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Independent components analysis as a means to have initial estimates for multivariate curve resolution-alternating least squares



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ABSTRACT

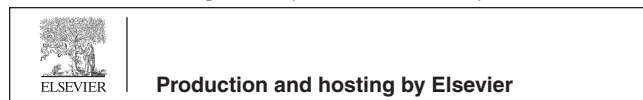
Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) is a curve resolution method based on a bilinear model which assumes that the observed spectra are a linear combination of the spectra of the pure components in the system. The algorithm steps include the determination of the number of components by rank analysis methods, initial estimates for the concentrations and/or spectra and an iterative optimization. Sometimes, suitable results may not be achieved when MCR-ALS is applied. One reason for this is the importance of the initial estimates of the spectral profiles. In that case, the MCR-ALS algorithm may reach a local minimum instead of a global minimum and this can result in ineffective curve resolution. The most popular algorithm used to find the initial estimates (PURE derived from SIMPLISMA) suffers from an essential drawback, which is the necessity to have “pure” variables related to a single spectral component, which cannot be expected in all cases because of the strong signal overlapping as in the Ultraviolet–Visible (UV–Vis) spectroscopy. This work summarizes this problem, presenting a case study based on UV–Vis spectroscopy of heated olive oil. To solve the problems of the need for “pure” variables and to avoid local minima with MCR-ALS, Independent Components Analysis (ICA) was used to calculate initial estimates for MCR-ALS. The results from this study suggest that this use of ICA prior to MCR-ALS improves the resolution for UV–Vis data and provides acceptable resolution results when compared to the most used method, PURE.

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**Introduction**

Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) is a curve resolution method based on a bilinear model which assumes that the observed spectra are a linear combination of the spectra of the pure components in the

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system [1]. The algorithm steps include the determination of the number of components by rank analysis methods, such as percentage of explained variance from Principal Component Analysis (PCA) [2], PCA-Loadings or Durbin-Watson (DW) criterion [3] and Singular Value Decomposition (SVD) [4]. PCA, PCA-Loadings and SVD are similar methods, while DW criterion to rank analysis has been proposed as a measure of the signal/noise ratio of the PCA loadings and regression vectors obtained by multivariate analysis of signals [3]. Then, an initial estimation for concentration and/or spectra with as many profiles as the number of components estimated from the rank analysis is constructed to start the iterative curve resolution process. Once the initial estimate is generated, the iterative optimization step can be started [5].

The initial estimate is found, normally, based on methods of finding the purest variables, as the PURE method that is derived from the simple-to-use interactive self modeling analysis (SIMPLISMA) [6], or on evolving factor analysis (EFA) [7]. However, these algorithms suffer from an essential drawback, which consists in the need for “pure” variables, which cannot be expected in all cases because of the possibility of strong signal overlapping [8]. This work offers an alternative to obtain initial estimates based on Independent Components Analysis (ICA) [9]. Here it is shown that the ICA improved the MCR-ALS resolution results when “pure” variables are not present due to the strong signal overlapping, as in the case of analyzing heated olive oil using Ultraviolet–Visible (UV–Vis) spectroscopy. The main objective is to verify the modifications that occur in olive oil samples when it is heated from room to high temperatures, such as happens during frying, without the need for physical separation, only by using curve resolution methods. This data set was used in order to show the problem of methods based on SIMPLISMA as initial estimates for MCR-ALS when “pure” variables are not present due to the strong signal overlapping, as occur at UV–Vis spectroscopy due the lack of selectivity in this technique.

