

24-Hour Diffusive Sampling of 1,3-Butadiene in Air onto Carbopack X Solid Adsorbent followed by Thermal Desorption/GC/MS Analysis—Feasibility Studies

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ABSTRACT

Diffusive sampling of 1,3-butadiene for 24 hr onto the graphitic adsorbent Carbopack X packed in a stainless steel tube badge (6.3 mm o.d., 5 mm i.d., and 90 mm in length) with analysis by thermal desorption/gas chromatography (GC)/mass spectrometry (MS) has been evaluated in controlled tests. A test matrix of 42 trace-level volatile organic compounds (VOCs) in humidified zero air was established by dynamic dilution of compressed gas standards flowing through an environmental chamber. Conditions for both automated thermal desorption of the badge, including pre-desorption dry purging, and GC/MS analyses (column flow rate and temperature programming profile) were optimized for specificity, precision, and sensitivity of response. Analytical system responses for sets of tubes exposed to a given 1,3-butadiene concentration were typically precise, e.g., a % RSD < 10% at 1.1 $\mu\text{g}/\text{m}^3$ (0.5 ppbv), and system response was approximately linear with concentration over the range 0–9 $\mu\text{g}/\text{m}^3$. No significant systematic variations of response were observed for changes in sample humidity and temperature (35% and 75% RH at 16, 20, and 29 °C). Loss of 1,3-butadiene from the tube badge due to reverse diffusion into clean air over 12 hr after an initial 12-hr exposure at 9 $\mu\text{g}/\text{m}^3$ gave an 11% response decrease. Adding 100 ppbv (~ 200 $\mu\text{g}/\text{m}^3$) of ozone during the second 12 hr caused no additional response change.

INTRODUCTION

Need for 1,3-Butadiene Monitoring

The need for monitoring 1,3-butadiene is based in its adverse health effects, i.e., a 10^{-6} lifetime risk level for cancer due to inhalation exposure of 0.03 $\mu\text{g}/\text{m}^3$ (12.4 pptv at 20 °C and 1 atm pressure).¹ This compound is very reactive in the ambient atmosphere with a short atmospheric lifetime, estimated to be 2–3 hr.² Ambient concentrations over a range of 0.02–314 $\mu\text{g}/\text{m}^3$ have been observed at different locations,³ with roughly 20% nondetects. Major sources are internal

combustion and tobacco smoking.² Vapor pressure of 3.3 atm at 25 °C makes it a very volatile compound.²

Desirability of Using Diffusive Sampling

Although ambient air sampling into specially prepared canisters is currently being successfully used to measure 1,3-butadiene in the U.S. National Air Toxics Trend Stations (NATTS) network, constraints related to cost, ease of use and deployment, and number of samples needed in exposure studies make diffusive sampling a compelling possibility. In fact, this possibility has been realized for other gases. Varns et al.⁴ used diffusive sampling onto chemically treated filters to study the distribution of ozone in the Dallas/Fort Worth metropolitan area. Chung et al.⁵ evaluated a commercially available diffusive sampling badge (Model 3520 organic vapor monitor, 3M Company, St. Paul, MN) for time-integrated sampling of several VOCs; compounds are solvent extracted from the adsorbent for analysis.

Diffusive Sampling of 1,3-Butadiene Using Thermally Reversible Adsorption

Thermally reversible adsorption involves physical adsorption during sampling, sealing and storage of the adsorbent, and heating the adsorbent to retrieve the adsorbed compounds. This avoids solvent use and typically leaves the adsorbent ready for subsequent sampling. Past studies using this procedure for 1,3-butadiene have often used active sampling over short-duration sampling periods. Kim et al.,⁶ for example, report 2-hr sampling at 30 mL/min and Sapkota and Buckley⁷ report 3-hr sampling at 25 mL/min. The Health and Safety Executive in the United Kingdom has published⁸ a laboratory method that uses active sampling up to 8 hr with a pre-filter for drying the sample. However, no thermally reversible adsorption method has so far proven adequate for 24-hr diffusive sampling of 1,3-butadiene. One obvious need has been for a hydrophobic adsorbent with a high specific retention volume. Supelco's recent characterization of the hydrophobic adsorbent Carboxen 1000 (Supelco, Bellefonte, PA) for adsorption of VOCs indicates a retention volume for 1,3-butadiene of at least 20 L in dry air.⁹

