# Spectroscopic screening of degradation process in edible oils and its mathematical evaluation

M. Buckova, H. Vaskova, M. Tobolova and V. Kresalek

Abstract—The purpose of the presented study is to verify applicability of Raman spectroscopy for the thermal degradation screening of edible oils and their identification. The statistical method Principal component analysis was performed for large spectral datasets evaluation as well as Partial least square regression. Raman spectroscopy as an effective tool for material identification offers benefits that are required for the process control of oils quality, both in terms of food technology and in terms of maintaining the nutritional value of edible oils. These are rapidity, independence on the number of chemicals, portability and possibility of automation of measurements - advantages over the conventional laboratory procedures. For the degradation process the most common types of oils used in the Czech Republic were used: sunflower, olive and canola oils. For the identification fourteen vegetable oils and oils from seeds and nuts were used. Mathematically processed spectral data indicate the worst effect of thermal load in terms of degradation process products formation and the loss of cis double bonds, i.e. the unsaturation for sunflower oils. Olive oils as the best and canola oil represent lesser risk due to a greater content of antioxidants. However, longer heat load leads to undesired decomposition and unsafe and unhealthy products generation even in these oils.

*Keywords*—Identification, PCA, Raman spectroscopy, thermal degradation, vegetable oils

## I. INTRODUCTION

HEALTHY diet and lifestyle are very popular topics lately. With the development and use of modern analytical methods, it is possible to become more knowledgeable and support common experiences by experimental data and scientific results.

Lipids are an irreplaceable part of the human diet because the role of lipids in organism is essential. They represent not only a major source of energy and mechanical and

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Vojtech Kresalek is with the Faculty of Applied Informatics, Tomas Bata University in Zlin, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic (e-mail: <u>kresalek@fai.utb.cz</u>) 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, (e.g. lipid-soluble vitamins). From this point of view 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, which can arise from industrial hydrogenation of edible oils and from biohydrogenation in ruminant animals [1].

Therefore it is very important to monitor changes in the quality of edible oils during processing, from the source of raw material (oil content in seeds, fruits, etc.) until their usage by the final user either as food or as highly popular dietary supplements. The most frequently observed adverse changes are just in oils with higher content of polyunsaturated fatty acids. Double bonds are sensitive to external factors causing the degradation of these double bonds to form degradation products and/or trans fatty acids formation. Edible oils can be degraded by oxygen, temperature, light, humidity, enzymes or trace of metals. These factors can be source of undesirable rancidity and decreasing of nutritional value [2].

The most often change in oil composition is due to oxidation process. Common chemical parameters used to determine the extent of oxidation in edible oils are peroxide value, spectrophotometric absorption at 232 and 270 nm for starting part of oxidation process and anisidine and 2-thiobarbituric acid value for aldehydes determination [3]. Most accurate methods are chromatography techniques, like a liquid chromatography (HPLC) and mainly gas chromatography coupled to FID or MS detector that can identify and quantify individual fatty acids and oxidation products. All these classical methods require the use of reagents and solvents that might be hazardous for people or the environment. These procedures are also time consuming, technician skill and expensive laboratory equipments are required [4]. 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 and vibrational spectroscopy [4], [5]. Olive oil production sector has recently experienced some technological and commercial changes e.g. the introduction of new production lines allowing continuously controlled process [6].

Primary experiments focused on terahertz technique application for edible oils classification can be found in [7]. Especially with the advent of the 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 [8]. Furthermore, the presently available portable Raman devices enable *in situ* analysis, what has undisputable relevance for application in food industry [9].

From this point of view Raman spectroscopy is a very promising technique in process analytical chemistry that is rapid, does not require any sample preparation, no reagents are needed, measurements are relatively simple. Another advantage is the possibility to obtain Raman spectra via transparent covering layers from glass or plastic. Raman spectroscopic measurements seem to be practically applicable for automated measurements on the basis of the features of this innovative method [8].

### II. SCOPE OF THE RESEARCH

The interest in the healthy use of edible oils has led to the study of oxidative degradation process accelerated by heating of oils. The objective was to use innovative method Raman spectroscopy both for thermal degradation and for rapid discrimination of 14 kinds of edible oils, to find correlation between the degree of saturation and classification of oils. Mathematical methods and chemometrics are needed since a mere visual examination of spectra is not sufficient.