Experimental

Samples of Portuguese olive oil (two samples from two different batches) were analyzed in triplicate. The samples were heated from 30 °C until 170 °C, increasing it by steps of 10 °C, and a first spectrum being taken at room temperature (25 °C). UV–Vis spectra were acquired in the range from 300 to 540 nm (steps of 2 nm) in a 1 mm quartz cuvette. Data were analyzed using MATLAB version R2007b (The Mathworks Inc., MA, USA) where curve resolution was performed by Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS). The MCR-ALS algorithm code and Graphical User Interface for MATLAB [10] are freely available from the home page of MCR at <http://www.mcrals.info/>. By this interface, there are two options to estimate the matrix rank: one is based on the percentage of variance captured by singular values decomposition (SVD) analysis and the other is the manual decision of it. Sometimes it is hard to decide the rank based only on these percentages and the decision can be improved by the graphical visualization of the PCA loadings [3]. ICA was performed using Joint Approximate Diagonalization of Eigenmatrices (JADE) algorithm [11], that involves matrix diagonalization. The MATLAB code of this algorithm can be found on

the website <<http://perso.telecom-paristech.fr/~cardoso/Algo/Jade/jadeR.m>>.

Chemometric methods

MCR-ALS

The usual assumption in multivariate curve resolution methods is that the experimental data follow a linear model similar to Lambert–Beer’s law in absorption spectroscopy. In matrix form this model can be written as [12]:

$$\mathbf{D}_{(i \times j)} = \mathbf{C}_{(i \times k)} \mathbf{S}_{(k \times j)}^T + \mathbf{E}_{(i \times j)} \quad (1)$$

where $\mathbf{D}_{(i \times j)}$ is the UV–Vis data matrix with “i” rows and “j” columns (where spectra are on the rows of \mathbf{D} and absorbance at different wavelength is on the columns of \mathbf{D}), $\mathbf{C}_{(i \times k)}$ is the matrix of the relative amounts or concentrations with “i” rows and “k” different species (in this case the relative concentration profile for each sample is placed in the rows of \mathbf{C} , while in the \mathbf{C} columns are the information concerning the different species), $\mathbf{S}_{(k \times j)}^T$ contains the pure spectra with “k” different species and “j” columns (recovered spectra are located in the columns of \mathbf{S} and the information about different species is in the rows of \mathbf{S}), and $\mathbf{E}_{(i \times j)}$ is the matrix associated with noise or experimental error with “i” rows and “j” columns.

To start the algorithm, the number of chemical species present in a particular system is determined based on the chemical rank associated with the data matrix \mathbf{D} . Here, the chemical rank was determined using PCA-Loadings [3], and confirmed by the Leverage analysis [13].

The main goal of curve resolution methods is the determination of the true \mathbf{C} and \mathbf{S} matrices only from the analysis of matrix \mathbf{D} . Initial estimates of the \mathbf{C} or \mathbf{S} matrices can be obtained using methods based on the detection of “purest” variables as methods based on SIMPLISMA [6], or from techniques based on evolving factor analysis [7].

Methods based on the choice of “purest” variables aim to the determination of the most representative series of different components in the experimental data set. If the choice is successful, the majority of similar algorithms offers a chance for qualitatively estimating the number of components in the system and also the relative concentrations and spectra of individual compounds. In the group of methods based on the choice of “purest” variable, the PURE algorithm is the most commonly used. However, algorithms of this group suffer from an essential drawback, which consists in the necessity of the presence of “pure” variables, which cannot be expected in all cases because of the strong signal overlapping [8]. To solve this problem, the use of ICA scores or signals is proposed as initial estimative to MCR-ALS. In this work, the scores and signals were tested as initial estimative for concentration (\mathbf{C}) and spectra (\mathbf{S}), respectively, and the results are identical.

These initial estimations of \mathbf{C} or \mathbf{S} are optimized solving Eq. (1) iteratively by alternating least squares optimization [12]. At each iteration of the optimization, a new estimation of the \mathbf{C} and \mathbf{S} matrices is calculated under the constraints of two least-squares steps [14]:

$$\mathbf{C} = \mathbf{D}\mathbf{S}(\mathbf{S}^T\mathbf{S})^{-1} \quad (2)$$

$$\mathbf{S}^T = (\mathbf{C}^T\mathbf{C})^{-1}\mathbf{C}^T\mathbf{D} \quad (3)$$

A reconstructed \mathbf{D}^* matrix, created from the product of the calculated \mathbf{CS}^T matrices obtained from Eqs. (2) and (3), is then compared with the original \mathbf{D} matrix, and the iterative optimization continues until the convergence criterion is attained (when the variation of results between consecutive iterations falls below a pre-set threshold value) or until a pre-selected number of iterations are exceeded. The default in the graphical user-friendly interface uses 50 iterations but, if after 10 cycles with no improvement, the best value found at the first iteration cycle is used to produce the spectra and concentration profiles. In this work, the convergence criterion used was 0.1% and 50 iterations as maximum. Alternatively, if 50 iterations were considered too small, it is possible to increase the number of iterations in the graphical interface.

