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Investigation of Charcoal Cloth as a Sorbent for Integrated Sampling of Solvent Vapors in Mixed-Expired Breath Using a New Stainless Steel Sampler*

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A stainless steel device for integrated sampling of solvents present in mixed-expired breath is described. During sampling, the subject inhales breathing air through commercial charcoal inhalation canisters. Exhaled breath is sampled from the mainstream using 45-mm wafers of charcoal cloth or from the sidestream on other sorbents. The device concentrates trace contaminants present in large volumes of breath. The charcoal cloth sorbent was evaluated for sampling and analysis of *m*-xylene and 1,1,1-trichloroethane under simulated physiological conditions. These samples were collected from atmospheres of either analyte generated at 35°-40° C and 80%-90% relative humidity to simulate an exhaled breath sample matrix. Concentrations sampled ranged from 2.2 to 190 mg/m^3 for 1,1,1-trichloroethane and from 0.44 to 35.6 mg/m^3 for *m*-xylene. Volumes sampled ranged from 10 to 50 L. The *m*-xylene samples were collected using a 3-wafer front and a 2-wafer backup bed of charcoal cloth; 1,1,1-trichloroethane samples were collected using a 10-wafer front and a 1-wafer backup bed. All samples were desorbed in carbon disulfide and analyzed via gas chromatography using a flame ionization detector. The volume of desorption solvent ranged from 1.7 to 2.5 mL per wafer of cloth. The quantitation limit is estimated to be 2.0 μg/L for 1,1,1-trichloroethane and 0.4 μg/L *m*-xylene for a 50-L sample. At least 80% recovery was obtained for *m*-xylene or 1,1,1-trichloroethane samples stored from 1 to 14 days after collection, if the samples were refrigerated at 0° C after an initial 7-day storage period at room temperature. The recovery of hexane, 1-hexene, ethyl acetate, isopropanol, methylene chloride, and methyl isobutyl ketone from the charcoal cloth also has been investigated and is reported. With the exception of isopropanol, all analytes were recovered quantitatively from the charcoal cloth by desorption with carbon disulfide following storage for 1 to 17 days at ambient temperatures.

Introduction

Human exposure to an organic solvent results in an uptake that is related not only to the time-weighted average exposure concentration and the duration of the exposure but also to such factors as "metabolic rate, cardiac output, blood perfusion of tissues, mass of fatty storage tissue, and the individual solvent blood-gas partition coefficients."[1] Percutaneous absorption also may occur through direct contact of the solvent with the skin.[1]

Environmental monitoring does not address the problem of total solvent uptake by an individual worker since neither dermal absorption nor worker-to-worker ergonomic differences are taken into account.

Biomonitoring of workers exposed to industrial solvents via collection of breath samples has gained a measure of acceptance. In the Federal Republic of Germany, exposure standards based upon analysis of exhaled breath have been proposed for tetrachloroethylene, carbon tetrachloride, and 1,1,1-trichloroethane.[2] Biological exposure indices have been recommended for carbon monoxide, ethyl benzene, styrene, toluene, trichloroethylene, benzene, and n-hexane in exhaled breath by the American Conference of Governmental Industrial Hygienists (ACGIH).[3] The sampling bag and the glass sample tube are the two major devices used for collection of exhaled breath samples. These devices may be used where the concentration of the analyte in the breath is relatively high, but do not permit samples to be directly concentrated. In addition, they may not permit the sample to be stored for extended periods.

In this paper, a solid sorbent sampler for direct sampling of large volumes of mixed-expired breath is described. Samples are collected on wafers of charcoal cloth sorbent—a carbonized viscose rayon fabric—that readily retains its mechanical integrity after being cut into wafers. The reported surface area of the charcoal cloth sorbent is 1300 m^2/g[4] and is comparable to that of coconut-shell charcoal.[5]

The charcoal cloth was evaluated as a sorbent for sampling solvents present in expired breath. The recoveries of eight representative compounds from the charcoal cloth were investigated. These compounds were hexane, 1-hexene, ethyl acetate, isopropanol, methylene chloride, methyl isobutyl ketone, *m*-xylene, and 1,1,1-trichloroethane; they include a variety of chemical functional groups to evaluate the charcoal cloth as a collection medium. *m*-Xylene and 1,1,1-trichloroethane were selected for further study based upon their potential for uptake into the bloodstream and storage in fat. *m*-Xylene is representative of those compounds that are very soluble in blood and fatty tissue, while 1,1,1-trichloroethane represents those solvents that are much less soluble in blood and fatty tissue.[1] The capacities of the charcoal cloth for both analytes were determined. The precision and accuracy of sampling and analysis for *m*-xylene and 1,1,1-trichloroethane under simulated physiological conditions were investigated separately.

*Disclaimer: Mention of products or manufacturers in this document does not constitute endorsement by the United States Government.

Description of the Sampler

The prototype sampler and sample canister, fabricated from stainless steel, are depicted in Figure 1. The device functions in the same manner as a respirator mask. Subjects, wearing a noseclamp, bite the mouthpiece and inhale air drawn through the two charcoal filter canisters. As the subject exhales, solvents are collected from the breath on 45-mm wafers of the charcoal fabric sorbent contained in the sample canister. The volume of exhaled breath is measured with a Wright respirometer (Ferraris Medical, Inc., Holland, N.Y.). One-way valves control directional flow. The compression fittings welded to the center of the main body allow sample collection from the sidestream. Sampling from either the mainstream with charcoal cloth or from the sidestream with other sorbents should permit concentration of trace levels of solvents present in large volumes of mixed-expired air, *e.g.*, 50 L. Recently, a face mask-based, mixed-expired breath sampler employing the charcoal cloth also was described. Solvents are sampled on two 72.5-mm diameter charcoal wafers; exhaled water vapor is collected on a bed of molecular sieves to provide an estimate of exhaled volume.[6] That sampler is apparently intended for sampling large volumes of mixed-expired breath, *e.g.*, 150 L. The stainless steel sampler described here provides an alternative for those situations where the collection of lower volume samples is feasible, thus not requiring the user to don a face mask.

