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A novel fast quality control strategy for monitoring spoilage on mayonnaise based on modeling second-order front-face fluorescence spectroscopy data

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ABSTRACT

The potential of front-face fluorescence spectroscopy along with chemometric algorithms was investigated for the non-destructive evaluation of mayonnaise spoilage stored at 5 °C and 37 °C during six days. Fluorescence excitation spectra on homemade and commercial mayonnaise samples were recorded between 230 and 400 nm, and emission wavelengths from 300 to 600 nm. Fluorescence spectra data were analyzed using parallel factor analysis (PARAFAC) capturing the changes occurred in the data set. The best PARAFAC model was obtained with 3 components, having 52% core consistency values and 98.8% of the explained variance. A chromatographic analysis was performed to know the specific compounds. Three compounds were presented in all the samples: tyrosine, tryptophan and riboflavin. The results confirm the decrease of the tyrosine and tryptophan concentrations in the time evaluated at 37 °C while the changes at 5 °C were not observed. The results obtained were evaluated by N-way partial least square discriminant analysis (NPLS-DA) on data set formed by all the fluorescence spectra at 37 °C in order to test the ability of the matrices to discriminate between each storage times. The results showed that 100% of good classifications were obtained using 3 PLS factors. This research confirms that the excitation-emission matrices (EEMs) provide information related to the mayonnaise fluorescent molecular structure, allowing the classification of the samples as a function of storage time.

1. Introduction

Mayonnaise is probably one of the most widely used sauces or condiments in the world today [1]. Mayonnaise is an oil-in-water emulsion and is traditionally prepared from a mixture of egg yolk, vinegar, oil and spices; it may also include salt, sugar or sweeteners, and other optional ingredients [2]. Mayonnaise spoils for a variety of reasons: separation of emulsion, oxidation and hydrolysis of the oils by strictly chemical foods processes and from the growth of microorganisms. Mainly, it is susceptible to deterioration due to autooxidation (lipid oxidation reactions) affecting to other molecules such as proteins, carbohydrates, and vitamins [3,4]. However, due to its low pH and high fat content, mayonnaise is relatively resistant to microbial spoilage [1,3,4].

Conventional methods for spoilage food detection and evaluation such as microscopy and plate count method and have been commonly used for quantitative microbial measurement together with physicochemical evaluations [1–5]. These traditional methods are tedious, laborious, destructive, and time-consuming, for this reason not very suitable for rapid measurement. Thus, methods more rapid for quality and safety detection and evaluation are necessary.

In this context, fluorescence spectroscopy has found wide applications in food analysis as well as food area research due to their nondestructive and noninvasive nature, and straightforward sample preparation and fast analysis time [5–8]. Besides, this technique has become in the last years quite popular as a tool related to food technology [9,10].

Particularly, front-face fluorescence spectroscopy (FFFS) provides very useful information on the presence of fluorescent molecules and their environment in food samples since traditional right angle

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fluorescence spectroscopic technique cannot be applied to thick substances due to large absorbance and scattering of light [11]. From this analytical technique, it is possible to obtain fingerprints of food changes to evaluate the degradation/modification of some native fluorophores and development of neoformed fluorophores derived from Maillard reaction [9] or lipid oxidation [10]. Presence of fluorophores in mayonnaise makes FFFS an ideal candidate to monitor the changes on mayonnaise during storage.

Excitation-emission matrices (EEMs) acquired by systematically varying the excitation and emission wavelengths and collecting the resulting data matrix can be obtained from FFFS. Relevant information about fluorophores derived from EEM data can be extracted by multivariate analysis. Applications of multiway methodology in the food authenticity have been increased in the last years. In this context, parallel factor analysis (PARAFAC) [11] is the most commonly used second-order algorithm to decompose EEMs and it has already been applied in many food systems [12–17]. Nevertheless, the ideal trilinear structure of EEM necessary to describe the data with a few factors, is commonly affected by the handling of Rayleigh and Raman scatter [17]. Several ways of removing the Rayleigh or Raman scatter have been proposed in the literature, and an interesting work exhibiting the advantages of the modeling of fluorescence data using interpolation versus inserting missing data has been recently presented [18].

