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

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Research Report for Hexachlorobutadiene

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ABSTRACT

This report describes the development of a sampling and analytical method for the determination of hexachlorobutadiene in air. The developed method is based on the collection of the compound from air with a solid sorbent, Amberlite XAD-2; desorption of the compound with hexane; and analysis of the extract by gas chromatography with electron capture detection. The overall method was evaluated in the concentration range of about 10 to 2000 $\mu g/m^3$ in 3-L air samples. The average bias from an independent analytical method was -7%; the pooled relative standard deviation was 9%.

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AN AIR SAMPLING AND ANALYTICAL METHOD FOR HEXACHLOROBUTADIENE

I. GENERAL CONSIDERATIONS

A. Background

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

Although no exposure limit has been promulgated for HCBD, there is a growing concern among environmentalists that exposure to the compound may present a serious health hazard. HCBD has been listed as a suspect carcinogen by the National Institute for Occupational Safety and Health (NIOSH). (C1) NIOSH is presently developing a criteria document for the compound that is due to be completed in 1979 or 1980. (C2) This document will recommend an exposure limit for HCBD. The Interagency Testing Committee (ITC) established by the Toxic Substances Control Act (TSCA) has selected the compound for priority attention by the Environmental Protection Agency (EPA) as a toxic point-source water effluent discharge.(C3) The toxicity data compiled by NIOSH and the EPA indicate that the compound is both an acute and chronic poison; this information along with other information pertinent to the toxicity of the compound has been summarized in a "Material Safety Data Sheet" appearing as Appendix 1.

The potential for the exposure of personnel to HCBD in air exists primarily in the commercial production of other chlorinated hydrocarbons. (G3) HCBD itself has not been produced in this country since 1972. In one study sponsored by the EPA, it was found that the major sources of HCBD emissions to the air were manufacturing sites for trichloroethylene and perchloroethylene. HCBD is produced as a waste or by-product. Carbon tetrachloride was usually manufactured along with trichloro- and perchloroethylene; however, at one site where carbon tetrachloride was the sole product, relatively small amounts of HCBD were found. The manufacturing processes for chlorine and triazine herbicides were observed to produce small but probably insignificant amounts of HCBD.

The commercial uses of imported HCBD also offer the potential for exposure to the compound. The primary uses of the compound have been summarized in a recent survey.(C9) Its largest use in the United States is as a solvent to recover chlorine gas at the liquefaction units in chlorine plants. (The study for the EPA cited above, however, reported insignificant amounts of HCBD in the air in chlorine manufacturing plants.)(G3) In the aerospace industry, HCBD has been recently used as a fluid for gyroscopes and as a chemical intermediate to produce high temperature lubricants. The compound has also been used as a chemical intermediate in the manufacture of rubber compounds.

B. Research Approach

The subsequent sections of this report describe work performed under contract with NIOSH to develop an air sampling and analytical method for the determination of HCBD in occupational environments. The method is to be used to obtain and analyze samples from the air breathed by individuals in the workplace.

The general approach to the development of the method involved several steps. First, a literature search for information relating to air sampling and analytical methodology for the compound was performed. Secondly, an experimental protocol was devised for development of the method according to NIOSH guidelines; the protocol was reviewed by NIOSH and revised. A method was then developed and evaluated according to the revised protocol. Upon the completion of the evaluation of the method, a written description of the method, a sampling data sheet, and 100 prototypes of the sampling device were submitted to NIOSH.

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

- Physical and chemical properties.
- Toxicity.
- Manufacture.
- Commercial uses.
- Analytical procedures.
- Air sampling and analytical procedures.
- Properties of candidate sorbent materials.

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

The protocol that was employed in the development and evaluation of the sampling and analytical method was comprised of the following tasks in the order in which they were carried out:

- Optimization of the analytical procedure.
- Calibration of the analytical procedure.
- Determination of desorption efficiencies of HCBD from solid sorbents by solvent extraction.

II. DEVELOPMENT AND EVALUATION OF THE ANALYTICAL METHOD

A. Optimization of Gas Chromatographic Procedure

The first step undertaken in the laboratory was to define the optimum procedure for determining HCBD by gas chromatography. The gas chromatograph employed was the HP 5750 (Hewlett-Packard Company) equipped with a ^{63}Ni electron capture detector. The column was 3% OV-1 on Gas-Chrom Q (100/120 mesh) in a glass coil (4 mm i.d. by 2 m). Operating conditions were altered as required to provide a reasonably sharp peak for HCBD while resolving the peak from those for five other organochlorine compounds—tetrachloroethylene; hexachloroethane; 1,2,4-trichlorobenzene; hexachlorocyclopentadiene (HCPD); and 4-chlorobiphenyl. (The listed compounds represent classes of compounds that may occur with HCBD in the workplace.) In the laboratory tests, hexane solutions of the compounds including HCBD were injected into the gas chromatograph.

The following operating conditions gave good resolution of the HCBD from the contaminants listed above:

Carrier gas: 5% methane, 95% argon, prepurified; 20 mL/min.

Detector purge gas: 5% methane, 95% argon; 80 mL/min.

Temperatures:

—injection port, 240 °C.

—column, 135 °C.

—detector, 250 °C.

A chromatogram of a mixture of hexane solutions of all of the organochlorine compounds except 4-chlorobiphenyl is presented in Figure 1. (The 4-chlorobiphenyl exhibited a retention time of about 12 min.) The amount of each potential interferent that was injected to produce this chromatogram was chosen to allow the same instrument attenuation for all of these compounds. The first large peak observed was the detector response to the solvent. The small unmarked peaks were the result of impurities in the reagents. As specified in Figure 1, the amount of tetrachloroethylene injected was only about 6% of the amount of HCBD injected. In other tests much larger amounts of tetrachloroethylene, which were comparable to the amount of HCBD injected, did not overlap the HCBD peak. Only one of these compounds, 1,2,4-trichlorobenzene, appears to have the potential to interfere with the determination of HCBD. Even at a level about four times that of HCBD, there was, however, no overlap of peaks.

B. Calibration of the Gas Chromatographic Method

Standard solutions for the calibration of the gas chromatographic method were prepared from reagent-grade HCBD (98% pure) obtained from Aldrich Chemical Company. A stock HCBD solution in hexane was frequently prepared

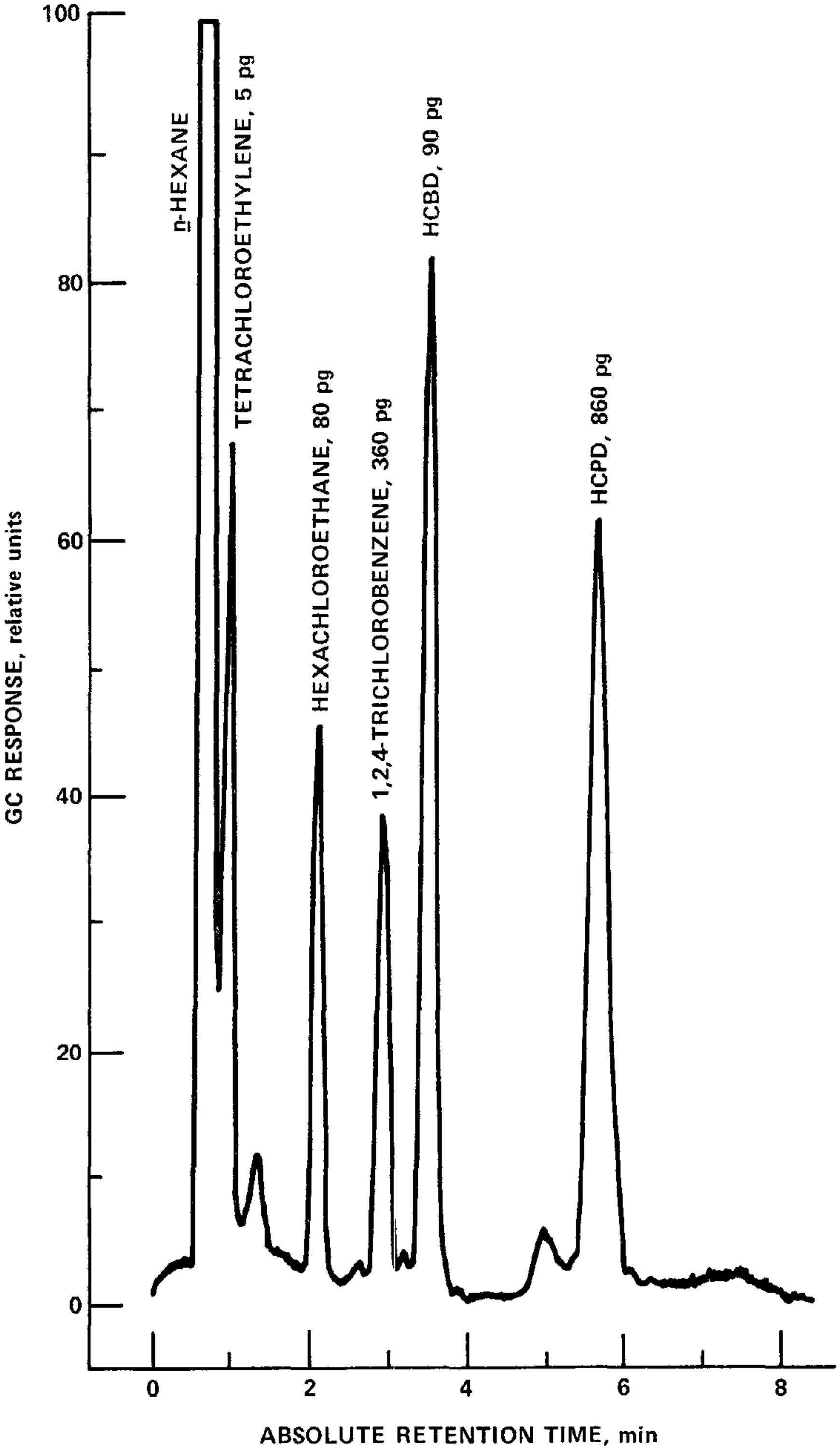

Figure 1. Chromatogram for mixture of organochlorine compounds.

by accurately weighing about 850 mg of HCBD in a tared 5-mL volumetric flask containing about 2 mL of hexane and then diluting the contents of the flask to the mark with hexane. Alternatively, a stock solution was made by diluting 1.00 mL of HCBD to 100 mL with hexane. The hexane was a high-purity reagent obtained from Burdick and Jackson Laboratories, Inc. Dilute working standards in the range of 0.14 to 168 ng/mL were prepared in glass-stoppered volumetric flasks by serial dilutions with hexane. The solutions appeared to be stable at room temperature (25 to 30 °C) for at least 2 wk with no precautions taken to shield the solutions from light.

