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Trends in Edible Vegetable Oils Analysis. Part B. Application of Different Analytical Techniques

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This review describes recent developments in edible oils analysis by using various instrumental techniques. Different analytical methods are applied to assess oil stability but none of them is good enough. Therefore, there is still a need to develop new combined techniques to improve the quality control of edible oils. The paper describes various sample preparation techniques and instrumental methods developed to analyse different components in edible oils.

SAMPLE PREPARATION METHODS

Most analytical techniques used in the analysis of vegetable oils require a special sample preparation step. This step is especially important, since individual operations related to the preparation of samples cannot lead to changes in their composition (oxidation process, decomposition, introduction of contaminants, proportional changes in individual components). They should also provide the best recovery of the analysed components from the sample matrix and cannot introduce interfering substances. These techniques should also enable obtaining a representative sample for further analyses.

Preparation of samples for determination using chromatographic techniques

In the case of chromatographic techniques, some compounds are analysed with the use of gas chromatography (volatile and semi-volatile compounds), and others using liquid chromatography, but both techniques require different sample preparation methods. In the case of volatile compounds analysis using gas chromatography, a sample preparation step is often unnecessary, and the sample or the compounds isolated with the help of a syringe or a suitable injector are directly introduced into the chromatographic column. However, in the case of a more complicated matrix, certain measures are required to allow for the analysis of a specific set of compound groups.

Head-space analysis (HSA) is a fast, universal, sensitive method, which does not require the use of solvents and is economical. It is very useful for preparing samples for chromatographic analysis [Michulec & Wardencki, 2004; Snow & Snack, 2002]. It can be conducted both in static conditions (*static headspace*) as well as dynamically (*dynamic headspace*). Static headspace is based on an analysis of collected gas phase, which is in an equilibrium with the sample. In turn dynamic headspace, often also called "purge and trap" (PT), consists in the enrichment of the volatile components in a cold trap or on any sorbent during constant analytes collection with gas flowing over the matrix [Plutowska & Wardencki, 2007; van Loon *et al.*, 2005]. The following fillings, earlier conditioned, are most often used as traps: Carbotrap-300, Tenax-TA or charcoal [Kanavouras *et al.*, 2005; Zunin *et al.*, 2004]. The attachment with the sorbent is most often connected to the gas chromatograph coupled with a mass spectrometer or a flame ionization detector (FID) [Povolo & Contarini, 2003]. Such an approach can be successfully used for the analysis of volatile compounds in edible oils with the aim of determining the level of their oxidative stability as well as their purity or even adulteration with other oils. The application of those methods enables successful detection of the residues of organic solvents sometimes used during the extraction of lipids and seeds [Michulec & Wardencki, 2004].

In order to identify adulterations as well as to determine sources of origin of olive oils, Lorenzo *et al.* [2002a,b] used the HS-MS method. In the result of the analysis, one peak of the whole volatile fraction was obtained. The increase in the value of individual characteristic ions in that peak can be used for detecting compounds, which characterise the origin, source of adulteration or the oxidation process of the oil.

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The proposed procedure is less expensive and faster than the traditional gas chromatography systems. In addition, it does not require earlier sample preparation or the use of organic solvents [Lorenzo *et al.*, 2002a,b].

Likewise, in order to monitor autooxidation of rapeseed oil, Jeleń *et al.* [2007] used Headspace – SPME directly coupled with mass spectrometry without the necessity of separating volatile compounds using gas chromatography.

Microextraction to the stationary phase was introduced as an alternative to dynamic headspace analysis. This rapid method, which does not require solvents, was developed by Arthur and Pawliszyn [Arthur & Pawliszyn, 1990; Pawliszyn, 1997; Pawliszyn, 2003]. It is based on analytes sorption process on a fused silica fiber covered with a sorbent, and then on their desorption in a heated gas chromatograph injector. Two methods are possible for analytes extraction using SPME: headspace extraction – HS-SPME and direct immersion extraction – DI-SPME. In HS-SPME, the fiber is placed directly in the headspace of a gas, liquid or solid sample. In the case of volatile component analysis from a complicated matrix with the aid of gas chromatography – mass spectrometry, the best extraction method is HS-SPME. The fiber is placed in the gaseous phase over the liquid or solid surface of a sample and is not in direct contact with the sample, because of which the fiber has a longer life cycle. In addition, the extraction time is significantly shortened and the risk of contamination with other sample components is minimal comparing to the purge and trap technique (PT) [Kalua *et al.*, 2006]. In the case of analytes extraction using direct mode DI-SPME, the fiber is directly immersed in the sample, which significantly shortens its life cycle. DI-SPME is, however, a more sensitive technique than HS-SPME for less-volatile analytes. Yet HS-SPME characterised by lesser background than DI-SPME is more suitable for more volatile analytes in most of gas, liquid and solid samples [Kataoka *et al.*, 2000].

A version of this extraction technique is "in-tube SPME" which uses a segment of capillary column coupled with HPLC or LC-MS for extraction. Analytes extraction in the case of classic SPME occurs on the outer surface of the fiber, whereas in the "in-tube" technique on the inner surface of the capillary column. This is why in the case of "in-tube SPME", it is important to prevent column against clogging, and to maintain a constant flow by earlier removal of larger molecules from the sample by filtration [Kataoka *et al.*, 2000].

However, SPME, in addition to many advantages, has also some drawbacks. Difficulties appear when comparing results obtained from extraction on different types of fibers. An evaluation of the extraction efficiency of the fiber and its life cycle is also problematic. A signal generated by the volatile compounds from a specific fiber changes with the quantity of fibre applied, due to decreasing adsorption capacity [Kalua *et al.*, 2006].

SPME is an easy technique for practical application in the analysis of vegetable oil samples. By determining the whole content of volatile lipid degradation products, both raw and refined oils can be characterised. This method enables also a quick differentiation of vegetable oils, an indication of their purity or adulteration with other oils, as well as allows to trace changes undergoing during oil storage [Doleschall *et al.*, 2001, 2003; Mildner-Szkudlarz *et al.*, 2003].

Application of SPME requires a selection of suitable extraction conditions: time, temperature, mixing rate, and most of all, a suitable fiber. A thick fiber is more effective for the removal of less-volatile components from a sample matrix, but the thicker the layer of a fiber, the longer the desorption time. In addition, a possibility exists of carrying analytes over to the next extraction [Wardencki *et al.*, 2004].

Based on studies performed by Jeleń *et al.* [2000] and Kalua *et al.* [2006], the best fiber for headspace extraction for volatile compounds originating from vegetable oil samples is a fiber covered with a Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) cross-linked polymer. Mixed DVB fibers are suitable for the analysis of volatile compounds because they diminish the discrimination of components caused by a difference in molecular mass. A CAR fiber shows a high sensitivity in relation to less-volatile molecules, whereas PDMS is characterised by high sensitivity towards non-polar components. Mixed DVB/CAR/PDMS fiber guarantees a high linear concentration range of the analysed components and a low detection limit, which makes it the best out of current, commercially available fibers meant for analysing volatile components of vegetable oils, such as olive oil or rapeseed oil [Jeleń *et al.*, 2000; Mildner-Szkudlarz *et al.*, 2003, Kalua *et al.*, 2006]. The CAR/PDMS and DVB/CAR/PDMS fibers are very useful for the isolation of sulphur compounds from a sample, especially methanethiol [Wardencki *et al.*, 2004].

In the case of less-volatile components, the possibility exists of derivatisation of the sample on the fiber by extraction of the derivatisation agent, and then the components of the analysed sample, or *vice versa* [Stashenko & Martinez, 2004; Plutowska & Wardencki, 2007]. The process of direct derivatisation on a fiber additionally shortens the time of individual analyses [Wardencki *et al.*, 2004].

