Development of a portable SERS tool to evaluate the effectiveness of washing methods to remove pesticide residue from fruit surface

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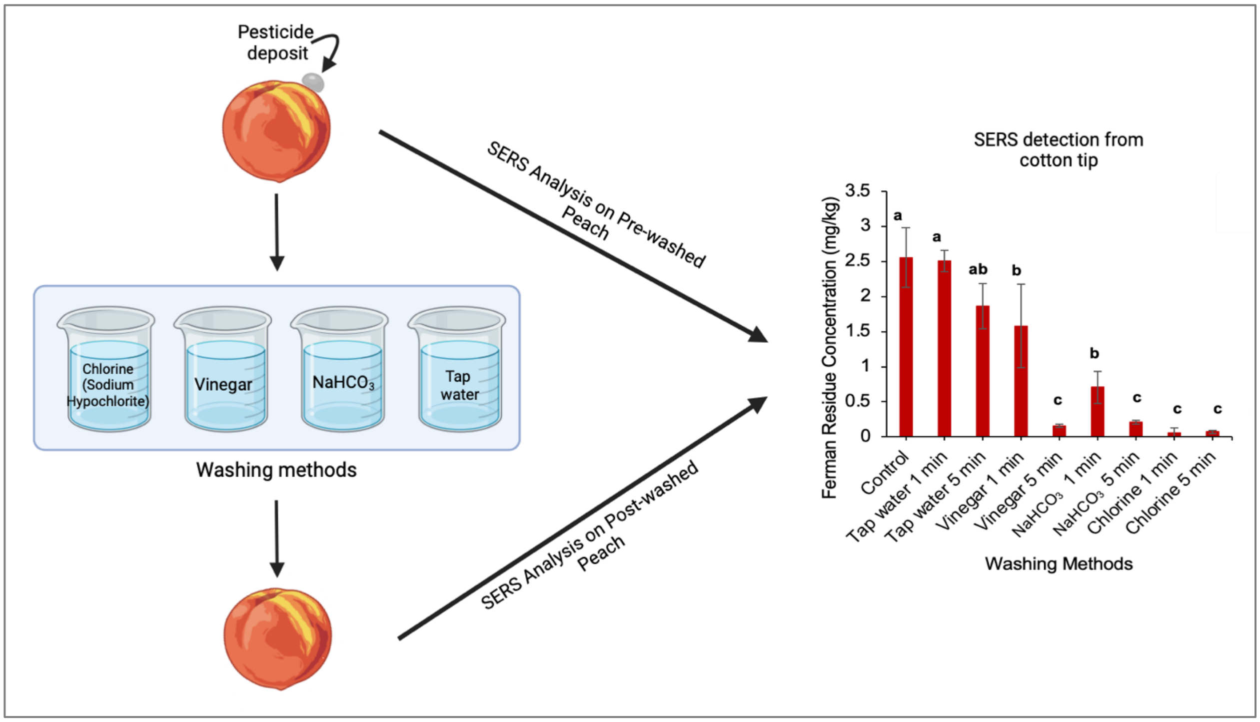
ABSTRACT:

Pesticides are commonly used to control pests and improve crop productivity in agriculture. Upon post-harvest, concerns have emerged regarding the potential harmful health effects resulting from the presence of pesticide residues. Analyzing these residues on crop surfaces is challenging due to their typically low concentration and potential interference from the complex matrix of the produce's surface. To address this challenge, we developed a portable surface-enhanced Raman spectrometer (SERS)-based approach that offers a fast turnover rate, simplified protocol, on-site capability, and high sensitivity. Further, this new approach was used to investigate the efficacy of various washing methods to remove a fungicide (ferbam) from peach surfaces. Household washing methods were compared with the chlorine wash used in the food processing industry (25 mg/L, sodium hypochlorite). The 1- and 5-minute chlorine wash (25 mg/L) proved most effective in removing pesticide residues, compared to tap water, sodium bicarbonate, and vinegar-soaking methods. Among household washing agents, sodium bicarbonate and vinegar provided superior removal effectiveness compared to tap water. In addition, SERS analysis on the flesh and backside of the skin revealed negligible penetration of ferbam into peaches. This study not only introduces an innovative method for measuring pesticide residues but also contributes to our understanding of pesticide removal and penetration. This knowledge is crucial for the effective use of pesticides and mitigation of their exposure through food sources.



Graphical abstract.

1 | INTRODUCTION

Pesticides are commonly used to prevent, destroy, or mitigate pests or to control plant growth.[1] According to the Food and Agriculture Organization of the United Nations (FAO), worldwide pesticide usage increased from 1.6 to 2.6 million tones between 1990 to 2020.[2] Fungicides, a class of pesticides that control fungal growth, are often used in agricultural settings to protect crops from fungal diseases that may damage them and cause them to be unfit for consumption. The application of fungicides to control fungal infestations is often considered indispensable to secure global food supply. However, like all pesticides, fungicides can reach bodies of water and distant soil easily.[3] Monitoring pesticide use on agricultural products is vital because while pesticides are designed to intercept the specific pests, the remaining portions of pesticide can leach into the environment, leading to potential entry into the food chain. Prolonged exposure to these compounds may lead to adverse health effects such as neurological disruptions.[4]

While the U.S. Food and Drug Administration Produce Safety Rule (PSR) does not mandate the washing of food produce before sale, if producers choose to wash their produce before taking it to market, the PSR requires that all agricultural water must be safe and of adequate sanitary quality for its intended use.[5,6] The most commonly available sanitizer washing solution for produce is chlorine (active ingredient: sodium hydrochloride) due to its inexpensiveness, ease of use, and relative safeness. As detailed by the United States Environmental Protection Agency (US EPA), fruits and vegetables should undergo soaking in a wash tank containing a sanitizing solution of 25 ppm available chlorine, followed by a final spraying rinse before packaging.[7] Once purchased, the most standard method to remove potential pesticide residues in households is through washing. Various washing methods have been proposed and developed over the years, yet the most common and familiar methods such as washing in tap water, sodium bicarbonate (baking soda), or acetic acid (vinegar) remain prominent. However, it is unclear about the efficacy of commercial chlorine sanitization and household washing methods in eliminating pesticide residues from fresh produce surfaces.