The purity of the HCBD used in the preparation of standards was checked by the analysis of hexane solutions with a gas chromatograph coupled to a mass spectrometer (the Hewlett-Packard Model HP 5985A). The gas chromatographic operating conditions were similar to those used in the optimization procedure. The resulting ion-chromatogram revealed that HCBD was the only compound present in the reagent at significant concentrations. Traces of hexachloroethane and an unidentified compound with the same molecular weight as HCBD were also found. The concentrations calculated from the relative ion currents of these compounds were 96.5% HCBD, 1.0% hexachloroethane, and 2.5% of the unidentified compound.

In the calibration of the GC procedure, 5-μL aliquots of the working standards were injected into the HP 5750 gas chromatograph. The gas chromatographic conditions were the same as those used in the optimization procedure. Multiple injections of each standard were performed by the solvent-flush technique. Peak heights and peak areas were measured.

A typical plot of detector response (peak height in amperes) as a function of solution concentration is presented in Figure 2. The plot indicates that the gas chromatographic response is a nonlinear function of HCBD concentration. The slight curvature is not uncommon for the response of an electron capture detector and is attributed to a decrease in the efficiency of ion formation in the detector as the concentration of the analyte increases.(F2)

Unknown concentrations were determined from the curve by two methods. Since the deviation from linearity was not large, unknown concentrations were determined accurately by the use of standard solutions that gave responses near those of the unknown solutions. Alternatively, determinations of unknowns were made with a curve obtained by plotting the logarithm of response as a function of the logarithm of HCBD concentration. The resulting plot was linear with a slope of about 0.9. A least squares fit of typical data allowed the prediction of concentrations within 5% of their actual values even at levels near 2 ng/mL. Peak area measurements gave a similar relationship.

The detection limit (X) was found to be about 0.8 ng/mL for 5 μL injections. At this concentration, the background noise caused the precision of peak height and peak area measurements to fall to a relative standard deviation of 10%. The ratio of the peak height to the background noise was about 6:1 at this level.

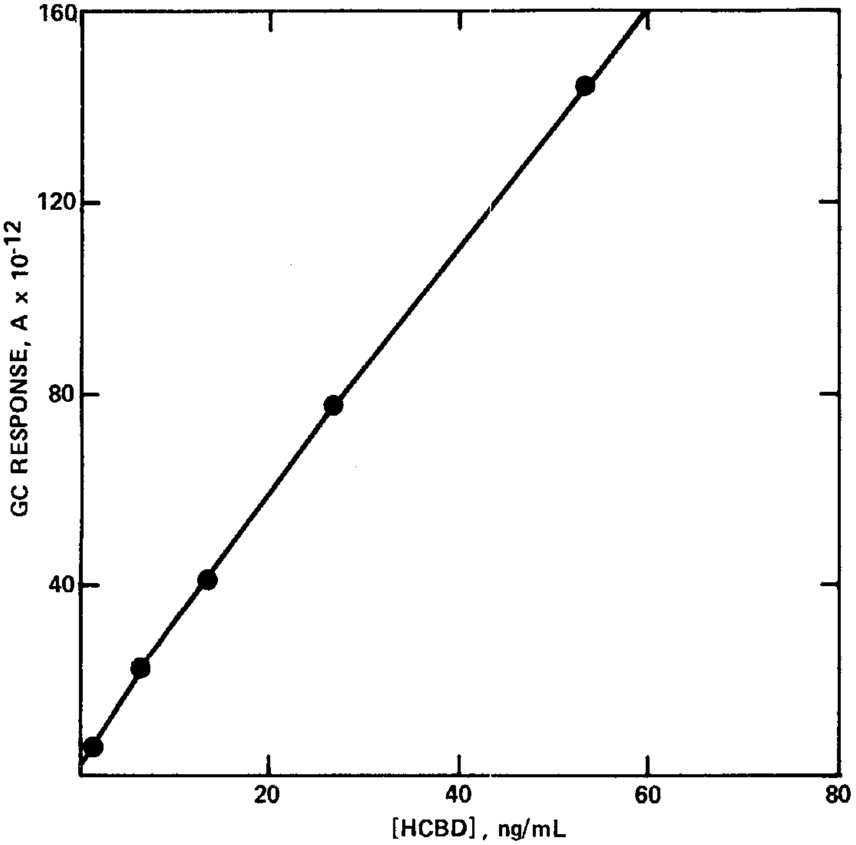

Figure 2. Calibration curve for GC determination of HCBD in hexane.

III. SELECTION OF COLLECTION MEDIUM AND PRELIMINARY EVALUATION

A. Choice of Candidate Sorbents

Two porous polymers, Tenax-GC and Amberlite XAD-2, were chosen for evaluation as collection media primarily because of their high affinity for chlorinated hydrocarbons. It was reported that Tenax-GC had demonstrated an affinity for chlorinated aliphatics, chlorinated benzenes, chlorinated phenols, and polychlorinated biphenyls.(H2,H5) Although specific applications of XAD-2 for the collection of chlorinated compounds from air were less numerous, the material had been found to have larger capacities than did Tenax-GC for many organic compounds including one chlorinated compound, dichlorobenzene.(H1) This result was attributed to the larger surface area of the XAD-2 sorbent.

Although we expected that both Tenax-GC and XAD-2 would prove to be suitable sorbents for HCBD, we believed that the evaluation of both materials was desirable since the behavior of either sorbent under all test conditions could not be predicted. The numerous successful applications of Tenax-GC to the determination of chlorinated hydrocarbons in air seemed to ensure that this polymer would be an excellent sorbent for HCBD. The potentially larger capacity of XAD-2 over Tenax-GC for organics appeared, however, to make it a more desirable choice. On the other hand, the purity of the XAD-2 available commercially did not compare with that of Tenax-GC. The significant amounts of hydrocarbon residues that could be extracted from unwashed XAD-2 with an organic solvent were potentially detrimental to the sensitivity and reproducibility of the determinations of HCBD.

The physical and chemical properties of Tenax-GC and XAD-2 are summarized as follows.(H1, H6) Tenax-GC is a polymer of 2,6-diphenyl-p-phenylene oxide with a surface area of 25 m^2/g, an average pore size less than 4 nm in diameter, and a low bulk density of 0.14 g/mL. Its primary attributes are its thermal stability and its inertness toward oxidation. In the presence of air, it is stable to temperatures as high as 400 °C.

Amberlite XAD-2 is a copolymer of styrene and divinylbenzene. Its surface area is about 350 m^2/g. It has an average pore size of 20 to 30 nm in diameter; its bulk density is about 0.38 g/mL. Its thermal stability is not as high as that of Tenax-GC, but it is stable up to about 210 °C in air. XAD-2 is chemically equivalent to Chromosorb 101, a sorbent that has been successfully employed as a collection medium for the determination of HCBD in air.(G4) XAD-2 appeared, however, to be a more attractive choice for inclusion in the method development than did Chromosorb 101. The reported surface area of Chromosorb 101 is approximately 30 m^2/g, less than one-tenth of that of XAD-2.

B. Evaluation of Candidate Sorbents for Selection of a Suitable Collection Medium

Three types of tests—desorption efficiency, stability, and capacity tests—were performed to determine the suitability of the candidate sorbents for use in a sampling and analytical method for HCBD. In the desorption efficiency tests, the two sorbent materials were spiked with HCBD in hexane and extracted with hexane. The extracts were then analyzed to determine the recovery of HCBD. From the results an estimate of the LAQL was made. In the stability tests, the two materials were spiked similarly, stored, and then extracted for analysis. In the capacity tests, the two sorbent materials and also a charcoal were challenged with test atmospheres of HCBD in humidified air until breakthrough was observed. (See Appendix 2 for a description of the HCBD-vapor generator employed to synthesize test atmospheres.) The results of these three types of tests were used in the design of a prototype sampling device described below.

1. Desorption efficiency tests

The materials employed in the tests were as follows. Purified XAD-2 resin (20/50 mesh), Lot No. 1006, and Tenax-GC (35/60 mesh), Lot No. 760511/10, were obtained from Applied Science Laboratories, Inc. (The XAD-2 was precleaned by the supplier by Soxhlet extraction with polar and nonpolar solvents.) Five-milliliter glass vials with crimp-on caps and Hycar and Teflon/rubber septa were obtained from Supelco, Inc., for use in the spiking and extraction of sorbent materials.

Before sorbent materials were spiked with HCBD, three unexposed 50-mg portions of XAD-2 and Tenax-GC were extracted with hexane for 20 min with agitation in an ultrasonic bath. When the extracts were analyzed by gas chromatography, traces of some volatile compounds were observed with the electron capture detector. In the extracts of XAD-2, small amounts of two compounds were observed with retention times of 2.1 and 2.7 min. In the extracts of Tenax-GC, small amounts of two other compounds were observed with retention times of 5 and 10 min. Since the retention times of these compounds differed enough from that of HCBD (3.6 min) to avoid interference, the sorbent materials were not washed to remove the contaminants.

The procedure employed for spiking, extracting, and analyzing the samples was as follows:

(1) Fifty milligrams of Tenax-GC or XAD-2 was added to a vial.

(2) Five microliters of hexane containing a specified amount of HCBD was injected into the sorbent bed in the vial.

(3) The vial was then sealed with a septum, usually a Teflon/silicone rubber septum.*

(4) The sealed vial was allowed to stand for several minutes at room temperature under incandescent lighting or was stored overnight under similar conditions.

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*The use of the Hycar septa was suspended after sorbent extracts became contaminated with compounds that were leached from the septa. These compounds interfered with the gas chromatographic determination of HCBD.

