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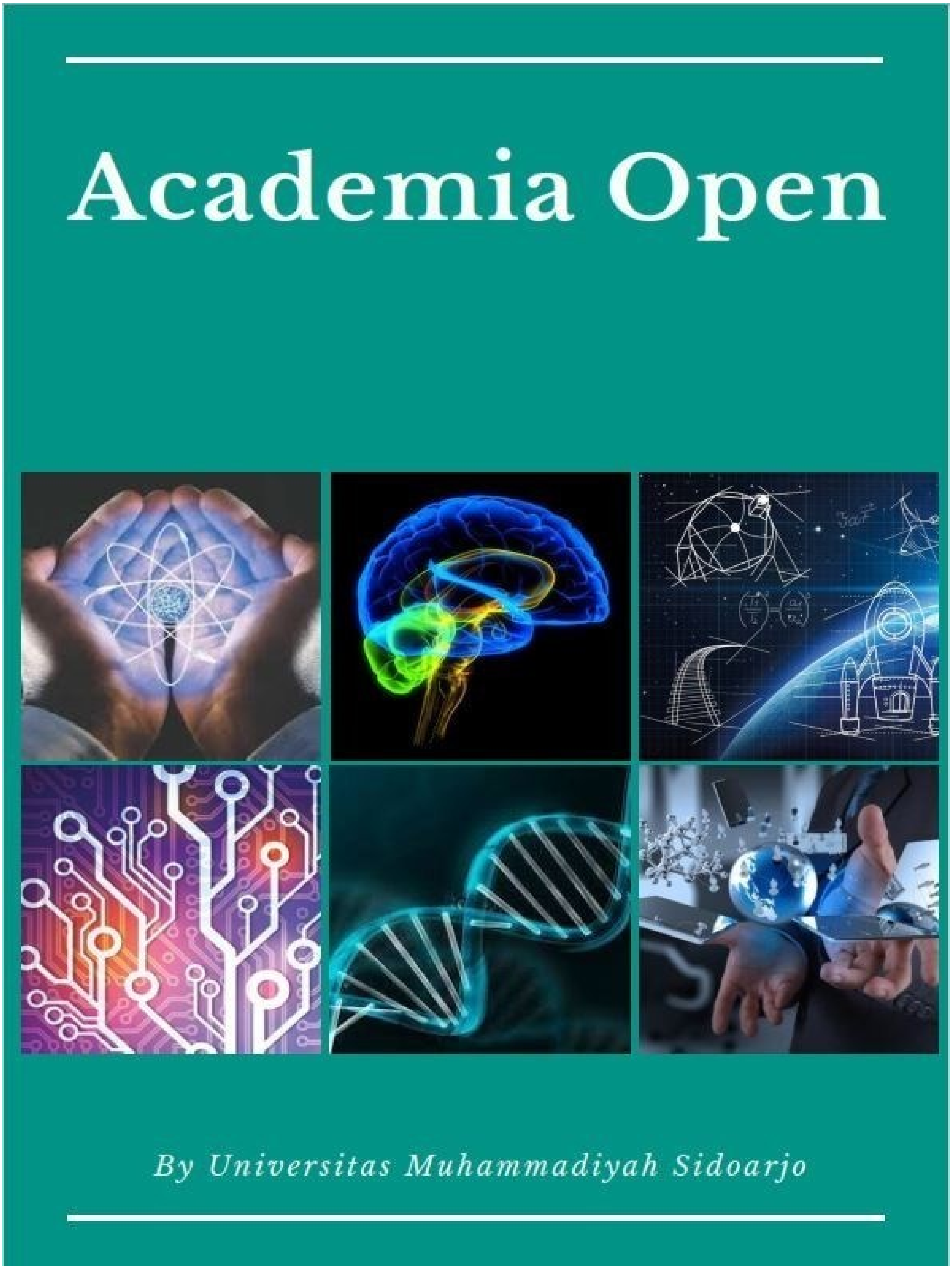

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Sensitive Food Pesticide Analysis Using Silver Nanostructured Raman Substrates

