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Analytica Chimica Acta 570 (2006) 129–135
ANALYTICA CHIMICA ACTA
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A new method for determination of the oxidative stability of edible oils at frying temperatures using near infrared emission spectroscopy

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Received 29 January 2006; received in revised form 30 March 2006; accepted 30 March 2006
Available online 18 April 2006

Abstract

This work proposes a new method for determination of the oxidative stability of edible oils at frying temperatures using near infrared emission spectroscopy (NIRES). The method is based on heating an oil sample at a fixed temperature, followed by the acquisition of the emission spectra with time using a home-made spectrometer with an acousto-optical tunable filter (AOTF) as monochromator. The induction time, related to the oxidative stability, is determined by means of the emission band at 2900 nm and its increase and broadening during the heating time. After the induction period, this band also provides information related to the oxidation rate of the sample. Twelve samples of edible oils, of different types and from different manufacturers, were analyzed for oxidative stability with mean repetitivity of 3.7%. The effects of nitrogen insertion, heating temperature and the presence of antioxidant compounds on the oxidative stability were evaluated.

Keywords: Near infrared emission spectroscopy; Edible oils; Oxidative stability; Instrumentation

1. Introduction

Oxidative stability is an important property of edible oils in food science. It is represented by the time in which an oil sample resists to oxidation and it can be used to evaluate when an oil reaches an oxidation level inadequate for human ingestion or even for its utilization in frying processes. This time, called induction time or induction period, has been determined by heating the sample to a constant temperature and measuring a physical or chemical parameter with time. Therefore, if this parameter is related to the degree of oxidation of the sample, it will remain practically constant during the stability period of the sample and, afterwards, it will start varying allowing the determination of the induction time.

There are several chemical parameters used to determine the degree of oxidation of an oil sample. They are based mainly on measurements of primary or secondary oxidation products. In general, lipid oxidation is described by a free-radical chain mechanism: (1) initial free radicals formation ($RH \rightarrow R^{\bullet} + H^{\bullet}$); (2) propagation of the free radicals and formation of primary oxidation products such as hydroperoxide ($R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$, $ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$); and (3) termination steps and formation of secondary oxidation products ($R^{\bullet} + R^{\bullet} \rightarrow R\text{–}R$, $R^{\bullet} + ROO^{\bullet} \rightarrow ROOR$, $ROO^{\bullet} + ROO^{\bullet} \rightarrow O_2 + ROOR$ or alcohol and carbonyl compounds) [1]. The peroxide value (PV) is based on determination of the hydroperoxide content, a primary oxidation product [2]. There are two important methods for determination of oxidative stability using PV. In the Schaal test [3], PV is determined every 24 h for a sample placed in an open cup in an oven at 60 °C until the induction time can be determined. In the Swift test [4], or active oxygen method (AOM), an air stream is passed through a sample heated at 98 °C and its PV is periodically determined by an iodometric procedure. Among the secondary oxidation products commonly measured, aldehydes, ketones and acids can be cited. The carbonyl value (CV) is based on determination of total carbonyl content, which is related to the sum of aldehydes and ketones. This has been made by means of chemical reactions with the formation of coloring products, such as reactions with hydrazines, or a gas-chromatographic procedure [5]. The anisidine value (AV) is based on the determination of α and β-alkenal content [6]. Some of these parameters can be also determined by quick tests based on colorimetric procedures [7]. The content of low molar mass acids is the basis of an important automatic method for determination of oxidative

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doi:10.1016/j.aca.2006.03.109

stability, the so-called Rancimat test [8], intensively employed since 1993 instead AOM. In Rancimat experiment, an air stream is passed through a sample, commonly heated up to 110 °C, and the effluent air is bubbled through deionized water. The conductivity of the water is continuously monitored. Therefore, the water conductivity increases when low molar mass acids, such as formic acid, are carried by the air and collected in the water. Among other methods for determination of oxidative stability, methods based on measurements of oxygen consumption [1,9] and thermal analysis [10–12], once the oxidation is an exothermal reaction, can also be cited. Melton et al. have presented a good review of the parameters used to determine the degree of oxidation of oils [7].