(5) After the appropriate time, the septum was removed and 1 mL of hexane was added.

(6) The vial was resealed and agitated in an ultrasonic bath for a specified time.

(7) A 5-μL aliquot was withdrawn from the vial with a syringe and injected into the gas chromatograph.

To establish a value for the LAQL, 50-mg portions of the sorbent materials were spiked with various amounts of HCBD. Initially, 84-ng amounts were added to six sorbent samples of each type. The spiked samples were allowed to stand for several minutes and then were extracted in an ultrasonic bath for 0.5 to 20 min. Values of the desorption efficiency were found to be 0.95 to 1.00 for Tenax-GC and 0.97 to 1.00 for XAD-2 with no significant dependence on extraction time. In another experiment, three sorbent samples of each type were spiked with 0.8-ng amounts of HCBD, allowed to stand several minutes, and then extracted for 0.5 min. Values of the desorption efficiency were again high, 0.95 to 1.08 for Tenax-GC and 0.98 to 0.99 for XAD-2. The gas chromatograms at this level, however, were not totally acceptable; peaks were often distorted by background noise. In a third experiment, sorbent samples were spiked with 4.2-ng amounts of HCBD. The samples were stored overnight to ensure that the analyte spikes had reached an equilibrium with the sorbent substrates. No effort was made to shield the samples from light during storage. After extraction of the samples for 0.5 min, the desorption efficiency averaged 1.003 for Tenax-GC and 0.968 for XAD-2. Precision was high; the RSD was 2.5% with Tenax-GC and 1.3% with XAD-2. The results appear in Table I.

Although levels slightly lower than 4 ng might have been recovered with acceptable accuracy and precision, the 4-ng level was chosen as the LAQL to allow for the expected variability in air sampling. (As described below in Section V.B, it was necessary to work at even higher levels in the evaluation of the overall sampling and analytical method to achieve the required accuracy and precision.)

2. Stability tests

The storability of HCBD on the two sorbent materials was compared in 7-d stability tests. Fifty-milligram amounts of Tenax-GC and XAD-2 were spiked with 4.2, 16.7, or 33.3 ng of HCBD. The samples were sealed and stored as in the previous tests. After storage, each sample was extracted with 1 mL of hexane.

The results with XAD-2 tubes are presented in Table II. It was found that the XAD-2 samples required agitation in an ultrasonic bath for about 30 min to obtain complete recovery of the HCBD. The average desorption efficiency over all three test levels was 0.990; the pooled relative standard deviation was 3.3%. The average desorption efficiency was about the same as that observed with spiked XAD-2 samples stored overnight (see Table I); the storage of the samples for 7 d, however, did decrease the precision somewhat.

Table I. Recovery of HCBD from Spiked Sorbent Samples Stored Overnight

Sorbent[a]	HCBD found, ng (4.20 ng added)	Desorption efficiency[b]
Tenax-GC	4.35	1.034
	4.30	1.023
	4.10	0.977
	4.13	0.983
	4.19	0.997
Mean	4.21	1.003
Std dev	0.11	0.025
RSD, %	2.6	2.5
XAD-2	4.10	0.976
	4.10	0.976
	4.00	0.952
	4.10	0.976
	4.10	0.976
	4.00	0.952
Mean	4.07	0.968
Std dev	0.05	0.012
RSD, %	1.3	1.3

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a. 4.20 ng of HCBD was applied to 50 mg of sorbent material and stored overnight at 25 to 28 °C.

b. HCBD found/HCBD added.

Table II. Recovery of HCBD from Spiked XAD-2 Samples Stored for One Week[a]

Test level	4.20 ng		16.7 ng		33.3 ng	
	HCBD found, ng	Desorption efficiency[b]	HCBD found, ng	Desorption efficiency[b]	HCBD found, ng	Desorption efficiency
	4.00	0.952	16.7	1.000	33.5	1.006
	4.30	1.024	16.4	0.982	32.2	0.967
	4.10	0.976	17.0	1.018	33.5	1.006
	4.20	1.000	16.7	1.000	32.6	0.979
	4.40	1.048	17.0	1.018	32.0	0.961
	-	-	16.5	0.988	30.0	0.901
Mean	4.20	1.000	16.7	1.001	32.3	0.970
Std dev	0.16	3.8	0.2	0.015	1.3	0.039
RSD, %	3.8	3.8	1.5	1.5	4.0	4.0

$\overline{DE}^{c} = 0.990$

$\overline{RSD}^{d} = 3.3\%$ ($\chi^2 = 4.55$; $\chi^2_{\text{critical}} = 9.21$ for three variances).

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a. HCBD was applied to 50 mg of 20/50-mesh XAD-2 and stored for 1 wk at 25 to 28 °C.

b. HCBD found/HCBD added.

c. Desorption efficiency averaged over the three test levels.

d. Pooled relative standard deviation. See Appendix 3.

The results for Tenax-GC samples are presented in Table III. Quantitative recovery of HCBD was obtained when these sorbent samples were extracted with hexane for 1 hr in an ultrasonic bath. With an extraction time of 30 min, recoveries from two samples each spiked with 16.7 ng of HCBD were only 70 to 80%. After extraction for another 30 min, the recoveries from these two samples rose to 97%. The average desorption efficiency was 0.987 for all three test levels with an extraction time of 1 h. The precision values were not pooled because they were inhomogeneous by Bartlett's test (see Appendix 3). In comparing Table III with Table I, it is evident that precision was decreased somewhat as the storage time was increased.

3. Capacity tests

Three sorbent materials—Amberlite XAD-2, Tenax-GC, and charcoal (Mine Safety Appliances, Inc.)—were included in the capacity tests. The charcoal was also evaluated because it was expected to offer a sorbing capacity greater than that of the porous polymers. The XAD-2 and Tenax-GC were used as received from their suppliers. The charcoal was taken from MSA organic vapor sampling tubes (Part No. 459004) and was also used without treatment.

To determine the capacity of a sorbent material for HCBD vapor, generator effluent was sampled into glass sorbent tubes, and the breakthrough of HCBD from the tubes was monitored. Two identical sorbent tubes were evaluated in each test. Each sorbent tube (3 mm i.d. by 7 cm long) contained 50 mg of a candidate sorbent material held in place with two plugs (about 2 mg) of silanized glass wool (Supelco, Inc., No. 2-0411). Each tube was followed in the sampling train by an impinger containing 10 ml of hexane. The impinger was immersed in an ice bath to prevent the loss of hexane during sampling. The test atmosphere was sampled through the tube and impinger at the rate of 0.2 L/min. The impinger was replaced periodically, and the hexane in the impinger was analyzed for HCBD to determine the amount of breakthrough. The temperature of the test atmosphere was 39 °C and the relative humidity was about 50%. The HCBD concentration was maintained between 715 and 850 $\mu g/m^3$. Prior to each test, the HCBD concentration was determined by sampling with impingers.

The results of these initial breakthrough tests are given in Table IV. The breakthrough from both XAD-2 and MSA charcoal was insignificant over the sampling periods employed; however, there were slight differences in the sorbing capacities of the two materials with XAD-2 exhibiting the greater sorbing efficiency. Tenax-GC was much less efficient than the other two sorbents, presumably because of its lower specific surface area. It was also found that the silanized glass wool used to hold the sorbent layers in the sorbent tubes retained approximately 2 ng of HCBD.

In Table V the calculated amounts of HCBD sampled are compared to the total amounts of HCBD recovered from the sorbent tubes plus the almost insignificant amounts recovered from the backup impingers. The recoveries from MSA charcoal and XAD-2 are in reasonable agreement with the predicted values. The anomalous high results with Tenax-GC apparently reflect a change in generator output or sampling rate during the simultaneous exposure of the two samples to HCBD.

Table III. Recovery of HCBD from Spiked Tenax-GC Samples Stored for One Week[a]

Test level	4.20 ng		16.7 ng		33.3 ng	
	HCBD found, ng	Desorption efficiency[b]	HCBD found, ng	Desorption efficiency[b]	HCBD found, ng	Desorption efficiency[b]
	4.20	1.000	16.2	0.970	32.0	0.961
	4.40	1.048	16.2	0.970	34.2	1.027
	4.00	0.952	16.3	0.976	33.0	1.000
	3.90	0.929	16.2	0.970	33.8	1.015
	4.40	1.048	16.2	0.970	34.0	1.021
	4.20	1.000	16.3	0.976	31.4	0.943
Mean	4.18	0.996	16.2	0.972	33.1	0.994
Std dev	0.20	0.049	0.1	0.003	1.2	0.034
RSD	4.9	4.9	0.3	0.3	3.5	3.5

$\overline{DE}^{c} = 0.987$

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a. HCBD was applied to 50 mg of 35/60-mesh Tenax-GC and stored for 1 wk at 25 to 28 °C.

b. HCBD found/HCBD added.

c. Desorption efficiency averaged over the three test levels.

Table IV. Initial Sorbent Capacity Tests for HCBD[a]

Sorbent[b]	Sample No.	Concn of HCBD,[c] $\mu g/m^3$	Exposure time, min	Break-through,[d] %
XAD-2				
(20/50 mesh)	1	780	130	0.0
	2	780	130	0.0
	3	715	250	0.4[e]
	4	715	250	0.3e
MSA charcoal	1	660	60	0.2
			115	0.2
	2	660	60	0.2
			115	0.3
Tenax-GC	1	830	60	11.0
(35/60 mesh)			80	13.2
	2	830	60	14.5
			80	16.4
Glass wool[f]	1	850	10	100

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a. In sampling chamber: temperature, 39 °C; relative humidity, 50%; sampling rate, 0.2 L/min.

b. Fifty milligrams of sorbent.

c. Determined by impinger sampling.

d. One hundred times the HCBD concentration in the tube effluent divided by the HCBD concentration in the tube influent.

e. After about 250 min of sampling, the rate of breakthrough, based on a limited number of samples, was approximately 0.06% per minute.

f. Approximately 2 mg of silanized glass wool (Supelco, Inc., No. 2-0411).

