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Comparison of Solid-Phase Microextraction and Stir Bar Sorptive Extraction for the Quantification of Malodors in Wastewater

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Malodors in wastewater from animal-rearing facilities are due to the presence of characteristic polar compounds. The efficiency and reproducibility of three solid-phase microextraction (SPME) fibers (Carboxen−PDMS, polyacrylate, and PDMS) as well as PDMS-coated stir bars for the measurement of some of these compounds in the liquid phase were compared. In initial experiments, the SPME fibers and stir bars were exposed to a standard water solution containing a mixture of 18 compounds with a range of octanol−water partition coefficients. The polyacrylate SPME fibers and PDMS-coated stir bars, having been found to possess the best combination of extraction efficiency and reproducibility of measurement, were compared for the extraction of a high-strength swine wastewater. Ten compounds, which are known contributors to malodors in wastewater, were quantified by both methods of extraction. For most compounds, greater levels were estimated by the PDMS-coated stir bars than by SPME, and measurement reproducibility was also greater. For both methods of extraction, there was greater variation in the measurement of volatile fatty acids than there was for aromatics.

KEYWORDS: CAFOs; concentrated animal-feeding operations; octanol−water partition coefficient; SBSE; stir bar sorptive extraction; SPME; solid-phase microextraction; VFA; volatile fatty acids

INTRODUCTION

Emission of malodorous compounds from concentrated animal-feeding operations (CAFOs) is due to the anaerobic metabolism of amino acids (*1*, *2*), production of volatile fatty acids (VFA) by fermentation (*3*, *4*), and dissimilatory sulfate reduction (*5*). The majority of compounds produced by these processes are polar and, therefore, relatively water-soluble. Typical management in many CAFOs is to flush animal manure from the barns with large amounts of water. These liquid wastes are stored and treated in anaerobic pits or lagoons (*6*).

By measuring malodors in wastewater, data can be obtained to correlate factors such as temperature, humidity, and wind speed to emission rates and odor fluxes from wastewater. For instance, the U.S. Environmental Protection Agency is using measurements of volatile compounds in lagoon wastewater as an aid for developing emissions models from CAFOs (*7*).

A number of techniques have been employed for measuring volatile compounds in water, including solvent extraction (*8*), supercritical fluid extraction (*9*), and various solid-phase extraction techniques such as partitioning onto a porous polymer (*10*). Newer techniques include solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) (*11*, *12*). In SPME, a polymer-coated fiber is extended into a headspace or liquid sample and analytes are thermally desorbed in a GC injection port. The sample may or may not be stirred with a magnetic stir bar during sampling. SBSE is similar to SPME except that the polymer coating is placed over a glass-coated magnetic stir bar.

SPME is rapidly becoming a favored method for the quantification of volatile organic compounds in water. It is relatively inexpensive, and the wide variety of coatings available allows for optimization of sample extraction. However, the amount of extraction phase in SPME is generally only a few microliters or less, which can limit sensitivity. The amount of extraction phase in SBSE, on the other hand, is of the order of 50−250-fold greater than that of SPME, which presumably affords this technique greater extraction efficiency (*12*). However, only one phase is available as a coating: poly(dimethylsiloxane) (PDMS). The hydrophobic nature of this phase would seem to be a hindrance in attempts to quantify polar analytes.

The present study was undertaken to compare the relative extraction efficiency and reproducibility of SPME and SBSE. The following two evaluations were performed: First, three SPME phases (PDMS, Carboxen−PDMS, and polyacrylate) were compared with SBSE extractors by exposing both SPME and SBSE to a standard mixture of compounds varying in octanol−water partition coefficients and, second, extractions of a high-strength wastewater were performed using polyacrylate SPME fibers and SBSE.

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MATERIALS AND METHODS

Extraction Efficiency for Model Compounds. Standards of 18 compounds were chosen to provide a range of polarities as measured by their estimated octanol−water partition coefficients, k_{ow} (*13*). One-milliliter water samples were spiked with 2 μL of CH_2Cl_2 (log k_{ow} = 1.25) containing 100 ng each of benzyl alcohol, phenol, *p*-anisaldehyde, benzyl acetate, *p*-cresol, indole, methyl benzoate, *p*-ethylphenol, methyl salicylate, skatole, linalool, borneol, octanol, *p*-propylphenol, fenchone, geraniol, γ-terpinene, and limonene.

