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Thin-film microextraction coupled to surface enhanced Raman scattering for the rapid detection of benzoic acid in carbonated beverages

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ABSTRACT

Benzoic acid (BA) is widely used as an antimicrobial preservative in carbonated beverages. In this study, silica gel thin-film microextraction (TFME) coupled to surface enhanced Raman scattering (SERS) was applied for the rapid detection of BA in carbonated beverages. The TFME process was performed by placing small pieces of silica gel substrate in a simple homemade device, and then the content of BA was detected using SERS after colloidal gold was uniformly dropped onto the substrate. The obtained SERS signals of BA were strong and of high reproducibility. A good linearity between the concentration of BA and the SERS signal intensity at 994 cm^{-1} in the range of 25–500 μg mL^{-1} was obtained under optimal experimental conditions. The detection limit value was found to be 3.6 μg mL^{-1} and the recovery of the spiked BA was in the range 85.0–103.0%. The developed method was successfully applied to detect BA in carbonated beverage samples as the results were consistent with those using high performance liquid chromatography, suggesting that it is a rapid, convenient and sensitive way to achieve BA detection in carbonated beverages.

1. Introduction

Benzoic acid (BA) is a commonly used antimicrobial preservative in food and beverages, especially in carbonated beverages as since it presents its strongest antibacterial activity at pH 2.5–4.0 [1–3]. BA has inhibitory effects on the proliferation of bacteria and yeasts, a major cause of food spoilage. Although the addition of BA can extend the shelf life of drinks and prevent nutritional losses, excessive intake of BA may cause diarrhea, abdominal pain and other symptoms, and even interfere with the intermediate metabolic processes of the body [2,4–6]. Therefore, the maximum permitted concentrations of BA in each type of food are limited by legislation. The US Food and Drug Administration states that the limit of BA addition in general food is 1000 mg kg^{-1} [7], whereas Chinese laws establish a limit for BA addition at 200 mg kg^{-1} in carbonated beverages [8]. Various traditional methods, such as high-performance liquid chromatography (HPLC) [9–11], gas chromatography (GC) [1,12], spectrophotometry [13] and thin layer chromatography [14], have been applied for the detection of BA. However, these methods are time-consuming with complicated pre-treatments and require expensive instruments [15–17]. Consequently, it was useful to develop a convenient and effective method to detect BA.

In recent years, surface enhanced Raman scattering (SERS) has been widely applied in chemical and biochemical analysis owing to its nondestructive and highly sensitive characteristic features [18,19]. Metallic colloids, especially silver and gold colloids, are often used as SERS active substrates [20–22]. The surface plasmon resonance excited between the nanoparticles (NPs) leads to strong enhancement of the SERS signal. Furthermore, the colloids can be easily synthesized using a reduction method [23–25].

Thin-film microextraction (TFME) is a novel approach of solid-phase microextraction (SPME) [26] and, comparing with the traditional fiber-based SPME technique, TFME possesses higher analytical sensitivity with shorter extraction equilibrium time due to the increase of available surface area and extractive phase volume [27]. TFME has been coupled with many types of analytical technology, including GC [28], HPLC [29,30], liquid chromatography electrospray ionization tandem mass spectrometry [31] and membrane introduction mass spectrometry [32] to achieve simpler or faster detection. In addition, the TFME-SERS method provides a more convenient and simple way for analysis in a number of aspects [33].

The extraction materials play an important role in the TFME-SERS process. In addition to the good stability, strong adsorption capacity and large surface area, it is also critical that the materials have the ability to combine with the SERS technique and ensure the

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reproducibility of the SERS signals. Silica gel ($mSiO_2{\cdot}nH_2O$) is an extraction material with open porous structure and an adsorption effect on organic substances [34]. It possesses strong chemical inertness under various conditions. Most importantly, there is no SERS background interference signal caused by silica gel. The commercial chromatography silica gel plate is a type of ideal TFME substrate because of its uniform surface and large extraction area. The holes in silica gel film allow metal NPs to become embedded into them and form abundant hot-spots to enhance analytical sensitivity.

In this study, we combined TFME with SERS to establish a rapid, convenient and sensitive method for the determination of BA in carbonated beverages. Commercial chromatography silica gel plates were used as the TFME substrates to accomplish the BA extraction in a homemade device [33]. SERS was then used to detect the BA content.

2. Experimental

2.1. Chemicals and materials

Analytical grade BA (C_6H_5COOH) was bought from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Different concentration stock solutions of C_6H_5COOH were prepared by dissolving it in pure water under ultrasonic conditions and gradually diluting it to the final concentrations in the range 25–500 μg mL^{-1}. Pure water was obtained from a Simplicity Water Purification Systems (Millipore, Molsheim, France). Carbonated beverage samples were obtained from local supermarkets.

Gold hydrosol was purchased from Push Nanotechnology Co., Ltd. (Xiamen, China). The average size of the gold NPs (AuNPs) was about 55 nm, and the concentration of the gold colloid was 0.3 mmol/L. The commercial gold hydrosol was concentrated before use. 1.0 mL of gold hydrosol were centrifuged at 4000 r/min for 10 min to obtain 30 μL of gold colloid by removing the supernatant.