Experimental Materials and Methods

The 1,1,1-trichloroethane (99.5%) was obtained from Fisher Scientific Co., Pittsburgh, Pa.; *m*-xylene (99%) was obtained from Aldrich Chemical Co., Milwaukee, Wis. Distilled-in-glass grade ethyl acetate, n-hexane, methylene chloride, and 2-butanol all were obtained from American Burdick and Jackson Co., Muskegon, Mich. Methyl isobutyl ketone (analytical grade) was obtained from J.T. Baker Chemical Co., Phillipsburg, N.J., and 1-hexene (96.1%) was obtained from Chem Service Co., West Chester, Pa. Isopropanol (99.8%) and distilled-in-glass grade carbon disulfide were obtained from MCB Chemicals, Norwood, Ohio.

The charcoal cloth used in these studies was supplied by Charcoal Cloth Ltd., Berkshire, England, or MDA Scientific Co., Park Ridge, Ill. The cloth was cut into 45-mm diameter wafers using a steel platen and a 45-mm diameter steel die. The charcoal cloth wafers were activated in the apparatus shown in Figure 2. Approximately 100 wafers were loaded into the purge chamber (C) on top of the distribution ring (B). The purging apparatus was placed inside a gas chromatograph oven and connected via the 6.4-mm O.D. tube (A) to the injector port outlet with compression fittings. Contaminants were removed by purging the cloth with nitrogen for 3-4 hr at 250° C, then for 15 min at 30° C. Sample wafers were desorbed in carbon disulfide and analyzed to assure complete removal of contaminants. After activation and prior to use, the wafers were stored in a clean, sealed, glass container.

Analytical Method

All analyses were conducted using a Hewlett-Packard Model 5730A gas chromatograph operated in the flame ionization detection mode. The instrument was calibrated by injection of standard solutions containing the analytes in carbon disulfide; the nominal injection volume was 5 μL. The detector was maintained at 250° C. For the analyses of the 1,1,1-trichloroethane samples, the temperature of the injector port was 150° C. For the remainder of the analytes, the injector port was maintained at 200° C. The carrier gas (N_2) flow was 25 mL/min. All sample concentrations were determined via analysis of peak areas using a Hewlett-Packard Model 3357 laboratory data system interfaced to the gas chromatograph via an analog-to-digital signal converter. Several columns and analytical conditions were used during this study. These columns were all made from 3-mm O.D.

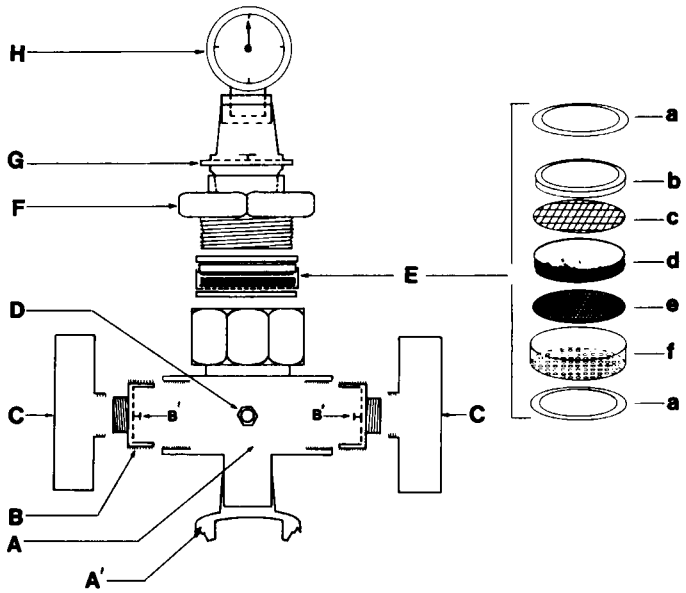

Figure 1—Prototype continuous mixed-expired breath sampler A. Main cross body of sampler, with bitewing mouthpiece (A') attached. B. Threaded end-fitting adaptors for attachment of inhalation canisters to the main sampler cross body. Inlet check valves (part 1001-1, Survivair, Santa Ana, Calif.) are held in place by the retainers (B'). C. Inhalation canisters (part 1001-00, Survivair Corp.) D. 6.4-mm (0.25-in.) compression fitting for collection of sidestream samples. On the opposite side of the sampler (not shown) are two additional 6.4-mm compression fittings. E. Sample stack, shown in the enlargement consists of (a) Teflon gaskets, (b) cylindrical stainless steel weight, (c) rear stainless steel retainer screen, (d) primary and secondary sorbent bed separated by large mesh stainless steel screen, (e) front stainless steel fine retainer screen (325 mesh × 325 mesh), (f) sample canister with 2.7-mm holes on face. F. Modified 51-mm (2.0-in.) compression-to-pipe fitting. The compression end of the fitting was shortened to provide sufficient clearance for the sample stack. G. One-way 'V' valve (Warren E. Collins Co., Braintree, Mass., P/N P-315) inserted into the pipe end of Fitting F. The pipe end of the fitting was shortened and honed along its internal axis to accept the 'V' valve. H. Wright respirometer (Ferraris Medical, Inc., Holland, N.Y.) press fit into one-way valve using bored out rubber stopper as an adaptor to make the connection.

