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# Gas-Phase Analysis of Trimethylamine, Propionic and Butyric Acids, and Sulfur Compounds Using Solid-Phase Microextraction

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**Complaints due to odors are an important problem for the wastewater, composting, and animal agriculture industries. Accurate, objective measurement techniques are needed to monitor emissions, to develop new waste handling procedures, and to reduce the production of these volatile gases. Solid-phase microextraction was investigated as a technique for the determination of representative odorous gases. A flow-through Teflon chamber was used to expose the fibers to certified gas standards. A 75-$\mu$m carboxen-poly(dimethylsiloxane) (Car-PDMS) coating was used for trimethylamine (TMA), carbon disulfide ($CS_2$), dimethylsulfide (DMS), and dimethyl disulfide (DMDS), and an 85-$\mu$m polyacrylate coating was used for propionic acid (PA) and butyric acid (BA). Using a 1-h fiber exposure time and a flow rate through the chamber of 72 mL/min, method detection limits were 2.38, 0.074, 0.150, 0.063, 1.85, and 1.32 ppbv for TMA, DMS, $CS_2$, DMDS, PA, and BA, respectively. Enhanced detector signal was observed for all analytes under flow conditions, as compared to static conditions, and the porous nature of the Car-PDMS coating appears to increase the time needed for analytes to reach equilibrium under flow conditions.**

Complaints from the public due to odors are an important problem for the wastewater, composting, and animal agriculture industries. Human health risks associated with odorous gases are currently being assessed, and state governments are implementing new regulatory systems to address odor issues.[1] Site managers need objective tools to measure odorous gases on a regular basis in the various treatment processes and in their final product. In the case of wastewater treatment plants, the odor quality of biosolids produced is important if the material is to be field-applied near residential areas. Daily monitoring of odors from treatment processes in the plant may be necessary to avoid complaint problems.

Historically, the most common approach to odor measurement is olfactometry, or the use of trained human panels, to determine the intensity and character of an air sample.[2] Although olfactometric methods reflect actual human response to odors, they do not provide information on the chemical components of a gas mixture, and there are large variations in results between laboratories.[3−5] The electronic nose is an alternate approach that has been developed. These devices can identify simple or complex gas mixtures using an array of electronic chemical sensors[5,6] and have been used to detect odorous chemicals, especially amines, volatile fatty acids, and sulfurs, from food, cattle, pig and chicken slurries, and wastewater.[7−9] However, this technology is still developing. A detailed review of the electronic nose technology was recently published by Ziegler et al.[10]

An understanding of the chemical components released from a particular waste treatment system can give scientists insights into the biological or chemical processes controlling odor release. Solid phase microextraction (SPME) is a relatively simple, inexpensive, solvent-free method to extract organic chemicals from different sample matrixes, for example, aqueous,[11−13] headspace,[14] and ambient air.[15] This method is an alternative to traditional extraction methods for the determination of the volatile com-

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Table 1. Physical Properties of Analytes, Mass Ions Used for GC/MS, Permeation Rate of Gas Standards, Method Detection Limits of Analytes, and Odor Threshold for Human Detection

| compd | mol wt (g/mol) | bp[a] (°C) | mass ions for GC/MS (*m*/*e*) | permeation rate[b](ng/min) | MDL[c] ppbv | odor threshold ppbv |
|---|---|---|---|---|---|---|
| | | | Acids | | | |
| propionic acid | 74 | 141.4 | | 407 | 1.80 | 28[d] |
| butyric acid | 88 | 163.5 | | 395 | 1.32 | 0.5[e] |
| | | | Amine | | | |
| trimethylamine | 59 | 2.87 | 58, 59 | 37.6 | 2.38 | 0.44[f] |
| | | | Sulfur Compounds | | | |
| carbon disulfide | 76 | 46.5 | 76, 78 | 7.00 | 0.189 | 16[g] |
| dimethyl sulfide | 62 | 37.3 | 47, 62 | 7.08 | 0.074 | 0.11[h] |
| dimethyl disulfide | 94 | 109.7 | 45, 94 | 4.78 | 0.063 | 6.4[i] |