In addition, fingerprint obtained when food samples are characterized by measuring properties that vary because of ageing, storage time and/or different stages of processing can be characterized using multiway tools [19]. In fact, multiway classification methods as multiway partial least squares discriminant analysis (NPLS-DA) have been used in food authentication [20,21].

In this paper, the modifications that occur in mayonnaise samples were monitored by FFFS at two different temperatures. The application of PARAFAC to these data makes it possible to recover the signals corresponding to the various mayonnaise fluorescent constituents, without the necessity of a physical separation. For this reason, a comparative study with several mayonnaise fluorescents components determined by HPLC was performed. In order to showcase the potential of EEM data in combination with NPLS-DA, the mayonnaise classification based on storage time was evaluated.

2. Materials and methods

2.1. Materials and reagents

Perchloric acid p.a. and chloroform p.a. were supplied by Cicarelli (San Lorenzo, Argentina). Acetonitrile and methanol HPLC–grade were obtained from Merck (Darmstadt, Germany). HPLC–grade water was obtained from a Milli–Q Biocel System (Millipore SAS, Molsheim, France).

Tryptophan, tyrosine, pyridoxine, riboflavin and nicotinamide adenine dinucleotide were purchased from Sigma (Sigma-Aldrich Inc., St Louis, USA). Solutions and solvents for mobile phase were always filtered through 0.45 μm nylon filters. Standards and sample solutions were also filtered through syringe 0.20 μm nylon membrane before injection in the chromatographic system.

The ingredients used in mayonnaise preparation were corn oil, white vinegar (6% w/v acetic acid), salt and chicken eggs purchased from a local supermarket.

2.2. Sampling and storage conditions

Homemade mayonnaise and commercial mayonnaises samples were analyzed. A total of 9 commercial mayonnaise trademarks with a fat content of 35.5–42% were purchased at local markets in packed form (Santa Rosa, La Pampa, Argentina). The samples were divided into two lots (10 samples per lot). One lot was stored at 5 °C, while the other lot was stored at 37 °C for both to be analyzed throughout six days in ten storage times. All samples were analyzed immediately after opening and it was considered as the starting point of the storage kinetics.

2.3. Homemade mayonnaise preparation

Mayonnaise was prepared from chicken eggs using the following formula: fresh egg yolk (15%), white vinegar (12%), corn oil (70%), and salt (2%). The mixing of ingredients was performed using an electric mixer (Philips HR7625/70). The dry ingredients were mixed separately in a container using one-third of the total amount of vinegar until a smooth paste was obtained. The paste was added to the egg yolk and mixed for 5 min. Oil was added slowly under continuous mixing to form the emulsion; after all the oil was added, mixing continued for 5 min. This was followed by the addition of the remaining vinegar and mixing continued for additional 5 min [2].

2.4. Instrumentation and procedure

2.4.1. Fluorescence spectroscopy

The measurements were performed on a Perkin Elmer LS-55 fluorescence spectrometer equipped with a front surface accessory with an incidence angle of the excitation radiation of 42°. Excitation and emission slits were both set at 5 nm and photomultiplier voltage set to 850 mV. Fluorescence excitation spectra were recorded between 230 and 400 nm (increment 5 nm), and emission wavelengths from 300 to 600 nm, spaced by 0.5 nm interval in the emission domain. Fluorescence measurements were done in triplicate for each sample. The spectrometer was interfaced to a computer supplied with FL Data Manager Software (Perkin–Elmer) for spectral acquisition and data processing.