Table V. Recovery of HCBD in Capacity Tests

Sorbent	Sample No.	Calculated HCBD sampled,[a] µg	Total HCBD recovered,[b] µg	Calculated recovery, %
XAD-2	1	19.1	19.1	100
	2	20.2	20.1	100
	3	34.8	31.5	91
	4	33.3	29.0	87
MSA charcoal	1	14.4	16.3	113
	2	14.0	14.7	105
Tenax-GC	1	12.7	18.1	143
	2	12.8	19.3	151

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a. Calculated from bubbler measurements made prior to sorbent exposure and the exposure time.

b. Total amounts recovered from tubes and impingers.

From these experiments, it appeared that XAD-2 was the sorbent of choice for sampling HCBD in air. At 39 °C and a relative humidity of 50%, the capacity of 50 mg of XAD-2 was more than 30 µg of HCBD when samples were taken at 0.2 L/min from a test atmosphere with an HCBD concentration of 715 $\mu g/m^3$.

Additional capacity tests were performed to determine the performance of XAD-2 under a variety of sampling conditions. Tests were performed at two temperatures—25 and 38 °C—and at two HCBD concentrations—1 and 10 mg/m^3. In the experiments at 38 °C, the relative humidity was 50%—a water vapor concentration of about 23 mg/L. In the experiments at 25 °C, the relative humidity was 80 or 90%—a water vapor concentration of 18 or 21 mg/L. There was, therefore, relatively little difference in the absolute water vapor concentrations in the experiments performed at the two temperatures.

The capacity was determined in a manner similar to that in previous experiments. Test gas from the vapor generator was drawn at a nominal rate of 0.2 L/min through sorbent tubes that each contained one 50-mg layer of XAD-2 in tandem with backup sorbent sections or bubblers containing hexane. The backup sorbent layers or bubblers trapped HCBD that passed through the sorbing section.

The results are given in Table VI. The weight capacity at an HCBD concentration of 1 mg/m^3 was lower than that at 10 mg/m^3; the maximum sampling volume and maximum sampling time, however, were higher. It is expected that at concentration levels lower than 1 mg/m^3 the maximum sampling volume and time would have been greater still. Increasing the sampling temperature had the most deleterious effect upon weight capacity and thus upon sampling volume and sampling time. The weight capacity was diminished by about a factor of five by increasing the temperature from 25 to 38 °C.

Table VI. Summary of Results on the Capacity of Amberlite XAD-2 for HCBD

Test conditions[a]			Observed sampling limits at indicated breakthrough			
Sampling temp, °C	Relative humidity, %	HCBD concn, mg/m^3	Weight capacity,[b] µg/50 mg	Maximum sampling volume, L	Maximum sampling time, h	Break-through,[c] %
25	80	1	238	234	19	3
25	80	1	254	245	19	4
38	50	1	58	71	6	2 to 3
38	50	1	49	66	6	2 to 3
25	90	10	1190	115	8	3
25	90	10	906	94	8	1

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a. Sampling rates were nominally 0.2 L/min.

b. Amount of HCBD collected by 50 mg Amberlite XAD-2 (20/50-mesh).

c. One hundred times the HCBD concentration in the tube effluent divided by the HCBD concentration in the tube influent.

From the results, it was concluded that air sampling with an XAD-2 sorbent tube at 0.2 L/min for at least 8 h is possible at 25 °C, at a relative humidity of 80 to 90%, and at HCBD concentrations ranging from 1 to 10 mg/m^3. At 38 °C, it appeared that sampling without significant breakthrough is feasible for several hours although the limit was not specifically defined.

4. Recommended sampling device

From the results of the desorption efficiency, stability, and capacity tests, XAD-2 (20/50 mesh) was deemed an appropriate collection medium for the determination of HCBD in air. At the chosen LAQL of 4 ng, the sorbent exhibited quantitative desorption efficiency, and provided an inert medium for storing collected HCBD. Fifty-milligram amounts of the material provided capacities high enough for sampling periods of at least several hours.

Although the tests with XAD-2 had been carried out with 50-mg portions of the material, it was considered advisable to recommend a larger sorbing layer to offset the reduction in capacity observed at elevated sampling temperatures with 50-mg layers (see Table VI). The following design was developed for the prototype sampling device. The size of the sorbing layer was increased to 100 mg. The size of the backup layer was arbitrarily chosen to be 50 mg. The sorbent layers were packed into a Pyrex tube (7 cm long by 6 mm o.d. and 4 mm i.d.) and held in place with three silanized glass wool plugs. The tubes were constricted slightly about 1 cm from the outlet end to facilitate packing. The ends of the packed tubes were sealed with Teflon tape and then with plastic caps to prevent contamination. During the packing of the sorbent into the tubes, it was necessary to avoid undue agitation of the sorbent to avoid the induction of a static charge. The charge was found to agglomerate the particles; this agglomeration could reduce the capacity of the sorbent tube through "channeling".

The pressure drop across nine separate sorbent tubes averaged 3.8 in. H_2O at 25 °C (1.0 kPa) at a sampling rate of 0.2 L/min. The relative standard deviation for the pressure drop measurements was 15%.

IV. INDEPENDENT METHOD FOR THE DETERMINATION OF HCBD IN AIR

The "true" HCBD concentration in the sampling chamber of the generator was determined by sampling the effluent with midget impingers containing hexane in an ice bath. For 3-L air samples, only 5 mL of hexane was used; for larger volumes of air, as much as 20 mL of hexane was employed. Sampling rates were 0.05 to 0.2 L/min. (At these low rates, the impingers functioned well as gas absorbers or bubblers; breakthrough was less than 5%.) The HCBD concentrations in the impinger solutions were determined by gas chromatography with electron capture detection. Although gas chromatography was also used in the developed method, the gas chromatographic method was deemed acceptably accurate by calibration daily with standard solutions of HCBD in hexane. The identities of the major peaks in the chromatogram were verified by gas chromatography with mass spectrometric detection.

HCBD levels in the sampling chamber were determined under a variety of generator operating conditions. The temperature of the HCBD reservoir in the generator, the flow rate of nitrogen over the neat HCBD in the reservoir, the relative humidity of the dilution air, and the temperature of the dilution air were varied. The dilution-air flow rate was not altered significantly from 10.5 L/min during the evaluation of the generator in all tests.

In the initial tests, the operating conditions employed were those given for Test Set No. 1 in Table VII. The observed HCBD concentration in the generator sampling chamber was 15 $\mu g/m^3$. This level was reproducible and steady over the period of a workday; however, the observed value was only about one-third the expected value of 50 $\mu g/m^3$ calculated from the equilibrium vapor pressure of HCBD and the gas flow rates.(B5)

Table VII. Results of the Evaluation of the HCBD Vapor Generator

Test Set No.	HCBD reservoir temp, °C	N_2 flow rate, ml/min	Calculated concn of HCBD, $\mu g/m^3$	Observed concn of HCBD, $\mu g/m^3$	RSD, %	No. of measurements
1	-34	45	50	15[a]	5.3	10
2	-34	45	50	15[b]	3.5	5
3	0	26	1060	710[b]	5.8	4
4	4	18	1020	865[b]	2.6	13
5	4	26	1470	860[b]	8.7	8

---

a. In sampling chamber: temperature, 27 °C; relative humidity, <1%.

b. In sampling chamber: temperature, 39 °C; relative humidity, 50%.

In Test Set No. 2, the temperature of the dilution air was raised from 27 to 39 °C, and the relative humidity was increased from <1 to 50%. At the same gas flow rates as those in the Test Set No. 1, the observed HCBD concentration was again 15 $\mu g/m^3$.

In later experiments with the neat HCBD maintained at 0 or 4 °C but with lower nitrogen flow rates, the agreement between theory and practice was better (see Test Sets Nos. 3 to 5 in Table VII). With a reservoir temperature of 0 °C and a nigtrogen flow rate of 26 mL/min, the observed concentration was 710 $\mu g/m^3$, and the calculated concentration was 1060 $\mu g/m^3$. Raising the temperature of the HCBD to 4 C and lowering the nitrogen flow rate to 18 mL/min produced an observed concentration of 865 $\mu g/m^3$ at a calculated value of 1020 $\mu g/m^3$. Maintaining the temperature of 4 °C and adjusting the nitrogen flow rate to 26 mL/min produced, however, an observed value of only 860 $\mu g/m^3$ at a calculated value of 1470 $\mu g/m^3$. The reproducibility and stability of the levels produced at 0 and 4 °C did appear to be acceptable throughout a given workday.

Since the HCBD concentrations appeared to be steady and covered a wide range, the performance of the generator was judged to be satisfactory for the exposure of sorbent tubes, even though discrepancies between the calculated and observed concentration values were observed.

V. EVALUATION OF TOTAL METHOD

The purpose of this portion of the research was to determine the desorption efficiency at widely separated levels of HCBD, to determine the storability of HCBD sorbed by XAD-2 from air, and to assess the accuracy and precision of the total sampling and analytical method developed.

A. Additional Desorption Efficiency Tests

The spiking and analysis procedure for these tests was similar to that employed in the earlier desorption efficiency tests described in Section III.B.1. Six 50-mg beds of XAD-2 were each spiked with 3000 ng of HCBD, stored overnight, and then extracted for 1 h in an ultrasonic bath. (The extraction time was increased from 30 min to 1 h to ensure quantitative recoveries during the long-term stability tests described below in Section V.B. Consequently, all subsequent tests including these were performed with 1-h extraction times.)

The resulting average value of the desorption efficiency at the 3000-ng level was 0.999 with a RSD of 0.8%. These results along with those obtained earlier at levels near 4-ng are presented together in Table VIII. The average desorption efficiency for both levels was 0.984; the pooled relative standard deviation (RSD) was 1.1% (see Appendix 3). (This pooled RSD is less than the value of 3.3% obtained after spiked XAD-2 samples were stored for 7 d before analysis; see Table II. The desorption efficiency, whether for samples stored overnight (0.984) or 7 d (0.990), was quantitative.)

