



ZnO nanorod coating for solid phase microextraction and its applications for the analysis of aldehydes in instant noodle samples

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ABSTRACT

Zinc oxide (ZnO) nanorods based solid-phase microextraction (SPME) coating was directly prepared on stainless steel wires using in situ hydrothermal growth method. This coating has high surface-to-volume ratio with a diameter in the range of 300–500 nm and a thickness of about 3–5 μm. A guiding tube was introduced into the laboratory-made SPME fiber to protect the ZnO nanorods coating from shaving, which significantly improved the method repeatability and prolonged the service life of the coating. The extraction properties of the prepared fiber were investigated using headspace SPME (HS-SPME) coupled to gas chromatography (GC) for the determination of aldehydes in instant noodle samples. The extraction efficiency of the coating for the five aldehydes was comparable to that of a commercial 85 μm Carboxen/Polydimethylsiloxane fiber, which has been reported to have best affinity towards aldehydes among all commercial fibers. The linear ranges of the proposed HS-SPME-GC method were from 0.05 to 5 μg g⁻¹ (hexanal, nonanal and decanal) and 0.1–5 μg g⁻¹ (heptanal and octanal), with the correlation coefficients from 0.990 to 0.999. The method developed was successfully applied to the determination of five aldehydes in instant noodle samples, and the recoveries were found to be 70.5–129% at the spiking level of 2 μg g⁻¹.

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1. Introduction

Since its introduction in 1989 [1], solid-phase microextraction (SPME) has gained widespread acceptance as a powerful sample preparation technique due to its simple, time-efficient, sensitive and solvent-free characteristics. Coupled with gas chromatography (GC) or high performance liquid chromatography (HPLC) [2–4], SPME has been successfully applied to environmental [5,6], clinical [7], biological [8], and food analysis [9]. Fiber coating is considered to be the key factor in SPME technique. In the past two decades, many efforts have been directed to the development of material as SPME coatings with remarkable thermal and chemical stability, enhanced sensitivity and selectivity for the specified analytes [10–14].

Zinc oxide (ZnO) is a promising material due to its wide bandgap, specific electrical property, and excellent chemical and thermal stabilities [15]. ZnO nanostructures, particularly one-dimensional

ZnO nanorods and nanowires, have shown considerable attraction in many fields, such as optoelectronics [16], nanomechanics [17,18], resonators [19], electric nanogenerator [20] and nanosensors [21–23]. Due to its high surface-to-volume ratio, good thermal stability, and easy preparation, ZnO nanorod is an ideal material for SPME coating, especially for headspace-SPME (HS-SPME) whose coating is requested to be gas adsorption materials. Recently, ZnO nanorods and nanotubes have been prepared on fused silica fibers as SPME coatings based on hydrothermal synthesis method [24–26]. The as-prepared ZnO nanorod and nanotube SPME fiber coatings proved to exhibit satisfactory extraction capability for the selected organic compounds. However, the SPME fiber based on the fused silica support is easily broken and its service life is therefore limited. Currently, stainless steel wire has gradually replaced fused silica fiber as the main substrate of laboratory-made SPME fiber [27,28], due to its excellent thermal and mechanical stabilities. However, stainless steel wires are generally ductile and thus lead to low straightness. As a result, the ZnO nanorod coating will be unavoidably shaved when the fiber is pushed out or drawn back through the needle tube of a SPME holder. So it is necessary to solve the problem of coating shaving in the case that stainless steel wire is used as fiber support.

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Instant noodle is a kind of popular food with high oil content, which always suffers a remarkable decrease in quality due to the oil oxidation. The oil autoxidations are non-enzymatic autocatalytic oxidations caused by free-radical chain reactions, resulting in the formation of hydroperoxide as a primary product. The primary product can be easily broken into the secondary products, including polymers, ketones and aldehydes [29]. Particularly, the generation of aldehydes is one of the deteriorative factors to the food quality. Thus, the aldehydes content can be taken as an indicator for the oxidation level of oil products or fried food samples [30]. Traditionally, the fats and oils in the instant noodle samples were extracted using Bligh and Dyer method [31], and then the deteriorated fats and oils were analyzed by potentiometry method. This method requires tedious processes with large amounts of organic solvent. For the analysis of volatile analyte as aldehydes in complex matrix samples, for example, instant noodles, HS-SPME can be considered as an ideal extraction method. Additionally, ZnO nanorods with high surface-to-volume ratio, polar surface [15], non-toxicity [32] and bio-compatibility [33], are also suitable to realize the direct extraction of aldehydes generated from the oil oxidation in foods.

