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Short communication

Evaluation of surface-enhanced Raman scattering detection using a handheld and a bench-top Raman spectrometer: A comparative study

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ABSTRACT

Surface enhanced Raman scattering (SERS) detection using a handheld Raman spectrometer and a bench-top Raman spectrometer was systemically evaluated and compared in this study. Silver dendrites were used as the SERS substrate, and two pesticides, maneb and pyrrolidine dithiocarbamate-ammonium salt (PDCA) were used as the analytes. Capacity and performance were evaluated based on spectral resolution, signal variation, quantitative capacity, sensitivity, flexibility and intelligence for SERS detection. The results showed that the handheld Raman spectrometer had better data consistency, more accurate quantification capacity, as well as the capacity of on-site and intelligence for qualitative and semi-quantitative analysis. On the other hand, the bench-top Raman spectrometer showed about 10 times higher sensitivity, as well as flexibility for optimization of the SERS measurements under different parameters such as laser power output, collective time, and objective magnification. The study on the optimization of SERS measurements on a bench-top spectrometer provides a useful guide for designing a handheld Raman spectrometer, specifically for SERS detection. This evaluation can advance the application of a handheld Raman spectrometer for the on-site measurement of trace amounts of pesticides or other chemicals.

1. Introduction

The surface enhanced Raman scattering (SERS) phenomenon was discovered in the 1970s when the Raman scattering of pyridine was markedly enhanced after being adsorbed on roughened silver surfaces [1,2]. It was later proven that the significant enhancement was mainly due to the local electric field around a nanoparticle, generated by localized surface plasmon resonance (LSPR) [3,4]. Since then, SERS has been a powerful vibrational spectroscopy technique for sensitive molecular characterization and as a signal conductor in sensors. It has found increasing uses in material science [5], chemistry [6], food safety [7,8], and bioscience [9] for a variety of applications [10].

In most published studies, SERS detection was accomplished using a bench-top Raman spectrometer in a laboratory. However, there are instances when on-site detection becomes a necessity, such as during time-sensitive emergencies, lack of transportation infrastructure, and when targets/analytes become prone to chemical instability over time. Specific examples may include security checks for warfare agents [11], drug screening at the border [12], contamination of pesticides and nerve agents on farms [13], and so on. Obviously, conventional analysis instruments (e.g., HPLC, GC, MS, NMR, and so on) are not conveniently suitable for field detection. On the other hand, current portable devices which utilize Raman and IR are primarily for bulk material identification in the field like geosciences [14] and mineralogy [15], as well as for quality control in pharmaceutical and food industry [16]. However, the use of portable devices is generally limited by its low sensitivity for detection of trace amounts of analytes.

Most recently, the feasibility of utilizing a handheld Raman spectrometer for SERS detection was evaluated on the pesticide ferbam, which was the first report that integrated the SERS technique with a handheld Raman spectrometer for semi-quantification of trace amounts of target molecules in a layman's format [17]. An on-site detection method was initially built up based on the sensitive SERS technique and the establishment of the straightforward 'answer box' on a handheld spectrometer. However, the report was based on early stage findings of a feasibility study. The detailed evaluation of the handheld Raman spectrometer performance compared with the bench-top one needs to be further investigated. Meanwhile, there have been a few studies on the comparison of a handheld and bench-top Raman spectrometer. However, they only tested normal Raman signals [18–21]. The comparison of SERS detection between two

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kinds of Raman spectrometers has never been systematically reported. In this study, we comprehensively compared a handheld Raman spectrometer (Truscan, Thermo Fisher Scientific) and a bench-top Raman microscope/spectrometer (DXR, Thermo Fisher Scientific) for their performance and capacity in SERS detection. Silver dendrites were used as the SERS substrate based on our previous study [17], and two pesticides, maneb (fungicide) and pyrrolidine dithiocarbamate-ammonium salt ('PDCA' for short, pesticide analog), were used as analytes. Herein, specific parameters (e.g. spectral patterns, linearity, signal variation, sensitivity, flexibility for adjusting SERS signals, and intelligence for data analyses) for SERS detection were carefully compared between the handheld (for field application) and bench-top (for laboratory use) Raman spectrometers. This evaluation can potentially greatly advance the application of a handheld Raman spectrometer for the on-site measurement of trace amounts of pesticides or other chemicals. To the best of our knowledge, it is the first study that systematically compared a bench-top and a handheld Raman spectrometer for SERS analysis.

