# *Supporting Information*

# *A facile method for in-situ detection of thiabendazole residues in fruit and vegetable peels using Surface-Enhanced Raman Spectroscopy*

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**Glassware cleaning procedure**

All glassware were exhaustively cleaned by immersion in a beaker with a hot alkaline potassium permanganate (Analar, England) solution for at least an hour and later rinsed first with distilled water, then with an acidic solution of hydrogen peroxide (Cicarelli, San Lorenzo, Santa Fe, Argentina), and finally with Milli-Q water. The glassware used with silver nanoparticles were cleaned in a bath of freshly prepared aqua regia ($HCl:HNO_3$=3:1, HCl (Cicarelli, USA) and $HNO_3$ (Cicarelli, San Lorenzo, Santa Fe, Argentina)) and later rinsed carefully with Milli-Q water.

**Preparation of the SERS substrate**

0.2 g of agar was mixed in a beaker with 10 mL of the as synthesized Ag NPs dispersion and then heated in a microwave oven at 700 W for few seconds until boiling. Then, the mixture was poured into a Petri dish reaching a height of about 0.5 cm. Once cooled, the Petri dish was wrapped with aluminum foil and storage in the fridge until being used.

**Table S1.** Wavenumber ($cm^{-1}$) and tentative assignment of selected bands of TBZ in the Raman spectra of a solid sample and of a saturated methanol solution ($4.0\times10^{-2}$ M) and in the SERS spectra of TBZ

| TBZ solid powder | TBZ in methanol solution | TBZ on Ag NPs gel SERS substrate | Tentative Assignment [a] |
|---|---|---|---|
| 3092 (w) | | Broad band at ~3075 $cm^{-1}$ | ν (C–H) Thi |
| 3065 (w) | | | ν (C–H) Thi |
| 3045 (w) | | | ν (C–H) Ph |
| 1620 (w) | 1592 (m) | 1622 (sh) | ν (C=C) Ph |
| 1588 (sh) | | 1596, 1588 (m or s depending on the TBZ concentration and/or spot) | ν (C=C) Ph |
| 1575 (vs) | 1576 (s) | 1574 (s) | ν (C3–C4) Ph |
| 1453 (s) | | | ν (C1=N2) Th |
| 1275 (s) | 1276 (s) | 1276 (s) | ν (C5–N3) Imi |
| 1010 (m) | | 1009 (m) | ν (C–C) Ph |
| 984 (m) | | 983 (m) | δ (NCN) Imi |
| 896 (w) | | 900 (m) | δ (C3N2C1)/δ (CC) Ph |
| 875 (w) | | 884 (m) | $\nu_s$ (C1SC2) Thi |
| 778 (m) | 779 (m) | 782 (m) | $\nu_{as}$ (C1SC2) Thi |

[a]Atom numbering of Figure S4. vs = very strong; s = strong; m = medium; w = weak; sh = shoulder; ν = stretching; as = antisymmetric; s = symmetric; δ = in-plane bending; γ = out-plane bending; Ph = vibrations of the phenyl group; Thi = vibrations of the thiazole ring; Imi = vibrations of the imidazole ring.

**Table S2.** Comparison of different SERS substrates for TBZ detection on fruit or vegetable peels

| SERS substrate | Matrix | LOD | References |
|---|---|---|---|
| Ag nanorods adhesive tape substrate | Spinach surface | $10^{-6}$ M | [S1] |
| Au nanorods array substrate | Apple surface | 0.06 ppm | [S2] |
| Au/Ag nanoparticles grown over cellulose acetate | Apple surface | 15.1 ng/cm$^2$ | [S3] |
| Polyurethane micelle/Ag colloid | Vegetables and fruit skin | 20 ng/mL | [S4] |
| Au colloid | Apple | 0.1 μg/g | [S5] |
| Ag dendrites in swab stick | Apple surface | 0.1 μg/g | [S6] |
| Cellulose nanofibers coated with AgNPs | Apple | 5 ppm | [S7] |
| AgNPs in hydrogel | Orange peel | 2.5 ng/cm$^2$ | [S8] |
| Ag NPs gel substrate | Apple peel | 0.20 μg/cm$^2$ | This work |
| Ag NPs gel substrate | Pear peel | 40 ng/cm$^2$ | This work |
| Ag NPs gel substrate | Eggplant and green pepper peels | 50 ng/cm$^2$ | This work |
| Ag NPs gel substrate | Tomato and strawberry peels | 0.50 μg/cm$^2$ | This work |

