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Surface-enhanced Raman spectroscopy study of commercial fruit juices

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Fruit juice and pulp characterization by SERS Spectroscopy

Characterization of fruit juice and pulp by SERS spectroscopy using visible light (λ = 632.8 nm) and a micro-Raman spectroscopy setup

Surface enhanced Raman Spectroscopy (SERS) using a home-made Gold nanoparticle-based substrate.

Numerical background subtraction by wavelet based algorithm.

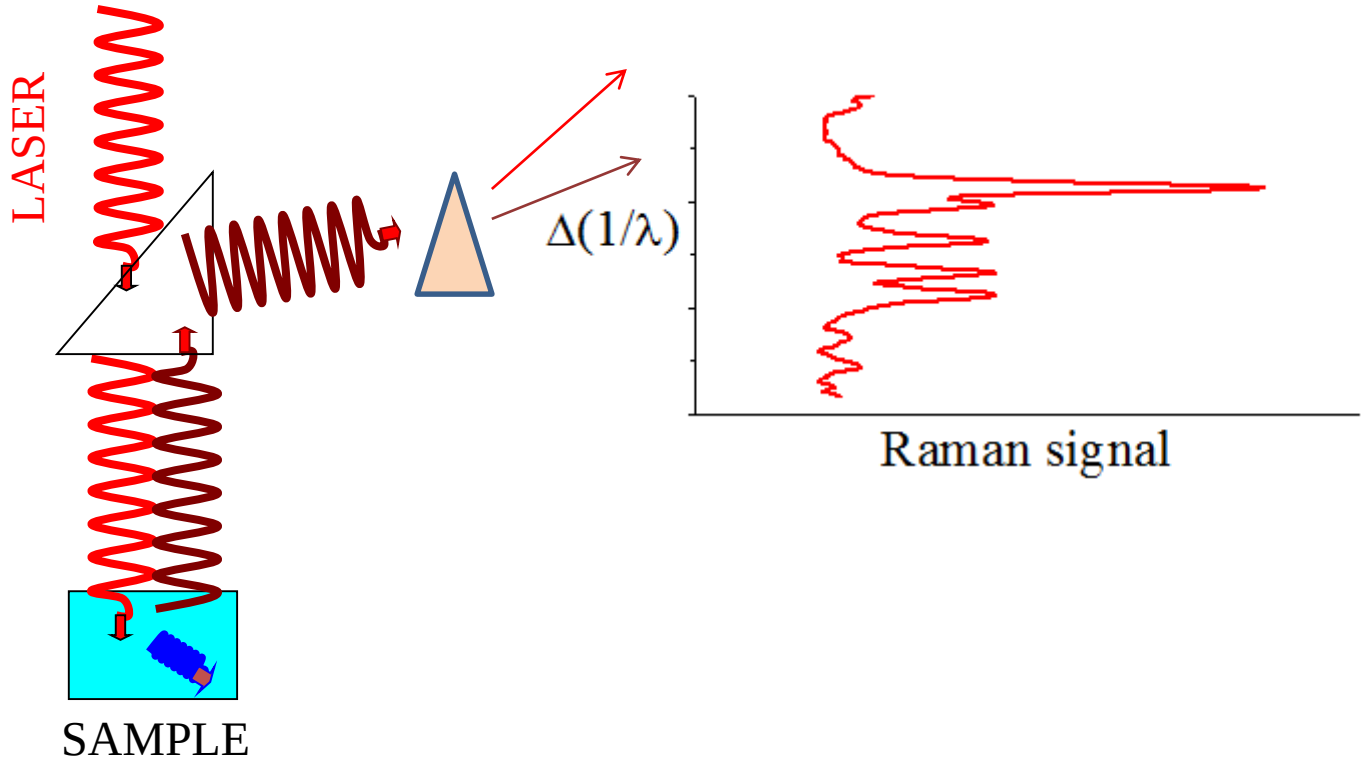
Evaluation of juice and pulp contents (glucose, fructose and pectin and so on)

Contamination or degradation processes

Territorial characterization

Micro-Raman Spectroscopy

Spectral analysis methods are FAST, NONINVASIVE and usually INEXPENSIVE: They are particularly suitable for food characterization and food process monitoring and food quality evaluation (also in situ and online).



