EVALUATION OF PASSIVE SAMPLING DEVICES (PSD's)

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing importance to EPA. The passive personal monitors evaluated in this study are possible candidate devices to be employed in future exposure monitoring studies. Such devices presently are being employed in industrial hygiene and have many characteristics which make them potentially very useful in ambient air investigations. However, since the requirements for ambient air monitoring are more stringent than those for industrial hygiene, the present investigation was undertaken to obtain an independent evaluation of a particular passive dosimeter developed for EPA by the Monsanto Research Corporation. A key goal of the program was to develop a sound understanding of the sampling performance of this device to serve as a basis for valid use of the passive monitors in ambient exposure monitoring.

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ABSTRACT

The basic objectives of this study were to evaluate the performance of
the EPA passive sampling device (PSD) for sampling of ambient level volatile
organic compounds (VOC's); to develop an understanding of the mechanics of
passive sampling using reversible adsorption; and to apply this understanding
to development of an improved PSD that is usable for sampling of VOC's over
periods of 8 to 24 hours. Laboratory and limited field evaluations of the
standard and modified PSD's were conducted and a model relating sorbent
properties and device design to sampling rates was developed. The results
show the standard PSD's to be useful for sampling of VOC's having large
retention volumes. Modified PSD's having greatly reduced sampling rates show
promise for sampling compounds having retention volumes as low as 5 to 10 L/g
over 8 to 24 hour sampling periods. The use of Spherocarb as an alternative
sorbent to Tenax® GC also was investigated as a means for improving the
performance of the PSD. This sorbent was found to be unsuitable because of
the high temperatures required for desorption. It is recommended that the
model which was developed be used for developing sampling plans for specific
applications, and that more extensive field evaluation of the reduced-rate
PSD's be conducted.

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SECTION 1

INTRODUCTION

In recent years, there has been an increased awareness of the need for monitoring individual or personal exposures to pollutants and toxic chemicals. This awareness has prompted the development of a variety of personal sampling devices including battery-driven pump systems, passive systems having high specificity for individual compounds, and generalized passive systems intended for the collection of volatile organic compounds. Within this latter category, the primary commercial emphasis has been on the use of carbon-based sorbents for monitoring of the relatively high concentrations of contaminants found in industrial workplaces. In two earlier programs for the Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (RTP), Battelle's Columbus Laboratories (BCL) explored the problems and limitations of using commercially available passive devices for monitoring ambient level organic chemicals. In addition, a detailed evaluation was made of the performance of one of these devices under simulated ambient conditions (1-2).

Results of these earlier studies have shown that the commercially available carbon-based devices are satisfactory for ambient monitoring of selected volatile organic compounds under some conditions, but they are by no means completely general in their applicability under realistic ambient conditions. For example, their performance is impaired under conditions of high relative humidity. The Environmental Monitoring Systems Laboratory therefore has undertaken, under separate contract with the Monsanto Research Corporation (MRC), the development of a passive sampler that is not subject to the same restrictions as the commercially available devices. The basic concept involved in the development of this new device has been to employ relatively hydrophobic porous polymer sorbents in order to evolve a system that is readily subject to thermal desorption for analysis. While much of the initial work with this device has been conducted using Tenax® GC as the sorbent, the fundamental applications concept is flexible to permit the use of other porous polymer sorbents, or even activated carbon, as may be required for specific applications.

This report addresses the findings of three Work Assignments conducted consecutively at BCL. The primary objective was an independent evaluation of the applicability of the MRC passive sampling device (PSD) with respect to monitoring of volatile organic compounds (VOC's) under ambient conditions. In the first Work Assignment, sampling rates were determined for chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, tetrachloroethylene, benzene, and chlorobenzene. A general model of passive sampling

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using thermally reversible adsorption also was developed. The second Work Assignment then was conducted to extend the list of chemicals to include acrylonitrile, 1,1-dichloroethylene, trichlorotrifluoroethane, 1,2-dichloro-ethane, α-chlorotoluene, and hexachlorobutadiene, and to test the general applicability of the performance model. In the third Work Assignment, the general precepts of the performance model were applied for the purpose of modifying the PSD to enable long-term (8-24 h) sampling of VOC's. Results of the first two work assignments and some of the developmental work performed by MRC are summarized in two papers accepted for publication in the January 1985 issue of Analytical Chemistry (3,4).

SECTION 2

OBJECTIVE

The basic objective of Work Assignment No. 13 was to provide an independent assessment of the efficacy of the MRC passive dosimeter. This assessment was to include:

1. Evaluation of dosimeter sampling rates and sampling precision at ppbv concentration levels.

2. Evaluation of the effect of air velocity on the sampling rate.

3. Evaluation of the effect of humidity on the sampling rate.

The basic objective of Work Assignment No. 21 was to:

1. Extend the body of information on sampling rates of the MRC dosimeter by consideration of ten additional compounds.

2. Evaluate the general applicability of the sampling performance model developed under WA-13.

The basic objective of Work Assignment No. 33 was to improve the overall performance of the PSD for sampling of volatile organic compounds by:

1. Replacement of the Tenax® GC sorbent with Spherocarb and/or

2. Redesign of the physical structure of the device.

A specific goal of Work Assignment No. 33 was to achieve accurate sampling of volatile organics for time periods of 8 to 24 hours.

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of this work, it is concluded that the EPA PSD's offer some distinct advantages over other available passive sampling devices for sampling ambient level volatile organic compounds. Thermal desorption of collected samples provides more than adequate amounts of sample for use with conventional GC and GC/MS analytical procedures. In addition the independence of these devices from high relative humidities yields more flexible field applicability than the commercially available devices using activated carbon. Finally, the Tenax® GC can be replaced easily with other sorbents for customized sampling applications. However, the PSD's should not be utilized without strict attention to the mechanics of reversible adsorption and their implications with the respect to particular sampling requirements. Specifically:

(1) The standard EPA PSD's can be used for sampling ambient levels of VOC's, but careful attention must be paid to the retention volumes of target compounds and the appropriate sampling period. In general, the standard PSD's are useful for chemicals having large retention volumes (>100 L/g), but can be used for only short sampling periods (a few hours or less) for compounds having small retention volumes.

(2) Reduced rate PSD's having nominal sampling rates of the order of 2.5 cc/min show promise for applications requiring the sampling of VOC's over extended periods of 8 to 24 hours. However, these reduced rate devices should not be used for compounds having retention volumes less than about 5-10 L/g. The current results also indicate potential blank problems with the use of the reduced rate devices over short sampling periods.

(3) In any case, the time-weighted average sampling rate for a particular sampling requirement should be estimated using the model presented in this report and should be used as a guide in designing the sampling plan for a particular application. In general, rates significantly less than about 70-80 percent of the initial rate (R_o) may indicate potential sampling error.

(4) The model of PSD performance presented in this report has been shown to correctly represent the effects of retention volume, sampling time, and air velocity on the effective time-weighted average sampling rates of the EPA PSD's.

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(5) The use of Spherocarb in the EPA PSD's may offer some advantages for sampling of a few selected VOC's, but general use of this sorbent is not recommended because of problems associated with the high temperatures needed for desorption. Contamination of the sorbent by unpyrolyzed polymer presents some special difficulties with cleanup and preparation of Spherocarb for use in the PSD's.

(6) Because the EPA PSD's are not affected by high humidities, they are not subject to the same limitations as the commercially available devices based on activated carbon.

(7) Protective shields developed for the EPA PSD's on this program can provide protection against contamination during handling of the devices in the field without significantly affecting their sampling rates.

(8) Blank contamination of the EPA PSD's has generally not been a problem, but a few instances of such have been observed. In recognition of the fact that the PSD's may not always be handled by trained laboratory personnel in the field, it is recommended that a formalized procedure and containment system be developed for cleanup and protection of the PSD's.

(9) It is recommended that further field testing of the reduced rate PSD's be considered.

(10) Investigation of the application of the EPA PSD to sampling of pollutants other than VOC's (e.g., NO_2, volatile polar organics, etc.) is recommended to take advantage of the capacity for use of different sorbents with this device.

SECTION 4

EXPERIMENTAL METHODS AND PROCEDURES

APPROACH

The experimental approach involved procedures very similar to those previously used (1-2) in evaluating commercially available passive dosimeters. In brief, the PSD's were exposed to mixtures of volatile organic compounds at ppbv concentration levels under well-controlled conditions. Exposure levels were monitored by two independent methods, direct GC analysis and active (pumped) sampling using Tenax® GC traps. Inasmuch as validated reference sampling rates were not available for the devices, apparent sampling rates based on the amounts of each chemical adsorbed and exposure times were used as a basis for comparison of PSD performance.

PASSIVE SAMPLING DEVICES

The EPA PSD is a cylindrical stainless steel (SS) sorbent container with a double layer of fine mesh SS screen fitted into each end of the cylinder. The volume between the screens is sufficient to permit filling with about 0.4 g of Tenax® GC. The screens serve as a diffusion barrier, and their dimensions determine the effective sampling rate of the device. An expanded view of the PSD is shown in Figure 1; critical dimensions of the device are shown for one face in Figure A-2 in Appendix A. The device is designed so that either one face or both faces can be exposed, as dictated by the sampling rate requirements. In use, the device is mounted in a circular ring clamp that is fitted with a spring clasp for attaching the device to the subject's clothing. After exposure, the ring clamp can be removed and the assembly can be stored in metal containers prior to analysis. For analysis, the device is placed in a close fitting desorption oven for thermal desorption and analysis by gas chromatography.

For this study, it was decided that prolonged storage was not necessary, and the exposed devices were mounted directly into desorption holders. Each holder consisted of two threaded SS halves with an internal O-ring seal and quick-disconnect fittings, as shown in Figure 2. Each dosimeter then was contained within its own holder at all times except during exposure. Several O-ring materials including Teflon, Kelrez, and Viton were tried during the program, with most of the work being conducted using Teflon O-rings. In all cases, the O-rings were baked out prior to use.

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CAP

STAINLESS STEEL
RETAINER RING

STAINLESS STEEL
PERFORATED PLATE

200 MESH
STAINLESS STEEL
DIFFUSION SCREEN

SORBENT
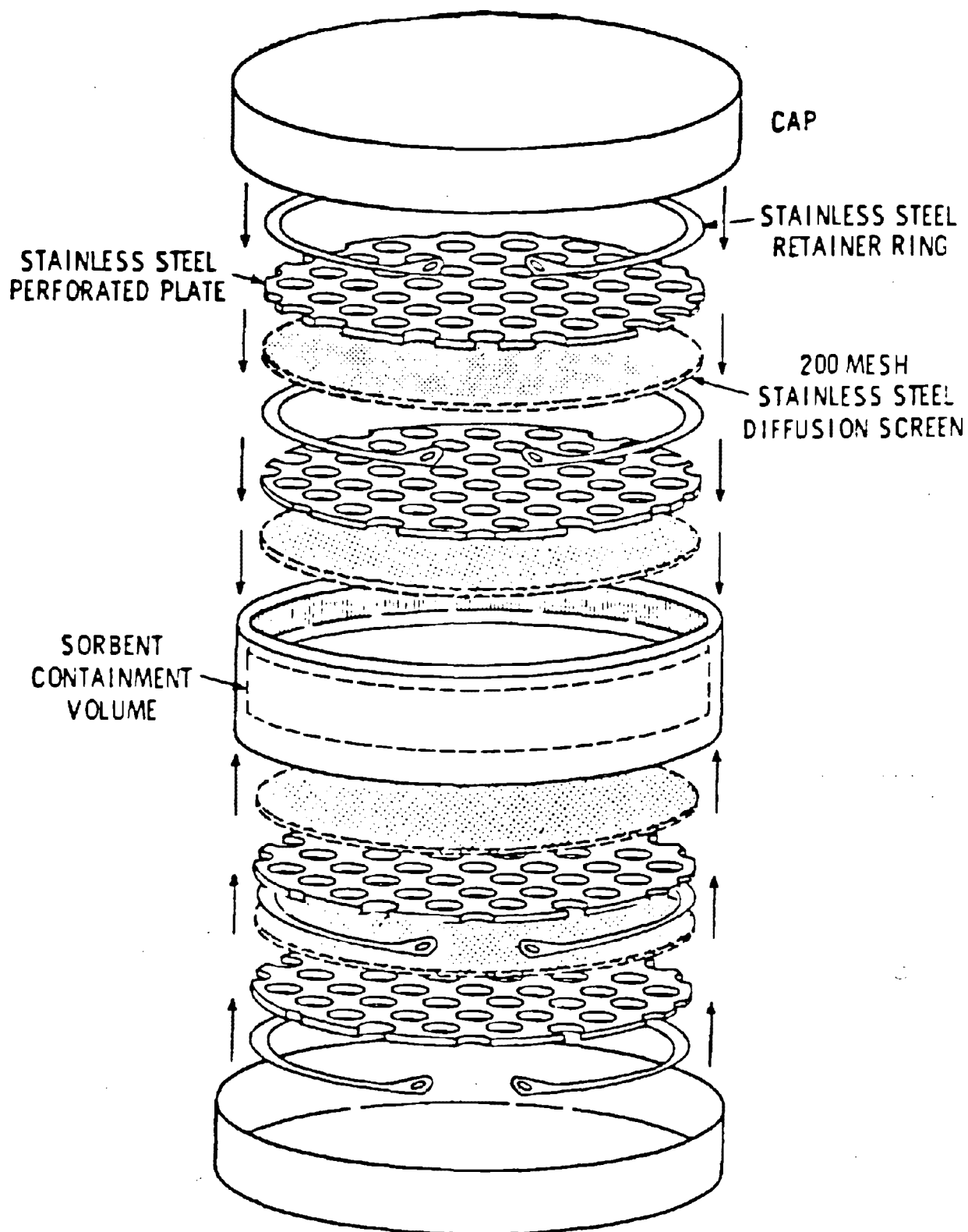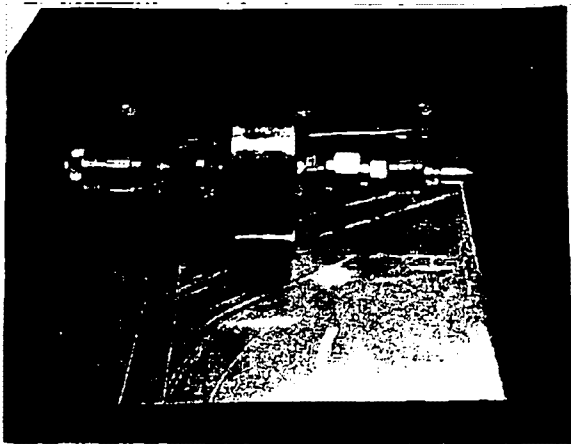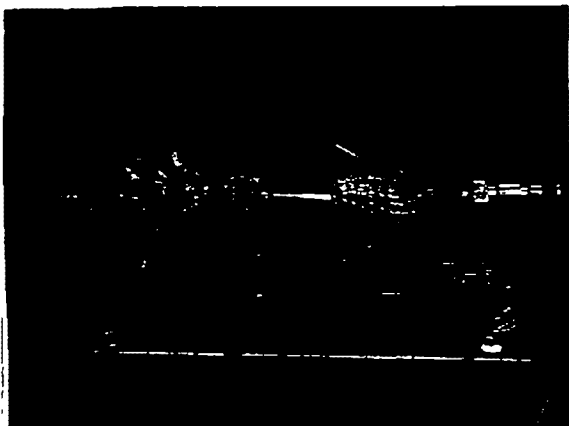CONTAINMENT
VOLUME

Figure 1.   EPA thermally desorbable passive dosimeter.

2a. PSD holder,
     closed for use

2b. PSD holder,
     open

2c. Tenax trap

2d. High temperature holder

Figure 2. Device holders.

The standard desorption holder described above could not be used for the experiments conducted with Spherocarb because of the high temperatures (350-450 C) needed for desorption of this sorbent. For those experiments, the special high temperature desorption holder shown in Figure 2d was used. This unit was constructed from a standard 1.5 in. stainless steel Swaglok cap and plug assembly. An annular shim was added to the inside of the assembly to provide a snug fit with the PSD, and the internal surfaces of the assembly were plated with nickel. The gas inlet tube was coiled flush with the top of the assembly so that the inlet gas was well-heated before contacting the PSD. Heating was provided by a commercially available ring heater of the same type used with the standard desorption holders. Inlet and outlet tubes were fitted with quick-disconnect fittings similar to those used with the standard holders. The total assembly provided a leak proof desorption holder that was capable of operation at temperatures as high as 700 C.

TENAX® GC TRAPS

Exposure dosages for the PSD's were monitored both by direct GC analysis of the test mixtures and by active sampling of the test gas using Tenax® GC traps. The traps for this purpose consisted of 5-inch sections of 1/4 inch O.D. SS tubing that were fitted on both ends with quick-disconnect fittings (see Figure 2c). The tubes were filled with approximately 1/3 g 60/80 mesh Tenax® GC, with glass wool plugs at the tube ends. During use, the traps were "plugged in" to the test chamber and were pumped at rates of 10 to 20 cc/min, with the actual rates for each run being measured by a soap-bubble flowmeter. Traps were always run in duplicate, and, in some cases, backup traps were used to test for breakthrough. In most cases, the total volume of gas sampled per trap was less than 2000 cc, and no breakthrough was detected. However, in some multiple hour exposure runs conducted later in the program, the retention volumes of several chemicals were exceeded. In these cases, primary emphasis was placed on the results of the direct analyses.

TRAP AND PSD CLEANUP

The routine procedure used for preparation of both Tenax® GC traps and the PSD's consisted of heating overnight at 200 C with zero-nitrogen (ZN2) flowing through the devices. Spherocarb-filled PSD's were heated at 450 C. Cleanup was always performed during the night directly preceding use of the devices. Blank contamination by compounds of interest was not detected on the Tenax® GC devices but was a problem with Spherocarb.

TRAP AND BADGE ANALYSIS

From an analytical viewpoint, the PSD's differ from most commercially available passive devices in that the entire amount of thermally desorbed sample (as opposed to an aliquot of solvent desorbed sample) is available for a single pass analysis. This means that the extreme detection sensitivity required for analysis of ambient samples collected on conventional passive

dosimeters is not needed or necessary for analysis of the PSD's. Conversely, if a highly sensitive detection system, such as a series combination of electron capture (ECD) and photoionization (PID) detectors is used, the PSD sample must be split in order to avoid detector saturation. Indeed, when the PSD is used to sample ppbv levels of volatile organic chemicals, it is advisable that less sensitive detectors, such as the flame ionization detector (FID), be operated at reduced sensitivity levels in order to avoid overly complex chromatograms caused by the myriad of minor components that are always present in ambient air samples.

In the current work, both a split sample approach and a whole sample analysis approach at reduced sensitivity were used with different groups of samples. The split sample approach was used with experiments with the first set of compounds, and the whole sample analysis was used for the second set of chemicals. Both approaches have faults; the use of a splitter requires special care in the characterization and/or elimination of selective splitting of the sample components, and the large amounts of sample available for whole sample analysis can cause retention time shifts that confound component identification. Although we obtained more consistent and reproducible results with the whole sample approach for laboratory samples of known composition, some procedure involving subdivision of the sample may be necessary for ambient field samples. The procedures used are discussed individually below.

