

Analytical evaluation of polyunsaturated fatty acids degradation during thermal oxidation of edible oils by Fourier transform infrared spectroscopy

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Abstract

The oxidative deterioration of polyunsaturated fatty acids (PUFAs) in culinary oils and fats during episodes of heating associated with normal usage (80–300°C, 20–40 min) has been monitored by Fourier transform infrared spectroscopy (FTIR). The thermal oxidation of PUFAs is a free radical chain reaction, in which hydroperoxides are generally recognized as the primary major products. Hydroperoxides of PUFAs are easily decomposed into a very complex mixture of secondary products with the decrease in unsaturation. The oxidative advance of PUFAs during heating was studied by the determination of unsaturation percentage at different temperatures and heating times. Oils frequently used in food frying such as olive oil, sunflower oil, corn oil and seeds oil (sunflower, safflower and canola seed) were studied. The results show there is a decrease in unsaturation starting at 150°C and becoming more pronounced at temperatures around 250°C. The following variations were found in the unsaturation percentage, expressed as methyl linoleate, between the original sample and the sample heated at 300°C for 40 min: olive oil (19–6%), sunflower oil (29–12%), corn oil (28–18%) and seeds oil (23–11%). This variation in unsaturation grade provides evidence of the transformation of essential PUFAs and subsequent decrease in the oils' nutritional value. The internal standard method is suitably precise when the *n*-valeronitrile is used as standard as shown by the 1–2% relative standard deviation (R.S.D.) found for seven replicates. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oils and fats are an important part of the human diet and more than 90% of global production is used as food or as ingredients in food

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products. Oils and fats in the diet are a rich source of energy, they contain certain fatty acids, which are nutritionally indispensable and their functional and textural characteristics add to the flavour and acceptability of many natural and processed foods. The polyunsaturated fatty acids (PUFAs) which can not be synthesised by the human body must be present in the diet to avoid symptoms caused by a shortage. They can be considered as vitamin factors and linoleic and linolenic acids must be considered specifically as they are PUFAs which are necessary for the normal development and functioning of human tissues and are known as essential fatty acids [1].

Oils and fats begin to decompose from the moment they are isolated from their natural environment when changes occur causing a disagreeable taste and smell. Atmospheric oxidation is the most important cause of deterioration in fats. This oxidative rancidity is accelerated by exposure to heat, light, humidity and the presence of trace transition metals [2]. The intense frying of oils causes an oxidizing thermal degradation with the formation of decomposition products [3–6], and a change in physical properties [7]. When oxygen travels through a fat, it is adsorbed by the fat and reacts mainly in the double links, thus the polyunsaturated components of fats oxidise much faster than saturated ones [8].

Spectroscopic methods can be employed to evaluate deterioration in oils subjected to intense heat [9]. Fourier transform infrared spectroscopy (FTIR) provides a quick and accurate way of evaluating thermal degradation in these lipids.

This paper reports a methodology to evaluate the degradation of the PUFAs initially present in the oil when it is subjected to intense heat (80–300°C, 20–40 min), and which are consequently related with the oxidative deterioration of the lipid. The unsaturation percentage was determined by FTIR for different temperatures and heating times, using *n*-valeronitrile as internal standard, so sample preparation was quick and optic pathlength does not have to be determined.

Four types of oils commonly used to fry food and high in unsaturated fats were studied, sunflower oil, corn oil, olive oil and seeds oil (canola, safflower and sunflower).

2. Experimental

2.1. Instrumentation

Perkin Elmer 1600 Fourier transform infrared spectrometer with deuterated triglycine sulphate (DTGS) detector. Number of co-added scans, 16; resolution: 4 cm⁻¹. Data acquisition and processing software Spectrum for Windows, Perkin Elmer.

2.2. Reagents

n-Valeronitrile Aldrich analysis grade; nujol Aldrich IR grade; methyl linoleate Aldrich analysis grade; and chloroform Baker analysis grade.

