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Characterization of Edible Oils Using Total Luminescence Spectroscopy

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Total luminescence spectroscopy was used to characterise and differentiate edible oils and additionally, to control one of the major problems in the oil quality—the effect of thermal and photo-oxidation. We studied several vegetable oils available on the Polish market, including soybean, rapeseed, corn, sunflower, linseed and olive oils. Total luminescence spectroscopy measurements were performed using two different sample geometries: front-face for pure oil samples and right-angle for transparent samples, diluted in *n*-hexane. All the samples studied as *n*-hexane solutions exhibit an intense peak, which appears at 320 nm in emission and 290 nm in excitation, attributed to tocopherols. Some of the oils exhibit a second long-wavelength peak, appearing at 670 nm in emission and 405 nm in excitation, belonging to pigments of the chlorophyll group. Additional bands were present in the intermediate range of excitation and emission wavelengths; however, the compounds responsible for this emission were not identified. The front-face spectra for pure oils included chlorophyll peaks for most samples, and some additional peaks in the intermediate range, while the tocopherol peaks were comparatively less intense. The results presented demonstrate the capability of the total luminescence techniques to characterise and differentiate vegetable oil products, and additionally, to characterize the effect of thermal and photo-oxidation on such products. In the photo-oxidation experiments, special attention was paid to possible involvement of singlet oxygen. Experiments were done to monitor the highly specific $O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-)$ singlet oxygen emission at 1270 nm. Thus, total luminescence spectroscopy presents an interesting alternative to time-consuming and expensive techniques such as gas or liquid chromatography, mass spectrometry and other methods requiring wet chemistry steps.

KEY WORDS: total fluorescence spectroscopy; edible oils; analysis of foodstuffs.

INTRODUCTION

Fluorescence spectroscopy is a rapid, selective and relatively simple method for characterising molecular environments and is much more sensitive than most other spectroscopic methods. The fluorescence measurements after appropriate sample preparations provide one of the most sensitive and selective methods of quantitative analysis for many compounds in a wide area of organic and inorganic analysis, biochemistry, agricultural and environmental chemistry, public health and clinical pathology. Fluorometry is a powerful detection method used in separation techniques like liquid chromatography and electrophoresis [1,2].

One of the most important advantages of the fluorescence method is its selectivity; however in its application to complex natural systems, the selectivity of conventional fluorescence techniques appears to be insufficient. Instead, multidimensional fluorescence techniques are used in such applications, providing additional information about the

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samples. One of such techniques is total luminescence spectroscopy (TLS), which involves simultaneous acquisition of multiple excitation and emission wavelengths in order to increase the method selectivity. The resulting emission-excitation data matrix (EEM) provides a total intensity profile of the sample over the range of excitation and emission wavelengths scanned [3].

The Total Luminescence Spectroscopy has been used, among others, for: identification and quantification of polyaromatic hydrocarbons (PAHs) in environmental samples [4], identification of oil spills by analysis of fluorescent PAHs, identification of oil and fuel samples in forensic studies [5], characterisation, differentiation and classification of natural organic matter such as humic matter in water [6], analysis and characterisation of pharmaceutical compounds, observation of luminescent properties of rocks and minerals, bacterial identification, and studies of marine phytoplankton [3].

Although fluorescence spectroscopy is a method, which has been exploited extensively for studies in chemistry and biochemistry and environmental analysis, the use of this method for non-invasive and non-destructive studies has not been fully recognised in food science. Only several papers have discussed the potential of fluorescence in the analysis of food products. Fluorescence spectroscopy was used for monitoring colour precursors in sugar industry processes [7–10], oxidation in fish and meat, flour, soap and frying oil [11].

This article explores the possibility of application of fluorescence methods in analysis of vegetable oils. Total luminescence techniques (TLS) were applied for characterisation and differentiation of commercially available vegetable oils. Note that we shall be using the terms Fluorescence and Luminescence as synonyms, given that no phosphorescence could be detected in the present experimental conditions.

Vegetable oils are predominantly (95–98%) tri-fatty acid esters of glycerol, commonly referred to as triglycerides. The remaining 2–5% is made of complex mixtures of minor compounds of a wide range of chemical classes, including: fatty alcohols, waxes, esters, hydrocarbons, volatiles, pigments, phenolic compounds, glyceridic compounds, phospholipids and triterpenic acids [12]. Characterization of these compounds is of great importance in establishing the oil quality, detecting adulteration and understanding the behaviour of oils during storage and processing. The most commonly used analytical techniques for analysis of these compounds are gas and liquid chromatography. These techniques are however expensive, time-consuming and require a pre-separation step before the analysis. In recent years, there have been a lot of research activities in developing new rapid methods for quality assessment of food products, which do not require separations steps. These methods include: mass spectrometry, infrared and near infrared spectroscopy, Raman and nuclear magnetic resonance spectroscopy [13,14]. There are also a few reports in literature on the application of fluorescence spectroscopy for vegetable oils analysis [11,15].

The objective of the present study was to investigate intrinsic fluorophores of edible oils, and to find general similarities and dissimilarities between different kinds of edible oils. The utility of fluorescence spectroscopy as the fingerprinting technique for vegetable oil analysis was examined. Comparative study of changes in fluorescent characteristic induced by thermal- and photo-oxidation was conducted.

EXPERIMENTAL

Materials

The studies were performed on eight commercially available edible oils, including refined oils (rapeseed 1, soybean, sunflower,) and those produced by mechanical pressing (rapeseed 2, corn, olive 1 and 2—two different brands, and linseed oil) The linseed and rapeseed 2 oils were obtained at a local oil manufacturer, other oils were acquired in a supermarket and had an expiry date exceeding the maximum duration of experiment. α-Tocopherol (97%), *n*-hexane, acetone were purchased from Aldrich. Bacteriopheophytin *c* was a gift from Prof. D. Frackowiak, Poznań University of Technology.