[a] Ref 22. [b] Certified to 70 °C ± 10% for VFAs, 30 °C ± 5% for TMA and sulfur compounds. [c] Method detection limit obtained using EPA standard procedure.[23] [d] Ref 24. [e] Ref 25. [f] Ref 26. [g] Ref 27. [h] Ref 28. [i] Ref 29.

pounds, for example, liquid−liquid extraction,[1,16] headspace, and purge-and-trap for aqueous samples,[17,18] or porous polyurethane foam or multiple-adsorbent tube traps for air sampling.[19,20]

Unlike other conventional methods, which require extensive sample preparation, SPME is a one-step extraction procedure in which the compounds of interest are absorbed by a thin polymer film or by porous carbonaceous materials that are bonded to a fused silica fiber. SPME is based on an equilibrium process, and at equilibrium the mass of analyte on the fiber is proportional to its concentration in the sample matrix.[21] The analysis can be carried out using either gas or liquid chromatography as needed, and the process can be automated.

The goal of this project was to develop a quantitative method to quickly measure odorous chemicals in the gas phase that are (1) commonly present in waste treatment systems, (2) have extremely low human detection thresholds, and (3) provide information to process managers or agricultural engineers as to the chemical conditions in the waste treatment system.

In this paper, we describe a method that utilizes two different SPME fiber coatings (carboxen-poly(dimethylsiloxane) and polyacrylate) for the analysis of trimethylamine (TMA), carbon disulfide ($CS_2$), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), propionic acid (PA), and butyric acid (BA). These chemicals have very low human detection thresholds (Table 1).[22−29] Amines, sulfides, and volatile fatty acids (VFAs) are three chemical classes that contribute to the odors released from waste treatment systems. These compounds are also frequently detected at biosolids land-application sites.[30]

Amines are produced from amino acids through the removal of the carboxyl (COOH) group.[5] The sulfur compounds are released when conditions in the waste system become anaerobic.[31] Volatile fatty acids are produced from carbohydrate fermentation and are associated with anaerobic treatment. Propionic and butyric acids can make up more than 50% of volatile acid gases released from a plant.[32] Although other chemicals from the amine, sulfur, and volatile fatty acid classes or from other compound classes such as the mercaptans, cresols, and indoles may be required to fully evaluate the odor character of various waste materials, this paper provides a critical evaluation of SPME as a tool for rapid measurement of these volatile odorous chemicals and a guide to other scientists or managers that have a need for this capability.

## EXPERIMENTAL METHODS

**Calibration of the SPME Fibers.** Gas standards were generated using certified Teflon membrane permeation devices (NIST traceable, VICI Metronics, Inc., Santa Clara, CA) for each compound (Table 1). Several studies on hydrocarbon gas analysis using permeation devices have been reported.[33,34] The permeation devices were placed together in a thermostated glass chamber (30 °C for TMA and sulfur compounds and 70 °C for fatty acids) of a model 320 Dynacalibrator (VICI Metronics, Inc.). The base flow of high purity (99.99%) nitrogen gas through the permeation chamber was 72 mL/min, and the concentration was varied using additional dilution gas.

Two SPME fibers were exposed to the gas standard in a temperature-controlled (20 °C), Teflon cylindrical collection chamber (i.d. = 4.1 cm, Savillex, Co., Minnetonka, MN) under atmospheric pressure (Figure 1). The average pressure at sampling site was 1 atm and was assumed to be constant. The temperature inside the chamber was measured by inserting a temperature probe (Traceable-4085, Control Com., Houston, TX)


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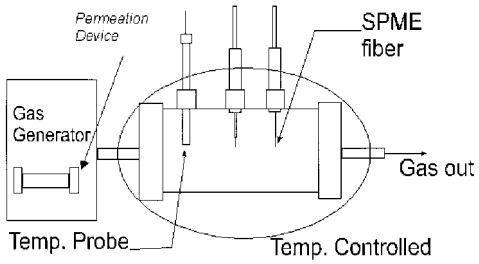


Figure 1. Experimental design for for SPME calibration.