2. Materials and methods

2.1. Regents

\Silver nitrate (99%), zinc (99%), and acetonitrile (HPLC grade) were bought from Fisher Scientific USA. Maneb and PDCA were purchased from Chem Service and Fisher Scientific (USA), respectively.

2.2. Sample preparation

The maneb and APDC were dissolved in acetonitrile (for maneb) and double distilled water (for PDCA) to make the 10 μg/mL (ppm) stock solutions, respectively. Then a series of concentrations were prepared by the consecutive double dilution method (i.e. 10, 5, 2.5, 1.25, 0.62, 0.31, 0.16, 0.08, 0.04, 0.02 and 0.01 ppm). Silver (Ag) dendrites were prepared by a simple replacement reaction between zinc and silver nitrate, which has been described before [22]. 1 mL of pesticide solution was gently mixed with 10 μL Ag dendrites on a consistent orbital rotator (Fisher Scientific, 24 rpm) for 3 min. Then, 5 μL of the Ag was deposited onto a microscopic glass slide and air-dried at room temperature for 2–3 min [23]. Ag without incubation with pesticides was used as a negative control.

2.3. Handheld Raman spectrometer

Truscan (Thermo Scientific USA), which weighs less than 2 Kg, was the handheld Raman spectrometer used in this study. It has a 785-nm excitation laser, and the spectral resolution is 7–10 cm^{-1} across range. All the data were collected in the range from 250 to 2875 cm^{-1} using 40 s collective exposure time and approximately 300 mW laser power. A nose cone was used to help manually position the device so that the focal point was in the right place when performing a point-and-shoot scan. The spot size was approximately 2 mm wide, and the focal point was more or less 5 mm beyond the tip of the nose cone. Intelligent analysis and determination were performed using the Software Version 1.3.x configured in the handheld device itself. Five spectra were collected for each sample.

2.4. Bench-top Raman spectrometer

The Thermo Scientific DXR Raman microscope was used as the bench-top Raman spectrometer in this study. This instrument is a research-quality instrument designed specifically for users who need high spatial resolution, ease of sample preparation and the power of Raman microscopy. To compare data with the handheld Raman spectrometer, we set up a representative program which involved a 780-nm excitation laser and a 10-fold objective. The resulting laser spot diameter was about 3 μm and the spectral resolution was 5 cm^{-1}. Raman measurement was taken with 2 mW of laser power and 50-μm slit aperture for 1 s collective time for 2 sample exposures in the range from 50 to 3400 cm^{-1}. Spectra were collected utilizing Thermo Scientific OMNIC™ Software. Five spectra were collected for each sample.

2.5. Linearity and signal variation

SERS spectral data taken from the handheld and bench-top spectrometers were analyzed using TQ Analyst software v8.0 (Thermo Fisher Scientific). Data pre-processing algorithms using second-derivative transformation were employed to subtract the baseline shift and eliminate high frequency noises from the instrument (or device) system. A multivariate statistical model (i.e. partial least square (PLS)), was constructed to predict analyte concentrations based on the actual (spiked) values using the pathlength of multiplicative signal correction (MSC). The constructed PLS model was validated by leave-one-out cross validation, which uses all but one sample to build a calibration model and repeats the procedure for each sample in the data set. The quality of the model was determined by root mean square error of calibration (RMSEC), root mean square error of cross-validation (RMSECV), and correlation coefficient (R). The higher the R value or the lower the RMSEC and RMSECV values, the better the predictability of the model. RMSEC and RMSECV represent the signal variation between systems. The closer the RMSEC value is to the RMSECV, the better robustness of the model [24].

