

# FTIR spectroscopy used for study the thermal degradation of lard

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## Aim

Recent developments in Fourier transform infrared (FTIR) spectroscopy instrumentation extend the application of this technique to the field of food research, in particular facilitating studies on edible oils and fats.

## Materials and methods

In this work, an attenuated total reflection-FTIR spectroscopy method was used as an effective analytical tool to monitor the oxidation process of lard samples during heating. The process was interpreted according to the peaks data.

## Results and discussion

FTIR spectroscopy has been found to be a versatile technique for evaluating the oxidative stability of lard and for providing information on the oxidation degree of a sample in a simple, fast and accurate way. To follow the oxidation process during the period of frying, about 40 min, the samples were subjected to increasing heat up to a temperature of 300°C, and samples were withdrawn every 10 min. Attenuated total reflection spectra were obtained and the process was interpreted according to the peaks data modifications.

## Conclusion

FTIR spectroscopy has been found to be a versatile technique for evaluating the oxidative stability of lard and for providing information on the oxidation degree of a sample in a simple, fast, and accurate way. A slight decrease in the intensity was observed for the band at 721 cm<sup>-1</sup>, which implies the loss of *cis* double bonds during oxidation, a fact also confirmed by the decrease in intensity at 3006 cm<sup>-1</sup>, assigned to the same *cis*-double bonds in C=CH.

## Keywords:

Fourier transform infrared analysis, lard, thermal degradation applications

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## Introduction

The increasing public demand for high-quality and safe food and globalization of food production, conducted to a global and interconnected system for the production and distribution of food demanded the development of appropriate and effective analytical tools for food analysis are required.

Frying is one of the most widely used practices in the preparation of food. During frying, the oil is exposed continuously to a high temperature in the presence of air and moisture, and in these conditions, some complex reactions (oxidation, polymerization, and hydrolysis) may occur.

Oils and fats are present in the diet and represent a rich source of energy. In their chemical composition, we can find some fatty acids, which are nutritionally indispensable, and their functional and textural characteristics add to the flavor and acceptability of many natural and processed foods.

Nowadays, due to its capability to act as a fingerprint technique, Fourier transform infrared (FTIR) spectroscopy has become a preferred method for the analysis of food [2], including studies in authentication of virgin olive oil [3,4], hazelnut [5], virgin coconut oil [6], and animal fat [7–9].

One of the most important objectives of these studies is to study the thermal degradation of oils [10,11].

Oils and fats begin to decompose from the first moment after they are isolated from their natural environment, so that some changes can occur that can cause a disagreeable taste and smell. Atmospheric oxidation is the most important cause of deterioration in fats, being accelerated by exposure to heat, light, humidity, and the presence of trace transition metals [12–14].

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Lard is a major constituent of most processed meat products. The composition of pig's adipose tissue widely contributes to the quality of meat products and it affects technological properties such as consistency. The fatty acid composition in adipose tissue of nonruminant animals such as pigs is influenced by the composition of the dietary fats [15]. Lard is also used in the preparation of pharmaceutical formulations.

The aim of the present study is to use FTIR spectrometry to investigate the thermal degradation of lard during the frying process.

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## Materials and methods

### Materials

The standard fatty acids, such as oleic and linoleic acid, were purchased from Sigma Chemical Co. (St Louis, Missouri, USA).

The lard sample was extracted by rendering adipose tissue of a slaughtered pig in a conventional oven (Electrolux, Bucharest, Romania). The melted fat was filtered through a Whatman filter paper and dried by the addition of anhydrous  $\text{Na}_2\text{SO}_4$ . The filtered samples were stored in a tightly closed container in a refrigerator until further analysis. The samples of pork bacon and lard were purchased from the local market.

All solvents were reagent grade and were obtained from Aldrich Chemical Co. (Milwaukee, Wisconsin, USA).

### Apparatus and procedure

A Perkin Elmer Spectrum 1000 FTIR spectrometer equipped with a horizontal attenuated total reflection (ATR) accessory with a ZnSe crystal was used to obtain the FTIR-ATR spectra. They were acquired using Spectrum software v. 5.01 (Perkin Elmer Co., Beaconsfield, Bucks, UK) and then processed using Spectrum software v. 10.5.1.581 (Perkin Elmer Inc., Boston, MA, USA), respectively.

