Electronic Supplementary Information (ESI)

Semi-quantification of Surface-enhanced Raman Scattering using a Handheld Raman Spectrometer: A Feasibility Study

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EXPERIMENTAL PROCEDURES

Sample preparation. The pesticide ferbam (Fisher Scientific) was spiked into acetonitrile (Fisher Scientific) at a serial level of 1, 2, 4, 6, 7, 8, 10, 14 and 50 μg/mL (ppm), respectively. The silver (Ag) dendrite nanosubstrates were prepared through a simple replacement reaction involving both zinc and silver nitrate according to a previously published method.[1] Then, SERS sample preparation was performed using the solution method in the prior method.[2] Briefly, 1 mL of ferbam solution was gently mixed with 10 μL Ag dendrites (~40 μg) for 10 minutes under consistent orbital rotation (Fisher Scientific). After centrifugation for a few seconds, 10 μL of the Ag was pipetted out and deposited onto a standard microscopic glass slide and air-dried at room temperature for 3 minutes. Ferbam sample at 50 ppm was used for qualitative analysis. Ferbam samples at other concentrations were utilized for semi-quantification. Ag without incubation with ferbam was used as a negative control.

Handheld Raman spectrometer. A handheld Raman spectrometer, Truscan (Software Version 1.3.x) from Thermo Fisher Scientific was used in this study. It is less than 4 pounds, and

has a 785-nm excitation laser. The line width of laser is 2 $cm^{-1}$and the spectral resolution is 7-10 cm^{-1}. All data were collected in the range from 250 to 2875 cm^{-1} using 10 s integration time and approximately 300 mW laser power. The nose cone was used to help manually position the unit so that the focal point was in the correct place when performing a point-and-shoot scan. The focal point was a little less than 5 mm beyond the tip of the nose cone. The Ag sample on glass was tested after 3 minutes of drying. Every sample was replicated three times.

Data acquisition. To set up the device to quantify ferbam in this study, we acquired reference 'signatures' from samples of four known concentrations (0, 4, 7, and 14 ppm), which were correspondingly named as 'No risk' (0 ppm), 'Low risk' (4 ppm), 'Risk' (7 ppm), and 'High risk' (14 ppm) according to the EPA tolerance levels for ferbam on fresh produce. When the method was run on a sample, the device executed the analytical tasks and verified its identity. Other sample concentrations, 1, 2, 6, 8, 10 ppm were used as test samples and analyzed for semi-quantification.

Data analysis. The data analysis can be performed in two ways. Spectra acquired from the handheld instrument can be transferred into a computer for advanced chemometics analysis using TQ analyst software v8.0 (Thermo Fisher Scientific), or directly analyzed using the built-in function on the handheld Raman device. The latter method is much more favorable and convenient in practice, which was the main objective of this study.

Chemometrics analysis. Partial least square (PLS) was used to evaluate the linearity and potential ability for quantification. It was constructed by predicting sample amount based on the actual (spiked) values. The higher the correlation coefficient and the smaller the root mean square error of calibration (RMSEC) value, the better the quality of the model. Principal

component analysis (PCA) was applied to analyze the variance of spectral data and to build the qualitative predictive model based on the standards. The smaller the cluster of one set of sample data, the smaller the data variance. If the two data clusters are not overlapped, it indicates there is statistical difference between the two samples. We used PCA to discriminate between the four references' spectra.

Semi-quantitative analysis. In practice, it would be much more convenient to get the result in a layman's format directly from the handheld instrument without showing the spectra. Herein, we utilized a built-in 'Selectivity' tool for semi-quantification of ferbam by analyzing it directly through the handheld device. The 'Selectivity' tool was utilized by comparing a measured sample against all four references. The semi-quantification of ferbam was obtained based on the *p*-value of the test sample when compared to the four reference concentrations (0, 4, 7 and 14 ppm for 'no risk', 'low risk', 'risk' and 'high risk', respectively) calculated by the built-in software in the spectrometer. When the analysis was complete, two useful reports were generated: 'Discover report' and 'Selectivity report'. In the 'Selectivity report', a *p*-value of 0.05 or greater means that there was no significant difference between the test sample and the reference; this was indicated by '(+)', which was termed as 'Positive matches'; a *p*-value between 0.001 and 0.05 was indicated by '(–)', which was also called 'Nearest neighbors'. In the 'Discover report', the relative probabilities (%) of all displayed outcomes indicated how much the measured data favored one reference over the others.