2.6. Sensitivity

Here we used principal component analysis (PCA) for determination of the limit of detection (LOD, sensitivity). PCA is a statistical technique normally applied to analyze the variance of spectral data and to build the qualitative predictive model based on the standards [25]. The information provided by PCA indicates any patterns or trends in the data. The minimum concentration with data points clearly separated from those of the blank control in the PCA plot was estimated to be the LOD value [26].

2.7. SERS spectra on bench-top Raman spectrometer under different key parameters

Laser power output, collective exposure time and objective were adjustable on a bench-top Raman spectrometer, which meant that the acquisition of spectra and subsequent results are relatively flexible. To further determine how these spectrometer parameters can influence the SERS spectra, we set up different parameters for SERS measurements, including laser power outputs (1, 2, 4, 8, and 16 mW), spectral collective times (1, 2, 4, 8, and 30 s). Three objectives (10-, 20- and 50-folds) were also tested.

3. Results and discussions

3.1. SERS spectra

The primary Raman and SERS spectra of maneb (Fig. S1) and PDCA (Fig. S2) were measured on the bench-top handheld spectrometer, respectively. The SERS signals came from samples at 10 ppm level (5 μL) of pesticides, and the normal Raman signals were taken from 10 mg solid samples. Spectral data were processed by a second-

derivative transformation with a 9 segment length and a 9 cm^{-1} gap to separate overlapping peaks, eliminate baseline effects, and enhance spectral resolution for better comparisons in this study. For both pesticides, the second-derivative signals of the solid samples and the solution samples agreed well with each other. For solid samples of maneb (Fig. 1**A**) and PDCA (Fig. 1**B**) at 10 mg, the handheld Raman device and the bench-top Raman instrument produced similar characteristic peaks and peak intensity except those over 2800 cm^{-1} (mainly by the symmetric/anti-symmetric CH_2/CH_3 stretch) due to its relatively narrow scanning range (250–2875 cm^{-1}). For the solution samples of maneb (Fig. 1**A**) and PDCA (Fig. 1**B**) at 10 ppm, the SERS spectral intensities on the handheld spectrometer were clearly lower than the ones from the bench-top spectrometer (indicated by the different scales). For both pesticides, the SERS signals from the solution samples at 10 ppm level was much stronger than the normal Raman signals of 10 mg solid samples (Fig. 1), which demonstrated the super sensitivity of the SERS technique. The spectral patterns of the two pesticides were different in the solid solution SERS spectra, which was due to the interaction between the analyte with the Ag dendrites. The strong peaks at 494 cm^{-1} of maneb and 456 cm^{-1} of PDCA structure were used for the following quantitative analysis.

3.2. Quantification

Maneb and PDCA at 5, 2.5, 1.25 and 0.62 ppm were used for establishing PLS models on the bench-top and handheld spectrometer, respectively (Table 1). The linearity and signal variation were evaluated by the *R*, RMSEC and RMSECV. For maneb, the RMSEC (0.368) and RMSECV (0.923) on the handheld spectrometer were lower than those (0.477 and 0.991) on the bench-top spectrometer (Fig. S3). Similar conclusions were obtained for PDCA: the RMSEC (0.307) and RMSECV (1.13) on handheld device were much lower than those (0.635 and 1.19) on the bench-top spectrometer. *R* values (0.93 and 0.72) on the bench-top Raman spectrometer were obviously lower than those (0.98 and 0.79) on the handheld spectrometer (Fig. S4). The results demonstrated that the SERS data generated from the handheld spectrometer were more consistent and hence the prediction model had a better linearity and robustness. This is probably due to the larger spot size of the handheld Raman spectrometer which averaged out the intrinsic "hot-spot" variance on the Ag dendrites.

