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Short communication

Use of solid-phase microextraction to detect and quantify gas-phase dicarbonyls in indoor environments

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Abstract

Solid-phase microextraction (SPME) was evaluated for the detection and quantification of the gas-phase dicarbonyls, glyoxal (GLY) and methylglyoxal (MGLY). Additionally, polydimethylsiloxane (PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), and carbowax/divinylbenzene (CW/DVB) fibers were tested to determine the optimum fiber for detection of these species. GLY and MGLY were derivatized with *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA), extracted with SPME from headspace or bag chamber and then analyzed by GC/MS. The PDMS/DVB SPME fiber for on-fiber derivatization and subsequent sampling for gas-phase methylglyoxal provided the optimum combination of analytical reproducibility and sensitivity. Linearity of the calibration curve was achieved across a range of 11–222 μg/m^3 (4–75 ppb).
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Keywords: Solid-phase microextraction; Derivatization; PFBHA; Dicarbonyls; Glyoxal; Methylglyoxal

1. Introduction

There is a need for new analytical techniques to measure the products of indoor chemistry that are short lived, highly reactive, thermally labile, or highly oxidized—"stealth chemicals" [1]. These "stealth chemicals" can be present in indoor environments when initiator species such as O_3 (ozone), for example, react with volatile organics compounds (VOCs) to form oxygenated organic compounds such as aldehydes, ketones, and dicarbonyls. In a recent paper by Jarvis et al., chemicals with carbonyl substructures (especially when the functional group was present twice or more in the same molecule) were associated with the potential to cause work-related asthma [2,3]. To characterize the indoor environment, industrial hygienists, for example, require analytical techniques that can adequately sample these species. Sampling and detecting the various carbonyl compounds in the indoor environment is an essential step to assessing health impacts [4]. Glyoxal and methylglyoxal are difficult to sample and detect due to their polarity and highly reactive nature. The greater the polarity of a compound; the more arduous it becomes to detect using direct GC analysis. Additionally, polar analytes are not suitable for thermal desorption-GC analysis [4]. In separation sciences, derivatization is used to improve the chromatographic properties and/or the sensitivity of the detection [5] and has other advantages that include: (1) providing analyte specificity based on key functional groups, (2) allowing detection with conventional detectors, and (3) acting as a method for conformation that the compound of interest is present in the sample [6]. An established method for detecting carbonyl compounds is to react them with *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) to form oximes which are then analyzed by GC with MS detection [7–12]. Solid-phase microextraction (SPME) with on-fiber derivatization supports the feasibility of coupling on-sorbent derivatization and subsequent sampling with thermal desorption anaylsis [4]. Martos and Pawliszyn have demonstrated that the combination of on-fiber derivatization and thermal desorption is a sensitive technique to sample and analyze airborne polar analytes [6]. More recently, gas-phase atmospheric research has effectively demonstrated the use of SPME fibers pre-coated with PFBHA for on-fiber derivatization of carbonyl-containing compounds [8,13].

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SPME is an extraction technology that combines sampling and sample preparation. Since conception, SPME has been widely used for research applications in pharmaceutical, food, fragrance, forensic, environmental and physicochemical areas [14]. Conventional air-sampling methods use sorbent tubes, impingers, vacuum canisters, gravimetric filters, pumps, and light scattering devices [15]. Many of these methods require considerable sampling expertise and costly equipment, lengthy sample collection and preparation periods, and complicated cleaning and extraction procedures [16]. SPME offers many advantages for air sampling and some of these are: high precision and sensitivity, wide range of sampling times, applicability to a wide range of compounds, reusability, possibility of automation, solventless extraction, and compatibility with conventional analytical equipment [14]. The primary objective of this research is to determine the potential for using PFBHA-loaded SPME fibers for detecting and quantifying glyoxal and methylglyoxal in the indoor environment.