Figure 1 presents a comparison of results obtained using headspace analysis and solid phase microextraction (SPME). Both methods are characterised by similar detection sensitivity, and the same number of separated peaks. Yet in the case of SPME, higher, thinner and better separated peaks are observed, which means that this technique is characterised by better selectivity, efficiency and separation in comparison with HSA.

Sample preparation for analyses with liquid chromatography and other instrumental techniques

The sample preparation step for samples to be analysed using liquid chromatography is usually very similar to sample preparation for spectroscopic methods, therefore these techniques will be discussed together.

In order to isolate analytes from a vegetable oil sample, extraction is very often conducted with the use of organic solvents or through saponification. During liquid-liquid extraction, a few different types of solvents are sometimes used, chosen according to the rise in polarity of the extraction agent [Romanik *et al.*, 2007]. Because of the use of various solvents, different fractions can be obtained for the same sample (*e.g.*, non-saponified and saponified fractions). In this

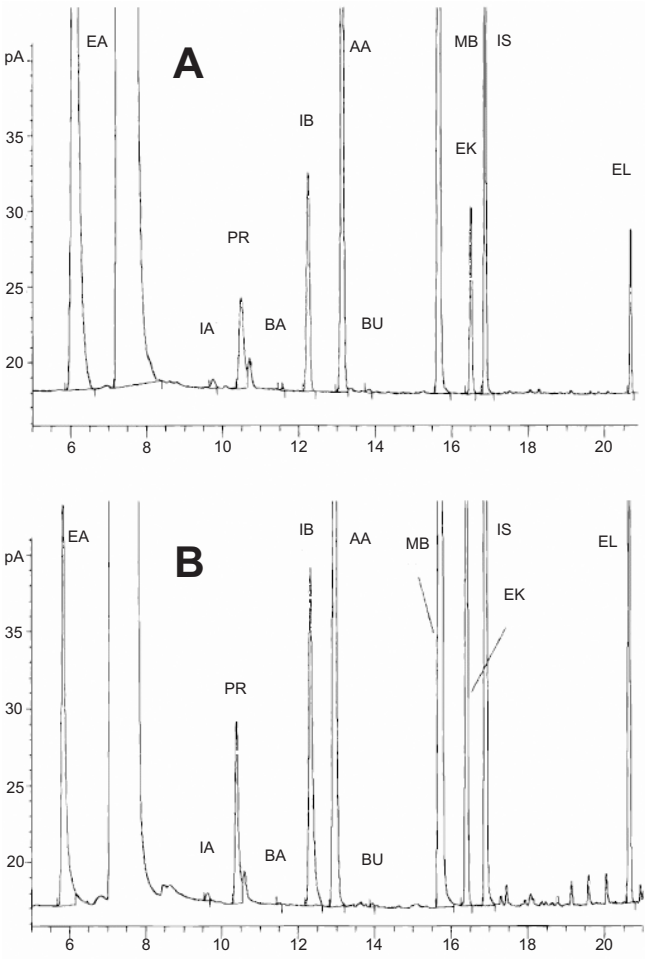

FIGURE 1. Chromatograms of Pilsner typed beer alcohols and esters determined by static headspace (SHS-A) and solid phase microextraction (SPME-B) methods. EA – ethyl acetate, IA – isobutyl acetate, PR – propanol, EB – ethyl butyrate, BA – butyl acetate, IB – isobutanol, AA – isoamyl acetate, BU – butanol, MB – methyl-1-bitanol, EK – ethyl caproate, EL – ethyl caprylate (Reproduced from Jeleń *et al.* [1998]).

way, one sample preparation step may provide analytes for analysis performed using various instruments (HPLC, GC, spectroscopic techniques). A disadvantage of this technique is the use of often toxic organic solvents, which increases the cost of analysis and pollution of the environment. This is the reason why for many years, studies have been ongoing with the aim of developing new techniques that would allow to significantly reduce the amount of solvents or even to eliminate or replace them with compounds which are less toxic and harmful to the environment, such as ethyl alcohol.

The solid phase extraction technique (SPE) has become popular because of the significantly limited amount of organic solvents applied. It is based on the adsorption of sample components on the surface of a solid sorbent placed in a glass or propylene columns or closed in extraction disks. Next, the adsorbed components are gradually rinsed out of the sorbent with the help of a small amount of appropriate solvents. This technique has many advantages, such as a reduced amount of organic solvents used in comparison with the liquid-liquid extraction. Furthermore, neither emulsions nor foams are formed during extraction, which is often observed in the case of liquid-liquid or gas-liquid extraction. The technique allows for the extraction, enrichment and also elimination of interfering substances in samples containing both volatile and non-volatile analytes. A disadvantage of this technique is incomplete analytes recovery [Camel, 2002].

Another, less commonly applied oil sample preparation technique is supercritical fluid extraction (SFE). Most often used extraction reagent in this technique is carbon dioxide because of its low cost, low toxicity and preferred critical parameters (T_c=31.1°C, P_c=74.8 atm). Because CO_2 is a non-polar compound, it is frequently used for the extraction of low and medium polar compounds with high volatility. In order to extract polar compounds, a CO_2 mixture with modifiers (polar solvents) is used. The main benefit of this technique is reduced usage of organic solvents, short extraction time, possibility of automatization and a small amount of samples needed for extraction [Romanik *et al.*, 2007].

ANALYTICAL TECHNIQUES USED IN OIL ANALYSIS

Gas and liquid chromatography

The most frequent and most popular techniques used in the analysis of vegetable oils are gas and liquid chromatography with different detection systems. The combined techniques are also often used, with the sample first undergoing separation with high-pressure liquid chromatography, and then the resultant fractions being analysed with the use of gas chromatography [Ruiz-Mendez & Dobarganes, 2007]. The most popular detectors are flame ionization detectors (FID) and UV-DAD because of their availability and cost, and also a mass spectrometer, which enables easy identification of an analysed sample's components [Destaillats & Cruz-Hernandez, 2007; Kawai *et al.*, 2007; Sullivan *et al.*, 2009]. These techniques enable the analysis of compounds which belong to different groups with the use of a single instrument. Table 1 lists examples of chromatographic techniques used for the analysis of individual component groups present in vegetable oils.

Scanning calorimetric techniques

A relatively new method, pressure differential scanning calorimetry (PDSC), has found application in the analysis of fats and oils, and especially oils with high oxidative stability, for which traditional analytical techniques are time-consuming and laborious. The specific heat of a vegetable oil is determined with the aid of a calorimetric technique, depending on its components and composition of fatty acids. A knowledge of the specific heat of a given oil is very useful during long-term oil storage in order to evaluate the transformation a given sample has underwent [Santos *et al.*, 2005]. With this technique, one can determine the oxidative induction time (OIT) of oils, by exposing them to high temperatures or pressure in the atmosphere of pure oxygen. OIT value indicates a good correlation with the oil stability index (OSI). A regression analysis of data allows for identifying a relationship between temperature and OIT in the form of equilibrium for every kind of oil [Kodali, 2005]. This analysis is possible when the oxidation process is an exothermic reaction, and the measurement of the released heat allows applying the differential scanning calorimetry (DSC) in the case of these analytes

TABLE 1. Application of chromatographic techniques in vegetable oils analysis.

