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Comparison of near-infrared emission spectroscopy and the Rancimat method for the determination of oxidative stability

This work presents a comparison between a new method for the determination of the oxidative stability of edible oils at frying temperatures, based on near-infrared emission spectroscopy (NIRES), and the Rancimat method at 110 °C. In the NIRES-based method, the induction time (IT) is determined by means of the variation of the emission band at 2900 nm during heating at 160 °C. The comparison between the IT values obtained with the two methods for 12 samples of edible oils shows some correlation for samples of the same type once there is an agreement on the sequence of highest to lowest IT values between the methods, but a poor correlation considering all samples (correlation coefficient of 0.78). This lack of correlation demonstrates that the results obtained with the Rancimat method cannot be used as an indication of the oxidative stability, or the resistance to degradation, of edible oils at frying temperatures. The difference in the heating temperatures used in the two methods leads to 20–36 times higher IT values for the Rancimat method in relation to the NIRES-based method, but with similar repeatabilities (2.0 and 2.8%, respectively).

Keywords: Near-infrared emission spectroscopy, edible oils, oxidative stability, Rancimat.

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 (IT) or induction period, has been determined by heating the sample to a constant temperature and measuring a physical or chemical parameter periodically 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 to vary, allowing the determination of the IT.

There are several parameters used to evaluate the degree of oxidation of oil samples [1] and several methods to determine their oxidative stability. Most of them are based on measurements of primary or secondary oxidation products, such as hydroperoxides, aldehydes and acids. In the Schaal method [2] and the active oxygen method (AOM) [3], the peroxide value (PV; related to hydroperoxide content) [4] is determined periodically for a sample heated at 60 and 98 °C, respectively, until the IT can be determined. The carbonyl value (CV; related to aldehydes and ketones) [5] and the anisidine value (AV; related to α- and β-alkenals) [6] can also be monitored with time in order to determine the IT. An important automatic method, based on the content of low-molar-mass acids, has been intensively employed since 1993, instead of the AOM, for determination of the oxidative stability: the so-called Rancimat method [7]. In a Rancimat instrument, an air stream is passed through a sample, usually heated at 110 °C, and the effluent air is bubbled through deionized water, whose conductivity is continuously monitored. The water conductivity increases when low-molar-mass acids, such as formic acid, are carried by the air and collected in the water, and the IT can be determined. Among other methods recently employed for the determination of oxidative stability, methods based on measurements of oxygen consumption [8], thermal analysis [9] (the oxidation is an exothermal reaction), and mid-infrared and near-infrared absorption spectroscopy [10–12] (infrared spectra depend on sample composition and undergo transformations due to the formation of oxidation products) can also be cited.

Despite the large number of methods for the determination of the oxidative stability of edible oils, papers dealing with its determination at frying temperatures (commonly

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between 140 and 180 °C) are still scarce. As the reactions and mechanisms taking place in the degradation of vegetable oils are very dependent on the heating temperature and most methods are carried out at temperatures below 120 °C, comparisons between the results obtained with new methods using frying temperatures and those obtained with methods using lower temperatures are very important. In addition, the official Rancimat method fails when used at frying temperatures because the low-molar-mass components of oils can be carried off by the air stream, and therefore standard methods for the determination of the oxidative stability at frying temperatures still have to be established. Recently, two methods using frying temperatures were proposed [13, 14], including one [14] based on near-infrared emission spectroscopy (NIRES). In the other work [13], the authors made a brief comparison between the results obtained with their new method at a frying temperature and the results obtained with the Rancimat method at 100 °C. However, their method does not determine an IT. It is based on the determination of the polymerized 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 IT, which can lead to errors in the evaluation of the oxidative stability. The PTG content says nothing about the period of stability of an oil sample. Consequently, the comparison with the Rancimat method is not applicable because the variables in comparison are very different. In addition, their comparison was made using only seven samples, and no discussion regarding the differences in the results due to the differences in the heating temperatures was provided.

The present work presents a comparison between the NIRES-based method for the determination of the oxidative stability of vegetable oils at frying temperatures and the Rancimat method at 110 °C, highlighting the differences in the results obtained using the two methods, which are, in part, explained by the difference in the heating temperatures.

2 Materials and methods

2.1 Samples analyzed

Using the two methods, twelve samples of edible oils were analyzed for oxidative stability. Eleven samples were obtained in 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 a degummed unrefined rice oil sample (L). All samples were stored at −10 °C in a refrigerator as soon as they were acquired and they were adapted to room temperature just before the analyses.