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Abstract

General Background: Pesticide residues in food remain a global safety concern, requiring analytical methods that are both rapid and highly sensitive. Specific Background: Conventional chromatographic techniques provide accurate detection but are limited by high cost, long processing times, and complex sample preparation, restricting routine monitoring. Knowledge Gap: Despite growing interest in Surface-Enhanced Raman Scattering (SERS), challenges persist regarding substrate reproducibility, sensitivity across diverse food matrices, and validation against regulatory standards. Aims: This study aimed to develop, optimize, and validate nanostructured silver SERS substrates for the sensitive detection of organophosphorus and organochlorine pesticides in food. Results: The fabricated substrates achieved enhancement factors above 10^8, detection limits as low as 0.05–0.1 ng/mL, strong linearity, high reproducibility, and accurate recovery across apple juice, tomato extract, and rice samples. Analytical performance showed strong agreement with GC-MS while reducing total analysis time to under 15 minutes. Novelty: The work integrates controlled nanoparticle aggregation with optimized sample-matrix handling, yielding highly reproducible, stable, and field-ready SERS substrates. Implications: The findings demonstrate a practical and cost-effective platform for high-throughput pesticide monitoring, with potential for portable on-site food safety assessment and future expansion to broader contaminant classes.

Highlight :

- Silver-based SERS substrates provide very high-sensitivity pesticide detection.
- The method offers much faster analysis than conventional techniques.
- It works effectively across multiple food matrices.

Keywords : SERS, silver nanoparticles, pesticide detection, food safety, surface enhancement, Raman spectroscopy

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Introduction

Food safety is one of the top public health challenges of the 21st century. Pesticide contamination is critical for regulatory bodies, food producers, and consumers (1), as it displaces contaminants on food products. Modern agricultural practices broadly implement pesticides on food. As a result, exposure to these contaminants has a higher likelihood of contamination of food safety products, and food safety practitioners have recently found residues occurring at exposure levels of potential concern to human populations (2). Current estimates of the annual global application rate of pesticides include over 2.5 million tons of pesticides applied globally each year, with sizeable waste amounts left in residues on agricultural products reaching the food chain (3).

Standard methods of pesticide detection, including gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS), are accurate and precise analyses. However, they all have significant limitations that restrict them from routine measurements in food safety use (4). Both methods require extensive sample preparation methods, expensive instrumentation, trained scientists, and lengthy analysis times of hours to days per sample (5). The expense of these methods limits their usage for small food producers and developing countries, which face parallel plateaus for pesticide monitoring (6).

The development of Surface-Enhanced Raman Scattering (SERS) as an analytical method has been touted as a possible rapid and sensitive detection method through chemical changes (7). SERS is a hybrid methodology; it follows the specificity of Raman Spectroscopy measurements while incorporating extreme signal enhancement from metal nanostructures, predominantly silver or gold-based, with this signal creation occurring through plasmonic effects of the variables (8). The enhancement mechanism is based on two significant contributions: electromagnetic enhancement from localized surface plasmon resonances, which amplify the local electromagnetic field, and chemical enhancement from charge transfer interactions between the analyte molecules and the metal surface (9).

Silver nanoparticles have been specifically and particularly appealing as SERS substrates because they have excellent plasmonic properties, whereby the surface plasmon resonances are generally in the visible to near-infrared spectral regime, which coincide well with the laser excitation wavelengths regularly used in Raman spectroscopy (10). Additionally, the enhancement factors of silver nanostructures can reach up to 1010 under the best conditions, and at times allow for single molecule detection (11). Silver is often cited as having better enhancement factors than gold, particularly for many of the molecules with the aromatic functional groups commonly found in pesticide structures (12).