2.3. Samples

Oils from the Mexican and Spanish market were analyzed: Virgin olive oil (Domeq), corn oil (Mazola), sunflower oil (Cristal), seeds oil (sunflower, safflower and canola, As).

2.4. Procedure

2.4.1. Thermal treatment

Approximately 80 ml of oil were placed in 9.7 cm diameter porcelain capsule and were subjected to heating on an electric device, stirring manually with a glass rod. A thermometer was introduced in the capsule and held by a support to control

Table 1
Thermal treatment of the oils

Sample	Temperature (°C)	Time (min)
1	T_{amb}	–
2	80	20
3	80	40
4	150	20
5	150	40
6	200	20
7	200	40
8	250	20
9	250	40
10	300	20
11	300	40

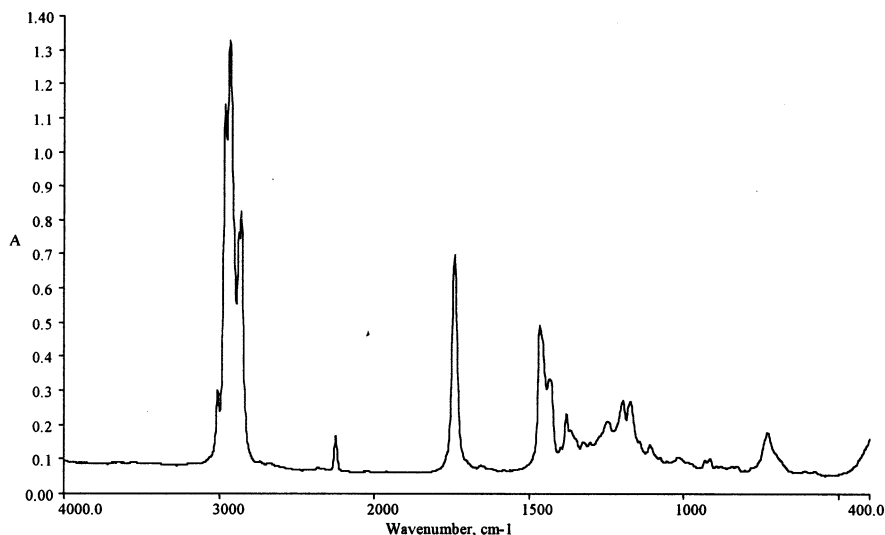


Fig. 1. Infrared spectrum of a methyl linoleate/n-valeronitrile/nujol mixture.

sample temperature. To follow the oxidation process in the oil during the period of frying, the samples were subjected to increasing heat up to a temperature of 300°C, during this process heating was maintained for 20 and 40 min at the following temperatures: 80, 150, 200, 250 and $300 \pm 5^\circ\text{C}$. Table 1 shows the samples analysed.

2.4.2. FTIR quantitative analysis

The oil samples and internal standard n-valeronitrile were mixed in a test tube, weighed on an analytical scale and the sample was shaken manually to ensure total homogenization. The proportion in weight of n-valeronitrile in the prepared samples was between 35 and 65%. To obtain the infrared spectra using a Pasteur pipette, one or two drops of the prepared samples were placed between two circular pieces of well polished potassium bromide crystal without using a spacer so sample thickness was not controlled but was variable in each prepared sample.

In the IR spectra of the prepared samples absorbance was measured as peak height at 3008 cm^{-1} with respect to the base line tangent at $3116\text{--}2718\text{ cm}^{-1}$ and the peak 2246 cm^{-1} , corresponding to n-valeronitrile, with respect to the base line tangent at $2408\text{--}2144\text{ cm}^{-1}$.

Eight mixtures of known composition of n-valeronitrile, methyl linoleate and nujol were prepared to obtain the calibration straight line. In these mixtures, the absorbance quotient $A(3008)/A(2246)$ was measured with respect to the above-mentioned base lines.