Based on these considerations, we directly synthesized ZnO nanorods on the surface of a stainless steel wire as an SPME coating using a one-step hydrothermal process. Meanwhile, to overcome the coating scraping problem as discussed above, we proposed a simple approach by attaching a guiding tube onto the stainless steel wire. Then, we for the first time applied HS-SPME with ZnO nanorod coating for the extraction of aldehydes generated from oil oxidation in instant noodles. The extraction efficiency and analytical performance for aldehydes using a ZnO nanorod fiber and commercial CAR/PDMS fiber were compared. Combined with a gas chromatography-flame ionization detector (GC-FID), five kinds of aldehydes in instant noodles including hexanal, heptanal, octanal, nonanal and decanal were quantitatively determined.

2. Experimental

2.1. Reagents and solutions

Stainless steel wires (O.D., 0.15 mm and 0.20 mm) were purchased from the AnTing Micro-Injector Factory (Shanghai, China). All chemicals and reagents used in the experiments were analytical grade. Zinc nitrate and hexamethylenetetramine (HMT) were obtained from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hexanal, heptanal, octanal, nonanal and decanal were purchased from J&K Scientific Ltd. (Beijing, China). Instant noodle samples were collected from local supermarkets in Xiamen. 100 mg L⁻¹ stock solutions of five aldehydes were prepared by diluting 1000 mg L⁻¹ of each compound with methanol. The standard working solutions were prepared by diluting the mixture with methanol to the required concentration. All the above-mentioned solutions were sealed and stored at 4 °C in a refrigerator.

2.2. Instrumentation

Commercial manual sampling SPME device was purchased from Supelco (Bellefonte, PA, USA), and the SPME fiber with 85 μm CAR/PDMS was selected for comparison in the experiments. The analysis of the selected aldehydes was carried on a Shimadzu GC-2010 GC system coupled with a flame ionization detector (FID). Before use, the CAR/PDMS fiber was conditioned in GC injector according to the instructions provided by the manufacturer. The prepared ZnO nanorod coated fiber was also conditioned at 220 °C. Separation was performed using a DB-5 capillary column (30 m × 0.25 mm I.D. and 0.25 μm, J&W Scientific, CA, USA).

The instrumental parameters for the analysis of the selected aldehydes were as follows: N₂ flow, 1.47 mL min⁻¹; column

temperature program: held at 40 °C for 3 min, then increased from 40 to 70 °C at 15 °C min⁻¹ and maintained for 1 min, finally increased to 220 °C at 30 °C min⁻¹ and stay for 1 min. The detector temperature was held at 280 °C. Under the optimized conditions, the temperature of the injector was set at 220 °C, and the desorption was performed in splitless mode for 1 min. An S4800 scanning electron microscope (SEM) (Hitachi, Tokyo, Japan) was used to obtain morphologies of the ZnO nanorod fiber coating. A Branson 200 ultrasonicator (Danbury, CT, USA) was used in this study.

2.3. Modification of stainless steel wire substrate

In order to protect the ZnO nanorod coatings from shaving, modification of the stainless steel wire support was carried out. On the end of the stainless steel wire, a 1.2 cm hollow stainless steel tube was fixed by adhesive. The diameter of the hollow stainless steel tube matched with the diameter of the stainless steel wire and the SPME holder needle. The stainless steel tube is taken as a guiding tube since it ensures the coated stainless steel wire position in the middle of the SPME holder needle. The modified stainless steel wires were used as the substrate for the ZnO nanorod coating.

2.4. Preparation of ZnO nanorod coated fiber

The preparation of ZnO nanorod coated fiber involved following processes: (1) prior to preparation of coating, the modified stainless steel wires (17 cm) were sequentially cleaned with acetone, then methanol and finally distilled water in an ultrasonicator for 5 min, and then air-dried at room temperature; (2) a 20 mL aqueous solution of equal amount (0.0125–0.050 mol L⁻¹) of Zn(NO₃)₂·6H₂O and HMT was ultrasonically mixed in a glass bottle. Several modified stainless steel wires were inserted through a foam cap, and a length of approximate 1.0 cm of stainless steel wires was left in the end for coating; (3) the foam cap with the stainless steel wires was inserted into the glass bottle, and the stainless steel wires were kept immersed in the solution for 2–12 h at a controlled temperature (70–95 °C). After the growth process completed, the ZnO nanorod coated fibers were rinsed by distilled water and then dried in oven for 2 h. The ZnO nanorod coated fiber was finally mounted into a laboratory-made SPME holder modified from a 5 μL micro-syringe [12].

