

Project Summary

Passive Sampling Device for Ambient Air and Personal Monitoring

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A high performance passive dosimeter has been developed and evaluated as a monitor for volatile organics in ambient air and for short-term, low-level personal monitoring applications. The dosimeter design was dictated by three major areas of concern: (1) diffusive mass transport considerations; (2) sorbent selection, and (3) chemical quantitation of the collected compounds, which intimately involves desorption procedures of the passive device.

Salient design features of the dosimeter included the following: (1) rugged, simple design and cost effective; (2) small size and simple operation; (3) high equivalent pump rate and high sensitivity; (4) multicomponent sampling capability; (5) ability to be reused and recharged; and (6) amenability to thermal desorption.

The results of laboratory and field evaluation studies of dosimeter performance are discussed in terms of the design criteria employed in the development of the device and its application to widely divergent sampling assignments. Detection sensitivity at the sub-ppb level was demonstrated for short exposure times (e.g., one hour) employing thermal desorption and halogen specific Hall detector/gas chromatography. Long-term exposures were conducted under ambient air (ppb range) and work station (ppm range) environmental conditions. Retention time windows and detector response factors for 24 halogenated compounds have been established for our computer program to increase compound recognition capabilities. The addition of a photoionization detector extended this

capability to nonhalogen compounds of current environmental interest.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The rapidly expanding needs of personal and area monitoring demand passive monitoring devices that offer the capability of detecting multicomponent vapors at low concentrations and are low-cost, lightweight, and convenient units. Properly designed passive dosimeters containing selected polymeric adsorbents can provide highly attractive performance with respect to multivapor capability and sensitivity to ppb levels.

The objective of this program was to design, develop and evaluate a prototype passive personal dosimeter based on diffusion principles and employing porous polymer sorbents that will meet all of the performance requirements stated above. The personal dosimeter was to be capable of monitoring the following toxic organic pollutants at the part-per-billion level in ambient air: benzene, vinyl chloride, trichloroethylene, tetrachloroethylene, chloroform, carbon tetrachloride, chlorobenzene, dichlorobenzene, 1,2-dichloroethane, and trichloroethane.

The personal monitor design was to be similar in size to a radiation badge so that it could be easily worn. The sorbent materials in the badge were to be chosen so that a wide range of toxic organic

pollutants could be monitored, or if more selective monitoring was desired, sorbents could be chosen to preferentially collect specific compounds. Laboratory tests and evaluations of the approved prototype were to be conducted to determine overall performance of the unit in the collection and analysis of the pollutants. Testing was to include determination of sensitivity limits, selectivity, shelf life, artifact formation, and other salient characteristics.

Dosimeter Design

The passive dosimeter consists of a stainless steel body, 3.8 cm diameter and 1.1 cm high, which makes the device amenable to thermal desorption, eliminates problems associated with adsorption of organics into plastic materials, and provides a rugged, reusable device. The internal body diameter is reduced to 3.0 cm to provide a precise containment volume (~0.4 g) for the porous polymer. Two sets of stainless steel screens (200 mesh wire) and perforated plates (28% open area) are located on each side of the polymer to confine the polymer and serve as diffusion barriers. Friction snap rings are used to hold the screen and plate tightly against the center of dosimeter body containing the polymer.

Application of the passive dosimeter involves three principal areas of technology: diffusion considerations, sorbent selection, and chemical quantitation of the sampled compounds.

The diffusion rate of organic compounds onto the adsorbent is based on the types of compounds of interest and their diffusion constants, the ambient concentration of the compounds, and the diffusion path the compounds must take to get to the adsorbent. Diffusion rates for several chlorinated organic compounds were calculated as well as defined by laboratory tests as part of this contract as discussed later in this report.

Selection of adsorbent materials is based on the ability of the sorbent to hold the compounds of interest at the sampling conditions and then readily release the compounds at the desorption conditions with minimum background interference.

Chemical quantification of exposed passive dosimeters entails a two-step procedure. The first step involves the removal (desorption) of collected compound(s) and the second involves the determination of compounds. Typically, the procedures used are thermal desorption and a gas chromatographic (GC) procedure with a specific detector (for example, electron capture or photoioniza-

tion detector) for the compounds of interest.

Test Equipment

Gas standards were generated for dosimeter evaluation studies using a sample generation system employing a syringe drive of fluids into heated blocks with three calibrated dilution stages.

Dosimeters were exposed to gas standards in one of two exposure chambers. The first chamber was a 2-liter borosilicate glass jar fitted with an "O"-ring-sealed Teflon lid and multiple Swagelok® fittings for gas injection, sampling, and gas outlet. Dosimeters hung in the center of the jar, sampling the contaminated air during grab type tests.

The second chamber was a thick-walled, flanged, borosilicate glass pipe by which dosimeters could be subjected to a range of concentrations, temperatures, humidities, and flow velocities. Sorbent tubes were used to collect known volumes of sample to validate gas constituent concentrations with either chamber during the tests.

