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Determination of Particulate-Bound Formaldehyde from Burning Incense by Solid Phase Microextraction

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Abstract This work studied the feasibility of using a solid phase microextraction (SPME) fiber for sampling and analysis of gaseous formaldehyde as well as particulate-bound formaldehyde from burning Chinese incense. The SPME fiber with PDMS/DVB coating were partially coated with o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA), and used for sampling formaldehyde. The sampling rate for formaldehyde and its dependence on temperature, relative humidity and sampling time were observed. The same PFBHA treated fibers were, in parallel, exposed to incense burning smoke with pre-filtration and without pre- filtration for 0.5–1 min. The NIOSH method 2541 using an XAD-2 tube at a flow rate of 0.1 Lpm was also applied for sampling simultaneously. The results demonstrate that commercially available PDMS/DVB fibers partially coated with PFBHA are capable of sampling the gas phase of formaldehyde as well as particulate-bound formaldehyde. The determined level of formaldehyde was close to the result obtained by the NIOSH method 2541. However, a reduction of the fiber's formaldehyde loading capacity in the aerosol sampling in comparison with gas sampling was noticed. This indicates that the particulate characteristics, and their bound chemicals other than formaldehyde may influence the maximum loading capacity of formaldehyde, and some characteristic particulates in high concentrations may even deteriorate the fiber coating.

Keywords Formaldehyde · Solid phase microextraction (SPME) · Sampling for particulate-bound formaldehyde · Burning Chinese incense

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Burning incense sticks, as a religious rite, produce indoor air pollutants, including gases, organic vapors and particulates. Incense burning is related to the growing incidence of lung cancer (MacLennan et al. 1977), childhood leukemia (Lowergard et al. 1987) and brain tumors (Preston-Martin et al. 1982). The Ames test has been performed to demonstrate the mutagenic effect of the incense smoke (Sato et al. 1980; Rasmussen et al. 1987; Chang et al. 1997). Of all the produced pollutants, particulate-bound chemicals are of the greatest concern because they easily enter the alveolar region of the respiratory system, resulting in biological effects.

Formaldehyde is a pollutant in incense smoke in either the gas phase or the particulate phase (Lin and Wang 1994; Lin and Tang 1994; Lee and Lin 1996; Chang et al. 1997). A pre-filter incorporated with a sampling tube that contains solid sorbent coated with a suitable derivative reagent such as 2,4-dinitrophenylhydrazine (DNPH) has been used to sample formaldehyde in aerosol-like incense smoke. Then formaldehyde in the particulate-loaded filter was extracted with a DNPH solution or other derivative reagent solutions. Conventional methods applied to characterize particulate bound chemicals are very strict and time-consuming.

Solid-phase microextraction (SPME) fibers can be successfully used in rapid air sampling (Martos and Pawliszyn 1998; Koziel et al. 1999; Pawliszyn 2000; Koziel et al. 2001a–c). This SPME method combines sampling, preconcentration and the direct transfer of the analytes into the analytical instrument in a series of steps, making it a promising alternative to conventional air sampling methods. Recent research has even demonstrated that adsorptive SPME fibers can be used in air samplers of particulate matter (Koziel et al. 2001a–c, Odziemkowski et al. 2001). This work establishes the feasibility of using PFBHA-coated SPME fibers in the sampling and analysis of formaldehyde in aerosol of burning Chinese incense.

Materials and Methods

The 65 μm PDMS/DVB SPME fiber, obtained from Sulpeco, USA, was coated with o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA, 98%, ALDRICH, Germany) before the formaldehyde was sampled. To coat the PFBHA, the SPME fiber housed in the needle of an SPME holder (Sulpeco, USA) was punched through the cap of a 4 mL vial (SUN, USA), containing 1 mL 17 mg/mL of PFBHA in water. Next, the fiber was pushed out of the needle and exposed to PFBHA for 2 min. The amount of PFBHA coated on the fiber was about 6 μg.