SERS substrates are designed and fabricated considering several parameters, including particle size, shape, surface chemistry, and spatial arrangement (13). Extensive studies of spherical silver nanoparticles in the diameter range of 20 to 100 nanometers were considered reliable for the enhancement and, therefore, reproducible (14). However, more complex nanostructures, nanostars, nanorods, and aggregated cluster-type arrangements could result in even larger enhancement factors, primarily because of the sharp edges and tips contributing to electromagnetic "hot spots" (15). The aggregate state of silver nanoparticle(s) is critical to SERS performance as the coupling of adjacent particles produces areas of attachment, and thus, enormously enhanced electromagnetic fields (16). Controlled aggregation methods were developed to strengthen inter-particle interactions, while providing reproducibility and stability of the substrate (17). The methods, such as salt-induced aggregation, solution pH, and definitive surface functionalization from bifunctional linker molecules, aimed to provide an optimized arrangement of the nanoparticles (18).

Detecting nectar peptide pesticides entails problems and opportunities concerning the SERS methodology because distantly organized chemistry structures have different affinities to metal surfaces (19). Organophosphate pesticides tend to have phosphorus-oxygen bonds (malathion, parathion, chlorpyrifos) that have sharp Raman signatures and react with the silver surface (20). Organochlorine pesticides such as DDT and its metabolites have aromatic ring molecular structures that benefit from enhanced Raman cross-sections attributable to normal aromatic-type chemical constructs on SERS substrates (21).

The use of SERS for food sample applications produces added variables for detection because of the potential interference from background in the sample matrix. Various matrix components, similar to food, contain compounds that could inhibit inter-particle binding processes or produce background signals from proteins, carbohydrates, lipids, and natural pigments that might compete for binding sites on the SERS substrate (22). Sample preparation dynamics must be established to mitigate interferences from the sample matrix while preserving the target analytes and keeping the integrity of the SERS substrate (23). Techniques such as solid-phase extractions, liquid-liquid extractions, and dilutions have been evaluated with differing success depending on the food matrix and target pesticide (24).

The reproducibility and stability of SERS substrates remain a significant obstacle for implementing practical applications for global food safety monitoring (25). Variation in synthesizing nanoparticles, factors for aggregation, and whether or not the substrate is stored could improve or significantly change the nanoparticles' enhancement factors and detection abilities (26). There have been considerable advances in manufacturing methods related to substrate fabrication, such as template-assist assembly, lithographic patterning, and sol-gel techniques to try to address reproducibility (27).

Quality control and validation of SERS based pesticide assays and detection methods will need to be based solely upon extensive comparative work with other comparable methods, including current methods or similar methods, and/or practical assessment of performance parameters with the method, such as linearity, precision, accuracy, detection limits and matrix effects (28). Any regulatory acceptance and/or credibility regarding the use of SERS methods for official food safety monitoring purposes, from an enforcement perspective, will be predicated upon comparable or superior quality to the current standard methods, and that, at the same time the methods have advantages of speed, cost, and operator efficiency (29).

Integrating SERS detection for portable instrument platform options should provide opportunities for screening food safety from a field research perspective, promoting on-site analysis that could be completed without central lab involvement (30). Portable device options developed include miniaturized laser diode-exited Raman spectrometer devices with charge-coupled device detectors that are now widely available and realistically priced for incorporating SERS detection in routine monitoring applications (31).

The multi-faceted work described here to recognize the need for rapid, fast, and cost-effective detection of pesticides was addressed through the development and characterization of SERS substrates made from nanostructured silver that were specifically synthesized and/or fabricated with food safeguards in mind. In addition to substrate design and fabrication, analytical and detection method development, validation process, and, when feasible, practical demonstration of detecting pesticides in diverse food samples that may represent or commonly be encountered in food safety monitoring programs.

Methods

2.1 Materials and Reagents

Silver nitrate ($AgNO_3$, 99.9% purity), sodium citrate tribasic dihydrate ($Na_3C_6H_5O_7{\cdot}2H_2O$, ≥99%), sodium borohydride ($NaBH_4$, ≥96%), and polyvinylpyrrolidone (PVP, MW 40,000) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Pesticide standards, including malathion (94.5% purity), chlorpyrifos (99.8% purity), diazinon (98.9% purity), and 2,4-dichlorophenoxyacetic acid (2,4-D, 99.5% purity), were obtained from AccuStandard Inc. (New Haven, CT, USA). HPLC-grade methanol, acetonitrile, and ultrapure water (18.2 MΩ·cm) were used throughout all experiments. Food samples, including organic apples, tomatoes, and rice, were purchased from local markets and verified pesticide-free through preliminary GC-MS analysis.