Three SPME fibers were exposed to the solutions: a PDMS fiber with a film thickness of 100 μm and polyacrylate and Carboxen−PDMS fibers, both with a film thickness of 85 μm (Sigma-Aldrich Inc., St. Louis, MO). Prior to first use, the PDMS fibers were thermally conditioned in the GC injection port as per the manufacturer's recommendations. During sampling, vial septa were pierced with the SPME sampler needle, and the fibers were extended into the water samples. The samples were extracted for 1 h at ambient temperature while being stirred at 500 rpm with a 1 cm Teflon-coated stir bar. The fibers were then desorbed in the GC inlet as described below.

Twister stir bars (10 mm × 3.2 mm) with a 1 mm thick PDMS coating (Gerstel Inc., Baltimore, MD) were preconditioned for 1 h at 250 °C under a stream of high-purity N_2. The stir bars/extractors were placed in the sample vials, the vials were closed, and wastewater was extracted for 1 h while being stirred at 500 rpm. After sampling, the Twisters were removed, rinsed with deionized water, blotted dry, and placed in 17.8 cm long by 4 mm i.d. thermal desorption tubes (Supelco Inc.) and desorbed as described below for wastewater analysis.

Extractions were repeated three times with separate fibers or stir bars to obtain mean recoveries and coefficients of variation (CV); that is, means divided by their standard deviation (SD). For each compound, recovery was expressed as the total ion current area integrated under the curve divided by the number of nanograms injected. Running averages of CVs for all four extractors were plotted versus log k_{ow} values using nearest-neighbor analysis with a sampling proportion of 0.3 (SigmaPlot for Windows, version 9.0, Systat Software, Richmond, CA).

Wastewater Samples. Samples were collected from an anaerobic pit that had been receiving waste for 6 months via the slatted floor of a 1200 pig finishing facility. On the day of collection, water within the pit was being stirred to facilitate sludge removal so that the waste could be applied to cropland by the use of subsurface injectors. Fifty-milliliter samples were placed in polypropylene centrifuge tubes and stored at 4 °C until analyzed. Water analyses were performed according to standard methods (*14*). Carbon and nitrogen analyses were performed on an Elementar Vario Max carbon−nitrogen analyzer (Elementar USA, Mt. Laurel, NJ), and other elemental analysis was performed by inductively coupled plasma spectrometry (ICP) on a Varian Vista-Pro ICP-OES after microwave digestion of a sample at 175 °C for 10 min.

Gas chromatography−mass spectroscopy (GC-MS) was performed on a Varian Saturn 2200 ion trap interfaced to a Varian model 3800 gas chromatograph (Varian Associates, Palo Alto, CA). For measuring the extraction efficiency of model compounds with a range of k_{ow} values, compound separation was performed on a 30 m × 0.25 mm Rtx-35 MS column (35% diphenyl−65% poly(dimethylsiloxane), Restek Corp., Bellefonte PA) with a film thickness of 0.25 μm. GC operating conditions were as follows: He carrier constant flow rate, 1 mL min^{-1}; column oven, 55 °C for 1 min, then programmed at 7 °C min^{-1} to 100 °C, and hence at 15 °C min^{-1} to 295 °C and held for 10 min; transfer line temperature, 300 °C. The mass spectrometer was run in electron ionization mode with an emission current of 10 μA using a scan time of 0.35 s per scan and a scan range of 45 to 225 amu. For SPME analyses, injections were performed in splitless mode for 2 min. with an injector temperature of 260 °C. For SBSE analyses, the stir bars were placed in thermal desorption tubes and placed in a model TDSA thermal desorption system (Gerstel Inc.). The stir bars were desorbed in splitless mode using an initial temperature of 25 °C with a delay time of 0.25 min and then heated at 60 °C min^{-1} to 225 °C with a final time of 3 min. Desorbed volatiles were transferred by a heated transfer line maintained at 240 °C to a glass wool packed injection liner maintained at −50 °C with liquid CO_2. After 5 min, compounds were transferred to the capillary column with a 20:1 split ratio by heating the injection liner at 10 °C min^{-1} to 300 °C with a final time of 3 min.