3. Results and discussion

The percentage of unsaturation expressed as a percentage in weight of methyl linoleate (l) was obtained for the eleven prepared samples, for each type of oil. The internal standard method was used with n-valeronitrile (v) as internal standard.

The infrared spectrum of n-valeronitrile shows an absorbance band at 2246 cm^{-1} , due to the stretching vibration of the triple $\text{C}\equiv\text{N}$ link which can be used as reference band as it does not interfere with any of the sample bands. The analytical signal used to determine unsaturation was the peak at 3008 cm^{-1} , due to the stretching vibration of the $\text{C}\text{--}\text{H}$ link adjoining the double $\text{C}=\text{C}$ link.

From eight mixtures of n-valeronitrile/methyl linoleate/nujol whose infrared spectrum is shown in Fig. 1, the calibration straight line was obtained representing the quotient $A(3008)/A(2246)$

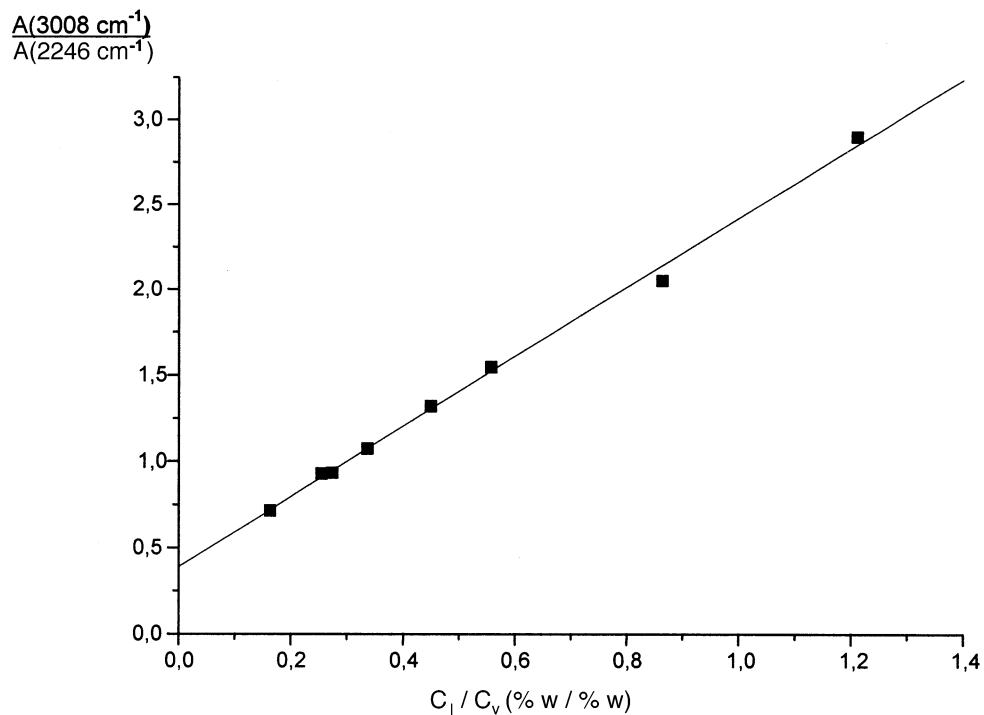


Fig. 2. Calibration straight line to obtain the unsaturation percentage of methyl linoleate.

