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Raman spectroscopy of chocolate using 1000 nm excitation

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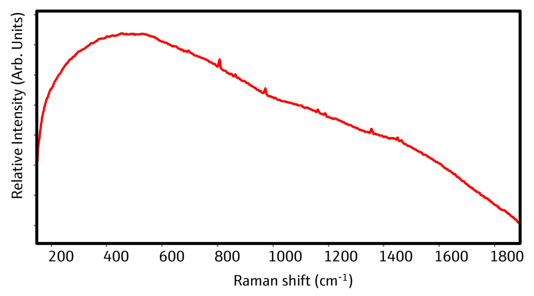
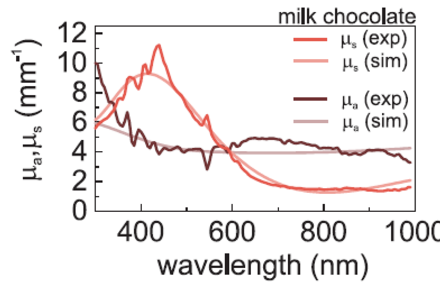
INTRODUCTION

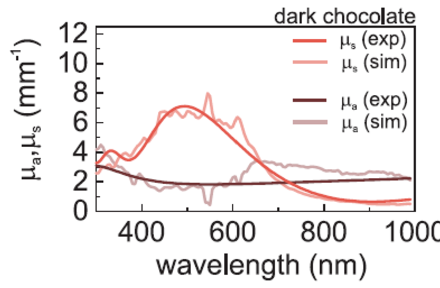
Lasers and chocolate: what can go wrong?

Even at low laser power densities using 785 nm excitation, laser-induced melting or bloom observed [1]



At 785 nm excitation, there is overwhelming background [2]





At NIR wavelengths, optical absorption becomes the dominant phenomenon [3]

EXPERIMENTAL

We hypothesized that 1000 nm excitation at low laser power could enable dispersive unenhanced Raman spectroscopy of milk and dark chocolate samples.

In the studies described, a Raman Rxn2 (λ=785 nm or 1000 nm) Raman analyzer (Kaiser Optical Systems, Ann Arbor, MI USA) was used. A 1000 nm non-contact optic or 785 nm PhAT probe (Kaiser Optical Systems, Ann Arbor, MI USA was used to collect Raman spectra of commercially-available chocolate samples

All samples were divided into two groups: one for taste testing and one for Raman analysis. Raman-measured samples were visually inspected for laser-related melting or blooming after the Raman measurement.

Raman spectra were preprocessed in GRAMS/AI (ThermoFisher Scientific, Waltham, MA USA).