(0.125-in.) stainless steel, and were obtained from Supelco Inc., Bellefonte, Pa. The first column was a 6.1-m (20-ft), 20% SP-2100/0.1% Carbowax 1500 column on 80/100 mesh Supelcoport® used in the determination of the limits of detection and quantitation of 1,1,1-trichloroethane and *m*-xylene and in the analysis of all 1,1,1-trichloroethane samples, *m*-xylene samples collected at the 36 mg/m^3 level, and the 1-hexene samples. The 1,1,1-trichloroethane samples collected at 19 or 190 mg/m^3 were analyzed isothermally at 110°C. Under these conditions, the analyte elutes in approximately 9.0 min. The presence of an unidentified interferent required that the 1,1,1-trichloroethane samples collected at the 1.9 mg/m^3 level be analyzed by programming the oven temperature at 4°C/min from 90°C (4-min hold) to 110°C (4-min hold). Under these conditions, the analyte elutes in approximately 11.1 min. The *m*-xylene samples analyzed using this column elute at 6 min at a temperature of 110°C. At a column temperature of 66°C, 1-hexene elutes at 11.4 min.

Another column was a 3.0-m (10-ft), 10% SP-2100 on 100/120 mesh Supelcoport column used to complete the analysis of the *m*-xylene samples generated at 0.4 and 4.4 mg/m^3 when problems were encountered with the SP-2100/0.1% Carbowax column listed above. The *m*-xylene eluted at 4.8 min at a column temperature of 113°C.

The third column was a 6.1-m (20-ft), 10% SP-1000 on 80/100 mesh Supelcoport used for the determinations of the recoveries and the limits of detection and quantitation for the remainder of the analytes. At a column temperature of 70°C, the elution times of each of the analytes were as follows: hexane, 2.3 min; ethyl acetate, 6.4 min; isopropanol, 7.3 min; methylene chloride, 7.5 min; and methyl isobutyl ketone, 12.4 min.

Prior to analysis all samples were stored in 10-mL, crimp-capped scintillation vials or in 59-mL ointment jars sealed with Teflon®-lined screw caps. The samples were desorbed for 0.5 hr with occasional agitation in carbon disulfide. The following volumes of carbon disulfide were used:

(1) 1,1,1-Trichloroethane—front beds (10 wafers), 25.0 mL; backup beds (1 wafer), 2.0 mL;

(2) *m*-Xylene—front beds (3 wafers), 5.0 mL; backup beds (2 wafers), 4.0 mL;

(3) Isopropanol—all samples (4 wafers) were desorbed in 6.0 mL of 1% or 2% v/v 2-butanol/carbon disulfide.

(4) All other samples of representative compounds (4 wafers) were desorbed in 6.0 mL of carbon disulfide.

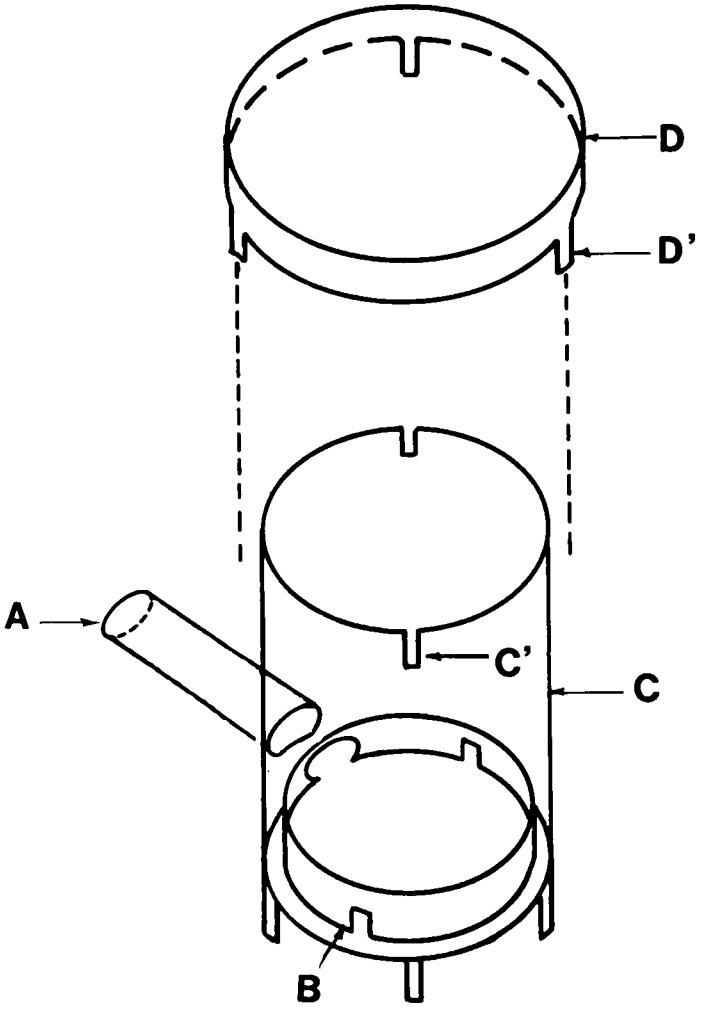

Figure 2—Apparatus for the purging of 45-mm charcoal cloth wafers A. 6.4-mm O.D. tube connected to inlet port of gas chromatograph. B. Removable support for charcoal cloth wafers with cutouts to distribute purge gas evenly through the bed of wafers. C. Purging chamber, 46-mm I.D. × 80-mm deep, with cutouts (C') for exhausting purge gas. This chamber rested on supports in the oven of the gas chromatograph. D. Heavy glass cover secured atop the purging chamber with the antislip studs (D').

Recovery Experiments

Samples were prepared by metering carbon disulfide solutions containing known amounts of each analyte onto the sample beds and determining recovery after storage for 1, 8, 10, 11, or 17 days at ambient temperatures. All of these samples were prepared separately for each analyte.

1,1,1-Trichloroethane and m*-Xylene*

Sorbent beds containing 10 wafers of charcoal cloth were used for 1,1,1-trichloroethane; 3 wafers of charcoal cloth were used as the sorbent beds for *m*-xylene. The masses of 1,1,1-trichloroethane spiked onto the sorbent bed were 95.4 μg, 190 μg, and 1903 μg. The corresponding masses of *m*-xylene spiked were 19.8 μg, 200.4 μg, and 993.2 μg. For both analytes, six samples were prepared at the two higher levels and recovery was determined after storage for 1 day. At the lowest levels, 12 samples were prepared: 6 were analyzed after storage for 1 day, 6 were analyzed after storage for 8 days.