LIGHT ⟷ (Electromagnetic interaction) NANOSCALE METALS

↓

collective oscillations of conduction electrons:
LOCALIZED SURFACE PLASMON RESONANCES

↓

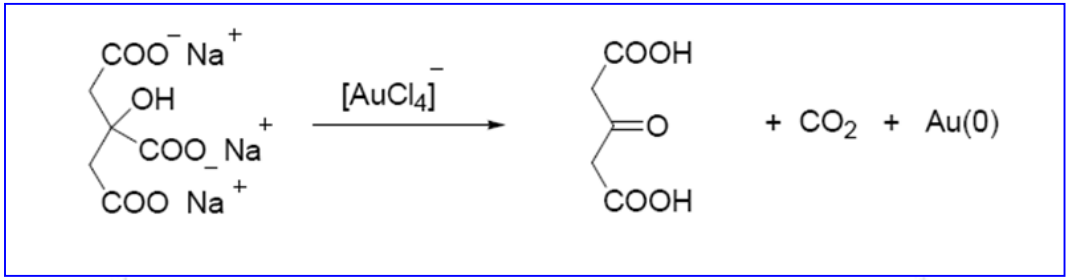
high local enhancements of the electromagnetic energy
(large enhancement of Raman signal)

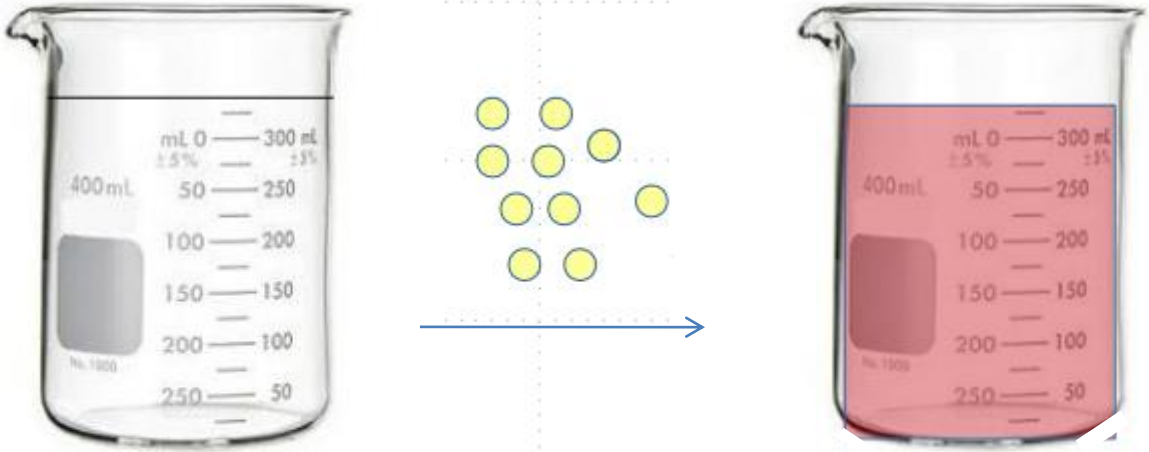
Au nanoparticles (GNPs): Fabrication process

