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Sampling and Determination of Formaldehyde Using Solid-Phase Microextraction with On-Fiber Derivatization

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Gaseous formaldehyde is sampled by derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) adsorbed onto poly (dimethylsiloxane)/divinylbenzene solid-phase microextraction fibers. The product of the reaction is an oxime which is thermally very stable and insensitive to light. The oxime can be analyzed by gas chromatography with flame ionization detection and other detectors. Loading PFBHA on the fiber is by room-temperature headspace extraction from aqueous solutions of PFBHA. The process of loading and desorption of unreacted PFBHA, and oxime formed, is both highly reproducible and reversible, with more than 200 loading, sampling, and analysis steps possible with one fiber. The standard formaldehyde gas concentrations studied ranged from 15 to 3200 ppbv with sampling times from 10 s to 12 min. Quantification can be achieved via interpolation from calibration curves of area counts as a function of formaldehyde concentration for a fixed sampling time. Sampling for 10 s yields a method detection limit of 40 ppbv and at 300 s the method detection limit is 4.6 ppbv. This is equal to or better than all other conventional grab sampling methods for gaseous formaldehyde employing sampling trains or passive sampling techniques. Alternatively, gaseous formaldehyde can be quantified with an empirically established apparent first-order rate constant (0.0030 ng/(ppbv s) at 25 °C) for the reaction between sorbed PFBHA and gaseous formaldehyde. This first-order rate constant allows for quantitative analyses without a calibration curve, only requiring detector calibration with the oxime. This new method was used for the headspace sampling of air known to contain formaldehyde, as well as other carbonyl compounds, and from various matrixes such as cosmetics and building products.

Formaldehyde is an ubiquitous airborne contaminant in the environment, primarily as a result of its use in various materials and processes. For example, it is used in, and is emitted from, plywood and particle board,[1] medium-density fiberboard, and adhesives used for tiling. Other sources include cosmetic products, ozone generators,[2] carpeting, fuel-burning appliances and fire place exhaust,[3] tobacco smoke,[4,5] as a preservative in some paints, insulation,[6] to add permanent-press qualities to clothing and draperies, in hospitals, laboratories, mortuaries, and others.[7−9] HCHO is a colorless gas with a pungent odor generally detectable at ∼1 ppmv; however, its toxicity in humans can be realized at concentrations significantly less than 1 ppmv. HCHO is a probable human carcinogen according to the United States Environmental Protection Agency (U.S. EPA) while the National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA) recognize it is a known animal carcinogen, and the American Conference of Governmental Industrial Hygienists (ACGIH) recognizes HCHO as a suspect human carcinogen.[10] At concentrations slightly greater than 100 ppbv, HCHO can cause watery eyes, itching skin, burning sensations in mucous membranes (eyes), nausea, difficulty breathing, and of concern, sensitization in a percentage of the population who are chronically, and sometimes acutely, exposed to it. Acceptable concentrations of formaldehyde in ambient air are reported to range from 20 to 100 ppbv.[11]

Sensitive sampling and analysis methods for formaldehyde at these levels presents a number of analytical problems specifically related to the difficulty in detecting HCHO. The sampling and analysis methods can be generally categorized as colorimetric, polarographic, and gas and liquid chromatographic (GC and HPLC).[12] In addition, the methods can be further divided according to whether detection of HCHO is required below 100

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ppbv, i.e., ambient air levels (in contrast to levels observed in occupational settings). For detection of ambient HCHO concentrations, there are standard methods which use active air sampling over solid adsorbent cartridges coated with dinitrophenyl hydrazine (DNPH) followed by analysis with HPLC.[13] A method that can be used to sample HCHO concentrations above 100 ppbv[14] makes use of active air sampling over a solid sorbent coated with (hydroxymethyl)piperidine (HMP) and analysis by GC. There are a number of other methods that can be used to sample HCHO at concentrations above 100 ppbv.[15] In addition, it is clear there is a requirement for better sampling and analysis methods for HCHO for large concentration ranges as demonstrated by the fact there are a number of recent methods that attempt to increase method sensitivity while undertaking to significantly reduce the time for sampling and analysis and simplifying the overall method.[16−19] Rapid and sensitive measures of HCHO levels during the manufacture of materials such as foods and cosmetics can provide enhanced process control.[20] Therefore, a sampling and analysis method for airborne or headspace levels of HCHO, which is simple to use, highly sensitive and extremely cost-effective, is required and would be of tremendous benefit.

The use of solid-phase microextraction (SPME) has expanded the range of analytical sampling tools available to scientists by providing a cost-effective sampling system while significantly enhancing overall analytical sensitivity and furnishing a large range of analyte flexibility and selectivity.[21] SPME has also been used for the air sampling of a number of hydrocarbons.[22] Sampling gaseous phases for target analytes with SPME provides a significant advantage over traditional methods, both active sampling and whole air sampling, since SPME requires no sampling pumps and is easy to deploy, reusable, and amenable to automation. At the heart of the SPME sampling device is a fixed polymeric phase which is directly exposed to target analytes. The analytes sorb, either via absorption for the fixed liquid films such as with the poly(dimethylsiloxane) (PDMS) coating or adsorption as with the PDMS/divinylbenzene (PDMS/DVB) coating. The dimensions of the typical SPME fiber coatings are 1 cm long and less than or equal to 100 μm thick. Following an appropriate sampling period, the fiber coatings are then directly inserted into the injector interface of common gas chromatographic equipment. SPME uses no solvents and is completely reusable, extremely accurate, and reproducible. In addition, there are a number of commercially available polymer phases and the list of analytes that can be sampled with SPME is constantly increasing; however, until now, no method employing SPME for the specific sampling of HCHO has been successful.

Shown in this paper is a novel sampling method for gaseous HCHO employing SPME and on-fiber derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA). It is not possible to sample and analyze HCHO with SPME and GC/FID without derivatization. Derivatization sampling for HCHO realizes a number of advantages over techniques not employing derivatization: (1) provides analyte specificity based on key functional groups, (2) allows for detection with conventional detectors (for those compounds that do not yield a response), (3) can provide for sampling based on first-order rate kinetics, and (4) can act as a method for confirmation that the compound of interest is present in the sample. This new sampling method can be used to sample HCHO in air and the off-gassing of HCHO from materials. In addition, it can be used to monitor ambient air levels of HCHO while the flexibility to quantify high HCHO concentrations is maintained. The sampling method is rapid and highly reproducible and can utilize an empirically obtained first-order rate constant for quantitative analyses without the need for interpolation from calibration curves; however, if required, the latter is possible. Data are also included on the use of SPME to sample HCHO under a number different conditions such as temperature, HCHO concentrations, and static versus dynamic gas sampling.