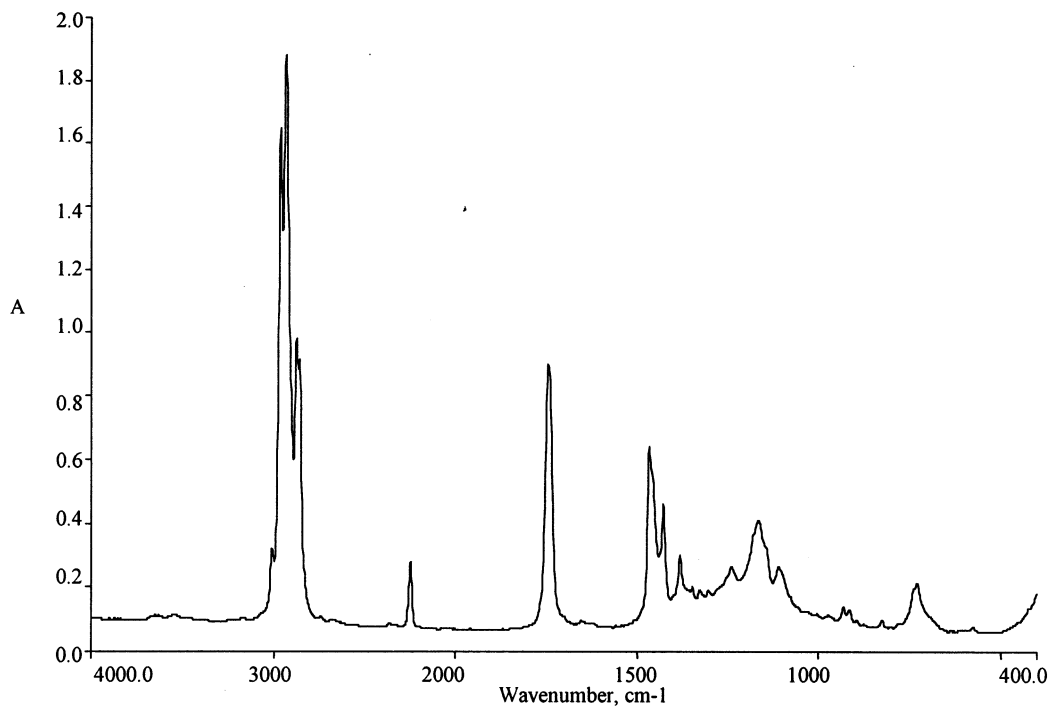


Fig. 3. Infrared spectrum of a prepared sample of corn oil unheated.

Table 2

Unsaturation expressed as percentage in weight of methyl linoleate, in the oils at different temperatures and heating times^a

Sample	Heating (°C min ⁻¹)	Olive oil	Sunflower oil	Corn oil	Seeds oil
1	T_{amb}	18.9	29.6	27.4	23.2
2	80–20	18.8	29.3	27.8	23.3
3	80–40	18.2	29.7	27.0	22.5
4	150–20	18.3	29.2	27.1	22.0
5	150–40	18.5	29.2	26.4	21.2
6	200–20	16.7	28.3	24.6	20.7
7	200–40	12.4	26.9	24.1	19.6
8	250–20	11.8	26.3	24.0	18.8
9	250–40	11.5	24.9	23.2	18.1
10	300–20	9.8	19.0	18.7	16.4
11	300–40	5.6	11.9	18.3	10.9

^a Results obtained by the internal standard method with Fourier transform infrared spectroscopy (FTIR).

against the C_l/C_v concentration quotient, where C_l is methyl linoleate concentration and C_v the n-valeronitrile concentration both expressed as % (weight/weight). This is shown in graph form in Fig. 2.

Linear regression provided the following behaviour with a correlation index 0.998 for the eight standard mixtures:

$$A(3008)/A(2246) = 0.3888 + 2.0326C_l/C_v$$

The unsaturation percentage was calculated from the spectra of the samples prepared with n-valeronitrile (Fig. 3) using the calibration equation. The values obtained are shown in Table 2. The precision for the different samples analyzed was studied, the relative standard deviation