2.5. HS-SPME procedure

Packaged instant noodle samples from different companies were purchased from local supermarkets in Xiamen. All the instant noodles were crushed into powders and then transferred to clean glass vials. Instant noodle samples and spiked samples were tested immediately. For HS-SPME experiments, 2.0 g instant noodle sample was placed in a 10 mL glass vial. The vial was closed with Teflon-lined septa (Supelco). This step is crucial for the application of HS-SPME, since it makes sure the airtightness. In the optimization of extraction process, the spiking concentration for each aldehyde is 5 μg g⁻¹ and for recovery experiments the spiking concentration is 2 μg g⁻¹. The instant noodle samples were pre-heated for 15 min, and then a ZnO nanorod coated fiber was introduced into the headspace of the vial for a period of time (1–15 min) at an experimental extraction temperature (28–95 °C). After extraction, the fiber was pulled out and inserted into the GC injector.

3. Results and discussion

3.1. Optimization of ZnO nanorod coated fiber preparation

A ZnO growth solution was prepared by modifying the method reported by Vayssiers [15]. To achieve a high effective surface

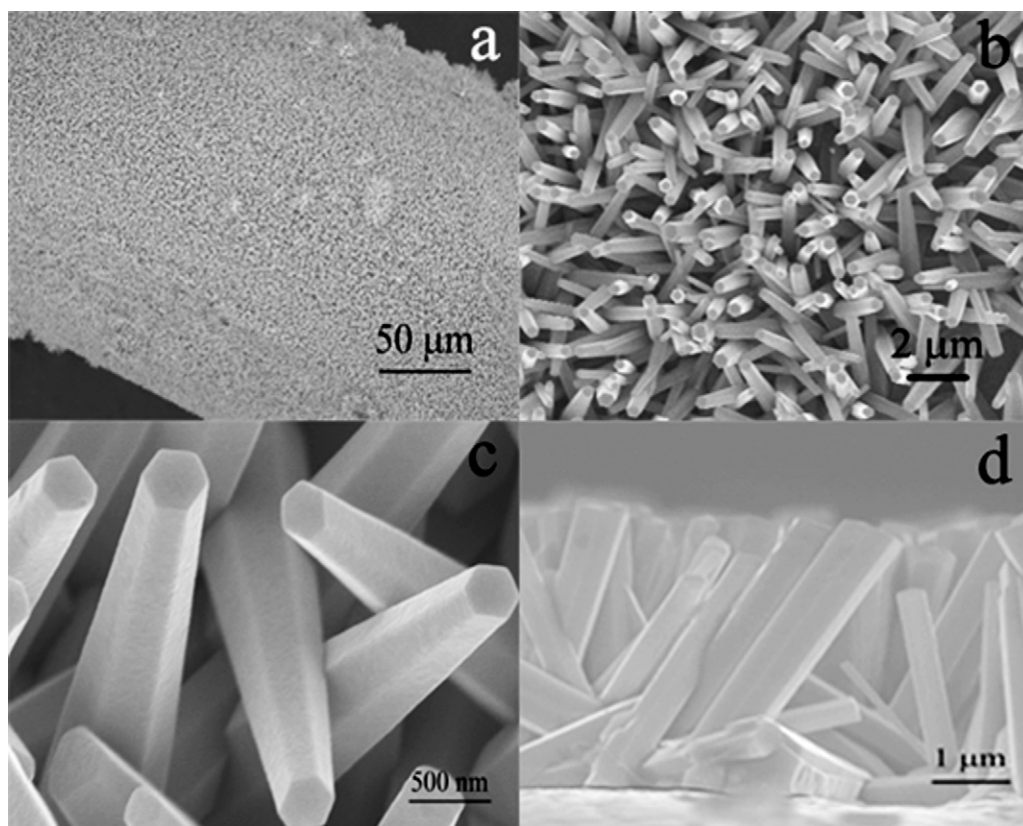


Fig. 1. SEM images of ZnO nanorod coating at (a) 200 \times magnifications (b) 5000 \times magnifications (c) 10,000 \times magnifications (d) 20,000 \times magnifications: precursor concentration, 0.025 mol L⁻¹; reaction time, 4 h; reaction temperature, 90 °C.