Table VIII. Recovery of HCBD at Two Levels from XAD-2 Samples Stored Overnight[a]

Test level	4.20 ng		3000 ng	
	HCBD found, ng	Desorption efficiency[b]	HCBD found, ng	Desorption efficiency[b]
	4.10	0.976	3000	1.000
	4.10	0.976	3040	1.013
	4.00	0.952	2980	0.993
	4.10	0.976	3000	1.000
	4.10	0.976	3000	1.000
	4.00	0.952	2970	0.990
Mean	4.07	0.968	2998	0.999
Std dev	0.05	0.012	24	0.008
RSD_1, %	1.3	1.3	0.8	0.8

$\overline{DE}$[c] = 0.984

$\overline{RSD_1}$[d] = 1.1% (χ^2 = 1.32; $\chi^2_{critical}$ = 6.64 for two variances.)

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a. HCBD was applied to 50 mg of 20/50-mesh XAD-2 and stored overnight at 25 to 28 °C.

b. HCBD found/HCBD added.

c. Desorption efficiency averaged over both test levels for samples stored overnight.

d. Pooled relative standard deviation. See Appendix 3.

B. Stability of HCBD Collected with XAD-2 from Test Atmospheres

XAD-2 tubes—each containing a 100-mg front (sorbing) section and a 50-mg backup section—were exposed to 3 L of generator effluent at a sampling rate of 0.2 L/min. The temperature of the test gas was 28 °C; the relative humidity was 80%. The exposed tubes were sealed with plastic caps and either analyzed soon after exposure or stored for up to 34 d prior to analysis. The stored tubes were maintained at room temperature for 7 d; tubes stored for more than 7 d were refrigerated (0 °C) after the seventh day.

In the initial set of these stability tests, the desired results were not obtained at an HCBD concentration of 3 $\mu g/m^3$. The average recovery was 70% with a RSD of 4% after sorbent samples were stored for 7 d; after 14 d, the average recovery was again 70% with an RSD of 14%.

The tests were repeated at a higher HCBD concentration, 10 $\mu g/m^3$. At this level it was also found to be necessary to increase the extractant volume from 1 to 2 mL and the extraction time from 30 min to 1 h to obtain adequate recovery of the HCBD. The backup sections from two of the freshly exposed tubes, from four of the tubes stored for 14 d, and from four of the tubes stored for 34 d were analyzed separately. For all other tubes, the front and backup sorbent sections were combined before analysis. (As usual, the glass wool plugs were analyzed along with the sorbent samples. No tubes were analyzed on the seventh day of storage because of instrument problems at the scheduled time.)

The results of the test at the 10-$\mu g/m^3$ level are presented in Table IX. The difference between the average concentration observed with freshly exposed tubes and the average concentration found with stored tubes on the fourteenth or the thirty-fourth day was found to be statistically insignificant at the 95% confidence level. No HCBD was found on any of the backup sorbent sections analyzed.

C. Determination of Accuracy and Precision of the Total Method

The procedure employed in the sampling and analysis tests was as follows. Sorbent tubes (front section, 100 mg; backup section, 50 mg) were exposed to test atmospheres of HCBD in air. The test atmospheres were generated as described in Appendix 2. The relative humidity of the gas was 80% or greater; the temperature was 25 to 28 °C. The sampling rates were nominally 0.2 L/min; about 3 L of test gas were sampled into each tube. The test gas was sampled simultaneously with bubblers containing hexane at 0 °C. After exposure, both sorbent sections in a tube were transferred along with the glass wool plugs to a 5-mL glass vial. The contents were then extracted with 2-mL of hexane and the extracts were analyzed.

The results of sampling and analysis are presented in Table X. The average recovery of HCBD with sorbent sampling relative to the independent method was 100%; the pooled relative standard deviation ($\overline{RSD_2}$) was 7%.

Table IX. Long-Term Stability of Sorbed HCBD

Sample Set No.[a]	HCBD found by independent method, $\mu g/m^3$	HCBD found by sorbent sampling, $\mu g/m^3$, in the indicated days of storage: 0	14	34
1	10.30	8.60	8.38	8.48
			10.27	9.55
2	-[b]	8.80	9.08	8.85
			9.83	8.87
3	10.28	8.81	9.48	8.92
			9.50	9.04
4	11.29	9.54	9.68	9.23
			9.79	8.89
5	-[b]	9.22	10.69	8.42
			9.69	8.60
6	10.86	9.32	9.32	9.20
			2.53[c]	9.05
Mean	10.68	9.05	9.60	8.93
Std dev	0.49	0.36	0.63	0.32
RSD, %	5	4	7	4
t		-	1.95[d]	0.72[e]
t (critical)		-	2.13	2.12

---

a. Sorbent tubes (front section, 100 mg; backup section, 50 mg).

b. Bubbler solutions were contaminated.

c. Rejected by the Grubb's test; see Appendix 3.

d. Comparison of means between the results of 0- and 14-d experiments by the student's <u>t</u> test at the 0.05 level of significance for a two-tailed test.

e. Comparison of means between the results of 0- and 34-d experiments by the student's <u>t</u> test at the 0.05 level of significance for a two-tailed test.

Table X. Sampling and Analysis of Sorbent Samples Exposed to Test Atmospheres

	HCBD FOUND				
Average test level[a]	Quantity, ng	Volume sampled, L	Concn, µg/m^3	HCBD taken,[b] µg/m^3	Recovery,[c] %
19 ng	15.5	2.15	7.22	7.94	91
	22.6	2.94	7.67		97
	18.6	2.70	6.90		87
	27.9	3.03	9.21	8.48	109
	17.9	1.98	9.04		107
	9.98	2.37	4.21	4.52	93
Mean	-	-	-	-	97
Std dev	-	-	-	-	9
RSD$_2^1$, %	-	-	-	-	9
237 ng	309	3.48	88.8	93.9	95
	235	2.66	88.3		94
	144	1.76	81.8		87
	343	3.32	103.5	98.2	105
	243	2.42	100.7		102
	147	1.35	109.0[d]		111[d]
Mean	-	-	-	-	97
Std dev	-	-	-	-	7
RSD$_2^2$, %	-	-	-	-	7
2990 ng	2200	1.97	1030	970	106
	3020	2.99	1010		104
	3480	3.47	1000		103
	3590	3.00	1200		124
	2710	2.74	990		102
	2920	2.87	1020		105
Mean	-	-	1040	-	107
Std dev	-	-	80	-	8
RSD$_2^3$, %	-	-	8	-	8

Table X. (continued)

Average test level[a]	Quantity, ng	Volume sampled, L	Concn, $\mu g/m^3$	HCBD taken,[b] $\mu g/m^3$	Recovery,[c] %
5575 ng	4900	2.61	1880	1920	98
	6330	3.26	1940		101
	5910	3.09	1910		99
	4130	2.01	2050		107
	6150	3.23	1900		99
	6030	3.09	1950		102
Mean	-	-	1940	-	101
Std dev	-	-	60	-	3
RSD_2^4, %	-	-	3		3

Mean recovery = 100%

$\overline{RSD}_2$,[e] % = 7% (χ^2 = 4.61; $\chi^2_{critical}$ = 11.34 for four variances)

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a. Average amount collected from test atmospheres with 20/50-mesh XAD-2 in sorbent tubes (front section, 100 mg; backup section, 50 mg).

b. Determined by the independent method. Each recorded value is the result of one bubbler sample.

c. Relative to the independent method.

d. Sample vial was cracked during analysis; therefore, this value was omitted from the statistical analysis.

e. Pooled relative standard deviation. See Appendix 3.

From the data in Tables VIII and X, the separate contributions of the sampling and analysis steps to the precision and accuracy of the total method over all test levels were statistically averaged. The overall precision was calculated according to the statistical procedures described in Appendix 3. Since the test air sample volumes were measured precisely with critical flow orifices, an assumed relative standard deviation of 5% was used to represent the precision of the metering of air sample volumes that would be experienced with personal sampling pumps (RSD_p). From $\overline{RSD}_2$ and RSD_p, the relative standard deviation of the total procedure ($\overline{RSD}_T$) over test levels ranging from about 10 to about 2000 $\mu g/m^3$ was calculated to be 9%. ($\overline{RSD}_1$, the precision of the analytical procedure, was not large enough to significantly affect the value of $\overline{RSD}_T$). A summary of the precision information follows:

$\overline{RSD}_1$ = 1.1% $\overline{RSD}_2$ = 7% $\overline{RSD}_p$ = 5%

$\overline{RSD}_T$ = 9%

There appeared to be little or no bias in the sampling and analytical method with XAD-2. The average recovery of HCBD with sorbent sampling relative to the independent method was 86% in stability tests and 100% in the sampling and analysis tests. The overall average was 93%.

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APPENDIX 1

4	Serious Health Hazard
0	Nonflammable
1	Low Reactivity

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.

ADDRESS

TRADE NAME Hexachloro-1,3-butadiene (Formula, C_6Cl_6)

SYNONYMS C-46, HCBD, Hexachlorbutadiene, Hexachlorobutadiene

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%	HAZARD DATA

III PHYSICAL DATA mol wt = 260.76

BOILING POINT, 760 mm Hg	210 to 220 °C	MELTING POINT	-19 to -22 °C
SPECIFIC GRAVITY (H_2O = 1)	1.6794 at 20 °C	VAPOR PRESSURE	0.15 torr at 20 °C
VAPOR DENSITY (AIR = 1)	9.05	SOLUBILITY IN H_2O, % BY WT	Insoluble
% VOLATILES BY VOL.		EVAPORATION RATE (BUTYL ACETATE = 1)	

APPEARANCE AND ODOR Clear, colorless liquid; odor of camphor.

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)	Nonflammable		AUTOIGNITION TEMPERATURE	618 °C	
FLAMMABLE LIMITS IN AIR, % BY VOL.		LOWER		UPPER	
EXTINGUISHING MEDIA					
SPECIAL FIRE FIGHTING PROCEDURES					
UNUSUAL FIRE AND EXPLOSION HAZARD					

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA Provisional Operational Limit, 1 ppm; Suspect Carcinogen

ROUTES OF EXPOSURE

INHALATION ihl-mus LCLo: 235 ppm/4 H

SKIN CONTACT skn-rat LD50: 2.99 g/kg; skn-rbt LD50: 126 mg/kg/6 H

SKIN ABSORPTION

EYE CONTACT irritant

INGESTION orl-rat LD50: 90 mg/kg; orl-mus LD50: 110 mg/kg; orl-gpg LD50: 90 mg/kg

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE

CHRONIC OVEREXPOSURE rat: renal damage, neoplasms at 20 mg/kg/day for 2 yr.

