



# SERS Spectra of Permethrin on Silver Nanofilm

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**Abstract:** Surface enhanced Raman scattering (SERS) has emerged as an ultrasensitive analytical tool for chemical, biological, and medical analysis. SERS spectra of permethrin, a common synthetic pyrethroid, were investigated for the first time. The SERS substrates used in this work were a silver nanofilm (AgNF) deposited on glass chips. The characteristic SERS bands of permethrin were analyzed and assigned to the corresponding modes. The strongest SERS band appeared at  $1003\text{ cm}^{-1}$  due to the breath vibration of benzene ring in the permethrin molecule. A detection limit of 10 ppm was obtained on the AgNF substrates. A good linear relationship between peak height of the  $1003\text{ cm}^{-1}$  band and permethrin concentration was observed in the range of 10 – 1000 ppm. The results obtained in this work indicate that SERS technique has a great potential for rapid, simple, *in situ*, and cost-effective detection and monitoring of permethrin in environment and on foods.

**Keywords:** SERS, Silver Nanofilm, Permethrin, Detection, Portable Raman

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## 1. Introduction

Since its discovery in the 1970s [1], interest in surface enhanced Raman scattering (SERS) has been growing exponentially [2]. SERS is a powerful vibrational spectroscopy technique that allows for highly sensitive detection of trace chemical and biological analytes through the amplification of an electromagnetic field near a nanostructured noble metal surface (such as nano-Ag or nano-Au, called a “SERS substrate”) generated by the excitation of localized surface plasmons [2-4]. Compared with conventional Raman, the intensity of the SERS signal excited by laser illumination can be observed with an enhancement factor (EF) on the order of  $10^5$ - $10^{14}$  when molecules are in close proximity to Ag and Au nanostructured surfaces, and under ideal conditions sufficient to detect single molecules [5]. SERS is an *in situ*, non-destructive technique, and can be easily used on-site or in the field when coupled with the portable/handheld Raman spectrometer [6, 7]. In recent years, SERS technique has emerged as one of the most promising analytical methods for environmental analysis and food safety [6-16].

Permethrin, a common synthetic pyrethroid, has been widely used as insecticide, acaricide, and insect repellent [17]. In healthcare, it is used to eradicate parasites such as head lice and mites responsible for scabies [18]. Additionally, the military combat uniforms are treated with permethrin to provide protection against the threat of biting insects and insect-borne

diseases [19]. Various methods, including gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), spectrophotometry, as well as immunology and electronic nose, have been well developed for permethrin determination [18, 20-24]. However, these methods are not suitable for field use because they require either bulky equipment, well-trained users, and use of chemical/biological reagents, or sophisticated and time-consuming separation/preparation of samples.

To the best of our knowledge SERS has not been reported for the detection of permethrin though it has been proven as a rapid, simple, and cost-effective method with high sensitivity and field-compatibility. In this work, we investigated SERS spectra of permethrin on silver nanofilm (AgNF) SERS substrates and demonstrated the feasibility of the SERS technique for quantitative permethrin analysis.

## 2. Materials and Methods

### 2.1. Materials

Permethrin (mixture of *cis* and *trans* isomers) and butylamine ( $\text{BuNH}_2$ ) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Silver nitrate ( $\text{AgNO}_3$ ) was obtained from Fisher Scientific (Fair Lawn, NJ, USA). Both anhydrous ethanol and methanol were supplied by Pharm Co. All other chemicals were analytical grade and purchased from Sig-

ma-Aldrich or Fisher Scientific and used as received. Deionized (DI) water with a resistivity of 18.2 M $\Omega$ -cm (Millipore Milli-Q System) was used throughout the experiments. Ethanol permethrin samples in the concentration range of 0 – 1000 mg L<sup>-1</sup> (ppm) were prepared by diluting a methanol solution of 10<sup>5</sup> ppm permethrin with anhydrous ethanol.

## 2.2. Preparation of AgNF SERS Substrates

The AgNF SERS substrates were prepared on glass slides by a one-step electroless deposition process according to the procedure reported in the literature [25]. Briefly, the glass chips (5×5 mm<sup>2</sup>) were cleaned in a piranha solution at ~80°C for 1 h, followed by rinsing with water. After sonicated in 1 M NaOH solution for 30 min, the glass chips were washed with water and ethanol, and then dried under a stream of compressed air. The cleaned glass chips were put into wells of a 6-well plate (20 chips in each well). Then 14 mL fresh prepared ethanolic AgNO<sub>3</sub>/BuNH<sub>2</sub> (5mM/2.5mM) solution was added into each well and allowed to react for 16 h. The AgNF deposited on the glass chips were rinsed thoroughly with ethanol and air-dried in the hood.

