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Independent components analysis applied to 3D-front-face fluorescence spectra of edible oils to study the antioxidant effect of *Nigella sativa* L. extract on the thermal stability of heated oils

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ABSTRACT

Independent Components Analysis (ICA) is one of the most widely used methods for blind source separation. In this paper we use this technique to facilitate the analysis of 3D- front face fluorescence spectra and to evaluate the efficiency of Nigella seed extract as a natural antioxidant compared with butylated hydroxytoluene (BHT) during accelerated oxidation of edible vegetable oils at 120 °C, 140 °C, 170 °C and 190 °C.

ICA has demonstrated its power to extract the most informative signals and thus to allow the interpretation of the differences observed in the corresponding IC scores between Control, BHT-spiked and Nigella-spiked samples.

The results of the study clearly indicate that the natural seed extract at a level of 800 ppm exhibited antioxidant effects similar to those of the synthetic antioxidant BHT at a level of 200 ppm and thus contributes to an increase in the oxidative stability of the oil.

1. Introduction

Oxidation of oils, which occurs during storage and heat treatment not only affects their organoleptic characteristics such as taste and aroma, making them unacceptable to the consumer, but also influences their nutritive value [1]. In fact, toxicity, mutagenicity and carcinogenicity of oxidized lipids have been discussed by Johnson and Cort. [2].

Thus, due to health concerns and for economic reasons, many investigations have been undertaken with the aim of enhancing the heat stability of lipids.

The addition of antioxidants is one of the technically simplest ways of reducing lipid oxidation [3,4].

Recently, the use of synthetic antioxidants such as butylated hydroxy anisol (BHA) and butylated hydroxy toluene (BHT), the most widely used anti-oxidants, has been decreasing because it is suspected that they may act as promoters of carcinogenesis, this is in addition to a general consumer rejection of the use of synthetic food additives [5,6]. The search for and development of other anti-oxidants from natural plant materials is therefore highly desirable.

In this study, *Nigella sativa* L. (Ranunculaceae) seed extract was used to enrich corn oil with a view to improving its thermal resistance during accelerated oxidation at 120 °C, 140 °C , 170 °C and 190 °C over 4 h. The modifications that occur in oil samples were monitored by front-face fluorescence spectroscopy (FFFS).

Over the last 10 years, fluorescence spectroscopy which is a fast, nondestructive, selective, and sensitive technique, has been shown to be able to provide important information about chemical and physical properties as well as changes in several types of complex food products [7,8]. The increased use of the technique has been facilitated by improved instruments and new data analysis techniques such as multivariate and even multiway chemometric data analyses [9]. In fact, the interpretation of fluorescence spectroscopic data is complex due to absorbance by several molecular groups, changes caused by variation in the sample matrix, etc. It is shown here how recent data analytical techniques are useful to improve the interpretation of the data.

In this paper, Independent Components Analysis (ICA) is used to analyse 3D- front face fluorescence spectra and facilitate monitoring the antioxidant effect of Nigella seed extract during the thermal evolution of samples.

ICA is a signal processing technique that aims at recovering the underlying source signals from a set of mixed signals based on the

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assumption that these source signals are statistically independent [10]. ICA has been applied, for example, to spectroscopic data [11–13], medical signal processing [14], speech recognition [15,16], fault detection [17], statistical process monitoring [18], and batch process monitoring [19].

Thus, in the present article, we intend to demonstrate the usefulness of ICA as a means to extract the pure underlying signals from a set of mixed signals with unknown proportions.

2. Materials and methods

2.1. Nigella sativa.L extract preparation (natural antioxidant)

Nigella seeds were washed and then dried in a hot-air oven at 40 °C. The dried seeds were ground into a fine powder in a mill. The material that passed through an 80 mesh sieve was retained for use. Ten grams of ground seeds were extracted with 100 mL of ethanol overnight in a shaker (Heidolph REAX 2) at room temperature. The extract was filtered and the residue was re-extracted under the same conditions. The combined filtrate was evaporated in a rotary evaporator (Rotavapor R110, Büchi, Switzerland) at below 40 °C. The extract obtained after evaporation of ethanol was used as the natural antioxidant [20,21].

2.2. Oil samples

Corn oils ("Safi" and "Nejma") were commercial brands bought in the Tunisian marketplace.

2.3. Experimental parameters and software

Corn oils were heated at 120, 140, 170 and 190 °C for 4 h to mimic frying conditions. Preliminary studies of *Nigella sativa* L seed extract at concentrations from 200 ppm to 4800 ppm having shown that enrichment with 800 ppm had a significant stabilising effect, this concentration was chosen. A relatively low concentration is preferable both for economic reasons and so as not to affect the organoleptic characteristics of the oil. For comparison, the synthetic antioxidant (BHT) was also tested at the legal limit of 200 ppm [22]. One 10 mL aliquot of each sample was taken every 15 min up to 180 min. A final aliquot was taken at 240 min which gives 14 samples for each oil as-is, with BHT or with Nigella (13 samples at after different heating times plus the unheated oil as the reference sample) resulting in 320 oil samples (40 samples × 4 temperatures × 2 oils).

Fluorescence landscapes (3D spectra) were measured directly on the samples without prior chemical treatment, using a Xenius spectrofluorometer (SAFAS, Monaco) equipped with a xenon lamp source, excitation and emission monochromators and a front face sample-cell holder. Measurements were carried out using acryl cuvettes. The instrumental settings were: bandwidth 10 nm, emission wavelengths 300 to 550 nm (recorded every 2 nm) and excitation wavelengths 280 to 500 nm (recorded every 2 nm). A photomultiplier (PM) voltage of 420 V was used to avoid detector saturation. The "Forcing" option was also applied in order to limit the emission range so that data acquisition started 15 nm above the excitation frequency, thus avoiding interference from Rayleigh scattering.