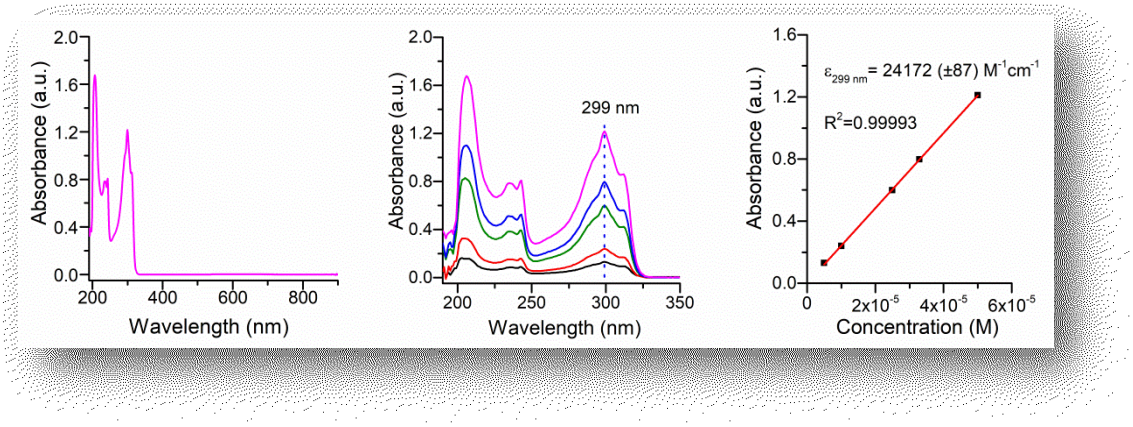


**Figure S1.** Left: UV-Vis absorption spectrum of thiabendazole in methanol solution $5.0\times10^{-5}$ M in 190–900 nm spectral region; Middle: UV-Vis absorption spectra of thiabendazole in methanol solutions in 190–350 spectral range, from bottom to top: $5.0\times10^{-6}$; $1.0\times10^{-5}$; $2.5\times10^{-5}$; $3.3\times10^{-5}$ and $5.0\times10^{-5}$ M. Right: linear calibration plot of absorbance at 299 nm against the TBZ concentration.

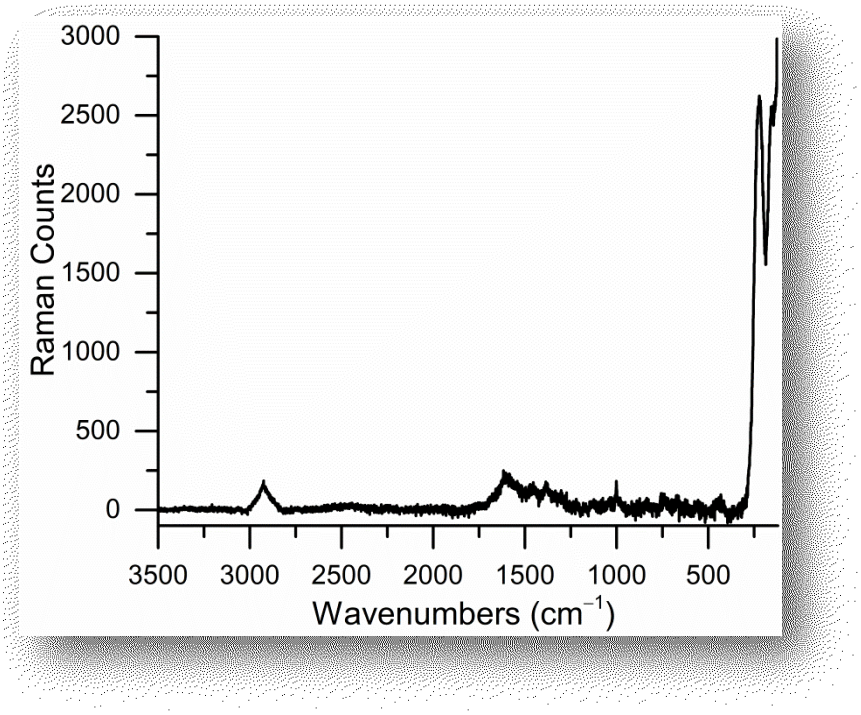


**Figure S2.** Blank Raman spectrum of dehydrated Ag NPs gel substrate. The sample was prepared dropping 20.0 μL of methanol onto 1 $cm^2$ of the substrate and subsequently allowed to dehydrate at room temperature. The spectrum baseline was corrected. (Excitation wavelength: 647.1 nm; laser power 100 mW; acquisition time: 10 s; 4 accumulations; 50× objective (0.75NA)).