2.4.2. HPLC analysis

2.4.2.1. Chromatographic conditions and data generation. All experiments were performed using an Agilent 1100 Series liquid chromatograph equipped with a quaternary pump, degasser membrane, thermostatted column compartment, autosampler and diode array detector (DAD) (Agilent Technologies, Waldbronn, Germany). The Chemstation version B 0103 was used for data acquisition and processing. The HPLC column was a Zorbax C18 (4.6 × 75 mm, 3.5 μm particle size) from Agilent.

The time-emission fluorescence data matrices (TEM) were registered in the emission spectral range between 300 and 600 nm, with the excitation wavelength fixed at 270 nm, which was selected as a compromise wavelength considering the excitation maximum of each analyte, in the elution time period from 0.0 to 15.0 min. The detector gain was set at 14. In this way, TEMs consisted of 217 × 301 data points for elution time and spectral dimension, respectively.

2.4.2.2. Sample preparation for HPLC analysis. In order to process each sample, 2.00 g of mayonnaise was accurately weighed and placed into a 10 mL plastic centrifuge tube. Then, 5.00 mL of the perchloric acid 1% were added and the mixture was vortered for 5 min, sonicated for 10 min, and then centrifuged at 3500 rpm for 10 min and the supernatant was transferred to centrifuge tube. After that, 1.00 mL of chloroform was added and the mixture was vortered for 5 min and then centrifuged at 3500 rpm for 10 min. Subsequently, the supernatant was filter and 5 μL were injected into the HPLC.

2.5. Statistical analysis

2.5.1. Preprocessing of spectra

EEM landscapes were preprocessed to reduce the scattering effects. A method for handling scattering using interpolation in the areas affected by first- and second-order Rayleigh scatter and avoid the so-called "inner-filter effects" was applied [23].

2.5.2. Parallel factor (PARAFAC) analysis

PARAFAC is a decomposition method used to higher-order arrays. A set of common factors can be used to describe simultaneously the variation occurring in several matrices albeit with different weighting coefficients for each matrix. In this work, PARAFAC analysis was used to analyze a data set when the spectra were recorded on mayonnaise sample under different conditions of temperature and storage time, in order to follow the storage kinetic evolution. Thus, the spectral data were arranged in a cube structure with sample storage time on the 1st mode, and emission and excitation wavelengths on the 2nd and 3rd mode, respectively. PARAFAC models of mayonnaise samples were developed for each storage temperature (three-way fluorescence array with 9 storage time, 302 emission wavelengths, and 35 excitation wavelengths).

The number of PARAFAC components necessary to reconstruct the data was determined through core consistency diagnostic (CORCONDIA) [24]. When the core consistency drops from a high value to a low value (below 50%), it indicates that an appropriate number of components has been attained. Furthermore non-negativity constraint was applied in three modes since both the spectral intensities and fluorophores concentrations are known to be positive [25].

2.5.3. N-PLS discriminant analysis (NPLS-DA)

N-PLS is an extension of PLS to handle data in three dimensional arrays [26]. The principles are similar to the PLS algorithm. N-PLS discriminant analysis (NPLS-DA) applies the N-PLS algorithm to classification. The aim of this technique is to predict the membership of an individual to a qualitative group defined as a preliminary [27]. Comparison of the predicted groups to the real group is an indicator of the quality of the discrimination and it is valued as the percentage of correct classification [19].

In order to build classification models, NPLS-DA was applied to spectra recorded on mayonnaise samples throughout storage at 37 °C. Data set was split into two sample sets. Training set for data modeling and internal validation with the full cross-validation procedure, and prediction set for evaluation the discriminative power of the models were randomly partitioned. Mayonnaise samples were classified into ten groups, according to their storage time.

2.5.4. Sofware

Chemometric analyses were performed using MATLAB version R2014b (The Mathworks Inc., Natick, Mass., U.S.A.). Data processing routine based on Optimized Warping Correction (COW) used to align the chromatogram peaks, was available in http://www.models.life.ku.dk/DTW_COW. The algorithms in use were from PLS_Toolbox ver. 8.2 (Eigenvector Research, Inc., WA). The correction function EEMscat available for Matlab, used to implement the interpolation methodology, was downloaded from http://www.models.life.ku.dk/EEM_correction.

