The Marines Project: A Laboratory Study of
Diffusive Sampling/Thermal Desorption/Mass Spectrometry
Techniques for Monitoring Personal Exposure to Toxic Industrial Chemicals

April 2002

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INTRODUCTION

The Force Medical Project Advanced Concept Technology Demonstration program was established in 1999 to determine the utility of existing and emerging technologies to monitor U.S. military personnel for exposure to toxic chemical substances. The technologies include real-time and non-real-time individual chemical exposure samplers and alarms, and biological detection systems. The demand for such samplers, alarms, and detection systems is evident in Presidential Review Directive 5, Department of Defense Directive 6490.2, Department of Defense Instruction 6940.3, and in a National Academy of Science study entitled "Strategies to Protect the Health of Deployed U.S. Forces". The toxic chemical substances to be monitored include chemical warfare agents (CWAs) and toxic industrial chemicals (TICs). Monitoring exposures to CWAs is the primary objective of the program. Monitoring TIC exposures is viewed as an important, but secondary, benefit of the program.

The Marine Corps was designated as technical manager for the program and has proposed use of diffusive sampling with analysis by thermal desorption and gas chromatography/mass spectrometry (GC/MS) to develop part of the monitoring program. Diffusive sampling has been shown to be a useful sampling technique for many volatile chemicals that does not require the use of cumbersome sampling pumps. Thermal desorption is an excellent means to extract many chemicals from the sampling medium with high efficiency. GC/MS is a method of analysis with the capability to simultaneously identify and to quantitate the vast number of possible toxic chemical exposures.

The U.S. Occupational Safety and Health Administration's Salt Lake Technical Center (OSHA SLTC) laboratory was contacted by the Marine Corps and asked to participate in a project to test two prototype diffusive samplers. SLTC was asked to perform laboratory research to test the sampling performance of the samplers with selected TICs, and also to test the proposed thermal desorption and GC/MS analytical technique. OSHA has no legal authority to protect the health of military personnel, but a decision was made to participate in the interests of interagency cooperation and in research that should result in a versatile sampling and analytical technique that may have application in OSHA's workplace monitoring program.

REAGENTS

The following TICs were jointly selected by the Marines Corps and by OSHA.

TICs   Benzene, (Bz), [CAS 71-43-2], Aldrich Chemical Company (Milwaukee, WI), 99.0%, A.C.S. Grade, lot no. BU 03051PS.

Ethylbenzene, (EtBz), [CAS 100-41-4], Aldrich Chemical Company (Milwaukee, WI), 99.8%, anhydrous, lot no. HI 03545DI.

1,1,2,2-Tetrachloroethane, (TCA), [CAS 79-34-5], Aldrich Chemical Company (Milwaukee, WI), 98%, lot no. 08330EI.

Mesitylene, (1,3,5-Trimethylbenzene), (TMB), [CAS 108-67-8], Aldrich Chemical Company (Milwaukee, WI), 98%, lot no. 00608TU.

(R)-(+)-Limonene, (1-methyl-4-isopropenyl-1-cylohexene), (LIM), [CAS 5989-27-5], Aldrich Chemical Company (Milwaukee, WI), 97%, lot no. 1006CI.

Undecane, (UND), [CAS 1120-21-4], Aldrich Chemical Company (Milwaukee, WI), 99+%, lot no. 1254AI.

2,2-Dichlorovinyldimethyl phosphate, (DDVP, also known as Dichlorvos), [CAS 62-73-7], Pfaltz and Bauer, Inc. (Waterbury, CT), 99%, lot no. 111084-2.

A TIC mixture was prepared in the following proportions: Bz 36 mL; EtBz 36 mL; TCA 20 mL; TMB 36 mL; LIM 37 mL; UND 42 mL; and DDVP 22 mL. This mixture was used to

generate test atmospheres, and to prepare analytical standards and test samples.

The following analytical reagents were used in analysis of samples.

Analytical
Reagents

Toluene-d_8, (tol-d_8), [CAS 2037-26-5], Scott Specialty Gases (Longmont, CO), Certified 0.1% in nitrogen gas, lot no. 11413CI. This gas was used as an internal standard for thermally-desorbed samplers. Tol-d_8 was selected for use as an internal standard because it does not exist in nature.

Methyl alcohol, [CAS 67-56-1], Fisher Scientific (Fair Lawn, NJ), HPLC Grade, lot no. 011264. This material was used to dilute the TIC mixture.

Carbon disulfide, [CAS 75-15-0], Aldrich Chemical Company (Milwaukee, WI), 99.9+%, low benzene, lot no. TI 01762PI. This material was a component of the solution used to desorb samples analyzed by GC/FID.

N,N-Dimethylformamide, (DMF), [CAS 68-12-2], Fisher Scientific (Fair Lawn, NJ), Certified A.C.S. Grade, lot no. 902902. This material was a component of the solution used to desorb samples analyzed by GC/FID.

Dodecane, [CAS 112-40-3], Aldrich Chemical Company (Milwaukee, WI), 99+%, lot no. EI 03040LU. This material was used as an internal standard for solvent-desorbed samples.

A solution of 99% carbon disulfide and 1% DMF was used to desorb samples that were analyzed by GC/FID. Dodecane (0.5 ΦL/mL) was added to this solution for use as an internal standard.

AIR SAMPLERS

Air samplers included project and non-project samplers. Project samplers were those that the Marine Corps selected for testing. Non-project samplers were selected for testing by OSHA SLTC.

Project
Samplers

Ultra Passive Sampler, SKC, Inc. (Eighty Four, PA). A prototype diffusive sampler based on the SKC 575 Series of samplers and containing 300 mg of Tenax TA, lot no. 1665.

GoreSorber, W.L. Gore and Associates (Elkton, MD). A proprietary diffusive sampler containing 30 mg of Tenax TA in each of two PTFE-like cartridges. Each GoreSorber sampler had a barcode label with a unique number beginning with the letters "AA", or "AAA".

Non-Project
Samplers

Ultra Passive Sampler-Reduced Sampling Rate, (SKC Ultra RSR), SKC, Inc. (Eighty Four, PA). A prototype diffusive sampler based on the SKC 575 Series of samplers and containing 300 mg of Tenax TA, lot no. 1665. This sampler is similar to the SKC Ultra Passive Sampler but has fewer holes in the inlet. These samplers were tested in a limited number of sampling rate experiments.

Perkin Elmer (PE)-type sampler, Marks international, (Pontyclum, UK). A diffusive sampler containing 200 mg of Tenax TA, or 400 mg of Carbopack B, or 300 mg of Chromosorb 106. Each sampler had a unique serial number that was etched onto the tube beginning with the letters "Mi". PE-type diffusive sampling caps containing membranes were used with these samplers. These samplers were not obtained directly from PE, but are referred to in this work as PE samplers. PE samplers have lower sampling rates than the project samplers and, therefore, should be capable of sampling for longer times. PE samplers containing sorbents other than Tenax TA were tested in limited work to provide supplementary information.

Carbon Molecular Sieve (CMS) sampling tubes, SKC, Inc. (Eighty Four, PA). An active sampling tube containing two sections (75/150 mg) of Anasorb CMS, SKC Catalog no. 226-121, lot no. 1879. These samplers were used to help establish actual concentrations of test atmospheres.

575-002 Passive Samplers, SKC, Inc. (Eighty Four, PA). A diffusive sampler containing 500 mg of Anasorb 747. Various lot nos. including lot no. 1840. These samplers were used as controls.

3520 Organic Vapor Monitor (OVM), 3M (St. Paul, MN). A diffusive sampler containing two charcoal wafers. Various lot nos. including lot no. 10-02 1120[10]. These samplers were also used as controls.

The Marine Corps requested that OSHA partially test SKC Ultra RSR samplers. The number of available SKC Ultra RSR samplers was insufficient for other than preliminary testing. The project samplers and PE Tenax TA samplers were those most tested in this work.

APPARATUS

Thermally-desorbed samples were analyzed using a Perkin Elmer (Norwalk, CT) TurboMatrix ATD (equipped with internal standard addition option) connected to the electronic-pressure controlled volatiles interface inlet of an Agilent Technologies (Wilmington, DE) 6890 Series GC system and an Agilent 5973 Network Mass Selective Detector (MSD). The ATD (automatic thermal desorber) and GC carrier gas was helium. Thermal-desorption tubes were loaded on the ATD carrousel-tray so that the end with the groove was upward. The groove identifies the front of the tube. ATD conditions: thermal-desorption tubes containing Tenax TA were desorbed at 275EC for ten min following a 1-min ambient purge. Tubes containing Chromosorb 106 were desorbed at 225EC, and Carbopack B at 350EC for the same

Figure 1. Perkin Elmer TurboMatrix ATD.

times. The focusing trap was flash heated from -30EC to 300EC and maintained at the upper temperature for 2 min. The GC transfer line temperature was 225EC and the valve temperature was 225EC. The inlet split flow was 22 mL/min, the desorb flow 58 mL/min, the internal standard tube load flow 23 mL/min, and the internal standard loop flow 1.3 mL/min. GC conditions: a Restek (Bellefonte, PA) Rtx-5 capillary GC column (30-m × 0.25-mm i.d. × 0.25-Φm df) was used for this work. The GC column was temperature programmed from 40EC (following a one-min hold) at 20EC/min to 230EC. The GC column was operated in the constant flow mode at 0.8 mL/min. The GC inlet temperature was 230EC, and the inlet split ratio was usually 67 to 1. MSD conditions: thermal auxiliary 2 temperature was 280EC, MS source was 230EC, MS quad was 150EC. The MSD was operated in the full scan mode from 24 to 350 AMU. Typically, a delay of 2 min was used to allow air and solvent used to prepare analytical standards to clear the MSD before the filament was energized. Electron multiplier (EM) voltage was automatically set by the MSD software via an "autotune" performed each week of operation. A photograph of the ATD is shown in Figure 1.

SKC CMS, SKC 575-002, and 3M 3520 samplers were analyzed (after desorption with carbon disulfide/DMF solution for one hour) using a Hewlett Packard (Avondale, PA) 5890 GC equipped with a Restek Rtx-5 capillary column (60-m × 0.32-mm i.d. × 1.5-Φm df), an automatic liquid injector, and an FID. The GC column was temperature programmed from 40EC (following a one-min hold) at 6EC/min to 190EC. The FID was maintained at 250EC and the injector at 220EC. The GC column flow was 4.0 mL/min hydrogen. The inlet split ratio was 50 to 1. The FID gases were 35-mL/min hydrogen, 415-

mL/min air, and 30-mL/min auxiliary nitrogen.

Test samples were collected from dynamically generated test atmospheres using an apparatus constructed from stainless steel. The apparatus consisted of either a large (cross-section area: 161 cm^2) or a small (cross-section area: 40 cm^2) exposure chamber designed to permit exposure of a large number of diffusive samplers to test atmospheres. The chambers were of different size to permit sample exposure at significantly different face velocities. A stainless-steel manifold was connected in-line and following the exposure chambers to permit collection of active samples.

Humid air for use with controlled-test atmospheres was generated using a Miller-Nelson Research (Monterey, CA) Model HCS 501 Flow-Temperature-Humidity Control System. This system was equipped with a 500-L/min mass flow controller.

Relative humidity and temperature of the test atmospheres were monitored with an Omega (Stamford, CT) Digital Thermo-Hygrometer meter and probe. The probe was calibrated by the manufacturer. Pressure within the exposure chambers was monitored with an Omega meter and pressure transducer. The transducer was calibrated to read ambient barometric pressure before each run. Ambient barometric pressure was measured with a Princo (Southampton, PA) NOVA mercury barometer.

Dilution air flow rates (50-360 L/min) were measured with an Equimeter (Rockwell International, Pittsburgh, PA) No. 750 gas meter. Equimeter readings at several different flow rates were compared to those of a Singer (Philadelphia, PA) DTM 115 gas meter (which had been tested by the local natural gas distributor and found to be accurate) that was connected in series before the Equimeter. Both meters gave very similar readings.

The TIC mixture was metered into the system with an Isco (Lincoln, NE) 100 DM syringe pump equipped with a cooling/heating jacket and an insulation cover package. The pump was operated in the constant flow mode. The temperature of water in the cooling/heating jacket was maintained at 23EC with a Forma Scientific (Marietta, OH) Model 2006 CH/P Bath and Circulator.

TIC vapors were generated by pumping the liquid mixture into a heated glass tube where it evaporated into the dilution air stream. This vapor generator consisted of a 10-cm length of ¼-inch diameter glass tubing with a small hole in the side. The hole was just large enough for $^1/_{16}$-inch diameter tubing to be inserted. The glass tubing was placed inside a ½-inch stainless steel Swagelok (Solon, OH) tee wrapped with heating tape that was heated when electricity was applied with a variable-voltage transformer. The $^1/_{16}$-inch tubing entered the third port of the tee through an adaptor and was inserted about $^1/_8$-inch (approximately in the center) into the glass tubing through the small hole. Solvent was pumped through the $^1/_{16}$-inch tubing and into the glass tubing. The liquid flow rate was slow enough (0.3 to 20 ΦL/min) so that it did not accumulate in the heated evaporation tube. The entire dilution air stream passed through the tee and swept generated vapors into the apparatus.

The following is a description of the arrangement of the apparatus, which was placed in a walk-in hood. Liquid from which vapors were to be dynamically generated was pumped with a precision Isco syringe pump (an identical pump and a small solvent mixing tee was available when its use was desired) into a heated glass tube where it evaporated. The generated vapors were swept from the glass tube with dilution air. Stainless steel tubing (½-inch o.d.) connected with stainless steel Swagelok fittings was used to transfer the test atmosphere. The dilution air was humidified (if desired) using a Miller-Nelson Flow-Temperature-Humidity controller. The vapor/dilution air mixture then passed into a 3×24-inch stainless steel mixing chamber. The test atmosphere next passed through ½-inch ball valves where it could be either diverted to waste,

Figure 2. Diffusive sampler exposure apparatus with small exposure chamber.

or directed into the exposure chamber. An additional ball valve allowed the chamber to be purged with room air. The transfer tubing diameter was increased from ½ inch to 1 inch at this point using a Swagelok adaptor attached to the chamber inlet. Tube and fitting diameter was increased to 1 inch after this fitting to help reduce any increased pressure to ambient. The 1-inch o.d. chamber inlets have small stainless steel deflectors to help insure that the test atmosphere completely fills the sampling chambers. Stainless steel screens were placed inside the chamber for the same purpose. This design should cause air flow through the chamber to be somewhat turbulent. Face velocities of the test atmospheres were calculated by dividing the volumetric flow of each atmosphere by the cross-sectional area available for air flow in each chamber. The cross-sectional area available for air flow was the cross-sectional area of each chamber reduced by the cross-sectional areas of the samplers. A photograph of the apparatus with the small sampling chamber is shown in Figure 2. Exposure chambers are used with removable doors (not shown in the photograph) to completely seal them when used with test atmospheres.

EXPERIMENTAL

This laboratory research was performed partially based on techniques and tests described in OSHA methods development protocols[1,2]. The TIC levels studied in this work were jointly selected by the Marine Corps and by OSHA. They are not associated with any military or OSHA exposure standard.

Preparation of Samples

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[1]   Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, http://www.osha.gov/dts/sltc/methods/chromguide/index.html, (accessed February 2002).

[2]   Development of a Protocol for Laboratory Testing of Diffusive Samplers, http://www.osha.gov/dts/sltc/methods/studies/3movm/3movm.html, (accessed February 2002).

SKC Ultra samplers were prepared for analysis by prying open the back of the sampler with a screwdriver to reveal the small end of the built-in aluminum funnel containing the sorbent. The small end of the funnel is sized to fit inside the thermal-desorption tube. The Tenax TA was then carefully transferred into the back of a clean, empty thermal-desorption tube using the funnel. The front of a thermal-desorption tube is the end with the groove and the back is the opposite end. A gauze screen was then carefully placed on top of the Tenax TA with the aid of a $^3/_{16}$-inch glass rod and a small screwdriver. The tube was not completely filled with the sorbent and an empty space of approximately ½ inch remained in the end of the tube. A retaining spring was placed into this space, and then seated on top of the gauze

Figure 3. SKC Ultra sampler.

screen and slightly below the end of the tube using the small end of the funnel to press the spring into position. A photograph of an SKC Ultra sampler is shown in Figure 3.

GoreSorber samplers were prepared for analysis by transferring one of the PTFE-like cartridges into the end of a clean, empty thermal-desorption tube and then pushing it forward with a $^3/_{16}$-inch glass rod. The other cartridge can then be placed in the same tube, or analyzed separately if desired. Both GoreSorber cartridges were usually analyzed in the same thermal-desorption tube in this work. A retaining spring is placed into the end of the tube, and then seated slightly below the end of the tube with the funnel from an SKC Ultra sampler. A photograph of a GoreSorber sampler and a thermal-desorption tube is shown in Figure 4. The tube endcaps shown are used to seal the samples for analysis with the ATD.

Figure 4. GoreSorber sampler.

