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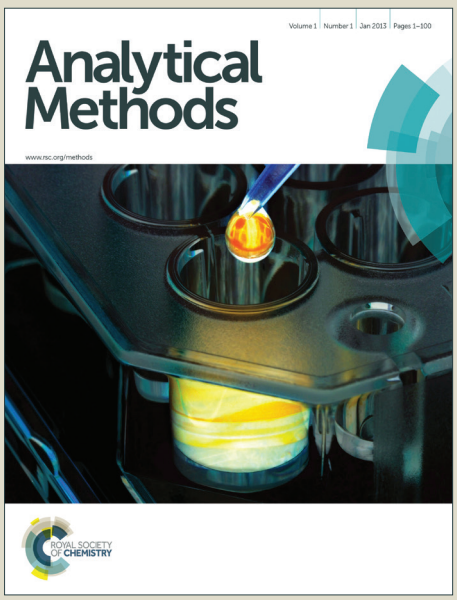

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Rapid detection of Chorpyriphos Residues in rice by Surface-Enhanced Raman Scattering

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Surface-Enhanced Raman Scattering (SERS) technology coupled with quick pre-treatment method is used to detect Chorpyriphos (CP) pesticides residues in rice. 72 rice samples containing CP pesticides residues are prepared for SERS spectra acquirement and GC-MS measurement. The lowest detection concentration of CP pesticides in rice is below 0.506 mg/L by SERS technology. Then three methods as Standard Normal Variate(SNV), Multiple Scattering Correction(MSC) and Normalization are used to preprocess the original SERS spectra, and the prediction models of Partial Least Squares (PLS) are established for detecting CP pesticides residues in rice. The PLS model with Normalization is the optimal, the correlation coefficient (Rp) is 0.9734, root mean square error of prediction (RMSEP) is 1.76 mg/L in the prediction, relative analysis deviation (RPD) is 4.58, higher than 3. The six unknown samples are prepared to verify the accuracy of the prediction model. The absolute values of relative deviation are calculated to be between 2.64%~4.47%, and the predicted recoveries are calculated to be between 96.59%~104.69%. The value of T test shows that the prediction model is accurate and reliable. This study demonstrates that the method can achieve rapid detection of CP pesticides residues

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in rice.

1. Introduction

In order to improve the yield of crops, pesticides had been used widely in greenhouses, farmlands, and orchards. It is estimated that 20~50% of crops are saved from infestation by pesticides application. However, the quantity of applied pesticides must be strictly controlled to insure public security, because the most common pesticides kill pests by assaulting the nervous system while they can contaminate the environment by water or soils. Consequently pesticides or their reactants exist in food, and pose a threat to human health.[1, 2] Chorpyriphos (CP), in which molecular formula is $C_9H_{11}C_{l3}NO_3PS$ containing benzene ring, pyridyl and phosphorothioate, is an efficient and moderately toxic organophosphorus pesticides.[3, 4] CP can effectively kill different pests such as cnaphalocrocis medinalis, planthopper, aphid and pieris rapae, which are pernicious to various plants such as rice, wheat, cotton, vegetable, fruits.[5] Currently conventional analytical methods have been applied for CP and related pesticides residues, such as HPLC,[6, 7] GC-MS,[8, 9] enzyme inhibition method.[10] Nevertheless, they are time-consuming, complex-preprocessed and labor- intensive, which makes these analytical methods less attractive, thus not suitable to screen and detect pesticides residues in field.[11, 12] So it is crucial to develop new rapid analytical methods for detecting trace amounts of CP in food.

Vibrational spectroscopic methods such as Surface enhanced Raman spectroscopy（SERS）have been obtained greatly increasing attention for rapid detection of trace substances.[13-15] SERS can avoid an intricate pretreatment, which