Vibrational absorbance spectroscopy in the infrared region also has been used to characterize edible oils. The vibrational modes and the ocurrence frequency of each vibrational mode depend on the chemical composition of the analyzed sample. Thus, infrared spectra show differences in the profile, maximum intensity and position of absorption bands according to the oil composition. Therefore, infrared absorption spectra have been used to classify different edible oils [13] and to determine some parameters related to the oxidation degree of these oils, such as the PV [14] and the AV [15]. In this way, oxidation monitoring and the determination of oxidative stability of vegetable oils using infrared absorption spectra is also possible and, in fact, they have already been employed [16,17]. As the near infrared (NIR) region is characterized by overtones and combinations of bands ocurring in the mid infrared region, near infrared absorption spectroscopy also has been used for classification [18] and determination of the degree of oxidation [19] of vegetable oils. An earlier work provided a good analysis of various infrared absorption bands, in both mid and near infrared regions, related to the oxidation degree of vegetable oils [20] and this was recently used for determination of oxidative stability [21].

Despite the large number of methods for determination of oxidative stability of edible oils, papers dealing with its determination at frying temperatures (commonly between 140 and 180 °C) are scarce. The reactions and mechanisms taking place in the degradation of vegetable oils are very dependent on the heating temperature. For instance, for temperatures up to 120 °C, the main reactions are hydrolysis and oxidation induced by moisture and atmospheric oxygen, whereas for temperatures above 120 °C polymerisation reactions also become important [22]. Therefore, as most methods are carried out at temperatures below to 120 °C, their results are not reliable in foreseeing oxidative stability at frying temperatures. In addition, most official methods are ineffective to evaluate the influence of the insertion of some antioxidant compounds or protective gases, like nitrogen, and the official Rancimat test fails when used at frying temperatures because the low molar mass components of oils can be carried off by the air stream. Another advantage of the determination of oxidative stability at frying temperatures would be a higher analysis throughput. As a rate of a reaction increases as the temperature increases, the induction time and, then, the analysis time decreases. For instance, the typical induction time values for methods based on daily determination of PV and AV at 60–70 °C are about 1–10 days [3,21] and it decreases to about 2–24 h in Rancimat test [8,12] due to the increase of about 45 °C in the heating temperature and it must decrease much more at frying temperatures.

Recently, a new method for determination of oxidative stability of vegetable oils at frying temperatures was proposed [23]. However, this method does not determine an induction time. It is based on determination of the polymerised triglyceride (PTG) content after heating an oil sample for 2 h. After this heating, one sample can possess a PTG content higher than another sample but its oxidation process can present a lower induction time and, consequently, a lower oxidative stability. The PTG content does not contain information on the induction time.

This work presents a new method for determination of oxidative stability of vegetable oils at frying temperatures based on acquisition of NIR emission spectra during heating.

2. Experimental section

2.1. Instrumentation

The NIRES instrument is based on an acousto-optical tunable filter (AOTF) made with a TeO_2 crystal, manufactured by Brimrose (TEAF_1.5–3.0), operating in the spectral region from 1500 to 3000 nm with nominal spectral resolution varying from 9 to 37 nm as the selected wavelength increases along its useful range. The AOTF was driven by a modulated (168 Hz) radio frequency (rf) signal generated by a digital synthesizer (Analog Devices–AD 9852), assembled to be controlled by a parallel interface (ICP-DAS A8111) placed into a micro-computer running a customized software written in Visual Basic 5.0. The detector is based on a thermoelectrically cooled (−10 °C) PbS element (Ealing Electro-Optics 043/035) aligned at 90° in relation to the plane of the output window of the AOTF, allowing measurement of both diffracted beams superimposed on the non-diffracted beam along the modulation. A lock-in amplifier (Stanford Research SR830 DSP) was employed for synchronous acquisition of the modulated signal of the detector. The analogue output of the amplifier was connected to the parallel interface, which was responsible for the conversion of the analogue signal to the digital domain with 12-bit resolution. The sample cell was a rod made of aluminum placed on the top of an aluminum cylinder, which contains a 60 W electrical heater used as excitation source. The heating system is within an acrylic tube which provides thermal isolation and the possibility of gas insertion at a low flow rate. The temperature of the sample was monitored by a calibrated thermocouple inserted in a small hole drilled in the body of the aluminum cylinder, at the point nearest to the sample cell. A digital meter was set to monitor the thermocouple signal, which was connected through a RS-232 serial interface to the computer. Fig. 1 shows the sample cell and the optical arrangement of the instrument. The instrument has been described in detail in an earlier work [24].

