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Fluorescent fingerprints of edible oils and biodiesel by means total synchronous fluorescence and Tucker3 modeling

Matías Insausti [a,*], Adriano de Araújo Gomes [b], José Manuel Camiña [c,d,**], Mario Cesar Ugulino de Araújo [e,*], Beatriz Susana Fernández Band [a]

[a] FIA Lab., INQUISUR – CONICET, Sector Química Analítica, Universidad Nacional del Sur. Av. Alem 1253, B8000CPB Bahía Blanca, Argentina
[b] Faculdade de Química, Instituto de Ciências Exatas da Universidade Federal do Sul e Sudoeste do Pará. Folha 17, Quadra 04, Lote Especial, Nova Marabá, CEP: 68505080 Marabá, Pará, Brazil
[c] Instituto de Ciencias de la Tierra y Ambientales de La Pampa (INCITAP), Mendoza 109, L6302EPA Santa Rosa, La Pampa, Argentina
[d] Facultad de Ciencias Exactas y Naturales, Universidad Nacional de La Pampa (UNLPam), Av. Uruguay 151, L6300CLB Santa Rosa, La Pampa, Argentina
[e] Universidade Federal da Paraíba, Departamento de Química, Laboratório de Automação e Instrumentação em Química Analítica/Quimiometria (LAQA), Caixa Postal 5093, CEP 58051-970 João Pessoa, PB, Brazil

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ABSTRACT

The present work proposes the use of total synchronous fluorescence spectroscopy (TSFS) as a discrimination methodology for fluorescent compounds in edible oils, which are preserved after the transesterification processes in the biodiesel production. In the same way, a similar study is presented to identify fluorophores that do not change in expired vegetal oils, to associate physicochemical parameters to fluorescent measures, as contribution to a fingerprint for increasing the chemical knowledge of these products. The fluorescent fingerprints were obtained by Tucker3 decomposition of a three-way array of the total synchronous fluorescence matrices. This chemometric method presents the ability for modeling non-bilinear data, as Total Synchronous Fluorescence Spectra data, and consists in the decomposition of the three way data arrays (samples $\times$ $\Delta\lambda$ $\times$ λ excitation), into four new data matrices: **A** (scores), **B** (profile in $\Delta\lambda$ mode), **C** (profile in spectra mode) and **G** (relationships between **A**, **B** and **C**). In this study, 50 samples of oil from soybean, corn and sunflower seeds before and after its expiration time, as well as 50 biodiesel samples obtained by transesterification of the same oils were measured by TSFS. This study represents an immediate application of chemical fingerprint for the discrimination of non-expired and expired edible oils and biodiesel. This method does not require the use of reagents or laborious procedures for the chemical characterization of samples.

1. Introduction

Currently it exist a great interest in the study of chemical composition from oils and biodiesel, since such information is valuable for the assessment of the quality and therefore, the final price of product. The European Standards (EN) and American Society for Testing and Materials (ASTM) propose high cost and off-line methodologies to this quality control [1,2]. Techniques like gas and liquid chromatography are the most commonly used for edible oil and biodiesel analysis. Spectroscopic methods present some alternatives to the established reference methods, which can be applied quickly and inexpensively. Advances in spectroscopy actually enable researchers to obtain information about chemical components in different samples at molecular level [3].

Fluorescence spectroscopy (FS) is one of the most promising techniques in complex analysis. Among the benefits of fluorescence spectroscopy, it can include an enhanced selectivity compared to others spectroscopic methods, a high sensitivity to a wide array of potential analytes, and to avoid a high consuming of reagents as else an extensive pretreatment of sample [4]. Due to these advantages there were numerous new methodologies taking advantages of the FS for biodiesel analysis [5–10]. However, conventional fluorescence techniques, which are based on the measurement of a single spectrum in emission or excitation way are often insufficient in the analysis of complex systems [11,12]. In such cases, Excitation-Emission Matrices of Fluorescence (EEMF) or Total Synchronous Fluorescence Spectra (TSFS) can improve the analytic potential of fluorescence measurements [13,14].