# III. THEORY

# A. Edible Oils

The most frequent forms in oils and fats are triacylglycerols, i.e. glycerol molecule is esterified by three fatty acids molecules. Vegetable oils are an important source of monounsaturated and polyunsaturated fatty acids, unlike animal fats that contain mainly saturated fatty acids. 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. From this point of view intake of polyunsaturated fatty acids is very important. Many of these PUFAs are essential for humans and many studies have focused on research of effect PUFAs in diet. The higher PUFAs intake is recommended by nutrition specialist also as the optimal proportion of  $\omega$ -3 and ω-6 PUFAs [1], [10].

Generally, each one of vegetable oils is characterized by its own specific fatty acids ratio content. Predominant presented fatty acids have 16 or 18 carbon atoms in straight aliphatic chains. There is palmitic acid (C16:0) and stearic acid (C18:0) as the main saturated fatty acids in vegetable oils, their concentration is quite low compare to unsaturated fatty acids except coconut and palm oil. Oleic acid is the major monounsaturated fatty acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3) are the major polyunsaturated fatty acids. [10] - [12]. The main characteristic fatty acids as compounds of edible oils used in this study are reported in Table 1.

Table 1 Percentual compositions of fatty acids in representative edible oil. C 12:0 lauric acid, C 16:0 palmitic acid, C18:0 stearic acid, C 18:1 oleic acid, C 18:2 linoleic acid, C 18:3 linolenic acid, C 20:0 arachidic acid, C 20:1 gadoleic acid; \* additional composition of coconut oil: C8:0 - 6,6, C10:0 - 5,1 and C14:0 - 5,1 [13] – [15].

	Oils	C12:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1
1	grape seed oil	-	6,6	3,5	14,3	74,7	0,2	-	-
2	groundnut oil	-	7,5	2,1	71	18,2	0	1	-
3	<u>canola oil</u>	-	4,6	1,7	63,3	19,6	1,2	-	9,1
4	sunflower oil	-	6,2	2,8	28	62,2	0,2	0,2	0,2
5	safflower oil	-	6,7	2,4	11,5	79	0,1	0,2	-
6	almond oil	-	6,8	2,3	67,2	22,8	-	-	0,2
7	wheat oil	-	17,4	0,7	12,7	59,7	4,1	-	-
8	sesame oil	-	9,7	6,5	41,5	41	-	0,6	-
9	pumpkin oil	-	13,1	5,7	24,9	54,2	-	0,5	1
10	rice oil	-	20	2,1	42,7	33,1	0,5	-	1,1
11	milk thistle oil	-	7,9	4,5	20,4	63,3	0,9	2,6	0,2
12	coconut oil*	47,7	8,4	2,7	6,2	1,6	-	0,3	-
13	hemp oil	-	6,4	2,6	11,5	59,4	3	0,5	16,5
14	olive oil	-	14,7	2,6	66,1	12,8	1	0,2	-

Contrary 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, oligomers and polymers. Many of them are now considered as toxic and potentially carcinogenic [16]. 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 [17]. Oxidation of unsaturated fatty acids is the main reaction responsible of the degradation of lipids [2]. This process is retarded by antioxidants such as tocopherols, and it can be accelerated by prooxidants such as trace metals and heat [3].

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 [10].

The oxidative degradation of oils can be increased by heating under 100°C. Using Raman spectroscopy chemical changes corresponding to C=C bond during oxidation as well as degradation products formation is expected to be reflected in spectral changes [18].

Edible oils analysis is actually developing field for

application of Raman spectroscopy. Collecting the real spectra is fast and quite easy, the quantitative determination is more difficult. The complexity of Raman spectra requires the use of advanced spectra treatment approaches [2]. Raman spectroscopy combined with chemometrics has been successfully used for characterization of different kinds of edible oils [19], for quantitative detection of extra virgin olive oils adulterated with cheaper edible oils [20], [21], for quantitative analysis of enriched virgin olive oil with other ingredients such as aromatic plant to improve its culinary, cosmetic and medicinal properties [2]. The quality control of olives for producing high-quality olives [22] and prediction of oil content of soybeans were published too [23]. Raman spectroscopy seems to be a suitable tool for recognizing oxidative deterioration of oil, for monitoring lipid oxidation process [4], [24].