2.2. Samples analyzed

Twelve samples of edible oils were analyzed for oxidative stability using the new method. Eleven samples were obtained in

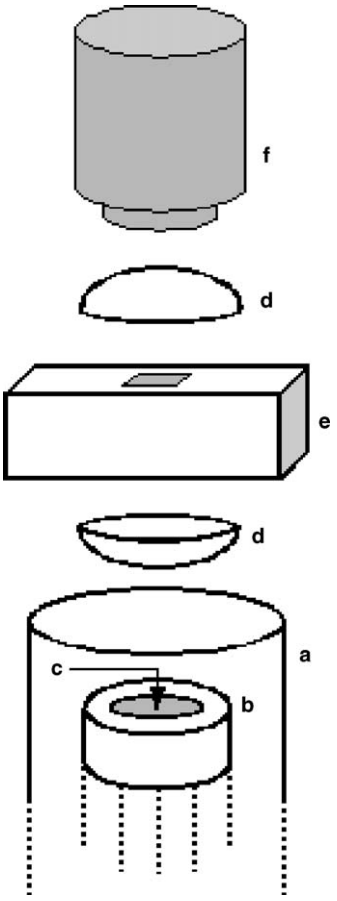

Fig. 1. Design of the sample cell and the optical arrangement of the instrument: (a) open acrylic tube containing the air or nitrogen stream; (b) sample cell; (c) circular groove to contain the sample; (d) CaF_2 lens; (e) AOTF; (f) PbS detector.

supermarkets, comprising different oil types and different manufacturers: two sunflower oil samples (called A and B), two soybean oil samples (C and D), two cottonseed oil samples (E and F), two corn oil samples (G and H), two canola oil samples (I and J) and one rice oil sample (K). The remaining sample was an unrefined rice oil sample (L). α-Tocopherol (Sigma) and γ-oryzanol (Tsuno) were added to one sample to evaluate their antioxidant effect.

2.3. Experimental procedure and data treatment

For each analysis, 10 μL of the sample were added to the sample cell. A nitrogen (99.99%) stream (1000 mL/min) was admitted around the heating system and the temperature was adjusted to 160 °C. The cell was then placed on the top of the heating system and the temperature was readjusted to 160 °C. After temperature stabilization, the nitrogen stream was substituted by a synthetic air stream (20% of oxygen) with same flow rate and raw emission spectra were continuously acquired as averages of five scans each in the region between 2650 and 3000 nm using a nominal resolution of 10 nm (5 s for each scan). Acquisition of the spectra was stopped when an appreciable increase of the band at 2900 nm was clearly visible. The intensities of raw emission spectra were converted to emissivity units using experimental blackbody spectra as reference [24]. The area of the emissivity signal between 2710 and 3000 nm divided by the area of the emissivity signal between 2650 and 2700 nm ($E_{2710–3000}/E_{2650–2700}$) was used as the parameter to determine the induction time during the oxidation process by means of a $E_{2710–3000}/E_{2650–2700}$ versus heating time graph, as discussed later.