The formaldehyde-o-PFBHA oxime, the derivative of formaldehyde and PFBHA, was prepared following Chou's procedure (Chou and Q Hee 1994), by mixing equal mole amounts of formaldehyde (36.5–38% w/v aqueous solution, SIGMA, USA) and PFBHA in water, heating the mixture in a microwave oven for 5 s; cooling it in an ice bath for 30 min; centrifuging it at 5°C, 2,000 rpm for 5 min; discarding the supernatant, adding two parts of 1 mL n-hexane for the extraction, centrifuging and transfer of the supernatant into a 4 mL vial, and drying. The final product was confirmed by GC/MS.

The formaldehyde-o-PFBHA oxime was dissolved in n-hexane to prepare a series of standard solutions with concentrations of between 1.84×10^{-4} and 9.22×10^{-2} mg/mL (equivalent to between 2.45×10^{-5} and 1.23×10^{-2} mg/mL formaldehyde). Gas chromatography with a flame ionization detector (HP 6890 series II, Agilent Tech., USA) was applied for quantification. The temperature of the the injection port was set to 250°C and that of the detector was set to 300°C. The flow rate of nitrogen was 1 mL/min. The column was DB-225 (30 m × 250 m × 0.25 μm, Agilent Tech., USA). The temperature program was from 60°C to 130°C at 10°C/min, to 220°C at a rate of 40°C/min, and then held for 1 min. The limit of detection for formaldehyde-o-PFBHA oxime was 2.03×10^{-5} mg/mL by 1.0 μL of injection volume into GC, which equivalent to 2.71×10^{-3} ng formaldehyde/sample for the method detection limit of SPME-fiber sampling. The calibration curve was plotted as response area versus concentration of formaldehyde.

To determine the rate at the SPME fiber which gaseous formaldehyde was sampled, a dynamic system was applied to generate ppm levels of formaldehyde (Chen et al. 2006). A known concentration of formaldehyde solution in a syringe was transferred to a heat block at a rate of 0.083, 0.166 or 0.332 μL/min. In the heat block, the formaldehyde vaporized at 250°C and was led to the exposure chamber at a flow rate of 500 mL/min. It merged with the dilution air to yield reference formaldehyde concentrations of 0.12, 0.62, and 1.23 mg/m^3. The temperature (15, 25, 35°C) and the relative humidity (25, 50, 80%) in the exposure chamber were regulated. In the exposure chamber, the SPME with the fiber pushed outside the needle was exposed to formaldehyde for 1, 5, and 10 min. Next, the needle was inserted into the injection port of a chromatograph for 5 min, which was determined to be enough time to enable all of heat oxime on the fiber to be desorbed.

Incense smoke was produced at a flow rate of 3 L/min in a cylindrical burning chamber (Yang et al. 2005) in which the distribution of particles, with a geometric mean of 95.35 nm, a geometric standard deviation of 1.61 and a coefficient of variance of 0.41 ($n = 3$), was reproducible (Yang 2005). Sampling was performed to quantify formaldehyde both with and without pre-filtration. Under the pre-filtration condition, incense smoke was passed through a mixed cellulose ester filter (MCE AF, 0.8 μm pore size, 37 mm diameter, SKC, USA) before entering an annexed exposure chamber that contained samplers. SPME samples were collected by exposing the SPME fiber for 10 s to 3 min. The NIOSH Method 2541 (NIOSH 1994) was followed for reference, using an XAD-2 tube (120 mg/60 mg, SKC, USA) at a flow rate of 1 L/min for 2 h.

Results and Discussion

The mass spectrum of formaldehyde-o-PFBHA oxime revealed features at *m/z* 181, 161, 195, 117, 44, and 223. Standard solutions were accordingly prepared and GC/FID analyses were conducted to obtain the chromatogram. The calibration curves were plotted as response area of GC/FID versus concentration of formaldehyde. The results indicated that the correlation coefficients exceeded 0.995 from 2.45×10^{-5} to 6.26×10^{-4} mg/mL and from 4.73×10^{-4} to 1.23×10^{-2} mg/mL.

The data in Table 1 were obtained by sampling the reference formaldehyde using the PDMS/DVB SPME fiber coated with PFBHA. The amount of adsorbed formaldehyde was positively related to the concentration of formaldehyde ($r = 0.98$) and the sampling time ($r = 0.99$).