## B. Raman Spectroscopy

In principle, Raman spectroscopy as a vibrational spectroscopic method has the potential to answer a number of questions related to chemical details of molecular structure what makes this technique definitely proper for material identification [25]. This method becomes a valuable part of laboratories around the world in recent years.

Raman spectroscopy provides very specific chemical "fingerprint" of every single chemical substance in the form of the Raman spectrum. The method is based on so called Raman scattering. Raman scattering is an inelastic scattering resulting from an interaction of a photon and a molecule. In inelastic scattering photons have slightly changed wavelengths that are characteristic for specific bonds in surveyed material. Since most photons are on molecules scattered elastically (Rayleigh scattering i.e. without changing the wavelength), it is necessary to filter out of the spectrum of the strongly present wavelength of laser. Diagram of the measurement using Raman

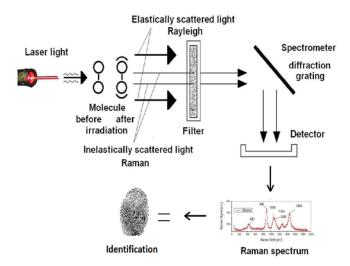


Fig. 1 Laser irradiate the sample, molecules vibrate, filter eliminates intense Rayleigh scattering, the grating disperses the light onto a detector to generate a spectrum, which gives the information about molecule bonding and provides a chemical fingerprint utilizable for identification.

spectroscopy is shown in Fig.1. Although the fundamental phenomenon is known since thirties of the 20th century, its effective use in Raman spectroscopy occurs in about last decade. The rebirth of this method goes hand in hand with advances in technology:

powerful lasers as sources of monochromatic light, efficient Notch filters transmitting all the wavelengths except the excitation wavelength of the laser, sensitive detectors and last but not least computer technology.

Raman spectroscopy brings many advantages. The method is:

- Relatively rapid, Raman spectra can be acquired within seconds.
- Non-destructive what allows undergoing investigated samples further analyses or simply repetition of Raman analyses.

• Contactless what is convenient, samples are not contaminated, also it is advantageous when toxic, dangerous samples or those with strong aroma are measured. There also exists a possibility of measuring samples through transparent glass or polymeric covering layers or containers.

Raman spectra of the covered sample and the cover can be then subtracted via software.

- Applicable to all states of matter and different its forms (crystals, powders, fibres, solutions, etc.).
- Without special requirements for sample preparation, what is convenient and prompt.
- Usable as in situ analysis.

The greatest drawback of the method is the fact that Raman scattering is a weak effect. Luminescence as much stronger quantum effect with bigger intensity can overlap Raman spectra and mask spectral information. Another disadvantage is eventual degradation of a sensitive sample when using intense laser beam [27].

Raman spectroscopy finds many applications in recent years [28] in a number of scientific areas such as chemistry, biochemistry, material science, mineralogy, arts, medicine, also is used for pharmaceutical or forensic and security purposes.

# IV. MATERIALS AND METHODS

## A. Samples

Fourteen samples of oils were used for spectroscopic analysis: pumpkin oil, grape seed oil, hemp oil, coconut oil, almond oil, olive oil, milk thistle oil, groundnut oil, wheaten oil, rice oil, canola, sesame oil, sunflower oil and safflower oil. All of these oils were purchased from common supermarkets.

Sunflower, canola and olive oils were used to monitor the thermal degradation process. Oils were heated up to 160 °C,

the temperature was maintained, while continually stirred, and after every 30 minutes the samples were taken and consequently analysed on a Raman microscope.

#### B. Raman instrumentation

Raman spectra of all samples were measured by Renishaw InVia Basis Raman microscope. The Raman instrument uses two lasers as light sources: argon ion laser with the excitation wavelength 514 nm and maximum output power of 20 mW and 785 nm NIR diode laser with maximum output power 300mW. Both were tested but more precise results were obtained using NIR laser.

A Leica DM 2500 confocal microscope with the resolution  $2\mu m$  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<sup>-1</sup> with 2 cm<sup>-1</sup> spectral resolution. After determining the principle peaks the spectral range was reduced approximately to the area 800 - 1800 cm<sup>-1</sup>.