In addition, gaining insight into the movement and migration of pesticides in edible plants enables us to anticipate the potential human exposure through food sources.[8–11] Pesticides can be categorized into two groups, nonsystemic and systemic, which differ in their physical characteristics and abilities to permeate the produce surface. Nonsystemic pesticides exhibit minimal or no capacity to infiltrate produce tissues while systemic pesticides possess that feature.[12] However, there is a scarcity of information available concerning the penetration behavior of fungicides in fruits.

As for the detection of pesticide residues in food, the most commonly applied methods are gas chromatography (GC) and high-performance liquid chromatography (HPLC)-based techniques; however, these methods are time-consuming and costly.[13] Alternatively, surface-enhanced Raman scattering (SERS) is a rapid, non-destructive analytical tool that has many advantages over regular Raman spectroscopy, which possesses limited detection sensitivity. SERS technique provides an electromagnetic and/or chemical enhancement to the original Raman signal by a magnitude up to 10^{15}. Thus, it can be employed for the detection and monitoring of inorganic, organic, and biological contaminants.[14] Noble metal nanoparticles such as silver, gold, and copper are often applied as the SERS nanosubstrate due to their ability to enhance Raman signals.[15] Materials such as paper-based and adhesive tapes are often used as the carriers of these noble metal nanoparticles. However, paper-based substrates and adhesive tapes suffer from low extraction efficiency, low sensitivity, and lack of reproducibility.[16] Chen et al. (2016) used flexible AuNP adhesive tape as their nanosubstrate due to its easy fabrication; however, there were strong background signals and little control over the morphology of the deposited nanoparticles.[17] Alternately, Li and Chin (2020) developed self-assembled silver nanocube arrays anchored onto a flexible poly(dimethylsiloxane) membrane which was a complex, multi-step procedure that required organic solvents as linkers.[18]

The overall goal of this study was to examine the effectiveness of the postharvest washing methods (both commercial and household) in eliminating the applied fungicide from the peach surface. Herein, we developed a portable SERS method to quantify pesticide presence, removal, and penetration on fruit surfaces. We used a rapid and simple protocol to create the SERS nanosubstrate on cotton swabs and integrate it with a portable Raman spectrometer for pesticide detection. In contrast to previous methods that demand several hours for nanosubstrate synthesis, the SERS nanosubstrate we utilized required only 10 minutes for preparation, demonstrating the high efficiency in both time and labor. The use of a portable Raman spectrophotometer allows for advantages such as convenience and compatibility for easy transport, on-site capabilities, and an inexpensive alternative to a benchtop spectrophotometer. To the best of our knowledge, this study is one of the first to use SERS as a portable and fast method to track pesticide exposure, removal, and translocation on fruit surfaces.

2 | MATERIALS AND METHODS

2.1 Materials

Silver nitrate ($AgNO_3$), sodium bicarbonate ($NaHCO_3$), and sodium hydroxide (NaOH) were obtained from Thermo Fisher Scientific (Ward Hill, MA, U.S.A.). Hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) was purchased from Sigma-Aldrich (St. Louis, MO, U.S.A.). Calcium chloride ($CaCl_2$) was purchased from J.T.Baker (Phillipsburg, NJ, U.S.A.). Iron(III) dimethyldithiocarbamate (fungicide ferbam) was purchased from TCI America

(Montgomeryville, PA, U.S.A.). Sodium hypochlorite yielding 12% available chlorine was purchased from Spectrum Chemical (New Brunswick, NJ, U.S.A.). The 6" Sterile Cotton-Tipped Applicators were purchased from Dealmed. Ultra-pure water from a MilliporeSigma™ Direct-Q™ 8 Ultrapure Water Purification System was used throughout this work. Organic peaches and distilled white vinegar (5% acidity) were purchased from a local market (NY, U.S.A.).

2.2 Synthesis of Silver Nanoparticles (AgNPs)

The synthesis of the silver nanoparticles was conducted following a procedure published by Wang et al.[19] Briefly, a 300 mM stock solution consisting of $NH_2OH{\cdot}HCl$, $AgNO_3$, and NaOH was made by dissolving the solid forms of the compounds in ultrapure water. In a 15 mL centrifuge tube, 9 mL of 2 mmol $NH_2OH{\cdot}HCl$ solution (containing 3 mmol NaOH) was mixed with 1 mL 10 mmol $AgNO_3$. Upon the addition of the $AgNO_3$, the solution became a deep yellow color to which it was then vortexed for about a minute.

From the 10 mL AgNP suspension, 2 mL was pipetted out and dispensed into a 2 mL microcentrifuge tube. The AgNPs were then centrifuged for 5 minutes at 10,000 *rpm*. The remaining supernatant liquid was decanted and disposed of without disturbing the AgNP precipitate at the bottom. The remaining precipitate left behind was redispersed in 0.2 mL of ultra-pure water and stored in the dark at 4º for future use.

2.3 Characterization of AgNPs:

Using a scanning electron microscope (SEM, Zeiss SUPRA 55-VP), the AgNP suspension with and without the addition of calcium chloride ($CaCl_2$) was characterized at an accelerated voltage of 10 kV. The SEM samples were prepared by depositing the required suspension on copper tape dried at room temperature in the dark before SEM analysis. Employing the technique of dynamic light scattering (DLS), a ZetaSizer Ultra was used to measure the average particle size and zeta potential of the AgNPs. Furthermore, UV-Vis absorbance of the AgNP suspension was measured to provide information about their optical properties.

