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Thermal Degradation of Vegetable Oils: Spectroscopic Measurement and Analysis

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Abstract

The paper deals with measuring of structural changes in edible oils during their heating giving arise to unsafe degradation products. The attention is paid to the major decomposition product of heated oxidized linoleate and content of carotenoids with antioxidant effects. Analysis is based on Raman spectral data that provide unique information about the structure of the oils. Raman spectroscopy offers effective and rapid way for oils quality control with respect to their health benefits and in terms of processes in food technology. Three most common vegetable oils were used for the thermal degradation study: sunflower, canola and olive oil. Measured were both, extra virgin and refined oils. Mathematically processed spectral data indicate the least action of thermal load for olive oils. Then due to a significant content of antioxidants it is canola oil. The worst effect in terms of thermal decomposition products formation and the loss of *cis* double bonds arise for sunflower oils.

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Keywords: Thermal degradation; Raman Spectroscopy;measurement; vegetable oils;carotenoids

1. Introduction

Vegetable oils as a source of lipids represent indispensable and permanent part of our daily diet. Interest in the health diet became an actual issue recently and is widely discussed both in scientific area but also in public media. Modern analytical tools enable application broadening in this area and contribution by faster, more available and precise experimental data that can complete, confirm or disprove already known coherency. Raman spectroscopy as an effective method for material identification brings advantages over conventional laboratory procedures and

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allows rapid, noncontact, specific, non-invasive analyses independent of number of chemicals and without requirement of special sample preparation. These features can also make measurement procedure to be automated. From this point of view Raman spectroscopy is a promising technique to be practically applicable in the area of food quality and assessments.

Besides proteins and carbohydrates, lipids are important and irreplaceable part of the human diet. The role of lipids in organism is essential. They represent not only a major source of energy and mechanical and temperature protection of organs and body, but their functional properties also participate in large extent in metabolism, they are components of biomembranes and other biologically active substances carriers. Hence the intake of vegetable oils is very important. Except saturated fatty acids they also contain a substantial proportion of mono- and polyunsaturated fatty acids. These unsaturated fatty acids represent on one hand the health benefit of edible oils in their consumption by humans or livestock, on the other hand also a source of instability of oils in the process of technological processing, storage or cooking. More recently health benefits of plant oils and margarines are discussed in relation to the content of undesirable trans fatty acids [1].

The interest of both general public and experts is focused on the optimal ratio of saturated to unsaturated fatty acids in human diet since it is associated with significant impact of the incidence of cardiovascular diseases, obesity and related diseases. High levels of saturated fatty acids in human diet are frequently considered to have influence on high concentration of low density lipoproteins (LDL) in blood circulation system. The intake of polyunsaturated fatty acids (PUFA) is very important since many of them are essential for humans (ω-3 and ω-6). [1]

Monitoring of the changes in the quality of edible oils during processing from the source of raw material until their usage by the final user either as food or as highly popular dietary supplements is therefore very reasonable. Edible oils can be degraded by oxygen, temperature, light, humidity, enzymes or trace of metals.

Most accurate methods for oxidation of edible oils are chromatography techniques, as HPLC and mainly gas chromatography coupled to FID or MS detector that can identify and quantify individual fatty acids and oxidation products and also UV-VIS spectrophotometry. All these classical methods require the use of reagents and solvents that might be hazardous for people or the environment. These procedures are time consuming, technician skill and expensive laboratory equipments are required [3]. Traditional methods do not provide possibility to couple with any automatic control element for process control introducing. This is the reason for searching for alternative methodologies which are based on direct sample analysis, such as nuclear magnetic resonance, chemiluminiscence, fluorescence, vibrational spectroscopy or terahertz spectroscopy [3-6]. Especially Fourier-transform vibrational techniques, both IR and Raman spectroscopy also in combination with chemometrics have potential to be rapid screening methods for lipid quality control purposes [7]. Furthermore, the presently available portable Raman devices enable *in situ* analysis, what represents undisputable relevance for application in food industry [8].