composes of sample preparation and separation as needed by other analytical methods.[16] Another superiority of the SERS can enhance the intensity of Raman spectroscopy by more than millions of times due to the electromagnetic mechanism and chemical mechanism.[17-19] Actually every compound can generate a characteristic Raman spectrum. Thus SERS as an available analytical method can be used to detect pesticides residues in food widely. Many applications have been developed with nanostructured substrates for SERS measurements. For example, the characterization of thiacloprid molecules has been conducted exhaustively in the state of solid and liquid. The SERS spectra of thiacloprid have been obtained in various experimental conditions.[20] SERS strategy coupled with gold nanoparticles (AuNPs) is used to detect melamine in milk powder, and the limit of detection is to be as low as 0.1 ppb with an excellent linearity of 0.5~100 ppb.[21] A rapid, non-destructive detection method used SERS technique is studied on apples. The linear regression model is set up with phorate and fenthion as investigative subjects.[22] SERS technique coupled with Ag and Au colloidal nanoparticles is recently recorded to analyze the organophosphate pesticides fonofos.[23] SERS with solid-phase extraction is used to detect CP-methyl factitiously added into orange juice, and the detection concentration is below 50 parts-per-billion.[24] Two significant organophosphate pesticides omethoate and dimethoate are analyzed with SERS, and their Raman characteristics peaks have been respectively assigned.[25] SERS technique is used to detect acetamiprid pesticides on apple surfaces and in apple juice respectively, and can detect successfully acetamiprid pesticides up to 0.5 mg/L in solvent, 0.125 μg/cm^2 on apple surfaces, and

3 mg/L in apple juice.[26] SERS technique is used to detect omethoate residues in orange skin, and the PLS model is established.[27] A sensitive method used SERS has been applied to determine tricyclazole pesticides residues in rice applying sliver colloid substrate, and calibration curves are established with the intensity of two characteristic peaks, and the tricyclazole solution used SERS can be determined to be as low as 0.002 mg/L.[28] It is feasible that SERS technology can be used to detect pesticides residues in food. While the detection of CP pesticides residues in rice is reported rarely.

In this paper, SERS technology combined with multivariate statistical methods is used for rapid detection of CP pesticides residues extracted from rice. In order to achieve this purpose, gold nanoparticles are used to enhance the Raman signal. Rice samples are prepared to extract CP pesticides residues. Anhydrous Magnesium sulfate, PSA and C18 are applied to remove the effects of protein, starch, amino acids and other substances. Then the SERS spectra of the samples are collected, and the actual values of the samples are obtained by GC-MS. Multivariate statistical method is used to analyze the SERS spectra and establish quantitative models of CP pesticides residues in rice by three preprocessed methods as SNV, MSC and Normalization. This study aims to provide a rapid, simple and accurate scheme that can be used to detect other pesticides residues in food by SERS.

2. Experimental

2.1 Reagents and Chemicals

CP is purchased from the National standards material information center in its analytical reagent and applied as received. Ethyl acetate, acetonitrile, sodium chloride are acquired and applied as received from Sinopharm Chemical Reagent Beijing Co., LTD. Anhydrous magnesium sulfate, PSA and C18 are obtained from CRM/RM Information center of China. OTR202 and OTR103 are bought from OptoTrace Technologies, Inc. Organic membrane (0.22um) and the analytical column (HP-5MS, 5% Phenyl Methyl Silox, 30m×250μm×0.25μm) are bought from the Agilent technologies co., LTD. The rice is provided by the agronomy experimental base of Jiangxi Agricultural University. All glassware are wished by aqua regia before using, and then cleaned drastically with deionized water, and then baked thoroughly.

2.2 Sample Preparation

100 mg/L stock solution of CP is prepared by ethyl acetate and diluted into the following working solutions of 50, 20, 10, 5, 1, and 0.5mg/L. Ethyl acetate without pesticides is used as the control. The solutions are stored in lucifugal environment at 4℃.

Simulated rice samples containing CP pesticides residues are prepared respectively according to the following steps. Firstly, 100g rice is weighed out, and placed in plastic wrap, and then sprayed proportionally the 100 mg/L stock solution of CP with sprinkling can. 72 different concentration gradient rice samples containing CP are manufactured severally. The samples are air-dried. After that, samples are crushed singly by pulverizer (MG100, Beijing Grinder Instrument Co., Ltd, China),

and then filtered by 80 mesh sieves respectively.

