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## Fast detection of fenthion on fruit and vegetable peel using dynamic surface-enhanced Raman spectroscopy and random forests with variable selection

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### ABSTRACT

Dynamic surface-enhanced Raman spectroscopy (D-SERS) based on the state change of the substrate not only significantly enhances but also provides a highly reproducible Raman signal. Hence, we develop a fast and accurate method for the detection of fenthion on fruit and vegetable peel using D-SERS and random forests (RF) with variable selection. With uniform Ag nanoparticles, the dynamic spectra of fenthion solution at different concentrations were obtained using D-SERS, and fenthion solution greater than or equal to 0.05 mg/L can be detected. Then, the quantitative analysis models of fenthion were developed by RF with variable selection for spectra of different range. The model of best performance is developed by RF and spectra of characteristic range with higher RF importance (top 40%), and the root mean square error of cross-validation is 0.0101 mg/L. Moreover, the fenthion residue of tomato, pear, and cabbage peel were extracted by a swab dipped in ethanol and analyzed using the above method to further validate the practical effect. Compared to gas chromatography, the maximal relative deviation is below 12.5%, and the predicted recovery is between 87.5% and 112.5%. Accordingly, D-SERS and RF with variable selection can realize the fast, simple, ultrasensitive, and accurate analysis of fenthion residue on fruit and vegetable peel.

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### 1. Introduction

Fenthion is widely used for the control of *Carposina niponensis* Walshingham, caterpillar, and aphid in fruits and vegetables [1,2]. However, its overuse and inappropriate application lead to residue. Excessive fenthion residue can induce intermediate syndrome with long-lasting and reiterative damage. The accurate detection of residue is a key approach for avoiding the above problem. The detection process must be rapid for large-scale residue. Moreover, the conventional method as gas chromatography (GC) is incapable for meeting the above requirement [3,4].

Surface-enhanced Raman spectroscopy (SERS), whose signal is largely enhanced based on the electromagnetic and chemical enhancement of nanoscale rough noble metal, allows highly sensitive detection. Furthermore, with the simple pretreatment and rapid spectrum-measuring procedure, SERS has been applied to the sensitive and fast detection of pesticides [5–7], drugs [8,9], food additives [10], and biomacromolecules [11]. Many researchers have detected fenthion

using SERS [4,12]. However, the conventional SERS measurement is performed on substrates of dry or wet state, and simultaneously ensuring good sensitivity and high reproducibility is highly difficult [13]. Recently, our group developed a novel method called dynamic SERS (D-SERS) [14–16], which originates from the two conventional methods as the dry film-based and solution-based methods. Dry film-based SERS detection: place the general colloidal nanoparticles on a solid substrate (silicon, glass wafer), dry the sample on the substrate, and obtain the SERS spectra. Generally, it gains the enormous SERS response accompanied with weak reproducibility and stability for fabrication of complicated substrates and damage of laser. Solution-based detection involves that analyte is mixed with colloidal nanoparticles and hot spots are generated through inducing particles aggregation prior to spectra measurement. Due to the hot spots of random distribution and low density, the high sensitivity is difficult to ensure. Measurement of D-SERS depends on the translation-based Raman substrate state from wet to dry. Under the critical state of wet to dry, the nanostructures can self-assemble to form hot spots driven by solvent capillary forces. Meanwhile, the aggregated nanostructures can provide a bigger capture space for the analyte molecules. The larger signal enhancement is obtained. In addition, self-assembled hot spots are of good uniformity,

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and the residual liquid at the critical state can prevent from damage of laser. Repeatability of D-SERS is also excellent. Previous results have proven that D-SERS can provide reproducible, stable, and sensitive SERS signals [12]. Accordingly, D-SERS is used for the fast and accurate detection of fenthion.

When spectra are obtained using D-SERS, the qualitative and quantitative analysis of analytes should be performed by professionals. Artificial intervention renders the fast detection difficult to achieve. However, the intelligent identification model obtained by chemometric methods can achieve automatic and rapid spectral analysis without experts [17–20]. Frequently used methods include artificial neural networks [21], support vector machine [18,19], and random forests (RF) [20]. Among them, RF possesses significant advantages of robustness and simple parameter optimization [22]. Moreover, RF can estimate the importance of variables during model construction, which is useful for variable selection [23]. In the present study, RF with variable selection is applied to analyze D-SERS spectra and intelligently obtain information on analytes.

With D-SERS and RF, we aimed to explore the ultrasensitive and fast detection of fenthion on fruit and vegetable peel. Firstly, the dynamic spectra of fenthion solution at different concentrations were measured using D-SERS with uniform Ag nanoparticles (AgNPs). Then, regression models for the quantitative analysis of fenthion were developed by combining RF with variable selection. Moreover, fenthion residue on peel of tomato, pear, and cabbage was extracted by wiping with a swab dipped in ethanol, then spectra were also measured using D-SERS. The established model and the obtained spectra were used to predict the residue concentration on peel.

## 2. Experiments and Methods

### 2.1. Reagents and Chemicals

Silver nitrate ( $\text{AgNO}_3$ , 99.9%), sodium citrate (99%), ethanol (99.9%), and fenthion powder (99.9%) were purchased from Beijing Century Aoke Biological Technology Co. Ltd. (Beijing, China). Tomato, pear, and cabbage were purchased from Hefei Hongfu market (Anhui, China).