3. Results and discussion

3.1. Emissivity spectra and oxidative stability

Fig. 2a shows a set of consecutive emissivity spectra obtained for a sunflower oil sample with heating time. As can be observed, the spectra remain practically unaltered at the beginning of the oxidation process but, after a determined time interval, the intensity and the width of the band at 2900 nm start to increase continuously. The band at 2900 nm is considered to be an overtone of glyceride ester carbonyl and its increase and broadening is due to the overlapping of two bands with it, one at a slightly higher wavelength related to hydroperoxides and another at a slightly lower wavelength related to alcohols [20]. Therefore, the area below the emissivity signal between 2710 and 3000 nm divided by the area below the emissivity signal between 2650 and 2700 nm ($E_{2710–3000}/E_{2650–2700}$) was used as the parameter related to the oxidation degree and the $E_{2710–3000}/E_{2650–2700}$ versus heating time graph (stability curve) was used to determine the induction time and, therefore, the oxidative stability. The area below the emissivity signal between 2650 and 2700 nm was used as a reference signal since this spectral region remains unaltered during the time interval monitored. The utilization of the areas is justified because the transformations in the peak at 2900 nm occur along a wide wavelength range (see Fig. 2a) and, furthermore, it improves the signal to noise ratio and allows a more precise location of the induction time instead of using peak heights. Fig. 2b shows the stability curve resulting from the emissivity spectra shown in Fig. 2a. The sudden increase of the $E_{2710–3000}/E_{2650–2700}$ ratio after a determined time interval, which defines the induction time, is clearly visible. The stability curve presents two distinct regions, one prior to the induction time, representing the stability period of the sample, and another after it, representing the oxidation period. Therefore, two linear regression curves can be defined, one for each region, and the induction time is calculated from the intersection between them, as shown in Fig. 2b. The curve slope in the oxidation period provides additional information related to the oxidation rate of the sample after the induction period. The stability curves for four samples with very different induction times are shown in Fig. 2c. The induction time (IT) values obtained for duplicates of the samples are shown in Table 1. Although the induction time is very dependent on the oil type, the differences between the values obtained for the two cottonseed oil samples or the two canola oil samples indicate that the induction time must be also dependent on crop time, the region where the seeds are picked and the manufacturing process of the oil. In general, as can be observed considering only the oil type, the more stable oils for frying processes were rice, canola and

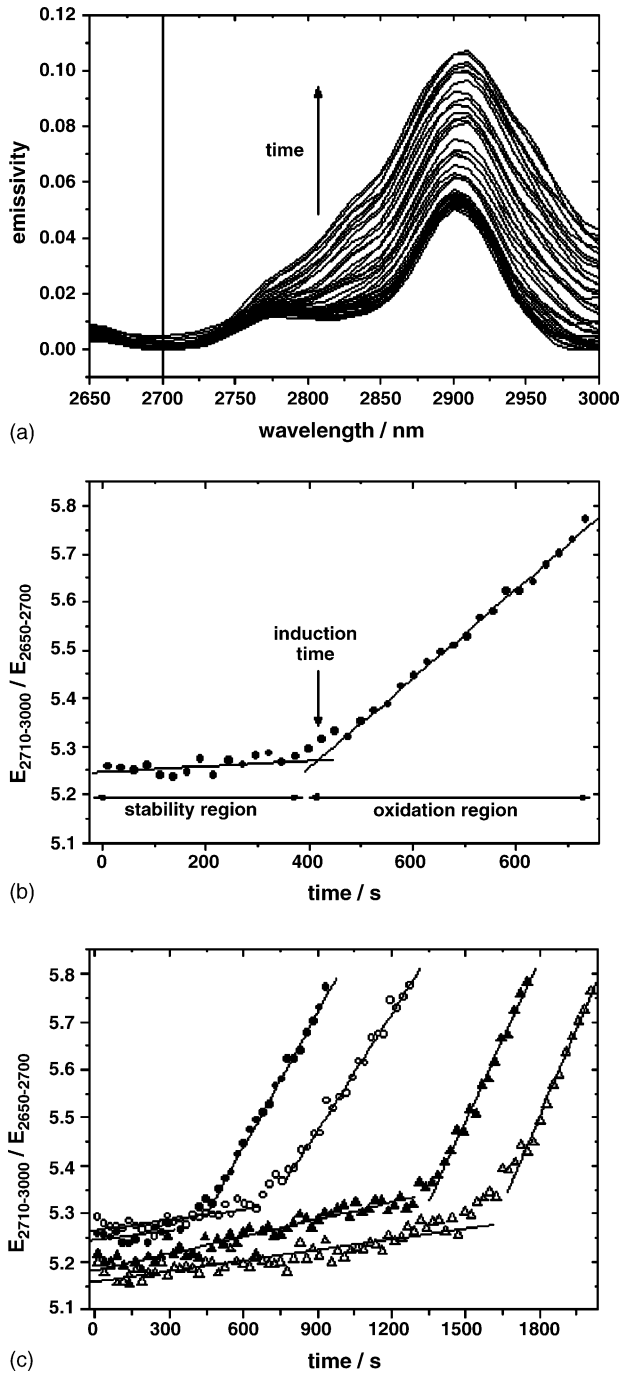

Fig. 2. (a) Emissivity spectra during the heating time for sample A and (b) resulting stability curve. (c) Stability curves for samples with different IT values: sample A (solid circles), sample E (open circles), sample G (solid triangles) and sample I (open triangles).

corn oils, whereas the less stable were sunflower and soybean oils.