The accuracy of diffusive sampling with thermal desorption is contingent on a knowledge of the diffusive sampling rate for target compounds during the sampling period.^{10,11,12} In practice, compounds are physically adsorbed during the period of diffusive sampling. Thermal desorption GC/MS analysis occurs in the laboratory and then all of the thermally desorbed compound is directed to the GC/MS. In practice, the rate must be essentially constant and verification of the degree to which this is true establishes the limits of confidence in the sampling results. The one-dimensional diffusion equation for the mass sampling rate is

$$dm/dt = DA/L [C - C_0] \quad (1)$$

where DA/L is the effective sampling rate in milliliters per minute, and m denotes mass, D denotes the diffusion coefficient, A is the open badge area, and L is the diffusion length. C denotes the ambient air concentration and C_0 the target gas concentration above the adsorbent,

which is considered in equilibrium with the compound on the adsorbent. For low adsorbent surface coverage, C_o is typically proportional to the amount of adsorbed target compound (a linear adsorption isotherm). As the target compound accumulates at the surface, and depending on the volatility of the compound (and the associated proportionality constant for the adsorption isotherm), the value of C_o can become high enough to decrease the mass sampling rate. The higher the retention volume (or adsorption energy) of the adsorbent/compound combination, the less likely C_o will depart significantly from zero.

In the current work, diffusive sampling with thermal desorption was selected for monitoring 1,3-butadiene at ambient levels. Temperature, humidity, composition of co-collected gases such as ozone, and target gas concentration variability were examined by altering conditions in an environmental chamber. The analysis of 1,3-butadiene was established under constraints that (1) accurate monitoring of other air toxic VOCs (benzene, carbon tetrachloride, trichloroethene, 1,2-dichloropropane, and tetrachloroethene) be possible and (2) the analysis cycle be limited to 1 hr.

EXPERIMENTAL METHODS

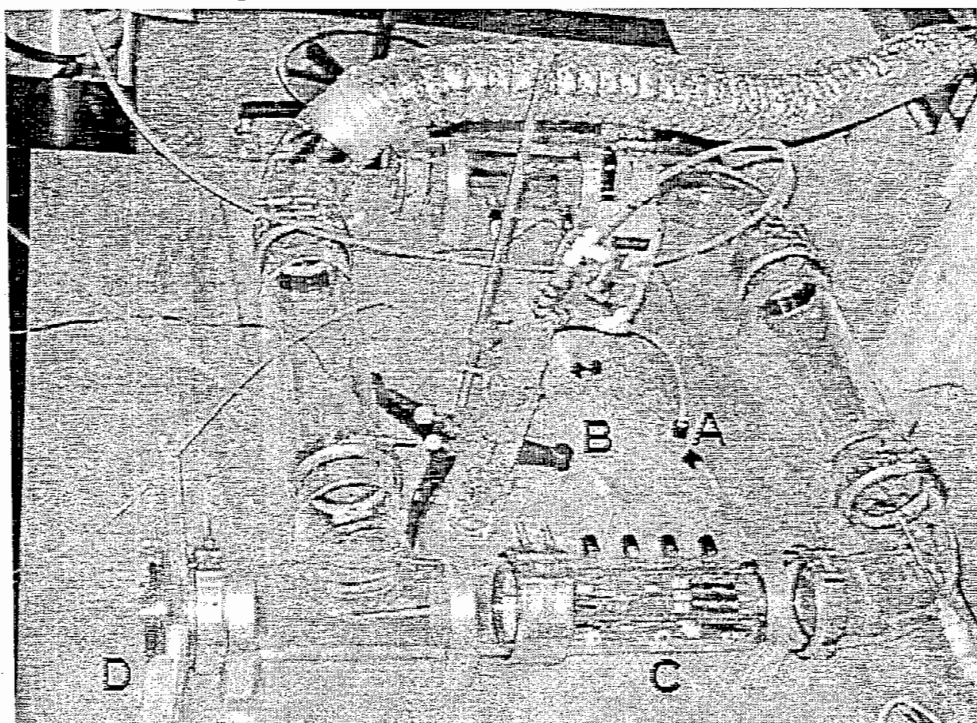
The graphitic solid adsorbent Carpack X (washed 60/80 mesh, 0.18–0.25-mm particle diameters) was evaluated for diffusive sampling of 1,3-butadiene. Based on experimental data from the commercial supplier, Supelco, Inc. (Bellefonte, PA), this adsorbent exhibits a retention volume of 20 L per gram for 1,3-butadiene in dry air, efficiently releases the compound upon heating at 325 °C, and is hydrophobic. Supelco product literature lists the specific surface area of the adsorbent as 240 m²/g, which is high compared to other graphitic carbons and may account for the comparatively high specific retention volume.