THEORY

There are four steps to consider in describing the overall rate of formation of oxime on solid sorbent SPME fiber coatings as a function of the concentration of gaseous carbonyl. Depicted below are the steps in the sampling system for PDMS/DVB fiber coatings loaded with PFBHA, followed by exposure to gaseous carbonyl (S is the available binding surface of the sorbent),

$$\text{PFBHA} + \text{S} \xrightarrow{k_1} \text{PFBHA*S} \quad \text{(adsorption)} \qquad \text{(A)}$$

$$\text{PFBHA*S} \xrightarrow{k_{-1}} \text{PFBHA} + \text{S} \quad \text{(desorption)}$$

$$\text{carbonyl} + \text{S} \xrightarrow{k_2} \text{carbonyl*S} \quad \text{(adsorption)} \qquad \text{(B)}$$

$$\text{carbonyl*S} \xrightarrow{k_{-2}} \text{carbonyl} + \text{S} \quad \text{(desorption)}$$

$$\text{carbonyl} + \text{PFBHA*S} \xrightarrow{K^*} \text{oxime*S} \quad \text{(reaction)} \qquad \text{(C)}$$

$$\text{oxime*S} \xrightarrow{k_3} \text{oxime} + \text{S} \quad \text{(desorption)} \qquad \text{(D)}$$

and where $K_A = k_1/k_{-1}$ and $K_B = k_2/k_{-2}$ (see below). The first step (A) is to load the sorbent with PFBHA. From experimental data, it is understood that following loading the sorbent with PFBHA, its rate of desorption is negligible, i.e., $k_1 \gg k_{-1}$. The second step to consider is the possibility that an approaching gaseous carbonyl molecule can bind to unoccupied surface sites (B); however, in step B, the rate of carbonyl adsorption is expected to be small, i.e., $k_2 \approx$ O, because almost all sorption sites are occupied by PFBHA. The third step to consider is C, where the rate of reaction between sorbed PFBHA and gaseous carbonyl is K^*. It is assumed that the PFBHA aromatic moiety provides the majority of binding affinity to the polymer while the hydroxylamine moiety is free to react with an approaching carbonyl compound (see Figure 1A for the structure of PFBHA). It is also assumed,

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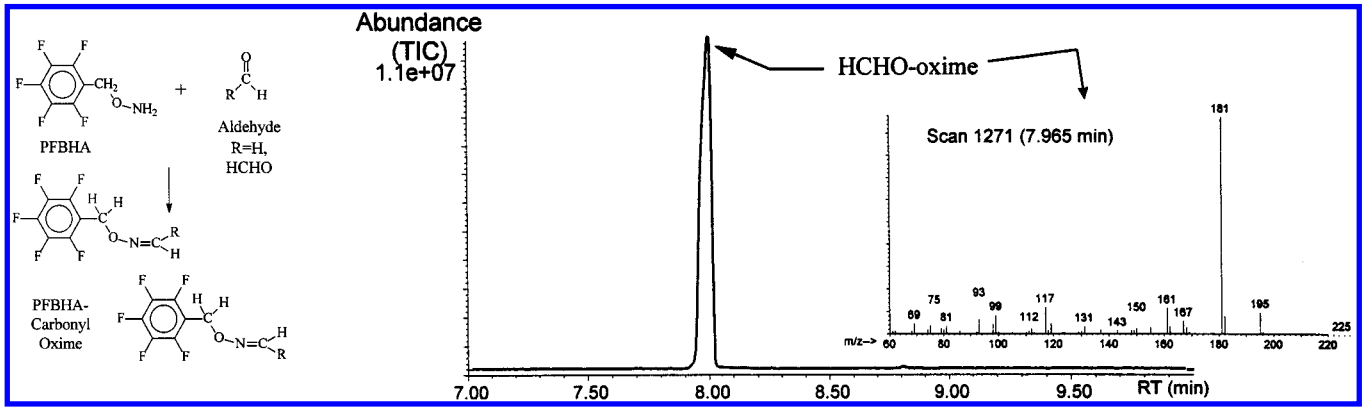

Figure 1. (A, left) Reaction between PFBHA and HCHO (R = H) forming the PFBHA−HCHO oxime. (B, right) GC/MS of 1.8 μL of 143 ng/μL PFBHA−HCHO oxime in hexane. The inset shows the mass spectrum of the peak at ~8 min.

from experimental findings, that K^* is rate limiting as opposed to the rate of gaseous carbonyl diffusion toward to the sorbent. When PFBHA-loaded sorbent is exposed to gaseous carbonyl, a reaction between the two (step C) is desired instead of the carbonyl binding to the sorbent (step B). To achieve this, the experimental sampling conditions are set to favor step C over step B by allowing short exposure times (10−300 s) to high concentrations of gaseous carbonyl and longer exposure times (>300 s) for low concentrations. The objective is to minimize the amount of PFBHA consumed from reaction while obtaining a sufficient quantity of the oxime for detection. As shown, these experimental conditions yield first-order rate kinetics of reaction, i.e., where the overall rate of reaction is dependent on the concentration of gaseous carbonyl. The last step to consider is step D. From experimental data (at room temperature), it is understood that the oxime formed has a very strong binding affinity for the sorbent; therefore, it is assumed that $k_3 \approx$ O. The presence of oxime on the sorbent, oxime*S, now occupies a sorption site. It then prevents adsorption of incoming gaseous carbonyl and can reduce the apparent overall rate of reaction. The reduction in reaction rate is possible because as the number of available PFBHA molecules decreases, so does the possibility of reaction between sorbed PFBHA and incoming carbonyl molecules. But, as stated, small consumptions of PFBHA are expected to have a negligible effect on the overall rate of reaction.

The Langmuir−Rideal mechanism can be used to describe the aforementioned mechanism.[23] This theory assumes there is a reaction between an adsorbed molecule and a gas-phase molecule on a surface, which is the case for the new sampling system described herein. Since the sorbent is first exposed to large concentrations of PFBHA, the sites are ostensibly saturated with PFBHA prior to exposure to gaseous carbonyl. The sorbent, therefore, acts as the surface and PFBHA is the adsorbed molecule. Then, the PFBHA-loaded sorbent is exposed to gaseous carbonyl. An approaching gaseous carbonyl can therefore either react with PFBHA or displace it due the possibility it has a stronger affinity than PFBHA for the sorbent. Consider that if θ is the fraction of surface covered by PFBHA and θ' is the fraction of the surface covered by the carbonyl, then $1 - \theta - \theta'$ is the fraction of the sorbent surface remaining unoccupied. The rate of adsorption and desorption of PFBHA is given by

$$\frac{\theta}{1-\theta-\theta'} = \frac{k_1}{k_{-1}} C_{\text{PFBHA*S}} = K_{\text{A}} C_{\text{PFBHA*S}} \qquad (1)$$