Kind of oil	Analytes	Potentialities of practical use	Techniques used	References
Hazelnut oil	Free fatty acids composition	To investigate acyl positional distribution in tri-acylglycerols	GC/FID	Alasalvar *et al.* [2003]
Vegetable edible oils	Free fatty acids composition	To estimate oils thermal stability, to determine fatty acids distribution of triglycerides, to determine hydrogenation level of edible oils	GC/FID	Miraliakbari *et al.* [2008]; Smith *et al.* [2007]; Pereira *et al.* [2002]; Naglic *et al.* [1997]; Allouche *et al.* [2007]
Hazelnut oil	Sterols		GC/FID	Alasalvar *et al.* [2003]
Sunflower, soybean, rapeseed oil, olive oil	Sterols	To assess oxidative stability of phytosterols in oil	GC/MS	Zhang *et al.* [2006]
Tree nut oil	Aldehydes	To assess oxidative stability of oil	HAS/GC/FID	Miraliakbari *et al.* [2008]
Sunflower, soybean, corn, peanut oils	Volatile hydroperoxides	To assess oxidative stability	HAS/GC/FID/TCD	Smith *et al.* [2007]
Soybean, sunflower oils	Tocopherols		HAS/GC/FID	Warner *et al*. [2005]
Olive oil		To detect, identify and quantify extra virgin olive oil adulteration by chemometric treatment of GC profile	GC/MS	Capote *et al.* [2007]
Edible oils	Volatiles	To analyse volatile compounds	GC/FID, GC/MS	Haiyan *et al.* [2007]
Tuna oil, milk fat, cocoa butter	Fatty acids	To apply for fast analysis of edible oils and fats or biological samples	Fast GC/FID	Destaillats *et al.* [2007]
Edible oils	Triacylglycerols, fatty acids	To determine fatty acids in polar lipids and TAGs	SPE/GC	Giacometti *et al.* [2002]
Hazelnut oil	Fatty acids, sterols, alcohols	To characterise hazelnut oils *versus* other edible oils	GC/FID, TLCxGC/FID	Benitez-Sanchez *et al.* [2003]
Vegetable oils	Volatiles	To determine qualitatively and quantitatively volatile compounds present in edible oils; to determine changes in oil volatiles during storage at elevated temperature and their relation with sensory characteristics of investigated samples	SPME/GC/MS	Jeleń *et al.* [2000]
Plant oils	Volatiles	To apply for rapid differentiation of various plant oils and for the monitoring of changes during their storage	SPME/GC/MS	Mildner-Szkudlarz *et al.* [2003]
Olive oils	Volatiles	To compare different olive oils by characterising their volatile compounds	SPME/GC/MS/FID	Lizzani-Cuvelier & Zarrouk [2007]
Extra virgin olive oil	Volatiles	To compare analytical techniques in the analysis of volatile compounds of olive oils	SPME/GC/TOF-MS; DSH-TD/GC/MS	Kanavouras *et al.* [2005]
Vegetable oils	Polycyclic aromatic hydrocarbons	To analysepolycyclic aromatic hydrocarbons in vegetable oils	SPME/GC x GC/TOF-MS	Purcaro *et al.* [2007]
Vegetable oils	Volatile solvents	To determine residues of solvents in vegetable oils	HAS/GC/FID/ECD; SPME/GC/FID/ECD	Michulec *et al.* [2004, 2005, 2007]
Pomegranate oil	Fatty acids, phytosterols, TAG	To apply for TAG fingerprinting in differential pomegranate from most other common edible oils	GC/MALDI-TOF/MS	Kaufman *et al.* [2007]
Argan oil	Vampesterol	To detect adulteration by campesterol level analysis	HPLC x GC/FID	Hilali *et al.* [2007]
Bergamot oil	volatiles	To compare oils obtained by different procedures	GC/MS	Belisto *et al.* [2007]
Edible oils	Unsaponifiable compounds	To analyse different groups of compounds (free sterols, tocopherols, squalene, erythrodiol, uvaol) in one chromatographic run or to analyse these compounds in different groups	RPLC – GC/FID	Cortes *et al.* [2006]
Edible oils	Volatile compounds	To evaluate the qualitative analysis of volatile compounds in edible oils	RPLC – GC/FID, SDE/GC-MS	del Mar Caja *et al.* [2000]
Olive oil	Erythrodiol, uvaol	To determine extra virgin olive oil adulterations	RPLC – GC	Blanch *et al.* [1998]
Edible oils	Acylglycerides, fatty acids, hydrocarbons, alkyl esters	To analyse deodorizer distillates from industrial refining of edible oils	AC x HPSEC x GC/FID	Ruiz-Mendez & Dobarganzez [2007]
Edible oils and fats	Triacylglycerides TAGs	To quantitatively analyse TAGs (fatty acids composition, number of double bonds) for analysis of target compounds or compounds groups, for fingerprinting of oil samples	LCxGC	Janssen *et al.* [2003]

Olive oil	Sterols		TLC x GC	Lopez-Lopez *et al.* [2008]
edible oils	Sterols		LC x GC	Senorans *et al.* [1998, 1996]; Villen *et al.* [1998]
Hazelnut oil	Tocopherols,		HPLC	Alasalvar *et al.* [2003]
Olive oil	Phenol compounds	To apply for qualitative and semiquantitative analysis, phenol compounds profiles of olive oils	HPLC/UV-DAD	Bonoli *et al.* [2004]; Carrasco-Pancorbo *et al.* [2007]; Gomez-Alonso *et al.* [2002]; Romero *et al.* [2002]
Olive oil, sunflower oil	Phenol compounds, tocopherols, carotenoids	To apply for qualitative and quantitative analysis	HPLC-UV-DAD	Allouche *et al.* [2007]; Mancebo-Campos *et al.* [2007]; Mateos *et al.* [2005]; Pellegrini *et al.* [2001]; Pereira *et al.* [2002]
Tree nut oil	Tocopherols		HPLC-UV-DAD	Miraliakbari *et al.* [2008]
Peanut oil		To analyse various classes of polar compounds in edible vegetable oils	HPSEC, GPC	Gomes & Caponio [1999]
Acai oil	Phenols	To characterise the main phenol compounds and to evaluate short- and long-term stability of these compounds	HPLC/MS	Pacheco-Palencia *et al.* [2008]
Olive oil	Tocopherols, phenols	To establish chemical changes occurring in oil after exposure to high temperature and air	HPLC/ FD, HPLC/ UV-DAD	Bester *et al.* [2008]
Pumpkin seed oil	Tocopherols		HPLC/ FD, HPLC/ UV-DAD	Gliszczyńska-Świgło *et al.* [2004]
Sunflower, corn, Olive oils			MLC	Noguera-Orti *et al.* [1999]
Vegetable oils	Fatty acids, triacylglycerols	To determine fatty acids and triacylglycerols composition in edible oils	HPLC/FID, HPLC/MS	Byrdwell *et al.* [2001]
Vegetable oils	Acrolein	To determine acrolein in heated vegetable oils	LC/PED	Casella *et al.* [2004]
Edible oils	Estrogen	To determine estrogen in selected edible oils using GPC followed by LC-MS	GPC/LC-MS	Tong *et al.* [2006]
Hazelnut oil	Tocopherols, tocotrienols	To characterise hazelnut oils *versus* other edible oils	NP-HPLC/MS	Benitez-Sanchez *et al.* [2003]
Vegetable oils		To apply for drug and oil analysis, phytochemistry and synthetic chemistry, forensics *via* reliable counterfeit detection and quality control	TLC/ EASI-MS	Haddad *et al.* [2008]
Conifer seed oils	Δ5-polyenoic fatty acids	To identify triacylglycerols containing Δ5 unsaturated polymethylene interrupted fatty acids (TGs Δ5-UPIFAs)	HPLC/MS	Lisa *et al.* [2007]

Abbreviations: HPSEC – high-performance size-exclusion chromatography, GPC – gel permeation chromatography, MLC – micelar liquid chromatography, PED – pulsed electrochemical detector, EASI – easy ambient sonic-spray ionization, AC – adsorption chromatography, RPLC – reversed phase liquid chromatography, SDE – steam distillation-solvent extraction, DSH-TD – dynamic headspace thermal desorption, TAGs – triacylglicerols, TOF – time of flight, FFA – free fatty acid, BHT – butylated hydroxytoluene, MS – mass spectrometry, GC – gas chromatography, TLC – thin layer chromatography, HPLC – high performance liquid chromatography, LC – liquid chromatography, SPME – solid phase microextraction, SPE – solid phase extraction, FID – flame ionization detector, ECD – electron capture detector, FD – fluorescence detector, DAD – photodiode array detector, UV – UV detector, TCD – thermo conductivity detector.

