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Analysis of aldehydes in water by solid-phase microextraction with on-fiber derivatization

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Abstract

The solid-phase microextraction (SPME) technique with on-fiber derivatization was evaluated for the analysis of aldehydes in water. The poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) fiber was used and *O*-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) were first loaded onto the fiber. The aldehydes in water sample were agitated into headspace and extracted by SPME with on-fiber derivatization. Gas chromatography/mass spectrometry (GC/MS) was used for the analysis of oximes formed and the adsorption-time profiles were examined. The precision, recovery and method detection limits (MDLs) were evaluated with spiked bidistilled water, chlorinated tap water as well as well water. The relative standard deviations from different spiked water sample were all less than 10% and the recoveries were 100 ± 15%. With 2 ml of water sample, MDLs were in the range of 0.12–0.34 μg/l. Compared with other techniques, the study shown here provided a simple, fast and reliable method for the analysis of aldehydes in water.

Keywords: Water analysis; Headspace analysis; Aldehydes

1. Introduction

Aldehydes (R–CHO where R is alkyl, aromatic, or alicyclic) are ubiquitous products of combustion [1–3], photodegradation of dissolved natural organic matter [4], and biological oxidations [5], and are mucous membrane irritants [6]. Formaldehyde, acetaldehyde, furfural, and crotonaldehyde are animal carcinogens [7]. Formaldehyde and glutaraldehyde expose embalmers [8,9], operating theater personnel [10] and pathologists [6]. In recent years, aldehydes are receiving increasing attention as disinfection and oxidation by-products formed during drinking water treatment processes, especially those with low molecular masses [11]. Formaldehyde, acetaldehyde, glyoxal, and methylglyoxal were the major organic by-products found in the ozonation of natural waters [12,13]. Besides the health affects mentioned above, these aldehydes may also cause taste and odor problems in drinking water [14].

For the determination in water, derivatizations prior to their detection by a spectroscopic or chromatographic technique are widely performed for the low-molecular-mass aldehydes [15]. For example, derivatization with 2,4-dinitrophenylhydrazine (2,4-DNPH) followed by liquid–liquid extraction (LLE) has been used by the US Environmental

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Protection Agency (US EPA) [16]. The 2,4-DNPH method potentially allows specific quantitation of different aldehydes and ketones through high performance liquid chromatography (HPLC)/ultraviolet (UV) detection of their hydrazones but not by gas chromatography (GC) since many hydrazones decompose at high temperatures [17]. Another commonly used method for determining aldehydes is based on the derivatization with *O*-2,3,4,5,6-(pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA).

PFBHA has been used to analyze aldehydes in water because of its fast quantitative reaction to form oximes suitable for detection at the picogram (pg) level by gas chromatography/mass spectrometry (GC/MS) and gas chromatography/electron capture detection (GC/ECD) [18]. PFBHA method has also been suggested by both the US EPA [19] and the US American Public Health Association (APHA) [20].

All the methods mentioned above involve complex procedures for sample preparations (solvent extraction, for example) and therefore very time-consuming. In recent years, a new extraction technique called solid-phase microextraction (SPME) has been developed by Pawliszyn [21,22]. SPME presents many advantages over conventional analytical methods by combining sampling, preconcentration, and direct transfer of the analytes into a standard gas chromatograph [23]. Sampling and analysis method for aldehydes in air which combined PFBHA with SPME technique have been reported [17,24,25]. For water sample, aldehydes derivatized with PFBHA to form oximes in solutions followed by extraction with SPME from liquid or headspace and analyzed by GC/ECD was also reported [11]. The research shown here reported another approach to determine the aldehydes in water, including butyraldehyde, formaldehyde, propionaldehyde, and *n*-valeraldehyde where PFBHA was first loaded onto the fiber of SPME followed by the headspace extraction of aldehydes solution with on-fiber derivatization.

2. Experimental

2.1. Materials

Butyraldehyde (99.5%), decafluorobiphenyl (99%), formaldehyde (37%), propionaldehyde (97.8%), valeraldehyde (99%), *O*-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine hydrochloride, *n*-hexane, and methanol were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Helium for GC/MS was 99.999% purity from Sanfu Co., Taiwan. All solid-phase microextraction fibers, holders and molecular sieve were from Supelco (St. Louis, MO, USA).

