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Quantitative Detection of Pesticides Based on SERS and Gold Colloid

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Abstract: The detection of pesticide residue in fruit is an important concern for consumers. Surface enhanced Raman spectroscopy (SERS) coupled with gold colloid was applied to analyze two kinds of pesticides (phosmet, chlorpyrifos) which were mainly used on the navel orange. The concentration of the phosmet samples of range from 3 to 33 mg/L and chlorpyrifos samples of range from 4 to 34 mg/L. Using Partial least squares (PLS) regression and the different preprocessing method for the spectral data analyses, and different pretreatment methods such as the Savitzky-Golay were compared. The optimal model of phosmet pesticide and chlorpyrifos pesticide were set up. The prediction correlation coefficient (R) and the root mean square error of prediction (RMSEP) of phosmet pesticide were 0.924 and 4.293 mg/L; The R and RMSEP of chlorpyrifos pesticide were 0.715 and 6.646 mg/L. It indicated that SERS technology is an effective method in the field of pesticide residue detection in fruit.

Keywords: SERS, gold colloid, pesticide residue

1. Introduction

SERS is an ultrasensitive testing technique, and It has achieved notable achievements in the last years in some areas such as food safety inspection[1-2], environmental monitoring[3], materials science, surface science, biomolecular Sensing[4] and analytical chemistry. With the

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photons as probes, SERS has the advantages of high sensitivity, good selectivity, non-destructiveness, and not require vacuum conditions. Now, SERS has become a widely used method of analysis. Organophosphosphate(OP) pesticides has been used for decades to protect the growth of crops, and made a great contribution to ensure the agricultural production and famers' income[5]. However, with the increasing scale of pesticide use, agricultural products with the pesticide residues have a negative impact on human health.

The common methods used to detect the pesticides residues in agricultural products are mature, such as Gas Chromatography (GC) [6,7], High Performance Liquid Chromatography (HPLC) [8-10], and etc. Although these methods have good accuracy, their sample pretreatment process is complex, time-consuming and testing cost is high. SERS has the advantages of faster, convenience, high sensitivity and nondestructive analytical method for determination of fruit pesticides. And the Raman analyses could be used in liquids [11-13]. For the past few years, SERS, which is a promising technology for the residues detection, has attracted much interest by researchers from the entire world. The theory of SERS is putting probed molecules onto the roughened surface of transition metals, enhancing the Raman signals more than one million times because of the chemical enhancement and electromagnetic field enhancement [14]. The strength of SERS depends on the interaction between analyte and Nanostructures substrate surface, and the most typical substrate is gold (Au), silver (Ag) and copper (Cu) [15].

Guerrini et al[16](2011) obtained the SERS spectra of dimethoate (DMT) and omethoate (OMT) by aggregated Ag hydrosols, and The result showed that the detection limit of DMT was 10^{-5} mol/L. Dhakal et al[17](2014) collected the Raman spectroscopy of organophosphorus (chlorpyrifos) pesticide. Detection limit for the chlorpyrifos residue in apple surface of the

developed system was 6.69 mg/kg .

The purpose of this study was to discuss the feasibility of choosing Gold Nanostructures as SERS substrates for qualitative and quantitative analysis of fruit residues. Ganan navel orange was selected as the object of research. Choose phosmet and chlorpyrifos as the experimental subject. Spectral data collected were qualitative and quantitative analyzed. Nowadays, there are many reports on the application of using Gold Nanostructures as SERS Substrates in the field of pesticide residues, and the goal was to detect and characterize pesticide residues using Gold Nanostructures as SERS substrates.

2. Experiments

2.1 Materials

Two OP pesticides (phosmet and chlorpyrifos) were purchased from AccuStandard, Inc. $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ was purchased from Sinopharm Chemical Reagent Co., Ltd. NaCl, acetonitrile, methanol and sodium citrate were analytically pure, and purchased from Nanchang huake Instrument Co. Ltd.

