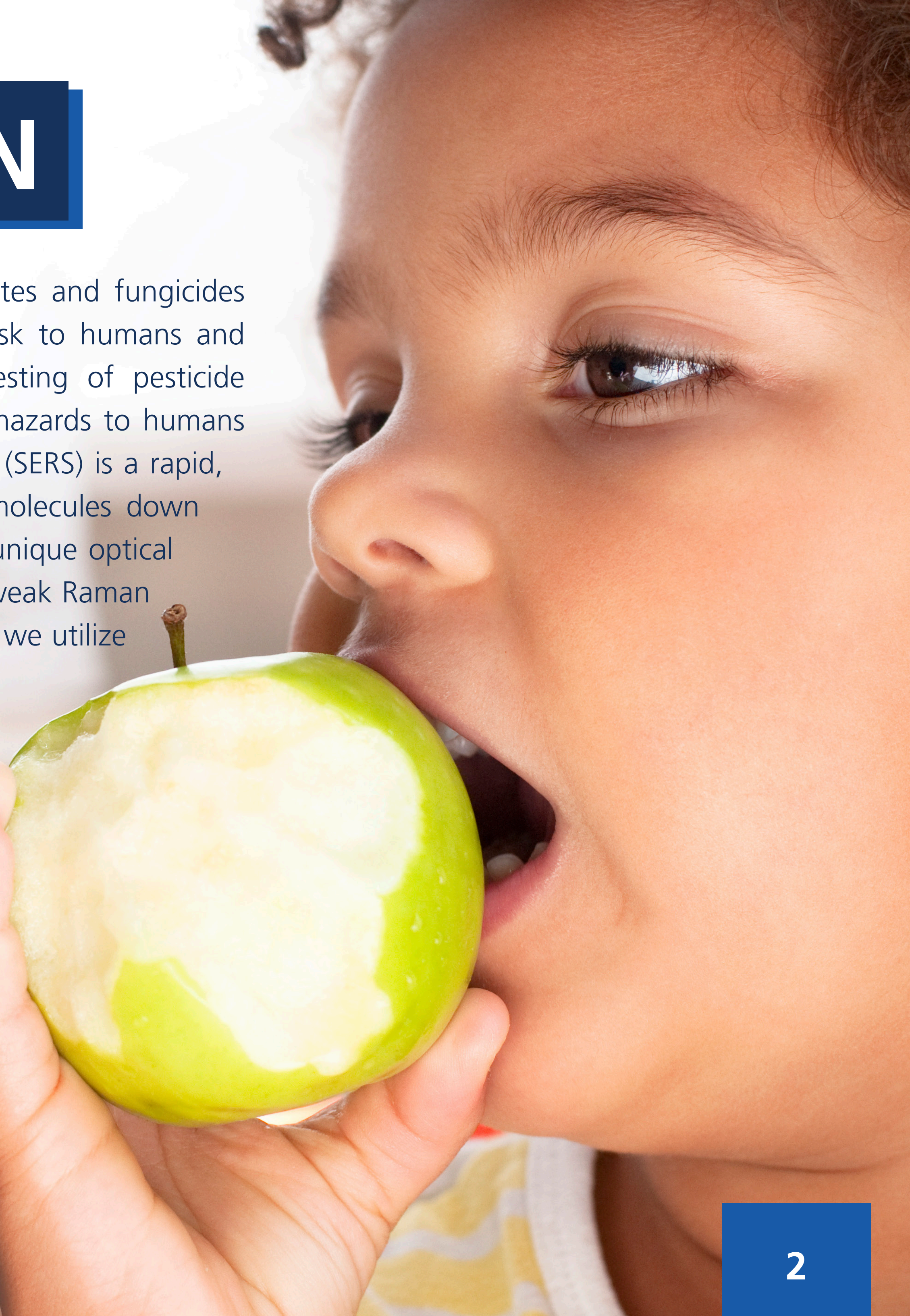
DETECTION OF PESTICIDE RESIDUES ON FRUIT SURFACES USING SURFACE ENHANCED RAMAN SPECTROSCOPY

Anne-Marie Dowgiallo and Derek Guenther
8060 Bryan Dairy Road | Largo, FL 33777 | USA