into the chamber. The chamber was equipped with two septa ports with Teflon-coated septa through which the needle of the SPME device was inserted so that duplicate measurements could be made for all of the calibration points. Care was taken not to expose any of the metal surfaces of the SPME probe, because excess analyte can be introduced into the GC injector port. All Teflon tubing and equipment were used to minimize possible adsorption of the compounds in the system. Excess gas was vented to a bypass valve in the Dynacalibrator to maintain the same flow rate in the collection chamber. The volumetric flow rate of gas flowing through the collecting chamber was measured with a bubble flow meter, and was controlled by a needle valve. The volumetric gas concentration under the experimental conditions in this study was calculated according to Nelson.[35]

**SPME and Gas Chromatography Conditions.** A 75-$\mu$m Car-PDMS coating was used to capture TMA, $CS_2$, DMS, and DMDS, and an 85-$\mu$m polyacrylate coating was used for propionic and butyric acids (Supelco, Bellefonte, PA). Analysis of propionic and butyric acids was performed using capillary gas chromatography with flame ionization detection using a Hewlett-Packard 5890 gas chromatograph. GC conditions were as follows: 30-m HP-Innowax column, 0.25-mm i.d.; 0.25-$\mu$m film thickness; injection port, 250 °C; 0.75-mm i.d. injection port liner; detector, 270 °C; 40-min desorption time; initial temperature, 32 °C for 5 min; 3.5 °C/min to 118 °C; hold for 10 min.

Trimethylamine and the sulfur compounds were analyzed using capillary gas chromatography with mass spectrometry detection in selected-ion monitoring mode. A Hewlett-Packard 5890 gas chromatograph, coupled to an HP 5970 mass spectrometer, was used. GC conditions were as follows: 60-m DB-1 (J&W Scientific, Folsom, CA) 0.25-mm i.d.; 1.0-$\mu$m film thickness; injection port temperature, 250 °C; 0.75 mm injection port liner; desorption time, 40 min; initial temperature, 32 °C for 5 min; 3.5 °C/min to 118 °C; hold for 0 min. Both GC systems were equipped with a Merlin microseal septum (Supelco, Bellefonte, PA) designed for SPME to ensure reproducibility between injections.

Prior to fiber exposure, the gas standard was equilibrated with the system for at least 30 min. Immediately after exposing the fiber to the gas standard, the fiber was desorbed in the GC injection port. The needle with the exposed fiber was left in the heated injector until the end of the GC run to eliminate any possible carry over of material. Fibers were cleaned prior to use by baking in the injector port for 30 min. The test for determining method detection limit (MDL) was performed based on EPA standard methods.[23]

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## RESULTS AND DISCUSSION

Analysis of volatile reactive chemicals such as those included in this study present many challenges. First, storing and handling these chemicals in pure form can be extremely dangerous, and even small spills can cause serious air quality problems in a building with a centralized air handling system. Second, many of these compounds are gaseous at room temperature; react with water, air, metal surfaces (such as syringe needles), or other solvents, in effect, making the creation of liquid standard solutions difficult. Third, they are susceptible to degradation on the surfaces of sorbents used to capture them from an air stream.

One approach that many scientists have used for volatile gas analysis is the use of containers such as Tedlar bags or stainless steel canisters.[2] Standards are created by adding a liquid solution or gas to the bag or canister, and an inert gas is added to the container to achieve a certain volume. However, the bags are permeable, and gas is lost over time, making storage impossible, and some chemicals may adhere or react with the bag or canister wall, changing the concentration in the standard.[36,37] Some specialty companies will create mixed gas standards in a traditional pressurized stainless steel gas tank, but reactions can occur in these tanks over time, and the cost is prohibitive.

The proposed method eliminates many of the problems with chemical handling, standard generation, and sample collection. A gas standard generator utilizing permeation devices eliminates the need for handling pure chemical reagents. The permeation rates are stable and certified to provide accuracy for analysis.