Split Sample Analysis

Traps and PSD's, in their holders were analyzed by identical procedures. First, they were checked for leakage of the holders by slight pressurization with GC carrier gas (ZN2). They were then heated to approximately 175 C and were plugged into the injection port of the GC using an O-ring-free quick disconnect fitting. Desorption was allowed to proceed for 5 minutes while flushing the sample with carrier gas. The desorbed sample was passed through a variable splitter and the sample was then cryofocused onto a fused silica capillary column maintained at -60 C. In some cases, a separate detector was used to monitor the unused splitter effluent. The output of that detector indicated that desorption was essentially complete within two minutes.

A Varian Model 3700 gas chromatograph equipped with three detectors (ECD and PID in series and FID in parallel) and coupled to three integrators was used for analysis. In the early experiments using the split sample approach, the FID was disconnected so that the sample components passed through only the ECD/PID pair. A pair of 50m fused silica capillary columns coated with SE-30 was used for component separation. One of these columns was operated in a splitless mode in conjunction with a 10cc gas sampling loop for analysis of test gas samples. The other column was connected to the inlet splitter, and both columns were common at the detector inlet. Split ratios of 150-200:1 were commonly used for PSD and trap analyses. Dual chromatograms obtained with the ECD/PID setup are shown in Figure 3a.
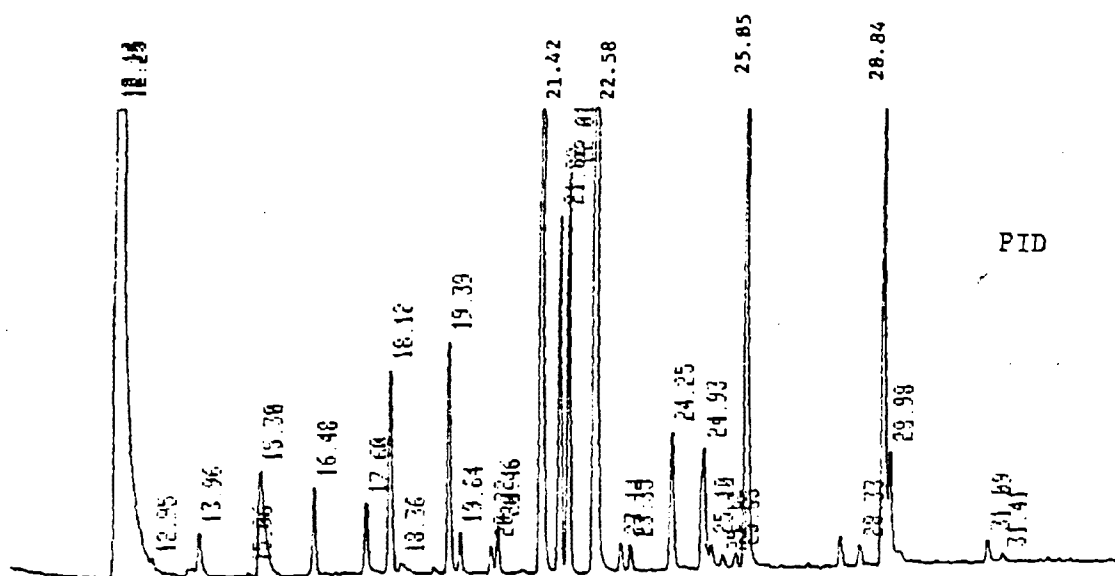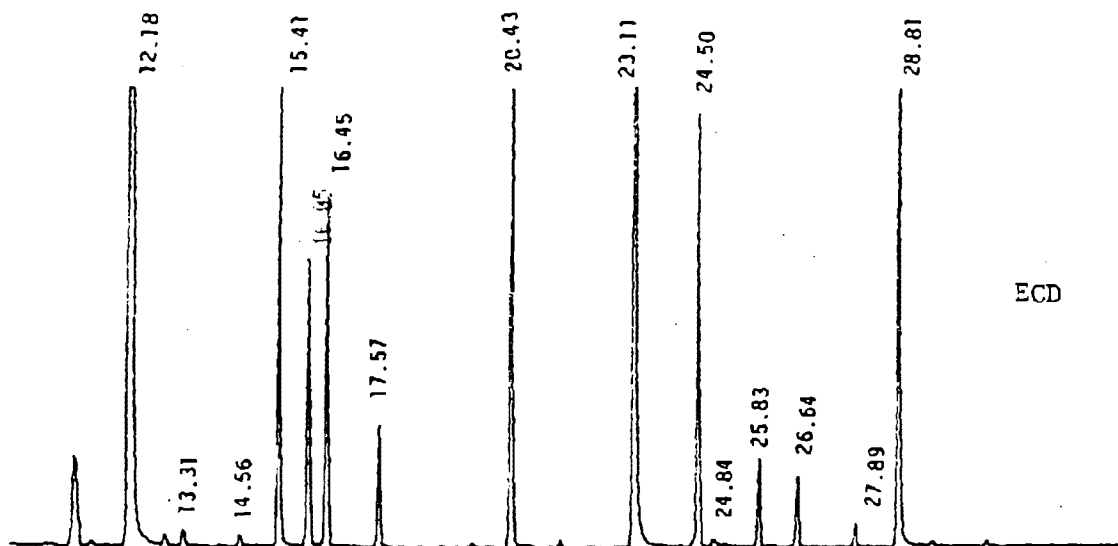
Sample: Spiked air
Run Conditions: Volume = 10cc
                  Column = 50m fused silica capillary
                  Flow Rate = 1 cc/min @ 25 C
                  Temperature = 5 min @ -60 C; 8 C/min to 150 C
Output Key: see Table 1

Figure 3a.   Dual chromatogram of gas sample.

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TABLE 1. KEY TO CHEMICALS IN FIGURE 3a

Chemical	Retention Time, min.	Decector[a] ECD	PID	Approximate[b] Concentration, ppbv	DL, ppbv
Chloroform	15.41	X	–	130	0.08
1,1,1-Trichloro-ethane	16.05	X	x	25	0.02
Carbon tetrachloride	16.45	X	–	4	0.005
Trichloro-ethylene	17.57	X	X	23	0.06
Tetrachloro-ethylene	20.43	X	X	27	0.01
1,1,2,2-Tetra-chloroethane	23.11	X	x	>58	(0.01)
1,1,1,2-Tetra-chloroethane	24.50	X	x	(27)	(0.01)
p-dichloro-benzene	24.84	x	–	–	–
o-dichloro-benzene	25.83	X	–	–	–
1,3,5-trichloro-benzene	27.89	x	–	–	–
1,2,4-trichloro-benzene	28.81	x	–	–	–
Benzene	16.48	–	X	3.6	0.1
Methylcyclo-hexane	20.46	–	x	–	–
Toluene	19.39	–	X	(10)	(0.1)
Chlorobenzene	21.42	–	x	36	0.13
Ethylbenzene	21.82	–	X	(15)	(0.1)
m&p-xylene	22.01	–	X	(16)	(0.1)
p-ethyltoluene	24.25	–	X	(6)	(0.1)
1,2,4-trimethyl-benzene	28.84	–	X	(37)	(0.1)

(a) X = good response; x = fair response; – = poor response.
(b) Estimated concentrations and detection limits in parentheses; – indi-cates no basis for estimate.

Whole Sample Analysis

For whole sample analyses, desorption and column loading were conducted in two steps. PSD's and traps were first desorbed into a cryogenic (LAr) trap, which was then flash heated for loading onto a cooled (-60 C) column. The same GC noted above was used, but a fixed splitter was used to divert approximately 90 percent of the column effluent to the FID. In contrast to results obtained with the inlet splitter (see Results Section) repeated tests of this outlet splitter showed no evidence of selective splitting. With this arrangement, the FID output was used for component quantification, and the ECD/PID outputs were used solely as an aid for component identification. An annotated chromatogram obtained with this system is shown in Figure 3b.

CHAMBER TEST PROCEDURES

Test Chamber

The chamber used for device exposure studies is shown in Figure 4. This chamber is a 200-L glass chamber constructed from two opposing bell jars that are joined to a central anodized aluminum ring. This ring is provided with numerous ports for loading, sampling, monitoring devices, etc. Stirring within the chamber is achieved using a completely sealed internal fan that is magnetically coupled to an external variable speed drive unit. For the current experiments, a stainless steel shroud and swirl dampener was placed over the fan in order to achieve well-directed flow within the chamber and a uniform flow pattern in the vicinity of the devices.

Devices were loaded into the chamber using the sample holder shown in Figure 5. This holder is a stainless steel cylinder with a central rod for attachment of the passive devices. For any experiment, the devices could be attached to the holder under a protective clean atmosphere; the cylinder was closed and was flushed with zero nitrogen; and the cylinder was inserted into the chamber, with one end locked in place while the other end protruded through a seal in the aluminum ring. The concentrations of test species could then be adjusted in the chamber without exposure of the PSD's. At the start of a chamber exposure, the outer shell of the cylinder was partially withdrawn through the seal, leaving the PSD's suspended from the central rod. At the completion of the run, this procedure was reversed, and the entire assembly was removed to a glove bag for disassembly and preparation of the collectors for analysis.

Prior to each chamber run, the chamber was thoroughly flushed with zero nitrogen and gas analyses were made by GC to confirm the initial condition of the chamber. Addition of the test species was made by direct injection of an appropriate liquid or gas mixture of the pure chemicals. Dilution then was carried out in the chamber as needed to obtain the desired concentrations. Once loaded, the chamber was operated in a dynamic mode with about 50 cc/min of gas being removed for GC analysis and appropriate makeup gas being added to maintain the chamber at about 0.25 cm H_2O above ambient pressure.

Figure 3b. Sample chromatogram of second series of chemicals (FID Detector).

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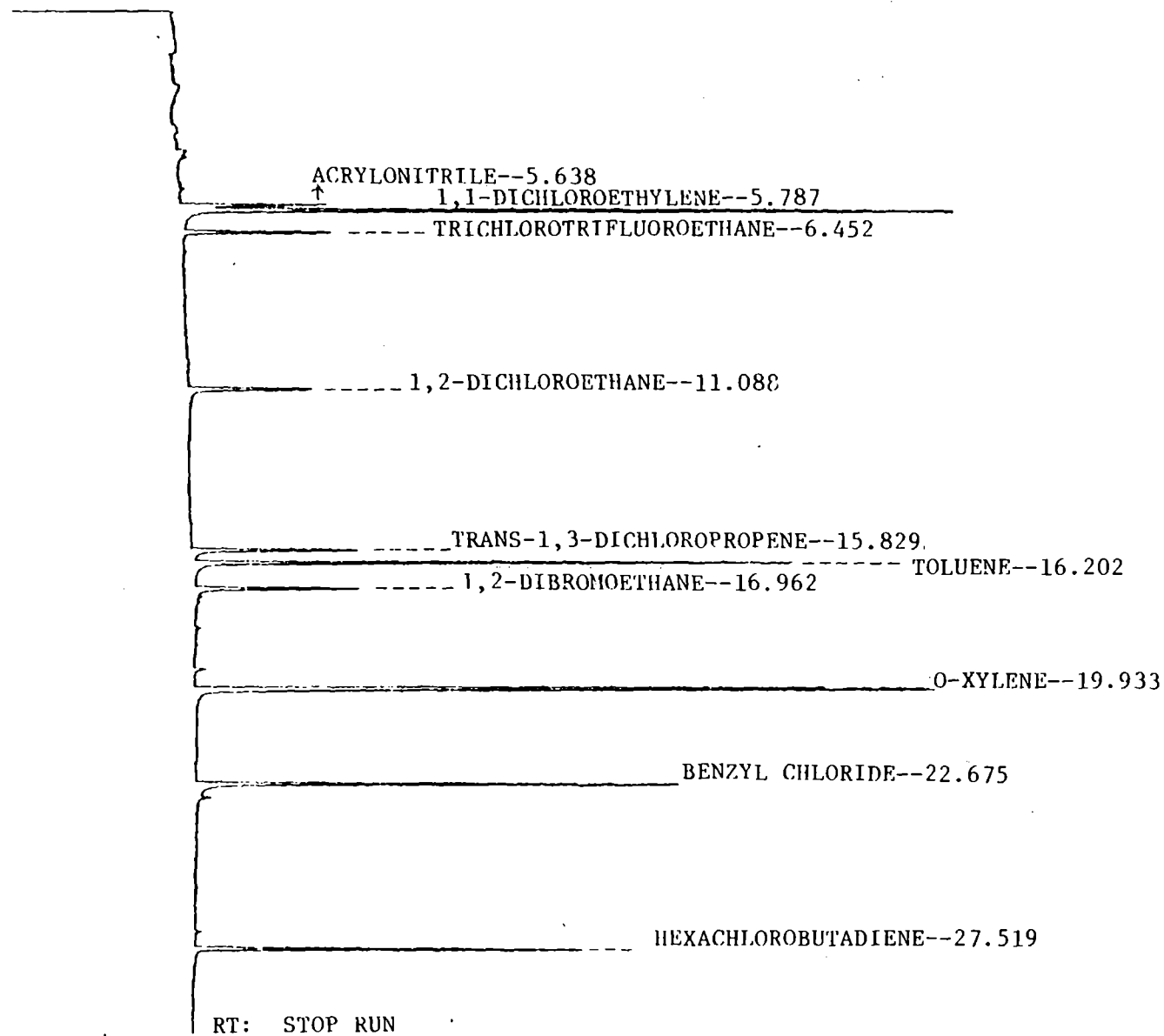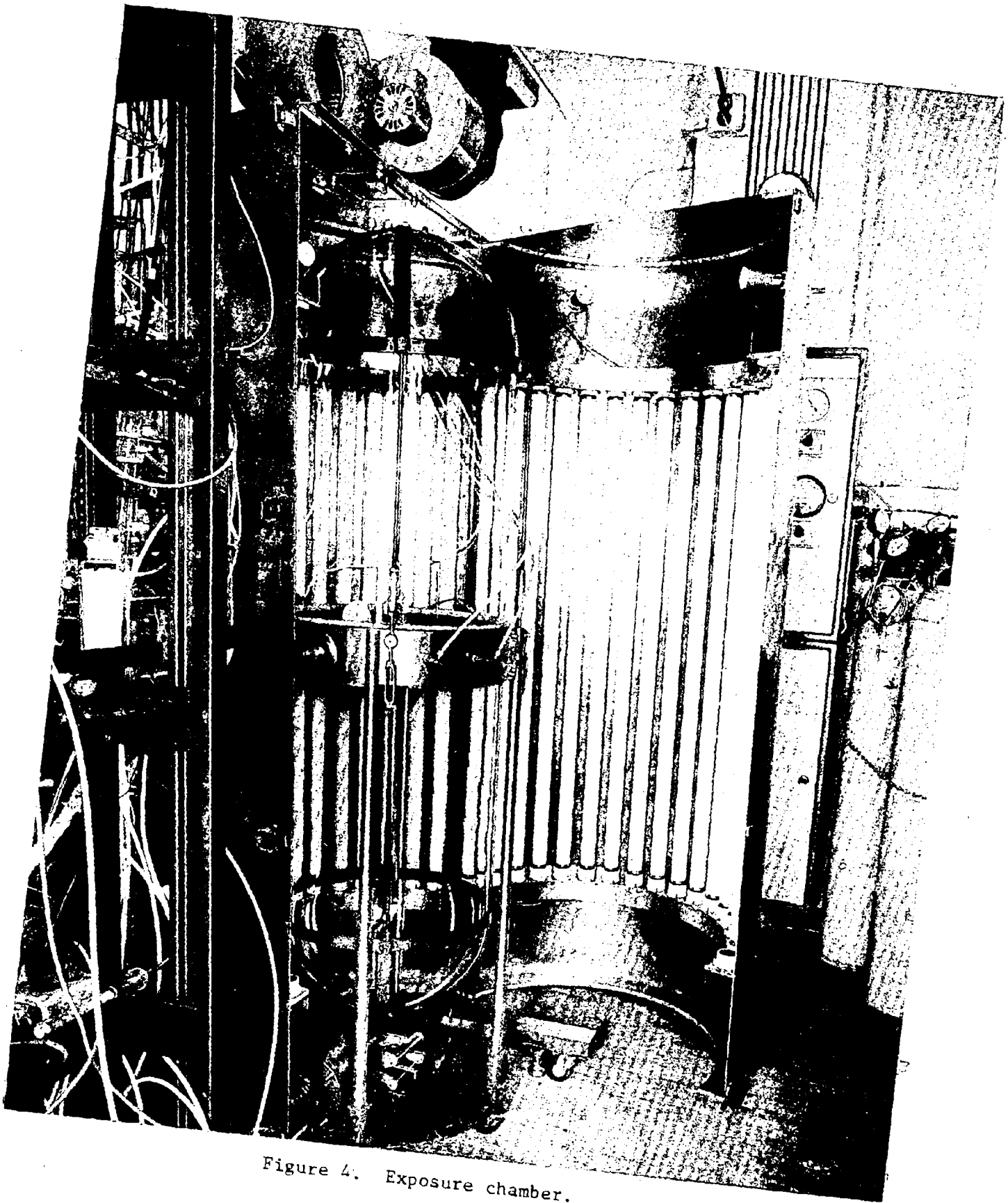
Figure 4. Exposure chamber.

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Teflon O-ring Seal

Stainless
Cylinder

Badge on Support Rod

Cylinder
Flushing Ports
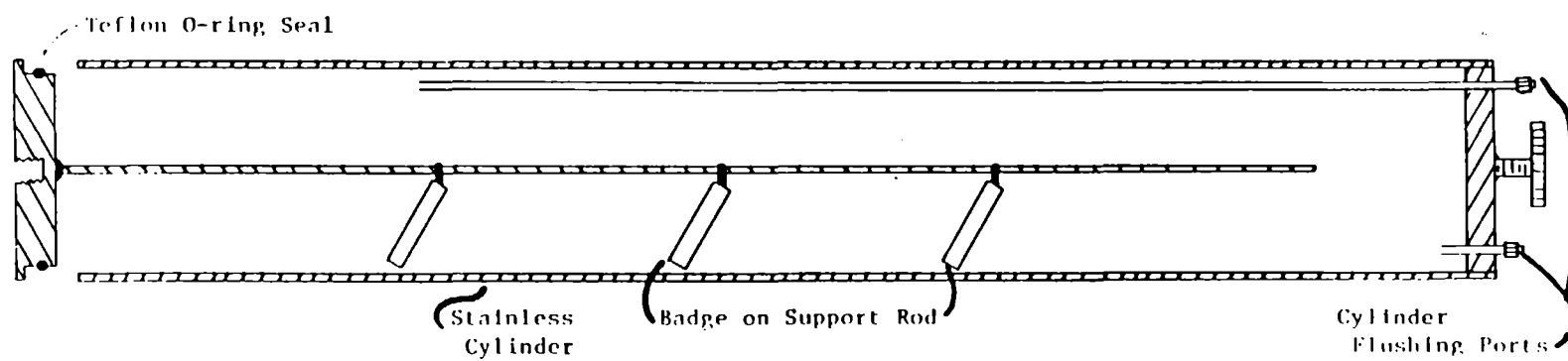
Figure 5. PSD loading and support device for chamber tests.