Edible oils analysis is actually developing field for application of Raman spectroscopy. Collecting the real spectra is fast and quite easy, however the quantitative determination is more difficult. Mathematical methods and chemometrics are necessary. This study is based on the interest in healthy use of vegetable oils. The objective of presented paper is then to perform Raman spectral determination of thermal degradation process in vegetable oils accelerated by heating.

2. Vegetable oils and degradation process

Vegetable oils are composed of glycerol molecule esterified by three fatty acids molecules. Each type of vegetable oils is characterized by its own specific fatty acids ratio content. Predominant fatty acids have 16 or 18 carbon atoms in straight aliphatic chains. Unlike to desirable health benefits of PUFAs there is higher ability to undergo degradation changes according to high level of double bonds presented. They are quite sensitive to oxidative conditions and generate many degradation products including aldehydes, ketones, epoxides, hydroxy compounds, etc. Many of them are now considered as toxic and potentially carcinogenic [9]. Oxidative stress can cause conjugated double bond system formation as well as evaluation of trans fatty acids. The content of these oxidation products can correspond to oil technological treatment, method and duration of storage and it has undesirable influence on nutritional quality, safety and sensory properties [10]. Oxidation of unsaturated fatty acids is the main reaction responsible of the degradation of lipids [2]. Therefore, it is essential to know the composition of

fatty acids to identify their characteristics and determining more precisely their stability during processing and storage, suitability for applications and possibility to verify their adulteration [11].

Oxidative degradation of oils can be increased by heating above 100°C. Chemical changes corresponding to C=C bond during oxidation as well as degradation products formation are expected to be reflected in Raman spectral changes [12].

Raman spectroscopy combined with chemometrics has been successfully used for characterization of different kinds of edible oils [13], for quantitative detection of extra virgin olive oils adulterated with cheaper edible oils [14], for quantitative analysis of enriched virgin olive oil with other ingredients such as aromatic plant to improve its culinary, cosmetic and medicinal properties [2]. Raman spectroscopy seems to be a suitable tool for monitoring lipid oxidation process.

3. Experimental part: thermal degradation monitoring

3.1. Materials

To monitor the thermal degradation process six common types of oils were used for spectroscopic measurements: sunflower oils, canola oils and olive oils; all of them extra virgin and refined. All oils were heated up to 160 ° C, the temperature was maintained, while continually stirred. Samples were taken immediately after reaching the desired temperature, after 30 minutes and after every other 30 minutes and consequently analysed on a Raman microscope.

3.2. Raman spectroscopy and Raman instrumentation

As an innovative vibrational spectroscopic method Raman spectroscopy provides a specific chemical fingerprint of every single chemical substance and its modifications in the form of Raman spectra. The method is based on so called Raman scattering - an inelastic scattering resulting from an interaction of a photon and a molecule. Vibrations of particular molecular bonds cause a slight characteristic changes in wavelengths in scattered photons. These wavelength shifts then facilitate the material identification and structural assessments. Substantial benefits arise from many advantages of the method: Raman spectroscopy is relatively rapid, non-destructive, contactless, applicable to all states of matter in different forms (crystals, powders, fibres, solutions, etc.), without special requirements for sample preparation, independent on chemicals, usable as *in situ* analysis, usable for measuring through transparent glass or polymeric covering layers. Since the Raman scattering is a weak effect, some adverse effects can influence the quality of spectral response. Luminescence, for instance, as much stronger quantum effect can overlap Raman spectra with its intensity and mask spectral information. Another disadvantage is eventual degradation of a sensitive sample when using intense laser beam.

Raman spectroscopy finds more and more applications across scientific areas such as chemistry, biochemistry, material science, mineralogy, arts, medicine; method is used for pharmaceutical, forensic and security purposes and recently starts to penetrate also to food industry [15 - 17].