At each iterative cycle, the chemical or mathematical properties that the \mathbf{C} and/or \mathbf{S}^T profiles must fulfill (constraints) can be applied. In MCR-ALS, many types of constraint, such as non-negativity, closure, unimodality, local rank, and trilinearity, can be easily applied to the solutions during the calculations [5]. The constraints used in this study were non-negativity for the concentrations and spectra while closure was applied to concentrations.

ICA

ICA is a Blind Source Separation method. It is based on the construction of latent variables or factors, called Independent Components (ICs), which are linear combinations of the original variables. The ICs are assumed to correspond to the signals of the “pure” source signals present in the analyzed mixtures. The hypothesis used to enable the extraction of the “pure source signals” is that these vectors are statistically independent, as opposed to PCA which is based on calculating orthogonal vectors that maximize the amount of variance extracted from the data (the dispersion of the samples) [15].

ICA searches for the decomposition of signals of a mixture into statistically independent components. However, the signals are not always independent, ICA always finds independent components which are not always pure signals, and signals are not always chemically independent. This can occur for example, if the signals of the different compounds do not evolve independently. Thus, the existence of “natural” mutual dependences of the mixture components means that ICA extracts signals corresponding to independent phenomena, and that the isolation of fully independent spectra of pure chemical compounds is not possible in such cases [8].

The general ICA model is [16] as follows:

$$\mathbf{X}_{(i \times j)} = \mathbf{A}_{(i \times c)} \mathbf{S}_{(c \times j)} \quad (4)$$

where $\mathbf{X}_{(i \times j)}$ is the matrix of observed spectra with “i” rows and “j” columns (where spectra are located in the rows of \mathbf{X} and absorbance at different wavelength in its columns), $\mathbf{S}_{(j \times c)}$ is the matrix of unknown “pure” source spectra with “c” ICs and “j” columns (recovered signals are in the columns of \mathbf{S} and the information about different sources in its rows), and $\mathbf{A}_{(i \times c)}$ is the mixing matrix of unknown coefficients with “i” rows and “c” ICs, related to the corresponding concentrations (where sample information is in the rows of \mathbf{A} and information concerning different sources in its columns).

The calculation of these source signals is based on the criterion of independence. As indicated above, if two components

with different characteristic signals evolve simultaneously in the matrix of the observed signals, these components are considered as a single source, and it is described by the same independent component. This kind of situation happens for example when a compound is converted in a chemical reaction to give rise to another compound, as during the *cis-trans* isomerization of fatty acids, where the spectra of the two isomers are not independent. For this reason, ICA is not comparable to the methods as MCR or methods based on SIMPLISMA [17,18].

Based on the Central Limit Theory, ICA assumes that the statistically independent source signals have intensity distributions that are less Gaussian than are their mixtures [9]. As there are several approaches in assessing statistical independence, there exist several different ICA algorithms and Joint Approximate Diagonalization of Eigenmatrices (JADE) [11] was used in this work.

Results and discussion

Fig. 1 shows the UV-Vis spectra of an extra virgin olive oil heated at different temperatures. It is possible to note that the absorbance is increasing or decreasing at some specific wavebands. In accordance with a previous study [19], the tocopherol shows a maximum absorbance peak at 325 nm, while the oxidation products, formed during heating oils, present absorbance around 400 nm. Although the absorbance is increasing or decreasing at some specific wavebands, it is hard to find differences in UV-Vis raw spectra due to the high degree of band overlapping and due to the lack of selectivity in UV-Vis spectroscopy. The difficulty to draw conclusions only by analyzing the spectra can be overcome by the use of the chemometric curve resolution methods that can contribute to the reliability of the results.