3.2. Repetitivity

Three samples with very different IT values, from the whole range of IT values, were analyzed in five replicates to evaluate the repetitivity of the proposed method. The results, shown in Table 2, present a mean relative standard deviation (% S.D.) of 3.7%, which is comparable to the reproducibility of the Racimat test [8]. In addition, as can be observed, the higher the IT value, the lower the relative standard deviation, improving the repetitivity.

Table 1
Induction time (IT) values obtained for duplicates of the samples

Sample	Type	IT (s)	
A	Sunflower	436	419
B	Sunflower	599	612
C	Soybean	846	898
D	Soybean	1168	1084
E	Cottonseed	651	709
F	Cottonseed	1060	1080
G	Corn	1345	1374
H	Corn	1383	1348
I	Canola	1523	1570
J	Canola	1181	1167
K	Rice	1629	1615
L	Rice	1765	1734

3.3. Effect of nitrogen insertion

The effect of nitrogen presence on oxidative stability was evaluated by keeping the nitrogen stream around the heating system during the acquisition of the emission spectra. The comparison between the stability curves obtained with an air stream or in a nitrogen stream for a sunflower oil sample is shown in Fig. 3a. As can be observed, nitrogen does not avoid the degradation of the sample, but the degradation rate is slower than in presence of an air stream and there is not a clear definition of the induction time along the stability curve. Degradation still happens because polymerisation reactions, such as those for tryglyceride polymerisation, which are important only at frying temperatures, do not require oxygen to occur [23]. However, it is clear that the presence of oxygen promotes the occurrence of several oxidation reactions, accelerating the degradation rate after the induction period.

3.4. Effect of heating temperature

The effect of temperature variation on oxidative stability was evaluated by acquiring stability curves for a canola oil sample heated at temperatures between 160 and 190 °C. The results are shown in Fig. 3b. A decrease of the induction time and an increase of the slope during the oxidation period were observed when increasing the heating temperature. This demonstrates that the heating temperature affects not only the sample stability, but also the oxidation rate after the induction period. The induction time decreases approximately by half for every increase of 10 °C in the heating temperature. In addition, the logarithm of the inverse of the induction time and the logarithm of the slope in the oxidation period decrease lineally with the inverse of the temperature in Kelvin, as predicted by Arrhenius law. This indicates that, for instance, for a manufacturer of oils with high IT values, such as canola or rice oils, the oxidation stability analyses could be made at 170 or 180 °C and the results could be extrapolated to

Table 2
Repetitivity of the induction time (IT) values for five replicates (% S.D. = relative standard deviation)

Sample	Type	IT (s)					Mean (s)	% S.D.
A	Sunflower	436	419	455	401	426	427	4.7
F	Cottonseed	1060	1080	1074	987	1029	1046	3.7
I	Canola	1523	1570	1642	1611	1576	1584	2.8

foresee their oxidative stabilities at 160 °C, increasing analysis frequency. In addition, we were able to calculate the Arrhenius parameters for the stability period, related to the antioxidant reaction responsible for the resistance to oxidation, and for the oxidation period, related to the oxidation reaction, for the canola oil sample used. We found $2.5 \times 10^9\ s^{-1}$ and $104\ kJ\ mol^{-1}$ for the antioxidant reaction and $6.0\ s^{-1}$ and $30.4\ kJ\ mol^{-1}$ for the oxidation reaction.