PE samplers require no preparation for analysis. A photograph of one of these samplers is shown in Figure 5. A diffusive sampling cap with membrane is shown in the upper right section of the figure. A gauze screen and retaining spring is shown in the right center. The vial shows the amount of sorbent contained within the tube. PE samplers are thermally preconditioned by the vendor and can be reused numerous times after thermal reconditioning.

CMS active sampling tubes were prepared for analysis by placing each section of sorbent into separate 2-mL glass vials and then adding 1 mL of 99/1 carbon disulfide/DMF solution. These vials were allowed to stand one hour before analysis, and were shaken by hand several times during this time.

Figure 5. PE Tenax TA sampler.

SKC 575-002 samplers were prepared for analysis by adding 2 mL of 99/1 carbon disulfide/DMF solution through one of the two sampler ports designed for that purpose. The sampler was then shaken on an

SKC Sorbent Extractor (also designed for that purpose) for one hour before analysis.

3M 3520 OVMs were prepared for analysis by removing the two charcoal wafers, placing each wafer into a separate 4-mL glass vial, adding 2 mL of 99/1 carbon disulfide/DMF solution to each vial, and then desorbing the sample on a tube rotator for one hour before analysis. The wafers were removed from the sampler to eliminate any possibility of desorption solvent loss from *in situ* desorption.

Analytical Standards

Media standards for thermally-desorbed samples were prepared by spiking 5-ΦL aliquots of a series of diluted TIC mixtures onto thermal-desorption tubes containing the same medium used for sampling. Standards used for SKC Ultra and GoreSorber samplers were spiked on the back of the thermal-desorption tube. Clean, room air was drawn through these tubes at 50 mL/min for about 10 seconds immediately after they were spiked to help ensure that the spiked TICs resided on the sampling medium. This air entered the thermal-desorption tube at the end spiked. The source of the media desorption tubes used to prepare standards for SKC Ultra and GoreSorber samplers was SKC Ultra samplers that had been previously analyzed, and then reconditioned for 10 min at 275EC using the ATD tube-conditioning feature. These thermal-desorption tubes were reused approximately three or four times before recycling. Recycling thermal-desorption tubes was accomplished by removing the retaining spring, the gauze screen, and the sorbent from previously analyzed samples. The empty tubes were washed twice with methyl alcohol and then air-dried overnight before reuse.

Analytical standards for PE samplers containing Chromosorb 106 or Carbopack B were prepared using reconditioned PE samplers containing the same medium used for sampling. PE samplers were thermally reconditioned by heating them at the same temperature used for desorption for 10 min. Standards for PE Tenax TA samplers were prepared using reconditioned SKC Ultra sampling medium. Standards for all PE samplers were prepared by liquid spiking the TIC mixture on the front of the tube.

Only limited work was performed to prepare standards using GoreSorber cartridges. Liquid spiking the cartridges would require a needle hole to be punctured in the PTFE-like cartridge wall and this would cause standards to be significantly different than samples. Some success was obtained by placing the cartridge in a glass vial, spiking the liquid standard into the vial, and allowing the vial to stand overnight at 40EC before transfer to the thermal-desorption tube and subsequent analysis. This technique was not fully developed.

Analytical standards for solvent-desorbed samples were prepared by injecting microliter volumes of diluted TIC mixtures into the same volume of 99/1 carbon disulfide/DMF desorption solution used to desorb the samples.

MSD Calibration

GC/MSD calibration curves were prepared for each TIC (for each sample set) by first calibrating the MSD software in terms of mass per sample with a single standard. MSD response was plotted against actual TIC mass per standard using an electronic spreadsheet. Sample results were calculated using the calibration-curve equation obtained for each TIC. The calibration range, in most cases, was one-half to two times the expected sample concentration. The MSD is saturated when approximately 50 ng of a TIC reaches the detector and accurate quantitation becomes impossible after this point. A combination of GC injector split and/or ATD split should be employed to reduce mass reaching the MSD when samples contain sufficiently high TIC levels. Alternatively, MSD EM voltage could manually be reduced to prevent premature saturation. All MSD results were calculated without internal standard correction.

GC/FID calibration curves were also prepared using an electronic spreadsheet for samples analyzed by solvent desorption. A Waters Associates Millennium Chromatography Manager data system was used to measure FID response. Dodecane was employed as an internal standard in the analysis of these samples.

MSD Detection Limits

Detection limits for the studied TICs were determined using the procedure described in OSHA methods development guidelines[3]. A series of standards was prepared with the highest giving a MSD response approximately ten times the MSD baseline noise. These standards were analyzed and MSD response plotted against mass injected on-column. The detection limit was defined as the mass equivalent to three times the SEE (standard error of estimate) of the regression line. SEE is the dispersion of data about a regression line, and it is mathematically similar to standard deviation for a data set.

Desorption Efficiency

Desorption efficiency studies can reveal adverse interactions between TICs and the sampling media. Desorption efficiencies for components of the TIC mixture were determined by liquid spiking the samplers with aliquots of the TIC mixture. No desorption efficiency work was performed for PE samplers because these spiked tubes would be identical to analytical standards. The spiking technique was routine except for GoreSorber samplers. The GoreSorber cartridges were removed from the outer pouch, one of the two cartridges was liquid spiked by penetrating the PTFE-like shell with a syringe needle, and then both were placed in a sealed glass vial. All spiked samples were allowed to equilibrate overnight before analysis. SLTC experience has shown that desorption efficiency results from wet sampling media can occasionally be different than from dry media. This is unlikely for Tenax TA because that sorbent is known to have low affinity for water. Desorption from wet SKC Ultra samplers was, however, tested to a limited degree. Wet media were prepared by sampling a clean atmosphere containing 80% relative humidity for four hours with dry samplers. Wet media were liquid spiked with aliquots of the TIC mixture after exposure to humid air. Dry samplers were as received from the vendors.

Desorption efficiency studies were performed using both wet and dry samplers for CMS sampling tubes, SKC 575-002 samplers, and 3M 3520 OVMs.

Sampling Rate

Sampling rates for the components of the TIC mixture were determined for project, non-project, and control samplers. Sampling rates were determined at ambient temperature and pressure, but all sampling rates presented in this work are expressed at 760 mmHg and 25EC. Three of each type of sampler was exposed to controlled test atmospheres for increasing time periods in the small exposure chamber for these experiments. The exposure times ranged from two to as long as 16 hours. The relative humidity of the test atmospheres was approximately 80% at ambient temperature. The face velocity of test atmospheres through the small exposure chamber was approximately 0.4 m/s. The concentration of each TIC in the test atmospheres was approximately 4 mg/m^3. Sampler orientation was parallel to the flow direction of the test atmosphere, except for PE samplers which was perpendicular. This orientation of PE samplers was necessitated because of space limitation within the small chamber.

Long-Term Sampling Capacity

A long-term sampling capacity experiment was performed with SKC Ultra, GoreSorber, and PE Tenax TA samplers. Twenty-one of each sampler were placed in the large exposure chamber, and three of each sampler were removed at approximately eight-hour intervals over a total exposure time of 54 hours. The relative humidity of the test atmospheres was approximately 80% at ambient temperature. The face velocity of the test atmosphere through the large exposure chamber was approximately 0.1 m/s. The concentration of each TIC in the test atmosphere was approximately 0.4 mg/m^3. Sampler orientation was parallel to the flow direction of the test atmosphere, except for PE Tenax TA samplers which was perpendicular.

Reverse Diffusion

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[3]   Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis,
http://www.osha.gov/dts/sltc/methods/chromguide/index.html, (accessed February 2002).

A reverse diffusion experiment was performed by exposing SKC Ultra, GoreSorber, and PE Tenax TA samplers (six of each) to a test atmosphere containing approximately 4 mg/m^3 of each TIC for four hours. The relative humidity of the test atmosphere was approximately 80% at ambient temperature and the face velocity was about 0.4 m/s. Following the four-hour exposure time, the samplers were removed and the chamber was flushed with clean, humid air. Then, three of each sampler was replaced in the chamber and exposure continued for an additional four hours with clean, humid air. The analytical results for samples exposed to the test atmosphere and then additionally to clean air were compared to results for samples exposed to only the test atmosphere.

Storage Stability

SKC Ultra and GoreSorber storage stability samples were simultaneously prepared by sampling a test atmosphere with 33 of each sampler. Thirty-three PE Tenax TA samplers were used to sample another, but similar, test atmosphere. The concentration of the test atmospheres was approximately 4 mg/m^3 for each TIC, and the exposure times were four hours. The relative humidity of the test atmospheres was approximately 80% at ambient temperature and the face velocity was about 0.4 m/s. Three of each type of sampler was analyzed on the day they were generated, and the remaining 30 of each type were split into two sets of 15 each. One set of each type of sampler was stored in a laboratory oven maintained at 40 EC to simulate hot ambient environments, and the other set in a refrigerator at -4EC to simulate cold environments, and to test if refrigeration could stabilize any TIC that might degrade at the higher temperature. The samplers were all sealed using original packaging materials as received from vendors. Three of each set of each type of sampler were removed from storage and analyzed at approximately three-day intervals.

Factor Test

A 16-run factor test was performed using a modified version of the test discussed in the NIOSH protocol for evaluation of diffusive samplers[4]. This test is performed primarily to observe the degree with which sampling rates change under the environmental conditions of the test. These conditions are significantly altered following a prescribed regimen for each run of the test. The pooled RSD of the sampling rates is called sampling rate variation[5] (SRV) by OSHA SLTC, and it has been established as a measure of sampling error for diffusive samplers. SRV is analogous to the often-cited ±5% sampling pump error used to estimate sampling error for active samplers.

Six factors were identified in the NIOSH protocol as having the potential to affect sampler performance. These factors are analyte concentration, exposure time, face velocity, relative humidity, interferant, and sampler orientation. Sixty-four experimental runs (2^6) would be required to fully evaluate combinations of each factor at two levels. NIOSH recognized that this would be an excessive number of tests, and has devised a 16-run fraction of the full factorial that is capable of revealing any of these factors having a significant effect, free of two-factor interactions, on sampler performance. Some two and three-factor interactions can also be screened by this design. The test is based on the comparison of each factor effect to experimental error so that the significance of that effect can be determined.

Experimental design and conditions are shown in Table 1. Interferant was provided by the components of the TIC mixture, for example, if EtBz was being examined then Bz, TCA, TMB, LIM, UND, and DDVP were the interferants, and the levels were declared either high or low. Each of the samplers has a slightly different cross-sectional area and this difference will slightly affect the face velocity to which that sampler is exposed. The following calculation is applicable only to high face velocity (1.5 to 2.1 m/s) experiments performed in the small exposure chamber. Experiments at low face velocity were performed in the large chamber, and the differences in sampler cross-sectional area are small compared to chamber cross-

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4   Cassinielli, M.E.; Hull, R.D.; Crabel, J.V.; and Teass, A. W., "Protocol for the Evaluation of Passive Monitors", *Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring,* Berlin, A,; Brown, R.H.; Saunders, K.J.; Eds., Royal Society of Chemistry, Burlington House, London, pp 190-202, 1987.

5   Development of a Protocol for Laboratory Testing of Diffusive Samplers, http://www.osha.gov/dts/sltc/methods/studies/3movm/3movm.html, (accessed February 2002).

sectional area. Face velocity shown in Table 1 is for SKC Ultra samplers. Multiply the value by 0.90 to calculate parallel orientation face velocity for GoreSorber samplers, and by 1.05 for perpendicular orientation. Exposure chamber size limitation necessitated that only perpendicular orientation be used for PE Tenax TA samplers. PE sampler orientation was either upward so that the test atmosphere first encountered the diffusion cap, or the sampler was inverted so that the test atmosphere first encountered the back endcap. Upward orientation was designated perpendicular orientation, and inverted designated parallel. Multiply by 0.91 to calculate parallel orientation face velocity for PE Tenax TA samplers, and by 0.86 for perpendicular orientation.

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Table 1 Experimental Design of the Factor Test													
run no.	concn (mg/m^3)	RH (%, EC)	inter level	time (min)	face vel (m/s)*	sampler orien	run no.	concn (mg/m^3)	RH (%, EC)	inter level	time (min)	face vel (m/s)*	sampler orien
1	2	24, 25	low	240	1.8	perp	9	7	78, 22	high	60	0.1	paral
2	7	10, 22	low	60	0.1	perp	10	2	81, 20	high	240	1.5	paral
3	2	81, 21	low	60	1.5	paral	11	7	8, 23	high	240	0.1	perp
4	7	75, 23	low	240	0.1	paral	12	2	7, 22	high	60	2.1	perp
5	2	9, 22	high	240	0.1	paral	13	7	66, 25	low	60	1.8	perp
6	7	26, 24	high	62	1.5	paral	14	2	72, 22	low	240	0.1	perp
7	2	75, 21	high	60	0.1	perp	15	7	22, 26	low	254	1.5	paral
8	7	66, 27	high	240	1.8	perp	16	2	11, 19	low	60	0.1	paral

inter = interferant, orien = orientation, perp = perpendicular, paral = parallel, vel = velocity, * face vel is for Ultra samplers

Precision and Accuracy

The NIOSH acceptability criterion (published in their diffusive sampler evaluation protocol[6]) for accuracy is that the method provide results within ±25% of the reference value at the 95% confidence level over the range 0.5 to 2 times the target level of the method. NIOSH specified which data to test against the criterion and those specifications were followed as closely as possible with data obtained in this work. Relative standard deviations (RSD) obtained from the analysis of three replicate samples of each type exposed at 2, 4, and 7 mg/m^3 for each TIC were pooled after first examining them for homogeneity at the 95% confidence level with the Cochran Test. RSDs from samples exposed at 0.4 mg/m^3 were pooled separately to evaluate precision and accuracy at lower levels.

OSHA methods acceptance criteria require that candidate sampling and analytical methods provide sample results at least 75% (±25%) of the method target level at the 95% confidence level, and that uncorrectable bias be less than 10%.   OSHA evaluates precision and bias using data from the storage stability test.

Precision and accuracy data were evaluated for SKC Ultra, GoreSorber, and PE Tenax TA samplers.

Packaging Integrity

An experiment was performed to determine if manufacturer's packaging is sufficient to prevent contamination of unused samplers placed in contaminated environments. Two each, SKC Ultra, GoreSorber, and PE Tenax TA samplers, unopened and as received from the vendors, were placed in the exposure chamber and allowed to remain undisturbed for 130 days. The samplers were exposed to test atmospheres for approximately 120 hours during the 130 days. The TIC concentrations of test atmospheres varied, but the average was about 4 mg/m^3 for each TIC.

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[6]   Cassinielli, M.E.; Hull, R.D.; Crabel, J.V.; and Teass, A. W., "Protocol for the Evaluation of Passive Monitors", *Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring,* Berlin, A.; Brown, R.H.; Saunders, K.J.; Eds. Royal Society of Chemistry, Burlington House, London, pp 190-202, 1987.

Concentrations of Test Atmospheres

Previous OSHA SLTC work[7] has shown that use of active samplers as an independent means to determine concentrations of test atmospheres gave more consistent experimental results than did calculation of concentrations from generation parameters. This is because of normal day-to-day variations in the operation of test equipment.

Theoretical concentrations of test atmospheres were calculated from the flow rate at which the liquid TIC mixture was pumped into the vapor generator, the TIC concentrations of the liquid mixture, and the dilution air flow rate. Actual concentrations of test atmospheres were determined from the analytical results of CMS sampling tubes. The CMS tube sampling rate was 0.1 L/min, and four samples were taken simultaneously with diffusive samples for every run. Average CMS results for the 16-run factor test, for example, were 100% of theoretical with a pooled RSD of 15%. Comparison of sampling rates for SKC 575-002 and 3M 3520 control samplers determined in this work with sampling rates published in the literature allows confirmation of the validity of this practice. A comparison of sampling rates is presented in Table 21.

RESULTS and DISCUSSION

MSD Calibration

MSD calibration data provides a means to estimate the contribution of the analytical procedure to overall method imprecision. Calibration was performed with MSD response at the following selected ions: Bz 78.1, EtBz 91.1, TCA 83.0, TMB 105.1, LIM 68.1, UND 57.1, DDVP 109.0, tol-d_8 98.1 m/z.

The concentration of standards used for MSD calibration is shown in Table 2. MSD response data obtained over this mass range is shown in Table 3. The combined GC and ATD split was 135 to 1.

The ATD automatic internal standard addition feature was activated for this calibration work, but MSD response data were not corrected for the internal standard. Internal standard data are presented for precision information only. No results obtained by thermal desorption presented in this report were corrected for internal standard. One reason for not using the internal standard option was that the uptake of tol-d_8 was about 115% for SKC Ultra samplers, about 60% for GoreSorber samplers, and about 105% for PE Tenax TA samplers, when compared to the uptake of standards. Use of an internal standard would obviously bias analytical results. Analytical standards would have to be prepared using blank samplers (including the PTFE-like shell for GoreSorber cartridges) in order to successfully employ the internal standard addition feature. Another reason was that the internal standard addition mechanism did not function properly until the work was fairly well advanced. Tol-d_8 was used in gas form after dilution by the vendor to 0.1% by volume in nitrogen gas. The ATD employs a 0.5-mL loop for internal standard addition, therefore, theoretically 2 Φg of tol-d_8 was injected with each standard.