In the absence of Raman scattering, EEMF are bilinear, this means that, all the fluorophores has a unique profile in excitation and emission modes that only changes in intensity. The individual EEM matrices may be stored in a trilinear three-way structure $\boldsymbol{X}_{(I \times J \times K)}$ or alternatively can be used augmented matrix or unfolded structure and modeled with multi-way methods like Parallel Factor Analysis (PARAFAC),

* Corresponding authors.
** Correspondence to: J. M. Camiña, Instituto de Ciencias de la Tierra y Ambientales de La Pampa (INCITAP), Mendoza 109, L6302EPA Santa Rosa, La Pampa, Argentina.
E-mail addresses: matiasi@conicet.gov.ar (M. Insausti), jcaminia@exactas.unlpam.edu.ar, jcaminia@gmail.com (J.M. Camiña), laqa@quimica.ufpb.br (M.C.U. de Araújo).

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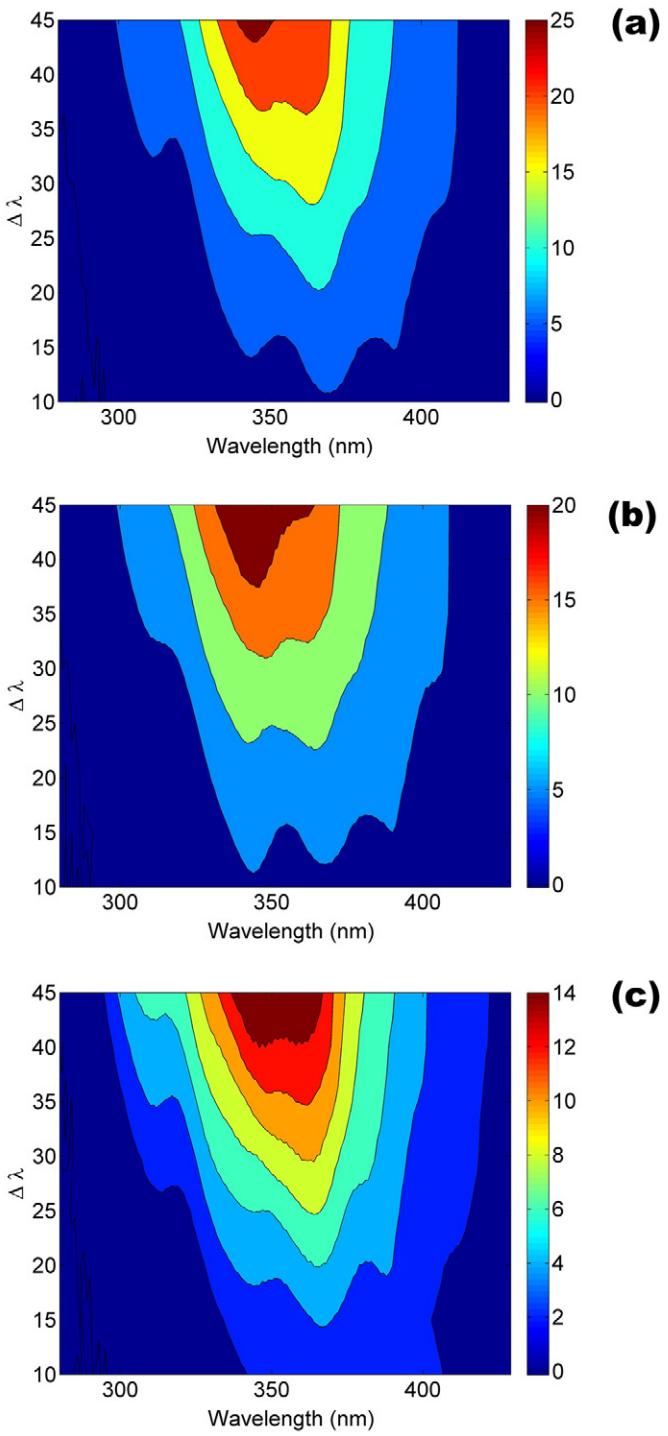

Fig. 1. Typical synchronic fluorescence landscape for (a) edible vegetable oil, (b) expired edible vegetable oil and (c) biodiesel.

