Development of a Solid-Phase Microextraction-Surface-Enhanced Raman Scattering Approach to Detect Ferbam

Shan Wang, Jinhui Zhao, Guoqiang Wu, Weijun Leng and Chunrong Wang*

School of Food Science and Technology, Jiangxi Agricultural University, Nanchang, 330045, China
Email: crwang07@126.com

Abstract. By coupling solid-phase microextraction (SPME) with surface-enhanced Raman scattering (SERS), a facile method was developed for the determination of ferbam, a pesticide often used in fruits and vegetables. It is a potential carcinogen. The SPME substrate was made by free settling of rod-like ZnO nanomaterials on a aluminum sheet. The extraction procedure for ferbam was performed in a simple solution, and then the ferbam was determined using SERS after uniformly dropping a SERS-active substrate (gold nanoparticles, AuNPs) onto the surface of the SPME substrate. In this method, qualitative measurement in extraction procedure takes only 5 minutes. The lowest detectable concentration of ferbam is 0.01 ppm. The newly developed method is fast, convenient and sensitive in the determination of ferbam in solution.

1. Introduction

Surface-enhanced Raman scattering (SERS) is a highly sensitive technique, based on the gaint electromagnetic enhancement induced by nanotechnology. SERS has been widely explored to detect organic chemicals. For example, the weak Raman molecular "fingerprint" can be tremendously enhanced through the placement of the analyte on gold nanostructures [1-4]. On the other hand, solid-phase microextraction (SPME) [5-8] is proved to be an effective method for gathering analyte and often used to detect organic compounds coupled with gas chromatography [9] and mass spectrometry [10-12]. In our study, we developed a new approach combining SPME with SERS to perform a simple, sensitive, and easy operation for the determination of ferbam. In the preparation of the extraction substrate, rod-like ZnO nanomaterials were deposited on an aluminum support sheet for SPME [13]. The ferbam was absorbed and concentrated by the ZnO, and the content of ferbam was then measured using SERS. Compared to other ferbam detecting methods such as GC and HLCP the SPME-SERS provided a simple, rapid, and sensitive approach for the determination of ferbam in solution.

2. Experimental Sections

2.1. Chemicals and Instruments

Chmicals such as Zn(CH$_3$COO)$_2$•2H$_2$O (99.0%), hydrogen tetrachloroaurate hydrate (99.999%) and sodium chloride (99.5%) were of analytical grade, and procured from Sigma Aldrich (St. Louis, MO). Hydrochloric acid (34 to 37.5%), acetone (99.9%), ethanol (100%), ammonia (25.0 to 28.0%), and methanol (99.9%) were purchased from Fisher Scientific (Fair Lawn, NJ).
2.2. Preparation of Gold Nanoparticles

Au nanoparticles were prepared through the reduction of trisodium citrate as described by Frens.[14] Briefly, 30 mL of HAuCl$_4$ aqueous solution (0.01%, w/w) was heated at 100 °C under vigorous stirring. While boiling, 0.6 mL of trisodium citrate aqueous solution (1%, w/w) was added very quickly. The solution turned wine red in colour within 2 min. After 15 min of reaction, the heating was stopped, but the stirring was maintained until the solution cooled to room temperature. The product was stored at 4 °C.

2.3. Preparation of Raman Substrate

The detailed experimental process is described as follows. Firstly, an aluminum foil (with dimensions of 10×10×0.1 mm$^3$) was pretreated by dilute hydrochloric acid and acetone assisted by ultrasonic to remove surface metal ions and surface oil contaminant, and was then used as the working substrate for the ZnO assemblage. The solution of 0.1 mol L$^{-1}$ Zn (CH$_3$COO)$_2$ with pH value of 11 was prepared. Then the solution of 0.3 mol L$^{-1}$ Zn (CH$_3$COO)$_2$ was prepared and sprayed onto the aluminium foil which was heated at 280 °C, and the spraying course was lasted for 30 min. This heated aluminium foil was cooled down and was submerge in the bottle containing 0.1 mol L$^{-1}$ Zn (CH$_3$COO)$_2$ solution. The bottle was sealed and heated to 90 °C for 4 h. After the bottle was cooled down, the aluminum foil covered with the synthesized crystal film (ZnO/Al) was taken out, washed with deionized water several times, and dried under vacuum at 80 °C for 4h.

