

Fast and Selective Detection of Trigonelline, a Coffee Quality Marker, Using a Portable Raman Spectrometer

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Quality control in the food industry is a key issue that requires rapid, efficient and selective methods that could discriminate the products, detect fraudulent or accidental adulterations, and identify the content of some biomarkers within a particular process of storage conditions. Along these lines, [Raman spectroscopy](#) in conjunction with the optical properties of metallic nanostructures is a powerful technique that can be implemented in food analysis.



[Surface-Enhanced Raman Spectroscopy \(SERS\)](#) is a technique that takes advantage of the optical properties of noble metal nanostructures (e.g. gold or silver nanospheres) to enhance the Raman signals of molecules adsorbed on the surface of the metal. Changes in the material, geometry and size of the metallic structures enable the modulation in enhancement of these unique nanoantennas. This advance has led to many applications, including the design of new and selective sensors with lower limits of detection for food metabolites in order to adapt to agriculture and industry needs. In addition, SERS minimizes acquisition time and reduces the amount of sample needed.

In this regard, this report shows how the portable Raman device [i-Raman Plus 785](#) can be used in combination with modified gold nanotriangles to develop an alternative quantification method for trigonelline. This alkaloid is a biomarker present in different food items, such as coffee and quinoa, that provides potential health benefits and whose thermal degradation (e.g. during the roasting process of the green coffee beans) makes the formation of different flavor and aroma compounds possible. For example, a coffee brew could contain around 2.3 mM of trigonelline, and there could be around 30-65 μmol of trigonelline in one gram of green coffee beans, which would be an indicator of quality and could be tested using this technique.



Gold nanotriangles modified with mercaptopropionic acid have been used as nanoantennas to quantify the concentration of trigonelline solutions from the SERS signal. The nanostructures have been optimized to enhance signals between 700-800 nm wavelength.

Calibration curves have been prepared using the 1034cm^{-1} peak area and compared with traditional Raman spectroscopy. The results show the advantages of the technique, which include lower limits of detection, and the potential of this method for quantifying trigonelline in food.

Experimental

Instrumentation: i-Raman Plus portable spectrometer with 785 nm laser excitation (BWS465-785H), Raman shift range $150\text{-}2800\text{ cm}^{-1}$, 50 sec integration time, 10 scans, and liquid cuvette holder (BCR100-A) with 10 mm optical path.
Samples: Standard trigonelline aqueous solutions ranging from 10.0 mM to 0.5 mM. Gold nanotriangles modified with mercaptopropionic acid and suspended in deionized water (AuNTs).

Results and discussion

A 250 mM solution of trigonelline was analyzed using conventional Raman spectroscopy. The spectrum in Figure 1 shows an intense signal at 1034 cm^{-1} , corresponding to the pyridine ring breathing mode, that could be used to monitor the concentration of this compound in water.

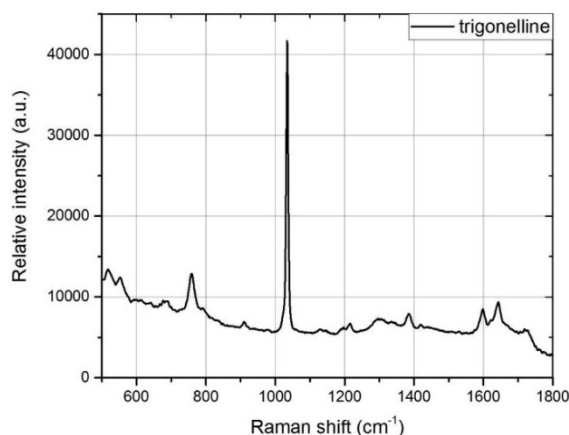


Figure 1: Raman spectrum of trigonelline solution at 250 mM

Four independent sets at five different concentrations were analyzed within the 0.5 mM and 10 mM range by conventional Raman spectroscopy and by SERS. The latter one requires an extra step where the modified gold nanotriangles are mixed with the trigonelline solutions (trigonelline: gold nanotriangles = 15:2) before samples are scanned. In all cases, the strong signal observed at 1034 cm^{-1} was monitored and the peak area within $1010\text{-}1045\text{ cm}^{-1}$ spectral window was used to determine the concentration of the alkaloid. Based on the results and the calibration curves (Figure 2) it was possible to observe an improvement on the signal to noise ratio of SERS over the conventional Raman spectra under the same

experimental conditions. The results show it is possible to detect concentrations below 0.5 mM using this method.

