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## Large-volume constant-concentration sampling technique coupling with surface-enhanced Raman spectroscopy for rapid on-site gas analysis



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### ABSTRACT

In this work, a portable large-volume constant-concentration (LVCC) sampling technique coupling with surface-enhanced Raman spectroscopy (SERS) was developed for the rapid on-site gas analysis based on suitable derivatization methods. LVCC sampling technique mainly consisted of a specially designed sampling cell including the rigid sample container and flexible sampling bag, and an absorption-derivatization module with a portable pump and a gas flowmeter. LVCC sampling technique allowed large, alterable and well-controlled sampling volume, which kept the concentration of gas target in headspace phase constant during the entire sampling process and made the sampling result more representative. Moreover, absorption and derivatization of gas target during LVCC sampling process were efficiently merged in one step using bromine-thiourea and OPA-NH<sub>4</sub><sup>+</sup> strategy for ethylene and SO<sub>2</sub> respectively, which made LVCC sampling technique conveniently adapted to consequent SERS analysis. Finally, a new LVCC sampling-SERS method was developed and successfully applied for rapid analysis of trace ethylene and SO<sub>2</sub> from fruits. It was satisfied that trace ethylene and SO<sub>2</sub> from real fruit samples could be actually and accurately quantified by this method. The minor concentration fluctuations of ethylene and SO<sub>2</sub> during the entire LVCC sampling process were proved to be <4.3% and 2.1% respectively. Good recoveries for ethylene and sulfur dioxide from fruit samples were achieved in range of 95.0–101% and 97.0–104% respectively. It is expected that portable LVCC sampling technique would pave the way for rapid on-site analysis of accurate concentrations of trace gas targets from real samples by SERS.

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### 1. Introduction

Surface-enhanced Raman spectroscopy (SERS), proposed by Fleischmann et al. [1] and Jeanmaire et al. [2], overcomes the major disadvantage on sensitivity of conventional Raman spectroscopy. Since then, SERS as a kind of nondestructive, sensitive, rapid and water interference-free detection technique has attracted much attention and been tentatively used for some typical analytical projects such as alkaline phosphatase [3], *Escherichia coli* [4], tyrosine [5], parietin [6], perchlorate [7], melamine [8], and so on. However, most of these works focused on SERS analysis of solid or liquid samples. It still remains a great challenge for rapid and accurate quantification of trace gases or volatile compounds with extremely low molecular weight and strong volatility from real samples with complex matrices.

Until now, there are still only a few works related with direct SERS analysis of gas targets such as carbon monoxide, nitrous oxide [9], ethanol [10] and acetone [11] in nitrogen or air by exposing substrates directly in gas phase. Hill and coworkers [12] attempted to detect

methyl mercaptane from atmosphere of rubber samples by a kinetic method. These works demonstrated the potential for real-time vapor sensing by SERS. However, due to the extreme volatility and mobility of trace gas targets and complex gas matrices of real samples, when SERS detection was applied for direct gas analysis, it was very difficult to generate strong bondings between target gases and SERS substrates, which would usually result in poor sensitivity and selectivity and greatly influence analytical accuracy finally. Thus, the above works could not actually realize the accurate quantification of gas targets from real samples by SERS. There is still a long way to achieve the accurate SERS methods for rapid on-site determination of trace gases from real samples.

It is well known that proper gas sampling process can usually give favor impact on greatly improving the concentrations of gas targets and removing matrix interference at the same time [13,14]. On the other hand, gas targets would be transferred, homogeneously dispersed or fixed in testing solutions or other sampling media via sampling process, which provides the possibility to generate bondings between targets and substrates and further strong SERS responses. A few recent works have proved the significance of sampling process on the improvement of the sensitivity and selectivity for SERS analysis of gas

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targets from real samples [15,16]. However, there are no reports focusing on the study of sampling accuracy and representativeness during the entire sampling process.

It is obvious that with the progress of sampling process the concentration of gas target will be gradually changed, since the dilution by complimentary carried gas and continuous releasing gas targets from samples during sampling process causes the non-equilibrium status of sample-gas phase. Thus, in order to achieve the accurate and representative sampling results, the ideal gas sampling technique for SERS analysis should be able to keep the concentrations of gas targets constant during the entire sampling process and collect the large volume of gas targets as much as possible. Currently, some negligible depletion sampling techniques reported in previous works such as solid-phase microextraction [17,18], liquid-phase microextraction [19] and liquid membrane extraction [20] could keep the concentrations of targets nearly constant during the sampling process due to very small amount of targets extracted. However, the slight concentration change of gas targets instantly during sampling process might cause big sampling error owing to their small sampling volumes. Thus, it'd better well control the pressure to keep the concentrations of gas targets constant during sampling large volume of gas target by use of flexible sampling cell whose sampling volume could be easily altered with the change of gas pressure. Nowadays, commercial sampling techniques for gas targets are usually based on single rigid sampling container such as stainless steel sampling canister [21] or elastic sampling bag [22]. In most cases they are only suitable for sampling gas targets from air [23] or atmospheric [24] samples but not solid or liquid samples. It is hard for rigid sampling container to well control gas pressure and concentration by flexibly changing chamber volume, and single elastic sampling bag is difficult for holding solid or liquid samples during sampling process without disturbing sample-gas equilibrium. The combination of large flexible sampling cell with the active pump-based sampling process can achieve the portable large-volume constant concentration (LVCC) sampling technique. It is expected that portable LVCC sampling technique coupled with portable SERS can actually applied for rapid on-site analysis of accurate concentration of trace gas targets from complex real samples.