2.4. SPME-SERS Measurement of Ferbam

In the SPME-SERS of ferbam, as described in Scheme 1, the as-prepared substrate preconcentrated the analyte in solution by the direct immersion solid-phase microextraction method for 10 min at ambient temperature. The substrate was dropped with 10 μl gold sol and allowed to air-dry, and Raman signals were collected.

Scheme 1. Graphical Sketch of the DSPME-SERS Process of Ferbam in solution

2.5. Characterization Techniques and SERS Detection

Scanning electron microscopy (SEM) images were obtained from a FEI Magellan 400 microscope (FEI, Oregon, USA). A DXR Raman microscope (Thermo Fisher Scientific, Madison, Wis., USA) with a 785 nm laser and a 50× confocal microscope objective was used in this study. OMNIC™
software version 9.7 was used to control the Raman instrument. SERS spectral data were analysed using the TQ Analyst software (version 9.7) from Thermo Scientific.

3. Results and Discussion

3.1. Preparation and Characterization of Nano ZnO
A simple and practicable one-step reaction procedure was used to prepare nano ZnO for SPME. As shown in Figure 1a, the surface contains lots of rod-like ZnO nanoparticles and form a rough substrate. This substrate is convenient for SERS measurements since the SERS-active substrate (AuNPs) could be well-dispersed on it. Figure 1b reported the typical Raman spectrum for ferbam (50 ppm). In fact, we can clearly observed the ferbam’s characteristic intensity increase of the ρ(CH₃), δ(CH₃) and ν(CN) at 1517.65 cm⁻¹, δ(CH₂) and ν(CN) at 1380.62 cm⁻¹, and ρ(CH₃) and ν(CN)1149.48 cm⁻¹, respectively. The highest peak of ferbam was observed at 1380 cm⁻¹ which was associated with CN stretching. As a result, it was chosen as the main characteristic peak for the following experiments.

![Figure 1](image.png)

Figure 1. (a) SEM image of ZnO/Al substrates and (b) typical Raman spectrum of Ferbam.

3.2. Analytical Performance of the SPME-SERS for Ferbam
No strong background signal was detected using SERS substrate (Figure 2). This is very beneficial for SERS detection because all detected peaks are from the analyte, which increases the sensitivity and makes the analysis easier and clearer. The effect of the extraction time was the most important parameter for the analytical Method. SERS signals of ferbam appeared after 5 min of extraction, which means that this method can greatly reduce the detection time, making this method of great significance for fast detection. The SERS signal intensity of the ferbam increased when the extraction time was increased to 60 min and then remained constant or slightly decreased, even when a longer extraction time was selected.
The lowest detectable concentration is one of the most important detection index for a new analyzing method. According to Figure 3, the lowest detectable concentration of ferbam was 0.01 ppm, which indicated that we were able to detect ferbam as low as 0.01 ppm for ferbam. The lowest detectable concentration at 0.01 ppm in a solution sample is comparable to the magnetic solid phase extraction with gas chromatography-flame photometric detection (GC-FPD) and high-performance liquid chromatography with diode array detection (HPLC-DAD).[15, 16]

4. Conclusion
In summary, we developed a simple and sensitive method combing SPME with SERS to analyze ferbam, a widely used in fruit. Rod-like ZnO nanomaterials were synthesized and used as the substrate for SPME. Coupled with SERS, the method was successfully applied in the investigation of ferbam in solution. As a result of the significant enrichment superiority of the nano ZnO toward ferbam and the characteristics of the ferbam SERS spectra, ferbam could be detected in solution at the lowest detectable concentration of 0.01 ppm, and the results were closely consistent with other reported methods. The characteristics of simpler operation, shorter analysis time, and less sample consumption make it a promising approach for the fast analysis.
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