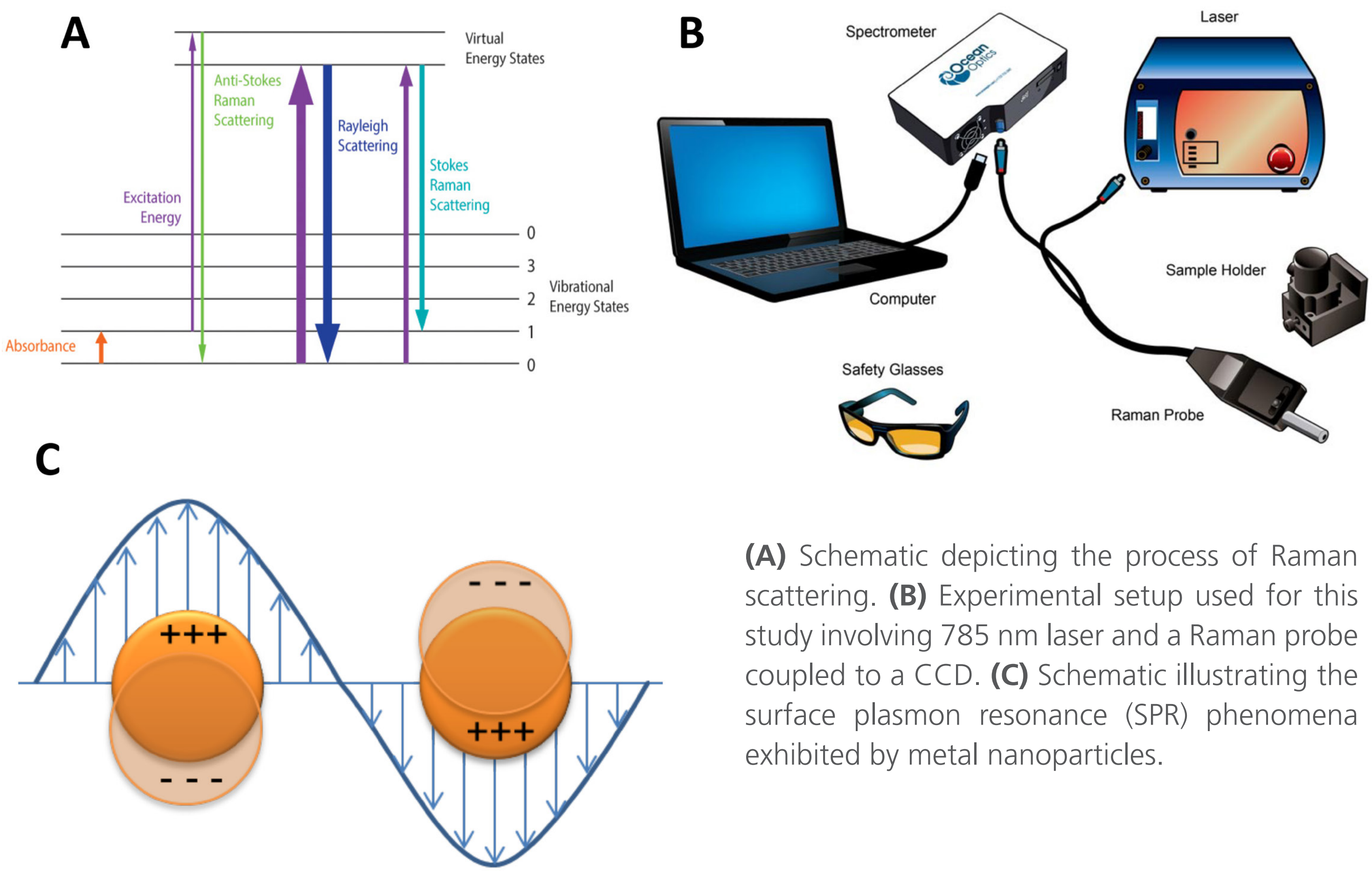
Ocean Optics

INTRODUCTION

Commonly used pesticides such as organophosphates and fungicides can attack the central nervous system, posing a risk to humans and other animals upon exposure. Hence, accurate testing of pesticide residues is imperative to minimize potential health hazards to humans and wildlife. Surface enhanced Raman spectroscopy (SERS) is a rapid, sensitive, and cost-effective tool for detection of molecules down to picogram or femtogram levels. SERS utilizes the unique optical properties of metallic nanoparticles to enhance the weak Raman scattering exhibited by most molecules. In this work, we utilize a swabbing technique to detect trace levels of pesticides on apple skin, including malathion, phosmet, imidacloprid, and thiram, using a gold nanoparticle based SERS substrate and a Raman experimental setup that involves 785 nm laser excitation and a thermoelectrically cooled CCD spectrometer. In addition, we demonstrate part-per-billion (ppb) detection of several other pesticides with another SERS substrate that consists of a gold/silver alloy thin film.