**Equilibration Time Measurements under Static Conditions.** The mass of chemical adsorbed by the SPME fiber coating is related to the concentration in the sample.[21] The chemical is adsorbed by the fiber coating over time until equilibrium is reached. The adsorption rate onto the fiber coating is initially fast and slows as equilibrium is approached. The time required to reach equilibrium is independent of concentration, but it is compound- and coating-dependent. The most volatile chemicals reach equilibrium very quickly, but the time increases for less volatile chemicals.[21]

It is desirable to expose the fiber coating to the sample until equilibrium is reached.[21] This provides the most reproducible results, and sample collection time does not have to be carefully monitored. Therefore, we investigated the time needed to reach equilibrium for our target analytes (concentrations used were 18−39 ppb for sulfur compounds, 210 ppb for TMA, and 860 and 560 ppb for PA and BP, respectively). Under static conditions (no flow through the Teflon chamber), equilibrium was achieved for the volatile fatty acids (VFAs) after 1.5 h (Figure 2). Three hours was required for TMA, $CS_2$, and DMS; however, DMDS did not reach equilibrium, even after 10 h.

Some researchers have reported rapid gas-phase equilibration times, for example, for hydrocarbons and several short chain amines.[37,38] However, others have also observed long equilibration times in studies with phenols (>50 min),[13] and aromatic amines in aqueous phase (>100 mins),[12] VFAs in headspace (>100 mins),[39] alkyl compounds (>15 h),[40] and sulfur compounds in the

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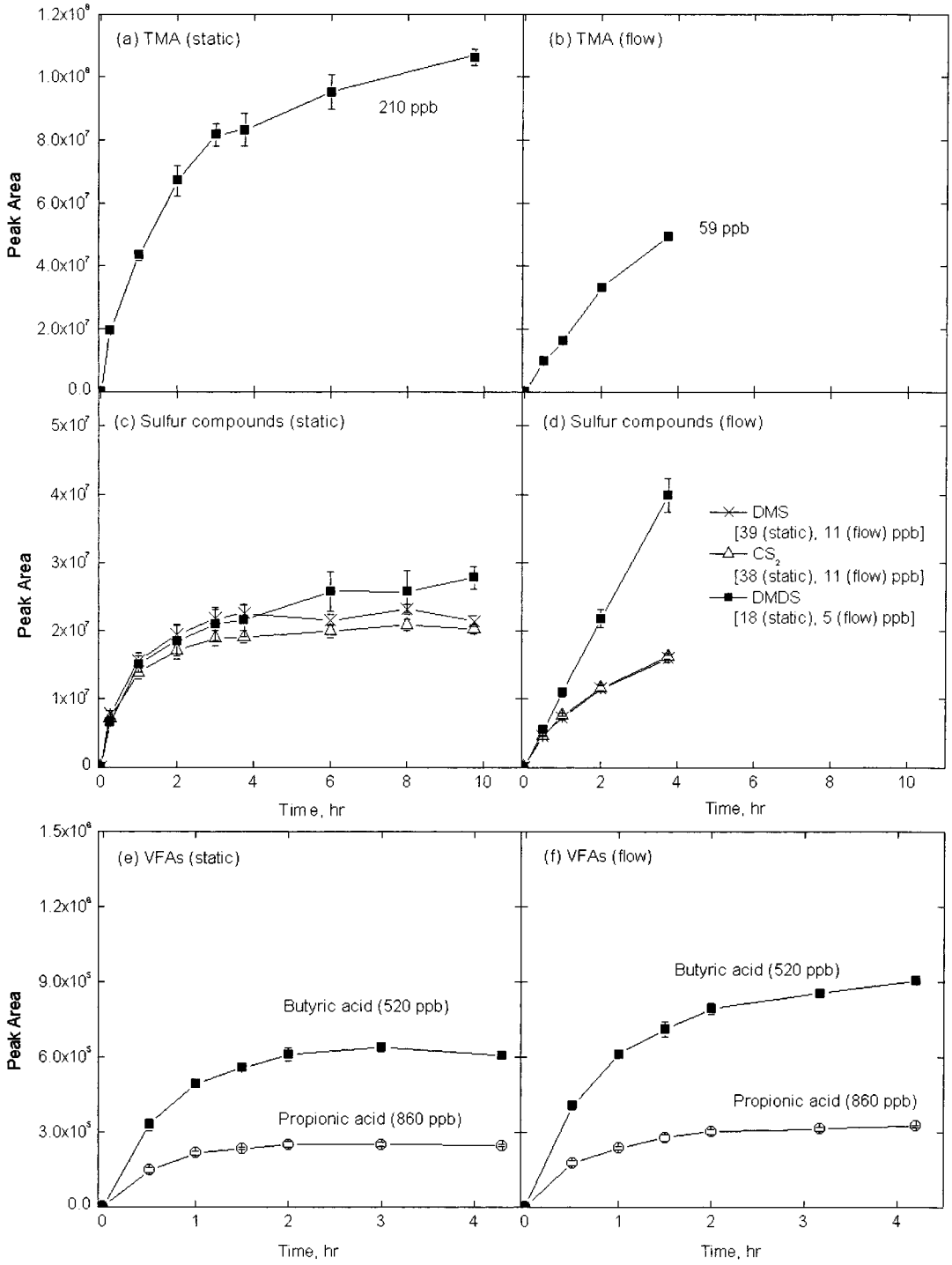