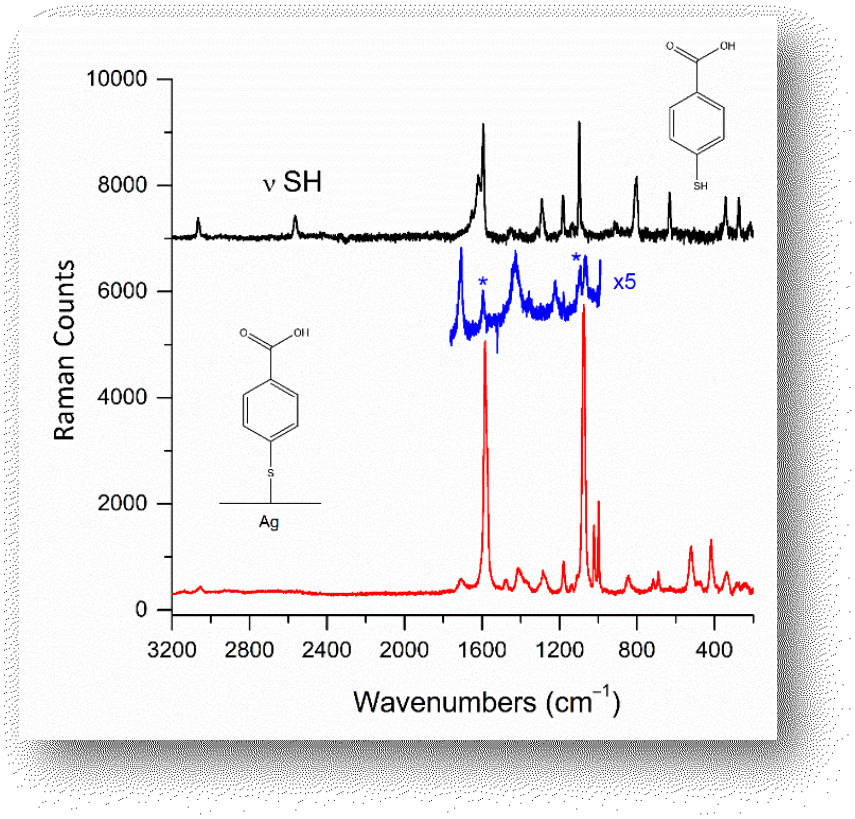


**Figure S3.** From top to bottom: Raman spectrum of 4-mercaptobenzoic acid (4-MBA) powder sample (black-trace, acquisition time: 40 s; 4 accumulations), the spectrum baseline was corrected; Raman spectrum of 0.16 M solution of 4-MBA in acetone (blue-trace, the bands of 4-MBA are indicated with an asterisk, acquisition time: 120 s; 4 accumulations) and SERS spectrum of 4-MBA on the Ag NPs gel substrate containing 3.1 μg/cm$^2$ of 4-MBA (20.0 μL of $1.0\times10^{-3}$ M solution, red-trace, acquisition time: 10 s; 4 accumulations), the spectrum baseline was corrected. Excitation wavelength of 647.1 nm; laser power: 100 mW; 50× objective (0.75NA).

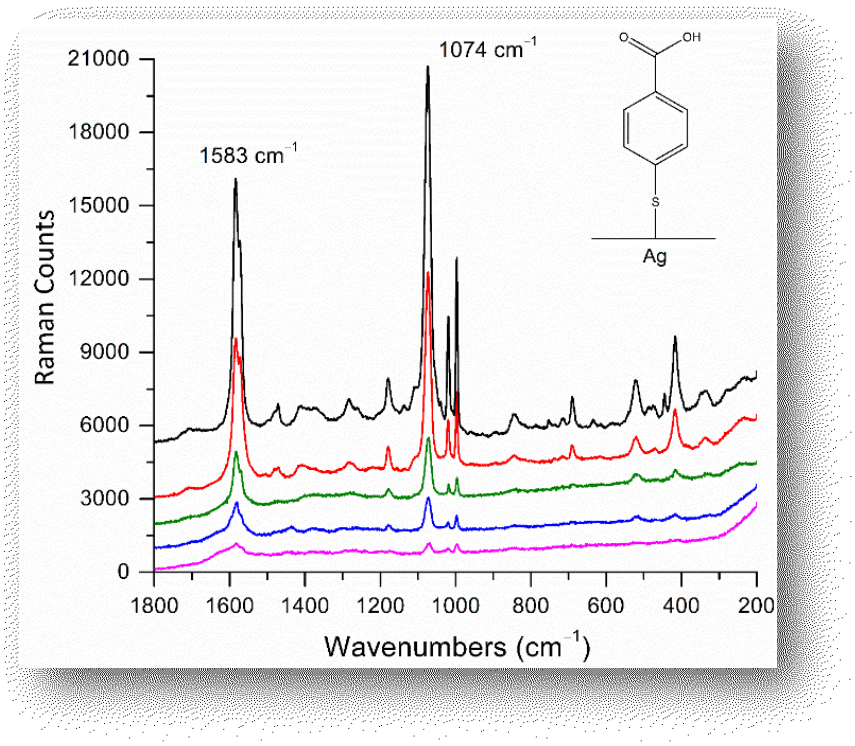


**Figure S4.** a) SERS representative spectra of 4-MBA on Ag NPs gels. Each spectrum correspond to a substrate containing a different amount of 4-MBA. The SERS substrate were loaded with 20.0 μL of 4-MBA ethanol solutions of (from top to bottom) $1.0\times10^{-2}$ (black-trace), $1.0\times10^{-3}$ (red-trace), $1.0\times10^{-4}$ (green-trace), $1.0\times10^{-5}$ (blue-trace) and $1.0\times10^{-7}$ M (magenta-trace). The spectra baselines were not corrected. Excitation wavelength: 647.1 nm; laser power: 100 mW; acquisition time: 10 s; 4 accumulations; 50× objective (0.75NA)).