For analysis of the wastewater samples, compound separation was performed on a 30 m × 0.25 mm VF-23MS column (50% cyanopropylmethylpolysiloxane) with a film thickness of 0.25 μm (Varian Inc.). GC operating conditions were the same as above, except that the column oven temperature was maintained at 40 °C for 2 min and then programmed at 2 °C min^{-1} to 115 °C and then at 15 °C min^{-1} to 250 °C and held for 10 min.

Odor compounds in the wastewater were quantified by injection of external standards of authentic compounds (Sigma-Aldrich Inc.) extracted from water at the same pH as the wastewater samples. For each odor compound in the wastewater, quantitation was based on its most prominent ion, whereas identification was based on computer matching of spectra. SPME and SBSE analyses were performed four times to obtain mean values for each compound.

Statistical Analyses. Tests of significance for correlations of compound yield versus log k_{ow} values were performed by analysis of variance using PROC MIXED in the Statistical Analysis System for Windows (*15*), whereas Pearson correlation coefficients were calculated in PROC CORR using mean values calculated in PROC SUMMARY.

RESULTS AND DISCUSSION

Extraction Efficiency for Model Compounds. The relative amounts of compounds collected on the three SPME fibers and PDMS stir bars are presented in **Table 1** along with the compounds' log k_{ow} values. There were, as expected, considerable differences between the different extractors' ability to retain detectable quantities of all 18 of the compounds contained in this standard mixture, for which estimated log k_{ow} values ranged from 1.05 (benzyl alcohol) through 4.57 (limonene). However, the Carboxen−PDMS and polyacrylate SPME phases were able to retain small but detectable amounts of the polar analytes benzyl alcohol and phenol that the PDMS SPME and SBSE phases were not. As expected, the PDMS SPME phase was unsuitable for analysis of polar analytes and did not retain appreciable amounts of any analytes with a log k_{ow} value of $\leq$1.96. On the other hand, the performance of the PDMS stir bars compared favorably to that of the polar SPME fibers at log k_{ow} values >1.50.

In these analyses, SPME fibers were desorbed in the injector in splitless mode, whereas the stir bars were transferred from the thermal desorption unit in splitless mode and from the cooled injector with a 20:1 split to accomplish the transition from the high flow rate of the thermal desorption unit to the low flow rate required by the capillary column. This complicates comparison of the relative response of SPME fibers and the stir bars. Furthermore, no attempt was made to account for relative detector response to the structurally diverse compounds in the standard mixture. However, given these limitations, some key observations were made about the amounts of analyte retained by each extractor as well as the reproducibility of extraction.

First, the amount of analyte retained by each of the four extractors tended to correlate with octanol−water partition coefficients despite the fact that no corrections were made for relative detector responses and that the compounds contained in the standard mixture were structurally diverse. For all extractors, the best correlations were obtained by log−log transformation of compound yield and k_{ow} (**Table 2**). This trend was strongest for the PDMS fiber (r = 0.98), but was also relatively strong for silicone stir bars (r = 0.70) and polyacrylate fibers (r = 0.67). The Carboxen−PDMS fibers did not show a strong correlation between log k_{ow} values and compound yields. This may be due to their biphasic adsorption matrix and

Table 1. Log k_{ow} and Relative Amount of Compounds Retained by SPME Fibers and SBSE Normalized to 100 for the Most Efficient Extractor