## C. Principal Component Analysis

Raman spectral data are multivariate, since they reflect the composition of material and its structure. Raman peaks/bands are assigned to the vibrations of chemical bonds in examined samples. For the evaluation it is advantageous to use multivariate mathematics.

Principal Component Analysis PCA is useful and powerful statistical method for analysing data. PCA finds application in various fields from chemistry via neuroscience to computer face recognition, image compression or social studies. Basically it is used to find and identify patterns in data of high dimension and highlight hidden similarities and differences, in other word extracting relevant information form confusing data sets. It would be challenging to find some specific patterns in large data sets without Multivariate data analysis. Principal Component Analysis and Partial Least Squares (PLS) method were used for monitoring the thermal degradation of vegetable oils and some features of oil identification.

#### D. Spectral Data Fitting

For some known spectral information a spectral fitting was used for their selection from data sets. Coming out of the quantum theory, transitions between energy levels in molecules after absorbing or emitting energy and related lifetimes it is proper to use for fitting Raman spectral data

#### Fig. 2 Raman spectrum of sunflower oil

different functions. Gaussian (1) is usually used for solids, Lorentzian (2) for gasses.

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{(x-\mu)^2}{2\sigma^2}}$$
(1)

$$L(x) = \frac{1}{\pi} \frac{\frac{1}{2}\Gamma}{(x - x_0)^2 + (\frac{1}{2}\Gamma)^2}$$
(2)

Where  $x_0$  represent the centre, parameter  $\Gamma$  specifies the width. In the case of oil – a liquid a combination of these functions the Gaussian-Lorentzian profile is an appropriate solution. Spectral line shapes has features of both Gaussian and Lorentzian character. The Gaussian-Lorentzian is represented

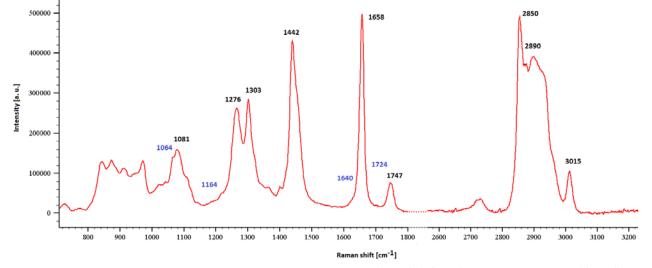
$$A * G + (1 - A) * L \tag{3}$$

Where *A* is a variable parameter in the fit being the fraction of Gaussian character  $(0 \le A \le 1)$ .

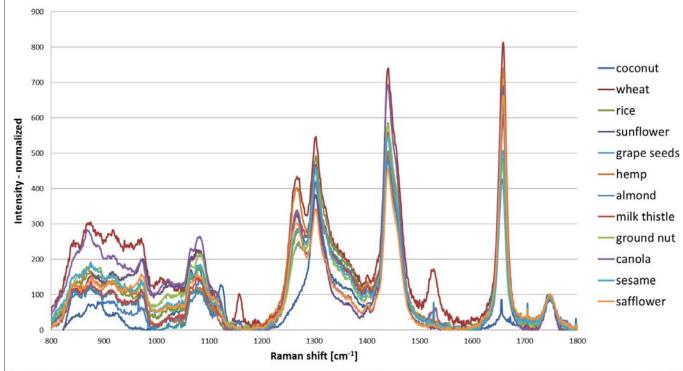
#### V. RESULTS

# A. Edible Oils Identification

Raman spectrum of sunflower oil is displayed in Fig.2. To evaluate and identify vegetable oils there are several essential bands in the range  $1200 - 1800 \text{ cm}^{-1}$  in Raman spectra related with the most important parts of the molecular structure.



Bands and their assignments are presented in Table 2.