The data consisting of 3D fluorescence spectra were exported in ASCII format for data treatment using MATLAB version 7.0.4 (The MathWorks, Natick, USA).

3. Chemometrics methods

3.1. Independent components analysis

Independent Components Analysis is a blind source separation (BSS) techniques developed to extract the pure underlying signals from a set of signals where they are mixed in unknown proportions. The general ICA model is [23,24]:

$$\mathbf{X} = \mathbf{A}.\mathbf{S}$$

where **X** is the matrix of observed spectra, **S** is the matrix of unknown "pure" source spectra and **A** is the mixing matrix of unknown coefficients, related to the corresponding concentrations. Based on the Central Limit Theorem, ICA assumes that statistically independent source signals have intensity distributions that are less Gaussian than are their mixtures [23,24]. For this reason, ICA aims to maximise the non-gaussianity of the extracted signals.

This method is now widely applied in the signal processing fields, such as biomedical signals [25], image processing [14] and financial data analysis [26]. Its applications in processing analytical signals, including NIR [12], MIR [13], fluorescence spectroscopy [27,28], photoacoustic spectroscopy [29], GC/MS [11] and electron paramagnetic resonance (EPR) [30], were also reported by some researchers in their recent works.

There are a large number of ICA algorithms such as FastICA, Joint Approximate Diagonalization of Eigenmatrices (JADE), Infomax ICA, Mean-field ICA (MF-ICA), Kernel ICA (KICA), often based on different definitions of independence and using different procedures to extract the Independent Components [24]. In this paper, the JADE algorithm was used [31]. JADE performs a joint diagonalization of matrices of the fourth-order cumulants calculated from the data and does not require any gradient searches, thus avoiding the convergence problems encountered with other procedures.

PARAFAC is the multi-way method commonly used to decompose 3-way fluorescence datasets [32,33]. However, ICA has several advantages over PARAFAC.

To obtain chemically interpretable results using PARAFAC, in the present case, it was necessary to impose non-negativity constraints on all three ways ("concentration", excitation and emission). No such *a priori* constraints are required when using ICA. If the extracted proportions ("scores") were negative, it was sufficient to multiply the scores and corresponding signals ("loadings") by −1.

As well, it was not possible to obtain a PARAFAC model which could extract all the components that were visibly present in the spectra. The Corcondia values used to determine the number of significant PARAFAC factors were already at the level of noise with only 3 or 4 Factors.

3.2. Choice of the number of ICA components

The choice of the optimal number of components to use in ICA is one of the crucial points in the analysis. In this work, the Durbin–Watson (DW) criterion was applied to the extracted signals to determine which ones had a high signal/noise ratio and could therefore be assumed to be informative ICs.

The DW statistic is a criterion which is classically used to test for the correlation of residuals after a regression [34] but which has been proposed as a measure of the signal/noise ratio of the loadings and regression vectors obtained by multivariate analysis of signals, in order to determine the optimal dimensionality of multivariate models [35,36]. The basic justification for the use of this criterion is that uninformative loadings and over fitted regression vectors contain more random noise. If the DW value is close to zero, the vector is structured and so the factor is significant and can be retained, while if DW value is close to 2, the vector is noisy and can be discarded [35].

The Durbin–Watson (DW) criterion which reflects the signals/noise ratio of the ICs is preferable to examining the scree plot of a Principal Components Analysis which only reflects the extracted variance. As well, the results of the PCA scree plot are ambiguous. In the present case, the number of significant PCs is 8 based on the percentage of the total variance divided by the total number of components; is 10 based on the

break in the slope; and is 20 based on the appearance of the almost horizontal plateau.

4. Results and discussion

The data corresponding to each oil heated at different times for a given temperature, with and without the Nigella extract or the BHT antioxidant is arranged in a (40×126×111) 3-way cubic array of 40 spectra, with 126 emission wavelengths and 111 excitation wavelengths. So as to simplify the interpretation of the data, all the elementary cubes of the two corn oils (Safi and Nejma) were gathered together giving a (320×126×111) 3-way cubic array. The final cube of data was unfolded to create a (320×13,986) matrix.

4.1. Choice of the number of ICA components

Although the *a priori* choice of the optimal number of ICs is a problem which has yet to be adequately solved, in the present case, *a posteriori* inspection can facilitate determining when there are either too many or too few. Extracting too many ICs produces uninformative ICs corresponding to noise. These can be detected by the Durbin-Watson criterion or by visual inspection of the structure of the IC signals.

Too few ICs results in some IC signals having contributions from several sources or in some sources not being extracted. By *a posteriori* examination of the IC it is possible to determine when all signal sources have been extracted.

Independent Components Analyses with from 1 to 20 Independent Components (ICs) was applied to the unfolded matrix. These components were used to calculate 20 approximation of the initial unfolded data matrix. Residuals matrices were then calculated by subtracting these approximations from the initial matrix. As progressively more ICs are extracted from the matrix, the resulting residuals become progressively noisier. The Durbin–Watson (DW) criterion was applied to the unfolded matrix of residuals for each spectrum in order to detect when all the informative signals had been removed, leaving just noise.

The residuals matrix was also refolded and the DW criterion calculated for each sample along the excitation and along the emission directions. The mean of these DW values were then calculated over all the samples to determine how many ICs needed to be extracted to detect the informative signals in each part of the excitation and the emission signals.

Fig. 1a shows the DW values for each unfolded residuals matrix for each sample, on abscissa, plotted as a function of the number of Independent Components, on ordinate. The samples are sorted into two main blocks, one per oil, each containing 4 sub-blocks, one per temperature, each containing the oils sorted as a function of heating time. It can be seen that all spectra give at least 5 structured ICs. Some matrices are still structured up to 10 ICs and a small number of them, towards the end of each block of heating times, remain structured even up to 15 ICs. The signals that require up to 15 ICs correspond to spectra obtained at the end of the heating (after 3 or 4 h) which can be explained by the formation of new oxidation products after long heating time.

