Feasibility of detection and quantification of gas-phase carbonyls in indoor environments using PFBHA derivatization and solid-phase microextraction (SPME)

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Solid-phase microextraction (SPME) was evaluated for the detection and quantification of the gas-phase carbonyls: citronellal, glyoxal, methylglyoxal, and β-ionone. Prepared air samples containing the carbonyl compounds were collected at a flow rate of 2.8 L min^{-1} in an impinger containing a 25% reagent water/75% methanol collection liquid. The aqueous samples were then derivatized with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA), extracted with a PDMS/DVB coated SPME fiber, and analyzed by GC-MS. Detection limits with a sample air volume of 76 L were calculated to be 0.03 ppbv, 0.34 ppbv, 0.12 ppbv, and 0.28 ppbv for citronellal, glyoxal, methylglyoxal, and β-ionone, respectively.

1. Introduction

Volatile organic compounds (VOCs) have received considerable interest because of the general availability of methods for sampling and analysis,[1] as well as their suggested association with health hazards in the indoor environment. Additionally, it has been reported that indoor VOC concentrations can be as much as 10 times higher than typically found in outdoor environments.[2] Previous research conducted on VOCs in the indoor environment has mainly focused on the individual VOCs and their specific health effects. However, the presence of individual VOCs does not completely explain elevated irritation levels.[3] These elevated irritation levels may be attributed to the formation of irritant products through oxidation reactions between unsaturated VOCs and indoor oxidants (*e.g.* ozone).[4]

VOCs in the indoor environment come from a number of different sources, but a significant portion results from the use of a variety of consumer products.[5–7] Experimental evidence has implicated that several initiator (reactant) species such as ozone (O_3), hydroxyl radicals (OH•), and nitrate radicals (NO_3•) are likely to be present indoors.[8] These indoor reactants can convert VOCs that are present (*i.e.* cleaning products, air fresheners) into other oxygenated organic compounds such as aldehydes, ketones, and other carbonyl-containing compounds. Recently, Jarvis *et al.* suggested that 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.[9] Furthermore, Anderson *et al.* identified the indoor oxidation products, glyoxal (GLY) and methylglyoxal (MGLY), as sensitizers using quantitative structure-activity relationship (QSAR) modeling, local lymph node assay (LLNA), and phenotypic analysis.[10]

Identification and quantification of the reaction products of indoor chemistry that are short lived, highly reactive, thermally labile, or highly oxidized—"stealth chemicals"[11] (*e.g.* GLY and MGLY) and require utilization of enhanced analytical techniques. Sampling and detection of GLY, MGLY, and other various carbonyl compounds in the indoor environment is difficult due to their polarity and highly reactive nature. Typically, these types of compounds degrade during analysis utilizing gas chromatography (GC), due to high temperatures and column interactions.[12] To circumvent these difficulties, derivatization techniques have been employed to improve the chromatographic properties and/or the sensitivity of the detection.[13] Additional advantages of derivatization techniques include: (1) providing analyte specificity based on key functional groups and (2) allowing detection with conventional analytical methods.[14] 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 mass selective (MS) detection.[12,15,16] Previous gas-phase atmospheric research has effectively demonstrated the use of SPME fibers pre-coated with PFBHA for on-fiber derivatization of carbonyl-containing compounds.[15,17] This technique was previously utilized in research evaluating the potential for using PFBHA-loaded SPME fibers for detecting and quantifying carbonyl-containing compounds such as GLY and MGLY in the indoor environment.[18] Because this previous research revealed the inherent difficulty of detecting GLY at low ppb concentrations, a further investigation to improve the overall sensitivity of this method was necessary.

The main objective of this research was to develop a method that could be easily used by scientists and industrial hygienists for characterization and evaluation of carbonyls in the indoor air environment. The present paper explores the feasibility of utilizing a gas-bubbler (impingement) with subsequent PFBHA derivatization, followed by extraction with SPME, to detect and

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quantify (by GC-MS analysis) gas-phase carbonyl compounds. Two methods of SPME extraction (direct immersion (DI-SPME) and headspace (HS-SPME)) were explored for the analysis of the compounds of interest, GLY, MGLY, and two other commonly used consumer product fragrance compounds, citronellal and β-ionone. HS-SPME is generally used to analyze volatile compounds while DI-SPME is more suitable for the extraction of semi- or less volatile analytes in liquid samples. The advantages of HS-SPME are typically lower fiber background and prolonged fiber life, while the advantages of DI-SPME are potentially higher sensitivity for semi-volatile compounds and typically shorter extraction times.[19,20]

2. Experimental

2.1 Reagents

All compounds were used as received and had the following purities: from Sigma–Aldrich (Milwaukee, WI, USA): methylglyoxal (MGLY) (40% aqueous solution), glyoxal (GLY) (40% aqueous solution), 3,7-dimethyl-6-octen-1-al ((*R*)-(+)-citronellal) (90%), *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) (98+%); from TCI America (Portland, OR, USA): 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone) (95+%); from Fisher Scientific (Fair Lawn, NJ, USA): methanol (HPLC Grade) (99+%). The reagent water was distilled and deionized to resisitivity of 18 MΩ cm, and filtered using a Milli-Q® filter system (Billerica, MA, USA). Compressed air from the NIOSH facility was passed through anhydrous $CaSO_4$ (Drierite, Xenia, OH, USA) and molecular sieves (Drierite, Xenia, OH, USA) 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, USA). Analysis of this treated compressed air by GC-MS revealed that no contaminants were present that would interfere with the experimental results. Helium (UHP grade), the carrier gas, was supplied by Amerigas (Sabraton, WV, USA). Experiments were carried out at 297 ± 3 K and 1 atmosphere pressure.