3.3. Sensitivity

The sensitivity (LOD value) was obtained from the PCA plot (Fig. 2). Briefly, the LOD value was determined at the minimum concentration with the data points clearly separated from those of the blank control. Utilizing this method, LOD values of maneb and PDCA were both 0.04 ppm in the test solution or 0.04 μg/mL using the bench-top spectrometer (Fig. 2**A** and **C**), while they were 0.62 and 0.31 ppm using the handheld spectrometer (Fig. 2**B** and **D**). Clearly, the handheld spectrometer possessed relatively low sensitivity, which is a distinct disadvantage compared with the bench-top spectrometer. However, it may not matter in this particular case for detecting these two pesticides, as LODs of both instruments were way below the EPA maximum allowable residue levels (MRL) [27,28].

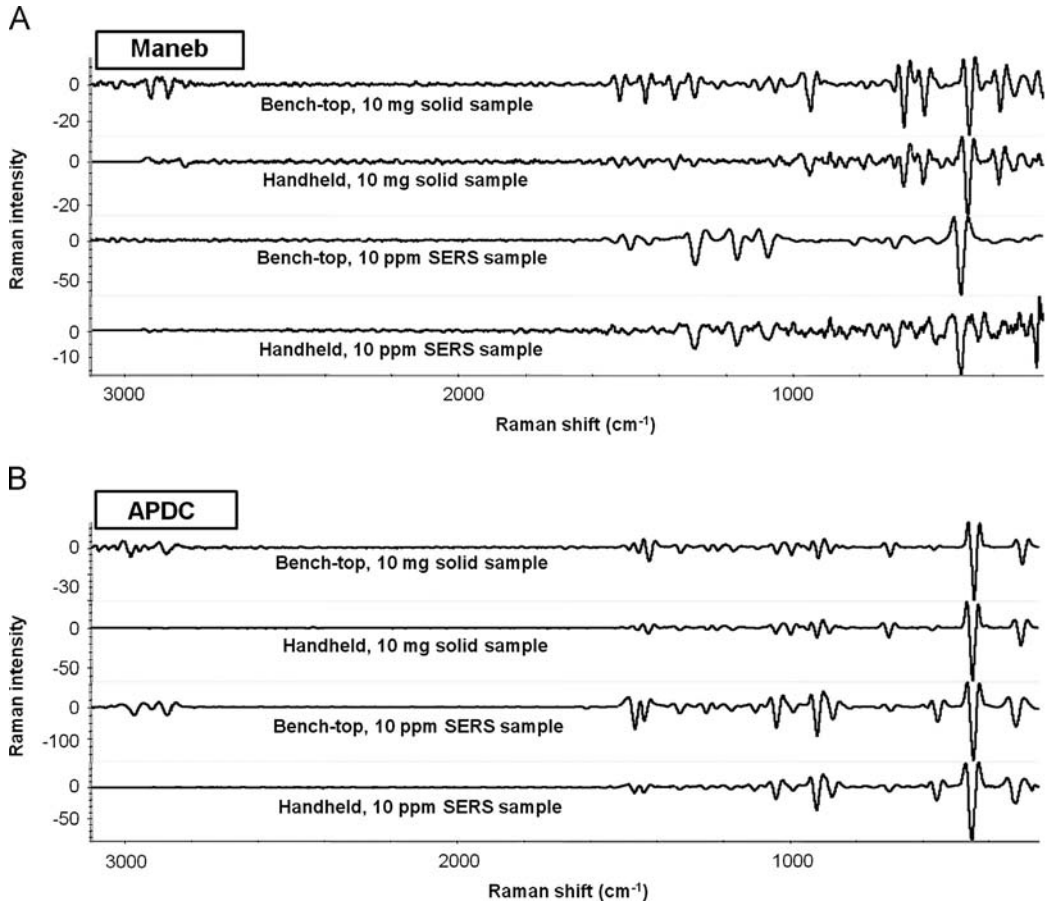

Fig. 1. The second-derivative SERS spectra of two analytes, maneb (A) and PDCA (B) measured on the bench-top and handheld spectrometers. The SERS signals from samples at 10 ppm level was even stronger than normal Raman signals of 10 mg solid samples.