Fig. 1b and c show the averages of the DW criteria over all oil samples, for each excitation and emission wavelength, and highlight which spectral regions require more Independent Components.

4.2. Independent components analysis

An Independent Components Analysis (ICA) with 17 Independent Components (IC) was applied to the unfolded matrix (320×13,986).

We present only figures corresponding to the significant signals. Certain figures are presented as supplementary information (SI).

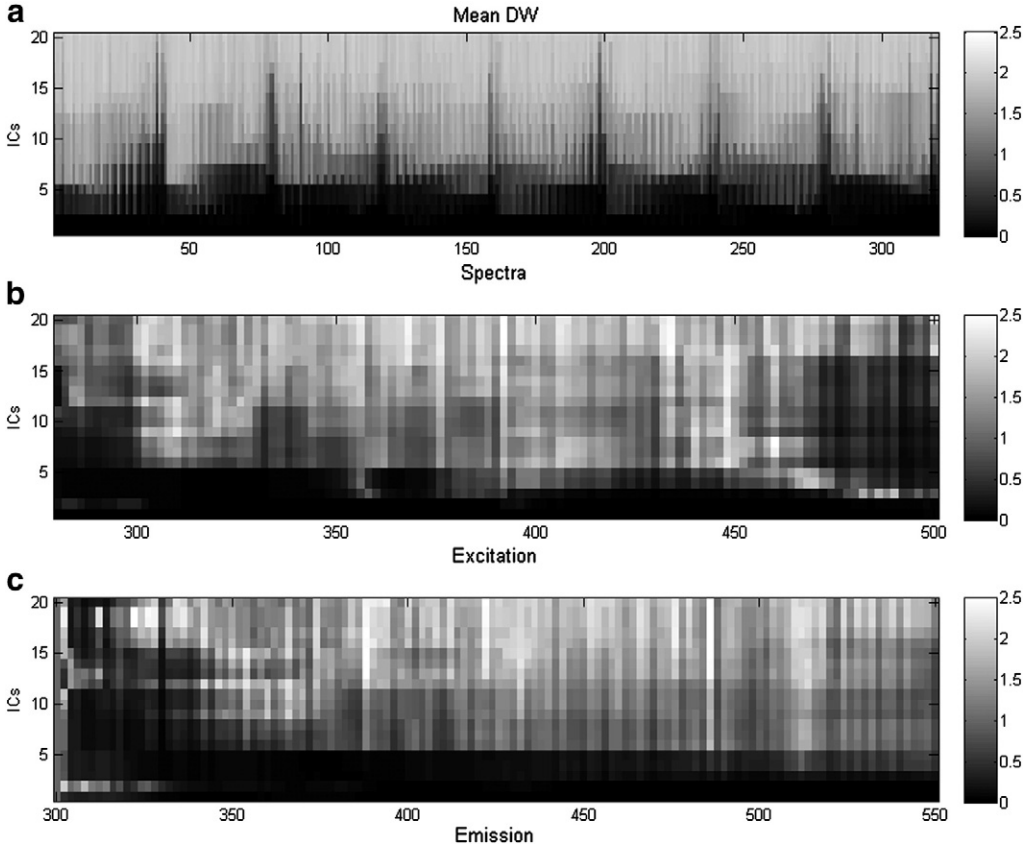

Fig. 1. a) Durbin-Watson values of the residual matrices for increasing numbers of extracted IC signals plotted as a function of the samples; b) mean DW values over all samples plotted as a function excitation wavelength; c) mean DW values over all samples plotted as a function emission wavelength.

Not all IC signals correspond to chemical components – some result from variations in base line and residual Raleigh diffusion; and several may correspond to the same chemical compound. However using ICA to decompose the dataset into 17 "pure signals" results in each IC signal plot (Figs. 2b–7b) presenting a single specific wavelength zone corresponding to individual fluorophores or