Representative Compounds

For each of the other six analytes, two sample sets of six samples each were prepared. One of the sample sets was prepared using dry charcoal cloth; the other was prepared from charcoal cloth that had been preconditioned by storage in an 80% relative humidity chamber for 4 hr. The quantities

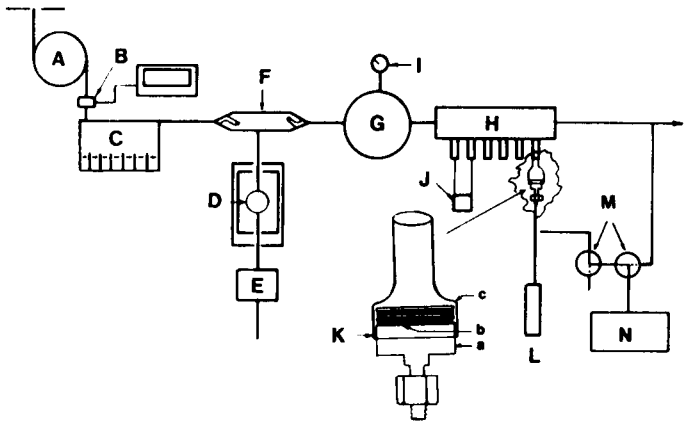

Figure 3—System used for the generation of synthetic atmospheres of *m*-xylene and 1,1,1-trichloroethane A. Blower with prefilter. B. Mass flow sensor with digital readout meter. C. Heated humidifier with specially installed wicks. D. Contaminant reservoir in constant-temperature bath. E. Mass flow controller. F. Mixing tube. G. Ballast tank. H. Sample manifold. I. Manometer. J. Dry/wet bulb apparatus. K. Sampler, enlarged to show (a) Teflon adaptor, 45-mm O.D. (43-mm I.D.) to 19-mm O.D. (17-mm I.D.); (b) Sampling stack showing 45-mm wafers of charcoal cloth, separated into front and backup sections with a stainless steel screen; (c) Main body of sampler, fabricated from glass 49-mm O.D. [45-mm I.D. to 25-mm O.D. (22-mm I.D.)]. L. Sample pump. M. Tandem two-way valves. N. Total hydrocarbon analyzer with strip-chart recorder.

of each analyte spiked onto each sample bed were as follows: hexane, 4.35 μg; 1-hexene, 3.88 μg; methyl isobutyl ketone, 6.24 μg; ethyl acetate, 16.2 μg; methylene chloride, 19.1 μg; and isopropanol, 22.6 μg. Three samples from each set were analyzed after storage for 1 day; the three remaining samples in that set were analyzed after storage for 10 to 17 days.

Generation System

Figure 3 depicts the system for the generation of dynamic atmospheres of *m*-xylene or 1,1,1-trichloroethane in humid air. Dilution air was provided at 100 L/min by the blower (A). This airflow was monitored by a mass flow sensor (B). The dilution air was humidified at (C) via passage through a humidifier that was equipped with a heater. The water reservoir in the humidifier had been specially fitted with cellulose fabric wicks to promote the evaporation of large quantities of water vapor. The reservoir was maintained in an insulated container. Three concentration levels of each analyte in humid air were generated: 2.2, 23, and 190 mg/m^3 for 1,1,1-trichloroethane and 0.43, 3.62, and 32.9 mg/m^3 for *m*-xylene. These experiments were carried out separately for each analyte. A reservoir (D) of either of the pure analytes was maintained in a constant temperature bath. The reservoir was either a bubbler or a diffusion tube. The two higher concentrations of either analyte were generated by passing nitrogen through bubblers at flows of 2 or 20 mL/min for 1,1,1-trichloroethane and of 8.7 or 87 mL/min for *m*-xylene. The temperature of the bubblers was maintained nominally at 25°C for both analytes. For the lowest concentrations, diffusion tubes filled with either analyte replaced the bubblers. Nitrogen was passed over the diffusion tubes at 30 to 60 mL/min. The tubes were maintained at 41.5°C for *m*-xylene and 26.5°C for 1,1,1-trichloroethane. Nitrogen flow over the tubes was regulated using a mass flow controller (E).

The contaminant stream then was introduced into the blender apparatus (F) where it was mixed with the humidified dilution air. From there it passed to a ballast tank (G) and then to a sampling manifold (H). A manometer (I) was used to assure that a positive pressure of approximately 0.02 kPa (0.1 in. H_2O) was maintained on the system. The relative humidity of the system was determined using the dry bulb/wet bulb apparatus (J). Samples were taken at 10 L/min from the manifold in specially designed glass samplers (K) connected to individual high-volume sampling pumps (L) (Gast, Benton Harbor, Mich.). The generation system was fabricated completely of glass and was wrapped with a layer of aluminum foil, then with heating tape, and finally, with fiberglass furnace duct insulation. The temperature of the system was maintained at 35°–40°C.

The effluent from the generator was monitored continuously with a total hydrocarbon analyzer (N) (Bendix, Lewisburg, W.Va.), attached to a strip-chart recorder, through the tandem two-way valving arrangement (M). This valving arrangement also permitted the hydrocarbon analyzer to be calibrated or the sidestream of the effluent from the sampler to be monitored during capacity studies. All transfer lines to the detector were heated with heating tape to prevent condensation of moisture. The monitor was calibrated with standard atmospheres containing 0.44 to 35.6 mg/m^3 *m*-xylene or 2.2 to 190 mg/m^3 1,1,1-trichloroethane. These standards were prepared by injection of known quantities of either analyte into dry air contained in polyvinylfluoride bags.