Table 1
The linearity (R value) and signal variation (RMSEC/RMSECV) were evaluated by the PLS model of Maneb and PDCA, which were separately prepared at series of concentration of 5, 2.5, 1.25 and 0.62 ppm. The amount predictions were performed on the bench-top and handheld spectrometers using calibration and cross-validation methods, respectively ($n=5$).

	Maneb				**PDCA**			
	Calibration		Validation		Calibration		Validation	
	R	RMSEC	*R*	RMSECV	*R*	RMSEC	*R*	RMSECV
Bench-top Raman spectrometer	0.96	0.477	0.83	0.991	0.93	0.635	0.72	1.190
Handheld Raman spectrometer	0.97	0.368	0.83	0.923	0.98	0.307	0.80	1.130

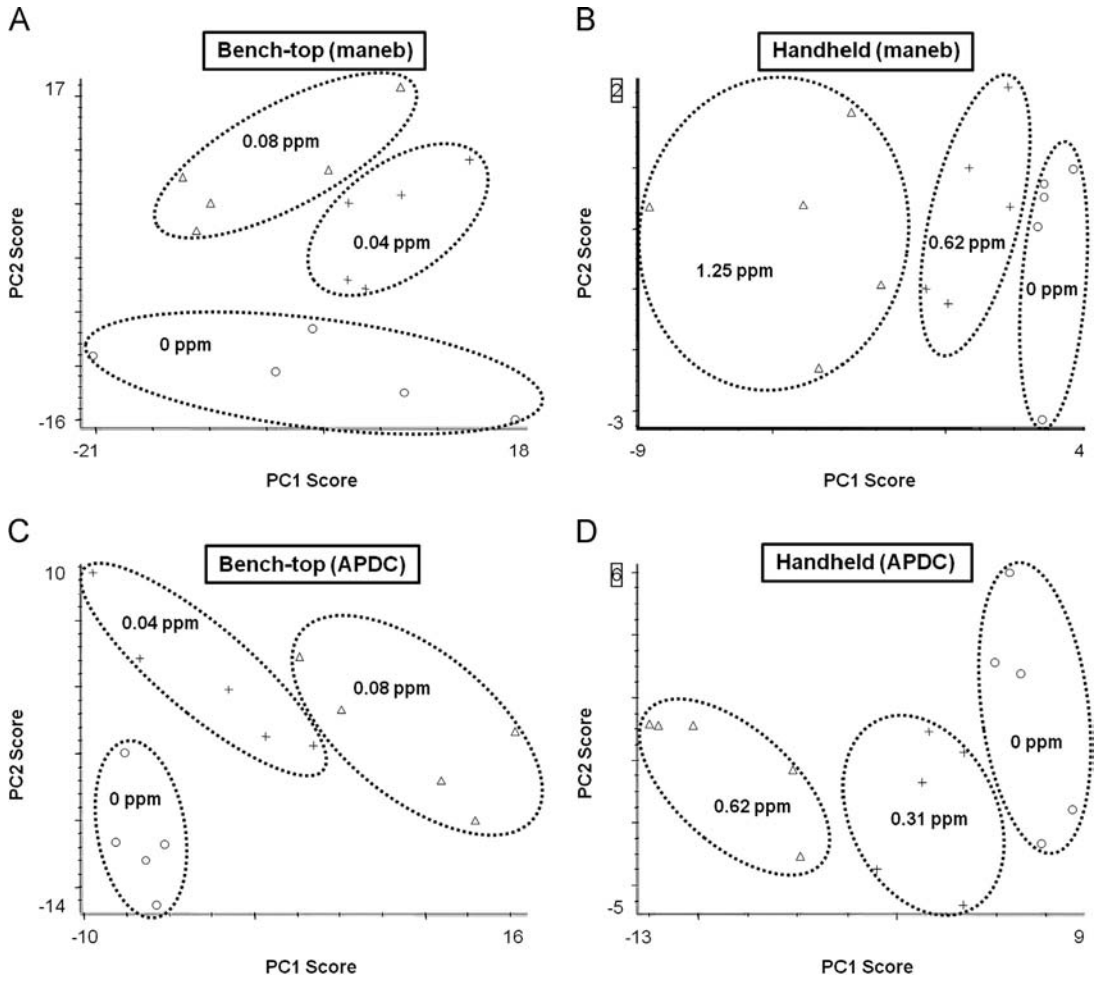

Fig. 2. The PCA plots from SERS spectra ($n=5$) of maneb (A and B) and PDCA (C and D) were used here to determine the limit of detection on a bench-top spectrometer (A and C) and a handheld spectrometer (B and D), respectively.