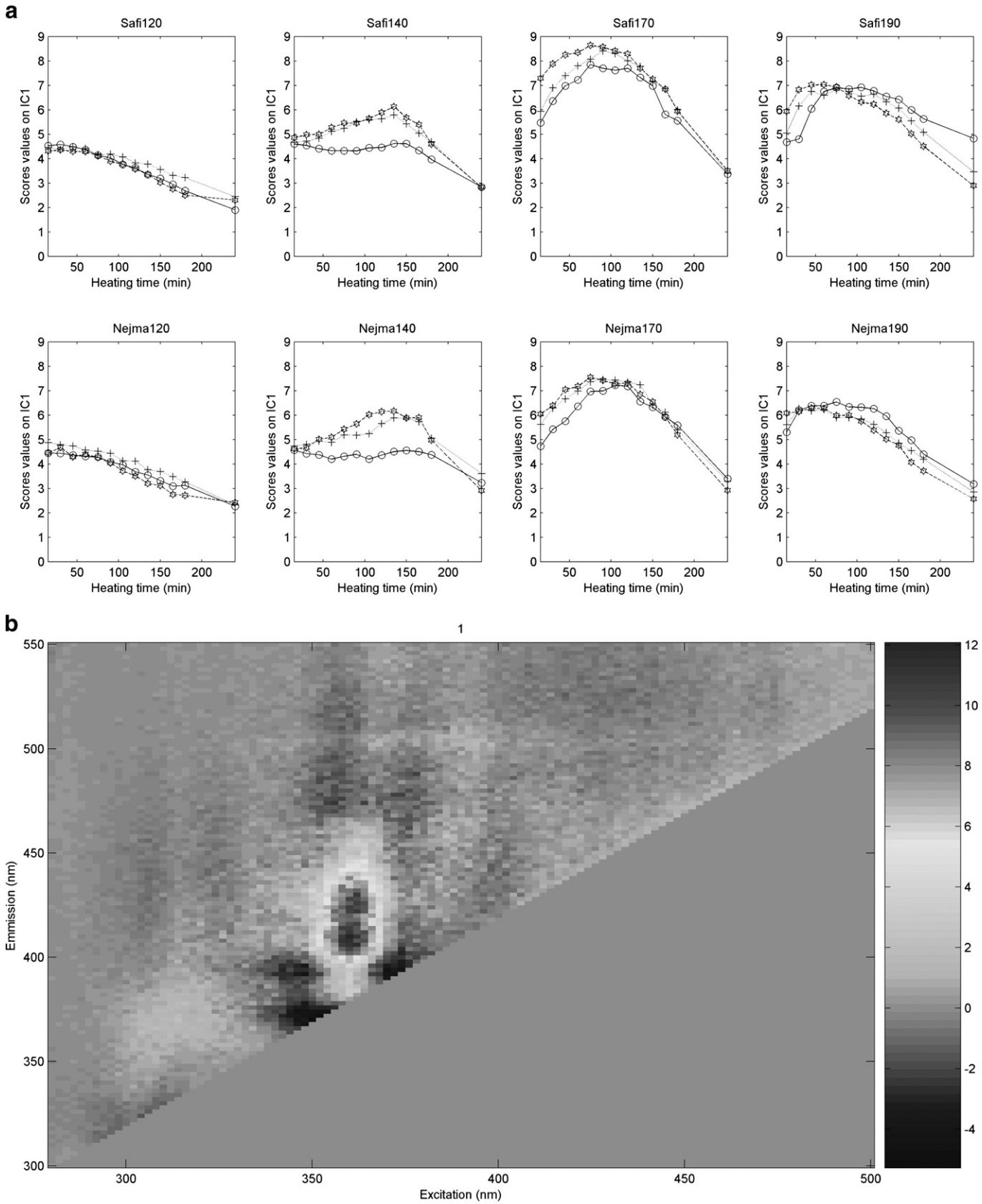

Fig. 2. a) Scores (−☆- Control; -O- Nigella; … + … BHT) and b) signals of IC1.

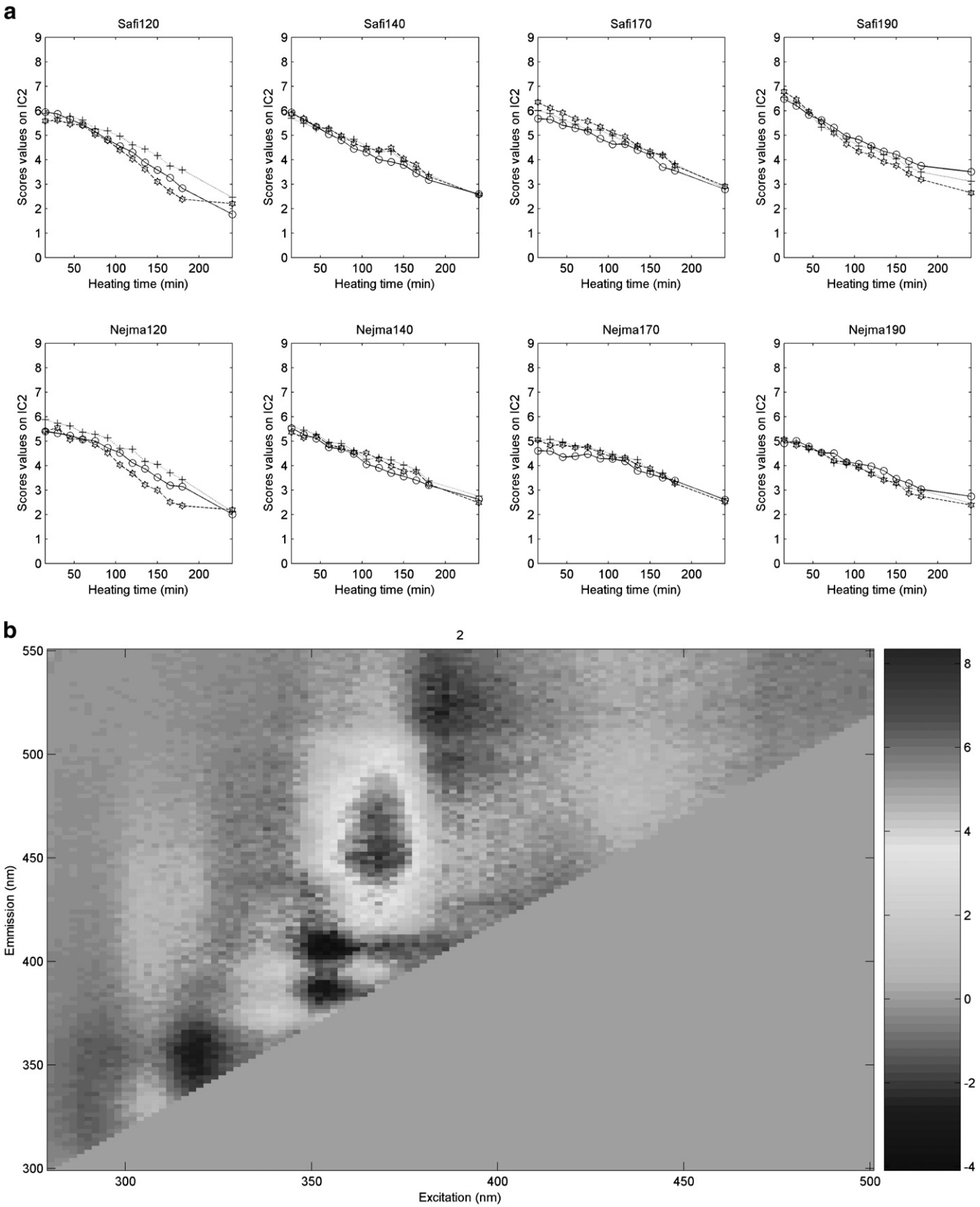

Fig. 3. a) Scores (—☼- Control; -O- Nigella; … + … BHT) and b) signals of IC2.

interpretable artefacts, thus facilitating the comprehension of the differences observed in the corresponding IC scores plot between Control, BHT-spiked and Nigella-spiked samples (See Table 1).

