the backup sections of the sorbent tubes.

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* An extra 50-mg backup sorbent section was included in each sorbent tube as a precaution against the possibility of breakthrough of 1,2,4-trichlorobenzene.

D. Additional Statistical Analysis of the Accuracy and Precision Data

The data obtained in all of the accuracy and precision tests with the prototype samplers were subjected to additional statistical analysis. The recoveries of each analyte were averaged over the various test levels and the average bias was calculated. The precision values were pooled after the computation of χ^2 by Bartlett's test. The resulting pooled values of precision ($\overline{RSD}_2$) were then combined with the pooled precision values for the GC analytical procedure ($\overline{RSD}_1$) reported earlier to yield the overall precision of the method ($\overline{RSD}_T$). Included in this computation, also, was an estimate of 5% for RSD_p, the approximate variability that would have been encountered if personal sampling pumps had been employed instead of critical orifices connected to vacuum pumps, which exhibit little variability in sampling.

The resulting values are presented in Table XIX and are segregated into three groups: (1) the results obtained with the use of hexane impingers in the independent sampling procedure, (2) the results obtained with the use of isooctane impingers in the independent sampling procedure, and (3) the combined results obtained with both sampling procedures. The average calculated biases relative to the independent method were all within ±10%. Values for $\overline{RSD}_T$ for the three analytes were no greater than 10.3%. The combined results for the sampling and analytical method meet the required statistical criteria limiting the net error of the method to ±25% or less at least 95% of the time [I1].

The method was, therefore, found to be valid for the determination of the vapors of the three analytes over a broad concentration range in air samples. Because no significant concentration level of either 1,2,4,5-tetrachlorobenzene or pentachlorobenzene was generated as particulate material in laboratory tests at levels 10 to 20 times the Industrial Hygiene Guides for these compounds (3.5 mg/m^3 for 1,2,4,5-tetrachlorobenzene and 1 mg/m^3 for pentachlorobenzene) as established by Dow Chemical Company [F19], it seemed unnecessary to carry out additional validation tests at even higher levels where particles of these compounds may have formed.

Table XIX. Summary of Statistical Analysis of Sampling and Analytical Methods for the Chlorinated Benzenes

		1,2,4-TCBz	1,2,4,5-TCBz	PCBz
Hexane impingers	$\overline{RSD}_2$	8.4	8.8	8.5
	χ_2^{2a}	2.58	0.36	0.81
	$\overline{RSD}_T{}^b$	9.9	10.3	10.1
	Av. recovery,[c] %	97.5	108.1	95.1
Isooctane impingers	$\overline{RSD}_2$	6.9	7.3	6.9
	χ_2^{2a}	2.97	1.43	0.53
	$\overline{RSD}_T{}^b$	8.7	9.0	8.8
	Av. recovery,[c] %	93.9	94.7	98.7
Both hexane and isooctane impingers	$\overline{RSD}_2$	7.6	8.1	8.1
	χ_2^{2a}	6.29	2.29	1.76
	$\overline{RSD}_T{}^b$	9.3	9.7	9.8
	Av. recovery,[c] %	95.7	101.4	96.8

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a. Computed value of χ^2 corresponding to $\overline{RSD}_2$ in Bartlett's test for homogeneity. The critical value of χ^2 is 9.21 for two degrees of freedom and 15.09 for five degrees of freedom.

b. Pooled precision for sampling and analysis in the laboratory.

$$\overline{RSD}_T = \{0.1667\ (\overline{RSD}_1)^2 + \overline{RSD}_2{}^2 + \overline{RSD}_p{}^2\}^{\frac{1}{2}}$$

where $\overline{RSD}_1$ = pooled precision for the analytical procedure. Values were taken from Table XV.

where $\overline{RSD}_p$ = estimated sampling precision obtainable with personal pump = 5%.

c. Average of the recoveries obtained during the accuracy and precision tests for the total sampling and analytical method.

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APPENDIX A

MATERIAL SAFETY DATA SHEETS

1,2,4-Trichlorobenzene
($C_6H_3Cl_3$)

*	Potentially serious health hazard
1	Slight fire hazard
1	Low reactivity

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME Dow Chemical Company**	REGULAR TELEPHONE NO. (517)636-1000 EMERGENCY TELEPHONE NO.
ADDRESS 2020 Dow Center, Midland, MI 48640	
TRADE NAME	
SYNONYMS <u>uns</u>-Trichlorobenzene	

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%	HAZARD DATA
Homogeneous chemical compound		

III PHYSICAL DATA mol. wt. = 181.5

BOILING POINT, 760 mm Hg	213 °C	MELTING POINT	17 °C
SPECIFIC GRAVITY (H_2O = 1)	1.4634 at 25 °C	VAPOR PRESSURE	1 torr at 38.4 °C
VAPOR DENSITY (AIR = 1)	6.26	SOLUBILITY IN H_2O, % BY WT	insoluble
% VOLATILES BY VOL.	–	EVAPORATION RATE (BUTYL ACETATE = 1)	None reported
APPEARANCE AND ODOR	Colorless liquid with pleasant aromatic odor		

* Tentative assignment

** Other manufacturers are listed in the 1980-81 OPD Chemical Buyers Directory, Schnell Publishing Company, Inc., New York, 1980.

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)	107 °C (closed cup)		AUTOIGNITION TEMPERATURE	None reported	
FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER	None reported	UPPER	None reported	

EXTINGUISHING MEDIA Water, foam, carbon dioxide, and dry chemical

SPECIAL FIRE FIGHTING PROCEDURES None reported

UNUSUAL FIRE AND EXPLOSION HAZARD When burned, releases hydrogen chloride and phosgene.

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA TLV-TWA = 40 mg/m^3 (5ppm) - ACGIH

ROUTES OF EXPOSURE

INHALATION Moderately toxic

SKIN CONTACT Moderately irritating

SKIN ABSORPTION None reported

EYE CONTACT None reported

INGESTION Oral LD50* (rat) = 756 mg/kg; oral LD50* (mouse) = 766 mg/kg; intraperitoneal LDLO** = 500 mg/kg (mouse)

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE
CHRONIC OVEREXPOSURE
Injury to liver and kidneys by ingestion

EMERGENCY AND FIRST AID PROCEDURES ***

EYES Irrigate immediately with water.

SKIN Wash promptly wih soap and water.

INHALATION Move to fresh air.

INGESTION Get medical attention. If concious, administer one pint or more of water and induce vomiting.

NOTES TO PHYSICIAN

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*Dose required to kill 50% of test population.

**Lowest published lethal dose.

***By analogy to procedures for o-dichlorobenzene.

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

Reacts vigorously with oxidizing agents.

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

When burned, may produce hydrogen chloride gas and phosgene.

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

None reported.

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

Contain spill; absorb with clay granules, saw dust, or the equivalent. Sweep up and collect in drums. Flush contaminated area with soap and water; collect washings.

NEUTRALIZING CHEMICALS None reported.

WASTE DISPOSAL METHOD

Controlled incineration, designated landfill, or other means of disposal in accordance with applicable local, state, and federal regulations.

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

Effective hood system

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL) "Organic vapor" cartridge respirator or self-contained breathing apparatus.

EYE

Chemical safety goggles

GLOVES

Neoprene or other impervious material

OTHER CLOTHING AND EQUIPMENT

Apron made of neoprene or other impervious material. Showers. Daily change of clothing.

IX SPECIAL PRECAUTIONS

PRECAUTIONARY
STATEMENTS

The effects of chronic exposures are not fully known.

OTHER HANDLING AND
STORAGE REQUIREMENTS

- Store bulk quantities of the chemical in a cool and well ventilated area.
- Do not breathe its vapor.
- Avoid contact of the chemical with the skin.
- Do not take the chemical internally.

