

Fast Ingredient Analysis of Edible Oils Using a Portable Raman Spectrometer

Edible oils are not only a major source of nutrition but also a key basic material in the food industry. Vegetable oils are increasingly important because of their high content in mono- and polyunsaturated fatty acids in comparison with animal fats. In this application note, the main ingredients of olive oil, camellia oil, arachis oil, sunflower seed oil, and colza oil are analyzed using a portable Raman spectrometer combined with chemometrics software from B&W Tek.

Traditional edible-oil analysis methods such as gas chromatography-mass spectrometry (GC-MS) are extremely time consuming and work only under laboratory conditions.

Raman spectroscopy, to the contrary, is rapid and do not require any sample preparation steps prior to analysis.

The samples studied include oils with different concentration of oleic, linoleic, mono- and polyunsaturated fatty acids. The aim of this study was to rapidly determine component concentration in several edible oils for at-line testing. Thus, it highlights the capability of portable Raman spectroscopy to provide information about the chemical processes taking place during lipid oxidation in a rapid and experimentally simple way.



Portable Raman spectrometer *i*-Raman and quantitative software BWIQ

B&W Tek is the leader in portable and handheld Raman spectrometers. The *i*-Raman[®] is equipped with B&W Tek's patented CleanLaze[®] technology for exceptional laser stabilization and narrow linewidth. Other features include a spectral resolution as fine as 3cm^{-1} , broad Raman shift coverage up to 4000cm^{-1} , and a TE-cooled 2048 pixel CCD array. With a convenient fiber optic interface, it can collect data to within 65cm^{-1} of the Rayleigh Line. It is unique for its high resolution combined with field-portability, with performance comparable to large bench-top Raman systems and weighing less than 7 lbs. Utilizing a series of dedicated accessories, one can measure samples with different physical states. For edible oil measurements, a Raman cuvette holder BCR100A is used to obtain Raman spectra.



BWIK® chemometrics software is a multivariate analysis package that analyzes spectral data for the discovery of internal relationships between spectra and response data and/or spectra and sample classes. By coupling new and transitional chemometrics methods with cutting edge computer science technology, BWIK provides speed, accuracy, and performance for qualitative and quantitative analysis. In this application BWIK with advanced spectral preprocessing and PLS regression allows for the quantitative determination of various components of a series of edible oils.

Experimental

Instrumentation: *i*-Raman portable spectrometer with 785nm laser excitation , Raman shift range 175-2600 cm^{-1} ,
Integration time: 9sec
Sampling accessory: Dedicated liquid cuvette holder, optical path 10mm.

Samples: olive oil, camellia oil, arachis oil, sunflower seed oil, and colza oil. 30 samples from each category were used for a total of 150 samples.