2.2 Sample Preparation

Pure pesticide solutions: 5000 mg/L of phosmet and chlorpyrifos solutions were prepared by methanol and H_2O (1:1, v/v).

Oranges were cleaned repeatedly with ultrapure, and dry naturally. Clean the orange skin and Cut it into square pieces ($2\text{cm} \times 2\text{cm}$), and a certain amount of standard pesticide solution of phosmet and chlorpyrifos were added on it. After waiting pesticides air-dry, the skin was grated and added to an acetonitrile solution. We could get the solution of pesticide after filter it. The 31

different concentrations of phosmet range from 3 to 33 mg/L at 1 mg/L interval. The 31 different concentrations of chlorpyrifos range from to 34 mg/L at 0.5 mg/L interval.

2.3 SERS Measurement

The SERS substrates of Gold Nanostructures were prepared by sodium citrate reduction method. The pesticide samples, colloidal gold and sodium chloride were mixed based on a certain volume ratio (10:3:3), shocked evenly on the shock tester. Mixed solution was put on the quartz plate, and collected SERS of it.

2.4 Data Analysis

The data analysis used Unscrambler v8.0 software. Pesticide original spectral data were processed by partial least squares (PLS) and the different pretreatment methods. The prediction model was established between the Raman spectrum and pesticide content using different modeling algorithms (PLS, PCR), and the effect of models was analyzed and evaluated using the following indicators:

$$R = \sqrt{\frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{\sum_{i=1}^n (\hat{y}_i - \bar{y})^2}}$$

$$RMSEC = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n - 1}}$$

$$RMSEP = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n - 1}}$$

In these equations, n is the number of samples, y_i is the reference pesticide concentration (mg/L), \hat{y}_i is the predicted pesticide concentration (mg/L), \bar{y} is the average of the reference pesticide concentration (mg/L).

The R, RMSEC and RMSEP were used to evaluate the model. In the same concentration

range, if the R value is higher and the RMSEP value is lower, the better predictability the model will get.

3. Results and discussion

3.1 Characteristic Raman shift of phosmet, chlorpyrifos

The chemical structures of phosmet and chlorpyrifos are quite similar (Fig. 1). Raman spectra of the phosmet powder were obtained, as shown in Fig. 2. The very strong peak at 650cm^{-1} is the $\text{P}=\text{S}$ stretching vibration; the strong peak at around 501cm^{-1} , 605cm^{-1} , 1189cm^{-1} , 1774cm^{-1} is attributed to CH_3 torsional vibration, $\text{C}=\text{O}$ in-plane deformation, $\text{P}-\text{O}-\text{CH}_3$ out-of plane deformation and $\text{C}=\text{O}$ stretch, respectively; the weak peak at around 1013 is attributed to $\text{P}-\text{O}-\text{C}$ deformation[18, 19].

Raman spectra of the chlorpyrifos powder were obtained, as shown in Fig. 3. The very strong peak at 631 and 678 cm^{-1} is the $\text{P}=\text{S}$ stretching vibration[20]. The peak at 1569 cm^{-1} is the $\text{C}=\text{C}$ stretching. The peaks at 160 and 1240 cm^{-1} is the $\text{P}-\text{O}$ vibration and ring breathing. [21]