All samples were homogenized and a small amount of sample was spread onto the ATR crystal to provide total coverage. The spectra were scanned in triplicate at room temperature over the wavenumber interval of  $4000\text{--}650\text{ cm}^{-1}$ , averaging 16 scans at a resolution of  $4\text{ cm}^{-1}$ , and were then averaged. A background air spectrum was scanned before each measurement session using the same instrumental conditions. For each sample, the absorbance spectrum was collected

against a background obtained with a dry and empty ATR cell. After acquiring each spectrum, the ATR crystal was cleaned with a cellulose tissue soaked in hexane and then rinsed with acetone.

### Thermal treatment

Approximately 100 ml of lard was placed in a porcelain capsule and heated on an electric device, while stirring manually with a glass rod. The temperature was monitored using a thermometer introduced into the capsule. To follow the oxidation process during the period of frying, the samples were subjected to increasing heat up to a temperature of  $300^\circ\text{C}$ ; during this process, heating was maintained up to 40 min. Samples were taken every 10 min.

### Biochemistry of thermodegradation

Frying is one of the oldest methods of food preparation, being used as early as 1600 BC by the ancient Egyptians [16,17]. Pliny (Gaius Plinius Secundus, 27–79 AD) recorded the first prescription that required eggs steeped in vinegar and then fried in oil. Authors in the middle ages (Chaucer, Cervantes) described cooking in oil in detail [16].

The intense frying of oils causes an oxidizing thermal degradation with the formation of decomposition products [18]. In this way, their quality is deteriorated by the oxidation that occurs during the heating process. Oxidation is a complex process, and involves three steps: initiation, propagation, and termination [19]. The overall process is initiated by heat, free radicals, light, photosensitizing pigments, and metal ions [20].

The chemistry of lipid decomposition in foods at elevated temperatures is complicated. Multiple reactions and interactions can occur rapidly and competitively. The rates of pathways of these degradation reactions are significantly affected by the temperature, reaction time, other constituents, sources of extraction, the environment, physical state, and molecular organization of lipids.

Most studies involving the effect of heat on lipids can be categorized as follows:

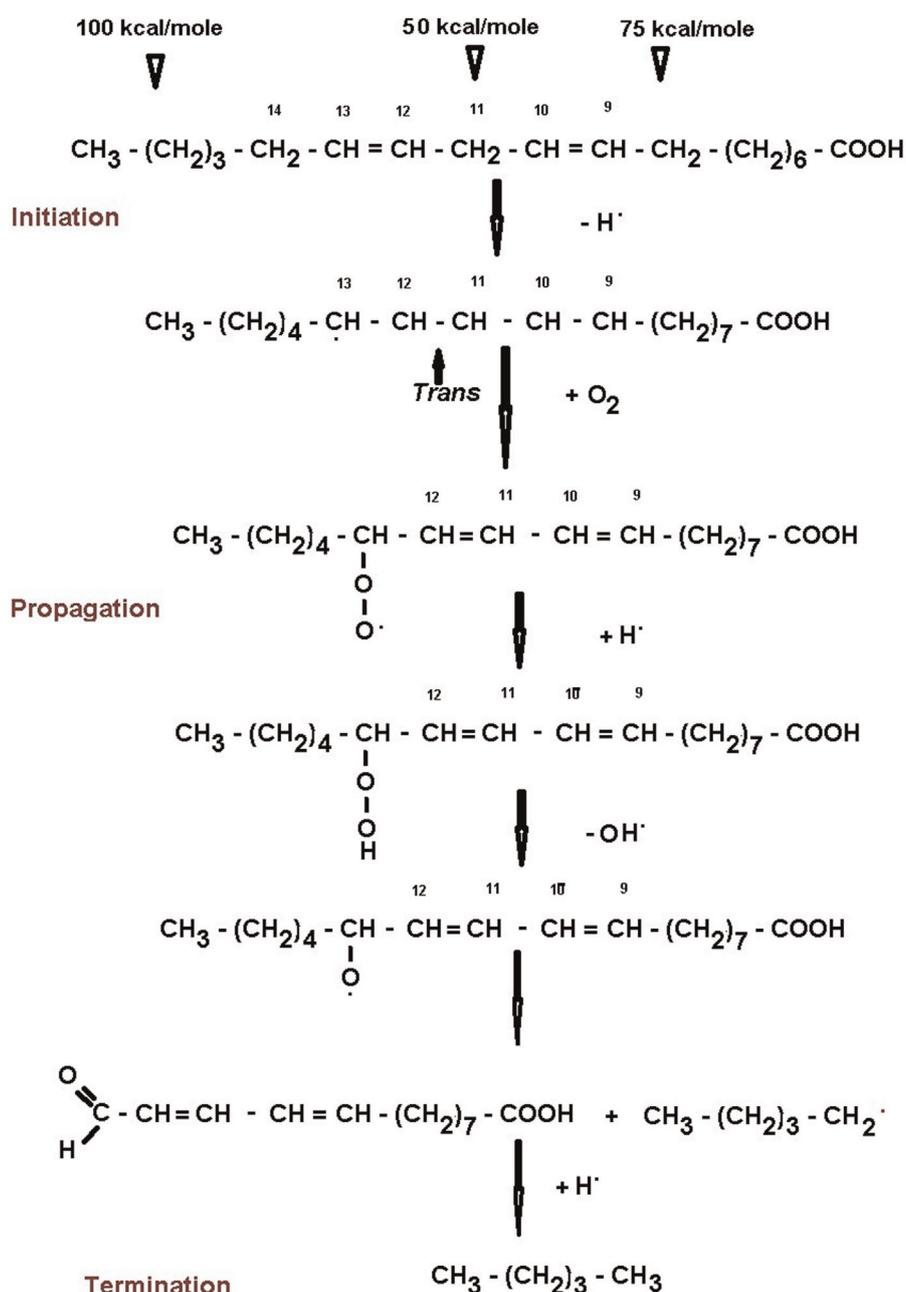
- (1) Studies in which heat was applied under strictly nonoxidative conditions with the objective of investigating the effect of heat alone [21].
- (2) Oxidative studies in which fats were oxidized under a flow of oxygen or air and various degrees of heating applied to speed up the reaction or to produce greater quantities of products [21].

