Two-dimensional correlation spectroscopy and multivariate curve resolution for the study of lipid oxidation in edible oils monitored by FTIR and FT-Raman spectroscopy

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Abstract

Accelerate oxidative degradation of six vegetable oils was monitored using FTIR and FT-Raman spectroscopy. Two-dimensional correlation spectroscopy and multivariate curve resolution alternating least squares (MCR-ALS) were applied to the analysis of the data. The use of heterospectral two-dimensional correlation of FTIR and FT-Raman data allowed the use of well established band assignments to interpret less clearly assigned spectral features. With a moving window approach it was possible to obtain simplified two-dimensional correlation maps and to detect compounds evolving with different kinetic. Simultaneous analysis of the oxidation experiments of the six different oils monitored by both spectroscopic techniques was performed using MCR-ALS. Although a complete resolution of the data was not possible, the spectral changes occurring during the oxidative degradation of the oils were described with a five-component model. The two fundamentally different chemometric approaches lead to coincident results.
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1. Introduction

Lipid oxidation is a major deteriorative reaction affecting edible oils and fats and consequently of primary concern to processors and consumers. Unsaturated lipids are particularly susceptible to oxidation. The oxidation process is extremely complex, involving numerous reactions that give rise to a variety of chemical and physical changes in lipids. The most common mechanism of oxidation is a free radical chain reaction. This process is retarded by antioxidants such as tocopherols, and accelerated by prooxidants such as trace metals and heat. Primary products in lipid oxidation are allylic hydroperoxides, in which the double bonds remain but may have changed position and/or configuration from their original form. Hydroperoxides decompose into secondary oxidation products such as aldehydes, ketones and epoxides [1].

Classical chemical parameters used to determine the extent of oxidation in edible oils are peroxide value and spectrophotometric absorption at 232 and 270 nm, for initial stages of oxidation; and anisidine and 2-thiobarbituric acid (TBA) value that measure aldehydes, oxidation products which are closely related to the development of rancidity. More sophisticated methods use gas and liquid chromatography to identify and quantify individual oxidation products [2].

It has been demonstrated that infrared spectroscopy is a useful tool to monitor the oxidation of edible oils due to the high information content of infrared spectra and the possibility to assign specific absorption bands to particular functional groups. Spectral changes in the mid-infrared region associated with oil oxidation have been described in detail and common oxidation products, such as aldehydes, alcohols and peroxides have been identified using representative reference compounds

[3]. Furthermore, quantitative and semi-quantitative approaches have been proposed to evaluate the oxidative alteration of oils using FTIR [4–6].

In a previous work we reported the possibility of monitoring oil oxidation using FT-Raman spectroscopy [7]. Formation of aldehydes was detected and isomerization of *cis* to *trans* double bonds, as well as formation of conjugated double bond systems was observed in the C=C stretching region. The time dependent intensity changes in certain Raman bands were compared to conventional parameters used to determine the extent of oxidation in oils, such as anisidine value and K_{270}, and showed good correlation.

Raman and IR are complementary techniques. Both techniques probe vibrational transitions but the selection rules applying for Raman scattering and IR absorption are different. Thus, the relative band intensities in IR and Raman spectra differ markedly, providing complementary information. Of particular significance in the field of vegetable oils is that stretching of C=C bonds give rise to strong Raman signals, whereas C=O stretching bands are very weak. The contrary is found in infrared spectra. The combined information provided from both techniques can be thus very useful in the study of vegetable oil oxidation, where these functional moieties are implicated in the major chemical changes.

The goal of the present work is to compare the IR and Raman spectral changes taking place during thermal oxidation of vegetable oils with different fatty acid compositions an to combine the information obtained from both techniques to gain insight on the chemical changes that occur. For this, two advanced chemometric tools for the analysis of evolving systems, two-dimensional correlation spectroscopy and multivariate curve resolution-alternating least squares will be used. Evolving data sets are frequently found in analytical chemistry, when spectroscopic techniques are applied to the monitoring of dynamic processes that proceed as a function of a modulation variable. In contrast to the univariate approaches analyzing specifically predetermined peaks, which were usually applied in the study of oil oxidation with infrared and in our previous study with Raman spectroscopy, these multivariate techniques allow comprehensive analysis of the whole spectra.

Two-dimensional correlation spectroscopy (2D-CoS) performs cross-correlation analysis of a series of spectra of a system that changes with a modulation variable. It spreads the one-dimensional spectra into a second spectral dimension, thus yielding two-dimensional maps of cross-correlations of a given spectral variable with every other spectral variable in the data [8]. In the most recent formulation, the synchronous correlation map is obtained as a covariance matrix of the measured spectra and the asynchronous correlation map as product of the matrix of measured spectra and a Hilbert–Noda transform [9,10]. 2D-CoS gives a descriptive picture of the data by visualizing and enhancing correlation (synchronous map) and disrelation (asynchronous map) in the data. It enhances spectral resolution and allows the establishment of unambiguous assignments of bands. Furthermore, the use of hetero-spectral correlation analysis provides a convenient mean to investigate the relationship

between dynamic variations observed by two different spectroscopic techniques [11,12].

The goal of curve resolution methods is to determine the number of significant chemical/physical components that contribute spectroscopically to the measured data matrix and recover the pure response profiles (pure spectra and pure concentration profile) of the modeled components [13,14]. This is done by decomposing the experimentally measured data matrix into the product of two smaller matrices containing the concentration profiles and the spectra. Various curve resolution approaches have been proposed, which differ in their principles and requirements to the data structure. Multivariate curve resolution-alternating least squares is a very flexible method that allows for the inclusion of several chemical constrains and for the simultaneous analysis of multiple data sets [15,16].

2. Experimental

2.1. Instrumentation

Raman spectra were recorded with a Bruker RFS (FT)-Raman spectrometer fitted with a liquid nitrogen cooled Ge detector. The samples were illuminated by an Nd:YAG laser line at 1064 nm with a power of 500 mW using a focused laser beam. All spectra were recorded with a resolution of $4\,cm^{-1}$ and averaged over 200 scans. Acquisition of one spectrum took 5 min. Infrared spectra were recorded with a Bruker Tensor 37 Fourier transform infrared spectrometer equipped with a horizontal DuraSamplIR II triple reflection ATR (SensIR Technologies) and a narrow-band mercury cadmium telluride (MCT) detector. All spectra were recorded at $4\,cm^{-1}$ resolution (128 scans, apodization function: Blackman-Harris-3-term). Spectra of the clean and dry ATR crystal against air were used for the background.

2.2. Samples

The six vegetable oils, virgin olive, corn, sunflower, rapeseed, peanut and safflower, were purchased from Austrian and Spanish supermarkets. C*is*-9, *trans*-11-linoleic acid standard was supplied by Sigma.

2.3. Oxidation and spectroscopic measurements

About 200 mL of the oils were heated at 160 (±2) °C and stirred continuously on a magnetic stirrer for 9 h. Every half an hour 4 mL were sampled, left to cool to room temperature for recording the FT-Raman and FT-IR spectra. No sample preparation was required.

2.4. Data evaluation

For all data evaluation the experimental data obtained for each oil are assembled in matrix **D**, which represents an $m \times n$ matrix with spectra (Raman or infrared) aligned in rows, thus yielding a time × wavenumber matrix.