## 2.3. Instruments and Methods

Normal Raman (NR) spectra of permethrin solid and its SERS spectra were collected with a portable PeakSeeker Pro-785 Raman spectrometer coupled with a fiber-optic probe and a microscope (Agiltron Inc, Woburn, MA). A 785 nm laser wavelength with 10 mW was used as an excitation source. A 50× microscope objective was used. The Raman band of a silicon wafer at 520 cm<sup>-1</sup> was used to calibrate the spectrometer. The measurements were conducted in the backscattering geometry.

For SERS analysis, 10  $\mu$ L of permethrin/ethanol solution was applied to the AgNF substrate with a pipette and the droplet was spread on the whole substrate surface. After air-drying within 5 min, the SERS spectra were collected. For reliable and reproducible SERS results, an averaged spectrum was obtained from 5 spectra collected on 5 randomly selected locations on the AgNF substrate for every sample in the quantitative SERS analyses.

## 3. Results and Discussion

### 3.1. NR Spectra of Permethrin

Permethrin has a molecular formula of C<sub>21</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>3</sub> (46 atoms), and a molecular structure as shown in Figure 1. It produces 132 normal vibration modes [17]. The NR spectrum of permethrin solid in the range of 200 – 2000 cm<sup>-1</sup> is shown in Figure 2. Characteristic Raman bands of permethrin can be observed in the spectrum, and assignments of the bands based on the literature are listed in Table 1 [17]. Typically, the strongest peak located at 1003 cm<sup>-1</sup> can be assigned to benzene ring breathing mode. The C=C stretching of benzene appears at 1595 cm<sup>-1</sup> as a shoulder of the peak of the alkenyl (C=C) stretching mode located at 1620 cm<sup>-1</sup>. The peaks at 1721 and 1213 cm<sup>-1</sup> are due to the C=O and C-O stretching

vibration modes, respectively. The peaks at 843 and 724 cm<sup>-1</sup> can be assigned to in-plane deformation modes of benzene ring and cyclopropyl ring, respectively. The symmetric stretching vibration of C-Cl appears at 661 and 622 cm<sup>-1</sup>.

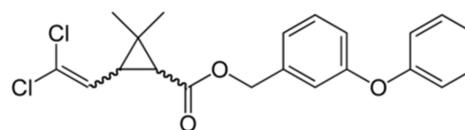


Figure 1. Molecular structure of permethrin.

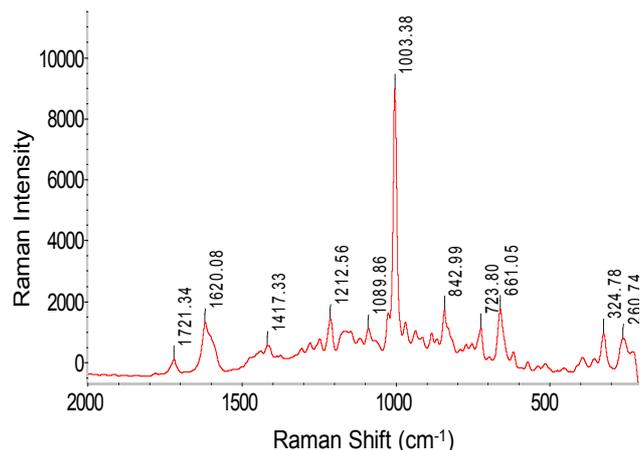


Figure 2. Normal Raman spectrum of permethrin solid.

Table 1. Normal Raman bands of permethrin and their assignments[17].