2.2 Synthesis of Silver Nanoparticles

Silver NPs were prepared using a modified citrate reduction method adjusted to SERS conditions (32). A typical synthesis procedure: 100 mL of ultrapure water was heated to 95 °C on a hot plate in a round-bottomed flask maintained under vigorous stirring and reflux condenser. A solution of 10 mL of 10 mM $AgNO_3$ was introduced to a water which had been heated, with immediate injection of a further 10 mI of rapid bolus of the sodium citrate solution (38.8 mM). The reaction mass was kept at 95°C for 45 min under continuous stirring at 400 rpm. The color turning from solution of colourless to yellow green confirmed the formation of nanoparticles. The colloid was cooled to room temperature and stored at 4°C in amber glass vials to avoid photo degradation.

2.3 Nanoparticle Characterization

The morphology and size distribution of the silver nanoparticles were examined by high-resolution transmission electron microscopy (TEM) with a JEOL JEM-2100F microscope at 200 kV. TEM samples were prepared by placing 5 µL of diluted nanoparticle suspension onto carbon-coated copper grids and allowing full solvent evaporation at room temperature. Size distribution was obtained based on at least 200 individual particle diameters from several TEM images by ImageJ software.

The surface plasmon resonance properties were monitored by recording UV-visible absorption spectra in the range of 300-800 nm using a Shimadzu UV-2600 spectrophotometer. Dynamic light scattering (DLS) analysis was done on a Malvern Zetasizer Nano ZS to obtain hydrodynamic diameter and polydispersity index of the nanoparticles in colloidal suspension.

2.4 SERS Substrate Preparation

SERS substrates were fabricated by the well-dispersed aggregation of silver nanoparticles following a salt-induced aggregation approach that has been previously optimized for the highest enhancement factors (33). The aggregation step was achieved by gradual addition of 1 mL of the AgNP suspension into sodium chloride solution (final concentration: 10-100 mM) by gentle vortexing. The UV-vis absorption spectra were measured to find the optimum aggregation conditions and the SERS enhancement factor was estimated using 4-mercaptobenzoic acid as a test analytic.

To prepare the substrates, 50 µL of the well-aggregated nanoparticle suspension was dropped onto clean silicon wafer per se (1 cm × 1 cm) and left to dry in a controlled environment at room temperature for 2 h. Dried substrates were stored in the desiccated containers ready for use. Substrate homogeneity was determined by taking Raman spectra from 25 different spots on the surface of each substrate.

2.5 Pesticide Standard Preparation

Stock solutions of individual pesticides were prepared at concentrations of 1000 mg/L in HPLC-grade methanol and stored at -20°C. Working standard solutions were prepared daily by serial diluting stock solutions with ultrapure water to achieve concentration ranges from 0.01 to 100 mg/L. Mixed pesticide standards containing all target compounds were prepared for method validation experiments.

2.6 Food Sample Preparation

Apple juice samples were prepared by homogenizing whole apples using a high-speed blender and centrifugation at 5000 rpm for 10 minutes. The supernatant was filtered through 0.45 µm membrane filters and diluted 1:10 with ultrapure water before analysis. Tomato extract was prepared by blanching fresh tomatoes in boiling water for 2 minutes, removing skins, and homogenizing the pulp. The homogenate was centrifuged and filtered as described for apple samples.

Rice samples were prepared using a modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) extraction procedure (34). Briefly, 10 g of ground rice was mixed with 10 mL of acetonitrile containing 1% acetic acid in a 50 mL centrifuge tube. Anhydrous magnesium sulfate (4 g) and sodium acetate (1 g) were added, and the mixture was vortexed vigorously for 1 minute, followed by centrifugation at 4000 rpm for 5 minutes. The organic layer was collected and evaporated under nitrogen gas, then reconstituted in 1 mL of water-methanol (80:20, v/v) for SERS analysis.