Table 1 Amount of formaldehyde adsorbed on SPME fiber under various exposure conditions (temperature, relative humidity, and sampling time)

Parameter of experimental trial					Amount of formaldehyde (ng), Mean ± Standard deviation (n = 3)
Trial	Concentration (mg/m^3)	Temperature (°C)	RH (%)	Sampling time (min)	
1	1.23	15	25	1	1.1417 ± 0.0512
2	1.23	25	50	5	4.0854 ± 0.2185
3	1.23	35	80	10	4.3055 ± 0.2001
4	0.62	15	50	10	4.1625 ± 0.1048
5	0.62	25	80	1	0.5754 ± 0.0390
6	0.62	35	25	5	1.8506 ± 0.1584
7	0.12	15	80	5	0.5306 ± 0.0240
8	0.12	25	25	10	0.9634 ± 0.0799
9	0.12	35	50	1	0.0302 ± 0.0050

The linear regression was $y = 0.7872x + 0.2394$ ($r = 0.99$) for samples at 15°C, $0.7802x + 0.1844$ ($r = 0.99$) for samples at 25°C, and $0.4069x + 0.3533$ ($r = 0.98$) for samples at 35°C, where y (ng) is the mass of formaldehyde and x (ng min/cm^3) is the product of the concentration and the sampling time. The sampling rates were 0.7872, 0.7802, and 0.4069 cm^3/min at 15, 25, and 35°C, respectively. The sampling rate (SR) depended on the sampling temperature ($T = 273 + t$°C) given by the equation $SR = 0.000448/T + 0.003060$ with correlation coefficient $r = 0.86$ (n = 3).

Table 2 shows the results of sampling formaldehyde in the incense smoke with and without pre-filtration. The amount of formaldehyde collected on the SPME fiber depended on the sampling time and the concentration, regardless of the pretreatment. Samples from incense smoke without pre-filtration contained more formaldehyde than those from incense smoke with pre-filtration for a given sampling time (Table 2). Similar results were obtained two samples subjected to GC-MS analysis; the abundance of formaldehyde-o-PFBHA oxime in the sample without pre-filtration was 1.5 times that in the sample with pre-filtration (Table 3).

The sample without pre-filtration contained diethyl phthalate and cedrol in addition to PFBHA, formaldehyde-o-PFBHA oxime and siloxanes. Diethyl phthalate and cedrol have previously been detected in extracts of incense but they have not been found in the gas phase during the burning of incense (Yang 2005). These two compounds are occasionally used as binders in incense sticks, and are present only in the form of particulate-bound chemicals when the incense stick is burning. The results imply that the particulate-bound formaldehyde and other chemicals are probably transported to the surface of the PDMS/DVB fiber, which is partially coated with PFBHA, where the formaldehyde reacts with PFBHA, while the other

Table 2 Amount of formaldehyde collected by SPME sampling incense smoke

Sampling time (min)	Amount of formaldehyde (ng), Mean ± Standard deviation	
	With pre-filtration (n)	Without pre-filtration (n)
1/6	0.2612 ± 0.0080 (3)	0.6965 ± 0.0912 (5)
1/3	0.4507 ± 0.0276 (3)	1.2113 ± 0.0149 (3)
1/2	0.5733 ± 0.0245 (3)	1.3849 ± 0.0461 (3)
1	1.2498 ± 0.1664 (11)	2.0969 ± 0.0271 (14)
2	2.1355 ± 0.1779 (3)	2.7789 ± 0.1482 (3)
3	2.9483 ± 0.0460 (3)	–

Table 3 PDMS/DVB sampling of incense smoke with/without pre-filtration to identify chemical species using GC/MS

Code no.	Without pre-filtration		With pre-filtration	
	Chemical species (RT: min)	Abundance	Chemical species (RT: min)	Abundance
1	HCHO-FFBHA (6.66)	8546649	HCHO-FFBHA (6.66)	5834854
2	FFBHA (7.57)	104714834	FFBHA (7.58)	123659054
3	Cyclopentasiloxane (8.08)	5145492	Cyclopentasiloxane (8.08)	3735088
4	Hydroxylamine-PFBHA (9.45)	2398196	Cyclohexasiloxane (9.77)	3101058
5	Cyclohexasiloxane (9.77)	5917801		
6	Cycloheptasiloxane (11.64)	2397001		
7	Diethyl phthalate (12.98)	3469240		
8	Cedrol (13.30)	2813034		