Multivariate Curve Resolution (MCR) and Principal Component Analysis (PCA), respectively [15,16].

On another hand, TSFS are intrinsically non-bilinear, because the excitation spectrum shape it is not unique to a single fluorophore, it changes every Δλ value. Consequently, the three-way structure $\boldsymbol{X}_{(I \times J \times K)}$ for TSFS do not fulfill with trilinearity [15]. This characteristic of TSFS makes a nontrivial modeling when using PARAFAC or MCR and it can also lead to non-reliable solutions. From a mathematical point of view unfolded TSFS can be modeled by PCA, but the high dimensionality of the data can make interpretation of the results very difficult [17]. Such drawbacks can be circumvented by using Tucker3 method proposed by L. Tucker [18] that is also known as a generalization of the PCA for multi-way data.

For three way data arrays $\boldsymbol{X}_{(I \times J \times K)}$, i.e., the model could be write like Eq. (1).

$$x_{ijk} = \sum_{p=1}^{P} \sum_{q=1}^{Q} \sum_{r=1}^{R} a_{ip} b_{jq} c_{kr} g_{pqr} + e_{ijk} \quad (1)$$

where x_{ijk} were the elements of $\boldsymbol{X}_{(I \times J \times K)}$, a, b e c had the elements associated to the factors p, q e r. The term g_{pqr} contains the weights of the relationships between the factors, whilst the term e_{ijk} represents the non-modeled information. Unlike the PARAFAC, the Tucker3 model allows calculation with different number of factors for the different modes, that is, $p \neq q \neq r$. Another feature that differentiates the Tucker3 to PARAFAC and also from PCA is that the factors could have interactions between them. These properties look very attractive from a mathematical point of view, in especial for the modeling of complex data as the non-bilinear TSFS matrices.

As well as in the PARAFAC decomposition, in the Tucker3 calculations some constraints could be applied to obtain mathematical solutions with chemical sense. In brief, the constraints are mechanisms to make that the loadings model be similar to the pure instrumental profiles of the constituents of the sample. In this case, the Tucker3 loadings must be the pure excitation spectra of the fluorophores present in the samples. As it does not make physical sense excitation spectra with negative intensity, therefore model solutions also must not contain negative values. This constrain is known as non-negativity, implemented in the Tucker3 method via non-negative least squares. Loadings that are the instrumental profiles of the constituents can then be used for diverse purpose like the estimation of fingerprint from complex samples and to generate discrimination and classification models [19,20].

The increasing awareness of consumers in food and fuel safety and quality issues has led to the development of new techniques for product authentication. However, most of these techniques require time consuming, extensive sample preparation, the use of hazardous chemicals, as well as skilled and experienced operators. These disadvantages have prompted for the adoption of new and simpler methods such as the fluorescence spectroscopy. In general, this technique is more frequently used to follow or mark a target at one wavelength that corresponds to a known compound, or to relate statistically the sum of the fluorescent bands with the values of certain quality parameters and deducing the origin of the luminescent signal. However, TSFS have been less used to describe fluorescent compounds. For this reason, this paper describes the use of the Tucker3 method that can discriminate compounds which can change or not during a chemical process in complex samples, such as in the transesterification or in the degradation of edible oils. This intrinsic knowledge was used to differentiate between expired and not expired edible oil and biodiesel.

2. Experimental

2.1. Samples

A total of 50 edible oil (O) samples from different lots and, manufacturers and raw material (14 samples of soybean, 20 of corn and 16 of sunflower) were acquired during a whole year. The transesterification

Table 1
Factors used in Tucker3 model.

