



# Rapid detection of pesticide residues in fruits by surface-enhanced Raman scattering based on modified QuEChERS pretreatment method with portable Raman instrument

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## Abstract

In this work, surface-enhanced Raman scattering (SERS) spectrum was used to build a rapid analytical method for pesticide residues in fruits. QuEChERS (quick, easy, cheap, effective, rugged and safe) method was modified by multi-walled carbon nanotubes as clean-up sorbents. Overall recoveries of selected pesticide phosmet ranged from 77 to 97% in apples at three spiking levels (0.5, 1 and 2 mg kg<sup>-1</sup>). The relative standard deviations were between 6.6 and 14%. The limit of detection for phosmet was 0.1 mg kg<sup>-1</sup> in standard solution and 0.5 mg kg<sup>-1</sup> in apples, which was below the maximum residue limits in fruits of USA, EU and China. The intensity of phosmet characteristic peak existed good linear relationship with the logarithm of concentration between 0.5 and 5 mg kg<sup>-1</sup>, with the calibration curve coefficients ( $R^2$ ) of 0.9994, which indicated quantitative potential for pesticide residue detection. The method was extended to other pesticides, and the obtained SERS results could be used to establish a spectra database. All the experiments were performed with a portable Raman instrument. Combining pretreatment method with spectra database, a sensitive, rapid and convenient method could be built for pesticide residues detection in fruits.

**Keywords** SRES · QuEChERS · Multi-walled carbon nanotubes (MWCNTs) · Fruit · Pesticide · Rapid detection

## 1 Introduction

Pesticides have been widely used to prevent or eliminate insects in agricultural products [1, 2]. However, pesticide residues have induced increasing attention due to their threat to life health and environment. Studies show that chronic contact pesticides might lead to adverse effects on the consumers [3–5]. Therefore, the detection of pesticide residues is extremely urgent. Researchers have dedicated to establish methods to detect trace pesticide residues on crops. Normally, current methods mostly used in laboratories are chromatography-based methods such as gas chromatography (GC), high-performance liquid chromatography (HPLC) and HPLC/GC coupled with mass spectrometry (MS) [6–8]. These methods are sensitive and capable

of detecting multiple pesticide residues quantitatively. However, several deficiencies of these methods restrict their applications, such as the need for sample preparation which is usually complicated and time-consuming; the experiment needs technical researchers, long measurement time and high cost. In many cases, such as in situ detections or in-filed measurements, establishing a fast, convenient and low-cost procedure to determine pesticide residues is significant [9]. In recent years, some novel detection methods such as enzyme inhibition assay, immunoassay or bio-sensor method have been developing quickly [10]. However, several defects such as short storage time and solution instability problem still exist [11], and the accuracy and cost have not been satisfactory.

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Vibration spectra such as Raman spectroscopy have been widely used as an effective method to estimate food safety [12]. Since its discovery in 1970s, surface-enhanced Raman scattering (SERS) became an important spectroscopic method [13, 14]. The studies showed that SERS spectra are ultra-sensitive, even could detect single molecules [15, 16]. Due to high sensitivity and fingerprint information about the chemical structure of analytes, SERS spectra have been employed to detect pesticides by several groups [11]. Li et al. [17] synthesized shell-isolated nanoparticles to detect pesticide residues parathion on the surface of fresh orange both by confocal microprobe and portable Raman system. Liu et al. [18] used SERS based on Au@Ag nanoparticles for rapid identification and detection of pesticides residues in the fruit peels. Tang et al. [19] prepared Ag colloid to obtained mixed pesticides SERS signals to identify them. He et al. [20] used SERS based on silver dendrites to detect thiabendazole on apple surface, which was swabbed to recover pesticides. Mandrile et al. [21] used gold nanoparticles to detect pyrimethanil on contaminated fruits surface-based optimized methodology by SERS and Raman mapping strategy.

However, most researches chose several points of the peers to evaluate the pesticide residues of the crops. As we know, the pesticide residues are not evenly distributed on the surface of crops; furthermore, they generally exist both at the surface and permeate into the inside of the crops. The detection results from one or several points on the surface of the crops are not representative. The crops normally contain several components and relatively low concentration of pesticides; in order to acquire typical results of the pesticide residues on the crops, pretreatment is necessary and important before detection. Fan et al. [22] showed the feasibility of applying SERS for detection pesticides in apples that were pretreated before detection, and the group also simplified sample preparation method based on QuEChERS later [23]. QuEChERS has been widely used as a pretreatment method to make the process quick, easy, cheap, effective and safe [24]. During the procedure, the clean-up performance is not always satisfactory to remove interferences [25]. Generally, primary secondary amine (PSA) sorbent was used to remove polar pigments, polar organic acids, some fatty acids and sugars, but the clean-up performance is not satisfactory [26]. Graphitized carbon black (GCB) or C18 was applied in modified QuEChERS to remove pigments or non-polar interfering substances, but it can adsorb planar pesticides [27, 28]. Multi-walled carbon nanotubes (MWCNTs) are a kind of novel carbonaceous materials; due to their huge surface area, they have been applied to adsorb interfering substances in fruit and vegetable during pesticides analysis [29, 30]. Our group has reported that MWCNTs as the clean-up material combined with GC-MS method to