Chromatography silica gel plates were purchased from the Qingdao Ocean Chemical Co., Ltd. (Qingdao, China), and were cut into 0.8 cm × 0.8 cm pieces before being used as the TFME substrate.

2.2. Instrumentation

Scanning electron microscope (SEM) images of the chromatography silica gel plates were captured using an S4800 field emission SEM (Hitachi, Tokyo, Japan). The SERS spectra were recorded using a commercial portable spectrometer (DeltaNu Inspector Raman, USA), of which the laser wavelength was 785 nm, the laser power was 120 mW, and the system resolution was 8 cm^{-1}. The SERS signal acquisition integration time was set as 1 s. All measurements were performed at room temperature.

The high performance liquid chromatography (HPLC) consisted of an LC-20AT machine (Shimadzu, Kyoto, Japan) equipped with a DGU-20A degasser and SPD-20A diode array detector. An HPLC Syncronis C_{18} column (250 × 4.6 mm, 5 μm) from Thermofisher USA was selected for the separation.

2.3. TFME and SERS measurement of BA

Samples were added directly to the glass vessel. The silica gel TFME substrate was hung in the center of the sample solution through a homemade device, and the solution stirred for 20 min to extract BA (1000 rpm) under room temperature (around 20 °C). Production of the homemade extraction device is shown in Fig. S1. An aluminum sheet was used as the trestle to hold the silica gel TFME substrate. After extraction, the silica gel TFME substrate was removed from the vessel and dried before SERS analysis. 10 μL of concentrated AuNPs was dropped onto its surface, and SERS measurements were collected 3 − 4 times randomly within the SERS-active substrate area and the data averaged.

2.4. HPLC measurement of BA

The HPLC measurement of BA was carried out following the Chinese national standard method to detect BA in carbonated beverages (GB/T 5009.29-2003) with minor modification. Briefly, 10 mL carbonated beverage was added into a beaker and heated slightly under stirring to remove carbon dioxide. The pH was adjusted to 7 by the addition of ammonia water (1 + 1). Then water was added to make the volume 20 mL. After filtering with a 0.22 μm membrane, the sample was directly injected into the HPLC system for detection. The injection volume was 10 μL. A binary mobile phase at a flow rate of 0.4 mL min^{-1} was used in the HPLC system. The mobile phase (A) was 2 mmol/L aqueous formic acid (pH 3.3), and the mobile phase (B) was acetonitrile. The elution program was set as follows: 0–20 min, 95% (A), 5% (B). The detection wavelength was 230 nm.

3. Results and discussion

3.1. Characterization of the silica gel TFME substrate

The silica gel TFME substrate was characterized using SEM. As shown in Fig. 1a, the surface of the substrate was rough and amorphous with many holes, indicating that the silica gel coating possessed a good number of adsorption sites and a large adsorption area. As indicated in Fig. 1b, the thickness of the silica gel coating was about 130 μm, which was thin enough to accelerate the mass transfer process.

3.2. SERS characteristics

The SERS detection of BA (500 μg mL^{-1}) in the liquid phase and the

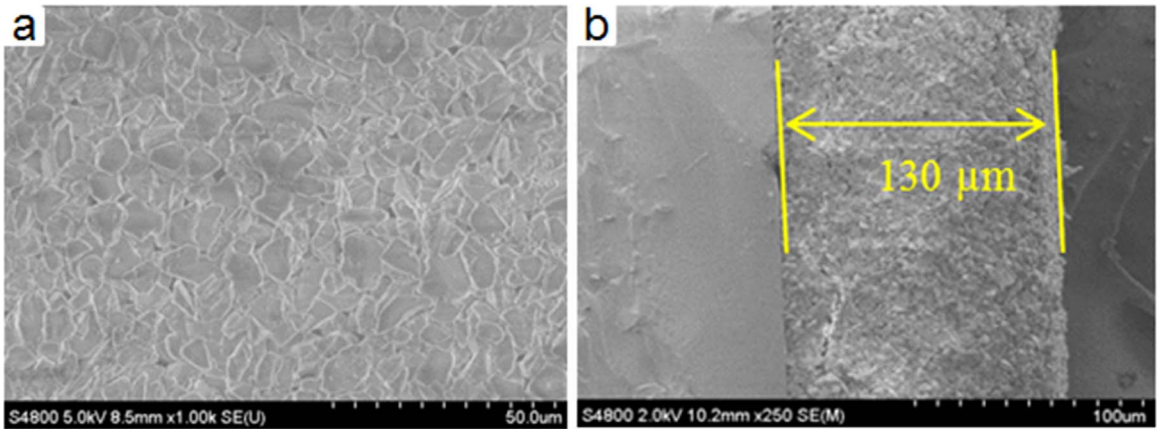

Fig. 1. (a) SEM image of the silica gel TFME substrate (× 1000); (b) Sectional view of the silica gel TFME material.