The same can be shown for the binding of gaseous carbonyl, e.g., HCHO, to the fiber without reaction

$$\frac{\theta'}{1-\theta-\theta'} = \frac{k_2}{k_{-2}} C_{\text{HCHO}} = K_{\text{B}} C_{\text{HCHO}} \qquad (2)$$

Solving eqs 1 and 2 for θ results in

$$\theta = \frac{K_{\text{A}} C_{\text{PFBHA*S}}}{1 + K_{\text{A}} C_{\text{PFBHA*S}} + K_{\text{B}} C_{\text{HCHO}}} \qquad (3)$$

It is emphasized that if the sorbent is almost completely coated with PFBHA before its exposure to HCHO, then a reaction between approaching gaseous HCHO and sorbed PFBHA is more likely to occur than binding of HCHO to the surface. This is especially true for short exposure times and when K_{B} is negligible in comparison to K_{A}. The velocity of oxime formation (weight/time) is proportional to the concentration of gaseous HCHO (C_{HCHO}), the rate of reaction between PFBHA and HCHO (K^*), and the total number of sorbent sites occupied by PFBHA (θ)

$$\nu = C_{\text{HCHO}} K^* \theta \qquad (4)$$

Substituting the fraction of sites occupied by PFBHA, θ, from eq 3 into eq 4 yields eq 5 for the velocity of the reaction,

$$\nu = \frac{K^* K_{\text{A}} C_{\text{PFBHA*S}} C_{\text{HCHO}}}{1 + K_{\text{A}} C_{\text{PFBHA*S}} + K_{\text{B}} C_{\text{HCHO}}} \qquad (5)$$

Equation 5 can be rearranged, isolating ν and C_{HCHO}, yielding

$$\frac{1}{\nu} = \frac{1}{C_{\text{HCHO}}}\left(\frac{1}{K^* K_{\text{A}} C_{\text{PFBHA*S}}} + \frac{1}{K^*}\right) + \frac{K_{\text{B}}}{K^* K_{\text{A}} C_{\text{PFBHA*S}}} \qquad (6)$$

(23) Laidler, K. J. *Chemical Kinetics*; McGraw-Hill Book Co: New York, 1965; Chapter 6.

A plot of $1/v$ as a function of $1/C_{HCHO}$ would yield a linear relationship where the slope and *y*-intercept are defined in eq 6 (see text). In addition, consider that when $K^* \ll K^*K_AC_{PFBHA^*S}$, eq 6 can be reduced to

$$\frac{1}{v} = \frac{1}{C_{HCHO}}\frac{1}{K^*} + \frac{K_B}{K^*K_AC_{PFBHA^*S}} \quad (7)$$

It is emphasized that the slope in eq 7 is dependent only on the rate of reaction between PFBHA and carbonyl. This condition is easily satisfied when the loss of PFBHA from the sorbent is negligible (from reaction and/or desorption). Further, eq 7 can be reduced to eq 8

$$\frac{1}{v} = \frac{1}{C_{HCHO}}\frac{1}{K^*} \quad (8)$$

when $K_B \ll K^*K_AC_{PFBHA^*S}$, i.e., particularly when the binding affinity of the gaseous carbonyl is negligible compared to that for PFBHA.

From eq 8, the direct relationship between the velocity of the reaction and the reaction rate as a function of the analyte concentration can be realized as shown in

$$v = C_{HCHO}K^* \quad (9)$$

Therefore, if the velocity of the reaction, *v*, is in weight/time of oxime formation and the C_{HCHO} is the concentration, K^* will be an apparent first-order rate constant, weight/(C_{HCHO} × time).

The inverse of the slope from eq 7 also yields an apparent first-order rate constant, K^*, when the amount of sorbed PFBHA consumed during the reaction is negligible (see text). Therefore, quantitative analyses of unknown HCHO concentrations is possible using this empirically determined first-order rate constant when the amount of PFBHA is negligibly consumed, i.e., during short sampling times for high C_{HCHO} and/or longer sampling times when the C_{HCHO} is low. Finally, with increasing sampling temperature, K^* increases, but conversely, k_3 increases and K_A decreases thus decreasing oxime*S and C_{PFBHA^*S}, respectively. This reduces the apparent rate of product formation.

EXPERIMENTAL SECTION

Chemicals. The carbonyl derivatization reagents PFBHA (>99%), DNPH (>99%), and HMP (>99%) and hexane (>99%) were from Sigma-Aldrich (Toronto, Canada). Formaldehyde, 37% stabilized with methanol, was from Fisher Scientific (Nepean, Canada).

Materials. All solid-phase microextraction fibers and holders, as well as vials, the GC column (SPB-5, 30-m, 0.25-mm i.d., 1.0 μm film thickness), syringes, bubble flow meter, 1-L gas sampling bulbs, charcoal filters, and molecular sieve were from Supelco (Supelco-Sigma-Aldrich). The stirrer, stir bars, and timer were from VWR. The 3-mL conical vials were from Kontes. The balance was from Sartorious and was proven to be linear from 1 mg to 10 g. Ultrahigh purity hydrogen (for the flame ionization detector and carrier gas) and ultrahigh purity nitrogen (for the standard gas generator) were from Praxair (Waterloo, Ontario). Caution should be exercised in using hydrogen as a carrier gas because unchecked leaks could result in explosion. Ultrapure air and nitrogen for the flame ionization detector were generated with gas generators from Balston.

Table 1. Ratios of Derivatization Reagent, PFBHA·HCl, and HCHO for the Synthesis of PFBHA−HCHO Oxime

aldehyde	HCHO
aldehyde vol (μL)/(mmol)	70.0/0.930
reaction vessel size	16 × 120 mm
mass of PFBHA·HCl (mg)/(mmol of PFBHA)	272.1/0.930
water vol (mL)	10
PFBHA·HCl/aldehyde molar ratio	1.0

Standard Gas Concentrations of Formaldehyde. A standard gas generator (model 491-MB, Kin-Tek, Texas City, TX) was used to generate all the standard gas concentrations of formaldehyde. It was equipped with a mass flow-controlled dilution gas system and temperature-controlled holding zone. National Institute of Standards and Technology (NIST) traceable certified HCHO permeation tubes were from Kin-Tek. Prior to entering the standard gas generator, the dilution gas (N_2) was scrubbed with a molecular sieve followed by a charcoal scrub.

Loading SPME Fibers with PFBHA. A solution of PFBHA·HCl (17 mg/mL) in formaldehyde-free water was placed in 4-mL amber Teflon-capped vials with a 1-cm stir bar. The solution was stirred at 1800 rpm. Then, various SPME fibers were placed in the headspace of the solution, for various times, above the center of the solution (vortex). The studied fibers were PDMS, PDMS/DVB for GC (65 μm), Carbowax/DVB, PDMS/DVB for HPLC (60 μm), and Carboxen 1006/PDMS.

