Food Chemistry 270 (2019) 494–501

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

A novel metastable state nanoparticle-enhanced Raman spectroscopy coupled with thin layer chromatography for determination of multiple pesticides

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ARTICLE INFO

Keywords:
Metastable state nanoparticle-enhanced Raman spectroscopy
Pesticide
Polyurethane
Micelle
Thin layer chromatography

ABSTRACT

A novel and highly sensitive metastable state nanoparticle-enhanced Raman spectroscopy (MSNERS) was reported in this work, which employed an amphiphilic polymer polyurethane-Ag nanoparticle (AgNPs) as the MSNERS substrate. Polyurethane could form micelle to incorporate nanoparticles and analytes, where targets could be in close contact with the metal surface, which was effective for further enhancing the detection sensitivity. Time-dependent visible absorption spectra and time-dependent Raman spectra indicated that polyurethane could greatly enhance the stability of AgNPs aggregates during the volatilization process, which was a great improvement of MSNERS substrate. Combining this MSNERS substrate with the rapid separation method of thin layer chromatography (TLC), this TLC-MSNERS was successfully applied to analyze mixed pesticides on fruit skin and the detection limits of thiabendazole, triazophos and phosmet were 0.02 μg/mL, 0.8 μg/mL, and 0.6 μg/mL, respectively. It enhanced 1 order of magnitude the signals of analytes in comparison to that of traditional TLC-SERS method.

1. Introduction

It is always a research hot topic in surface enhanced Raman spectroscopy (SERS) by controlling hot spots of Au or Ag nanoparticles to enhance SERS signal. Recently, highly sensitive SERS signal was obtained based on a state translation process of Au or Ag colloid: from wet state to dry state, namely metastable state nanoparticle-enhanced Raman spectroscopy (MSNERS) (Liu et al., 2014; Yang et al., 2011). It was reported that nanoparticles tended to approach closer to generate hot spots during the solvent volatilization process. In this case, the target analytes could be trapped in the gap of hot spots and strong SERS signal could be obtained at this moment (Dong, Weng, Yang, & Liu, 2015; Yang, Li, Liu, Tang, & Liu, 2015; Zhu, Li, Yu, & Yang, 2014). The strongest SERS signal was observed when the droplet tended to become dry. Therefore, it is critical to seize the moment before the solvent complete drying to collect the best SERS signal. In the previously reported literature, the common method to obtain the optimal signal was by continuous recording the Raman spectra during the solvent evaporation process and chose the strongest signal. Although many studies have demonstrated that the MSNERS substrate showed higher detection sensitivity compared with the traditional SERS method due to forming appropriate hot spots and the volatilization-induced automatic concentration of the target molecules during the detection process (Li et al., 2014; Wu, Zhou, Yang, & Liu, 2013; Yang, Liu, Ma, & Liu, 2012), the signal intensity fluctuated a lot during the acquiring process due to the evaporation process changing with time in real application. In other words, the optimal signal could only be observed spontaneously. Robust control over the accurate acquiring time to seize the strongest signal remains a challenge because of the fluctuations of hot spots' state and analyte concentration. Customarily, it needs to acquire a large number of spectra to screen the most intense signal. Therefore, although MSNERS is a sensitive technique, there is still room for improvement of the substrate to obtain stable signal.

In fact, keeping SERS signal stable for a longer time is quite challenging in the dynamic evaporation process due to the difficulty in tuning the balance between persistent solvent evaporation and stability of the resulting nanoparticles aggregates. In this work, we adopted a novel method to improve the performance of the MSNERS substrate by adding a polymer surfactant, polyurethane, which is a water soluble amphiphilic polymer. Polyurethane could form micellar cluster in the volatilization process, which could reduce the effect caused by volatilization-induced automatic concentration of the target molecules

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https://doi.org/10.1016/j.foodchem.2018.07.070
Received 25 January 2018; Received in revised form 4 June 2018; Accepted 11 July 2018

during the detection process. More importantly, according to the results from the time-dependent visible diffuse spectra, it was found that the presence of polyurethane could stabilize different forms of nanoparticle aggregates for a great while in the dynamic evaporation process. It was proposed that polyurethane-bridged nanoparticles in the 3D hotspot matrix were predominant in the aggregates in our system and this structure could be kept stable for a great while in the evaporation process. Due to the stability of aggregates, the optimal SERS signal with slight fluctuation was obtained in this work during the acquisition process before droplet became dry and this strong signal could be kept stable for several minutes. This feature was of great help and convenience for building up the quantitative relationship between the Raman intensity and the corresponding concentration of analytes. The enhancement in stability of this MSNERS substrate was a great improvement in comparison to that of previous reported metastable substrates, which was believed to provide bright future for practical application of MSNERS substrate.