2.4 Nano-substrate creation and pesticide detection via a portable Raman Spectrometer:

6" Sterile Cotton tips were used as the supporting material for the nano-substrate. The cotton tips were immersed into a centrifuge tube containing the AgNP suspension for roughly 5 seconds, subsequently removed, and left to dry. To increase the number of SERS hotspots, we evaluated the effect of aggregating salt ($CaCl_2$, 0.1-0.5mM) on the performance of AgNPs.

To measure the pesticide on peach surfaces, the nano-substrate was wetted by adding 35 μL of ethanol using a micropipette onto the surface of the cotton tip. Directly after, the cotton tip was gently rubbed onto the ferbam-contaminated peach skin and measured using an EZRaman-I Series Portable Raman Analyzer (Enwave Optronics Inc., laser of 785 nm at a laser power of 221 mW). Each run had a 10-second integration time, with spectra collected through a single scan. A total of three spectra were collected on three spots randomly selected on the nano-substrate. Each data file was exported and saved as an Excel file.

2.5 Preparation of Calibration Curve:

To quantify the pesticide, a matrix-assisted calibration curve was constructed. The ferbam standard solutions at different concentrations were spiked onto slices of peach skin, with each slice receiving three 10 μL droplets for each concentration. Once the ferbam droplets had dried, the cotton tip nano-substrate was used to swab the surface. The nano-substrates were detected by the portable Raman spectrometer as described above in 2.4.

2.6 Evaluation of Washing Methods

The preparation of peach slices followed the identical procedure described in subsection 2.5 above. In total, there were eight washing methods conducted with four washing solutions for 1 min or 5 min: tap water (pH 7.61), sodium bicarbonate ($NaHCO_3$, 10 mg/mL), white distilled vinegar (3:1 water/vinegar, v/v), and sodium hypochlorite (12.5% available chlorine, 25 mg/L,). Additionally, a non-washed pesticide control group was used as a comparison. For each washing method, once the ferbam droplet had dried on the peach skin surface, the peach was submerged into a clean beaker and left to soak for either 1 or 5 min in one of the above washing solutions. Once the set time had elapsed, the peach slice was gently removed from the beaker, placed on a clean glass slide, and left to dry before being swabbed by the prepared nanosubstrate.

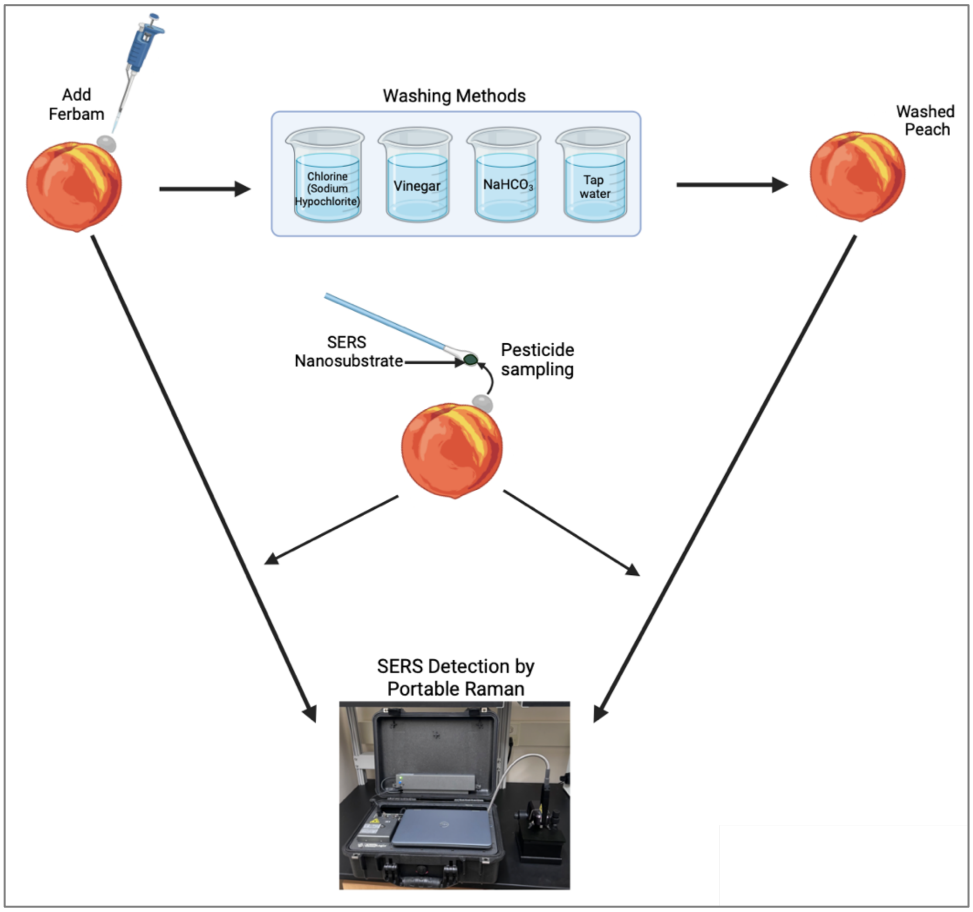


Figure 1. Experimental procedure for pre-washing and post-washing sample preparation and analysis.

2.7 Testing Pesticide Penetration

With the purchased peaches, each whole peach was gently washed with distilled water to remove any potential contaminants and air-dried. Afterwards, slices of the skin (approximately 8.3 cm^2 area and 0.25 cm thickness) were cut from the peach using a knife and placed on a clean glass slide. A 10 µL aliquot of the 10 mg/L ferbam solution was placed in three locations per slice and allowed to dry in air at room temperature before being moved to the dark at 4˚C.