PREPARED BY H. Kenneth Dillon

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

DATE January 1981

1,2,4,5-Tetrachlorobenzene
($C_6H_2Cl_4$)

*	Potentially serious health hazard
1	Slight fire hazard
2	Low reactivity

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME Dow Chemical Company**	REGULAR TELEPHONE NO. (517) 636-1000 EMERGENCY TELEPHONE NO.
ADDRESS 2020 Dow Center, Midland, MI 48640	
TRADE NAME	
SYNONYMS Benzene tetrachloride	

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%	HAZARD DATA
Homogeneous chemical compound		

III PHYSICAL DATA mol. wt. = 215.9

BOILING POINT, 760 mm Hg 245 °C	MELTING POINT 138 °C
SPECIFIC GRAVITY (H_2O = 1) 1.734 (temperature not specified)	VAPOR PRESSURE <0.1 torr at 25 °C
VAPOR DENSITY (AIR = 1) 7.4	SOLUBILITY IN H_2O, % BY WT Insoluble
% VOLATILES BY VOL. –	EVAPORATION RATE (BUTYL ACETATE = 1) None reported
APPEARANCE AND ODOR White solid with pleasant aromatic odor	

*Tentative assignments

**Other manufacturer's are listed in the 1980-81 OPD Chemical Buyers Director, Schnell Publishing Company., Inc., New York, 1980.

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)	311 °F (closed cup)		AUTOIGNITION TEMPERATURE	None reported	
FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER	None reported	UPPER	None reported	
EXTINGUISHING MEDIA	Water, foam, carbon dioxide, and dry chemical				
SPECIAL FIRE FIGHTING PROCEDURES	None reported				
UNUSUAL FIRE AND EXPLOSION HAZARD	When burned, releases hydrogen chloride and phosgene				

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA Industrial Hygiene Guide = 3.5 mg/m^3 (0.4 ppm) - Dow Chemical Company

ROUTES OF EXPOSURE

INHALATION None reported

SKIN CONTACT None reported

SKIN ABSORPTION None reported

EYE CONTACT None reported

INGESTION Oral LD50* (rat) = 1500 mg/kg; oral LD50 (mouse) = 1035 mg/kg

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE
CHRONIC OVEREXPOSURE } Injury to liver, kidneys, lungs, and possible blood abnormalities

EMERGENCY AND FIRST AID PROCEDURES **

EYES Irrigate immediately with water.

SKIN Wash promptly with soap and water.

INHALATION Move to fresh air.

INGESTION Get medical attention. If concious, administer one pint or more of water and induce vomiting.

NOTES TO PHYSICIAN

---

*Dose required to kill 50% of test population.

**By analogy to procedures for o-dichlorobenzene.

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

Reacts vigorously with oxidizing agents

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HAZARDOUS DECOMPOSITION PRODUCTS

When burned, may produce hydrogen chloride gas and phosgene

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

None reported

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

Sweep up and collect in drums. Flush contaminated area with soap and water; collect washings.

NEUTRALIZING CHEMICALS None reported

WASTE DISPOSAL METHOD

Controlled incineration, designated landfill, or other means of disposal in accordance with applicable local, state, and federal regulations.

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

Effective hood system

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL) "Organic vapor" cartridge respirator or self-contained breathing apparatus.

EYE

Chemical safety goggles

GLOVES

Neoprene or other impervious material

OTHER CLOTHING AND EQUIPMENT

Apron made of neoprene or other impervious material. Showers. Daily change of clothing.

IX SPECIAL PRECAUTIONS

PRECAUTIONARY STATEMENTS

The effects of chronic exposures are not fully known.

OTHER HANDLING AND STORAGE REQUIREMENTS

- Store bulk quantities of the chemical in a cool and well ventilated area.
- Do not breathe its vapor.
- Avoid contact of the chemical with the skin.
- Do not take the chemical internally.

PREPARED BY H. Kenneth Dillon

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

DATE January 1981

Pentachlorobenzene

*	Potentially serious health hazard
1	Slight fire hazard
1	Low reactivity

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME Koch Chemical Company

REGULAR TELEPHONE NO. (617) 237-5477

EMERGENCY TELEPHONE NO.

ADDRESS 400 Blue Hill Drive, Westwood, MA 02090

TRADE NAME

SYNONYMS QCB

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%	HAZARD DATA
Homogeneous chemical compound		

III PHYSICAL DATA

mol. wt. = 250.35

BOILING POINT, 760 mm Hg	276 °C	MELTING POINT	85 °C
SPECIFIC GRAVITY (H_2O = 1)	1.8342 at 16.5 °C	VAPOR PRESSURE	1 torr at 98.6 °C
VAPOR DENSITY (AIR = 1)	8.7	SOLUBILITY IN H_2O, % BY WT	Insoluble
% VOLATILES BY VOL.	–	EVAPORATION RATE (BUTYL ACETATE = 1)	None reported

APPEARANCE AND ODOR White solid with little odor

*Tentative assignment

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)	None reported	AUTOIGNITION TEMPERATURE	None reported

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

EXTINGUISHING MEDIA	Water, foam, carbon dioxide, and dry chemical
SPECIAL FIRE FIGHTING PROCEDURES	None reported
UNUSUAL FIRE AND EXPLOSION HAZARD	When burned, releases hydrogen chloride and phosgene.

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA Industrial Hygiene Guide = 1 mg/m^3 (0.1 ppm) - Dow Chemical Company

ROUTES OF EXPOSURE

INHALATION None reported

SKIN CONTACT None reported

SKIN ABSORPTION None reported

EYE CONTACT None reported

INGESTION Oral TDLO* (rat) = 2000 mg/kg / (6 to 15 days of pregnancy)

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE } None reported
CHRONIC OVEREXPOSURE }

EMERGENCY AND FIRST AID PROCEDURES

EYES Irrigate immediately with water.

SKIN Wash promptly with soap and water.

INHALATION Move to fresh air.

INGESTION Get medical attention. If concious, administer one pint or more of water and induce vomiting.

NOTES TO PHYSICIAN

*The lowest level published that has been shown to exhibit a toxic effect.

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

Reacts vigorously with oxidizing agents.

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

When burned, may produce hydrogen chloride gas and phosgene

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

None reported

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

Sweep up and collect in drums. Flush contaminated area with soap and water; collect washings.

NEUTRALIZING CHEMICALS None reported

WASTE DISPOSAL METHOD

Controlled incineration, designated landfill, or other means of disposal in accordance with applicable local, state, and federal regulations.

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

Effective hood system

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL) "Organic vapor" cartridge respirator or self-contained breathing apparatus.

EYE

Chemical safety goggles

GLOVES

Neoprene or other impervious material

OTHER CLOTHING AND EQUIPMENT

Apron made of neoprene or other impervious material. Showers. Daily change of clothing.

IX SPECIAL PRECAUTIONS

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- Store bulk quantities of the chemical in a cool and well ventilated area.
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- Do not take the chemical internally.