Table 2 Standard Concentrations (Φg per standard)							
std	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
1	4.10	4.10	3.95	4.00	3.95	4.05	3.90
2	3.25	3.25	3.15	3.20	3.15	3.25	3.15
3	2.45	2.45	2.35	2.40	2.35	2.40	2.35
4	1.65	1.65	1.60	1.60	1.60	1.60	1.55
5	0.80	0.80	0.80	0.80	0.80	0.80	0.80

Table 3 MSD Calibration Data (MSD response)								
std no.	Bz	EtBz	TCA	TMB	LIM	UND	DDVP	tol-d_8
1	28641636	43454042	14312933	38846452	13247783	17202956	23440848	569535
1	30643376	45257645	14858385	41196355	13683133	18115700	26580610	560406
1	30445154	44581695	14725691	40398411	13658798	17827207	27048673	547299
ave	29910055	44431127	14632336	40147073	13529905	17715288	25690044	559080
RSD	3.69	2.05	1.94	2.98	1.81	2.63	7.64	2.00

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[7] Development of a Protocol for Laboratory Testing of Diffusive Samplers, http://www.osha.gov/dts/sltc/methods/studies/3movm/3movm.html, (accessed February 2002).

std no.	Bz	EtBz	TCA	TMB	LIM	UND	DDVP	tol-d_8
2	26286654	36684939	12022473	33621744	11224307	14781093	20340921	546155
2	26096894	36726922	11965531	33337284	11180821	14792399	20191208	548792
2	26964735	37238709	12012397	33915663	11539267	14889760	20662368	562188
ave	26449428	36883523	12000134	33624897	11314798	14821084	20398166	552378
RSD	1.73	0.84	0.25	0.86	1.73	0.40	1.18	1.56
3	19767705	27856077	9007271	25398185	8621183	11296994	14195664	562952
3	20450297	28375303	9257640	26174815	8986079	11737467	15031324	560481
3	20932034	29042523	9526675	26680928	9043854	11778283	15988129	575954
ave	20383345	28424634	9263862	26084643	8883705	11604248	15071706	566462
RSD	2.87	2.09	2.80	2.48	2.58	2.30	5.95	1.47
4	13046706	19682445	6383122	18079294	5839289	8156706	10839043	559044
4	13481463	20146261	6516168	18157601	6210200	8293435	10137451	577749
4	13021364	19539209	6308035	17353238	5966648	7870290	10786881	520656
ave	13183178	19789305	6402442	17863378	6005379	8106810	10587792	552483
RSD	1.96	1.60	1.65	2.48	3.14	2.66	3.69	5.27
5	7332528	10204191	3273858	9255749	3223915	4351088	4884348	610041
5	7410959	10084991	3208730	9378546	3195213	4288999	4553462	630170
5	7309025	10020740	3227673	9203708	3136032	4281767	5133310	630563
ave	7350837	10103307	3236754	9279334	3185053	4307285	4857040	623591
RSD	0.73	0.92	1.04	0.97	1.41	0.88	5.99	1.88
pooled RSD	2.42	1.59	1.76	2.14	2.23	2.01	5.38	1.74

Table 3
MSD Calibration Data (MSD response)

The individual RSDs in Table 3 were tested for homogeneity with the Cochran Test and, with the exception of tol-d_8 data for std no. 4, found to be homogeneous. The homogeneous RSDs were pooled and the result is shown in Table 3. These pooled RSDs are similar to those obtained for FID calibration data which are typically 1 to 2%. Instrument calibration was not a significant source of analytical error.

An example calibration curve for TMB is shown in Figure 6. SEE (standard error of estimate) shown in Figure 6 is equivalent to 87 ng over the calibrated range. Calibration is not performed using total-ion MSD response; it is accomplished using MSD software for optimum response and selectivity. A total-ion chromatogram for std no. 4 is shown in Figure 7.
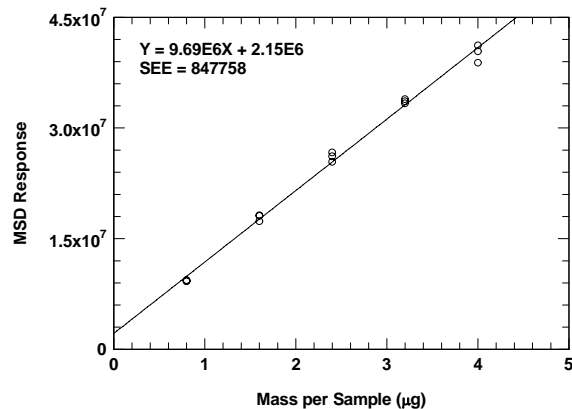
Figure 6. Calibration curve for TMB.
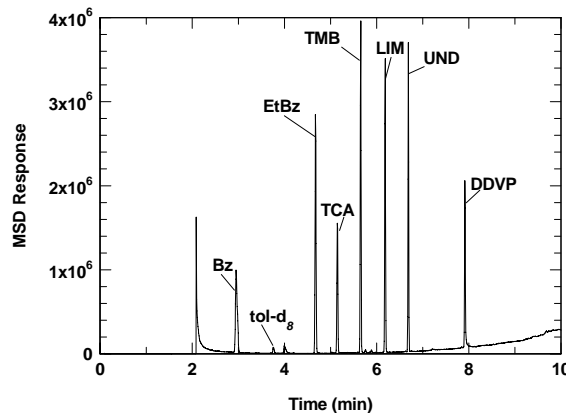
Figure 7. Total-ion chromatogram for std no. 4.

MSD Detection Limits

MSD detection limits are shown in Table 4. These amounts are mass injected on-column and not mass per sample. The detection limits are based on precision of the analysis, and on spectral quality of the resultant mass spectra.

Table 4 MSD Detection Limits (ng)						
Bz	EtBz	TCA	TMB	LIM	UND	DDVP
0.16	0.10	0.06	0.10	0.07	0.06	0.24

An example of plotted data used to determine MSD detection limit for TMB is shown in Figure 8. A total-ion chromatogram from the analysis of a standard spiked at approximately the MSD detection limits is shown in Figure 9.
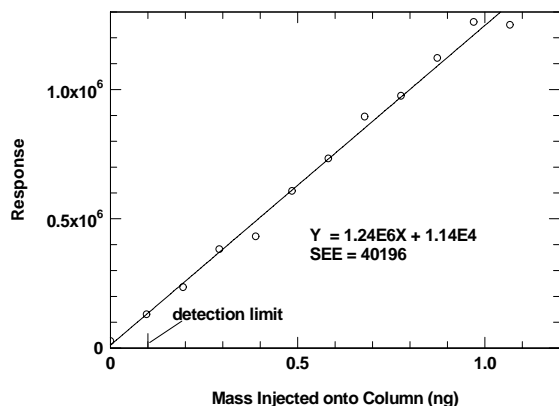
Figure 8. Determination of MSD detection limit for TMB.
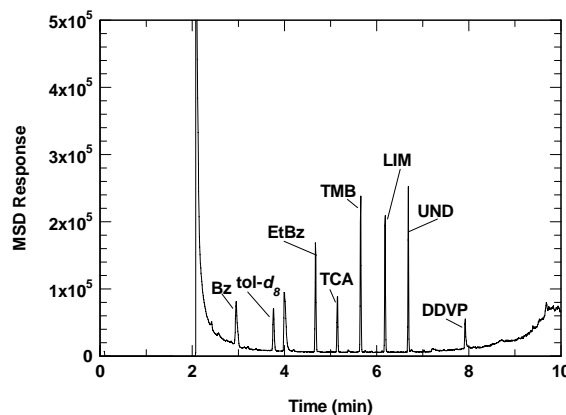
Figure 9. Total-ion chromatogram of the analysis of a standard at approximately the detection limits.

Media standards for project samplers were prepared using the sampling medium from previously analyzed Ultra samplers that have been thermally reconditioned. Analysis of reconditioned Ultra samplers gives clean chromatograms. SKC conditions the Tenax TA to be packaged within Ultra samplers by solvent extraction and subsequent heating to remove the solvent. The sorbent is not thermally conditioned at a sufficiently high temperature, and the analysis of a sampler blank reveals many artifact peaks. An SKC representative has stated that they intend to begin thermally conditioning the sorbent to reduce artifacts[8]. Analysis of blank GoreSorber samplers also shows a significant number of artifacts. Total-ion chromatograms from the analysis of SKC Ultra and GoreSorber blank samplers are shown in Figures 10 and 11. Chemicals identified on the SKC Ultra blank include trioxane, 1-methyl-2-propyl acetate, and 2-ethyl-1-hexanol. Present on the GoreSorber blank are 2-ethyl-1-hexanol, 1-decene, and butylated hydroxytoluene. Attaining the detection limits in Table 4 for blank and field samples could be challenging because of co-eluting artifacts and other species. For example, satisfactory MSD spectra for EtBz and for TCA were not obtained for blank SKC Ultra samplers spiked at approximately the detection limits. Almost 2 ng of each TIC was required to obtain good spectra, and this required spectral subtraction of the interfering species. Good spectra were obtained for the other TIC components spiked on a blank SKC Ultra sampler at the stated detection limits. This data emphasizes the need for samplers with low artifact levels.

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8   Coyne, L. SKC Inc., Eighty-Four, PA. Personal Communication, 2002.
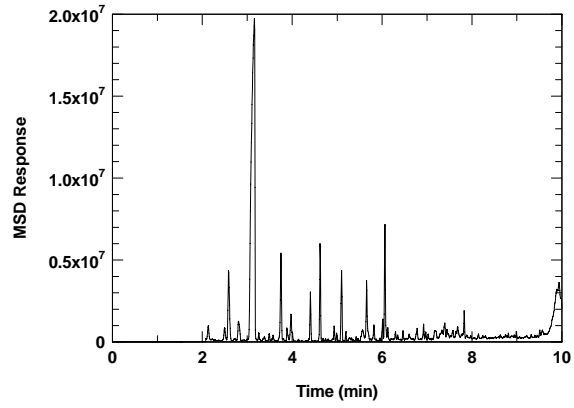
Figure 10. Total-ion chromatogram from the analysis of a blank Ultra sampler.
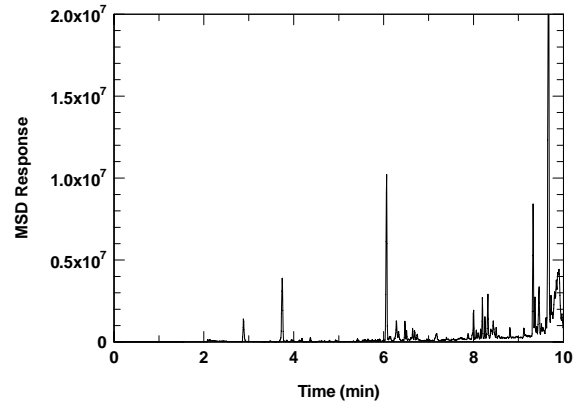
Figure 11. Total-ion chromatogram from the analysis of a blank GoreSorber sampler.

Desorption Efficiency

Average desorption efficiencies for SKC Ultra samplers are shown in Table 5. The mass range studied was 13 to 32 Φg for each TIC per sample. Wet samplers were prepared by exposing them to clean, humid air for four hours prior to spiking. Some results from wet samplers were lower than from dry samplers for unknown reasons. These results were not used to correct SKC Ultra sampler results presented in this report because it was assumed that desorption was 100%. This assumption was supported by the fact that a second desorption of several SKC Ultra samples showed no TICs present in significant amounts.

Table 5 Desorption Efficiency From SKC Ultra Samplers (%)							
	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
dry	102.5	100.4	97.0	100.6	99.7	98.4	99.2
wet	92.3	93.1	94.1	94.3	95.6	95.7	99.7

Average desorption efficiencies for GoreSorber samplers are shown in Table 6. The mass range studied was 13 to 30 Φg for each TIC per sample. A study using wet samplers was not performed. These results were not used to correct GoreSorber results presented in this report because it was assumed that desorption was 100%. This assumption was again supported by the fact that a second desorption of several GoreSorber samples showed no TICs to be present in significant amounts. The low desorption efficiency obtained for Bz was probably caused by the relatively low affinity of Tenax TA for Bz, and its subsequent loss through the hole punctured in the PTFE-like shell of the cartridge by liquid spiking the sample.

Table 6 Desorption Efficiency From GoreSorber Samplers (%)							
	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
dry	74.7	99.2	98.3	100.1	99.7	99.8	100.8

Average desorption efficiencies for the front section (150 mg) of SKC Anasorb CMS sampling tubes are shown in Table 7. The mass range studied was 10 to 165 Φg of each TIC per sample. Wet samplers were prepared by drawing clean, humid air through the samplers at 0.1 L/min for four hours prior to spiking.

Table 7 Desorption Efficiency From Anasorb CMS (%)							
	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
dry	96.0	96.7	93.6	96.4	97.1	99.3	91.3
wet	94.2	95.8	80.4	95.2	92.7	98.3	68.6

All CMS results presented in this report were corrected using the appropriate desorption efficiency. Results for DDVP desorbed from wet samplers were low and would necessitate use of another solvent or desorption technique in routine analytical work because a minimum recovery of 75% is usually required for NIOSH and OSHA methods. The reason for low DDVP wet results is unknown but could be due to hydrolysis. The low desorption was deemed adequate for this work because samples were analyzed immediately after generation. Results for TCA from wet CMS were lower than from dry CMS, but they were greater than 75% and, therefore, adequate for conditional use.

Average desorption efficiencies for SKC 575-002 samplers are shown in Table 8. The mass studied was 13 Φg of each TIC per sample. Wet samplers were prepared by exposing them to clean, humid air for four hours prior to spiking. All SKC 575-002 samplers in this study were exposed to humid air and, therefore, analytical results were corrected using only the wet desorption efficiencies. A chromatographic interference prevented the analysis of DDVP. This co-eluting interference was identified as cyclohexyl isothiocyanate by GC/MS. The low wet desorption efficiency obtained for TCA would necessitate use of another solvent or desorption technique in routine analytical work, however, it was also deemed adequate for this work because these samples were analyzed immediately after generation.

Table 8 Desorption Efficiency From SKC 575-002 Samplers (%)							
	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
dry	96.6	101.5	87.7	100.0	103.9	109.4	inter
wet	94.0	95.9	47.3	94.0	95.2	100.3	inter

Average desorption efficiencies for 3M 3520 OVM charcoal wafers are shown in Table 9. The mass studied was 26 Φg of each TIC per sample. Wet samplers were prepared by exposing them to clean, humid air for four hours prior to spiking. All 3M 3520 OVM

Table 9 Desorption Efficiency From 3M 3520 OVM Charcoal Wafers (%)							
	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
dry	96.7	101.5	91.2	94.8	94.4	95.0	86.2
wet	98.1	98.2	62.1	98.0	97.4	99.9	57.4

samples in this study were exposed to humid air and, therefore, analytical results were corrected using only the wet desorption efficiencies. The low wet desorption efficiencies for TCA and DDVP would necessitate use of another solvent or desorption technique in routine analytical work, however, they were again deemed adequate for this work because these samples were analyzed immediately after generation.

Sampling Rate

Sampling rates were determined by exposing samplers to test atmospheres containing approximately 4 mg/m^3 of each TIC (about 1 ppm) for increasing time intervals

Sampling rates were calculated with the following equation and then converted to mL/min:

ambient sampling rate = average mass collected/(concn of test atm × sampling time)

Mass was corrected for desorption efficiency only for SKC 575-002 and 3M 3520 OVM samplers.