Raman spectra of different oils are mostly alike in the distribution of characteristic peaks, shown in Fig.3. This is due to the content of similar components such as triacylglycerols, saturated and unsaturated fatty acids with straight aliphatic chains and predominantly with 16 or 18 number of carbon atoms in chains. Each oil has, however various ratios of these

1526	C=C stretching of carotenoids	
1640	C=C trans, trans 2,4 decadienal C=C cis double bond stretching	
1658		
1747	C=O ester-carbonyl stretching	
2850	C-H symmetric stretching of methylene groups	
2890	C-H asymmetric stretching of methylene groups	
3015	=C-H stretch	

## Fig. 3 Data collection - Raman spectra of oils

components what affects the intensity of the peaks and can be used for their identification. These differences for Raman bands 1267 cm<sup>-1</sup> and 1303 cm<sup>-1</sup> for different types of oil can be noted in Fig. 4. The relative intensity ratio of the bands at 1265 and 1300 cm<sup>-1</sup> is usually used to determine the degree of unsaturation in the oil [8]. Raman band 1747 cm<sup>-1</sup> was taken as an internal standard for normalization. This band does not exhibit any changes in the structure corresponding to C=O ester carbonyl band. It is obvious that oils such as sunflower, wheaten, safflower, pumpkin or grape seed have higher share of linoleic acid than for example groundnut, almond, rice or olive oil and also coconut oil which has the

Raman peak [cm-1]	Assignment		
1267	=C-H symmetric rocking		
1303	CH <sub>2</sub> in-plane twist		
1442	CH <sub>2</sub> scissoring		

most dissimilar composition. These results can be confirmed by the known amounts of fatty acids with one or two double bonds in the chain, see Tab. 1 [10], [12], [17]. Correlation of spectral intensity for bands 1267 cm<sup>-1</sup> and 1658 cm<sup>-1</sup> both related to the *cis* C=C bonds content is depicted in Fig. 5.

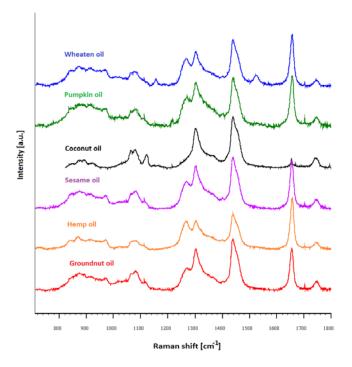


Fig. 4 Raman spectra of six different oils: wheaten, pumpkin, coconut, sesame, hemp and groundnut

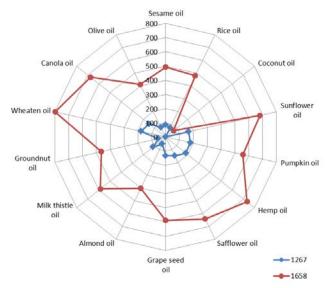


Fig. 5 Correlation of spectral response to *cis* C=C bonds for Raman bands 1267  $\text{cm}^{-1}$  and 1658  $\text{cm}^{-1}$ 

B. Thermal degradation of oils

Raman spectroscopy was also performed for monitoring thermal degradation of edible oils. Attention was given to two features of degradation manifested in the spectra. Firstly to changes of characteristic peaks corresponding to the formation of degradation products observed mainly at 1640 cm<sup>-1</sup>, secondly to the decrease of unsaturated carbon *cis* double bonds affecting especially peaks at 1267 and 3015 cm<sup>-1</sup>.

Formation of the degradation product at 1640 cm<sup>-1</sup> is shown in Fig. 6. This band can be assigned to formation of *trans*, *trans*-2,4-decadienal as a major decomposition product of heated oxidized linoleate which corresponds to the C=C stretching vibration in conjugated system [2]. This 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 non-smoking female lung adenocarcinoma in Asia and with various respiratory diseases in kitchen workers in Norway [16], [28]. Therefore it is the important reason for looking for appropriate methods for volatile aldehydes determination [29].

Other degradation products are reflected in the generation of Raman peaks at 1064 cm<sup>-1</sup> for epoxystearic acids, 1164 cm<sup>-1</sup> is C=C stretching from heated oxidized linoleate but in a much lesser extent than the peak 1640 cm<sup>-1</sup>, C=O for stretching of aldehyde arises at 1724 cm<sup>-1</sup> [2].

The first stage of thermal degradation can be described by a linear dependence of increasing Raman intensity at 1640 cm<sup>-1</sup> on time. These increases for sunflower, canola and olive oil are shown in in Fig. 7. Intensities were acquired from fitting using normalization via 1747 cm<sup>-1</sup> band and subtraction of the intensity at the room temperature.