Velocity Effect Experiments

Most of the runs in the chamber were performed with the air velocity set at about 100 fpm in the vicinity of the PSD's, as determined by measurements made with an Alnor hot-wire anemometer. In attempting to determine the effect of air velocity on the apparent PSD sampling rates, initial experiments were performed by simply reducing the fan speed. However, we found that the air flow became poorly defined in the chamber at low fan speeds, and an alternative procedure was adopted. In this procedure, a single PSD was mounted in the loading cylinder, and the cylinder was withdrawn only a few inches at the start of the exposure period. An external SS bellows pump was then used to draw chamber air through the cylinder and over the PSD, with the pumping rate being determined by a rotometer. The exhaust from the rotometer was then recycled back into the chamber.

Relative Humidity Effects

Most of the experiments for this study were performed at low relative humidities (in the range of 7 to 10 percent). However, for two runs the chamber air was humidified to a level of approximately 90 percent RH.

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SECTION 5

EXPERIMENTAL RESULTS

ANALYTICAL SYSTEM

Initial work on this study consisted of checking the analytical system with respect to the desorption and injection procedures used for the Tenax® GC traps. Because of time delays in obtaining PSD's and the ring heaters used for PSD desorption, PSD's were not included in this initial checkout, and it was assumed that the performance of the system was similar for the traps and PSD's because of the similarities in materials and construction of the two types of devices. However, after making a number of chamber runs, it was noted that although reasonably good precision was being obtained with the PSD's, the absolute quantities of adsorbed test compounds apparent from the PSD analyses were somewhat higher than expected. At that point, a series of runs was performed in which both PSD's and traps were used in an active mode to sample the chamber mixture. The results indicated that even though identical procedures were being used and the trap data indicated essentially complete recovery, the apparent recoveries of each of the test chemicals from the PSD's were consistently greater than could be accounted for in terms of normal analytical error. Indeed, the apparent recovered amounts of chlorobenzene were approximately twice the anticipated amounts. Furthermore, the apparent recoveries appeared to be subject to seemingly subtle changes in the desorption and injection procedure. In the interest of utilization of the early data and maintaining continuity, a set of "calibration" runs was made using the PSD's in an active mode and employing the same procedures used in the early runs. Chamber runs made after this point in time also were per-formed using this standardized set of procedures for desorption and injection. Although this approach is less than ideal from an analytical viewpoint, it is believed that the correction factors (shown in Table 2) derived from this approach are valid for the procedures used. In any case, all raw data shown for the first set of compounds in this report are numbers actually observed, and the correction factors have been applied only in data analysis.

A similar set of active sampling experiments was conducted with the second set of compounds, for which the analytical procedure was changed. This second set of compounds contained both more volatile, acrylonitrile and 1,1-dichloroethylene, and less volatile, hexachlorobutadiene, chemicals. However, the average "correction factor" found was 1.00 ± 0.10, and we con-clude that the necessity for a correction factor is due to an interaction in the desorption and inlet splitter operation rather than some function unique to the PSD's.

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TABLE 2. BADGE ANALYSIS CORRECTION FACTORS
(First Set of Chemicals)

Chemical	Correction factor[a]
Chloroform	1.28
1,1,1-Trichloroethane	1.07
Carbon Tetrachloride	1.35
Trichloroethylene	1.98
Tetrachloroethylene	1.36
Benzene	1.74
Chlorobenzene	2.12

(a) To be divided into quantities of each chemical
     recovered from PSD desorption.

SAMPLING RATES

    The normal procedure for use of a passive sampler involves the use of
known sampling rates for each compound to relate the analytical results to
exposure concentrations. In principle, the effective sampling rates for each
compound can be calculated from knowledge of the physical dimensions of the
device, the diffusion coefficient for each compound, and an understanding of
the fundamental mechanics of the sampling system. For many of the commer-
cially available passive systems, the assumption of irreversible sorption and
application of Fick's first law suffice for reasonable estimates of the sam-
pling rates. However, in some cases, characterization of the effective dif-
fusional resistance of the physical structure is not perfectly straight-
forward and such estimates bear considerable uncertainty. For example, with
dosimeters employing porous membranes as the diffusion barrier, pore size
distributions and total porosity of the membranes are not easily measured
with sufficient accuracy, and it is more expeditious to determine effective
sampling rates experimentally. In most cases, estimates of sampling rates
neglect the effects of air velocity on mass transport to the surface of the
device, and the effects of interaction between the air velocity and the
physical structure of the device. In the case of reversible sorption, as is
the case with the EPA PSD's, there are, to the best of our knowledge, no
published procedures for estimating passive device sampling rates. Rates
estimated for the EPA PSD's are, therefore, based on the procedure advanced
in Appendix A of this report.

    Because of the fact that sampling rates for some of the compounds consi-
dered in this study had not previously been determined for the EPA PSD's,

this parameter was chosen as the basis for comparison of the experimental data. The current data include three separate measures of the gas phase concentrations in the test chamber: (1) direct GC gas phase analysis, (2) active sampling via the Tenax® GC traps, and (3) passive sampling via the EPA PSD's. These data can be ratioed in several different ways to yield desorption efficiencies and apparent sampling rates:

$$\text{desorption efficiency} = DE = \frac{Q_T V_g S}{Q_g V_T} \tag{1}$$

$$\text{sampling rate} = Q_B R_T / Q_T \equiv R_{BT} \tag{2}$$

$$\text{sampling rate} = Q_B V_g S / Q_g DE\ t \equiv R_{Bg} \tag{3}$$

In equations (1), (2), and (3), the subscripts B, T, and g refer to PSD, trap, and gas phase, respectively. Q represents the quantity of an individual compound detected by the GC; S is the split ratio; V is the volume of gas sampled; R is the sampling rate; and t is the sampling time. For the core set of data shown in Table 3, V_g has a value of 10 cc and S = 167; Q_g values are time weighted average values based on 3-4 measurements made during the course of a given run.

The values of sampling rates and desorption efficiencies derived from the data in Table 3 using equations (1), (2), and (3) are shown in Table 4. In making these calculations, values of Q_B were adjusted by dividing the observed values by the correction factors shown in Table 2. Also listed in Table 4 are the one-hour dual-sided sampling rates estimated from the PSD dimensions and published Tenax® GC retention volumes (3) using the procedures outlined in Appendix A. Each derived value of a sampling rate given in Table 4 is a mean value, and is accompanied by the number of points used and the standard deviation, expressed as a percentage of the mean. The numbers of points used varies principally because of the fact that different numbers of combinations were available for the different calculations. However, some of the observed values were rejected as outliers. The criterion used for rejection was that no point should differ from the mean by more than 50 percent or twice the standard deviation, whichever was greater. Although this criterion is quite severe, it permits retention of most of the data.

It can be seen from Table 4 that R_{BT} and R_{Bg} values generally agree reasonably well with each other, with R_{BT} values probably being more representative because of the larger number of points involved. In most cases, R_{BT} values also agree with the estimated sampling rates, with values for carbon tetrachloride and tetrachloroethylene being the exceptions. In the case of carbon tetrachloride, difficulties with accurate sampling by both passive and active samplers have been noted by ourselves (2) and other investigators (5), but this phenomenon has not yet been satisfactorily explained. To the best of the author's knowledge, similar difficulties with sampling of tetrachloroethylene have not been reported previously, and the low rates seen in the current data may reflect analytical difficulties, or the effect may be real.

TABLE 3. CORE DATA SET FOR MRC BADGE PERFORMANCE

Run Number	628	702	707	708	709	712	728	804	819
Time, hr	1/2	1	1	1	1	1	2	1-1/2	1
Trap Rate, cc/min	10	16.7	16.7	16.7	16.7	16.7	16.7	16.7	21.0/19.0
Chemical									
Chloroform	0.024/0.030	0.019/0.021	0.044/0.040	.032/.032	.269/.322	.051/.054	.221/.296	.140/.127	.832/.576
	0.063	0.035	0.069	0.052	0.543	0.103	0.164	0.103	1.11
	0.200/0.117/0	0.103/0.131/0	.233/.212/.264	.136/.156/.190	1.48/1.49/1.62	.218/.316/.403	.844/.973/0	.442/.464/.575	1.995/2.06/2.28
1,1,1-Trichloroethane	0.108/0.102	0.086/0.125	.201/.154	.128/.132	.591/.654	.198/.220	.386/.443	.218/.207	.652/.586
	0.185	0.118	0.262	0.213	1.075	0.377	0.303	0.149	1.02
	0.554/0.488/0	0.547/0.582/0	.794/.728/.753	.495/.461/.549	1.173/1.20/1.277	.723/.778/.838	1.105/1.013/0	.536/.535/.545	1.11/1.17/1.26
Carbon tetrachloride	0.051/0.059	0.039/0.040	.080/.075	.065/.064	.188/.203	.095/.097	.100/.107	.109/.103	.208/.184
	0.109	0.074	0.133	0.109	0.318	0.170	0.110	0.118	0.331
	0.132/0.118/0	0.109/0.125/0	.168/.158/.171	.132/.142/.154	.325/.328/.339	.177/.186/.203	.172/.171/0	.177/.183/.066	.316/.326/.344
Trichloroethylene	0.019/0.022	0.016/0.018	.057/.044	.038/.037	.219/.258	.047/.048	.074/.087	.193/.169	1.00/0.800
	0.051	0.031	0.082	0.065	0.458	0.093	0.062	0.142	1.39
	0.252/0.162/0	0.158/0.163/0	.431/.435/.495	.268/.325/.401	1.50/1.58/1.66	.551/.684/.776	.703/.748/0	1.09/1.18/1.20	2.52/2.52/2.68
Tetrachloroethylene	0.025/0.028	0.019/0.021	.062/.055	.040/.040	.221/.237	.085/.089	.255/.281	.112/.099	.302/.281
	0.077	0.037	0.103	0.071	0.359	0.156	0.289	0.095	0.418
	0.207/0.197/0	0.170/0.176/0	.237/.243/.255	.197/.212/.224	.508/.523/.533	.275/.321/.363	.519/.545/0	0/.316/0	.608/.582/.603
Benzene	0.014/0.019	0.112/0	.036/.025	.016/.016	.124/.142	.031/.032	.185/.219	.061/.056	.302/.211
	0.038	0.019	0.037	0.027	0.226	0.057	0.152	0.048	0.372
	0.184/0.162/0	0.113/0.144/0	.164/.165/.185	.104/.132/.144	.946/1.04/1.13	.271/.335/.379	1.05/1.14/0	.331/.421/.921	1.66/1.67/1.88
Chlorobenzene	0.023/0.024	0.068/0.078	.052/.057	.034/.034	.214/.240	.130/.118	.316/.409	.051/.043	.311/.276
	0.050	0.143	0.091	0.062	0.419	0.103	0.273	0.049	0.401
	0.285/0.275/0	0.701/0.696/0	.359/.380/.422	.232/.269/.299	1.81/2.00/2.18	.367/.446/.534	2.24/2.59/0	.357/.418/.337	2.29/2.06/2.20

Table Key: 1. For each chemical data group represents –   trap 1/trap 2 (Q_{T1}/Q_{T2})
gas TWA (Q_g)
Badge 1/Badge 2/Badge 3 $(Q_{B1}Q_{B2}Q_{B3})$

2. Units are nanograms per sample

3. Sample sizes: a. trap = trap rate x time/split ratio
b. gas = 10 cc
c. badge = badge rate x time/split ratio

TABLE 4. SAMPLING RATES[a] AND DESORPTION EFFICIENCIES

Chemical	$R_{est}^{(b)}$	$R_{BT}^{(c)}$	RSD[d]	N[e]	$R_{Bg}^{(f)}$	RSD[d]	N[e]	DE[g]	RSD[d]	N[e]
Chloroform	59.0	59.5	20	39	63.8	21	22	0.95	11	13
1,1,1-Trichloroethane	46.8	45.1	25	40	47.4	32	20	1.02	14	13
Carbon-tetrachloride	53.9	23.8	17	44	22.4	19	21	0.93	9.4	16
Trichloro-ethylene	67.7	68.2	23	38	73.2	20	18	0.97	15	15
Tetrachloro-ethylene	71.5	39.0	31	34	34.4	30	17	0.97	14	16
Benzene	72.2	70.1	22	41	77.0	16	22	1.03	12	13
Chloro-benzene	66.0	61.3	19	45	61.3	13	22	0.98	12	14

[a] All R's in units of cc/min.
[b] Estimated using procedure of Appendix A.
[c] Mean of rates calculated by Equation 2.
[d] Standard deviation expressed as percentage of mean.
[e] Number of points included in set.
[f] Mean of rates calculated by Equation 3.
[g] Mean of DE's calculated by Equation 1.

Each of the derived values in Table 4 is based on the results of two separate analyses, and it might be expected that the standard deviations would reflect roughly twice the estimated analytical precision of $\pm$ 5 percent plus any uncertainty intrinsic in the sampling method (e.g., in the pumping rates of the traps). The standard deviations shown for the desorption efficiencies therefore appear to be reasonable, but the deviations in the sampling rates may be higher than expected. At least a part of the imprecision in the sampling rates can be explained by further analysis of the data in Table 3. In each case where the data in Table 3 reflect the use of three PSD's, the same three badges were employed (EPA numbers 120, 121, and 122), and the ordering of data for the three PSD's is the same for each experiment. The frequency of ranking of results obtained with the three PSD's is shown in Table 5; Badge 120 consistently yielded relatively low results, and Badge 122 was consistently high. It can be seen that the relative precision of the

TABLE 5. COMPARISON OF INDIVIDUAL PSD's

| Badge Number | Frequency of ranking | | | Relative[a] response |
	Low	Medium	High	
120	31	5	4	0.84 ± .14
121	8	31	1	0.90 ± .10
122	1	4	35	1.0
			Average =	0.92 ± 13%

[a] Relative to PSD number 122.

individual PSD's are reasonably consistent with the precision observed for the traps, but the process of averaging over all three PSD's contributes additional apparent imprecision. Inasmuch as the PSD's evaluated in this program are prototype devices, it is likely that this source of variation in PSD responses could be reduced significantly by refined manufacturing and assembly techniques.

Velocity Effects

In principle, the performance of any passive sampler should be affected by the velocity of air passing over the device. This is caused by the fact that the sampling process tends to deplete the concentrations of sampled species in the vicinity of the PSD, and these species must be replenished in order to establish a steady-state sampling process. The nature of the effect can be formalized in terms of boundary-layer theory as we have indicated previously (2). The magnitude of the sampling rate is determined by the dimensions and construction details of the individual passive device. However, inasmuch as most commercially available passive dosimeters, including the EPA device, have similar gross physical structures and similar intrinsic sampling rates, it is to be expected that the velocity effects would be roughly the same for all of these devices. Qualitatively, only a minor effect of air velocity on the sampling rate at velocities above about 30 to 50 fpm would be expected, but significant decrease in sampling rate should result at velocities below 30 fpm (see Appendix A). In the current work, most of the PSD evaluation experiments were performed using an air velocity of about 100 fpm, i.e., a typical velocity for a person moving about or even sitting in a well-ventilated area. However, additional experiments were performed at reduced velocities in order to document the existence of the velocity effect with the EPA PSD.

Initial experiments to evaluate the velocity effect were conducted with the PSD's suspended in the chamber in the normal manner and the fan speed reduced. The results of these experiments showed poor reproducibility however, and a re-examination of flow patterns in the chamber revealed seemingly random fluctuations in flow at the low fan speed. The procedure therefore was changed to permit exposure of one PSD at a time under conditions of a well-directed flow (see section on procedures). Three PSD's were exposed under these conditions at a linear velocity of 10 fpm, with the results shown in Table 6.

Based on the considerations given in Appendix A, it is estimated that the effective rate at 10 fpm should be approximately 0.64 times the rate at 100 fpm--a value that is in good agreement with the data in Table 6.

Relative Humidity Effects

In previous studies of passive devices that employ activated carbon as the sorbent, it was found that the apparent sampling rates of the devices were significantly diminished at relative humidities greater than about 80 percent (2). This result was not unexpected because of the well-recognized affinity of activated carbons for water. On the other hand, porous polymer sorbents such as Tenax® GC are generally considered to be hydrophobic, and it was expected that passive devices using Tenax® GC as the sorbent would be relatively unaffected by high relative humidities. In the current work, two exposure tests of the PSD's were made at relative humidities of 87 and 92 percent, with the results as summarized in Table 7. With only six data points available for each chemical, median apparent sampling rates and mean values are both cited in Table 7. Although the scatter is somewhat greater for some of the chemicals than was observed for the core data set given in

TABLE 6. VELOCITY EFFECT
(v = 10 fpm)

| Chemical | Apparent sampling rate, cc/min | | | $\bar{R}_{10}$ | R_{10}/R_{100} |
	1	2	3		
Chloroform	47.7	45.6	52.4	48.6	0.82
1,1,1-Trichloroethane	23.9	23.6	23.5	23.6	0.52
Carbon tetrachloride	13.6	13.3	14.0	13.7	0.58
Trichloroethylene	38.3	39.9	37.7	38.6	0.57
Tetrachloroethylene	21.2	21.6	21.4	21.4	0.55
Benzene	49.3	51.8	54.3	51.8	0.74
Chlorobenzene	41.8	45.2	43.2	43.4	0.71

Mean = 0.64 ± 0.11
Median = 0.58

TABLE 7. RELATIVE HUMIDITY EFFECT[a]

| Chemical | Apparent sampling rates, cc/min | | | |
	Mean	RSD, %	N	Median
Chloroform	95.3	15	6	96.1
1,1,1-Trichloro-ethane	68.4	33	6	67.6
Carbon tetrachloride	28.2	30	6	29.1
Trichloro-ethylene	77.3	13	5	80.8
Tetrachloro-ethylene	40.4	12	6	40.4
Benzene	66.1	37	6	62.6
Chlorobenzene	59.9	9.1	6	60.9

[a] Rates obtained at RH = 87 and 92 percent

Table 3, the mean apparent rates (or the medians) compare favorably with
those obtained at low humidities in all cases except for chloroform and
1,1,1-trichloroethane. With the latter two materials, the apparent sampling
rates were significantly higher at the high humidities. A re-examination of
the raw data for 1,1,1-trichloroethane reveals that the results obtained at
92 percent relative humidity yield an average apparent sampling rate of
47.3 cc/min (shown in parentheses in Table 7) which agrees quite well with
the low humidity data. On the other hand, very high results were obtained in
the 87 percent humidity experiment. The latter results may be due to spuri-
ous contamination, but such cannot be supported within the framework of the
current results. However, in the case of chloroform, all of the results
indicated higher sampling rates than those obtained at low humidities. In
experiments conducted later in this program, it was noted that hexane was
sometimes a system contaminant that interfered with the chloroform GC peak.
Such contamination may have affected the results of these humidity
experiments.