Sampling

An enlarged drawing of the sampler (K), used for collection of samples from the generation system, is shown in Figure 3. This sampler, fabricated from Teflon and glass, accepts up to 15 wafers of charcoal cloth. It was attached to the sampling manifold via 19-mm I.D. (0.75-in.) Teflon tubing. The wafers of charcoal cloth were separated into front and back sections via large mesh, 45-mm diameter, stainless steel screens.

The 1,1,1-trichloroethane samples were collected by packing the sampler with 11 wafers of charcoal cloth—10 in the front and 1 in the back. The *m*-xylene samples were collected using 5 wafers of charcoal cloth—3 in the front and 2 in the back. Each sampler was connected to a single sampling pump; all samples were obtained at 10 L/min. At the two higher levels studied for each analyte, six 1-min samples (10 L) were taken; at the lowest level studied for each analyte, twelve 5-min samples were taken (50 L).

Capacity Studies

The capacities of the charcoal cloth for both 1,1,1-trichloroethane and *m*-xylene were determined at nominal challenge concentrations of 190 mg/m^3 1,1,1-trichloroethane or 40 mg/m^3 *m*-xylene in air humidified to 80%–90% of saturation at temperatures ranging from 35°–40°C. Challenge flows

TABLE I
Calibration Curves for Eight Analytes with Estimated Limits of Quantitation as Determined Using Gas Chromatography[A] with Flame Ionization Detection

Analyte	Calibration Curve Range (μg/mL)	S_r (%) for Lowest Standard[B]	Linear Correlation Coefficient (r)	LOQ[C] (μg/mL)
Hexane	0.527 to 8.44	5.3	.9997	0.73
1-Hexene	0.19 to 3.88	10.5	.9989	0.60
Ethyl acetate	1.80 to 28.9	0.6	.9999	1.4
Isopropanol	1.57 to 25.1	5.3	.9991	3.9
Dichloromethane	0.53 to 42.4	8.1	.9999	1.5
Methyl isobutyl ketone	0.32 to 25.6	4.7	.9999	1.1
1,1,1-Trichloroethane	1.07 to 21.4	2.8	.9987	3.8
m-Xylene	0.21 to 4.16	5.3	.9990	0.63

[A]A 6-m, 20% SP-2100/0.1% Carbowax 1500 column was used for the analysis of 1,1,1-trichloroethane, *m*-xylene, and 1-hexene. A 6-m, 10% SP-1000 column was used to analyze the remainder of the analytes.

[B]The percent relative standard deviation (S_r) for the average of three injections of the standard solutions.

[C]Limit of quantitation = 3.3 times the limit of detection.[7]

ranged from 10 to 20 L/min. The capacities of 3 or 5 wafers of charcoal cloth for *m*-xylene were determined. The capacities of 5, 10, or 15 wafers of charcoal cloth for 1,1,1-trichloroethane were determined. Each capacity experiment was performed by sampling the effluent from a single sampler. One to seven replicate runs were made. The 5% breakthrough volume, *i.e.*, the volume sampled at the time that the concentration of analyte exiting the sorbent bed was 5% of the challenge concentration, was measured. Pressure drops across the sampling train were determined at each bed depth and flow rate.

Results and Discussion

Limits of Quantification

Table I summarizes the calibration curve information obtained for each analyte studied. These curves were used to estimate the limits of detection for each analyte using methodology outlined in Reference 7. Those detection limits were multiplied by 3.3 to obtain the limits of quantitation given in Table I.

Since carbon disulfide was used to desorb the samples, the most efficient mode of analysis for the test compounds was a flame ionization detector. Co-eluting contaminants that respond to a flame detector will interfere with the analysis and raise the detection limit. Other desorbing solvents that permit the use of selective detectors should reduce the detection limit, however, and minimize problems with interference.

Recovery and Sample Stability Studies

The results of the storage studies for 1,1,1-trichloroethane and *m*-xylene are presented in Table II. These studies demonstrate that at least 20 μg of *m*-xylene and 95 μg of 1,1,1-trichloroethane could be recovered quantitatively from the sorbent after storage for 7 or 8 days at ambient temperatures. These masses correspond to the limit of quantitation for 1,1,1-trichloroethane and to six times the limit of quantitation for *m*-xylene.

TABLE II
Recovery of *m*-Xylene and 1,1,1-Trichloroethane from Spiked Charcoal Cloth Wafers after Storage for 1 to 8 Days[A]

Analyte	Loading Level (μg)	Storage Period (days)	Percent Recovery	
			Average[B]	S_r (%)
1,1,1-Trichloroethane	1903	1	100	1.7
	190	1	101	2.9
	95.4	1	96	5.6
		7	100	4.3
	pooled[C]			3.8
m-Xylene	965	1	100	2.9
	195	1	97	6.5
	19.8	1	102	4.8
		8	100	7.2
	pooled[C]			5.0

[A]All samples were prepared by spiking sorbent beds containing dry charcoal cloth with carbon disulfide solutions containing either of the analytes. Ten wafers of cloth were spiked to prepare the trichloroethane samples; three wafers were spiked to prepare the *m*-xylene samples. All samples were stored in closed containers at ambient temperatures prior to analysis. The trichloroethane samples were desorbed in 25 mL of carbon disulfide. The *m*-xylene samples were desorbed in 5 mL of carbon disulfide. All samples were analyzed via GC-FID.