2.2 Apparatus and materials

The following SPME fibers mounted in a manual syringe holder were obtained from Supelco (Bellefonte, PA, USA): a 100 μm film thickness polydimethylsiloxane (PDMS) coated fiber; a 65 μm film thickness polydimethylsiloxane/divinylbenzene (PDMS/DVB) coated fiber; and a StableFlex 70 μm film thickness carbowax/divinylbenzene (CW/DVB 70 μm) coated fiber. The fibers were conditioned prior to experimental use, according to manufacturer's recommendations, with a two channel SPME conditioner: Model CN 301 Conditioner 2X by Field Forensics (St. Petersburg, FL, USA). Two methods were utilized to agitate the derivatized liquid (impinged) samples. Before SPME sampling, the samples were agitated for approximately 60 s at max speed utilizing a mini vortexer (Fisher Scientific, Pittsburgh, PA, USA). During SPME sampling, the samples were agitated by magnetic stirring. A 3 × 10 mm magnetic micro stir bar (Fisher Scientific, Pittsburgh, PA, USA) was placed in a pre-cleaned 7 mL amber sample vial (Supelco, Bellefonte, PA, USA) and a magnetic stirrer, (Corning, Corning, NY, USA) set at approximately 600 rpm, was used.

The PFBHA derivatized oximes[12,15,16] of the carbonyl 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 conditions were as follows: 70 eV for electron impact/positive ion mode, 25 to 550 (*m*/*z*) mass range, and 280 °C. 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, Inc. (Deerfield, IL, USA). Compound separation was achieved by a J&W Scientific (Folsom, CA, USA) DB-5 MS (0.25 mm i.d., 30 m, 1 μm film thickness) column and the injection port was set to 250 °C. The GC oven temperature program was as follows: initial 40 °C (hold 6 min), 10 °C min^{-1} to 260 °C (hold 3 min).

The chambers (80–90 L sample bags) were made of five-mil fluorinated ethylene propylene copolymer (FEP) Teflon-film. The bag filling apparatus was equipped with a heated syringe injection port facilitating the introduction of a target compound mixture into the Teflon-film bag with the flowing, treated, dry air stream as described above. All study mixtures and calibration curves were generated using this bag filling apparatus. Experiments conducted to recover the known concentrations of carbonyl compounds from a sample bag were collected through a 100 mL glass gas bubbler (impinger) obtained from Kontes (Vineland, NJ, USA; p/n 652650–2440) utilizing an Airchek sampling pump (Model 224-PCXR4) acquired from SKC, Inc. (Eighty Four, PA, USA). An Agilent Technologies (Rockaway, NJ, USA) DC power supply (Model E3611A) was used to power the pump instead of a battery pack. A BF1/A bag filling pump obtained from BGI Incorporated (Waltham, MA, USA) was used in all field investigations.

All glassware and micro stir bars used in this study were cleaned with methanol (triple rinsed) and then dried in an oven (Fisher Scientific, Pittsburgh, PA, USA) at 120 °C for at least one hour before each use.

The target compounds (citronellal, GLY, MGLY, and β-ionone) were introduced into a sample bag with concentrations ranging between 0.3 and 37.0 μg m^{-3} (0.09 and 5.3 ppbv) using the bag filling apparatus described above. After each experiment, the sample bags were cleaned by filling with clean, dry air and then evacuated for a total of six times. Four experimental parameters were evaluated to maximize the effectiveness of target compound detection by SPME: method of extraction, fiber type, impinger collection liquid, and laboratory sampling pump flow rate.

2.3 Derivatization of collected samples and optimization of method procedures

Sample extraction and detection of the target carbonyl compounds in the liquid sample were facilitated by the addition of 300 μL of a derivatization agent (PFBHA, 23 mM in reagent water) and subsequent oxime collection by SPME. Two methods of SPME extraction were investigated: (1) DI-SPME and (2) HS-SPME. Results of fiber exposure were evaluated for each technique. Each experiment consisted of collecting a specified volume of a sample from a bag containing a concentration

between 119.8–1338.2 μg m^{-3} (50–170 ppbv) of each of the target compounds in an impinger utilizing one of five selected collection liquids. The following collection liquids were chosen: (1) 100% reagent water, (2) 25% reagent water/75% methanol, (3) 50% reagent water/50% methanol, (4) 75% reagent water/25% methanol, and (5) 100% methanol. Due to changes in the evaporation rate associated with each collection liquid, initial collection liquid volumes were adjusted to ensure that final volumes after sampling were approximately 4 mL. PFBHA was added to the samples after impingement and allowed to react overnight to derivatize the target compounds into their respective PFBHA-oximes for subsequent extraction by SPME. Extraction times of 60 min and 120 min were chosen for DI-SPME and HS-SPME, respectively, based on work by Bao *et al.*[21] DI-SPME was selected as the optimal SPME method of extraction based on the higher GC-MS signal response for all of the target compounds using each of the five selected collection liquids. The DI-SPME method of extraction was used for all subsequent evaluations.