Model Evaluation

Because of the apparent success in using the model presented in Appendix
A to predict the effects of retention volume and sampling time on the

time-averaged sampling rates of the EPA PSD's, additional exposure experiments were conducted to provide a more severe test of the model. In these tests, ten more chemicals, including three very volatile compounds, acrylonitrile, 1,1-dichloroethylene and trichlorotrifluoroethane were added to the test set. At the same time, the desorption procedure was changed (see the Procedures Section) to permit less ambiguous quantification of the analytical results.

The initial plan of these additional experiments was to conduct PSD exposures to all eighteen chemicals for various time periods, ranging from 15 minutes to 24 hours. However, after conducting several such experiments at time periods up to 4 hours, two faults in this plan became apparent:

1. With several of the more volatile chemicals, the total volumes being sampled with the traps exceeded the retention volumes for these compounds even at the low sampling rates being employed (ca. 10 cc/min).

2. The large amounts of sample being collected by the PSD's caused shifts in the GC retention times. These shifts along with the complexity of having to identify 18 chemicals amidst an array of minor system contaminants made peak identification uncertain or even impossible in many cases.

For these reasons, the initial data were discarded and two changes were made in the experimental plan:

1. Trap samples were still collected, but were used only as crosschecks on the data for the less volatile compounds (those for which retention volumes were not exceeded in any given experiment). The direct gas analyses then became the primary reference for determining sampling rates.

2. The list of chemicals was limited to the ten new compounds to facilitate visual comparisons of chromatogram patterns.

Exposures of the EPA devices, in triplicate, then were made using ppbv levels of the ten chemicals for time periods of 1/4, 1/2, 1, 2, 4, 12, and 24 hours. The results of these tests are given in Table 8. The median values of the apparent sampling rates are used in this table because only three data points were obtained for each sampling condition. In most cases, there were at least two points close to the indicated median values.

Although there is some scatter in the data, the variation is not generally significant with respect to the expected experimental error, i.e., ± 10 percent. As predicted by the model given in Appendix A, the apparent sampling rates of the very volatile compounds decline sharply as the sampling time is increased, while those compounds having large retention volumes display only slowly declining sampling rates. A better picture of the correspondence between the model and the experimental data can be gained by consideration of Figures 6 to 10. These curves depict the experimental

TABLE 8. TWA SAMPLING RATES OF PSD's (Median Values, cc/min)

Chemical	Averaging Period, hr							
	0[a]	0.25	0.5	1	2	4	12	24
Acrylonitrile	94.7	72.3	50.8	26.9	16.2	9.3	2.4	1.1
1,1-Dichloroethylene	82.2	37.9	19.8	10.1	4.5	2.7	0.5	0.2
Trichlorotrifluoroethane	62.1	10.7	7.3	3.7	3.1	2.3	1.0	0.7
1,2-Dichloroethane	81.2	95.8	67.0	55.9	41.4	21.2	11.9	6.9
trans-1,3-Dichloropropene	71.0	86.2	71.0	66.7	53.6	74.8	54.3	32.9
Toluene	75.9	75.5	71.2	65.9	45.0	43.0	34.9	25.4
1,2-Dibromoethane	69.5	80.3	61.0	64.7	48.1	60.8	57.7	--
o-Xylene	65.1	74.8	70.3	57.2	62.5	75.2	44.1	28.5
α-Chlorotoluene	83.9	63.0	73.8	62.0	68.2	72.7	45.8	55.3
Hexachlorobutadiene	(42.0)[b]	40.5	40.3	41.3	41.9	40.4	(27.1)	31.4

(a) Estimated based on device dimensions and chemical diffusion coefficients (see Appendix A).

(b) Estimated from current data.

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Ro = 94.7 cc/min.
V_b = 4.9 ± 0.8 L/q
SDEV = 2.8 cc/min.

R,
cc/min.

Figure 6. Acrylonitrile.

Ro = 82.2 cc/min
V_b = 1.5 + 0.1 L/q
SDEV = 2.8 cc/min.

R,
cc/min.
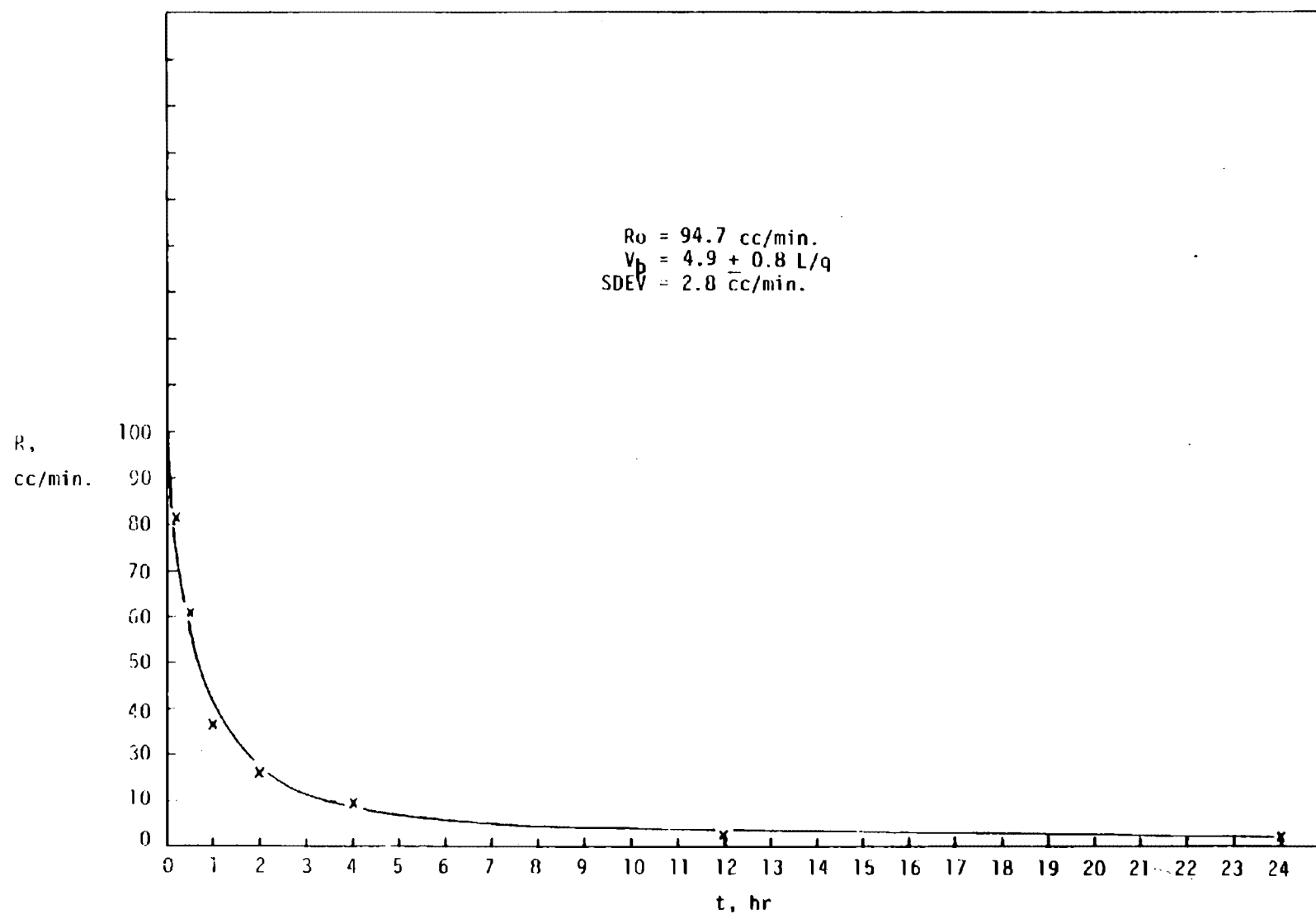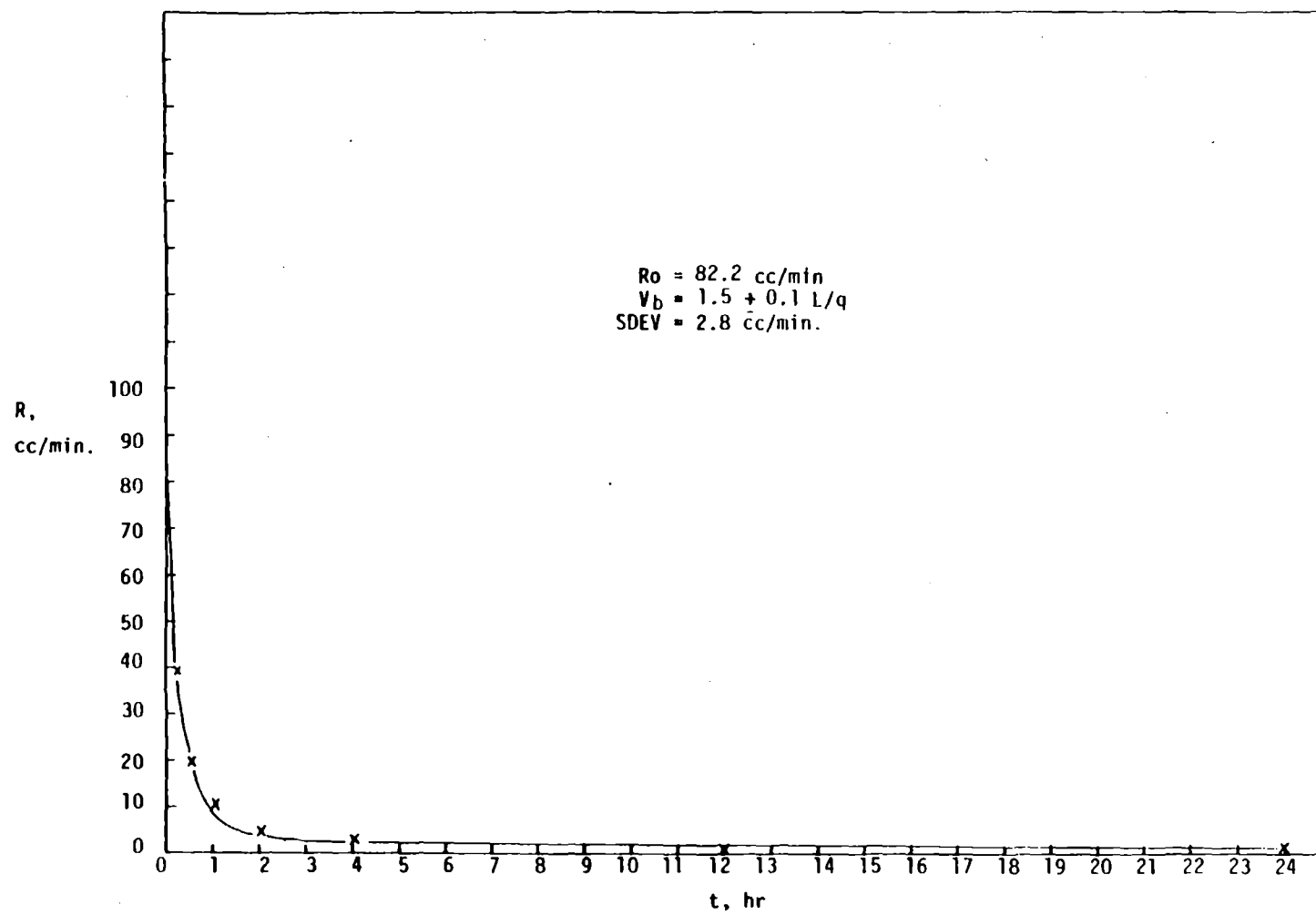
Figure 7. 1,1-Dichloroethylene,

R,
cc/min

Ro = 62.1 cc/min.
V_b = 0.5 + 0.08 L/q
SDEV + 1.3 cc/min.

100
90
80
70
60
50
40
30
20
10
0

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

t, hr.
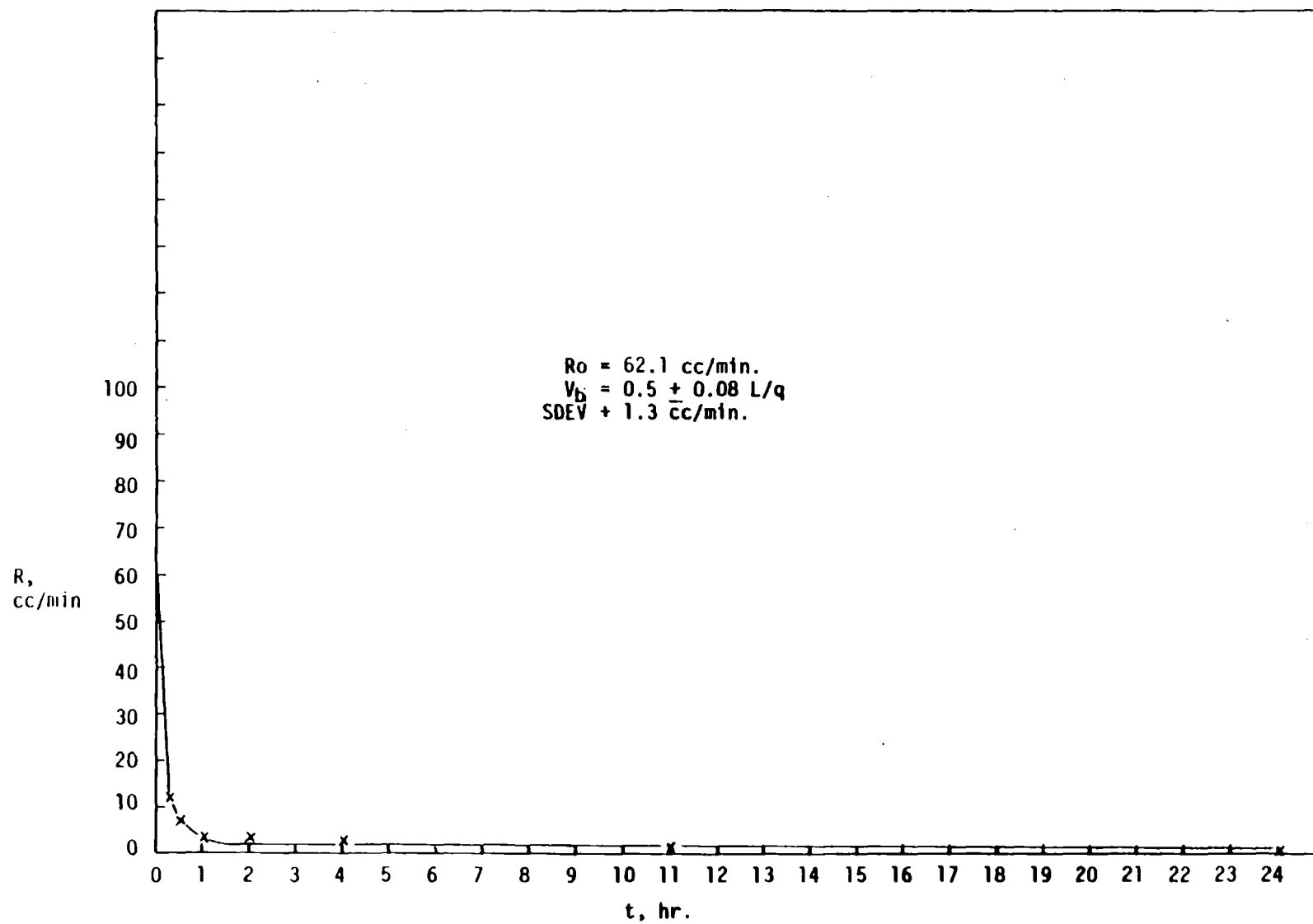
Figure 8.   Trichlorotrifluoroethane.

Figure 9.   1,2 Dichloroethane.

Ro = 42 cc/min.
V_b = 324 L/q
SDEV = 1.3 cc/min.

100

90

80

70

R,
cc/min

60

50

40

(x)

30

20

10

0

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

t, hr

Figure 10.   Hexachlorobutadiene.

points and curves calculated for several compounds using equation A-8'. Retention volumes (V_b) for these calculations were derived from the experimental data by solving equation A-8' at each point followed by averaging the resultant values of V_b to obtain a best overall value. The experimentally derived retention volumes for the more volatile compounds in comparison with values cited in the literature are shown in Table 9.(5) In principle, the same approach could be used to calculate the retention volumes of the less volatile compounds, but, for those compounds, the experimental fluctuations are of a magnitude equal to or greater than the expected declines in sampling rates. Thus meaningful calculations cannot be made.