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APPENDIX B

TEST ATMOSPHERE GENERATOR

TEST ATMOSPHERE GENERATOR

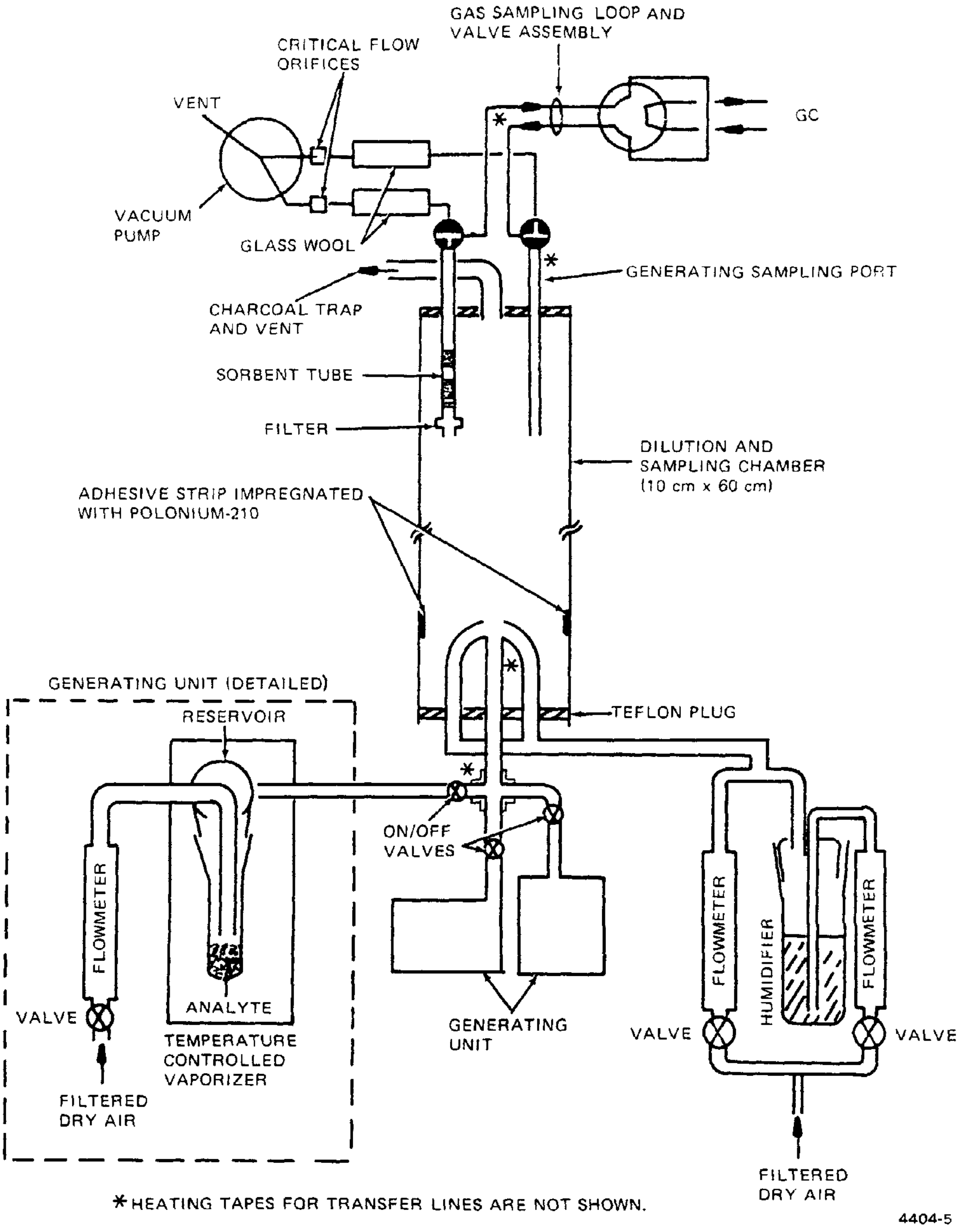
A test atmosphere generator was required for the evaluation of sampling devices. The generation system was designed to produce vapors of all three of the chlorinated benzenes and to allow the formation of condensation aerosols if the volatilities of the compounds were exceeded during testing. The volatilities of the substances at 25 °C as extrapolated from vapor pressure data follow: 3000 mg/m^3 for 1,2,4-trichlorobenzene; 140 mg/m^3 for 1,2,4,5-tetrachlorobenzene, and 24 mg/m^3 for pentachlorobenzene [A3, B10]. These estimates seemed to suggest that the compounds would be present primarily in the vapor state at concentrations near the concentrations of interest (i.e., concentrations near a TWA of 40 mg/m^3 for 1,2,4-trichlorobenzene as established by the ACGIH or concentrations near the Industrial Hygiene Guides of 3.5 mg/m^3 for 1,2,4,5-tetrachlorobenzene and 1.0 mg/m^3 for pentachlorobenzene as established by Dow Chemical Company [C1, F19]). It was, however, expected that particles of 1,2,4,5-tetrachlorobenzene or pentachlorobenzene might form in measurable quantities at levels somewhat above these standard concentrations.

The generation system was also designed to provide test concentrations over wide concentration ranges and at relative humidities between 10 and 80 to 90% and at temperatures between 25 and 40 °C.

Construction of the Generator. The generation system is depicted in Figure B1. To control the concentration of each analyte independently, three separate generating units were necessary. Each generating unit consisted of a reservoir containing one of the three analytes maintained at a constant temperature to regulate the vapor pressure of the compound precisely. Compressed air was metered into the reservoirs and became laden with the vapors of the compounds. The vapor-laden air from the three reservoirs was mixed with additional air in the dilution and sampling chamber to obtain the test atmosphere.

To eliminate potential problems due to contamination, the compressed air supply was cleaned prior to introduction into the system. 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 contained beds of molecular sieves for removing water vapor.) The air was then passed sequentially through a felt filter, a Gelman Acroflow membrane filter cartridge, and finally a bed of charcoal. (The filter membrane was a copolymer of acrylonitrile and vinyl chloride coated on a nylon web.)

The dry dilution air was rehumidified by metering a portion of the dilution airstream through a heated Greenburg-Smith impinger containing distilled, deionized water and by then mixing the humidified airstream with the appropriate proportion of dry air to obtain the desired relative humidity. The humidified air was transferred to the dilution and sampling chamber through heated Teflon tubing to avoid condensation of the water vapor.



*HEATING TAPES FOR TRANSFER LINES ARE NOT SHOWN.

Figure B1. Test atmosphere generator and sampling system.

The reservoirs for the analytes were modified midget impingers. The impingers were modified by shortening the inlet nozzle to permit the introduction of larger quantities of the solid analytes than would have been possible otherwise. (All three analytes were solids under some conditions of vaporization.)

To control the temperatures of the reservoirs, and thereby the vapor pressures of the analytes inside, the impingers were submerged in constant temperature baths. A coil of copper tubing (18 in. long by 0.125 in. o.d.) was attached to each impinger inlet and also submerged in the appropriate bath to maintain the compressed air that was flushed through each impinger at the bath temperature.

The constant temperature baths were two FTS Systems, Inc., Model No. MC-2-84 refrigerated coolers, each equipped with a proportional temperature controller—FTS Model No. TCH-1—and a resistance heater. One bath was used for generating 1,2,4-trichlorobenzene; isopropanol was used as the heat transfer medium. The other bath was used for generating the two other analytes; propylene glycol was employed as the heat transfer medium.

All analyte transfer lines and connectors were made of nickel, stainless steel, or glass with the exception of brass shut-off valves with Teflon seals for the three reservoirs. These lines and connectors were heated externally with electrical heating tapes to maintain the compounds in the vapor state in the transfer lines.

The vapor-laden air was mixed with dilution air in a cylindrical glass dilution and sampling chamber. (The cylinder was a glass pipe 60 cm long by 10 cm o.d. with Teflon discs for end caps.) The chamber was mounted vertically with the end caps at top and bottom. The effluent from the generating units and the dilution air entered through openings in the bottom end of the chamber near two small ^{210}Po strips to dissipate electrostatic charge. Eight sampling ports and a vent were located in the top cap. The design of the top end cap allowed sorbent tubes with or without filter discs to be mounted vertically through the ports so that the collection material was actually inside the chamber during sampling. When sampling temperatures greater than ambient were required, the glass cylinder was heated with an electrical heating tape.

Evaluation of the System. Several tests were conducted to determine the general performance of the generator in producing the vapors of the analytes. These test results were largely based on bubbler sampling at about 0.2 L/min with midget impingers containing hexane and on the determination of the analytes by GC/ECD.