2.2. Instrumentation

All analyses were performed on a Perkin-Elmer Autosystem XL Chromatograph equipped with a 30 m × 0.25 mm i.d. 0.25 μm film DB-225 chemically bonded fused-silica capillary column (J&W Scientific, Folsom, CA, USA) and a Perkin-Elmer Turbo Mass, mass spectrometer. The carrier gas was helium with flow rate of 1.0 ± 0.1 ml/min in the 1:20 split mode. The temperature for the injector was 250 °C. The column temperature programs was: 60–95 °C at 10 °C/min, and hold for 29.5 min. The temperature of mass spectrometer was 220 °C.

2.3. Loading SPME fibers with PFBHA

Poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) SPME fiber (65 μm) was selected because it adsorbed PFBHA with greater reproducibility [24]. A solution of PFBHA (17 mg/ml) in aldehydes-free water was placed in 4 ml PTFE-capped vials with a 1 cm stir bar [24]. The magnetic stirrer used was MIRAK 7 × 7 stir plate from Barnstead International (Dubuque, Iowa, USA) which also allowed temperature control. The solution was stirred at 1100 rpm. Then the PDMS/DVB SPME fiber (65 μm) for GC was placed in the headspace of the solution above the center of the solution. To get the adsorption-time profile, the SPME fibers were exposed to the vapors of the aqueous for 0.5, 1, 1.5, 2, 5, 10, 20, and 30 min, respectively. Chromatographic peak areas and calibration curves were used for adsorbed PFBHA quantification. To ensure the desorption was complete when the SPME needle was inserted into the heated GC injector, different desorption times were tested to examine the desorption efficiencies. For successive analysis of samples, the SPME fiber was always first heated in the GC injector and a blank run was performed right before the loading of PFBHA to make sure the fiber was clean as well as to avoid the carryover effects.

2.4. Derivatization and SPME procedures

Headspace extraction was used in this research to avoid possible contamination and damage to the fiber that might occur through direct liquid contact [26]. Aldehydes of different concentrations (1 μg/l to 5 mg/l) were prepared as standard solutions and 2 ml of each solution was placed in a 4 ml PTFE-capped vial with 1 cm stir bar, respectively. The solutions were stirred at 1100 rpm for at least 5 min before further procedures were performed to allow the equilibrium of analytes between the aqueous phase and the headspace phase. After loading with PFBHA, the SPME fiber was inserted in the headspace of the solutions. Aldehydes with concentrations of 5 mg/l which were higher than the normal concentration ranges found in the drinking water [19] were first tested. Different periods of time for extraction were performed to obtain the adsorption-time profiles. Besides 5 mg/l, different concentrations of aldehydes ranged from 0.01 to 50 mg/l were also tested to obtain the adsorption-time profiles. Appropriate time for further headspace extraction of each aldehydes was then determined to establish the calibration curves from the adsorption-time profiles.

The internal standard solution (48 mg/ml) was prepared by dissolving decafluorobiphenyl [18,20] into a solution of hexane. The internal standard solution was then placed in a 4 ml PTFE-capped vial with 1 cm stir bar and stirred at 1100 rpm. After the headspace extraction of aldehydes solutions followed by 1 min exposures of the internal standard solution, the SPME fiber was inserted into the injector of GC/MS for analysis. The selective ion monitoring in mass spectrometer utilized *m*/*z* 181 and 234 while total ion monitoring utilized *m*/*z* 50–300 [18]. All the experiments were performed in triplicates.

To determine the precision and recovery of current technique, spiked samples (10 μg/l and 1 mg/l) of bidistilled water, chlorinated tap water, and well water for each aldehydes were analyzed 10 times based on the processes mentioned above. The relative standard deviation (R.S.D.) and recovery for each aldehydes were then calculated. Another spiked samples (1 μg/l) of bidistilled water were also analyzed eight times to determine the method detection limits (MDLs) based on the calculation procedures suggested by the US EPA (where MDL = standard deviation of replicate analyses × Student's *t*-value for the 99% confidence level with $n - 1$ degrees of freedom) [19].