Determination of the optimum collection liquid and SPME fiber for detection and quantification of the derivatized oximes was achieved by conducting a series of experiments utilizing the DI-SPME method of extraction combined with each of the five collection liquids and three different SPME fibers (PDMS, PDMS/DVB, CW/DVB 70 μm,). Each sample bag utilized in these experiments contained a concentration of 4.8–15.4 μg m^{-3} (approximately 2 ppbv) of each of the target compounds. A 76 L sample was then pulled through an impinger containing 1 of the 5 collection liquids (described above), PFBHA was added, and the sample was left to react overnight. This new sample containing the PFBHA–oximes was agitated with a magnetic stirrer and extracted with one of the three SPME fibers (described above) for 60 min. After sampling, the SPME fiber was removed from the sample and injected into the GC-MS for analysis. All experiments for evaluating this SPME method were conducted in this manner. Each fiber/collection liquid study was tested in triplicate. The PDMS/DVB SPME fiber combined with 10 mL of the 25% reagent water/75% methanol collection liquid exhibited the best overall performance for all of the target compounds. This combination was selected for all further experiments.

Determination of the optimum laboratory pump flow rate was conducted by evaluating four flow rates: 1.0, 2.3, 2.8, and 3.3 L min^{-1}. The concentration of the bag samples used in this portion of the study was 4.8–15.4 μg m^{-3} (approximately 2 ppbv) for each of the target compounds. One experiment at each flow rate was conducted. An optimal laboratory pump flow rate of 2.8 L min^{-1} was selected since it produced the highest GC-MS signal response for all of the target compounds when coupled with the PDMS/DVB SPME fiber and a 10 mL starting volume of the 25% reagent water/75% methanol collection liquid.

An experiment was conducted to determine the optimal flow rate necessary to minimize sample loss during field sampling. Target compound generation consisted of filling a sample bag with a concentration of 3.8–10.8 μg m^{-3} (approximately 1.5 ppbv) of the target compounds listed above. The contents of this sample bag were then transferred *via* the BF1/A sampling pump into a second bag. The second bag was then processed in the same manner as all other samples in the study as described above. The pump was tested at 3 flow rates: 210, 506, and 991 mL min^{-1}. Two experiments at each flow rate were conducted comparing the second bag to a reference sample bag of the same concentration. The reference sample bag contained the same target compounds as the second bag, but was not subject to any sample transfer or further sample manipulation. Selection of the most favorable pump flow rate for field sampling (991 mL min^{-1}) was determined by evaluating which flow rate produced the least amount of target compound loss when compared to the reference sample bag.

Reproducibility was evaluated by determining the relative standard deviation (RSD) across each concentration/compound combination. Each test within a concentration study was repeated 12 times and an RSD was calculated. Repeatability was evaluated utilizing a Bland–Altman plot, to indicate agreement between any two measurements, which in this case meant looking at measures from the same procedure, as opposed to paired measures between a new procedure and a primary standard.[22–24] Confidence intervals for recovery were also produced for each compound, not only to display recovery potential, but also to show recovery variability.

A relative recovery (%) study was conducted to determine the variance efficiency of the new SPME method as well as evaluating relative recovery rate variance over the concentration range. A 100% reference standard was created by making a blank sample bag which contained treated compressed air only. The blank sample bag was then pulled through the impinger collection liquid and the resultant sample was then spiked with the desired concentration of the target compound stock solution mix. PFBHA was then added to the sample to derivatize the target compounds into their respective PFBHA-oximes for subsequent extraction by SPME. The 100% reference standard was repeated at least three times for each of the six concentrations. The relative recovery (%) was calculated by comparing the 12 sample tests within each concentration study to the 100% reference standards at the same concentration.

A calibration curve was created for each of the target compounds in order to determine if the SPME sampling method would be useful for sampling carbonyl compounds in an indoor air environment. Each calibration curve consisted of a minimum of 4 concentrations between 0.7 and 37.0 μg m^{-3} (0.22 and 5.3 ppbv) with 12 data points at each concentration. All calibration curves, except the GLY curve, were linear regression plots. Trend lines were not forced through zero.

Method blanks were run in conjunction with the 12 sample tests and 100% reference standards within each concentration level. A method blank is a sample that contains only treated dry air which was handled exactly in the same manner as sample tests and 100% reference standards. A method blank provides information on the background levels of the target compounds in all steps of the sampling/analytical procedure. Three method blanks were run for each of the concentration studies. Approximately fifteen measurements were collected at each concentration level, therefore method blanks were typically run at the beginning (before any other measurements were collected), in the middle (approximately the seventh or eighth measurement), and at the end (after all other measurements were completed). All raw data were corrected before statistical evaluation by subtracting the method blank average.

The absolute limit of detection (LOD) for each of the target compounds, except GLY, utilizing the DI-SPME method

coupled with GC-MS detection, was determined from the calibration curves described above. The LOD, expressed in ppbv, was determined by using the following equation:[25] LOD = $3.3\sigma/s$, where σ is the standard deviation of the blank and s is the slope of the calibration curve.