Synthesis of PFBHA−HCHO Oxime and Standard Solutions in Hexane. The oxime formed from the reaction between PFBHA and HCHO (Figure 1A) was synthesized using a modified literature method.[24] The oxime is extremely stable and freely soluble in hexane while the PFBHA is essentially insoluble in hexane. It should be noted that when R is not H, there are syn and anti isomers of the oxime,[24] which was observed for the reaction between PFBHA and asymmetrical carbonyl compounds such as *n*-valeraldehyde and acrolein. Table 1 summarizes the ratios of HCHO and PFBHA·HCl used to synthesize ~160 mg of PFBHA−HCHO oxime. Solutions of PFBHA were prepared according to Table 1. The appropriate amount of HCHO was added slowly while shaking. Once all of the HCHO was added, the solution was vigorously shaken and heated for 5 s. The solution was then cooled on an ice bath prior to centrifuging for 5 min. When the tubes were cold, the HCHO oxime appeared as a solid layer at the bottom but turned liquid upon warming to room temperature. The upper layer was removed with a disposable transfer tube. The bottom layer (the PFBHA−HCHO oxime) was extracted with three 900 μL portions of hexane and pooled into preweighed 3-mL conical vials. The hexane extract was evaporated to constant weight with a gentle stream of nitrogen. In addition, the upper aqueous layer was extracted with three 900-μL portions of hexane, pooled into a 3-mL graduated conical vial, and then dried with N_2, but a negligible amount of the product was recovered. The PFBHA−HCHO oxime was stored in a conical vial and then wrapped in aluminum foil. The density of

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Table 2. Mass Spectral Information of PFBHA−HCHO Oxime[a]

	m/*e* (%)							
	181	195	161	117	182	99	167	93
lit.	100	11	10	9	7	7	5	5
obsd	100	12	10	9.9	6.7	9.6	5.4	6.3

[a] The literature data for PFBHA−HCHO oxime[24] are compared to those obtained from the synthesized oxime. The formula weight is 225. The *m*/*e* and the percent of base peak, *m*/*e* 181, are presented.

the PFBHA−HCHO oxime was determined to be 1.431 g/mL (23 °C). Figure 1B shows the total ion chromatogram for a liquid-injected aliquot of synthesized PFBHA−HCHO oxime analyzed by GC/MS (see below). Also shown is the mass spectrum for the peak which is almost identical to that previously reported[24] (Table 2). Injection of this oxime to the GC/FID showed the product was better than 99% pure (based on FID response). Standard PFBHA−HCHO oxime solutions (0.143−14300 ng/μL) were prepared and used to calibrate the GC/FID. The synthesized PFBHA−HCHO oxime confirmed the oxime's retention time and provided for detector calibration (see Results and Discussion). Typical amounts injected ranged from 0.14−1430 ng. The equation for the dependence of response (area counts, AC) as a function of weight of oxime injected (ng) was AC = 2630 (ng) + 1640 with $R^2 = 0.9998$.

Instrumentation and Methods for SPME and Liquid Injections of PFBHA−HCHO Oxime. For identification of the PFBHA−HCHO oxime, a Hewlett-Packard 5890 Series II gas chromatograph coupled to a Hewlett-Packard 5970 mass-selective detector (MSD) was used. The GC column used was a DB-5 column (25 m, 0.25-μm film thickness, 0.32-mm i.d.). The carrier gas, helium, was set at 25 cm/s. The temperature program was 45 °C (hold 1 min), 10 °C/min to 200 °C (hold 5 min). For liquid injections, the standard split/splitless liner was used, but for SPME injections, the 0.75-mm-i.d. narrow-bore insert was used. The MSD scan range was set from 40 to 350 amu. The MSD was autotuned to FC-43 prior to all runs and checked following the runs.

Except for the mass spectrometric data, all the experiments used a Varian Star computer-controlled Varian 3400 gas chromatograph equipped with a carbon dioxide-cooled Septum-equipped programmable injector (SPI). The column effluent was split with a Y-connector and coupled to an FID and an electron capture detector. The connection from the Y-connector to the detectors was facilitated with two identical lengths of deactivated 0.25-mm-i.d. pieces of fused-silica tubing. Confirmation that 50% of the column eluant entered the FID was achieved by injecting a standard without the Y-connector and with the Y-connector. The ECD was only used to confirm the retention time of the PFBHA−HCHO oxime from hexane liquid injections and as a quality control check of the oxime's retention time from liquid injections. The injector was maintained at 210 °C for SPME injections but at 70 °C for hexane liquid injections which was then ramped to 250 °C at 300 °C/min. The column temperature program for SPME and hexane liquid injections was 45 °C for 1.00 min., 30 °C/min to 200 °C, then 50 °C/min to 290 °C, and held for 4.0 min. The column head pressure was set to 26 psi hydrogen, which resulted in a flow rate of 1.7 mL/min and a carrier gas velocity of ~58 cm/s. Care should be taken to ensure that all connections are properly sealed when working with hydrogen as a carrier gas. The detector gas flow rates were set to 300 mL/min for air, 30 mL/min for nitrogen, and 30 mL/min for hydrogen and were all measured daily. The instrument was checked daily for calibration using a liquid midpoint calibration standard, and any deviations in area counts greater than 10% required reinjection of that standard, and if still greater than 10%, the instrument was recalibrated with a six-point calibration. In addition, quality of peak shapes, resolution, and retention times were carefully monitored to ensure all chromatography was within all required specifications.

Sampling the HCHO Standard Gas. The HCHO standard gas effluent from the standard gas generator was directed into a 1-L gas sampling bulb equipped with a sampling port from which the SPME device could be exposed to the gas. The bulb was maintained at 25 °C for all experiments, except for the temperature study. All sampling times were accurately measured with a NIST traceable timer.

Analysis of Headspace Samples of Hair Gel and Particle Board. Approximately 3 g of hair gel known to contain formaldehyde (according to the manufacturer's label) were placed in a 40-mL vial and allowed to reach equilibrium for 1 min before sampling. Approximately 3 g of four-year-old particle board were placed in 40-mL vials and allowed to reach equilibrium. For the hair gel, the PFBHA-loaded SPME fiber was introduced into the headspace for 10 s and then analyzed. New samples were prepared and the process was repeated for other sampling times, e.g., 120 s. For the particle board sample, the PFBHA-loaded SPME fiber was exposed to the headspace for 2 min and then the fiber was analyzed. This was repeated on the same sample after the vial was heated for 15 s in a microwave oven on high until condensate was observed on the inside of the vial.