A standard stainless steel tube badge (STB), 6.3-mm outer diameter (o.d.) (5-mm inner diameter [i.d.]) by 90 mm in length, was packed with 650 mg of Carpack X. This badge is described in the open literature¹³ and is identical to that shown in the EPA Compendium Method TO-17¹⁴ for active sampling with solid adsorbents. The STB is designed for a low diffusive sampling rate that is consistent with a small exposed adsorbent area, A , and a long diffusion channel ($L = 1.5$ cm). The STBs used in these experiments (Supelco custom order) were preconditioned by Supelco by heating for 8 hr at 350 °C with a 40–50 mL/min nitrogen purge. Specially designed PTFE caps from PerkinElmer (part number N6200119, PerkinElmer Life and Analytical Sciences, Shelton, CT) were used to seal the STBs during storage prior to analysis in the laboratory. Swagelok fittings with Teflon ferrules are used to seal the tubes during long storage times (days to weeks). For controlled experiments, the STBs were held at room temperature after sampling, and analyses were performed usually within 24 hr and no later than 7 days afterward.

An environmental chamber for controlled testing of the STBs, which consists of 10.2-cm-o.d. glass tubing, is shown in Figure 1. Humidified zero air and trace gas mixtures from compressed gas cylinders are introduced at position A, mixed at B, and directed into the chamber at a flow rate of 5.8 L/min. Based on the volume of the chamber and independent measurements with a Model 1440-4 digital air velocity meter (Kurz Instruments, Inc., Monterey, CA), the air speed through the chamber was approximately 5 cm/sec. The sample air moved around the chamber,

through the volume occupied by the STBs at position C, and then into a fume hood. STBs were introduced and retrieved through the sliding door at D. Temperature, humidity, and air-speed measurements as well as active sampling with adsorbent tubes or with an automated gas chromatograph with flame ionization detection (GC/FID) system were accomplished through ports in the chamber wall at position C. The automated GC/FID system was operated to sample from the chamber before and after exposures to document the stability of the 1,3-butadiene concentrations.

Figure 1: The Environmental Chamber Used for Testing Diffusive Samplers. Position A: gas mixture introduced, B: gases mixed, C: volume occupied by STBs, and D: sliding Teflon door.



Tubes were thermally desorbed using the PerkinElmer TurboMatrix automated thermal desorber (ATD). This process involves (1) dry purging the STB with helium in the sampling direction (exhaust goes to vent) for 4 min at 15 mL/min; (2) thermally desorbing the retained compounds at 325 °C while back-flushing the tube with helium for 10 min at 30 mL/min to transfer target gases into a small-volume, glass tube trap containing a length of Carbopack X (40/60 mesh) at 27 °C; and (3) heating the trap (325 °C) while back-flushing with helium onto a GC column at a flow rate of 1.65 mL/min at room temperature (flow rate changes with column temperature). A fused silica capillary GC column (Agilent Technologies, Wilmington, DE), 60 m in length with a 0.32-mm i.d. and a 1-micron DB-1 (dimethylpolysiloxane) stationary phase, was used for compound separation. The mass spectrometer was operated in the mode referred to by

PerkinElmer as the SIFI mode, which allows both selected ion monitoring and full scan during the same run. The scan mode was used to determine the occurrence of any co-eluting compounds and the selected ion mode was set to use the 54 m/z mass ion for quantitation of 1,3-butadiene. A PerkinElmer AutoSystem XL GC/TurboMass Gold MS system was used for the analyses. The complete set of operational parameters for thermal desorption is shown in Table 1 along with MS parameters. Using these parameters, repeat thermal desorption of tubes showed low carryover for 1,3-butadiene.

Table 1. ATD and MS Operating Conditions

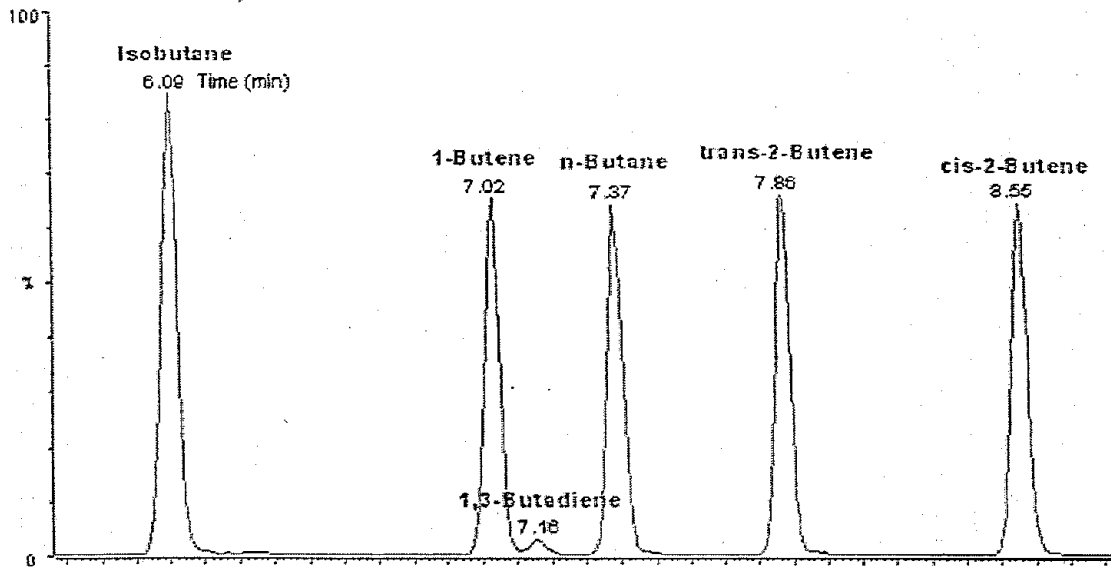
TurboMatrix ATD Optimized Operating Conditions			
Transfer line	225 °C	Valve	225 °C
Tube desorb	325 °C	Trap low	27 °C
Trap rate	40 °C/sec	Trap high	325 °C
Tube purge	4 min	Purge flow	15 mL/min
Tube desorb	10 min	Desorb flow	30 mL/min
Trap hold	10 min	Cycle time	62 min
Inlet split	Off	Min psi	8
Outlet split	Off	Operating mode	2-stage desorb
Std. injection	Off	Injections/tube	1
TurboMass Gold MS Operating Conditions			
Source temp (°C)	180	LM resolution	12.8
GC line temp (°C)	200	HM resolution	12.4
Electron energy	70	Ion energy (V)	2.2
Trap emission	100	Ion energy ramp	3.4
Repeller	1.0	Multiplier (V)	398.0
Lens 1	5.0		
Lens 2	55.0		