0.01% $HAuCl_4$ solution

+

1% sodium citrate

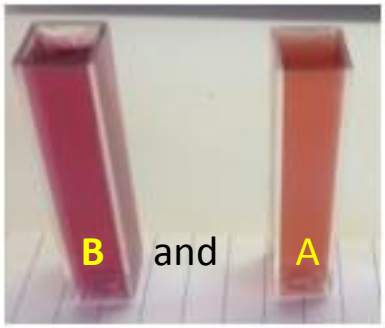




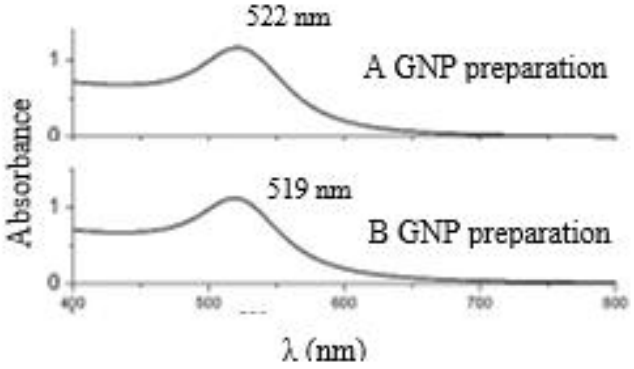
Turkevich and Frens method: the reducing agent (sodium citrate) acts as stabilizing agent by adsorbing onto the metal surface and avoiding nanoparticle aggregation through electrostatic repulsions.

I. Delfino, M. Lepore, R. Taté, M. Portaccio, Int. Electronic Conference on Sensors and Applications 2014 (www.mdpi.com/journal/sensors/)

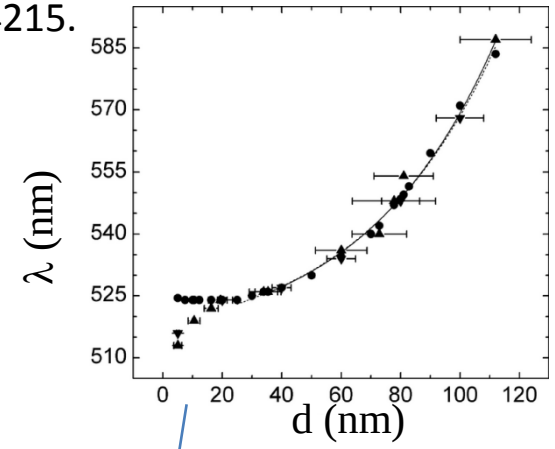
GNPs of different sizes can be obtained, depending on the amount of sodium citrate. They were characterized by using DLS, TEM and absorption spectroscopy



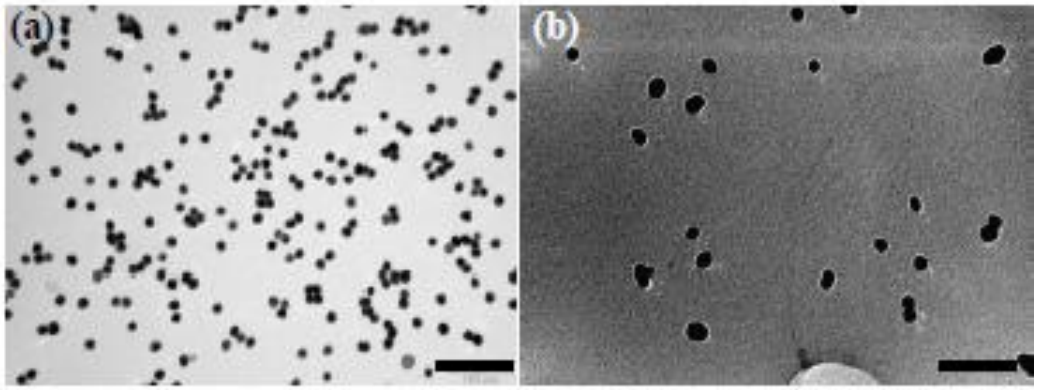
GNP preparations



W. Haiss et al, Anal. Chem. 79 (2007) 4215.



Position of the Plasmon Resonance peak as a function of the particle diameter for GNPs in water.