RESULTS AND DISCUSSION

Selection of a Carbonyl-Specific Derivatization Reagent Suitable for Loading onto SPME Fiber Coatings. The first objectives of the work were to obtain a carbonyl-specific derivatization reagent that could be reversibly loaded onto selected SPME fibers. The product of the reaction between the derivatization reagent and the carbonyl compound should also be (thermally) stable and amenable to analysis with conventional chromatographic equipment and detectors, such as GC/FID. A thermally stable product would allow for ambient-temperature storage conditions so that samples could be field acquired and then analyzed in the laboratory or if sampling occurred at above ambient temperatures. Further requirements were that the derivatization reagent should be preferably nontoxic and insensitive to light, heat, and oxygen.

The commercially available derivatization reagents selected for study were DNPH, HMP, and PFBHA; however, of these three derivatization reagents, only PFBHA was found to satisfy all of the aforementioned criteria for the study. For example, after loading various PDMS and PDMS/DVB fibers with each of the three selected derivatization reagents, only PFBHA on either coating yielded a chromatogram showing only one GC peak associated with the derivatization reagent and another peak from the product of the reaction between PFBHA and HCHO (see

below). In contrast, both DNPH and HMP loaded on either fiber types yielded a significant number of peaks from which the product of the reaction could not be identified. The use of PFBHA is also highly desirable due to the fact it is water soluble, thus allowing a highly controlled loading of the free amine onto various SPME fibers via headspace extraction from aqueous solutions. Preliminary experiments also showed that >97% of sorbed PFBHA desorbed from the SPME fibers following 1-min desorption at 210 °C and that an extremely reproducible amount of PFBHA could be loaded onto the fiber even after 20 injections. In addition, the PFBHA−HCHO oxime is a halogenated aromatic compound, which allows for photoionization detection. The compound yields characteristic electron impact fragmentation patterns with base peak daughter ions at *m*/*e* 181 and it shows an excellent response with FID (see below). The electronegative fluorine atoms stabilize the ring structure making PFBHA and its reaction products are stable under a large range of conditions, such as exposure to water and elevated temperatures. Therefore, on the basis of the aforementioned points, PFBHA was selected as the derivatization reagent for HCHO, but what was next required was an SPME fiber coating best suited for loading PFBHA.

Fiber Selection for Loading PFBHA. A number of different SPME fiber coatings were examined to establish one (see Experimental Section), or more, that would provide the highest loading and stability of PFBHA and oxime retention characteristics.

The first screening was based on the extent the fiber would load PFBHA and the carry-over following one desorption step. Each of the fibers were consecutively exposed to an aqueous headspace of a PFBHA solution (17 mg/mL), in random order, ensuring that each fiber extracted from the solution at least three times. The largest mass loading of PFBHA was on the Carboxen/PDMS fiber, followed by the PDMS/DVB for GC and HPLC fibers and the Carbowax/DVB fibers, each having similar mass loading yet only half of that observed for the Carboxen/PDMS fiber, and with the lowest loading observed for the PDMS fiber coating, approximately half of that observed for the DVB fibers. The Carboxen/PDMS fiber coating would have been selected for the remainder of the studies were it not for the fact that the optimum desorption temperature for this fiber was found to be ∼310 °C, with a 2-min desorption time to overcome low desorption yields; however, this resulted in significant peak tailing. Attempts to reduce the observed peak tailing then required cooling the column to 0 °C and/or changing the column. Both were attempted, with the latter proving unsuccessful and the former approach being dismissed because of the desire to maintain the analysis method as simple as possible. In addition, given the mass loading of PFBHA on the Carboxen/PDMS fiber coating was only ∼2 times that observed for the PDMS/DVB fiber, there was no advantage to using Carboxen/PDMS given all of its affiliated issues.

The next criterion for fiber selection was to select a coating that would retain the largest amount of PFBHA with time. This was accomplished by loading the PFBHA on each of the fibers for a given time, exposing the fibers to aldehyde free air for 10 min, and then comparing the amount of remaining PFBHA to the amount of PFBHA without exposure to the air. The results showed that PDMS lost more than 90% of the PFBHA while the Carbowax/DVB and the different PDMS/DVB fibers only showed

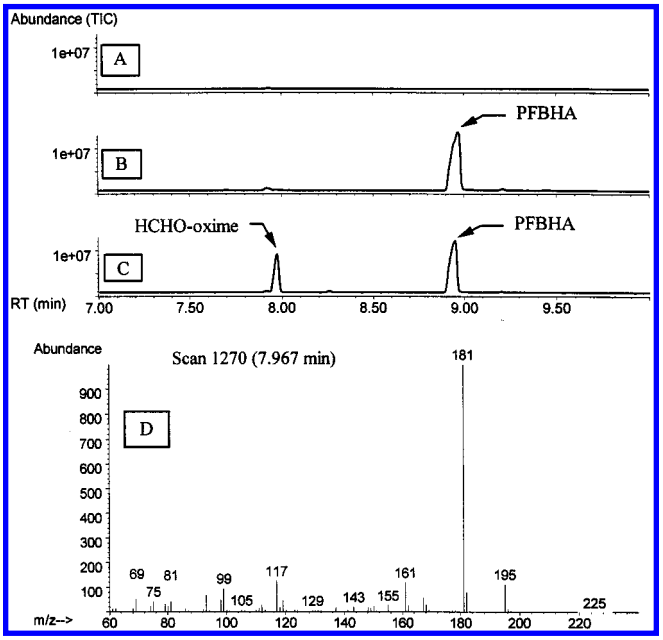

Figure 2. GC/MS of PFBHA-loaded PDMS/DVB fibers (65 μm) with and without exposure to 650 ppbv HCHO. The run conditions here were the same as those for the data shown in Figure 1B.

a loss of ∼30%. Increasing the time to 30 min resulted in essentially no further loss in PFBHA for the PDMS/DVB and Carbowax/DVB fiber coatings, while the PDMS fiber coating retained ∼3% of the original amount. In addition, the stability study was carried out by placing PFBHA-loaded fibers, with the coating retracted into the needle, overnight in clean air at room temperature. The finding was that the PDMS fiber lost more than 70% of the PFBHA while the other fibers only lost ∼15%. Therefore, the results indicated that Carbowax/DVB and the two PDMS/DVB fibers could be used to load PFBHA. Finally, the PFBHA·HCl solution pH was increased with the addition of Na_2CO_3, which resulted in a significantly larger mass loading of PFBHA on all the fibers, but which also resulted in higher background; however, no further enhancements in loading PFBHA were required since an appropriate level of method sensitivity was achieved without it.

The Carbowax/DVB fiber coating was ultimately not selected because the coating proved to be less rugged than either PDMS/DVB fiber coating. Finally, the PDMS/DVB fiber coating for GC was selected over the one designed for HPLC because the former showed greater reproducibility from one lot to another even though the latter was structurally more rugged than the former. With care, the PDMS/DVB fiber for GC was used for more than 200 loading and desorption steps without failure. Following the selection of the PDMS/DVB fiber coating for GC, the PFBHA-loaded fibers were exposed to standard concentrations of HCHO.