Experimental sampling rates were determined at ambient temperature (T_{amb}) and barometric pressure (P_{amb}), and were converted to their equivalent at 760 mmHg and 298K with the following equation:

$$\text{sampling rate}_{760 \text{ mmHg, } 298K} = \text{sampling rate}_{amb}(298/T_{amb})^{3/2}(P_{amb}/760)$$

Sampling rates for the components of the TIC mixture were determined for SKC Ultra and GoreSorber project samplers. Sampling rates were also determined for SKC Ultra RSR, PE Tenax TA, PE Chromosorb 106, and PE Carbopack B non-project samplers. They were also determined for the 3M 3520 and SKC 575-002 samplers that were used as controls. DDVP was not thermally desorbed from PE Carbopack B samplers at its recommended maximum desorption temperature. A chromatographic interference that eluted at the same time as DDVP prevented its determination in SKC 575-002 samplers. Relative standard deviations (RSD) were calculated for the three samplers of each type that were exposed for each time interval. RSD was excessive in some cases, but all data were retained because of the small sample size and also to preserve the integrity of precision results. Part of this work was to test and evaluate the analytical method.

time	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
2	13.92	6.13	12.19	4.88	10.71	6.01	11.14	5.68	10.38	5.54	9.79	4.40	8.59	5.75
4	11.07	13.39	12.30	19.34	11.38	16.14	11.51	18.48	10.52	16.55	9.98	13.61	10.25	14.56
6	12.51	0.32	14.80	0.63	13.63	1.03	14.03	1.29	12.77	1.59	11.76	1.31	11.17	2.36
8	9.91	2.51	13.01	3.00	12.49	2.45	12.14	3.14	11.16	3.12	10.79	2.04	9.89	2.85
10	8.29	2.12	12.46	1.03	10.69	1.44	13.41	5.79	10.66	1.00	10.28	1.26	10.58	2.61
14	5.48	3.19	10.90	3.62	11.04	2.50	11.82	2.02	10.69	1.71	10.53	0.19	10.04	1.41

Table 10
Sampling Rate Data for SKC Ultra Samplers

time	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
2	9.29	7.64	23.78	4.93	21.58	5.50	21.02	5.06	19.11	4.53	21.35	4.66	22.12	6.86
4	4.16	6.93	19.32	11.07	19.74	14.45	18.46	13.75	16.25	12.50	18.91	13.23	21.27	15.37
6	1.30	13.17	20.12	12.84	20.38	14.21	19.34	15.23	16.20	15.01	19.96	12.84	21.31	17.78
8	0.83	3.19	11.53	8.24	15.97	4.52	15.55	4.63	13.07	3.66	18.07	2.75	21.58	1.80
10	0.77	14.99	7.11	26.00	13.74	6.81	12.23	9.42	9.97	12.46	15.54	8.24	21.19	6.12
14	0.45	11.58	6.04	13.77	10.64	8.57	10.72	8.31	9.32	9.26	14.70	8.09	18.20	6.48

Table 11
Sampling Rate Data for GoreSorber Samplers

	Table 12 ||||||||||||||
	Sampling Rate Data for SKC Ultra RSR Samplers ||||||||||||||
time	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
2	6.28	5.74	5.07	6.39	4.15	6.35	4.40	6.75	4.06	7.12	3.59	5.25	2.41	6.15
8	5.49	17.53	4.80	21.88	4.26	19.36	4.35	25.41	3.85	21.64	3.45	18.99	2.56	25.58
10	4.98	4.19	4.74	2.69	4.43	2.56	4.34	2.51	3.98	2.60	3.74	4.28	3.54	6.84
14	4.17	4.41	2.72	20.55	4.68	7.01	4.71	8.86	4.22	5.90	3.65	5.45	3.17	6.82
16	3.52	0.68	3.90	3.90	3.90	4.34	3.97	2.47	3.67	2.14	3.42	0.70	3.09	3.50

	Table 13 ||||||||||||||
	Sampling Rate Data for PE Tenax TA Samplers ||||||||||||||
time	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
2	0.51	7.77	0.50	6.00	0.43	3.23	0.44	3.45	0.42	5.59	0.38	17.44	0.43	24.74
4	0.42	2.74	0.48	2.86	0.45	6.03	0.45	1.21	0.41	4.03	0.36	4.56	0.34	5.98
6	0.46	13.28	0.46	12.86	0.41	10.80	0.39	14.64	0.37	10.50	0.32	12.07	0.25	18.50
8	0.46	3.01	0.50	2.26	0.48	1.85	0.45	2.17	0.42	2.00	0.38	5.26	0.35	18.49
10	0.45	2.35	0.50	2.76	0.48	3.20	0.45	3.47	0.42	2.52	0.39	2.46	0.38	18.84
14	0.42	12.57	0.45	4.44	0.42	4.08	0.41	3.39	0.38	1.98	0.35	1.30	0.32	10.94
16	0.46	4.07	0.47	4.59	0.46	5.03	0.44	6.06	0.39	6.58	0.37	6.31	0.30	32.28

	Table 14 ||||||||||||||
	Sampling Rate Data for PE Chromosorb 106 Samplers ||||||||||||||
time	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
2	0.56	9.61	0.54	4.09	0.47	1.71	0.48	3.13	0.43	14.26	0.33	40.32	0.34	43.30
4	0.74	2.76	0.64	4.81	0.58	10.52	0.68	16.22	0.56	23.11	0.75	33.88	0.63	39.26
6	0.59	1.27	0.55	2.91	0.58	2.76	0.48	2.40	0.49	3.29	0.47	11.69	0.79	35.53
8	0.58	11.55	0.56	6.67	0.52	6.23	0.52	6.33	0.51	5.87	0.46	9.72	0.47	60.12
10	0.52	16.94	0.52	10.06	0.50	8.74	0.49	7.72	0.48	10.07	0.45	12.54	0.73	12.92
16	0.62	3.61	0.55	2.45	0.54	1.69	0.51	2.22	0.48	1.37	0.44	0.85	0.57	6.75

	Table 15											
	Sampling Rate Data for PE Carbopack B Samplers											
time	Bz		EtBz		TCA		TMB		LIM		UND	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
2	0.53	3.70	0.48	6.18	0.39	7.14	0.42	7.62	0.41	7.81	0.36	11.02
4	0.50	8.97	0.42	11.45	0.35	10.14	0.36	13.58	0.32	11.18	0.26	24.74
6	0.55	10.21	0.49	11.24	0.42	10.05	0.43	11.90	0.41	8.86	0.36	6.76
8	0.58	3.83	0.54	7.33	0.52	2.83	0.49	5.06	0.44	3.14	0.40	6.72
10	0.56	6.18	0.52	8.48	0.47	8.63	0.47	9.02	0.42	9.59	0.37	12.93
16	0.58	23.19	0.49	11.51	0.50	14.04	0.47	7.39	0.40	10.76	0.34	11.00

DDVP not desorbed at maximum temperature

	Table 16											
	Sampling Rate Data for SKC 575-002 Samplers											
time	Bz		EtBz		TCA		TMB		LIM		UND	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
2	19.51	3.35	14.61	2.43	19.08	6.50	13.19	3.12	11.78	3.39	10.85	4.24
4	17.23	1.31	14.25	0.92	18.73	1.30	12.91	1.06	10.62	0.41	10.79	0.70
6	17.71	0.56	13.97	2.17	18.41	1.41	11.79	4.13	10.75	4.97	10.11	6.31
8	17.21	5.68	13.40	6.97	17.41	4.67	11.74	4.75	10.22	5.03	10.05	5.99
10	17.29	3.70	14.46	1.11	15.50	2.65	13.15	0.92	11.06	0.54	10.93	1.75
14	17.41	2.68	14.08	2.46	17.00	3.41	12.80	2.84	10.86	2.46	10.64	2.81
16	17.03	3.84	14.12	5.26	17.78	5.22	13.15	5.60	11.11	6.34	10.94	6.22

chromatographic interference for DDVP

Table 17 Sampling Rate Data for 3M 3520 OVM Samplers														
time	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
2	36.83	1.42	28.38	1.71	34.37	0.75	25.67	1.22	23.27	1.37	21.30	1.03	20.97	5.82
4	32.44	7.10	27.20	4.86	33.62	5.94	24.56	6.24	20.52	6.20	20.02	5.56	20.36	4.82
6	34.00	4.64	27.71	2.03	34.53	2.21	25.02	2.04	22.46	2.20	20.30	2.15	19.78	6.19
8	33.84	2.91	28.62	2.26	33.12	3.08	26.11	2.28	23.49	2.21	21.20	1.76	19.11	5.34
10	34.50	0.23	29.74	0.47	32.29	4.14	28.80	15.08	23.71	0.61	21.40	0.49	22.51	4.29
14	35.18	4.76	28.63	4.32	33.19	5.72	25.88	4.25	23.39	4.56	20.95	4.12	20.83	4.88
16	33.42	0.58	28.12	0.30	34.08	7.34	26.12	0.19	23.51	0.36	21.16	0.21	21.93	4.18

Average sampling rates were calculated over the time intervals that they were judged to remain relatively constant. RSDs were calculated for these averages. These data are presented in Tables 18-19, together with the time interval range for which sampling rates were averaged. Sampler capacity was not exceeded in most cases. Cases in which sampler capacity was judged to have been exceeded are indicated with an asterisk (*). GoreSorber samplers had insufficient capacity for Bz and were declared not applicable for this TIC.

Table 18 Sampling Rate Summary												
sampler	Bz			EtBz			TCA			TMB		
	mL/min	RSD	range	mL/min	RSD	range	mL/min	RSD	range	mL/min	RSD	range
SKC Ultra	12.5	11.4	2-6*	12.4	3.1	2-10*	11.3	6.1	2-14	12.0	6.5	2-14
GoreSorber	NA			21.1	11.3	2-6*	20.6	4.5	2-6*	19.6	6.6	2-6*
SKC Ultra RSR	5.9	9.5	2-8*	4.9	3.6	2-10*	4.4	5.3	2-14	4.5	3.9	2-14*
PE Tenax TA	0.45	6.7	2-16	0.48	4.3	2-16	0.45	6.3	2-16	0.43	5.5	2-16
PE Chromosorb 106	0.60	12.5	2-16	0.56	7.4	2-16	0.53	8.3	2-16	0.53	14.6	2-16
PE Carbopack B	0.55	5.6	2-16	0.49	8.4	2-16	0.44	15.0	2-16	0.44	10.8	2-16
SKC 575-002	17.6	4.9	2-16	14.1	2.8	2-16	17.7	6.9	2-16	12.7	5.0	2-16
3M 3520	34.3	4.1	2-16	28.3	2.8	2-16	33.6	2.4	2-16	26	5.2	2-16

NA = not applicable

Table 19 Sampling Rate Summary									
sampler	LIM			UND			DDVP		
	mL/min	RSD	range	mL/min	RSD	range	mL/min	RSD	range
SKC Ultra	10.8	3.0	2-14	10.5	5.3	2-14	10.1	8.6	2-14
GoreSorber	17.2	9.7	2-6*	20.1	6.1	2-6*	21.5	1.8	2-10*
SKC Ultra RSR	4.0	3.8	2-14*	3.6	3.8	2-16	3.0	15.7	2-16
PE Tenax TA	0.40	5.3	2-16	0.36	6.5	2-16	0.34	17.0	2-16
PE Chromosorb 106	0.49	8.7	2-16	0.48	29.0	2-16	0.59	28.3	2-16
PE Carbopack B	0.40	10.4	2-16	0.35	13.6	2-16	NA		
SKC 575-002	10.9	4.4	2-16	10.6	3.6	2-16	NA		
3M 3520	22.9	4.9	2-16	20.9	2.6	2-16	20.8	5.7	2-16

NA = not applicable

Sampling rates for SKC Ultra and SKC 575-002 samplers should be similar providing the sampling medium is adequate. This is because the SKC Ultra sampler design is based on the SKC 575 Series of samplers. The main difference is that the SKC Ultra sampler contains Tenax TA and the SKC 575-002 sampler contains carbon-based Anasorb 747. The greatest disagreements are for Bz and TCA, and to a lesser degree, EtBz. Bz and EtBz differences are due to low affinity of Tenax TA for Bz and EtBz as evidenced by the reverse diffusion experiment results presented in Table 25. The reason for the TCA difference is unknown, but the presence of water may be a contributing factor. Comparison of sampling rates was excellent for TMB, LIM, and UND. These results indicate that Tenax TA is not suitable for more volatile TICs.

Sampling rates for PE Tenax TA, PE Chromosorb 106, and PE Carbopack B samplers should also be similar if the sampling medium is adequate. The only difference in these samplers is the sampling medium. Except for Bz, PE Tenax TA and PE Carbopack B sampling rates were similar. The difference for Bz is due to the low affinity of Tenax TA for Bz. Sampling rates for PE Chromosorb 106 samplers were higher than were the other two for unknown reasons.

Sampling rates for some TICs and some of the samplers tested in this report are published in the literature[9] and are presented in Table 20 for comparison with those obtained in this current work (CW). Literature (Lit) values cited in Table 20 for SKC 575-001/2 samplers were determined for the SKC 575-001 sampler which is similar to the SKC 575-002 sampler tested in this study. The difference is that the SKC 575-001 sampler contains 350 mg of coconut-shell charcoal and the SKC 575-002 sampler contains 500 mg of Anasorb 747. The 3M 3500 OVM is similar to the 3M 3520 OVM, except the 3M 3520 OVM contains two charcoal wafers. Lit sampling rates cited in Table 20 for PE samplers were obtained using diffusive sampling caps without membranes. It is interesting to note that Lit Chromosorb (Chrom) 106 sampling rates are higher than those for Tenax TA which generally supports results obtained in this work. Blank spaces in Table 20 mean that no Lit data were found.

Table 20 Sampling Rates Comparison (mL/min)														
Sampler	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
	CW	Lit	CW	Lit	CW	Lit	CW	Lit	CW	Lit	CW	Lit	CW	Lit
SKC 575-001/2	17.6	16.0	14.1	12.9	17.7	11.8	12.7	12.1	10.9	11.4	10.6			
3M 3500/20	34.3	35.5	28.3	27.3	33.6	28.4	26.0	26.3	22.9	21.9	20.9		20.8	
PE Tenax TA	0.45	0.41	0.48	0.46	0.45		0.43	0.45	0.40		0.36		0.34	
PE Chrom 106	0.60	0.54	0.56	0.56	0.53		0.53	0.47	0.49		0.48		0.59	

Control samplers were employed to test some of the practices used in this work. If the test atmosphere generation apparatus was functioning properly, and if concentrations of the test atmospheres were correctly known, then sampling rates for control samplers should be in agreement (within experimental error) with those previously determined.

OSHA SLTC has previously determined Bz sampling rates for SKC 575-002 and 3M 3520 samplers[10]. They were 17.1 and 34.3 mL/min, respectively. OSHA SLTC has also determined the EtBz sampling rate for SKC 575-002 samplers to be 13.8 mL/min[11].

Lit values from Table 20 were divided by CW values for the Lit comparison, and values determined from previous work were divided by CW values for the OSHA comparison. Both comparisons are presented

Table 21 Control Sampler Comparison					
	Bz	EtBz	TCA	TMB	LIM
Lit					
575-002	90.9	91.5	66.7	95.3	104.6
3M 3520	103.5	96.5	84.5	101.2	95.6
OSHA					
575-002	97.2	105.0			
3M 3520	100.0				

in terms of percent in Table 21. No comparison data were available for UND and DDVP. Except for TCA, the agreement between Lit, OSHA, and CW sampling rates for TICs that were tested is good. Low desorption efficiency from wet carbon-based sampling media obtained in this work is a possible reason for the TCA difference. Many laboratories do not investigate desorption from wet media. Low desorption would cause the calculated sampling rate to increase because analytically determined mass would also increase.

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9   Health and Safety Executive, *The Diffusive Monitor*, **12**, Workplace Applications, 6-13, (July 2001).

10 Eide, M. *OSHA Method No.1005 Benzene*; OSHA Salt Lake Technical Center, unpublished, Salt Lake City, UT 84115-1802, November 2001.

11 http://www.osha.gov/dts/sltc/methods/mdt/mdt1002/1002.html, (accessed February 2002).

The overall good comparison of sampling rates for control samplers with sampling rates available in the literature values support the techniques used to in this work.

Long-Term Sampling Capacity

The possibility of long-term sampling was investigated by exposing 21 each SKC Ultra, GoreSorber, and PE Tenax TA samplers to a test atmosphere containing approximately 0.4 mg/m^3 of each TIC (about 0.1 ppm) for up to 54 hours. Three of each type of sampler was removed for analysis at approximately eight-hour intervals. Results in terms of sampling rates for the long-term sampling experiment are shown in Tables 22-24.