3. Results and discussion

3.1. Replacing scattering areas with interpolated data

The interpolation method selected to remove first and second-order Rayleigh scatter consists of defining the window width for the affected areas (parameters required in the interpolation). Then, the measured signal in the width-defined window is removed around the scatter lines for every emission spectrum. Subsequently, the window is replaced with the interpolated values [18,23]. In order to remove the scattering effects, the width of the scatter areas was assessed. The widths used for first and second-order Rayleigh scatter areas for dataset were ±20 and ±25 nm, respectively. First and second-order Rayleigh scattered areas were replaced with interpolated values, as shown in Fig. 1.

3.2. Evolution of EEMs during storage

Fluorescence spectra recorded on mayonnaise samples provide information about the fluorescent molecules environment. NADH, vitamin A, and proteins containing fluorescent amino acids such as tryptophan, tyrosine, and phenylalanine residues are the best-known fluorescent molecules in foods [5].

Changes in spectra on a homemade mayonnaise samples during storage time at 5 °C and 37 °C can be observed by visual inspection of EEMs in Fig. 2. It can be clearly seen some mayonnaise components increasing and others decreasing over time. These assessments are well-observable in mayonnaise maintained at 37 °C. Mayor visual differences in the EEMs from mayonnaise samples stored at 5 °C were not appreciated during the evaluation time. In addition, commercial samples presented similar spectral evolution (plot not shown).

3.3. Decomposition of three-way spectral data using PARAFAC

Fluorescence data sets were arranged into two three-way fluorescence arrays (storage time × emission spectra × excitation spectra), i.e., one for each storage kinetic, and PARAFAC analysis was implemented. Thus, these two arrays were decomposed to evaluate the pure spectra of fluorophores contributing at mayonnaise storage time. Consequently, a PARAFAC model with 3 factors was used to describe the matrices formed by spectra data recorded at 5 °C and 37 °C, exhibiting 52% robustness and 98.8% of explained variance. The results, in terms of loadings plots for the three first factors, are shown in Fig. 3. The loading profiles of the first three PARAFAC components model showed maximum emission at 348 nm, 426 nm, and 398 nm, with a maximum excitation at 295 nm, 355 nm, and 320 nm for the first, second and third factors, respectively (Fig. 3).

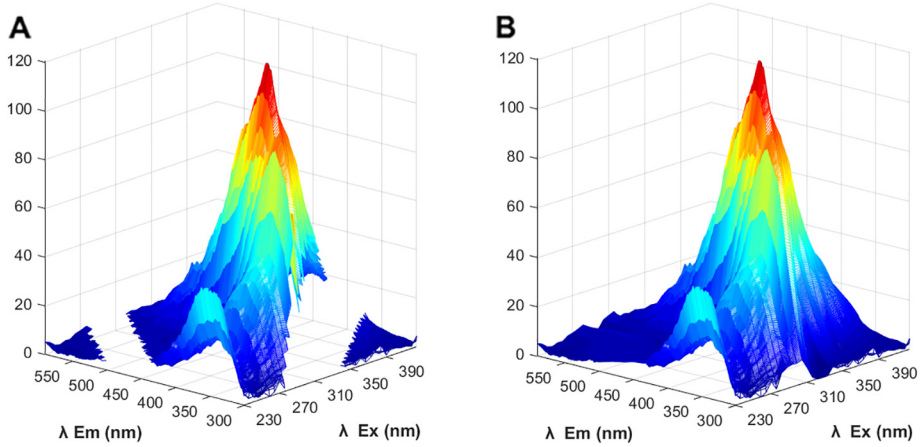

Fig. 1. An example of the EEM of one mayonnaise sample landscape: (A) EEM after scattering areas has been set to missing. (B) The same EEM after interpolation.