Samples	Model complexity			ExVar (%)*
	Mode 1	Mode 2	Mode 3	
Oil	3	3	3	99.43
Expired oil	3	3	3	99.34
Biodiesel	2	2	2	98.35

* Explained variance.

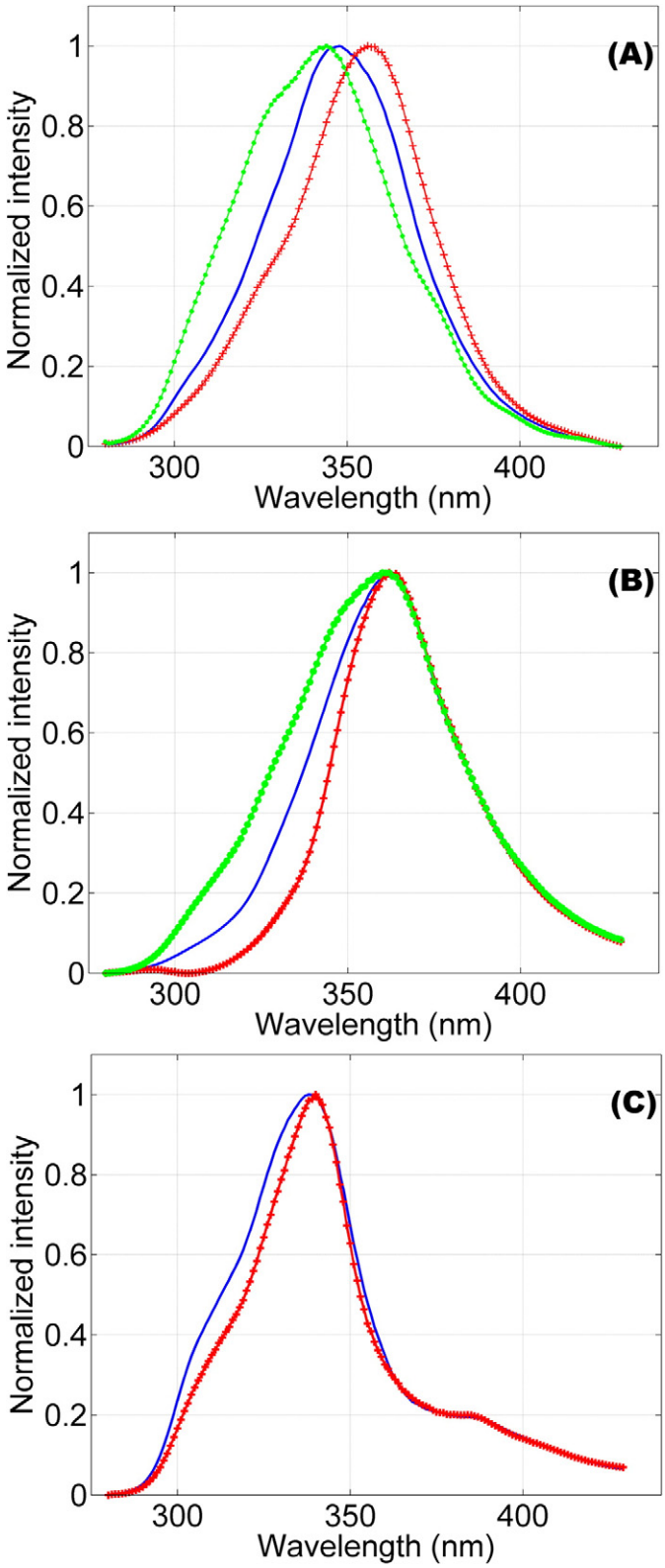

Fig. 2. Loading profiles in the spectral mode recovered by the Tucker3 method for (a) factor 1, (b) factor 2 and (c) factor 3. The colors and type of the lines correspond to oil (solid blue line), expired oil (cross red line) and biodiesel (circle green line).

of biodiesel (B) samples were carried out by using the methylic route with KOH as catalyzer, at a temperature of 60 °C with molar ratio of 6:1 (methylicalcohol:oil). The catalyzer/oil ratio was 0.5% w/w. After 1 hour, the glycerin byproduct was separated and the resulting biodiesel was washed with water and dried. The same 50 samples of edible oils were stored in the original commercial flask without strict environmental control for 18 months after acquired, and then were measured to obtain the expired oil (EO) samples spectra.