2.2 Rancimat method procedure

The Rancimat instrument used was an Omnion ADM Oxidative Stability instrument. Each analysis was performed using 5.0 g of sample heated at 110 °C.

2.3 NIRES-based method procedure and data treatment

The NIRES instrument basically consisted of an electrical heater (60 W) attached to an aluminum rod containing a circular groove for sample insertion (sample cell), an acousto-optical tunable filter (AOTF – Brimrose TEAF_1.5–3.0) [15] used as monochromator for the region between 1500 and 3000 nm, and a thermoelectrically cooled PbS detector (Ealing Electro-Optics 043/035). The instrument also employs a modulated radio frequency signal generator (based on the digital synthesizer Analog Devices AD 9852) for AOTF control, a thermocouple inserted near the sample cell and connected to a digital meter to monitor the heating temperature, a lock-in amplifier (Stanford Research SR830 DSP) for synchronous acquisition of the modulated signal of the detector, and a microcomputer containing a communication interface (ICP-DAS A8111) and running a home-made software for data acquisition and hardware control. The heating system containing the sample cell was placed within an acrylic tube which provided thermal isolation and the possibility of gas insertion at a low flow rate. The instrument has been described in previous papers [14, 16]. For each analysis, 10 μL of the sample were heated to 160 °C and, after temperature stabilization, emission spectra were continuously acquired, as averages of 5 scans each in the region between 2650 and 3000 nm using a nominal resolution of 10 nm (5 s for each scan), until an increase of 90% in the emissivity at 2900 nm in relation to the first spectrum was reached. Before the temperature stabilization at 160 °C, a nitrogen (99.99%) stream (1000 mL/minute) was passed around the heating system to avoid oxidation, which, after temperature stabilization, when starting acquisition of emission spectra, was replaced by a synthetic air (20% of oxygen) stream with the same flow rate. 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 IT.

3 Results and discussion

3.1 Near-infrared emission spectra and oxidative stability

Fig. 1 shows a set of consecutive emissivity spectra obtained during the heating of a sunflower oil sample and the resulting $E_{2710-3000}/E_{2650-2700}$ *versus* heating time graph. The spectra remained 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 started to increase continuously due to an overlapping with two other bands, one related to hydroperoxides and the other related to alcohols, as reported by previous papers using Fourier transform infrared absorption spectroscopy for the determination of the degree of oxidation and the oxidative stability of edible oils [11, 17]. 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 degree of oxidation, and the $E_{2710-3000}/E_{2650-2700}$ *versus* heating time graph (stability curve) was used to determine the IT. For each stability curve, two linear regression curves could be defined (one prior and another after the IT), allowing the calculation of the IT (Fig. 1b) [14].

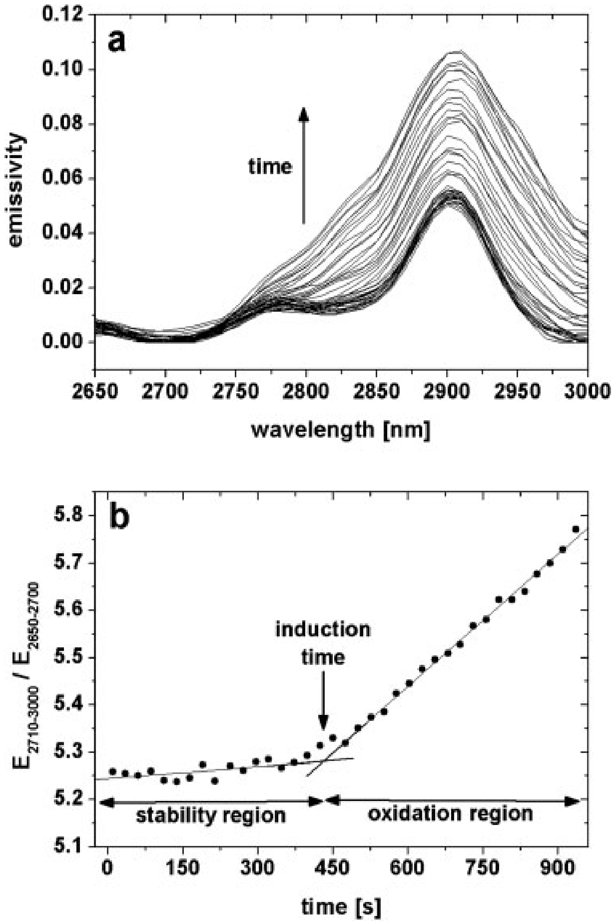

Fig. 1. (a) Consecutive near-infrared emission spectra obtained during the heating of sample A and (b) resulting stability curve.