During initial controlled tests in which co-collected compounds did not interfere with detection, the temperature programming of the GC oven began at 35 °C and followed the temperature profile of 35 °C for 5 min, 6 °C/min to 210 °C, and a 0.84-min hold at 210 °C, for a total GC analysis time of 35 min. For the VOC mixtures encountered in real-world conditions, subambient column temperatures were required to separate 1,3-butadiene from other C-4 hydrocarbons. As a result, the GC oven temperature program was changed to -21 °C initially, 3 °C/min to 12 °C, 5 °C/min to 155 °C, 45 °C/min to 240 °C, which was held for 3.5 min. The resulting separation from a mixture containing several C-4 hydrocarbons at 40 ppbv along with 1,3-butadiene at 2 ppbv is shown in Figure 2A as a total ion chromatogram. Although not shown in Figure 2A, isobutene elutes just prior to 1-butene. Figure 2B shows the same mixture in the selected ion monitoring mode using the 54 m/z ion.

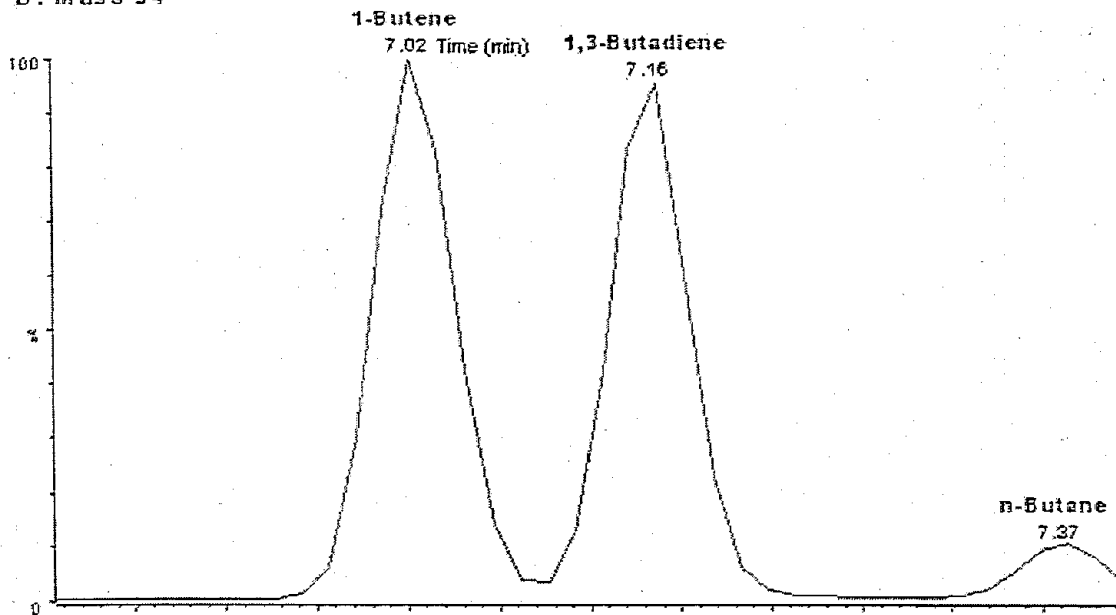
Temperature changes in the environmental chamber over a range of 16–29 °C were achieved using the extremes of temperature range available at the EPA facility. Humidity changes were

Figure 2: GC Separation of Potentially Interfering Compounds from 1,3-Butadiene (2 ppbv 1,3-butadiene and 40 ppbv of C-4 hydrocarbons). A: Separation on the total ion chromatogram, and B: Separation using 54 ion for quantitation.