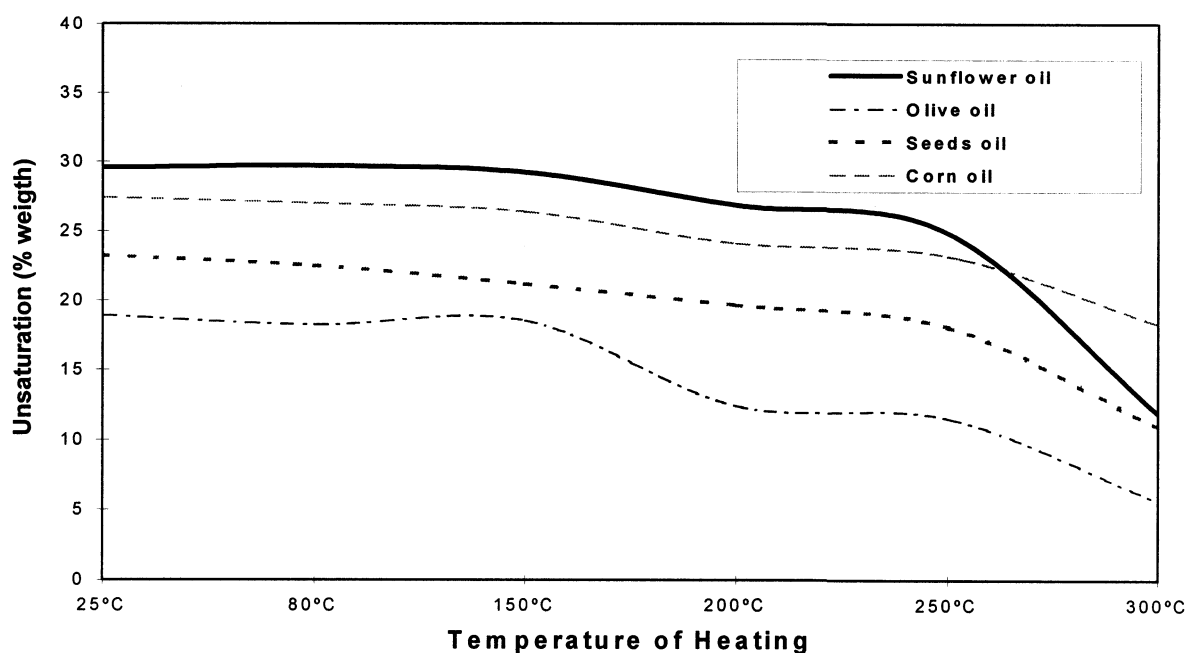


Fig. 4. Unsaturation expressed as percentage in weight of methyl linoleate, in the studied oils at different temperatures and 40 min heating time.

(R.S.D.) obtained for seven replicates was statistically satisfactory, with values between 1 and 2%.

The difference in unsaturation can be seen for each type of oil, at ambient temperature sunflower oil and corn oil have the highest content of unsaturates and the lowest is olive oil. The results obtained show how the intense heating of oils causes a decrease in unsaturation. It has been possible to establish that in all the oils studied this degradation starts becoming considerable after 150°C (Fig. 4) and at higher temperatures, a more significant decrease in unsaturation of between 40 and 70% is apparent.

The peroxide index obtained for each sample by the iodimetric method [10], reveals that the decrease in unsaturation coincide with the decomposition of hydroperoxides. Fig. 5 shows the variation of unsaturation grade and peroxide value in sunflower oil when subjected to different temperatures. The same behaviour is observed in the rest of the studied oils.

4. Conclusions

FTIR provides very useful information on the composition and extent of thermal self-oxidation

in oils subjected to intense heat, equivalent to that used in the ordinary preparation of food.

The methodology developed in this study permitted determination of the percentage of unsaturated components in the samples at different heating temperatures, with no prior treatment. The use of absorbance quotient measurements permitted quantitative analysis without requiring a constant and known cell thickness thus facilitating sample handling and reducing analysis time. Furthermore, it permits quantification in cases where it is impossible to know the optic path-length accurately.

The determination of unsaturation in oils makes it possible to classify them and evaluate their oxidative deterioration which is directly related with the degradation of polyunsaturated fatty acids in the lipids and which are indispensable nutrients in human tissue development.