Fluorescence Measurements

Fluorescence spectra were obtained on a Fluorolog 3-11 Spex-Jobin Yvon spectrofluorometer. Xenon lamp source was used for excitation.

Right-angle geometry was used for oil samples diluted in *n*-hexane (1% v/v) in 10 mm fused-quartz cuvette. Front-face geometry was used for neat oil samples and measurements were performed in a triangular fused-quartz cuvette.

All the three-dimensional spectra were obtained by measuring the emission spectra in the range from 290 to 700 nm repeatedly, at excitation wavelengths from 250 to 450 nm, spaced by 5 nm intervals in the excitation domain. Excitation and emission slit width was 2 nm for all the samples. The acquisition interval and the integration time were maintained at 1 nm and 0.1 s, respectively. A reference photodiode detector at the excitation monochromator stage compensated for the source intensity fluctuations. Individual spectra were corrected for the wavelength

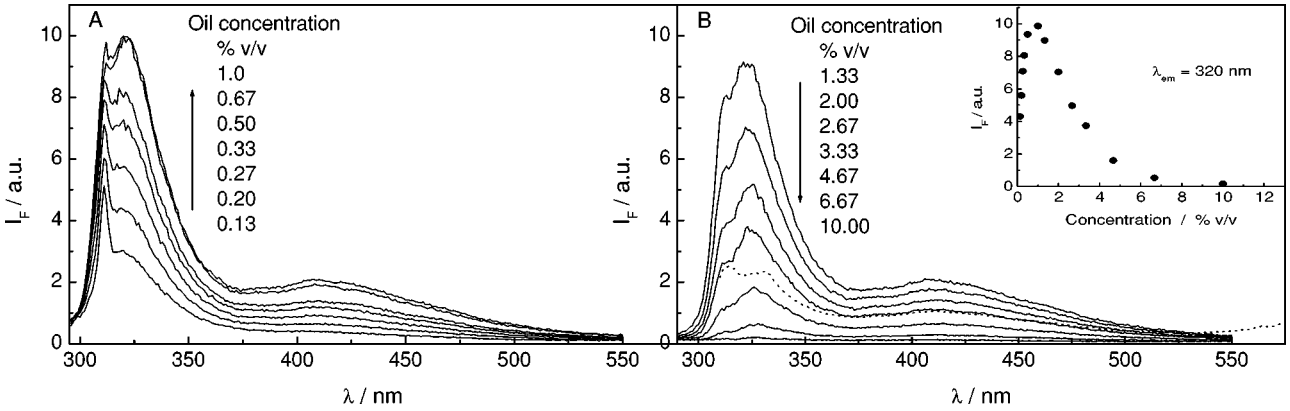

Fig. 1. Effect of oil concentration on the emission spectra of soybean oil, in *n*-hexane, $\lambda_{exc} = 295$ nm; A—increase of fluorescence intensity for concentration range 0.13–1.00% v/v; B—decrease of fluorescence intensity for concentration range 1.33–10% v/v; dotted line—emission spectrum of neat soybean oil measured using front face geometry; inset—changes in the emission intensity at 320 nm depending on oil concentration.

response of the system. Fully corrected spectra were then concatenated into an excitation-emission matrix.

Three-dimensional plots and contour maps of total luminescence spectra were produced using DataMax Grams/32 program. Each set of contour maps was plotted using the same scale range of fluorescence intensities, and number of contours. For diluted oils, neat samples and oxidized oils, respectively, the scales of 0 to 3×10^7, 0 to 8×10^7, 0 to 1×10^7 intensity units (counts per second) were applied. The data along the *Z* axis were interpolated to improve appearance.

Photo- and Thermal Oxidation of Oils

In photo-oxidation experiments the samples of neat oils (20 cm^3) were placed in open glass vessels, and exposed directly to light from two tungsten lamps, 100 W each, for 176 hr at 20°C.

In thermal oxidation experiments, the neat oil samples were heated at 200°C in darkness for 20 hr.

Singlet Oxygen Measurements

Singlet oxygen luminescence experiments were carried out by excitation of the sample with the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Spectron Laser Systems, UK; 20 mJ per pulse, ca. 9 ns FWHM). The excitation energy was attenuated using solutions of sodium nitrite in water. Detection was using an EO-980P LN_2-cooled germanium photodiode detector (North Coast Scientific), with a 1270 nm interference filter (Melles Griot) interposed between sample and detector to reduce detection of laser scatter and sensitizer emission, and to isolate the singlet oxygen phosphorescence. Data capture was with a 250MS/s digitising oscilloscope (Tektronix 2432A) and data analysis used Microcal Origin. Perinaphthenone (Aldrich) was used as a reference standard, $\phi_\Delta = 0.95 \pm 0.05$, independent of solvent [16].

RESULTS AND DISCUSSION

Total Luminescence Spectra of Vegetable Oils

Vegetable oils are complex mixtures of non-fluorescent and fluorescent compounds and the molecular interactions between components like energy transfer and self-quenching via solvent collisions are expected. These interactions may distort the characteristic fluorescence of individual components, especially in concentrated samples. Thus, first of all the effect of concentration on fluorescence spectra was checked.