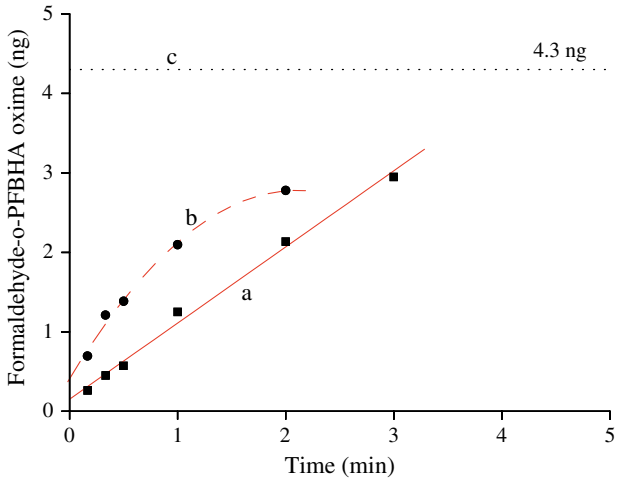

Fig. 1 Amount of formaldehyde-o-PFBHA oxime collected on SPME fiber (**a**) with pre-filtration; (**b**) without pre-filtration by sampling incense smoke. The loading capacity is much less than the 4.3 ng of formaldehyde-o-PFBHA oxime of sampling reference formaldehyde

Table 4 Determination of formaldehyde in aerosol sample from incense burning

Concentration of formaldehyde determined by using two methods*, Mean ± Standard deviation (mg/m^3)			
Sampling aerosol with pre-filtration		Sampling aerosol without pre-filtration	
SPME, n = 14	NIOSH-2541 with XAD-2 tube, n = 5	SPME, n = 17	NIOSH-2541 with XAD-2 tube, n = 4
1.91 ± 0.26 (CV = 13.75%)	2.84 ± 0.38 (CV = 13.32%)	3.44 ± 0.49 (CV = 14.23%)	3.73 ± 0.68 (CV = 18.10%)

* Sampling time for using SPME = 0.5 or 1 min; Sampling time for using XAD-2 tube at flow-rate of 100 cm^3/min = 60, 90, 110, or 120 min

chemicals are retained via adsorption. According to Fig. 1, the mass of formaldehyde (w) increased linearly with sampling time (t) when incense burning smoke was sampled with pre-filtration, according to $w = 0.96t + 0.15$ ($r = 0.997$). However, the uptake rate (ng/min) increased and the relationship between the mass of formaldehyde and the sampling time became $w = 1.94 \log t + 2.12$ ($r = 0.993$) when the fiber was exposed to the incense smoke without pre-filtration.

Particulates from burning incense are oily particles (Cheng et al. 1995), which not only adhere easily to the SPME fiber coating, but are also are likely to reduce loading capacity. As presented in Fig. 1, the loading curve reaches a plateau when the loading of formaldehyde in the aerosol sample exceeds 2.1 ng. Unexpectedly, this loading capacity is much less than that (4.3 ng) of the PDMS/DVB SPME fiber used for sampling the reference formaldehyde. Moreover, the aerosol sample from burning incense without pre-filtration contained more siloxanes than that with pre-filtration according to GC-MS analysis (Table 3).

Levels of formaldehyde determined by the NIOSH method using XAD-2 tubes, and by the SPME method, did not statistically differ among samples of incense smoke without pre-filtration but did statistically differ among those with pre-filtration (Table 4). In the latter case, the greater level of formaldehyde, as determined by NIOSH method 2541, implies that the active air flow (100 cm^3/min) that flushes the particulates onto the pre-filter may move some of the particulate-bound formaldehyde during relatively long periods of sampling (60–120 min), in contrast to the SPME method with sampling times of 0.5–1 min.