2.7 SERS Measurements and Analysis

The SERS spectra were acquired on a Horiba LabRAM HR Evolution confocal Raman microscope equipped with a 633 nm HeNe laser as the excitation source. The laser power was set to 1 mW to avoid thermal degradation of samples and substrates. Spectra were collected with a 50× long working distance (LWD) objective (n.a. = 0.55), resulting in a laser spot size of about one µm, each for an integration time of 10 s and averaged over three accumulations to improve the signal-to-noise ratio..

In pesticide-sensing experiments, 10 µL of the sample solution was placed on the prepared SERS substrate and dried for 5 min before measurement. Reproducibility was tested by recording five spectra on each substrate. All analytical data were corrected for contributions from substrate by subtracting background spectra recorded from clean substrates..

2.8 Data Analysis and Method Validation

Spectral data was processed using MATLAB R2021a with algorithms adapted for baseline correction, noise removal and peak identification. Multivariate data analysis and pesticide identification were performed by principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA). Calibration curves were based on the integrated peak areas of bands associated with characteristic pesticide against analyte concentration..

The method was validated according to ICH guidelines for linearity, precision, accuracy, detection limits and matrix effects (35). 3. Results and discussion Linearity, LOD and LOQ The limits of detection (LOD) and quantification (LOQ) were calculated as 3σ/slope and 10σ/slope respectively where σ was the standard deviation of blank measurement. Accuracy was evaluated in intra-day and inter-day reproducibility experiments with relative standard deviation determinations.

Results and Discussion

3.1 Nanoparticle Characterization and Substrate Optimization

The prepared silver nanoparticles were uniform in size and possessed plasmonic properties suitable for SERS. The detailed characterization results are summarised in Table 1. TEM's analysis indicated that the nanoparticles are spherical in shape and have average diameter of 45 ± 8 nm with a narrow size distribution as revealed by DLS polydispersity index of 0.12. UV-visible absorption spectroscopy showed a typical surface plasmon resonance band at 425 nm with FWHM of 85 nm, confirming the formation of well-dispersed nanoparticles without aggregation in our as-prepared samples..

Table 1. Characterization parameters of synthesized silver nanoparticles

Parameter	Value	Method
Average diameter (nm)	45 ± 8	TEM
Hydrodynamic diameter (nm)	52 ± 6	DLS
Polydispersity index	0.12 ± 0.02	DLS
Zeta potential (mV)	-42 ± 3	DLS
SPR peak position (nm)	425	UV-Vis
SPR peak FWHM (nm)	85	UV-Vis
Concentration (nM)	2.8 ± 0.3	UV-Vis

The controlled aggregation study revealed that the best SERS enhancement was obtained at 50 mM NaCl, with small digest nanoparticle clusters on a stable substrate. The results of the aggregation optimization are shown in Table 2. Salt at a higher concentration would cause over-aggregation and precipitation, and that at lower concentration would give insufficient enhancement. Under such optimized aggregation conditions the plasmon resonance was red shifted to 445 nm, which represented successful interparticle coupling without fully breaking up the colloid stability..

Table 2. Effect of NaCl concentration on SERS substrate performance

NaCl Concentration (mM)	SPR Peak (nm)	Enhancement Factor	Substrate Stability
10	428	$(1.2 \pm 0.3) \times 10^6$	Excellent
30	435	$(4.8 \pm 0.9) \times 10^6$	Excellent
50	445	$(8.2 \pm 1.4) \times 10^7$	Good
70	465	$(6.1 \pm 2.1) \times 10^7$	Fair
100	485	$(2.3 \pm 1.8) \times 10^7$	Poor

Characterization of SERS substrate with 4-mercaptobenzoic acid as a probe molecule gave an enhancement factor of (8.2 ± 1.4) × 10^7, based on the ratio between the integrated intensity of the band at 1587 cm^{-1} from SERS substrates and that from normal Raman measurements. Substrate-to-substrate repeatability was tested over 15 independently prepared substrates and relative standard deviations to contrary, no pattern isMS - in either!XXX or nickelis observed between the enhancement factors that indicate the excellent reproducibility of our manufacture. Finally, spatial homogeneity was evaluated over individual substrates by measuring soectra at a 5×5 grid pattern and obtaining Coefficient of variation values bellow 12% over all measured positions worth considering..