Fig. 1 Chemical structures of phosmet and chlorpyrifos

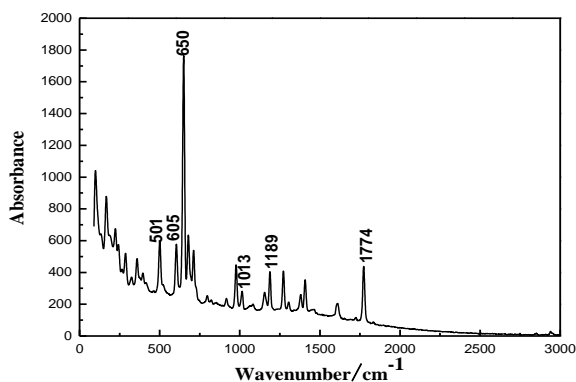


Fig.2 Raman spectra of Phosmet powder

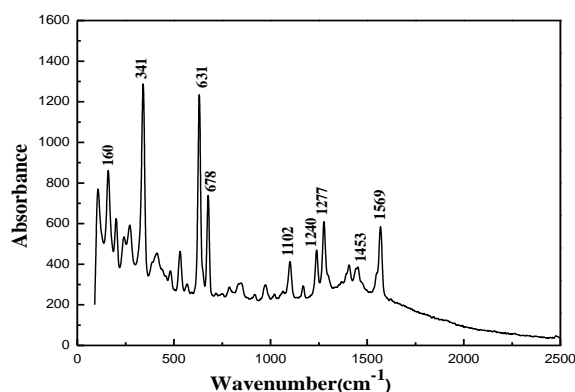


Fig.3 Raman spectra of chlorpyrifos powder

Table 1 Band assignments of major peak in Raman spectra acquired from chlorpyrifos

Band (cm ⁻¹)	Assignment
160	P-O vibration
341	N-cyclopropyl bending vebration
411	C-Cl stretch
631	P=S
678	P=S
1102	P-O-C stretch
1240	Ring mode
1277	Ring mode
1453	C-H deformation
1569	Ring stretching mode

3.2 SERS spectra of phosmet and chlorpyrifos

Raman spectrum has fingerprint characteristics, namely the spectrum of each substance has a specific peak. Its characteristic peak should be identified before the quantitative analysis about this two pesticides. With the increase of phosmet content in solution, the corresponding peak intensity was rise accordingly as shown in Fig.4. In addition to differences in signal intensity, the peak shape and peak value remained the same. According to the peak position, the main characteristic

peaks of phosmet was at 501cm^{-1} , 605cm^{-1} , 798cm^{-1} , 1013cm^{-1} , 1189cm^{-1} , 1774cm^{-1} . Compared with the Raman spectra of phosmet solid, the SERS spectra of phosmet solution were not obvious peak appeared at 650cm^{-1} , and the intensity of peak vibration at 1013cm^{-1} , 1189cm^{-1} , 1774cm^{-1} also significantly decreased in phosmet solution.

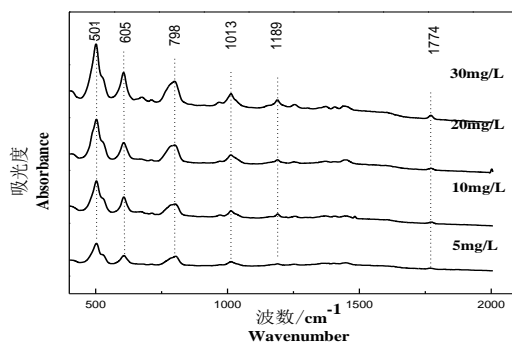


Fig.4 Contrast of phosmet in different concentrations

Using gold colloid as SERS substrates, enhanced spectrum of chlorpyrifos in orange skin was collected, the average SERS spectrum as shown in Fig.5, and the spectral range was $400\text{cm}^{-1}\sim 1800\text{cm}^{-1}$. Compared with SERS spectra of chlorpyrifos and the Raman spectra of chlorpyrifos solid, as shown in Fig.6, there were enhanced effect in multiple bands using gold colloid. The intensity of peak vibration at 970cm^{-1} , 1013cm^{-1} , 1164cm^{-1} , 1443cm^{-1} as shown in Fig.6, and the spectrum peaks belonging as shown in table 1. With the increase of chlorpyrifos content in solution, the corresponding peak intensity was rise accordingly. Some peaks displacement of SERS spectra of solution changed in chlorpyrifos pesticide residues solutions, but the drift range was less than 10cm^{-1} and not affect the accuracy of the model.