The penetration of ferbam was monitored at 1, 5, and 7 days. Following the various exposure periods, the prepared nano-substrates were used to swab the surface where ferbam was deposited, as well as the skin directly beneath it, and the flesh of the fruit below. The pesticide was measured by SERS using the method described in 2.4.

3 | RESULTS AND DISCUSSION

3.1 SERS nanosubstrate preparation and optimization

In this study, the Raman signal enhancer we used was made of AgNPs. It provided electromagnetic enhancement induced by hotspots and the chemical enhancement produced by the charge transfer between AgNPs and ferbam through the Ag-thiol groups. The highest SERS peak of ferbam was detected at 1380 cm^{-1} and chosen as the characteristic peak for ferbam detection. The peak observed at 1380 cm^{-1} in the Raman spectrum of ferbam is associated with this symmetric stretching vibration of the dithiocarbamate (DTC) group's C-N bonds. As shown in Figure S1 of the Supporting Information, the peach surface alone yielded a negligible Raman signal. Meanwhile, the characteristic Raman peaks of ferbam were hard to observe from Raman spectra when AgNPs were absent from the cotton tip (Figure S2). To increase the Raman hotspot number, we added $CaCl_2$ to the AgNP suspension to generate nanoclusters. The optimal $CaCl_2$ concentration was determined by evaluating two concentrations, with 0.5 mM exhibiting the most significant improvement in Raman signal (Figure S3). With the addition of 0.5 mM $CaCl_2$ to the AgNP suspension, the signal intensity of ferbam at 1380 cm^{-1} increased by 68.9% (Figure 2A) confirming the generation of more hotspots induced by $CaCl_2$.[20] We speculate that when $CaCl_2$ was dispersed in the AgNP suspension, it reduced the surrounding negative charge on AuNPs resulting in their aggregation and more SERS hotspots.[21]

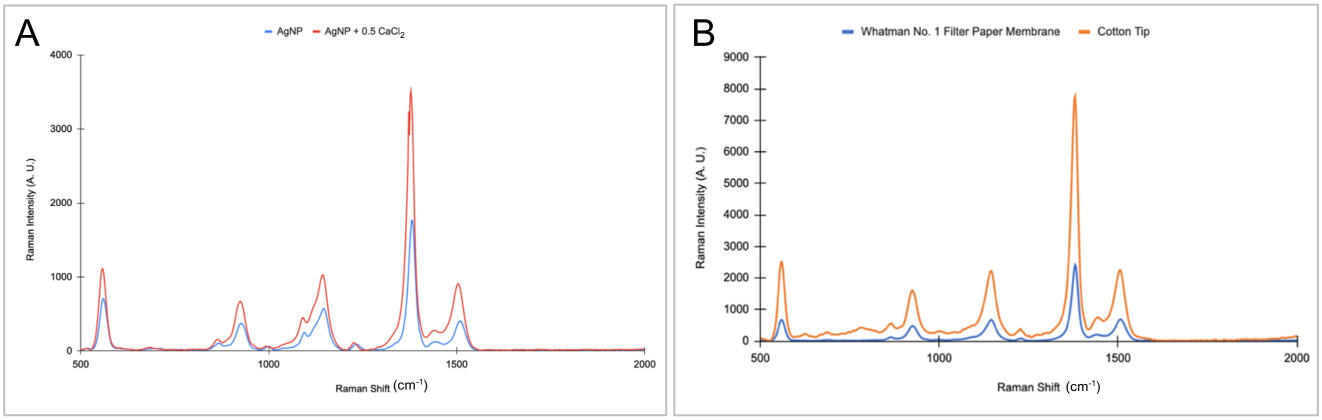


Figure 2. (A) SERS spectra on nanosubstrate created with AgNPs alone (blue) or AgNPs + 0.5 mM $CaCl_2$ (red). Both contained ferbam (10 mg/L) as the analyte of interest. With the addition of 0.5 mM calcium chloride to the AgNP suspension, the Raman single enhancement increased by 68.9%. **(B)** SERS spectra on nanosubstrate created with the 0.5 mM $CaCl_2$ on a Whatman No. 1 Filter Paper Membrane and on a sterile cotton tip with 10 mg/L ferbam deposition. The use of a cotton tip as a nano-substrate allows for higher Raman enhancement, as well as more flexibility and accessibility by the users when removing pesticide residue from fruit surfaces.

To confirm the speculation, we characterized AgNPs with and without using $CaCl_2$ by DLS, UV-visible spectroscopy, and SEM. Using DLS (ZetaSizer), we determined that the original suspension of AgNPs had a Z-average of 42.58 ± 0.55 nm and increased to 288.56 ± 20.31 nm with the addition of $CaCl_2$. When salts are added to a nanoparticle suspension, the ions in the salt solution can shield the surface charges of the nanoparticles, reducing the electrostatic repulsion between particles. As a result, the nanoparticles can approach each other more closely, leading to aggregation.[22,23] We discovered that the original suspension of AgNPs had a zeta potential of -42.09 ± 0.40 mV and increased to -21.06 ± 0.48 mV with the addition of $CaCl_2$, confirming that the particles in the suspension exhibited less electrostatic repulsion and formed more aggregates with high Raman enhancement.