An indoor air evaluation was conducted within an office building at two locations, an office cubicle and an atrium area. Both locations were sampled using an 80–90 L Teflon-film sample bag and the BF1/A bag filling pump. The relative humidity and temperature at both locations were 60% and 22 °C, respectively. All of the indoor air samples were collected between 12 and 21 h after the sampling locations were cleaned. The ozone concentration was not measured. The air exchange rate was approximately 10 h^{-1}. Indoor air samples were collected through the sampling pump at a flow rate of 991 mL min^{-1} for a total of 77 min. An evacuated sample bag was suspended inside a wooden chamber box. One port of the sampling bag was attached to the outlet port of the sampling pump. The inlet port of the sampling pump was attached to the bulkhead external sampling port of the chamber box. Each test location was sampled in duplicate.

3. Results and discussion

3.1 Compound identification and optimization of method procedures

Fig. 1 represents a typical GC-MS chromatogram of a sample bag with a concentration of 3.8–10.8 μg m^{-3} (approximately 1.5 ppb) of the target compounds overlaid with a representative method blank. The chromatogram displays resolved PFBHA–oxime peaks for each of the target compounds as well as uniform peak shapes. In the case of non-symmetrical carbonyls, PFBHA forms two geometric isomers due to the rigid nitrogen–carbon double bond, whereas more than two isomers are possible for dicarbonyls such as MGLY.[16] In this study, the following was observed: one PFBHA-citronellal peak, four PFBHA-GLY peaks (three were singly derivatized – *m/z* 181 and 253; one was doubly derivatized – *m/z* 181 and 448), five PFBHA-MGLY peaks (one singly derivatized – *m/z* 181 and 267; four were doubly derivatized – *m/z* 181 and 462), and two PFBHA–β-ionone peaks. One peak for each compound was selected for quantification: PFBHA–citronellal at 26.6 min, PFBHA–GLY (doubly derivatized) at 28.1 min, PFBHA–MGLY (doubly derivatized) at 28.5 min, and PFBHA–β-ionone at 29.6 min.

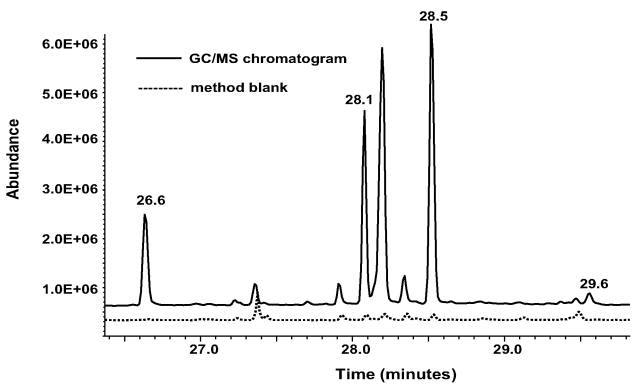

Fig. 1 A typical GC-MS chromatogram of a sample bag with a concentration of 3.8–10.8 μg m^{-3} (approximately 1.5 ppb) of the target compounds overlaid with a representative method blank. The sample and blank chromatograms were offset for clarity. The chromatogram peaks are identified as follows: citronellal (26.6 min), GLY (28.1 min), MGLY (28.5 min), β-ionone (29.6 min).

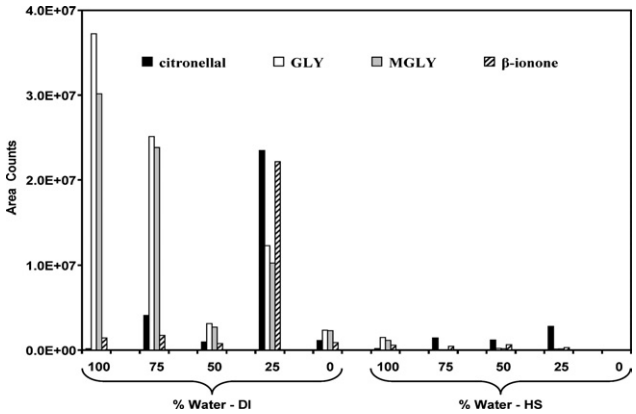

Fig. 2 Comparison of two extraction techniques, direct immersion SPME (DI) and headspace SPME (HS), utilizing each of the five proposed collection liquids: 100% reagent water; 75% reagent water/25% methanol; 50% reagent water/50% methanol; 25% reagent water/75% methanol; and 100% methanol.

Fig. 2 shows the performance of DI-SPME *versus* HS-SPME utilizing each of the five collection liquids. The collection liquid mixture of 25% reagent water/75% methanol exhibited the best general response for all of the target compounds utilizing DI-SPME. The 100% reagent water collection mixture demonstrated the best general results for all of the target compounds utilizing HS-SPME. Considering the target compounds of interest, the information displayed in Fig. 2 indicates that DI-SPME is a more sensitive method of extraction than HS-SPME.