[Simon & Kolman, 2001]. Conducting a process of accelerated oxidation under non-isothermal conditions is important because of the similarity of the process to domestic conditions, where oil is exposed to different temperatures. An analysis of the increase in the oxidation temperature with the increase in the heating level under non-isothermic DSC conditions allows for the indication of the kinetic parameters of the oxidation process of oils [Simon & Kolman, 2001].

The melting and freezing curves obtained using DSC can serve for the evaluation of quality, geographic origin as well as storage conditions of the analysed oils [Angiuli *et al.*, 2006; Tan & Che Man, 1999], as they are very sensitive to the presence of other compounds in lesser quantities in a sample matrix, often indicating the ageing process or illegal additives. They can also be used to discover adulterations of oils with less expensive oils, and also to evaluate the quality of olive oil (whether it was mixed with oil that was refined, filtered or renewed) [Ferrari *et al.*, 2007]. A calorimetric method proposed by Ferrari *et al.* [2007] for indicating olive oil adulterations is easy, fast, inexpensive and allows for conducting tests in commercial conditions [Ferrari *et al.*, 2007].

The quality and origin of olive oil can also be determined using other calorimetric techniques, such as high sensitivity isothermal calorimetry (TAM) or modulated adiabatic scanning calorimetry (MASC) [Angiuli *et al.*, 2006]. Modulated calorimetry provides information regarding the reversibility of processes and the polymorphic crystal structure. Each of the mentioned calorimetric techniques can be applied for vegetable oil analysis. DSC allows for a differentiation of olive oil from other vegetable oils. TAM analysis is time-consuming, but allows for determination of such parameters as induction time (IT) and enthalpy of freezing (H),

which are unusually sensitive towards defects and the source of origin of olive oil. On the other hand, modulated calorimetry with a modulated temperature and work in an adiabatic system widens the analytical possibilities to detailed studies of the crystallization process, as opposed to the remaining two calorimetric techniques [Angiuli *et al.*, 2006].

Among the benefits of calorimetric techniques, apart from a short time of analysis, a few other advantages should also be mentioned, such as the small amount of samples needed for analysis and the minimal step of their preparation, as well as a lack of toxic solvents and other chemical compounds [Tan & Che Man, 1999].

Nuclear magnetic resonance (NMR)

Considering the demands of contemporary analysis, where the time for conducting a single analysis, as well as the amount of sample needed for analysis, the lowest detection limit and the easiest application of the method are important, the benefits, possibilities and limitations of high-resolution nuclear magnetic resonance (NMR) should be discussed. Complex vegetable oil samples often require laborious, time-consuming methods for explicit classification, they additionally require suitable sample preparation steps for analysis with the use of large quantities of toxic organic solvents. An alternative technique is spectroscopy, specifically NMR. Both ^{1}H and ^{13}C NMR enable simultaneous analysis of different components present in vegetable oils [Hidalgo *et al.*, 2002; Khallouki *et al.*, 2008]. The NMR spectrum delivers much information obtained during a short analysis with a short or even no sample preparation step. Different signals present in the NMR spectrum deliver two types of information regarding chemical changes and their intensity in analysed samples. The first delivers qualitative data and is related to different atoms present in samples, whereas the second delivers quantitative data, which allows for a good characterisation of the oil and opens a wide field of application for this technique [Hidalgo & Zamora, 2003].

One of the first applications of NMR for the analysis of vegetable oils was the determination of fatty acid composition, with the aim of determining oil authenticity. However, with better techniques applied to analyse adulterated oils, quantitative analysis becomes more important, and in the case of NMR, appears in the form of the intensity of a specific peak, which is characteristic for a specific oil [Hidalgo & Zamora, 2003].

Using differentiation analysis and ^{13}C NMR data from the olefin group, the majority of adulterations with other vegetable oils, which can be met in olive oil, can be determined [Alonso-Salces *et al.*, 2010; Smejkalova & Piccolo, 2010]. Similarly, analysing the whole spectrum or ^{1}H NMR data, genuine oil can be differentiated from those with even 5% added hazelnut oil, which is the hardest adulteration to uncover [Zamora *et al.*, 2001; Mannina *et al.*, 2009]. The geographic region of origin can also be determined, as well as the type and quality of the oil (extra virgin, virgin, olive oil) [Shaw *et al.*, 1997]. ^{13}C NMR analysis can be a powerful tool for evaluating the oxidative stability of oil samples which earlier underwent the process of chromatographic enrichment. Minor components, which were concentrated using the triacylglycerols fraction elimination step with the use of liquid chromatography [Hidalgo *et al.*, 2002].

Similarly, the application of coupled ^{1}H NMR and ^{31}P NMR as well as multidimensional statistical analysis allowed for the classification of 13 types of vegetable oils, and enabled the discovery of adulterations of olive oils with these oils at a 5% level. It was feasible because of the quantitative determination of 1,2-diacyloglycerol concentrations for the entire content of diacylglycerol in the analysed samples [Vigli *et al.*, 2003].

Near infrared spectroscopy (NIR), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy

Spectroscopic techniques are widely widespread in the analysis of basic food components. They have also become popular in the analysis of vegetable oils because of their benefits, which include: rapidity, directness, relative cost-effectiveness, and usually no need for sample preparation [Beaten *et al.*, 2001]. Near infrared spectroscopy (NIR) was used to indicate tocopherols in vegetable oils as an alternative to HPLC. Samples, similarly to liquid chromatography, were extracted with an organic solvent (ethanol). Results of the precision determination (RSD) and accuracy obtained by Szłyk *et al*. [2005] are comparable with the standard HPLC method, in addition, this technique allows to perform a single analysis in a very short time (1–4 min), which argues in favor of technology NIR used in routine analysis of tocopherols in vegetable oils. In order to compare both methods, oil samples were prepared in exactly the same manner, and then tocopherols extracted with ethanol were analysed by HPLC (identification based on comparing retention time with the standard) and NIR (spectrum-based identification). The correlation coefficient for both methods was very high, *i.e.* $R^2 = 0.9989$ (n=8). The proposed method does not require the use of toxic organic solvents (ethanol extraction), and the cost of the instrument is essentially lower than in the standard HPLC method.

The discussed technique, in connection with chemometric analysis, has also found application in the direct determination of acidity and peroxide index screening in vegetable oils. This is possible because a single analysis takes less than 30 s and does not require earlier sample preparation for analysis [Armenta *et al.*, 2007]. Oil samples were scanned within a range of 4,000 to 12,500 cm^{-1} at a temperature of 30°C, and then the spectra obtained were evaluated using chemometric analysis. Liescheski [1996] found a correlation between the adsorption intensity with bonded vinyl C-H and the relation of the vinyl bonded C-H and symmetric CH_2 bond and the iodine value, which describes the saturation level of vegetable oils. The absorption relation of the two mentioned bonds indicates a correlation coefficient of an even 0.995 with the iodine value, determined in accordance with the standardised method [Liescheski, 1996].