The AuNP suspensions were further measured by UV-Vis spectrophotometer (Figure S4). The presence of silver in its colloidal form was evidenced by the absorption spectrum of AgNPs, which exhibits a distinct peak at approximately 400 nm. The effect of $CaCl_2$ on the spectra could distinctly be seen as the peak intensity was reduced by 78.9%. Furthermore, the broadening of the peak suggests that the aggregated nanoparticles interacted more heavily with light of a longer wavelength than non-aggregated nanoparticles.[20]

In addition, scanning electron microscopy (SEM) was employed to investigate AgNP morphology before (Fig. 3A, B) and after (Fig. 3C, D) adding 0.5 mM $CaCl_2$. In the absence of $CaCl_2$, the AgNPs were less populated and distributed more sparsely. With the addition of $CaCl_2$, a more cohesive and uniform layer of particles could be seen (Fig. 3C). In addition, the AgNPs exhibited a densely populated array of nanoscale features nearby a central nanoparticle (Fig. 3D), indicative of core-satellite assembly on nanoparticles which provide additional multiple enhanced electromagnetic field locations (hot spots).[24] This can be attributed to the role of $CaCl_2$ in promoting controlled aggregation or assembly of the nanoparticles. $CaCl_2$ may act as bridges, facilitating attractive interactions between the silver nanoparticles. This controlled aggregation leads to the creation of core-satellite structures, where one central nanoparticle (core) is surrounded by smaller satellite nanoparticles.[25,26] The presence of $CaCl_2$

likely influences the surface charge and interparticle forces, fostering the development of these well-defined nanostructures and enhancing the electromagnetic field at specific regions, ultimately resulting in the observed hotspots.[27]

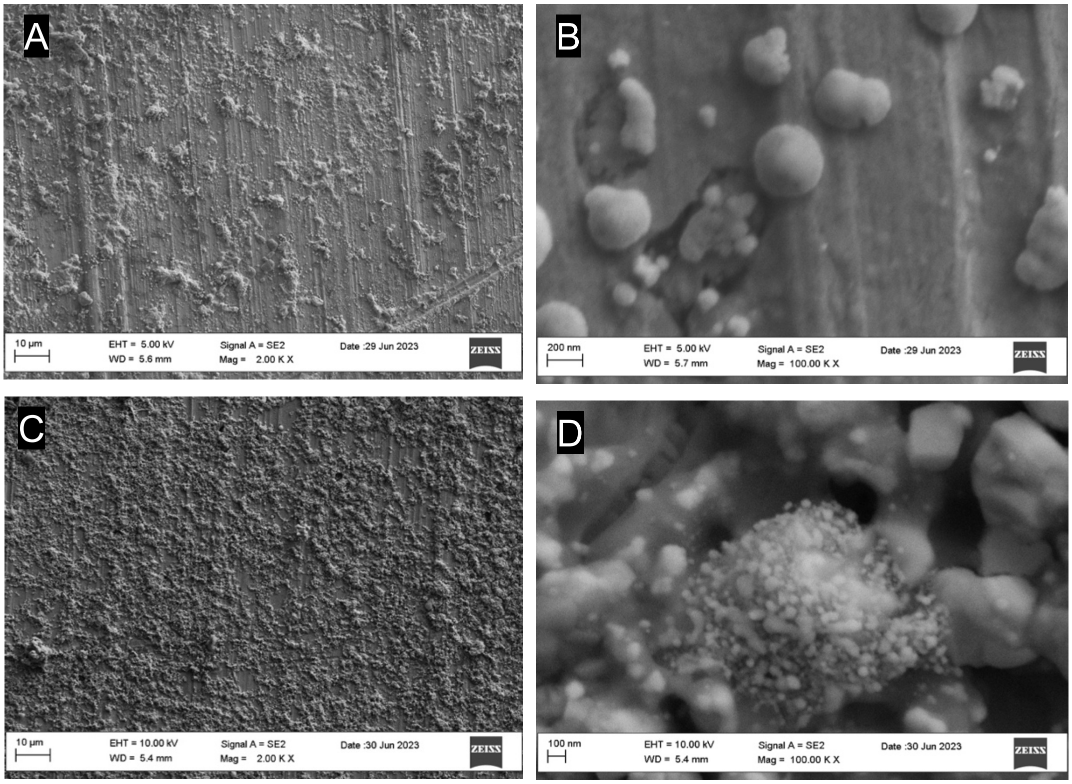


Figure 3. SEM images of AuNPs before (A, B) and after (C, D) mixing with 0.5 mM $CaCl_2$. The scale bar is denoted in the bottom left corner of each image.

To fully develop the SERS nanosubstrate, we elevated two types of low-cost carrier materials (Whatman No. 1 Filter Paper and cotton tip) to support $CaCl_2$-aggregated AgNPs. As shown in Figure 2B, the nanosubstrate prepared on the cotton tip caused a substantial SERS signal increase at the peak of 1380 cm^{-1} compared with the one on the Whatman Filter Paper. This increase is likely due to the flexibility and ease of the cotton tip when applying it to food produce surfaces, leading to more effective sample collection. Therefore, the nanosubstrates prepared on the cotton tips were used for the following experiments.

3.2 Development of Calibration Curve to Quantify Pesticide Residue on Fruit Surface.

To evaluate the ferbam removal from peach surfaces following each washing method, a linear calibration curve ($R^2 = 0.9821$, Figure 4) was created to quantify ferbam surface concentration based on the Raman intensity at 1380 cm^{-1}, the strong feature band of ferbam.

To define the lowest ferbam concentration that can be reliably detected, the limit of detection (LOD) was calculated using the equation, $LOD = 3\sigma/S$, where σ is the standard deviation of the response from the blank control and S is the slope of the calibration curve. Upon calculating, we received an LOD of 0.01195 mg/kg. Based on U.S. Environmental Protection Agency, the existing tolerance for ferbam residue on peaches is 7 mg/kg.[28] Since our LOD is lower than 7 mg/kg, our method is sensitive enough to detect concentrations lower than the regulated concentration.