The optimum fiber was selected according to overall performance with each collection liquid. The factors that influenced fiber selection for this study were as follows: sensitivity, reproducibility, fiber deterioration, and carry over. The PDMS/DVB SPME fiber displayed the best combination of the factors mentioned above when coupled with the 25% reagent water/75% methanol collection liquid. Additionally, tests were conducted to determine if any analytes remained on the PDMS/DVB SPME fiber after desorption. Complete desorption was achieved for all analytes, except for the PFBHA–oxime of citronellal, which exhibited less than 1% carry over. Furthermore, it was observed during preliminary tests that the CW/DVB 70 μm SPME fiber was the only fiber that displayed signs of deterioration.

3.2 Precision, relative recovery, and calibration

The RSDs for all compounds at each of the five concentrations are shown in Fig. 3. All of the RSD values were less than 30% except for β-ionone at a concentration of 2.1 μg m^{-3} (0.27 ppbv). The RSDs of the lowest concentration (not shown) of 0.3 to 0.8 μg m^{-3} (approximately 0.1 ppbv) were higher, with an average RSD of greater than 30%. This indicates that this concentration was close to or below the limit of detection for most of the target compounds and therefore was not used in creating the

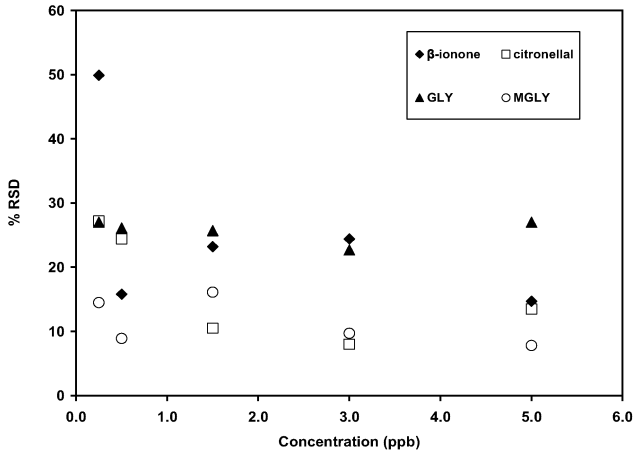

Fig. 3 Actual %RSD for citronellal, GLY, MGLY, and β-ionone at each of the five concentrations studied.

calibration curves. The calculated LOD results for citronellal, MGLY, and β-ionone were 0.17 μg m^{-3} (0.03 ppbv), 0.35 μg m^{-3} (0.12 ppbv), and 2.2 μg m^{-3} (0.28 ppbv), respectively. Because the calibration curve for GLY was non-linear and a slope could not be determined, a calculated LOD for GLY could not be reported. Therefore, the lowest calibration point of the curve, 0.8 μg m^{-3} (0.34 ppbv), was reported as the LOQ. The LOQ for citronellal, MGLY, and β-ionone were 1.3 μg m^{-3} (0.22 ppbv), 0.73 μg m^{-3} (0.25 ppbv), and 2.2 μg m^{-3} (0.28 ppbv), respectively, which corresponds to the lowest concentration points on the calibration curve for each compound.

A Bland–Altman plot (Fig. 4) was created by taking the average and difference of consecutive log transformed (natural log) data pairs and graphing the ordered pair (average, difference). This plot was generated using the sample results from the five concentrations studied for each compound. The outside bands of the plot are two standard deviations away from the mean, creating an approximate 95% confidence band. Approximately 3% (7 out of 220) of the data points fall outside of this 95% confidence interval, indicating good repeatability. Out of these 7 points, only two were GLY data points. There were no MGLY data points outside of the bands. The graph also indicates that there was little or no systematic bias or trend.

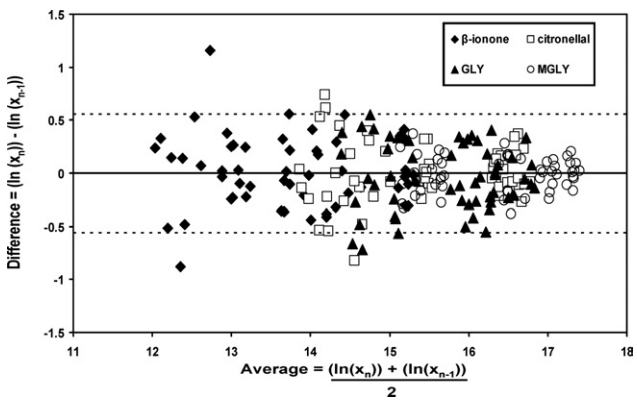

Fig. 4 Bland–Altman plot including data points from five concentrations. The outside bands are two standard deviations away from the mean, creating an approximate 95% confidence interval.

Relative recovery (%) was calculated by comparing 12 sample tests within each concentration study to a 100% reference standard at the same concentration. This calculation was conducted over the entire concentration range of the investigation and the result was an estimated recovery average. The percent recoveries, utilizing a 95% confidence interval, for citronellal, GLY, MGLY, and β-ionone were (54 ± 4), (70 ± 6), (83 ± 4), and (41 ± 4), respectively.