We conclude that the commercially available PDMS/DVB fiber partially coated with PFBHA could be used to sample gaseous formaldehyde and particulate-bound formaldehyde from burning incense when the fiber was pushed outside the needle of an SPME holder and exposed to the aerosol sample for less than 3 min. The detected level of formaldehyde was close to that obtained by the NIOSH method 2541 However, in aerosol sampling, the fiber's loading capacity for formaldehyde was lower than that in gas sampling, a result that probably follows for the characteristics of the particulates and their bound chemicals other than formaldehyde. Some characteristic particulates at high concentration may even facilitate the deterioration of the fiber coating.

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References

Chang HJ, Kuo ML, Lin JM (1997) Mutagenic activity of incense smoke in comparison to formaldehyde and acetaldehyde in *Salmonella typhimurium*. Bull Environ Contam Toxicol 58: 394–401

Chen CY, Hsiech C, Lin JM (2006) Diffusive sampling of methylene chloride with solid phase microextraction. J Chromatogr A 1137:138–144

Cheng YS, Bechtold WE, Yu CC, Hung IF (1995) Incense smoke: characterization and dynamics in indoor environments. Aerosol Sci Technol 23:271–281

Chou CC, Q Hee SS (1994) Saliva-available carbonyl compounds in some chewing tobacco. J Agric Food Chem 42:2225–2230

Koziel J, Jia M, Khaled A, Noah J, Pawliszyn J (1999) Field air analysis with SPME device. Analytica Chimica Acta 400: 153–162

Koziel J, Augusto F, Pawliszyn J (2001a) Air sampling with solid phase microextraction. ASAE Annual International Meeting

Koziel J, Noah J, Pawliszyn J (2001b) Field sampling and determination of formaldehyde in indoor air with solid-phase microextraction and on-fiber derivatization. Environ Sci Technol 35:1481–1486

Koziel J, Odziemkowski M, Pawliszyn J (2001c) Sampling and analysis of airborne particulate matter using in-needle trap and SPME devices. Aanl Chem 73:47–53

Lee RS, Lin JM (1996) Gaseous aliphatic aldehydes from burning raw materials of Chinese incense smoke. Bull Environ Contam Toxicol 57:361–366

Lin JM, Tang CS (1994) Characterization and aliphatic aldehyde content of particulates in Chinese incense smoke. Bull Environ Contam Toxicol 53:895–901

Lin JM, Wang LH (1994) Gaseous aliphatic aldehydes in Chinese incense smoke. Bull Environ Contam Toxicol 53:374–381

Lowengard RA, Peters JM, Cinioni C, Buckley J, Bernstein L, Preston-Martin S, Edward R (1987) Childhood leukemia and parent's occupation and home exposure. J Natl Cancer Inst 79(1):39–46

Maclennan R, Costa JD, Day NE, Law CH, Ng YK, Shanmugaratnam K (1977) Risk factors for lung cancer in Singapore Chinese, a population with high female incidence rate. Int J Cancer 20: 854–860

Martos P, Pawliszyn J (1998) Sampling and determination of formaldehyde using solid-phase microextraction with on-fiber derivatization. Anal Chem 70:2311–2320

NIOSH (National Institute for Occupational Safety and Health) (1994) Manual of analytical methods, 4th edn. Centers for Disease Control and Prevention

Odziemkowski M, Koziel J, Irish D, Pawliszyn J (2001) Sampling and Raman confocal microspectroscopy analysis of airborne particulate matter using polydimethylsiloxane solid phase microextraction fibers. Aanl Chem 73:3131–3139

Pawliszyn J (2000) Theory of solid-phase microextraction. J Chromatogr Sci 38:270–278

Preston-Martin S, Yu MC, Benten B, Henderson BE (1982) N-nitroso compounds and childhood brain tumors: a case–control study. Cancer Res 42:5240–5245

Rasmussen RE (1987) Mutagenic activity of incense smoke in *Salmonella typhimurium*. Bull Environ Contam Toxicol 38: 827–833

Sato S, Makino R, Takahashi Y, Sugimura T, Miyazaki T (1980) Mutagenicity of smoke condensates from joss sticks. Mut Res 77:31–36

Yang TT (2005) Development of less-pollution incense: characterization of aerosol and gas emission from burning incenses. National Taiwan University, Taiwan

Yang TT, Chen CC, Lin JM (2005) Effect of air flow on emission of smoldering incense. Bull Environ Contam Toxicol 74:456–463