Exposure of PFBHA-Loaded PDMS/DVB Fibers to HCHO Standard Gases. Figure 2 shows typical GC/MS data obtained following exposing PFBHA-loaded PDMS/DVB fibers to ∼650 ppbv HCHO for 10 min, with comparative chromatograms showing the fiber blank and the PFBHA-loaded fiber alone. Figure 2A shows the PDMS/DVB fiber blank while Figure 2B shows the chromatogram from the PFBHA-loaded PDMS/DVB fiber and Figure 2C shows the chromatogram with the PFBHA−HCHO oxime and unreacted PFBHA. Figure 2D shows the mass

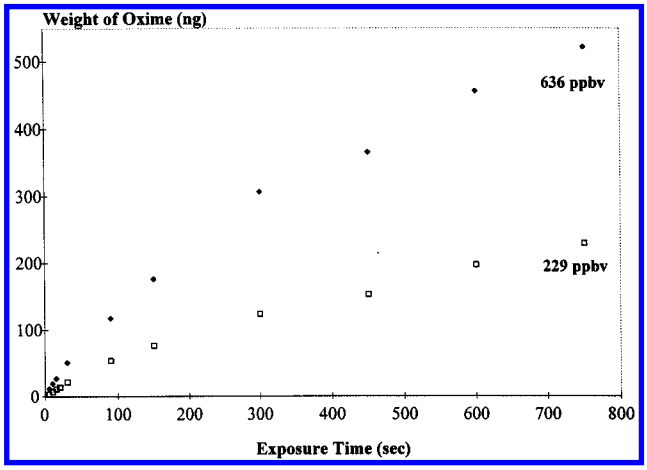

Figure 3. Representative exposure time profiles for PFBHA-loaded PDMS/DVB fibers (65 μm) for 636 and 229 ppbv HCHO. Not shown are those for 45 and 15 ppbv HCHO.

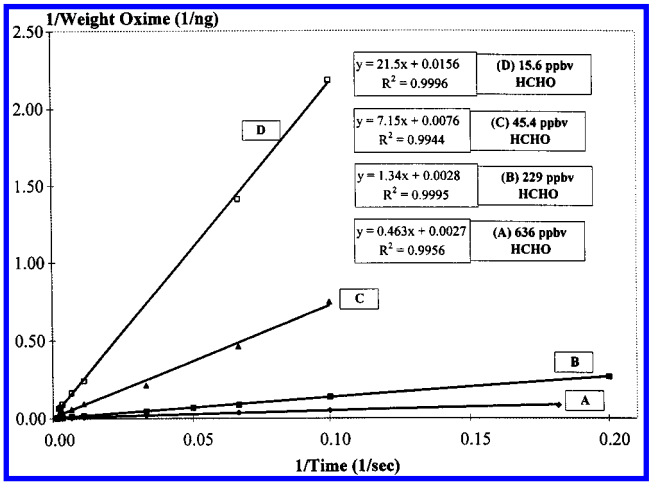

Figure 4. Inverse of the amount PFBHA−HCHO oxime formed (1/ng) as a function of the inverse of time (1/s). The equations for each of the curves is presented on the chart with its associated [HCHO] (ppbv).

spectrum of the PFBHA−HCHO oxime, which is ostensibly identical to that obtained from the injection of pure PFBHA−HCHO oxime (Figure 1B) and that from the literature[24] (Table 2). Therefore, the identity and retention time of the PFBHA−HCHO oxime formed on the SPME fiber coating were established.

Exposure Time Profiles. Two of the typical exposure time profiles obtained from the reaction between PFBHA sorbed onto PDMS/DVB-coated fibers after exposure to various concentrations of HCHO standard gas concentrations are presented in Figure 3. The HCHO concentrations studied this way were 636, 229, 45, and 15 ppbv at 25 °C. The ordinate depicts the weight of HCHO oxime (ng) formed as a function of time (s). The data indicate that a steady-state level of product formation was not observed even after 12-min extraction times and was not dependent on the gas velocity (see below). As can be seen from the curves, for short exposure times, e.g., from approximately 10 to 90 s, the data points follow a straight line relationship. The extent of this linear range increases with decreasing HCHO concentration, e.g., from 10 to 150 s for 15 ppbv HCHO. After some time, the curves become nonlinear as observed (Figure 3). This is consistent with the fact the reaction is pseudo first order in the linear region because the derivatization reagent, PFBHA, is negligibly consumed and is in significant excess to the amount of PFBHA−HCHO oxime formed. This aspect was exploited in establishing the apparent first-order rate constant for the reaction between PFBHA and HCHO which would allow for quantitative determinations without the need for fiber calibration curves. From eq 7, we see that a plot of $1/v$ as a function of C_{HCHO} should yield a linear relationship; however, before this can be done, the velocities of product formation (ng/s) have to be established using the data shown in Figure 3. This could be done with either of two ways. First, the initial slopes of each exposure time profile could have been determined directly from the data in Figure 3 and then the inverse of the slopes taken. Alternatively, the reciprocal of weight of oxime formed as a function of the reciprocal of time could be plotted, the slopes of which would be the inverse of velocity for each HCHO concentration. Both methods worked similarly; however, the second method was chosen and is discussed below.

Establishing the Apparent First-Order Rate Constant for the Reaction between PFBHA Loaded onto PDMS/DVB Fibers and HCHO. Figure 4 shows the plots of the inverse of amount of PFBHA−HCHO oxime formed (1/ng) as a function of the inverse of exposure time (1/s). The slopes for each of the curves represent the inverse of the reaction velocity (s/ng) of PFBHA−HCHO oxime product formation from the reaction between sorbed PFBHA and gaseous HCHO. Following this, a plot of the slope of each curve (from Figure 4) as a function of the inverse of the HCHO concentration yields a curve where the *inverse* of the slope is the apparent first-order rate constant, 0.00297 ng/(ppbv s), for the reaction between sorbed PFBHA and gaseous HCHO (Figure 5) (see Theory). It is this apparent first-order rate constant which can be used to quantify unknown concentrations of airborne HCHO. For example, the amount of PFBHA−HCHO oxime product formed following a given exposure time (ng/s), e.g., 10 s, for an unknown HCHO concentration is divided by the apparent first-order rate constant (0.00297 ng/(ppbv s), the result being the unknown HCHO concentration. In this way, no SPME fiber calibration curve is required for quantification, provided the sampling time is accurately known and that the amount of derivatization reagent consumed does not exceed ~5% of the original amount of PFBHA. Of interest is that this first-order rate

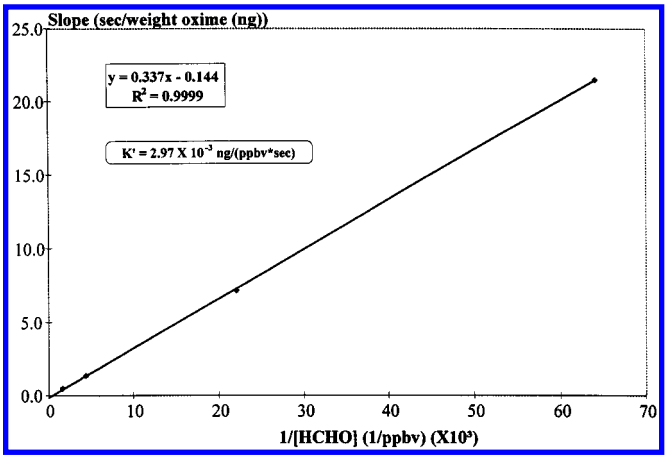

Figure 5. Slope for each of the curves from Figure 6 as a function of the inverse formaldehyde concentration (1/[HCHO]). The equation for the line is presented as well as the inverse of the slope, which represents the apparent first-order rate constant.