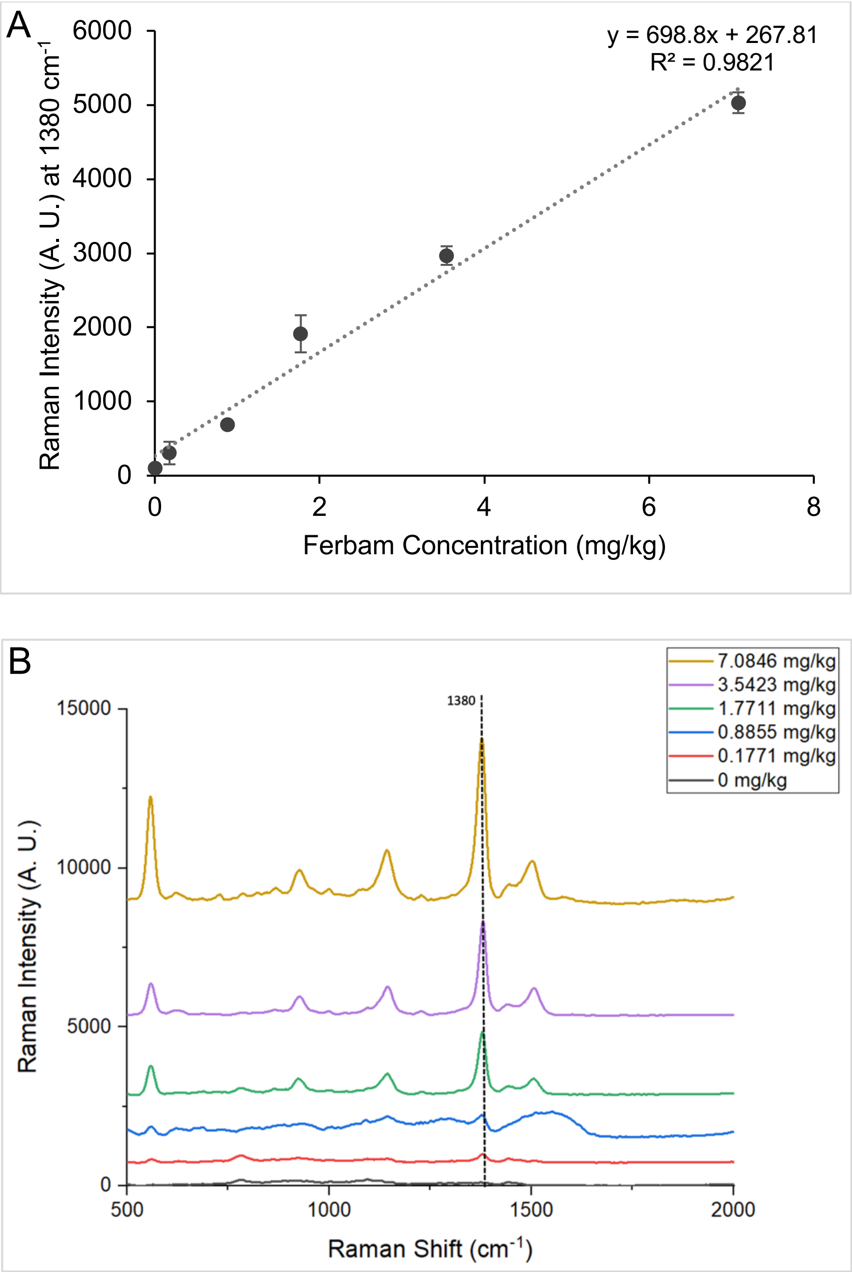


Figure 4. (A) The linear relationship between SERS peak intensity (at 1380 cm^{-1}) and ferbam concentrations (0, 0.1771, 0.8856, 1.7712, 3.5423, 7.0947 mg/kg). The error bars represent the standard error of three replicates at each concentration. **(B)** Raman spectra of ferbam concentrations.

3.3 Effectiveness of Different Washing Methods on Pesticide Removal from Fruit Surface.

To determine the most effective method to remove pesticide residues from fruit surface, we conducted tests comparing eight methods, including tap water-1 min, tap water-5 min, $NaHCO_3$-1 min, $NaHCO_3$-5 min, vinegar-1 min, vinegar-5 min, chlorine-1 min, and chlorine-5 min. The time indicates the soaking period, mimicking a typical at-home wash time. After washing, the remaining ferbam concentration was quantified using the SERS nanosubstrate developed above. As a basis of comparison, a non-washed sample was used as the control. The concentration of the remaining pesticide after each washing method is shown in Figure 5A. Among the eight methods, the tap water washing for 1 min is the least effective method to remove ferbam, without significant difference from the control group. In contrast, vinegar-5 min, $NaHCO_3$-5 min, chlorine-1 min, and chlorine-5 min are the most effective, showing similarly low levels of ferbam residue on the surface. Increasing the soaking time improved the pesticide removal for the tap water, vinegar, and $NaHCO_3$ group while in the chlorine group, the effect was not significant. Figure 5B illustrates the effectiveness of the washing methods in removing ferbam residues from the peach surface. As for the two vinegar washing treatments (1 min and 5 min), they exhibited pesticide removal of 38.2 and 93.8%, respectively. Pesticide removals of 72.4 and 91.8% were observed for the 1-min and 5-min $NaHCO_3$ treated groups, respectively. The significantly higher removal effectiveness by vinegar and $NaHCO_3$ than the 1.9 and 27.2% displayed by the tap water 1 min and 5 min, respectively, is likely due to the pH difference. The stability of pesticides, including fungicides such as ferbam, can be pH-dependent. The chemical properties of a pesticide may change under different pH conditions, which can influence its solubility, persistence, and effectiveness. Specifically, ferbam is a dithiocarbamate fungicide, and the stability of dithiocarbamates is often influenced by pH. Dithiocarbamates can undergo hydrolysis reactions when exposed to alkaline conditions, which leads to the breakdown of the compound. [29,30] Alternately, certain pesticides may undergo acid hydrolysis which involves the use of an acid to break the chemical bonds in the pesticide. [29,30] Regarding our washing agents, baking soda is basic and vinegar is acidic, which may cause alkaline or acid hydrolysis of the pesticides and facilitate the pesticide removal.