analysis pesticide residues; and as an alternative absorbent for removing interfering substances in the crops, MWCNTs have been validated to be as superior clean-up material to PSA [31, 32].

In this paper, based on SERS spectra, we focused on detecting pesticide residues such as phosmet, which is a kind of pesticides widely used as protective fungicides in fruits [33]. Before SERS measurement, the fruits are planned to be pretreated with modified QuEChERS method to obtain the purified analyte which could represent typical fruits. The procedure has been extended to other pesticides such as thiabendazole and thiram. In order to establish a fast detection method for field application, all SERS experiments were intended to be performed by a portable Raman instrument.

## 2 Experimental

### 2.1 Materials

Tetrachloroauric acid ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), sodium citrate and (3-aminopropyl) trimethoxysilane (APS) were purchased from Sigma. Acetonitrile of HPLC grade was purchased from Fisher Chemicals (Fair Lawn, NJ, USA). Magnesium sulfate anhydrous ( $\text{MgSO}_4$ , 98%) and sodium chloride ( $\text{NaCl}$ , 99.5%) of analytical grade were purchased from Sinopharm Chemical Reagent (Beijing, China). Analytical standards of the pesticides in this study were provided by the Institute of the Control of Agrochemicals, Ministry of Agriculture and Peoples' Republic of China. Primary secondary amine (PSA) and C18 were purchased from Agilent. Multi-walled carbon nanotubes (MWCNTs) with average external diameters of 10–20 nm were obtained from Tianjin Bonna-Agela Technologies Co., Ltd. (China). All chemicals were of analytic grade and were used without further purification. Ultra-pure water was obtained from a Milli-Q water purification system and used for all aqueous. The 0.22  $\mu\text{m}$  nylon syringe filters were used to filter the extracts.

The stock solution of the pesticides ( $1000 \mu\text{g mL}^{-1}$ ) was prepared by exact weighing of the powder and dissolved in 10 mL acetonitrile, and stored at  $-20^\circ\text{C}$  in the dark. A serial of working standard solutions were prepared by dilution from the stock solution and used for spiking fruits samples, studying the linear dynamic range of SERS analysis. The working solutions were stored at  $4^\circ\text{C}$  in darkness.

### 2.2 Synthesis of Au nanoparticles

Au@SiO<sub>2</sub> core-shell nanoparticles (NPs) were prepared according to the procedure of Li et al.'s method [17]. Briefly, Au NPs cores were first synthesized by a sodium

citrate reduction method [34]. Under vigorous magnetic stirring, 1 mM APS was added to the as-prepared Au solution. After 15 min stirring, sodium silicate solution (0.54%) was added to the solution and kept stirring at 90 °C for 1 h. The obtained Au@SiO<sub>2</sub> NPs solution was stored at 4 °C for further detections. Before each SERS measurement, 1.5 mL Au@SiO<sub>2</sub> NPs solution was added in a tube and centrifuged for 5 min at 8000 r min<sup>-1</sup>; the bottom deposit was obtained for further SERS experiments.

### 2.3 Characterization and instruments

The UV–Vis absorption spectroscopy of the Au@SiO<sub>2</sub> NPs was recorded on a GBC Cintra-10e spectrophotometer. TEM images were performed using JEOL JEM-2100F microscope with an accelerating voltage of 200 kV. Raman spectra were recorded with a Nuctech Portable Raman inspection instrument (Nuctech RT5000), with a laser wavelength of 785 nm and a charge-coupled device (CCD) detector. The initial laser power was about 450 mW. Raman equipment is calibrated by a software-controlled method. The samples were placed in a 2 mL glass vial, which was put in the sample room of the instrument to reduce interference from ambient light. The laser illuminated the samples through the side of the vial. The acquisition time for each spectrum was 5 s.