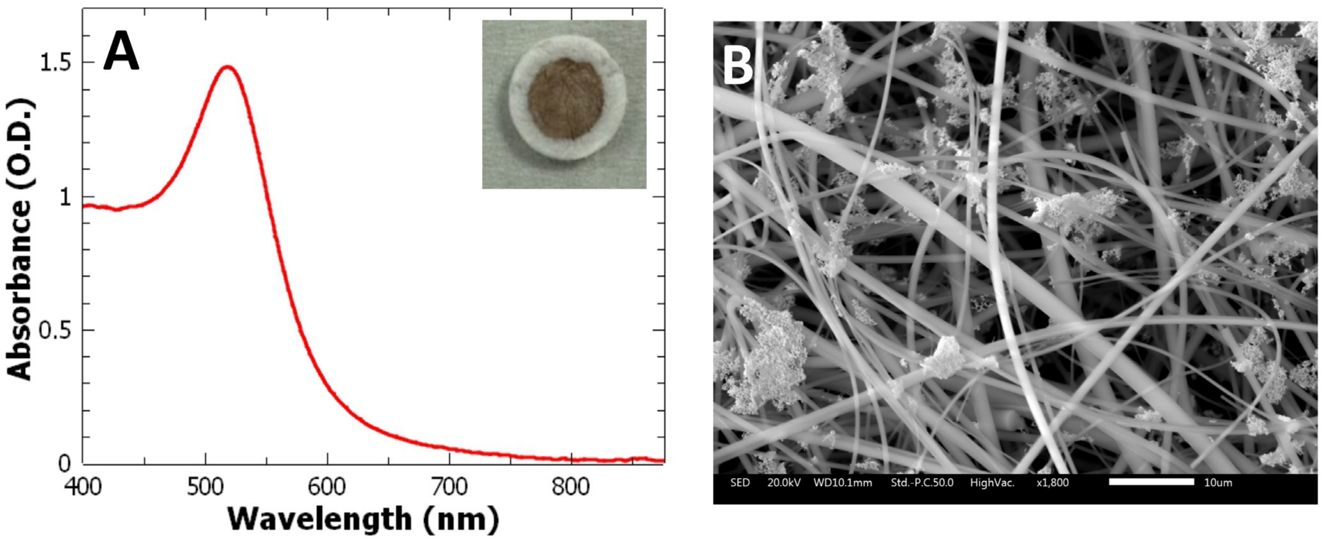
SURFACE ENHANCED RAMAN SPECTROSCOPY



(A) Schematic depicting the process of Raman scattering. **(B)** Experimental setup used for this study involving 785 nm laser and a Raman probe coupled to a CCD. **(C)** Schematic illustrating the surface plasmon resonance (SPR) phenomena exhibited by metal nanoparticles.