Table 22													
Long-Term Sampling Experiment for SKC Ultra Samplers													
time	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
7.23	11.29	3.76	14.45	16.07	12.45	2.60	12.91	3.02	14.96	26.93	11.31	1.52	11.65	2.75
15.55	8.26	7.89	14.01	17.91	11.97	3.63	11.82	6.52	9.96	6.58	9.34	5.61	12.47	4.48
23.57	7.98	5.32	11.83	3.19	11.64	6.14	11.51	2.12	8.99	1.52	9.21	1.63	13.08	1.34
30.23	6.36	5.09	12.20	5.38	12.17	2.12	11.96	1.65	9.66	1.56	10.03	0.55	13.25	1.79
39.40	4.92	3.26	10.99	10.67	11.07	7.15	10.94	10.85	8.81	8.53	9.32	6.70	11.28	6.93
47.68	4.30	5.89	10.97	3.17	11.64	0.88	10.88	0.95	8.37	1.67	9.36	1.34	11.04	2.72
53.77	3.69	4.82	10.38	5.90	11.19	4.67	10.58	4.87	8.27	4.52	9.02	3.98	11.03	3.98

Table 23													
Long-Term Sampling Experiment for GoreSorber Samplers													
time	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
7.23	4.50	7.35	22.77	3.21	22.15	3.73	21.13	3.44	17.93	3.70	22.06	3.46	21.08	1.96
15.55	0.54	43.98	19.71	1.97	20.63	3.56	19.46	3.31	14.84	2.88	20.24	3.68	23.55	5.57
23.57	1.16	27.47	16.99	9.48	19.33	6.16	18.51	7.30	14.02	8.88	19.75	5.92	24.97	5.37
30.23	0.45	24.02	13.77	2.65	16.60	6.53	16.40	7.96	12.20	7.74	17.78	9.78	22.30	12.06
39.40	0.30	7.26	11.49	3.73	14.63	3.16	14.59	3.82	11.13	4.02	16.46	2.32	19.90	4.00
47.68	0.52	16.70	9.67	7.87	14.32	5.92	13.48	6.63	10.09	4.16	15.88	4.71	20.33	7.00
53.77	0.31	18.75	7.56	9.26	12.08	2.30	12.06	2.46	9.03	3.72	14.40	1.45	19.43	3.62

Table 24													
Long-Term Sampling Experiment for PE Tenax TA Samplers													
time	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
hours	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
7.23	0.49	0.00	0.57	5.41	0.53	0.00	0.56	0.00	0.54	0.00	0.51	0.00	0.44	0.00
15.55	0.47	2.79	0.56	5.33	0.51	5.97	0.49	3.15	0.48	5.88	0.32	0.00	0.37	16.88
23.57	0.37	4.42	0.48	3.23	0.49	3.89	0.45	4.17	0.41	10.34	0.39	4.17	0.48	14.43
30.23	0.35	6.44	0.50	3.88	0.51	5.53	0.47	7.56	0.41	3.33	0.40	6.67	0.42	21.17
39.40	0.36	3.67	0.46	6.45	0.48	7.40	0.42	9.31	0.37	13.09	0.36	5.71	0.38	1.84
47.68	0.32	3.20	0.47	2.94	0.54	4.22	0.48	3.76	0.41	4.84	0.36	0.00	0.49	4.46
53.77	0.32	4.55	0.46	6.66	0.52	6.92	0.45	6.35	0.41	6.33	0.35	9.58	0.51	14.73

Results for the long-term sampling experiment are shown graphically in Figures 12-14. The data show that sampling rates for most TICs generally decrease over the extended sampling time. The decrease is probably due to reverse diffusion and to exceeded sampling capacity. The decrease for SKC Ultra samplers is most severe for Bz, then LIM, and then EtBz. Sampling rates for other TICs all decrease, but at a much slower rate. The GoreSorber sampler has almost no capacity for Bz. Sampling rate decrease for GoreSorber samplers is severe for all the tested TICs, except DDVP. Sampling rate decrease for PE Tenax TA samplers is most severe for Bz, then LIM, and then EtBz.
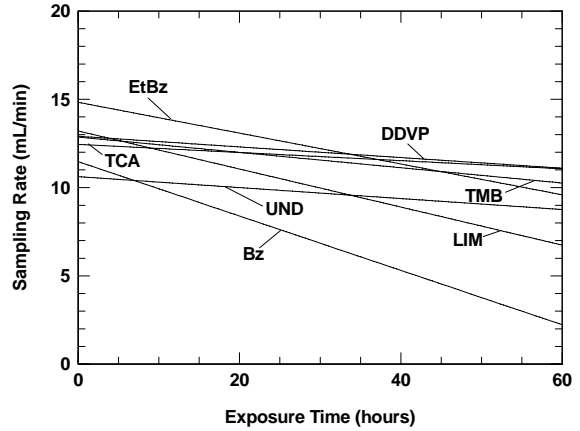
Figure 12. Long-term sampling experiment for SKC Ultra sampler.
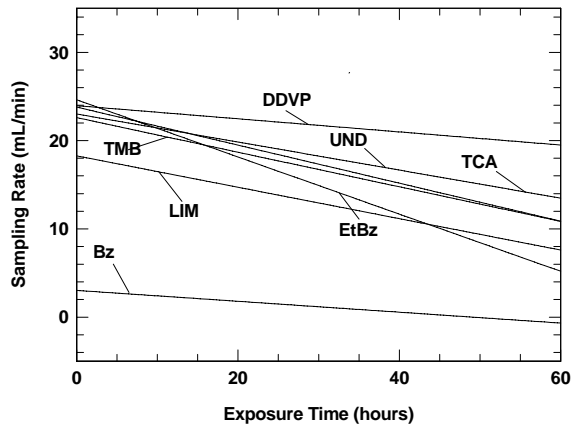
Figure 13. Long-term sampling experiment for GoreSorber sampler.
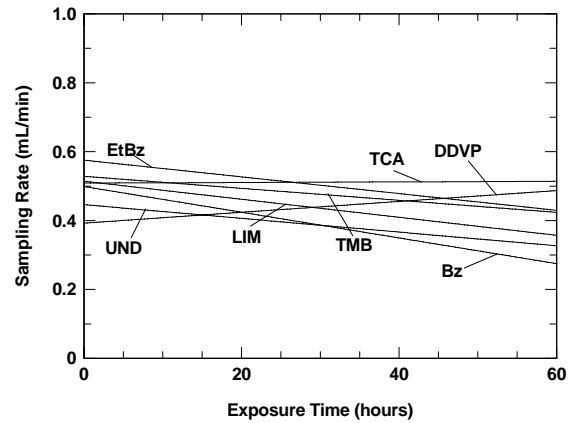
Figure 14. Long-term sampling experiment for PE Tenax TA samplers.

Long-term sampling capacity for a particular sampler depends on the concentration of TIC in the sampled atmosphere and on the affinity of the sampling medium for that TIC. Sampling error will increase as sampling time increases because almost all sampling rates for the tested TICs were observed to decrease with increasing time. Inspection of the graphed data shows that long-term sampling for Bz is not appropriate with either SKC Ultra or GoreSorber samplers.

Reverse Diffusion

Results in Table 25 are expressed as TIC retention by samplers that were exposed to contaminated air for four hours and then additionally to clean air for four hours, compared to samplers exposed only to contaminated air for four hours. Loss greater than 10% (90% retention) is considered to be significant. These results show that Tenax TA is not a good sampling medium for Bz, and that reverse diffusion must be considered when setting maximum sampling times for other TICs.

Table 25 Reverse Diffusion (percent retention)							
sampler	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
SKC Ultra	56.9	88.9	97.5	95.8	96.3	95.6	100
GoreSorber	0	74.3	85.3	91.6	89.8	95.0	100
PE Tenax TA	87.7	96.7	96.9	99.2	99.1	99.5	100

Storage Stability

Sampling rates used to calculate storage stability sample results were taken from Tables 18-19 and were converted to their equivalents at sampling site temperature and pressure. Results from the three samples analyzed on the designated days are presented as percent of the concentrations of the test atmosphere. GoreSorber sampler results for Bz on Day 0 and subsequent samples were very low, less than 25% of the expected mass, and are not presented because no meaningful recovery data could be calculated. Storage stability data were examined statistically, and those results are presented following graphical representation of the storage data.

Table 26
Ambient Temperature Storage Stability for SKC Ultra Samplers

day	Bz			EtBz			TCA			TMB			LIM			UND			DDVP		
0	93.8	96.1	98.4	101.7	106.6	109.8	106.1	109.9	113.4	100.6	104.6	108.3	105.9	110.4	113.7	102.0	107.5	109.9	111.8	115.0	120.5
4	71.8	79.1	85.2	104.5	104.6	109.2	107.2	105.1	111.4	98.9	98.5	104.2	104.8	103.5	110.2	103.1	101.0	106.7	106.4	106.0	112.0
8	74.4	94.2	79.7	112.9	111.2	109.0	112.4	112.3	109.7	113.2	115.3	114.3	114.2	114.9	114.4	107.6	108.9	108.3	134.7	132.6	129.7
11	59.7	81.3	82.4	103.9	106.5	117.0	77.1	108.3	112.5	103.9	108.0	115.0	107.0	110.2	116.5	83.7	106.9	112.0	129.4	130.2	142.1
16	49.7	55.7	46.4	100.8	98.3	85.6	104.9	97.8	90.0	106.9	100.1	89.2	109.2	102.8	95.1	104.5	97.7	90.8	122.4	114.3	104.6
23	50.8	55.3	50.7	97.1	94.3	102.2	97.5	93.4	97.6	101.4	97.3	102.5	101.2	96.9	102.8	97.1	95.3	99.4	114.1	119.0	118.8

Table 27
Refrigerated Temperature Storage Stability for SKC Ultra Samplers

day	Bz			EtBz			TCA			TMB			LIM			UND			DDVP		
0	93.8	96.1	98.4	101.7	106.6	109.8	106.1	109.9	113.4	100.6	104.6	108.3	105.9	110.4	113.7	102.0	107.5	109.9	111.8	115.0	120.5
4	106.4	95.6	103.4	121.0	109.4	119.9	114.0	102.3	112.1	112.5	102.1	114.0	116.8	106.8	115.4	110.3	103.4	109.7	112.6	104.1	114.5
8	106.4	100.6	104.9	113.8	108.2	110.3	115.5	108.6	112.1	116.6	108.9	114.4	117.2	111.5	114.9	108.9	105.1	106.4	128.5	124.1	126.8
11	105.2	101.3	102.2	118.2	120.7	111.8	118.0	115.4	112.1	117.4	116.2	111.5	119.5	118.6	113.3	112.9	112.3	107.2	137.4	140.0	122.4
16	96.8	101.2	89.6	111.2	105.8	93.5	108.9	109.6	96.3	109.5	109.9	96.8	126.2	126.6	111.6	107.4	105.2	94.9	123.0	121.4	106.2
23	91.9	97.2	98.1	101.5	108.0	112.9	100.8	105.6	102.1	100.9	107.0	113.0	104.6	107.3	111.5	99.7	100.7	104.8	115.8	119.2	123.7
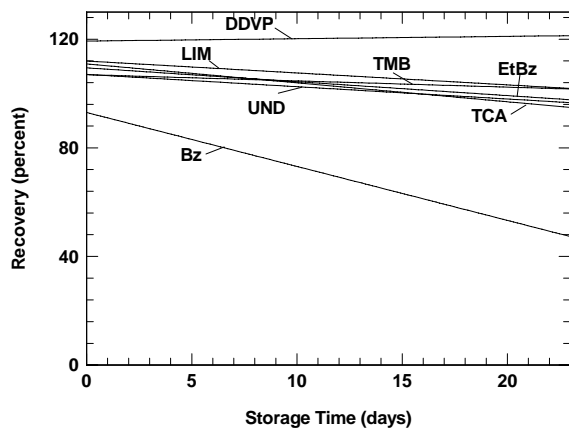
Figure 15. Ambient temperature storage stability test for Ultra sampler
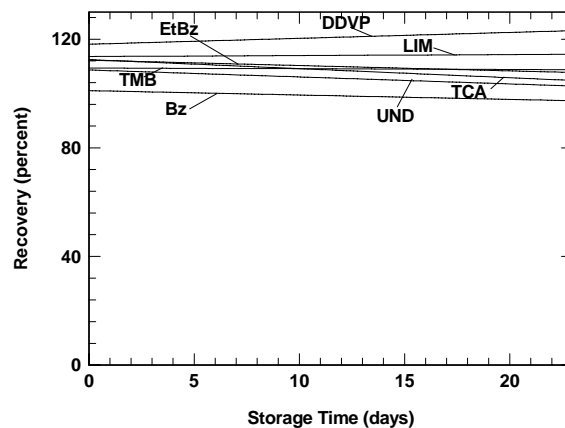
Figure 16. Refrigerated temperature storage stability test for Ultra samplers

SEE_R (standard error of estimate) is defined as the dispersion of data about the regression line for the plotted storage data, and it is mathematically similar to standard deviation for a data set. SEE_p is the pooled RSD of the numerical values for SEE_R and sampling rate variation (Table 41). SEE_p is multiplied by 1.96 to calculate the 95% confidence interval (conf int) for the storage test.

Table 28
Statistical Data for SKC Ultra Sampler Ambient Temperature Storage Stability Test

TIC	equation of line	$SEE_R(\pm\%)$	$SEE_p (\pm\%)$	95% conf int (%)
Bz	Y = -1.99X + 93.0	9.31	13.56	26.6
EtBz	Y = -0.511X + 109.5	6.42	11.77	23.1
TCA	Y = -0.697X + 110.9	8.31	12.89	25.3
TMB	Y = -0.230X + 106.9	6.97	12.07	23.7
LIM	Y = -0.439X + 112.0	5.41	11.25	22.0
UND	Y = -0.452X + 107.0	6.64	11.89	23.3

		Table 28			
		Statistical Data for SKC Ultra Sampler Ambient Temperature Storage Stability Test			
TIC	equation of line	$SEE_R(\pm\%)$	$SEE_D\ (\pm\%)$	95% conf int (%)	
DDVP	Y = 0.0865X + 119.3	11.16	14.89	29.2	

		Table 29			
		Statistical Data for SKC Ultra Sampler Refrigerated Temperature Storage Stability Test			
TIC	equation of line	$SEE_R(\pm\%)$	$SEE_D\ (\pm\%)$	95% conf int (%)	
Bz	Y = -0.162X + 101.1	4.94	11.03	21.6	
EtBz	Y = -0.197X + 112.3	7.23	12.23	24.0	
TCA	Y = -0.334X + 112.5	5.38	11.23	22.0	
TMB	Y = -0.0262X + 109.4	6.25	11.67	22.9	
LIM	Y = 0.0356X + 113.6	6.43	11.77	23.1	
UND	Y = -0.257X + 108.7	4.31	10.76	21.1	
DDVP	Y = 0.217X + 118.1	9.54	13.72	26.9	

Table 30
Ambient Temperature Storage Stability for GoreSorber Samplers

day	EtBz			TCA			TMB			LIM			UND			DDVP		
0	94.3	98.3	96.3	97.5	100.0	98.5	101.0	103.5	103.1	97.3	99.4	100.7	100.3	101.8	100.9	112.5	115.9	113.0
4	98.7	95.7	85.2	108.2	101.4	87.2	105.0	98.9	89.7	103.9	95.7	80.3	117.2	108.8	96.7	132.5	119.7	106.7
8	88.2	88.5	82.0	88.4	91.1	83.6	92.4	95.4	85.5	88.9	91.5	80.4	94.9	96.5	88.3	112.4	119.2	110.4
11	88.6	87.2	80.9	91.5	90.6	82.8	93.7	93.9	85.0	91.3	90.5	81.4	96.8	95.0	88.9	124.2	123.0	125.6
16	83.4	90.2	72.4	82.7	91.8	71.5	87.5	95.5	73.3	82.2	90.9	71.4	89.2	99.8	79.1	100.2	120.4	88.3
23	77.5	80.2	77.7	79.8	83.3	79.7	84.2	85.0	84.2	78.6	83.3	80.5	89.5	94.0	89.5	106.7	106.8	100.6

Table 31
Refrigerated Temperature Storage Stability for GoreSorber Samplers

| day	EtBz			TCA			TMB			LIM			UND			DDVP		
0	94.3	98.3	96.3	97.5	100.0	98.5	101.0	103.5	103.1	97.3	99.4	100.7	100.3	101.8	100.9	112.5	115.9	113.0
4	99.5	91.7	96.8	102.4	92.0	100.3	102.4	89.8	99.0	100.1	84.2	96.0	105.9	99.9	104.1	111.4	104.7	111.9
8	83.6	88.1	92.2	84.3	89.2	94.1	86.0	92.1	98.9	84.8	89.8	98.4	89.2	92.8	98.4	102.2	106.9	117.1
11	89.5	91.4	90.7	91.2	94.1	94.2	93.1	96.3	96.6	91.2	94.3	94.6	92.9	98.2	99.0	112.7	120.3	123.6
16	87.6	90.2	101.4	89.9	93.3	111.8	92.6	96.0	105.6	92.0	95.6	114.5	94.7	97.9	124.5	110.0	115.8	138.2
23	81.5	87.7	86.9	85.0	91.8	88.0	85.3	93.2	91.9	94.9	94.0	91.6	90.6	99.4	95.9	105.8	111.3	100.2

Figure 17. Ambient temperature storage stability test for GoreSorber Samplers.
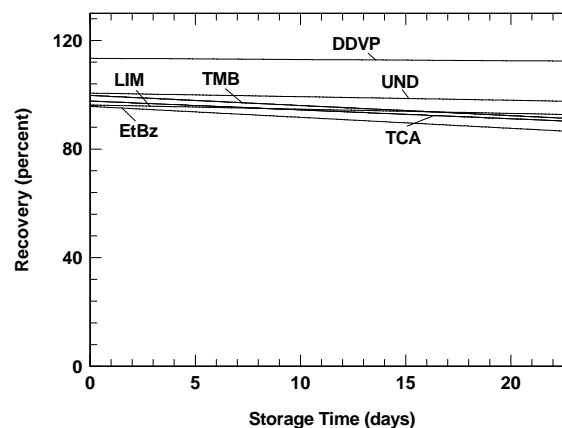
Figure 18. Refrigerated temperature storage stability test for GoreSorber samplers.