From this spectral data set, the chemical rank (pseudorank, a mathematical rank in absence of experimental noise) was estimated using the PCA-loadings [3], shown in Fig. 2. Based on the observations in the PCA loadings, the chemical rank for these spectra sets are four, since the loadings from Principal Component 5 (PC5) presented only noise. The scores plot with 95% confidence level *versus* leverage, shown in Fig. 3, was

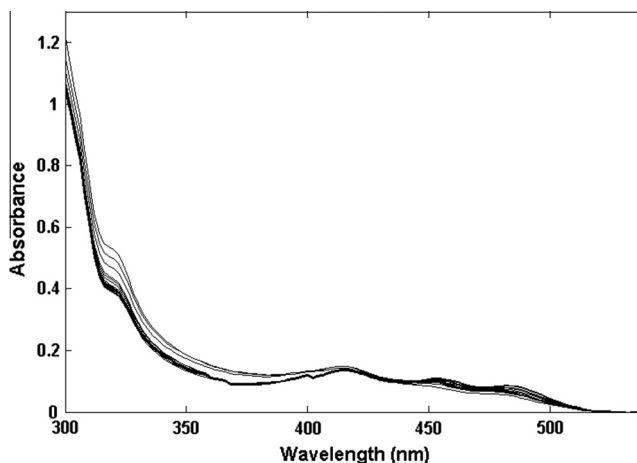


Fig. 1 UV-Vis spectra to extra virgin olive oil heated at different temperatures.

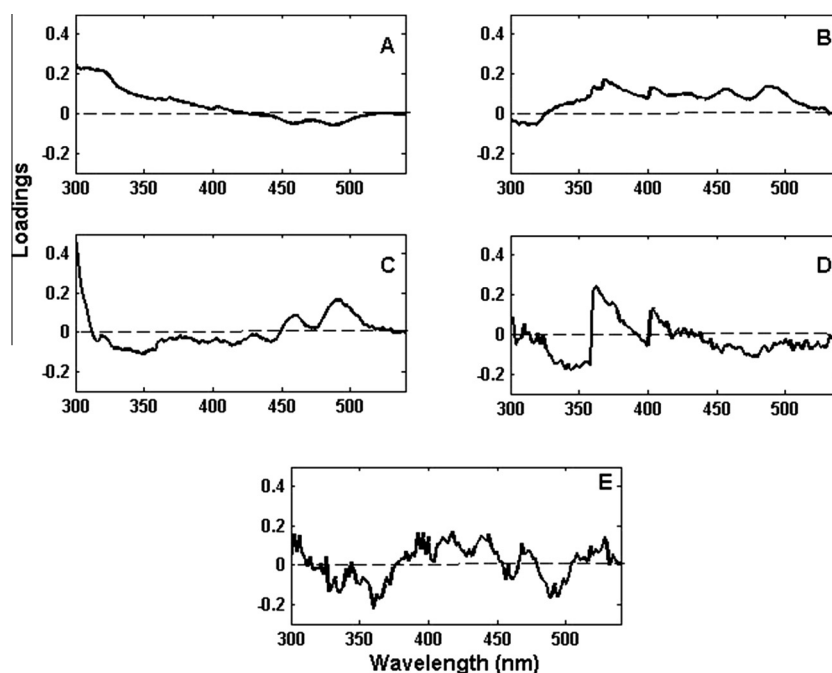


Fig. 2 PCA Loadings, (A) on PC1 (96.79%), (B) on PC2 (2.16%), (C) on PC3 (0.87%), (D) on PC4 (0.09%), and (E) on PC5 (0.03%).

done in order to confirm that the PC5 is not important in this case. In this way, when a PC is referred as belonging to a sample with high leverage or score values which is outside of the confidence level considered, this PC is informative in the rank analysis.