EMERGENCY AND FIRST AID PROCEDURES

EYES Wash with water immediately; get medical attention

SKIN Wash with soap and water; get medical attention

INHALATION Move to fresh air; keep warm. If not breathing, give oxygen. Get medical attention.

INGESTION Do not induce vomiting. Give a saline cathartic and a demulcent if conscious. Get medical attention.

NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

Destructive chlorination in light, accelerated by $FeCl_3$

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

Hexachloroethane in presence of light.
Phosgene in an electric discharge.

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

Does not occur easily.

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

Evacuate area and allow liquid compound to evaporate, or use protective equipment specified below during cleanup and removal.

NEUTRALIZING CHEMICALS

WASTE DISPOSAL METHOD

Incineration

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

Filtered exhaust system

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL) For even low concentrations, self-contained breathing apparatus or mask with organic vapor canister.

EYE Goggles or mask

GLOVES Rubber; change frequently

OTHER CLOTHING AND EQUIPMENT

Lab coat when handling neat liquid.

IX SPECIAL PRECAUTIONS

PRECAUTIONARY STATEMENTS	
OTHER HANDLING AND STORAGE REQUIREMENTS	Store in ventilation hood.

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DATE July 1978

APPENDIX 2

Vapor Generation System

The generator was operated as follows: A reservoir of HCBD was maintained at a constant temperature to regulate the vapor pressure of the compound precisely. Nitrogen was flushed over the compound and became laden with HCBD vapor. The nitrogen was then diluted with air to obtain the desired concentration. A schematic of the system is given in Figure 3. A photograph of the actual generator appears in Figure 4; the HCBD generator is inside the dotted lines of the figure.

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

The reservoir for HCBD was a small impinger constructed from stainless steel tubing and Swagelok stainless steel joints, as shown in Figures 5 and 6. A coil of copper tubing (12 in. long by 0.125 in. o.d.) and a section of stainless steel tubing (4 in. long by 0.25 in. o.d.) containing glass beads (80/100-mesh) cooled the nitrogen to the bath temperature before the gas flowed into the impinger. (These features of the apparatus are not shown in Figures 3 and 4.)

The temperatures of the nitrogen gas and the stainless steel impinger were regulated in a constant temperature bath with the FTS Systems Inc. Model No. MC-2-84 refrigerated cooler and the proportional temperature controller—FTS Model No. TCH-1—equipped with a resistance heater. A mixture of isopropanol and ethanol served as the heat transfer medium.

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

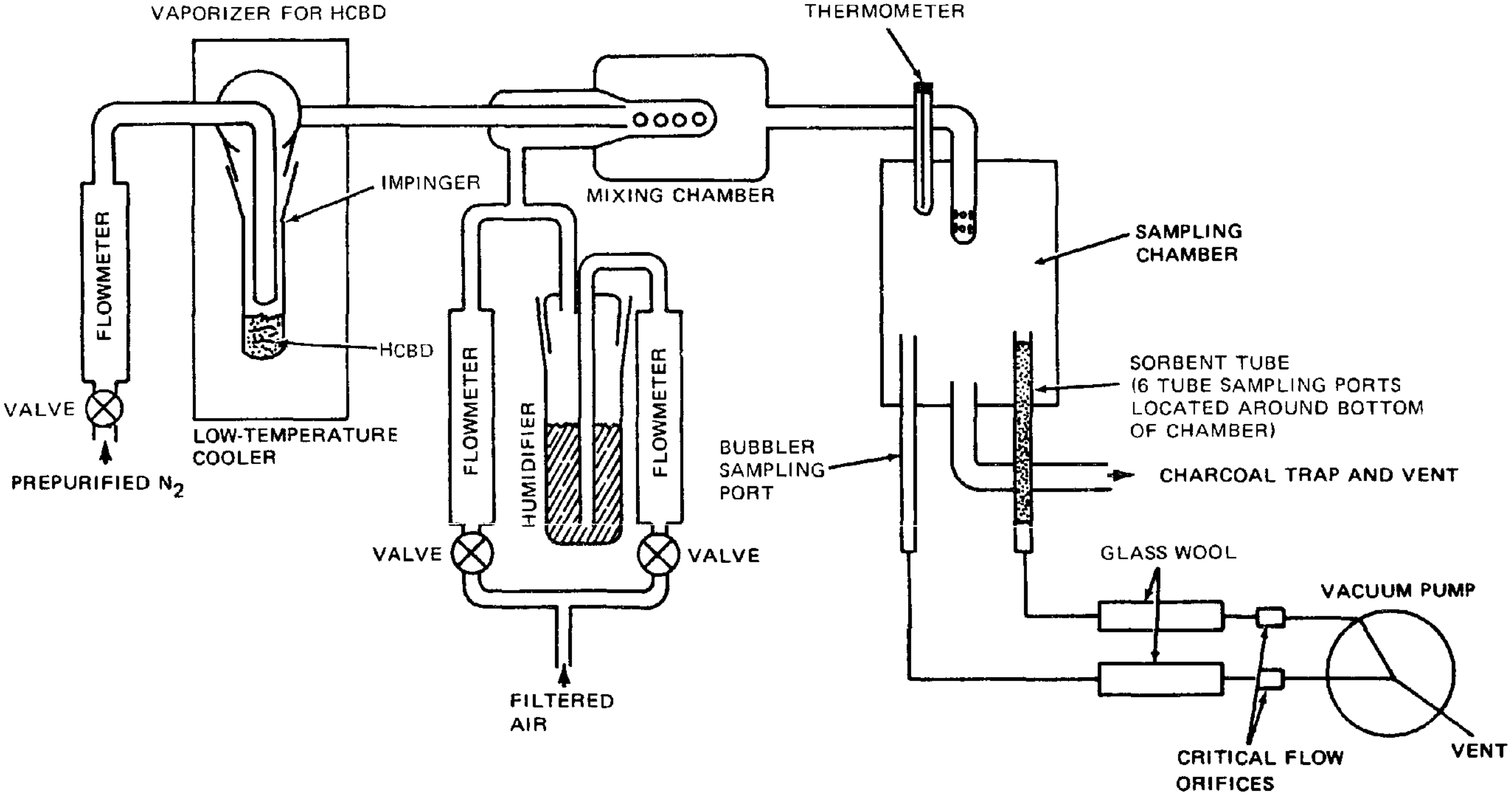

Figure 3. Schematic of vapor generator and sampling system.

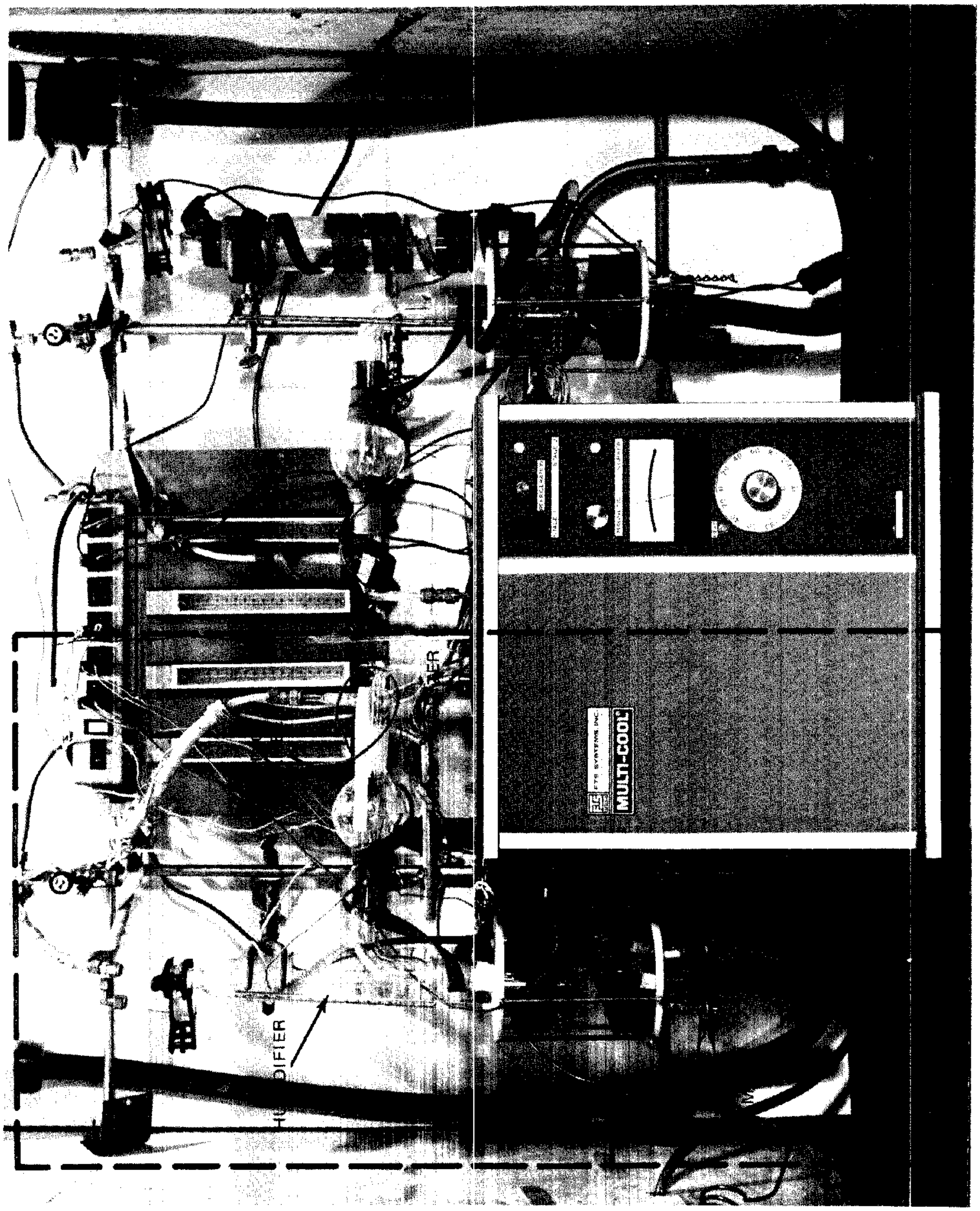

Figure 4. Vapor generator and sampling system (inside dotted line).

