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Stability of Avocado and Pequi oil During Heating: Study Using Ultraviolet Visible Spectroscopy and Chemometrics Methods of Curve Resolution

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Abstract

Avocado and pequi oils were analyzed by UV-Vis spectroscopy and chemometric methods of curve resolution. When vegetable oils are heated at high temperatures, oxidation products are formed, which besides being harmful to human health strongly accelerates the antioxidants degradation. In this sense, monitoring antioxidants and oxidation products can provide information about the best conditions to its consumption. Therefore, this study aimed to evaluate antioxidants and oxidation products behavior in avocado and pequi oils. By applying Independent Component Analysis (ICA) in the avocado oil it was detected that antioxidant concentration decreased after 90°C. To the pequi oil, by applying Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) it was possible to detect that the transformations between antioxidant/oxidation products took place at 70°C. The results suggested that avocado oil is more resistant to high temperatures then pequi oil. Moreover, the methods used in this study suggest that chemomstric tools are feasible to accomplish spectrophotometric techniques in food quality evaluation.

Keywords: Avocado oil; Pequi oil; Oxidative stability; UV-Vis spectroscopy; MCR-ALS; ICA

Introduction

The development of analytical chemistry and in particular spectroscopy can be strongly improved through the development and application of mathematical methods of complex data analysis [1]. The progress in this issue has provided a huge toolbox named chemometrics, which implies in the use of mathematical, statistical, and formal logics methods to extract the most important information from the experimental data [2]. One of the most complex problems has been multicomponent spectral analysis of complex mixtures, which deals with the detection of a number of important components in a system with its identification and quantification being carried out without using any additional information [1] besides not using physical separation or isolation of the sample constituents. To solve complex mixtures in multicomponent spectral analysis, different methods as the ones based on self-modeling curve resolution, such as simple to-use interactive self-modeling analysis (SIMPLISMA) [3] and Evolving Factor Analysis (EFA) [4], methods represented by iterative algorithms such as multivariate curve resolution alternating least squares (MCR-ALS) [5] and methods based on blind source resolution as Independent Component Analysis (ICA) [6] are proposed.

Oils extracted from avocado and pequi naturally provides complex mixtures. Avocado (Persea americana Mill.) is an oleaginous fruit, which has a lipid content on approximately 25% of the edible portion with an energy density can be compared to the amount provided from a chicken breast. The principal components of the lipid fraction are monounsaturated fatty acids, which have been studied focusing on their cardiovascular benefits potential, including effects on serum lipids. In addition to its high content of monounsaturated fats, avocados contain several bioactive phytochemicals, including some carotenoids, B vitamins, vitamins C and E, terpenoids, d-manno-heptulose, hsitosterol, persenone A and B, and phenols. The bioactive substances in this fruit and in its extract or individual components have been shown antioxidant and radical suppressing activity [7]. In a study regarding on edible oils, the stability of the saponifiable and unsaponifiable fractions of avocado oil under drastic heating treatment (180°C) was compared to that of olive oil using gas chromatography with FID detection, where the stability of avocado oil showed similar behavior to that of olive oil [8]. The pequi fruit (Caryocar brasiliense) can be found in closed vegetation areas, and is explored mainly in extractive manners [9], displaying considerable quantity of carotenes which are responsible for the colors, varying from the yellow to red, presented by the oil. Besides pigmentation, carotenes are precursors of vitamin A and some of them presents antioxidant activity, being considered in between the functional foods. Epidemiologic evidences demonstrates that diets rich in carotenes are related to the decrease of cancer incidence and cardiovascular diseases, as well as protecting membrane cells and lipoproteins against oxidative damages [10]. The pequi oil has being used in the popular medicine thanks to its medicinal properties and now at the cosmetic industry [11]. Moreover, pequi oil is used as a food fryer [9] and as sauce in Brazilian regional typical dishes [12].