2.2. Spectrum Acquisition

A computer-controlled spectrofluorimeter SLM Aminco Bowman series 2 (Thermo, Madison, USA), equipped with a xenon discharge light source (150 W), was used to obtain the spectra. Wavelength accuracy and wavelength repeatability were ±0.5 and ±0.25 nm, respectively. Excitation and emission slits of 8 nm were used. The scan rate was 5 nm/s.

For each sample, eight synchronous spectra were obtained by scanning both monochromators simultaneously at constant wavelength differences ($\Delta\lambda = \lambda_{emission} - \lambda_{excitation}$) of 10, 15, 20, 25, 30, 35, 40, 45 nm. The excitation range 280–600 nm was the same for all spectra, whereas the emission range varied from 285 to 605 nm to 330–650 nm according to the wavelength difference ($\Delta\lambda$) employed. All spectra from O, B and EO were recorded using a standard 600 μl quartz cell. None sample pretreatment were used to perform the scans.

2.3. Software

Three-way array decomposition was carried out by Tucker3 using N-way toolbox [21] available in http://www.models.life.ku.dk/nwaytoolbox in MatLab® environmental [22].

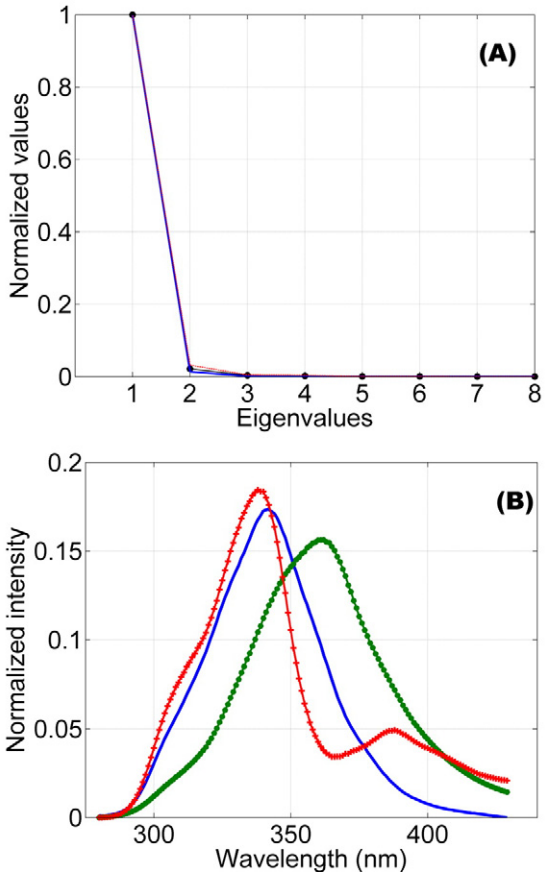

Fig. 3. Tucker3 decomposition for all samples (a) eigenvalues plots of the. Eigenvalues plot for (solid blue line) mode 1; (dotted red line) mode 2 and (circle black line) mode 3. (b) Profiles recovered in the spectral mode: first (solid blue line), second (circle green line) and third (cross red line) factors.

3. Results and Discussion

3.1. Data Set

The data set, used like input for Tucker3 model, consisted in 50 STFS matrices for each sample group, (edible oil (O), expired edible oil (EO) and biodiesel (B)) with dimension 8 (Δλ) × 150 (excitation wavelength). These matrices were arranged in a three-way structure, for all cases the size were (50 × 8 × 150). Initially, each sample group was submitted to a Tucker3 decomposition. The results obtained were compared with respect to each other for the fingerprint purpose. In addition for discrimination use, a new three-way structure, containing all STFS matrices was used. This approach allows to estimate the individual rank of each samples group and full rank of the data. Typical synchronic fluorescence contour plot for are displayed in Fig. 1.