3.5. Antioxidant effect

The antioxidant effect of some compounds present in edible oils was evaluated. This was done by comparison between two soybean oils where one of them was enriched with Vitamins A, D and E by the manufacturer (sample D), two rice oils where one of them was of an unrefined type (sample L), and by adding α-tocopherol and γ-oryzanol to a sunflower oil sample. The soybean oil enriched with vitamins showed a higher induction time (see Table 1) than the other soybean oil sample (sample C), as expected, due to the antioxidant action of the vitamins. Fig. 4 shows the stability curves for the rice oil samples. As the unrefined rice oil contains antioxidant compounds that are eliminated in the purification process, its stability curve presented a higher induction time and a lower slope after the induction period than the other rice oil sample. Fig. 5 shows the stability curves for a sunflower oil sample in which α-tocopherol or γ-oryzanol were added, with final concentrations of 1000 mg kg^{-1} or 1%, respectively, in comparison with the stability curve of the

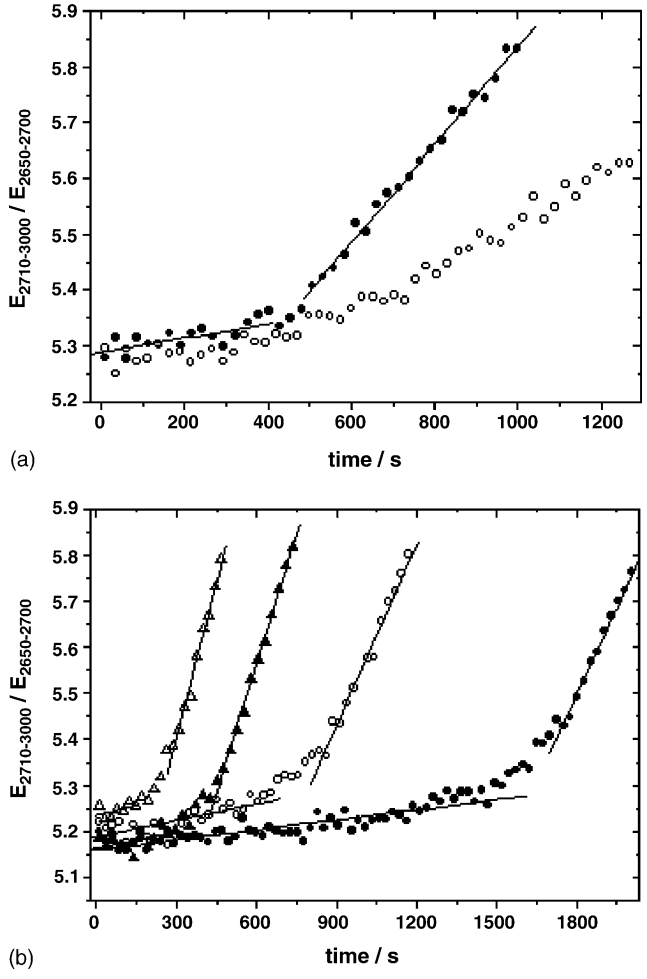

Fig. 3. (a) Stability curves obtained in a synthetic air stream (solid circles) and under a nitrogen stream (open circles) for sample A. (b) Stability curves obtained at various temperatures for sample I: 160 °C (solid circles—IT = 1611 s), 170 (open circles—IT = 830 s), 180 (solid triangles—IT = 424 s) and 190 °C (open triangles—IT = 250 s).

