Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 418 (2004) 11–15
thermochimica acta
www.elsevier.com/locate/tca

Oxidizability of different vegetables oils evaluated by thermogravimetric analysis

E. Coni*, E. Podestà, T. Catone

Food Department, Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Rome, Italy

Received 24 February 2003; received in revised form 15 July 2003; accepted 25 November 2003

Available online 2 March 2004

Abstract

With thermogravimetric analysis (TGA) it is possible to have an estimation of vegetable oil resistance to oxidation, having a measure of weight gain percent (Δ%) due to oxygen caption of oil sample during the oxidation, and of initial and final oxidation temperatures (T_i and T_f). The following samples were examined: extra-virgin olive oil, olive oil, sunflower seed oil, soybean oil, maize oil, peanut oil, rapeseed oil, grape seed oil, hazelnut oil, rice oil and four different kinds of oils for frying. An assessment of data obtained so far makes it possible to point out some interesting outcomes. With regard to weight gain percent, the peanut, rice and extra-virgin olive oils showed the lowest values, whereas the highest one has been detected for one of the oils for frying. As concerns the initial oxidation temperature the rice oil has displayed the maximum value, whereas the same oil for frying above said the minimum. The experimental approach and analytical method developed in this study appear adequate for the purpose, and compared to older techniques offers definite advantages.

Keywords: Vegetable oil stability; Lipid autoxidation; Natural antioxidant; Thermogravimetric analysis

1. Introduction

Food products undergo a chain of changes in the natural matrix due to ripening, harvesting, processing and storage. These changes are caused by several factors including browning reactions, microbial spoilage and lipid autoxidation. Of the various factors, lipid autoxidation contributes significantly to the deterioration and reduction of the shelf life of many products. Lipid oxidation is a free-radical chain reaction that causes a total change in the sensory properties and nutritive value of food products. Changes in color, texture, odor and flavor, loss of vitamins, and damage to proteins are some of the effects of lipid oxidation. The beginning of lipid oxidation can be delayed by the presence of natural antioxidants or by addition of synthetic antioxidants. Antioxidants are a group of chemicals effective in extending the shelf life of a wide variety of food products. Naturally occurring antioxidants impart a certain amount of protection against oxidation but they are often lost during processing or storage, necessitating the addition of exogenous antioxidants.

The protective role from free-radical-mediated disease of some vegetables oils is mainly attributed to natural antioxidant compounds which are present in their polar fraction. These compounds, which play an important role in oil stability during storage, could also be used as stabilizer of food matrices. The antioxidant ability of natural antioxidant compounds has been recently confirmed by different studies. Virgin olive oil stability to autoxidation, for example, is mainly due to phenolic compounds naturally occurring in oil or arising from the glycated precursors present in the olive fruit before extraction. The oil stability to oxidation has been correlated to the total amount of natural antioxidant components as well as fatty acid composition [1–4]. Tocopherols and complex phenols make up a part of the so-called "polar fraction" of vegetable oil and little is known about the contribution of each component to the stability of the oil [1].

The relative contribution of tocopherols, phenols, γ-oryzanol and other antioxidant compounds in determining vegetable oil stability during storage and heating has been investigated by different methods. Contrasting data have been published on the effectiveness of the same antioxidant

* Corresponding author. Tel.: +39-064-990-2713; fax: +39-064-990-2712.
E-mail address: e.coni@iss.it (E. Coni).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2003.11.038

compound depending on the various conditions and methods used to evaluate the oxidation rate [5–7]. Valid comparison of antioxidant activity depends on condition of oxidation and on which analytical method is used to determine the extent and endpoint of oxidation [6]. The aim of this study was to measure oil resistance to oxidation using a method that employs a thermogravimetric balance; in this system changes in sample weight are monitored continuously while the sample is temperature programmed in an oxygen environment. The procedure essentially imitates the simple technique of heating oil in an oven and weighing it periodically, but weight changes can be permanently recorded. It was proved that with thermogravimetric methods, it is possible to have an estimation of oil resistance to oxidation, having a measure of weight gain percent due to oxidation, and of initial and final oxidation temperatures [8–10].