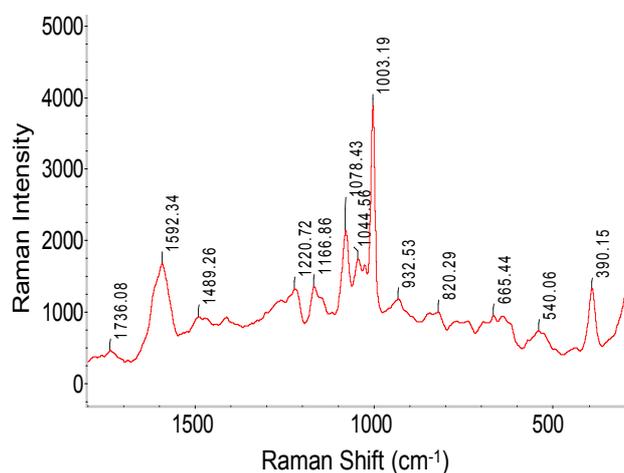
Bands (cm <sup>-1</sup> )	Assignments	Bands (cm <sup>-1</sup> )	Assignments
1721	$\nu$ (C=O)	915	in-plane def. of cp
1620	$\nu$ (C=C)	884	$\nu$ (C-C)
1595(shoulder)	$\nu$ (C=C) <sub>ben.</sub>	867	$\gamma$ (C-H) <sub>ben.</sub>
1439	$\delta$ <sub>asym</sub> (CH <sub>3</sub> )	843	in-plane def. of ben. ring
1418	$\delta$ (C-H) <sub>cp</sub>	791	in-plane def. of cp
1388	$\delta$ <sub>sym</sub> (CH <sub>3</sub> )	771	$\gamma$ (C-H) <sub>ben.</sub>
1376	$\delta$ (CH <sub>2</sub> )	753	$\gamma$ (C-H) <sub>ben.</sub>
1279	breath of cp	724	in-plane def. of cp
1247	$\nu$ <sub>asym</sub> (C-O-C)	661	$\nu$ <sub>sym</sub> (C-Cl)
1213	$\nu$ (C-O)	618	$\nu$ <sub>sym</sub> (C-Cl)
1170	$\nu$ (C-O)	571	in-plane def. of ben. ring
1147	$\delta$ (C-H) <sub>ben.</sub>	540	out-of-plane def. of ben. ring
1117	$\nu$ (C-C)	514	$\delta$ (C-C-C)
1090	$\delta$ (C-H) <sub>ben.</sub>	453	$\gamma$ (=C-Cl)
1066	in-plane def. of cp	395	$\delta$ (C-C-C)
1026	$\nu$ (C-O)	355	$\tau$ (C-O-C-C)
1003	breath of ben. ring	325	$\delta$ (C-O-C)
969	$\gamma$ (C-H) <sub>cp</sub>	261	$\tau$ (C-C-C-C)
937	$\rho$ (CH <sub>3</sub> )	230	$\tau$ (C-C-C-C)

$\nu$ : stretching;  $\delta$ : scissoring;  $\gamma$ : out-of-plane bending;  $\rho$ : rocking;  $\tau$ : torsion; ben.: benzene; cp: cyclopropyl; def.: deformation; asym: asymmetric; sym: symmetric.

### 3.2. SERS Spectra of Permethrin

The SERS spectrum was recorded at a high concentration of permethrin at the beginning of the study to obtain a clear

SERS spectrum. The SERS sample was prepared by dropping 10  $\mu\text{L}$  of 1250 ppm methanolic permethrin solution on the AgNF SERS substrate and then air-dried prior to the SERS measurement. The measured SERS spectrum is shown in Figure 3. Compared with Figure 2, the SERS spectrum has a similar profile to the NR spectrum. The primary characteristic SERS bands of permethrin are marked in the figure. The strongest peak still appears at  $1003\text{ cm}^{-1}$  due to the benzene ring breathing mode. The bands of the C=C stretching of benzene, the scissoring vibration of C-H on benzene ring and the scissoring vibration of C-C-C are observed to be moderately enhanced in the SERS spectrum, but have shifted from 1595, 1090 and  $395\text{ cm}^{-1}$  to 1592, 1078 and  $390\text{ cm}^{-1}$ , respectively. Some of other characteristic peaks are also observed in the SERS spectrum, exhibiting the shifts of a few to  $>10\text{ cm}^{-1}$ . However, for low concentrations of permethrin, only the  $1003\text{ cm}^{-1}$  peak due to the breath vibration of benzene ring was significantly enhanced in the SERS spectra. Therefore, this SERS band will be used for the quantitative SERS detection of permethrin and the determination of detection limit.