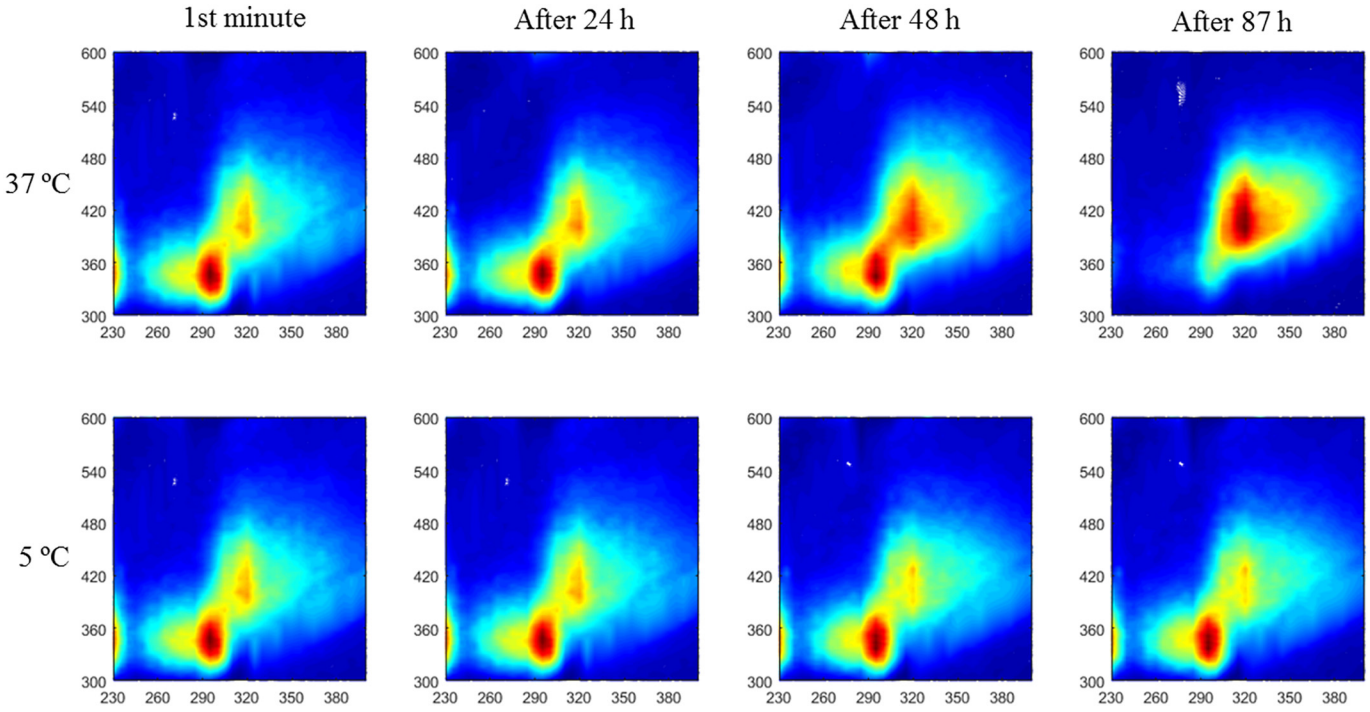

Fig. 2. Contour plots of EEMs from homemade mayonnaise sample at the first minute of analysis, after 24, 48, and 87 h, respectively. Stored at 37 °C (up) and 5 °C (bottom).

Interestingly, these PARAFAC profiles can be related to some specific fluorophores if an inspection of a list of food-relevant single compounds containing fluorescence spectral properties is carried out [7]. Thus, the excitation and emission profiles of PARAFAC factor 1 could be related to tryptophan (Em = 357 nm/Ex = 280 nm) and/or vitamin E (Em = 326 nm/Ex = 298 nm). On the other hand, nicotinamide adenine dinucleotide (NADH-Em = 465 nm/Ex = 344 nm) present fluorescent properties that could be associated to PARAFAC factor 2. Lastly, PARAFAC factor 3 profiles could be attributed to the excitation and emission spectra of the vitamin B6 (Em = 393 nm/Ex = 328 nm) owing to their similarity.