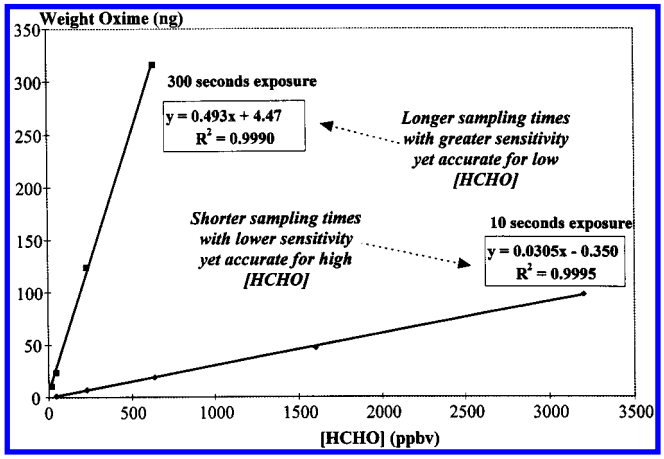

Figure 6. Weight of PFBHA−HCHO oxime formed at 10- and 300-s exposure times as a function of various [HCHO] (ppbv). The equations for the curves are presented. Note that the slope of the curve obtained from 10-s sampling times is essentially identical to that obtained from the inverse of the slope from the plot shown in Figure 5.

constant was independently confirmed with SPME calibration curve data provided in the next section.

SPME Fiber Calibration Curve Data for HCHO. Plots for the amount of HCHO oxime formed for 10- and 300-s sampling times of various concentrations of HCHO are provided in Figure 6. The data show that, as expected, long sampling times, e.g., 300 s, result in a larger mass of oxime formed compared to shorter sampling times, e.g., 10 s. The slopes of the two curves indicate that sampling for 300 s results in ~16 times greater sensitivity compared to sampling for 10 s. This is consistent with the concept that an increased exposure time will result in a increased amount of product formed, thus increasing method sensitivity and decreasing detection limits.

Of particular interest is that the slope from the curve obtained for 10-s sampling of the various HCHO concentrations is 0.0305 ng/(ppbv 10 s), yielding an apparent first-order rate constant of 0.00305 ng(ppbv s). This is significant because it independently confirms the first-order rate constant reported in the previous section where the two values differ by <3%.

Finally, these data indicate it is should be possible to obtain first-order constants for other PFBHA carbonyl reactions by exposing the PFBHA-loaded SPME fibers to various concentrations of the carbonyl compounds of interest for very short times where the slopes represent the apparent first-order rate constants.

Temperature Dependence. The dependence of amount of PFBHA−HCHO oxime formed as a function of the inverse of temperature ($\times 10^3$) (1/kelvin) for a given HCHO concentration was found to follow the following equation: (ng) = 245(1/T) − 684 with R^2 = 0.9963. With increasing temperature there is a decrease in the amount of detected PFBHA−HCHO oxime for a fixed sampling time. It is understood that increasing sampling temperature results in an increase in the rate of reaction, K^*, between the PFBHA and HCHO but the increase in temperature also decreases the binding affinity of PFBHA and PFBHA−HCHO oxime to the fiber coating (see eq 6). Of significance is that a temperature variation of ±5 °C from 25 °C does not significantly affect the amount of HCHO oxime detected, thus potentially reducing the requirement to correct for sampling temperature; however, this option is available.

Table 3. Summary of Data Obtained from the Method Detection Limit Study of PFBHA-Loaded PDMS/DVB Fiber Coatings[a]

no.	HCHO-oxime (ng)	HCHO (ppbv)
1	10.5	11.7
2	11.8	14.3
3	11.1	12.9
4	12.1	15.0
5	10.4	11.5
6	10.6	12.0
7	9.9	10.2
8	10.7	12.2
av	10.9	12.5
std dev	0.73	1.5[b]
% RSD	6.7	12

[a] The study was carried out with n = 8 at 10 times the expected method detection limit, yielding 7 degrees of freedom. A two-tailed t-test of the data was carried out where t = 2.998; 5-min exposure, at 25 °C, to 15 ppbv HCHO. [b] MDL (ppbv) 4.6 (std dev × t).

Dynamic versus Static Sampling. The question as to whether there was a difference between sampling a constant source of standard HCHO (from the standard gas generator) and sampling the standard gas concentration under static conditions gas was addressed. First, one standard concentration of gaseous HCHO was dynamically generated and sampled with PDMS/DVB fibers loaded with PFBHA. Second, the same HCHO standard gas concentration was sampled under static conditions with the same fibers sorbed with fresh PFBHA. The data indicate the amount of PFBHA−HCHO oxime formed for a given sampling time was identical for each sampling type. This is because the reaction rate between sorbed PFBHA and gaseous HCHO is slower than the rate of HCHO diffusion. In addition, these data indicate that sampling HCHO under static conditions, such as from small or large vessels, should yield highly accurate HCHO concentrations.

Method Precision. The overall method precision was established to be 12% RSD for 15 ppbv HCHO at 300-s sampling and better than 2% RSD for 3200 ppbv at 10-s sampling. The data indicate that the complete method of loading PFBHA, sampling, and analysis is highly reproducible. It is this excellent precision which allows the method to achieve significantly low detection limits for 300-s sampling times.

Method Detection Limits. Table 3 summarizes the data obtained from a two-tailed t-test of eight replicate analyses carried out at 15 ppbv, yielding 7 degrees of freedom. The data estimate an overall method detection limit (MDL) of 4.6 ppbv for 300-s sampling and 40 ppbv for 10 s (data not shown for the latter). These MDL values are equal to or better than all other rapid sampling methods for HCHO.

Interfiber Reproducibility. The use of a number of different PDMS/DVB fibers during the course of the study raised questions regarding possible fiber to fiber variations. Four different fibers from a number of different lot productions were used to consecutively load PFBHA and then sample 640 ppbv HCHO for 300 s. The results (data not shown) indicate there was no difference in the amount of PFBHA−HCHO oxime formed on any of the fibers.