TEM images; size bar 100 nm

Estimated GNP Size by Absorption

A: 20±2 nm B: 47±5 nm

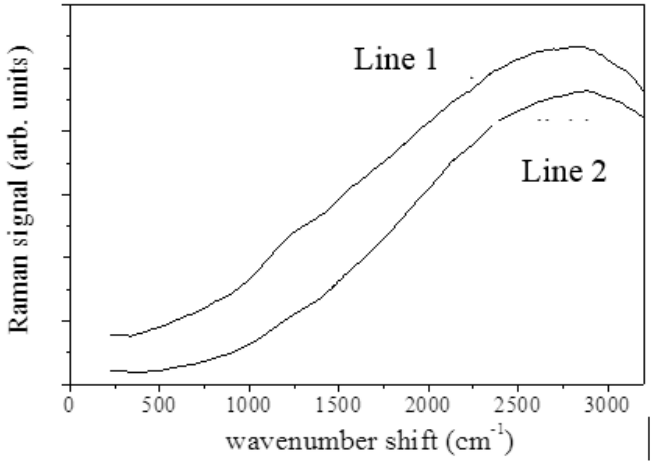
Estimated GNP Size by TEM and DLS

A: 18±10 nm B: 47±13 nm

(greater dispersion)

GNP preparation based SERS Substrates

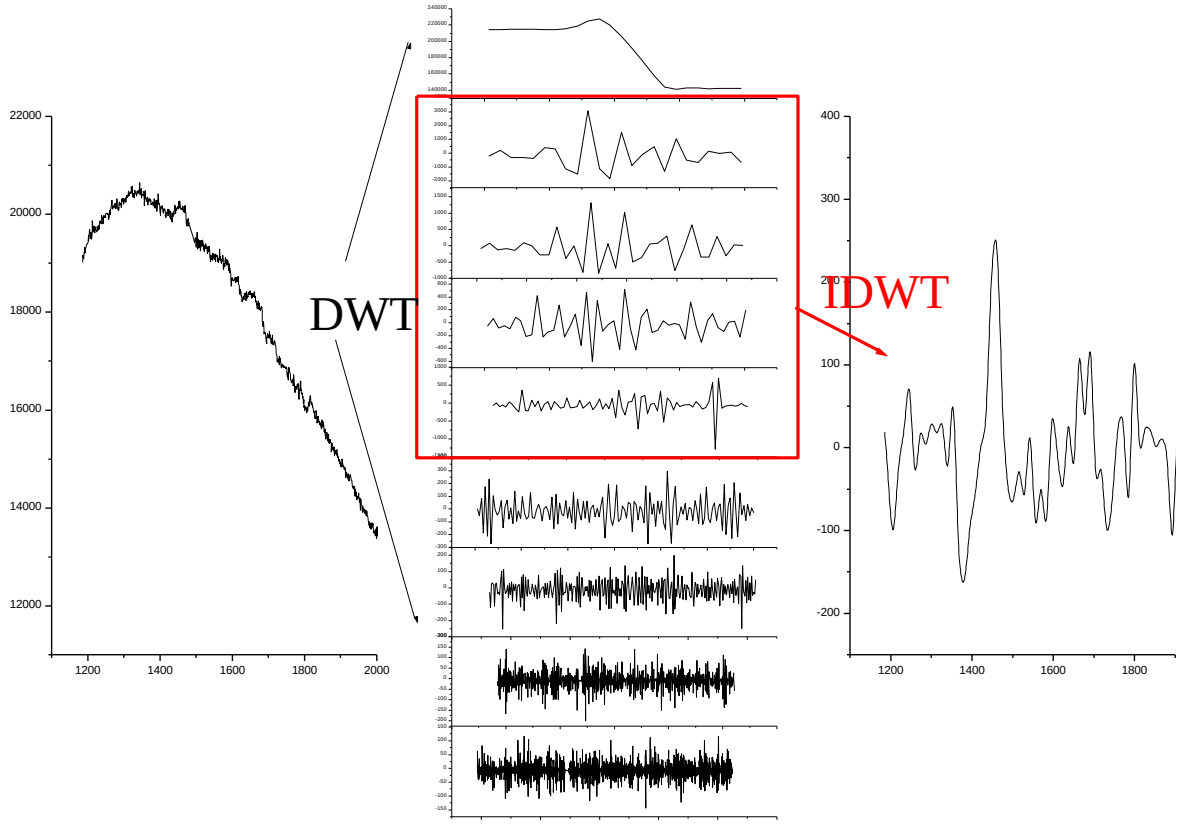
Raman signal from GNP based substrates



Line 1: GNP A preparation
Line 2: GNP B preparation