### 2.4 Sample preparation and SERS measurement

As mentioned before, apples were pretreated before SERS measurements with QuEChERS method. A schematic illustration is shown in Scheme 1 of sample pretreatment and measurements of pesticides. Apples were obtained from supermarkets in Beijing. Editable portion was homogenized for 1 min by a blender at high speed. Homogenized apple (10.0 ± 0.1 g) was weighed in a 50 mL centrifuge tube. Ten milliliters of acetonitrile was added afterward, and the tube was then vortexed for 1 min at

room temperature. After that, 1 g NaCl and 4 g MgSO<sub>4</sub> were added. The tube was shaken for 1 min and put into ice-water bath immediately until cooled to room temperature. After extraction, the tube was centrifuged for 5 min (3800 rpm). Then, 1 mL aliquot of supernatant was transferred into a 2.0 mL micro-centrifuge tube which contained 10 mg of MWCNTs and 150 mg of MgSO<sub>4</sub>. The tube was shaken vigorously for 30 s before centrifugation at 10,000 rpm for another 30 s. The supernatant was filtered by a membrane (0.22 μm) and transferred to a HPLC vial. In order to search for a better purification result, we also used 50 mg C18 or 50 mg PAS as sorbents, to replace MWCNTs in the above procedure.

For recovery determination, the apple samples (10.0 ± 0.1 g) were spiked with 50, 100 and 200 μL standard stock solutions (100 mg kg<sup>-1</sup>) in 50 mL centrifuge tubes, to obtain three samples with concentration levels of 0.5, 1 and 2 mg kg<sup>-1</sup>, respectively. The spiked samples were set aside for 30 min before extraction. Other spectra were obtained from the pesticide samples spike with the above-pretreated fruits.

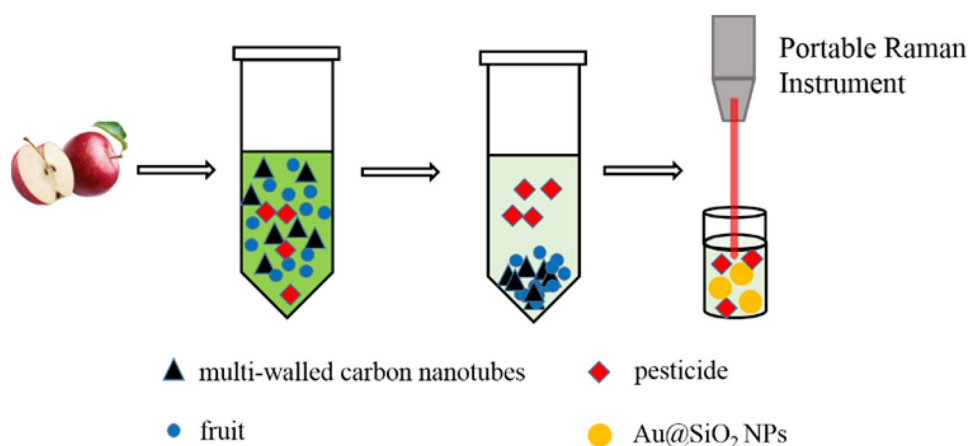
The samples were prepared using the following procedure for SERS measurements: 400 μL analyte solution, which was obtained by the above QuEChERS method, was mixed thoroughly with the above Au@SiO<sub>2</sub> NPs deposit and 20 μL NaCl (0.1 M) in a standard HPLC sample glass vial of 2 mL. Each spectrum was measured four times. The characteristic peaks of apple without pesticide residues were obtained first as blank sample data.