The following sample preparation steps are implemented for both Gas chromatography–mass spectrometry (GC-MS) measurements and SERS, and each sample is repeated twice. (1)5g crushed rice sample, 10mL water, 10mL acetonitrile and 5g sodium chloride are successively blended in 50mL centrifuge tube, and shaken on a vortex mixer (Vortex-Genie 2, The United States Scientific Industries co., LTD, USA) until a symmetrical mixture is acquired, and the symmetrical solution is centrifuged for 5 min at a speed of 4200 r/min (Mini-10K, Hangzhou AoSheng instrument co., LTD, China). (2) 2 mL of the supernatant is loaded into a 15 mL centrifuge tube containing moderate mixtures of PSA, anhydrous Magnesium sulfate and C18. The centrifuge tube is shaken for 1 min on a vortex mixer to remove the effects of protein, starch, amino acids and other substances, and then centrifuged for 5 min at a speed of 4200 r/min. Then the resulting supernatant is filtered by 0.22um organic membrane. The filtrate is used for SERS measurement. (3) 1mL of the filtrate is added into a 10mL centrifuge tube and evaporated with termovap sample concentrator (PHC-12R, Shanghai Qiqian Electronic Technology Co. Ltd, China). (4)The extracted pesticide is eluted using 1 mL of ethyl acetate. The eluted solutions is swayed for a moment, and loaded into a vial, and used for GC-MS measurement.

2.3 SERS Measurement

SERS spectra are acquired using a portable Raman apparatus（RamTracer-200-HS, OptoTrace Technologies, Inc. China）with an electrical charge-coupled device (CCD).

The measurements are implemented employing the following configuration: an excitation light of 785nm, the spectral distinguishability of 4 cm^{-1}, the laser power of 200mW, the integration time of 10s with two accumulations and the spectral acquisition range 0f 400～1800cm^{-1}. A compound solution is prepared by adding 500uL OTR202, 20uL analytic solution and 100uL OTR103 into a quartz bottle and lightly shaken, and then placed in the sample cell. The laser beam is focused inside the sample cell containing the solution for SERS measurement. Each sample is scanned respectively three times.

2.4 GC-MS measurement

The GC-MS instrument (Agilent GC700, Agilent technologies co., LTD, USA) is used to measure actual values of samples. The measurements are executed with a flame ionization detector. The oven is heated at 50°C for two min, then raised to 150 °C at 50°C/min, then ascended to 300°C at 10°C/min. 1μL sample is injected into the instrument using high purity helium as a carrier gas. The pressure is 9.7853 psi. The gas flow rate is 1.2 mL/min. Interface temperature is 230°C, and quadrupole temperature is 150°C, and transfer line temperature is 280°C. Collision gas is high purity nitrogen (purity ≥99.999%).

2.5 Data Analysis

In order to eliminate the interferences of baseline shift, stochastic noise and background signal, and original spectra are pre-processed using MSC, SNV and

Normalization. Prediction models of pesticides residues in rice are established using the regression method of Partial Least Squares (PLS), and appraised comprehensively by the parameters of RMSEP, Rp and RPD. The model of the higher Rp value and the lower RMSEP value has a better predictability. The accuracy of the model is verified using the six unknown samples. Paired-samples T test is implemented with the actual values of GC-MS and the prediction values of the model. Data analysis is achieved based on MATAB R2010a (Matworks Inc., Natick, MA, USA) and SPASS V17.0 (International Business Machines Corporation, USA).

3. Results and discussion

3.1 Spectroscopic characterization

To affirm that no interfering signals are produced by solvent or other factors, SERS spectra of 50mg/L CP solution, as well as the background spectra of Aceticether and Nano-enhanced reagents (OTR202 and OTR103) for comparison are displayed as shown Fig.1(a), (b) and (c). The background SERS spectra from Fig.1 (b) and (c) are quite weak and it does not have superposition with the peaks of CP. The SERS spectrum of CP coupled with Nano-enhanced reagents is acquired easily, which indicats that a strong interaction happens immediately when CP is absorbed onto metal surfaces. This is a compelling evidence manifesting that SERS can be applied to detect CP molecules without any disturbances from the background. As shown in Fig.1 (a), the strong peaks at 527, 606, 674, 1094, 1264 and 1552 cm^{-1} are attributed as follows.[23, 29-31] Intensity of the band at 674 cm^{-1} is highly enhanced and it is

assigned the mode of ring breathing vibration coupling to deformation mode of the C–Cl bond. The band at 527 cm^{-1} is assigned the stretching mode of the P–O bond. The band at 606 cm^{-1} may consist of the stretching mode of the P=S and C–Cl bond. The band at 1094 cm^{-1} is assigned the stretching mode of the P–O–C bond. The band at 1264 cm^{-1} may actually be a C–H deformation mode. The band at 1552 cm^{-1} is due to a ring stretching vibration. In general, our results agreed well with previous reports. It can be observed that the wide baseline shift from 1000 to 1600 cm^{-1} is likely due to the luminescence produced by the quartz bottle. These characteristic peaks may be used as qualitative and quantitative evidences of determination CP molecules.