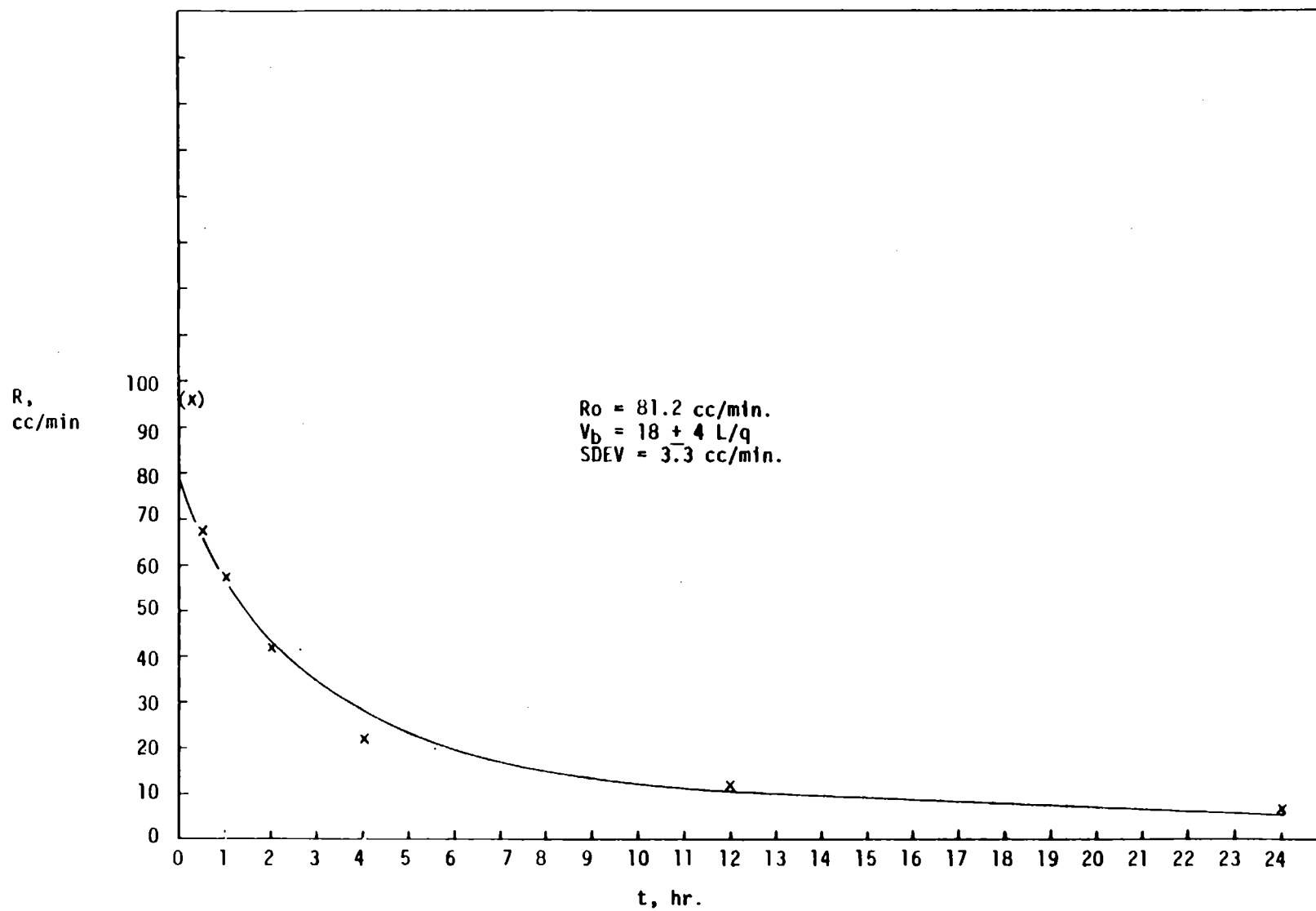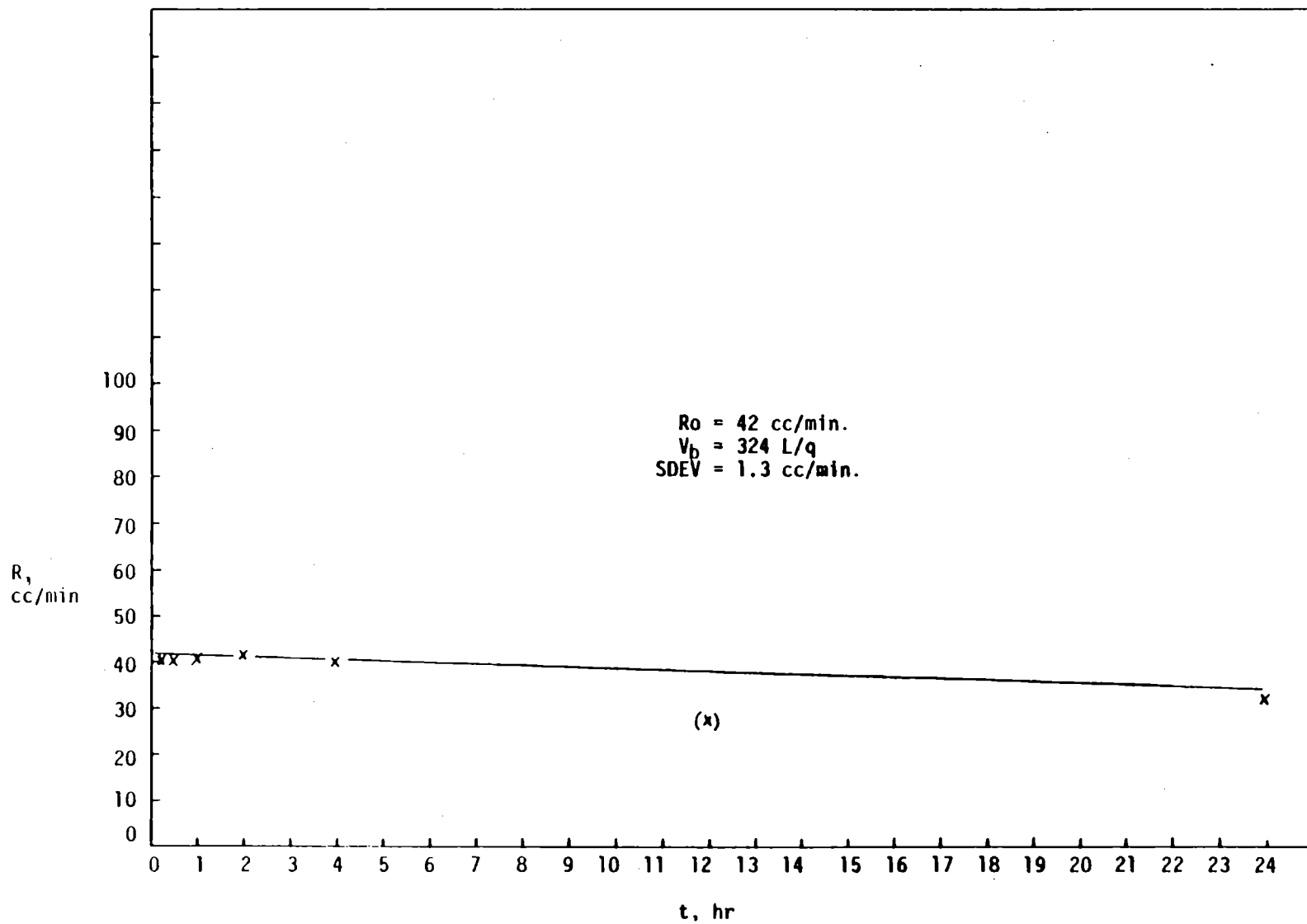## SPHEROCARB-FILLED PSD's

As indicated in the previous sections of this report, the Tenax® GC-filled PSD's exhibit severely declining sampling rates when used for multiple hour sampling of compounds having low retention volumes. One approach to solution of this problem involves the use of a sorbent having larger retention volumes. Ideally, the sorbent selected would have a uniform retention volume of say 500 liters/gram for all compounds. Unfortunately, such a sorbent is fundamentally infeasible. A sorbent having increased retention volumes for some compounds will necessarily have larger retention volumes for all compounds, and there is the risk that in enhancing the ability to sample certain compounds the ability to recover some of the less volatile compounds in a practical manner may be lost.

Some preliminary work conducted with Spherocarb under a separate contract with EPA (Contract No. 68-02-3745(WA7)) indicated that this sorbent might be suitable for sampling of compounds as volatile as vinyl chloride and acrylonitrile, and that compounds such as toluene and tetrachloroethylene still could be recovered at desorption temperatures below their decomposition temperatures.

TABLE 9. RETENTION VOLUMES[a]

Chemical	V_b(cal),L/g	V_b(Lit),L/g
Acrylonitrile	4.9+0.8	0.3-7.0
1,1 Dichloroethylene	1.5+0.1	2.6
Trichlorotrifluoroethane	0.5+0.08	0.23-0.47
1,2-Dichloroethane	18+4	24.4

(a) Calculated from PSD data.

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Retention Volumes

Spherocarb is a relatively new sorbent material, and little was known about the retention volumes for many of the compounds of interest. Therefore, measurements of retention volumes were undertaken for the set of 12 organic compounds identified as test compounds for Task 33. These were measured by the standard chromatographic procedure involving determination of the retention times as a function of temperature and column flow rate. Also included in this series of experiments was the determination of the retention volume of water vapor as an indicator of the possible susceptibility of Spherocarb to humidity. The results of these measurements are shown in Table 10. It can be seen that retention volumes for all of the compounds in Table 10 are significantly larger than those shown for Tenax® GC in Table A-1, indicating potentially good sampling ability for these compounds. The retention volume for water vapor is relatively low, suggesting that sampling with Spherocarb should be relatively insensitive to humidity.

Preliminary Evaluation of Spherocarb

Initial tests of Spherocarb involved the use of a Spherocarb-filled PSD as an active sampler to determine appropriate desorption conditions and efficiencies. For these experiments, the PSD was mounted in the high-temperature holder described above, and was kept sealed at all times. At this point, several problems associated with the use of Spherocarb became obvious:

1. Apparent desorption efficiencies for the test compounds were not readily reproducible, and were quite low for several of the chlorinated hydrocarbons. In particular, the recovery efficiency of 1,1,1-trichloroethane was very sensitive to temperature, with recoveries steadily decreasing at temperatures above 300 C.

2. Recoveries of hydrocarbons, notably benzene, on the other hand exceeded 100 percent in all tests, and benzene was always found in blank runs in spite of extensive bakeout periods at temperatures up to 500 C.

These observations illustrate two separate problems with the use of Spherocarb. A close examination of the sorbent, as received from the manufacturer, revealed the presence of unpyrolyzed polymer beads mixed in with the Spherocarb. Examination of several different batches of the sorbent showed some variability in the amount of polymer present, but all batches examined contained at least some of this material.

Several attempts were made to clean the 1.5 grams of sorbent in one PSD by pyrolyzing the material while flushing with UHP nitrogen. In these experiments, the output gas from the desorption cell was connected directly to a flame-ionization detector so that progress in cleaning the sorbent could be monitored continuously. Large amounts of hydrocarbon (full-scale deflection on the least sensitive FID range) were observed in heating the PSD from 500 to 600 C. After several days at 600 C, the FID had still not returned to baseline. After three additional 8-hour periods at 700 C, the output

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TABLE 10. SPHEROCARB RETENTION VOLUMES

Chemical	t,C/Vb,L/g			Vb(298 K)[a]	Vb(311 K)[a]
Acrylonitrile	250/0.231	225/0.413	200/0.804	1700	720
1,1-Dichloroethylene	300/0.117	250/0.315	200/1.14	2400	1000
Methylene Chloride	250/0.137	225/0.230	200/0.421	415	190
Trichlorotrifluoro-ethane	300/0.294	275/0.494	250/0.900	14×10^3	5600
Chloroform	275/0.324	250/0.533	225/1.01	4300	1800
1,2-Dichloroethane	30/0.266	275/0.443	250/0.779	8500	3400
1,1,1-Trichloroethane	300/0.132	250/0.386	225/0.740	5000	2000
Benzene	350/0.342	325/0.521	300/1.07	5×10^5	2×10^5
Trichloroethylene	350/0.199	325/0.365	300/0.638	4×10^5	1×10^5
trans-1,3-Dichloro-propene	375/0.217	350/0.353	325/0.605	4×10^5	1×10^5
Toluene	350/0.336	325/0.576	300/1.05	5×10^5	2×10^5
Tetrachloroethylene	375/0.463	350/0.799		6×10^6	2×10^6
Water	60/0.143	45/0.323	30/0.740	1.02	0.47

[a] Estimated by extrapolation of high temperature results.

appeared to be clean, and subsequent blank desorption runs at temperatures up to 450 C revealed no benzene or other hydrocarbons being emitted. However, further tests of desorption efficiencies of the other compounds still showed low and erratic recoveries.

It was suspected that a part of the problem in low recoveries of the chlorinated hydrocarbons might be due to catalytic dehydrochlorination occurring on the stainless steel surfaces of the PSD and desorption holder. This hypothesis was tested by placing an empty PSD (no sorbent) in the holder, and sampling gas from the chamber through the holder. During this process, the temperature of the holder was increased stepwise from ambient to 400 C. At temperatures up to about 250 C, the apparent gas composition was essentially the same as measured directly in the chamber. However, at temperatures above 250 C, progressive degradation of the chlorinated hydrocarbons was noted, with 1,1,1-trichloroethane appearing to be most affected. Indeed, at temperatures between 250 and 350 C, the gas analyses suggested the conversion of 1,1,1-trichloroethane to 1,1-dichloroethylene.

Catalytic dehydrochlorination is not an uncommon problem when dealing with chlorinated hydrocarbons, and one common solution is to use nickel or silica in place of stainless steel. We therefore proceeded to replace the stainless screens of the PSD with nickel screen of the same size, and all other exposed parts of the PSD and the desorption holder were plated with nickel. The experiment noted above was then repeated. Results indicated better resistance to degradation and suggested that good recoveries might be possible if the desorption temperatures could be held below 400 C.

Further tests of the desorption efficiencies then were conducted using different temperature ramps in an attempt to gain the best compromise between obtaining good recovery and accomplishing the desorption in a reasonable amount of time. A comparison of desorption efficiencies obtained by three different procedures is presented in Table 11. The first two of these involved stepwise temperature programming, with isothermal operation at selected temperatures during the process. The main difference between the first two procedures lies in the higher final temperature for the first method. The last two sets of data represent results of ballistic programming of the desorption holder to 400 C. All of these data were obtained using the PSD in an active mode, with the direction of gas flow during desorption being opposite of that during sampling. These are not individually typical data, but rather illustrate some of the extreme variability observed in these experiments.

Passive Sampling with Spherocarb

Despite of the inconsistent results obtained with Spherocarb in the preliminary experiments, conflicting information from other programs suggested that this sorbent might still be useful for passive sampling of volatile organics. Therefore a series of exposures of the nickel-plated Spherocarb-filled PSD's in the 200 L chamber facility was conducted. Tests were conducted for 0.5, 1, 8, and 24 hr. Mechanical problems related to handling of the PSD's in the chamber were experienced in both the 0.5 and

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TABLE 11. SPHEROCARB DESORPTION EFFICIENCIES
(active mode)

Chemical	Run A	Run B	Run C	Run D
Acrylonitrile	102	90	NA	NA
1,1-Dichloroethylene	9.6	35	22	18
Methylene Chloride	19	30	52	41
Trichlorotrifluoroethane	9.4	33	26	17
Chloroform	49	(488)	14	10
1,2-Dichloroethane	93	98	20	15
1,1,1-Trichloroethane	28	41	18	14
Benzene	82	88	107	78
Trichloroethylene	74	77	27	23
trans-1,3-Dichloropropene	62	59	51	49
Toluene	82	78	49	42
Tetrachloroethylene	71	74	33	33

Run key: A. 5-minute hold at 150 C; 5-minute hold at 250 C; 10-minute hold at 350 C; 40-minute total cycle.
B. Similar to A, but with additional 10 minutes at 400 C; 60-minute total cycle.
C. Ballistic program to 400 C, with 10 minutes at 400 C; 45-minute total cycle.
D. Same as C.
NA = acrylonitrile not analyzed because of interference.
Numbers in parentheses represent probably misidentified peaks.

1 hour runs, and the 1 hour run was repeated. With the second 1 hour run, we experienced analytical problems. A review of the results from the 8 and 24 hour runs led us to the conclusion that additional attempts to complete the short term exposure work would not be meaningful.

The results of the 8 and 24 hr runs are cited in Table 12. In this table, the results are expressed as the apparent percentage recovery for each chemical based on the known time-weighted average concentrations and the sampling rates derived from the physical properties of the PSD's. With the large retention volumes for all chemicals listed in Table 12, the 8 and 24 hr sampling rates should be essentially the same as the Ro values listed for the Tenax® GC-filled PSD's in Table A-1. Also listed in Table 12 are average recoveries, standard deviations and number of points used for each chemical. These data suggest that the Spherocarb PSD's may be satisfactory for a few selected chemicals such as methylene chloride, 1,1-dichloroethylene, and tetrachloroethylene, but for most of the other compounds, the devices are clearly unsatisfactory. It also should be noted that the apparent recoveries listed in Table 12 generally do not correspond well with those listed in Table 11. This may be due--in part--to the fundamental difference in desorption from an active sampler as opposed to desorption from a passive sampler. (With a highly effective active sampler, most of the sample is concentrated on the inlet edge of the sorbent bed, and desorption is effected most easily by reversing the flow direction.) More generally, it is believed that the lack of correspondence between the two tables reflects a persistent inability to obtain good reproducibility with Spherocarb.

REDUCED RATE PSD's

Another possible solution to the problem of poor sampling of the very volatile compounds by the standard PSD's is to reduce the sampling rates by alteration of the diffusion barrier. This approach was taken as an alternative to the use of Spherocarb in place of Tenax® GC.

In the current work, several different alternative diffusion barriers were considered. These included: (1) filter paper between the screen assemblies of the standard PSD's; (2) finer screen; (3) compound plate assemblies with the holes in the first plate being offset from those in the second plate; and (4) simple plates having a single small hole. Simple calculations utilizing the precepts outlined in Appendix A indicated that in order to meet the objective of 8-24 hr sampling of compounds having retention volumes as low as say 5 L/g, the sampling rates of the PSD's would have to be reduced to the order of a few cc/min. Such a reduction is not possible with the first two approaches cited above, but can be achieved with either the compound plate or single plate approaches.

Both approaches were tried, with the result that it was demonstrated that rates of the order of 2-10 cc/min could easily be achieved. However, it quickly became obvious that the reproducibility of sampling rates between separate PSD's was not good. A careful examination of barrier plates and PSD's revealed irregularities in the physical dimensions of the PSD's. For

TABLE 12.   PERCENTAGE RECOVERIES FROM SPHEROCARB PSD's

| | PSD No. | | | | | | |
| | 8 hr | | | 24 hr | | | |
Chemical	102	115	121	102	115	121	Ave/RSD/N[a]
1,1-Dichloroethylene	150	78	60	750	39	250	82/48/4
Methylene Chloride	107	101	68	122	101	59	93/24/6
Trichlorotrifluoro-ethane	14	5	1	46	14	22	13/6/5
Chloroform	53	33	23	(253	103	144)[b]	36/15/3
1,2-Dichloroethane	16	7	9	202	33	109	16/12/4
1,1,1-Trichloroethane	6	4	3	26	15	11	8/5/5
Benzene	412	230	360	(all >1000)			700
Trichloroethylene	55	27	14	11	19	14	15/3/4
Toluene	24	17	13	(all >1000)[c]			18/6/3
Tetrachloroethylene	91	81	82	300	53	99	88/8/4

[a] Average value of percentage recovery; relative standard deviation; and number of points included in average.
[b] Chloroform believed to be obscured by interfering hexane peak.
[c] Possible blank or interference problem.

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example, most of the PSD's in hand have I.D.'s within 0.002 in. of the average values, but at least one PSD was found to vary in I.D. by 0.005 in. from the average. Also, several of the PSD's were found to be slightly irregular in shape. These variations are insignificant with respect to normal usage of the standard PSD's but are very important when the barrier plates are used to reduce the sampling rates.

For example, the hypothetical case where a barrier plate having a central hole of 0.5 mm I.D. is used to replace the outer screen assembly of a standard PSD may be considered. If a mismatch of 0.001 in. occurs between the O.D. of the plate and the I.D. of the PSD because of an irregularity in shape of the PSD, the area of the gap at the edge of the barrier plate (1.5 cm radius) would amount to 0.024 cm^2 as compared with an area of 0.0079 cm^2 for the center hole. That is, the sampling rate due to edge leakage would be 3 times as great as the rate through the center hole. It is obvious from this example that either tolerances must be kept very close, or some mechanism must be used to seal the edges of the barrier plate. Optional approaches considered for sealing the edges included the use of thin copper and aluminum gaskets and high temperature soldering. The latter approach gave a good seal, but resulted in contamination of the PSD by the flux that was necessary and presented potential difficulties in replacement of the Tenax® GC bed. The gaskets appeared to give good seals initially, but these failed after a few normal temperature cycles in the desorption unit.

The final approach used was to carefully select PSD's that were free of shape irregularities and which had closely matched I.D.'s. Barrier plates then were machined to O.D.'s that were very slightly greater than the I.D., of the PSD's, and were "sprung" into the PSD's in place of their standard outer screen assemblies.