		Table 32			
		Statistical Data for GoreSorber Sampler Ambient Temperature Storage Stability Test			
TIC	equation of line	$SEE_R(\pm\%)$	$SEE_D\ (\pm\%)$	95% conf int (%)	
EtBz	Y = -0.785X + 95.1	4.83	18.34	35.9	
TCA	Y = -0.875X + 98.5	6.38	18.81	36.9	
TMB	Y = -0.803X + 100.3	5.88	18.64	36.5	
LIM	Y = -0.794X + 96.4	6.66	18.90	37.0	
UND	Y = -0.640X + 102.6	7.13	19.07	37.4	
DDVP	Y = -0.600X + 119.4	9.97	20.31	39.8	

Table 33				
Statistical Data for GoreSorber Sampler Refrigerated Temperature Storage Stability Test				
TIC	equation of line	$SEE_R(\pm\%)$	$SEE_p\ (\pm\%)$	95% conf int (%)
EtBz	Y = -0.403X + 95.7	4.54	18.26	35.8
TCA	Y = -0.326X + 97.7	6.38	18.81	36.9
TMB	Y = -0.373X + 99.8	5.31	18.47	36.2
LIM	Y = -0.155X + 96.2	7.23	19.11	37.5
UND	Y = -0.132X + 100.6	7.87	19.36	37.9
DDVP	Y = -0.0452X + 113.4	8.96	19.83	38.9

Table 34																					
Ambient Temperature Storage Stability for PE Tenax TA Samplers																					
day	Bz			EtBz			TCA			TMB			LIM			UND			DDVP		
0	110.8	112.4	110.8	97.0	102.1	98.7	96.7	91.4	89.7	88.1	103.7	105.7	93.7	95.8	112.9	105.6	110.3	103.3	92.0	99.4	84.5
5	107.5	102.5	115.7	108.7	112.1	112.1	123.1	117.8	119.6	123.3	125.3	133.1	117.1	121.4	123.5	110.3	115.0	131.4	67.1	106.9	116.8
9	109.1	94.2	110.8	105.4	103.7	107.1	102.0	98.5	100.2	117.4	105.7	107.6	112.9	119.2	119.2	105.6	103.3	105.6	87.0	96.9	116.8
14	107.5	107.5	90.9	117.1	105.4	88.7	112.5	110.8	93.2	105.7	113.5	86.1	129.9	100.1	91.6	117.4	124.4	105.6	89.5	106.9	96.9
21	99.2	110.8	104.1	100.4	107.1	93.7	103.8	110.8	89.7	113.5	117.4	97.9	108.6	115.0	91.6	103.3	119.7	103.3	129.2	94.4	111.8
26	94.2	104.1	104.1	97.0	107.1	100.4	110.8	112.5	107.3	105.7	113.5	107.6	93.7	110.7	102.2	119.7	122.1	110.3	101.9	87.0	54.7

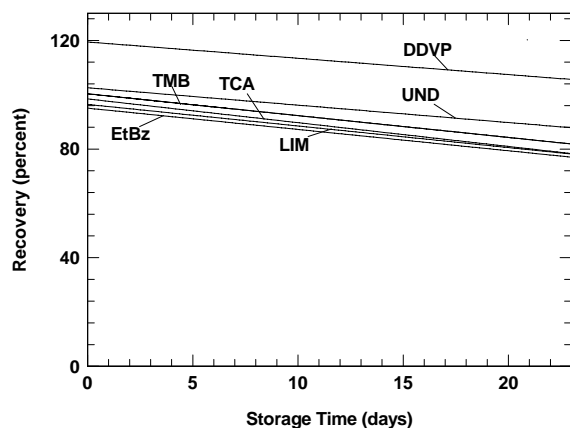| Table 35																					
Refrigerated Temperature Storage Stability for PE Tenax TA Samplers																					
day	Bz			EtBz			TCA			TMB			LIM			UND			DDVP		
0	110.8	112.4	110.8	97.0	102.1	98.7	96.7	91.4	89.7	88.1	103.7	105.7	93.7	95.8	112.9	105.6	110.3	103.3	92.0	99.4	84.5
5	114.1	107.5	109.1	108.7	110.4	113.8	116.1	114.3	117.8	119.4	113.5	121.3	104.3	110.7	123.5	124.4	110.3	117.4	109.4	109.4	101.9
9	100.8	112.4	115.7	107.1	115.4	112.1	100.2	103.8	116.1	113.5	131.1	119.4	117.1	136.3	136.3	112.7	115.0	115.0	124.3	114.3	99.4
14	124.0	119.0	104.1	110.4	118.8	102.1	116.1	112.5	98.5	117.4	123.3	111.6	115.0	123.5	112.9	110.3	126.8	103.3	96.9	111.8	104.4
21	119.0	107.5	104.1	110.4	105.4	110.4	107.3	110.8	105.5	105.7	103.7	117.4	110.7	106.5	108.6	112.7	100.9	108.0	96.9	89.5	119.3
26	104.1	99.2	92.6	107.1	100.4	105.4	112.5	98.5	109.0	111.6	103.7	113.5	115.0	102.2	112.9	122.1	103.3	105.6	134.2	141.7	64.6
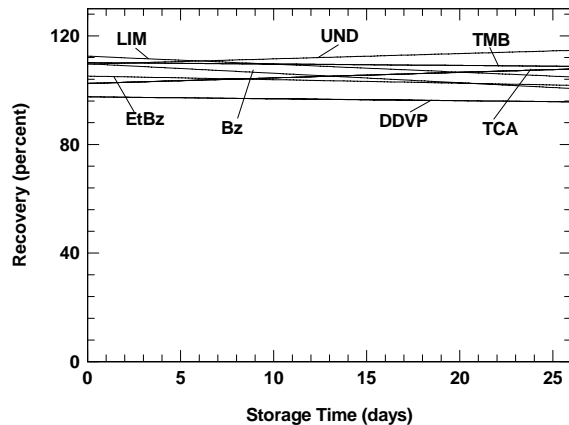
Figure 19. Ambient temperature storage stability test for PE Tenax TA samplers.
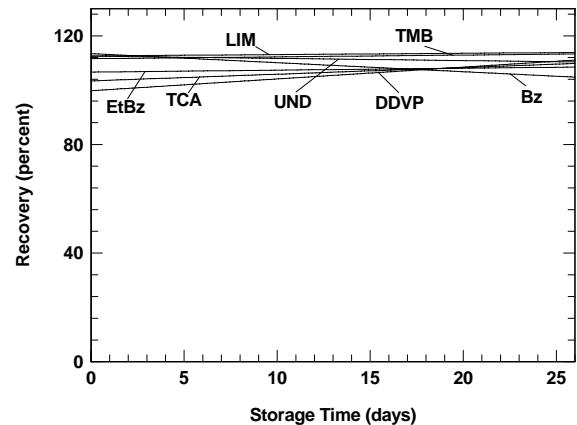
Figure 20. Refrigerated temperature storage stability test for PE Tenax TA samplers.

Table 36				
Statistical Data for PE Tenax TA Samplers Ambient Temperature Storage Stability Test				
TIC	equation of line	$SEE_R(\pm\%)$	$SEE_p\ (\pm\%)$	95% conf int (%)
Bz	Y = -0.350X + 109.7	6.30	13.60	26.7
EtBz	Y = -0.130X + 105.2	7.18	14.03	27.5
TCA	Y = 0.205X + 102.5	10.61	16.06	31.5
TMB	Y = -0.0515X + 110.1	12.26	17.19	33.7
LIM	Y = -0.293X + 112.5	12.23	17.17	33.7
UND	Y = 0.195X + 109.6	8.69	14.86	29.1
DDVP	Y = -0.0711 X + 97.5	18.34	21.94	43.0

Table 37 Statistical Data for PE Tenax TA Sampler Refrigerated Temperature Storage Stability Test				
TIC	equation of line	$SEE_R(\pm\%)$	$SEE_p (\pm\%)$	95% conf int (%)
Bz	Y = -0.333X + 113.5	7.39	14.14	27.7
EtBz	Y = 0.0716X + 106.6	6.04	13.48	26.4
TCA	Y = 0.247X + 103.4	8.86	14.96	29.3
TMB	Y = 0.0663X + 111.6	10.01	15.67	30.7
LIM	Y = 0.0485X + 112.6	11.88	16.92	33.2
UND	Y = -0. 0813X + 112.5	7.77	14.34	28.1
DDVP	Y = 0.435X + 99.8	18.27	21.89	42.9

Storage tests showed good stability for all TICs on the three tested samplers, except for Bz stored at 40ᴇC on SKC Ultra samplers. The observed loss of Bz was probably due to physical loss, and not to chemical instability. Bz was not retained by the GoreSorber sampler and, therefore, was not tested. The stability data were not as precise as that obtained in other OSHA SLTC work performed with different diffusive samplers containing carbon-based sampling media. The overall SEE_R for those tests was about 3%, compared to the 9% obtained in this work.

Factor Test

The results of the factor test are shown in Tables 38-40.   RSDs for the three samplers exposed for each test are presented for information. RSDs were also calculated for the averaged sampling rates.

Table 38 Factor Test Results for SKC Ultra Samplers														
test	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
1	13.17	2.82	13.83	2.02	13.53	2.09	13.94	2.00	13.01	2.03	11.51	1.98	11.60	1.49
2	16.33	1.82	13.13	0.89	13.58	1.17	15.17	0.46	13.30	9.68	10.14	9.38	16.22	3.79
3	18.24	4.49	15.90	3.79	12.84	2.77	15.23	1.40	15.34	2.60	12.30	3.49	11.83	2.87
4	11.07	2.14	12.16	0.77	11.14	1.86	11.89	1.29	12.23	1.96	10.69	1.62	11.15	2.52
5	12.99	7.53	11.74	11.45	12.64	8.81	11.43	8.94	11.45	8.94	10.49	7.65	11.49	9.61
6	15.86	3.84	14.36	2.34	12.71	3.31	13.28	2.17	12.65	1.46	11.01	0.64	11.37	9.02
7	15.17	0.94	12.42	6.25	10.86	3.85	12.84	2.88	13.08	3.06	11.16	1.26	11.13	3.97
8	9.68	15.07	14.22	12.24	13.46	13.74	15.18	14.61	13.85	12.30	13.45	11.89	12.18	12.85
9	16.37	6.33	15.09	12.25	12.67	11.79	14.10	7.93	13.27	7.98	10.84	17.64	11.63	9.75
10	18.56	3.43	15.60	6.28	12.94	5.98	14.93	4.06	14.08	4.13	11.70	6.90	12.83	2.81
11	10.91	3.20	13.54	5.19	12.34	19.07	12.87	5.00	9.74	5.00	10.63	2.65	11.26	18.10
12	19.54	10.22	12.78	4.64	11.91	1.67	11.63	7.97	11.08	6.19	8.68	1.65	12.91	0.50
13	11.86	14.40	13.26	11.93	11.55	5.14	11.73	6.43	12.25	8.50	10.95	8.57	10.06	11.08
14	13.01	3.49	13.81	3.80	12.22	2.97	13.49	4.03	12.07	1.88	10.97	4.37	10.80	2.90
15	11.95	10.36	13.41	7.72	12.80	1.82	12.98	1.56	11.86	2.13	10.82	4.75	11.26	4.95
16	16.40	4.50	12.15	4.65	11.81	1.56	13.29	2.41	12.76	3.30	10.86	2.53	15.08	2.81
ave	14.44		13.59		12.44		13.37		12.63		11.01		12.05	
RSD	20.86		9.04		6.55		9.78		10.33		9.13		13.13	

Table 39 Factor Test Results for GoreSorber Samplers														
test	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
1	4.23	11.51	18.87	7.86	19.71	7.69	17.95	8.44	15.72	9.04	17.16	8.28	22.32	10.16
2	16.39	4.82	25.08	4.61	24.79	4.00	22.95	4.19	21.07	4.50	22.48	3.84	23.54	6.98
3	23.14	7.73	32.56	4.52	27.67	5.74	27.93	5.25	26.76	5.00	25.29	4.26	26.72	4.80
4	3.15	3.09	14.91	3.13	16.62	5.17	15.31	3.76	15.85	0.57	17.34	5.01	19.58	5.01
5	6.99	8.50	19.94	7.82	20.41	10.10	18.65	8.99	16.36	5.88	18.68	6.77	20.28	8.71
6	16.25	8.18	25.63	1.67	24.25	3.08	18.80	25.43	19.57	3.29	20.50	3.17	27.53	1.45
7	19.89	10.59	26.04	6.33	24.94	7.46	23.94	7.41	22.43	7.59	24.08	6.97	27.42	7.44
8	1.99	4.94	20.43	5.04	21.83	7.99	23.62	17.48	18.94	8.38	25.72	8.68	27.64	8.71

Table 39 Factor Test Results for GoreSorber Samplers														
test	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
9	17.81	1.73	33.00	5.16	28.45	5.22	27.69	5.62	26.15	3.98	27.07	4.00	31.15	4.62
10	3.38	64.86	22.11	43.88	20.62	47.32	19.11	45.28	16.90	46.51	20.99	55.30	27.84	62.36
11	2.32	8.72	18.83	5.46	17.71	18.35	20.45	22.68	15.04	8.47	19.08	8.13	24.13	7.17
12	24.17	5.94	25.95	4.84	23.91	4.32	20.88	3.97	18.64	3.88	20.52	3.56	27.42	5.76
13	15.12	8.34	27.41	2.00	24.28	1.08	24.31	2.33	21.91	3.12	25.03	3.27	26.48	5.91
14	6.07	10.76	21.89	1.23	24.02	0.31	22.92	1.38	21.68	1.15	24.83	1.19	25.14	0.89
15	1.01	13.78	15.15	5.07	16.95	6.70	15.45	5.59	13.79	6.32	18.25	5.76	21.56	6.34
16	19.91	8.99	22.72	9.40	22.98	7.82	21.43	8.84	20.09	7.34	21.98	2.10	32.24	6.70
ave	11.36		23.16		22.45		21.34		19.43		21.81		25.69	
RSD	73.95		22.83		15.79		17.61		19.56		14.77		14.02	

Table 40 Factor Test Results for PE Tenax TA Samplers														
test	Bz		EtBz		TCA		TMB		LIM		UND		DDVP	
	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD	mL/min	RSD
1	0.59	3.07	0.52	3.03	0.52	3.77	0.48	4.03	0.44	4.50	0.39	4.95	0.37	9.76
2	0.45	0.00	0.44	3.82	0.43	0.00	0.37	0.00	0.37	4.88	0.27	12.86	0.25	74.18
3	0.54	21.65	0.51	28.39	0.43	22.91	0.47	22.91	0.52	22.91	0.47	22.91	0.47	37.80
4	0.46	12.87	0.50	6.02	0.47	9.94	0.46	4.95	0.45	5.96	0.40	7.33	0.28	10.80
5	0.50	0.00	0.50	4.22	0.54	3.57	0.49	2.28	0.44	2.55	0.39	2.79	0.30	25.80
6	0.64	5.33	0.55	6.45	0.51	5.41	0.48	5.00	0.45	6.30	0.38	6.25	0.33	12.06
7	0.52	6.93	0.49	7.53	0.47	7.53	0.49	7.87	0.46	8.66	0.38	26.96	0.28	13.32
8	0.42	7.12	0.47	2.73	0.42	2.87	0.44	3.42	0.41	2.22	0.37	3.78	0.36	8.00
9	0.55	1.95	0.56	6.19	0.50	2.25	0.52	6.93	0.51	10.19	0.37	8.81	0.20	21.53
10	0.51	10.19	0.46	0.00	0.41	2.47	0.42	4.55	0.53	0.00	0.52	0.00	0.32	18.33
11	0.41	5.48	0.45	6.33	0.46	11.36	0.43	6.24	0.42	9.48	0.39	3.46	0.24	40.20
12	0.60	0.00	0.64	0.00	0.67	0.00	0.46	0.00	0.48	0.00	0.44	12.37	0.41	15.75
13	0.53	3.15	0.54	3.15	0.48	3.33	0.50	3.53	0.45	4.03	0.40	0.00	0.30	26.96
14	0.43	9.12	0.45	8.00	0.43	6.28	0.43	6.74	0.41	4.76	0.34	6.54	0.18	41.81
15	0.58	8.96	0.54	9.17	0.51	8.73	0.49	9.18	0.45	8.50	0.38	10.49	0.39	27.12
16	0.57	4.95	0.57	5.09	0.59	5.09	0.52	17.32	0.52	11.95	0.48	43.30	0.28	0.00
ave	0.52		0.51		0.49		0.47		0.46		0.40		0.31	
RSD	13.39		10.49		14.00		8.55		9.91		14.65		24.85	

The RSDs for the averaged sampling rates were examined using the Cochran Test for homogeneity. The Bz RSD for the SKC Ultra sampler, Bz for the GoreSorber sampler, and DDVP for the PE Tenax TA sampler were found to be non-homogenous at the 95% confidence level and were not pooled. This application of a pooled RSD is called sampling rate

Table 41 Sampling Rate Variation	
sampler	SRV (%)
SKC Ultra	9.86
GoreSorber	17.69
PE Tenax TA	12.05

variation (SRV) by OSHA, and it was established as a measure of sampling error for diffusive samplers[12]. SRV is analogous to the often-cited ±5% sampling pump error used to estimate sampling error for active samplers. SRV can be combined with analytical error to estimate total uncertainty in results for field samples by the addition of variances. It has been suggested that SRV is independent of the contained sampling medium, and that it depends entirely on sampler design. SRV for SKC 575 Series Samplers was determined to be 8.71% in previous work[13]. The close agreement of SRVs for the SKC 575 Series and SKC Ultra samplers supports that concept.

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[12] Development of a Protocol for Laboratory Testing of Diffusive Samplers, http://www.osha.gov/dts/sltc/methods/studies/3movm/3movm.html, (accessed February 2002).

[13] Determination of the Sampling Rate Variation for SKC 575 Series Passive Samplers, http://www.osha.gov/dts/sltc/methods/studies/skc575/skc575.html, (accessed February 2002).