However, emission and excitation wavelengths values informed correspond to specific spectral value of pure fluorophores. For that, it is relevant to consider the phenomena related to the food nature that will influence the fluorescence signal such as the concentration and the molecular environment of the inherent fluorophores. A specific fluorophore studied in different foods can present different spectral signals. In addition, temperature also affects the fluorescence signal through its impact on dynamic quenching [17,28]. For this reason, the wavelength values found in this work for the fluorophores present in mayonnaises are not exactly equal to the values reported for pure fluorophores.

These same fluorophores have been studied in food, and have been related to changes with the growth of microorganisms, thermal changes, stored conditions and packaging [12,15,28]. It should be taken in account that the shelf-life of mayonnaise is not limited by microbial spoilage, but its quality is strongly influenced by oxidative changes of their fat component; the fluorescent compounds could be correlated with lipid oxidation products. In fact, fluorescence spectra which could be used for monitoring spoilage on mayonnaise can be detected for monitoring lipid oxidation.

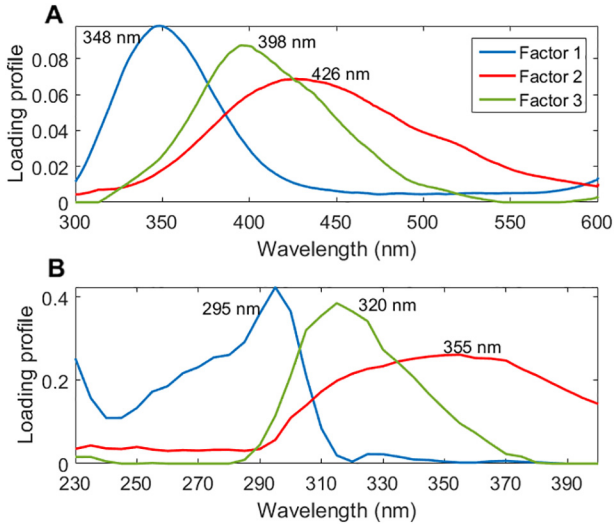

Fig. 3. Loading plot for first three components PARAFAC models constructed on EEMs of mayonnaise sample stored 5 °C and 37 °C. (A) Emission profiles and (B) excitation profiles.

3.4. Comparison of evolutionary profiles in mayonnaise stored at 5 °C and 37 °C

Loading plots of the relative concentration profiles for the three PARAFAC models components of the homemade mayonnaise samples maintained at 5 °C and 37 °C are displayed in Fig. 4.

For mayonnaise stored at 37 °C, factor 1 shows a concentration relatively constant in the first evaluation times, and an abrupt growth from 48 h, approximately (Fig. 4A). This increment along the time axis indicates that this fluorescent oxidation product is being formed during storage time. The situation is entirely different for Factor 2 and 3, exhibiting similar behavior. Both factors decrease fast and continuously afterward first storage time (15 h). This decrease along the time axis indicates the degradation of oxidation products. Changes describing the evolution of these components along time are correctly correlated with the visual changes observed on the contour plots indicating the mayonnaise spoilage (Fig. 2). Furthermore, profiles of relative