2. Experimental

2.1. Reagents

The following reagents were used as received from Sigma-Aldrich (St. Louis, MO) and had the following purities: methylglyoxal (MGLY) 40% aqueous solution, glyoxal (GLY) 40% aqueous solution, and *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride 98+%. The reagent water was distilled and deionized to resisitivity of 18 MΩ cm, and filtered using a Milli-Q filter system (Billerica, MA). Compressed air from the National Institute for Occupational Safety and Health (NIOSH) facility was passed through anhydrous $CaSO_4$ (Drierite, Xenia, OH) and molecular sieves (Drierite, Xenia, OH) to remove both moisture and organic contaminants. This dry compressed air was added as a diluent to the reaction chambers and measured with a 0–100 L min^{-1} mass flow controller (MKS, Andover, MA). Analysis of this treated compressed air by gas chromatography/mass spectrometry revealed that if contaminants were present they would be below the parts per trillion range. Helium (UHP grade), the carrier gas, was supplied by Amerigas (Sabraton, WV, USA). Experiments were carried out at (297 ± 3 K) and 1 atm.

2.2. Apparatus and materials

The following SPME fibers mounted in a manual syringe holder were obtained from Supelco (Bellefonte, PA): a 100-μm film thickness Polydimethylsiloxane (PDMS) coated fiber; a 65-μm film thickness polydimethylsiloxane/divinylbenzene (PDMS/DVB) coated fiber; a 65-μm film thickness Carbowax/Divinylbenzene (CW/DVB 65 μm) coated fiber; and a Stable Flex 70-μm film thickness (CW/DVB 70 μm) coated fiber. The fibers were conditioned using a two-channel SPME conditioner: Model CN 301 Conditioner 2× by Field Forensics (St. Petersburg, FL, USA) according to manufacturer's recommendations prior to experimental use.

The PFBHA derivatized oximes of the dicarbonyl compounds were analyzed using a Hewlett-Packard (HP) 5890 gas chromatograph with a 5972 mass selective detector (GC/MS) and HP Chemstation software. The MS scan parameters were set to a range of 25–550 (*m*/*z*) and the acquisition mode was TIC. The SPME fibers/holders were inserted at a depth of 2.5 on the holder into the heated injection port equipped with a Merlin Microseal septum purchased from Alltech Associates (Deerfield, IL, USA). Compound separation was achieved by a J&W Scientific (Folsom, CA) DB-5MS (30 m × 0.25 mm I.D., 1 μm film thickness) column and the following GC parameters: injection port was set to 250 °C, and oven temperature began at 40 °C for 6 min and ramped 10 °C min^{-1} to 260 °C and held for 3 min. The chambers used in this study were constructed at the NIOSH facility and made of 5-mil fluorinated ethylene propylene copolymer (FEP) Teflon-film. The chambers, which varied in size between 90 and 95 L, were cleaned before each new concentration by utilizing six cleaning cycles. Each cycle consists of evacuating the chamber by a NIOSH facility house vacuum and then filling the chamber with treated air as described above.

2.3. Derivatization and SPME procedures

2.3.1. PFBHA-fiber saturation optimization

Optimization of PFBHA saturation of fibers was determined using the PDMS/DVB fiber. The aqueous PFBHA solution (0.2 mM) was shaken vigorously for 15 s before each and every exposure to ensure regeneration of the PFBHA headspace concentration. Care was taken to avoid immersion of the fiber in the liquid. The fiber was exposed to the headspace of the PFBHA solution for 5, 15, and 30 min exposure times. The fiber-PFBHA exposure concentration level was determined by the PFBHA chromatographic peak areas at a retention time of 17.38 min. Each fiber exposure time experiment was duplicated.

2.3.2. GLY/MGLY mixture saturation optimization

The headspace of 0.5 ml of the 4% aqueous GLY/MGLY solution was sampled with a PFBHA saturated PDMS/DVB fiber for the following exposure times: 30 s, 1, 2, 3, and 4 min. The optimum dicarbonyl sampling time was determined by evaluating the chromatographic peak areas at retention times: 18.54, 18.92, and 19.03 min for PFBHA-GLY and 20.24, 20.44, and 28.77 min for PFBHA-MGLY. Each saturation experiment was duplicated.