NIR, thanks to its low cost and short time of individual analysis, has also found application in the discovery of camellia oils adulterations with soybean oil [Wang *et al.*, 2006], as well as at the differentiation and classification stages of vegetable oils [Yang *et al.*, 2005]. Using mid-infrared (IR) spectroscopy the detection limit of extra virgin olive oil adulteration was determined as 5 % for corn – sunflower binary

mixture, cottonseed and rapeseed oils [Gurdeniz & Ozen, 2009].

Similarly, it is hard to detect, using traditional methods, adulterations of olive oils with hazelnut oil, which can be determined using near-infrared spectroscopy, Raman spectra or Fourier transform infrared spectroscopy (FTIR) [Concha-Herera *et al.*, 2009]. Raman's dispersion emerges as a result of changes in polarization or the shape of the electron layout in the vibrating molecule; meanwhile infrared radiation absorption requires internal changes in the dipolar moment during the molecule's vibration [Beaten *et al.*, 2005]. Not only were oil samples analysed, but also the unsaponifiable matter [Beaten *et al.*, 2005]. Coupling the above-mentioned technique with a statistical analysis of the results obtained, it is possible to determine an addition of over 8% of hazelnut oil or even 5% of sunflower, corn or soybean oil to olive oil [Lerma-Garcia *et al.*, 2010]. These techniques also allow for the classification as well as determination of purity and authenticity of other vegetable oils, such as corn, peanut, canola, soybean, safflower and coconut oils [Yang *et al.*, 2005; Beaten *et al.*, 2005, 1998; Lankmayr *et al.*, 2004]. The proposed techniques are easier to use and deliver results in a shorter time than the chromatographic techniques or nuclear magnetic resonance [Beaten *et al.*, 2005].

Another important question in the analysis of oils is their oxidative stability. Guillen & Cabo [1999] developed a respective method which is based on Fourier transforms infrared spectroscopy (FTIR), and assumes that frequency changes in specific bonds allow for the differentiation of stages of the oxidation process and determination of the oxidation level of the analysed oil sample. The proposed method is fast, easy and precise [Guillen & Cabo, 1999]. Moreno, Olivares, Lopez, Adelantado and Reig [1999] also conducted similar studies to determine the influence of heating vegetable oils on the changes in oxidation levels and the emergence of *trans* isomers of fatty acids [Moreno *et al.*, 1999]. Van de Voort *et al.* [2008] also determined the content of *trans* isomeric fatty acids in vegetable oils, on the basis of a method developed based on the FTIR technique. They concluded that after applying two-dimensional correlation analysis, the fast and precise FTIR method for determining *trans* isomers in fats and oils could also compete with gas chromatography [van de Voort *et al.*, 2008]. For quantitative and qualitative determinations of *trans* isomers undergoing the hydrogenation process in vegetable oils, a combination of Fourier transform and Raman spectroscopy technique proved to be useful [Johnson *et al.*, 2002]. Two-dimensional analysis connected with FTIR and FT-Raman was also used by Muik *et al*. [2007] in order to trace the lipid oxidation process in vegetable oils. The FTIR technique enables also the determination of the peroxide value (informing of the primary oxidation products). This method is based on a rapid reaction of triphenylphosphine with hydro peroxides present in oil samples, resulting in the emergence of triphenylphosphine oxide (TPPO), which displays absorption at 542 cm^{-1} [Yu *et al.*, 2007]. However, when analysing the primary spectra in infrared for absorption of the bond between carbonyl (1740 cm^{-1}) and the double carbon-carbon bond (1651 cm^{-1}) a quick determination of the iodine value is possible, characterised by the content of unsaturated fatty acids in oils [Hendl *et al.*, 2001]. Similarly to other procedures of determinations with the use of infrared spectra, in this case there is also no need for sample preparation for analysis. In addition, the automated FTIR technique, with the use of an auto sampler, allows conducting even 90 analyses within one hour. Such an automated technique was used for the determination of free fatty acids in vegetable oils. The identification of fatty acids is done on the basis of absorption of the carbonyl group (1573 cm^{-1}) [Al-Alawi *et al.*, 2006].

CONCLUSIONS

Based on the collected and presented literature, it can be concluded that there is constant development of new analytical methods for vegetable oil analysis. Asides from traditional, normalized methods, new methods are appearing which use modern instruments, which are partially or fully automated. Most often their main advantage is the simplicity of performance and short times needed for individual analyses. Such methods include chromatographic techniques, which are very popular techniques in vegetable oil analysis. Very promising techniques with a great potential are spectroscopic techniques, especially near infrared spectroscopy (NIR) coupled with different techniques. Also nuclear magnetic resonance is gaining better recognition, being initially a technique, which was not easily accessible and considered as very expensive. Newly developed methods, however, require further studies and the development of methods that would enable using one instrument for the determination of compounds from different groups. A constantly increasing pressure from consumers and competition on the market also require new methods to be developed, which can be characterised by low limits of detection and quantification, and also high precision and accuracy of the results obtained.

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REFERENCES

1. Al-Alawi A., van de Voort F.R., Sedman J., Ghetler A., Automated FTIR analysis of free fatty acids or moisture in edible oils. J. Assoc. Lab. Automat., 2006, 11, 23–29.
2. Alasalvar C., Shahidi F., Ohshima T., Wanasundara U., Yurttas H.C., Liyanapathirana C.M., Rodrigues F.B., Turkish Tombul hazelnut (*Corylus avellana L.*). 2. Lipid characteristics and oxidative stability. J. Agric. Food Chem., 2003, 51, 3797–3805.
3. Allouche Y., Jimenez A., Gaforio J.J., Uceda M., Beltran G., How heating affects extra virgin olive oil quality indexes and chemical composition. J. Agric. Food Chem., 2007, 55, 9646–9654.
4. Alonso-Salces R.M., Heberger K., Holland M.V., Moreno-Rojas J.M., Mariani C., Bellan G., Reniero F., Guillou C., Multivariate analysis of NMR fingerprint of the unsaponifiable fraction of virgin olive oils for authentication purposes. Food Chem., 2010, 118, 956–965.