Figure 2. Results from equilibrium experiments under static and flow conditions.

gas phase (>100 mins).[34] Pan et al.[41] reported longer than expected equilibrium times (50−100 min) in their study with gaseous acids and attributed it to the adsorption of acids on the wall of the vial. However, in our study, the chamber and tubing are Teflon, limiting adsorption to the walls. In experiments to determine if chemicals were adhering to the walls, the chamber was purged with clean gas for 30 min. Afterward, none of our analytes were detected in the exit air stream. This indicates that there is no serious adsorption of analytes within the system.

**Equilibration Time Measurements under Flow Conditions.** SPME extraction efficiency of liquid solutions is often improved through agitation of the fiber to reduce the thickness of the static diffusion layer around the fiber.[21] Agitation reduces the time required for chemicals to reach equilibrium in liquid solutions. It is logical to assume that a static diffusion layer of air around the fiber is created in the gas phase as well and slows the

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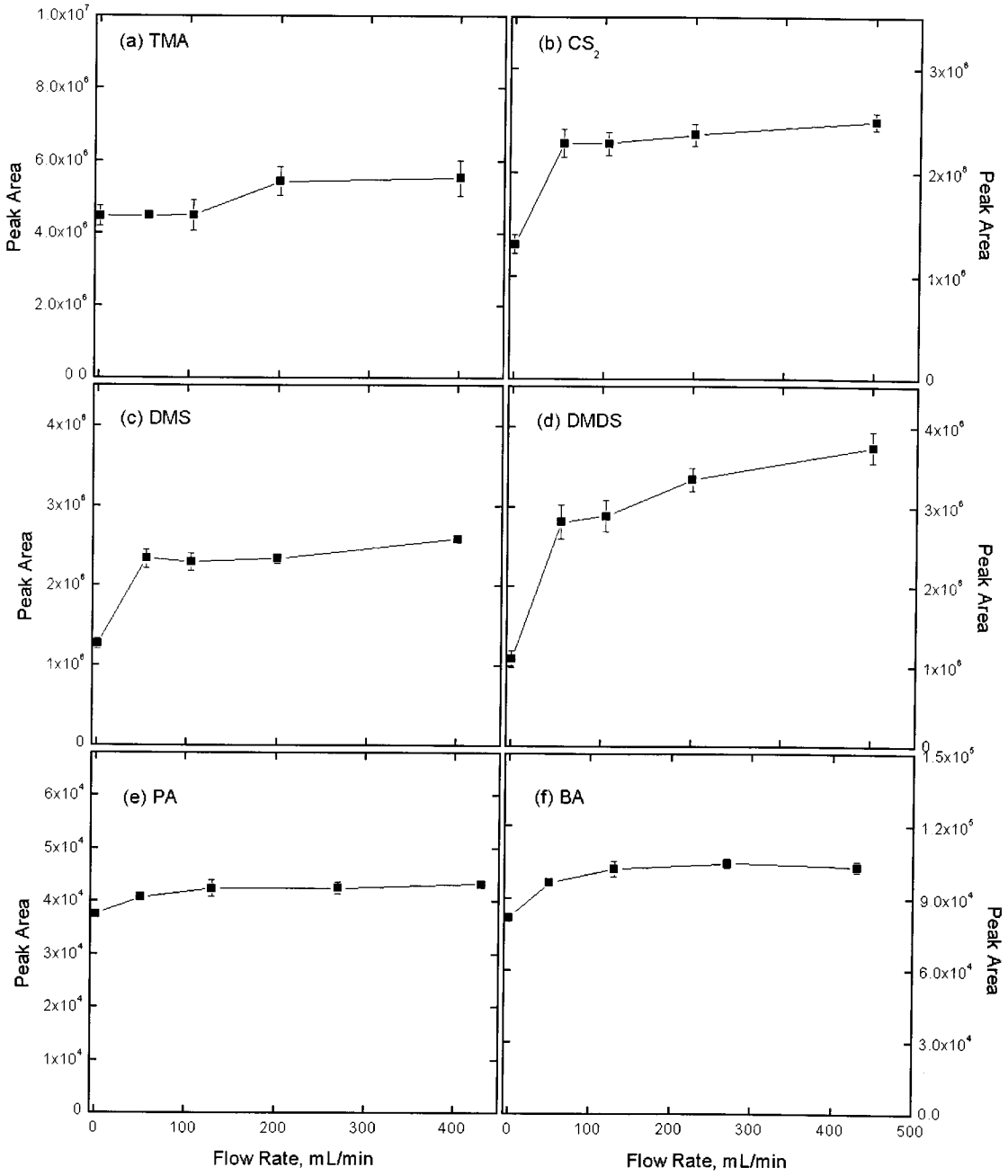