		integrated area per nanogram[a] with extractor			
compound	log(K_{ow})	Carboxen–PDMS SPME	polyacrylate SPME	PDMS SPME	PDMS SBSE
benzyl alcohol	1.05	9 ± 10 a	9 ± 7 a	nd[b]	nd
phenol	1.50	52 ± 57 a	17 ± 2 a	nd	nd
p-anisaldehyde	1.65	1150 ± 514 a	224 ± 25 b	nd	997 ± 193 a
benzyl acetate	1.96	2138 ± 532 a	386 ± 63 b	125 ± 107 b	2520 ± 390 a
p-cresol	1.97	441 ± 243 a	184 ± 47 ab	nd	14 ± 3 b
indole	2.14	922 ± 257 ab	1389 ± 579 a	39 ± 27 c	668 ± 71 b
methyl benzoate	2.20	3353 ± 741 a	571 ± 55 b	201 ± 154 b	2800 ± 150 a
p-ethylphenol	2.50	704 ± 364 a	493 ± 200 a	nd	227 ± 108 a
methyl salicylate	2.55	2675 ± 283 b	1045 ± 10 c	321 ± 235 d	3741 ± 311 a
skatole	2.60	1164 ± 307 c	3249 ± 910 a	277 ± 114 c	2297 ± 172 b
linalool	2.97	704 ± 231 b	303 ± 77 c	120 ± 103 c	1731 ± 95 a
borneol	3.01	126 ± 128 bc	434 ± 35 b	63 ± 54 c	1823 ± 310 a
octanol	3.07	24 ± 41 b	264 ± 79 b	nd	823 ± 279 a
p-propylphenol	3.20	1311 ± 467 a	854 ± 1063 a	nd	1279 ± 272 a
fenchone	3.52	671 ± 162 b	299 ± 12 b	436 ± 146 b	3409 ± 599 a
geraniol	3.56	217 ± 111 b	344 ± 77 b	26 ± 35 b	1320 ± 333 a
γ-terpinene	4.36	1832 ± 2395 b	3111 ± 285 ab	4354 ± 651 a	4888 ± 682 a
limonene	4.57	2281 ± 2395 a	2555 ± 341 a	3764 ± 515 a	3136 ± 486 a

[a] Data represent the average of three determinations ± standard deviation. [b] Compound not detected.

Table 2. Effect of k_{ow} Values on Extraction Efficiencies of Three SPME Fibers and Stir Bar Sorptive Extractors[a]

extractor	*F* value	Pr > *F*	Pearson correlation coefficient
Carboxen–PDMS SPME	2.93	0.1054	0.35
polyacrylate SPME	14.42	0.0014	0.67
PDMS SPME	723.8	<0.0001	0.98
PDMS SBSE	16.10	0.0009	0.70

[a] Correlation coefficients were obtained by log–log transformation of compound yield versus k_{ow}.

competing modes of adsorption. This fiber has been shown to give good estimates of k_{ow} values for compounds with k_{ow} values <3.5 (*16*).

Although there have been a number of studies that have correlated partitioning on SPME fibers and k_{ow} values in a more critical manner (*16*, *17*), it was found that adding structurally diverse analytes with a selected range of k_{ow} values to water served as a convenient guide for the selection of an appropriate extraction phase. Of the extractors used, both of the two polar SPME phases performed reasonably well over a broad polarity range and especially well at log k_{ow} values <3.0. Furthermore, the performance of SBSE was comparable to that of the polar SPME fibers except for the analysis of benzyl alcohol, phenol, and *p*-cresol.

A particularly important observation was that the four extractors showed considerable differences in extraction reproducibility as represented by the running averages of their coefficients of variation (**Figure 1**). Of the SPME fibers, the polyacrylate phase showed the most reproducibility, having an average CV of 27.7%, whereas average CVs of the Carboxen−PDMS and PDMS fibers were over 63.1 and 64.9%, respectively. SBSE had the least variability with an average CV of 17.9%. Interestingly, the plots of average CV for all four extractors were similar, showing less variation in a log k_{ow} range of roughly 1.5−3.0 and more variability in the range of 3.0−4.0.

Extractions were done with three separate SPME fibers or stir bars from a single lot for the determination of each mean in order to gain an appreciation of the inherent variation that might be encountered when needs dictate changing extractors. For automated SPME, a single extractor is used until fiber breakage occurs or loss of fiber performance is noted. For typical automated SBSE, on the other hand, a series of stir bars are used. From the viewpoint of reproducibility, the best extractors used in the present study were polyacrylate SPME and SBSE.