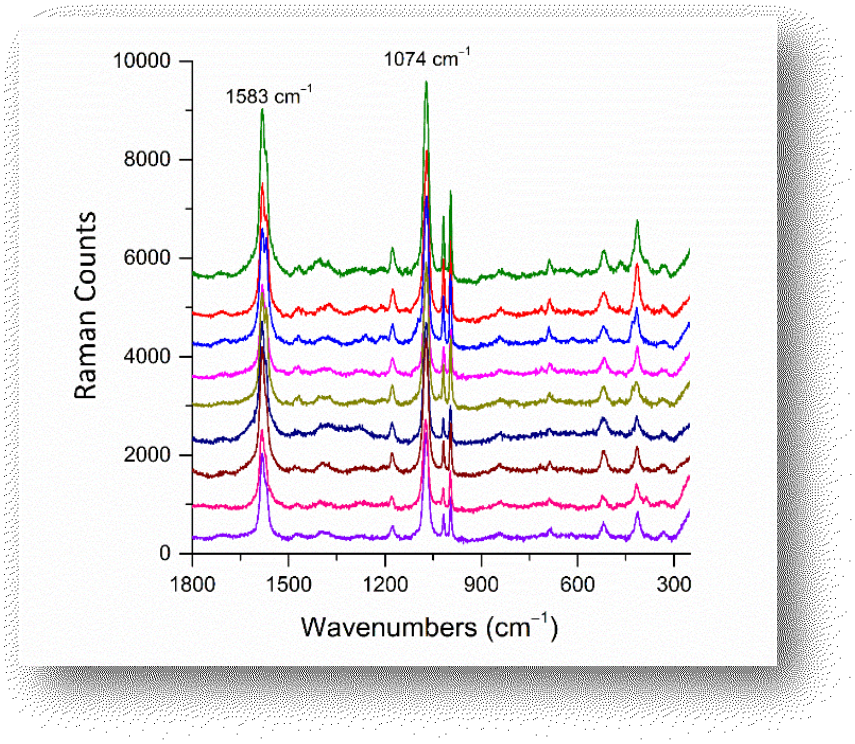


**Figure S5.** a) SERS spectra of Ag NPs gel substrate containing 0.30 μg/cm$^2$ (20.0 μL of $1.0\times10^{-4}$ M solution) collected at different spots of the substrate. (Excitation wavelength: 647.1 nm; laser power: 100 mW; acquisition time: 10 s; 4 accumulations; 50× objective (0.75NA)).