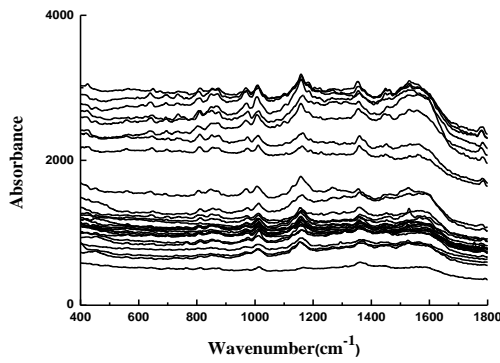


Fig.5 Average Raman spectra of chlorpyrifos sample

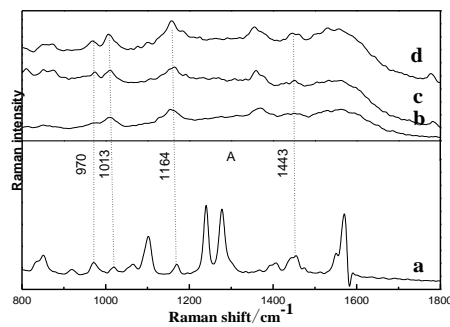


Fig.6 Raman spectra of chlorpyrifos standard sample and SERS of chlorpyrifos solutions , 5 (b), 10 (c) and 20mg/L (d)

3.3 SERS spectral pretreatment of phosmet and chlorpyrifos

The SERS spectra of phosmet samples ranged from 3 mg/L to 33 mg/L was collected by confocal Raman spectroscopy using gold colloid as SERS substrate. The original spectra data were pretreated by Savitzky-golay smoothing, baseline processing, first derivative, second derivative and multiple scatter correction etc. The quantitative analysis mode of phosmet was built by PLS, in which 24 samples for calibration set and 7 samples for prediction set. Compared six different pretreatment methods, the models were evaluated by R_p and RMSEP as shown in table 2. The best prediction model was achieved with R_p of 0.924 and RMSEP of 4.293 mg/L, with the Savitzky-golay smoothing and 2nd derivative data preprocessing.

Table 2 Comparison results for phosmet solution

Preprocessing method	Calibration Set		Prediction Set	
	R_C	RMSEC(mg/L)	R_P	RMSEP(mg/L)
Savitzky-golay smoothing	0.897	3.726	0.835	4.705
Base line	0.898	3.706	0.827	4.738
1st derivatives	0.968	2.120	0.873	4.754
2nd derivatives	0.966	2.173	0.883	4.662
MSC	0.890	3.853	0.665	6.017
S. G smoothing+ 2nd	0.988	1.254	0.924	4.293

3.4 Building model of phosmet

The original spectral data were processed by different modeling algorithms combined with the savitzky gold smoothing and second derivatives data preprocessing. The analysis model of Raman spectroscopy and phosmet content was established using PLS and principal component regression(PCR), the prediction effect of the model was evaluated by R_P and RMSEP, as shown in table 3. The value of factor lower resulted in that the information of model was not complete, and the predictive ability of model was lower; on the other hand, the value of factor higher resulted in that the model was too complex, and fitting phenomenon appeared in the training. As shown in Fig.7, when the factor is 6, the RMSEP of PLS model is minimum. The PLS model predicted values of chlorpyrifos concentrations were showed in Fig.8.

Table 3 Modeling comparison results for phosmet pesticide residues

modeling algorithm	PCs	Prediction set	
		R_P	RMSEP(mg/L)
PCR	8	0.893	4.527
PLS	6	0.924	4.293