Oxidation of lipids presented in oils is an undesirable chemical change that may impact on flavour, aroma and consequently on nutritional quality of oils with significant implication on human health and deeply in the product commercial value. The major compounds produced during vegetable oil oxidation are hydroperoxydes, aldehydes, alcohols and some acids. The oxidation processes are generally considered to occur following the radicalar organic reactions steps: an initiation or induction, a propagation, and a termination step. The products of each of these steps will increase and decrease over time making it difficult to quantitatively measure lipid oxidation [13]. Therefore, it is becoming imperative to be able to check the evolution of oils quality which can be altered by oxidation processes induced by

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oxygen presence and especially accelerated by heating of avocado and pequi oils. In this paper, transformations that occurred in avocado and pequi oil samples when heated from ambient to high temperatures, such as happens during frying (~170°C) [14], were monitored by ultraviolet-visible spectroscopy (UV-Vis). The application of chemometric curve resolution methods such as MCR-ALS and ICA made it possible to resolve the signals corresponding to the pure spectra and relative concentration of the oil sample constituents without resorting to physical separation methods. The aim of this work is to show the possibility of applying different curve resolution methods to analyze oils during heating in order to monitor its oxidation products.

Material and Methods

Samples

Commercially-available avocado and pequi oils were purchased in the Brazilian marketplace. To these samples, in accordance to the label information found on the flask, no stabilizers or additives are present.

Experimental parameters and software

The samples were heated from 30°C until 170°C, increasing from 10 to 10°C, being the first spectrum taken at the room temperature (25°C). UV-Vis spectra were acquired in the range of 200 to 900 nm (2 nm resolution) in a 1mm pathway quartz cuvette, using a PG Instruments LTd T80+. After organizing the data into matrix, it was analyzed using MATLAB version R2007b (The Mathworks Inc., MA, USA). Chemometric curve resolution was performed by Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) and Independent Component Analysis (ICA). The MCR-ALS algorithm code and Guidelines User Interface for MATLAB are freely available at MCR-ALSwebpage at http://www.mcrals.info/. The Independent Components Analysis (ICA) was performed using the JADE algorithm.

Theory

Independent component analysis

Independent Component Analysis is one of the several blind source separation techniques that have been developed with the aim of extracting the pure underlying signals from a set of signals mixed in unknown proportions.

Based on the Central Limit Theory, ICA assumes that the statistically independent source signals have intensity distributions that are less Gaussian than their mixtures [15]. The general ICA model is obtained trough [16]:

$$\mathbf{X = AS} \quad (1)$$

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.

Multivariate curve resolution alternating least squares

There are many multivariate curve resolution (MCR) techniques and all of them have as main objectives the isolation, resolution, and relative quantification of the main sources of variation in a particular data set. The outstanding feature of this technique is that no a priori chemical assumption about the contribution of the different components is necessary [17]. Mathematically, multivariate curve resolution methods are based on a bilinear

Model like the one given in equation (2)

$$\mathbf{D=CS^T+E} \quad (2)$$

The goal of MCR-ALS is the bilinear decomposition of the data matrix D into the true pure response profile associated with the variation of each contribution in the row and the column directions, represented by matrices C and ST, respectively, which are responsible for the observed data variance. MCR-ALS solves iteratively equation (2) by an alternating least squares algorithm which calculates concentration C and pure spectra ST matrices optimally fitting the experimental data matrix D. This optimization is carried out for a proposed number of components and using initial estimates of either C or ST [18]. Initial estimates of C or ST can be obtained either using EFA [4] or, like in this study, using SIMPLISMA [3]. During the ALS optimization, several constraints can be applied to model the shapes of the C and ST profiles, such as non-negativity, unimodality, closure, trilinearity, selectivity or/and other shape or hard-modeling constraints [19]. The constraints used in this study were non negativity for the concentration and spectra while unimodality were applied to concentration.

Convergence is achieved when in two consecutive iterative cycles, relative differences in standard deviations of the residuals between experimental and ALS calculated data values are less than a previously selected value, usually chosen as 0.1% [18].

Results and Discussion

MCR-ALS was applied to resolve the pure spectra and concentration profiles of the two different components in each oil sample, in accordance with ST initial estimative performed by SIMPLISMA. The constraints applied during ALS optimization were non-negativity (for both spectra and concentration profile) and closure only to the concentration profile. ICA, applied from JADE algorithm, does not requires constraints and initial estimative. For the two different components, considered in this study, it is known that the antioxidants, as in the case of tocopherol, shown the maximum absorbance peak at 325 nm while oxidation products presented absorbance band from 390 to 550 nm [20]. The UV-Vis spectra of the heated avocado oil are shown in Figure 1(A). In Figure 1(B-D), the concentration profiles resolved to the avocado oil is given in detail (Figure 1).