area for the remarkable adsorption of analytes, the precursor concentration, reaction time and temperature were optimized during the synthesis procedure. The precursor concentrations of Zn(NO₃)₂·6H₂O and HMT are critical factors affecting the diameter and alignment of nanorods. The shape of ZnO has transformed from wire-like to rod-like with the precursor concentration from 0.0125 to 0.50 mol L⁻¹. When the precursor concentration of Zn(NO₃)₂·6H₂O and HMT was 0.0125 mol L⁻¹ (Fig. S1a–c), the grown nanorods were scattered and their shapes were irregular. When the precursor concentration reached 0.025 mol L⁻¹ (Fig. S1d–f), the nanorods oriented in a perpendicular fashion and arranged in very large and uniform arrays on the stainless steel wire. After the concentration increased to 0.050 mol L⁻¹ (Fig. S1g–i), the length and density of nanorods stayed unchanged while the diameter increased irregularly. In addition, it can be found that nanorods stacked up and made the surface area decreased. In order to obtain high surface-to-volume ratio, the precursor concentration of Zn(NO₃)₂·6H₂O and HMT were chosen as 0.025 mol L⁻¹.

The reaction temperature and time were also optimized and set at 90 °C for 4 h. By controlling these experimental conditions, we have successfully synthesized well-oriented ZnO nanorods. Fig. 1 shows electron micrographs of the coating obtained from the aqueous chemical growth of ZnO under 90 °C for 4 h with the concentration of 0.025 mol L⁻¹ Zn(NO₃)₂·6H₂O and HMT. It can be found that the novel nanorod array coating has a high surface-to-volume ratio with a diameter in the range of 300–500 nm and the length of about 3–5 μm.

3.2. Modification of laboratory-made SPME device

As discussed in the introduction section, stainless steel wire is a good alternative for SPME fiber substrate, but its lower straightness

causes fiber bend and coating shaved easily. As shown in Fig. 2a, the coated stainless steel wire contacts with the wall on the end of the SPME holder needle. When the fiber was pushed out or drawn back, the inside wall of the needle easily contacted with some part of the coating and scratched it off. It reduced the fiber service life. To solve this problem, we developed a modified SPME fiber by introducing a guiding tube (Fig. 2b), whose internal and outer diameter is equivalent to the outer diameter of the stainless steel wire support and the internal diameter of the SPME holder needle, respectively. This minor modification ensured the coated stainless steel wire position in the middle of the SPME holder needle. Fig. 2c shows the condition of the modified fiber, which kept straight while being pushed out or drawn back. After the modification, the ZnO nanorod coating could be protected from shaving effectively. The mechanical stability of the coating was enhanced effectively, and the service life was prolonged greatly (more than 100 injections).

3.3. Extraction efficiency of the ZnO nanorod coated fiber

To investigate the extraction ability of the ZnO nanorod coated fiber for aldehydes, a commercial fiber (85 μm CAR/PDMS) was selected for the comparison, since it is reported to be of high affinity for aldehydes [34]. Compared to the commercial fiber, ZnO nanorod coated fiber presented practically equivalent extraction efficiency towards the most selected aldehydes (Fig. 3). It should be noted that the ZnO nanorod coating thickness is only 3–5 μm. It could be estimated that higher extraction efficiency of fiber could be attained if the coated thickness increased. The high extraction efficiency of ZnO nanorod fiber towards the aldehydes may be due to its large surface area and polarity. The well-oriented nanorod structure increased the available surface area and thus increased the available adsorption sites of the fiber. The results indicated that