Three of the reduced rate devices were prepared by replacing the outer screen assemblies of standard PSD's with 0.030 in thick stainless plates having single 0.5mm I.D. holes to serve as the diffusion barriers. These then were exposed for time periods of 0.5, 4, 8, and 24 hours to the twelve challenge compounds at nominal concentrations of 10 ppbv each.

A cursory examination of the results obtained with these PSD's indicated good precision, but poor correspondence with Ro values calculated by the usual procedures. This was not unexpected because of the extreme difficulty of providing a perfect seal at the edge of the device, while maintaining the flexibility of exchangeable diffusers. The following approach was therefore adopted:

1. It was assumed that the literature values of the diffusion coefficients were correct, and that our model for reversible adsorption is applicable. (Appendix A)

2. The apparent value of A/L was calculated for each data point.

3. The raw data was screened to eliminate obviously incorrect points. For example, all of the trichlorotrifluoroethane data was totally

inconsistent with all previous experience with this chemical. Also, there was an obvious problem with integration of some of the chloroform peaks, and these data were dropped from this analysis.

4. An iterative sorting procedure involving successive rejection of points more than two sigma from a floating mean was used to identify the most consistent value of A/L.

5. This value of A/L was used to calculate values of Ro, and the data for each chemical were analyzed as a group, by reducing the data to relative values of R/Rcal. (This approach increases the sizes of the data sets by removing the time dependence of the data.)

The iterative sorting procedure yielded a value of A/L of 0.482 ± 9.8 percent with 87 points included in the analysis. Examination of data for the individual devices gave values as shown in Table 13. It can be seen that there is no significant difference between the three devices. Apparent rates and values used in the analysis of the data are shown in Table 14.

Limited Field Study

The reduced rate PSD's were designed for use over extended sampling periods of 8 to 24 hours. Inasmuch as the field intercomparison study permitted sampling periods of only 2 hours, and results suggested a possible blank problem with the use of the reduced rate devices for short sampling periods, a limited field study was conducted to give preliminary evaluation of the potential of these devices. In this field experiment, reduced-rate PSD's were exposed in triplicate at three different sites, and active samples were collected simultaneously using Tenax® GC traps. The three sites were:

1. At a BCL employee's home

2. In a hallway near the main BCL shop facility.

3. In a 5th floor BCL office complex, well removed from laboratory activities.

TABLE 13.   A/L VALUES FOR REDUCED RATE PSD's

Device No.	A/L, cm	RSD, %	N
23	0.497	9.1	32
30	0.453	20	37
52	0.476	9.5	32
all	0.482	9.8	87

TABLE 14.   SUMMARY OF REDUCED RATE PSD RESULTS[a]

Chemical	D[b]	V_b[c]	Apparent Rate				R_o	R/R_{cal}[d]	8h	24h
			0.5h	4h	8h	24h				
Acrylonitrile	6.35	4.9	2.34	8.79	3.55	1.46	3.06	1.15	0.75	0.46
			2.26	5.64	3.31	2.04		+/-28%		
			2.45	7.38	3.27	1.70		n=9		
1,1-Dichloroethylene	5.51	2	2.34	2.02	1.81	1.23	2.66	1.17	0.57	0.26
			2.12	1.65	1.62	1.13		+/-36%		
			2.34	1.90	1.61	1.20		n=12		
Methylene Chloride	(6.31)	5.5	1.54	2.65	2.02	1.53	3.04	0.89	0.78	0.50
			1.42	2.07	1.69	1.57		+/-19%		
			1.77	1.90	1.71	1.81		n=9		
Trichlorotrifluoroethane	4.16	0.5	0.72	1.91	1.73	1.26	2.01	3.0	0.25	0.09
			1.50	1.53	1.48	1.42		+/-250%		
			1.45	1.63	1.51	1.84		n=11		
Chloroform	5.33	18.9	(ND)	2.28	2.20	1.73	2.57	0.95	0.94	0.83
			2.82	1.62	1.91	2.57		+/-20%		
			3.25	2.18	1.86	2.41		n=11		
1,2-Dichloroethane	5.44	24	2.68	2.84	3.20	2.70	2.62	1.10	0.95	0.86
			2.18	1.94	2.79	2.47		+/-4.7%		
			2.73	2.74	2.85	2.48		n=9		
1,1,1-Trichloroethane	4.76	11.8	2.11	2.09	2.34	2.39	2.29	1.06	0.91	0.77
			2.53	1.50	2.06	2.29		+/-19%		
			2.14	2.17	2.08	2.31		n=12		
Benzene	5.59	42.5	2.82	2.76	2.79	2.35	2.69	0.96	0.97	0.91
			4.19	2.12	2.49	2.27		+/-8.6%		
			4.79	2.57	2.43	2.17		n=10		
Trichloroethylene	5.25	39.3	2.53	2.57	2.54	2.67	2.53	0.98	0.97	0.91
			2.37	1.90	2.11	2.42		+/-11%		
			3.40	2.42	2.21	2.56		n=11		
trans-1,3-Dichloropropene	4.76	335	2.30	2.74	2.63	2.57	2.29	1.19	1.0	0.99
			2.46	1.80	2.50	2.93		+/-8.2%		
			3.15	2.58	2.65	2.90		n=10		
Toluene	5.09	193	2.34	2.57	2.56	2.33	2.45	1.00	0.99	0.98
			3.12	1.79	2.27	2.50		+/-5.2%		
			3.90	2.28	2.39	2.53		n=9		
Tetrachloroethylene	4.97	254	1.32	2.35	2.26	2.53	2.40	0.91	0.99	0.98
			1.78	1.63	2.10	2.24		+/-13%		
			2.18	2.17	2.14	2.50		n=11		

(a) Results for PSD's 23, 30, and 52 listed in sequence.
(b) Diffusion coefficient, cm^2/min.
(c) Retention volume, L/g.
(d) Mean, relative standard deviation, and number of included points for ratio of observed rate to calculated rate.
(e) Expected ratio of time averaged rate at 8 and 24 h to initial rate.

Results of this limited study are shown in Table 15. Data for the run near the BCL shop is restricted to two PSD samples; the third sample was lost because of a power outage during the analysis. Trap analyses for the more volatile components of the target set of compounds are considered questionable because, in many cases, the retention volumes of these compounds were approached or exceeded by the sample volumes.

For this series of runs, the reproducibility of Tenax® GC trap analyses was very poor, with reasonable duplication being obtained in only seven of the pairs. However, the average precision of the PSD analyses is quite reasonable and is in generally good agreement with precision observed in the field intercomparison study and with earlier laboratory work. Because of the tenuous nature of the Tenax® GC trap results, estimation of accuracy of the PSD collection is arguable, and has been attempted only for the last 5 (least volatile) compounds as shown in the last column of Table 15. These data suggest that the reduced-rate PSD's have some promise for accurate sampling of VOC's, but considerably more data will be required to validate their use. It is particularly recommended that further evaluations of the reduced-rate PSD's in the field include the use of a reference method that can be shown to reliably sample the more volatile compounds. One possibility might be to use pumped canister samples or Tedlar bag samples as references.

SHIELDED PSD's

While no special problems related to handling of the PSD's have been observed in our laboratory evaluation, field tests conducted in conjunction with other EPA programs have indicated the desirability of physical protection of the devices during exposure. In particular, it would be desirable to have a light weight protective shield that would prevent direct handling and contamination of the PSD during its field exposure. Several designs for such a protective shield were considered, with the final design as shown in Figure 11. This simple shield consists of a thin aluminum shell that was machined from 1.25 in. rigid aluminum conduit and end plates made from commercially available chromium-plated sink strainers. The aluminum conduit was bored out to accommodate the PSD, leaving a thin lip at one end to retain one end plate. At the other end, the end plate is held in place by a snap ring. The result is a rugged light-weight shield with end plates that present very little restriction to air access to the PSD.

A total of five attempts were made to determine if the protective shields influence the sampling rates of the normal PSD's. However, problems were encountered in handling of these shielded devices because of the increased overall dimensions of the devices -- they are too large to fit easily into our loading device for the chamber. In each of the first four attempts, at least one shielded PSD was displaced from the suspension rod because of rubbing against the loading device. In the fifth trial, we did manage to recover the devices. This run included 2 shielded PSD's and one unshielded PSD for comparison. Results for this run are shown in Table 16.

TABLE 15. REDUCED-RATE PSD FIELD SAMPLES[a]

| Chemical | Sampling Site, time | | | PSD[b] Precision, % | PSD/Trap[c] |
	Shop, 4h	Home, 8h	Office, 8h		
Acrylonitrile	21/5.5 / 51.4/45.1	ND/ND[d] / 1.98/1.63/1.95	3/ND / 2.0/.52/.95	29	
1,1-Dichloroethylene	6.14/1.3 / 15.2/19.5	9.2/2.5 / 31.2/45.3/4.3	ND/ND / 16/22/6.1	27	
Methylene Chloride	5.55/7.20 / 17.9/14.1	11.9/49.2 / 103/122/36	ND/ND / 1.3/8.8/7.9	12	
Trichlorotrifluoroethane	1.4/ND / 10.1/10.1	ND/ND / 7.2/10.2/8.7	ND/ND / ND/7.1/9.7	13	
Chloroform	316/92 / 405/169	117/26 / 35/48/50	285/35 / 81/111/97	17	
1,2-Dichloroethane	31.4/1.1 / 23.1/18.0	25.6/4.2 / 8.92/11.8/13.8	19.2/2.5 / 8.6/11.2/100	17	
1,1,1-Trichloroethane	3700/720 / 3100/2600	11.9/ND / ND/7.84/8.07	22.3/ND / 9.6/14.1/11.3	11	0.64/0.13/7
Benzene	10.0/8.2 / 13.1/105	13.5/7.3 / 4.0/11.5/9.5	12.9/2.4 / 2.8/3.4/3.8	23	1.26/0.25/5
Trichloroethylene	20.6/15.0 / 13.0/15.1	5.6/7.7 / 4.8/2.0/2.7	13.6/5.7 / 4.7/5.3/.65	22	0.89/0.09/5
Toluene	27.2/30.2 / 18.9/39.4	1.5/35 / 1.7/0.76/19	31.1/25.2 / 7.5/11.8/12.6	(26)	0.69/0.41/7
Tetrachloroethylene	15.2/14.5 / 18.3/13.7	15.5/2.8 / 0.96/1.08/10.6	10.1/8.4 / 2.3/4.8/6.3	25	0.69/0.34/6
			Total Average	22	0.81/0.23/23

a. Concentrations in ng/L; data group format = $\frac{\text{Trap Concentrations}}{\text{PSD Concentrations}}$

b. Average of relative standard deviations within PSD groups

c. Relative concentrations/standard deviations/number of points included; Trap concentrations for lighter chemicals considered inappropriate because of small retention volumes.
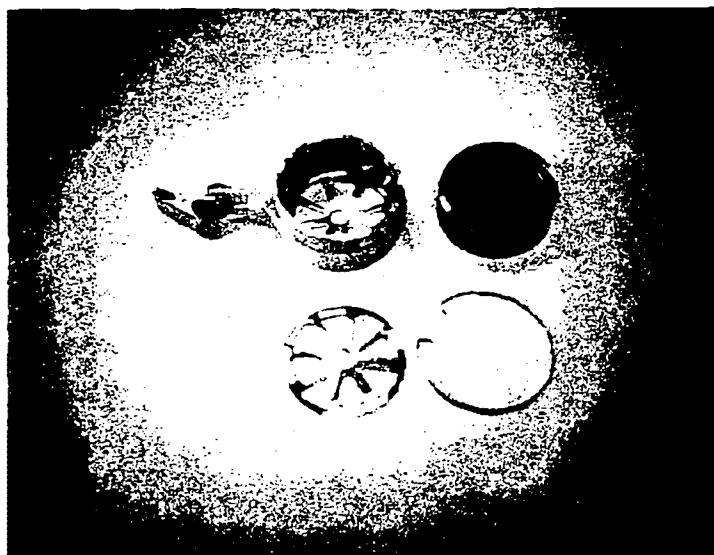
d. ND = not detected.

Figure 11. PSD shield assembly.

TABLE 16. COMPARISON OF SHIELDED AND
UNSHIELDED PSD's

Chemical	Rsh/Runsh	+/-
1,1,1-Trichloroethane	1.04	0.03
Benzene	0.97	0.01
Trichloroethylene	0.92	0.06
Toluene	0.98	0.20
Tetrachloroethylene	1.51	0.05

With the exception of the case of tetrachloroethylene, these results indicate little or no effect of the shields on the sampling rates of the PSD's. The high results obtained for tetrachloroethylene are believed to be due to an analysis anomaly.

INTERCOMPARISON FIELD STUDY

A brief intercomparison field study was conducted at BCL during July and August, 1984, with the primary purpose of comparing cryogenic sampling methodology with active sampling using several different sorbents. The bulk of this study was conducted under Work Assignment 37 of this contract, and the general results of the study were included in the Final Report for that Work Assignment. However, a limited field study of the performance of Tenax® GC-filled PSD's also was conducted in conjunction with this intercomparison study.

Briefly, a sampling station was set up in the BCL parking lot, with instrumentation for cryogenic sampling, multiple active sampling, and collection of pressurized air samples. The air was collected through a common manifold with provision for fortification of the air with standard mixtures of the VOC's of interest. This permitted fortification of selected samples as a part of the quality assurance program. A cylinder of air containing selected components of interest was prepared as a blind sample by EPA/EMSL as a further check on sampling and analytical quality. Analyses of the cryogenic samples and pressurized air samples were conducted within the sampling station by gas chromatography using flame ionization, electron capture, and mass selective detectors. Active samples collected as a part of the main body of this study were returned to the laboratory and were analyzed by GC/MS.

It was inappropriate to collect the passive samples within the station's manifold system. Therefore, PSD's were exposed in triplicate on the roof of the station at a point close to the manifold inlet. Separate active samples were collected at the same point using two Tenax® GC trap samplers. Standard high-sampling rate PSD's were used in all runs, and additional low-rate PSD's were exposed in selected runs. PSD and Tenax® GC traps were returned to the laboratory and were analyzed by thermal desorption/gas chromatography, using a flame ionization detector. A pressurized gas sample collected within the station also was analyzed using the same GC system for purposes of comparison with results obtained at the sampling station. All exposure periods were of 2 hours duration. Additional data collected were air temperature, wind velocity, relative humidity, and barometric pressure. The sampling rates for the PSD's were corrected for temperature and wind velocity, and concentrations were corrected to 25 C, 760 torr, and 0 percent relative humidity for purposes of comparison of the data with results of the main body of the study. The temperature correction for the PSD sampling rates included corrections of the diffusion coefficients and the Tenax® GC retention volumes.

Calibrations for the three separate analytical facilities used on the study were referenced to N.B.S. standards for benzene and tetrachloroethylene, and to a BCL prepared standard mixture of all components of interest. Cross checks of analyses on the pressurized gas samples and on the EPA audit cylinder showed generally good agreement between the different analytical facilities.

A summary of the results of the PSD study is shown in Table 17. Data in this table are grouped in the following format:

<div align="center">

Canister Concentration
Tenax® GC Trap Concentrations
PSD Concentrations

</div>

where the canister concentration refers to the pressurized gas sample taken within the sampling station. Only six chemicals were considered; a number of other chemicals were included in the overall intercomparison study, but these included very volatile chemicals for which (a) the retention volumes were exceeded with the external active samplers, and (b) the standard PSD's are known to be inaccurate because of the low retention volumes.

In the last 5 columns of Table 17 the apparent precision and accuracy of the PSD's are summarized. Precision here is defined as the reproducibility within each group of 3 PSD's, and is calculated separately for the standard and low rate devices for each chemical. Accuracy is defined relative to the canister analyses, with the relative accuracy of the Tenax® GC trap samples being shown also.

A cursory examination of the data in Table 17 reveals several apparent inconsistencies. Except for the cases of 1,2-dichloroethane and toluene, data for the low rate PSD's are generally much higher than corresponding data for the standard PSD's, Tenax® GC traps and canister samples. This may be due to the relatively short duration of the sampling period -- the low-rate devices are designed to sample over periods of 8 to 24 hours. Because of their low sampling rates, the accuracy of blank corrections is very critical when they are used for short-term sampling. Indeed, for several of the samples in Table 17 where "not-detected" is indicated, the chemicals were actually detected, but at levels below the blank correction.

A second problem is evident in consideration of the Tenax® GC trap results. The reproducibility of the traps was less than desirable in a number of cases. Finally, there appears to have been a consistent problem with the GC analyses for tetrachloroethylene on the standard PSD's, with appreciably more tetrachloroethylene being recovered than was present in the canister and trap samples.

In general, the Tenax® GC trap results are of the order of 20-25 percent lower than corresponding canister analyses. This is consistent with the observations made on active sample and canister analyses made within the sampling station. Results for the standard PSD's are, on the average, intermediate between the trap and canister results. The standard deviations for

TABLE 17. SUMMARY OF PSD/TENAX TRAP DATA: FIELD INTERCOMPARISON STUDY[a]

Chemical	Concentration, ng/L Run Number								
	731	731L[d]	719	806	806L	809	809L	814	814L
1,2-Dichloroethane	31.9 2.76/25.3 8.37/3.76	34.3/24.5/29.6	36.3 32.1/32.1 18.3/20.7/21.6	12.4 8.21/1.5 5.76/4.59/2.67	13.5/15.0/16.8	20.2 11.0/1.8 9.2/9.7/8.5	14/20/30	12.4 2.89/0.45 1.56/0.72/0.64	8.34/12.4/10.1
1,1,1-Trichloroethane	32.6 2.57/24.1 26.9/14.5	ND/ND/ND	88.4 78/81 124/134/137	15.5 9.02/1.7 14.7/18.1/13	ND/ND/ND	22.5 13.6/2.6 29.6/33.2/27.5	ND/19.3/7.6	8.0 2.53/0.32 16/11/6.3	17.2/24.6/12.4
Benzene	4.8 4.39/6.05 2.65/ND	49/55/45	375 376/394 388/386/391	9.1 5.93/2.92 4.94/4.34/3.72	22.5/13.7/30	8 6.3/4.3 6.9/6.6/12.3	15.5/30/165	8.4 1.69/0.53 0.87/0.81/1.27	5.3/6.9/5.4
Trichloroethylene	2.0 ND/2.90 ND/ND	0.72/0.14/0.14	30 15.6/14.7 26/22.6/26.2	11.4 10.2/5.96 7.7/ND/6.0	14.2/16.4/13.5	5.0 2.1/0.3 2.1/2.9/1.6	ND/5.4/1.7	3.4 0.91/0.74 ND/ND/ND	4.6/1.0/1.0
Toluene	14.5 13.8/15.1 19.3/17.7	14.4/14.1/14.7	22 20.6/20.9 23.9/24.4/26.8	20.4 14.3/14.8 24.6/ND/24.4	14.2/24.1/22.6	16.6 13.5/14.6 24/23/22	23.9/22/20	10.3 9.45/5.51 11.1/10.7/11.0	9.1/11.9/12.7
Tetrachloroethylene	10.4 3.10/5.32 13.3/12.5	23.4/ND/ND	12 12.2/12.2 17.5/4.4/36.7	3.9 1.2/1.8 22.8/17.2	ND/13.2/ND	7.1 5.56/4.65 19.4/19.5/22	7.1/ND/ND	3.73 3.90/2.43 13.8/25.5/19.9	11.4/14.3/9.8

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TABLE 17. (Continued)

Chemical	Precision, z [b]		Accuracy [c]		
	Standard PSD's	Reduced Rate PSD's	Trap/ Canister	PSD/ Canister	LPSD/ Canister
1,2-Dichloroethane	27	14	.75/.15/5	.46/.10/9	.92/.18/10
1,1,1-Trichloroethane	21	(34)	.74/.15/5	1.20/.29/12	(1.6/1.1/5)
Benzene	20	(21)	.82/.20/6	.75/.26/9	(.72/.12/3)
Trichloroethylene	20	(15)	.72/.40/6	.67/.17/7	(.72/.53/11)
Toluene	4	15	.85/.15/10	1.19/.12/12	1.08/.17/10
Tetrachloroethylene	(19)	(19)	.80/.23/7	2.4/.96/8	(3.0/.62/5)
	Total		.77/.23/39	.91/.33/48	

(a) Format of data group = Canister/Traps/PSD's; Canister and trap results not repeated for reduced rate PSD data groups.