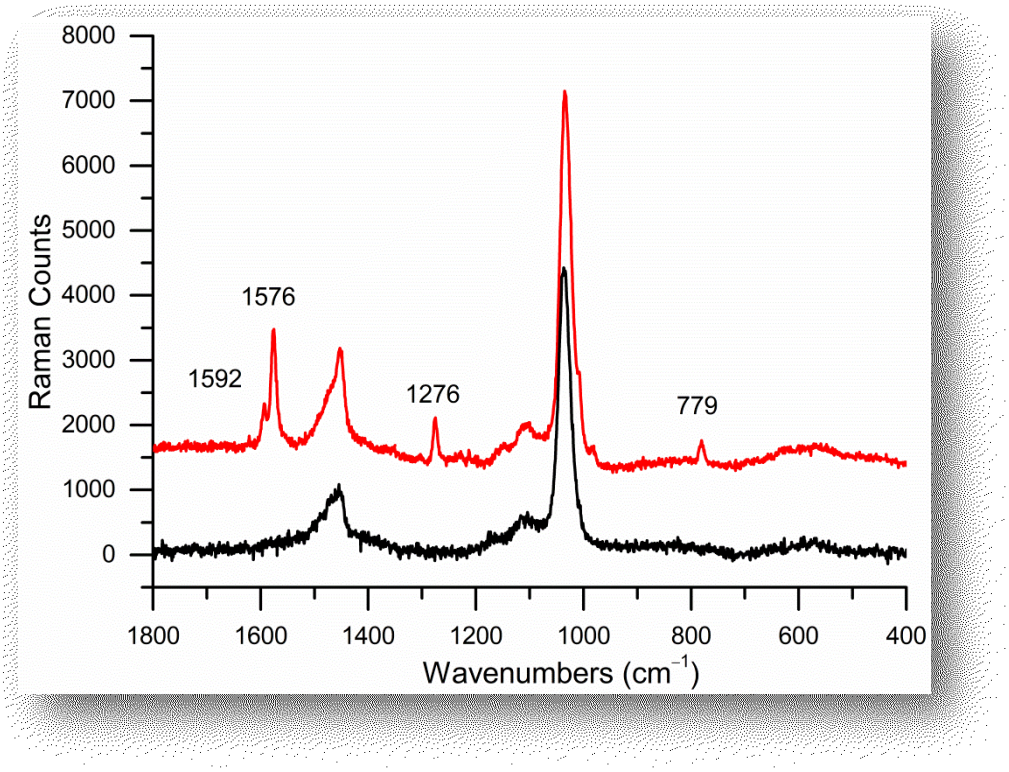


**Figure S6.** Raman spectra of a solution of thiabendazole in methanol $4.0\times10^{-2}$ M (red-trace) (excitation wavelength: 647.1 nm; laser power 200 mW; acquisition time: 120 s; 8 accumulations; 10× objective (0.25NA)) compared with methanol (black-trace) (excitation wavelength: 647.1 nm; laser power 200 mW; acquisition time: 20 s; 8 accumulations; 10x objective (0.25NA)).

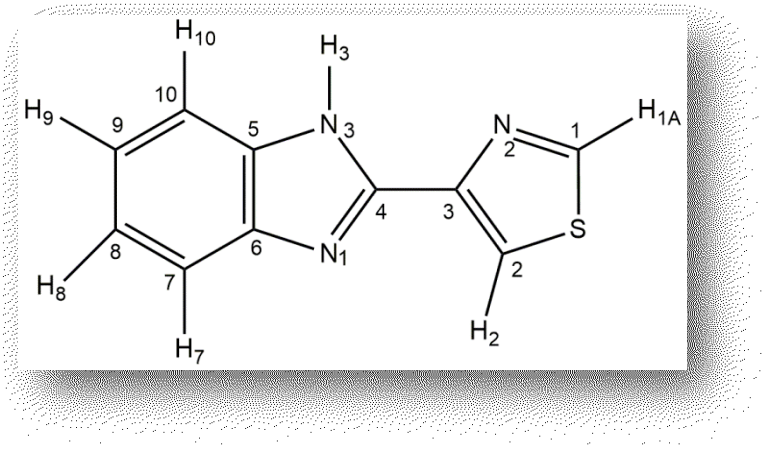


**Figure S7.** Schematic representation of the thiabendazole molecule ($C_{10}H_7N_3S$).

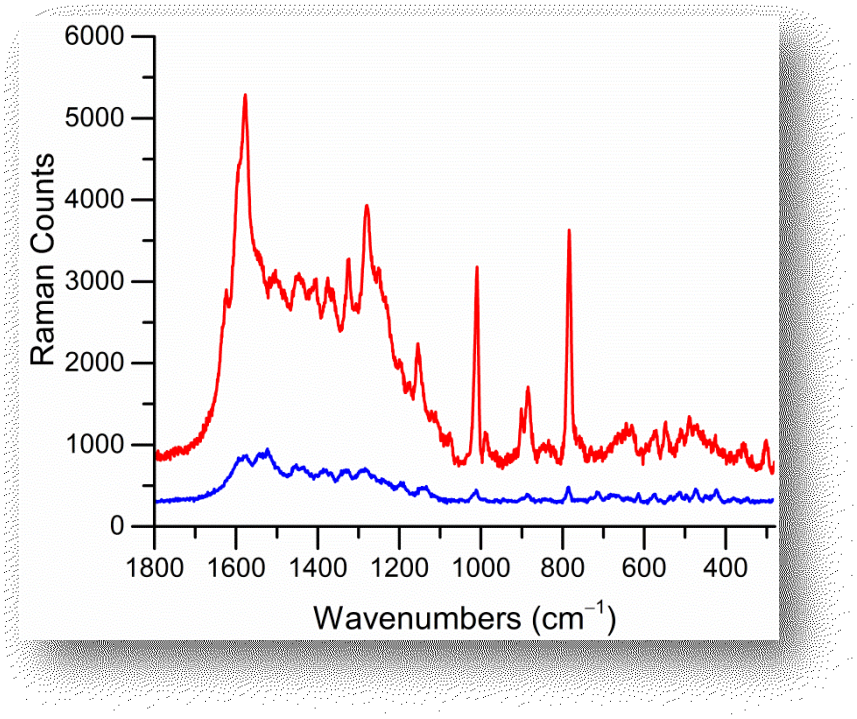


**Figure S8.** Selected SERS spectra of thiabendazole on the Ag NPs gel substrate containing 4.0 μg/cm$^2$ of thiabendazole before (botton, blue-trace) and after (top, red-trace) dehydration of the substrate (Excitation wavelength: 647.1 nm; laser power: 100 mW; acquisition time: 10 s; 4 accumulations; 50× objective (0.75NA)).