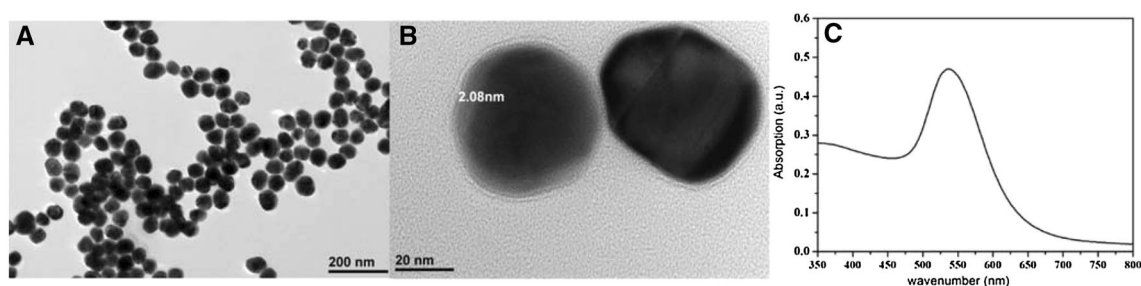
## 3 Results and discussion

### 3.1 SERS spectra of phosmet

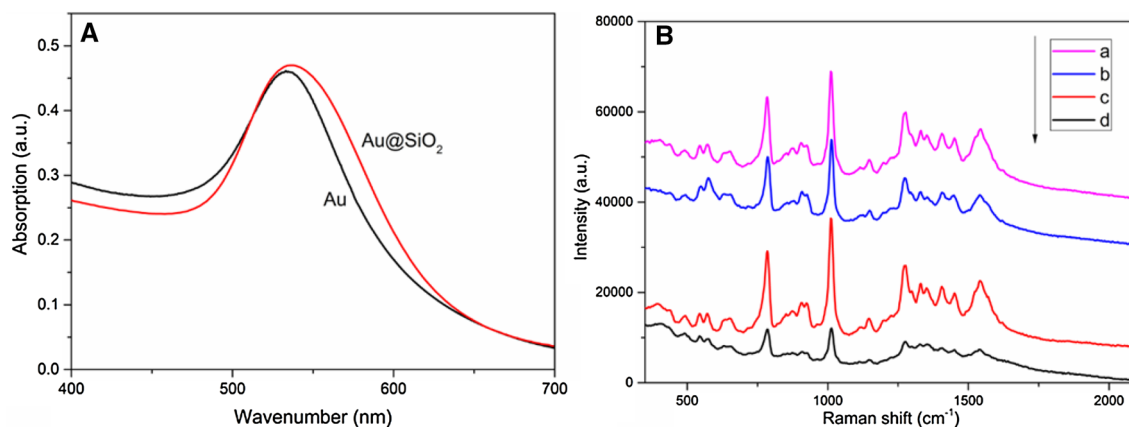
Figure 1 shows a typical TEM image of the as-prepared Au NPs, which clearly show that the average diameter of the Au NPs is estimated to be 45 ± 5 nm. Figure 2 shows

**Scheme. 1** Sample pretreatment and detection with SERS by portable Raman instrument





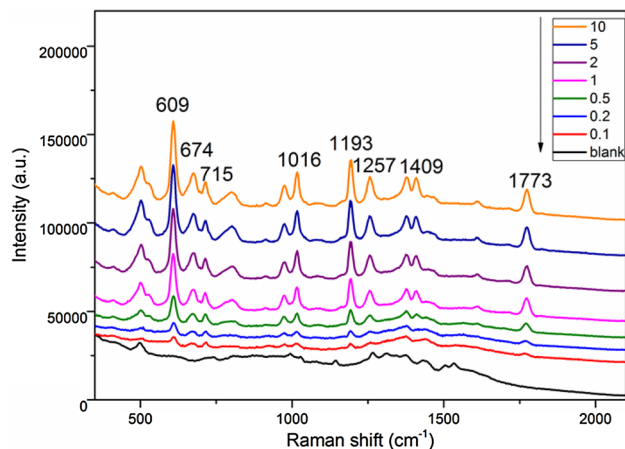
**Fig. 1** The TEM images of the Au NPs (a) and Au@SiO<sub>2</sub> NPs (b); c UV-Vis absorption spectra of the Au@SiO<sub>2</sub> NPs



**Fig. 2** **A** UV-Vis absorption spectra of AuNPs and Au@SiO<sub>2</sub> nanoparticles. **B** SERS spectra of thiabendazole stand solution (1 mg kg<sup>-1</sup>): with newly prepared Au@SiO<sub>2</sub> nanoparticles (a) and

Au@SiO<sub>2</sub> nanoparticles stored in the bottle for 45 days (b); with newly prepared AuNPs (c) and AuNPs stored in the bottle for 45 days at room temperature (d)

the TEM image of the Au@SiO<sub>2</sub> NPs, as can be seen, the thickness of the SiO<sub>2</sub> shell is about 2–3 nm. The UV-Vis spectra of the as-prepared Au@SiO<sub>2</sub> NPs is shown in Fig. 1c, which exhibited one band at about 540 nm; the spectrum was with a slight shift to red compared to that of Au NPs (Fig. 2A), and the result was similar to Ref. [17]. As Li et al. [17] reported, with the protection of thin SiO<sub>2</sub> shell, less interference would induce during the detection for the complicated system such as fruits. Furthermore, Au@SiO<sub>2</sub> NPs were more stable for storage and transportation during the process of in-field measurements. We used new prepared Au@SiO<sub>2</sub> and AuNPs to detect the same pesticide solution (1 mg kg<sup>-1</sup> thiabendazole); the intensity of SERS spectra obtained by AuNPs (Fig. 2B c) was slightly stronger than that of Au@SiO<sub>2</sub> NPs (Fig. 2B a). However, while both NPs were stored in the bottle for 45 days at room temperature, the spectra intensity of the same pesticide solution was decreased significantly for AuNPs (Fig. 2B d), while for Au@SiO<sub>2</sub> NPs it was slightly decreased (Fig. 2B b). As we were trying to build a rapid pesticide detection method that could be used in field, we need more stable Au@SiO<sub>2</sub> NPs for further detection.