Leverage represents how far a sample is distant from the center of the data. A low leverage (lower than a limit value calculated as: $3 \frac{A+1}{n}$, where A is the number of PCs and n is the number of samples) for an object shows that the object is near to the center of the data set in \mathbf{X} with respect to the A -dimensional component space, and consequently this object is a good leverage point, because it stabilizes the model. However, a leverage larger than a limit value shows that the object is far from the mean and this may have had a very high importance on the resulting A -dimensional model. In calibration models, an object with leverage larger than an established limit can indicate that this object is an outlier due to an extreme analyte concentration or extreme value of an interferent which was also modeled [13]. In exploratory analysis, an object with high leverage is caused by the fact that this object is particularly informative. Therefore, it is possible to conclude that the PC has some importance in the analysis and in this case, that the PC represents a chemical species which is present as result from rank analysis. In this data set, no samples presented high leverage, since all samples are above the vertical dash line in Fig. 3. However, until PC4 it is possible to observe samples with score values outside a 95% confidence level (horizontal dash lines). Therefore, in Fig. 3 it is possible to observe that it can be considered informative from PC 1 to 4, while in PC number 5 all objects present leverage lower than the limit and inside the confidence level. This analysis confirms that the rank for the UV-Vis matrix from heated olive oils is four.

The next step was to make an initial estimate for \mathbf{S}^T containing as many profiles as the number of components estimated by the rank analysis. Here, the initial \mathbf{S}^T was

determined using either PURE and ICA. Once the initial estimate was generated, the iterative optimization step was started, under constraints of non negativity for \mathbf{C} and \mathbf{S}^T and closure for \mathbf{C} , performed by alternating least squares.

Fig. 4 shows the spectra recovered by MCR-ALS when using PURE for the initial estimates. Here one can note that there is practically no resolution, particularly by expanding the spectra using an approaching zoom. Sometimes, suitable results may not be achieved when MCR-ALS is applied [20]. The main reason for this is the importance of the initial estimates of the spectral profiles. In this particular application of PURE initializing MCR-ALS, the algorithm has reached a local minimum instead resulting in insufficient curve resolution [21]. This was probably due to the high degree of band overlapping and the lack of selectivity in UV-Vis spectroscopy technique.

In order to evaluate the extent of rotation ambiguity (Sets of \mathbf{C} and \mathbf{S}^T profiles with shapes different from the real ones can reproduce the data set \mathbf{D} with optimal fit) associated with MCR-ALS solutions, the MCR-BANDS was applied [22]. This procedure allows for checking up the effect of applied constraints in the results of a particular system solved by MCR-ALS. The results obtained are shown in the Fig. 5. Although a possible improved resolution for the profiles 1 and 4 in Fig. 4, no improvement was achieved for the profiles 2 and 3. One solution from MCR-BANDS for the profile 1 resembles the spectra of phenolic and polyphenolic compounds [23] while for the profile 4 one solution resembles hydrolysis products spectra [24].

When using ICA as an alternative method to calculate the initial estimates for MCR-ALS, a very appropriate resolution was obtained, as shown in Fig. 6. The recovered spectra were compared to those in the literature and it could be verified that they are very similar to the spectra of phenolic and polyphenolic compounds (270–330 nm) [23], tocopherol (maximum