5. Angiuli M., Ferrari C., Lepori L., Matteoli E., Salvetti G., Tombari E., Banti A., Minnaja N., On testing quality and traceability of virgin olive oil by calorimetry. J. Therm. Anal. Calorim., 2006, 84, 105–112.
6. Armenta S., Garrigues S., de la Guardia M., Determination of edible oil parameters by near infrared spectrometry. Anal. Chim. Acta, 2007, 596, 330–337.
7. Arthur C., Pawliszyn J. Solid-phase microextraction with thermal desorption using fused silica optical fibers. Anal. Chem., 1990, 62, 2145–2148.
8. Baeten V., Pierna J.A.F., Dardenne P., Meurens M., Garcia-Gonzalez D.L., Aparicio-Ruiz R., Detection of the presence of hazelnut oil in olive oil by FT-Raman and FT-MIR spectroscopy. J. Agric. Food Chem., 2005, 53, 6201–6206.
9. Baeten V., Dardenne P., Meurens M., Aparicio R., Interpretation of Fourier transform Raman spectra of the unsaponifiable matter in a selection of edible oils. J. Agric. Food Chem., 2001, 49, 5098–5107.
10. Baeten V., Hourant P., Morales M.T., Aparicio R., Oil and fat classification by FT-Raman spectroscopy. J. Agric. Food Chem., 1998, 46, 2638–2646.
11. Belsito E.L., Carbone C., di Gioia M.L., Leggio A., Liguori A., Perri F., Siciliano C., Viscomi M.C., Comparison of the volatile constituents in cold-pressed bergamot oil and a volatile oil isolated by vacuum distillation. J. Agric. Food Chem., 2007, 55, 7847–7851.
12. Benitez-Sanchez P.L., Leon-Camacho M., Aparicio R., A comprehensive study of hazelnut oil composition with comparisons to other vegetable oils, particularly olive oil. Eur. Food Res. Technol., 2003, 218, 13–19.
13. Bester E., Butinar B., Bucar-Miklavcic M., Golob T., Chemical changes in extra virgin olive oils from Slovenian Istra after thermal treatment. Food Chem., 2008, 108, 446–454.
14. Blanch G.P., Villen J., Herraiz M., Rapid analysis of free erythrodiol and uvaol in olive oils by coupled reversed phase liquid chromatography-gas chromatography. J. Agric. Food Chem., 1998, 46, 1027–1030.
15. Bonoli M., Bendini A., Cerretani L., Lercker G., Toschi T.G., Qualitative and semiquantitative analysis of phenolic compounds in extra virgin olive oils as a function of the ripening degree of olive fruits by different analytical techniques. J. Agric. Food Chem., 2004, 52, 7026–7032.
16. Byrdwell W.C., Neff W.E., List G.R., Triacylglycerol analysis of potential margarine base stocks by high-performance liquid chromatography with atmospheric pressure chemical ionization mass spectrometry and flame ionization detection. J. Agric. Food Chem., 2001, 49, 446–457.
17. Camel V., Extraction techniques. Anal. Bioanal. Chem., 2002, 372, 39–40.
18. Capote F.P., Jimenez J.R., de Castro M.D.L., Sequential (step-by-step) detection, identification and quantitation of extra virgin olive oil adulteration by chemometric treatment of chromatographic profiles. Anal. Bioanal. Chem., 2007, 388, 1859–1865.
19. Carrasco-Pancorbo A., Cerretani L., Bendini A., Segura-Carretero A., Lercker G., Fernandez-Gutierrez A., Evaluation of the influence of thermal oxidation on the phenolic composition and on the antioxidant activity of extra-virgin olive oils. J. Agric. Food Chem., 2007, 55, 4771–4780.
20. Casella I.G., Contursi M., Quantitative analysis of acrolein in heated vegetable oils by liquid chromatography with pulsed electrochemical detection. J. Agric. Food Chem., 2004, 52, 5816–5821.
21. Concha-Herrera V., Lerma-Garcia M.J., Herrero-Martinez J.M., Simo-Alfonso E.F., Prediction of the genetic variety of extra virgin olive oils produced at La Comunitat Valenciana, Spain, by Fourier transform infrared spectroscopy. J. Agric. Food Chem., 2009, 57, 9985–9989.
22. Cortes J.M., Sanchez R., Villen J., Vazquez A., Analysis of unsaponifiable compounds of edible oils by automated on-line coupling reversed-phase liquid chromatography-gas chromatography using the through oven transfer adsorption desorption interface. J. Agric. Food Chem., 2006, 54, 6963–6968.
23. Destaillats F., Cruz-Hernandez C., Fast analysis by gas-liquid chromatography. Perspective on the resolution of complex fatty acid compositions. J. Chromatogr. A, 2007, 1169, 175–178.
24. Doleschall F., Kemeny Z., Recseg K., Kovari K., Monitoring of lipid degradation products by solid-phase microextraction. J. Microcolumn Sep., 2001, 13, 215–220.
25. Doleschall F., Recseg K., Kemeny Z., Kovari K., Comparison of differently coated SPME fibres applied for monitoring volatile substances in vegetable oils. Eur. J. Lipid Sci. Technol., 2003, 105, 333–338.
26. Ferrari C., Angiuli M., Tombari E., Righetti M.C., Matteoli E., Salvetti G., Promoting calorimetry for olive oil authentication. Thermochim. Acta, 2007, 459, 58–63.
27. Giacometti J., Milosevic A., Milin C., Gas chromatographic determination of fatty acids contained in different lipid classes after their separation by solid-phase extraction. J. Chromatogr. A, 2002, 976, 47–54.
28. Gliszczyńska-Świgło A., Sikorska E., Simple reversed-phase liquid chromatography method for determination of tocopherols in edible plant oils. J. Chromatogr. A, 2004, 1048, 195–198.
29. Gomes T., Caponio F., Effort to improve the quantitative determination of oxidation and hydrolysis compound classes in edible vegetable oils. J. Chromatogr. A, 1999, 844, 77–86.
30. Gomez-Alonso S., Salvador M.D., Fregapane G., Phenolic compounds profile of Cornicabra virgin olive oil. J. Agric. Food Chem., 2002, 50, 6812–6817.
31. Guillen M.D., Cabo N., Usefulness of the frequency data of the fourier transform infrared spectra to evaluate the degree of oxidation of edible oils. J. Agric. Food Chem., 1999, 47, 709–719.
32. Gurdeniz G., Ozen B., Detection of adulteration of extra-virgin olive oil by chemometric analysis of mid-infrared spectral data. Food Chem., 2009, 116, 519–525
33. Haddad R., Milagre H.M.S., Catharino R.R., Eberlin M.N., Easy ambient sonic-spray ionization mass spectrometry combined with thin-layer chromatography. Anal. Chem., 2008, 80, 2744–2750.
34. Haiyan Z., Bedgood Jr. D.R., Bishop A.G., Prenzler P.D., Robards K.R., Endogenous biphenol, fatty acid and volatile profiles of selected oils. Food Chem., 2007, 100, 1544–1551.
35. Hendl O., Howell J.A., Lowery J., Jones W., A rapid and simple method for determination of iodine values using derivative Fourier transform infrared measurements. Anal. Chim. Acta, 2001, 427, 75–81.
36. Hidalgo F.J., Zamora R., Edible oil analysis by high-resolution nuclear magnetic resonance spectroscopy: recent advances and future perspectives. Trends Food Sci. Technol., 2003, 14, 499–506.