Normal Raman spectrum of ferbam. The normal Raman spectrum was shown in figure S1 using a DXR Raman microscope (Thermo Scientific) with a 780 nm laser. There were some differences between the normal Raman and SERS spectra. Though both spectra show a peak at 1384-1388 cm^{-1}, the relative intensity of this peak was much higher in the SERS spectra than the

one in the normal Raman spectrum. The highest peak in the normal Raman spectrum was observed at 968 cm^{-1}, while this peak nearly disappeared in the SERS spectrum. The highest peak in the SERS spectra was at 563 cm^{-1}, while in the normal Raman spectrum, a close peak at 576 cm^{-1} was observed. The differences between the normal Raman and SERS spectra were likely resulted from the interaction between the ferbam molecules and the Ag dendrites.

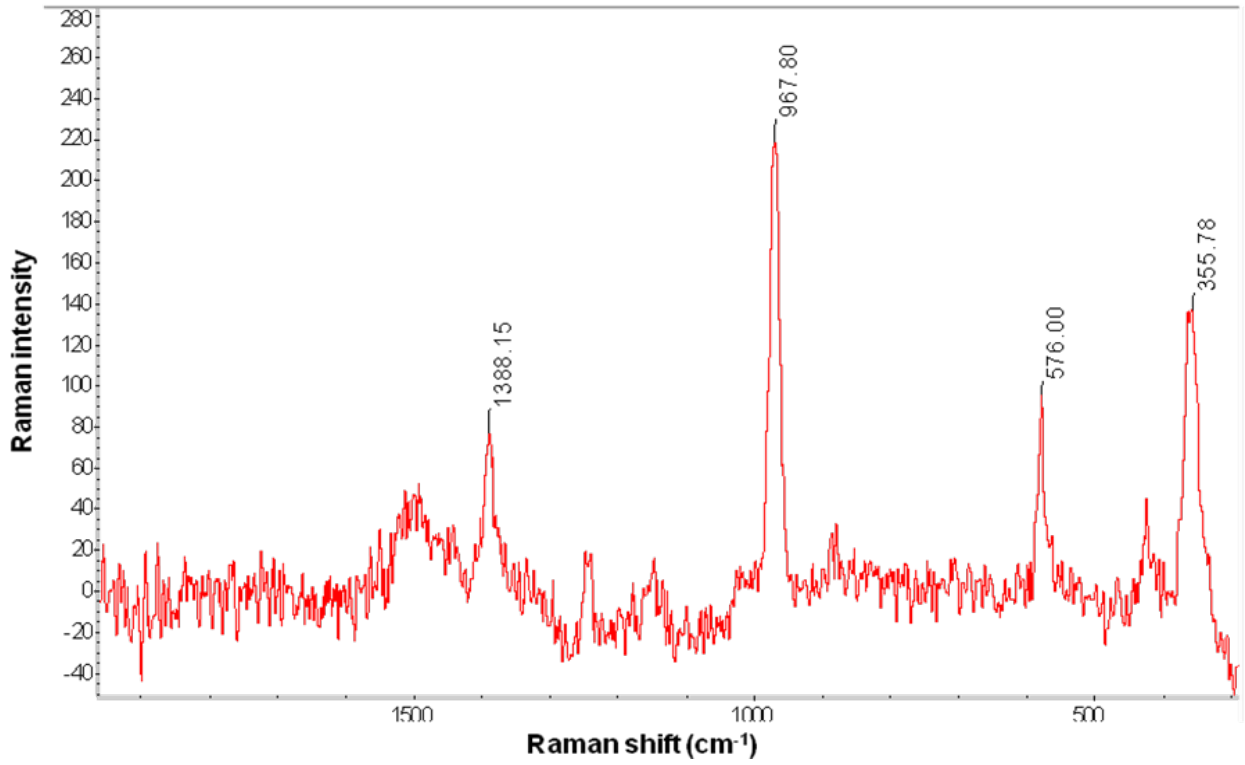

Figure S1. The normal Raman spectrum of solid ferbam (50 mg).

REFERENCES

1 L. L. He, M. S. Lin, H. Li and N. J. Kim, *J. Raman Spectrosc.*, 2010, **41**, 739–744.

2 L. L. He, J. K. Zheng, T. P. Labuza and H. Xiao, *J. Raman Spectrosc.*, 2013, **44**, 531–535.