Raman spectra of all samples were measured on Renishaw InVia Basis Raman microscope using NIR diode laser (785 nm) with maximum output power 300mW. Leica DM 2500 confocal microscope with the resolution 2μm was coupled to the Raman spectrometer. All measurements were collected with 30 s exposure time and 10 accumulations. The samples were firstly scanned in range 100 to 3200 cm^{-1} with 2 cm^{-1} spectral resolution. After determining the principle peaks the spectral range was reduced approximately to the area 800 - 1800 cm^{-1}.

4. Results

Raman spectra of different oils are mostly alike in terms of contribution of characteristic peaks due to similar chemical composition. However every oil has various ratio of MUFA and PUFA and other components, what affects intensity of Raman bands. Essential bands for vegetable oils assessments are listed in Table 1.

Table 1. Raman bands and their assignments.

Raman peak [cm^{-1}]	Assignment to vibrations of chemical bonds
1159	C-C stretch of carotenoids
1164	C=C stretching of oxidized linoleate
1267	=C-H symmetric rocking
1303	CH_2 in-plane twist
1442	CH_2 scissoring
1526	C=C stretching of carotenoids
1640	C=C *trans, trans* 2,4 decadienal
1658	C=C *cis* double bond stretching
1747	C=O ester-carbonyl stretching

Thermal decomposition of oils was demonstrated on two features manifested in the spectra. Firstly on changes of characteristic peaks corresponding to the formation of degradation products observed mainly at 1640 cm^{-1}, secondly on the decrease of C=C stretching of carotenoids at 1526 cm^{-1}. Further analysis could be conducted on the basis of unsaturated carbon *cis* double bonds affecting especially intensity reduction of peaks at 1267 cm^{-1} and 3015 cm^{-1} and current rise of peak at 1303 cm^{-1} for saturated CH_2.

Formation of the degradation product at 1640 cm^{-1} is shown in Fig. 1(a). C=C stretching from heated oxidized linoleate exhibit at 1164 cm^{-1} however in a much lesser extent than the peak 1640 cm^{-1}. This band is assigned to formation of *trans, trans*-2,4-decadienal as a major decomposition product of heated oxidized linoleate corresponding to C=C stretching vibration in conjugated system. Mentioned aldehyde is readily detected in heated oils, stored food products as well as on restaurant and kitchen emissions. Cooking oil fumes are a complex mixture of chemicals, among the *trans, trans*-2,4-decadienal is the most abundant and cytotoxic. Recent epidemiological studies have demonstrated that exposure to cooking oil fumes is strongly associated with respiratory diseases and non-smoking female lung adenocarcinoma in kitchen workers [18].

Obtained spectral data indicates that the first stage of thermal oxidation exhibits a linear trend for increasing Raman intensity at 1640 cm^{-1} on time as displayed in Fig. 2(a). The steepest increase is indicated for sunflower oil.

Carotenoids are known for their anti-oxidative properties as radical scavengers and singlet oxygen quenchers in lipid oxidation. Out of three types of tested oils it is canola oil with the greatest share of carotenoids, and sunflower oil with the lowest [20]. Raman spectra of canola oil degradation process indicate the decrease of both 1526 cm^{-1} and less intense 1159 cm^{-1} band for carotenoids C-C stretch. These bands show a gradual decrease in intensity in