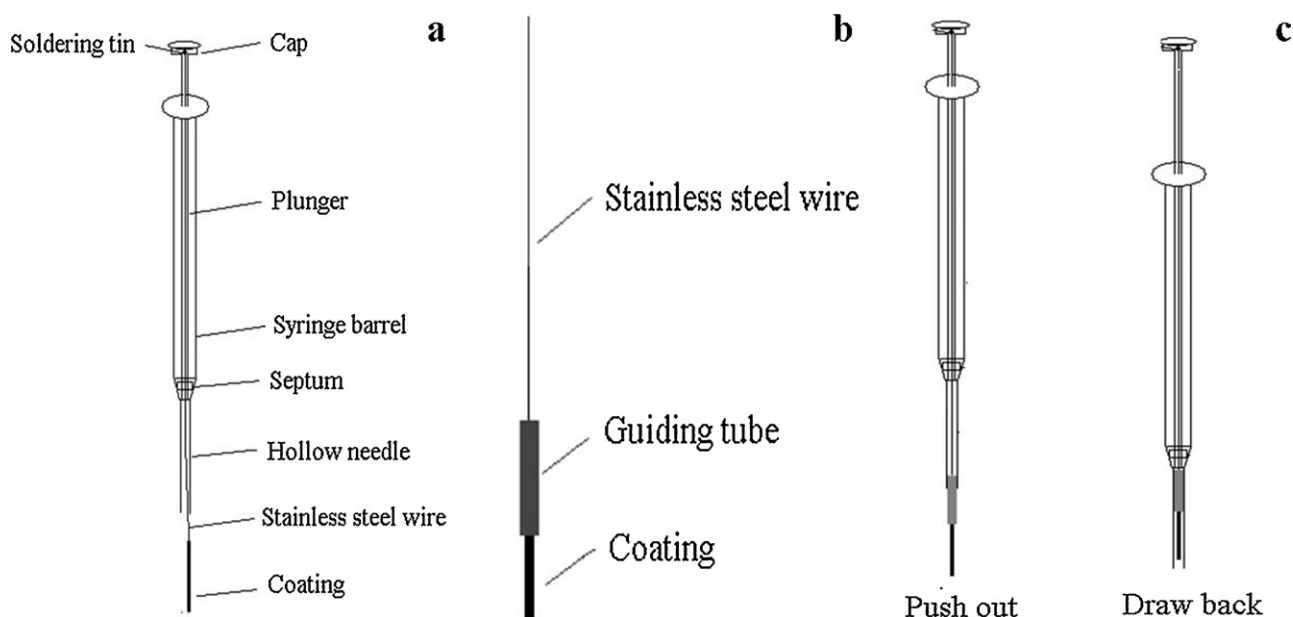


Fig. 2. Schematic diagram of laboratory-made SPME devices. (a) laboratory-made fiber without modification; (b) the condition of modified SPME fiber; (c) the operation of the modified fiber: push out (left), draw back (right).

the ZnO nanorod coated fiber could be a good choice for HS-SPME of polar aldehydes generated from foods with complex matrix.

3.4. Optimization of extraction process for aldehydes

3.4.1. Extraction time

The effect of extraction time on the extraction efficiency for the selected aldehydes was investigated at 1, 2, 4, 6, 8, 10, and 15 min. Fig. 4 shows that the peak areas of the analytes increased with the extraction time from 1 to 10 min, and most of the aldehydes reached equilibrium after 10 min. This short equilibrium time is attributed to the thin coating of ZnO nanorods (3–5 μm). In the following experiments, an extraction time of 10 min was selected as a compromise between the analysis time and the method sensitivity.

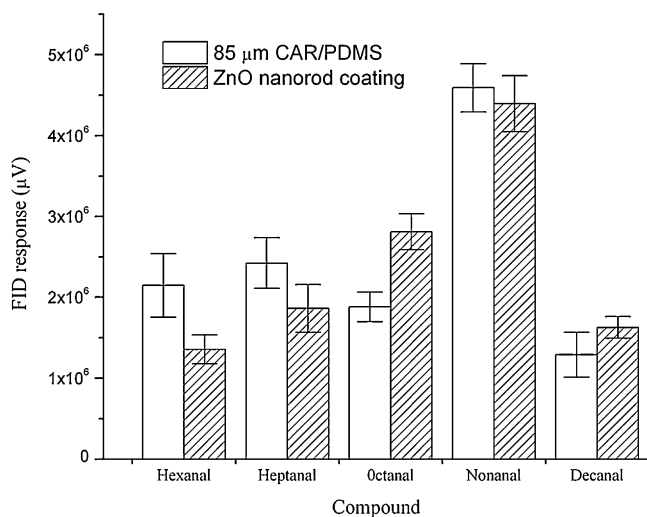


Fig. 3. Comparison of extraction amounts using a ZnO nanorod coated fiber and a CAR/PDMS fiber. HS-SPME conditions: sample weight, 2 g; extraction temperature, 45 $^{\circ}\text{C}$; extraction time, 10 min; desorption temperature, 220 $^{\circ}\text{C}$; and desorption time, 2 min. Concentration of each aldehydes, 5 $\mu\text{g g}^{-1}$.