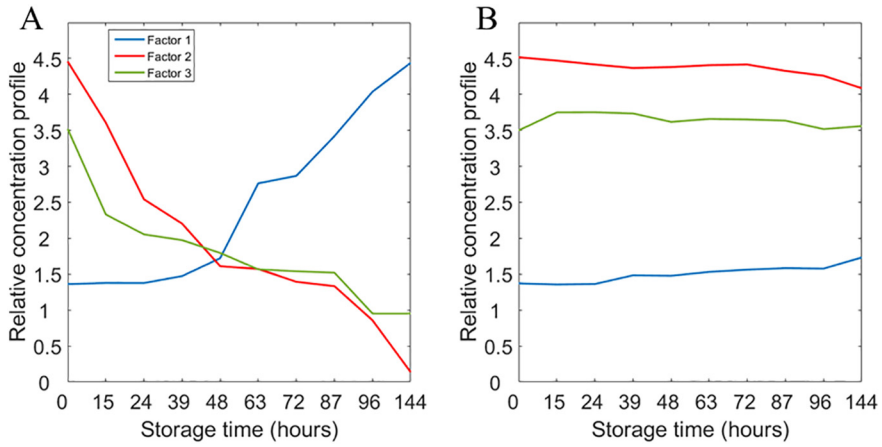

Fig. 4. Relative concentration profiles of the three main compounds extracted with PARAFAC describing the mayonnaise quality evolution time at 37 °C (A) and 5 °C (B).

concentrations for mayonnaise stored at 5 °C were relatively constant along the time for this storage temperature (Fig. 4B).

3.5. HPLC analysis

After confirming the changes produced in mayonnaise components observed in the EEMs, and in order to know the specific compound concentrations which decrease or increase, a chromatographic analysis was performed. The chromatograms were performed at every storage condition.

In this analysis, five standard fluorescent compounds were determined with the following elution order: pyridoxine (B6), tyrosine (Tyr), tryptophan (Try), nicotinamide adenine dinucleotide (NADH) and riboflavin (B2). The chromatographic peaks of B6, Tyr, Try, and NADH were observed at emission wavelength = 350 nm, while the B2 peak was detected at 500 nm. Four chromatograms acquired throughout 87 h of homemade mayonnaise storage are shown superimposed in Fig. 5. Three of the five analyzed compounds (Tyr, Trp, and B2) were presented in all the samples, while NADH was only presented in the commercial mayonnaise samples. This find was expected due to that it is used as antioxidant to prolong the shelf-life of commercial mayonnaise products [29]. Pyridoxine was not presented in none of the samples. The chromatographic analysis confirm the decrease of the tyrosine and tryptophan concentrations in the time evaluated, while the B2 and NADH concentrations were maintained relatively constant. Both, Tyr and Trp can be directly related to the second and third PARAFAC factors because the decreasing of other compounds was not observed. Moreover, after 48 h storage time the presence of two unidentified compounds was detected, some of them related to the first PARAFAC component.

3.6. Discriminant ability evaluation of EEMs

The previous experiments confirmed the ability of the EEMs modeling as a simple and fast tool to know about the stability of the mayonnaise. Thus, a new experiment was conducted in order to test the