From this plot it was possible to see the antioxidants and oxidation product components spectra and its stability during heating by monitoring its relative quantity profiles. The profiles changed according to the nature of the UV-Vis absorbent responsible for the constituent and evolved with the increasing of the temperature. The results showed that the antioxidants concentration decreased and oxidation products increased by increasing the temperature. These results are in agreement with previous studies [13,21-24] that show spectral profiles changing and evolving accordingly with heating. In that study, to all cases antioxidant concentration decreased while oxidation products concentration increased as the temperature was increased up to 170°C.

In the avocado oil the ICA method was applied and the results are presented in Figure 1. It indicates that antioxidants concentration started to decreased at 90°C, which are also in agreement with previous studies about olive oils [8,21] indicating that avocado oil and olive oils are similar, according to the formation of products derived from fatty acids oxidation and lipid profile. The UV-Vis spectra of the pequi oil heated in different temperatures are shown in Figure 2(A). In Figure 2(B), the concentration profiles resolved by MCR-ALS are given in detail, where it is shown that antioxidants concentration has decreased while oxidation products increased trough the temperature.

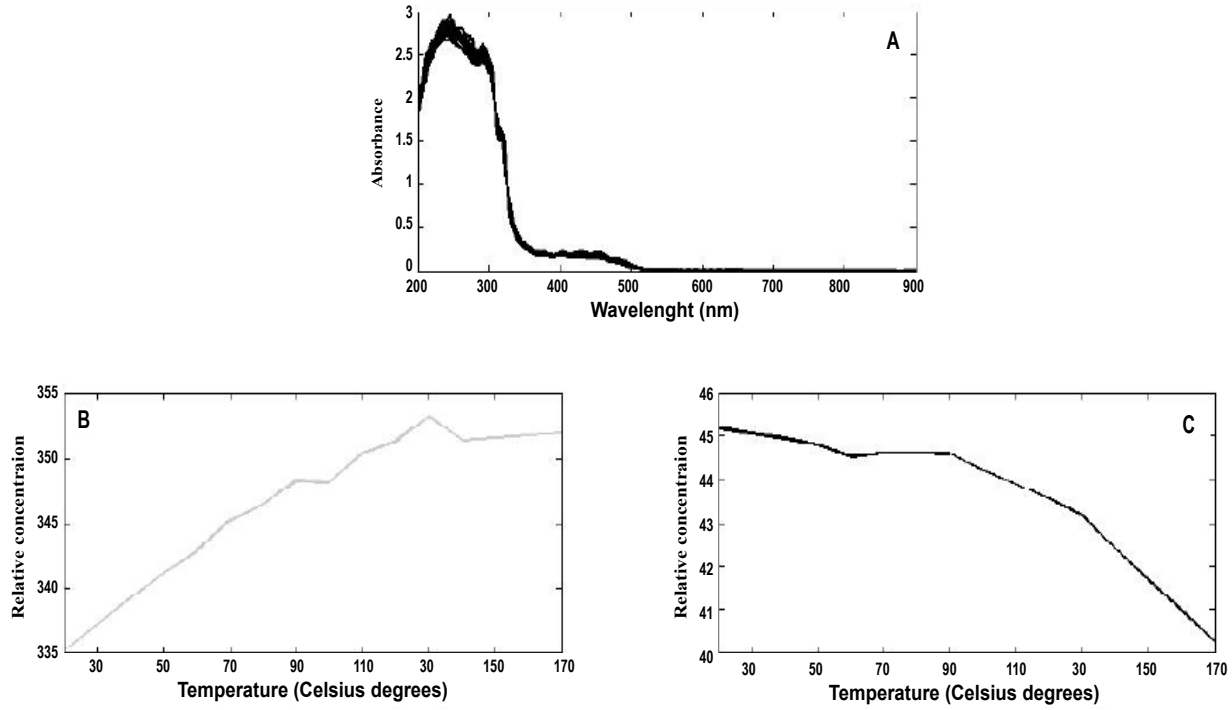

Figure 1: (A) Avocado oil spectra, (B) and (C) ICA results (----) oxidation Products (---) tioxidants.