3. Results and discussion

To upload PFBHA onto PDMS/DVB fiber, a solution of PFBHA in aldehydes-free water was placed in a 4 ml PTFE-capped vial with a 1 cm stir bar and the solution was stirred at 1100 rpm [17,24]. As shown in Fig. 1, the mass of PFBHA loaded on the fiber increased as the loading time increased and the equilibrium time was around 20 min. To assure the amount of PFBHA loaded, complete equilibrium was not necessary as long as the extraction conditions were reproduced [27]. Therefore 2 min of loading time was first arbitrarily used in the current study based on previous experience [17]. More PFBHA can be loaded on the fiber if the time for extraction is increased. The condition for thermal desorption of the SPME fiber was also determined. At temperature of 250 °C, the desorption efficiency was found to be 99.96% when the desorption time was 2 min.

Fig. 2 showed the SPME adsorption-time profiles from the on-fiber derivatizations of aldehydes with PFBHA. The equilibrium time was similar for most of the oximes formed on the fiber except formaldehyde. The reason why formaldehyde showed a different adsorption-time profile was not clear. Besides the data shown in Fig. 2, different spiked aldehydes samples with concentrations ranged from 0.01 to 50 mg/l were also tested and the results showed that the shapes of the adsorption-time profiles were all similar to Fig. 2 even the concentrations were different. It was reported that no single classical adsorption isotherm including Langmuir, BET, Dubinin–Radushkevich, and Freundlich could predict the passive chemisorptive system between aldehydes and PFBHA [28]. Therefore what was found in this study suggested that more researches are needed to establish the chemisorption model for headspace extraction of aldehydes with on-fiber derivatization by PFBHA-coated PDMS/DVB. For the purpose of the current technique, a 10 min extraction time was employed since it was not necessary to reach an adsorption equilibrium for quantitative analysis [27] and a 10 min extraction time yielded sufficient extraction (>80%) for most of the aldehydes.

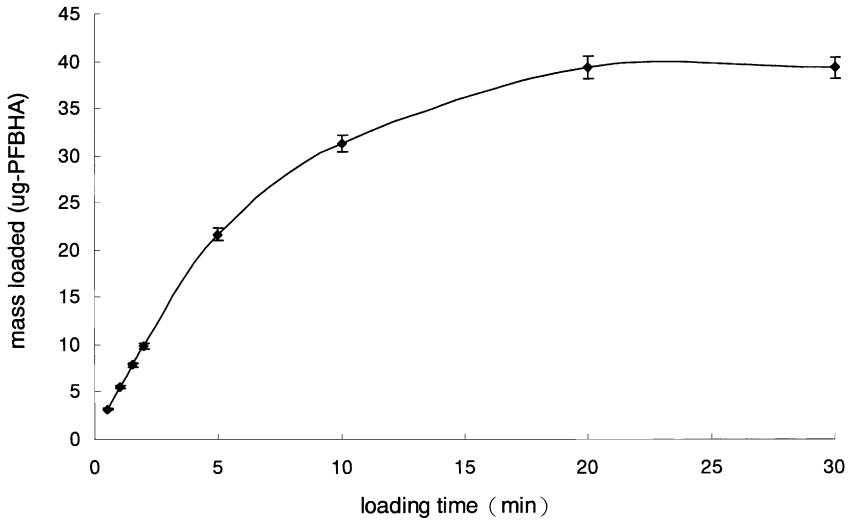

Fig. 1. PFBHA loading time vs. mass loaded.

Fig. 3 showed a typical GC/MS chromatogram of spiked samples at concentration equaled 10 μg/l. Further experiments showed that large peak of PFBHA was still observed after reaction when the loading time for PFBHA was 2 min and the spiking level was 5 mg/l which were higher than the normal concentration ranges found in drinking water [19]. Therefore increasing loading time for PFBHA was not necessary