### 2.2. SERS Substrate

AgNPs sol solution was synthesized using chemical reduction [24]. Firstly, 1 mL 0.1 M silver nitrate was added into 99 mL deionized water and heated to slight boiling. Then, 4 mL 1% sodium citrate was

added, and kept boiling for 1 h after the color change. Finally, the solution was centrifuged for 10 min at 7500–8000 rpm, and dark green and transparent colloid was obtained. Ultraviolet and visible (UV–vis) absorption spectrum was shown in Fig. 1, and the inset is the corresponding SEM image of silver colloid nanoparticles. According to Fig. 1, the absorption peak of the silver colloid was about 425 nm with a full width at half maximum (FWHM) of 115 nm. The size of silver particle was uniform, and the average diameter was about 40–50 nm.

### 2.3. Sample Preparation and Measurement

D-SERS measurement: fenthion powder was dissolved in ethanol to obtain concentrations of 50, 10, 5, 1, 0.5, 0.1, 0.05, and 0.01 mg/L. Samples of fruit and vegetable peel: tomato, pear, and cabbage were sprayed with 1 mL of 50, 10, 5, 1, 0.5, 0.1 mg/L fenthion solution on the labeled  $3 \times 3 \text{ cm}^2$  region. After the solution dried, the labeled region was wiped by a swab dipped in ethanol, and the swab was vortexed in ethanol to release the pesticide [25]. The total amount of ethanol was 1 mL, and ten samples were collected for each fruit and vegetable. The testing solution and AgNPs colloid solution ( $V/V = 1:1$ ) were mixed adequately and dropped on the silicon chip, and the dropping volume of the mixture was 2  $\mu\text{L}$ . During the wet-to-dry state of the mixed solutions, 18 spectra were collected on the Raman spectrometer (Lab-RAM HR800) with a 5 s integration time and a 5 s interval time. During interval time of 5 s, the focus was corrected on the droplets. For the Lab-RAM HR800, a 532 nm laser was used as the excitation source with a measured power of 3.5 mW at center of mixing droplet surface with a focal spot of about 1  $\mu\text{m}$  in diameter. And temperature and relative humidity were kept at 25  $^\circ\text{C}$  and 40% to reduce the fluctuation of signals. Two spectra were selected from the obtained 18 spectra, which were regarded as dynamic spectra for the subsequent analysis. Samples that underwent the same treatment were also analyzed by GC to validate the results.

GC measurement: the obtained ethanol solution was removed into centrifuge tube of 5 mL and evaporated with a termovap sample concentrator (GIPP-AUTO-12S, Jipu, Shanghai). The extractive was eluted using 1 mL ethyl acetate and used for GC measurement. A GC instrument (ThermoFinnigan Trace GC 2000, USA) was used to measure fenthion residue with a flame photometric detector. The oven was heated at 110  $^\circ\text{C}$  for 1 min, then raised to 220  $^\circ\text{C}$  at 40  $^\circ\text{C min}^{-1}$ , and then ascended to 222  $^\circ\text{C}$  at 1  $^\circ\text{C min}^{-1}$ . Sample of 1 mL was injected into the instrument using high purity nitrogen as a carrier gas. The gas flow rate was 3.0  $\text{mL min}^{-1}$ . Interface temperature was 230  $^\circ\text{C}$ , and detector temperature was 250  $^\circ\text{C}$ . The collision gas was high purity nitrogen.

### 2.4. RF

RF is a powerful algorithm for solving classification and regression problems. In specific, RF takes advantage of multiple classification and regression tree (CART) to construct the recognition model, which was first developed by Leo Breiman [26] and Adele Cutler [27]. When the RF model identifies the unknown objects based on some properties, every CART provides its own conclusion, and the final output of the model is the most selected option (classification) or the mean value of all results (regression).

Furthermore, the main parameters of RF [28], such as the number of CART ( $n_{tree}$ ) and the number of features ( $m_{try}$ ), significantly affect the performance of the RF model. According to experience,  $n_{tree}$  was set to traverse between 400 and 1000 with an interval of 100, and  $m_{try}$  was set to the round number of the square root of feature dimension (dimension of spectrum). The prediction accuracy of the models was quantitatively evaluated using root mean square error of cross-validation (RMSECV). Additionally, the dual fold cross-validated method was adopted in this study to verify the effect of variable selection based on the estimation of variable importance (Fig. 2). The dataset

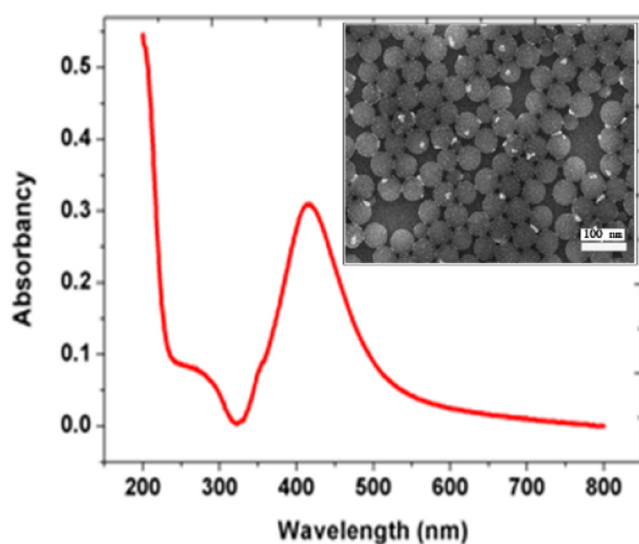


Fig. 1. UV–vis absorption spectrum of silver colloid, and the inset is SEM image of silver colloid nanoparticles.

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