A typical set of spectra shown on Fig. 1 illustrates the changes in emission with increasing concentration of soybean oil in *n*-hexane, recorded at right-angles geometry; an emission spectrum recorded using front-face geometry is presented for comparison. As expected, initially the oil fluorescence intensity increases with increasing concentration, with a maximum intensity achieved at about 1% v/v. At higher concentrations, the fluorescence intensity decreased and band shape changes were observed. These effects may result from molecular interactions in concentrated samples as well as from screening effects e.g. inner filter effects. The comparison of the spectra recorded for concentrated samples using right-angles geometry with those of neat oils measured using front-face arrangement, points out that the interactions occurring in the concentrated samples influence the shape of the emission bands. A relative reduction of fluorescence intensity

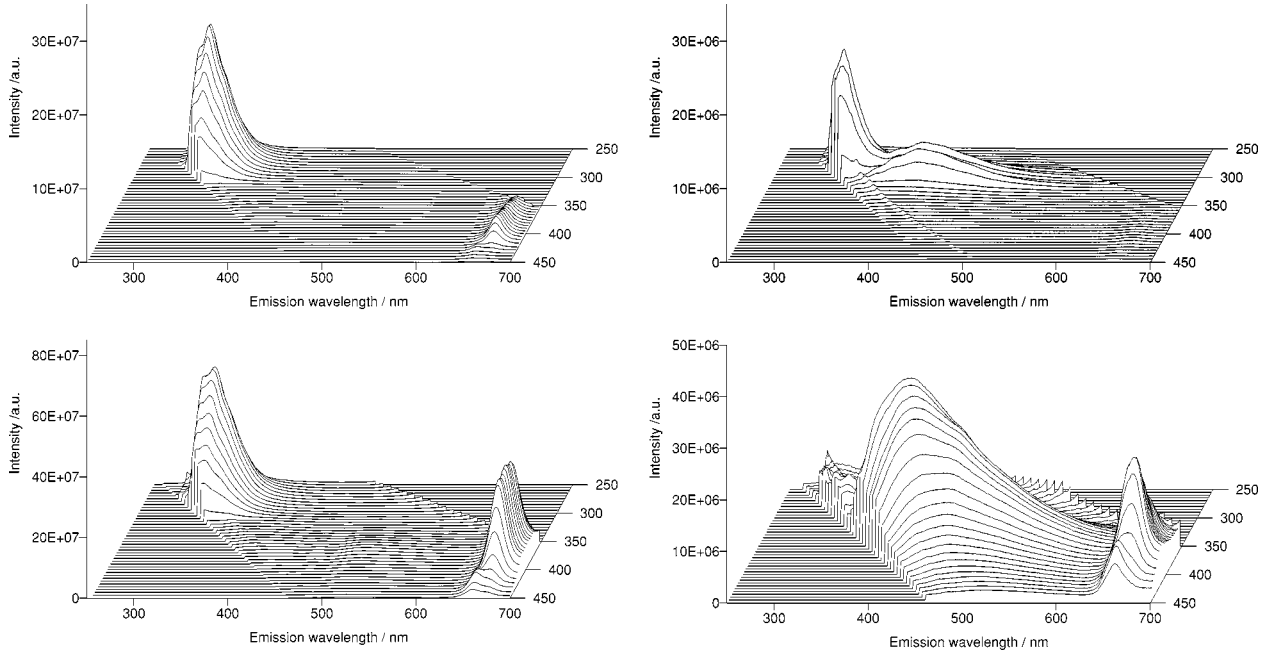

Fig. 2. Three-dimensional total luminescence spectra of rapeseed (left) and soybean (right) oils in *n*-hexane, 1% v/v (top), and for neat oils (bottom).

in the right-angles arrangement may result from primary and secondary inner filter effects; e.g.: attenuation of the emission intensity due to the absorption of the incident excitation light and to absorption of the emitted light. However, these effects are avoided in the front-face illumination; as the entire incident light is absorbed close the sample surface due to high optical densities. On the other hand, the high concentration of sample results in a variety of molecular interactions, such as collisional quenching and energy transfer, which can distort the fluorescence spectrum [17].

To avoid such distortions, we made most of the measurements for oils diluted in *n*-hexane at 1%, v/v. The spectra of undiluted oils, on the other hand, despite of their distortions, may be of interest for the sake of differentiation and characterisation of oils. Moreover, such spectra might contain additional information due to reduced excited-state quenching by oxygen or other species in viscous oils as compared to diluted solutions. Hence, we also measured total luminescence spectra directly on neat oil samples, using front-face geometry in order to reduce the inner filter and self absorption effects.

Figure 2 shows three-dimensional spectra of rapeseed and soybean oils in *n*-hexane. Such spectra are known as excitation-emission matrix or total luminescence spectra, in which one axis represents the excitation wavelength, another—the emission wavelength, and the third—the intensity. Alternatively, three-dimensional spectra may be transformed into two-dimensional contour maps, in which one axis represents the emission and another—the excitation wavelength. The contours are plotted by linking points of equal fluorescence intensity. Such a presentation is more practical for analysing the fluorescence patterns. Figure 3 shows contour maps of total luminescence of oils diluted in *n*-hexane (1%, v/v).

All the samples studied exhibit a strong characteristic band with excitation at about 270 nm–310 nm and emission at about 300 nm—350 nm. This band has been ascribed to tocopherols and tocotrienols. This assignment is based on its similarity to the total luminescence spectrum of α-tocopherol dissolved in *n*-hexane, Fig. 4.