Results

Sorbent Selection

Porapak R and Tenax GC were evaluated as sorbent materials for use in the dosimeters, based on their high breakthrough volumes and clean background on the thermal desorption. The Porapak R sorbent provided good results at most concentration levels, however, at low concentration levels (~1 ppb), recovery of spiked samples for several chlorinated compounds was low (40% to 50%). Exposure studies using Tenax GC were more encouraging with recovery efficiencies for all components greater than 93%. Tenax GC was subsequently chosen as the adsorbent material for all future dosimeter tests.

Performance Testing

Initial tests performed on the dosimeter defined the response of the analytical systems with compound mass collected on the dosimeter, the sample concentration range, equivalent sampling rates, effects of concentration and exposure time on dosimeter sampling rates, and storage of samples.

A linear response was verified for the quantity of organic compound on sorbent and the GC response. This response was verified for chloroform, carbon tetrachloride, 1,1,2-trichloroethane, chlorobenzene, 1,2-dichloroethane, trichloroethylene, and tetrachloroethylene.

Dosimeter calibration curves were developed for the low concentration range (1-50 ppbv) and extended up to approximately 10 ppmv (see Figure 1). These curves were established by exposing dosimeters in the sample exposure chambers for varying times and concentrations.

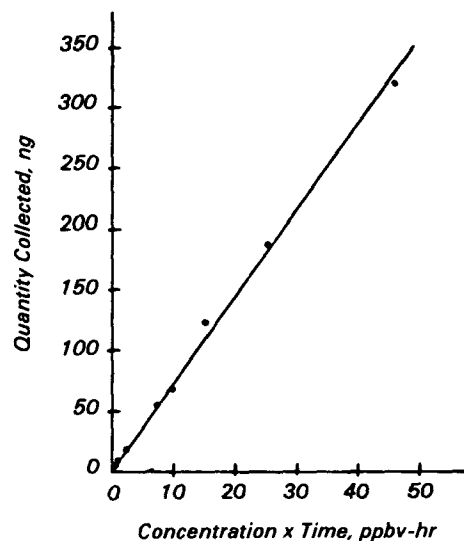


Figure 1. Example response curve (1,2-dichloroethane).

Sampling rates for dosimeters were defined by comparing the dosimeter with active sorbent sampling tubes. Simultaneous samples were collected by exposing dosimeters within the chamber and by withdrawing gas samples from sample ports into the sorbent tubes. Sampling times were varied between one and four hours. Two-sided dosimeter exposure resulted in equivalent sampling rates of 50 to 60 cc/min. Averaged equivalent sampling rates for one-sided exposure ranged 25 to 34 cc/min as shown in Table 1.

To determine the effect of concentration and time on dosimeter performance, triplicate exposures were made at 1-, 2-, 4-, 8-, and 16-hour durations and at concentrations of 1, 10, and 100 ppbv. Typically, there is a decrease in sampling rate for the more volatile compounds (i.e., chloroform, 1,2-dichloroethane, and carbon tetrachloride) at the ppb level as exposure time is increased above approximately 4 hours.

Studies to determine the extent in which compounds were lost during storage was also evaluated. Exposed dosimeters were capped with friction-tight Teflon caps, sealed in screw-cap

Table 1. Average Equivalent Sampling Rates (Single-Faced Sampling)

	Chloroform	1,2-Dichloroethane	Carbon tetrachloride	Trichloroethylene	1,1,2-Trichloroethane	Tetrachloroethylene	Chlorobenzene
Pump rate, cc/min	25.0	26.8	21.8	28.3	27.7	29.5	34.3
Std. dev.	±5.0	±2.9	±5.2	±1.5	±0.6	±1.9	±4.0

glass jars, and maintained under ambient laboratory conditions for twelve days. Only 10 to 18% decrease was observed from the 30 ng spike after the 12 days, except for carbon tetrachloride which showed a 50% decrease.

Sampling Tests

Laboratory validation tests were conducted by varying sampling times and concentrations for single- and dual-faced exposures. Multiple dosimeters and tubes were typically used for each test. Typical results for the validation tests, shown in Tables 2 and 3, indicate that the dosimeters have the ability to identify compounds and concentrations similar to the tube results or the expected gas standard concentrations.

Small-scale field studies were performed to provide additional dosimeter validation information. The first study conducted found good recoveries of the laboratory spikes. In addition, clean dosimeter blanks were found. Variation in temperatures (80°F to 90°F), relative humidities (50% to 80%), and wind velocity (5 mph to 25 mph) appeared not to effect results.

Work station monitoring conducted in a second field study showed good comparisons between dosimeter and charcoal and solid sorbent tubes. As shown in Table 4, good agreement was shown for 1,2-dichloroethane between the dosimeter and charcoal tubes with one exception (attributed to the fact that the dosimeter may have been shielded by protective clothing). Table 5 shows additional results from this study comparing sorbent tube and dosimeter. In addition, one 5-hour sample compared well with the sum of five consecutive 1-hour samples.