3.4.2. Extraction temperature for HS-SPME sampling

In order to investigate the effect of the extraction temperature on the extraction efficiency in HS-SPME sampling for the selected aldehydes, different extraction temperatures of 28, 32, 45, 55, 75 and 95 $^{\circ}\text{C}$ was studied (Fig. 5). The temperature range was selected based on the equilibrium between the fiber coating, analytes and the sample matrix. As shown in Fig. 5, the extraction efficiency increased as the temperature increased from 28 to 55 $^{\circ}\text{C}$, and tended to equilibrium when the temperature was higher than 55 $^{\circ}\text{C}$. Lower temperature favors the adsorption to the fiber, but higher temperature is beneficial for the transfer of the analytes into the headspace part [35]. Due to the high volatility of the aldehydes, lower extraction temperature is enough to bring these compounds up into the headspace. Furthermore, for instant noodle samples containing high level of oils, too high extraction temperature might cause side reactions (such as oxidation) and competition adsorptions from co-existing substances. Consequently, the optimal extraction temperature of 55 $^{\circ}\text{C}$ was chosen.

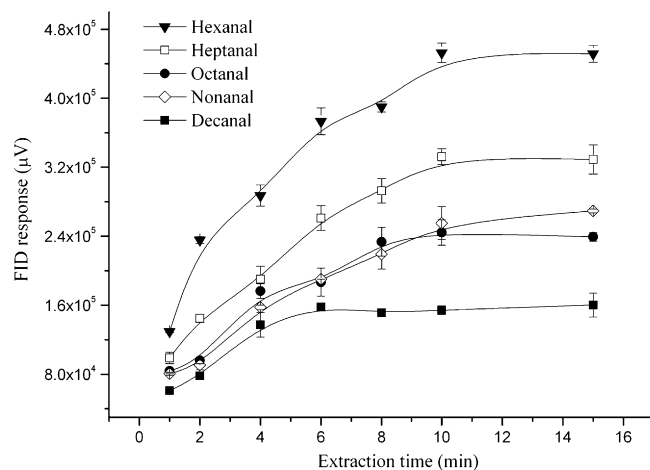


Fig. 4. SPME extraction time profiles for aldehydes using a ZnO nanorod coated fiber. HS-SPME conditions: sample weight, 2 g; extraction temperature, 45 $^{\circ}\text{C}$. Concentration of each aldehyde, 5 $\mu\text{g g}^{-1}$.

Table 1
Detection limits, linear range, correlation coefficients, repeatability and reproducibility of the proposed HS-SPME-GC-FID method using a ZnO nanorod coated fiber and a commercial CAR/PDMS fiber.

Analytes	LOD (ng g ⁻¹)		Linear range (μg g ⁻¹)		Correlation coefficients		Repeatability (n = 5, %)		Reproducibility (n = 3, %) ^a	
	ZnO	CAR/PDMS	ZnO	CAR/PDMS	ZnO	CAR/PDMS	ZnO	CAR/PDMS	ZnO	CAR/PDMS
Hexanal	36	11	0.05–5.0	0.05–5.0	0.999	0.996	8.2	17.3	3.9	7.2
Heptanal	37	23	0.1–5.0	0.05–5.0	0.990	0.999	13.3	10.4	10.0	5.3
Octanal	28	34	0.1–5.0	0.05–5.0	0.996	0.998	11.5	8.9	6.1	8.9
Nonanal	10	5	0.05–5.0	0.05–5.0	0.994	0.993	9.7	16.0	10.2	9.4
Decanal	17	29	0.05–5.0	0.1–5.0	0.998	0.995	12.6	15.1	8.3	12.1

^a The concentration of the aldehydes was 2 μg g⁻¹ in blank instant noodle sample, and other conditions were the optimized conditions.

3.4.3. Desorption temperature

In order to effectively release analytes from the fiber, the desorption temperature must be high enough. A desorption temperature ranged from 200 °C to 240 °C was studied in the experiments. The peak areas of all five aldehydes remained nearly unchanged above 220 °C. Although a higher desorption temperature was helpful to reduce the desorption time, the higher temperature might cause the fiber coating and injector damaged. The desorption temperature for subsequent experiments was set at 220 °C.

The desorption time was checked at 0.1, 0.5, 1, 2, and 3 min. The peak areas of the analytes increased from 0.1 to 2 min and reached equilibrium after 2 min. The analytes remaining in the coating after desorption at 220 °C for 2 min were checked and none could be found. These results showed that the analytes had been released completely. The rapid desorption of analytes was mainly attributed to their high volatility, thus the desorption time was set at 2 min.