A. TIC



B. Mass 54



achieved by bubbling a portion of the zero air supplied to the environmental chamber through water. Ozone concentrations were established by passing a portion of the zero air supply through a commercially available TEI Model 49 PS ozone calibrator (Thermal Environmental Instruments, Inc., Franklin, MA), which mixed with humidified zero air to achieve a concentration of $200 \mu\text{g}/\text{m}^3$ (100 ppb of ozone at STP). The ozone concentration was monitored at the position of the STBs using a calibrated TEI Model 49 ozone analyzer.

Calibration standards for TO-14A compounds and 1,3-butadiene were established by diluting and blending two commercially obtained trace gas mixtures, one containing 2 ppm each of 1,3-butadiene and acrolein in nitrogen and a second containing 2 ppm each of the 41 target VOCs identified in the EPA Compendium Method TO-14A¹⁵ in nitrogen. The variability in calibration concentrations was no greater than $\pm 5\%$ about the mean value as established by periodic sampling from the manifold with a GC/FID system. The 1,3-butadiene standard concentration was verified by measuring the FID response and comparing it with the response of a known propane concentration from a National Institute of Standards and Technology (NIST) Standard Reference Material.¹⁶

RESULTS

Blanks and Measurement Precision

Blank values for 1,3-butadiene were generated by exposing six STBs to humidified zero air ($22 \pm 2 \text{ }^\circ\text{C}$ at 35% RH) for 24 hr in the environmental chamber. The mean blank value was 79 pg. The precision for this data set as measured by the relative standard deviation (RSD) was 4.9%. Precision values for other tube sets were comparable. Three different sets of seven STBs exposed to 1,3-butadiene levels of $1.1 \mu\text{g}/\text{m}^3$ (0.5 ppbv) exhibited RSDs of 3.1%, 5.8%, and 7.1%, while the RSD of another set of seven STBs exposed to $9.0 \mu\text{g}/\text{m}^3$ (4.0 ppbv) was 2.7%. The average RSD for the last three tube sets was 4.6%.

MDL Determination

A method detection limit (MDL) was established by generating 1,3-butadiene concentrations at $1.1 \mu\text{g}/\text{m}^3$ in the exposure chamber under conditions of $22 \pm 2 \text{ }^\circ\text{C}$ and 75% RH. The MDL was determined from seven replicates and formula 2,

$$\text{MDL} = t_{(n-1, 1-\alpha=0.99)} \sigma, \quad (2)$$

where σ is the standard deviation of replicate analysis and t is the Student's t -value at the 99% confidence level and $n-1$ degrees of freedom ($t = 3.143$). The resulting MDL was $0.11 \mu\text{g}/\text{m}^3$. Based on guidance for determination of the MDL, the challenge concentration should be within a factor of 5 of the MDL. In this case, a redetermination of the MDL is warranted.