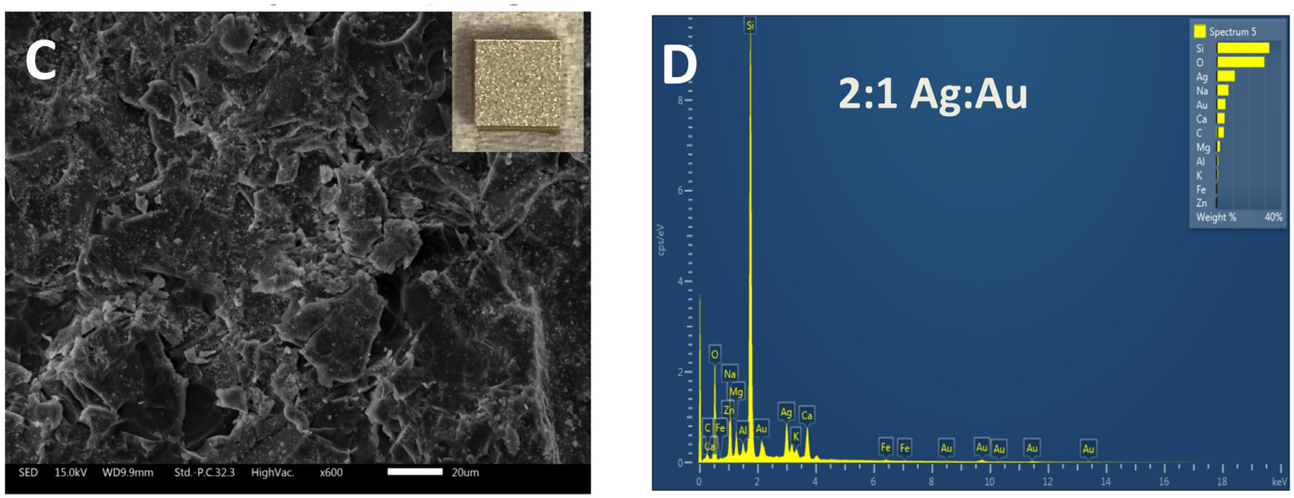
SERS SUBSTRATES

Gold nanospheres embedded in quartz paper

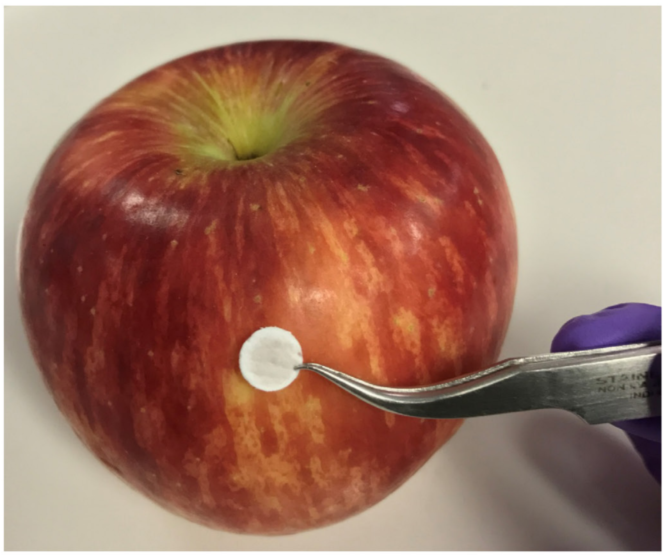


(A) Absorption spectrum of gold nanoparticles with photograph of gold SERS paper substrate (inset). **(B)** SEM image of gold SERS paper substrate. **(C)** SEM image of gold/silver alloy nanosponge substrate, with inset showing an image of the substrate having 4 x 4 mm dimensions. **(D)** EDS analysis of gold/silver nanosponge substrate.