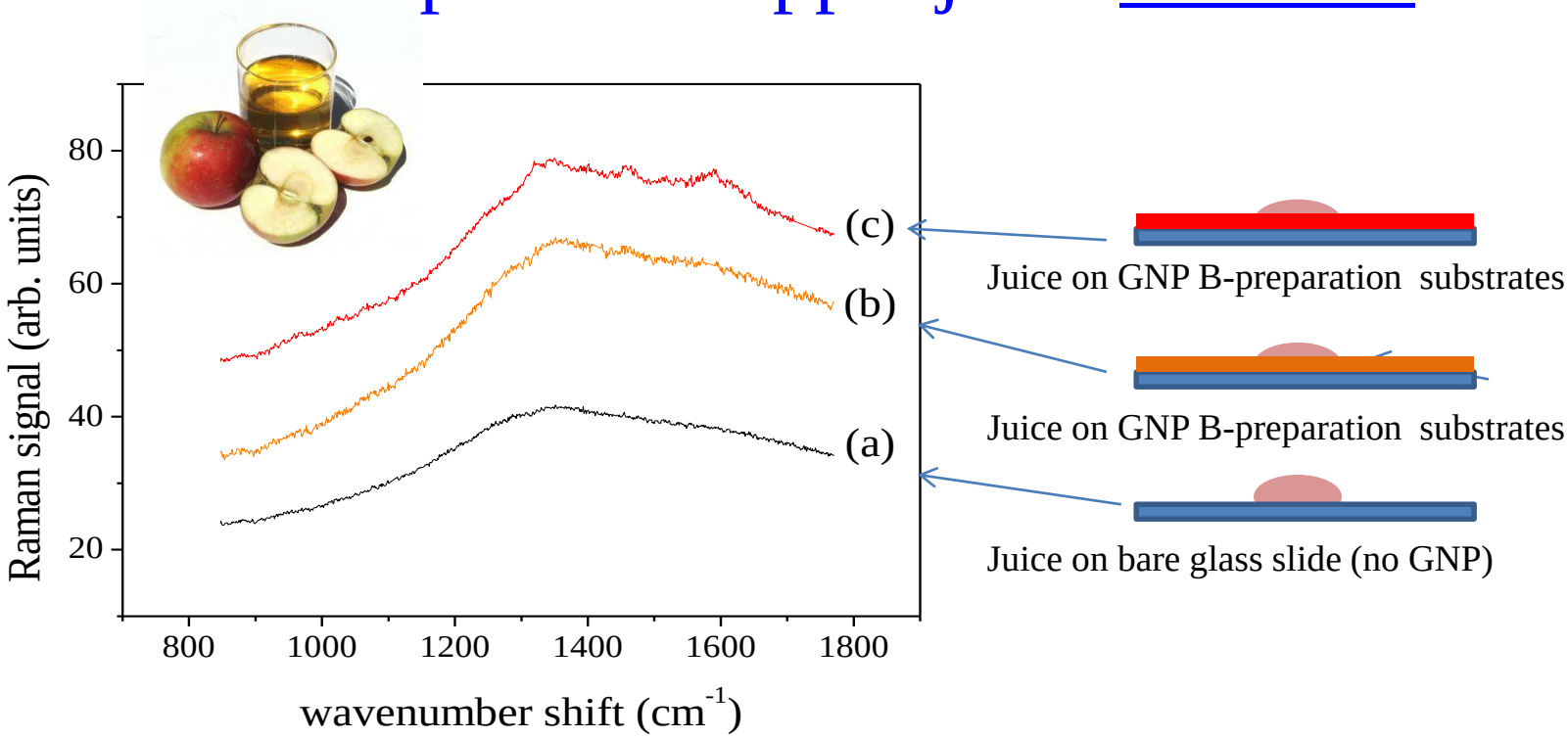
NO SPECIFIC FEATURES

Numerical Data treatment based on wavelet algorithm



C. Camerlingo et al, Meas. Sci. Technol. 17 (2006) 298.

Raman and SERS spectra of apple juice



Raman spectra of clear apple juice (data not treated) for bare juice drop (a), juice drop on A-preparation based substrate and for (b) juice drop on B-preparation based substrate (c).