Conventional excitation and emission spectra obtained for the studied oils in the wavelength range mentioned are also similar to those of α-tocopherol, Fig. 5. Moreover, the excitation spectra are in good agreement with the absorption spectrum of α-tocopherol in *n*-hexane. Exact positions of maxima of tocopherol emission vary slightly from one oil to another, which may result from differences in the respective tocopherol composition. Tocopherols are present in most vegetable oils in widely variable amounts, from 70 to 1900 mg/kg [12]. The vitamin E group includes: four natural tocopherols (α, β, γ, δ) and four tocotrienols (αT3, βT3, γT3, δT3), all—in the R-configuration. The two classes differ by the presence of

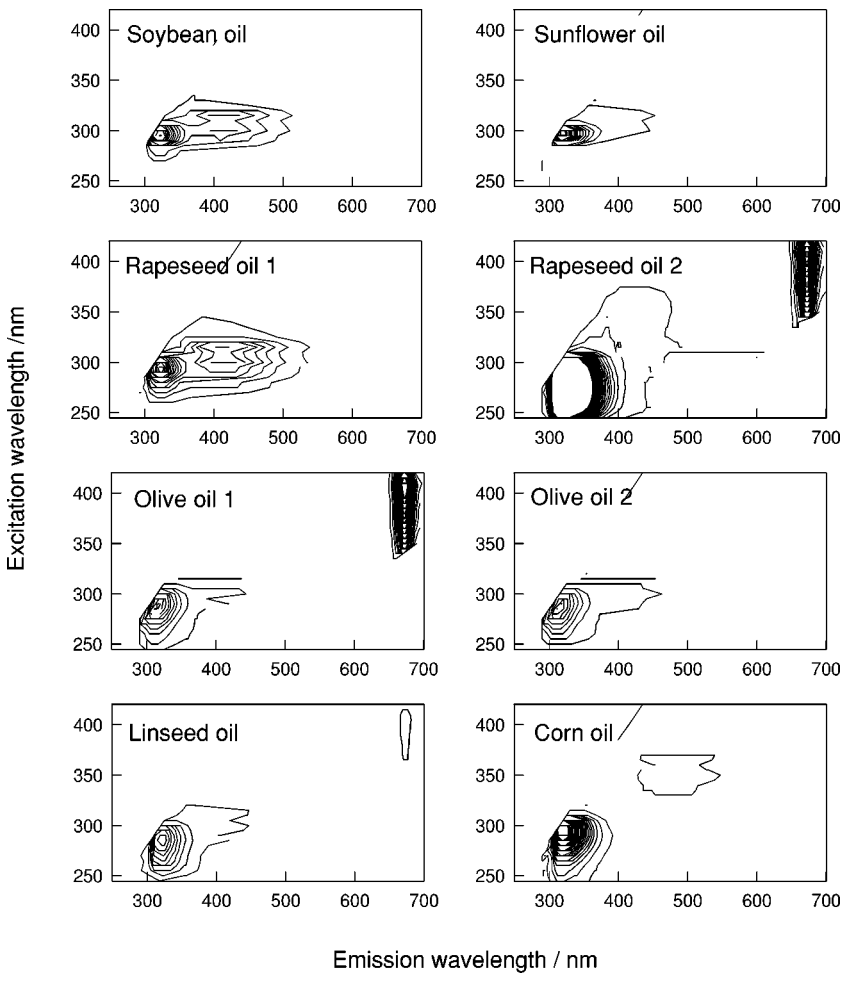

Fig. 3. Contour maps of total luminescence of edible oils diluted in *n*-hexane, 1% v/v.

three double bonds in the side-chain in tocotrienols [18]. Due to their structure similarity, all these compounds exhibit very similar UV-absorption spectra and are expected to have similar fluorescence properties. It is interesting to note that the oils obtained by physical methods (cold pressing): linseed, olive 1 and 2 and rapeseed 2 oil—have fluorescence maxima of the tocopherol band blue-shifted by about 10 to 25 nm as compared to other oils, indicating variation in chemical composition, which may result from differences in manufacturing technology.

For some oils, namely linseed, rapeseed 2 (obtained by physical methods) and olive oil 1, a long-wavelength band is observed with excitation at about 350 nm–420 nm and emission at about 660 nm–700 nm. This band was attributed to pigments of chlorophyll group, based on its excitation and emission characteristics [19]. This group includes chlorophylls *a* and *b*, and pheophytins *a* and *b*, derived from chlorophylls by loss of magnesium [12]. Fig. 4 presents the total luminescence spectrum of bacteriopheophytin *c*, related to bacteriochlorophyll *c*. These pigments differ in structure from pheophytins and chlorophylls *a* and *b*, in that the pyrrole ring IV is not reduced, and the position 17 is esterified by an acrylic residue—instead of a propionic group, the terminal carboxylic group being generally not esterified [19]. However, the absorption and emission spectra of chlorophylls *a* and *b* are very similar to those of chlorophyll *c*, thus the respective spectra are shown for the sake of comparison.

Another emission band is observed in the spectra of soybean and rapeseed 1 oils, with emission in the 350 to 480 nm range, and excitation in the 280 to 330 nm range. The respective single excitation (see Fig. 5) and emission spectra for this fluorescence are very similar to each other, suggesting that the same or similar fluorophores are present in both these oils. The compounds responsible for this band were not identified; we should note, however,