As for the postharvest washing method using a 25 mg/L sodium hypochlorite solution, it effectively removed surface ferbam by 97.2% and 97.7% for both the 1- and 5-minute wash times, respectively. Yang et al. (2017) studied apple surfaces contaminated by phosmet and thiabendazole and did not detect a considerable increase in the removal of their selected pesticide residues by sodium hypochlorite.[31] In contrast to our findings, it is possible that a certain portion of their pesticides might have penetrated the wax layer on the surface of the apple, making it inaccessible while soaking in the sodium hypochlorite solution. In addition, the research paper lacks quantification or calculation of removal effectiveness, which poses a challenge in comparing it with our data. While chlorine (active ingredient sodium hypochlorite) is widely used within industrial washing practices, it is commonly only used in small-scale operations.[32] Despite the solution showing impressive removal effectiveness, there are drawbacks. Currently, only registered formulations are permitted for use on produce; household bleach is not an authorized substance for treating produce.[32] Moreover, applying sodium hypochlorite repeatedly to recirculating water may result in excessive sodium accumulation, leading to potential damage to delicate produce.[28] When chlorine is used for pesticide washing treatments, it interacts with organic substances present in the water, leading to the formation of disinfection byproducts (DBPs).[33–35] The formation of DBPs is a concern because some of them may pose adverse health effects, particularly if present in elevated concentrations. Water treatment facilities and agricultural practices may employ strategies to minimize the formation of DBPs, such as using alternate disinfectants or optimizing chlorine dosage. Our findings suggest that implementing an alternative washing method, like vinegar-5 min or $NaHCO_3$-5 min, could yield a removal rate almost identical to that achieved with a chlorine wash.

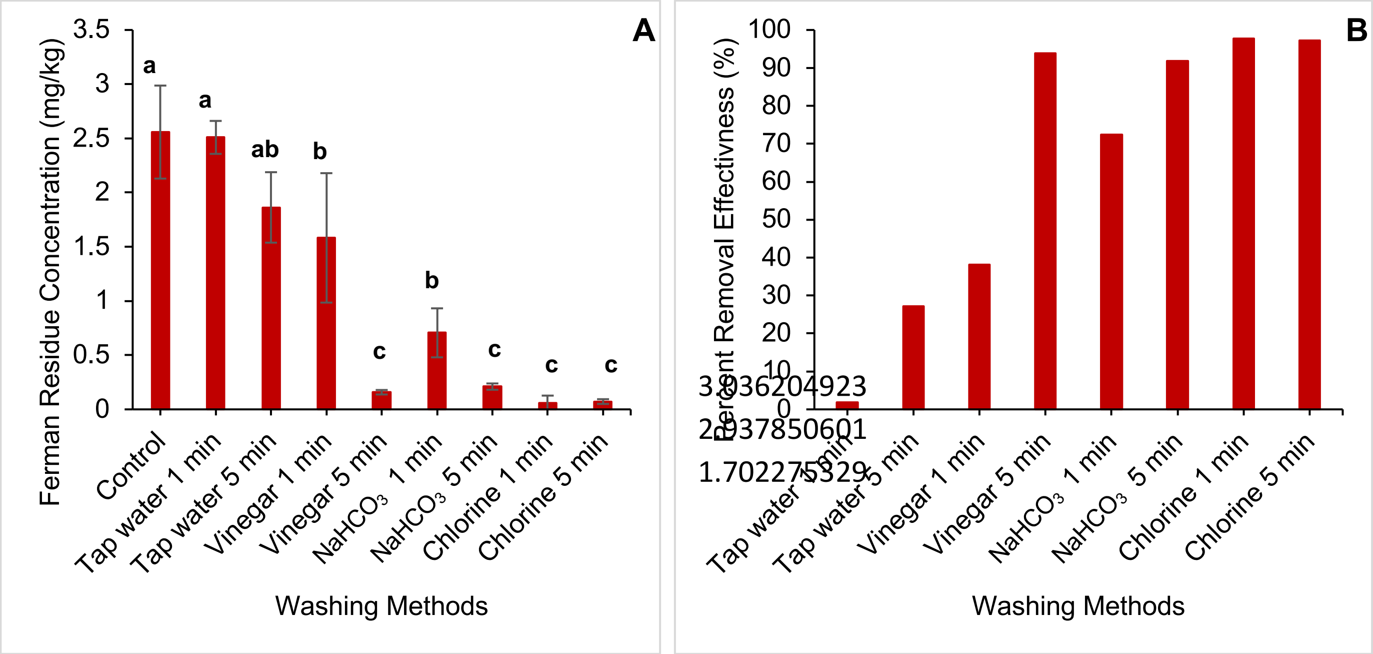


Figure 5. (A) The ferbam residue concentrations on peach surfaces after washing by different methods. A control group without washing was used for comparison. The sodium hypochlorite

washing was performed at a concentration of 25 mg/L. The vinegar solution maintained 3:1 ratio (water/vinegar, v/v), while the $NaHCO_3$ solution had a concentration of 10 mg/mL. The error bars represent the standard error of three replicates in each group. The significance of the differences was analyzed by Tukey's test with $p<0.05$ considered to be statistically significant. **(B)** Effectiveness (%) of washing methods to remove the ferbam residue from peach surfaces.