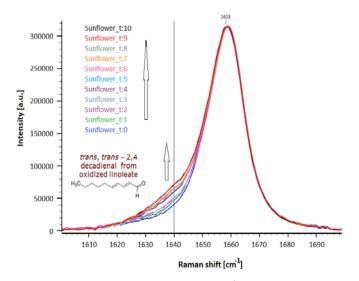


Fig. 6 Raman spectra of increasing 1640 cm<sup>-1</sup> band pertaining to the product of thermal degradation

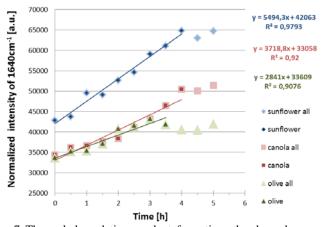


Fig. 7 Thermal degradation product formation: the dependence of normalized intensity of 1640 cm<sup>-1</sup> on time for sunflower, canola and olive oil.

Raman spectra of canola oil degradation process indicate the decrease of peak 1526 cm<sup>-1</sup> corresponding to carotenoids which have antioxidative effects. There are three bands around 1008 cm<sup>-1</sup> attributed to carotenoids: 1008 cm<sup>-1</sup> the C-CH<sub>3</sub> band, 1150 cm<sup>-1</sup> for C-C stretch and 1525 cm<sup>-1</sup> for C=C stretch. These bands show a gradual decrease in intensity in correlation to short time temperature stress [30] – [32].

After 2 hours of heating already a very small share of remaining carotenoids can be observed, see Fig. 8. After 5 hours of heating the peak totally disappears. Carotenoids have antioxidant properties as radical scavengers and singlet oxygen quenchers in lipid oxidation. The antioxidative behaviour of carotenoids is closely related to its own oxidation. Corresponding loss of carotenoids during 90 min heating period at 1525 cm<sup>-1</sup> was observed elsewhere [2].

This trend quite accurately correlates with the rise of degradation product in 1640cm<sup>-1</sup>. When following points for

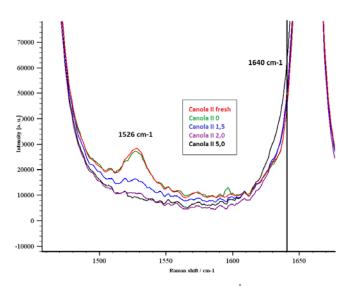


Fig. 8 The influence of carotenoid  $(1526 \text{ cm}^{-1})$  on the formation of *trans*, *trans*-2,4-decadienal  $(1640 \text{ cm}^{-1})$  during heating of canola oil.

canola oil in Fig. 7 just a slight increase in first two hours is obvious then it starts to grow much more rapidly as the share of antioxidants is reduced.

The PCA statistical method was applied to the share of carotenoids content in all oils used for identification. Six out of 14 vegetable oils exhibit non-negligible carotenoid content: wheaten, canola, pumpkin, olive, safflower and sunflower oils [33] – [35]. These are the most spread in the PCA results in Fig. 9, bounded by rectangle. The characteristic carotenoids profiles can be used for the authenticity assessment of some types of oils using HPLC-TLS method [33].

The decrease of carbon cis double bonds, caused by thermal degradation appears mainly at Raman peaks 1267 cm<sup>-1</sup> and

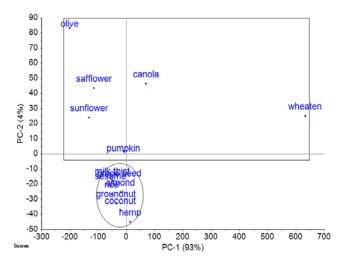


Fig. 9 PCA of the share of carotenoids in edible oils. Rectangle: a significant share of carotenoids; oval: negligible amount of carotenoids.

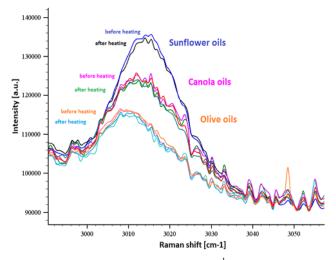


Fig. 10 Raman intensity of peak 3015  $\text{cm}^{-1}$  assigned to *cis* double bond related to the loss of unsaturation during heating load.