The changes observed are in many cases explained on the basis of classic oxidative mechanisms such as the theory of Leningher Biochemistry of lipids [22], and modifications or extensions of this theory.

The chemical mechanism of thermal oxidation is principally the same as the autoxidation mechanism. The thermal oxidation rate is faster than the autoxidation, but specific and detailed scientific information and comparisons of oxidation rates between thermal oxidation and autoxidation are not

available. Ordinary oxygen in air is a diradical compound and requires radical oil to react. Taking into account the energy to break the carbon–hydrogen bond in stearic, oleic, linoleic, and linoleic acids during thermal oxidation or autoxidation [23,24], the mechanism can be represented in Fig. 1. Unsaturated fatty acids are more susceptible to oxidation than saturated fatty acids; the level of polyunsaturated fatty acid such as linoleic or linolenic acids should be low and the level of oleic acid should be high, with moderate amounts of saturated fatty acid [25,26].

Figure 1



Initiation, propagation, and termination steps of thermal oxidation of oil.

## Results and discussions

Figure 2 shows a comparison of the FTIR spectra of fresh lard and pork bacon.

As can be seen, the spectra are similar and for a better visualization, they were scaled.

All the details on the association between the bands and the chemical structure of the sample have been described earlier [1,27–31].

Next, we will present only some of them:

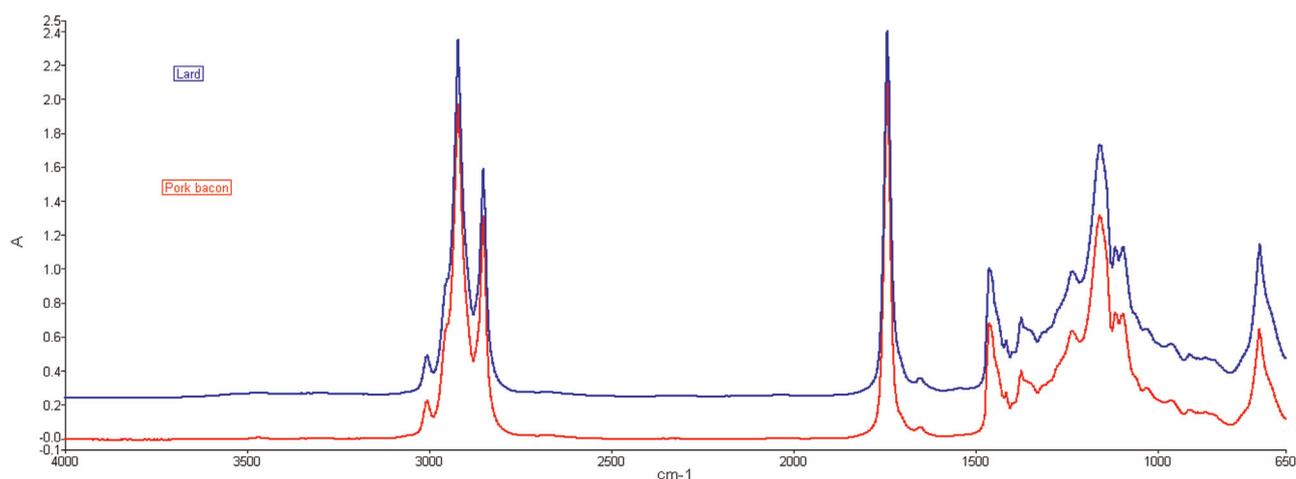
- (1) The shoulder presented at  $3006\text{ cm}^{-1}$  is associated with the stretching vibration of *cis* olefinic double bonds.
- (2) The C=O group of triglycerides shows a stretching vibration band, at about  $1746\text{ cm}^{-1}$ .