37. Hidalgo F.J., Gomez G., Navarro J.L., Zamora R., Oil stability prediction by high-resolution 13C nuclear magnetic resonance spectroscopy. J. Agric. Food Chem., 2002, 50, 5825–5831.
38. Hilali M., Charrouf Z., El Aziz Soulhi A., Hachimi L., Guillaume D., Detection of argan oil adulteration using quantitative campesterol GC-analysis. J. Am. Oil Chem. Soc., 2007, 84, 761–764.
39. Janssen H-G., Boers W., Steenbergen H., Horsten R., Floter E., Comprehensive two-dimensional liquid chromatography x gas chromatography: Evaluation of the applicability for the analysis of edible oils and fats. J. Chromatogr. A, 2003, 1000, 385–400.
40. Jeleń H.H., Mildner-Szkudlarz S., Jasińska I., Wąsowicz E., A headspace-SPME-MS method for monitoring rapeseed oil autoxidation. J. Am. Oil Chem. Soc., 2007. 84, 509–517.
41. Jeleń H.H., Obuchowska M., Zawirska-Wojtasiak R., Wąsowicz E., Headspace solid-phase microextraction use for the characterization of volatile compounds in vegetable oils of different sensory quality. J. Agric. Food Chem., 2000, 48, 2360–2367.
42. Jeleń H.H., Wlazły K., Wąsowicz E., Kamiński E., Solid-phase microextraction for the analysis of some alcohols and esters in beer: comparison with static headspace method. J. Agric. Food Chem., 1998, 46, 1469–1473.
43. Johnson G.L., Machado R.M., Freidl K.G., Achenbach M.L., Clark P.J., Reidy S.K., Evaluation of Raman spectroscopy for determining *cis* and *trans* isomers in partially hydrogenated soybean oil. Organic Proc. Res. Develop., 2002, 6, 637–644.
44. Kalua C.M., Bedgood D.R. Jr., Prenzler P.D., Development of a headspace solid phase microextraction-gas chromatography method for monitoring volatile compounds in extended time–course experiments of olive oil. Anal. Chim. Acta, 2006, 556, 407–414.
45. Kanavouras A., Kiritsakis A., Hernandez R.J., Comparative study on volatile analysis of extra virgin olive oil by dynamic headspace and solid phase micro-extraction. Food Chem., 2005, 90, 69–79.
46. Kataoka H., Lord H.L., Pawliszyn J., Applications of solid-phase microextraction in food analysis. J. Chromatogr. A, 2000, 880, 35–62.
47. Kaufman M., Wiesman Z., Pomegranate oil analysis with emphasis on MALDI-TOF/MS triacylglycerol fingerprinting. J. Agric. Food Chem., 2007, 55, 10405–10413.
48. Kawai Y., Takeda S., Terao J., Lipidomic analysis for lipid peroxidation – derived aldehydes using gas chromatography – mass spectrometry. Chem. Res. Toxicol., 2007, 20, 99–107
49. Khallouki F., Mannica L., Viel S., Owen R.W., Thermal stability and long-chain fatty acid positional distribution on glycerol of argan oil. Food Chem., 2008, 110, 57–61.
50. Kodali D.R., Oxidative stability measurement of high-stability oils by pressure differential scanning calorimeter (PDSC). J. Agric. Food Chem., 2005, 53, 7649–7653.
51. Lankmayr E., Mocak J., Seret K., Balla B., Wenzl T., Bandoniene D., Gfrerer M., Wagner S., Chemometrical classification of pumpkin seed oils using UV-Vis, NIR and FTIR spectra. J. Biochem. Biophys. Methods, 2004, 61, 95–106.
52. Lerma-Garcia M.J., Ramis-Ramos G., Herrero-Martinez J.M., Simon-Alfonso E.F., Authentication of extra virgin olive oils by Fourier-transform infrared spectroscopy. Food Chem., 2010, 118, 78–83.
53. Liescheski P.B., Supercritical fluid extraction coupled to infrared spectroscopy for iodine number analysis of edible oils. J. Agric. Food Chem., 1996, 44, 823–828.
54. Lisa M., Holcapek M., Rezanka T., Kabatova N., High-performance liquid chromatography-atmospheric pressure chemical ionization mass spectrometry and gas chromatography-flame ionization detection characterization of Δ5-polyenoic fatty acids in triacylglycerols from conifer seed oils. J. Chromatogr. A, 2007, 1146, 67–77.
55. Lizzani-Cuvelier L., Zarrouk M., Profiles of volatile compounds from some monovarietal Tunisian virgin olive oils. Comparison with French PDO. Food Chem., 2007, 103, 467–476.
56. van Loon W.A.M., Linssen J.P.H., Legger A., Posthumus M.A., Voragen A.G.J., Identification and olfactometry of French fries flavor extracted at mouth conditions. Food Chem., 2005, 90, 417–425.
57. Lopez-Lopez A., Montano A., Ruiz-Mendez M.V., Garrido-Fernandez A., Sterols, fatty acids and triterpenic alcohols in commercial table olives. J. Am. Oil Chem. Soc., 2008, 85, 253–262.
58. Lorenzo I.M., Pavon J.L.P., Laespada M.E.F., Pinto C.G., Cordero B.M., Detection of adulterants in olive oil by headspace–mass spectrometry. J. Chromatogr. A, 2002a, 945, 221–230.
59. Lorenzo I.M., Pavon J.L.P., Laespada M.E.F., Pinto C.G., Cordero B.M., Henriques L.R., Peres M.F., Simoes M.P., Lopes P.S., Application of headspace-mass spectrometry for differentiating sources of olive oil. Anal. Bioanal. Chem., 2002b, 374, 1205–1211.
60. Mancebo-Campos V., Salvador M.D., Fregapane G., Comparative study of virgin olive oil behavior under Rancimat accelerated oxidation conditions and long-term room temperature storage. J. Agric. Food Chem., 2007, 55, 8231–8236.
61. Mannina L., D'Imperio M., Capitani D., Rezzi S., Guillou C., Mavromoustakos T., Vilchez M.D.M., Fernandez A.H., Thomas F., Aparicio R., ^{1}H NMR-based protocol for the detection of adulterations of refined olive oil with refined hazelnut oil. J. Agric. Food Chem., 2009, 57, 11550–11556.
62. del Mar Caja M., del Castillo M.L.R., Alvarez R.M., Herraiz M., Blanch G.P., Analysis of volatile compounds in edible oils using simultaneous distillation-solvent extraction and direct coupling of liquid chromatography with gas chromatography. Eur. Food Res. Technol., 2000, 211, 45–51.
63. Mateos R., Trujillo M., Perez-Camino M.C., Moreda W., Cert A., Relationship between oxidative stability, triacylglycerol composition and antioxidant content in olive oil matrices. J. Agric. Food Chem., 2005, 53, 5766–5771.
64. Michulec M., Wardencki W., Validation of SPME-GC and HS--GC procedures for the determination of selected solvent residues in edible oil matrices. Accred. Qual. Assur., 2007, 12, 94–104.
65. Michulec M., Wardencki W., Development of headspace solid-phase microextraction-gas chromatography method for the determination of solvent residues in edible oils and pharmaceuticals. J. Chromatogr. A, 2005, 1071, 119–124.
66. Michulec M., Wardencki W., Determination of solvents residues in vegetable oils and pharmaceuticals by headspace analysis and capillary gas chromatography. Chromatographia, 2004, 60, 273–277.
67. Mildner-Szkudlarz S., Jeleń H.H., Zawirska-Wojtasiak R., Wąsowicz E., Application of headspace—solid phase microextraction and multivariate analysis for plant oils differentiation. Food Chem., 2003, 83, 515–522.
68. Miraliakbari H., Shahidi F., Oxidative stability of tree nut oils. J. Agric. Food Chem., 2008, 56, 4751–4759.