Initially, generator conditions were set to establish effluent levels of the vapors of the analytes near 0.5 mg/m^3. To achieve this level, the following generating conditions were required for each analyte: The 1,2,4-trichlorobenzene bath temperature was set at 0 °C with a flow rate of 25 mL/min of air through the analyte reservoir. The bath temperature for the two other analytes was set at 39 °C with an airflow rate of 95 mL/min through the 1,2,4,5-tetrachlorobenzene reservoir and a flow rate of 120 mL/min through the pentachlorobenzene reservoir. The dilution air flow rate was about 5 L/min at a temperature of 28 °C.

The resulting concentrations of the three analytes were between 0.3 and 0.7 mg/m^3 and were found to be reasonably stable. The data in Table B1 indicate that within each test day the measurements were fairly precise. During the 4-h test period on the first day, values of the RSD of 10 to 11% were obtained. On the second and third days of testing, only two air samples were taken, but the measurements appeared to be more precise than those taken on the first day. The concentration levels that were observed for all three analytes changed by about 20% between the first and second day; the 1,2,4-trichlorobenzene concentration decreased but the concentrations of the other two analytes increased. There were no significant differences in the observed average concentration levels found on the second and third days. All of the observed levels were significantly lower than the concentrations predicted from estimated volatilities and airflow rates. There was no visual evidence of the production or accumulation of particles inside the dilution and sampling chamber during any of these tests.

To raise the generator output to about 10 mg/m^3 of each analyte, the concentration required in sorbent screening, the generating conditions were then adjusted as follows: The bath temperature for 1,2,4-trichlorobenzene was raised from 0 to 30 °C and the airflow through the reservoir for the compound from 25 to 45 mL/min. The bath temperature for the other two analytes was raised from 39 to 72 °C, and the airflow through the reservoirs for both compounds was set at 210 mL/min. The dilution airflow rate was kept at 5 L/min.

The resulting concentrations of the three analytes were found to be near or above about 10 mg/m^3 by bubbler sampling. The data in Table B2 indicate that the concentrations of each analyte were constant (within experimental error) on each day. There was a slight difference ($\leq$10%) between the corresponding average values found on Test Day 1 and those found on Test Day 2. Again, the observed levels were much less than predicted.

After operation of the generator at these levels for 2 d, a small amount of particulate material began to accumulate on the walls of the generator. Analysis of a portion of this particulate material revealed that it was essentially all pentachlorobenzene with only traces of 1,2,4,5-tetrachlorobenzene. When the pentachlorobenzene level was reduced to about 5 mg/m^3, with an increase in temperature to 40 °C and with the relative humidity maintained at 80%, the accumulation cleared and did not form again. In later tests at a temperature of about 30 °C and a relative humidity of about 80%, no particles were observed to accumulate at concentrations of 12 mg/m^3 of trichlorobenzene, 28 mg/m^3 of 1,2,4,5-tetrachlorobenzene, and 23 mg/m^3 of pentachlorobenzene.

Additional tests with bubbler sampling were conducted to examine the effect of water vapor upon the generation of the analyte vapors. At relatively low concentrations (0.3 to 0.8 mg/m^3) and relatively high

Table B1. Determination by Bubbler Sampling of Chlorinated Benzenes in Generator Effluent at Relatively Low Concentrations[a]

		Concentration of specified analyte, mg/m^3		
Test Day	Sample No.[b]	1,2,4-TCBz	1,2,4,5-TCBz	PCBz
1	1	0.484	0.528	0.560
	2	0.404	0.483	0.560
	3	0.437	0.582	0.591
	4	0.479	0.549	0.617
	5	0.368	0.458	0.455
	Average	0.434	0.520	0.557
	RSD, %	11	10	11
2	1	0.377	0.635	0.748
	2	0.338	0.653	0.693
	Average	0.358	0.644	0.682
3	1	0.332	0.583	0.642
	2	0.353	0.637	0.705
	Average	0.353	0.637	0.673
Theoretical concentration[c]		3	4	7

---

a. The sampling rate was 0.2 L/min; the sampling time was 15 min. The temperature in the dilution and sampling chamber was 28 °C; the relative humidity was <10%.

b. Air samples were taken 1 h apart.

c. As calculated from estimated volatilities and airflow rates.

Table B2. Determination by Bubbler Sampling of Chlorinated Benzenes in Generator Effluent at Relatively High Concentrations[a]

		Concentration of specified analyte, mg/m^3		
Test Day	Sample No.[b]	1,2,4-TCBz	1,2,4,5-TCBz	PCBz
1	1	19.5	9.0	11.7
	2	19.9	9.0	11.6
	Average	19.7	9.0	11.6
2	1	16.7	8.7	10.5
	2	18.9	9.0	11.3
	Average	17.8	8.8	10.9
Theoretical concentration[c]		50	160	110

---

a. The sampling rate was 0.2 L/min; the sampling time was 5 min. The temperature in the dilution and sampling chamber was 28 °C; the relative humidity was <10%.

b. Air samples were taken 1 h apart.

c. As calculated from estimated volatilities and airflow rates.

concentrations (12 to 32 mg/m^3), determinations were made at 28 °C at a low relative humidity (<10%) and at a high relative humidity (>85%).

The results are compared in Table B3. At the low concentration levels, the change in relative humidity appeared to have no significant effect upon the observed concentrations. As humidity was increased at the high concentration levels, the observed concentration of 1,2,4-trichlorobenzene increased by about 10%; the concentration of 1,2,4,5-tetrachlorobenzene remained about the same; and the concentration of pentachlorobenzene decreased by about 13%.

Table B3. Effect of Water Vapor on Analyte Concentration in Generator Effluent

Relative humidity,[a] %	Concentration of specified analyte, mg/m^3		
	1,2,4-TCBz	1,2,4,5-TCBz	PCBz
<10	0.353	0.637	0.705
>85	0.323	0.650	0.760
<10	13.3	32.1	14.3
>85	15.2	31.6	12.4

---

a. The sampling rate was 0.2 L/min; the sampling time was 5 min. The temperature of the dilution and sampling chamber was about 28 °C.

With the pentachlorobenzene concentration at 5 mg/m^3; the 1,2,4,5-tetrachlorobenzene concentration at 8 mg/m^3; and the 1,2,4-trichlorobenzene concentration at 14 mg/m^3, an experiment was conducted to study the physical state of the analytes in the generator effluent at 40 °C and at a relative humidity of 80%. The analytes were determined by sampling approximately 0.1 mL aliquots of the generator effluent with the gas sampling loop and then injecting the samples into the GC/ECD (see Section IV). In one test, the generator effluent was sampled through a 13-mm glass fiber particulate filter placed in the sampling line upstream from the sampling loop. In a second test the filter was omitted.

Initially, the concentration levels observed with the filter in the sampling line were less than those levels found without the filter by about 20% for 1,2,4-trichlorobenzene and 1,2,4,5-tetrachlorobenzene and 40% for pentachlorobenzene. With time, the differences decreased and, after about 3 to 4 h of sampling through the filter at 0.2 L/min, the differences stabilized. The concentration levels were, however, still somewhat higher than those observed with no filter in the sampling line. With the filter in the sampling line, the apparent concentration losses were about 8% for 1,2,4-trichlorobenzene; 4% for 1,2,4,5-tetrachlorobenzene; and 12% for pentachlorobenzene. These relatively small differences were possibly due to the adsorption of vapor by the filter. Significant levels of particles in the generator effluent were apparently not formed under these operating conditions.

It was concluded that, under the operating conditions that were evaluated, the analytes existed primarily in the gaseous state. Also, it was found that reasonably stable concentration levels were obtainable although some drift in the output concentrations was observed.

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 $\underline{n-1}$ degrees of freedom for $\underline{n}$ 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 $\underline{n-1}$ degrees of freedom was used:

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

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).

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

k = degrees of freedom (i.e., the number of variances tested minus one).