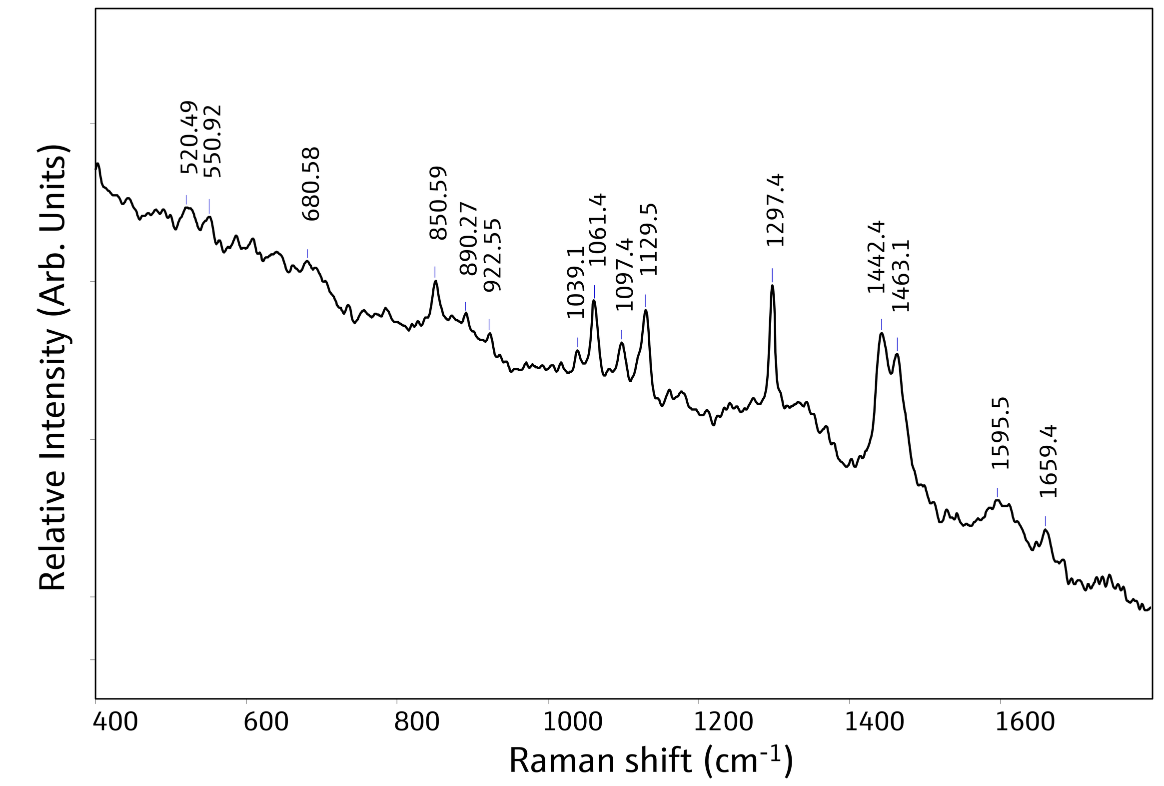
RESULTS AND DISCUSSION

Overview of chocolate samples

Manufacturer Sample name	Total fat (g) Saturated fat (g)	Sugars	Protein	Extra ingredients?
Mindo Pure 67%	8 5	8	3	Yes
Mindo Pure 87%	11 7	3	3	No
Vosges Mo's Milk Bacon. 45% cacao	11 6	12	3	Yes
Vosges Raw Honey Cacao, 100% cacao	13 8	6	2	Yes
Lindt Classic White Chocolate	10 6	16	2	Yes
Lindt Classic Milk Chocolate	9 5	15	3	Yes
Ghirardelli Intense Dark Toffee Interlude	8 4.5	13	1	Yes
Ghirardelli Unsweetened Baking Chocolate 100% cacao	8 4.5	0	2	No

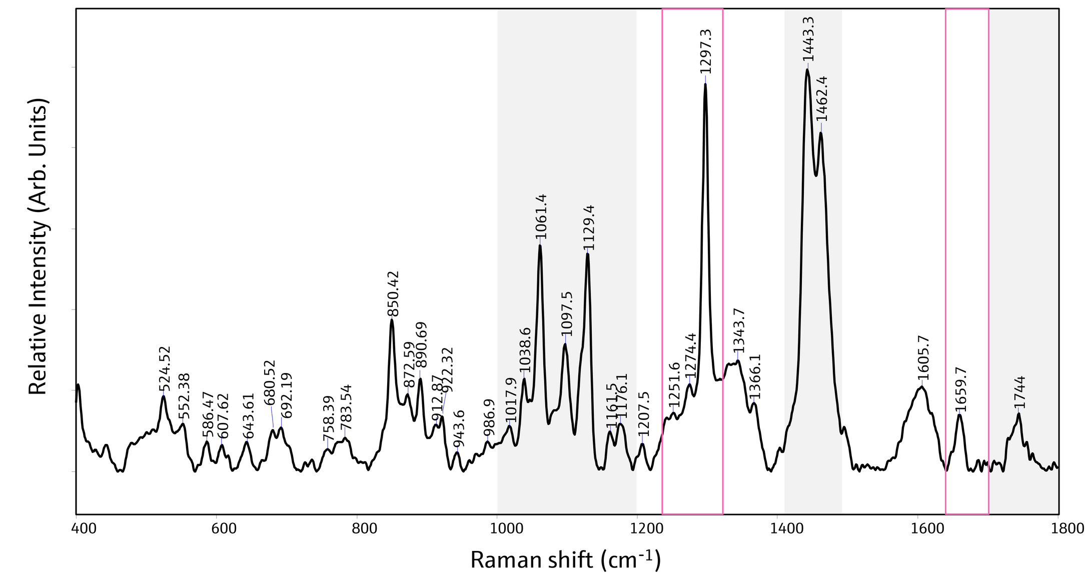
Milk, dark, and white chocolate samples were measured, spanning a range of fat, sugar, and protein content. Chocolate samples were measured as-received at ambient temperature and % relative humidity conditions.