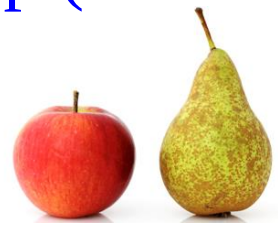
The spectra are arbitrarily shifted along the y-axis.

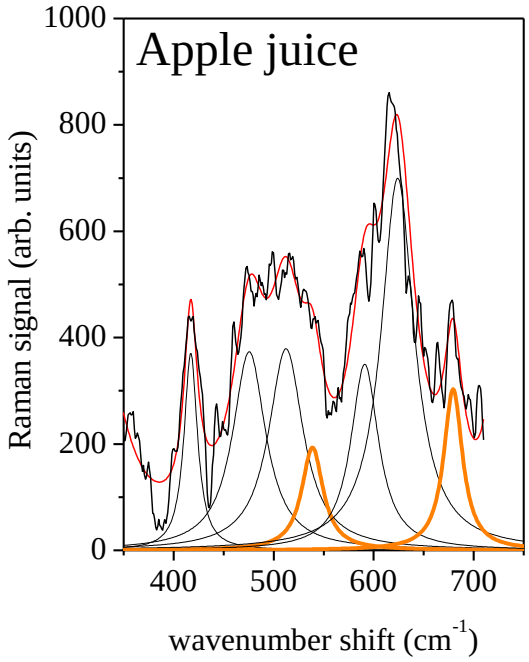
When B-preparation GNP based substrates is used Raman features are observed

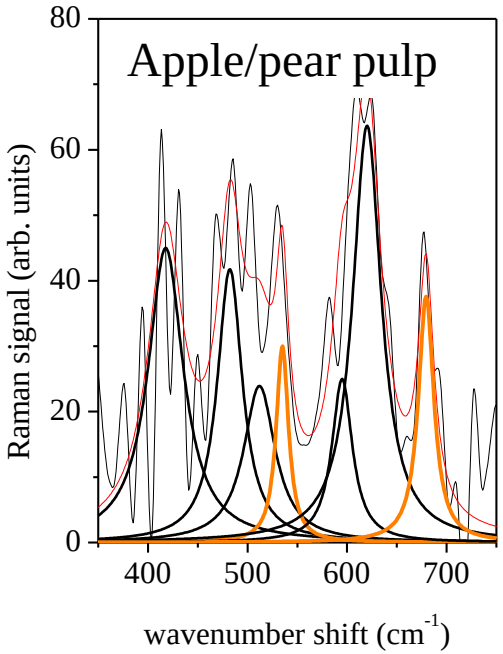
→ SERS

By using this substrate SERS spectra are detected also for commercial pulp (NO GNP based substrate = undetectable Raman signal)

SERS spectra of apple juice and pulp (low frequency range)