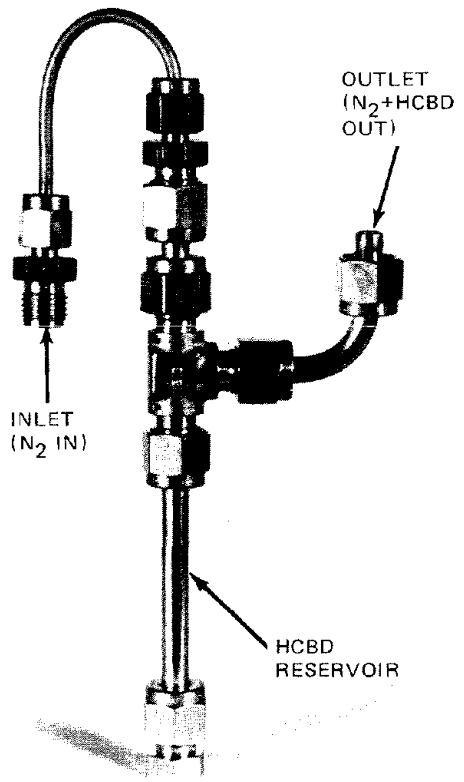

Figure 5. Assembled HCBD vaporizer.

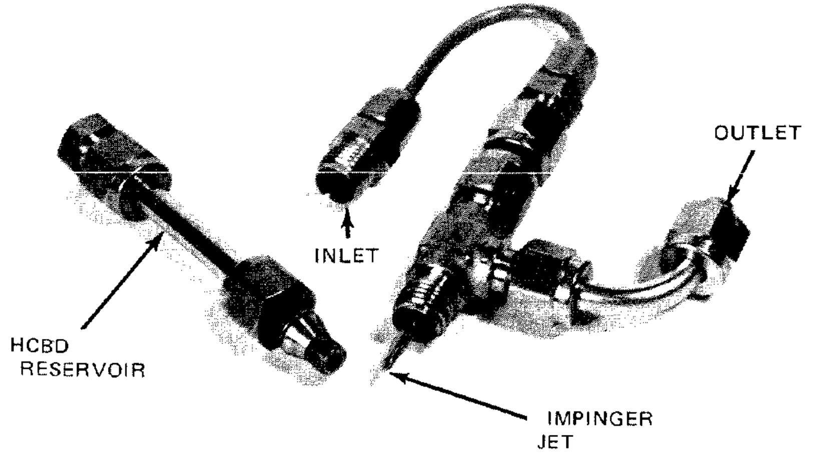

Figure 6. Disassembled HCBD vaporizer.

The nitrogen laden with HCBD was mixed with the dilution air in a glass splash trap—the mixing chamber—and was then passed into a cylindrical glass sampling chamber. (The cylinder was a glass pipe 6 in. long by 4 in. o.d. with Teflon discs for end caps.) The chamber was mounted vertically with the end caps at top and bottom. The generator effluent entered through an opening in the top cap of the chamber. Seven sampling ports and a vent were located in the bottom cap. Sorbent tubes were mounted vertically through the ports so that the front (sorbing) sections of the tubes were inside the chamber during sampling. The test atmosphere was sampled at rates ranging from about 0.05 to 0.2 L/min through tubes and bubblers with critical flow orifices connected to a vacuum pump.

APPENDIX 3

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."* 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).

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*Taylor, D. G.; Kupel, R. E.; Bryant, J. M. "Documentation of the NIOSH Validation Tests"; National Institute for Occupational Safety and Health: Cincinnati, Ohio, April 1977. DHEW (NIOSH) Publication No. 77-185, pp 4-11.

$\overline{RSD}$ - 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%.

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*See footnote on p 39.

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

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

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 $\underline{n}$ degrees of freedom for $\underline{n}$ observations.

For any six observations, a value can be rejected if $B_1' \geq 2.130$. 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 2.130 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:

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

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 = number of variances being tested.

In order to pass Bartlett's test at the 1% significance level, χ^2 must be less than or equal to 6.64 when k = 2, 9.21 when k = 3, or 11.34 when k = 4.

APPENDIX 4

HEXACHLOROBUTADIENE

Measurements Research Branch

Analytical Method

Analyte:	Hexachlorobutadiene	Method No.:	P&CAM 307
Matrix:	Air	Range:	10 to 2000 μg/m³ in 3 L of air
Procedure:	Adsorption on Amberlite XAD-2, desorption with hexane, GC/ECD	Precision:	9%
Date Issued:	6/28/79		
Date Revised:		Classification:	B (Accepted)

1. Synopsis

1.1 A known volume of air is drawn through an XAD-2 tube to trap the hexachlorobutadiene present.

1.2 The XAD-2 in the tube is transferred to a small vial where the hexachlorobutadiene is desorbed with hexane.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The height of the resulting peak is determined and compared with the peak heights obtained from the injection of standards.

2. Working Range, Sensitivity, and Detection Limit

2.1 The sampling and analytical method was tested with nominal sample loadings of 20 to 6000 ng of hexachlorobutadiene per 100-mg bed of XAD-2. The samples were collected from atmospheres containing hexachlorobutadiene in the approximate range of 10 to 2000 μg/m³ at 25 to 28 °C and at a relative humidity of 90% or greater.

2.2 The slope of the analytical calibration curve was 5×10^{-13} A/pg when peak heights were plotted as a function of the amount of hexachlorobutadiene injected. (There was a slight curvature in the calibration curve. See Section 9.)

2.3 The lowest analytically quantifiable level for this method was determined to be 20 ng of hexachlorobutadiene per sorbent sample extracted with 2.00 mL of hexane. At this level, the relative standard deviation for replicate samples was found to be less than 3%, and desorption was quantitative. The instrumental detection limit was

0.8 ng/mL of hexachlorobutadiene in hexane; the relative standard deviation of replicate determinations of standards at this level was 10%.

3. Interferences

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

3.2 Any substance that has the same retention time as hexachlorobutadiene with the gas chromatographic operating conditions described in this method is an interferent. Therefore, retention time data on single or multiple columns cannot be considered proof of chemical identity.

3.3 If the possibility of interference exists, separation conditions (column packing, temperature, carrier flow, detector, etc.) must be changed to circumvent the problem.

3.4 The gas chromatographic operating conditions described below will separate tetrachloroethylene, hexachloroethane, 1,2,4-trichlorobenzene, hexachlorocyclopentadiene, octachlorocyclopentene, and 4-chlorobiphenyl from hexachlorobutadiene. These compounds are among those likely to be collected along with hexachlorobutadiene in air (see Reference 11.1).

4. Precision and Accuracy

4.1 For the overall sampling and analytical method, the pooled relative standard deviation was 9% for 24 sorbent samples collected in the approximate range of 10 to 2000 μg/m^3. The pooled relative standard deviation for the analytical method was 3.3% for 18 sorbent samples spiked with 4 to 33 ng of hexachlorobutadiene and stored for 7 d. For 12 sorbent samples spiked with 4 or 3000 ng and stored overnight the pooled relative standard deviation for the analytical results was 1.1%.

4.2 The concentration of hexachlorobutadiene in test atmospheres was determined in control experiments by sampling the bubblers containing hexane and subsequently analyzing the bubbler solutions by gas chromatography. The determinations with sorbent sampling gave values that averaged 93% of those found by bubbler sampling over the range of the method.

4.3 The breakthrough volume of the sorbent tube was found to be greater than 100 L with a sampling rate of 0.2 L/min at a hexachlorobutadiene concentration of 10 mg/m^3, a sampling temperature of 25 to 28 °C, and a relative humidity greater than 90%. Elevation of the sampling temperature to 38 °C significantly reduced the capacity; however, the breakthrough volume of a 100-mg sorbing section was still estimated to be greater than 100 L at a hexachlorobutadiene concentration of about 1 mg/m^3 and a relative humidity of about 50%.

4.4 Samples of hexachlorobutadiene on XAD-2 were found to be stable at 25 °C for 7 d and for 28 d if stored at 0 °C after the seventh day. These samples were stored in the dark.

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 gas chromatographic procedure. The samples are analyzed by means of a quick instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the capacity of the XAD-2 tube. When the sample value obtained for the backup section of the XAD-2 tube exceeds 20% of that found on the front section, the possibility of sample loss exists. During sample storage the analyte may migrate throughout the tube until equilibrium is reached; however, no migration of 20- to 30-ng amounts of hexachlorobutadiene was observed after storage for 28 d when the samples were refrigerated (0 °C) after the seventh day.

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

6. Apparatus

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

6.2 XAD-2 tubes: Pyrex tubes, 7 cm long with a 6 mm o.d. and a 4 mm i.d. containing two sections of Amberlite XAD-2 (20/50 mesh)—a 100-mg sorbing section and a 50-mg backup section—held in place with three silylated glass wool plugs. The tubes are constricted slightly about 1 cm from the outlet end to facilitate the packing of the tube with sorbent material. The ends of the tubes are sealed with Teflon tape and then with plastic caps to prevent contamination during storage. The pressure drop across a typical sorbent tube is less than 4 in. H_2O at 25 °C, 1.0 kPa, at a sampling rate of 0.2 L/min. During the preparation of sorbent tubes, avoid undue agitation of the sorbent particles. A static charge can be induced that will cause the particles to agglomerate. This may reduce the capacity of the sorbent tube.

6.3 Purified XAD-2 (available from Applied Science Laboratories, Inc.) is used to pack the tubes without further treatment. If the purified XAD-2 is unavailable, gram quantities of the XAD-2 should be cleaned by Soxhlet extraction as follows:

- Extract with an acetone-methanol mixture (80:20) for 4 h.
- Extract with hexane for 4 h.

- Dry the sorbent material under vacuum at 50 to 75 °C overnight.

- Cool and store in a clean desiccator.

(If 2-mL hexane extracts of 100-mg amounts of the washed XAD-2 yield anomolous peaks in the GC analysis procedure, repeat the cleaning procedure.)