Each IC signal plot (Figs. 2b–7b) presents a specific wavelength zone corresponding to individual fluorophores, which facilitates the interpretation of the differences observed in the corresponding IC

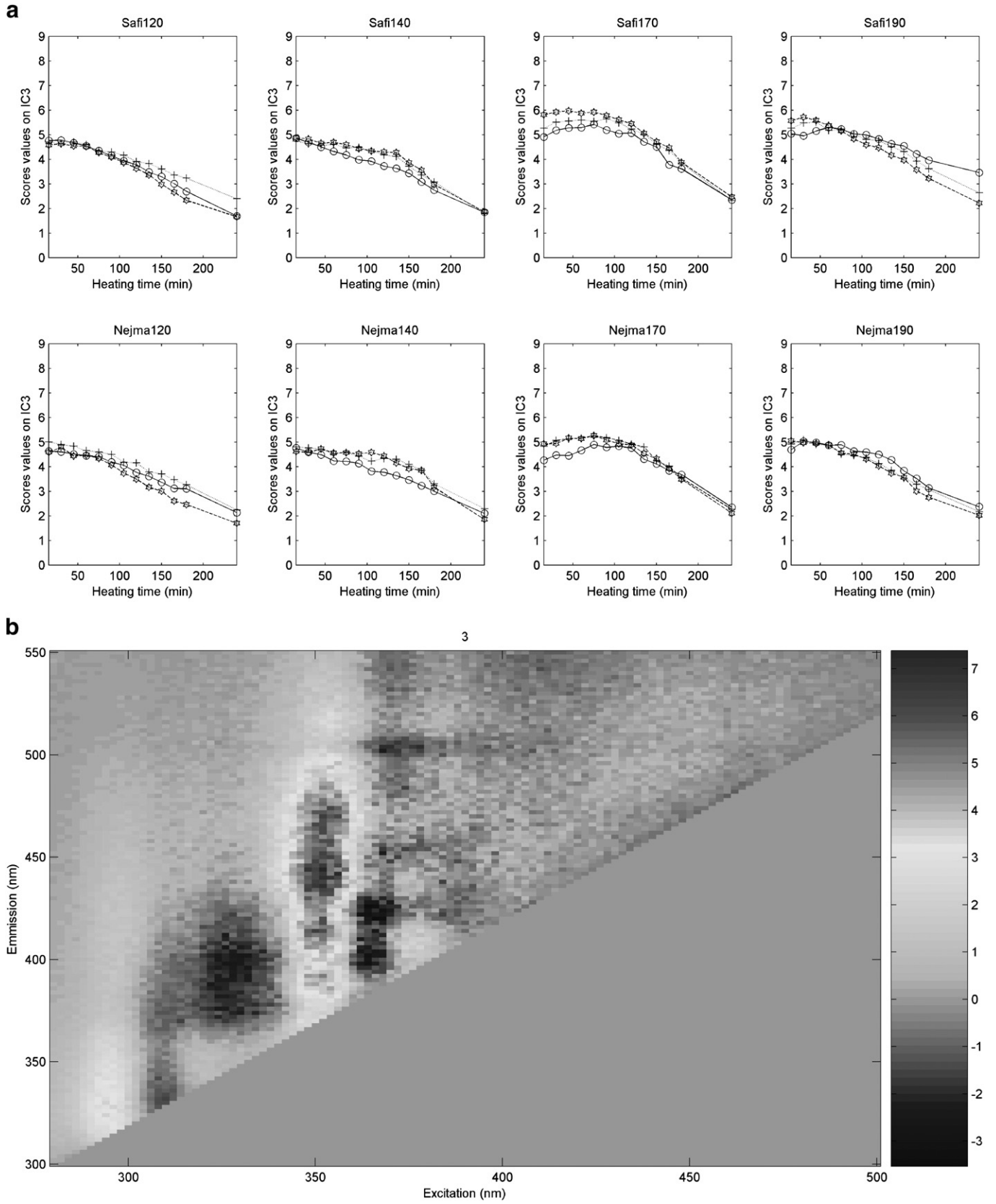

Fig. 4. a) Scores (—☼- Control; -O- Nigella; … + … BHT) and b) signals of IC3.

scores plot between Control, BHT-spiked and Nigella-spiked samples (See Table 1).

All ICs (Figs. 2a–7a) show that during the heating, the scores corresponding to the Nejma corn oil and Safi corn oil evolve in the same way. This shows that the two corn oils are similar. It also demonstrates that front-face fluorescence spectroscopy, the controlled heating of the samples and the data processing using ICA produce repeatable results. The effect of the addition of antioxidant is also repeatable.

