



## Project Summary

# Method for Collection and Analysis of Chlorobenzenes

G. W. Wooten, J. E. Strobel, R. C. Gable, J. V. Pustinger, and C. R. McMillin

To measure individual exposures to potentially hazardous organic compounds including halogenated hydrocarbons and benzene, personal monitors using sorbent-based passive samplers (passive exposure monitors) and analytical methodology using gas chromatographic analytical techniques were developed. The sampling/analytical techniques were evaluated under laboratory conditions with generated vaporous samples of known concentration for the compounds of interest and optimized for detection and quantitation. The passive dosimeter and analytical technique used for this project was found to be capable of detecting 0.5 ppb of the subject compounds after as little as one-half hour of sampling. Passive dosimeter results correlated well with results obtained on pumped sorbent tubes collected in parallel. The sampling/analytical methods were further validated with field samples, focusing on a quantitative analysis of the halogenated hydrocarbons and benzene.

*This Project Summary was developed by EPA's Environmental Sciences Research 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 U.S. EPA instituted the Public Health Initiative (PHI) in 1980 with the goal of establishing an ongoing human exposure monitoring capability within the

EPA. The basic approach of this program is to measure individual exposures to toxic substances through the main exposure pathways of air, drinking water, and food. The ultimate results of the initiative will be a field-tested methodology for measuring human exposure to toxic substances in defined geographical areas.

This report addresses one portion of the PHI program, the development of atmospheric monitoring techniques for potentially hazardous organic compounds, including chloroform, chlorobenzene, benzene, carbon tetrachloride, 1,1,1-trichloroethane, 1,1-dichloroethane, tetrachloroethylene, and trichloroethylene.

In conjunction with another EPA contract, Monsanto Research Corporation (MRC) developed the passive exposure monitor (PEM or passive dosimeter) as a sampling device to measure the exposure to halogenated hydrocarbon and benzene compounds at low concentrations (low parts per billion level). Experimental test chambers were built to test the PEMs to demonstrate sensitivity and specificity of the approach. Laboratory studies also were conducted to define the effects of ultraviolet light, water, and ozone on the chemical integrity of the compounds of interest in generated vaporous samples.

### Procedures

Three test facilities were constructed to test the dosimeters and identify their sensitivity to various compounds. These facilities included a standard generation system, a laboratory test exposure chamber, and an environmental test chamber. Standards were prepared by

mixing stock solutions of compounds diluted to various volumes. Both liquid and gas standards could be generated using the syringe drive of fluids into a heated block with three calibrated dilution stages

The laboratory test exposure chamber consisted of a two-liter Pyrex reaction kettle filled with an "O"-ring-sealed Teflon lid, and three ports for gas inlet, gas outlet, and temperature and humidity monitoring. The chamber provides for evaluation of the dosimeter capabilities under the lab chamber conditions. The passive dosimeter is inserted into the Pyrex chamber, the chamber is sealed, and the standard gas is passed through the chamber at defined rates and durations. Effluent gas passes through a sorbent tube and measurements are made of the particular organic compound for mass in, mass out, and mass absorbed by the dosimeter.

The environmental test chamber consisted of a thick-walled, flanged Pyrex pipe in a concentric tube arrangement in which the gas flowed down the center tube, back through the space separating the two tubes, and down the center tube again. This facility provided for the detailed evaluation of the effects of temperature, humidity, and flow velocities, all of which could be controlled and monitored

MRC developed a miniature passive dosimeter containing a solid sorbent. Chlorinated organic vapors diffuse to the solid sorbent in the dosimeter and are thereby concentrated over a period of time. Subsequently, the trapped vapors are removed by thermal desorption and quantitated via gas chromatography (GC) or tandem-coupled gas chromatography/mass spectroscopy (GC/MS) or a specific detector (i.e., electron capture or photoionization). Solid porous polymers have found wide acceptance as means for collecting and concentrating organic compounds in ambient air and other sampling environments. Sorbent-based active (pump-drive) sampling systems as well as passive sampling devices are customarily employed for such assignments where compound concentrations are encountered.