2. Experimental

2.1. Samples

The following specimens were examined: extra-virgin olive oil, olive oil, sunflower seed oil, soybean oil, maize oil, peanut oil, rapeseed oil, grape seed oil, hazelnut oil, rice oil and four different kinds of oil for frying, all available on the market. To avoid influence coming from storage conditions all samples were obtained from freshly processed oil through industry.

It is not necessary any preliminary treatment of the oil samples before the analysis.

2.2. Thermogravimetric analysis

A thermobalance (Mod. TGA 7, Perkin-Elmer) coupled with a thermal analysis controller (Mod. TAC 7/DX, Perkin-Elmer) was employed. The instrument was calibrated with “alumel” alloy and nickel for temperature setting, and with a 100 mg standard for weight accuracy. Approximately 3 mg of each sample were added to a tared aluminium balance pan. The pan was then placed in the furnace at room temperature and the exact sample weight was determined. The temperature was then increased to 70 °C at the rate of 10 °C min^{-1} and the sample was held at this temperature for conditioning it. Thereafter, sample was heated until 250 °C at the rate of 2 °C min^{-1}. In order to establish an environment suitable for the oxidation process, O_2 was chosen as sample purge gas (flow of 50 cm^3 min^{-1}) during all the analysis, whereas as balance purge gas was used N_2 at the flow of 75 cm^3 min^{-1}. Sample weight variation was recorded on a plotter (Mod. ColorPro, Hewlett-Packard).

2.3. Statistical analysis

In order to evaluate if the results relative to the different vegetables oils were significantly different, analysis of variance (ANOVA test) was applied. Data processing was performed by means of Statgraphics software package (Version 7 for DOS, Manugistic).

3. Results and discussion

A typical thermogravimetric curve for vegetable oil is shown in Fig. 1. It is opportune to point out that, under the analysis conditions adopted in this study, the noise of the recorded signal has always been very low varying between 0.5 and 1% of the signal. The line AB indicates isothermal heating at 70 °C of oil sample. In correspondence of point B starts temperature program. The line from B to T_i represents the static condition of oil resistance to oxidation when temperature is increasing. During this step and previous isotherm the sample weight undergo a slight decrease probably due to loss of residual water and volatile compounds. T_i is the “initiation temperature”; the temperature at which the rate of oxidation increases fast, as shown by a weight gain. T_f is the “final temperature”, the point of maximum gain in sample weight (Δ). As temperature increases beyond T_f, the sample continually loses weight until the recorder pen is no longer on scale, and the run is finished. The ratio (weight at T_f − weight at T_i/weight at $T_i \times 100$) represents the sample weight gain percent (Δ%).

The results of thermogravimetric analysis for all samples taken into consideration in this study are shown in Tables 1 and 2. Each mean value is accompanied by its standard deviation (S.D.) and relative standard deviation (R.S.D.). The values of these last prove that the precision of the method is more than satisfactory for what concerns the temperatures (T_i and T_f). In fact R.S.D. values range from 0.9 to 3.0% and from 0.6 to 2.0% for T_i and T_f, respectively. On the contrary, R.S.D. related to weight gain percent since measured levels were very close to the detection limits of the technique employed, have evidenced a lower precision (up to ±35%). In the same tables the significance level values (P) obtained by ANOVA test are also indicated. The comparisons have been made all versus rice and peanut oil for T_i and Δ%, respectively.

An assessment of data obtained so far makes it possible to point out some interesting outcomes. With regard to weight gain percent, the peanut, rice and extra-virgin olive oils showed the lowest values with 0.13, 0.15 and 0.17%, respectively. This means that the extent of lipid autoxidation process is minor for these three kinds of oil. On the contrary, the highest value of weight gain percent has been detected for one of the oils for frying (0.53%). As regards the initial oxidation temperature the rice oil has displayed the maximum value (171.00 °C) followed by rapeseed oil (166.68 °C) and extra-virgin olive oil (166.20 °C) whereas the same oil for frying above said the minimum (148.60 °C).