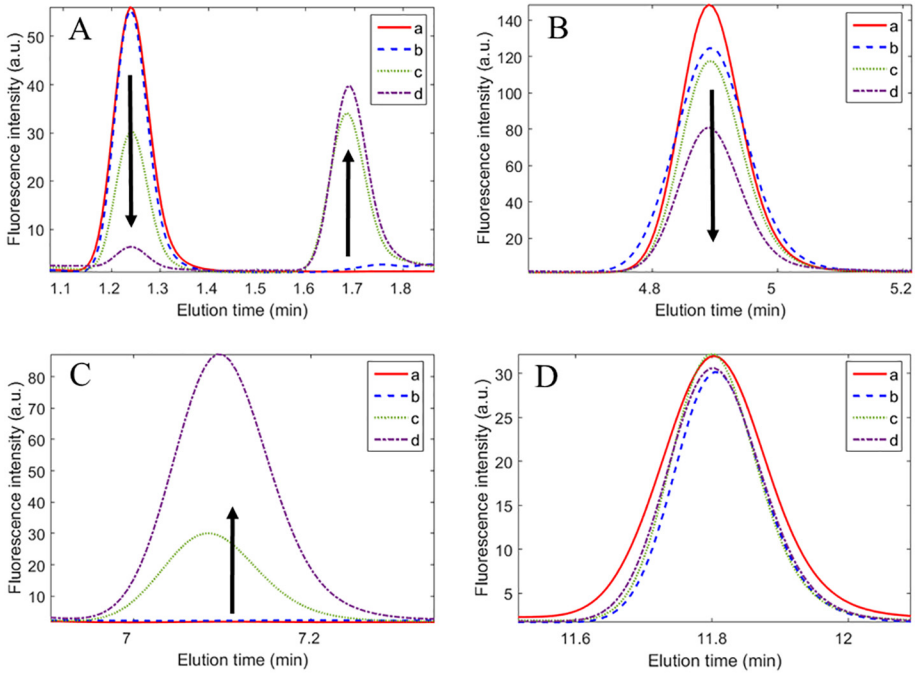

Fig. 5. Chromatograms corresponding to a homemade mayonnaise sample stored at 37 °C containing (A) tyrosine at λ_{em} = 350 nm plus one unidentified peak, (B) tryptophan at λ_{em} = 350 nm, (C) unidentified peak, and (D) riboflavin at λ_{em} = 500 nm; (a) opening in the first minute, (b) after 12 h, (c) after 48 h, and (d) after 87 h. The arrows show the concentration modification of the compound during the storage time.

ability of the EEMs to discriminate between each of the ten storage times.

Fluorescence data collected during the storage kinetic at 37 °C were combined in a three-dimensional array (100 samples × 302 emission wavelengths × 35 excitation wavelengths). Then, NPLS-DA was applied on the data set considering the following classes:1 (0 h), 2 (15 h), 3 (24 h), 4 (39 h), 5 (48 h), 6 (63 h), 7 (72 h), 8 (87 h), 9 (96 h) and 10 (144 h).

In order to build classification models, the data set was randomly partitioned into two samples set. The training set containing seventy samples, seven for each storage time, was used for data modeling and internal validation with the full cross-validation procedure. The prediction set (including independent samples) with thirty samples, three for each storage time, to evaluate the model discriminative power.

NPLS-DA results showed a highly discriminant model using three PLS factors, capable to obtain 100% of correct classification for both training and prediction sets from the data set recorded at 37 °C.

The data sets obtained from fluorescence methods contain information about kinetic of mayonnaise spoilage which could be used for reliable determination of mayonnaise quality. Interestingly, several research evaluating food changes under different conditions have found good classifications from fluorescence spectral data, but none of them have dealt classification methods of multiway arrays [12–15,30]. The models obtained through this methodology consider the contemporary contribution of multiple effects. Data analysis applying multiway methods is more efficient in order to capture and interpret the underlying structure in a data set [19].

4. Conclusions

The obtained results were encouraging and showed a promising potential of FFFS for detecting spoilage on mayonnaise during storage kinetic at different temperatures. PARAFAC allows obtaining wide information about EEMs and the results suggest that the spectral information is originating from the mayonnaise spoilage. In addition, through chromatographic analysis it was possible to know some compounds related to mayonnaise storage kinetic.

As a result, a good discrimination of mayonnaise samples stored under different conditions can be achieved by studying spectral data sets according to their storage time and, the obtained models could be employed to determine the mayonnaise shelf life. For that, these results must be also complemented with sensory analysis to check for the presence of off-odors and off-flavors in mayonnaise stored under temperature to determinate the time in which mayonnaise maintain adequate quality attributes.

In the present study, the proposed method is shown as a simple and fast way to obtain information about the mayonnaise oxidative stability, allowing analytical time and cost reduction compared to the traditional physical-chemical analysis.

Thereby, FFFS along with multi-way chemometric approaches is a potential innovative method to monitor lipid oxidation changes taking place in the mayonnaise during storage. In addition, it could be used as a screening method for the mayonnaise quality assessment stored under temperature.

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