69. Moreno M.C.M.M., Olivares D.M., Lopez F.J.A., Adelantado J.V.G., Reig F.B., Determination of unsaturation grade and trans isomers generated during thermal oxidation of edible oils and fats by FTIR. J. Molec. Struc., 1999, 482–483, 551–556.
70. Muik B., Lendl B., Molina-Diaz A., Valcarcel M., Ayora-Canada M.J., Two-dimensional correlation spectroscopy and multivariate curve resolution for the study of lipid oxidation in edible oils monitored by FTIR and FT-Raman spectroscopy. Anal. Chim. Acta, 2007, 593, 54–67.
71. Naglic M., Smidovnik A., Use of capillary gas chromatography for determining the hydrogenation level of edible oils. J. Chromatogr. A, 1997, 767, 335–339.
72. Noguera-Orti J.F., Villanueva-Camanas R.M., Raims-Ramos G., Direct injection of edible oils as microemulsions in a micellar mobile phase applied to the liquid chromatographic determination of synthetic antioxidants. Anal. Chim. Acta, 1999, 387, 127–134.
73. Pacheco-Palencia L.A., Mertens-Talcott S., Talcott S.T., Chemical composition, antioxidant properties and thermal stability of a phytochemical enriched oil from acai (*Euterpe oleracea Mart.*). J. Agric. Food Chem., 2008, 56, 4631–4636.
74. Pawliszyn J., Sample Preparation: Quo Vadis? Anal. Chem., 2003, 75, 2543 – 2558.
75. Pawliszyn J., Solid Phase Microextraction: Theory and Practice. 1997, first edition, Wiley-VCH, New York, pp. 43–192.
76. Pellegrini N., Visioli F., Buratti S., Brighenti F., Direct analysis of total antioxidant activity of olive oil and studies on the influence of heating. J. Agric. Food Chem., 2001, 49, 2532–2538.
77. Pereira J.A., Casal S., Bento A., Oliveira M.B.P.P., Influence of olive storage period on oil quality of three Portuguese cultivars of *Olea europea cobrancosa*, *madural* and *verdeal transmontana*. J. Agric. Food Chem., 2002, 50, 6335–6340.
78. Plutowska B., Wardencki W., Aromagrams – Aromatic profiles in the appreciation of food quality. Food Chem., 2007, 101, 845–872.
79. Povolo M, Contarini G., Comparison of solid-phase microextraction and purge-and-trap methods for the analysis of the volatile fraction of butter. J. Chromatogr. A, 2003, 985, 117–125.
80. Purcaro G., Morrisom P., Moret S., Conte L.S., Marriott P.J., Determination of polycyclic aromatic hydrocarbons in vegetable oils using solid-phase microextraction-comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry. J. Chromatogr. A, 2007, 1161, 284–291.
81. Romanik G., Gilgenast E., Przyjazny A., Kamiński M., Techniques of preparing plant material for chromatographic separation and analysis. J. Biochem. Biophys. Methods, 2007, 70, 253–261.
82. Romero M.P., Tovar M.J., Girona J., Motilva M.J., Changes in the HPLC phenolic profile of virgin olive oil from young trees (*Olea europaea L.* cv. *Arbequina*) grown under different deficit irrigation strategies. J. Agric. Food Chem., 2002, 50, 5349–5354.
83. Ruiz-Mendez M.V., Dobarganes M.C., Combination of chromatographic techniques for analysis of complex deodorizer distillates from an edible oil refining process. Food Chem., 2007, 103, 1502–1507.
84. Santos J.C.O., Santos M.G.O., Dantas J.P., Conceicao M.M., Athaide-Filho P.F., Souza A.G., Comparative study of specific heat capacities of some vegetable oils obtained by DSC and microwave oven. J. Therm. Anal. Calorim., 2005, 79, 283–287.
85. Senorans F.J., Villen J., Tabera J., Herraiz M., Simplex optimization of the direct analysis of free sterols in sunflower oil by on-line coupled reversed phase liquid chromatography-gas chromatography. J. Agric. Food Chem., 1998, 46, 1022–1026.
86. Senorans F.J., Tabera J., Herraiz M., Rapid separation of free sterols in edible oils by on-line coupled reversed phase liquid chromatography-gas chromatography. J. Agric. Food Chem., 1996, 44, 3189–3192.
87. Shaw A.D., di Kamillo A., Vlahov G., Jones A., Bianchi G., Rowland J., Kell D.B., Discrimination of variety and region of origin of extra virgin olive oils using ^{13}C NMR and multivariate calibration with variable reduction. Anal. Chim. Acta, 1997, 348, 357–374.
88. Simon P., Kolman L., DSC study of oxidation induction periods. J. Therm. Anal. Calorim., 2001, 64, 813–820.
89. Smejkalova D., Piccolo A., High-power gradient diffusion NMR spectroscopy for the rapid assessment of extra-virgin olive oil adulteration. Food Chem., 2010, 118, 153–158.
90. Smith S.A., King R.E., Min D.B., Oxidative and thermal stabilities of genetically modified high oleic sunflower oil. Food Chem., 2007, 102, 1208–1213.
91. Snow N.H., Snack G.C., Head-space analysis in modern gas chromatography. Trends Anal. Chem., 2002, 21, 608 – 617.
92. Stashenko E.E., Martinez J.R., Derivatization and solid-phase microextraction. Trends Anal. Chem., 2004, 23, 553–561.
93. Sullivan J.C., Budge S.M., St-Onge M., Determining ethyl esters in fish oil with solid phase microextraction and GC-MS. J. Am. Oil Chem. Soc., 2009, 86, 743–748.
94. Szłyk E., Szydłowska-Czerniak A., Kowalczyk-Marzec A., NIR spectroscopy and partial least-squares regression for determination of natural α-tocopherol in vegetable oils. J. Agric. Food Chem., 2005, 53, 6980–6987.
95. Tan C.P., Che Man Y.B., Differential scanning calorimetric analysis for monitoring the oxidation of heated oils. Food Chem., 1999, 67, 177–184.
96. Tong P., Kaługa Y., Khoo C.S., Liquid chromatographic-mass spectrometric method for detection of estrogen in commercial oils and in fruit seed oils. J. Food Comp. Anal., 2006, 19, 150–156.
97. Vigli G., Philippidis A., Spyros A., Dais P., Classification of edible oils by employing ^{31}P and ^{1}H NMR spectroscopy in combination with multivariate statistical analysis. A proposal for the detection of seed oil adulteration in virgin olive oils. J. Agric. Food Chem., 2003, 51, 5715–5722.
98. Villen J., Blanch G.P., del Castillo M.L.R., Herraiz M., Rapid and simultaneous analysis of free sterols, tocopherols and squalene in edible oils by coupled reversed-phase liquid chromatography-gas chromatography. J. Agric. Food Chem., 1998, 46, 1419–1422.
99. van de Voort F.R., Sedman J., Sherazi S.T.H., Correcting for underlying absorption interferences in Fourier transform infrared trans analysis of edible oils using two-dimensional correlation techniques. J. Agric. Food Chem., 2008, 56, 1532–1537.
100. Wang L., Lee F.S.C., Wang X., He Y., Feasibility study of quantifying and discriminating soybean oil adulteration in camellia oils by attenuated total reflectance MIR and fiber optic diffuse reflectance NIR. Food Chem., 2006, 95, 529–536.
101. Wardencki W., Michulec M., Curyło J., A review of theoretical and practical aspects of solid-phase microextraction in food analysis. Int. J. Food Sci. Technol., 2004, 39, 703–717.

102. Warner K., Effects on the flavor and oxidative stability of stripped soybean and sunflower oils with added pure tocopherols. J. Agric. Food Chem., 2005, 53, 9906–9910.
103. Yang H., Irudayaraj J., Paradkar M.M., Discriminant analysis of edible oils and fats by FTIR, FT-NIR and FT-Raman spectroscopy. Food Chem., 2005, 93, 25–32.
104. Yu X., van de Voort F.R., Sedman J., Determination of peroxide value of edible oils by FTIR spectroscopy with the use of the spectral reconstitution technique. Talanta, 2007, 74, 241–246.
105. Zamora R., Alba V., Hidalgo F.J., Use of high-resolution ^{13}C nuclear magnetic resonance spectroscopy for the screening of virgin olive oils. J. Am. Oil Chem. Soc., 2001, 78, 89–94.
106. Zhang X., Julien-David D., Miesch M., Raul F., Geoffroy P., Aoude-Werner D., Ennahar S., Marchioni E., Quantitative analysis of β-sitosterol oxides induced in vegetable oils by natural sunlight, artificially generated light and irradiation. J. Agric. Food Chem., 2006, 54, 5410–5415.
107. Zunin P., Boggia R., Lanteri S., Leardi R., De Andreis R., Evangelisti F., Direct thermal extraction and gas chromatographic–mass spectrometric determination of volatile compounds of extra-virgin olive oils. J. Chromatogr. A, 2004, 1023, 271–276.

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