In order to pass Bartlett's test at the 1% significance level, χ^2 must be less than or equal to 9.21 for $k = 3$, 11.34 for $k = 4$, 13.28 for $k = 5$, and 15.09 for $k = 6$.

APPENDIX D

SAMPLING AND ANALYTICAL METHOD

1,2,4-TRICHLOROBENZENE; 1,2,4,5-TETRACHLOROBENZENE; AND PENTACHLOROBENZENE

Measurements Research Branch
Analytical Method

Analytes: 1,2,4-Trichlorobenzene (1,2,4-TCBz); 1,2,4,5-tetrachlorobenzene (1,2,4,5-TCBz); and pentachlorobenzene (PCBz)

Matrix: Air

Procedure: Collection on Teflon filter and Amberlite XAD-2, elution with hexane, analysis by GC/ECD

Date Issued:

Date Revised:

Method No.: P&CAM 343

Range: In 10 to 12 L of air, 0.002 to 100 mg/m^3 for 1,2,4-TCBz; 0.003 to 31 mg/m^3 for 1,2,4,5-TCBz; and 0.008 to 22 mg/m^3 for PCBz

Precision:
0.093 for 1,2,4-TCBz
0.097 for 1,2,4,5-TCBz
0.098 for PCBz

Classification: B (Accepted)

---

1. Synopsis

1.1 A known volume of air is drawn through a two-stage sampler consisting of a Teflon fiber mat filter followed by a tube containing two sections of Amberlite XAD-2 sorbent material to collect the analytes as aerosols or vapors.

1.2 The Teflon filter and sorbent sections are each transferred to a separate vial where the analytes are desorbed with 2 mL of hexane.

1.3 Aliquots of the resulting solutions are injected into a gas chromatograph equipped with an electron capture detector (GC/ECD).

1.4 The height or area of the peak corresponding to each analyte is determined and compared with the peak heights or areas obtained from the injection of standard solutions of the analytes in hexane.

2. Working Range, Sensitivity, and Detection Limit

2.1 The overall method was validated by collecting 10- to 12-L samples of test atmospheres containing the three analytes in the following concentration ranges: 0.002 to 100 mg/m^3 for 1,2,4-trichlorobenzene; 0.003 to 31 mg/m^3 for 1,2,4,5-tetrachlorobenzene; and 0.008 to 22 mg/m^3 for pentachlorobenzene. In these evaluations, the temperature of the test atmosphere was 28 to 30 °C and the relative humidity was >80%. The corresponding average quantities of the analytes recovered from the sampling devices in these tests ranged as follows: 0.023 to 1200 µg of 1,2,4-tetrachlorobenzene; 0.028 to 280 µg of 1,2,4,5-tetrachlorobenzene; and 0.076 to 231 µg of pentachlorobenzene.

2.2 With a Perkin-Elmer Model 910 Gas Chromatograph, the slopes of the analytical calibration curves (peak height as a function of quantity injected) were as follows on an instrument attenuation of one: 2.5 mm/pg of 1,2,4-trichlorobenzene; 4 mm/pg of 1,2,4,5-tetrachlorobenzene; and 4.5 mm/pg of pentachlorobenzene.

2.3 The lowest analytically quantifiable level (LAQL) of each analyte was determined to be about 0.02 µg when extracted from the 100-mg sorbent section of the sampler with 2 mL of hexane. The LAQL would correspond to a concentration of about 0.002 mg/m^3 in a 12-L air sample. (Neither the filter nor the filter holder sorbed significant quantities of the analytes when exposed to the analytes at the .02-µg level.) The instrumental detection limit was found to be about 20 pg of each analyte, corresponding to a solution concentration of 10 ng/mL with a 2-µL injection volume. At this concentration level, a relative standard deviation of about 10% was obtained for replicate injections. The ratio of the peak height to the background noise was about 5:1. The ratio was about 2:1 at concentrations near 1 ng/mL (2 pg injected).

2.4 The breakthrough volume of the 100-mg sorbent section of the sampler for 1,2,4-trichlorobenzene (the most volatile of the three analytes) was found to be approximately 24 L with a sampling rate of 0.2 L/min at a 1,2,4-trichlorobenzene concentration of about 45 mg/m^3, a sampling temperature of 40 °C, and a relative humidity of >80%. During the determination of this capacity, the other two analytes were also present in the test atmosphere. Their concentrations were 22 mg/m^3 of 1,2,4,5-tetrachlorobenzene and 15 mg/m^3 of pentachlorobenzene. The capacity of the 100-mg sorbing section was not specifically determined for these two analytes; however, their breakthrough volumes were greater than 24 L.

3. Interferences

3.1 The gas chromatographic operating conditions described below will separate the three analytes from each other and from all but one of the nine remaining isomers of the chlorinated benzenes. No set of operating conditions nor alternate packed column could be found that would separate 1,2,4,5-tetrachlorobenzene from 1,2,3,5-tetrachlorobenzene.

3.2 When substances other than the analytes are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample because these substances may interfere with the determination of the analytes.

3.3 Any substance that has the same retention time as one of the three analytes 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 packing, temperature, carrier flow, detector, etc.) may circumvent the problem.

4. Accuracy and Precision

4.1 For the overall sampling and analytical method, the pooled relative standard deviations (RSDs) for six replicate measurements of each analyte in six or seven separate tests in the specified concentration ranges were as follows:

Analyte	Concentration, mg/m^3	RSD, %
1,2,4-Trichlorobenzene	0.002 - 100	9.3
1,2,4,5-Tetrachlorobenzene	0.003 - 31	9.7
Pentachlorobenzene	0.008 - 22	9.8

The pooled RSDs for the analytical method obtained with 36 samplers, each spiked with all three analytes in the specified ranges and stored for 1 d prior to analysis, were as follows:

Analyte	Quantity, µg	RSD, %
1,2,4-Trichlorobenzene	0.0189 - 502	4.4
1,2,4,5-Tetrachlorobenzene	0.0209 - 506	4.2
Pentachlorobenzene	0.0209 - 513	5.7

4.2 The concentrations of the analytes in the test atmospheres were determined in control experiments primarily by impinger sampling. The average ratios of the determinations with the developed sampler to the determinations by impinger sampling were 0.96 for 1,2,4-trichlorobenzene; 1.01 for 1,2,4,5-tetrachlorobenzene; and 0.97 for pentachlorobenzene.

4.3 Thirty-five nanograms of 1,2,4-trichlorobenzene; 63 ng of 1,2,4,5-tetrachlorobenzene; and 43 ng of pentachlorobenzene were found to be stable at room temperature (25 to 30 °C) for at least 14 d.

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 Another advantage is that the two-stage sampling device may be used to collect both particulate and gaseous air contaminants.

5.3 One disadvantage is that the precision of the method is limited by the reproducibility of the pressure drop across the samplers. 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 sampler only.

5.4 Another disadvantage of the method is that the quantities of the vapors of the analytes that can be sampled are limited by the capacity of the sorbent tube. When the quantity of an analyte that is found on the backup section of the sorbent tube exceeds 20% of that found on the front section, the possibility of sample loss exists.

6. Apparatus

Disclaimer: Mention of company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health.

6.1 Personal sampling pump capable of accurate performance (±5%) at 0.025 to 0.2 L/min and calibrated with a representative tube in the line.

