Determination of unsaturation in food oils and fats

Benefits at a glance
- Non-invasive, non-destructive measurement of food oil and fat unsaturation
- Raman-predicted unsaturation levels agree with off-line iodine value measurements
- In-line capability enables real-time process control

Introduction

Knowing the degree of unsaturation and relative amounts of *cis* and *trans* isomerization in edible oils and fats is important in today's food industry. This is necessary for both process and quality control, and is required nutritional information in food labeling.

Total oil and fat unsaturation is presented as the Iodine Value (IV). The IV is currently determined by titration or chromatographic techniques. These approaches are only used in the laboratory for off-line analysis because they require extensive sample preparation and take a long time to perform the measurements. However, there is a growing need for off-line process monitoring and control.

Raman spectroscopy is a technique for laboratory or process measurements in oils and fats.[1,2] We present evidence that this analysis can be conducted with dispersive Raman instrumentation designed for process control.

Experimental

A Raman analyzer, operating at 532 nm, was used to collect the Raman data. Depending on the sample, signal was collected for 60-300 seconds.

Determination of total unsaturation

Figure 1 shows the Raman spectra of butter, margarine, vegetable oil and vegetable shortening between 1150 and 1775 cm^{-1}. Total unsaturation can be determined quantitatively by measuring the ratio of the C=C stretch (νC=C) centered at 1661 cm^{-1} to the CH_2 scissoring deformation (δCH_2) at 1444 cm^{-1}.[1-3] Calculating band intensity ratios is a straightforward approach to quantifying total unsaturation. Visual inspection of the spectra provides a quick initial understanding of lipid saturation. The position and width of the band at ~1444 cm-1 and ~1661 cm-1 will shift to a lower Raman shift and become more narrow with increasing saturation.

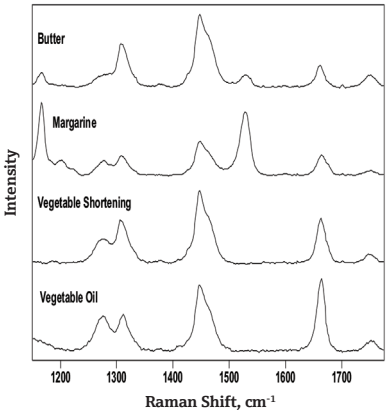

Figure 1: Background-corrected Raman spectra of commercial food oils and fats. The bands at 1165 and 1525 cm^{-1} of the butter and margarine spectra are attributed to the coloring agent ß-carotene.

Cis isomer content

Cis isomer content can also be determined from the Raman spectrum. The band at 1272 cm^{-1} is attributed to in-plane =C–H deformation in an unconjugated *cis* double bond. The intensity of this band ratioed to the in-phase methylene twisting vibration at 1306 cm^{-1} provides a direct *cis* isomer measurement. This is illustrated by comparing the Raman spectrum of vegetable oil with that of partially hydrogenated vegetable shortening. Hydrogenation results in a preferential decrease in the *cis/trans* isomer ratio.[3] In Figure 1, unhydrogenated vegetable

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

oil contains significantly more *cis* isomer character than partially hydrogenated vegetable shortening.

Background correction in highly fluorescent samples

Figure 2 shows the background-corrected, full Raman spectra of vegetable and peanut oils. The ratio of background level to the δCH_2 vibration intensity appears in parentheses by each spectrum. The fluorescence observed from commercial samples has been attributed to assorted coloring agents.[1–3] Figure 2 illustrates that, even in the presence of significant background, Raman spectra from these sample classes are readily observable.

This study used 532 nm excitation, which offers two advantages of increased sensitivity and detector efficiency. However there is also increased fluorescence signal at 532 nm. In some samples, fluorescence at 532 nm from the material itself or from additives may overwhelm the Raman signal. Using a longer wavelength laser either at 785 nm or 1000 nm will reduce the fluorescence for those samples.

Conclusion

The high-throughput Raman analyzer permits the use of low laser powers and short exposure times for remote Raman measurements. Its rugged construction and compatibility with fiber optic sampling probes make it well suited to applications outside the laboratory environment. This technique is well suited to the on-line determination of total unsaturation and *cis* isomer level in commercial oil and fat samples.

References

1. Lee, H.; et.al. Prediction of Crude Protein and Oil Content of Soybeans Using Raman Spectroscopy. *Sensors and Actuators B: Chemical* **2013**, 185, 694–700.

2. Jiménez-Sanchidrián, C.; Ruiz, J. R. Use of Raman Spectroscopy for Analyzing Edible Vegetable Oils. *Applied Spectroscopy Reviews* **2016**, 51 (5), 417–430.

3. Dymińska, L.; et.al. Quantitative Determination of the Iodine Values of Unsaturated Plant Oils Using Infrared and Raman Spectroscopy Methods. *International Journal of Food Properties* **2017**, 20 (9), **2003–2015**.

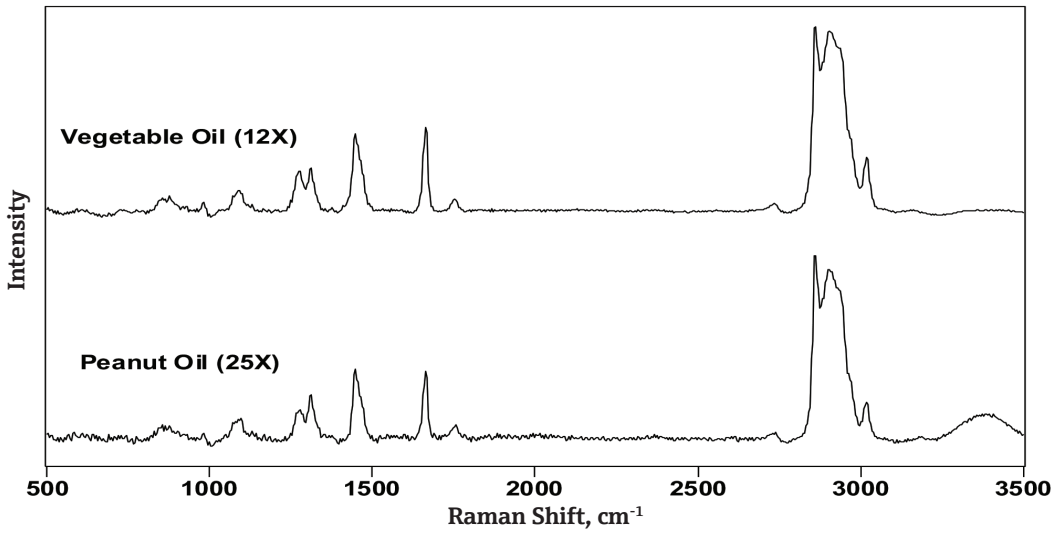

Figure 2: Background-corrected spectra of vegetable and peanut oils. The number in parenthesis indicates the background-corrected intensity of the 1444 cm-1 band.