



# Study of the heat stability of sunflower oil enriched in natural antioxidants by different analytical techniques and front-face fluorescence spectroscopy combined with Independent Components Analysis

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## ABSTRACT

The aim of this study was to find objective analytical methods to study the degradation of edible oils during heating and thus to suggest solutions to improve their stability. The efficiency of *Nigella* seed extract as natural antioxidant was compared with butylated hydroxytoluene (BHT) during accelerated oxidation of edible vegetable oils at 120 and 140 °C. The modifications during heating were monitored by 3D-front-face fluorescence spectroscopy along with Independent Components Analysis (ICA), <sup>1</sup>H NMR spectroscopy and classical physico-chemical methods such as anisidine value and viscosity. 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.

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## 1. Introduction

Lipid oxidation is one of the major factors resulting in losses in fatty food quality by the formation of products with negative effects on taste, aroma and nutritional value of the food, which are associated with many types of biological damages in living tissues and may increase the risk of cardiovascular disease [1,2]. Antioxidants are major ingredients that protect the quality of oils and fats by retarding oxidation [3]. Synthetic antioxidants are used within regulated limits to reduce deterioration, rancidity and oxidative discoloration [4]. Butylated hydroxyl anisol (BHA) and butylated hydroxyl toluene (BHT) are two widely used synthetic antioxidants but are quite volatile and decompose easily at high temperatures [5].

Questions have been raised concerning the safety and toxicity of such synthetic antioxidants in relation to their metabolism and possible absorption and accumulation in organ and tissues [6,7]. Therefore, the search for and the development of other antioxidants from natural plant materials is highly desirable.

In this study, *Nigella sativa* L. (Ranunculaceae) seed extract was used to enrich sunflower oil with a view to improving its thermal resistance during accelerated oxidation at 120 °C and 140 °C over 3 h. The modifications that occur in oil samples were monitored by front-face fluorescence spectroscopy (FFFS), by <sup>1</sup>H NMR spectroscopy and by measurements of viscosity and anisidine values.

Spectroscopic techniques such as Fourier transform infrared spectroscopy have been largely used for the determination of oil degradation [8–10]. However, vibrational techniques lack sensitivity in comparison to fluorescence spectroscopy.

Fluorescence spectroscopy has been successfully used for olive oil characterization and adulteration assessment [11–13].

The advantages of this technique are its speed of analysis, lack of solvents and reagents, and requirement of only small amounts of sample. In addition, it is a noninvasive, a highly selective and sensitive technique. In fact, the sensitivity of fluorescence is 100–1000 times higher than that of the absorption techniques, enabling to measure concentrations down to parts per billion levels technique. The front-face (FF) technique was shown to be the method providing the most accurate results for the fluorescence of edible oils in nondiluted samples [14,15].

The interpretation of fluorescence spectral data is complex due to the presence of many fluorophores and by changes caused by variation in the sample matrix, etc. In this paper, Independent

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Components Analysis (ICA) was applied to the 3D-front-face fluorescence spectra to facilitate monitoring the antioxidant effect of *Nigella* extract during heat treatment.

Independent Components Analysis is a blind source separation (BSS) technique developed to extract the pure underlying signals from a set of signals where they are mixed in unknown proportions. The general ICA model is [16,17]:

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

where  $\mathbf{X}$  is the matrix of observed signals (the spectra in our case),  $\mathbf{S}$  is the matrix of unknown “pure” source signals and  $\mathbf{A}$  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 [16,17]. For this reason, ICA aims to maximize the non-gaussianity of the extracted signals.

This method is now widely applied in the signal processing fields, such as biomedical signals [18], image processing [19] and financial data analysis [20]. Its applications in processing analytical signals, including NIR [21], MIR [22], fluorescence spectroscopy [23,24], photoacoustic spectroscopy [25], GC/MS [26] and electron paramagnetic resonance (EPR) [27] have also been reported.

Several ICA algorithms exist, 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 [17]. In this paper, the JADE algorithm was used [28]. JADE performs a joint diagonalization of matrices extracted from the fourth-order cumulants calculated from the data and does not involve gradient searches, thus avoiding the convergence problems encountered with other procedures.

It is shown here how ICA may be useful to simplify the interpretation of the data.

## 2. Materials and methods

### 2.1. *N. 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 [29,30].

### 2.2. Oil samples

Sunflower oil was a commercial brand bought in the French marketplace.

### 2.3. Experimental parameters and software

Non-enriched sunflower oils and sunflower oils enriched with 800 ppm of *N. sativa* L. extract were heated at 120 and 140 °C for 3 h. For comparison, the synthetic antioxidant (BHT) was also tested at a legal limit of 200 ppm [30]. The samples taken after each hour of heating during 3 h are then analyzed by 3D-front-face fluorescence.

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 acrylic cuvettes. The instrumental settings were: bandwidths 10 nm, emission wavelengths 300–550 nm (every 2 nm) and excitation wavelengths 280–500 nm (every 2 nm). A photomultiplier (PM) voltage of 420 V was used to avoid detector saturation. The “Forcing” option was also used in order to limit the emission range so that data acquisition started 15 nm beyond the excitation wavelength, 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).

### 2.4. Viscosity and anisidine value Measurements

A Houillon viscometer (S. Lauda, LAUDA France S.A.R.L.) was used to study the kinematic viscosity of the oils after heat treatment. Measurements were performed in duplicate at 40 °C using “Houillon” capillary tubes.

Anisidine values were determined by the standard 2504 IUPAC method (IUPAC, 1987) by measuring absorbance at 350 nm using a single beam U.V./visible spectrophotometer (UV-vis Roucaire SHIMADZU UV-1205). Measurements were carried out in duplicate.

### 2.5. <sup>1</sup>H NMR spectroscopy

The oil samples were placed in 5 mm diameter NMR tubes for the analysis. TSP (Trimethylsilyl propanoic acid) was dissolved in deuterated water, placed in a 200 μL NMR capillary and used as a chemical shift reference. The spectra were acquired using a Bruker 300 MHz spectrometer with a relaxation delay of 3 s, an pulse angle of 90° and 64 scans.

The baseline corrections of the spectra were performed manually and the chemical shifts are expressed in δ scale (ppm). Each sample was analyzed three times.

## 3. Chemometrics methods: 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, two methods were used in order to determine the number of independent components.

The first method is based on the Durbin–Watson (DW) criterion which was applied to the residual matrices after removing the contributions of the calculated signals to find out which ones had a low signal/noise ratio and could therefore be assumed to no longer contain informative ICs. The DW statistic is a criterion which is classically used to test for the correlation of residuals after a regression [31] 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 [32,33]. 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 the DW value is close to 2, the vector is noisy and can be discarded [32].

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