In general, for SERS analysis, only those molecules readily adsorbed or close to the surface of nanoparticles can be detected. However, there are many interference components in real samples. The signal from the low concentration of analytes or weak adsorbates is likely to be buried in the signal from high concentration of analytes or strongly adsorbed molecules. Therefore, it is best to separate the targets from a mixed system prior to the SERS detection for real-world applications. Thin layer chromatography (TLC) is a facile, rapid and cost-effective technique for separating different components from mixtures (Dawan, Satarpai, Tuchinda, Shiowatana, & Siripinyanond, 2016; Sokolović & Šimpraga, 2006). Often the developed TLC spots are scraped off and extracted from the TLC plate by means of repeated rinsing and centrifugation, and further examined by infrared spectroscopy (Sharma & Kumar, 2017) or mass spectrometry (Stanger et al., 2017) for further identification, which are time-consuming and labor-intensive. SERS in conjunction with TLC has achieved on-site detection. It is easy to acquire Raman signal of multiple targets after the components are separated by the TLC plate. TLC-SERS technique has been used for detecting kinds of targets in different fields, such as environmental aromatic pollutants (Li et al., 2011), fiber of artist dyestuffs (Brosseau et al., 2009), drugs (Fang, Qi, Lu, & Yang, 2016; Lucotti et al., 2012; Lv et al., 2015; Xiao, Hui, Zhu, Yan, & Feng, 2016; Zhu, Cao, Cao, Chai, & Lu, 2014), pesticides (Yao et al., 2013), biochemistry (Xie et al., 2017), polycyclic aromatic hydrocarbons (Chen, Huang, & Zhao, 2015), dyes (Kong, Squire, Chong, & Wang, 2017; Wang et al., 2014). Although this coupling technique possesses great potential for rapid analysis in complex system, the sensitivity of traditional SERS substrates still needs to be improved. In this work, coupling TLC with this improved MSNERS technique (TLC-MSNERS), good correlations between targets concentration and intensity were obtained. A highly reliable, sensitive and practical analysis method was established for rapid detection of multiple pesticides on fruit skin, which demonstrates that this method possesses great potential to realize the quantitative detection of different targets in real samples.

2. Materials and methods

2.1. Materials

Silver nitrate, sodium citrate and sodium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further purification. Isopropanol, petroleum benzin and dichloromethane were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Phosmet, thiabendazole, triazophos and all other reagents of analytical grade were obtained from Aladdin-Reagent Co., Ltd. (Shanghai, China). Polyurethane was purchased from Shanghai Xian Ding Biotechnology Co., Ltd. (Shanghai, China). All solutions were prepared with Milli-Q water (18 MΩ·cm, Billerica, MA, USA). TLC plates of silica gel 60-F254 (Ø: 200 nm, LT: 0.2 mm) with glass back plate were purchased from Shanghai Jijusheng Chemical Co., Ltd. (Shanghai, China). The plate containing fluorescing additive, F254, was used for easy spot visualization. Various eluents were prepared by mixing petroleum benzin, dichloromethane and isopropanol in different proportions to elicit the best separation of pesticides on TLC plates.

2.2. Preparation of AgNPs

AgNPs were prepared by reducing silver nitrate using sodium citrate (Lee & Meisel, 1982). In a typical experiment, 18 mg $AgNO_3$ was dissolved in 100 mL of H_2O and brought to boiling. A solution of 1% sodium citrate (2 mL) was added drop by drop to the $AgNO_3$ solution. The mixed solution was kept on boiling for 45 min. The prepared colloid was rinsed with water and ethanol for several times and stored at −4 °C. Before the SERS measurements, the colloid was brought to different concentrations for use.

2.3. Chromatography and detection method

The TLC-MSNERS method was designed for the detection of multiple pesticides. All the TLC plates were directly used as received. On each plate, a line parallel to the short side was drawn with a pencil and the distance to the edge was about 5 mm, slightly higher than the unfolding reagent. For the separation of different pesticides, 200 μL of sample solution containing different concentrations of pesticides was spotted onto the line, along with three standard solutions of 200 μL of 50 μg/mL thiabendazole, 50 μg/mL triazophos and 50 μg/mL phosmet spotted side by side, respectively, allowing to develop at the same time. The latter served as position marks, through which the exact spots of different pesticides in the mixture after development were found. Chromatography was performed in a vial with an optimized mobile phase (proper ratio of petroleum benzin, dichloromethane and isopropanol). After that, the positions of high concentration standards could be easily distinguished under 254 nm illumination with a handheld UV lamp (Shanghai Jihui Scientific Analyze Instrument CO., Ltd., China). The mixture was separated and their positions of three pesticides in the sample were then marked out according to the locations of standards. Later, 50 μL mixture of AgNPs and polyurethane as the SERS substrate was dropped to each spot and the SERS spectra were recorded using Raman spectrometer allowing qualitative and quantitative analysis of the components of the analyte mixture.

2.4. Sample preparation

Cherries were purchased from a local supermarket in Shanghai. After thoroughly cleaning the cherries with ultrapure water, 1 mL mixture of 5 μg/mL thiabendazole, 5 μg/mL phosmet and 5 μg/mL triazophos was evenly sprayed on the surface and dried at room temperature. Then, 10 mL solution of methanol and dichloromethane (1:1, v/v) were employed as the extracting reagent. The sample was immersed in the extracting solution under ultrasound (Shanghai Shengyan Ultrasonic Equipment, China) for 20 min and extracted 2 times. Finally, the extracts were filtered and concentrated for use. 100 μL of concentrated extracts were spotted onto the TLC for developing.

2.5. Instrumentation and characterization

SERS experiments were conducted using a Renishaw InVia Reflex confocal microscope (Renishaw, UK) equipped with a 50× objective and a high-resolution grating with 1200 grooves/mm. Acquisition of SERS spectra employed laser of 785 nm as the excitation source and laser power of approximately 3 mW. Time-dependent visible diffuse reflection absorption spectra were recorded by VIS miniature optical fiber spectrometer (Insion, Germany).