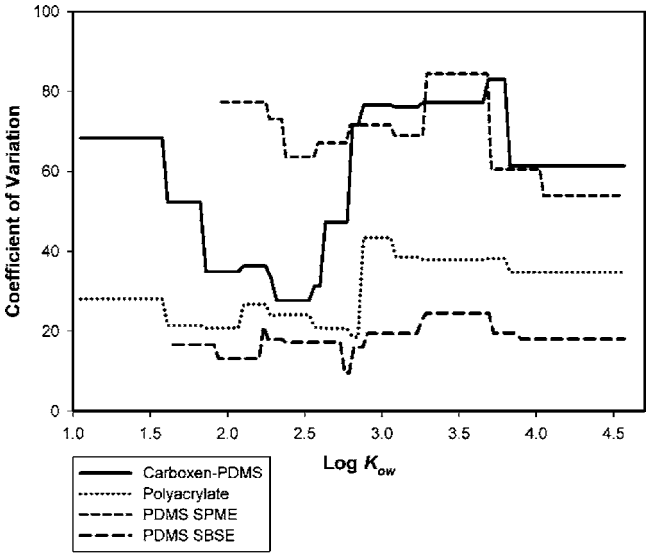

Figure 1. Smoothed running averages of coefficients of variation for SPME extractors and SBSE as a function of octanol–water partition coefficients.

Table 3. Characteristics of Wastewater from Swine Housing Anaerobic Pit

characteristic	value	characteristic	value
pH	7.78	sodium	956 mg L^{-1}
total solids	34 g L^{-1}	phosphorus	1370 mg L^{-1}
total suspended solids	18.8 g L^{-1}	potassium	3980 mg L^{-1}
carbon	22 g L^{-1}	iron	81.7 mg L^{-1}
nitrogen	4.3 g L^{-1}	copper	24.2 mg L^{-1}
calcium	826 mg L^{-1}	sulfur	404 mg L^{-1}
magnesium	526 mg L^{-1}		

Wastewater Analyses. Characteristics of the wastewater obtained from the swine anaerobic pit are shown in **Table 3**. The water had a pH of 7.78, total suspended solids of 18.8 g L^{-1}, and total solids content of 34 g L^{-1}. High levels of plant nutrients were present in the water, with phosphorus occurring at >1300 mg L^{-1} and potassium at almost 4000 mg L^{-1}. The

Table 4. Levels of Malodorous Compounds in a Model Wastewater As Measured by Polyacrylate SPME Fibers and PDMS Stir Bars

compound	compound yield[a] (ng mL^{-1}) with extractor	
	polyacrylate SPME	PDMS SBSE
aromatics		
phenol	3250 ± 123	1990 ± 31.0
p-cresol	32000 ± 2620	135000 ± 412
p-ethylphenol	6050 ± 152	12500 ± 135
p-propylphenol	22.0 ± 1.5	36.8 ± 0.6
indole	759 ± 41.1	837 ± 17.8
skatole	3720 ± 182	9920 ± 66.4
volatile fatty acids		
butanoic acid	18700 ± 5830	173000 ± 15500
2-methylpropanoic acid	40200 ± 4270	28200 ± 4130
3-methylbutanoic acid	51000 ± 1940	36100 ± 12100
hexanoic acid	9540 ± 7740	nd[b]

[a] Data represent the mean of four determinations ± standard error of the mean. [b] Compound not detected.

level of most elements were in the range found in the sludge portion of a wastewater in an anaerobic pit studied by Zahn et al. (*9*), so the wastewater might more properly be described as a sludge.

Malodors from wastewater are complex mixtures of compounds that arise from the anaerobic degradation of wastes by diverse microbial populations (*1*−*5*). Because the characteristic odorants of animal wastes tend to be polar, a more polar chromatographic phase than the Rtx-35MS column was desirable to improve chromatographic performance. Whereas Carbowax-type columns are generally preferred for the analysis of polar compounds, and in particular VFA (*18*), a cyanopropyl-modified column (VF-23MS) was chosen because this column exhibits lower bleed than cross-linked poly(ethylene glycol) columns and was the highest polarity GC-MS phase available from the manufacturer.

The VF-23MS column proved to be superior to the nonpolar column for the analysis of wastewater odor compounds. Although VFA exhibited considerable fronting on the Rtx-35MS column, which rendered quantification problematic, on the cyanopropylmethylpolysiloxane column, VFA peaks exhibited less fronting and greater spectral integrity. In addition to VFA, six aromatic compounds with strong malodors were also quantified.