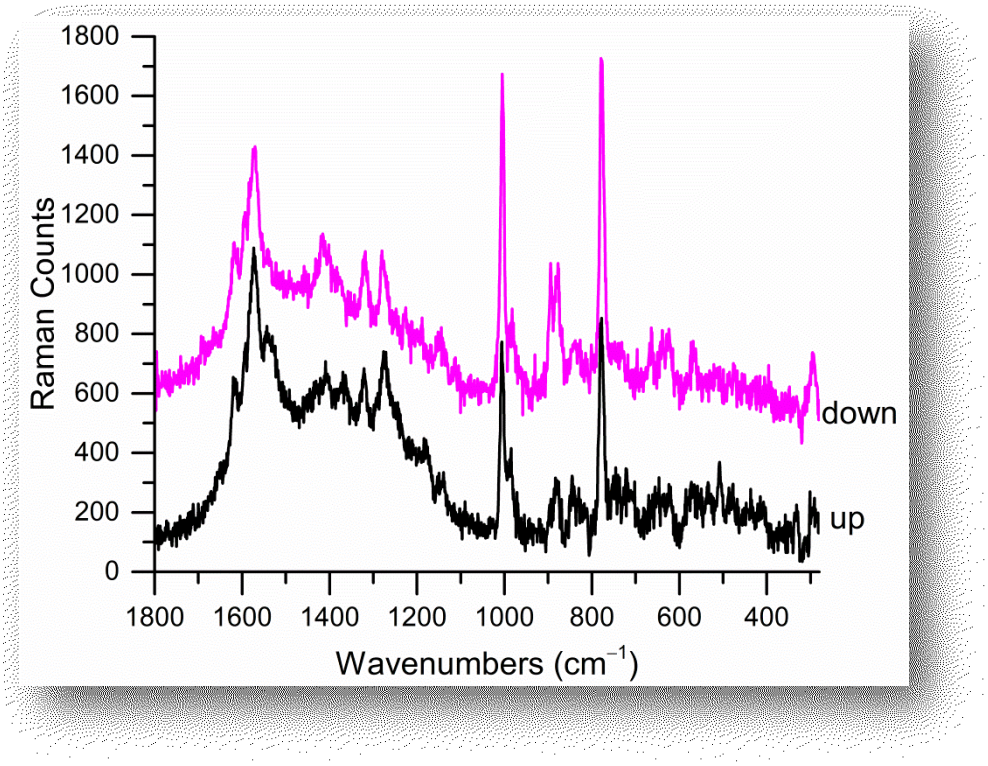


**Figure S9.** Selected SERS spectra of thiabendazole on the Ag NPs gel substrate containing ~ 2 μg/cm$^2$ of thiabendazole measured in both sides of the dehydrated gel substrate (up and down). (Excitation wavelength: 647.1 nm; laser power: 100 mW; acquisition time: 10 s; 4 accumulations; 50× objective (0.75NA)).