3015 cm<sup>-1</sup> as mentioned above. The intensity at 3015 cm<sup>-1</sup> also correlate with the amount of PUFA, see Table 3 and Fig. 10. The gradual decrease of the intensity of the band at 3015 cm<sup>-1</sup> is related to the loss of unsaturation and this band can be used

to estimate the degree of the total *cis* unsaturation. This loss of the unsaturation degree could be due to the degradation of the natural antioxidants (carotenoids) contained in oils [31].

The result of oil heating is *cis* C=C double bonds downgrade. This behavior is represented by the changes of Raman intensity: decrease at 1276 cm<sup>-1</sup> and coincidental rise up at 1303 cm<sup>-1</sup>. That means the ratio  $I_{1267}$  / $I_{1303}$  drops in time as demonstrated in Fig. 11.

The thermal degradation can be then observed on several

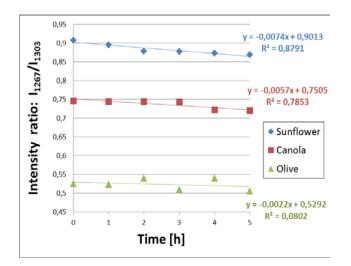


Fig. 11 Thermal degradation related to the decrease of Raman intensity ratio  $I_{1267}/I_{1303}$  on time corresponding to variety amount of unsaturated and saturated bonds.

Table 3 Amounts of MUFA, PUFA, magnitudes of normalized Raman intensity and slope (Fig. 11) for thermal degradation of tested vegetable oils

Oil	MUFA [%]	PUFA [%]	Δ 1267 [a.u.]	Δ 1303 [a.u.]	Slope
Sunflower	24	64	10,4	5,0	-0,0074
Canola	60	28	4,3	6,6	-0,0057
Olive	77	8	1,5	13,8	-0,0022

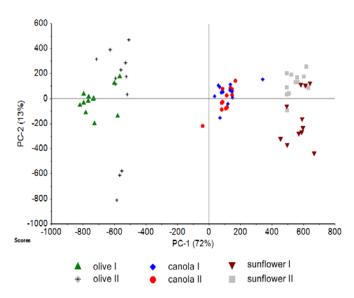


Fig. 12 PCA of two sets of thermally degraded olive, canola and sunflower oil.

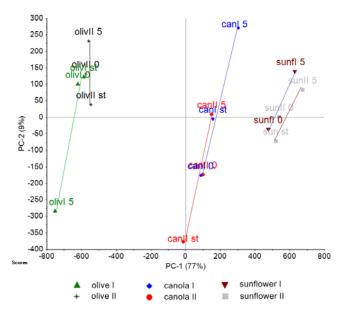


Fig. 13 PCA of fresh cold oils (st), just heated up to  $160^{\circ}$ C (0), heated for 5 hours (5).

different spectral parameters. Here the correlations between normalized intensity decrease at 1267cm<sup>-1</sup> ( $\Delta$  1267) and the changing content of PUFA, and also normalized intensity increase at 1303cm<sup>-1</sup> ( $\Delta$  1303) and changing content of MUFA can be revealed (Table 3). The linear decrease of this ratio in consequence of increasing temperature reflects a neat loss of the lipid chain unsaturation during the heating process is also mentioned in other study [31].

Finally the Principal Component Analysis applied to spectral data sets for thermally degraded sunflower, canola and olive oils show the clear diversity among these oils, Fig. 12. The fresh samples, just being heated and samples heated for 5

hours were picked from all data and are shown in Fig. 13. All except of the olive oil sample I show similar trends sharply distinguished from other species.

## VI. CONCLUSION

Raman spectroscopy was used as a modern spectroscopic method for edible oils identification and monitoring their thermal degradation. Multivariate statistical method PCA and PLS were used for spectral data evaluation. Results acquired in this study show that on the basis of characteristic ratios of unsaturated fatty acids contained in oils it is possible to distinguish different species. Further the thermal stress of vegetable oils can be monitored and evaluated via the amount of arising degradation products. The study was carried out for sunflower, canola and olive oil resulting, and confirmed by several features, in the most evident degradation for sunflower oils, then for canola and olive oils as the most suitable for thermal load. However, prolonged heat load causes the formation of degradation products that may undesirably affect the human health. Raman spectroscopic evaluation of mentioned 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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