6.2 Two-stage sampler: The sampler is described schematically in the figure; the assembled unit consists of a 13-mm Teflon fiber mat (the Millipore Type LS [Mitex] filter disc, Catalog No. LSWP01300) in a stainless steel filter holder (the Millipore Swinny Stainless Disc Filter Holder, Catalog No. XX3001200) in tandem with a Pyrex sorbent tube (7 cm long with a 6.4 mm [0.25 in.] o.d. and a 4 mm i.d.). The filter holder and tube are coupled with a nylon Swagelok union (Crawford Fitting Company, Catalog No. NY-400-6). To attach the outlet of the filter holder to the union, a Teflon Swagelok reducing ferrule (Alltech Associates, Catalog No. RF-400/200-T) is bored out to 4 mm (0.156 in.) i.d. and the filter holder outlet is inserted into the ferrule. Standard 0.25 in. o.d. front and back Teflon Swagelok ferrules (Crawford Fitting Company, Catalog Nos. T-404-1 and T-403-1) are used to attach the sorbent tube to the union; however, the union is bored out to 7.1 mm (0.28 in.) to allow the insertion of the end of the tube for a butt-to-butt fit with the reducing ferrule. The sorbent tube contains two sections of 20/50-mesh Amberlite XAD-2—a 100-mg sorbing section and a 50-mg backup section. The sorbent sections are separated by a 4-mg plug of silanized glass wool. Two additional 4-mg plugs of the glass wool, one near each end of the sorbent tube, serve to hold the sorbent sections in place. The sampling device is sealed at each end, first with Teflon tape and then with plastic caps. The pressure drop across an assembled sampler is typically 4 in. H_2O (1 kPa) at a sampling rate of 0.2 L/min. The filter disc and sorbent tube are disposable; the filter holder, connector, and plastic caps are reusable.

Before sorbent tubes are packed, bulk quantities of the Amberlite XAD-2 are cleansed of impurities by Soxhlet extraction in a 4:1 (v/v) mixture of acetone and methanol for 4 h followed by Soxhlet extraction in hexane for 4 h. The washed material is then dried overnight at 70 to 100 °C under vacuum.

Commercially available sorbent tubes containing Amberlite XAD-2 may not exhibit as high a capacity for the analytes as do sorbent tubes prepared as described above.

6.3 A gas chromatograph equipped with a ^{63}Ni electron capture detector.

6.4 A 2.0 m by 2 mm i.d. nickel column containing 10% Carbowax 20M-TPA on 80/100-mesh Chromosorb W AW.

6.5 Vials, 5-mL, with crimp-on caps containing Teflon-lined silicone rubber septa.

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

6.7 Volumetric flasks, 5.00-mL and convenient sizes for making dilutions.

6.8 Ultrasonic bath.

6.9 Syringes, 10-μL.

7. Reagents

7.1 1,2,4-trichlorobenzene, 98% pure.

7.2 1,2,4,5-tetrachlorobenzene, 98% pure.

7.3 Pentachlorobenzene, 98% pure.

7.4 Hexane, distilled in glass.

7.5 Ultra high purity nitrogen (99.999%) for GC carrier and purge gas.

7.6 Stock Standard Solution. Prepare a stock standard solution containing each of the three analytes in hexane as follows: Add an accurately weighed quantity (about 500 mg) of each analyte to a 5-mL volumetric flask. Add hexane to the mark and dissolve the compounds. Store in an airtight container. The solution is stable indefinitely.

8. Procedure

8.1 Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis, empty sorbent tubes, and the components of the stainless steel filter holders and nylon unions should be thoroughly cleaned and rinsed with 5% nitric acid, tap water, distilled water, acetone, and hexane (in that order). The materials should then be dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, remove the plastic caps and Teflon tape from the ends of the sampler.

8.2.2 Connect the outlet of the sorbent tube to the sampling pump with Tygon or rubber tubing.

8.2.3 Place the sampler in a vertical position during sampling to prevent channeling through the sorbent tube.

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

8.2.5 Sample the air at 0.025 to 0.2 L/min. Measure and report the flow rate and time or volume sampled. The maximum volume sampled should not exceed 12 L.

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

8.2.7 Immediately after sampling, separate the filter holder from the sorbent tube and seal the ends of each device with Teflon tape and plastic caps. Save the union for future usage.

8.2.8 To obtain a blank sample, process one unused sampler in the same manner as the exposed samplers (open, seal, and transport) but do not sample air through this sampler. Submit one blank sampler for every ten exposed samplers with a minimum of three blank samplers.

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 Teflon filter discs and sealed sorbent tubes so that desorption efficiency studies can be performed on the same type and lot of Teflon filters and Amberlite XAD-2 used for sampling.

8.2.11 Refrigerate all samples stored longer than 7 d.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the sealed filter holders and sorbent tubes from the refrigerator and permit them to equilibrate to room temperature to prevent water condensation inside the devices. Transfer each section of Amberlite XAD-2 in a sorbent tube to a separate 5-mL vial. Add the glass wool plug near the sorbent tube inlet to the vial containing the sorbing section; add the other two glass wool plugs to the vial containing the backup section. Transfer each Teflon filter to a separate 5-mL vial.

8.3.2 Desorption of Samples. To each vial add 2.00 mL of hexane. Cap each vial immediately with a Teflon-lined silicone rubber septum. Extract the sealed samples in an ultrasonic bath for 30 min at room temperature. Also, wash the inside surfaces of the filter holder with 2 to 3 mL of hexane. Transfer the washings of the filter holder to a 5-mL volumetric flask and dilute to the mark with hexane.

8.3.3 Operating Conditions for the Gas Chromatograph

- Carrier gas flow rate, 30 mL/min of nitrogen.
- Detector purge gas flow rate, 90 mL/min of nitrogen.
- Injection port temperature, 220 °C.
- Column temperature, 160 °C.
- Detector temperature, 300 °C.
- Injection volume, 2 µL.
- Under these conditions, the analytes elute with the following retention times:
  2.0 min for 1,2,4-trichlorobenzene,
  3.3 min for 1,2,4,5-tetrachlorobenzene,
  7.5 min for pentachlorobenzene.

8.3.4 Injection. Inject a 2-µL aliquot of a sample extract or standard into the gas chromatograph by the solvent flush technique. Use 1 µL of hexane as the solvent flush. Maintain a 1-µL air gap between the solvent flush and the 2-µL aliquot.

8.3.5 Measurement of Peak Height. The product of peak height and attenuation setting is linear over the concentration range of about 10 to 100 ng/mL of each analyte in hexane. The peak height is multiplied by the attenuator setting necessary to keep the peak on scale. Results are read from a standard curve prepared as discussed in Section 9. If peak heights indicate an apparent concentration above about 100 ng/mL, dilute the sample solution appropriately for reanalysis.

8.4 Determination of the Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiencies of the three chlorinated benzenes can vary from one laboratory to another and also from one batch of samplers to another. It is necessary to determine the fraction of each analyte that can be recovered from the samplers. In laboratory tests, the mean overall desorption efficiencies for the three analytes when extracted from exposed samplers were found to be as follows: 0.908 for 1,2,4-trichlorobenzene; 0.901 for 1,2,4,5-tetrachlorobenzene; and 0.917 for pentachlorobenzene.

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels of each of the three analytes 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 all three of the analytes in hexane to give stock solutions with concentrations such that 20 ng to 500 µg of each compound will be injected onto the sampler in no more than 5 µL of a stock solution. Inject an aliquot of the appropriate solution onto the filter in an assembled sampler while drawing 12 L of analyte-free air through the sampler at 0.2 L/min to volatilize the analytes and flush their vapors onto the 100-mg sorbing layer. Separate the filter holder and the sorbent tube, seal each device with Teflon tape and plastic caps, and store the devices overnight at room temperature. Then extract the components of the sampler as described in Section 8.3. Prepare a standard at each level by injecting an identical amount of the corresponding stock solution into 2 mL of hexane. Analyze the samples and standards as described in Section 8.3.

The desorption efficiency at each level is taken to be the ratio of the sum of the average amounts of each analyte found on the various components of the samplers to the total amount spiked. The quantities of the analytes found on the backup sorbent sections should be negligible and, therefore, should make a negligible contribution to the computation of the desorption efficiency. A blank correction is not expected to be necessary but should be checked. The desorption efficiency curve for each analyte is constructed by plotting the total amounts of each compound found in the samplers versus the desorption efficiency.