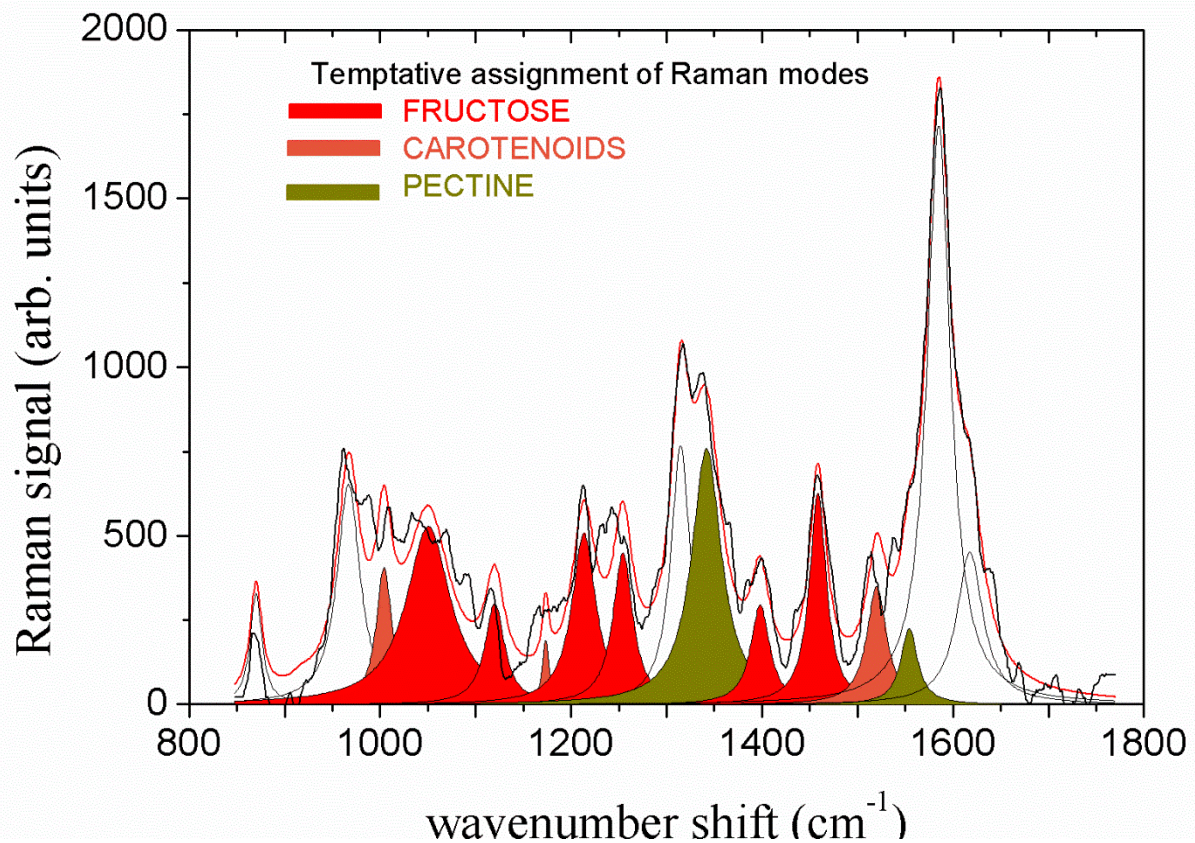






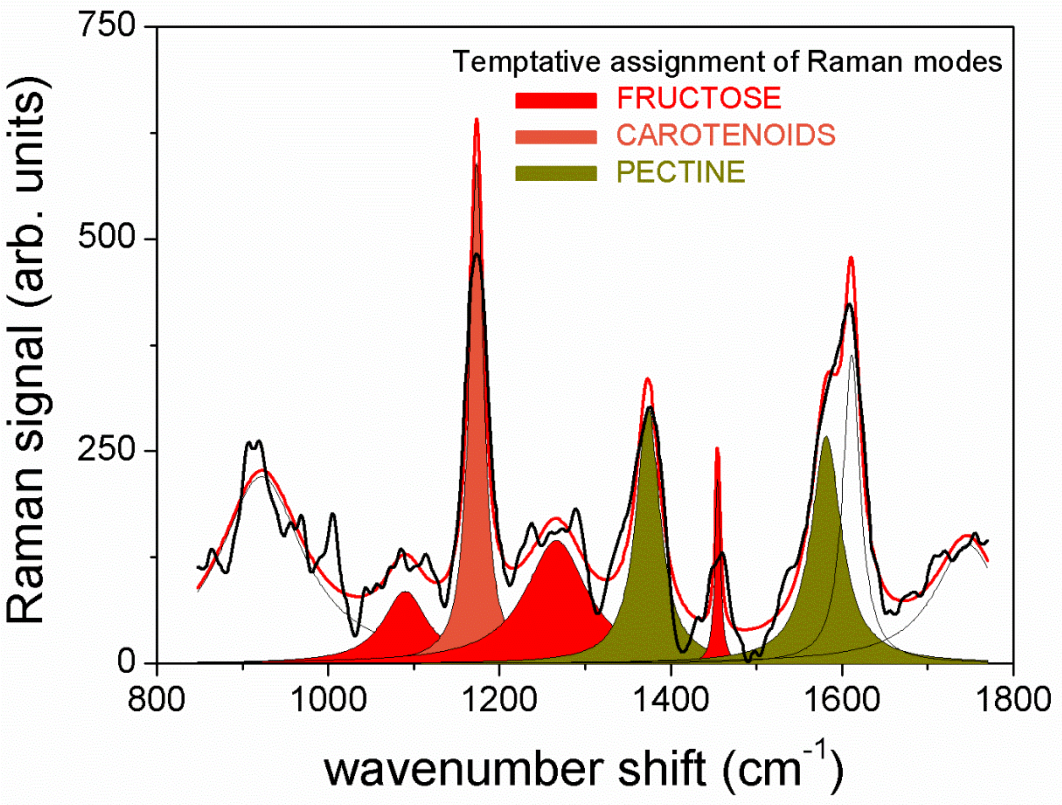
Deconvolution in Lorentzian functions of SERS spectrum in the range 350-700 cm^{-1} of clear apple juice on B-preparation based substrate. Red line is the convolution of the peaks found. Black peaks are assigned to fructose (peaks at 417, 475, 512, 591, 624 cm^{-1}) , while orange ones refer to pectin (539, 679 cm^{-1}) .

SERS spectrum of apple juice (high frequency range)



Deconvolution of Raman (SERS) spectrum of apple juice. An attempt of assignment of Raman modes for the main components of the apple juice is indicated. The strong peak at about 1600 cm^{-1} is presumably generated by residual fiber content (lignite).

SERS spectrum of apple/pear smashed pulp (high frequency range)



Deconvolution of SERS spectrum of apple/pear smashed pulp. An attempt of assignment of Raman modes for the main components is indicated.

Tentative assignment of main Raman modes found in apple juice spectra

Peak wavenumber (cm^{-1})	Pectin	Fructose	β–carotene	Refs.
845	C-O-C antisymmetric stretching of the glycoside linkage	-	-	21
918	In-plane bending of CH_2	Furanose isomer	-	20
1004	-	-	Methyl component rocking	23