Application of the solid sorbent sampling approach to specific sampling problems involved three principal areas of technology: pump rates and/or diffusion considerations, sorbent selection, and chemical quantitation of sampled compounds. The latter area intimately involved desorption of the compounds from the sorbent sampling tube or passive device.

Basically, the passive dosimeter consists of a stainless steel body, with a 3.8-cm outer diameter, a 3.5-cm inner diameter and 11 cm high. The stainless steel construction makes the device amenable to thermal desorption, avoids possible absorbance or reactant problems associated with plastic materials, and provides a rugged, strong device. Two stainless steel screens (200-mesh) and two perforated plates (28% open area) on each side of the polymer serve to confine the polymer within the dosimeter body and provide diffusion barriers. A measured amount of sorbent (~0.4 g) commonly Tenax GC, is used in the dosimeter. Friction snap rings seal the screens and backup plates on each side of the adsorbent within the dosimeter body.

The thermal desorption oven required for dosimeter desorption/analysis was designed to ensure reliable performance, to handle a large number of dosimeters, and to handle the desorption of sorbent sampling tubes (dynamic flow) as well as the newly designed passive dosimeters. The oven unit operates based on two manual high-temperature (300°C max) Valco valves which direct helium purge gas through either the sorbent tube or the passive dosimeter path to the second valve that selects the "desorb/trap" or "analyze" mode of operation. The "desorb/trap" mode diverts the purge gas through a cryogenically cooled sample loop to provide off-line trapping which, in addition, provides better carrier gas flow rate control. The "analyze" mode backflushes a second gas stream (helium carrier gas) through the sample loop, which is now ballistically heated to transfer the trapped compounds to the analytical column for high-resolution chromatographic analysis.

Chromatographic conditions employed for the analysis of dosimeters and sorbent sample tubes are given in Table 1. The GC column effluent is split and sent to both a Hall electrolytic conductivity detector (EC) and a photoionization detector (PID) for selective determination of halogens and semi-selective determination of aromatics, respectively.

## Results and Discussion

Preliminary studies were conducted to evaluate sorbent selection. Based on previous success in both active and passive sampling modes Porapak R and Tenax GC adsorbents were evaluated. Studies of one-hour exposures of seven-compound test gas showed Tenax GC had recoveries exceeding 93% and was a better choice of sorbent.

Continued development of the passive dosimeter as a sampling device for low-concentration hazardous organic compounds including halogenated and aromatic compounds was conducted and tested extensively at the laboratory and field scale under several EPA-MRC contracts. The development work results are presented in the reports of the EPA contract number 68-02-3469 and 68-02-3699.

**Table 1.** GC/EC Detector Conditions for Dosimeter Analysis

*Instrument:* Chromatograph: Hewlett-Packard Model 5711  
Hall Detector Tracor Model 700 (in chlorine mode)  
Auto Sampler: Hewlett-Packard Model 7671-A

*Column* 2.44- x 2-mm (ID) glass packed with 1% SP1000 on 60/80 mesh Carbopak B

*Temperature Program:* 60 to 210°C at 8°C/min, hold at 210°C for 15 min

*Other Conditions:*

Parameter	Temperature, °C
Injection Port	200
Transfer Line	250
Hall Reactor	850

	Flow rate, mL/min
Helium (carrier)	40
Hydrogen (reactor gas)	45
Electrolyte (n-propanol)	0.75

G. W. Wooten, J. E. Strobel, R. C. Gable, J. V. Pustinger, and C. R. McMillin are with Monsanto Company, Dayton, OH 45407.

**Bruce W. Gay, Jr.**, is the EPA Project Officer (see below).

The complete report, entitled "Method for Collection and Analysis of Chlorobenzenes," (Order No. PB 84-189 646; Cost: \$8.50, subject to change) will be available only from:

National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:  
Environmental Sciences Research Laboratory  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

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