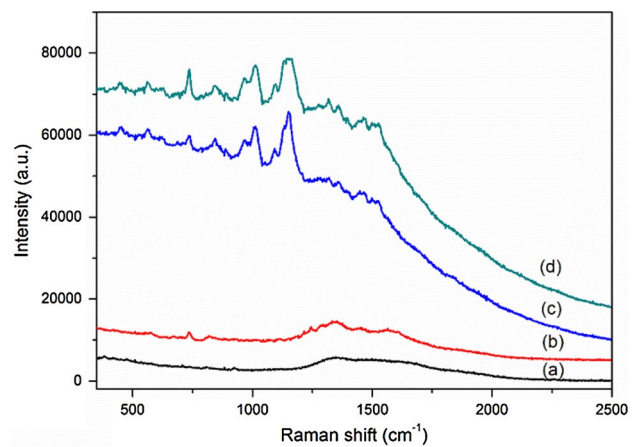
**Fig. 3** SERS spectra of phosmet stand solution with serial concentrations (0–10 mg kg<sup>-1</sup>)

Figure 3 shows SERS spectra of phosmet stand solution with serial concentrations from 10 to 0.1 mg kg<sup>-1</sup>. Several characteristic peaks were shown obviously [35]. A strong peak at 609 cm<sup>-1</sup> was attributed to the C=O

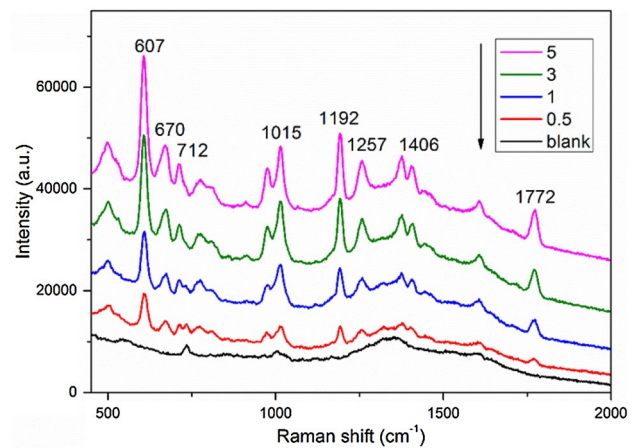
in-plane deformation vibration mode. The  $674\text{ cm}^{-1}$  peak was from P=S stretching. The band at about  $715\text{ cm}^{-1}$  arose from benzene ring breathing mode. The peak at about  $1016\text{ cm}^{-1}$  may due to asymmetric P-O-C deformation vibration. The peaks at  $1193\text{ cm}^{-1}$  and  $1409\text{ cm}^{-1}$  were C-H out-of plane deformation vibration in P-O-CH<sub>3</sub> and S-CH<sub>2</sub>-N, respectively. The peak at  $1257\text{ cm}^{-1}$  can be attributed to C-N stretching in S-CH<sub>2</sub>-N. The peak appeared at around  $1773\text{ cm}^{-1}$  was attributed to C=O stretching. As is seen in Fig. 3, the intensity of characteristic peaks decreased with the concentration of phosmet and were still distinguishable, while the concentration decreased to as low as  $0.1\text{ mg kg}^{-1}$ . The spectra of Au@SiO<sub>2</sub> NPs without pesticide were obtained as blank spectra. There were several weak peaks in these blank spectra, and in order to avoid inference of these bands, the peaks of phosmet shown at 609, 674, 1193 and  $1773\text{ cm}^{-1}$  were chosen as characteristic bands for the phosmet detection.

#### 4 Pretreatment of fruits

As mentioned before, the fruits normally contained organic acids, pigments and other non-targeted compounds, which would interfere with the SERS spectra of the targets. A good clean-up procedure is indispensable for the pesticide residue analysis in fruits. Due to its unique structure and huge surface area, MWCNTs have been used as an alternative absorbent in our previous work; compared to PSA, the clean-up effect and recoveries of pesticide of MWCNTs were better [31, 32]. Our group has used TEM to observe MWCNTs before and after the adsorption of interference of fruits [36]. The results show that some large interference appears on the surface of the nanotube and small matrix substances in the hollow cylindrical structures of nanotubes. Thus, the interaction probably occurs on both the surface of MWCNTs and absorptive action of the nanotubes. In this work, we applied modified QuEChERS approach by using MWCNTs as clean-up sorbents for pesticide residues extraction from the fruits. PSA and C18 were induced to compare the clean-up efficiency for SERS measurement. In order to simplify the procedure and reduce the pretreatment time, QuEChERS method was modified to be suitable for SERS measurements. Figure 4 shows the SERS spectra of fruits purified with above three sorbents. As can be seen, compared to the spectra of apples without sorbents (Fig. 4d), and purified with C18 (Fig. 4c) or PSA (Fig. 4b), the spectra of analyte extract clean-up by MWCNTs (Fig. 4a) show low basement and less peaks that would interfere with SERS detection of pesticide residues. MWCNTs have achieved the best