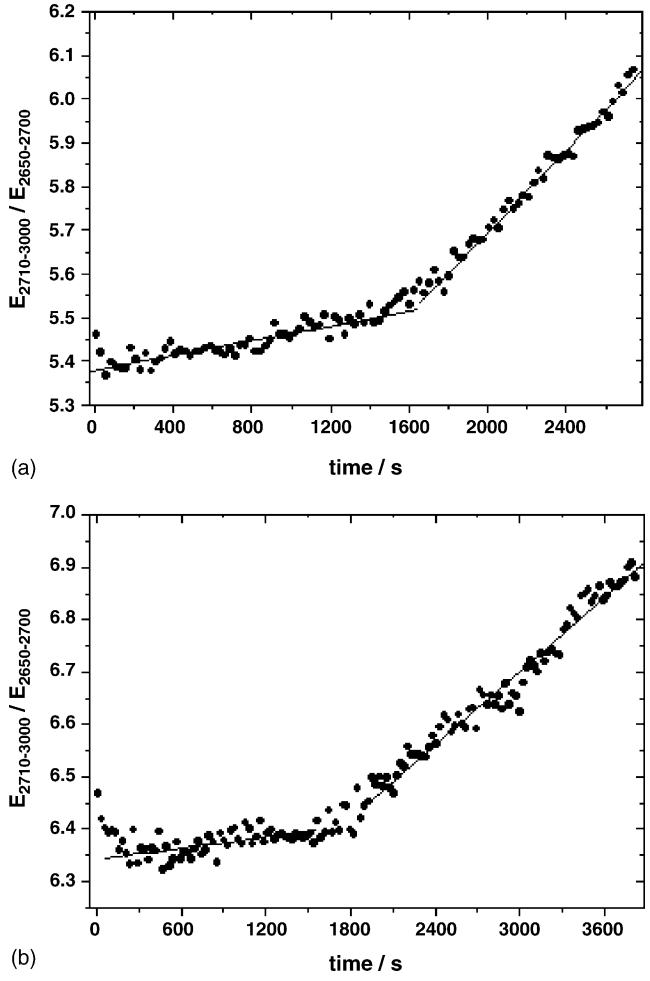

Fig. 4. (a) Stability curve for rice oil K. (b) Stability curve for unrefined rice oil L.

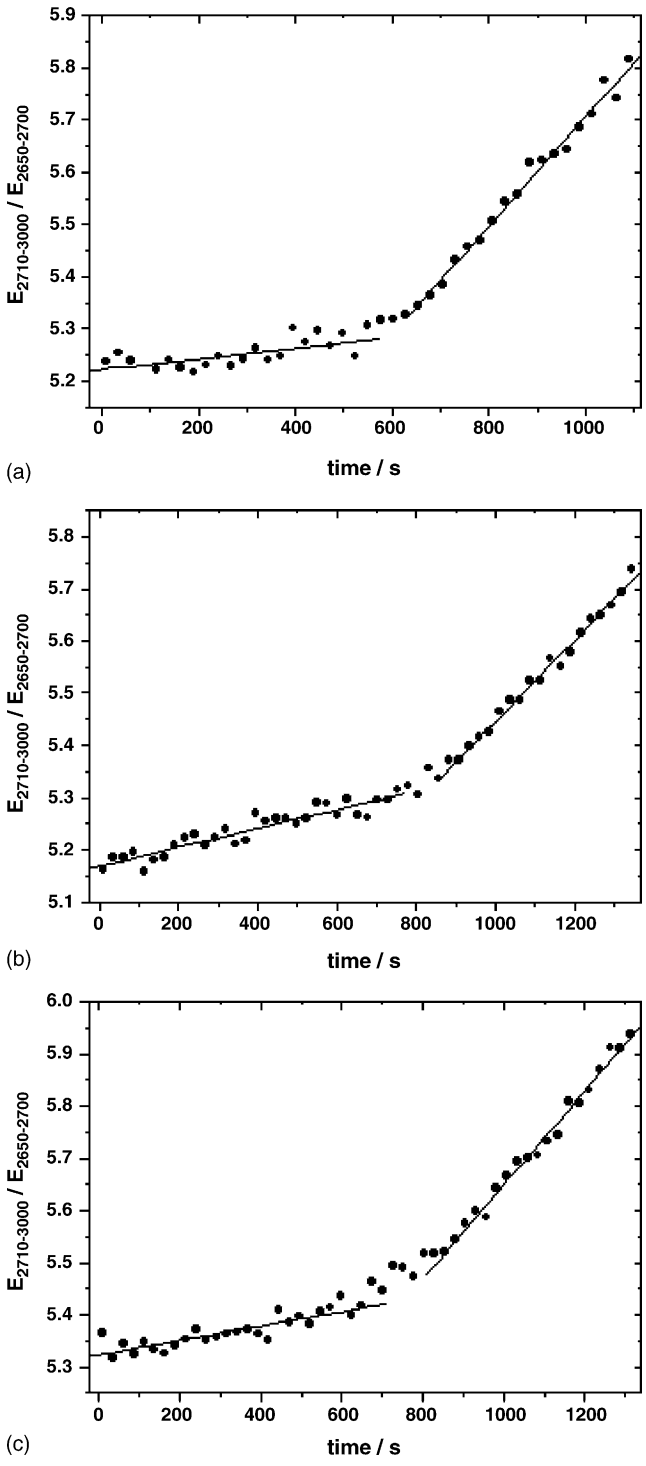

Fig. 5. Effect of antioxidant addition to sample B: (a) without antioxidant addition (IT = 599 s); (b) after adding α-tocopherol (IT = 843 s); (c) after adding γ-oryzanol (IT = 738 s).