The rice and extra-virgin olive oil have therefore shown a good resistance to lipid autoxidation both as concerns T_i and Δ%. This outcome corroborates the hypothesis that the

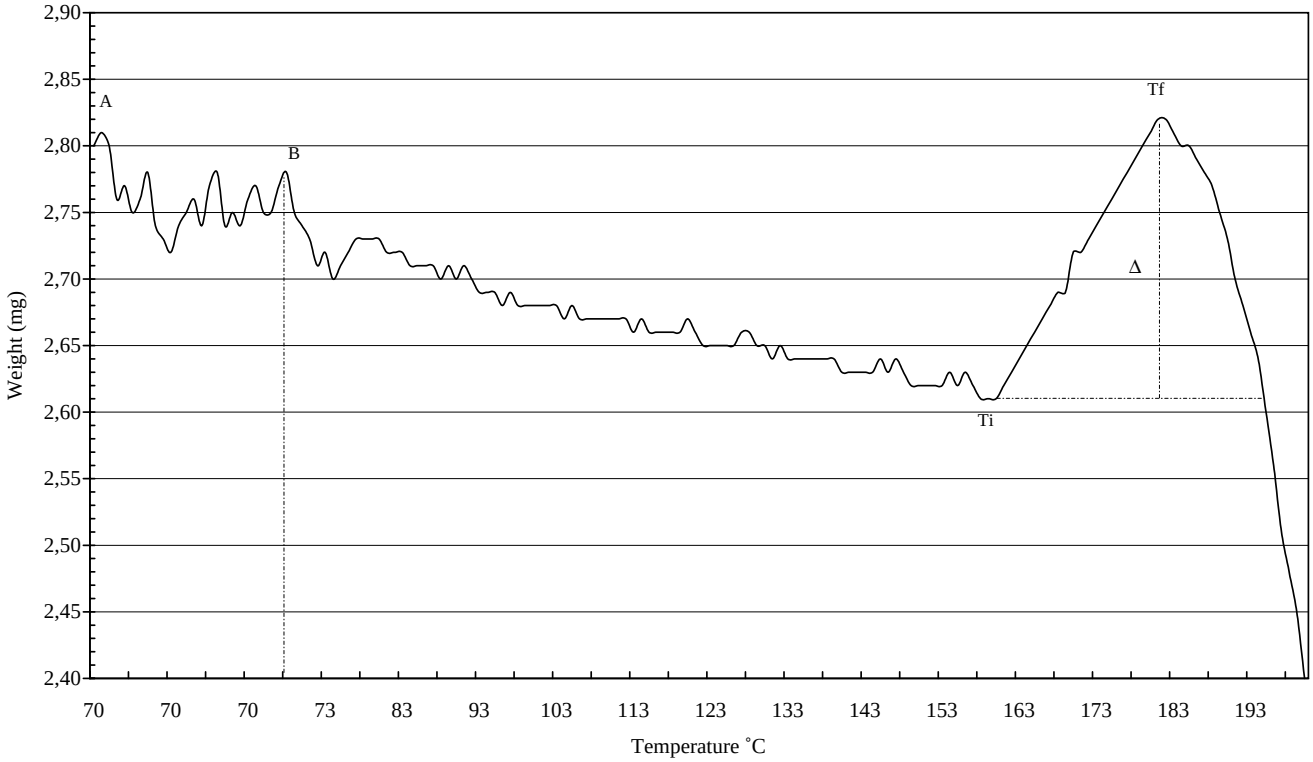

Fig. 1. Typical thermogravimetric curve for a vegetable oil sample (olive oil). See text for description.

presence of natural primary antioxidant as polyphenols in olive oil and γ-oryzanol in rice oil positively influence oil stability. The antioxidant activity is particularly strong in the case of γ-oryzanol considering that rice oil has a high content of polyunsaturated fatty acids (average value of 38% versus 8.6% of olive oil) and a low content of tocopherols (average value of $270\,mg\,kg^{-1}$ versus $1400\,mg\,kg^{-1}$ of maize oil).