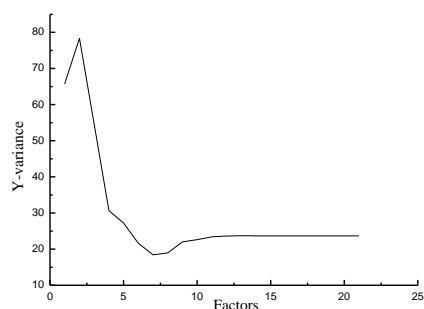


Fig.7 Determination of principal factor number for detection of phosmet content

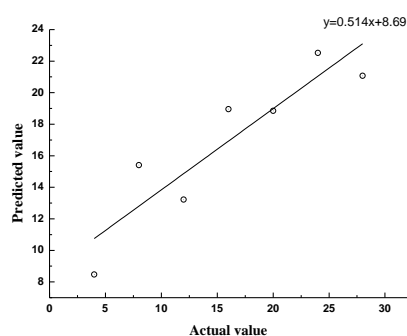


Fig.8 Validation results of phosmet pesticide residues

3.5 SERS spectral pretreatment of chlorpyrifos

The SERS spectra of chlorpyrifos samples ranged from 4 mg/L to 34 mg/L was collected by confocal Raman spectroscopy using gold colloid as SERS substrate. The quantitative analysis mode of chlorpyrifos was established by PLS, in which 23 samples for calibration set and 8 samples for prediction set. Table 3 shows the results of the models with different preprocessing methods obtained by PLS regression. The optimal model of chlorpyrifos pesticide was R_p of 0.715 and RMSEP of 6.646 mg/L, with the baseline and MSC data preprocessing.

Table 3 Comparison results for chlorpyrifos solution

		Calibration set		Prediction set	
Pretreatment method	PC	R_C	RMSEC	R_P	RMSEP
			(mg/L)		(mg/L)

Origin	3	0.837	4.829	0.640	7.066
smoothing	3	0.837	4.827	0.640	7.067
MSC	7	0.974	1.980	0.714	6.743
Baseline	5	0.922	3.409	0.682	7.031
1st	5	0.990	1.192	0.686	7.216
2nd	4	0.987	1.380	0.797	7.918
Baseline+MSC	8	0.989	1.273	0.715	6.646

3.6 Building model of chlorpyrifos

The original spectral data were processed by different modeling algorithms combined with baseline and MSC data preprocessing. The analysis model of Raman spectroscopy and chlorpyrifos content was established using PLS and PCR, the prediction effect of the model was evaluated by R_p and RMSEP, as shown in table 4. As shown in Fig.9, when the factor is 13, the RMSEP of PLS model is minimum. The PLS model predicted values of chlorpyrifos concentrations were showed in Fig.10.

Table 4 Modeling comparison results for chlorpyrifos pesticide residues

Modeling algorithms	PC	R_C	RMSEC (mg/L)	R_p	RMSEP (mg/L)
PLS	8	0.989	1.273	0.715	6.646
PCR	13	0.941	2.981	0.780	6.006

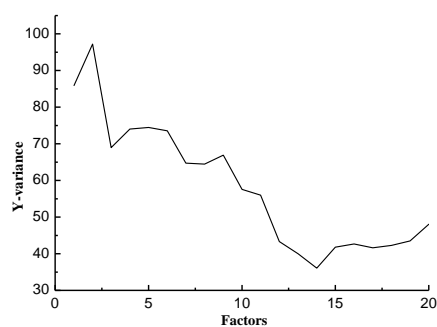


Fig.9 Determination of principal factor number for detection of chlorpyrifos content

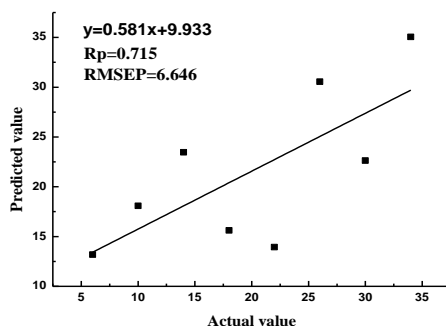


Fig.10 Validation results of chlorpyrifos pesticide residues

4. Conclusions

Two kinds of pesticides (phosmet, chlorpyrifos) can be quantitatively measured and distinguished using SERS coupled with gold colloid. Pesticide residues on the surface of orange could be measured and the model has a good effect in the qualitative analysis of their SERS spectral data. It indicated that determination of pesticide residues using SERS coupled with gold colloid is feasible, compared the SERS method and other chemical detection methods such as GC and HPLC. But two kinds of pesticides are not enough for determination of pesticide residues, so we need to rich the kinds of pesticides.

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