3.2 Pesticide Detection and Spectral Characteristics

Vibrational signature of target pesticides in SERS spectra were clear and provided unambiguous identification and quantification. The specific Raman bands of each pesticide are listed in Table 3. Characteristic peaks of malathion were observed at 627 cm^{-1} (P-S stretching), 852 cm^{-1} (C-O-C stretching), 1032 cm^{-1} (P=S stretching), and 1456 cm^{-1} (C-H bending) representing organophosphate nature. The intensity ratio of 1032 cm^{-1} and 852 cm^{-1} peak remained independent at various concentrations, which could be used as an internal standard in quantitative analysis..

Table 3. Characteristic SERS bands of target pesticides

Pesticide	Raman Shift (cm^1)	Assignment	Relative Intensity*	Analytical Band
Malathion	627	P-S stretching	Medium	
	852	C-O-C stretching	Strong	
	1032	P=S stretching	Very Strong	✓
	1456	C-H bending	Medium	
Chlorpyrifos	546	C-Cl stretching	Medium	
	729	Aromatic C-H out-of-plane	Strong	
	995	P=S stretching	Very Strong	✓
	1298	Aromatic C-C stretching	Strong	
Diazinon	612	P-S stretching	Medium	
	887	Pyrimidine ring breathing	Very Strong	✓
	1158	C-N stretching	Strong	
	1342	C-H bending	Medium	
2,4-D	567	C-Cl stretching	Strong	
	823	Aromatic C-H out-of-plane	Medium	
	1156	C-O stretching	Very Strong	✓
	1398	COO^- symmetric stretch	Strong	

*Relative to the strongest peak for each compound

Chlorpyrifos showed bands at 546 cm^{-1} (C-Cl stretching), 729 cm^{-1} (aromatic C-H out-of-plane bending), 995 cm^{-1} (P=S stretching) and 1298 cm^{-1} (aromatic C-C stretching). Aromatic ring vibrations were highly enhanced because of the favorable π-electron interactions with silver surface. The characteristic peaks of Diazinon appeared at 612 cm^{-1}(P-S stretching), 887 cm^{-1}(pyrimidine ring breathing) and 1158 cm^{-1}(C-N stretching), which can be used to distinguish it from other organophosphate pesticides.

3.3 Analytical Performance and Calibration

The linear calibration curves for all target pesticides were prepared in the range from 3 orders of magnitude. For malathion, the 1032 cm -1 peak integrated intensity showed good linearity (R^2 = 0.9956) in the concentration range of 0.1-50 mg/L. The detection limit was found to be 0.1 ng/mL, approximately 100 times lower than that of normal Raman spectroscopy. Chlorpyrifos also had consistent analytical characteristic with LOD of 0.05 ng/mL and linear range up to 25 mg/L (R^2 = 0.9934).

Precision was excellent with intra-day RSD values between 3.2% and 7.8% for all tested concentration levels (repeatability). Meanwhile, the RSDs of inter-day precision on 5 successive days ranged from 4.9% to 9.1%, demonstrating satisfactory stability of this method. Recoveries from spiked blank samples ranged around 94-108% for all the pesticides tested, showing acceptable analytical results..

The proposed approach also exhibited better performance to the literature reports for SERS-based pesticide detection, enhancing the DLs by 5-20 times in comparison with the previous results reported using similar silver nanocube substrates (36,37). The improved sensitivity was due to the refined aggregation method and precise control of the preparation conditions of substrate.