1056	Nonlocalized, highly coupled vibrational modes of polysaccharide backbones	-	-	21
1132	-	Pyranose isomer	-	20
1153	-	-	C-C stretching	23
1265	-	D- fructose	-	20
1361	C-H bending	-	-	21
1427	COO^- symmetric stretching	-	-	21
1520	-	-	C=C stretching	23
1552	Amide II: N-H deformation Contribution from C-N stretching	-	-	21

Table taken from C. Camerlingo, F. Zenone, I. Delfino, N. Diano, D.G. Mita, M. Lepore, Investigation on clarified fruit juice composition by using visible light micro-Raman spectroscopy, Sensors **7** (2007) 2049-2061.

20. Cerchiaro, et al *Carbohydrates Research* ***2005, 340, 2352-2359.***
21. Engelsen, S.B.; Noorgard L. *Carbohydrates Polimers* ***1996, 30,***9-24.
23. Koyama, Y. et al. *J. Raman Spectrosc.* ***1988, 19, 37-49.***

Summary

- ✓ The realized home-made GNP based substrate has enabled to obtain clear Raman spectra of commercial apple juice and pear/apple smashed pulp, that feature a low Raman signal.
- ✓ The detected good SERS spectra enabled to evidence the presence of fructose and pectin in the untreated samples.
- ✓ The overall inspection of the results has confirmed the potentialities of SERS in food industry especially for the eventual on-line product evaluation.