3.4. Flexible adjustability of SERS spectra on bench-top Raman instrument

The influence of SERS measurement on the bench-top Raman spectrometer by three important parameters (i.e. laser power output, collective exposure time, and objective magnification) were carefully analyzed by shifting one of the variables. The result showed that laser power output, collective exposure time, and objective magnification can significantly affect SERS signals. As shown in Fig. 3**A**, the intensity of SERS signals of 5 ppm maneb had an increasing trend with increased laser power output (1, 2, and 4 mW), however it decreased with further increase in laser output (8 and 16 mW). This could be interpreted by the degradation of the Ag dendrites or the pesticide molecule resulting from the strong laser power. Analogously, increasing collective time (1, 2, 4 and 8 s) resulted in stronger SERS signals to some extent, but prolonged time (30 s) weakened the signals (Fig. 3**B**). Moreover, higher magnification of the objectives (50- and 20- fold) can significantly improve the sensitivity and resolution of SERS signals compared to the 10-fold objective (Fig. 3**C**). However, there is relatively low signal variation in the PCA plot (Fig. 3**D**) under 10-fold objective compared with others. This is because of the large laser spot size ($\sim$3 μm) of the 10-fold objective, which could average out the intrinsic "hot-spot" variance, which explains again that SERS signal variation on the handheld spectrometer (with the spot size about 2 mm) is much lower than those on a bench-top spectrometer. Furthermore, the laser excitation wavelength (e.g., 514, 633, and 785 cm^{-1}) can also affect SERS spectra, which has been described in another study [29]. This data not only demonstrated the importance of optimizing the parameters for