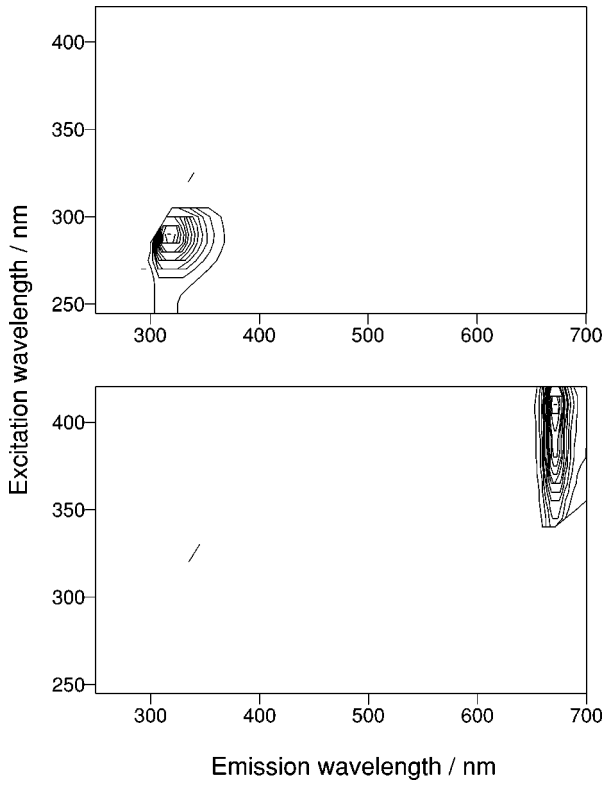

Fig. 4. Contour maps of total luminescence of α-tocopherol in *n*-hexane and bacteriopheophytin *c* in acetone.

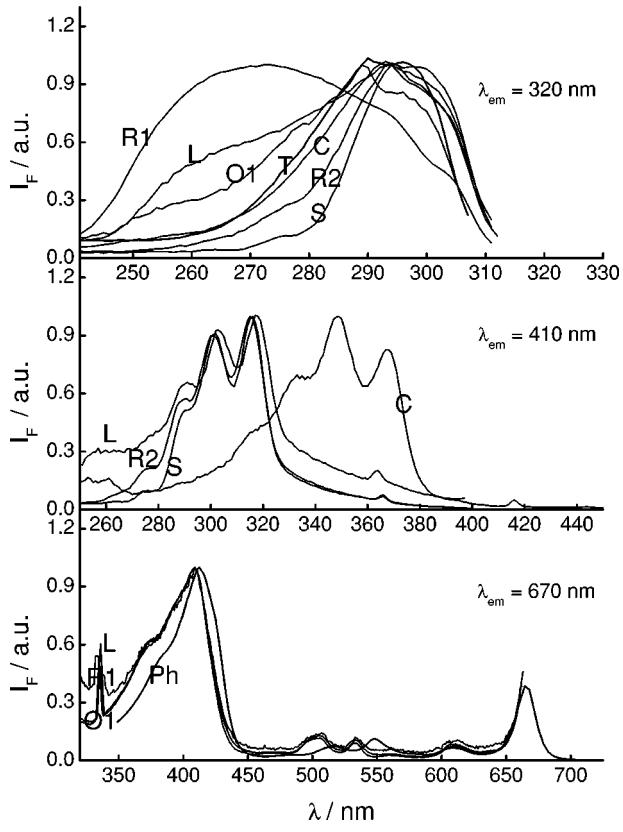

Fig. 5. Excitation spectra of various fluorophores of studied oils, samples diluted in *n*-hexane, 1% v/v; L—linseed oil, R1—rapeseed oil 1, R2—rapeseed oil 2, S—soybean oil, O1—olive oil, C—corn oil, T—α-tocopherol in *n*-hexane, Ph—bacteriopheophytin *c* in acetone.

that their presence might result from the technological process used, as the two oils exhibiting this band were manufactured by the same producer. Another possibility is that these additional fluorescent constituents originated from a particular batch of the raw plant material. The total emission spectra of the other oils studied reveal emission bands in the similar range, with similar excitation spectra, Fig. 5, although with low intensity. A different band is present in the corn oil spectrum, with emission at 450 nm–550 nm and excitation at 320 nm–380 nm, characteristic to this sample only.

Total luminescence spectra of virgin and refined olive oils in isooctane were reported by Giungato *et al.* [15]. They found for virgin olive oils an emission band with the excitation maximum at 285 nm and the emission maximum at about 315 nm, attributed to tocopherols, and a second band with the excitation maximum at 410 nm and emission maximum at 669 nm, identified as the chlorophylls emission. For refined oils, the tocopherol band was observed with excitation and emission maxima at 295 nm and 331 nm respectively, while the chlorophyll emission was not detectable. Additionally, another emission was observed for this oil with two excitation maxima at 300 and 315 nm and an emission maximum at 406 nm, the origin of this emission having remained uncertain.

Although presenting distinct mixtures of fluorescent compounds, the presently studied oils also exhibit differences in relative fluorescent intensities for particular compounds. It is interesting to note that intensity of tocopherol emission is lowest for the two olive oils, in agreement with the known low tocopherol contents of these oils [18]. The highest tocopherol emission intensity was observed for rapeseed oil 2, produced by mechanical means. However at this stage, without a full understanding of the factors influencing fluorescence intensity of individual components in the oil matrix, any quantitative conclusions have to be drawn with great caution.

The preceding analysis of the total luminescence spectra of diluted oils leads to a conclusion that other fluorescent components are present in oils, in addition to tocopherols and chlorophylls, depending on their nature, brand, origin and processing technology.