2.3.3. Selection of SPME fiber for quantifying derivatized dicarbonyls

Determination of the optimum SPME fiber for detection and quantification of the derivatized oximes was achieved by comparing the oxime chromatographic peak areas at the retention times previously mentioned for GLY and MGLY using four different SPME fibers: PDMS; PDMS/DVB; CW/DVB (65 μm); and CW/DVB (70 μm). After conditioning, each fiber was exposed 15 min to PFBHA aqueous solution headspace followed immediately by a 2 min exposure of the 4% GLY/MGLY aqueous solution headspace. Immediately following the exposure each fiber was desorbed on the HP GC/MS system using the

parameters described above. Each fiber was exposed six separate times to check for sampling variability.

2.3.4. Identification of peaks at lower GLY/MGLY headspace concentration

A PFBHA saturated PDMS/DVB fiber was exposed 10 separate times to a 0.4% aqueous solution of GLY/MGLY and desorbed on the GC/MS system. Three oxime peaks were chosen to identify and quantify PFBHA-GLY (18.54, 18.92, and 19.03 min) along with five other peaks (20.24, 20.44, 28.40, 28.57, and 28.77 min) which were chosen to identify and quantify PFBHA-MGLY.

2.3.5. Chamber saturation optimization of PFBHA-fiber with GLY/MGLY solution

In order to simulate sampling in an indoor air environment, a 90 L Teflon-film chamber was prepared with 264 μg/m^3 (111 ppb) GLY and 264 μg/m^3 (90 ppb) MGLY in air. The preparations of the standard gases for this study were achieved by injecting aliquots of a 0.4% GLY/MGLY solution into a chamber via a heated injection port that was inline with the treated diluent air line mentioned and described in Section 2.1. Optimization of GLY/MGLY saturation time was determined by exposing a PFBHA saturated PDMS/DVB SPME fiber to the GLY/MGLY chamber concentration for time periods of 10, 30, 60, 120, and 180 min.

2.3.6. Calibration curve creation

In order to determine if the SPME sampling method would be useful for sampling dicarbonyl compounds in an indoor work environment, a calibration curve was created for PFBHA-MGLY using five concentration points: 11, 31, 67, 160 and 222 μg/m^3 (4, 11, 23, 54, and 75 ppb). A 90 L Teflon bag with two ports was used for each of the five concentrations. Two PFBHA saturated PDMS/DVB SPME fibers were exposed simultaneously therefore each fiber was sampled twice for each concentration for a total of four samples per concentration. In reference to a sampled pair, one of the fibers was desorbed on the HP GC/MS system immediately after exposure while the other fiber was desorbed 30 min after exposure to check for potential oxime loss.

3. Results and discussion

3.1. Derivatization and SPME procedures

3.1.1. PFBHA-fiber saturation optimization

An optimum PFBHA loading time ensured that the maximum amount of PFBHA derivatizing agent could be adsorbed onto the fiber while minimizing the PFBHA exposure time. The saturated level of PFBHA adsorbed on the SPME fiber was necessary to ensure that there was a sufficient amount of PFBHA available to derivatize the sampled dicarbonyls. A 15 min fiber exposure time produced 91% of the maximum PFBHA-fiber loading while keeping the exposure time to a minimum. Therefore, all subsequent PFBHA-fiber loading exposures were 15 min.

3.1.2. GLY/MGLY mixture saturation optimization

There were a total of 4 PFBHA-GLY peaks (retention times of 18.54, 18.92, 19.03 and 28.30 min) and eight PFBHA-MGLY peaks (retention times of 20.13, 20.24, 20.33, 20.44, 27.92, 28.40, 28.57, and 28.77 min) that could have been used to