Figure 3. Detector response under different flow rate conditions.

adsorption rate of the chemical under static conditions. Thus, the effectiveness of a flow-through gas standard system was investigated in order to achieve shorter equilibration times.

Using a constant flow rate (72 mL/min) of gas standard through the Teflon chamber, the equilibration time for propionic and butyric acid on the polyacrylate fiber was unchanged when compared to static conditions (Figure 2). This indicates that a static diffusion layer for these chemicals does not limit equilibrium. However, the detector signal under flow conditions was increased by 10% when compared with static conditions (Figure 2). A significant increase in mass adsorbed was not expected, since the same gas standard concentration was used in both static and flow experiments. Bartelt et al.[42] reported that the amount of analyte absorbed on a PDMS fiber increased with volumetric flow rate, especially for high-molecular-weight chemicals. This indicates that diffusion into the fiber coating may be more efficient under flow conditions.

Interestingly, equilibration times for the other analytes using Car-PDMS were much longer under flow conditions. After 4 h under flow conditions, the detector signal for TMA and all of the sulfur compounds are beginning to plateau, but the signal for DMDS, the highest-molecular-weight analyte, continues to increase in a linear fashion (Figure 2). In addition, the detector signal for all of the chemicals for which the Car-PDMS fiber was used was also higher under flow conditions, as compared to static conditions, even though the gas standard concentrations were a factor of 3 times lower than the static experiments.