The results for the factor test were further analyzed to reveal those factors that have significant effect on sampling rate[14]. Minimum significant effect (MSE) is calculated by multiplying experimental error of the factor test by the appropriate t statistic for nine degrees of freedom. MSE is compared to the factor effect, and if MSE exceeds that effect, then that sampling factor effect is significant and should be evaluated further. A different MSE is determined for each TIC and for each sampler. Results of this analysis are shown in Tables 42-44. A ratio of the absolute value of each factor to MSE was calculated, therefore, any tabulated result greater than 1 is significant and should be further evaluated. Experimental error was somewhat excessive and ranged from 3 to 8% of the average sampling rates. Therefore, this experiment was capable of detecting only those factors that had sampling rate effects greater that 8 to 18% of the average sampling rates. Face velocity had the most significant impact on diffusive sampling rates in previous work[15,16]. Generally, factors other than face velocity were more significant in this work. Interferant (inter) results may be somewhat equivocal because components of the TIC mixture provided the studied interference. A detailed discussion of the Plackett-Burman screening design and of the mathematical treatment of factor test data are presented in the Appendix.

Significant factors for the SKC Ultra sampler were concentration and sampling time for Bz.

Table 42 Analysis of Factor Test Data for SKC Ultra Samplers							
factor	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
concn	1.25	0.09	0.19	0.03	0.37	0.10	0.17
RH	0.17	0.71	0.45	0.33	1.02	0.90	0.63
inter	0.38	0.19	0.01	0.10	0.36	0.03	0.21
samp time	1.54	0.07	0.39	0.04	0.54	0.49	0.50
face vel	0.36	0.87	0.56	0.26	0.62	0.53	0.31
orien	0.64	0.32	0.01	0.02	0.52	0.14	0.03
interaction	none	none	None	none	none	none	none

Significant factors for the GoreSorber sampler were sampling time for all TICs, and concentration for Bz. The E1 interaction was significant for TMB, LIM, and UND. This interaction is completely confounded between concentration, relative humidity, and interferences.

Table 43 Analysis of Factor Test Data for Gore Samplers							
factor	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
concn	1.96	0.35	0.47	0.44	0.61	0.21	0.37
RH	0.04	0.95	0.89	0.81	1.17	1.14	0.36
inter	0.22	0.49	0.26	0.46	0.17	0.50	0.65
samp time	7.18	2.42	2.19	1.59	2.36	1.43	1.29
face vel	0.19	0.21	0.04	0.07	0.01	0.21	0.24
orien	0.08	0.06	0.16	0.76	0.30	0.70	0.01
interaction	none	none	none	E1: 0.99	E1: 1.08	E1: 1.06	None

Significant factors for the PE Tenax TA sampler were relative humidity, sampling time, face velocity, and sampler orientation for Bz; relative humidity for TCA; sampler orientation and concentration for LIM and UND; and face velocity for DDVP. The E7 interaction was significant for Bz, and the E3 for TCA. The E7

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[14] Cassinielli, M.E.; Hull, R.D.; Crabel, J.V.; and Teass, A.W., "Protocol for the Evaluation of Passive Monitors", *Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring,* Berlin, A.; Brown, R.H.; Saunders, K.J,; Eds. Royal Society of Chemistry, Burlington House, London, pp 190-202, 1987.

[15] Development of a Protocol for Laboratory Testing of Diffusive Samplers, http://www.osha.gov/dts/sltc/methods/studies/3movm/3movm.html, (accessed February 2002).

[16] Determination of the Sampling Rate Variation for SKC 575 Series Passive Samplers, http://www.osha.gov/dts/sltc/methods/studies/skc575/skc575.html, (accessed February 2002).

interaction is completely confounded between sampling interferences and sampling time or between relative humidity and face velocity. The E3 interaction is confounded between concentration and relative humidity or between face velocity and orientation. Exposure chamber size limitation necessitated that only perpendicular orientation be used for PE Tenax TA samplers. PE sampler orientation was either upward so that the test atmosphere first encountered the diffusion cap, or the sampler was inverted so that the test atmosphere first encountered the back endcap. Upward orientation was designated perpendicular orientation, and inverted designated parallel orientation. Therefore, the sampler orientation factor results are somewhat equivocal.

Table 44 Analysis of Factor Test Data for PE Tenax TA Samplers							
factor	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
concn	0.55	0.20	0.51	0.18	1.12	1.10	0.55
RH	0.95	0.52	1.12	0.03	0.65	0.31	0.38
inter	0.00	0.11	0.22	0.03	0.35	0.26	0.17
samp time	1.24	0.92	0.58	0.42	0.81	0.02	0.17
face vel	1.29	0.61	0.11	0.08	0.58	0.79	1.98
orien	1.00	0.43	0.15	0.62	1.65	0.98	0.38
interaction	E7: 1.09	none	E3: 0.98	none	none	none	none

Packaging Integrity

The results of the packaging integrity test, together with analysis of blank samplers, are shown in Table 45. Only those TIC components that gave satisfactory MSD spectra were reported as present. Most sample results were similar to blank results, and the contamination that occurred was not severe.

Table 45 Results of Packaging Integrity Test (ng per sample)							
sampler	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
SKC Ultra 1	72	19	nd	110	163	34	nd
SKC Ultra 2	63	11	nd	55	79	nd	nd
GoreSorber 1	12	6	3	6	nd	nd	nd
GoreSorber 2	12	8	3	6	nd	nd	nd
PE Tenax TA 1	6	nd	nd	nd	2	2	5
PE Tenax TA 2	3	nd	nd	nd	2	nd	nd
blanks							
SKC Ultra	39	11	nd	34	38	22	nd
GoreSorber	12	7	nd	nd	nd	nd	nd
PE Tenax TA	8	4	nd	nd	nd	3	nd

nd = none detected

Precision and Accuracy

The NIOSH methods acceptability criterion for accuracy is that the candidate method must provide results within ±25% (pooled RSD #10.5%) of the reference value at the 95% confidence level over the range 0.5 to 2 times the target level of the method. Low-level data are pooled separately to assess method performance at these levels. There is no criterion for low-level data.

Data in Tables 46, 48, and 50 are from high-level experiments. The levels for each TIC were: 4 mg/m^3 for the sampling rate (SR) tests; 4 mg/m^3 for the reverse diffusion test; 7 mg/m^3 for Factor Tests 2, 4, 13, and 15; 4 mg/m^3 for storage test day 0; and 2 mg/m^3 for Factor Tests 1, 3, 14, and 16.

SKC Ultra data for Bz reverse diffusion, and Factor Tests 13 and 15; EtBz Factor Test 13; TMB Factor Test 13; LIM Factor Tests 2 and 13; and DDVP Factor Test 13 were non-homogenous by the Cochran Test at the 95% confidence level and were not pooled.

Table 46 RSDs for High-Level Data for SKC Ultra Samplers							
data source	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
6 hour SR	0.32	0.63	1.03	1.29	1.59	1.31	2.36
8 hour SR	2.51	3.00	2.45	3.14	3.12	2.04	2.85
reverse diffusion	8.23	2.71	2.00	2.11	2.23	1.97	2.91
Factor Test 2	1.82	0.89	1.17	0.46	9.68	9.38	3.79
Factor Test 4	2.14	0.77	1.86	1.29	1.96	1.62	2.52
Factor Test 13	14.40	11.93	5.14	6.43	8.50	8.57	11.08
Factor Test 15	10.36	7.72	1.82	1.56	2.13	4.75	4.95
storage day 0	2.39	3.88	3.32	3.68	3.56	3.82	3.77
Factor Test 1	2.82	2.02	2.09	2.00	2.03	1.98	1.49
Factor Test 3	4.49	3.79	2.77	1.40	2.60	3.49	2.87
Factor Test 14	3.49	3.80	2.97	4.03	1.88	4.37	2.90
Factor Test 16	4.50	4.65	1.56	2.41	3.30	2.53	2.81
pooled RSD	2.99	3.66	2.58	2.37	2.52	4.59	3.14

Data in Tables 47, 49, and 51 are from low level, long-term sampling capacity tests that were conducted at 0.4 mg/m^3 for each TIC.

SKC Ultra data for LIM 7.23 and 15.55 hours; and for UND 15.55 hours were non-homogenous by the Cochran Test at the 95% confidence level and were not pooled.

Table 47 RSDs for Low Level Data for SKC Ultra Samplers							
data source	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
7.23 hours	3.76	16.07	2.60	3.02	26.93	1.52	2.75
15.55 hours	7.89	17.91	3.63	6.52	6.56	5.61	4.48
23.57 hours	5.32	3.19	6.14	2.12	1.52	1.63	1.34
30.23 hours	5.09	5.38	2.12	1.65	1.56	0.55	1.79
pooled RSD	5.71	12.43	3.94	3.84	1.54	1.33	2.86

GoreSorber data for reverse diffusion for Bz and for 6-hour sampling rate for DDVP were non-homogenous by the Cochran Test at the 95% confidence level and were not pooled.

Table 48 RSDs for High-Level Data for GoreSorber Samplers							
data source	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
6 hour SR	13.17	12.84	14.21	15.23	15.01	12.84	17.78
8 hour SR	3.19	8.24	4.52	4.63	3.66	2.75	1.80
reverse diffusion	29.40	11.90	11.26	12.67	11.03	9.60	12.00
Factor Test 2	4.82	4.61	4.00	4.19	4.50	3.84	6.98
Factor Test 4	3.09	3.13	5.17	3.76	0.57	5.01	5.01
Factor Test 13	8.34	2.00	1.08	2.33	3.12	3.27	5.91
Factor Test 15	13.78	5.07	6.70	5.59	6.32	5.76	6.34
storage day 0	17.81	2.18	1.29	1.31	1.74	0.74	1.64
Factor Test 1	11.51	7.86	7.69	8.44	9.04	8.28	10.16
Factor Test 3	7.73	4.52	5.74	5.25	5.00	4.26	4.80
Factor Test 14	10.76	1.23	0.31	1.38	1.15	1.19	0.89
Factor Test 16	8.99	9.40	7.82	8.84	7.34	2.10	6.70
pooled RSD	10.36	7.14	7.03	7.43	7.04	6.06	6.54

GoreSorber data for EtBz for 23.57 hours test were non-homogenous by the Cochran Test at the 95% confidence level and were not pooled.

data source	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
Table 49 RSDs for Low-Level Data for GoreSorber Samplers							
7.23 hours	7.35	3.21	3.73	3.44	3.70	3.46	1.96
15.55 hours	43.98	1.97	3.56	3.31	2.88	3.68	5.57
23.57 hours	27.47	9.48	6.16	7.30	8.88	5.92	5.37
30.23 hours	24.02	2.65	6.53	7.96	7.74	9.78	12.06
pooled RSD	28.81	2.66	5.18	5.90	6.34	6.25	7.23

PE Tenax TA data for Factor Test 3 for Bz, EtBz, TCA, LIM, and UND; Factor Test 16 for UND; and Factor Test 2 for DDVP were non-homogenous by the Cochran Test at the 95% confidence level and were not pooled.

data source	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
Table 50 RSDs for High-Level Data for PE Tenax TA Samplers							
6 hour SR	13.28	12.86	10.80	14.64	10.50	12.07	18.50
8 hour SR	3.01	2.26	1.85	2.17	2.00	5.26	18.49
Rev diffusion	3.16	3.91	4.06	4.40	3.26	4.23	15.29
Factor Test 2	0.00	3.82	0.00	0.00	4.88	12.86	74.18
Factor Test 4	12.87	6.02	9.94	4.95	5.96	7.33	10.80
Factor Test 13	3.15	3.15	3.33	3.53	4.03	0.00	26.96
Factor Test 15	8.96	9.17	8.73	9.18	8.50	10.49	27.12
storage day 0	0.86	2.57	3.95	9.74	10.42	3.37	8.11
Factor Test 1	3.07	3.03	3.77	4.03	4.50	4.95	9.76
Factor Test 3	21.65	28.39	22.91	22.91	22.91	22.91	37.80
Factor Test 14	9.12	8.00	6.28	6.74	4.76	6.54	41.81
Factor Test 16	4.95	5.09	5.09	17.32	11.95	43.30	0.00
pooled RSD	7.19	6.30	6.16	10.57	7.18	7.74	23.03

Low-level PE Tenax TA data were homogenous by the Cochran Test and all were pooled.

data source	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
Table 51 RSDs for Low Level Data for PE Tenax TA Samplers							
7.23 hours	0.00	5.41	0.00	0.00	0.00	0.00	0.00
15.55 hours	2.79	5.33	5.97	3.15	5.88	0.00	16.88
23.57 hours	4.42	3.23	3.89	4.17	10.34	4.17	14.43
30.23 hours	6.44	3.88	5.53	7.56	3.33	6.67	21.17
pooled RSD	4.15	4.56	4.51	4.60	6.18	3.93	15.34

OSHA methods acceptability criteria requires that the candidate method provide sampling results that are at least 75% (±25%) of the target level at the 95% confidence level, and also have less than 10% bias. This data is derived from the storage stability tests. SKC Ultra samplers, with the exception of DDVP, generally met OSHA methods requirements. SKC Ultra samples for Bz must be stored at refrigerated temperature, or analyzed within five days of sampling. GoreSorber and PE Tenax TA samplers did not meet OSHA methods requirements.

Precision in terms of SEE or RSD was calculated from the ambient temperature storage stability tests, the factor tests, and the Precision and Accuracy high-level tests, and is presented in Table 52. The data may not be directly comparable because it was obtained in considerably different tests. Factor test data have higher imprecision because this test is performed by significantly altering exposure conditions during the 16-run experiment, and it is intended to spotlight sampler inadequacies. The data in Table 52 may be useful, though, to compare the magnitude of precision values obtained by different means. It shows that Bz is not a good application for SKC Ultra and GoreSorber samplers, nor is DDVP a good application for PE Tenax TA samplers.

Table 52								
Precision Summary for SKC Ultra, GoreSorber, and PE Tenax TA Samplers								
sampler	source	Bz	EtBz	TCA	TMB	LIM	UND	DDVP
SKC Ultra	ambient storage SEE$_R$	9.31	6.42	8.31	6.97	5.41	6.64	11.16
	Factor Test	20.86	9.04	6.55	9.78	10.33	9.13	13.13
	Precision	2.99	3.66	2.58	2.37	2.52	4.59	3.14
GoreSorber	ambient storage SEE$_R$	NA	4.83	6.38	5.88	6.66	7.13	9.97
	Factor Test	73.95	22.83	15.79	17.61	19.56	14.77	14.02
	Precision	10.36	7.14	7.03	7.43	7.04	6.06	6.54
PE Tenax TA	ambient storage SEE$_R$	6.30	7.18	10.61	12.26	12.23	8.69	18.34
	Factor Test	13.39	10.49	14.00	8.55	9.91	14.65	24.85
	Precision	7.19	6.30	6.16	10.57	7.18	7.74	23.03

SUMMARY

Preparation of SKC Ultra samplers for analysis was fast and easy. Suitable care must be exercised when transferring the sorbent within the SKC Ultra sampler to the thermal-desorption tube. Most TICs are probably retained near the sampler inlet and that part is transferred last. The aluminum funnel built into the SKC Ultra sampler made transfer of the sorbent easy. Tenax TA sampling medium did not clump on transfer, even after sampling humid atmospheres for extended times. Preparation of GoreSorber samplers was especially easy. The option of analyzing each of the two GoreSorber cartridges separately is very attractive. No preparation of PE Tenax TA samplers is required for analysis.

The body of the SKC Ultra sampler is probably recyclable. The inlet of the sampler is not disturbed when removing the sampling medium for analysis, therefore, sampling performance should not be altered. It seems likely that the SKC Ultra sampler could be refilled with fresh Tenax TA and successfully reused. PE samplers are reusable for as-many-as 100 times[17] after thermal reconditioning.

Preparation of analytical standards was quick and easy. Calibration of the MSD was straightforward and the resultant calibration curves were linear unless the MSD was saturated. Detector saturation will obviously interfere with quantitation. The internal standard option of the ATD should be used cautiously because uptake of the internal standard can be somewhat different for field samples compared to standards prepared using reconditioned sampling medium. It might be possible to avoid uptake differences if analytical standards were prepared with unused samplers of the same type used for field samples. An internal standard should be employed if a significant amount of time will elapse between initial analysis and subsequent quantitation because identical internal standards analyzed separately can link MSD response for both analyses.

MSD detection limits were generally sufficiently low to permit detection about one-ppb of each TIC in a four-hour SKC Ultra air sample. Detection limits for some TICs could be dependent on the presence of interfering sampler artifacts and other co-eluting species. Sampler artifacts should be reduced to the lowest feasible level.

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[17]   Perkin Elmer, Inc. *TurboMatrix Thermal Desorbers*, Instrument Manual Part Number M041-3331, Norwalk, CT, 2000, pp 206-7.

Thermal desorption efficiencies were all high, except for Bz from the GoreSorber sampler. The 75% recovery was probably caused by loss of Bz through the hole punctured in the cartridge wall when liquid spiking the GoreSorber cartridge. Tenax TA does not have a high affinity for Bz[18].

