Application Note 410000013-A

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

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 1034 cm^{-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, Raman shift range 150-2800 cm^{-1}, 50 sec integration time, 10 scans, and liquid cuvette holder 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.

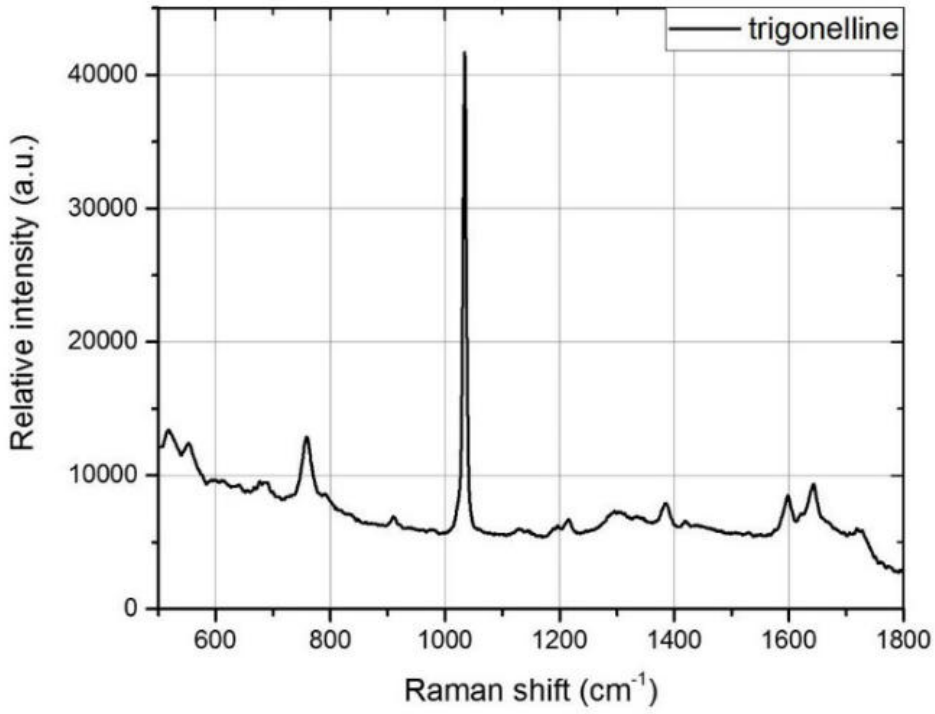


Figure 1. Raman spectrum of trigonelline solution at 250 mM

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 1010-1045 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.

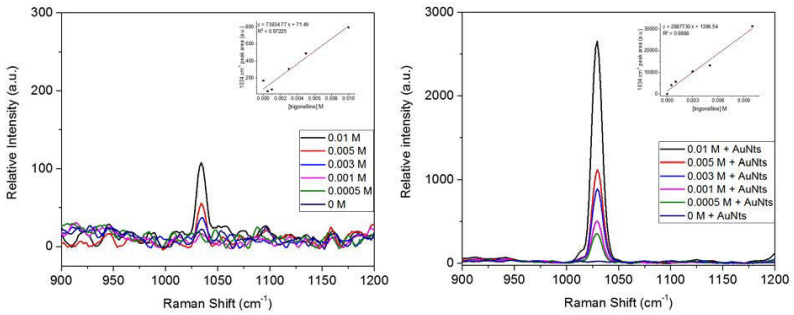


Figure 2. Raman spectra of trigonelline solutions without gold nanotriangles (left) and with gold nanotriangles (right). Inserts show the calibration curves of trigonelline solutions using the 1034 cm-1 peak area within a 1010-1045 cm-1 spectral window.

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.

FURTHER READING

Related application notes

Portable Raman instrumentation for SERS applications

Choosing the most suitable laser wavelength

Analysis of Edible Oils by a Portable Raman Spectrometer

Other related documents

Raman vs SERS... What's the Difference?

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We would like to thank Angeline Saldana Ramos, Yulán Hernandez, and Prof. Betty C. Galarreta of the Departamento de Ciencias – Sección Química, Pontificia Universidad Católica del Perú for sharing their research results.

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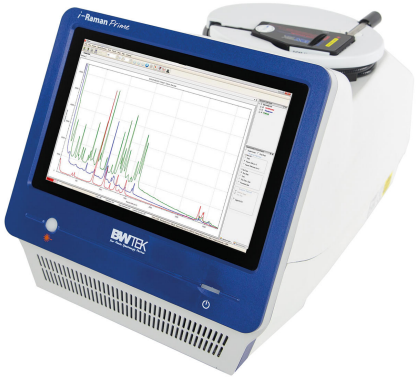
CONFIGURATION



i-Raman Plus 785S Portable Raman Spectrometer

The i-Raman® Plus 785S is part of our award-winning series of i-Raman portable Raman spectrometers powered by our innovative intelligent spectrometer technology. Using a high-quantum-efficiency CCD array detector with TE cooling and high dynamic range, this portable Raman spectrometer delivers excellent performance with low noise, even at integration times of up to 30 minutes, making it possible to measure weak Raman signals.

The i-Raman Plus 785S features the unique combination of wide spectral range and high resolution with configurations which allow measurements from 65 cm^{-1} to 3,350 cm^{-1}. The system's small footprint, lightweight design, and low power consumption ensure research-grade Raman analysis capabilities at any location. The i-Raman Plus is equipped with a fiber probe for easy sampling, and can be used with a cuvette holder, a video microscope, an XYZ positioning stage with a probe holder, as well as our proprietary BWIQ® multivariate analysis software and BWID® identification software. With the i-Raman Plus, you always have a high precision Raman solution for qualitative and quantitative analysis.



i-Raman Prime 785S Portable Raman Spectrometer

The i-Raman® Prime 785S is a low-noise, high-throughput, and fully integrated Raman system with an embedded tablet computer and a fiber-optic sampling probe. Using a high-quantum-efficiency CCD array detector with TE deep cooling (-25 °C) and high dynamic range, this portable Raman spectrometer delivers research-grade Raman analysis capabilities, including real-time quantitation and identification. The high throughput gives Raman spectra with excellent signal-to-noise ratio, making it possible to measure rapid processes and to measure even the slightest Raman signals, detecting subtle sample differences.

In addition to its portable construction, the i-Raman Prime 785S features the unique combination of wide spectral coverage and high resolution, thus enabling measurements from 150 cm^{-1} to 3,350 cm^{-1}. The i-Raman Prime can be battery-operated for easy portability, providing research-grade Raman analysis capabilities for high-precision qualitative and quantitative work wherever needed. The system is optimized for use with our STRaman® technology for analyses through non-transparent packaging.



Raman Video Micro-Sampling System (785 nm)

Video microscope sampling system for use with B&W Tek's lab and industrial Raman probes. Includes a 20x objective at a working distance of 16 mm. Offers manual rough and fine adjustment on the X, Y, and Z-axes, coaxial LED illuminator for target alignment, video camera for sample observation, and is compatible with standard microscope objectives. Probe not included, available separately. 785 nm configuration.

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