It can be said then, that when an edible oil is subjected to a heating process or frying, the initial nature of the triglyceride changes significantly and the decrease in unsaturation is evidence of the transformation occurring in the essential PUFAs which the oil initially contains, thus indicating a decrease in the oils' nutritional value.

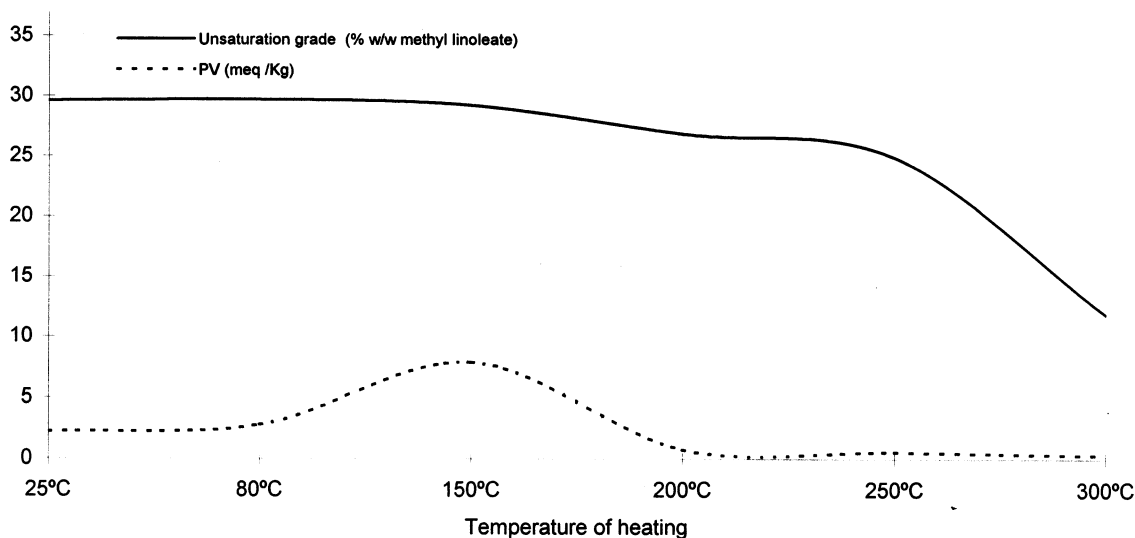


Fig. 5. Variation in unsaturation grade and peroxide value in sunflower oil when subjected to different heating and 40 min heating time.

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References

- [1] Dietary Fats and Oils in Human Nutrition. Food and Nutrition Paper, Rome, FAO, 1978.
- [2] E. Primo Yúfera, Química Agrícola III, Alimentos, E. Alhambra, Madrid, 1978.
- [3] A. Kamal-Eldin, L.A. Appelqvist, *Grasas y Aceites* 47 (5) (1996) 342–348.
- [4] G. Takeoka, C. Perrino, R. Buttery, *J. Agri. Food Chem.* 44 (3) (1996) 654–660.
- [5] G.R. Takeoka, G.H. Full, L.T. Dao, *J. Agri. Food Chem.* 45 (8) (1997) 3244–3249.
- [6] G. Dobson, W.W. Christie, J.L. Sebedio, *Chem. Phys. Lipids* 82 (2) (1995) 101–110.
- [7] V.K. Tyagi, A.K. Vasishtha, *J. Am. Oil Chem. Soc.* 73 (4) (1996) 499–506.
- [8] G. Dobson, W.W. Christie, M.C. Dobarganes, *Grasas y Aceites* 47 (1–2) (1996) 34–37.
- [9] S.B. Engelsens, *J. Am. Oil Chem. Soc.* 74 (4) (1997) 1495–1508.
- [10] Official press of European Community, No 1248, 8–9, 5 September 1991.