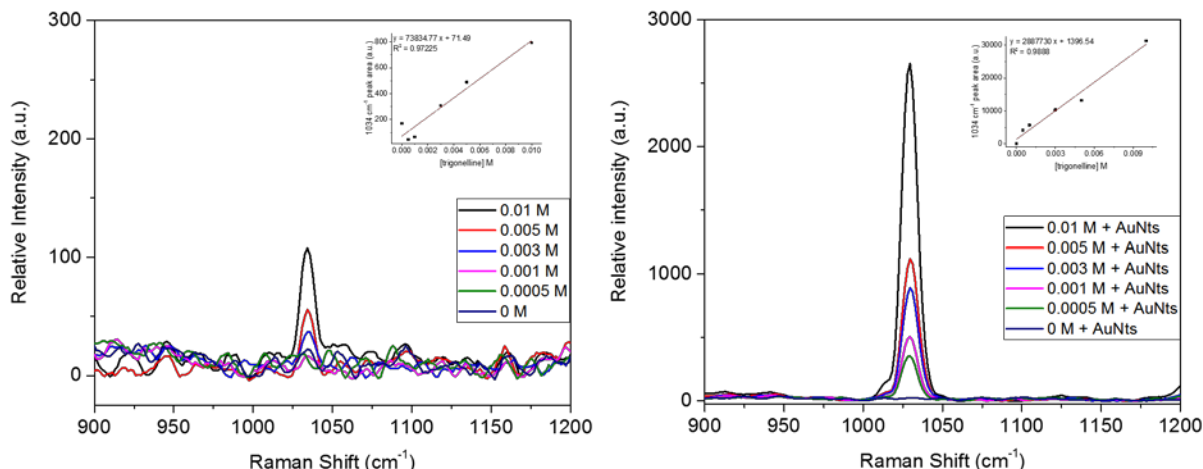


Figure 2. Raman spectra of trigonelline solutions without gold nanotriangles (left) and with gold nanotriangles (right). Inserts show the calibration curves of trigonelline solutions using the 1034 cm^{-1} peak area within a 1010-1045 cm^{-1} spectral window.

In summary, we describe a simple method to quantify the presence of diluted trigonelline in solutions using surface enhanced Raman spectroscopy as a tool could potentially improve the quality control process of food items such as coffee and quinoa.

References

- Galarreta, B.C.; Hernandez, Y.; Saldaña Ramos, A. "Síntesis y aplicación de nanotriángulos de oro en el desarrollo de un método de cuantificación de un potencial alcaloide terapéutico: la trigonelina" Dirección de Gestión de la Investigación (DGI-2016-352) PUCP.
- Galarreta, B.C.; Maruenda, H. "Espectroscopía vibracional y de resonancia magnética nuclear en el control de calidad de café orgánico peruano y café instantáneo" Dirección de Gestión de la Investigación (DGI-2014-078) PUCP.
- Aroca, R. "Surface-enhanced vibrational spectroscopy" John Wiley & Sons, 2016.
- Jaworska, A.; Malek, K.; Marzec, K.M.; Baranska, M. "Nicotinamide and trigonelline studied with surface-enhanced FT-Raman spectroscopy" *Vibrational Spectroscopy* (2012) 63,469-476.

Further Reading:

[Portable Raman for SERS Applications](#)

[Choosing the Most Suitable Laser Wavelength](#)

[Analysis of Edible Oils by a Portable Raman Spectrometer](#)

Additional Resources:

[Raman Spectroscopy overview](#)

[i-Raman Plus datasheet](#)

[Portable Raman for Agricultural Products & Cultural Heritage in Peru](#)