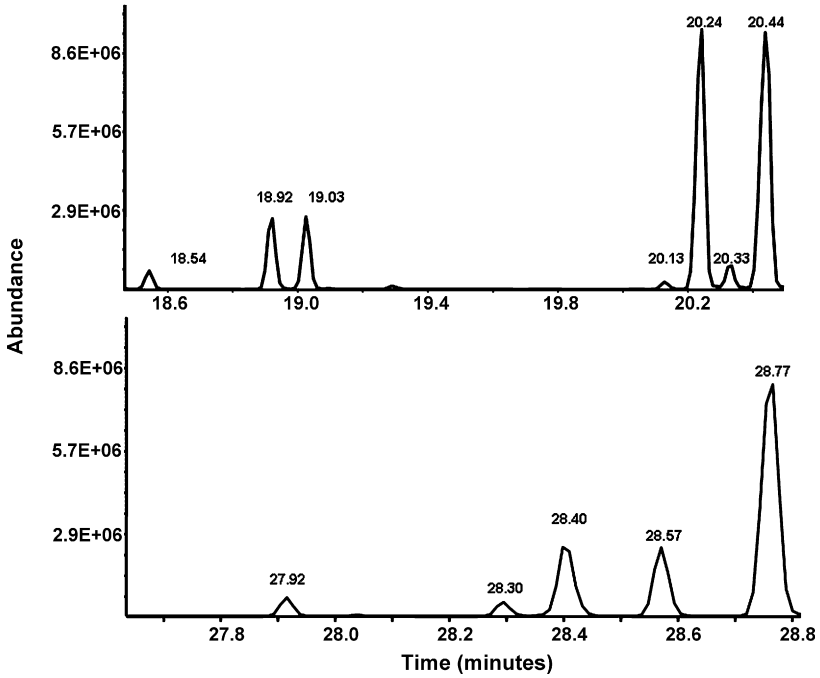

Fig. 1. Chromatogram showing resolved peaks of the PFBHA derivatives for GLY (single derivatized at 18.54, 18.92, and 19.03 min; double derivatized at 28.30 min) and MGLY (single derivatized at 20.13, 20.24, 20.33, and 20.44 min; double derivatized at 27.92, 28.40, 28.57, and 28.77 min).

evaluate saturation optimization. With respect to GLY, the peaks at 18.54, 18.92, and 19.03 min are singly derivatized PFBHA-GLY (*m/z* 181 and 253) while the peak at 28.30 min was a doubly derivatized PFBHA-GLY (*m/z* 181 and 448). Singly derivatized PFBHA-MGLY peaks were at retention times 20.13, 20.24, 20.33, and 20.44 min (*m/z* 181 and 267) and doubly derivatized PFBHA-MGLY peaks were at 27.92, 28.40, 28.57, and 28.77 min (*m/z* 181 and 462). All of the PFBHA-GLY and PFBHA-MGLY derivative peaks were baseline resolved and exhibited good peak shapes (Fig. 1). The GLY saturation curves show that the PFBHA-GLY signal reached a maximum at a 30 s exposure time and did not significantly change for exposure times up to 4 min. The result for the MGLY curves show that a headspace saturation exposure time of 2 min would allow maximum saturation for all peaks observed.

3.1.3. Selection of best SPME fiber for quantifying derivatized carbonyls

Fig. 2A–C show the performance of each of the four fibers for three of the largest GLY chromatographic peak responses, while Fig. 3A–C show the same for the three largest MGLY peak responses. All graphs in Figs. 2 and 3 are on the same scale. Since the PDMS/DVB SPME fiber exhibited the best reproducibility and sufficient signal response for both PFBHA-GLY and PFBHA-MGLY it was selected as the optimum fiber for this investigation.

3.1.4. Chamber saturation optimization of PFBHA-fiber with GLY/MGLY solution

The resulting chromatographic peak areas for the three identifying peaks for PFBHA-GLY (18.54, 18.92, and 19.03 min) were less than three times the noise level. The highest PFBHA-GLY signal response (peak at 18.54 min for a 180 min exposure) was 12% of the response of the lowest PFBHA-MGLY signal response (peak at 28.57 min for 10 min exposure). Since the PFBHA-GLY signal responses were so low in comparison to PFBHA-MGLY responses the optimization of saturation time in the chamber could only be achieved by focusing on PFBHA-MGLY results. The results showed that 120 min was the optimum time for PFBHA-MGLY saturation on the fiber using the identifying peaks for PFBHA-MGLY at retention times of 20.24, 20.44, 28.40, 28.57, and 28.77 min.