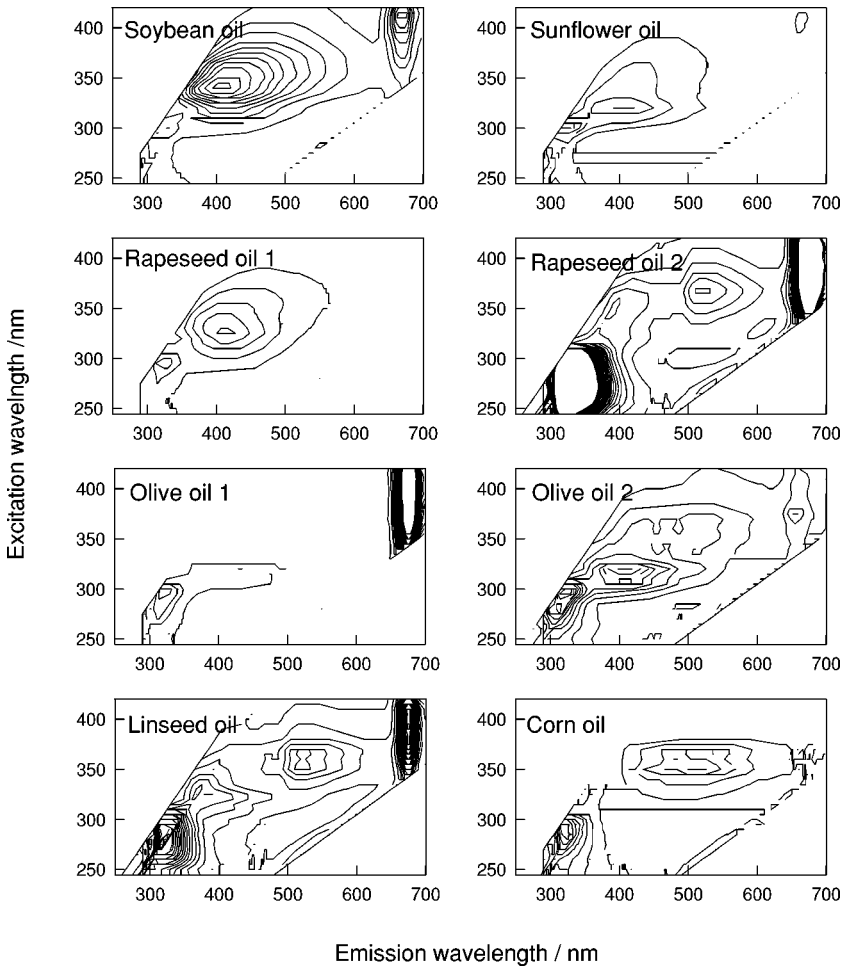

Fig. 6. Contour maps of total luminescence of neat edible oils.

The presence of fluorophores other than tocopherols and pheophytins is even more evident from total luminescence spectra of neat oils recorded using the front-face arrangement, Fig. 6. In these spectra, the intensity of tocopherol emission is reduced as compared to diluted samples. On the contrary, the chlorophyll fluorescence is more intense and present in all oils with an exception of corn and refined rapeseed oils. Moreover, in almost every sample, with the exception of one of the olive oils, additional intense fluorescence bands in the intermediate wavelength range are observed. Consequently, the front-face analysis has been found more informative as compared to diluted *n*-hexane solutions in the right-angles geometry. A linear feature noticeable at the right-hand boundary of the contour maps is a system artefact and should be disregarded.

The changes evident when comparing the diluted oil spectra to those of the concentrated oils should result from the energy transfer and collisional quenching effects. Similar phenomena have been noted in the fluorescent studies of crude petroleum oils [20–23], and can significantly complicate quantitative analysis of the fluorescent constituents. Clearly, much additional work will be required to clarify these fundamental issues. On the other hand, the lack of such fundamental knowledge does not preclude the use of fluorescent analysis techniques for the purposes of authentication and quality control.

Vegetable oils are known to contain other classes of compounds, besides tocopherols and chlorophylls. The group of carotenoids includes non-polar hydrocarbons—carotenes and xanthophylls, which are oxygenated at the outermost carbon atoms. Another group of minor constituents present in vegetable oils includes polyphenols with one or more aromatic rings, substituted with hydroxyl groups. Some of these compounds may contribute to the emission observed. Clearly, further studies are needed to

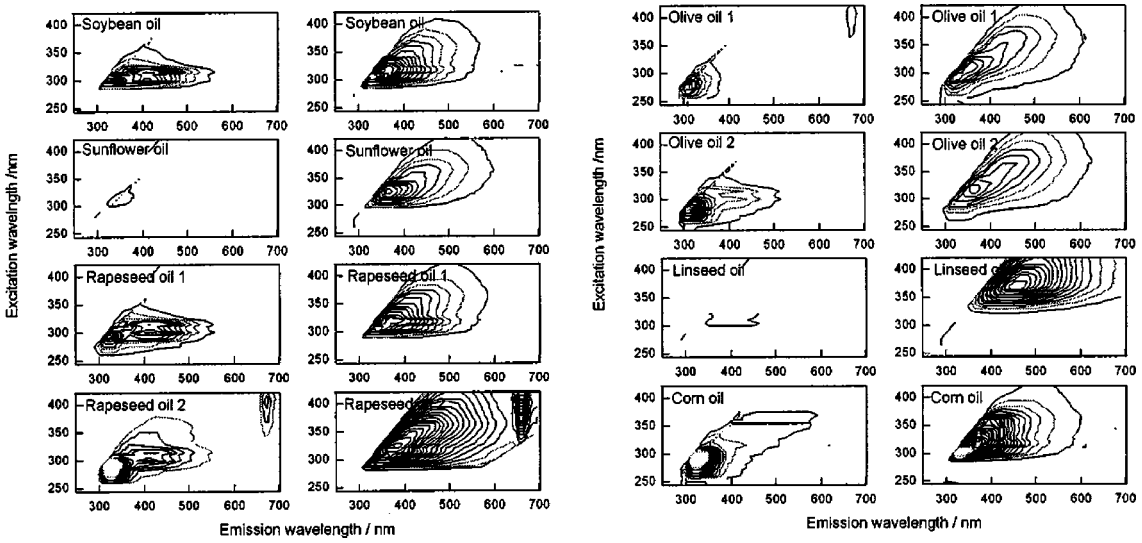

Fig. 7. Contour maps of total luminescence of edible oils after photo-oxidation (left) and thermal-oxidation (right), samples diluted in *n*-hexane 1% v/v.

identify the fluorophores responsible for the unidentified emission bands.