(b) Average reproducibility with PSD triplets (numbers in parentheses indicate limited data group).

(c) Average ratios of traps, PSD's and reduced-rate PSD's to canister results formatted as: average/standard deviation/number of points included.

(d) Reduced-rate groups denoted by "L".

the PSD/canister ratios are somewhat larger than the precision calculated for the PSD's, but this is to be expected because of the additional analytical uncertainty associated with the canister concentrations. The apparent precision for both the standard and low-rate PSD's are consistent with those observed in the laboratory evaluations of these devices (see Tables 4 and 14).

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APPENDIX A

MECHANICS OF PASSIVE DOSIMETER SAMPLING
WITH REVERSIBLE ADSORPTION

MECHANICS OF PASSIVE DOSIMETER SAMPLING

A general model of the mechanics of passive sampling with reversible adsorption is given in reference 3. The following discussion summarizes the simplified model that is appropriate for the EPA PSD.

Passive dosimeters in general rely on diffusion-limited sampling to achieve their characteristic, compound selective "pumping" rates. It is normally assumed that the function of these devices can be expressed in terms of Ficks first law, i.e.,

$$\dot{m}_i = D_i \, A \left(\frac{\partial C_i}{\partial X} \right) \tag{A-1}$$

where $\dot{m}_i$ and D_i are the mass flow rate and diffusion coefficients of the i-th species and A is the sampling area, i.e., the face area, A_o, times the porosity, ε.

$$\left(\frac{\partial C_i}{\partial X} \right) = (C_i^s - C_i^c)/\ell \tag{A-2}$$

where C_i^s and C_i^c are the concentrations at the surface of the device and at the surface of the collection medium, respectively. ℓ is then the distance from the surface of the device to the surface of the collection medium. C_i^c is effectively the equilibrium concentration of the i-th species over the collection medium under a given condition of loading of the collection medium.

When the collector is an activated carbon, the value of C^c is usually taken to be zero because of the strong chemisorption that occurs with that substrate. With a polymeric collector, however, C^c may not be effectively zero ($C^c \leq 0.1 \, C^s$). This is especially the case when the sorbent is chosen to permit thermal desorption. In such cases, it is desirable that only physical adsorption be involved in the collection process. With physical adsorption, however, the adsorbed material is energetically not much different from a condensed liquid phase and the equilibrium value of C^c may

have a significant dependence on the amount of adsorbed material. If the adsorption isotherm of a given species is represented by a plot of the weight of adsorbate per gram of sorbent, W_s, versus the equilibrium gas phase concentration, C^c, the slope of the curve at any point has the units of volume. Walling, et al. (J. F. Walling, R. E. Berkley, D. H. Swanson, and F. J. Toth, <u>Sampling Air for Gaseous Chemicals Using Solid Adsorbents,</u> <u>Application to Tenax</u>, EPA 600/5-4-82-059, 1982) show that this volume parameter is equivalent to the familiar GC retention volume, V_b. That is,

$$dW_s = V_b dC^c \quad . \tag{A-3}$$

Further, Walling notes that V_b can be considered constant at low surface coverages and in the absence of interfering species.

The significance of Equation (A-3) is that we can expect C^c to increase as the surface becomes loaded and that the rate of increase is inversely proportional to the retention volume. In terms of passive monitor operation, this means that the effective sampling rate will decrease at a rate that is inversely proportional to the retention volume. For species that have large retention volumes, the rate of sampling will be relatively insensitive to loading, but we can expect the sampling rates of weakly bound species to change with time. An estimate of the magnitude of this effect can be gained from the following considerations.

In accord with Equation (A-1), the mass flow per unit weight of sorbent into the device can be expressed as

$$\frac{1}{W}\left(\frac{dm}{dt}\right) = \frac{R_o}{W}(C^s - C^c) \tag{A-4}$$

where R_o is the intrinsic diffusion limited rate under irreversible conditions, DA/ℓ. Part of the mass flow to the device will result in an increase in surface loading and part of the mass will contribute to an increase in C^c, i.e.,

$$\frac{1}{W}(dm) = dW_s + \frac{\ell A}{2W}(dC^c) \quad . \tag{A-5}$$

Combining Equations (A-3), (A-4), and (A-5), we obtain

$$\frac{dC^c}{(C^s - C^c)} = \frac{R_o/W}{V_b + \ell A/2W} \quad . \tag{A-6}$$

For a sorbent/device combination that is of any practical significance, $V_b \gg \ell A/2W$, we can simply neglect the latter term. Making the substitution $k = R_0/WV_b$, we can integrate Equation (A-6) between the limits of $C^c = 0$ at $t = 0$, and C^c at $t = t$ to obtain

$$\frac{C^c}{C^s} = 1 = e^{-kt} \ . \tag{A-7}$$

Now the quantity $1 - C^c/C^s$ represents the effective relative sampling rate, R/R_0 at any instant in time. Inasmuch as the passive sampler is an integrating device, it is more appropriate to know the time weighted average relative sampling rate, $\bar{R}_t$.

$$\bar{R}_t = \frac{\int_0^t e^{-kt} dt}{\int_0^t dt} = \frac{1 - e^{-kt}}{kt} \ . \tag{A-8}$$

We see then that for small k's, i.e., for large retention volumes, the sampling rate is inversely proportional to R_0 and directly proportional to V_b, i.e., a relatively constant sampling rate is favored by the combination of a large retention volume, a property of the sorbent/sorbate combination, and a relatively low intrinsic sampling rate, a property determined by the physical design of the device.

For the sake of completeness, it is necessary to include one more effect that is usually ignored in considerations of passive dosimeter mechanics -- the velocity effect. Obviously, when a passive dosimeter removes molecules of some species from the air space surrounding the device, the concentrations of those species must be replenished by bulk movement of the air in order to achieve a steady-state sampling condition. Whenever there is bulk flow over a surface, there is drag between the gas stream and the stationary surface, with the result that a relatively stagnant boundary layer develops near the surface. The thickness of this boundary layer depends on the velocity and the distance from the leading edge of the surface. (Surface shape and roughness also affect the boundary layer development, but are ignored in this elementary treatment.) The significance of this boundary layer is that it does present a small diffusional resistance that is additional to the intrinsic resistance that is determined by the physical structure of the dosimeter (noted above in terms of R_0).

The velocity effect for dosimeters previously has been treated employing irreversible adsorption (2), and use a similar approach for the reversible case:

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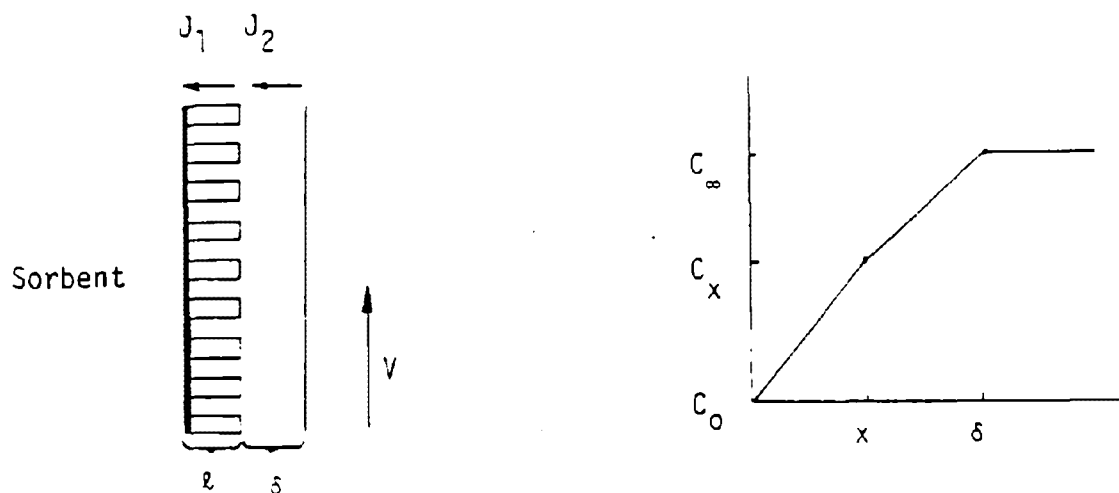Consider the simplified representation of a dosimeter given in Figure A-1.

Figure A-1. Boundary layer over badge surface.

Here the boundary layer thickness is represented by δ, and x represents the position of the surface of the dosimeter. Under steady-state conditions, the mass fluxes J_1 and J_2 must be equal. Therefore,

$$DA_o(C_\infty - C_x)/\delta = DA_o\epsilon(C_x - C_o)/\ell \ . \tag{A-9}$$

Defining the quantity $\epsilon\delta/\ell$ as z, we then find that

$$C_x = (C_\infty + zC_o)/(1+z) \ . \tag{A-10}$$

Inasmuch as $C_x = C^s$ and $C_o = C^c$, as used in Equation A-4,

$$\frac{dC^c}{(C_s - C_c)} = \frac{R_o/W(1+z)}{V_b}dt \tag{A-6'}$$

where Equation 6' is now the equivalent of Equation A-6, but including the contribution of the boundary layer. We can see then that this effect merely amounts to reduction of R_o by a factor of $1/(1+z)$, or

$$R_o' = R_o/(1 + \frac{\epsilon\delta}{\ell}) \ . \tag{A-11}$$

Equation A-8 can then be corrected for the velocity effect,

$$\bar{R}' = \frac{1}{t} \cdot \frac{1 - e^{-k't}}{k't}.$$ (A-8')

In order to apply Equation A-8', the following relationship given by Bird, Stewart and Lightfoot (6) is used:

$$\delta = 4.64 \left(\frac{\mu x}{v\rho}\right)^{1/2}/1.026 \; S_c^{1/3} \approx 3.94 \left(\frac{\mu x}{v\rho}\right)^{1/2} \text{ for air}$$ (A-12)

where μ is the viscosity, x is the mean distance from the leading edge, v is velocity, ρ is the gas density, and S_c is the Schmidt number. (For an average organic molecule in air at 25 C, $S_c \approx 1.5$).

The EPA Device

The diffusion barrier of the EPA device is a multilayer structure and in determining the effective ϵ/ℓ, the several layers must be treated as a series of diffusional resistors. Thus,

$$(\epsilon/\ell)^{-1} = \sum_i (\epsilon_i/\ell_i)^{-1}.$$ (A-13)

The structure and parameters for the EPA device are shown in Figure A-2. (One face shown, normal use employs both faces.)

Referring to the dimensions in Figure A-2,

$$(\epsilon/\ell)^{-1} = 2\left(\frac{1}{.127}\right)^{-1} + 2\left(\frac{.379 \times .395}{.0107}\right)^{-1} + 2\left(\frac{.395}{.0655}\right)^{-1}$$

$$= 0.729$$

or $\qquad \epsilon/\ell = 1.37$

and

$$A_0 \epsilon/\ell = 9.70 \text{ cm for single sided sampling}$$

$$\text{or } 19.40 \text{ cm for two sided sampling.}$$

It should be noted that the open recess at the face of the device is included in these calculations. If this recess is not included, $A_0 \epsilon/\ell = 11.75$ cm for single sided sampling.
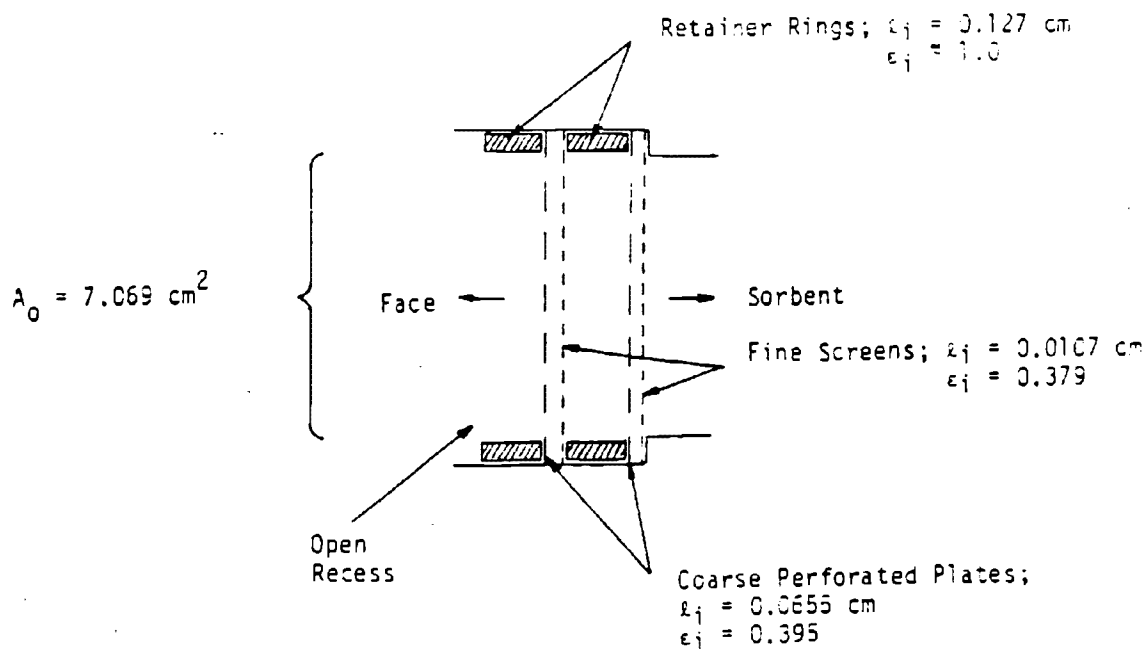
Figure A-2. Schematic representation of PSD diffusion barrier.

For the circular MRC dosimeter, $x \approx \frac{d}{\pi}$ (diameter) ≈ 0.96 cm, and $\delta = 1.55/v^{1/2}$ (v in cm/sec). Therefore the velocity correction factor is

$$f\left(\frac{v\epsilon}{\ell}\right) = \frac{1}{1 + 1.37(1.55/v^{1/2})}$$

or, @100 fpm, $f\left(\frac{v\epsilon}{\ell}\right) = \frac{1}{1 + 0.30} = 0.76_9$

and the effective sampling rate for two sided sampling is

$$R_i' = D_i \ 14.92 \ cm^3/min. \tag{A-14}$$

The rates calculated for some volatile organic compounds using Equation (A-14) are shown in Table A-1. Relative velocity effects, expressed as R_v/R_{100} are shown in Figure A-3.

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TABLE A-1. CALCULATED PSD SAMPLING RATES

Compound	(a) D_i, cm^2/min	(b) R^{100}, cc/min	(c) V_b, L/g	(d) R_t', cc/min
Chloroform	5.33	79.5	18.9	59.0
1,1,1-Trichloroethane	4.76	71.0	11.8	46.8
Carbon Tetrachloride	4.97	74.2	16.5	53.9
Trichloroethylene	5.25	78.3	39.3	67.7
Tetrachloroethylene	4.97	74.2	154.0	71.5
Benzene	5.59	83.4	42.5	72.2
Chlorobenzene	4.48	66.8	372.0	66.0
Acrylonitrile	6.35	94.7	0.3-7	23.0
1,2-Dichloroethylene	5.51	82.2	2-6	25.0
Trichlorotrifluoroethane	(4.16)	62.1	0.23-0.47	2.0
1,2-Dichloroethane	5.44	81.2	24.4	63.9
trans-1,3-Dichloropropene	4.76	71.0	335.0	69.9
Toluene	5.09	75.9	193	73.7
1,2-Dibromethane	(4.66)	69.5	183.0	67.6
o-Xylene	4.36	65.1	2800.0	64.9
α-Chlorotoluene	4.28	63.9	1984.0	63.7
Hexachlorobutadiene	(3.3)	49.2	324.0	48.7

(a) Diffusion coefficients taken from Lugg (Anal. Chem., 40, 1072 (1968)) except for estimated values given in parentheses.

(b) Calculated sampling rates at zero time and face velocity of 100 fpm.

(c) Retention volumes of Tenax GC taken from Pellizari, et. al., (Anal. Chem. 54 810-817 (1982)) except where range of values is indicated.