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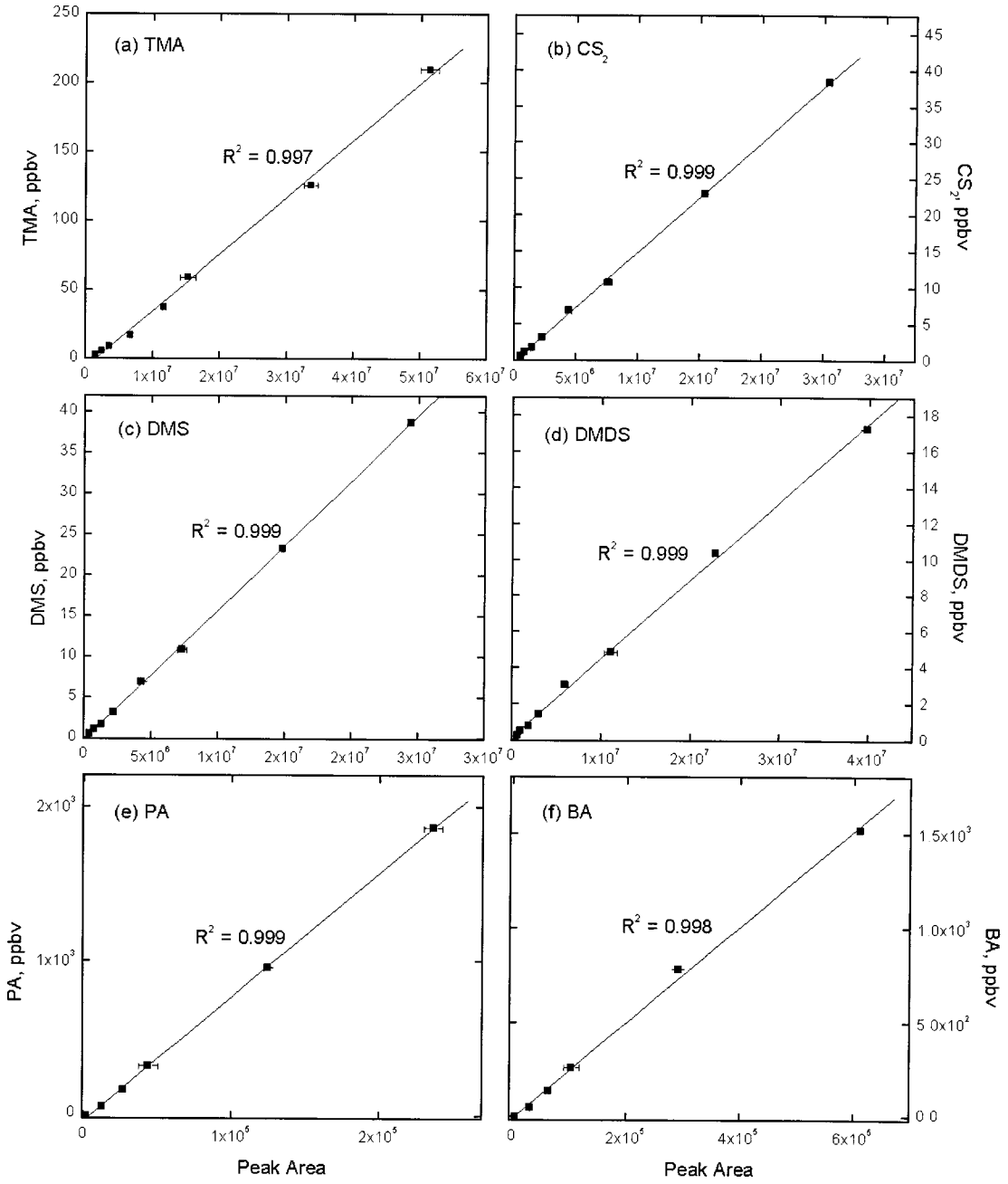


Figure 4. Calibration curves generated for target analytes.

Page et al.[43] recently described the relationship between extraction efficiency and porosity of the Car-PDMS fiber coating. Carboxen is porous in nature, whereas the conventional PDMS or polyacrylate coatings act as a liquid film.[44] Therefore, under flow conditions, analyte molecules may be able to penetrate further into the fiber pores, resulting in higher extraction efficiency and longer equilibration times. Initially, attempts were made to use Car-PDMS fibers for the volatile fatty acids in this study. The detector response was 2−3 times higher than with the polyacrylate (data not shown); however, the chromatographic retention times were unstable, the peak shapes were wide, and equilibration times were >4 h under flow conditions. Therefore, the carboxen-based fiber coatings do not behave in the same manner as the liquid polymer coatings and must be carefully calibrated.