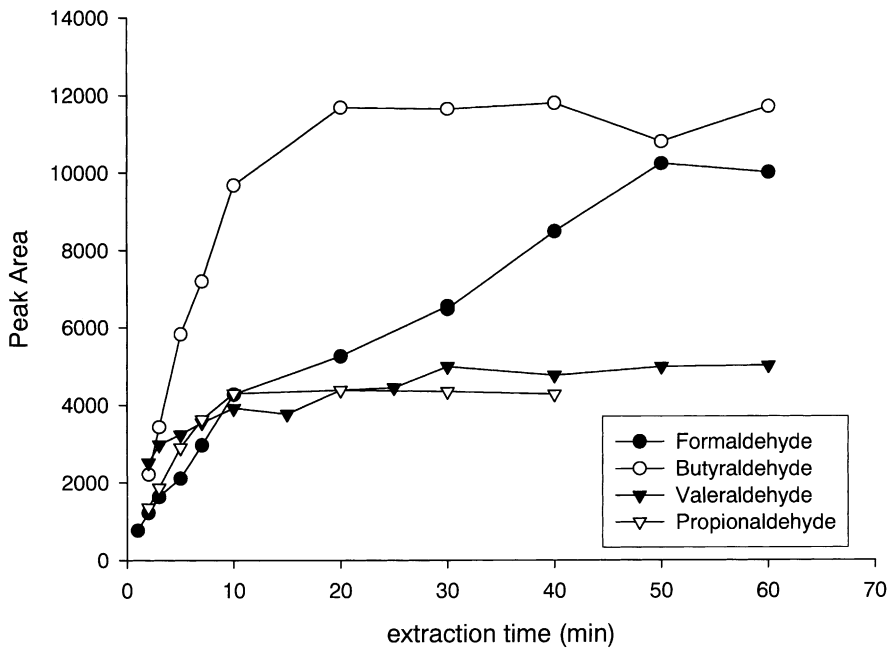

Fig. 2. Adsorption-time profiles for aldehydes in water using headspace SPME with on-fiber derivatization. Sample volume was 2 ml and spiking level was 10 μg/l.

