Supplementary

Surface-Enhance Raman Spectroscopy Detection of Thiabendazole in Frozen Food Products: The Case of Blueberries and Their Extracts

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Table S1. Detection of pesticides from fruits and vegetables using SERS substrates.

Pesticides	SERS substrates [ref.]	Limit of detection	Observation
Parathion-methyl, thiram, chlorpyrifos	Au NPs [35]	2.6, 0.24, 3.51 ng/cm^2	Apple, orange peels
	Au@Ag NPs [36]	0.025~7.23 ng/cm^2	Apple, grape, mango, pear, peach peels
Thiram, 4-polychlorinated biphenyl, methyl parathion	Ag-NC@PE composite film [37]	10 nM, 1 μM, 10 nM	Orange surface
Thiram	Au NPs grafted on dendritic α-Fe_2O_3 [38]	5×10^{-6} M	Apple peels
	TiO_2 supported silver Nanoparticles [39]	240 ng/cm^2	
	Ag nanoshells (Ag NSs) [40]	38 ng/cm^2	
	Fe_3O_4@NRs [41]	10^{-7} M	
	AgNRs embedded PDMS [42]	2.4×10^{-9} g/cm^2	
Thiabendazole	Au nanostar/ polydimethylsiloxane (PDMS) film [43]	20 ppb	Apple skin
	Ag dendrites [44]	5 ppm μg/g per weight	Apples (Gala)
	Cellulose nanofibers coated with Ag NPs [45]	5 ppm	Apples
	Ag nanoparticles [27]	10^{-11} mol l^{-1}	Orange, grapefruit, lemon, bio lemon, and banana peels
	electrochemically (EC) roughened, gold-based screen-printed electrodes (AuSPEs) [46]	0.061 ppm	Apple juice
	metal liquid-like 3D plasmonic arrays on O/W interface [47]	0.1 ppm	Fresh juice
	novel gold nanomaterial-based substrates [48]	149, 216, and 179 μg/L	lemon, carrot, and mango juice
Acetamiprid	Ag dendrites/swab method [49]	0.125 μg/cm^2	Apple surfaces
Carbaryl	Au-coated Klarite [50]	0.5 μg/g	Apples (Fuji)
	Au nanopopcorn [51]	0.35 mg/kg	Pear surface

Chlorpyrifos	Ag_2O@Ag NPs/PMMA [52]	10^{-7} M	Apple peels
	Au NPs [53]	0.13 mg/kg	Apples (Fuji) surface

Table S2. The proposed assignment of SERS peaks of frozen blueberry extracts.

Anthocyanidins pH4 *	**Blueberry**	**Blueberry filtered with bentonite**	**Assignments** [25]
1639 (s)	1633 (s)	1640 (s)	ν (CC)
1594 (s)	1591 (s)	1592 (w)	ν (CC)
1528 (s)	1527 (vs)	1523 (s)	ν (CC)
1496	1490 (s)	1480 (s)	ν (CC)
1325 (s)	1322 (m)	1324 (m)	ν (CC); i; δ (CH)
	1281 (s)	1287 (m)	
1247 (s)	1241(vs)	1244 (w)	ν (CO)
1194 (s)	1195 (s)	1193 (m)	δ (OH)
1082	1083 (m)	1082 (w)	
870 (m)	867 (s)	862 (m)	γ (CH)
710 (s)	713 (s)	718 (w)	
649 (s)	643 (s)	649 (w)	
539 (s)	541 (m)	541 (m)	δ (CC)

* Data from reference from Yaffino et al. [25].

Table S3. The proposed assignment of the main Raman and SERS bands of TBZ on the hydroxylamine-reduced AgNPs [19, 26-28].

Solid /cm-1	**SERS - Ag (cm-1)**	**Vibrational assignments**
778 (w)	778 (vs)	υ (C-S) and breathing mode of pentaring
1010 (w)	1005 (vs)	δ(C-H) in-plane
1276 (m)	1275 (w)	υring + δ(CH) in-plane
1300 (w)	1318 (w)	δ(C-H) in-plane
1398 (vw)	1400 (m)	υ (C-C)
1453 (m)	1452 (w)	υ (C–N)
1490 (w)	1489 (w)	υ(C=C) + δ(N-H) in-plane
1575 (vs)	1571 (vs)	υ(C=N)
1590 (m)	1592 (w)	υ(C=N)
1619 (w)	1618 (m)	υ(C=N)

Note: vs = very strong; s = strong; m = medium; w = weak; υ = stretching, δ = bending

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