Gold/silver alloy nanosponge



SWABBING TECHNIQUE



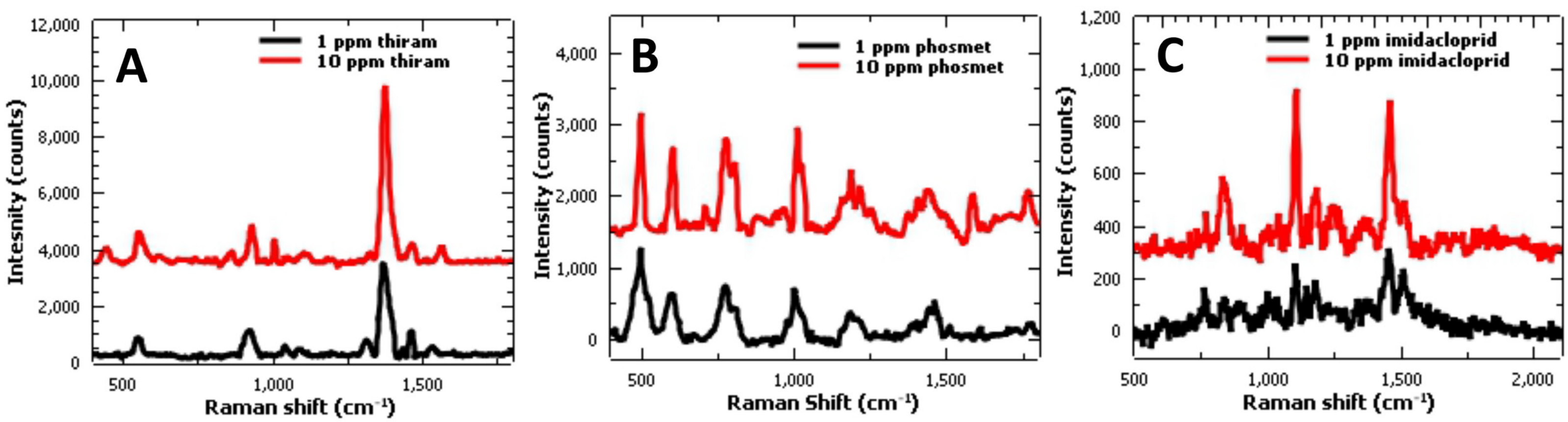
Background

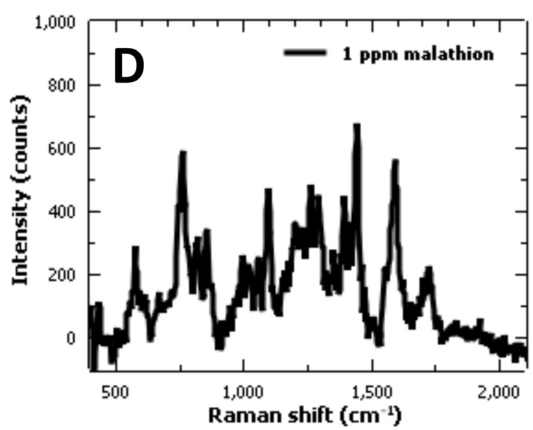
Apple skin
+
Solvent

Sample

Apple skin
+
Pesticide

TRACE LEVEL DETECTION OF PESTICIDES



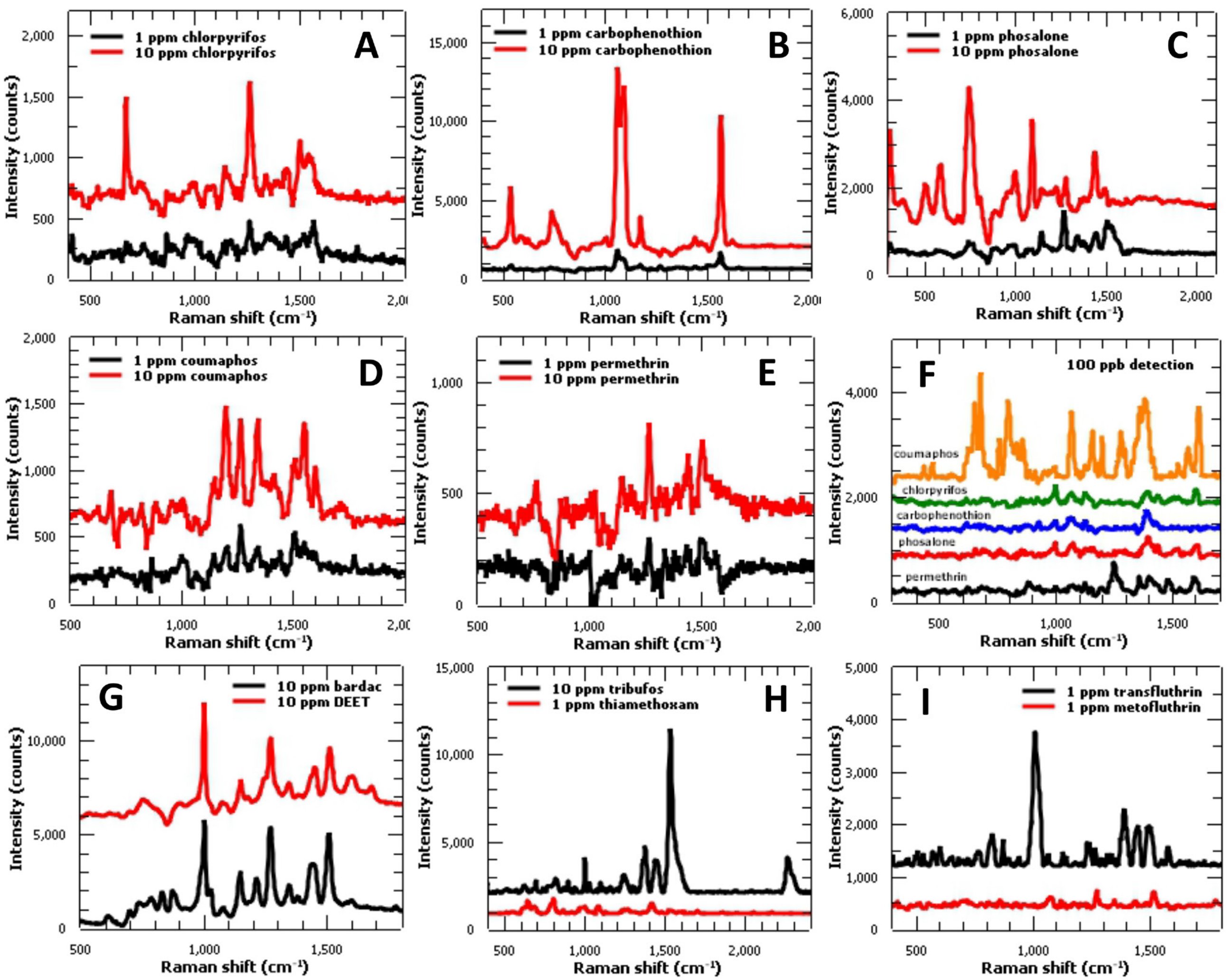


Thiram		Malathion		Imidacloprid		Phosmet	
552	ν(SS)	860	ν(C–O–C)	830	δ (C–C–C)	500	ρ(CH_2) + ρ(PO_2)
931	ν(CH_3N) + ν(C=S)	1100	ν(C–C)	1110	(C–C–C)	601	δ(C=O)
1380	δ_s(CH_3) + ν(CN)	1446	δ(CH_2) + δ(CH_3)	1458	δ(CH)	1012	ν_{as}(P–O–C)
		1720	ν(C=O)			1188	δ(C–N)
						1768	ν(C=O)

ν: stretching, δ: deformation vibration, ρ: rocking, s: symmetric, as: asymmetric

Raman spectra of surface swabs of the pesticides **(A)** thiram, **(B)** phosmet, **(C)** imidacloprid, and **(D)** malathion after 785 nm laser excitation using 3 seconds integration time and 15 mW power. The limit of detection for these four pesticides is 1 ppm using the swab method.

TRACE LEVEL DETECTION OF PESTICIDES



SERS spectra of the pesticides **(A)** chlorpyrifos, **(B)** carbophenothion, **(C)** phosalone, **(D)** coumaphos, **(E)** permethrin, **(G, black)** Bardac™, **(G, red)** DEET, **(H, black)** tribufos, **(H, red)** thiamethoxam, **(I, black)** transfluthrin, and **(I, red)** metofluthrin after applying 15 μL of each to a gold nanoparticle substrate and interrogating with 785 nm laser excitation using 3 seconds integration time and 15 mW power. Some of these pesticides **(A – E)** were then detected at 100 ppb using gold/silver alloy nanosponge substrates with 638 nm laser excitation, 3 seconds integration time, and 20 mW power **(F)**.

SUMMARY

We present a swab method that utilizes a gold nanoparticle based SERS substrate to detect trace levels of thiram, malathion, imidacloprid, and phosmet on apple skin. The current technique can detect each of these pesticides down to 1 ppm, where the pesticide residue tolerances on apples as established by the 2016 Code of Federal Regulations for imidacloprid, thiram, malathion, and phosmet are 0.5, 7, 8, and 10 ppm, respectively. Raman spectroscopic measurements were carried out using a cost-effective experimental setup consisting of a 785 nm laser, Raman probe, and thermoelectrically cooled spectrometer. Additional experiments on several other pesticides demonstrate the versatility of the gold SERS paper substrates, and tests with gold/silver alloy nanosponge substrates indicate that ppb-level detection is also possible with some of these pesticides. The results presented here indicate that SERS is a useful tool for identifying pesticide residues on the surface of fruits for food quality and safety control.