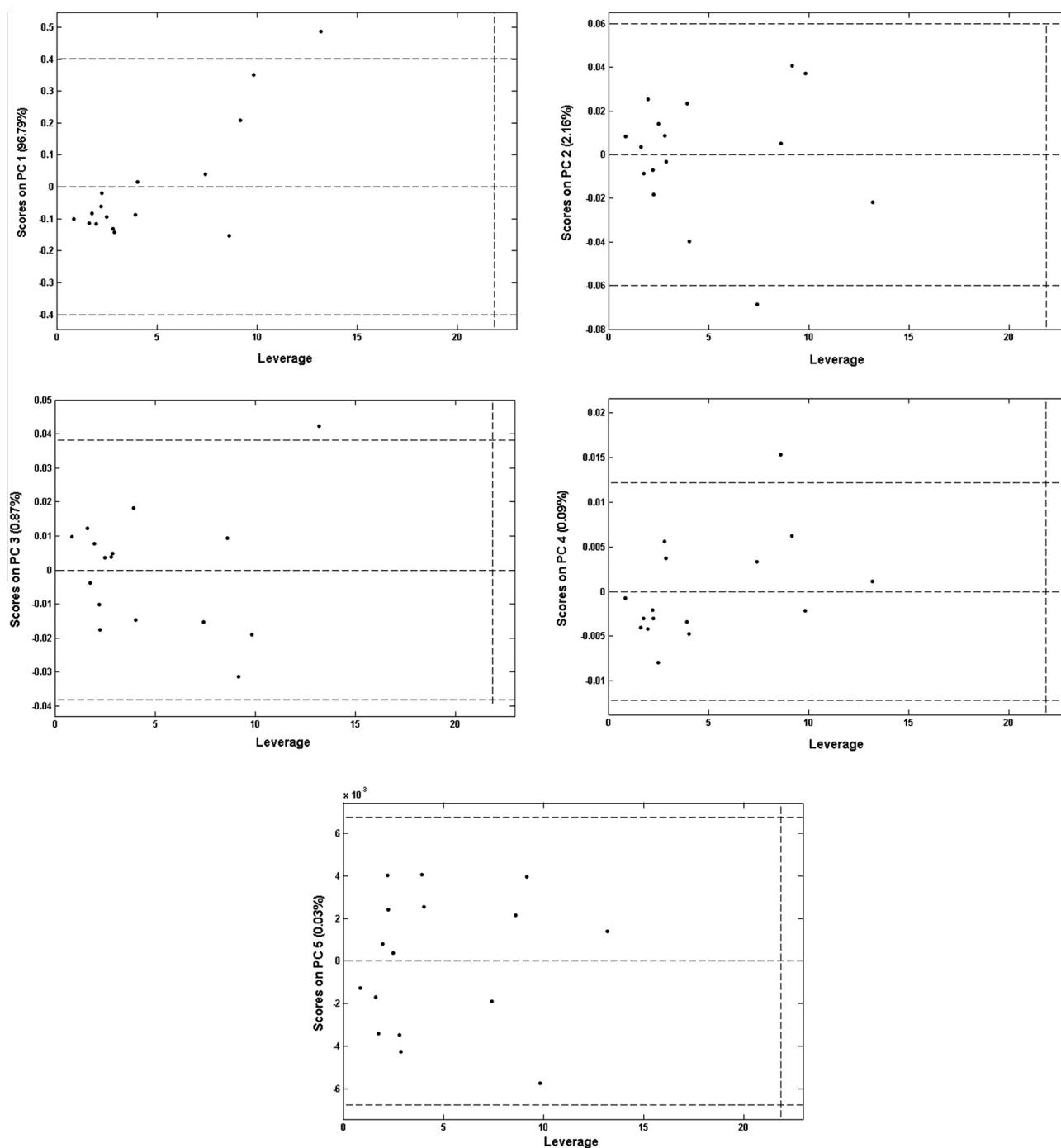


Fig. 3 Leverage against scores.

absorbance peak at 325 nm [19], hydrolysis products produced by oxidized triacylglycerols (monomers) and dimeric and polymerized triacylglycerols during frying [19,24], and carotenes (α -carotene with maximum absorbance peak at 447 nm, β -carotene with maximum absorbance peak at 451 nm, and γ -carotene with maximum absorbance peak at 462 nm) [25]. These compounds present chromophore groups with transitions $\delta \rightarrow \delta^*$, $n \rightarrow \delta^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ or combination of these [25].

These results suggest that the use of ICA prior to MCR-ALS could be an efficient way to improve the resolution of

curves. ICA promotes the minimization of the statistical dependence of the signals, and solves the problems as the necessity of the presence of “pure” variables and local minimum instead of global minimum by MCR-ALS. Gonçalves et al. [19] evaluated olive oils by UV-Vis spectroscopy and they recovered only two spectral profiles by using MCR-ALS and PURE as initial estimates. In other studies, Valderrama et al. [3] also studied olive oil degradation but using molecular fluorescence spectroscopy. In this case, the authors reached to recover five spectral profiles by applying Parallel Factor Analysis (PARAFAC). Thus, considering the difference of