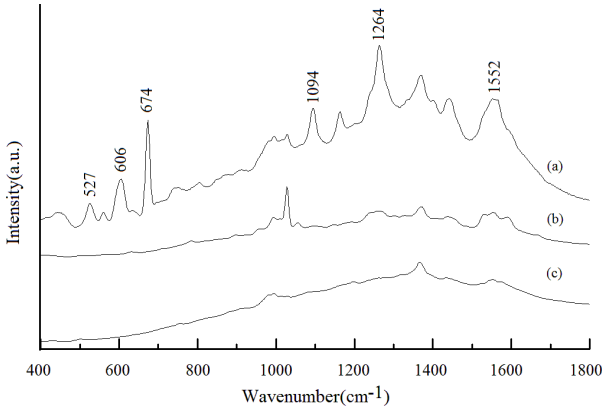

Fig. 1 SERS of (a) 50 mg/L CP solution, (b) Aceticether and (c) Nano-enhanced reagents

3.2 SERS analysis of stock solutions

SERS is used to measure the different concentration stock solutions of CP. Average SERS spectra of CP are shown in Fig.2 at the 400–1800cm^{-1} ranges. The intensities of characteristic peaks constantly reinforce with increasing concentration, and the alterative rates of characteristic peak intensity are different. The SERS spectra are consistent with a previous report using Silver (Ag) dendrites as SERS substrate, in

which the peak intensity weakens as concentration of pesticides decreases.[14, 20] The peaks at 527 and 606cm^{-1} have a faster change with concentration, and the peaks at 674, 1094 and 1264cm^{-1} have a slower change relatively. This may be the cause of the CP molecules attached on the nanoparticles substrate surface with different absorbability and different orientations.[32] These characteristic peaks can be used for quantitative analysis of CP pesticides residues.

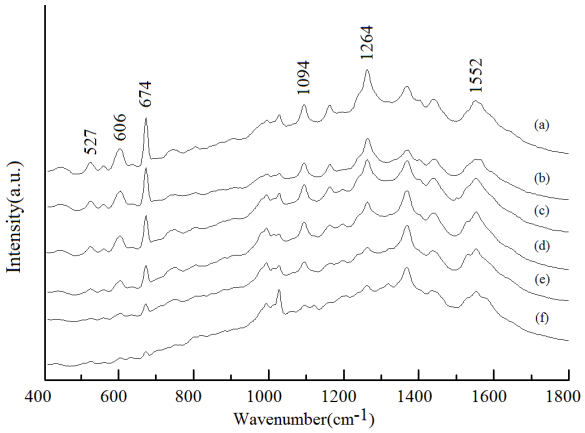

Fig. 2 SERS spectra of CP solutions with different concentrations, (a)~(f): 50, 20, 10, 5,1, 0.5mg/L

3.3 Comparison of SERS with purified and unpurified

The SERS of 5.764 mg/L CP solution extracted from rice with purified and unpurified, the substrate background of rice solution without CP for contrast are respectively shown in Fig.3 (a), (b) and (c). The CP characteristic peaks at 524, 604 and 672 cm^{-1} are visible while relatively weak from Fig.3 (b). These characteristic peaks can be easily observed and stronger from Fig.3 (a), furthermore no significant baseline shift, which suggests that the CP Raman signal is weakened because of the interference of proteins, starch, amino acids and other substances in rice.[33] The characteristic peaks

have been enhanced, which is beneficial to quantitative analysis of CP residues in rice.