Specificity of the Method for HCHO. It has been demonstrated that acrolein can interfere with the uptake of HCHO from a sampling system using DNPH on a solid sorbent.[9] Therefore,

Table 4. Specificity of the Sampling Method for HCHO with and without Exposure to High Concentrations of Reactive Aldehydes

aldehyde[a]	exposure time (s)	aldehyde (ppbv)	consecutive exposure (area counts)	individual	% of orig AC[b]
HCHO (3)	60	640	2.19×10^5	2.42×10^5	91
acrolein (2)	20	72000	9.86×10^4	1.31×10^5	75
n-valeraldehyde (1)	20	45000	4.41×10^5	4.87×10^5	90

[a] Number in parentheses is the sequence of fiber exposure. [b] AC refers the area counts obtained from FID.

the possibility of interference from other reactive aldehydes with the new sampling method presented herein was addressed. Table 4 summarizes the data from this study. First, PDMS/DVB fibers sorbed with PFBHA were exposed to 46 000 ppbv *n*-valeraldehyde for 20 s, then to 75 000 ppbv acrolein for 20 s, and then to 640 ppbv HCHO for 60 s, followed by analysis. These data were then compared to those when the fiber was exposed to each aldehyde separately and then analyzed. The data indicate the sampling system can still sample for HCHO even when the fiber is exposed to 100-fold higher concentrations of other very reactive aldehydes. The oximes formed from the reaction between PFBHA and acrolein and *n*-valeraldehyde eluted later than the PFBHA peak, unlike the PFBHA−HCHO oxime which eluted earlier than PFBHA.

Actual Samples with the Method. Figure 7A shows the chromatogram obtained from the GC/FID analysis of HCHO oxime formed after PFBHA-loaded PDMS/DVB fibers were exposed to hair gel known to contain HCHO according to the list of ingredients. The results indicate that HCHO was indeed present in the headspace of the hair gel, thus presenting an additional source of potential exposure of HCHO to those individuals in the vicinity of where the hair gel may be applied. Therefore, the sampling can be potentially used as a method of estimating exposure to HCHO from cosmetics. Figure 7B shows the chromatograms obtained from the sampling of HCHO from four-year-old laminated particle board. The data indicate that HCHO is still emitting from this material, even after four years and that heating the material only exacerbates the emission of HCHO.

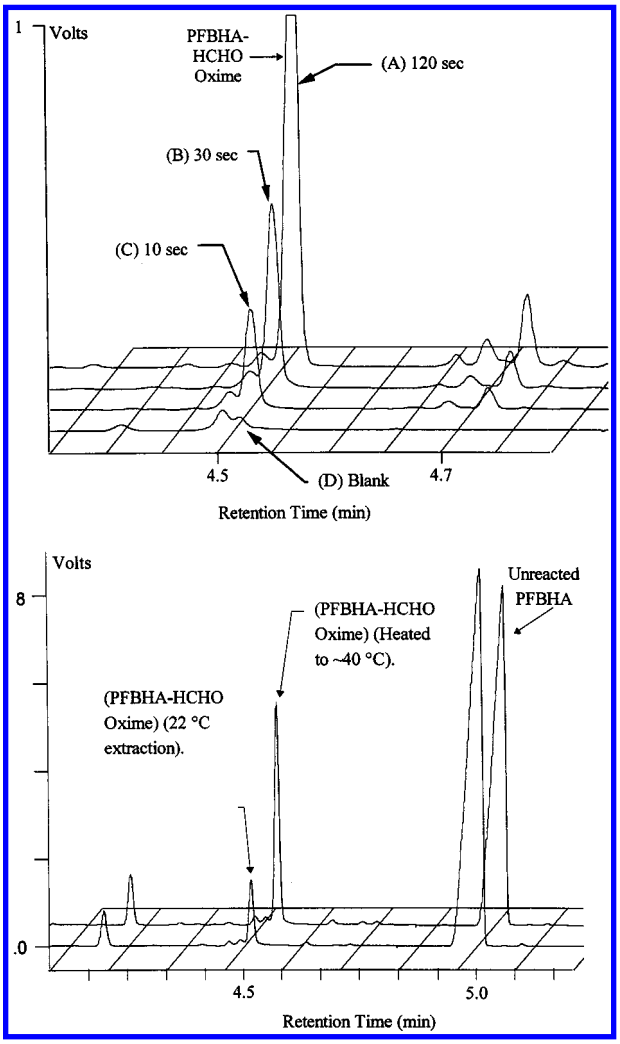

Figure 7. (A, top) Exposure of PDMS/DVB fibers (65 μm) sorbed with PFBHA to the headspace of ~3.5 g of hair gel. The various times presented are different sampling times. (B, bottom) Exposure (120 s) of PDMS/DVB fibers (65 μm) sorbed with PFBHA to the headspace of ~3 g of four-year-old particle board before (22 °C) and after heating.

CONCLUSIONS

The use of SPME with PFBHA for the on-fiber derivatization of gaseous formaldehyde provides a number of distinct advantages over traditional formaldehyde sampling methods. For example, the method requires no alterations to conventional gas chromatographic equipment and can be used with flame ionization detectors for concentrations ranging from 15 ppbv to greater than 3000 ppbv formaldehyde. This new sampler is extremely small, yet very sensitive, which allows for easy placement of the sampler in areas previously not amenable to other samplers. Also, this new method is both extremely rapid and accurate and allows for 10-s grab sampling times, with quantitative analyses possible using empirically determined first-order rate constants, obviating the need for SPME fiber calibration curves. Short sampling times, while yielding accurate results, decrease the overall time necessary for quantitative analyses, thus increasing sample throughput. Another advantage with this new method is that it is reusable. One fiber was used for more than 200 samples, thus reducing the materials cost to ~30 cents per sample. In addition, since the consumption of formaldehyde from a sample is minimal, the sample can be reanalyzed multiple times without significantly affecting the actual formaldehyde gas concentration.

The new sampling method presented herein is valuable not only for use as a grab sampling device to allow for an estimate of the instantaneous concentration of formaldehyde but also as a

time-weighted average sampling device for HCHO (data to be published). Preliminary data indicate that 10−1000-min time-weighted average sampling for HCHO is possible with the same sampling method by simply retracting the fiber into the needle during sampling with field data showing an excellent correlation to standard methods. Again, a first-order rate constant is used for quantitative analyses. The small size of the SPME sampler lends itself to personal monitoring and/or easy placement anywhere to allow for indoor air measurements of formaldehyde and/or potential occupational exposures. Finally, the sampler may be useful for ambient air monitoring of formaldehyde generated from secondary reactions in the atmosphere.

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