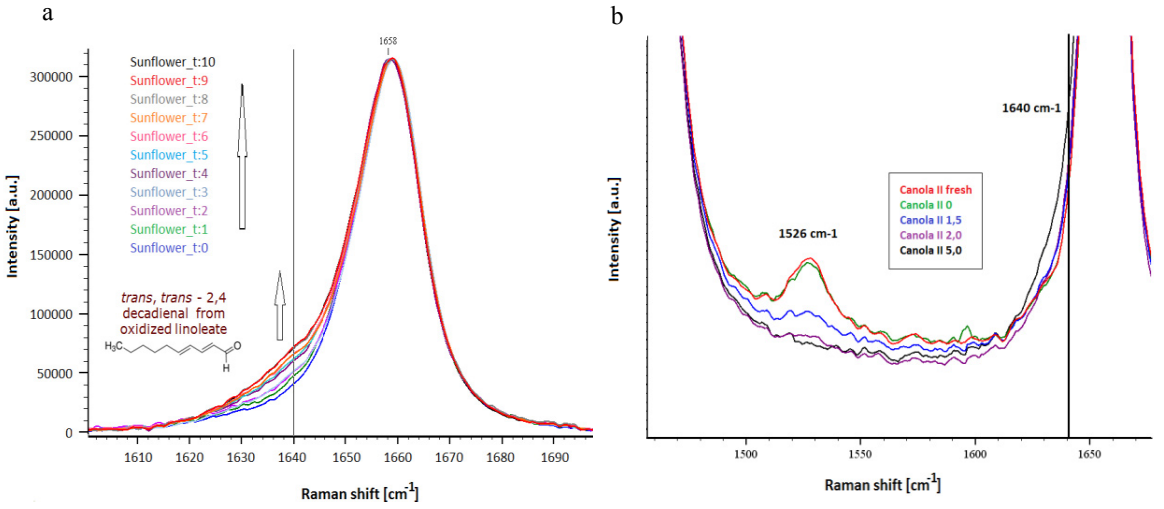

Fig. 1 (a) Raman spectra of increasing 1640 cm^{-1} band of product of thermal degradation; (b) influence of carotenoid (1526 cm^{-1}) on the formation of *trans, trans*-2,4-decadienal (1640 cm^{-1}) during heating of canola oil.

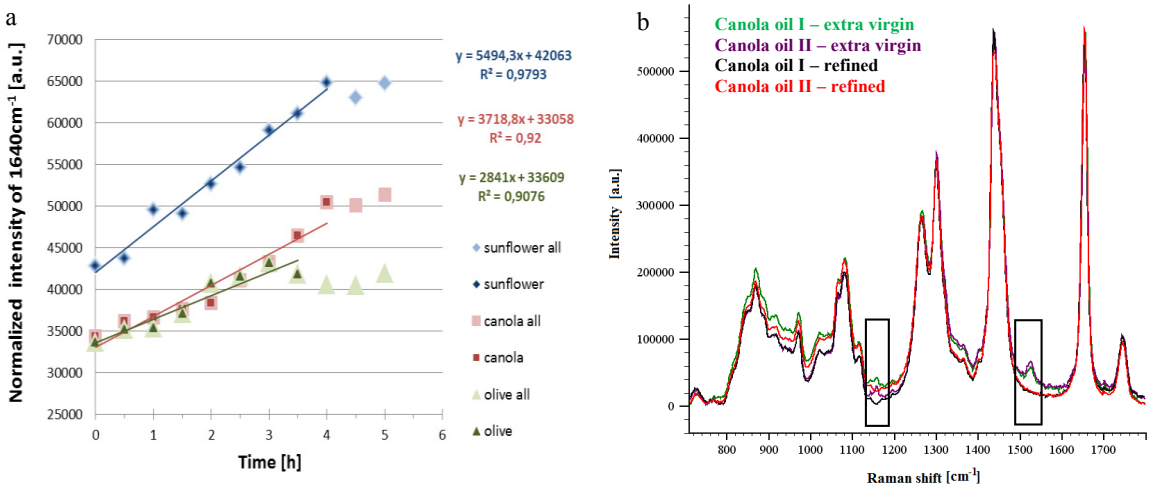

Fig. 2 (a) Thermal degradation product formation; (b) Raman spectra of extra virgin and refined canola oil, (bands for carotenoids in boxes).

correlation to short time temperature stress [21]. Results show only a very small share of remaining carotenoids observed after heating for 2 hours, complete disappearance of the peak after 5 hours, see Fig. 1(b). Corresponding loss of carotenoids during 90 min heating period at 1525 cm^{-1} was observed elsewhere [2].