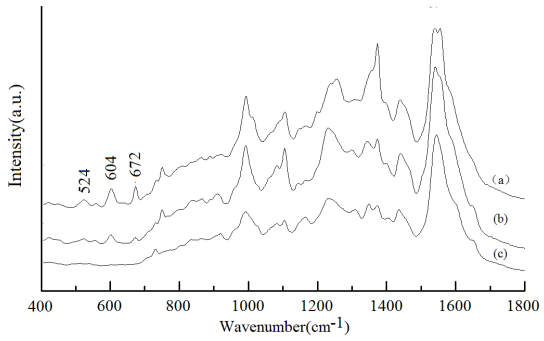

Fig. 3 SERS spectra of (a) 5.764 mg/L CP solution extracted from rice with purified, (b) 5.764 mg/L CP solution extracted from rice with not purified and (c) rice solution without CP

3.4 CP Detection

The SERS spectra of CP solutions extracted from rice samples are shown in Fig.4. Several bands in the 400-800cm^{-1} range compared with the SERS of CP standard solution are shifted to smaller wavenumbers: 527-524, 606-604 and 674-672cm^{-1}. This is due to the effect of rice complex matrix composition.[34, 35] These bands at 524,604 and 672cm^{-1} are obviously observed in both Fig.4(a) and (b).The bands at 604 and 672cm^{-1} are observed only in Fig.4(c), but the characteristic peak intensities are weakened, and the band at 524cm^{-1} can not be identified. The bands at 604 and 672cm^{-1} are still observed but very weak in Fig.4(d). The bands at 524,604 and 672cm^{-1} are not observed in Fig.4(e), and the Raman spectra are almost consistent in both Fig.4(e) and (f). All of these indicate that the method used SERS technique detecting CP solution in rice is feasible even in concentration below 0.506mg/L. As

shown in Fig.4, there may be a linear relationship between Characteristic peak intensity and concentration of CP pesticide residues in rice.

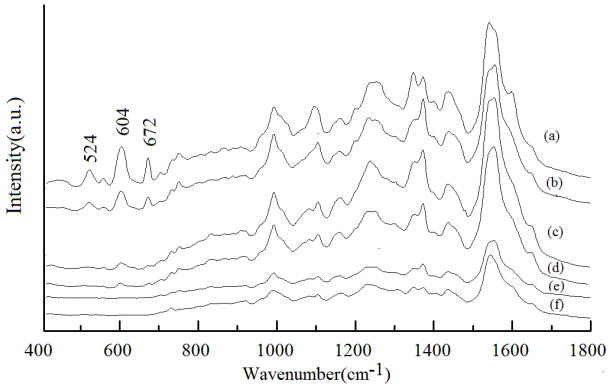

Fig. 4 SERS spectra of CP solution, (a)~(f): 19.842, 10.108, 0.996, 0.506, 0.427mg/L, blank

3.5 Actual values by GC-MS

The actual values of 72 samples are obtained using GS-MS. The data range is 0.427~66.426 mg/L. In order to establish a model, 72 samples are divided into two subclasses. One subclass named calibration set is used to establish the model, and the other named the prediction set is used to validate the dependability of the model. All 72 samples are classified according to their actual values. A 1:2 prediction/calibration division is implemented. Two samples from every three samples are picked as the calibration set, and the remaining sample as the prediction set. Therefore, the calibration set includes 48 samples and the prediction set includes 24 samples. As shown in Table 1, the range of the calibration set nearly includes the range of the prediction set, and the distributions in the calibration and prediction sets are coincident.

Table 1 The actual values of CP pesticides residues in rice in the calibration and prediction set

Two Subsets	Number	Units	Range	Mean	Standard deviation
Calibration	48	mg per kg	0.427~66.426	25.874	2.37
Prediction	24	mg per kg	0.506~65.972	26.186	2.26

3.6 PLS models with SERS spectra preprocessing

As the original spectra may be subject to the impacts of random noise, baseline shift, external stray light, thermal stability noise of CCD and other factors, and then the reliability and stability of the prediction model would be possibly disturbed.[36] Therefore, the original spectra are pretreated by three methods as MSC, SNV and Normalization, then prediction models of CP in rice are established using the regression method of Partial Least Squares (PLS), and appraised comprehensively by the parameters of Rc, RMSECV, RMSEP, Rp and RPD. From Table 2, the models with three preprocessing methods are better than the original spectra, the predictive performance of the model by Normalization is the optimal.