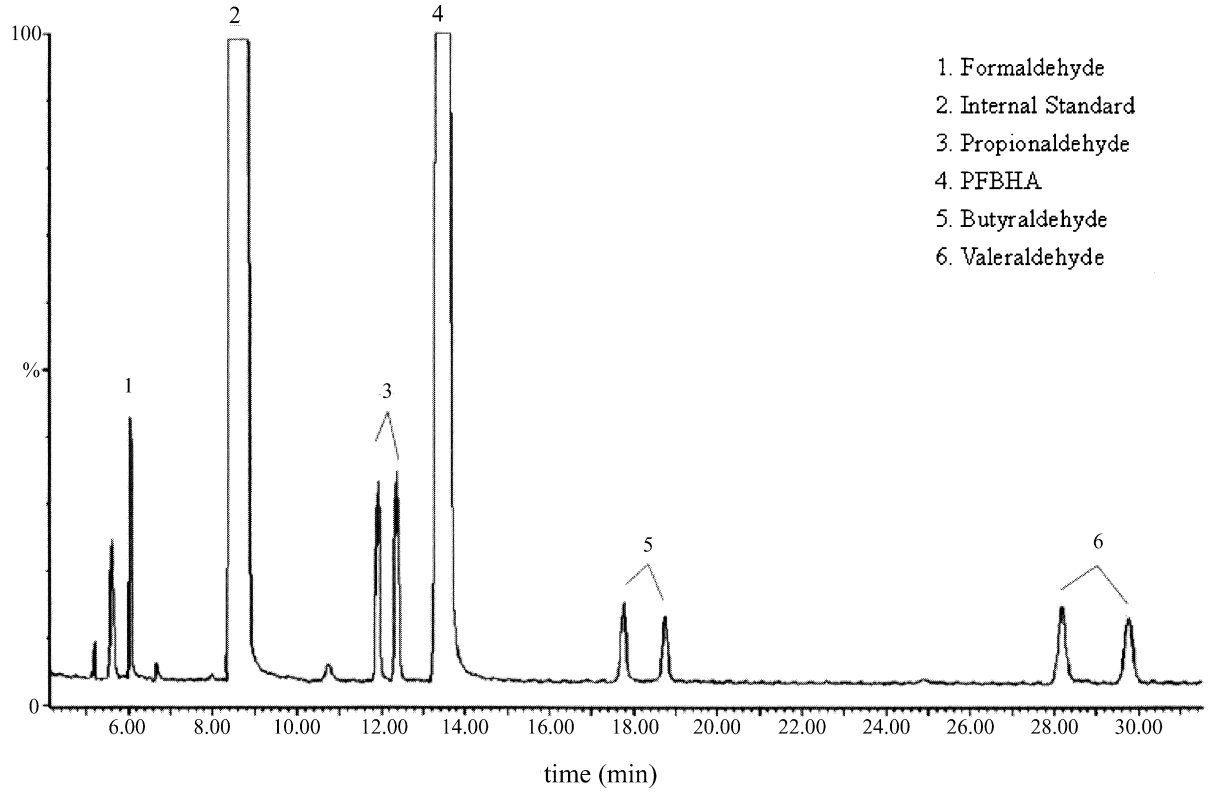

Fig. 3. Typical GC/MS chromatograms of spiked samples in bidistilled water. Sample volume was 2 ml and spiking level was 10 μg/l.

in this research. It was also observed that there were syn and anti isomers of the oximes because aldehydes were asymmetrical carbonyl compounds, except formaldehyde.

Table 1 showed the data of precision and recovery from three different water matrices, including bidistilled water, chlorinated tap water, and well water, respectively. All the data from this table met US EPA's

Table 1
Precision and recovery in bidistilled, well, and chlorinated tap water[a]

	Bidistilled water		Well water		Chlorinated tap water	
	10 μg/l[b]	1 mg/l[c]	10 μg/l	1 mg/l	10 μg/l	1 mg/l
Butyraldehyde	96 (9.2)[d]	106 (7.1)	110 (9.7)	93 (8.8)	105 (7.2)	102 (8.6)
Formaldehyde	90 (8.1)	99 (3.9)	106 (5.1)	105 (3.4)	101 (9.6)	97 (5.5)
Propionaldehyde	105 (7.3)	108 (1.9)	98 (8.5)	99 (2.9)	108 (8.3)	103 (9.7)
Valeraldehyde	103 (6.6)	94 (6.4)	102 (3.8)	106 (4.0)	115 (7.4)	94 (8.2)

[a] $n = 10$, sample volume = 2 ml; ranges for standard curves = 1 μg/l to 5 mg/l; the *x*-axis of the standard curves were concentrations of aldehydes in μg/l; the *y*-axis were the ratio of peak area from oximes divided by the peak area from the internal standard; slopes and regression coefficients were 0.0032 and 0.996 (butyraldehyde); 0.0054 and 0.997 (formaldehyde); 0.0084 and 0.999 (propionaldehyde); 0.0037 and 0.997 (valeraldehyde).

[b] Spiked concentration = 10 μg/l for each aldehydes.

[c] Spiked concentration = 1 mg/l for each aldehydes.

[d] Recovery = 96%, relative standard deviation = 9.2%.

Table 2
Method detection limits

	MDL in current research[a] (μg/l)	MDL in EPA method[b] (μg/l)
Butyraldehyde	0.28[c]	0.35
Formaldehyde	0.22	0.36
Propionaldehyde	0.34	0.41
Valeraldehyde	0.12	0.47

[a] Spiked concentration = 1 μg/l, $n = 8$, column = 30 m × 0.25 mm J&W DB-225 ms.

[b] Spiked concentration = 2 μg/l, $n = 8$, column = 30 m × 0.25 mm J&W DB-5 ms, 0.25 μm film thickness [19].

[c] MDL = $St_{(n-1,1-\alpha=0.99)}$ [19], where $t_{(n-1,1-\alpha=0.99)}$ is the Student's t-value for the 99% confidence level with $n-1$ degrees of freedom, n the number of replicates, S the standard deviation of replicate analyses for $n = 8$ and $\alpha = 0.01$, $t_{(n-1,1-\alpha=0.99)} = 2.998$ for the analysis of butyraldehyde, the standard deviation of replicate analysis = 0.0933, therefore MDL = 0.0933 × 2.998 = 0.28.

±20% requirements [19]. Table 2 showed the data of method detection limits and it was found that the current method had better sensitivities than the US EPA's method [19]. Besides the data from different spiked water matrices, three samples from rain water were also collected and analyzed without the spiking of aldehydes. The analytical procedures mentioned above were performed and GC/MS with SIR detection was utilized. Only formaldehyde were found in these rain water samples with concentrations between 30 and 125 μg/l. Compared with other SPME methods for the determination of aldehydes in water [11], the use of GC/MS with SIR detection in the current study apparently decreased the background interference from the real samples.