9. Calibration and Standardization

By serial dilution of the stock standard solution with hexane, prepare a series of five working standards varying in concentration over the range of 10 to 100 ng/mL of each analyte. Prepare fresh working standards daily. 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 height or area.

10. Calculations

10.1 Determine the weight of each analyte in a sample (μg) from the standard curve. If the sample solution was diluted for analysis, use the appropriate dilution factor.

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

$$W_i = W_s - W_b$$

where: W_i = corrected amount (μg) of the analyte of interest on the ith component of the sampler, either the filter, filter holder, or a sorbent section.

W_s = amount (μg) actually found.

W_b = amount (μg) found on the corresponding component of a blank sampler.

Follow a similar procedure for each component of the sampler and for each analyte.

10.3 Make a correction for desorption efficiency as follows:

$$M_F = \frac{\sum_i W_i}{D}$$

where: i = the index summed over the components of the sampling device excluding the backup sorbent section.

M_F = the sum of the corrected amounts (μg) of the analyte of interest on the components of the sampler excluding the backup sorbent section.

W_i = amount (μg) of the analyte of interest on the ith component of the sampler after blank correction.

D = desorption efficiency corresponding to the weight $\sum_i W_i$.

Follow an analogous procedure for the backup sorbent section.

10.4 Express the concentration, C, of each of the three analytes in mg/m^3, which is numerically equal to (µg/L).

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

where: M_F = the sum of the corrected amounts (µg) of the analyte of interest found on the components of the sampling device excluding the backup sorbent section.

M_B = corrected amount (µg) of the analyte found on the backup sorbent 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.

$$C(\text{ppm}) = C(\text{mg/m}^3) \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

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.

M.W. = molecular weight of the analyte of interest (181.46 for 1,2,4-trichlorobenzene; 215.90 for 1,2,4,5-tetrachlorobenzene; and 250.35 for pentachlorobenzene).

11. Reference

Dillon, H.K.; Bryant, M.L. "Analytical Methods Evaluation and Validation for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; Pentachlorobenzene; and Polychlorinated Terphenyls: Research Report for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; and Pentachlorobenzene"; NIOSH Contract No. 210-79-0102; Southern Research Institute: Birmingham, Alabama; May 1981.

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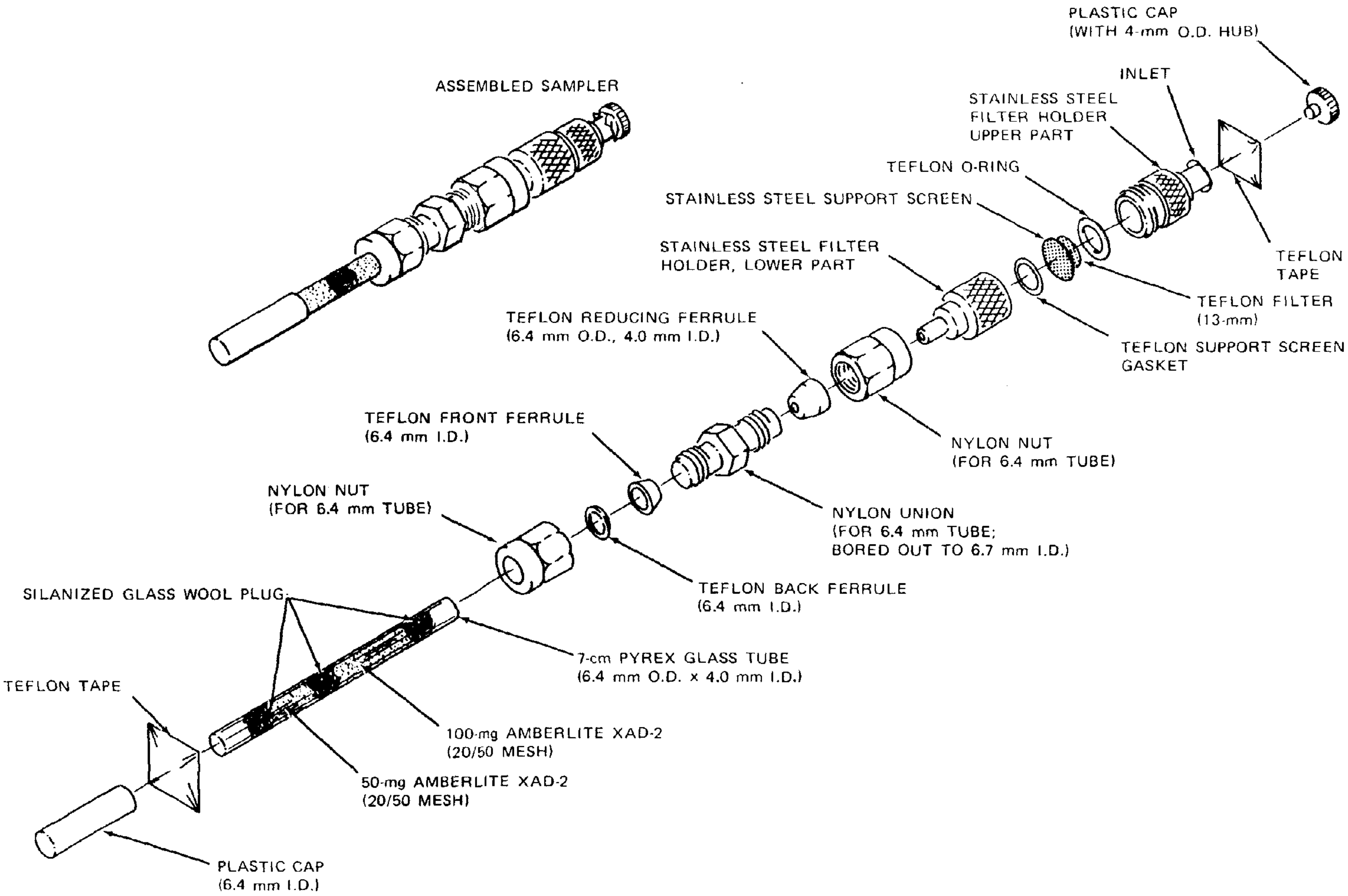

Schematic diagram of the two-stage sampler for the chlorinated benzenes.

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APPENDIX E

NIOSH SAMPLING DATA SHEET

NIOSH SAMPLING DATA SHEET NO. 343 CLASS B

Substances

1,2,4-Trichlorobenzene; 1,2,4,5-tetrachlorobenzene; and pentachlorobenzene

Standard

The American Conference of Governmental Industrial Hygienists has established an 8-h time-weighted average (TWA) of 40 mg/m^3 for occupational exposures to 1,2,4-trichlorobenzene (see Reference 2). Dow Chemical Company has established Industrial Hygiene Guides of 3.5 mg/m^3 at 25 °C (0.4 ppm by volume) for 1,2,4,5-tetrachlorobenzene and 1.0 mg/m^3 at 25 °C (0.1 ppm by volume) for pentachlorobenzene (see Reference 3).

Sampling Equipment

Disclaimer: Mention of company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health.

1. Personal sampling pump capable of accurate performance (±5%) at 0.025 to 0.2 L/min and calibrated with a representative tube in the line.