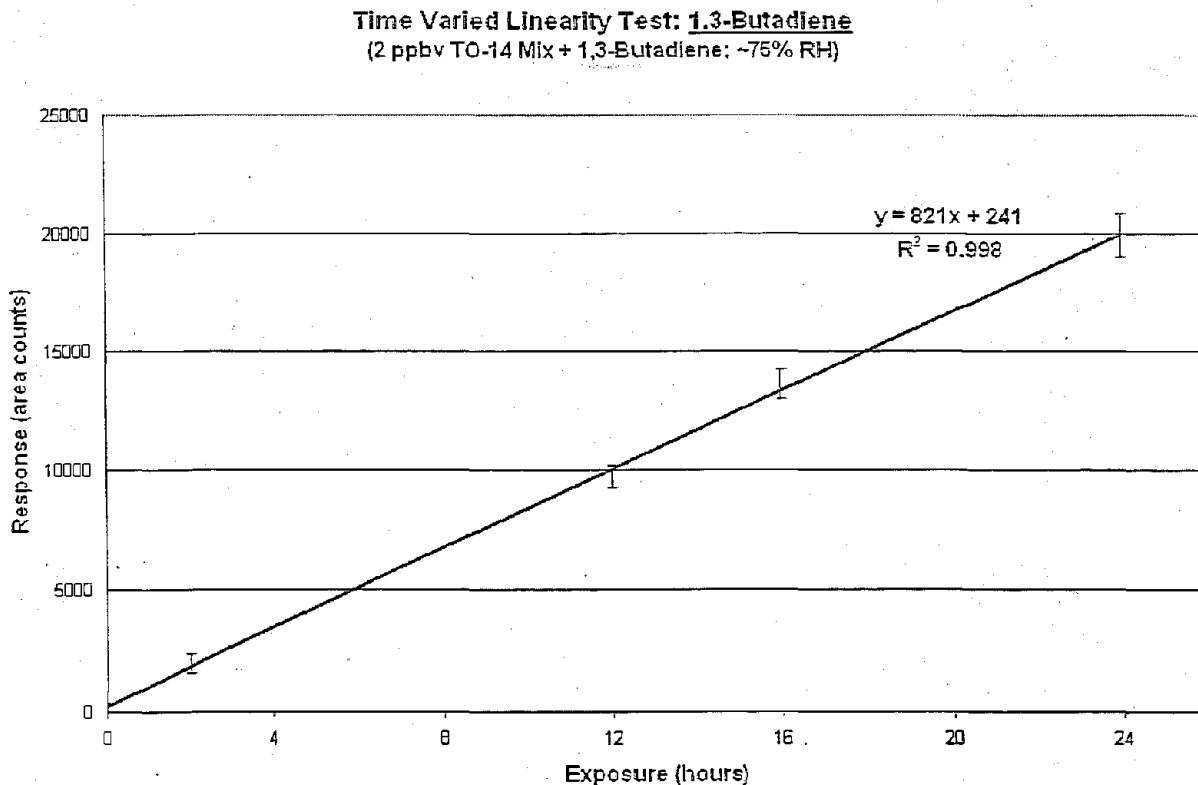
Calibration

Sampling conditions to be used in exposure studies were simulated by implementing 24-hr sampling of 1,3-butadiene concentrations over a range of $0-9 \mu\text{g}/\text{m}^3$ (0-4.0 ppbv). Each data

point was an average of the response values for a set of five to seven tubes that were exposed simultaneously during a single run. The response for each tube set was precise, but day-to-day variations were observed in the average response for a given concentration. This variation was traced to analytical system variation from one run sequence to another, usually separated by two or more days. This issue was addressed by using an external standard to correct for day-to-day MS response variation.

Since calibration using 24-hr sampling runs was very time-consuming, a one-day calibration was demonstrated in which exposure time was varied for a given concentration. Two STBs were removed from the exposure chamber after exposures of 2, 12, 16, and 24 hr (see Figure 3). The error bars in Figure 3 represent $\pm 4.6\%$ of the average response (the %RSD measurement precision as determined earlier) except at the 2-hr exposure, in which the error bars are \pm RSD for the tube blanks. To determine whether this calibration was equivalent to a calibration using different concentrations for 24 hr, 1 ppbv of 1,3-butadiene (six tubes) was sampled for 24 hr and compared to 3 ppbv sampled for 8 hr (six tubes). The latter sample averaged 15% higher.

Figure 3: Example Calibration Curve of Response vs Sampling Time for Constant 2 ppbv Environmental Chamber Concentration



Effect of Humidity and Temperature on Apparent Sampling Rate

Considerable optimization of thermal desorption conditions was necessary to achieve close agreement for identical 24-hr sampling exposures for both 35% and 75% RH at 22 °C in the environmental chamber. After optimization, five tubes were exposed to 2-ppbv gas mixtures at 35% RH, giving a mean area count of $18,570 \pm 1041$ (1 standard deviation). This test was repeated at 75% RH with the same tubes six days later to obtain $16,394 \pm 306$, or 6.2% below the average value. Temperature variations from 16 to 29 °C at 75% RH gave essentially identical responses. Other research^{10,11,17} indicates that the effect of temperature and humidity on sampling rate is no more significant than found in these tests.

Effect of Reverse Diffusion on Diffusive Sampling Rate

Eight STBs were exposed for 12 hr in the environmental chamber to a mixture of 1,3-butadiene and the 41 Method TO-14A compounds at nominal concentrations corresponding to 4 ppbv in humidified zero air at 22 ± 2 °C and 75% RH. The tubes were removed and the chamber was flushed with humidified zero air. Four of the tubes were then returned to the chamber and exposed to humidified zero air for an additional 12 hr. Subsequently, all eight tubes were analyzed. Results indicated that the effect of reverse diffusion was to reduce the apparent 1,3-butadiene concentration by 11%. This experiment was repeated with 40 ppbv of the mixture for 1 hr followed by 23 hr of exposure to humidified zero air, which resulted in an average response reduction of 22%.