[B]Six samples at each level studied

[C]One-day samples only

TABLE III
Recovery of Six Representative Compounds after Storage on Charcoal Cloth for Periods Ranging from 1 to 17 Days[A]

Analyte	Loading (μg)	Sorbent[A] Treatment	Storage Period (days)	Percent Recovery		Recovery Ratio[C] (%)
				Mean[B]	S_r (%)	
Hexane	4.35	dry	1	97	2.7	
			10	103	12.1	107
		humid	1	89	8.4	
			10	100	5.5	111
1-Hexene	3.88	dry	1	93	4.7	
			17	91	5.2	98
		humid	1	93	1.6	
			17	78[D]	5.6	84
Ethyl acetate	16.2	dry	1	87	3.8	
			10	88	18.6	101
		humid	1	96	14.4	
			10	82	9.9	86
Methyl isobutyl ketone	6.24	dry	1	93	3.2	
			10	99	1.6	106
		humid	1	87	4.4	
			10	91	1.2	104
Methylene chloride	19.1	dry	1	94	1.4	
			11	86[D]	1.5	91
		humid	1	93	4.9	
			11	88	2.9	95
Isopropyl alcohol	22.6	dry	1	74	3.1	
			10	84	2.9	
		humid	1	65	2.4	
			10	78	3.4	

[A]The samples were prepared by spiking carbon disulfide solutions containing the analytes onto sorbent beds prepared either from dry charcoal cloth (dry) or charcoal cloth that had been preconditioned at 80% relative humidity for 4 hr (humid). The sorbent bed for each sample was four wafers of the charcoal cloth. For each solvent, 12 samples were prepared—one set of 6 from the dry sorbent and a second set of 6 from the preconditioned sorbent. Next, 3 samples from each set were analyzed after storage for 1 day; the other 3 samples in each set were analyzed after storage for the period indicated.

[B]All 1-day storage samples of isopropanol were desorbed in 1% 2-butanol in carbon disulfide; 2% 2-butanol in carbon disulfide was used to desorb all of the 10-day isopropanol storage samples. All other samples were desorbed with carbon disulfide.

[C]Recovery, Day 10, Day 11, or Day 17 divided by recovery, Day 1, and multiplied by 100.

[D]Average recovery is significantly different from that at Day 1 at the 95% level of confidence.

Data obtained from the recovery experiments conducted with the other six compounds are presented in Table III. These experiments were conducted to determine the feasibility of storing and recovering each solvent at a level corresponding to its estimated limit of quantitation as given in Table I. Preliminary tests indicated that recoveries of methylene chloride and ethyl acetate from samples stored for 1 day at these levels were 73.3% (S_r = 13.7%, 6 samples) and 78.5% (S_r = 7.1%, 2 samples), respectively. Therefore, storage stability of these two analytes at twice the quantitation limit was investigated.

The tests with the water-vapor preconditioned charcoal cloth were conducted to simulate the effect of co-adsorbed water from the breath upon the recovery of the representative compounds. With the exception of 1-hexene, long-term storage of all of the analytes on prehumidified charcoal cloth did not result in recoveries that were significantly lower than those obtained after storage for 1 day. The average recovery of methylene chloride stored on dry charcoal cloth, however, was significantly lower after long-term storage. The reasons for these lower recoveries are not clear. Loss of methylene chloride caused by evaporation into the void volume of the desorption vessel was minimized by carrying the desorptions out in 10-mL, crimp-capped vials. Separate experiments had shown that lower recoveries were obtained for 20-μg samples of methylene chloride spiked onto the charcoal cloth and desorbed in 59-mL ointment jars after storage for 1 day—84.2% (S_r = 1.3%, 3 samples). This loss presumably is

caused by volatilization of the analyte into the void volume of the desorption vessel.

As with coconut-shell charcoal,[8] it was necessary to add 2-butanol to the carbon disulfide (1% to 2% v/v) in order to quantitatively recover isopropyl alcohol from the charcoal cloth. Desorption of isopropanol from the charcoal cloth with carbon disulfide alone gave an average recovery of 27.8% (S_r = 3.5%, 6 samples).

Generation Conditions

The generation system shown in Figure 3 was constructed to simulate those physiological conditions under which a sample of human breath might be expected to be collected. Synthetic atmospheres were generated over the range from 0.44 to 38 mg/m^3 for *m*-xylene and from 1.9 to 190 mg/m^3 for 1,1,1-trichloroethane. These concentrations correspond to approximately 0.001 to 0.1 times the current Occupational Safety and Health Administration (OSHA) permissible exposure limits of 434 mg/m^3 and 1900 mg/m^3 for *m*-xylene and 1,1,1-trichloroethane, respectively.[9] The National Institute for Occupational Safety and Health (NIOSH) recommends exposure levels of 434 mg/m^3 and 1091 mg/m^3 for *m*-xylene[10] and 1,1,1-trichloroethane,[11] respectively. The range of concentrations generated is reflective of concentrations found in samples of expired breath following human exposures to controlled atmospheres of *m*-xylene[12] or 1,1,1-trichloroethane.[13] The analyte generation experiments described in this paper were conducted at constant flow rates ranging from 3 to 20 L/min; these are reasonable for resting tidal breathing flow rates.[14] It was not feasible to simulate experimentally a pulsating dilution airflow.

Samples were generated at 35° to 40° C at 80% to 90% relative humidity. Relative humidities of expired human breath are reported to range from 80% to 90% of saturation at temperatures ranging from 30° to 33° C.[15] A major limitation of the generation system was that only 100 L/min of air could be humidified to 80%–90% of saturation at these temperatures. In order to maintain a positive pressure of 0.02 kPa (0.1 in. H_2O) on the generation system, only 30 L/min of the atmosphere were sampled. For this reason, only three samples could be withdrawn simultaneously at 10 L/min.

Capacity Studies

The capacity of the charcoal cloth was evaluated at a maximum anticipated breathing flow rate of 20 L/min. It was not experimentally feasible to conduct these studies at flows higher than 20 L/min or to evaluate the sorbent capacity using more than one sampler at a time.