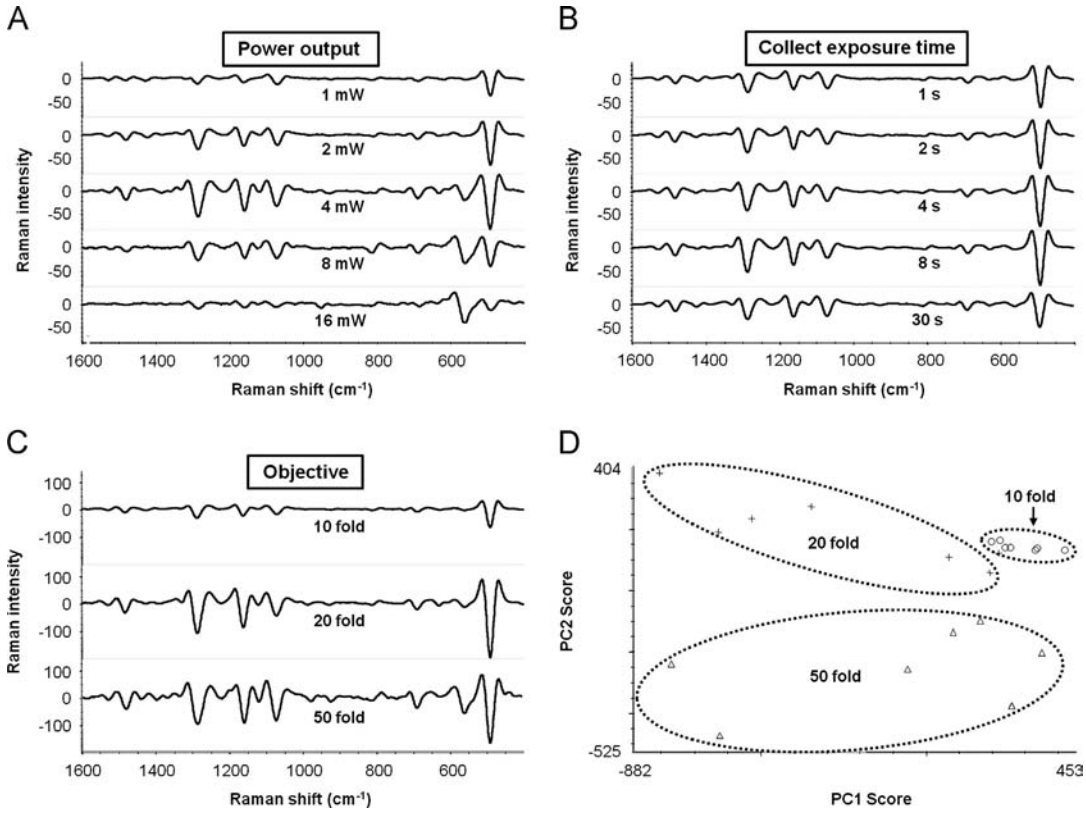

Fig. 3. The flexible adjustability of SERS spectra on the bench-top Raman spectrometer. (A–C) The secondary-derivative SERS spectra were influenced by the laser power output (1, 2, 4, 8, and 16 mW), collective exposure time (1, 2, 4, 8, and 30 s), and magnification of objective (10-, 20-, and 50-fold), respectively. (D) The PCA plot of secondary-derivative SERS spectra affected by different magnification of objective. Scores 1 and 2 explained 81% and 6% of the data variance, respectively.

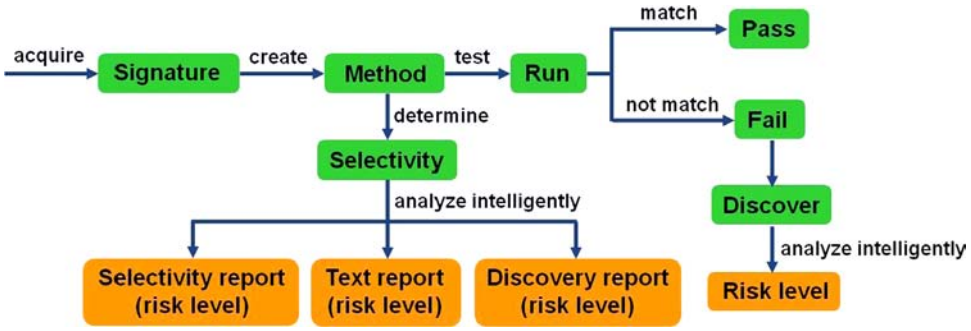

Fig. 4. The analysis procedure using the handheld spectrometer.

measuring SERS signals using a bench-top spectrometer, but also suggested the possible guidance towards rational design of a handheld Raman device specifically for SERS measurements.

3.5. *Efficient and intelligent identification and semi-quantitative determination on the handheld Raman spectrometer*

To take full advantage of the intelligent function from the handheld Raman spectrometer, we tested many different procedures so that identification and semi-quantification could be achieved conveniently and efficiently. The procedure of identification and semi-quantitative analysis by the handheld spectrometer is illustrated in Fig. 4. Before analysis, a sample reference referred to as 'signature' was acquired and a 'method' was created. For SERS identification, the procedure is the same as the traditional method for bulk material identification, which is to click 'run' and select the 'method' to give a 'Pass' or 'Fail' result. For SERS quantification, we have previously demonstrated the use of the asymmetry characteristic peaks between pesticide and nitrate on the surface of Ag dendrites to realize the distinct pattern at different concentrations in order to distinguish them using a handheld Raman spectrometer [17]. Compared against the references spectra set up based on the *p*-Values, we were able to semi-quantify the level using the 'Selectivity' (in the form of 'selectivity report', 'discovery report', and 'text report') and 'Discover' function. Both of them can provide a semi-quantitative analysis based on the references in a layman's format.