**Effect of Flow Rate on Adsorption into Fiber Coating.** To further evaluate the effect of flow rate on adsorption into the fiber coating, a constant gas standard concentration was maintained while varying the flow rate through the Teflon chamber from 0 to 400 mL/min. SPME fibers were exposed to the gas standard for 1 h at each flow rate. The detector signal for the sulfur compounds increased 70−150% when the flow rate was raised from 0 to 50 mL/min (Figure 3). However, the increase for these chemicals is less dramatic in going from 50 to 400 mL/min, with the exception of DMDS, which increased another 27%. On the other hand, the detector signal increased only 10, 26, and 17% for PA, BA, and TMA, respectively. It appears that the influence of flow rate on adsorption is greatest for less volatile chemicals. This

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is a logical result, since those compounds with the slowest molecular diffusion rates (highest molecular weights) would be affected most dramatically by the reduction in static diffusion layer thickness.

**Competitive Adsorption.** Another factor to consider in the use of porous fiber coatings is the problem of competitive adsorption. Koziel et al.[33] described the replacement of low-molecular-weight molecules with heavier ones on the fiber surface in their study with benzene compounds. Page et al.[43] also reported the replacement of analytes, that is, volatile organics, with methanol in their study with carboxen PDMS fiber. During the calibration of the fiber coating, we carried out experiments to compare the mass adsorbed by the fiber when a single permeation device was placed in the permeation chamber versus all devices placed in the chamber together. There was no observable difference between the calibration curves produced from single devices versus combined conditions. These results indicate that competition between our analytes on the fiber coating is not a problem under the conditions used in the calibration. Limiting exposure times to 1 h versus equilibrium conditions may have prevented this effect from developing. More experiments under real world conditions are needed to determine if the exposure time should be reduced even further.

**Calibration Results.** Since equilibrium was not achievable in a reasonable time period for our analytes, an arbitrary fiber exposure time of 1 h was used for all analytes. And since flow-through conditions of >50 mL/min enhanced detector response, the base flow conditions for the Dynacalibrator (72 mL/min) were used for calibration of the SPME fibers. At low concentrations, excess diluted standard was vented to the bypass valve of the Dynacalibrator to maintain a constant flow rate through the Teflon chamber. Use of nonequilibrium conditions is commonly used for SPME analysis.[12,45] Accurate quantification still can be achieved as long as exposure time is exactly the same for standards and samples.

Resulting calibration curves were linear ($R^2 = 0.997 \sim 0.999$) (Figure 4) over the range of ~3.2−210 (TMA), 0.6−40 ($CS_2$), 0.6−39 (DMS), 0.3−18 (DMDS), 2−860 (PA), and 2−520 (BA) ppbv. $R^2$ for TMA was slightly lower than other compounds becaue of substantial tailing of the chromatographic peak. The method detection limits (MDL) for the compounds ranged from 0.063 ppbv for DMDS to 2.38 ppbv for TMA (Table 1). MDLs from this study are lower than published olfactory threshold values (Table 1)[22−29] except for TMA, indicating that this approach will be useful in measuring levels of chemicals at the limit of human perception.

Reproducibility with the same fiber and between fibers was measured to determine the error associated with the procedure. For polyacrylate, the average error between duplicate fibers was 5.4 (3.3−7.4)% ($n = 8$). The error produced from the same fiber was 4.9 (2.9−7.2)% ($n = 4$). For Car-PDMS, the average error between fibers was 3.7 (2.0−7.6)% ($n = 8$). The error from the same fiber was 2.9 (1.4−5.8)% ($n = 4$).

## CONCLUSIONS

Results of this study indicate that SPME can be a powerful tool for measuring low levels of reactive gases that cause an odor response in humans. This methodology can be expanded to include other key chemicals that can provide important information to scientists and managers as to the chemical processes occurring in a waste treatment system that might contribute to the perceived odor of their final product. However, special attention must be paid to the performance of the carboxen-based fiber coatings under flow conditions because of its porous nature. Competitive adsorption between analytes on the carboxen coating is also an important issue to investigate with various types of samples. Further experiments are needed to calibrate the fiber coatings under a range of temperature, humidity, and flow conditions so that accurate concentration measurements can be made under ambient conditions.

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