3.5. Evaluation of the proposed HS-SPME-GC-FID method for determination of aldehydes in instant noodles

3.5.1. Evaluation of method performance

Under the optimized conditions, the ZnO nanorod coated fiber was used for the extraction of five aldehydes, followed by the determination using GC-FID. The analytical characteristics of the proposed method are presented in Table 1, and the data was compared with that using a commercial CAR/PDMS fiber. Solutions used in linearity studies were prepared by diluting the stored solution with the blank instant noodle samples. The linear ranges of the method were from 0.05 to 5 μg g⁻¹ (hexanal, nonanal and decanal) and 0.1 to 5 μg g⁻¹ (heptanal and octanal), with the correlation coefficients from 0.990 to 0.999. The limits of detection

(LODs), which was defined as three times the baseline noise, were found in the range of 10 ng g⁻¹ (nonanal) to 37 ng g⁻¹ (heptanal). The repeatability for the method was evaluated through extracting blank instant noodles spiked at 2 μg g⁻¹ of five aldehydes (five replicates), and the relative standard deviations (RSDs) were presented to be 8.2–13.3%. In the preparation, several ZnO nanorod coated fibers could be simultaneously prepared in one batch using a foam cap, which improved the reproducibility of fiber to fiber. The reproducibility of fiber-to-fiber (three replicates) was evaluated and ranged 3.9–10.2%. It was clearly found from Table 1 that the proposed method using ZnO nanorod as SPME coating presented practically equivalent performance with the CAR/PDMS, even though the thickness of the ZnO coating was obviously thinner than the CAR/PDMS. The results are also consisted with Fig. 3, and proved that this fiber coating satisfied with the quantitative requirements of aldehydes generated from food oxidation.

3.5.2. Application to instant noodle samples

As mentioned in Section 1, aldehydes are the most important degraded products of hydroperoxides, and thus could be used as an indicator of lipid oxidation in foods. To test the method applicability, the proposed method was used to determine five aldehydes in real instant noodle samples. As shown in Table 2, the detected content of five aldehydes was different in instant noodles manufactured from different companies, ranging from 0.13 (decanal) to 1.35 μg g⁻¹ (hexanal). The recovery of the five aldehydes in the instant noodle samples spiked at 2 μg g⁻¹ ranged from 70.5% to 129%. Considering the low concentration of aldehydes and the

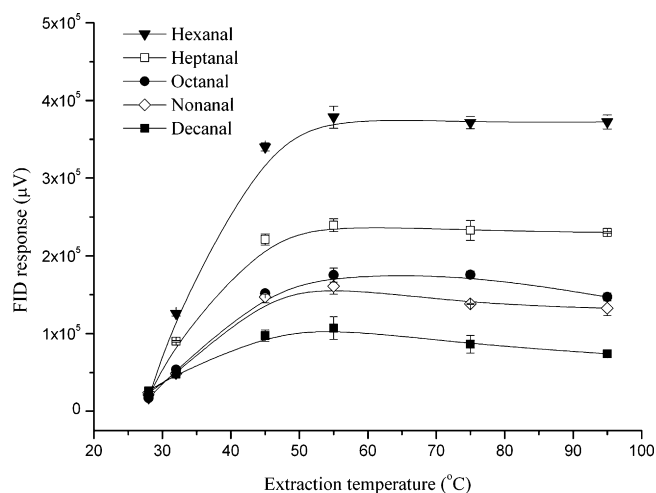


Fig. 5. Effect of extraction temperature on the extraction efficiencies of aldehydes using a ZnO nanorod coated fiber. HS-SPME conditions: sample weight, 2 g; extraction time, 10 min. Concentration of each aldehyde, 5 μg g⁻¹.