When the salt concentration in the solutions is increased, the amount extracted is increased frequently because the fiber/matrix distribution constant increases [21]. However, a decrease in the amount extracted is sometimes observed when analytes are in dissociated form [21]. Some researchers also found that the addition of salt might have no significant effect on the amount extracted. For example, the addition of 10% NaCl had no significant effects on the extractability of the PFBHA derivatives [11]. In current study, the

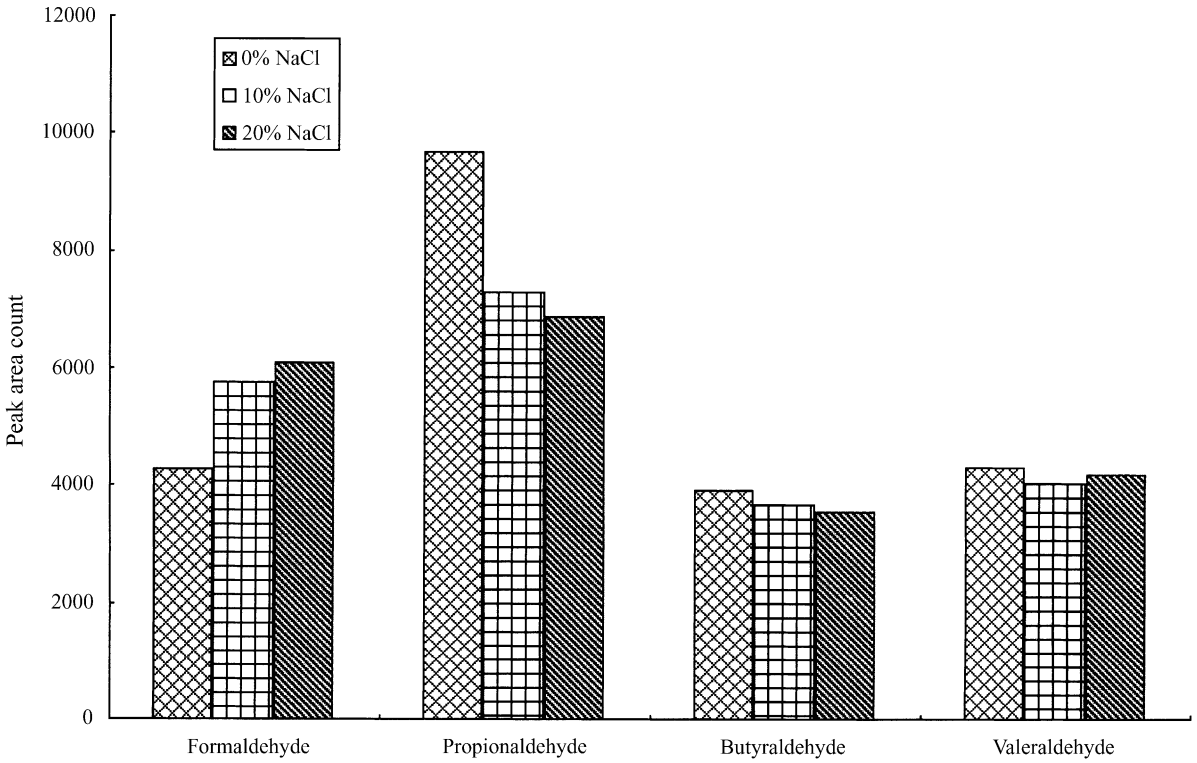

Fig. 4. Effects of salt (NaCl) addition of spiked samples in bidistilled water. Sample volume was 2 ml and spiking level was 10 μg/l.

effects of salt additions were also investigated and Fig. 4 showed the results when the spiking level was 10 μg/l for bidistilled water. Only the test on formaldehyde showed the effects of extraction increased as the concentration of salt added increased. Besides Fig. 4, well water and chlorinated tap water were also tested for the effects of salt additions and the results were all similar to Fig. 4. This founding was expected since the equilibrium of adsorption-time profile for formaldehyde shown in Fig. 2 was not reached at the extraction time of 10 min.