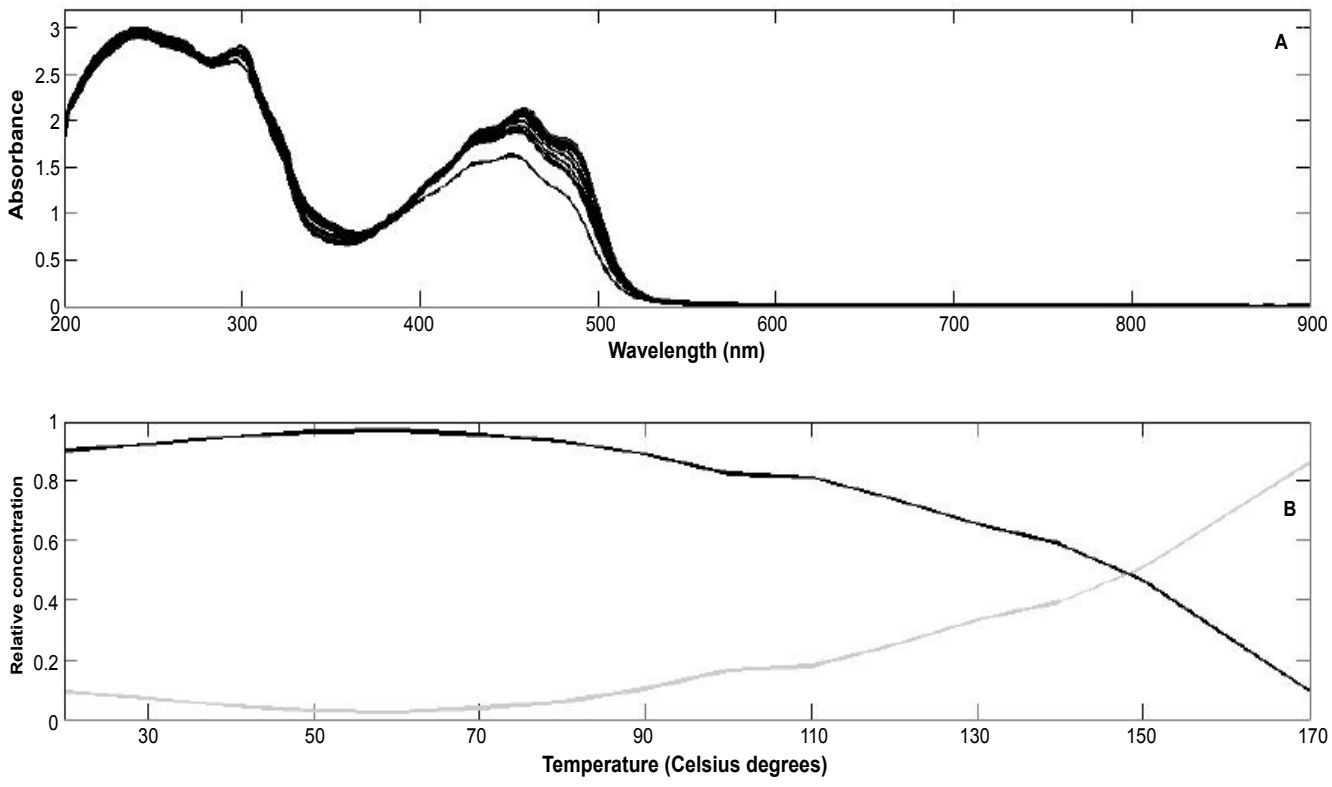

Figure 2: (A) pequi oil spectra, (B) MCR-ALS results (----) oxidation products (----) antioxidants.

The methods used here to monitor the oils transformations are feasible tools once there are only spectroscopic equipment available. Nonetheless, a significant drawback should take place when there is no information about thespectra of the analytes of interest because of rotational ambiguity intrinsic inresolution methods [25] (Figure 2).

These transformations observed in pequi oil started at 70°C. The results obtained from this study also indicate that the concentration of monounsaturated fatty acids in pequi oil was lower than in the avocado oil.

Conclusion

This paper reports the use of UV-Vis spectroscopy as a tool to determine and compare the oxidative stability of avocado and pequi oils. The use of the MCR-ALS and ICA methods provided the description of two principle issues, degradation of antioxidants and the appearance of oxidation products, implicated in the oxidation process. Based on these data, MCR-ALS and ICA could be used to determine the contribution of various chemical compounds to oxidative phenomena and the comparison of oils according to its stability. The advantages of ICA, with JADE algorithm, compared with MCR-ALS are no use of constraints and no need initial estimative. Nonetheless, the use of ICA in chemical data is always questionable regarding on the independence criteria required to the usage of this tool.

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