Raman spectroscopy at 1000 nm for chocolate measurements

Benefits at a glance

- The use of 1000 nm excitation effectively reduced fluorescence of chocolate
- Quantitative and qualitative assessment of cocoa butter can be performed within minutes using non-contact instrumentation
- Rapid and non-contact chocolate quality measurements now possible in a laboratory, at-line, or in-line environment

Introduction

Understanding the chemical composition of chocolate has important implications in its production, shelf life, sensory properties, and possible health effects. Raman spectroscopy brings a non-destructive, multi-attribute, and process-ready measurement to chocolate manufacturing and quality assurance. However, the extensive fluorescence of milk and dark chocolates has prohibited Raman using visible or near-infrared excitation using microscopy or fiber optic probes, necessitating the use of surface-enhanced Raman spectroscopy (SERS) or Fourier transform (FT) Raman approaches. Our studies showed that using 1000 nm excitation effectively reduced fluorescence and enabled dispersive Raman measurements of white, dark, and milk chocolate samples.

Materials and methods

A 1000 nm Raman Rxn2 analyzer (laser intensity = 100mW) equipped with a Rxn-10 probe and non-contact optic, resulting in a spot size of 150 µm, was used to collect Raman spectra from commercially-available white, dark, and milk chocolate samples.[1] Raman spectra were compared with literature studies in cocoa butter polymorphs, lipid extractions of chocolate, and chocolate samples.[2–4] Qualitative analysis of several functional groups of cocoa butter and sucrose was performed directly from the chocolate Raman spectrum without further sample preparation. Quantitative analysis was performed to understand the relative populations of *gauche* (distorted) and *trans* conformers, the relative amount of saturated fatty acids, and the relative amount of sugar to lipids.

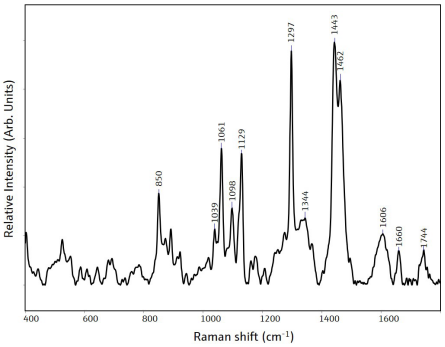

Figure 1: Raman spectrum of dark chocolate

Results and discussion

The 1000 nm results showed effective fluorescence reduction in dark and milk chocolates and enabled visualization of many sharp Raman bands with good signal-to-background. No sample melting was observed after measurement using 1000 nm excitation with 100 mW laser intensity. The resulting Raman spectra have a remarkable amount of spectral detail, which was used to provide qualitative and quantitative information on cocoa butter and sugar. Figure 1 shows a Raman spectrum of a representative dark chocolate sample in the 400-1800 cm^{-1} region. Table 1 presents Raman band assignments. Bands in the 400-800 cm^{-1} spectra region are dominated by sucrose bands, with some overlap with cocoa butter fatty acids in a few bands in the 1200-1800 cm^{-1} region. These initial studies support the use of Raman to understand cocoa butter and sucrose directly in white, milk, and dark chocolate with no sample preparation.

Spectral region Raman shift (cm^{-1})	Assignment	Component
600-900 403 525 640 850	δ(C9–C3–O2), δ (O14–C4–C3) βR_2 (A5) βR_1 (A5) τCH_2	**Sucrose**
1000-1200 ~1060 ~1080 ~1097 ~1130	**Skeletal v C-C** v_{as} C-C v_s C-C v_s C-C C-C, C-OH C-N stretch	**Cocoa butter** All-*trans* extended chains *gauche* extended chains *gauche* extended chains All-trans extended chains
1250-1300 ~1267, 1275 ~1300	**τCH_2** =C-H deformation, *cis* isomer τCH_2	**Cocoa butter** Unsaturated fatty acids in cocoa butter Chain-chain coupling
1420-1480 ~1442 ~1460	CH_2/CH_3 deformation δCH_2 and δCH_3 δCH_2	**Cocoa butter, sugar** Saturated fatty acids in cocoa butter Sucrose
~1650-1670	v_s C=C, *cis* isomer v_s C=C, *trans* isomer	Cocoa butter
1700-1780	Ester carbonyl stretch (v_s C=O)	Cocoa butter

Table 1. Raman band assignments for chocolate samples

Conclusions

Raman spectroscopy brings a non-destructive, multi-attribute, and process-ready measurement to chocolate laboratory and manufacturing applications. The utility of dispersive unenhanced Raman in the laboratory or process environment for chocolate measurements has historically been limited due to laser-induced sample heating and an overwhelming background at visible and near-infrared excitation wavelengths (532 nm - 785 nm). Our results showed that Raman spectra collected at 1000 nm demonstrated sufficient background reduction to enable observation of bands throughout the fingerprint region for cacao nibs and white, milk, and dark chocolate samples. These feasibility studies establish the experimental basis for future studies involving more samples and understanding cocoa butter polymorphism directly in milk or dark chocolate without sample preparation or extraction.

References

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3. de Oliveira, L. N.; Castro, J. C. de R.; de Oliveira, M. A. L.; de Oliveira, L. F. C. Lipid Characterization of White, Dark, and Milk Chocolates by FT-Raman Spectroscopy and Capillary Zone Electrophoresis. *J. AOAC Int.* **2015**, 98 (6), 1598–1607. https://doi.org/10.5740/jaoacint.15-083.
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