Fig. 5(A–D) are calibration curves for citronellal, GLY, MGLY, and β-ionone. The citronellal and GLY calibration curves were created by plotting the average of 12 data points collected at 5 concentration levels between 0.8 and 28.1 μg m^{-3} (0.22 and 5.3 ppbv) for each compound. The citronellal curve was linear throughout the concentration range studied. The MGLY and β-ionone calibration curves were created by plotting the average of 12 data points collected at 4 concentration levels between 0.7 μg m^{-3} and 21.7 μg m^{-3} (0.25 and 2.8 ppb) as this was the linear range. The GLY calibration curve was not linear throughout the 5 concentration levels evaluated. Since GLY has the lowest molecular weight amongst the target compounds, it is possible that evaporation losses may have affected the GLY concentrations during impinger sampling. Calibration curves were also constructed for the 100% reference standards (collected air samples which were spiked with known concentrations of the target compounds after impingement). This was done in order to examine how the impingement step in the sampling procedure might affect the overall method. The 100% reference standard calibration curves for citronellal, GLY, MGLY, and β-ionone were linear throughout the same concentration ranges mentioned above for each compound. Error bars on each graph represent the average %RSD for each compound across the entire concentration range of the study. The results are as follows: citronellal 16.7%, GLY 25.7%, MGLY 11.4%, and β-ionone 25.6%.

3.3 Method comparison

The primary carbonyl compounds of interest in this investigation were GLY and MGLY. Previous research by Bao *et al.*[21] evaluated sampling and detection of carbonyl compounds, including GLY and MGLY, in water by utilizing PFBHA derivatization coupled with DI-SPME. Ho *et al.*[26] explored the feasibility of sampling and detecting airborne carbonyls, also including GLY and MGLY, by on-sorbent PFBHA derivatization and thermal desorption. Both studies demonstrated new approaches for sampling these specific carbonyl species in water and air, respectively. Although these two studies differ from the work presented here, the use of PFBHA derivatization coupled with DI-SPME as an alternative method for sampling GLY and MGLY in air creates a link between these studies. Table 1 shows a comparison of results from this investigation to the results of the two studies mentioned above. Considering MGLY only, the LOD reported by Bao *et al.*[21] was approximately 500 times lower than the sensitivity achieved for the same compound in the work presented here. This difference in the reported LOD could be explained by the use of an electron capture detector (ECD) in the research by Bao *et al.*[21] compared to a mass selective detector (MSD) utilized in this study. The MSD was chosen in this work for the advantage of qualitative identification power.

The thermal desorption (TD) technique utilized by Ho *et al.*[26] displays an overall higher precision for MGLY when compared

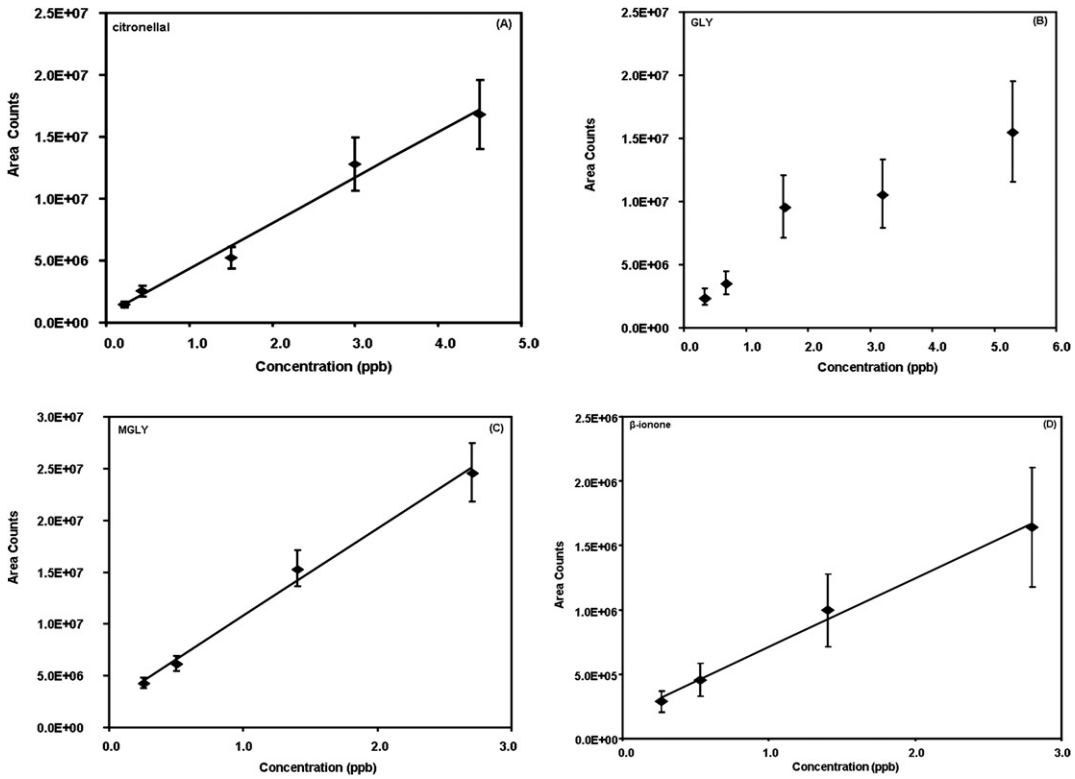

Fig. 5 (A–D). Calibration curves for citronellal, GLY, MGLY, and β-ionone. The GLY calibration curve was non-linear throughout the concentration range studied. The MGLY and β-ionone calibration curves were created using 4 calibration points. Error bars represent average %RSD for each curve: 16.7%, 25.7%, 11.4%, and 25.6%, respectively.

