



## Project Summary

# Evaluation of Passive Sampling Devices (PSDs)

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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 (VOCs); 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 VOCs over periods of 8 to 24 hours. Laboratory and limited field evaluations of the standard and modified PSDs were conducted and a model relating sorbent properties and device design to sampling rates was developed. The results show the standard PSDs to be useful for sampling of VOCs having large retention volumes. Modified PSDs 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 Sphero Carb 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 PSDs be conducted.

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*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

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. The performance of one of these devices under simulated ambient conditions also was subjected to a detailed evaluation.

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 (13, 21, and 33) 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 (VOCs) 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 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-dichloroethane,  $\alpha$ -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 VOCs. 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*.

## Procedures

### Exposure Studies

The U.S. EPA passive sampling devices (PSDs) were exposed in triplicate to controlled compositions of the test chemicals at ppbv concentration levels in the

Battelle dosimeter test facility. This facility consists of a 200 L chamber in which air velocity, gas composition, relative humidity, and temperature can be controlled. Associated with this chamber is appropriate monitoring equipment including a capillary GC facility having a triple detector (in series electron capture and photoionization with parallel flame ionization) arrangement to provide both high sensitivity and selectivity for component analysis. The devices were handled under a protective atmosphere of zero-nitrogen at all times except during the actual exposures to the test atmospheres. Test compositions in the chamber were monitored both by periodic direct analysis with the GC and by a pair of Tenax® GC traps that were used to sample the chamber gases in an active mode. The PSDs and Tenax traps were analyzed by thermal desorption into the GC. Exposures were conducted at different relative humidities, different concentrations (in the low ppbv range), different air velocities, and for various lengths of time (up to 24 hr).

## Results

Inasmuch as sampling rates for most of the compounds studied had not previously been determined for the EPA PSD, this parameter was used as the basis for comparison of the device performance. A generalized model relating sampling rate to the device geometry and chemical retention volumes was developed. This model takes into account the reversible nature of the adsorption of volatile organics on Tenax® GC, and permits the prediction of the time weighted average sampling rate as a function of time. Conversely, it has been demonstrated that the model can be used to derive Tenax retention volumes from measurements of the apparent sampling rates with the MRC device. More importantly, the model provides guidelines for design and application of passive dosimeters employing reversible adsorption.

Apparent sampling rates measured for the 18 test chemicals agreed well with those predicted by the model (generally within about 6 percent), except in the cases of carbon tetrachloride and tetrachloroethylene. With the latter chemicals, the apparent rates were only about one-half those expected. Battelle researchers previously have noted difficulties with passive sampling for carbon tetrachloride and other authors have noted similar problems with active sampling for this chemical. No appreciable effect of relative

humidity was found at humidities as high as 90 percent. The precision of measured sampling rates was generally of the order of 20-25 percent, with approximately one-half of this variation being traceable to differences between individual devices. The remainder of this variation can be associated with analytical error.

Two approaches to modification of the PSDs were pursued for the purpose of improving their performance for long-term (8 to 24 hour) sampling. These consisted of (1) replacement of the Tenax® GC with Spherocharb in order to increase the retention times of VOCs and (2) alteration of the diffusion barrier to yield sampling rates reduced by a factor of 30 in comparison with the standard PSDs. The use of Spherocharb proved unsatisfactory because of the high temperatures required for desorption of most of the target compounds. Results obtained in the laboratory tests of the reduced-rate PSDs showed promise for the use of these devices in sampling of chemicals having retention volumes as low as 5 to 10 L/g.

Limited field studies of the performances of both the standard and reduced-rate PSDs yielded overall precisions comparable to those determined in the laboratory tests. These field studies illustrated problems associated with the inappropriate use of the standard PSDs for sampling of very volatile chemicals, and also indicated potential problems with using the reduced-rate devices for very short time periods. In the latter case, uncertainties in blank levels impact severely on the relatively small amounts of sample collected by the reduced-rate devices when they are used for times that are too short. In any case, these results emphasize the need to use the model as an aid to design of a sampling plan for a particular application.

## Conclusions and Recommendations

Based on the results of this work, it concluded that the EPA PSDs offer some distinct advantages over other available designs of passive sampling devices in application to sampling of ambient level volatile organic compounds. The ability to thermally desorb collected samples provides more than adequate amounts of sample for use with conventional GC and GC/MS analytical procedures, and their independence from high relative humidities yields more flexible field applicability than the commercially available devices using activated carbon. Finally, the

Tenax® GC can easily be replaced with other sorbents for customized sampling applications. The PSDs should not, however, 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 PSDs can be used for sampling of ambient levels of VOCs, but careful attention must be paid to the retention volumes of target compounds and the appropriate sampling period. In general, the standard PSDs are useful for chemicals having large retention volumes ( $\geq 100$  L/g), but can be used only for short sampling periods (a few hours or less) for compounds having small retention volumes.
2. Reduced rate PSDs having nominal sampling rates of the order of 2.5 cc/min show promise for applications requiring the sampling of VOCs over extended periods of 8 to 24 hours. These reduced rate devices, however, should not be used for compounds having retention volumes less than about 5-10 L/g. Also, the current results show 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 ( $R_0$ ) may indicate potential sampling error.
4. The model of PSD performance presented in this report has been shown to represent correctly the effects of retention volume, sampling time, and air velocity on the effective time-weighted average sampling rates of the EPA PSDs.
5. The use of Sphero carb in the EPA PSDs may offer some advantages for sampling of a few selected VOCs, but general use of this sorbent is not recommended because of problems generally associated with the high temperatures needed for desorption of this sorbent. Contamination of the sorbent by unpyrolyzed polymer presents

some special difficulties with clean-up and preparation of this sorbent for use in the PSDs.

6. The EPA PSDs are not affected by high humidities, and therefore are not subject to the same limitations as the commercially available devices based on activated carbon.
7. Protective shields developed for the EPA PSDs on this program provided protection against contamination during handling of the devices in the field without significantly affecting their sampling rates.
8. Blank contamination of the EPA PSDs has generally not been a problem, but a few instances of such have been observed. In recognition of the fact that the PSDs 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 PSDs.
9. It is recommended that further field testing of the reduced rate PSDs be considered.
10. Investigation of the application of the EPA PSD to sampling of pollutants other than VOCs (e.g.,  $\text{NO}_2$ , volatile polar organics, etc.) is recommended to take advantage of the capacity for use of different sorbents with this device.

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*The complete report, entitled "Evaluation of Passive Sampling Devices (PSD's)," (Order No. PB 85-196 418/AS; Cost: \$10.00, subject to change) will be available only from:*

*National Technical Information Service  
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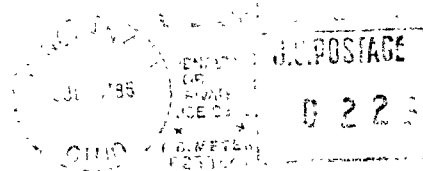
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