As can see, fluorescence profiles for O, EO and B had similar shape, being remarkable the change of the fluorescence intensity (more intense in oil samples and less intense in biodiesel samples). These variations in fluorescence signal may be accessed by chemometric approaches and used like useful information for purpose of the discrimination between O, EO and B.

3.2. Tucker3 Fingerprint

Tucker3 decomposition was carried out on data set separately (O, EO and B). The initial step in Tucker3 modeling, it was to choose the number of factors in each instrumental mode. In this work was used the eigenvalues examination approach for the matrices $\mathbf{X_a}_{(I \times JK)}$, $\mathbf{X_b}_{(J \times IK)}$ and $\mathbf{X_c}_{(K \times IJ)}$ obtained with the frontal plane of the $\boldsymbol{X}_{(I \times J \times K)}$. In addition, it was observed the increase in the explained variance with the increasing of the complexity of models. In all cases, it is preferable to choose the calculated model less complex. The selected number of factors in each case is summarized in Table 1.

Table 2
LDA fit parameters.

True class	Estimated class			
	O	EO	B	NER (%)*
O (50 samples)	37	13	0	74
EO (50 samples)	13	36	1	72
B (50 Samples)	0	3	47	94

* NER: non error rate.

As it can be seen in Table 1, in all cases a high percentage of variance explained was obtained for the selected factors. The next step was the evaluation of the loading profiles retrieved by Tucker3 method in spectral mode under non-negativity constraint (see Fig. 2). It is important to take into account that, profiles displayed in Fig. 2 are normalized. The contribution of each one vary of the sample to sample, this information (or be the relative concentration) is stored in matrix A, output of the Tucker3 model.

Numerous published works have attributed the fluorescence of oil and biodiesel to molecules such as tocopherols, free fatty acids, carotenoids, and degradation products of chlorophyll *a* and b [23,24]. In our case, due all samples proceed from refined oils, carotenoids (fluorescence range of 500–650 nm) were not recorded.

The decomposition of unsaturated methyl esters is a similar process to oxidation of edible oils [25]. The oxidation of these compounds produces conjugated double bonds carbon = carbon, which could be responsible of fluorescence signal. As previously described by Magalhães et al. [26], fluorescence spectra found in this work, suggest that conjugated tetraenes could be produced from a previous degradation of unsaturated triglycerides (edible oil) as well as of unsaturated methyl esters (biodiesel), which are more related to methyl linolenates, justifying the fluorescence spectra in the 350–550 nm.

Comparing Fig. 1 and Fig. 2, it can be notice that the first profile calculated explains the highest fluorescence with an excitation wavelength of 348, 356, 344 nm (O, EO, B), that correspond to the dienes, trienes and tetraenes of the carbon chain of triglycerides and esters constituents of