Table 1 Summary of results comparing LOD, %RSD, and relative recovery (%) for GLY and MGLY. Since the LOD for GLY could not be calculated, the reported value for GLY (this study) reflects the lowest concentration of the calibration curve (LOQ). Data was obtained from research conducted by: Bao *et al.*,[21] Ho *et al.*,[26] and research from this investigation

Previous work	Bao *et al.*	Ho *et al.*	This study
Experimental method	Sample vol. 4 mL (aqueous) DI-SPME (PDMS) GC-ECD	Sample vol. 4.8 L (air) thermal desorption GC-MS	Sample vol. 76 L (air) DI-SPME (PDMS/DVB) GC-MS
LOD			
GLY (# of molecules)	0.04×10^{13}	1.2×10^{13}	65×10^{13}
MGLY (# of molecules)	0.03×10^{13}	6.6×10^{13}	23×10^{13}
% RSD	Int. std.; $n = 7$	No int. std.; $n = 12$	No int. std.; $n = 60$
GLY	6.7	2.2–5.3	22.7–7.0
MGLY	9.8	0.7–6.4	7.8–16.1
Relative recovery (%)			
GLY	95–103 Conc. = 5 mg L^{-1}	98 ± 2 Conc. = 20 ppbv	70 ± 6 Conc. range = 0.34–5.3 ppbv
MGLY	108–116 Conc. = 5 mg L^{-1}	93 ± 5 Conc. = 20 ppbv	83 ± 4 Conc. range = 0.25–4.9 ppbv

to the SPME technique utilized by Bao *et al.*[21] and this study. The lower overall precision obtained in the two latter studies could be explained by the difficulty in maintaining consistency in the positioning of the SPME fiber, sample mixing conditions, competitive sorption and/or incomplete analyte trapping.[21] Despite these difficulties in SPME positioning and sample mixing conditions, the method described in this study has a distinct advantage in comparison to the TD method. In the TD method, a laborious process is required to clean the Tenax TA sorbent, coat the sorbent with the appropriate amount of PFBHA derivatizing agent, dry the sorbent in the tube, and finally seal the tube before sampling. The glass sampling tubes can be reused. However, the sorbent has to be removed, recleaned, recoated with PFBHA, and repacked before the next use. In addition to this labor intensive process to prepare the sampling tubes, loading the sorbent with too much PFBHA could overload the GC column and detector. Since the method described in this study utilizes an impinger containing an easily prepared collection liquid, reusing the impinger requires only cleaning the impinger. Due to the small sample size used in SPME sampling/analysis the possibilities for GC column or detector overload from PFBHA are minimized. The advantages of decreased sample

preparation time coupled with increased protection for analytical equipment creates a simplified analytical procedure that can be easily adapted for indoor air evaluations. Although the MGLY recoveries from this study are lower in comparison to work by Bao *et al.*[21] and Ho *et al.*,[26] the large sample size ($n = 60$) along with the fact that all of the MGLY data points were inside of the 95% CI, indicate that this method could be used for sampling MGLY with confidence within the concentration range studied.

3.4 Concentrations of GLY and MGLY in indoor air and field sampling

Recent research has explored the significance of air pollutant exposures among building occupants resulting from the use of cleaning products.[7] Many consumer cleaning products contain terpenoids and related compounds, such as terpinolene, α-terpineol, and *d*-limonene, as active ingredients or fragrances that volatilize during product use.[6,7] Some of the products that might be formed from the oxidation of these cleaning product additives could include: carbonyls (such as GLY and MGLY), organic acids, hydrogen peroxide, secondary organic aerosols, and the hydroxyl radical (OH•).[7,8] In order to further evaluate the effectiveness of this proposed SPME method, it was necessary to consider previous research, as well as make some general assumptions. Concentration estimations of GLY and MGLY produced in an office building after a facility has been cleaned requires knowledge of the following: the amount and components of the applied cleaning product, the air exchange rate, %RH, temperature, ozone concentration, and GLY and MGLY molar yields. In a typical office building where a pine oil-based general-purpose cleaner might be utilized, Singer *et al.* suggested possible time-averaged concentrations of terpinolene, α-terpineol, and *d*-limonene (given 50 g of the general purpose cleaner applied, an air exchange rate of 1 h^{-1}, 53% RH, 22 °C, and an ozone concentration of 120 ppb) within thirty minutes of initial application of 134, 105, and 159 ppb, respectively.[5] To the best of our knowledge, the GLY and MGLY molar yields from the ozonolysis of terpinolene, α-terpineol, and *d*-limonene, have not been reported in the literature. However, Fick *et al.*[27] have reported the molar yields of GLY and MGLY from the ozonolysis of α-pinene at 0.0009 and 0.0003, respectively. Assuming the GLY and MGLY molar yields of the ozonolysis of terpinolene, α-terpineol, and *d*-limonene are similar to the reported molar yields for α-pinene, a rough estimate of the potential GLY and MGLY concentrations can be calculated. If a cleaning product is applied in the same manner and with the same conditions and concentrations as the investigation by Singer *et al.*[5] described above, an estimated concentration of 0.85 and 0.35 μg m^{-3} (approximately 0.36 ppbv and 0.12 ppbv) can be calculated for GLY and MGLY, respectively.