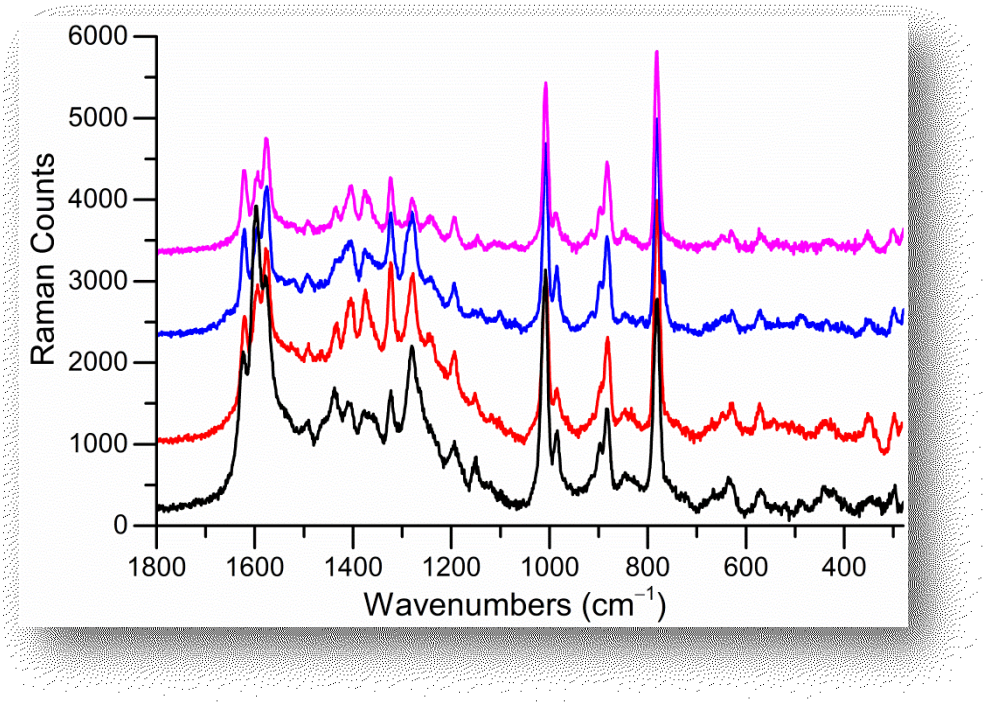


**Figure S10.** Selected SERS spectra of a dehydrated Ag NPs gel substrate containing ~ 2 μg/cm$^2$ of thiabendazole, from bottom to top: freshly prepared (bottom, black-trace), after 5 months (red-trace), 16 months (blue-trace) and 22 months (top, magenta-trace). (Excitation wavelength: 647.1 nm; laser power: 100 mW; acquisition time: 10 s; 4 accumulations; 50× objective (0.75NA)).

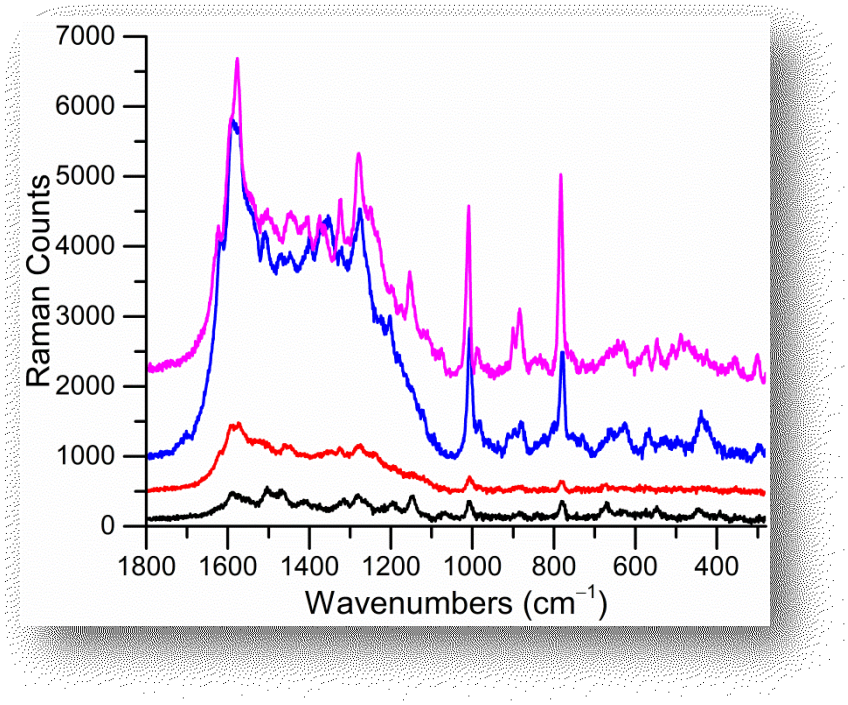


**Figure S11.** Selected SERS spectra of different dehydrated Ag NPS gel substrates all containing 4.0 μg/cm$^2$ of thiabendazole, from bottom to top: 3 months old substrate (bottom, black-trace), 2 months old substrate (red-trace), 1 month old (blue-trace) and 4 days old substrate (top, magenta-trace). (Excitation wavelength: 647.1 nm; laser power: 100 mW; acquisition time: 10 s; 4 accumulations; 50× objective (0.75NA)).