Thus, a total luminescence spectrum gives a comprehensive description of the fluorescent components of the mixture, exhibiting different features for various oils. Such a spectrum incorporates all information present in the absorption and fluorescence spectra of fluorescent oil constituents. The resulting spectral resolution depends on the number of conventional emission scans at different excitation wavelengths, used to construct the contour plot. Due to these features, the total luminescence contour map may serve as a unique fingerprint for identification and characterization of various oils.

OXIDATION OF VEGETABLE OILS

The susceptibility of lipids to oxidation is a major cause of quality deterioration in many types of natural and processed foods. Lipid oxidation causes changes in the type and concentration of molecular species present in food. This in turn alters the quality attributes of foodstuffs, such as texture, taste, shelf life, appearance and nutritional profile. Lipid oxidation is undesirable because it leads to the development of an off-flavour, and results in potentially toxic compounds.

Therefore, we investigated changes of fluorescence characteristics of edible oils resulting from thermal and photo-oxidation. Figures 7 and 8 show the total luminescence spectra of oils exposed to light or high temperatures.

Both types of oxidation produce a general reduction of fluorescence intensity, which may result from decomposition of the fluorophores. Interestingly, the qualitative changes observed in oils exposed to light or high temperatures are markedly different for every oil studied. For photo-oxidised oils, an intensity decrease of the tocopherol and chlorophyll fluorescence is accompanied by various qualitative changes, depending on the oil. For example, in linseed and rapeseed 2 oils, both obtained by mechanical means, a new emission band is formed, shifted to longer excitation and emission wavelengths as compared to the tocopherol band. The qualitative changes in fluorescence caused by photo-oxidation are rather small in some oils. Resulting from thermal oxidation, the tocopherol band intensity is reduced to a variable extent, depending on the oil studied. The most common feature in the fluorescence of oils exposed to high temperatures is the emergence of a new broad fluorescence band, spread over the central part of the contour plot. This band appears in all oils after thermal oxidation, although its exact location depends on the sample. Differences in fluorescent characteristics of thermally- and photo-oxidised oils point out different mechanisms of the two processes.

Lipid oxidation is a complex process, in which polyunsaturated lipids undergo reaction with molecular oxygen to form lipid hydroperoxides. Oils containing polyunsaturated fatty acids undergo spontaneous peroxidation by way of thermal auto-oxidation reaction involving ground-state oxygen, which leads initially to the formation of lipid hydroperoxide products. The lipid hydroperoxides can undergo further oxidation, eventually forming aldehydes, ketones and other species via a complex series of radical reactions. Peroxidation can be also initiated photochemically. Photosensitised oxidation results from the production of singlet oxygen generated by

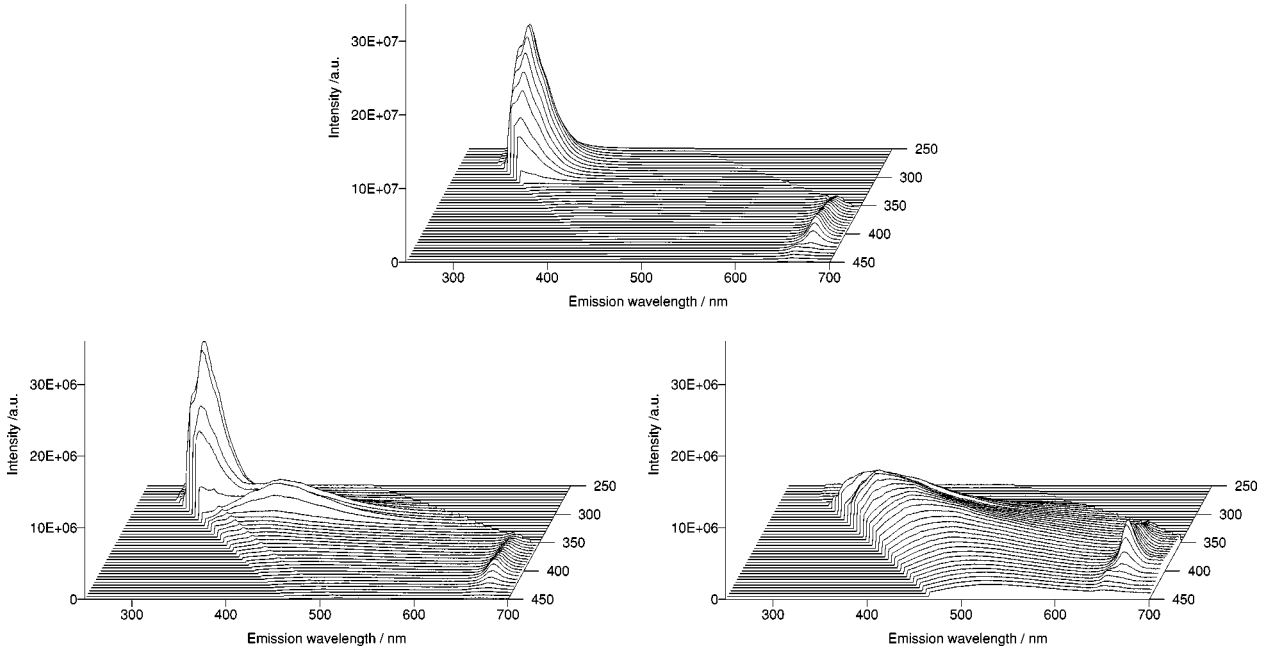

Fig. 8. Effect of thermal- and photo-oxidation on total luminescence spectra of rapeseed oil; untreated oil (top), exposed to light (bottom left) and to heat (bottom right), samples diluted in *n*-hexane 1% v/v.