3.2 Comparison between the Rancimat and the NIRES-based method

The IT values obtained using the two methods for all samples analyzed, as averages of duplicates, are shown in Tab. 1. Considering the empirical rule that for every increase of 10 °C in the temperature, the reaction rate is doubled [18], the IT must decrease by half for each 10 °C rise. Therefore, as the heating temperature is 50 °C lower in the Rancimat method, the IT values obtained using that method must be approximately 32 times higher than those obtained with the NIRES-based method. This behavior was confirmed by the results, since the IT values obtained with the Rancimat method divided by the IT values obtained with the NIRES-based method ranged approximately from 20 to 36. The IT values obtained with the NIRES-based method continued to decrease by half for every increase of 10 °C in the heating temperature up to 190 °C, which was demonstrated for sample I [14]. Despite the higher degradation rate occurring in the NIRES-based method, the repeatabilities of both methods, obtained by the analysis of sample I in five replicates, were similar, with a relative standard deviation between replicates of 2.0% for the Rancimat method and 2.8% for the NIRES-based method. A comparison between the IT values obtained with the two methods showed some correlation, mainly for samples of the same type where there is an agreement on the sequence of highest to lowest IT values between the methods. However, a general correlation considering all samples (shown

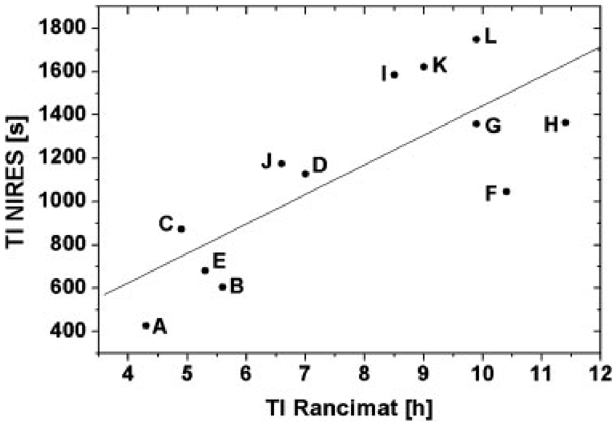

Fig. 2. Correlation between the IT values obtained using the Rancimat and the NIRES-based method.

Tab. 1. Induction time values obtained with the Rancimat and the NIRES-based method.

Oil sample	$IT_{Rancimat}$ [h]	IT_{NIRES} [s]	Oil sample	$IT_{Rancimat}$ [h]	IT_{NIRES} [s]
Sunflower (A)	4.3	427	Corn (G)	9.9	1359
Sunflower (B)	5.6	605	Corn (H)	11.4	1365
Soybean (C)	4.9	872	Canola (I)	8.5	1584
Soybean (D)	7.0	1126	Canola (J)	6.6	1174
Cottonseed (E)	5.3	680	Rice (K)	9.0	1622
Cottonseed (F)	10.4	1046	Rice (L)	9.9	1749

in Fig. 2) presented a correlation coefficient of only 0.78. This occurs in part because the reactions and mechanisms taking place in the degradation of vegetable oils are very dependent on the heating temperature. For temperatures up to 120 °C, the main reactions are hydrolysis and free-radical-induced autoxidation initiated by moisture and atmospheric oxygen, whereas for elevated frying temperatures, polymerization reactions by non-radical mechanisms like elimination or nucleophilic substitution become predominant. In addition, the Rancimat method is based on measurements of other oxidation products and it is carried out with an excess of oxygen, while the frying conditions frequently involve a more reduced contact with air (only by the surface of the sample), which is best simulated by the NIRES-based method [19]. As a result, for instance, the only unrefined oil sample (L) presented the higher IT value by the NIRES-based method, which can probably be explained by its high content of antioxidant compounds in relation to the other samples, but it presented an IT value lower than those for the corn oil samples (G and H) and for one of the cottonseed oil samples (F) by the Rancimat method. As antioxidants are expected to be more efficient in free-radical processes, these results also demonstrate that the Rancimat method is ineffective when evaluating the action of antioxidant compounds on the oxidative stability once these compounds can be partially carried off by the air stream in the Rancimat instrument, increasing the conductivity of the deionized water and leading to an oxidative stability lower than the real one, as reported in previous papers [13, 19]. Other differences between the results obtained with the two methods were inversions in the order of the IT values for some samples, as occurred for the samples C, E and B. The results obtained with the Rancimat method provide good information about the shelf life, rancidity development, and oxidative resistance of oils at temperatures below 120 °C, but they cannot be used as an indication of the oxidative stability, or the resistance to degradation, of oils at frying temperatures. In addition to results that better represent the oxidative stability at frying conditions, the NIRES-based method, compared to the Rancimat method, presents the advantages of higher analytical throughput, lower sample consumption, and better simulation of the real frying process by heating the sample over a metallic surface and under an air atmosphere.