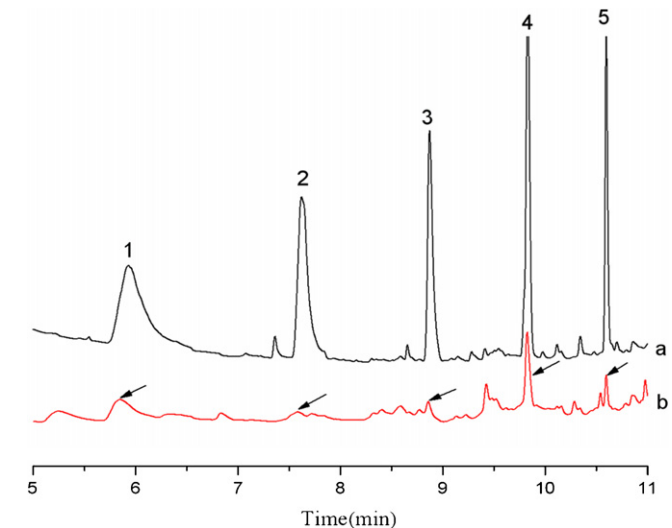


Fig. 6. Chromatograms of ZnO nanorods based HS-SPME-GC-FID analysis of (a) instant noodles spiked with 2 μg g⁻¹ standard solutions of each aldehydes and (b) instant noodle samples. (Peaks: 1. Hexanal 2. Heptanal 3. Octanal 4. Nonanal 5. Decanal.)

Table 2

Analytical results for the determination of five aldehydes in three kinds of instant noodles using the proposed HS-SPME-GC-FID method.

Analyte	Sample 1 ^a		Sample 2		Sample 3	
	Detected (SD ^b , n = 3) (μg g ⁻¹)	Recovery ^c (SD, n = 3) (%)	Detected (SD, n = 3) (μg g ⁻¹)	Recovery ^c (SD, n = 3) (%)	Detected (SD, n = 3) (μg g ⁻¹)	Recovery ^c (SD, n = 3) (%)
Hexanal	0.99 (0.04)	82.4 (7.8)	1.07 (0.04)	96.8 (8.9)	1.35 (0.07)	78.5 (1.1)
Heptanal	ND ^d	70.5 (6.4)	ND	129 (1.5)	0.21 (0.08)	76.6 (8.9)
Octanal	ND	97.1 (2.5)	ND	97.4 (8.9)	0.18 (0.05)	96.7 (3.3)
Nonanal	0.33 (0.09)	114 (7.8)	1.21 (0.16)	78.9 (9.0)	1.16 (0.43)	75.5 (8.1)
Decanal	0.13 (0.05)	92.8 (3.0)	0.29 (0.04)	89.1 (6.9)	0.26 (0.04)	85.4 (6.8)

^a Instant noodle samples manufactured from different companies.^b Standard deviation.^c The spiked concentration of each aldehyde was 2 μg g⁻¹, and the recovery was calculated based on the equation: Recovery = (C_{found} - C_{detected})/C_{added} × 100% (C_{found}: total concentration of the aldehydes after spiking; C_{detected}: original concentration of the aldehydes in samples; C_{added}: spiking concentration).^d Not detected.

severe interfering effect from the complex matrix, this recovery range is acceptable. It should be noted that the content of hexanal was the highest in all three instant noodle samples and increased with the storage time (the storage time was increased from sample 1 to sample 3). There are high amounts of polyunsaturated fatty acids (PUFA) in oils and oil products. Hexanal is a typical volatile oxidation product of n-3 PUFA, n-6 PUFA, n-9 PUFA, thus it can be used as an indicator of lipid oxidation in foods [36]. The results demonstrated that the instant noodle storage time presented correlation with hexanal concentration. Fig. 6 showed typical HS-SPME-GC-FID chromatograms of standard aldehydes solution and one of the instant noodle samples. It could be seen that all the target analytes could be extracted using the ZnO nanorod coated fiber. It must be emphasized that all the aldehyde peaks from the chromatogram of instant noodle sample (Fig. 6b) were qualitatively confirmed using GC-MS.

4. Conclusions

In this study, using in situ hydrothermal growth method, ZnO nanorods were directly synthesized onto a stainless steel wire as an SPME coating. Simultaneously, the laboratory-made SPME fiber is modified by introducing a guiding tube to protect the ZnO nanorod coating from shaving. This modification effectively improves the extraction reproducibility and prolongs the fiber lifetime. The extraction efficiency of the ZnO nanorod coated fiber towards five selected aldehydes was comparable to that of a commercial SPME fiber (85 μm CAR/PDMS). The prepared ZnO nanorod coated fiber features the characteristics of low cost, easy preparation, large surface-to-volume ratio and high extraction efficiency towards aldehydes. The content of hexanal was found to be related to the storage time of oil fried products as instant noodles. These results indicated that the ZnO nanorod coated fiber of HS-SPME combined with GC-FID can be potentially set as a standard method to identify the extent of oil oxidation in foods. Additionally, it could be predicted that ZnO nanorod coated fiber would also show high affinity towards other volatile and semi-volatile compounds in foods and other complex matrix.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2012.01.080.

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