Sampling rate and long-term sampling capacity experiments showed that sampler capacity depended on sampling rate, mass of sampling medium, affinity of the sampling medium for the TIC, and concentration of that TIC in the test atmospheres. SKC Ultra samplers had limited capacity for Bz and slightly more capacity for EtBz and LIM. Capacity for the other TICs was adequate. GoreSorber samplers had almost no sampling capacity for Bz, and limited capacity for the other TICs. The SKC Ultra sampler has the higher sampling capacity of the two project samplers. Long-term sampling for Bz using either SKC Ultra or GoreSorber samplers is not recommended. Selection of maximum sampling times is a compromise between economy and the required quality of the sample results. Sampling performance was adequate for the non-project PE Tenax TA sampler with the possible exception of Bz.

The SKC Ultra RSR sampler has fewer holes in the inlet than the SKC Ultra sampler and this results in lower sampling rates compared to the SKC Ultra sampler. Lower sampling rates should permit longer sampling times for some TICs.

Limited work performed with PE samplers containing either Chromosorb 106 or Carbopack B gave promising preliminary results. Chromosorb 106 does have a large number of sampler artifacts that could make interpretation of field sample results time consuming. DDVP did not desorb from Carbopack B at its recommended maximum desorption temperature. SKC 575-002 and 3M 3520 OVM control samplers both performed satisfactorily. An SKC 575-002 sampler artifact prevented determination of DDVP. These two control samplers could be useful, but they are not amenable to thermal desorption.

Storage tests showed good stability for all TICs on the three tested samplers, except for Bz stored at 40EC on SKC Ultra samplers. The observed loss of Bz was probably due to physical loss, and not to chemical instability. Bz was not retained by the GoreSorber sampler and, therefore, was not tested. The stability data were not as precise as that obtained in other OSHA SLTC work performed with different diffusive samplers containing carbon-based sampling media. The overall SEE_R for those tests was about 3%, compared to the 9% obtained in this work.

Factor tests were performed to determine sampling rate variation (SRV). SRV has been established as an estimate of sampling error for diffusive samplers that can be combined with analytical error to calculate overall sampling and analytical error by the addition of variances. The SRV obtained for SKC Ultra samplers was comparable to that obtained in other work for a sampler that is similar in design.

Manufacturer's packaging was sufficient to prevent severe contamination of samplers when sealed SKC Ultra, GoreSorber, and PE Tenax TA samplers were exposed to test atmospheres for an extended time. Some contamination did occur. The glass container used by the manufacturer for GoreSorber samplers is not appropriate for rugged field use.

Data from the analysis of SKC Ultra samplers met the NIOSH methods acceptability criterion for precision and accuracy. GoreSorber samplers, with the exception of Bz, also met the standard. PE Tenax TA samplers, with the exceptions of TMB and DDVP, also met the NIOSH criterion.

The precision of ambient temperature storage stability data showed that SKC Ultra samplers, with the exception of DDVP, generally met OSHA methods requirements. SKC Ultra samples for Bz must be stored at refrigerated temperature, or analyzed within five days of sampling. GoreSorber and PE Tenax TA samplers did not meet OSHA methods requirements.

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18   Perkin Elmer Thermal Desorption Data Sheet No. 10, "A Guide to Adsorbent Selection".

PROJECT CONCLUSIONS

The prescribed thermal desorption/MSD analytical method provided acceptable sample results for both project samplers. The addition of an internal standard is potentially extremely useful, but must be done cautiously, and then results must be carefully interpreted.

Use of the project samplers has been shown to be an effective means to monitor personal exposure to the tested TICs with the exception of benzene. The SKC Ultra sampler generally provided more reliable sampling results than did the GoreSorber sampler. Both of these samplers contain Tenax TA sorbent. This sorbent may be the best overall sampling medium for many chemicals, but its capacity is limited for relatively volatile species that may constitute significant personal exposures. Length of permissible sampling time was shown to be a compromise between economy and required accuracy of sample results. The SKC Ultra sampler is probably reusable three or four times when refilled with fresh adsorbent.

SUPPLEMENTARY DISCUSSION

A limitation of relatively long-term diffusive sampling is that exposures will be determined as time-averaged results. Short and possibly very high-level exposures to extremely toxic materials would be averaged over the entire sampling period and could be dismissed as inconsequential.

The large number of personnel to be monitored will likely require each individual to be involved in sample collection. This process has been termed self-assessment. There is precedent for the use of diffusive sampling in self-assessment of chemical exposures. A Swedish study[19] reported good agreement between self-assessment sample results and results from expert monitoring in several surveys. Several issues were raised in this report. Among them were the necessary degree of worker training and motivation, the validity of sample results, and the acceptance of sample results by regulatory authorities. Self-assessment fraud was not found to be a serious problem. Simple, robust diffusive samplers and strong organizational support were seen as prerequisites for such a monitoring program to succeed.

An expert MSD operator given sufficient time can correctly identify most exposures. SLTC experience has shown that it is often the minuscule chromatographic peak that is of the most toxicological interest. For example, exposure to a few picograms of chemical agent is of much more concern than exposure to a few nanograms of an innocuous chemical.

The vast number of possible chemical exposures causes difficult technical problems. This number will cause most sampling rates to remain unknown. A single surrogate-sampling rate could be established for each project sampler, and then used to calculate air concentrations for all detected TICs. The surrogate sampling rate could be partially based on literature data, and have a large uncertainty factor attached to it.

Calibration of the MSD to provide accurate sample quantitation will be difficult and time consuming, and it can only be done after the offending chemical has been identified. Perhaps quantitation results could be expressed in terms of internal standard equivalents. Third parties using project equipment could establish TIC/internal standard response ratios for the MSD response for all possible TICs. Each TIC/internal standard ratio would be numerically different and would be confirmed from time-to-time. In this way, internal standard equivalents can be related to TIC concentration without the need to calibrate the MSD used to analyze samples. Results obtained using a surrogate sampling rate and response ratios would be approximate. Advantages to this approach are much-improved sample turn-around-time and significantly reduced analytical costs.

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[19] Levin, J.O., Liljelind, I., Stromback, A. Sunesson, A.L., Sundgren, M., Lindahl, R. Diffusive Sampling as a Tool for Self-Assessment of Chemical Exposure. Presented at International Conference Measuring Air Pollutants by Diffusive Sampling, Montpellier, France, 2001.

Non-project PE samplers have good potential for extended-time sampling, but they appear to have precision limitations. The imprecision may be somehow related to use of membranes in the diffusive sampling caps. Most literature data addresses sampling caps used without membranes. Membranes, or windscreens, in other diffusive samplers are designed to reduce effects of wind speed on sampling rate. The windscreen also acts as a diffusion barrier and will reduce sampling rates.

The GoreSorber sampler might have more application for TICs if one of the two cartridges containing Tenax TA could be replaced with another cartridge containing a sampling medium more suitable for TICs. Undoubtedly, there would be sampling competition between the two cartridges and the modified sampler would require testing. The cartridges could retain their present diameter, but be lengthened so that they could contain more sampling medium. The two cartridges would be analyzed separately, one for CWAs and the other for TICs.

APPENDIX

Analysis of Factor Effects

NIOSH has identified six factors (analyte concentration, exposure time, face velocity, relative humidity, interferant, and monitor orientation) that can affect diffusive sampling performance. Sixty-four experimental runs (2^6) would be required to evaluate combinations of each factor at two levels per factor. NIOSH has recognized that this is an excessive number of experimental runs, and has devised a 16-run fraction of the full factorial experiment that is capable of revealing any of these factors having a significant effect on performance, free of two-factor interactions[20]. Some two and three-factor interactions, in which the combined effect of certain factors are compared to their separate effects, can also be tested by this experimental design. This fraction of the full factorial is based on the Plackett-Burman screening design. A Plackett-Burman screening design is a specific fraction of the full factorial that has properties that allow efficient estimation of the effects of the variables under study[21]. Table 53 is a representation of the experimental design, and this format is suitable for use in an electronic spreadsheet. The effects of the factors are examined at two levels. The two levels are a high level (designated by a "1"), and a low level (designated by a "-1"). Columns X1 through X6 represent the factors, for example, X1 is analyte concentration. The E columns provide an estimate of experimental error, a means to calculate minimum significant effect (MSE), and estimates of two and three-factor interactions. Columns E1 and E2 depict the three-factor interactions, and columns E3 through E9 represent two-factor interactions. Rows 1 through 16 are the experimental runs. Experiments are performed under the conditions specified in the appropriate row. For example, experiment 1 is conducted at low analyte concentration, low relative humidity, low interference level, high exposure time, high face velocity, and perpendicular monitor orientation. Three monitors are exposed under the required conditions for each experimental run. Average analytical results are calculated in terms of sampling rate, and are placed in the R column (or in a separate array with the same format). Each experimental result (R) is multiplied by the number (either 1 or -1) in each cell, and that cell content is replaced by the result. For example, if the result for run 1 was 13.94 mL/min, X1 (run 1) would become -13.94, X2 (run 1) become -13.94, X3 (run 1) become -13.94, X4 (run 1) become 13.94...E9 (run 1) become -13.94. Alternatively, the results could be entered in another table. The sum of the positive numbers in a column (for example, the X1 Column) is entered in the "Sum+" row under each column. The sum of the negative numbers in a column (for example, the X1 Column) is entered in the "Sum-" row under each column. Add the absolute values of the "Sum+" and "Sum-" numbers for each column and place that result in the "Total" row. The "Total" result should be the same for all columns. Add the "Sum+" number and the "Sum-" number and place that result in the "Diff" row. Divide the "Diff" number by 8 (the number of positive numbers in each column, and put that result in the "Effect" row. The "Effect" number is the factor effect for the X columns, and an estimate of experimental error for the E columns. The experimental error is calculated by the following equation:

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[20] Cassinielli, M.E.; Hull, R.D.; Crabel, J.V.; and Teass, A.W., "Protocol for the Evaluation of Passive Monitors", *Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring,* Berlin, A.; Brown, R.H., Saunders, K.J,; Eds. Royal Society of Chemistry, Burlington House, London, pp 190-202, 1987.

[21] E.I. du Pont de Nemours & Co. (Inc.). *Strategy of Experimentation,* Revised ed.; Wilmington, DE October 1975.

$(1/9\times(E1^2+E2^2+E3^2+...+E9^2))^{0.5}$. The minimum significant effect (MSE) is calculated by multiplying the experimental error by the *t* statistic at the 95% confidence level for the number of E columns (degrees of freedom). In this case the *t* statistic is 2.26 because there are nine degrees of freedom. Factors with "Effect" numbers (absolute value) exceeding "MSE" have significant effect on the sampling performance of the monitors and should be further studied. E columns with "Effect" numbers (absolute value) exceeding "MSE" are an estimate of factor interactions. The ratio "absolute value of Effect/MSE" is calculated and any result greater than 1 is significant. The factor interactions are shown in Table 54. A worked example for TMB and SKC Ultra samplers is shown in Table 55.

Table 53 Factor Effects Experimental Design															
	X1	X2	X3	X4	X5	X6	E1	E2	E3	E4	E5	E6	E7	E8	E9	R
run	concn	RH	inter	time	face vel	orien										
1	-1	-1	-1	1	1	1	-1	1	1	1	-1	-1	-1	1	-1	
2	1	-1	-1	-1	-1	1	1	1	-1	-1	-1	-1	1	1	1	
3	-1	1	-1	-1	1	-1	1	1	-1	1	1	-1	1	-1	-1	
4	1	1	-1	1	-1	-1	-1	1	1	-1	1	-1	-1	-1	1	
5	-1	-1	1	1	-1	-1	1	1	1	-1	-1	1	1	-1	-1	
6	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	-1	1	
7	-1	1	1	-1	-1	1	-1	1	-1	-1	1	1	-1	1	-1	
8	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
9	1	1	1	-1	-1	-1	1	-1	1	1	-1	-1	-1	1	-1	
10	-1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	1	1	1	
11	1	-1	1	1	-1	1	-1	-1	-1	1	1	-1	1	-1	-1	
12	-1	-1	1	-1	1	1	1	-1	1	-1	1	-1	-1	-1	1	
13	1	1	-1	-1	1	1	-1	-1	1	-1	-1	1	1	-1	-1	
14	-1	1	-1	1	-1	1	1	-1	-1	1	-1	1	-1	-1	1	
15	1	-1	-1	1	1	-1	1	-1	-1	-1	1	1	-1	1	-1	
16	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	
Sum+																
Sum-																
Total																
Diff																
Effect																
Error																
MSE																
|Effect/ MSE|																

Table 54 Factor Interactions			
E column	factor interaction	E column	factor interaction
E1	X1X2X3	E6	X1X5 or X2X6
E2	X1X2X4	E7	X3X4 or X2X5
E3	X1X2 or X5X6	E8	X2X3 or X4X5
E4	X1X3 or X4X6	E9	X2X4 or X3X5
E5	X1X4 or X3X6		

Factor interactions are completely confounded. For example, the E3 interaction is confounded between concentration and relative humidity or between face velocity and sampler orientation. These interactions cannot be resolved without additional experimental work.

	X1	X2	X3	X4	X5	X6	E1	E2	E3	E4	E5	E6	E7	E8	E9	R
run	concn	RH	inter	time	face vel	orien										
1	-13.94	-13.94	-13.94	13.94	13.94	13.94	-13.94	13.94	13.94	13.94	-13.94	-13.94	-13.94	13.94	-13.94	13.94
2	15.17	-15.17	-15.17	-15.17	-15.17	15.17	15.17	15.17	-15.17	-15.17	-15.17	-15.17	15.17	15.17	15.17	15.17
3	-15.23	15.23	-15.23	-15.23	15.23	-15.23	15.23	15.23	-15.23	15.23	15.23	-15.23	15.23	-15.23	-15.23	15.23
4	11.89	11.89	-11.89	11.89	-11.89	-11.89	-11.89	11.89	11.89	-11.89	11.89	-11.89	-11.89	-11.89	11.89	11.89
5	-11.43	-11.43	11.43	11.43	-11.43	-11.43	11.43	11.43	11.43	-11.43	-11.43	11.43	11.43	-11.43	-11.43	11.43
6	13.28	-13.28	13.28	-13.28	13.28	-13.28	-13.28	13.28	-13.28	13.28	-13.28	13.28	-13.28	-13.28	13.28	13.28
7	-12.84	12.84	12.84	-12.84	-12.84	12.84	-12.84	12.84	-12.84	-12.84	12.84	12.84	-12.84	12.84	-12.84	12.84
8	15.18	15.18	15.18	15.18	15.18	15.18	15.18	15.18	15.18	15.18	15.18	15.18	15.18	15.18	15.18	15.18
9	14.10	14.10	14.10	-14.10	-14.10	-14.10	14.10	-14.10	14.10	14.10	-14.10	-14.10	-14.10	14.10	-14.10	14.10
10	-14.93	14.93	14.93	14.93	14.93	-14.93	-14.93	-14.93	-14.93	-14.93	-14.93	-14.93	14.93	14.93	14.93	14.93
11	12.87	-12.87	12.87	12.87	-12.87	12.87	-12.87	-12.87	-12.87	12.87	12.87	-12.87	12.87	-12.87	-12.87	12.87
12	-11.63	-11.63	11.63	-11.63	11.63	11.63	11.63	-11.63	11.63	-11.63	11.63	-11.63	-11.63	-11.63	11.63	11.63
13	11.73	11.73	-11.73	-11.73	11.73	11.73	-11.73	-11.73	11.73	-11.73	-11.73	11.73	11.73	-11.73	-11.73	11.73
14	-13.49	13.49	-13.49	13.49	-13.49	13.49	13.49	-13.49	-13.49	13.49	-13.49	13.49	-13.49	-13.49	13.49	13.49
15	12.98	-12.98	-12.98	12.98	12.98	-12.98	12.98	-12.98	-12.98	-12.98	12.98	12.98	-12.98	12.98	-12.98	12.98
16	-13.29	-13.29	-13.29	-13.29	-13.29	-13.29	-13.29	-13.29	13.29	13.29	13.29	13.29	13.29	13.29	13.29	13.29
Sum +	107.20	109.39	106.26	106.71	108.90	106.85	109.21	108.96	103.19	111.38	105.91	104.22	109.83	112.43	108.86	
Sum -	-106.78	-104.59	-107.72	-107.27	-105.08	-107.13	-104.77	-105.02	-110.79	-102.60	-108.07	-109.76	-104.15	-101.55	-105.12	
Total	213.98	213.98	213.98	213.98	213.98	213.98	213.98	213.98	213.98	213.98	213.98	213.98	213.98	213.98	213.98	
Diff	0.42	4.80	-1.46	-0.56	3.82	-0.28	4.44	3.94	-7.60	8.78	-2.16	-5.54	5.68	10.88	3.74	
Effect	0.053	0.600	-0.183	-0.070	0.478	-0.035	0.555	0.493	-0.950	1.098	-0.270	-0.693	0.710	1.360	0.468	
Error	0.802															
MSE	1.812															
|Effect/ MSE|	0.029	0.331	0.101	0.039	0.264	0.019	0.306	0.272	0.524	0.606	0.149	0.382	0.392	0.751	0.260	

Table 55
Analysis of Factor Test Data for TMB for SKC Ultra Sampler