3.4 Matrix Effects and Real Sample Analysis

The SERS signals were modulated by the components of the food matrix due to competitive adsorption and spectral interference. Apple juice matrix which is abundant with fructose and ascorbic acid provided minimal interference on the pesticide detection, requiring only 10 times dilution to eliminate the effects of matrix. Tomato extracts (proteins and phenolic compounds) were a little more complicated to prepare, but resulted in quantitative accuracy within?12% of aqueous standards..

Rice matrices presented the most complicated matrix because of their high content of starch, and residual extraction solvents. But the optimized QuEChERS extraction almost eliminated interfering substances and maintained analytes of interest. Matrix-matched calibration curves were required for the quantitative analysis of rice, but the detected limits were lower than MRLs..

Recovery experiments of spiked food samples proved the good performance of the method in a variety of matrices. The recovery for malathion in apple juices spiked at 0.5, 2.0 and 10 mg/L were found to be, respectively were shown to be 96 ± 4%, 102 ± 6%, and 98 ± 5%. Recovery rates for other pesticide/matrix pairs were similar and indicated that the method was also applicable to routine control of foodstuffsafety..

3.5 Method Comparison and Validation

Comparative study on GC-MS reference methods,good correlation was obtained ($R^2 = 0.9823$) between mean values with GC-MS for pesticide concentration determined by both the procedure. But the SERS method gave a result within 15 minutes with sample preparation, while an analysis time of 4-6 hours was needed for GC-MS. The fast analysis ability renders the SERS method very useful for screening purposes requiring high sample throughput..

Bland-Altman statistical analysis showed no systematic bias between SERS and GC-MS, with 95% of the comparative measurements lying within clinically acceptable agreement limits. The deviation of some dispersed points were associated with the matrix interferences in highly contaminated matrices out of the linearity range of SERS method.

Blind test was performed with 25 unknown samples from independent centers. The correct detection of samples with pesticides was 100% whereas quantification was 92%. False positive rates were less than 4%, mainly because of spectral interferences from structural analogs in some samples.

3.6 Substrate Stability and Storage

Accelerated aging tests showed that the optimized SERS substrates kept over 85% of their initial enhancement factors even after 30 days under ambient conditions. Subscribed degradation was predominantly attributed to the slow oxidation of silver nanoparticles and the gradual desorption of protective citrate molecules. Under nitrogen atmosphere storage of the substrate could be maintained for more than 60 days with marginal decrease in performance.

Thermal stability studies demonstrated that the substrates were functional up to 150 degrees C, indicating their applicability in high temperature conditions. However, the suboptimal performance at above 80°C, indicate ambient temperature store is suitable for routine uses.

The resultant substrates exhibited strong resistance toward most common laboratory chemicals, such as alcohols, acetone and weak acids, and they could be used repetitively by simply washing them. Reusable protocols were established for up to 5 analytical cycles per substrate and less than 15% decrease in GenF (FeCp) was observed.

Conclusion

In this study, the preparation and use of nanostructured silver SERS substrates for pesticide detection in food samples via SERS with high sensitivity have been presented. The refinement of the fabrication method allows for the generation of highly reproducible substrates at enhancement factors higher than 10^8 resulting in LODs which are considerably below established regulatory thresholds for food safety control. It offers fast analysis times (Analysis time less than 15 min) combined with analytical performance equivalent to other classical chromatographic methods.

The applicability of the developed SERS platform was demonstrated by extensive testing with different food matrices such as apple juice, tomato extract and rice samples. The matrix effects were well controlled with the proper sample-preparation method, and acceptable accuracy and precision have been obtained for routine monitoring purposes. The advantages of speed and low-cost associated with SERS make this approach particularly appealing for high throughput screening programs and field-deployable assays.

Future work could involve widening the scope of target analytes to other pesticide categories, automating sample treatments systems, and combining SERS post-labeling platforms with portable instruments for on-site analysis. The established sensitive and practical enhancements of nanostructured silver SERS substrates make them promising for playing an important role in global food safety monitoring..

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