Effect of Ozone on Diffusive Sampling Rate

Ozone is known to react with some VOCs when the VOCs are adsorbed on carbon-based sorbents.¹⁸ Kim et al.⁶ have shown that in active sampling of 1,3-butadiene with another graphitic carbon solid adsorbent (Carbopack B at 1000 mg), ozone levels as high as 240 ppb do not change the recovery. To determine the effect of ozone for 1,3-butadiene adsorbed on Carbopack X, eight STBs were placed in the exposure chamber for a 12-hr period and exposed to 4 ppbv of 1,3-butadiene. Environmental chamber conditions were 75% RH at 22 ± 2 °C. The tubes were removed from the environmental chamber and the chamber was flushed with humidified zero air. Four of the tubes were then returned to the chamber and exposed to $200 \mu\text{g}/\text{m}^3$ (~ 100 ppb) of ozone in humidified zero air for 12 hr. The eight tubes were then analyzed. Comparison of results show that the effect of ozone plus reverse diffusion was to reduce the apparent 1,3-butadiene by 11%. Hence, the combined effect was indistinguishable from reverse diffusion alone.

Effect of Storage on Sample Integrity of 1,3-Butadiene

Dettmer et al.¹⁹ provide storage stability data for 1,3-butadiene on Carbotrap X (20/40 mesh). Sample loop injections of 5 ng 1,3-butadiene in helium followed by 75 mL of helium purge onto Carbotrap X (20/40 mesh) held in glass tubes were made at room temperature. Ten other low-boiling-point hydrocarbons, each at approximately the same concentration, were simultaneously loaded. Recoveries averaged $95\% \pm 1.5\%$ (average of five measurements) after 7 days of storage at room temperature. Recoveries of 50-ng samples averaged $100\% \pm 1.5\%$. The Health and Safety Executive Method 53/2 indicates no loss of 1,3-butadiene retained on Carbopack X for 14

days.⁹ The storage stability for 1,3-butadiene using diffusive samplers may differ somewhat from these results because the distribution of adsorbed 1,3-butadiene is expected to be nearer the front of the badge and different results are possible with the current tube sealing and storage procedures.

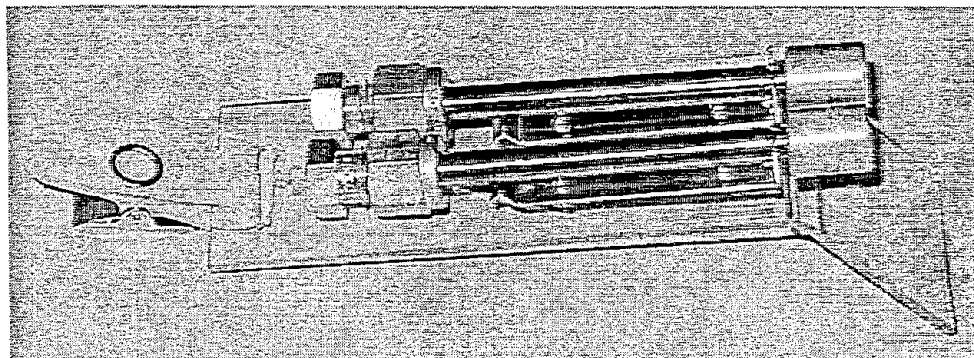
Effect of Wind Speed and Badge Orientation

Based on studies conducted at low wind speeds in our environmental chamber, no orientation effects were noted for STBs facing into the airflow compared with those facing the opposite direction. Variations of wind speed were not tested; however, because the STBs have a relatively low sampling rate, such variations are known to be insignificant.¹¹

Holder for Duplicate Sampling

Some duplicate samples were taken with adsorbent tubes to determine the precision of diffusive sampling. For use in estimating the overall precision of the sampling and analytical process, a duplicate badge holder was fabricated (see Figure 4). The badge holder was designed for the sampling end of a tube to be pointing downward and slightly elevated so as to promote unimpeded sampling when the badge is placed next to a surface, e.g., an outer garment worn by a human subject. Limited results to date indicate excellent precision at the low-pptv concentrations for several common air toxic VOCs. All metal holders are now being fabricated to eliminate the possibility of outgassing from the plastic in the original badge.

Figure 4: Duplicate Sampling Tubes with Tube Holder for Clip-on Sampling



DISCUSSION

Based on the reverse diffusion tests, the average 1,3-butadiene field concentration is expected to be lower than the actual concentration, but not more than the 22% reduction observed when the badge was exposed to 40 ppbv for 1 hr followed by 23 hr of zero air. Apparent losses may be caused by variable temporal patterns of 1,3-butadiene accumulation at the front of the STB as explained by Coutant et al.^{20,21} They applied differential equations for diffusion to predict the

performance of diffusive sampling badges based on badge design parameters and the compound/solid adsorbent combination. Using the "thin" badge assumption that the adsorbed and gas phases are in equilibrium throughout the adsorbent, the ratio of sampling rate, R , after a time, t , to the initial rate, R_o , is simply

$$R/R_o = \exp [-R_o t/WV_b]. \quad (3)$$

Further, the ratio of the average rate over time, t , to the initial rate is

$$R_{avg}/R_o = \{1 - \exp [-R_o t/WV_b]\} / [R_o t/WV_b], \quad (4)$$

where W denotes mass of adsorbent in the thin badge and V_b denotes the specific retention volume of Carbo-pack X for 1,3-butadiene. This assumption, when originally applied to a large-diameter badge with a "thin" section of solid adsorbent (0.35 cm), successfully predicted experimental results. However, the STB is a "thick" badge and an extension of this mathematical treatment is warranted to address the diffusion of 1,3-butadiene from the front of the STB into the remainder of the 6 cm of adsorbent. Application of Equation 4 to an arbitrary 1-cm length of the adsorbent indicates that $R_{avg} = 0.85 R_o$ for a 24-hr sampling period.