Besides the effects of salt addition, the influences of different extraction temperatures were investigated as well and Fig. 5 showed the results. The data for formaldehyde showed the dependence of extraction temperatures as expected. However, as mentioned above, a 10 min extraction time without any further salt addition and temperature control also yielded sufficient efficiencies and provided acceptable sensitivities (Table 2), therefore the addition of salt and the increasing of extraction temperature can also be omitted in the future.

Various derivatization techniques including direct derivatization in sample matrix, derivatization in GC injector port, and derivatization in SPME fiber coating can be implemented combined with SPME [21]. On-fiber derivatization technique was used in this research where simultaneous derivatization and extraction were performed directly in the fiber coating. This approach allows high efficiencies and can be used in remote field applications [21].

Compared with other PFBHA-SPME method for the analysis of aldehydes in water where oximes were formed in solutions and vaporized to headspace by magnetic stirring [11], aldehydes were stirred to headspace and reacted with PFBHA on-fiber in the current research. It was obvious that vaporizing aldehydes were easier than oximes because the molecular masses were far different (e.g. 30 g/mol for HCHO while 225 g/mol for HCHO–PFBHA oxime). This might explain why a 10 min extraction time could be used here to yield over 80% of extraction efficiencies while other researcher had to use a 30 min extraction time [11]. On the other hand, reactions between

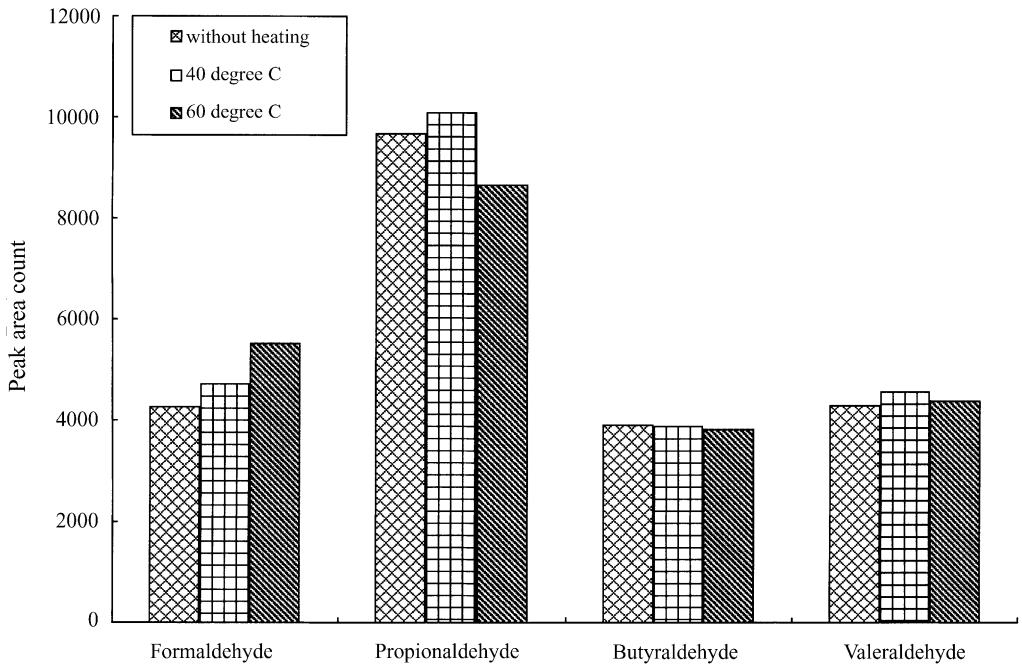

Fig. 5. Effects of headspace extraction temperatures of spiked samples in bidistilled water. Sample volume was 2 ml and spiking level was 10 μg/l.

aldehydes and PFBHA in air were observed to be very fast [24], compared to 2 h were needed to complete the derivatization process in water [11]. This also made the current technique favorable in terms of time saving.

4. Conclusions

The research shown here demonstrated that the analysis of aldehydes in water by SPME with on-fiber derivatization provided acceptable precision and sensitivity with simple and fast procedures. When sample volume is limited, only 2 ml of water sample needed makes this technique more favorable than other methods. For water samples containing more aldehydes and/or ketones, the loading time for PFBHA onto fiber can be simply increased to provide enough amount for reaction. The time saving procedure also makes the proposed method suitable for routine analysis of water samples.

Acknowledgements

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