interaction of light with a photosensitizer such as chlorophyll. Singlet oxygen reacts with double bounds of unsaturated fatty acids to form hydroperoxides. Since photosensitised oxidation and free-radical auto-oxidation proceed by different pathways, different products are formed in these processes [24].

The presence of pheophytin, chlorophylls and carotenoids influences auto-oxidation and photo-oxidation of the oils. Chlorophylls and their derivatives as singlet oxygen sensitizers enhance the process of oil deterioration, whereas tocopherols and carotenoids prevent it by quenching the reactive oxygen species. Oils also possess other natural antioxidants which may affect photo- and thermal oxidation of oils [25–29].

SINGLET OXYGEN

We measured the emission at 1270 nm, which is highly specific to the $O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-)$ transition, under laser excitation at 355 nm of air-equilibrated samples of all the oil products. The first set of measurements was performed for neat oils without any preparation using the front face geometry. Because of complex composition of the samples and resulting different optical densities, quantitative measurements were extremely difficult to conduct. Thus, no attempts to estimate limits of singlet oxygen quantum yield were made for front-face geometry experiments. However, the lifetime of singlet oxygen phosphorescence in the range of several microseconds was obtained for all samples by fitting the decay curve to a single-exponential function.

In the second set of experiments, quantum yields and lifetimes of the singlet oxygen formed were determined by exciting air-equilibrated oil samples dissolved in *n*-hexane, all optically matched (OD = 0.5) at the excitation wavelength (355 nm). Singlet oxygen was detected by monitoring the 0,0 vibronic band of its phosphorescence centred at 1270 nm using a germanium photodiode detector. The phosphorescence was detected at right angles to the exciting beam. The intensity of singlet oxygen phosphorescence (I_0) at time $t = 0$ was obtained by fitting the decay curve to a single-exponential function. All the results of oil product samples were compared to results of standard reference air-equilibrated solution of perinaphthenone, also optically matched at the excitation wavelength (355 nm). The upper limits of the quantum yield of singlet oxygen production, ϕ_Δ, were determined from the ratios of I_0 for the oil product and perinaphthenone samples. These results provided some estimates of the singlet oxygen formation. The highest quantum yield of singlet oxygen was obtained for olive oil 1 in *n*-hexane, as being almost 1, with the short lifetime of singlet oxygen of 7 μs indicating its high reactivity towards the molecular species present. Quantum yields of the singlet oxygen for all the other oil products were quite low, including olive 2

(0.002). These values depended very little on the oil product, being the highest (0.007) for rapeseed 1 and lowest or even undetectable for the sunflower, soybean and corn oils. The emission lifetime values recorded at 1270 nm in air-equilibrated solutions were in a range of 20 to 50 μs, with the lifetime for perinaphthenone experiments being 29 μs, typical for singlet oxygen in *n*-hexane [30]. Olive oil 1 was an exception, having the shortest lifetime of singlet oxygen and also considerable amounts of chlorophyll, as indicated by total luminescence spectra. The singlet oxygen data confirm that singlet oxygen involvement can be a viable path in the photo-oxidation of at least some oils.

CONCLUSIONS

Due to their molecular structure, which includes conjugated double bounds, tocopherols, tocotrienols and chlorophylls are good fluorescent probes. Tocopherol and chlorophyll content is also an important quality control parameter in the edible oils industry. Chlorophylls, tocopherols and carotenoids are considered to play an important role in keeping the quality of edible oils, mainly due to their action as photo-sensitizers or singlet oxygen quenchers and free radical scavengers, respectively. Tocopherols protect vegetable oils from oxidation, thus the extent of the reduction in their emission should be a good indicator of the extent of oxidation processes in the oil samples, with their complete disappearance pointing with certainty to the start of oxidation of the main constituents.

The type and amount of pigments in vegetable oils depend fundamentally on the species, cultivars, state of ripeness, and agronomic conditions; and undergo a considerable variation during storage and preparation of edible oils. Fluorescence characteristic of oils may thus be used for authentication of these products as well as monitoring their quality, and could be an interesting alternative for other spectroscopic methods: IR and NIR spectroscopies, used widely in the oil industry. However, one has to bear in mind that fluorescence spectroscopy provides no information regarding the non-fluorescent constituents, which are the majority constituents of the oils. Moreover, the application of this technique for identification is based on the assumption that different oils will contain different relative concentrations of fluorescent compounds at the very least, and preferably significantly different fluorescent compounds. Present results, however, demonstrated that there exist certain groups of fluorescent substances, that tend to be present in vegetable oils of different origins and subjected to different treatment during the manufacture cycle. Then again, there are other emission bands, more sensitive to the origin, manufacturing technology and oil oxidation, providing a possibility to identify the oils and evaluate their quality.

Although the present results look very promising as regards applicability of the TLS to the edible oil analysis, additional experiments are clearly needed to obtain comprehensive correlations between origin, manufacturing technology, consumer qualities and the emission spectra, employing more oil samples of different origin and from different producers. For such purposes various chemometric approaches should be tested [10,31].

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