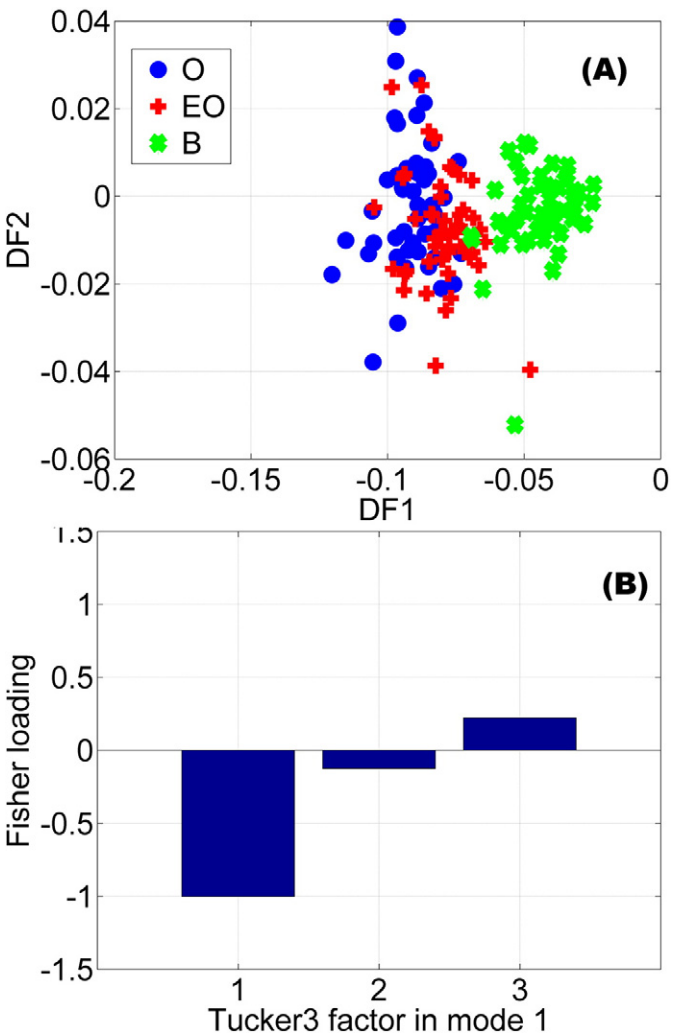

Fig. 4. LDA results: (a) DF1 × DF2 score plot and (b) Fisher loading plot for DF1.

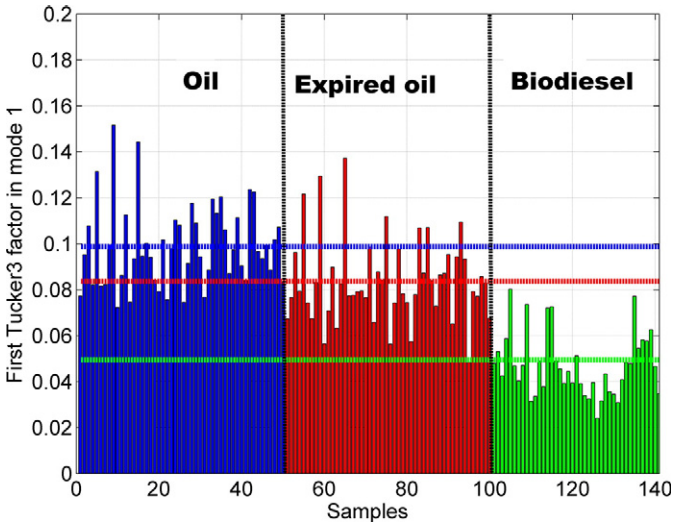

Fig. 5. Bars plot for first Tucker factor in mode 1. The horizontal lines are the average loading.

this type of samples. The responsible of the shift is the different viscosity [27]. The band at 330 nm that appears in biodiesel with high intensity and in expired oil with lesser signal, corresponds exactly with the maximum of excitation wavelength of the tetraenes derived from methyl linolenate in biodiesel or free linolenic acid in expired oil.

The second and third factors show the profiles of the fluorescent compounds with a maximum in 362 nm, corresponding to conjugated carbon-carbon double bonds. The overlapped signals from 310 to 340 nm are product of isomers of tocopherol, butylated hydroxyanisole (BHA) and ter-butylhidroquinone (TBHQ) that are commonly added to edible oils to prevent the rancidity, but they diminish with the increasing of the degradation time. The 310 nm band that appears in the third factor corresponds to α-tocopherol, a form of vitamin E. Different percentages of tocopherol isomers are present according to the diverse sources of edible oils: α-tocopherol in sunflower oilsor γ-tocopherol in soybean and corn oils [28]. Finally, the band at 393 nm corresponds to conjugate dienes.