The results of an indoor air evaluation for GLY and MGLY consisting of duplicate measurements in a cubicle and atrium area, corrected for recovery, were as follows: GLY (cubicle) < 0.34 ppbv, < 0.34 ppbv; GLY (atrium) < 0.34 ppbv, < 0.34 ppbv; MGLY (cubicle) 0.25 ppbv, 0.24 ppbv, and MGLY (atrium) 0.26 ppbv, 0.26 ppbv. GLY peaks were observed in the cubicle and atrium samples. However, the concentrations could not be determined with a high level of certainty because the observed peaks were approximately 3 times lower than the LOQ. Actual MGLY concentrations, before correction for recovery, were between the LOD (0.12 ppbv) and LOQ (0.25 ppbv). The estimated concentrations of GLY and MGLY compared to those observed in the indoor air evaluation of this investigation showed that the indoor air results for GLY were approximately 4 times lower than the estimated concentration of 0.36 ppbv while the MGLY results were approximately 2 times higher than the estimated concentration of 0.12 ppbv. It is important to keep in mind that the estimated GLY and MGLY concentrations were derived by incorporating many assumptions into the estimation calculations. The largest assumption was that the GLY and MGLY molar yields for the ozonolysis of α-pinene were similar to the GLY and MGLY yields for the ozonolysis of terpinolene, α-terpineol, and *d*-limonene. Even with the assumptions made in order to estimate these dicarbonyl concentrations, the results of the indoor air evaluation were within one order of magnitude of the estimated concentrations. Since the indoor air results obtained for GLY were lower than the estimated GLY concentration and the MGLY results obtained from the indoor air evaluation were higher than the estimated MGLY concentration, it was worth considering what factors might create the difference between the field sample results and the estimated concentrations for both compounds.

Because the air exchange rate in a typical office building is approximately 1 h^{-1} and the highest concentration of a cleaning constituent is within 30 min of the initial cleaner application,[5] it was important to determine how the difference in the air exchange rate might impact the lifetimes of terpinolene, α-terpineol, and *d*-limonene. In the ozonolysis of terpinolene, α-terpineol, and *d*-limonene, without taking into account the impact of the air exchange rate, a calculation of the estimated pseudo first-order lifetimes for all three compounds can be made using the following terpene/O_3 rate constants: (1) $k_{\text{terpinolene/O3}} = 4.7 \times 10^{-5}$ ppb^{-1} s^{-1}, $k_{\alpha\text{-terpineol/O3}} = 7.4 \times 10^{-6}$ ppb^{-1} s^{-1}, and $k_{d\text{-limonene/O3}} = 5.2 \times 10^{-6}$ ppb^{-1} s^{-1}[17,8] and (2) an ozone concentration of 100 ppb. The estimated pseudo first-order rate constants (k') for terpinolene, α-terpineol, and *d*-limonene were calculated to be 17, 2.7, and 1.9 h^{-1}, respectively. Taking into account the office building air exchange rate of 10 h^{-1}, the estimated pseudo first-order lifetimes of all three compounds were reduced to less than 6 min. The information presented here suggests that the observed indoor air concentrations of GLY and MGLY in this example should be lower than the estimated GLY and MGLY concentrations. The observed indoor air concentration of GLY was lower than the estimated concentration which is in agreement with the data presented here. However, the higher than expected MGLY concentrations observed from the indoor air evaluation could be due to (1) MGLY formation from other secondary products, (2) surface chemistry (ozone reactions with carpet and other building materials), and/or (3) outdoor sources of MGLY transported into the facility.

4. Conclusion

The results of this study show that there is great potential for the detection and quantification of gas-phase carbonyls, particularly MGLY, in indoor air environments. The impingement, PFBHA derivatization, DI-SPME, GC-MS procedure for the sampling and detection of citronellal, GLY, MGLY, and β-ionone

provided a useful combination of analytical reproducibility and sensitivity. Linearity of the calibration curves was achieved across a range of 1.3–28.1 μg m^{-3} (0.22–4.5 ppbv) for citronellal and 0.7 μg m^{-3}–21.7 μg m^{-3} (0.25–2.8 ppb) for MGLY and β-ionone. A linear calibration curve for GLY was not achieved across the range of 0.8 μg m^{-3}–12.7 μg m^{-3} (0.34–5.3 ppbv). Additional studies are required to investigate the non-linearity of GLY in the concentration range studied. The use of a GC-ECD system might further improve sensitivity, and may be investigated in future research. In addition to this, further studies may also include improving precision by maintaining consistency in the positioning of the SPME fiber and by maintaining sample mixing conditions. In the course of this investigation it was realized that there is an important data gap that remains to be filled in order to improve the characterization of the indoor environment. There is a need to determine the molar yields of GLY and MGLY with respect to the ozonolysis of the high volume terpenoid compounds (*i.e.* terpinolene, α-terpineol, and *d*-limonene) found in commercial air fresheners, cleaners, and degreasers. Because air samples can be collected in sample bags (or sampled directly into an impinger) and subsequently derivatized with PFBHA, this procedure can be easily adapted for indoor air evaluations.

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