It is interesting to note the difference observed between extra-virgin olive oil and olive oil. In fact the two kinds of oil have exactly the same gliceride composition and structure. In this case it is clear that T_i and Δ% differences may be ascribed to the fact that the process of olive oil manufacture causes a more or less pronounced decrease in the phenols concentration. In effect, phenols content of extra-virgin olive oil, measured according to the method of Vázquez Roncero

Table 1
Figures of merit for the initial and final oxidation temperatures (T_i and T_f)

Sample	T_i[a] (°C) ± S.D.	R.S.D. (%)	T_f[a] (°C) ± S.D.	R.S.D. (%)
Rice oil	171.00 ± 4.61	2.7	186.93 ± 3.76	2.0
Rapeseed oil	166.68 ± 2.91*	1.7	180.87 ± 1.05	0.6
Extra-virgin olive oil	166.20 ± 1.89*	1.1	183.43 ± 1.52	0.8
Oil for frying D	164.03 ± 1.62**	1.0	178.42 ± 2.14	1.2
Peanut oil	163.54 ± 2.14**	1.3	176.65 ± 1.95	1.1
Maize oil	162.48 ± 3.61**	2.2	182.46 ± 1.92	1.0
Olive oil	161.60 ± 3.58**	2.2	181.90 ± 2.73	1.5
Oil for frying B	160.52 ± 4.69**	2.9	179.37 ± 2.59	1.4
Oil for frying A	159.48 ± 4.57***	2.9	178.29 ± 3.27	1.8
Hazelnut oil	158.36 ± 1.76***	1.1	177.36 ± 2.18	1.2
Soybean oil	158.34 ± 3.85***	2.4	178.63 ± 2.06	1.1
Sunflower seed oil	153.87 ± 4.56***	3.0	173.34 ± 1.19	0.7
Grape seed oil	149.89 ± 1.99***	1.3	169.17 ± 2.63	1.5
Oil for frying C	148.60 ± 1.38***	0.9	172.00 ± 2.89	1.7

[a] Each value of T_i, T_f is the mean of 10 determinations.
* Significant at $P < 0.05$.
** Significant at $P < 0.01$.
*** Significant at $P < 0.001$ compared to rice oil.

Table 2
Figures of merit for the weight gain percent

Sample	Δ[a] (%) ± S.D.	R.S.D. (%)
Peanut oil	0.13 ± 0.03	23
Rice oil	0.15 ± 0.03	20
Extra-virgin olive oil	0.17 ± 0.06*	35
Hazelnut oil	0.21 ± 0.02*	9.5
Oil for frying D	0.22 ± 0.02*	9.1
Olive oil	0.22 ± 0.03*	13
Maize oil	0.24 ± 0.07*	29
Soybean oil	0.28 ± 0.06**	21
Rapeseed oil	0.29 ± 0.06**	21
Oil for frying A	0.36 ± 0.04***	11
Sunflower seed oil	0.38 ± 0.03***	7.9
Grape seed oil	0.44 ± 0.03***	6.8
Oil for frying B	0.45 ± 0.06***	13
Oil for frying C	0.53 ± 0.03***	5.7

[a] Each value of Δ (%) is the mean of 10 determinations.
* Significant at $P < 0.05$.
** Significant at $P < 0.01$.
*** Significant at $P < 0.001$ compared to peanut oil.

et al. [11], was found to be 139.5 mg kg^{-1}, while the olive oil one was 47.2 mg kg^{-1}. The phenomenon is also interesting under a technological point of view because it testify that a greater content of natural phenols, besides to extend the olive oil shelf life, could limit the extent of oil decomposition during cooking processes.

Rapeseed oil has revealed a high temperature of oxidation starting probably due its high content of tocopherols (average value of 1200 mg kg^{-1}) but the lipid autoxidation extent, pointed out by Δ%, was rather elevated. On the contrary, peanut oil has shown the smallest oxidation extent in spite of its high content of polyunsaturated fatty acids but a low T_i.

Obviously both T_i and Δ% depend on many factors among which gliceride composition and structure, amount and kind of natural antioxidants contained (primary, synergistic, secondary, etc.) presence of transition metal ions (pro-oxidants) and chelators and so on. Thus, no easy explanation can be given for the behaviors found in this study. The difficulty lies in fully comprehending the different influence exerted by several factors affecting oxidation and their interaction but this does not invalidate the reliability and validity of results.