**Fig. 4** SERS spectra of fruits purified with different pretreatment clean-up materials: (a) MWCNTs, (b) PSA, (c) C18 and (d) without sorbents



**Fig. 5** SERS spectra of apple pretreatment sample spiked with phosmet of different concentrations: 5, 3, 1, 0.5 and  $0\text{ mg kg}^{-1}$ , respectively

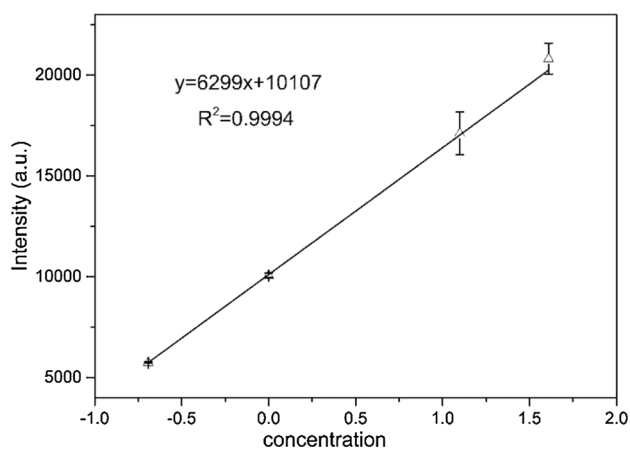
performance for fruits clean-up. Similar clean-up performance has been found in cowpea in our earlier research [32]. The subsequent experiments would choose MWCNTs as a clean-up material.

##### 4.1 SERS spectra of phosmet in fruits

Apples spiked with  $0.5\text{--}5\text{ mg kg}^{-1}$  phosmet were pretreated by the method illustrated in the sample preparation part. SERS spectra of the result samples are shown in Fig. 5. The apples contain no detectable phosmet residues which were used as blank sample for comparison. As can be seen, the spectra of blank (Fig. 5 blank) have several

weak peaks, which appeared in different bands and did not interfere with the characteristic peaks of phosmet. The major characteristic bands of phosmet such as 607, 670, 1192 and 1772  $\text{cm}^{-1}$  can be identified clearly and were consisted with the SERS spectra of phosmet standard solutions (Fig. 3). As we know, the limit of detection was determined as the concentration of analyte giving a signal-to-noise ratio ( $S/N$ ) of 3 for the characteristic peaks. At 0.5  $\text{mg kg}^{-1}$ , the peaks at 607  $\text{cm}^{-1}$ , 670  $\text{cm}^{-1}$ , 1192  $\text{cm}^{-1}$  and 1772  $\text{cm}^{-1}$  were still distinguishable, and the  $S/N$  beyond 3. Generally, as for phosmet, the maximum residue limit in apple of USA, EU and China is above 3  $\text{mg kg}^{-1}$ , which is above the detection limit of our method (0.5  $\text{mg kg}^{-1}$ ).

The results showed a great potential of using the method for quantitative analysis of phosmet residues in apples. Similar to the standard solution of phosmet, Fig. 5 shows that the intensities of main peaks decreased as the concentration of phosmet in the apple decreased; the intensities of the peaks were



**Fig. 6** Linear relationship between intensity of 607  $\text{cm}^{-1}$ ( $y$ ) and concentration of spike phosmet in apples ( $x=\text{Inc}$ ), the unit of  $c$  is  $\text{mg kg}^{-1}$

linearly related to the concentration of phosmet in the apples. Choosing the strongest characteristic band at 607  $\text{cm}^{-1}$ , Fig. 6 shows the relationship between Raman intensity and the concentration of phosmet between 0.5 and 5  $\text{mg kg}^{-1}$ . It is interesting to find out a good linear relationship existed between  $y$  and  $x$ , where  $y$  was intensity of Raman peak and  $x$  was  $\text{Inc}$  ( $c$  stands for phosmet concentration), with the calibration curve coefficients ( $R^2$ ) of 0.9994. The results indicated that this method could be used to quantitatively detect phosmet residues in apples, and the detection limitation is 0.5  $\text{mg/L}$ , far more beyond maximum residue limits in stand demands.