3.4 Evaluation of Pesticide Penetrating Fruit Surface.

We further examined the ability of ferbam to penetrate the peach skin using the developed SERS approach. Peach samples were subjected to a 10 mg/L ferbam solution and measured at 1 day, 5 days, and 7 days, respectively by SERS. The results of ferbam penetration through the peach surface, the skin underneath, and fruit flesh are demonstrated in Figure 6. We found that ferbam exhibited non-detectable penetration beyond the treated surface and into the underlying flesh across all exposure durations. The result agrees with an earlier study, which observed negligible penetration of 20 mg/L ferbam in spinach leaves.[10] In contrast, another study employed a 100 mg/L ferbam concentration and detected an internalized signal in basil leaves, likely due to the higher ferbam concentration applied on the leaf's surface.[11] The variation in collected data suggests that the penetration behavior fluctuates depending on the pesticide nature and the matrices of the produce.[36] The different penetration abilities observed in produce may be attributed to discrepancies in the cuticle and epicuticular wax composition. The plant cuticle, which consists of a polymeric cutin matrix and soluble cuticular waxes, is a nonliving and nonuniform plant structure acting as a barrier against foreign substances.[37] Additionally, the cuticular membranes of fruits, composed of cutin and waxes, are generally thicker than those of leaves.[38] Another key finding we observed is that the ferbam concentration on the peach skin decreased over time. Since our samples were saved in a dark condition, photo-induced degradation is excluded. However, microbial degradation is possible given that a variety of microbes may grow on peach surface over time. Future studies are needed to reveal the chemical and biological changes of ferbam on fruit surfaces.

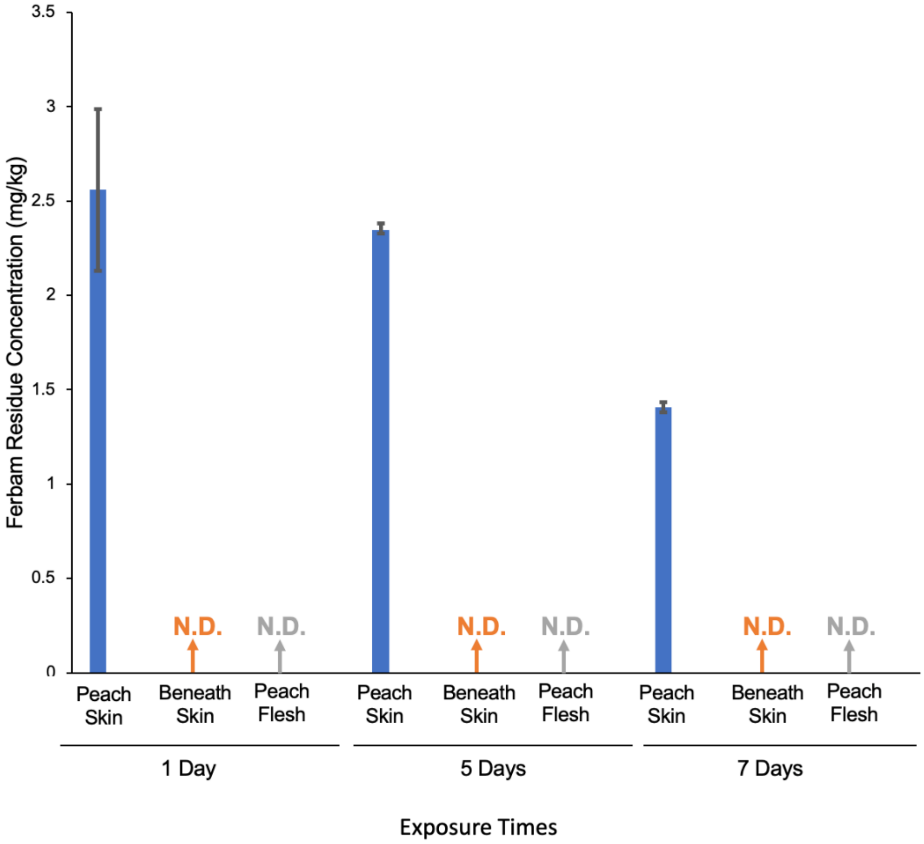


Figure 6. Tracking of ferbam penetration through peach layers (peach surface (blue), beneath skin (orange), peach flesh (gray) at varying exposure times using SERS. Ferbam was not

detectable (N.D.) under the fruit skin or in the flesh. The error bars represent the standard error of three replicates per group.

4 | CONCLUSION

In this study, we quantified the pesticide removal effectiveness of varying washing agents on fruit surfaces using a SERS nanosubstrate deposited on a cotton-tip. By implementing the use of the cotton tip as our substrate, we achieved high sensitivity, quick and simple assembly, as well as flexibility for delicate fruit surfaces. Due to its fast and straightforward construction, this substrate has high potential to be used in conjunction with a portable Raman spectrometer for fieldwork. Our experimental results have shown that the home-accessible washing agents, such as $NaHCO_3$ and vinegar, provided effective removal of ferbam residue from peach surfaces, whereas tap water alone did not successfully eliminate the pesticide. Regarding the commercial post-harvest chlorine washing (25 mg/L sodium hypochlorite), ferbam was swiftly and effectively removed from the fruit surface. Nevertheless, produce is not always guaranteed to be washed well nor washed at all before being released to the market thus it is vital to wash produce after purchase.

As suggested by our findings, it is evident that tap water in isolation exhibits limited efficacy in reducing pesticide residue. Thus, it is advisable to include supplementary cleansing agents, such as vinegar and $NaHCO_3$, as exemplified in this research. Furthermore, while not investigated in this study, the potential benefits of incorporating physical force, such as mechanical tools like scrub brushes or manual friction using one's hands, should be considered for future research.

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Conflict of Interest: The author has declared no conflict of interest.

List of Acronyms:

Abbreviations	**Meaning**
SERS	Surface-enhanced Raman spectroscopy
FAO	Food and Agriculture Organization of the United Nations
PSR	Produce Safety Rule
US EPA	United States Environmental Protection Agency
GC	Gas chromatography
HPLC	High-performance liquid chromatography
AuNP	Gold nanoparticles
AgNP	Silver nanoparticles
SEM	Scanning electron microscope
DLS	Dynamic light scattering
DTC	Dithiocarbamate
LOD	Limit of detection
DBPs	Disinfection byproducts

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