1000 nm Raman spectrum of chocolate



1000 nm Raman spectrum of a representative chocolate sample (Mindo Pure 87%). Spectrum collected for 30 s and presented without baseline correction.

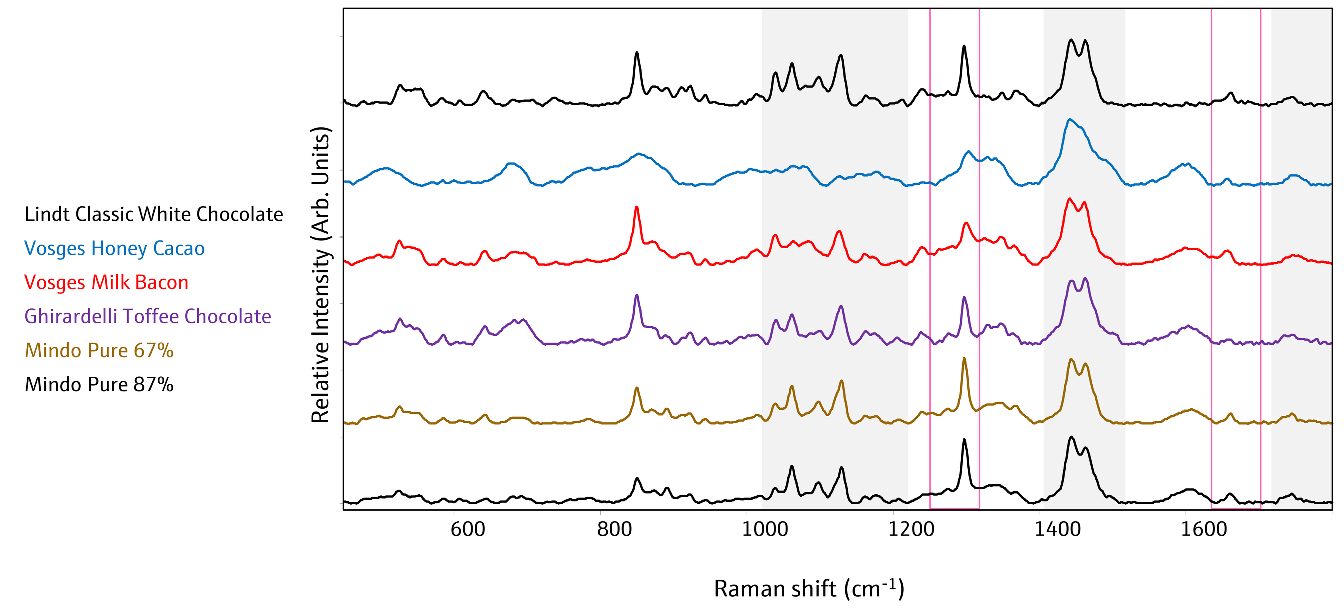
Raman band assignments

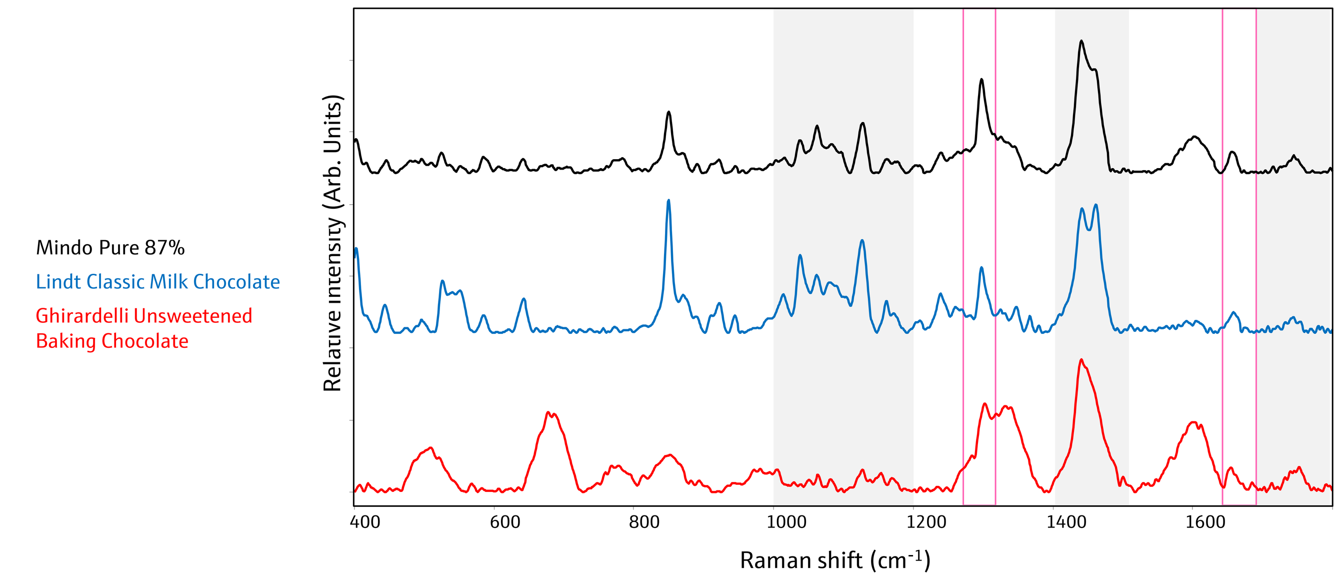


Raman band location(cm⁻¹)	Assignment	Component
1000-1200 ~1060 ~1097 ~1130	**Skeletal ν C-C** ν_{as} C-C ν_s C-C	**Cocoa butter** All-*trans* extended chains *gauche* extended chains All-*trans* extended chains
1250-1300 ~1267, 1275 ~1300	**τCH_2** =C-H in plane deformation, *cis* isomer τCH_2	**Cocoa butter** UnFa in cocoa butter Chain-chain coupling
1420-1480 ~1442 ~1460	**CH_2/CH_3 deformation** δCH_2 δCH_3	**Lipids, organic material** SaFA in cocoa butter Cocoa butter
~1660	ν_s C=C, *cis* isomer	Cocoa butter
1700-1780	Ester carbonyl stretch (ν_s C=O)	Cocoa butter

Major spectral contributions observed arise from cocoa butter.[4,6-8] In chocolate samples with ingredients other than cocoa butter and sugar, there are additional but minor contributions from milk proteins, other fatty acids, soy lecthin, and flavorings.

Raman spectra of various chocolate samples





Raman spectra from various chocolate samples reveal subtle differences in the spectral regions informing on cocoa butter composition and molecular structure. Possible sources of variation include differences in raw material composition, the use of fats other than cocoa butter, and processing operations such as conching.

CONCLUSIONS

Raman spectroscopy brings a non-destructive, multi-attribute, and process-ready measurement to chocolate manufacturing. Surface-enhanced Raman, FT-Raman, or Handheld Raman at 1064 nm has been used was used in order to measure cocoa beans, cacao, or chocolate samples.[1,4,5 8] However, the utility of dispersive unenhanced Raman in the laboratory or process environment has been limited because laser-induced sample heating and an overwhelming background at visible excitation wavelengths (532nm-785nm).[2]

We hypothesized that dispersive Raman spectroscopy at 1000 nm would effectively reduce the background, enabling dispersive Raman measurements of white, dark, and milk chocolate.

Raman spectra collected at 1000 nm demonstrated sufficient background reduction to enable observation of bands throughout the fingerprint region for white, milk, and dark chocolate samples. The fluorescence reduction and specificity of 1000 nm Raman spectra enables non-contact assessment of cocoa butter and other chocolate components with the measurement ease of lab-to-process dispersive Raman spectroscopy.

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