Table 2 Results of PLS models for CP in rice by different pretreating methods

Pre-processing method	Principal components	Calibration		Prediction		
		Rc	RMSECV(mg/L)	Rp	RMSEP(mg/L)	RPD
Original spectrum	5	0.9718	1.82	0.9567	2.56	3.88
MSC	6	0.9851	1.42	0.9711	1.93	4.49
SNV	7	0.9837	1.54	0.9712	1.87	4.53
Normalization	4	0.9868	1.26	0.9734	1.76	4.58

The lowest RMSEP value is obtained when four latent variables are used, which indicates that the best number of latent variables to construct a PLS model is 4. As shown in Fig.5, Rc is 0.9868, and RMSECV is 1.26 mg/L in the calibration curve. Rp is 0.9734, RMSEP is 1.76 mg/L, and RPD is 4.58, higher than 3 in the prediction curve, which shows that the PLS model can accurately predict the CP residues in rice.

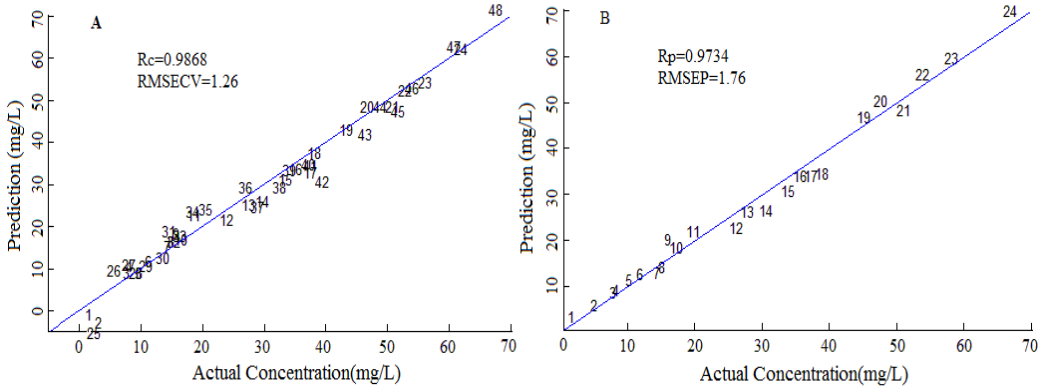

Fig.5 PLS plots of the calibration curve (A) and the prediction curve (B)

3.7 Model validation

In order to verify the method accuracy, six rice samples of unknown CP concentration are pretreated and obtained their actual values by GC-MS methods. The results compared the actual values with the predicted values are listed in Table 3. The absolute values of relative deviation are calculated to be between 2.64%~4.47%, and the predicted recoveries are calculated to be between 96.59%~104.69%, the predicted values of model are basically consistent with the actual values. This indicates that the method is receivable and credible for rapid detection of CP pesticide residues in rice by SERS.

Table 3 Predicted value and actual value of CP solution in rice

Sample (n)	Measured value (mg/L)	Predicted value (mg/L)	Relative Deviation (%)	Predicted Recovery (%)
1	2.198	2.311	-4.47	104.69
2	4.768	4.627	3.08	97.04
3	9.231	8.917	3.52	96.59
4	12.672	12.346	2.64	97.43
5	15.94	16.562	-3.76	103.90
6	19.778	19.213	2.94	97.14

The paired-samples T test is implemented with the actual values of GC-MS and the predicted values of PLS model. The Sig value is 0.389, higher than 0.05. It shows that the difference between SERS and GC-MS is not significant. This indicates that the method by SERS is reliable and rapid.

4. Conclusions

The study demonstrates that SERS coupled with quick pre-treatment method can be used to detect CP residue in rice. This concentration of below 0.506 mg/L is able to meet the tolerance levels for CP in rice. MSC, SNV and Normalization are used to pretreat the original spectra, and then the PLS models are established respectively, the predictive performance of model by Normalization is the optimal. Six rice samples of unknown CP concentration are used to verify the model accuracy, and the predicted values of the model are basically consistent with the actual values. The paired-samples T test result indicates that the difference between SERS and GC-MS is not significant. The whole analysis, including solvent extraction and SERS

measurement, is achieved in approximately 12 min. Therefore, Raman technique can be used to determine pesticides residues in rice, particularly as a rapid screening instrument for food inspectors. The field measurements could be achieved because of the pretreatment simplicity and the portable Raman apparatus. Current study can provide an analytic idea extending to other pesticides in food.

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