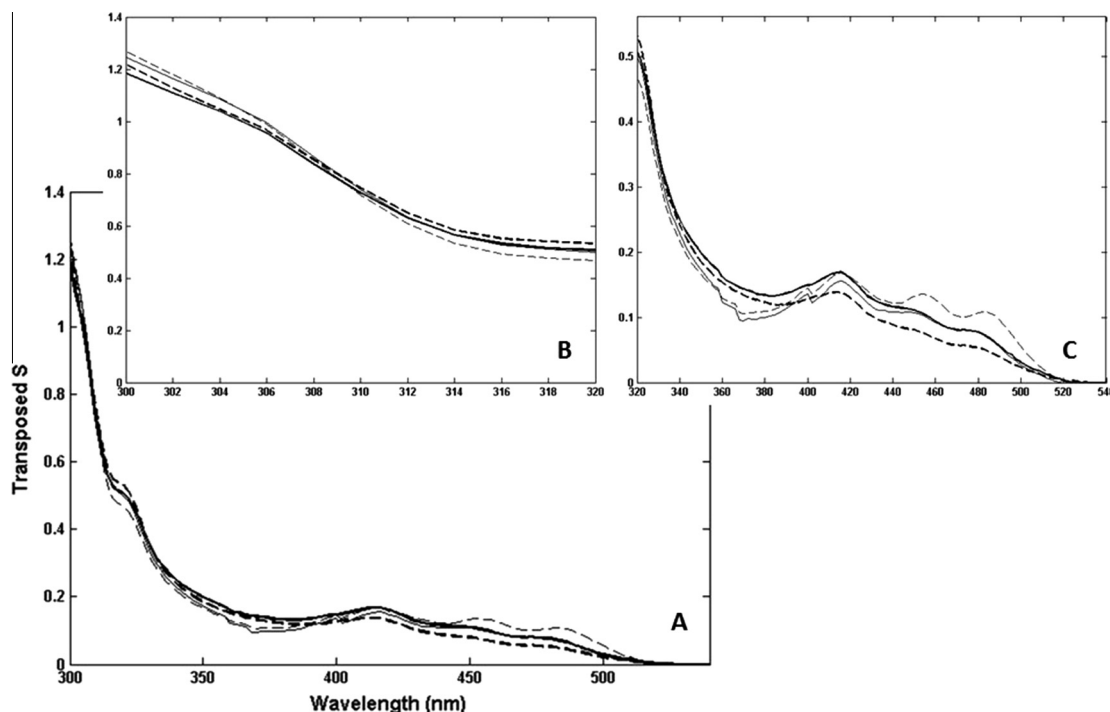


Fig. 4 (A) Spectral profiles recovered from MCR-ALS when PURE was used to obtain initial estimates. (B) Spectral profiles zoom from 300 to 320 nm. (C) Spectral profiles zoom from 320 to 540 nm. (—) unknown profile 1, (---) unknown profile 2, (— · —) unknown profile 3, and (---) unknown profile 4.

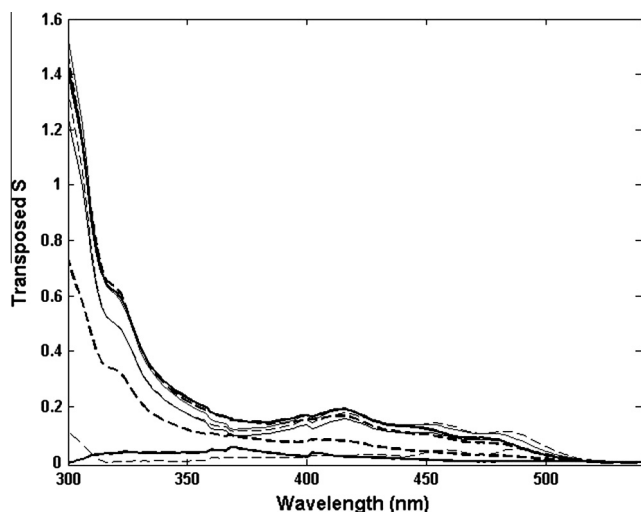


Fig. 5 Spectral profiles obtained from MCR-BANDS. (—) unknown profile 1, (---) unknown profile 2, (— · —) unknown profile 3, and (---) unknown profile 4.

sensitivity among these techniques, it is notorious that UV-Vis spectroscopy coupled with MCR-ALS, employing ICA to the initial estimates, could provide more reliable information about complex systems.