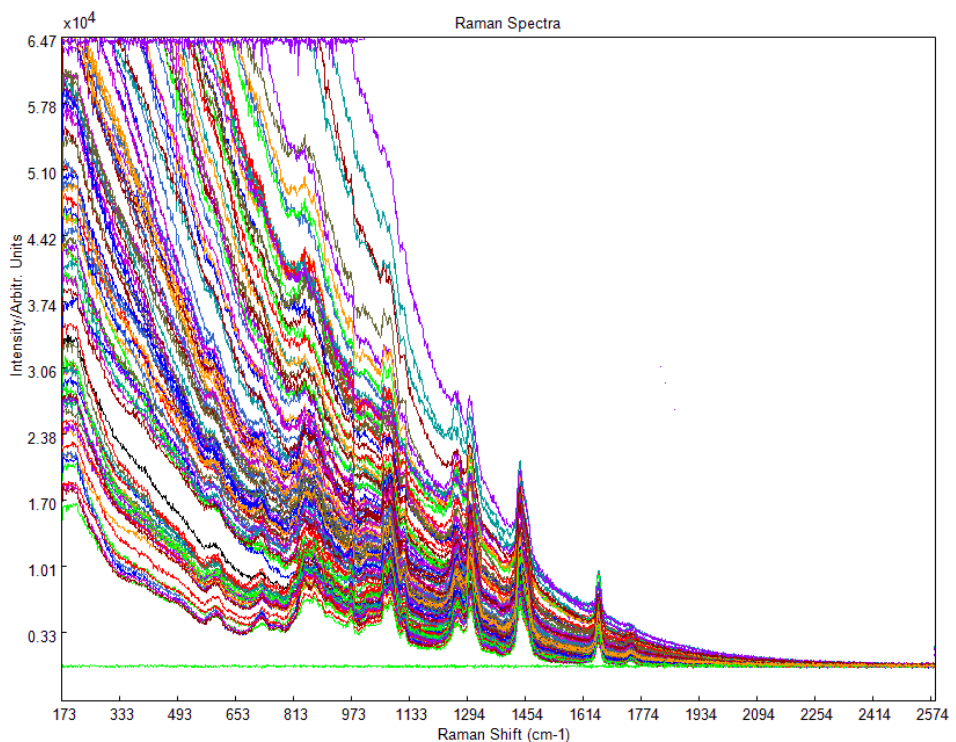


Figure 1: Raw Raman spectra of different types of edible oil



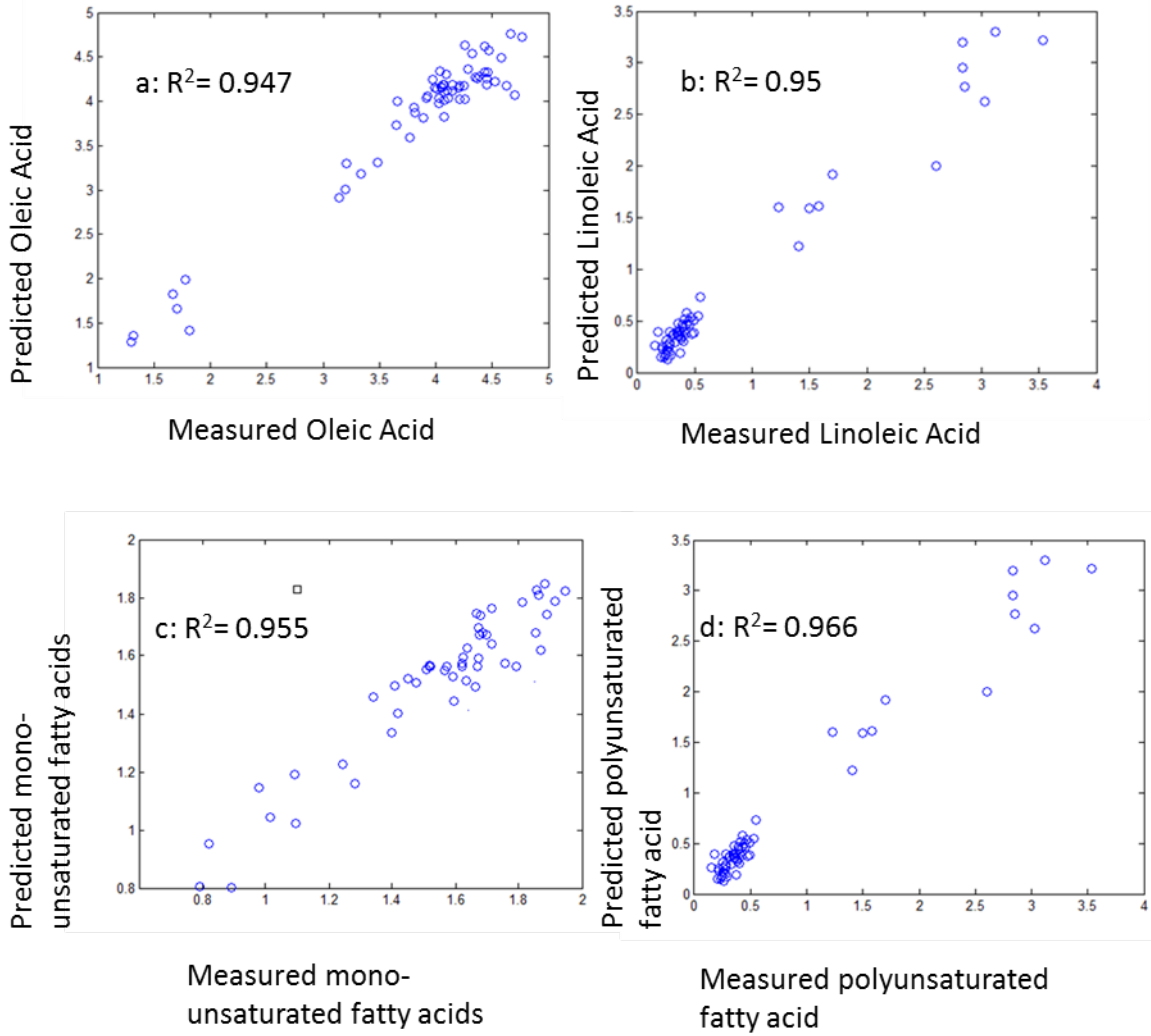
Result and Discussion

Raman spectra of different edible oils were collected and quantitative analysis for the concentration of the composition of the oils was accomplished. The reference values for the concentration of edible-oil ingredients, including oleic acid, linoleic acid, mono-unsaturated fatty acids, polyunsaturated fatty acid and saturated fatty acid, were measured by GC-MS. A quantitative PLS regression model was constructed in BWIQ software based on the Raman spectra for 150 samples. - Preprocessing including background removal and Savitzky-Golay smoothing were employed to improve the signal-to-noise ratio of the Raman spectra. PLS regression was used to build the model for all five ingredients (PLS2). The characteristic Raman bands were manually selected to focus on the spectral regions associated with bands attributable to the saturation, unsaturation, and backbone of the different acids. Table 1 shows a summary of the PLS regression results for all chemical values of ingredients mentioned above.

Table 1: PLS model results

Ingredients	coefficient of correlation	RMSEP
oleic acid	0.95	0.24
linoleic acid	0.97	0.17
mono-unsaturated fatty acids	0.96	0.23
polyunsaturated fatty acid	0.98	0.15
saturated fatty acid	0.84	0.15

Both RMSEP (Root Mean Square Error of Prediction) and coefficient of correlation show the quality of this model is sufficient to predict the ingredients in the edible oils. is a key index to evaluate the prediction quality. Samples of different types were then measured by an i-Raman portable spectrometer to predict the chemical values in BWIQ software using this model. Figures 2 and 3 show the results of prediction for each ingredient.