(d) Time-weighted-average sampling rates (cm^3/min) calculated for one hour sampling times;

$$\bar{R} = R_0 \left[\frac{1 - e^{-kt}}{kt}\right], \text{ where } k = R_0/0.4V_b$$
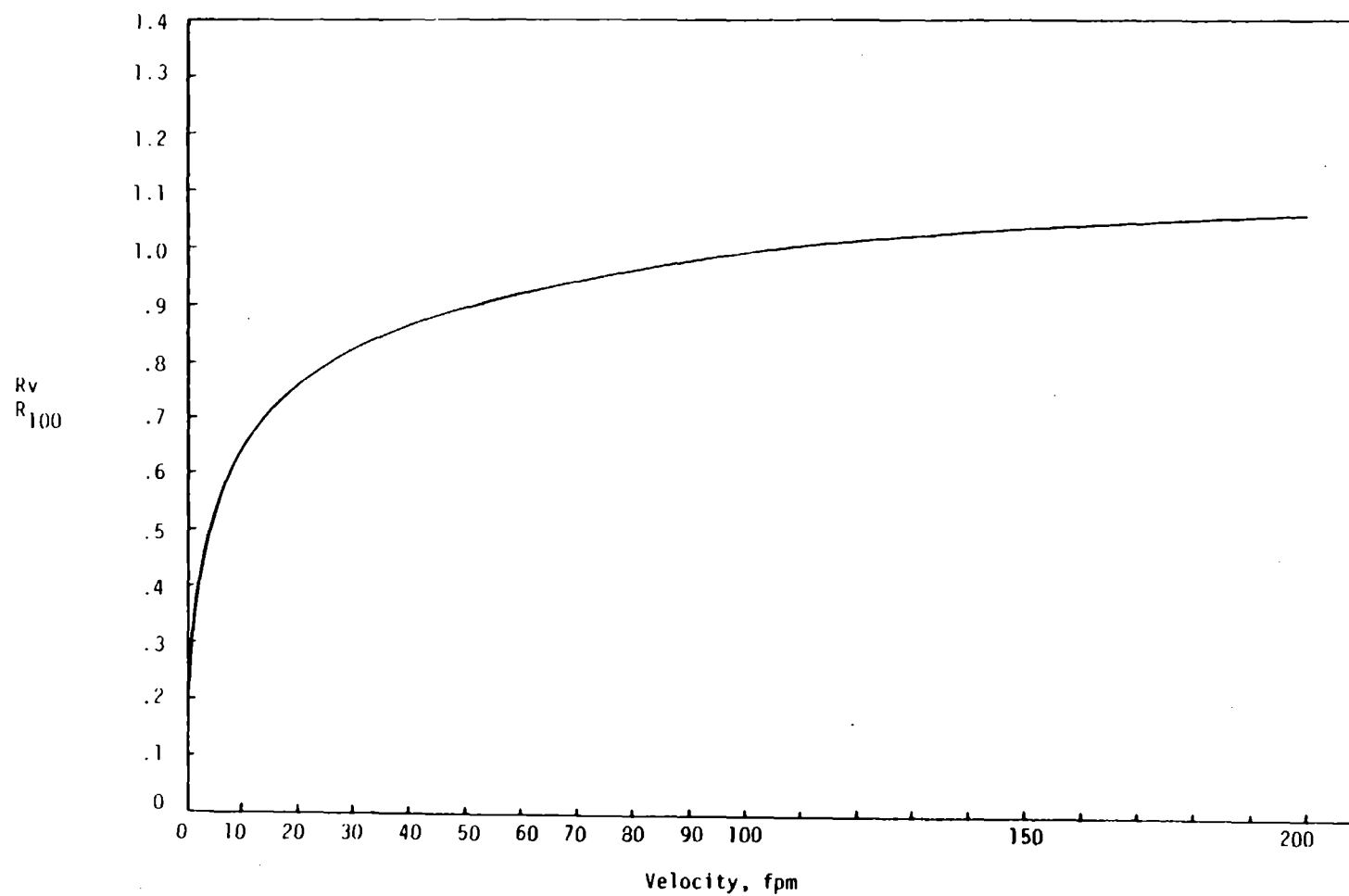
Figure A-3. Calculated Effect of Velocity on MRC Badge Sampling Rate (ϵ/ℓ = 1.37).

It should be noted that the rates given in Table A-1 are minimum rates for the MRC device, i.e., they are based on the assumption that the open recess at the face of the badge is part of the diffusion barrier. An upper limit estimate of these rates would yield values about 20 percent higher.

The calculations shown in Figure A-3 imply that the sampling rate approaches zero as the velocity goes to zero. This is somewhat misleading because the calculated rate represents only the steady-state rate. Under perfectly quiescent sampling conditions, the diffusion layer would continuously expand to infinity, taking an infinite time to do so. During this time, the device would continue to sample in a transient mode at an ever decreasing rate.

Normal air velocities are likely to range from about 10-20 fpm in a passive indoor situation to 440 fpm (5 mph) in outdoor applications. The expected variation in rates is thus $0.65 \, R_{100}$-$1.15 \, R_{100}$. Under normal indoor working conditions the expected rate is $R_{100} \pm 5$ percent.

The effect of sampling time on the time weighted average sampling rate can be seen in Figure A-4. In this figure $\overline{R}_t$ is plotted vs t/τ, where

$$\tau = \frac{WV_b}{R_o} .$$

This approach allows the performance of the reversible sorption passive dosimeter for different chemicals to be compared on the same graph once the characteristic values of τ are calculated for chemicals of interest. Also indicated in Figure A-4 are the values of τ calculated for single sided sampling of the chemicals used in this program on the EPA PSD.

In principle, Figure A-4 could be used to correct sampling data taken over various time periods to a common basis. If this type of correction is deemed undesirable, however, it is likely that $\overline{R}_t$ values less than say 0.8 would be acceptable. Arbitrary selection of such a limit would determine the allowed sampling time for each chemical. For example, choice of $\overline{R}_t = 0.8$ would allow a 39 hour sampling time for chlorobenzene but only 1 hour sampling of 1,1,1-trichloroethane.

The most useful aspect of Figure A-4 may lie in its use for device design. For any chemical having a known characteristic value of V_b, Figure A-4 specifies the ratio of W/R_o that is needed to obtain relatively time insensitive sampling.

Effect of Fluctuating Concentration

Although Equation A-8' correctly applies to sampling of relatively constant concentrations of volatile organics (C^S constant), it does not apply when C^S varies significantly during the sampling period. For example, if the species being sampled is initially at say C^S for the first half of the sampling period, and then drops to $C^S=0$ during the second half of the sampling

$$\bar{R}_t = \frac{1-e^{-t/\tau}}{(t/\tau)}$$

$$\tau = \frac{1}{k} = \frac{W\ V_b}{R_o} \quad (W=0.4g)$$

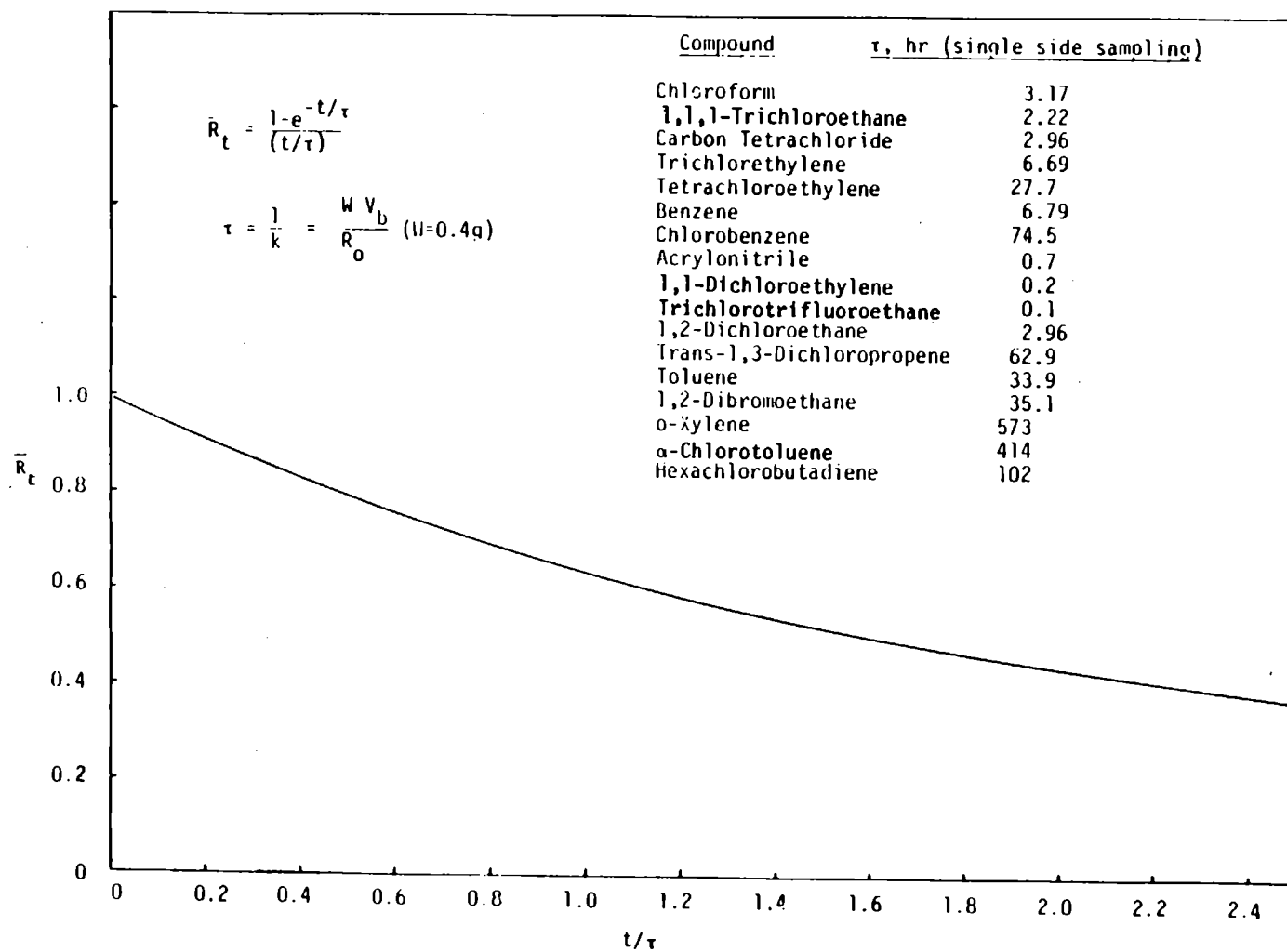| Compound	τ, hr (single side sampling)
Chloroform	3.17
1,1,1-Trichloroethane	2.22
Carbon Tetrachloride	2.96
Trichlorethylene	6.69
Tetrachloroethylene	27.7
Benzene	6.79
Chlorobenzene	74.5
Acrylonitrile	0.7
1,1-Dichloroethylene	0.2
Trichlorotrifluoroethane	0.1
1,2-Dichloroethane	2.96
Trans-1,3-Dichloropropene	62.9
Toluene	33.9
1,2-Dibromoethane	35.1
o-Xylene	573
a-Chlorotoluene	414
Hexachlorobutadiene	102

Figure A-4. Effect of Time on Sampling Rate.

time (e.g., when the user moves from one building to another) some of the chemical adsorbed during the first exposure condition will be lost because of the reversible nature of the adsorption process. The rate of loss will not be as great as the initial rate of adsorption however because of the fact that the concentration gradient will be smaller $((C^c-0)/\ell)$ during the second period. Indeed, the error induced by fluctuating concentrations can be either positive or negative, depending on the way in which the exposure condition changes. In principle, we could express C^s as a function of time and numerically integrate Equation A-6, but this would require prior knowledge of C^s for each sampling condition. A more reasonable approach is to consider some specific examples and use the results to provide further guidelines to use the PSD. Consider the following simple cases:

Case 1: C^s = 1 ppbv for t = 0-1 hr; C^s = 0 for t = 1-2 hr

R_o = 81.2 cc/min; k = 0.676 hr^{-1} (two sided sampling for 1,2-dichloroethane).

During the first hour, the time-weighted average sampling rate is correctly given by Equation A-8' and is equal to 59.0 cc/min. The amount adsorbed is therefore 60 min x 59 cc/min x 1 ppbv = 3.54 x 10^{-6} cc. During the second hour, Equation A-6 reduces to

$$C^c/C^c_o = \exp{-kt}$$

so that 50.9 percent of the adsorbed chemical will be lost during the second hour. That is, 1.74 x 10^{-6} cc will remain at the end of the 2-hr sampling period. If the user does not know that the concentration change has occurred, he will assume that the correct sampling rate is the 2-hr time-weighted rate (TWR) or 44.5 cc/min and he would calculate the TWR concentration as

1.74 x 10^{-6}/(120 x 44.5) = 0.326 ppbv .

The true TWR for this sampling condition is 0.5 ppbv; a negative error of 34.8 percent has occurred.

Case 2: Same concentration profile as Case 1; $\bar{R}_{2hr}$ = 0.8 R_o = 70 cc/min

In this case, the Newton-Raphson method can be used to solve Equation A-8' for k with the result that k = 0.232 hr^{-1}. The amount sampled during the first hour is then 3.75 x 10^{-6} cc. The amount left after the second hour is 2.97 x 10^{-6} cc. The user will assume that the badge sampled at a TWR of 56 cc/min and will calculate the TWR as 0.442 ppbv. The true TWR is again 0.5 ppbv, so that a negative error of 11.6 percent occurs.

Case 3: Concentration profile reversed from Case 2, i.e., $C^S = 0$ for $t = 0-1$ hr; $C^S = 1$ ppbv for 1-2 hr; R_O and k remain as in Case 2

This time there is no material lost, but the device does not begin to sample until the second hour, during which time it samples at the 1-hr TWR. The amount adsorbed is therefore 3.75×10^{-6} cc. Again, the user assumes that the 2-hr TWR is appropriate, and he calculates a TWR of 0.558 ppbv, or a positive error of 11.6 percent.

These three cases probably represent extreme exposure conditions; more gradual changes with less total change in C^S would be more realistic, and we would expect that the error would therefore generally be less than found in these examples. However, the results serve to illustrate the effect of a large value of k on the sample integration accuracy. The results also suggest that the restriction of the TWR to 0.8 R_O may be a reasonable choice.

APPENDIX B

CHROMATOGRAPH INLET SYSTEM

CHROMATOGRAPH INLET SYSTEM

As noted in the text of this report, analytical procedures used for the PSD's were upgraded several times during the course of the 3 work assignments covered by this report. One of the more significant changes involved the development of a multi-purpose chromatograph inlet system that incorporates capabilities for: (1) PSD desorption, (2) direct sampling of external gas streams, and (3) cryogenic preconcentration of gas samples. A schematic of this inlet system is shown in Figure B-1. Briefly, this unit consists of the following components:

1. A quick-disconnect inlet for PSD connection.

2. A gas sample inlet.

3. An outlet to a vacuum or pumping station.

4. An outlet to a capillary column.

5. A fixed volume loop for capture of gas samples.

6. A resistance wound cryogenic loop for trapping and release of PSD or gas samples.

7. Two 6-port Carle valves for switching of flow directions and injection of samples into the chromatograph.

The complete assembly, except for the cryogenic loop is contained within an insulated temperature controlled box. When using the cryogenic sampling capability, the pumping outlet is connected to an evacuated fixed volume system that is fitted with a Wallace and Tiernan gage for accurate determination of sample volume.
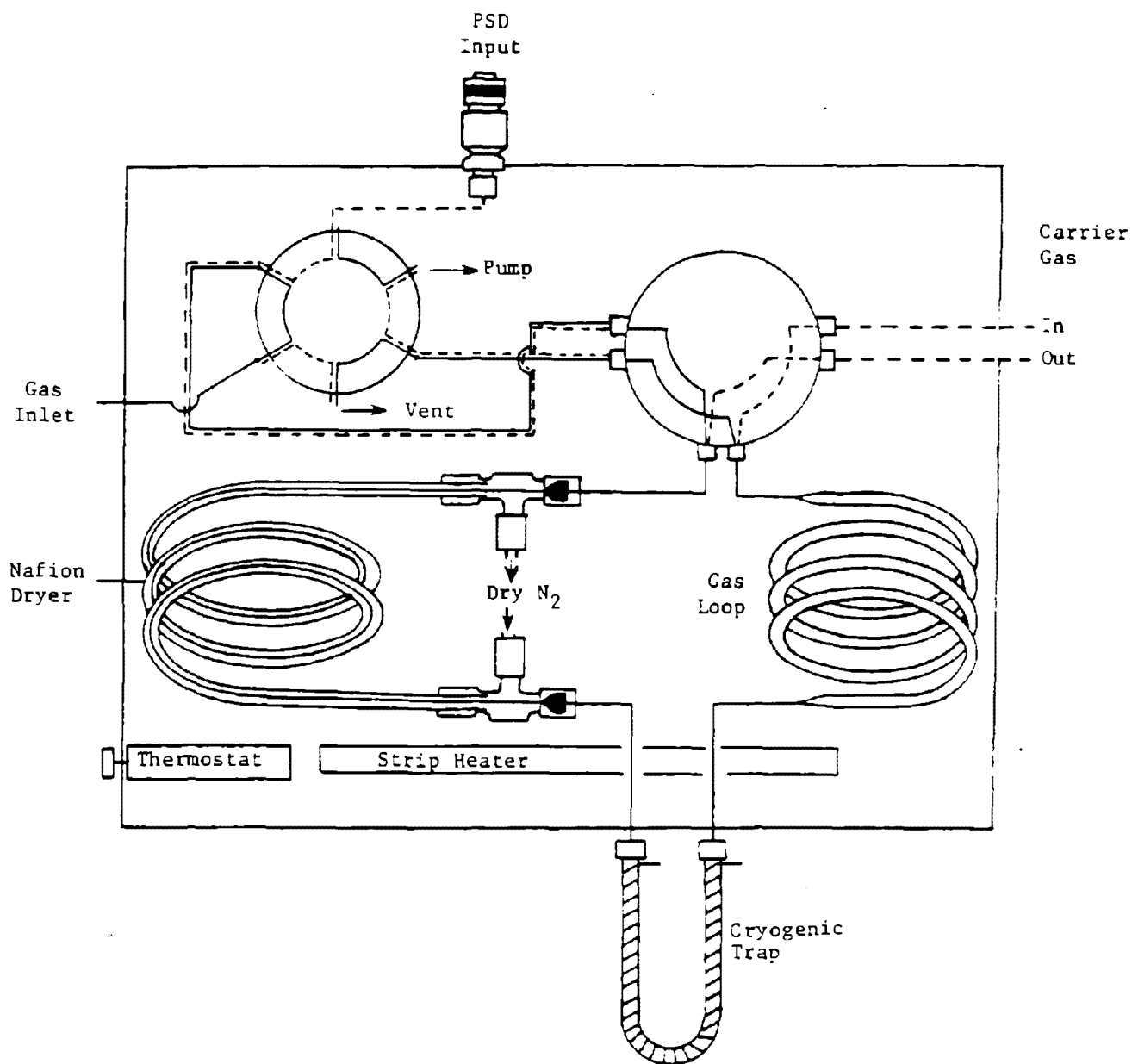
Figure B-1.   General purpose GC inlet.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The basic objectives of this study were to evaluate the performance of the EPA passive sampling device (PSD) for sampling of ambient level volatile organic compounds (VOC's); to develop an understanding of the mechanics of passive sampling using reversible adsorption; and to apply this understanding to development of an improved PSD that is usable for sampling of VOC's over periods of 8 to 24 hours. Laboratory and limited field evaluations of the standard and modified PSD's were conducted and a model relating sorbent properties and device design to sampling rates was developed. The results show the standard PSD's to be useful for sampling of VOC's having large retention volumes. Modified PSD's having greatly reduced sampling rates show promise for sampling compounds having retention volumes as low as 5 to 10 L/g over 8 to 24 hour sampling periods. The use of Spherocarb as an alternative sorbent to Tenax GC also was investigated as a means for improving the performance of the PSD. This sorbent was found to be unsuitable because of the high temperatures required for desorption. It is recommended that the model which was developed be used for developing sampling plans for specific applications, and that more extensive field evaluation of the reduced-rate PSD's be conducted. This report is being submitted in fulfillment of Contract No. 68-02-3487 by Battelle Columbus Laboratories under the sponsorship of the US Environmental Protection Agency. It covers a period of April 15, 1982 to October 31, 1984, and work was completed as of October 31, 1984.

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