At 35° C, the vapor pressures of 1,1,1-trichloroethane and *m*-xylene are 27 kPa (109 in. H_2O) and 1.9 kPa (7.6 in. H_2O), respectively.[16] Since 1,1,1-trichloroethane also has the higher exposure criteria, it was selected as the model compound for determination of the maximum bed depth of sorbent. The selection of an optimal bed depth for 1,1,1-trichloroethane required that two factors be balanced: (1) the depth of the sorbent bed had to provide adequate capacity but (2) could not be so great as to restrict breathing during sample collection. Therefore, the capacity studies were conducted using a factorial experimental design in order to explore the relationship of the capacity and pressure drop to the depth of the sorbent bed and sampling flow rate. The capacities of the sorbent for 1,1,1-trichloroethane were determined at flow rates of 10, 15, and 20 L/min and at bed depths of 5, 10, and 15 wafers.

Table IV lists the 5%-breakthrough volumes and pressure drops for the sorbent bed configurations at the flow rates studied. These data indicate that the cloth has an extremely high capacity for 1,1,1-trichloroethane and *m*-xylene in humid air, at flow rates up to 20 L/min, even under conditions of high relative humidity. For 1,1,1-trichloroethane, Table IV indicates that the average capacities of a 5-wafer bed depth were very imprecisely determined at the flows investigated. The source of this imprecision is not clear.

TABLE IV
Pressure Drops and 5%-Breakthrough Volumes for Sorbent Beds of 45-mm Charcoal Cloth Wafers Challenged with Synthetic Atmospheres of 1,1,1-Trichloroethane or *m*-Xylene in Air[A]

Analyte	Bed Depth (wafers)	Flow (L/min)	Pressure Drop		Breakthrough Volume (L)		
			Average kPa (in. H_2O)	S_r (%)	Average	S_r (%)	n
1,1,1-Trichloroethane	5	10	0.10 (0.4)	1.3	6.3	42.6	3
	5	20	0.32 (1.3)	12	3.6	31.5	4
	15	10	0.40 (1.6)	6.1	63	17.0	4
	15	20	0.90 (3.6)	6.7	59	22.4	5
	10	15	0.47 (1.9)	4.3	39	10.7	7
	10	10	0.25 (1.0)	2.3	45	17.1	4
	10	20	0.67 (2.7)	4.3	31	3.5	3
m-Xylene	5	20			238	15.0	3
	3	20			89		1

[A]Nominal challenge concentrations were 190 mg/m^3 for 1,1,1-trichloroethane and 40 mg/m^3 for *m*-xylene in air humidified to 81%–91% relative humidity at 35°–40° C.

Variation in the relative humidity or analyte challenge concentration was less than or equal to ± 5% for all measurements. With the exception of the capacity studies conducted at 20 L/min with 5 wafers of the cloth, the pressure drops across the sorbent beds were determined with about the same degree of precision, indicating uniform packing of the sorbent beds.

The first four rows of data in Table IV were analyzed using the procedures described in Reference 17. Equations were developed that predict the 5%-breakthrough volumes for 1,1,1-trichloroethane and also the sorbent bed pressure drops for given sampling bed depths and flow rates:

$$V = -20 - 0.2F + 5.75D - 0.01(F)(D) \quad (1)$$

$$P = -0.13 + 0.008F + 0.002D + 0.0028(F)(D) \quad (2)$$

where V = the 5%-breakthrough volume (L), P = the pressure drop across the sorbent bed (kPa), F = flow rate (L/min), and D = bed depth (number of wafers). In the selection of an optimal bed depth for the collection of 1,1,1-trichloroethane, a minimum sample volume of 20 L was assumed. Equation 1 predicts 5%-breakthrough volumes of 34.5 L and 31.5 L for a 10-wafer sorbent bed at flows of 10 or 20 L/min, respectively. A 20-L sample, therefore, can be obtained using a 10-wafer bed at 10 to 20 L/min and still provide a realistic margin of error equal to one-third of the estimated 5%-breakthrough volume. Table IV shows that the experimentally determined 5%-breakthrough volumes for a 10-wafer sorbent bed were 31 L at 20 L/min and 45 L at 10 L/min.

The breakthrough data for *m*-xylene, also listed in Table IV, indicate that 3 wafers of the charcoal cloth should be adequate for the collection of a 50-L sample. Therefore, the sample bed configuration for collection of generated samples of *m*-xylene was a 3-wafer front and a 2-wafer back section. The 1,1,1-trichloroethane was sampled with a 10-wafer front and a 1-wafer back section.

Since each charcoal cloth wafer is 0.05-cm thick, the depth of the sorbent beds in the capacity experiments ranged from 0.1 to 0.5 times the 1.5-cm bed depth of sorbent in a conventional charcoal tube. Given that the surface areas of the cloth and of coconut-shell charcoal are comparable, the capacities reported here for such low bed depths may appear to be very large, especially at the high flow rates studied in the breakthrough experiments. Further considerations, however, indicate that the capacities are not unreasonable. For one thing, the charcoal cloth may have a lower capacity for water vapor than does coconut-shell charcoal.[4] The linear velocity through a 45-mm diameter bed of charcoal cloth at 20 L/min is 21 cm/sec; this is comparable to the linear velocity of 26.5 cm/sec through a conventional 4-mm I.D. charcoal sample tube at a flow of 0.2 L/min. Furthermore, the exposed cross-sectional area (1590 mm^2) of a 45-mm diameter sorbent bed is approximately 126 times that of a 4-mm diameter sampling tube (12.6 mm^2). Finally, the capacity experiments were conducted using 3 to 15 wafers of charcoal, weighing approximately 0.2 g/wafer. The sorbent beds, therefore, contained from 4 to 20 times the mass found in a conventional 150-mg charcoal tube.

The capacity experiments were conducted at a single challenge concentration and constant flow rates for two test analytes only. In field sampling, it is likely that expired breath will be simultaneously sampled for a number of solvents that are present in varying concentrations. In addition, the breath samples will not be delivered at a single, fixed flow rate but in pulsating patterns at a variety of flow rates. Both of these factors will affect sample capacity. Therefore, the sorbent bed configurations described in this paper should be regarded as guidelines. The authors used a sampling bed containing a 4-wafer front and a 2-wafer back section configuration of charcoal wafers in the stainless steel sampler in a study of the method using human subjects exposed to *m*-xylene. Results of this study will be presented in a future publication.