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References

[1] S. L. Melton, S. Jafar, D. Sykes, M. K. Trigiano: Review of stability measurements for frying oils and fried food flavour. *J Am Oil Chem Soc.* 1994, **71**, 1301–1308.

[2] J. Pokorny, S. Dobiasova, J. Davidek: Repeatability of the determination of oxidative stability of vegetable-oils using the Schaal test. *Sb Vys Sk Chem Techn.* 1985, **58**, 163–173.

[3] *AOCS: Official Methods and Recommended Practices of the American Oil Chemists' Society.* AOCS Press, Champaign, IL (USA) 1983, Method Cd 12–57.

[4] G. Barthel, W. Grosch: Peroxide value determination – comparison of some methods. *J Am Oil Chem Soc.* 1974, **51**, 540–544.

[5] E. Kuruczlusztig, M. Prepostffy, M. Jeranek: Comparison of analytical methods used for the characterization of carbonyl content of fats. *Acta Aliment Hung.* 1981, **10**, 1–9.

[6] M. A. Grompone: Anisidine value as a measurement of the latent damage of fats. *Grasas Aceites.* 1991, **42**, 8–13.

[7] *AOCS: Official Methods and Recommended Practices of the American Oil Chemists' Society.* AOCS Press, Champaign, IL (USA) 1983, Method Cd 12b–92.

[8] K. Tian, P. K. Dasgupta: Determination of oxidative stability of oils and fats. *Anal Chem.* 1999, **71**, 1692–1698.

[9] C. P. Tan, Y. B. C. Man, J. Selamat, M. S. A. Yusoff: Comparative studies of oxidative stability of edible oils by differential scanning calorimetry and oxidative stability index methods. *Food Chem.* 2002, **76**, 385–389.

[10] T. A. Russin, F. R. van de Voort, J. Sedman: Rapid determination of oxidative stability of edible oils by FTIR spectroscopy using disposable IR cards. *J Am Oil Chem Soc.* 2004, **81**, 111–116.

[11] M. D. Guillén, N. Cabo: Fourier transform infrared spectra data *versus* peroxide and anisidine values to determine oxi-

dative stability of edible oils. *Food Chem.* 2002, **77**, 503–510.

[12] G. Yildiz, R. L. Wehling, S. L. Cuppett: Method for determining oxidation of vegetable oils by near-infrared spectroscopy. *J Am Oil Chem Soc.* 2001, **78**, 495–502.

[13] C. Gertz, S. Klostermann, S. P. Kochhar: Testing and comparing oxidative stability of vegetable oils and fats at frying temperature. *Eur J Lipid Sci Technol.* 2000, **102**, 543–551.

[14] F. B. Gonzaga, C. Pasquini: A new method for determination of the oxidative stability of edible oils at frying temperatures using near infrared emission spectroscopy. *Anal Chim Acta.* 2006, **570**, 129–135.

[15] C. D. Tran: Acousto-optic tunable filter: A new generation monochromator and more. *Anal Lett.* 2000, **33**, 1711–1732.

[16] F. B. Gonzaga, C. Pasquini: Near-infrared emission spectrometry based on an acousto-optical tunable filter. *Anal Chem.* 2005, **77**, 1046–1054.

[17] M. D. Guillén, N. Cabo: Usefulness of the frequency data of the Fourier transform infrared spectra to evaluate the degree of oxidation of edible oils. *J Agric Food Chem.* 1999, **47**, 709–719.

[18] P. W. Atkins, L. L. Jones: *Chemistry – Molecules, Matter, and Change*. Freeman, New York, NY (USA) 1997.

[19] S. P. Kochhar, C. Gertz: New theoretical and practical aspects of the frying process. *Eur J Lipid Sci Technol.* **2004**, 106, 722–727.

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