The contents of gas targets in headspace phase are usually at trace levels with strong volatility, and also most of gas targets are non-SERS responsive compounds. Thus, it is difficult to directly analyze gas targets in headspace phase by SERS. It is a good choice to use analytical derivatization method to absorb and convert gas targets in headspace into SERS responsive products [15]. Through analytical derivatization, gas targets can be greatly enriched, and some interference compounds can be effectively cleaned up at the same time. Therefore, analytical derivatization coupled with suitable gas sampling technique would make SERS analysis of gas targets from real samples possible with improving sensitivity and selectivity. There have been some reports using derivatization to realize SERS analysis of gas targets from real samples [25,26]. Zhang et al. [15] proposed a typical derivatization based SERS method for rapid determination of trace formaldehyde in aquatic products with high selectivity and sensitivity. These works successfully analyze the average releasing amounts of gas targets, but it still remains a great challenge to achieve rapid SERS analysis of instant accurate content of gas targets from real samples without suitable sampling techniques.

Ethylene and sulfur dioxide are two typical gas molecules with extremely low molecular weight and strong volatility which are of utmost importance in fruit storage. Ethylene is a well-known important plant hormone for the indication of fruits ripeness and freshness [27,28]. Sulfur dioxide is also widely used as a preservative to control the fruit freshness during fruit storage, especially for grape storage [29,30]. In this study, a portable LVCC sampling technique was well designed and developed based on a simple and special sampling cell combining a rigid sample container and a flexible gas sampling bag. Then, a portable LVCC sampling-SERS detection system based on efficient and selective

derivatization method was developed and successfully applied for rapid on-site analysis of trace ethylene and SO<sub>2</sub> from fruits under optimal sampling, derivatization and detection conditions.

## 2. Experimental Section

### 2.1. Chemicals and Materials

Saturated bromine aqueous solution (ACS grade), *o*-phthalaldehyde (OPA, 98%) and H<sub>2</sub>AuCl<sub>4</sub>·3H<sub>2</sub>O (Au ≥ 48%) were purchased from Aladdin Company (Shanghai, China). Methanol, ethanol, propanol, isopropanol, ethyl formate, ethyl acetate, ethyl propionate, diethyl ether, trisodium citrate dehydrate, carbon tetrachloride, thiourea, triethanolamine, ammonium acetate, potassium phosphate monobasic and sodium phosphate dibasic dodecahydrate were all of analytical grade and purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Water used in this work was produced by a Unique-R20 water purification system (RSJ Scientific Instruments Co., Ltd., Xiamen, China). Other chemical reagents were all of analytical grade.

Standard gases of ethylene (1250 µg/L) and SO<sub>2</sub> (1.49%) and high-purity nitrogen (99.999%) were purchased from Changzhou Jinghua Industry Gases Co., Ltd. (Changzhou, China). Working gases of ethylene and SO<sub>2</sub> were prepared by gradual dilution of corresponding standard gases using nitrogen at different concentrations. Gold nanoparticles (AuNPs, 55 nm) were prepared as enhancement substrate for SERS analysis according to a previous hydrothermal reduction method in our lab using sodium citrate [31]. Fruit samples including black plums, peaches, Gala apples, Kyoho grapes, and white grapes were obtained from a local market (Guangzhou, China). White grapes and red grapes were wrapped with preservative paper imported from South Africa for analysis of SO<sub>2</sub> by LVCC sampling-SERS detection technique.

### 2.2. Instrument

A magnetic stirrer (IKA, RET basic C, Germany) was used for agitation of the reaction reagent. A vortex shaker (IKA, Germany) was used to shake up the extraction tube for homogenizing mixture. A gas flowmeter and a QC-2B portable air sampling pump were purchased from Beijing Municipal Institute of Labour Protection (Beijing, China) for development of portable LVCC sampling techniques. Gas sampling bags were purchased from Shanghai Eler Economy and Trade Co. Ltd. (Shanghai, China). SERS spectra were recorded based on a portable DeltaNu (Laramie, WY) battery-powered Raman spectrometer (model Inspector Raman, diode laser excitation wavelength  $\lambda_{ex} = 785$  nm) with a CCD detector (Model Spec-10:400B, Roper Scientific, Trenton, NJ), and a data-acquisition system (Photometrics, Tucson, AZ). Laser intensity was set at the 'High' level. Each spectrum was the average of three scans with exposure time of 3 s per scan. Tangent partitioning method was utilized for the integration of the characteristic SERS peaks during quantification.

An HP 4890D gas chromatography (Agilent, Palo Alto, USA) equipped with the Flame Ionization Detector (FID) was employed as a comparison method for analysis of ethylene according to our previous method [32] with slight modification. GC/FID conditions were as follows: injector temperature, 200 °C; injection volume, 1.00 mL; detector temperature, 200 °C; nitrogen flow, 1.5 mL/min; air flow, 400 mL/min; hydrogen flow, 35 mL/min. GC/FID temperature program was set at 40 °C for 6 min. A DB-5 (Agilent Scientific, USA) capillary column (30 m length × 0.25 mm i.d. × 0.25 µm film thickness) was used for the chromatographic separation of ethylene. A QP2010 gas chromatography/mass spectrometer (GC/MS, Shimadzu, Japan) was employed as a comparison method for analysis of SO<sub>2</sub> according to an analytical method in the previous work [33]. GC/MS conditions were as follows: injector temperature, 100 °C; injection volume, 1.00 mL; split ratio, 5:1; carrier gas pressure, 123.2 kPa; carrier gas flow, 2.0 mL/min; purge gas flow, 3.0 mL/min; column oven temperature, 40 °C hold for 3 min;

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