3.6. *Detailed comparison of SERS detection between handheld device (on-site) and bench-top instrument (in-lab)*

To get a better understanding and to further promote the SERS detection of on-site testing, the detailed information (e.g., key spectrometer parameters, advantages, disadvantages) between the

Table 2
Detailed comparison of SERS detection between the handheld and bench-top Raman spectrometers.

	Handheld Raman spectrometer	Bench-top Raman spectrometer
Spectrometer parameters		
Laser excitation wavelength	(785 ± 5) nm	780 (replicable with 532 and 633) nm
Wavenumber range	250–2875 cm^{-1}	50–3400 cm^{-1}
Estimated resolution	7.0–10.5 cm^{-1}	4.7–8.7 cm^{-1}
Exposure time	~40 s	adjustable as needed
Estimated spot size	1–2 mm	1–3 μm (adjustable by objectives)
Power output	300 mW or lower	0–24 mW (adjustable as needed)
Weight (size)	1.7 kg ($30 \times 15 \times 7.6$ cm^3)	56.7 kg ($97 \times 69 \times 61$ cm^3)
Price	~50,000 $	~100,000 $
Advantages (A) and disadvantages (D)		
Intelligence	Intelligent identification and semi-quantification (**A**)	Manual analysis with the help of software (**D**)
On-site detection	Portable (**A**)	Not portable (**D**)
Signal variation	Relatively low (**A**)	Relatively high (**D**)
Price	Economic (**A**)	Expensive (**D**)
Adjustability	Fixed (**A or D**)	Adjustable (**D or A**)
Sensitivity	Relatively low (**D**)	Relatively high (**A**)
Scanning range	Relatively narrow (**D**)	Relatively broad (**A**)

handheld and bench-top Raman spectrometers were carefully compared in Table 2. As expected, higher sensitivity, resolution and broader scanning range can be obtained using the bench-top spectrometer. In addition, the optimal SERS spectra can be read directly on a bench-top spectrometer by adjusting different spectrometer parameters, such as exposure time, power output, and objective. This means that we can acquire high-quality SERS spectra in a lab. Compared with the bench-top spectrometer, however, the handheld spectrometer showed its exclusive advantages for SERS detection through the following: 1) The handheld Raman device is convenient (portable) and economical (lower price), and fit for on-site detection, especially for analyzing samples during time-sensitive emergencies, lack of transportation infrastructure, and when targets/analytes become prone to chemical instability over time. This is the most obvious advantage. 2) We also demonstrated an easy and reliable method to carry out not only identification but also semi-quantification using the handheld spectrometer coupled with silver dendrites, which is much more intelligent than the manual data analysis on bench-top spectrometer with the help of software, more suitable for the workers without the knowledge of Raman scattering and data analysis. 3) Interestingly, the SERS signal variation obtained on the handheld spectrometer was much lower than those on the bench-top spectrometer, which indicated better signal consistency and accuracy to use a handheld Raman spectrometer for SERS analysis. The parameters on the handheld Raman device are fixed, which is designed to be more applicable for real applications by workers or farmers without scientific background, though it is not flexible for adjustments in different applications. Therefore, further development and optimization on the handheld Raman spectrometer specifically for SERS detection is needed.

4. Conclusions

A handheld Raman spectrometer for SERS detection is promising for on-site measurement of trace amounts of analytes. A comprehensive evaluation of utilizing a handheld Raman spectrometer for SERS detection was carried out by comparing it with a bench-top spectrometer. The handheld Raman spectrometer is not only convenient and economical for on-site detection, but also possesses intelligent function for both identification and semi-quantification, and produces consistent and robust data, which are advantageous compared with the bench-top spectrometer. However, there were also some disadvantages, e.g., relatively low sensitivity. To advance the handheld Raman spectrometer for real on-site SERS measurements, it is important to couple a good SERS substrate and to set optimized parameters on the handheld Raman spectrometer specifically for SERS detection.

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Appendix A. Supporting information

Supplementary data associated with this paper can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.05.015.

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