Conclusions and Recommendations

A high performance passive dosimeter was developed to meet the rapidly expanding needs of ambient air and short-term, low-level, personal monitoring. This device, employing a porous polymer as the sorbent medium, satisfies the stringent requirements imposed by ambient air sampling. Detection sensitivities in the part-per-trillion (ppt) to part-per-billion (ppb) range have been demon-

Table 2. Single-Face Sampling for One Hour

Compound	Concentration ppbv		Percent recovery	Concentration, ppbv Dosimeter	Ratio dosimeter/tube
	Theory	Tube			
Chloroform	11.6	11.1	96	12.9	1.17
1,2-Dichloroethane	13.7	13.7	100	13.8	1.00
Carbon tetrachloride	8.8	10.6	120	9.7	0.91
Trichloroethylene	10.4	10.2	98	12.1	1.19
1,1,2-Trichloroethane	10.2	11.1	109	12.5	1.13
Tetrachloroethylene	8.2	8.6	105	13.7	1.59
Chlorobenzene	12.1	11.0	91	12.4	1.13

Table 3. Dual-Face Sampling Integration Experiment B (1 ppbv - 45 min; 100 ppbv - 15 min)

Compound	Concentration, ppbv		Percent recovery	Concentration, ppbv Dosimeter	Ratio dosimeter/tube
	Theory	Tube			
Chloroform	28.0	26.5	95	26.7	1.01
1,2-Dichloroethane	33.8	33.6	99	28.1	0.84
Carbon tetrachloride	21.7	22.6	104	24.0	1.06
Trichloroethylene	25.4	24.3	96	27.7	1.14
1,1,2-Trichloroethane	25.0	26.7	107	29.8	1.12
Tetrachloroethylene	20.1	19.8	99	28.8	1.43
Chlorobenzene	29.7	32.0	108	33.9	1.06

Table 4. 1,2-Dichloroethane Sampling with Charcoal Tubes and Passive Monitors

Parameter	Charcoal Tube No.			
	1	2	3	4
Flow rate, mL/min	47.2	46.2	50.2	49.0
Amount collected, µg	81	456	305	17,865
Exposure time, hr	5.6	5.6	5.6	5.6
Concentration, µg/L	5.1	27.8	18.2	1,027
ppmv	1.3	6.9	4.5	254
Parameter	Dosimeter No.			
	90	91	92	93
Equivalent, mL/min pump rate	30.0	30.0	30.0	30.0
Amount collected, µg	64.0	277	212	1,536
Exposure time, hr	5.6	5.6	5.6	5.6
Concentration, µg/L	6.3	25.9	21.0	144.0
ppmv	1.6	6.4	5.2	35.6

strated for seven halogenated organic compounds at exposure times of about one hour. Retention time and detector response data for twenty-four halogenated compounds were developed to extend compound recognition capabilities. This simple, inexpensive monitor demonstrates multicomponent sampling capabilities. Sampling performance of the passive device is comparable to active "pumped"

sampling tubes. Device performance is provided by the equivalent pump rate characteristics, the high sample recovery via a thermal desorption process, and the detection sensitivity and specificity afforded by multiple specific detector GC analysis.

While in-depth laboratory and field evaluation studies have been conducted with the monitor, more comprehensive

field studies should be completed to demonstrate the practical applicability of the monitor to real sampling problems. Hazardous waste sites represent a timely sampling problem that would provide a good practical evaluation of the monitor.

Table 5. Work Station Sampling Studies

Compound	Mass collected, μg					Σ	Dosimeter 5-hr exposure
	1 hr	2 hr	3 hr	4 hr	5 hr		
<i>Passive dosimeter</i>							
1,2-Dichloroethane	0.27	0.29	0.24	0.20	~0.10	~1.1	0.67
Trichloroethylene	0.58	0.38	0.25	0.11	0.16	1.48	1.47
1,1,2-Trichloroethane	0.16	0.48	-	0.38	0.48	1.50	0.90
Tetrachloroethylene	0.25	0.38	-	0.15	0.12	0.90	0.66
Chlorobenzene	8.4	18.2	10.4	8.6	6.7	51.0	51.0
<i>Pumped tube</i>							
1,2-Dichloroethane	0.34		0.14		0.13		
Trichloroethylene	0.43		0.22		0.15		
1,1,2-Trichloroethane	0.49		-		0.59		
Tetrachloroethylene	0.11		-		0.17		
Chlorobenzene	7.5		9.6		5.4		

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James D. Mulik is the EPA Project Officer (see below).

The complete report, entitled "Passive Sampling Device for Ambient Air and Personal Monitoring," (Order No. PB 84-210 046; Cost: \$10.00, subject to change) will be available only from:

National Technical Information Service
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