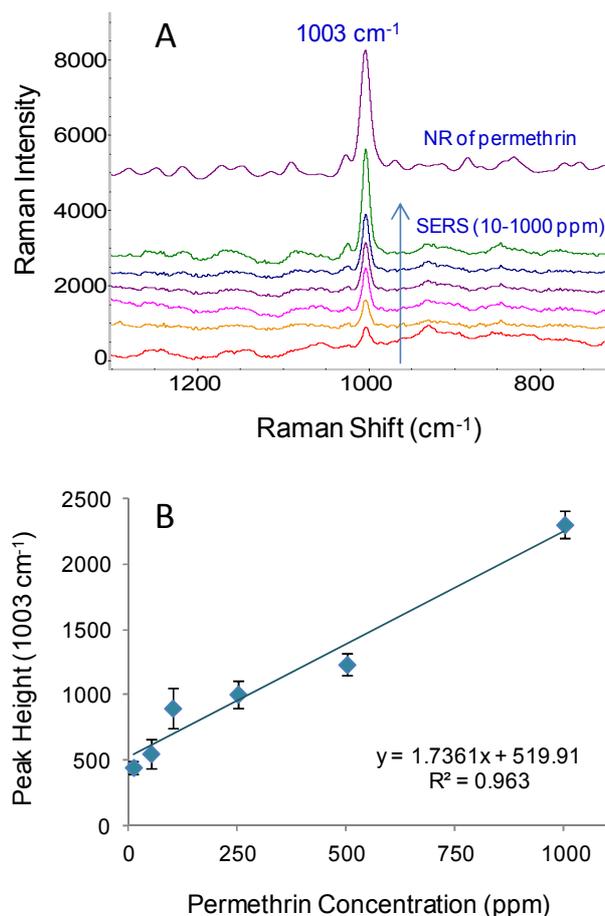
**Figure 3.** SERS spectrum of permethrin on AgNF SERS substrate. 10  $\mu\text{L}$  of 1250 ppm permethrin solution was dropped onto the AgNF and air-dried prior to SERS measurement.

### 3.3. Quantitative Detection of Permethrin

Figure 4A shows the SERS spectra of permethrin on the AgNF SERS substrates recorded for the concentrations of 10 to 1000 ppm in the region from 700 to  $1300\text{ cm}^{-1}$ . In the background spectrum of the AgNF substrate, there exists a very weak Raman band around  $1000\text{ cm}^{-1}$  (data not shown). This band may interfere with SERS detection of low concentration permethrin because the characteristic SERS band of permethrin appears at  $1003\text{ cm}^{-1}$ . Due to its interference, the permethrin SERS band for low concentrations ( $< 10\text{ ppm}$ ) is difficult to be discerned. Thus, 10 ppm was determined to be the detection limit of the AgNF substrate towards permethrin.

From Figure 4A, it can be seen clearly that a steady increase in SERS intensity or peak height of the permethrin  $1003\text{ cm}^{-1}$  Raman band is observed as the permethrin concentration increases from 10 to 1000 ppm. To evaluate the Ag films for quantitative analysis, the peak heights of the permethrin Ra-

man bands are plotted as a function of the permethrin concentrations (Figure 4B). A linear regression was fit to the plot and is also shown in Figure 4B. The fitting equation is  $y = 1.7361x + 519.91$  ( $y$  is the peak height at  $1003\text{ cm}^{-1}$ , and  $x$  is the permethrin concentration in ppm). A high regression coefficient ( $R^2$ ) value of 0.963 indicates a high goodness of fit. These results indicate that permethrin peak intensity increases linearly and proportionally with the permethrin concentration in the dynamic range between 10 to 1000 ppm. This linear dependence indicates a potential of the SERS approach for quantitative permethrin analysis.



**Figure 4.** (A) SERS spectra of different concentrations of permethrin deposited on the AgNF SERS substrates (from bottom to top: 10, 50, 100, 250, 500, and 1000 ppm) and NR spectrum of permethrin solid. The SERS Spectra were baseline-corrected and shifted vertically for clarity but the relative intensities were kept unchanged. (B) Plots of the peak height of the  $1003\text{ cm}^{-1}$  band against the permethrin concentration. The linear regression line was obtained by fitting the experimental data with a linear Eq.  $y = kx + b$ .

## 4. Conclusions

The SERS spectra of permethrin were measured on the AgNF SERS substrates. The characteristic SERS bands of permethrin were analyzed and assigned to the corresponding modes based on the NR spectra of permethrin. The SERS band at  $1003\text{ cm}^{-1}$  was identified for the evaluation of quantitative analysis. The detection limit was determined to be 10 ppm on the AgNF substrates. In the range of 10 – 1000 ppm,

a good linear relationship between the peak height of the 1003  $\text{cm}^{-1}$  band and the permethrin concentration is observed. In summary, the results obtained in this work indicate that SERS is a promising technique for the identification and quantification of permethrin.

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