Quantification of Malodors. The results of quantification are presented in **Table 4**. In general, for the aromatics, both methods were relatively reproducible, having standard errors of <10% that of the mean, although standard errors were less for SBSE than for SPME analysis. However, SBSE estimated higher levels for all aromatics except phenol. SPME and SBSE are often used as equilibrium samplers; that is, upon reaching equilibrium, the rate that analytes are lost from the sampler is equal to the rate at which they are gained. At equilibrium, therefore, the amount of analyte adsorbed by the sampler is proportional to that amount contained in the liquid and gaseous phases, as well as the amount sorbed to solid matter (*19*). SBSE, by virtue of its greater amount of extraction phase, may effectively compete for more analyte than does SPME. For both methods, therefore, a suitable matrix needs development for calibration that effectively mimics the partitioning found in environmental samples.

Five VFA were detected in the samples. Of these, however, propanoic acid was not quantified due to the presence of an interfering compound that hindered quantitation. For polyacrylate SPME, high levels of all VFA were estimated, with 3-methylbutanoic acid occurring at >50 μg mL^{-1}. Standard errors were high for butanoate and hexanoate, being 31 and 81% of the mean. The standard error of measurement for 3-methylbutanoate was only 3.8% of the mean, however.

For SBSE, an interfering peak also hampered quantitation of propanoic acid and no hexanoic acid was detected in the samples. For 2-methylpropanoate and 3-methylpropanoate, the results obtained by SPME and SBSE were in reasonable agreement. For butanoic acid, however, levels were estimated at almost 10-fold that of SPME. It is possible that, as for the aromatics, the greater amount of extraction phase present in SBSE facilitates extraction of this compound. At the alkaline pH of the wastewater (7.78), however, I feel that neither SPME nor SBSE is capable of rendering more than semiquantitative results for VFA. At low pH (<5.0) quantitation of VFA is improved considerably for both SPME and SBSE (data not shown). Of course, sample dilution to lower pH, even with a strong mineral acid, will also affect the analyte equilibrium with solids, water, and sample headspace, and so will influence quantitation.

The levels of acids and aromatics measured in the present study are comparable to those found by Zahn et al. (*9*) in a swine waste anaerobic pit as measured by SPME using a Carbowax/divinylbenzene fiber. In general, they estimated higher levels of VFA than were found in the present study, especially in the case of butanoate (106 000 ng mL^{-1}). In addition, using this SPME fiber Zahn et al. were able to quantify acetic acid in their samples. The pH of their samples was considerably lower (7.2), which may have facilitated extraction of the VFA. On the other hand, the levels of aromatics found in that study are quite comparable to those found here. Zahn et al. did not present standard errors for their measurements of volatile compounds in wastewater.

No volatile sulfides were extracted from the wastewater samples by either the polyacrylate fibers or PDMS stir bars, although these compounds are often important contributors to fecal malodor (*5*, *9*). Hydrogen sulfide is undoubtedly too volatile to be measured by SPME, but higher molecular weight compounds such as dimethyl sulfide and dimethyl disulfide should be detected (*9*). Interestingly, however, a peak corresponding to elemental octacyclic sulfur was detected in the SBSE analyses. This may, even in the oxygen-limited environment of the pit, indicate activity of chemoautotrophic bacteria such as *Thiobacillus*, which oxidize sulfide ions to elemental sulfur (*20*). More likely, however, sulfides were lost in the wastewater by volatilization and oxidation that occurred as the pit was being agitated and pumped out prior to land application.

Although it has been suggested that SBSE affords greater sensitivity for analysis that does SPME (*11*, *12*, *21*), the necessity of performing split injections onto the capillary mass spectroscopy column negates quite a bit of this advantage because SPME injections can be performed in splitless mode. In the present work, it appears that the greater amount of extraction phase in SBSE may serve as an advantage in competing with the sample matrix for analyte. Furthermore, measurement reproducibility is higher in SBSE than in SPME.

In conclusion, either a polyacrylate or Carboxen−PDMS SPME fiber is suitable for analysis of polar compounds in wastewater, but the polyacrylate phase generates more reproducible results. For the analysis of polar aromatics, SBSE affords more reproducible results than does SPME. For the analysis of VFA at high pH, neither SPME nor SBSE appears to be capable of providing more than semiquantitative results.

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