3.1.5. Calibration curve creation

Fig. 4 shows two of the five calibration curves which were created for PFBHA-MGLY, one for each of the five identifying peak retention times. Four exposures were conducted at each of the five concentration levels. The average of the four exposures was used in creating each of the points at the five concentrations: 11, 31, 67, 160 and 222 μg/m^3 (4, 11, 23, 54, and 75 ppb). Error bars on the graph represent the average %RSD which was 17.7% for curve at 28.77 min and 21.7% for curve at 28.57 min. The results for the curves at 20.24, 20.44, and 28.40 min, not shown on the graph, are 36.1, 23.8, and 17.6 %RSD, respectively.

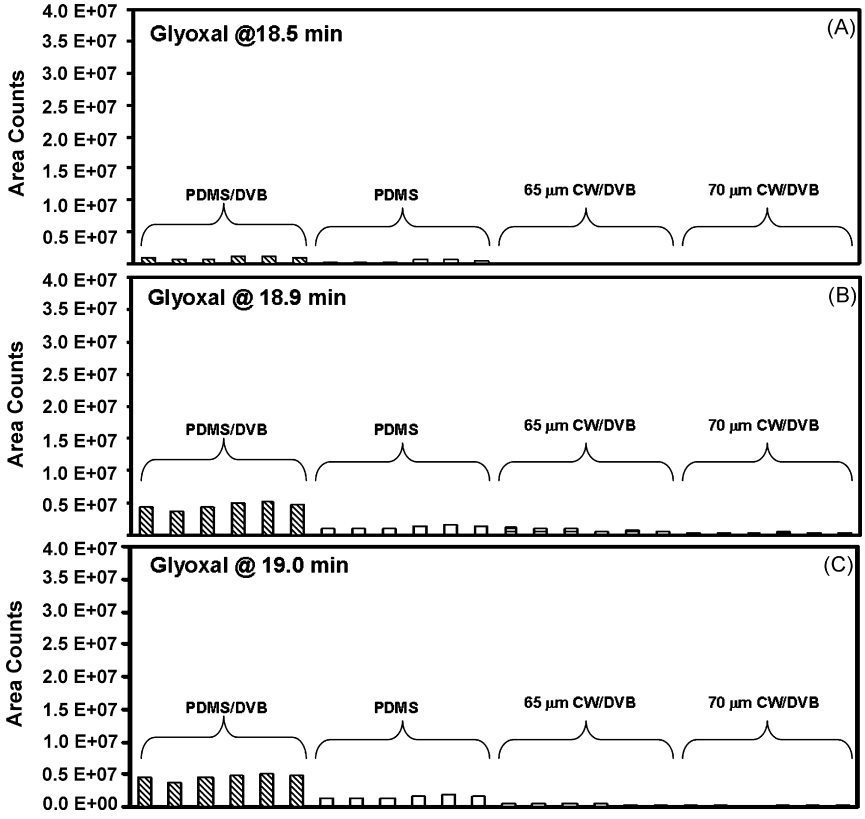

Fig. 2. Comparison of SPME fibers for optimum SPME fiber selection using PFBHA-GLY chromatographic signal responses at 18.54, 18.92, and 19.03 min. No response for 65 μm CW/DVB or 70 μm CW/DVB at 18.54 min was noted. Note: All figures are on the same scale.