**Figure 2: a) oleic acid b) linoleic acid
c) mono-unsaturated fatty acids d) polyunsaturated fatty acid prediction results**

The Saturated fatty acid prediction sample set showed a large deviation which may be an outlier in the system.

In BWIQ software, one can easily find the outlying samples both graphically and from model statistics. In this work an outlying sample was rejected and a new model was built in BWIQ software. Figure 3 shows the prediction results for saturated fatty acid.

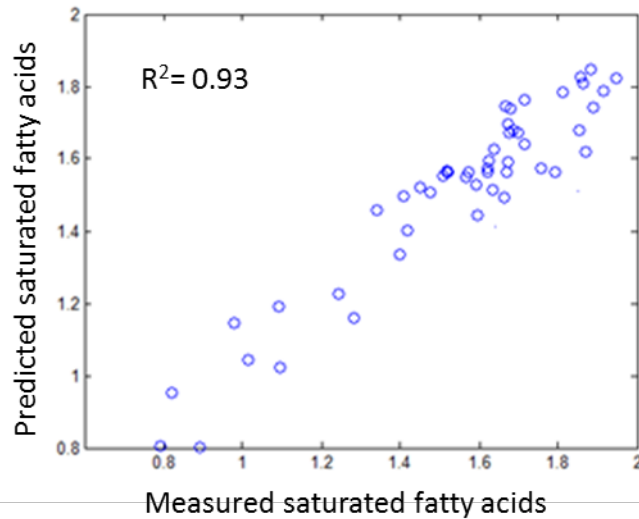


Figure 3: Saturated fatty acid prediction result

In this work it is shown that calibration models for five ingredients in edible oils can be developed using the portable i- Raman spectrometer and BWIQ chemometric software. The prediction results are acceptable for all ingredients compared to GC-MS, and can be obtained quickly and nondestructively - using the portable Raman spectrometer. The oil samples can be measured in disposable glass vials of cuvettes, without any further sample preparation. In addition, the results could also be improved if the model is built for each ingredient respectively.

Reference

- Bruno Bernuy, Marc Meuren, et.al. Determination by Fourier Transform Raman Spectroscopy of Conjugated Linoleic Acid in I2-Photoisomerized Soybean Oil. J. Agric. Food Chem., 2009, 57 (15), pp 6524–6527 DOI: 10.1021/jf9003237
- Barbara Muik; Bernhard Lendl; Antonio Molina-Diaz Direct monitoring of lipid oxidation in edible oils by Fourier transform Raman spectroscopy. 2005(2) doi:10.1016/j.chemphyslip.2005.01.003
- BWIQ Raman quantitative software: <http://www.bwtek.com/products/bwig/>
- AppNote: 20120710C, B&W Tek Shanghai, Central South University, and ChemSolve Ltd.