Fig. 7 presents the initial estimates obtained from PURE and ICA. The results reinforce that PURE suffers from an essential drawback, which consists in the necessity of “pure” variables, which cannot be expected in the UV-Vis spectroscopy data of complex samples, as olive oil, due to the

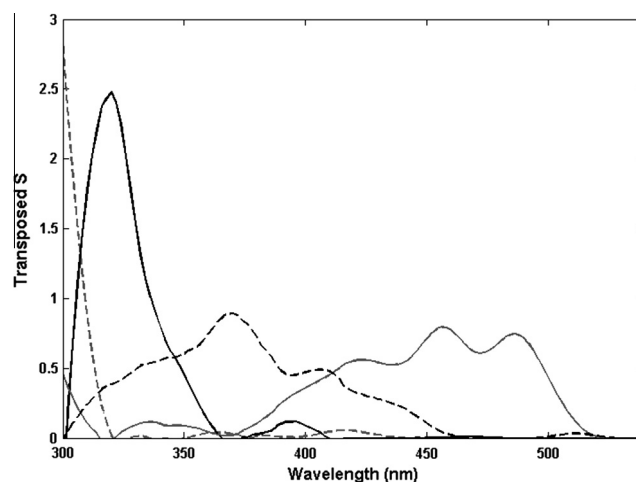


Fig. 6 Spectral profiles recovered from MCR-ALS when ICA was used to calculate initial estimates. (—) Tocopherol, (---) Hydrolysis products, (— · —) Carotenes, and (---) Phenolic and polyphenolic compounds.

strong signal overlapping and due to the lack of selectivity in UV-Vis technique. The strong signal overlapping for heated olive oil samples and the lack of selectivity in UV-Vis spectroscopy reinforce the existence of natural mutual dependences of the mixture components in this data set. The results confirm that the signals of the different compounds found in heated olive oil do not evolve independently. In cases like this, the ICA can promote the minimization of the statistical dependence of the signals and by employing the results from ICA as initial estimates for MCR-ALS it is possible to solve both

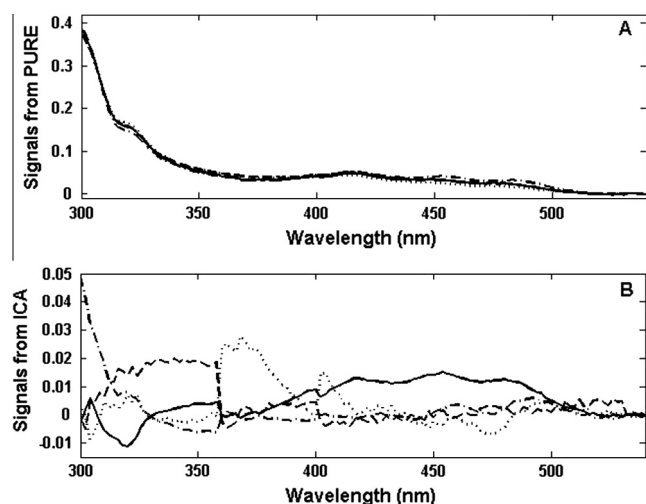


Fig. 7 Initial estimates obtained from (A) PURE and (B) ICA. (—) specie 1, (---) specie 2, (···) specie 3, and (-·-·-) specie 4.

the need for “pure” variables of the PURE method and the problem of local minimum instead of global minimum of the MCR-ALS.

Conclusions

The results from this study suggest that using ICA as a mean to obtain initial estimates for the MCR-ALS algorithm results can improve the resolution for UV–Vis data besides providing better resolution results when compared with the most commonly used method. Furthermore, this strategy would be used as an interesting alternative when the most used tools do not provide appropriate resolution.

Conflict of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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