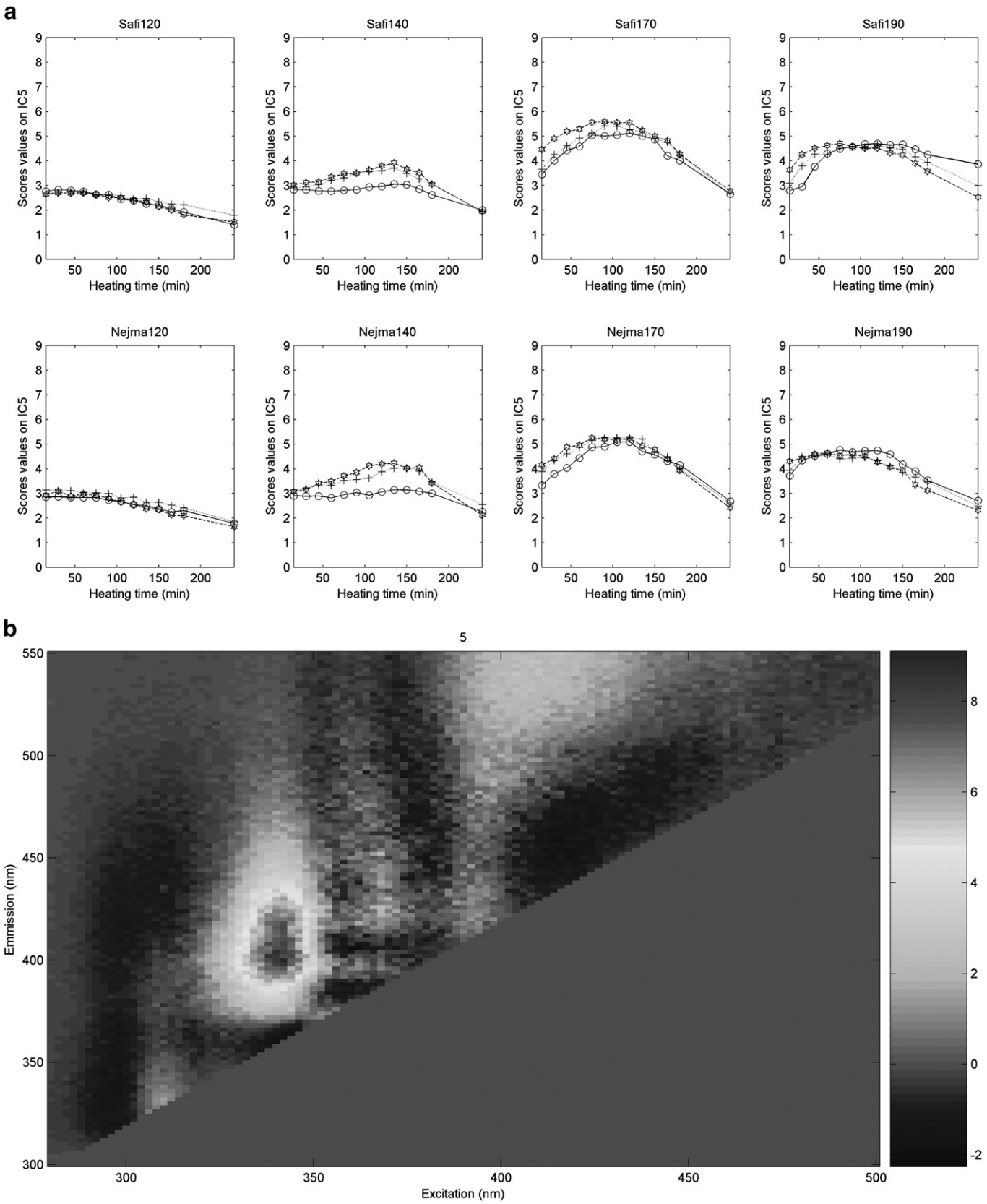

Fig. 5. a) Scores (—☼- Control; -O- Nigella; … + … BHT) and b) signals of IC5.

The fact that the time courses of the IC scores are dramatically different at different temperatures shows that the heat treatment has a strong effect on oil oxidation reactions.

For the two corn oils heated at 120 °C, we notice that the scores of almost all ICs decrease with the heating time indicating that the corresponding fluorophore is being degraded. Enriched oils (with