At this regards it is worth mentioning that the oils sold as suitable for frying have, except one, displayed bad results both as concerns T_i and Δ%. This experimental evidence confirms once more the complexity of assessing all variables that affect the oil oxidizability. To blend different vegetable oils, as in the case of oils for frying, on semi-empirical basis considering only some factors (e.g. unsaturated fatty acid amount) often does not give expected outcomes.

Finally, it generates some surprise to find that some vegetable oils considered suitable and suggested for frying, e.g. grape seed oil, have not shown been able to reduce lipid oxidation process in significant manner, as expected. No simple justification can be given for this behavior, but it must be stated that the methodological approach adopted in this study completely differs by those applied in previous investigations that, in the majority of cases, are not be able to monitor the oxidation process in continuous manner.

4. Conclusions

The experimental approach and analytical method developed in this study appear adequate for the purpose, and compared to older but still used techniques as, for example, the active oxygen method (AOM) [12], the schaal oven method [13] or the A.S.T.M. Oxygen bomb method [14] offers the advantages of (i) very shorter analysis time (about 80 min); (ii) smaller sample amount (approximately 3 mg); (iii) good precision; (iv) the possibility of following, in a continuous manner, the oxidation process.

The experimental results gained sheds further light on the resistance to oxidation of the most common vegetable oils. Moreover, the antioxidant activity of natural antioxidant present in some of these oils has been even put in evidence. This could constitute a notable starting point for sound and effective action in replacing artificial antioxidant additives, normally employed for vegetable oils (i.e. BHA and BHT), with natural compounds so as enhance safety and quality of foodstuffs. Under this point of view, it must be considered, for example, that a large amount of biophenols are present in olive oil mill waste waters (WWs), the by-product of olive oil production, currently discarded at high running expenses. The WWs disposal is origin of problems in olive oil producing countries, mainly due their toxicity. Consequently, the possibility of finding methods to recycle WWs could be very interesting for two orders of reasons. The first concerns the prospect to detoxify a dangerous and polluting by-product. The second one is related to the fact that, at the same time, WW recycling could be a profitable operation if carried out to obtain natural antioxidant.

References

[1] G. Papadopoulos, D. Boskou, J. Am. Oil Chem. Soc. 68 (1991) 669–671.
[2] M. Tsimidou, G. Papadopoulos, D. Boskou, Food Chem. 44 (1992) 53–60.
[3] M.T. Satue, S. Huang, E.N. Frankel, J. Am. Oil Chem. Soc. 72 (1995) 1131–1137.
[4] P. Zunin, F. Evangelisti, M.A. Pagano, E. Tiscornia, R. Petacchi, Riv. It. Sost. Grasse LXXII (1995) 55–59.
[5] E.N. Frankel, Trends Food Sci. Technol. 4 (1993) 220–225.
[6] E.N. Frankel, S. Huang, J. Kanner, J.J. Bruce German, J. Agric. Food Chem. 42 (1994) 1054–1059.

[7] S.W. Huang, A. Hopia, K. Schwarz, E.N. Frankel, J.B. German, J. Agric. Food Chem. 44 (1996) 444–452.
[8] H.J. Nieschlag, J.W. Hagemann, J.A. Rothfus, Anal. Chem. 46 (1974) 2215–2217.
[9] L. Gennaro, A. Piccioli Bocca, D. Modesti, R. Masella, E. Coni, J. Agric. Food Chem. 46 (1998) 4465–4469.
[10] E. Rudnik, A. Szczucinska, H. Gwardiak, A. Szulc, A. Winiarska, Thermochim. Acta 370 (2001) 135–140.
[11] A. Vázquez Roncero, C. Janer del Valle, M.L. Janer del Valle, Grasas y Aceites 24 (1973) 350–357.
[12] R.W. Riemenschneider, J. Turer, R.M. Speck, Oil and Soap 22 (1943) 169–171.
[13] N.T. Joiner, J.E. McIntyre, Oil and Soap 15 (1938) 184–186.
[14] W.M. Gearhart, B.N. Stuckey, J.J. Austin, J. Am. Oil Chem. Soc. 34 (1957) 427–430.