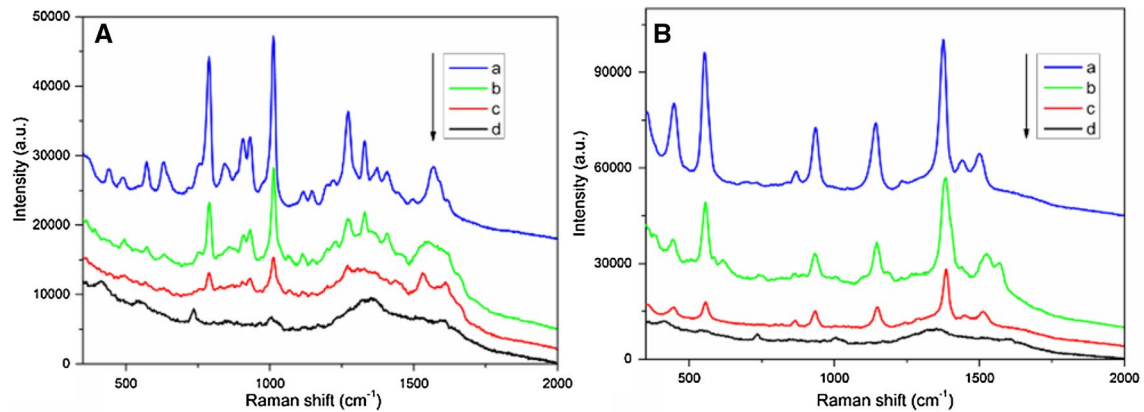
The accuracy and precision of the above method were assessed by apple samples fortified with three different concentration levels (0.5, 1 and 2  $\text{mg kg}^{-1}$ ). Four repetitive samples were set for each concentration. The result recoveries are shown in Table 1. The average recoveries ranged from 77 to 97% with RSDs between 6.6 and 14%. The recoveries were in acceptable range (70–120%) [37]. The result showed that the detection method has good corrected recoveries for phosmet in apple. The pretreatment method meets the requirement of phosmet residue analysis in apple.

### 4.2 Other pesticides in apples

The above procedure was applied to detect other pesticides in apples. Thiabendazole and thiram were spiked in apples, pretreated and analyzed using the above method. Figure 7 shows the result SERS spectra of the analyst samples. Using the above procedure, SERS spectra of the apples containing no pesticide residues were used as blank sample for comparison (Fig. 7A, B d), as compared to the SERS spectra of thiabendazole stand solution (Fig. 7A a); similar characteristic peaks

**Table 1** Recoveries and RSDs of phosmet spiked in apples at levels 0.5, 1 and 2  $\text{mg kg}^{-1}$  ( $n=4$ )

Spiked ( $\text{mg kg}^{-1}$ )	Recovery (%) [ $n=4$ ]				Average recovery (%)	RSD (%)
	1	2	3	4		
0.5	83	101	101	100	97	9.3
1	73	73	93	94	83	14
2	72	84	77	76	77	6.6