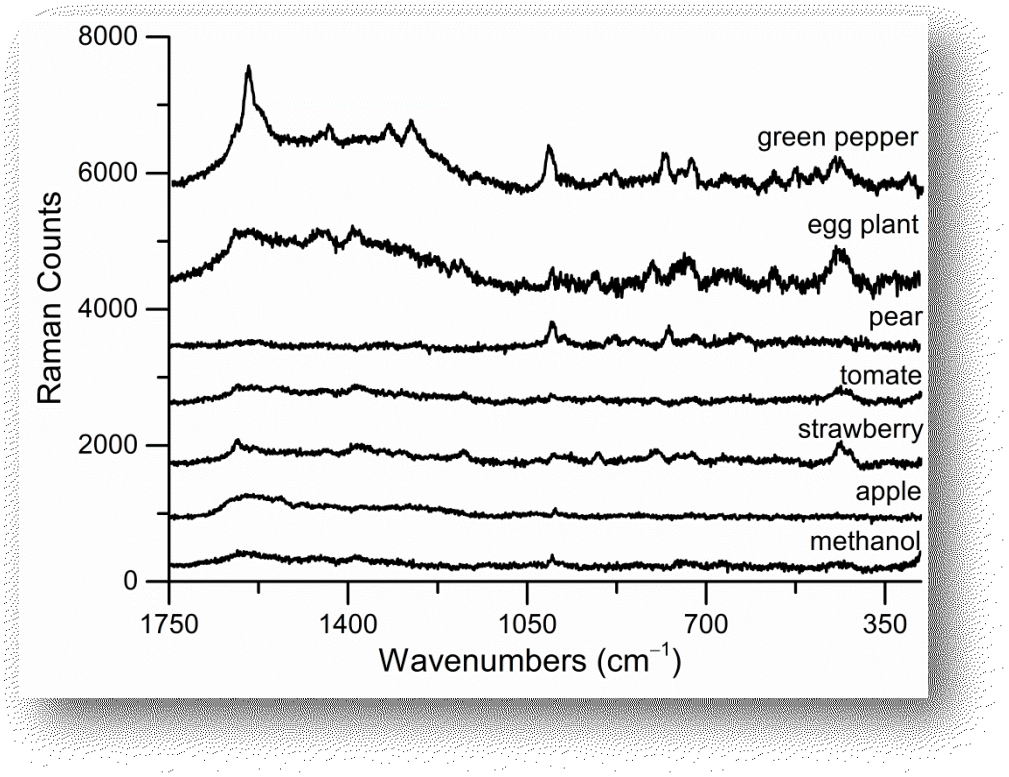


**Figure S12.** Blank Raman spectra of dehydrated Ag NPs gel substrates rubbed over 1 $cm^2$ of each washed fruit or vegetable peel using methanol for the extraction process. The surfaces were first treated with the same volume of methanol employed in the contamination process. The spectrum of dehydrated Ag NPs gel substrate is also shown for comparison purposes. (Excitation wavelength: 647.1 nm; laser power: 100 mW; acquisition time: 10 s; 4 accumulations; 50× objective (0.75NA)). The spectra baselines were corrected.

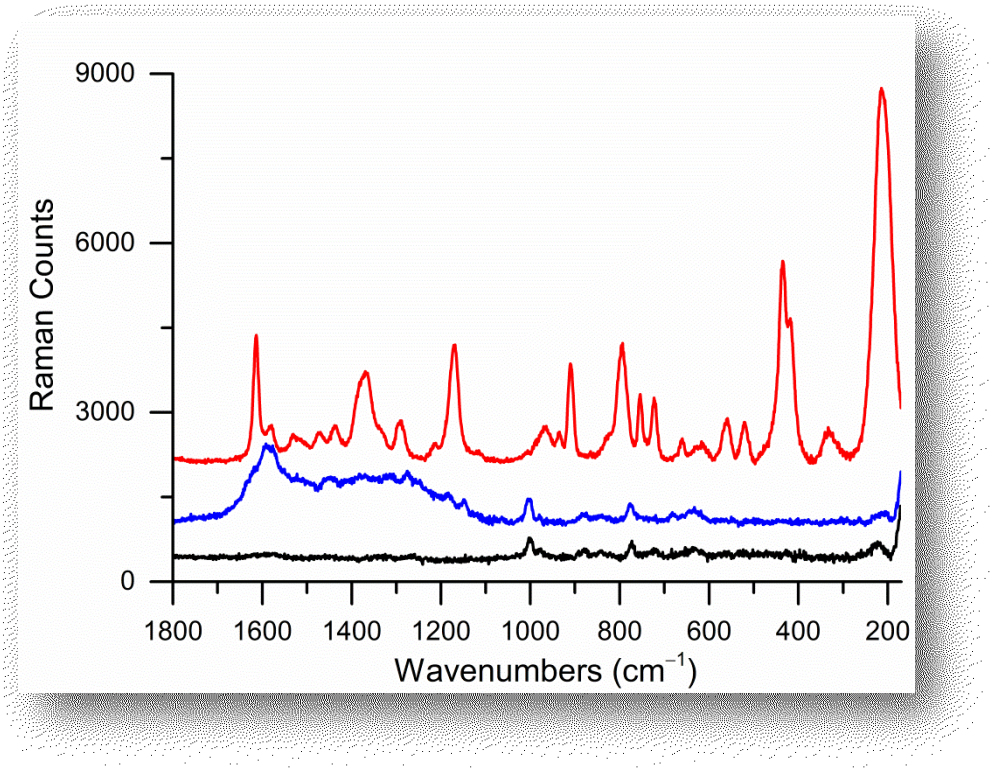


**Figure S13**. Blank Raman spectra of dehydrated Ag NPs gel substrates rubbed over 1 $cm^2$ of pear peels using methanol for the extraction process; each spectrum corresponds to a different pear bought in a different shop. The surfaces were first treated with the same volume of methanol employed in the contamination process. (Excitation wavelength: 647.1 nm; laser power: 100 mW; acquisition time: 10 s; 4 accumulations; 50× objective (0.75NA)). The spectra baselines were corrected.

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