2. Two stage sampler: The sampler is described schematically in the figure; the assembled unit consists of a 13-mm Teflon fiber mat (the Millipore Type LS [Mitex] filter disc, Catalog No. LSWP01300) in a stainless steel filter holder (the Millipore Swinny Stainless Disc Filter Holder, Catalog No. XX3001200) in tandem with a Pyrex sorbent tube (7 cm long with a 6.4 mm [0.25 in.] o.d. and a 4 mm i.d.). The filter holder and tube are coupled with a nylon Swagelok union (Crawford) Fitting Company, Catalog No. NY-400-6). To attach the outlet of the filter holder to the union, a Teflon Swagelok reducing ferrule (Alltech Associates, Catalog No. RF-400/200-T) is bored out to 4 mm (0.156 in.) i.d. and the filter holder outlet is inserted into the ferrule. Standard 0.25 in. o.d. front and back Teflon Swagelok ferrules (Crawford Fitting Company, Catalog Nos. T-404-1 and T-403-1) are used to attach the sorbent tube to the union; however, the union is bored out to 7.1 mm (0.28 in.) to allow the insertion of the end of the tube for a butt-to-butt fit with the reducing ferrule. The sorbent tube contains two sections of 20/50-mesh Amberlite XAD-2—a 100-mg sorbing section and a 50-mg backup section. The sorbent sections are separated by a 4-mg plug of silanized glass wool. Two additional 4-mg plugs of the glass wool, one near each end of the sorbent tube, serve to hold the sorbent sections in place. The sampling device is sealed at each end, first with Teflon tape and then with plastic caps. The pressure drop across an assembled sampler is typically 4 in. H_2O (1 kPa) at a sampling rate of 0.2 L/min. The filter disc and sorbent tube are disposable; the filter holder, connector, and plastic caps are reusable.

Before sorbent tubes are packed, bulk quantities of the Amberlite XAD-2 are cleansed of impurities by Soxhlet extraction in a 4:1 (v/v) mixture of acetone and methanol for 4 h followed by Soxhlet extraction in hexane for 4 h. The washed material is then dried overnight at 70 to 100 °C under vacuum.

Commercially available sorbent tubes containing Amberlite XAD-2 may not exhibit as high a capacity for the analytes as do sorbent tubes prepared as described above.

Sample Size

The volume of air sampled should not exceed 12 L.

Sampling Procedure

1. Immediately before sampling, remove the plastic caps and Teflon tape from the ends of the sampler.

2. Connect the outlet of the sorbent tube to the sampling pump with Tygon or rubber tubing.

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

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

5. Sample the air at 0.025 to 0.2 L/min. Measure and report the flow rate and time or volume sampled.

6. Record the temperature and pressure of the air being sampled.

7. Immediately after sampling, separate the filter holder from the sorbent tube, and seal the ends of each device with Teflon tape and plastic caps. Save the union for future usage.

8. To obtain a blank sample, process one unused sampler in the same manner as the exposed sampler (open, seal, and transport) but do not sample air through this sampler. Submit one blank sampler for every ten exposed samplers with a minimum of three blank samplers.

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

10. Ship nine to twelve Teflon filter discs and sealed sorbent tubes so that desorption efficiency studies can be performed on the same type and lot of Teflon filters and Amberlite XAD-2 used for sampling.

Special Considerations

1. The identities of all substances that are known or suspected to be present in the air that is sampled should be transmitted with the exposed samplers.

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

3. High humidity might cause a reduction in breakthrough volumes; however, as long as a maximum of 12 L at 0.025 or 0.2 L/min is sampled, no breakthough should occur. If the sorbent material becomes coated with water, the analytes will not be trapped quantitatively.

Bulk Samples

If samples of material containing the analytes are shipped to the laboratory they should be submitted in glass containers with Teflon-lined caps. Do not transport these samples in the same container with the samplers.

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 samples in the same container as the samplers. When the samplers are received by the laboratory, they should be stored under refrigeration to avoid any chance of loss of the analytes. Store the samplers during refrigeration in an airtight container to prevent contamination by the diffusion of chemicals through the plastic end caps.

References

1. 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; and Pentachlorobenzene. NIOSH Method No. P&CAM 343.

2. American Conference of Governmental Industrial Hygienists. "Threshold Limit Values for Chemical Substances in Workroom Air"; ACGIH: Cincinnati, Ohio, 1979.

3. Langhorst, M.L; Nestrick, T.J. "Determination of Chlorobenzenes in Air and Biological Samples by Gas Chromatography with Photoionization Detection." Anal. Chem. 1979, 51, 2018-25.

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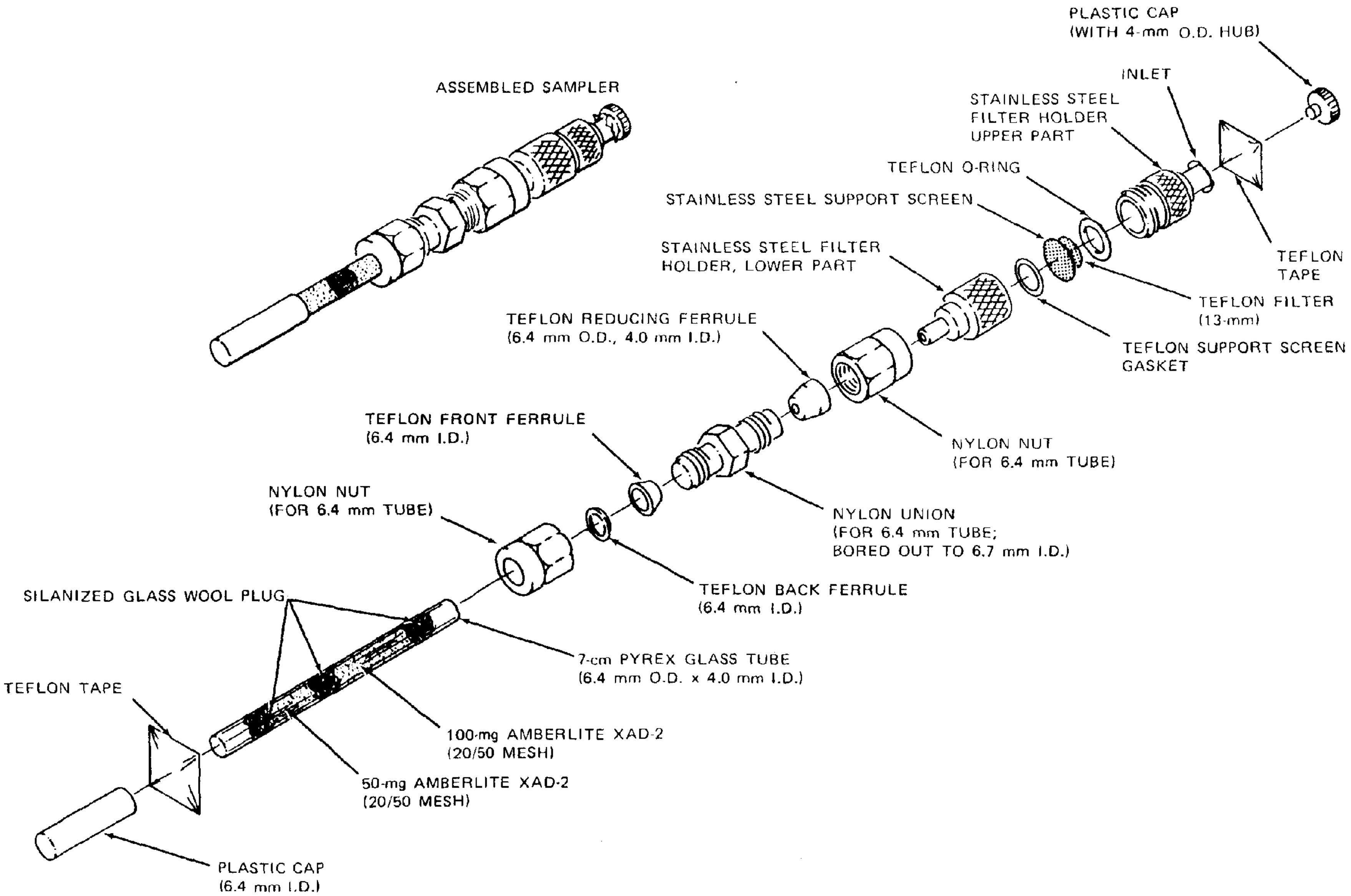

Schematic diagram of the two-stage sampler for the chlorinated benzenes.

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