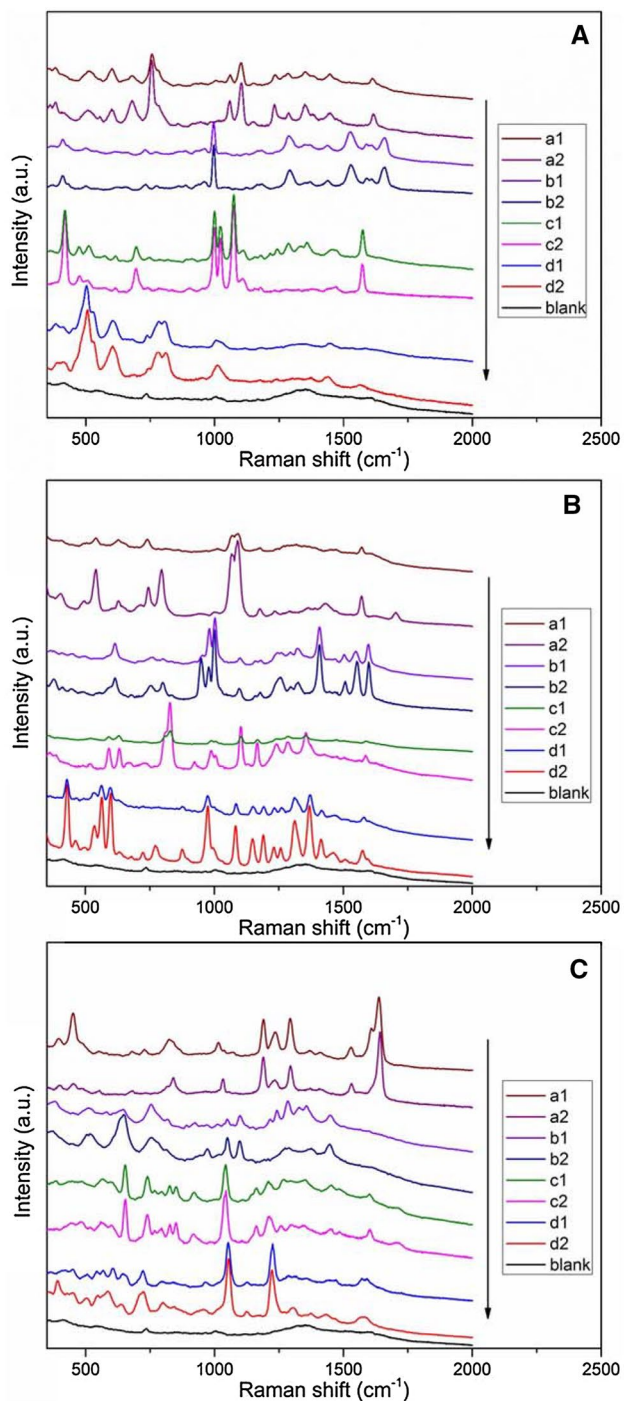
**Fig. 7** SERS spectra of thiabendazole (**A**): (a) stand solution ( $10 \text{ mg kg}^{-1}$ ), (b) spike in apple of  $1 \text{ mg kg}^{-1}$ , (c)  $0.5 \text{ mg kg}^{-1}$ , (d)  $0 \text{ mg kg}^{-1}$ ; thiram (**B**): (a) stand solution ( $10 \text{ mg kg}^{-1}$ ), (b) spike in apple of  $10 \text{ mg kg}^{-1}$ , (c)  $1 \text{ mg kg}^{-1}$ , (d)  $0 \text{ mg kg}^{-1}$

could be seen clearly in SERS spectra of apples spike with  $1 \text{ mg kg}^{-1}$  and  $0.5 \text{ mg kg}^{-1}$  thiabendazole (Fig. 7A b, c), and identical results were found for thiram spiked in apple of  $10 \text{ mg kg}^{-1}$  and  $1 \text{ mg kg}^{-1}$  (Fig. 7B b, c). The detection limits were below the residue limit in fruits of thiabendazole and thiram, which were  $3 \text{ mg kg}^{-1}$  and  $5 \text{ mg kg}^{-1}$ , respectively.

The above detection method was extended to more pesticides. Figure 8 shows SERS spectra of 12 pesticides. As can be seen, several characteristic peaks of pesticides spiked with apple pretreatment sample (a1–d1) were consistent with the corresponding stand solutions ( $1 \text{ mg kg}^{-1}$ ) (a2–d2). Moreover, the characteristic peaks of these pesticides were different from each other. The SERS spectra of these pesticides could be created to be a database, combined with the portable Raman instrument, and a convenient method for pesticide residues detection could be built.

## 5 Conclusions

In summary, a sensitive, rapid and convenient method based on SERS, QuEChERS pretreatment and portable Raman instrument has been built for pesticide residues detection in fruits. Overall recoveries of pesticide phosmet ranged from 77 to 97% in apples at three spiking levels ( $0.5$ ,  $1$  and  $2 \text{ mg kg}^{-1}$ ), with RSDs between 6.6 and 14%. The detection limitation of phosmet was  $0.1 \text{ mg kg}^{-1}$  in standard solution and  $0.5 \text{ mg kg}^{-1}$  in apples; the intensity of characteristic peak in phosmet showed good linear relationship with logarithm concentration between  $0.5$  and  $5 \text{ mg kg}^{-1}$  ( $R^2 = 0.9994$ ). The detection limits were all below the maximum residue limits in standard requirements. The method could be extended to other pesticides such as thiabendazole and thiram. All the spectra could be used to create a database, combined with portable Raman instrument and the simple pretreatment method, and a fast, ultra-sensitive and convenient method for pesticide residues detection could be built.



**Fig. 8** SERS spectra of apple pretreatment sample spiked pesticide and pesticide stand solution, **A** (a1–a2) phosalone, (b1–b2) propyzamide, (c1–c2) fonofos, (d1–d2) methidathion, **B** (a1–a2) trithion, (b1–b2) triazophos, (c1–c2) flusilazole, (d1–d2) tricyclazole, **C** (a1–a2) paraqua, (b1–b2) phorate, (c1–c2) isocarbophos, (d1–d2) fenthion, blank: SERS spectra of apple pretreatment sample spiked without pesticide

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## Compliance with ethical standards

**Conflict of interest** The author(s) declare that they have no conflict of interest.

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