same sample without antioxidant addition. These concentrations were chosen according to the naturally occurring concentration ranges. For instance, γ-oryzanol is commonly found in the concentration range of about 0.2–2% in refined rice oils [25] and α-tocopherol is commonly found in the concentration range of about 100–600 mg kg^{-1} in most vegetable oils [26]. Although both compounds have presented some antioxidant action, which can be shown by the increases in induction time, α-tocopherol was more efficient than γ-oryzanol. As it is generally accepted that natural antioxidants, as γ-oryzanol, present a more potent antioxidant activity than synthetic antioxidants, as α-tocopherol, at temperatures up to 110 °C [27], the non-observation of that behavior, even with the higher concentration of γ-oryzanol than α-tocopherol, indicates that γ-oryzanol must have a lower thermal stability than α-tocopherol. Therefore, the thermal degradation of γ-oryzanol would explain its lower antioxidant power at frying temperatures.

4. Conclusions

The acquisition of emission spectra in the NIR spectral region during the heating of edible oil samples was used for the first time for determination of oxidative stability. The increase and broadening of the band at 2900 nm after a determined induction time, which is related to oxidative stability, allowed establishing a parameter for the degree of oxidation during the heating time based on the area of the emissivity signal within this band. The resulting stability curves presented two regions that provided information about the oxidative stability and also about the oxidation rate of the vegetable oils. The induction time could be determined by the intersection of two linear regression curves established in these two regions and the oxidation rate is directly related to the slope after the induction period. The induction time values for several edible oils of different types, coming from different manufacturers, were determined with relative standard deviations lower than 5%.

The effects of nitrogen insertion, temperature variation and the presence of antioxidant compounds over oxidative stability could be evaluated. Nitrogen insertion reduces the oxidation rate but did not avoid the degradation of the oils because some polymerisation reactions do not need oxygen to occur. The higher the temperature, the lower the induction time and the higher the oxidation rate. The logarithm of the inverse of the induction time and the logarithm of the slope after the induction period decreased lineally with the inverse of the temperature. The stability curves for samples with high contents of antioxidant compounds presented higher induction times and lower oxidation rates than similar samples with lower antioxidant content. Among the antioxidant compounds added to an oil sample, the increase of the induction time was higher for α-tocopherol addition than with γ-oryzanol.

This new method for determination of oxidative stability of vegetable oils presents several advantages compared to other methods. It is one of the few methods described for determination of oxidative stability at frying temperatures. The analysis throughput is higher than other methods working at lower temperatures and each induction time determination is made in 15–35 min, depending of the oxidative stability, with a precision comparable to other proposed methods. Besides, methods working at lower temperatures cannot supply reliable information about oxidative stability at frying temperatures and sometimes they cannot evaluate the presence of a protective gas or an antioxidant compound. In comparison with other methods for determination at frying temperatures, the analytical signal

related to the oxidation degree is acquired in real-time in the present method, resulting in the determination of an induction time, as proposed by official tests such as Rancimat, whereas some other methods are based on determination of the content of an oxidation product after a pre-defined heating time. In addition, it is possible to think of a multiplexed instrument, which could monitor more than one sample simultaneously by using optical fibers to collect the emitted radiation and to send it to the AOTF. Finally, sample consumption in the present method is the lowest among the methods described in literature, since each analysis is done using only 10 μL of sample, and the design of the sample cell, with the sample disposed over an aluminum surface and under a renewable air atmosphere (see Fig. 1), best simulates a real frying procedure.

Acknowledgements

The authors are grateful to Dr. C.H. Collins for manuscript revision and to Dr. A.J.A. Meirelles and Dr. C.E.C. Rodrigues for supplying the antioxidants and the unrefined rice oil sample. F.B.G. wishes to thank UNICAMP (pilot program for graduate instructors) for a fellowship.

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