The range of controlled conditions used in the environmental chamber covers a majority of expected ambient and indoor environmental conditions. However, extension of the temperature range from the current 16–29 °C to 10–35 °C and the humidity from 35–75% RH to 10–95% RH is needed to complete this type of testing. This is particularly important because of the apparent 6% decrease in average diffusive sampling rate at 75% RH.

CONCLUSIONS

The characteristics of 24-hr diffusive sampling of 1,3-butadiene followed by thermal desorption and GC/MS analysis have been investigated through controlled testing with a sample matrix of 42 compounds. For sampling with washed 60/80 mesh Carbo-pack X and the current analytical system, we concluded the following:

- The experimentally determined average blank value is 79 pg and the MDL is 0.11 µg/m³ (0.05 ppbv).
- The average method precision was 5.3% at 1.1 µg/m³ based on three multi-tube experiments and 2.7% at 9.0 µg/m³ for one multi-tube experiment.
- Water vapor effects indicate an increase in sampling rate of 12.4% at room temperature in going from 75% RH to 35% RH. No change in sampling rate was observed with temperature over the range 16 °C to 29 °C at 75% RH.
- The badges are insensitive to orientation in a directed airstream at flow velocities of approximately 5 cm/sec.
- Loss of 1,3-butadiene from the STBs due to reverse diffusion was observed during 24-hr sampling runs. Tests included high concentrations followed by zero concentrations of 1,3-butadiene. In the case of 12 hr at 4 ppbv followed by 12 hr of clean air, the overall effect was

to reduce analytical response by 11%; 1 hr at 40 ppbv followed by 23 hr of clean air gave a 22% reduction.

- Ozone does not react with adsorbed 1,3-butadiene.
- For a "thin" adsorbent, the application of diffusion theory predicts a decrease in average mass sampling rate when adsorbed compound accumulates rapidly. The same theory explains losses using the STB (a "thick" badge), although this effect is moderated by longitudinal diffusion into the adsorbent.

Based on these facts, the diffusive sampling rate of 1,3-butadiene onto Carbopack X in the STB is relatively insensitive to environmental conditions, and accumulation of sample is expected to be approximated by Equation 3 for low loadings. Although the existing theory considered here is inadequate for describing the STB performance, indications are that nonzero values of C_0 can occur at modest and variable concentrations and will reduce the effective sampling rate during 24-hr sampling. The C_0 values are lowest (and mass sampling rate the highest) at the initiation of sampling and subsequently depend on the exposure history. Initial experimental work indicates that sample losses are unlikely to be greater than 22% for the STB, and that calibration results for the STBs may depend somewhat on how a given microgram loading of 1,3-butadiene is obtained.

In summary, diffusive sampling for 1,3-butadiene is feasible with the STB and current analytical equipment, although 24-hr average concentration measurements may be as much as 22% low due to the nature of diffusive sampling. External standards for tracking system response changes must be used as well as periodic calibration to ensure linearity of response under typical loading conditions.

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KEY WORDS

1,3-butadiene

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diffusive sampling

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solid adsorbent

sorbent tube

VOCs

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DISCLAIMER

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16. Abstract Diffusive sampling of 1,3-butadiene for 24 h onto the graphic adsorbent Carbopack X packed in a stainless steel tube badge with analysis by thermal desorption/gas chromatography(GC)/mass spectrometry(MS) has been evaluated in controlled tests. A test matrix of 42 trace-level volatile organic compounds in humidified zero air was established by dynamic dilution of compressed gas standards flowing through an environmental chamber. Conditions for both automated thermal desorption of the badge and GC/MS analyses were optimized for specificity, precision, and sensitivity of response. Analytical system responses for sets of tubes exposed to a given 1,3-butadiene concentration were typically precise, e.g., a %RSD<10% at 0.5 ppbv, and system response was approximately linear with concentration over the range 0-4 ppbv. No significant systematic variations of response were observed for changes in sample humidity and temperature. Loss of 1,3-butadiene from the tube badge due to reverse diffusion into clean air over 12 h after an initial 12-h exposure at 4 ppbv gave an 11% response decrease. Adding 100 ppbv of ozone during the second 12 h caused no additional response change.		
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