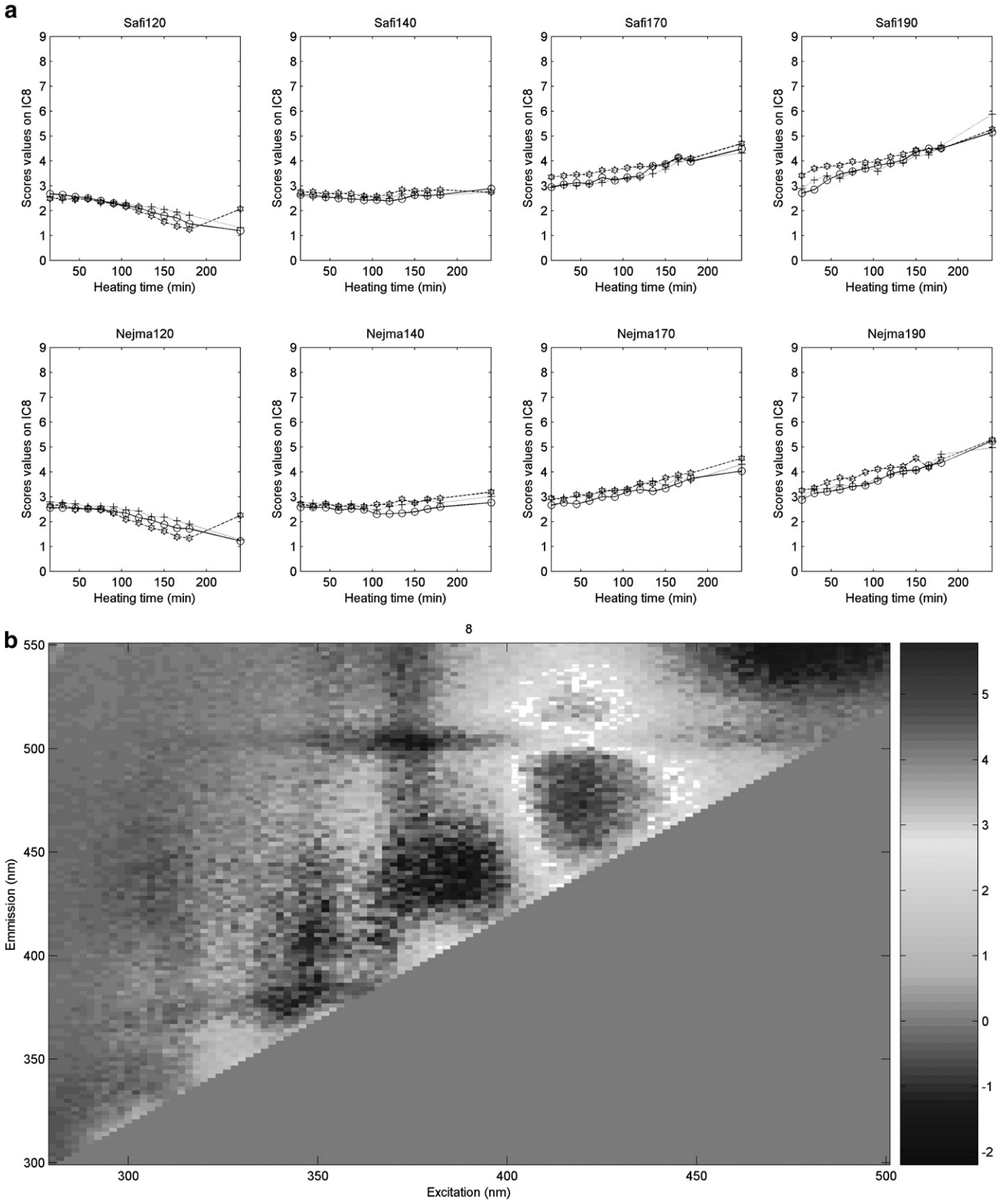

Fig. 6. a) Scores (—☼- Control; -O- Nigella; … + … BHT) and b) signals of IC8.

either Nigella seeds extract or BHT) evolve less as a function of heating time. In fact, the oxidation products in non-enriched oils are in greater quantity than in the enriched oils.

IC2 (Fig. 3), IC9 (SI) are associated to oxidation products and decrease with time indicating that the corresponding fluorophore is degraded during heating.

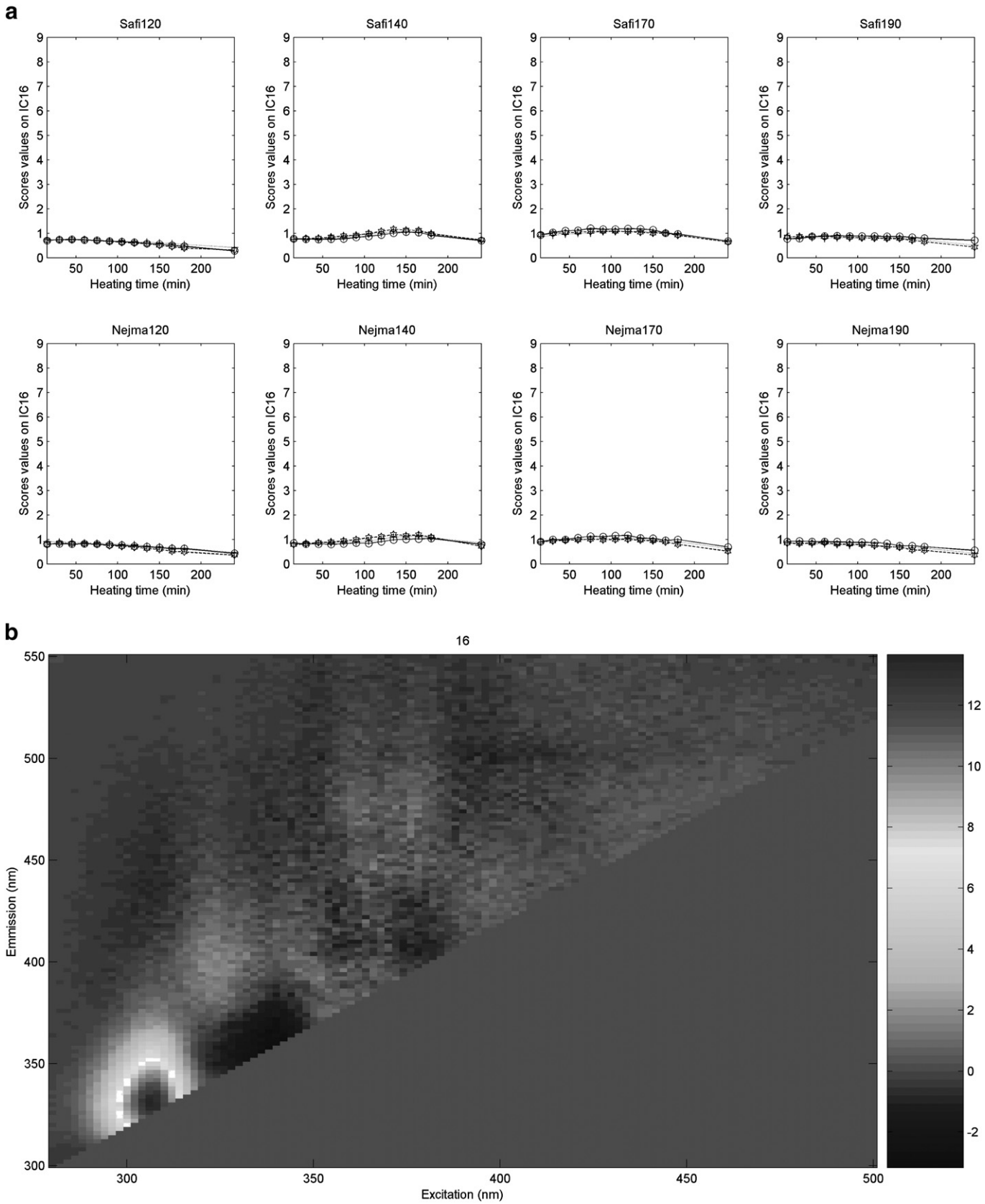

Fig. 7. a) Scores (—☼- Control; -O- Nigella; … + … BHT) and b) signals of IC16.