This trend quite accurately correlates with the rise of degradation product in 1640cm^{-1}. When following points for canola oil in Fig. 2(a) just a slight increase in first two hours is obvious, but then it begins to grow more rapidly as the share of antioxidants is reduced.

The presence of carotenoids is also a significant attribute to distinguish extra virgin oils from refined oils since refining remarkably reduce the share of antioxidants. Raman spectra of extra virgin and refined oils are shown in Fig. 2(b).

Finally PCA applied to spectral data sets for thermally degraded sunflower, canola and olive oils show the clear diversity among these oils, see Fig. 3(a). The fresh samples, just being heated and samples heated for 5 hours were picked from all data and are shown in Fig. 3(b). All except of the olive oil sample I show similar upward trends sharply distinguished from other species.

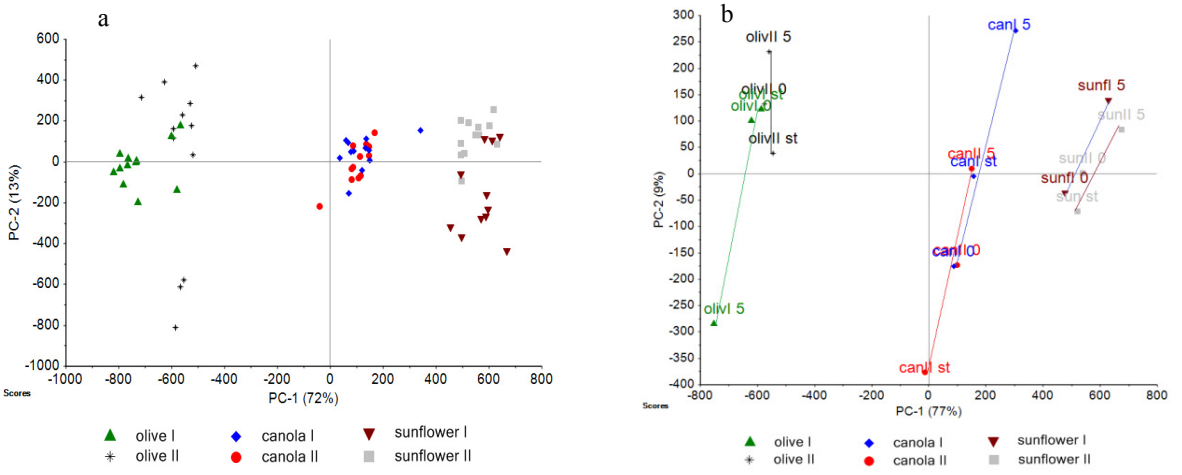

Fig. 3 (a) PCA of two sets of thermally degraded olive, canola and sunflower oil; (b) PCA of fresh cold oils (st), just heated up to 160°C (0), heated for 5 hours (5).

Conclusion

Raman spectroscopic study of oxidative degradation of edible oils shows that thermal stress of vegetable oils can be monitored via the amount of rising degradation products. Multivariate statistical method PCA and PLS are an efficient tool for spectral data evaluation. Analyses carried out for sunflower, canola and olive oils leads to the conclusion that the most evident degradation occurs for polysaturated sunflower oils. Canola oils give better results due to negligible content of carotenoids and the best results exhibit olive oils. These two represent greater health benefits as rather monosaturated oils and are more suitable for thermal stress. However, prolonged heat load of all types of cooking oils causes the formation of degradation products that may undesirably affect the human health. Raman spectroscopic evaluation of discussed features brings advantages over traditional methods mainly in sense of rapidity, simplicity and no need of chemical reagents and sample preparation, what saves time and costs.

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