3.3. Discrimination Based on Tucker3

In order to evaluate the discrimination power of fluorescence synchronic matrices, Tucker3 decomposition was simultaneously carried out on data set ($\times_{150 \times 8 \times 150}$) of the three types of samples (O, EO and B). Again, the number of factors was determined by the procedure described above. The eigenvalues plot for full data is showed in Fig. 3.

As can be seen in Fig. 3a, after the third factor, in all modes no significant changes were observed. In addition, the rank suggested by the eigenvalues for all samples were in agreement with the value rank of those observed when samples are modeled by Tucker separately (see Table 1). The loading profiles recovered by Tucker3 (Fig. 3b) were jointly for all samples identical to those obtained when analyzing samples separately.

The loading matrix in mode 1 of Tucker3 model was used as input data for linear discriminant analysis (LDA) to evaluate the discriminating power of the STFS. As can be seen in the Fisher score plot for LDA displayed in Fig. 4a, the discrimination of oil, expired oil and biodiesel samples was obtained along the first discriminant function (DF1).

On the other hand, in general, oil samples had higher absolute score values, while biodiesel samples had the lower ones. Expired oils samples presented intermediate values between oil and biodiesel samples. This behavior was similar to the fluorescence intensities observed in Fig. 1. In Table 2 is presented a summary of the LDA fit.

Based on the results of Table 2, it can notice that samples of oil and biodiesel were better discriminated with success rates of 74% and 94%, respectively, but the expired oil showed an overlapping with oil and biodiesel samples. In the plot of Fisher loadings (Fig. 4b) for DF1, it could be seen remarkable influences in the first variable, that is, the first factor of Tucker3 model. On the other hand, the contribution of the third factor was bigger than the second one, but negligible in comparison with first one. In other words, this means that the firstTucker3 factor in mode 1 had the most discriminant information.

The significant score elements (g_{mnl}) for m = 1 were $g_{(111)}$ and $g_{(113)}$. This means that the first and third loading profiles in spectral mode were related to the discrimination of edible oil, expired oil and biodiesel samples (see Fig. 3b). The first factor (blue solid line in Fig. 3b) corresponds to the fluorophores that were present in all samples and were related to the discrimination of edible and expired oil. The third factor (red solid line in Fig. 3b) corresponds to the fluorophores that could be discriminated in oil/expired oil and biodiesel. As was showed in Fig. 2c, the third factor was absent in biodiesel samples. This justify why B samples were better discriminated than O and EO.

The first factor in mode 1 had significant interactions with the factors 1 and 2 in spectral mode. This suggests that score values for the first factor in mode 1were the sum of the concentrations of the fluorophores corresponding to 1 and 3 in the loading profile retrieved by Tucker3 method in mode 3. In Fig. 5 is shown the loading values of Tucker3 model for the first factor in mode 1.

It can see that these values change for the different type of samples. However, it can be noted that these changes were more pronounced among oils (O and EO) and biodiesel (B). This fact can be attributed to the presence of fluorophores corresponding to the third profile recovered by the method Tucker3, which were absent in the biodiesel samples. The blue, red and green horizontal dotted lines represent the mean scores of values for each type of samples. Notice that all biodiesel samples are below of the oils average scores.

4. Conclusions

This work showed the reduction of antioxidants levels and the increasing of fluorescence signal due the conjugated diens, triens and tetraens in edible and expired oils. Biodiesel samples were easily discriminated from O and EO due the presence of conjugated double bounds associate to methyl esters. In addition, it is important to remark that it was not necessary sample pretreatment, reducing time consuming analysis. On the other hand, the total absence of reagents, include to this method into the green chemistry principles. The biodiesel samples could be successfully discriminated from edible and expired oil samples. Tucker3 was able to find spectral fingerprints using three-way data and second order analysis of non bilinear matrices, reaching chemical information from the retrieved loadings. Therefore, the combination of fluorescence (TSFS) and chemometrics (Tucker3) may be useful to assess the transesterification or degradation process for quality control of biodiesel and edible oils, with the additional advantage that it is not destructive method and can be used in modes in-line or on-line.

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