On the one hand, IC1(Fig. 2), IC6 (SI), corresponding to secondary, and on the other hand IC5 (Fig. 5), IC10 (SI), corresponding to primary oxidation products, increase and then decrease along the time axis, indicating that new fluorescent oxidation products are formed and are then degraded during heating.

Table 1
Chemical interpretation of IC signals calculated by the JADE algorithm.

IC	Wavelength region	Possible fluorophores	References
1	λex = 350–370 nm, λem = 400–450 nm	Oxidation products (oxidation of conjugated dienes and trienes)	[28,29,38]
2	λex = 350–380 nm, λem = 420–500 nm		
3	λex = 345–360 nm, λem = 380–500 nm		
4	λex = 375–395 nm, λem = 440–520 nm		
5	λex = 330–350 nm, λem = 380–450 nm		
6	λex = 365–385 nm, λem = 380–440 nm		
7	λex = 390–410 nm, λem = 410–480 nm		
8	λex = 410–450 nm, λem = 440–540 nm		
9	λex = 355–380 nm, λem = 480–550 nm		
10	λex = 350–370 nm, λem = 370–410 nm		
11	λex = 380–400 nm, λem = 390–450 nm		
12	λex = 320–350 nm, λem = 350–390 nm		
13	λex = 310–330 nm, λem = 390–490 nm		
14	λex = 430–490 nm, λem = 495–550 nm		
15	λex = 290–315 nm, λem = 355–455 nm		
16	λex = 295–315 nm, λem = 315–350 nm	Antioxidants (tocopherols + polyphenols)	[28,38,39]
17	Noise		

It can be seen from the IC1 scores (Fig. 2) that oxidation products decrease to a level which is below the initial level. In fact since corn oil is refined it already contains oxidation products which can be degraded by heating to give new oxidation products.

It is the same evolution for IC3 (Fig. 4), but with a less significant formation.

At 170 °C, and especially at 140 °C, the antioxidant effect of *Nigella sativa* L. is very clear. Indeed, the newly formed oxidation products are definitely lower for the enriched samples. This effect is less discernible at 190 °C.

At 120 °C, oil does not undergo much oxidisation. The protective effect of the Nigella extract is therefore not very noticeable. However, at higher temperatures (140 °C and 170 °C), the oxidation reactions are accelerated and the antioxidant effect of Nigella extract becomes more visible. However, at 190 °C, the oxidation reactions rates are so much higher that the Nigella extract is no longer as effective in slowing it down.

Except for the non-enriched oil at 170 °C and 190 °C which starts at a higher level, the IC1 scores (Fig. 2) all start at approximately the same intensity level even for the two different oils. Since this initial point corresponds to unheated oils, this discrepancy is probably an artefact introduced by the ICA decomposition. Nevertheless, the evolutions of the curves as a function of oil, heating time, temperature and presence of anti-oxidant are interpretable. These evolutions are very similar for the two oils, indicating that the oils behave in very similar manners and that the observed changes are greater than the experimental errors.

At 120 °C, existing oxidation products are degraded by the heating and the anti-oxidants have little effect. At 140 °C, oxidation products are newly formed more quickly than they are degraded, and Nigella extract has a strong anti-oxidant effect. At 170 °C, the formation of new oxidation products is even faster, leading to a higher and earlier maximum concentration. At 190 °C, this maximum is attained even sooner.

IC8 (Fig. 6), and IC14 (SI) illustrate that at 140 °C scores remain stable. However, at 170 °C and 190 °C (Fig. 6), the scores increase indicating that at these higher temperatures new fluorescent oxidation products are being formed. These new products are definitely lower for the BHT-spiked and Nigella samples.

At relatively low temperatures (120 °C), the oxidation products already present in the corn oil undergo degradation during the heat treatment.

At higher temperatures, there is either formation of new oxidation products due to the degradation of primary oxidation products or development of new oxidation products which undergo additional degradation especially at higher temperatures (170 °C and 190 °C).

IC16 (Fig. 7) scores corresponding to the naturally present antioxidants (polyphenols and tocopherols) [28,37–39] remain almost stable throughout heating, which may seem strange because, normally antioxidants are degraded during heating. This could be due to the fact that these products are present in very small quantities in refined oils and so the variations are masked by the effect of baseline changes due to other much larger peaks in the spectra.

All ICs show (Figs. 2–7) that during heating, the scores corresponding to the oils enriched with Nigella extract or with BHT evolve in the same way, which confirms that the addition of the extract plays the same role as the addition of synthetic antioxidant. In certain cases, for example IC1 and IC5 (Figs. 2 and 5), Nigella exhibited an antioxidant effect more powerful than that of the BHT, thus assuring a better protection of corn oil against the effects of heat treatment.

5. Conclusion

ICA is an effective tool to facilitate the analysis of 3D- fluorescence spectra and simplifies monitoring the antioxidant effect during the thermal evolution of samples with or without addition of Nigella extract or synthetic antioxidant.

Based on the results of this study, the addition of Nigella seed extract to edible oils may improve their thermal stability and shelf-life. Thus, Nigella extract could be an interesting alternative to the use of synthetic antioxidants. The next step in this study will be to verify the innocuity of the Nigella extract through toxicological tests before proposing its use in food product applications.

Supplementary materials related to this article can be found online at doi:10.1016/j.chemolab.2011.06.005.

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