Recovery of Generated Samples

Results of the analyses of samples of *m*-xylene and of 1,1,1-trichloroethane collected from the generation system are given in Table V. Over the ranges studied, the concentrations determined with charcoal cloth sampling averaged 91% (S_r = 10.1%) for *m*-xylene and 107% (S_r = 8.88%) for 1,1,1-trichloroethane relative to those determined using the hydrocarbon analyzer. It should be noted that the collection of a 50-L sample of 1,1,1-trichloroethane at the 2 mg/m^3 level exceeded the 5%-breakthrough volume guidelines mentioned previously. These samples, however, were collected from a 100-fold lower concentration of 1,1,1-trichloroethane than those generated for capacity testing. No breakthrough to the backup section was observed for any of the 1,1,1-trichloroethane samples. Of the twelve 50-L samples of *m*-xylene collected at the 0.44 mg/m^3 level, however, eleven samples exhibited breakthrough to the back section ranging from 3% to 6% of the total mass collected. Large-volume samples were collected at each of the lowest concentrations generated for either analyte so that the concentrations of the desorbed samples would be equal to or greater than the established limits of quantitation.

The storability of samples of each analyte collected at the lowest concentrations generated was evaluated. Of the 12 samples collected, 6 were analyzed after storage for 1 day, 6 after storage for 14 days. The 14-day samples were refrigerated at 4°C after storage for 7 days at room temperature. For *m*-xylene, the mean recovery following storage for 14 days was not statistically different from the mean recovery determined following storage for 1 day. The mean recoveries of the 1,1,1-trichloroethane samples stored for 14 days on the charcoal cloth, however, were statistically lower than those determined after storage for 1 day. A similar reduction in recovery was not encountered for the samples of 1,1,1-trichloroethane that were spiked at the 95-μg level and stored at ambient temperatures for 7 days (Table II).

Estimation of Sampling and Analytical Method Imprecision

Estimates of the sampling and analytical method imprecision were determined from Table V for each analyte over the three concentrations generated. For sampling and analysis

TABLE V
Results of Sampling and Analysis for 1,1,1-Trichloroethane over the Range 2.2 to 190 mg/m³ and for *m*-Xylene over the Range 0.44 to 35.6 mg/m³ Using Charcoal Cloth Wafers[A]

Analyte	Concentration (mg/m³)		Storage Period (days)[D]	Percent Recovery[B]	
	Reference[C]	Recovered[C]		Mean	S_r (%)
1,1,1-Trichloroethane	190	197	1	104	6.6
	23	28	1	120	11.2
	2.16	2.44	1	113	8.1
		1.93	14	89[E]	13.2
	pooled[F]				8.9
m-Xylene	35.6	32.9	1	92	7.2
	4.35	3.62	1	83	6.1
	0.435	0.428	1	98	14.7
		0.392	14	90	8.7
	pooled[F]				10.1

[A]Samples were collected from atmospheres of the analytes maintained at a relative humidity of 80%-90% and temperatures ranging from 35°-40° C. All samples were collected on 45-mm cloth wafers at 10 L/min. The 1,1,1-trichloroethane samples were collected using 10 wafers; the *m*-xylene samples were collected with 3 wafers.

[B](Average recovered/reference) × 100%. For both solvents, 12 samples were collected and analyzed at the lowest concentration level; 6 at each of the two higher levels. Average recovery of trichloroethane collected at the 2.16 mg/m³ level and stored 1 day is based on analysis of 5 samples.

[C]Reference concentration was determined using a total hydrocarbon analyzer. Recovered concentration was determined by charcoal cloth sorbent sampling.

[D]All of the 1-day samples were stored at ambient temperatures; the 14-day samples were stored for 7 days at room temperature and then for 7 days under refrigeration at 0° C.

[E]The 14-day recovery is statistically lower than the 1-day recovery at the 95% level of confidence.

[F]One-day samples only.

of *m*-xylene and 1,1,1-trichloroethane, the total method imprecision (percent relative standard deviation) was estimated to be 11% and 10%, respectively. These estimates were made using the 1-day storage data in Table V and an assumed maximum imprecision of 5%[18] for measurement of tidal volumes using the Wright respirometer.

Sampling exhaled breath with the stainless steel sampler is likely to be less precise than indicated by the above estimates. For one thing, breath samples will be delivered in a pulsed flow pattern over a wide range of flow rates. The above estimates of the method imprecision reflect collection of samples only at a constant flow rate of 10 L/min. Furthermore, the subject rebreathes a portion of the previously delivered breath from the void volume of the sampler. It was not feasible to simulate experimentally such a sample rebreathing pattern.

Conclusions

Experiments described in this paper indicate that a 3-wafer or a 10-wafer primary sorbent bed can be used to sample *m*-xylene or 1,1,1-trichloroethane, respectively, in 10 to 50 L of exhaled breath. The concentrations sampled ranged from 2.2 to 190 mg/m³ for 1,1,1-trichloroethane and from 0.44 to 35.6 mg/m³ for *m*-xylene. Desorption of samples in carbon disulfide and analysis using gas chromatography with a flame ionization detector provided adequate sensitivity for analysis of the samples, if the volume of desorption solvent ranged from 1.7 to 2.5 mL per wafer of cloth. Quantitative recovery of either analyte from the sorbent was obtained after storage for 1 to 8 days.

From 78% to 103% of trace quantities of five representative compounds were recovered from the charcoal cloth following storage for 10 to 17 days if the samples were desorbed with carbon disulfide. Trace quantities of a sixth compound, isopropanol, were recovered (78% to 84%) following long-term storage on the sorbent if 2-butanol was added to the carbon disulfide. These experiments suggest that the sorbent may be used for sampling a wide range of organic solvents present in expired breath.

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