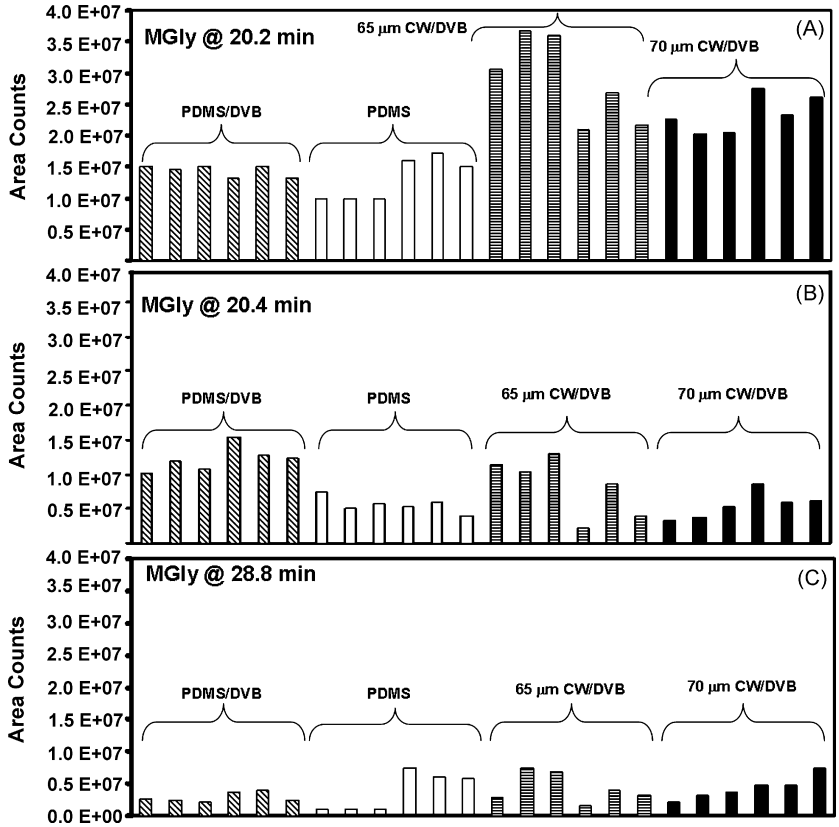

Fig. 3. Comparison of SPME fibers for optimum SPME fiber selection using PFBHA-MGLY chromatographic signal responses at 20.24, 20.44, and 28.77 min. Note: All figures are on the same scale.

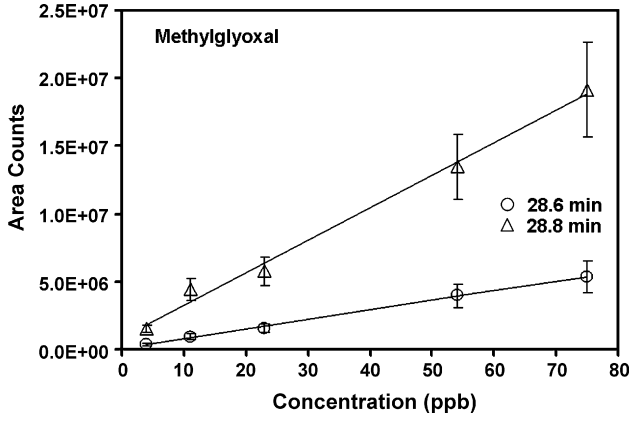

Fig. 4. MGLY calibration curve for the five identifying peaks. The curve at 28.6 min was very similar to the data collected for curves at 20.2, 20.4, and 28.4 min. These curves were omitted for clarity. Error bars represent average RSD; 17.7% for curve at 28.8 min and 21.7% for curve at 28.6 min.

4. Conclusion

There is great potential for the use of PFBHA-loaded SPME fibers for detecting and quantifying gas-phase dicarbonyls, particularly MGLY, in indoor air environments. The results of this study show that using the PDMS/DVB SPME fiber for on-fiber derivatization and subsequent sampling for MGLY provides a good combination of analytical reproducibility and sensitivity. Linearity of the calibration curve was achieved across a range of 11–222 $\mu g/m^3$ (4–75 ppb). The results obtained by using the PDMS/DVB SPME fiber for on-fiber derivatization and subsequent sampling for GLY at the same concentration range as MGLY were not equivalent. The difference in results is due to decreased sensitivity for GLY which makes sampling and detecting PFBHA-GLY very difficult. Additional studies are required to investigate the difficulty in sampling low ppb concentrations of GLY with a PFBHA-coated SPME fiber. The use of a GC/MS system with Negative Chemical Ionization (NCI) capabilities might improve sensitivity, and this is something that may be investigated in future research. Because PFBHA-loading of the SPME fiber can be achieved in 15 min and regeneration of the PFBHA headspace concentration can be maintained with vigorous shaking, this procedure can easily be adapted for field sampling (i.e. indoor air evaluation).

Disclaimer: The findings and conclusions in this paper are those of the author and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

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