6.4 Gas chromatograph equipped with a ^{63}Ni electron capture detector.

6.5 Glass GC column (4 mm i.d. by 2 m long) packed with 3% OV-1 on Gas-Chrom Q (100/120 mesh).

6.6 Vials, 5 mL, with serum caps containing Teflon-lined silicone rubber septa.

6.7 Microliter syringes, 10 µL and convenient sizes for making dilutions.

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

6.9 Glass wool, silanized.

6.10 Ultrasonic bath.

7. Reagents

All reagents used should be ACS Reagent Grade or better.

7.1 Hexane, spectroquality.

7.2 Hexachlorobutadiene, 98% or purer.

7.3 A mixture of 5% methane and 95% argon (or other appropriate carrier and purge gas for the electron capture detector).

8. Procedure

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

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, open the ends of the tube by removing the plastic caps and Teflon tape. Examine the ends of the tube to ensure that the openings are at least one-half the internal diameter of the tube (2 mm).

8.2.2 Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of XAD-2 is the backup layer and is positioned nearest the sampling pump.

8.2.3 Place the XAD-2 tube in a vertical position during sampling to prevent channeling through the tube.

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

8.2.5 Measure and report the flow rate and time or volume sampled. The sample is taken at 0.05 to 0.2 L/min. The maximum volume sampled should not exceed 100 L at 0.2 L/min at temperatures near 25 °C. At high humidity (>90%) accompanied by temperatures near 40 °C, do not sample more than about 50 L.

8.2.6 The temperature and pressure of the air being sampled are measured and reported.

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

8.2.8 For every 10 samples taken, process one XAD-2 tube not exposed to hexachlorobutadiene in the same manner as the samples (break, seal, and transport). Do not sample air through this tube. The tube should be labeled as a blank.

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

8.2.10 Ship 6 to 12 unopened XAD-2 tubes so that desorption efficiency studies can be performed on the same type and lot of XAD-2 used for sampling.

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

8.3 Analysis of Samples

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

8.3.2 Desorption of Samples. After the two sections of a tube are transferred to small vials, pipet 2.00 mL of hexane into the vial containing the sorbing section and 1.00 mL into the vial containing the backup layer. Crimp a serum cap into place immediately after the hexane has been added. Extract the sealed sorbent samples by ultrasonification for 1 h at room temperature.

8.3.3 GC Conditions

- Carrier flow, 30 mL/min.
- Purge flow, 80 mL/min.
- Injection port temperature, 150 °C.
- Detector temperature, 250 °C.
- Column temperature, 135 °C.

8.3.4 Injection. Inject a 5-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 5-μL aliquot.

8.3.5 Measurement of Peak Height. Multiply the peak height by the attenuator setting necessary to keep the peak on scale. Determine the apparent concentration from a standard curve prepared as discussed in Section 9. If the peak height indicates an apparent concentration above 100 ng/mL, dilute the sample solution appropriately for reanalysis.

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound may vary between laboratories and batches of XAD-2. Also, for a given batch of XAD-2 the desorption efficiency may vary with the weight of contaminant adsorbed. (The XAD-2 used for the study of this method gave a desorption efficiency of 1.000 for a loading of 16.7 ng of hexachlorobutadiene on a 50-mg bed of sorbent material.)

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third is an intermediate level. Dissolve hexachlorobutadiene in hexane to give stock solutions with concentrations such that 20 to 6000 ng of hexachlorobutadiene will be injected onto the sorbent in no more than 5 μL of a stock solution. Place XAD-2 in an amount equivalent to that found in the larger section of the tube (100 mg) in a small vial and cap the vial. Inject an aliquot of the appropriate stock solution into the vial. Allow each vial to stand overnight to assure complete adsorption of hexachlorobutadiene onto the XAD-2. Prepare standards by injecting an identical amount of hexachlorobutadiene solution into 2.00 mL of hexane. Analyze the samples and standards as described in Section 8.3.

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

9. Calibration and Standardization

CAUTION: Hexachlorobutadiene has been identified as a suspect carcinogen. Precautions must be taken while handling this compound to prevent contamination of personnel and the working area.

To make a stock standard solution, dilute 1.00 mL (1.67 g) of hexachlorobutadiene to 100 mL with hexane. By serial dilution with hexane prepare a series of working standards varying in concentration over the range of 1-100 ng/mL. Follow the dilution scheme presented below:

Initial concn	Aliquot volume, mL	Final diluted volume, mL	Final concn
1.67 g/mL	1	100	16.7 mg/mL
16.7 mg/mL	1	100	167 μg/mL
167 μg/mL	1	100	1.67 μg/mL
1.67 μg/mL	1	10	167 ng/mL
167 ng/mL	1	10	16.7 ng/mL
167 ng/mL	2	10	33.4 ng/mL
167 ng/mL	4	10	66.8 ng/mL
167 ng/mL	6	10	100.2 ng/mL
16.7 ng/mL	2	25	1.34 ng/mL
16.7 ng/mL	5	10	8.35 ng/mL

Analyze the standard solutions under the same GC conditions and during the same time period as the samples. Alternate standards and samples during the analysis. To establish a calibration curve plot the concentration of the standards in ng/2 mL (or ng/sample) versus peak height. The plot has a slight curvature but the deviation from linearity is small below a concentration of 100 ng/mL (200 ng/2 mL). To ensure accurate analyses, determine standards at concentrations about 25% above and below the apparent sample concentration.

10. Calculations

10.1 Read the sample weight in ng from the standard curve.

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

$$W_F = W_s - W_b$$

where: W_F = corrected amount (ng) on the front section of the XAD-2 tube.

W_s = amount (ng) found on the front section of the XAD-2 tube.

W_b = amount (ng) found on the front section of the blank XAD-2 tube.

Follow a similar procedure for the backup section.

10.3 Make a correction for desorption efficiency as follows:

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

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

W_F = amount (ng) after blank correction.

D = desorption efficiency corresponding to the weight W_F.

Calculate the corrected amount on the backup section, M_B, similarly.

10.4 Express the concentration, C, of hexachlorobutadiene in the air sampled in µg/m³, which is numerically equal to ng/L.

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

where: M_F = amount (ng) of hexachlorobutadiene found on front section.

M_B = amount (ng) of hexachlorobutadiene found on backup section.

V = volume (L) of air sampled.

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

$$C(\text{ppb}) = C(\text{ng/L}) \times \frac{24.45}{260.76} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled.

T = temperature (°C) of air sampled.

24.45 = molar volume (L/mol) at °C and 760 torr.

260.76 = molecular weight ($\underline{M}_r$) of hexachlorobutadiene.

11. References

11.1 Dillon, H. K. "Research Report for Hexachlorobutadiene"; September 7, 1979; NIOSH Contract 210-78-0012; Southern Research Institute: Birmingham, Alabama.

11.2 Taylor, D. G.; Kupel, R. E.; Bryant, J. M. "Documentation of the NIOSH Validation Tests"; National Institute for Occupational Safety and Health; Cincinnati, Ohio, April 1977. DHEW (NIOSH) Publication No. 77-185.

H. Kenneth Dillon, Ph.D., CIH
Southern Research Institute
NIOSH Contract No. 210-78-0012

APPENDIX 5

NIOSH SAMPLING DATA SHEET NO. 307 Class B

June 28, 1979

Substance

Hexachlorobutadiene

Standard

A standard has not been established.

Analytical Method

A known volume of air is drawn through an Amberlite XAD-2 tube to trap the hexachlorobutadiene (HCBD) vapor present. The analyte is desorbed from the sorbent with hexane, and an aliquot of the solution is analyzed with a gas chromatograph with an electron capture detector. The front and rear sections of the sorbent tube are analyzed as individual samples. The rear section is used as a breakthrough indicator. The supporting analytical method has been evaluated for sample loadings between 4 and 3000 ng per sorbent tube. The complete sampling and analytical method has been tested with air containing about 10-2000 $\mu g/m^3$ of HCBD at 25 to 28 °C and at a relative humidity of 90% or greater. Details are provided in Reference 2.

Sampling Equipment

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

2. XAD-2 tubes: Pyrex tubes, 7 cm long with a 6 mm o.d. and a 4 mm i.d. containing two sections of solvent-extracted Amberlite XAD-2 (20/50 mesh)—a 100-mg sorbing section and a 50-mg backup section—held in place with silylated glass wool plugs. The tubes are constricted slightly about 1 cm from the outlet end to facilitate the packing of the tube with sorbent material. The ends of the tubes are sealed with Teflon tape and then with plastic caps to prevent contamination during storage. The pressure drop across a typical sorbent tube is less than 4 in. H_2O at a sampling rate of 0.2 L/min.

Sample Size

The recommended sample size should not exceed 100 L at 0.2 L/min at temperatures near 25 °C. At high humidity (>90% R.H.) accompanied by temperatures near 40 °C, do not sample more than about 50 L.

Sampling Procedure

1. Immediately before sampling, open the ends of the tube by removing the plastic caps and Teflon tape. Examine the ends of the tube to ensure that the openings are at least one-half the internal diameter of the tube (2 mm).

2. Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of XAD-2 is the backup layer and is positioned nearest the sampling pump.

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

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

5. Measure and report the flow rate and time or volume sampled. The sample is taken at 0.05 to 0.2 L/min.

6. The temperature and pressure of the air being sampled are measured and reported.

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

8. For every ten samples taken, process one sorbent tube in the same manner as the samples (break, seal, and transport). Do not sample air through this tube. The tube should be labeled as a blank.

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

10. Ship 6 to 12 unopened sorbent tubes so that desorption efficiency studies can be performed on the same type and lot of XAD-2 used for sampling.

Special Considerations

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

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

3. High humidity in conjunction with temperatures near 40 °C may reduce the breakthrough volume to less than 100 L. Under these sampling conditions, reduce the maximum sampling volume to about 50 L. If the sorbent material becomes coated with water, the analyte will not be trapped quantitatively.

Bulk Samples

If bulk samples of material containing HCBD 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 sorbent tubes.

Shipping Instructions

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

References

1. Hexachlorobutadiene, NIOSH Method P&CAM 307.

2. Dillon, H. K. "Research Report for Hexachlorobutadiene"; September 7, 1979; NIOSH Contract 210-78-0012; Southern Research Institute: Birmingham, Alabama.