- (3) Absorption at  $1650\text{ cm}^{-1}$  is attributed to deformation bands of OH bonds of water [32].

The following group of bands was observed at about  $1238$ ,  $1163$ ,  $1118$ , and  $1097\text{ cm}^{-1}$ , respectively, and a shoulder at  $1033\text{ cm}^{-1}$  could be assigned to the stretching vibrations of the C–O group in esters [32]:

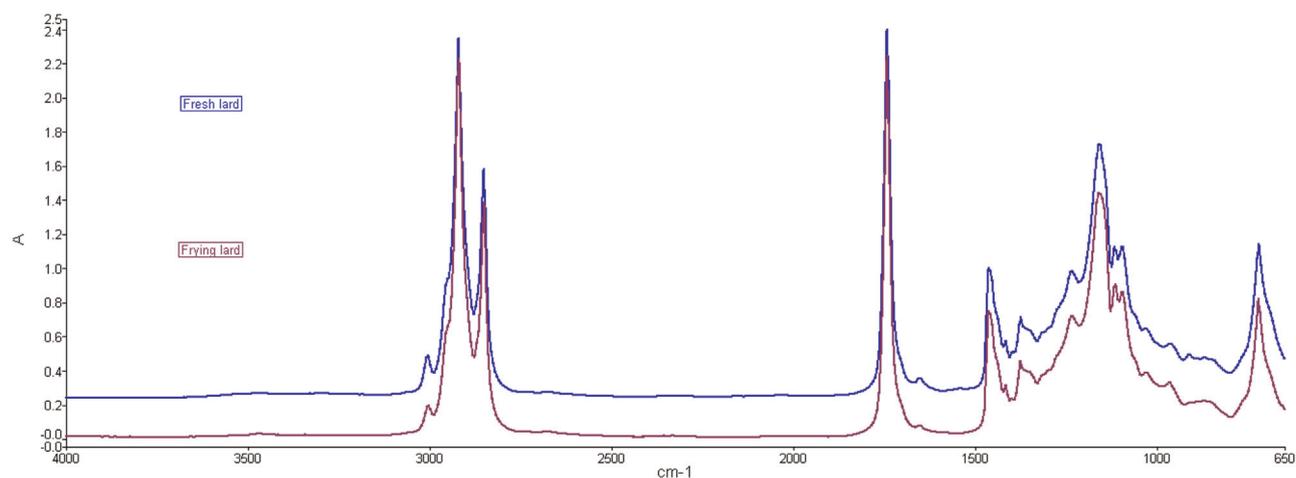
- (1) Lard had approximately equal proportions of saturated acyl groups and the oleic acyl group, which was reflected in the lard spectra, in which peaks of  $1119$  and  $1100\text{ cm}^{-1}$  appeared to have the same height [33].
- (2) Some other authors assign the band at  $1238\text{ cm}^{-1}$  to the bending vibration out-of-plane of the methylene group [34].
- (3) Finally, at  $\sim 723\text{ cm}^{-1}$ , there is a band, as a result of the overlapping of the methylene rocking vibration

**Figure 2**



FTIR spectra of fresh lard and pork bacon. FTIR, Fourier transform infrared.

**Figure 3**

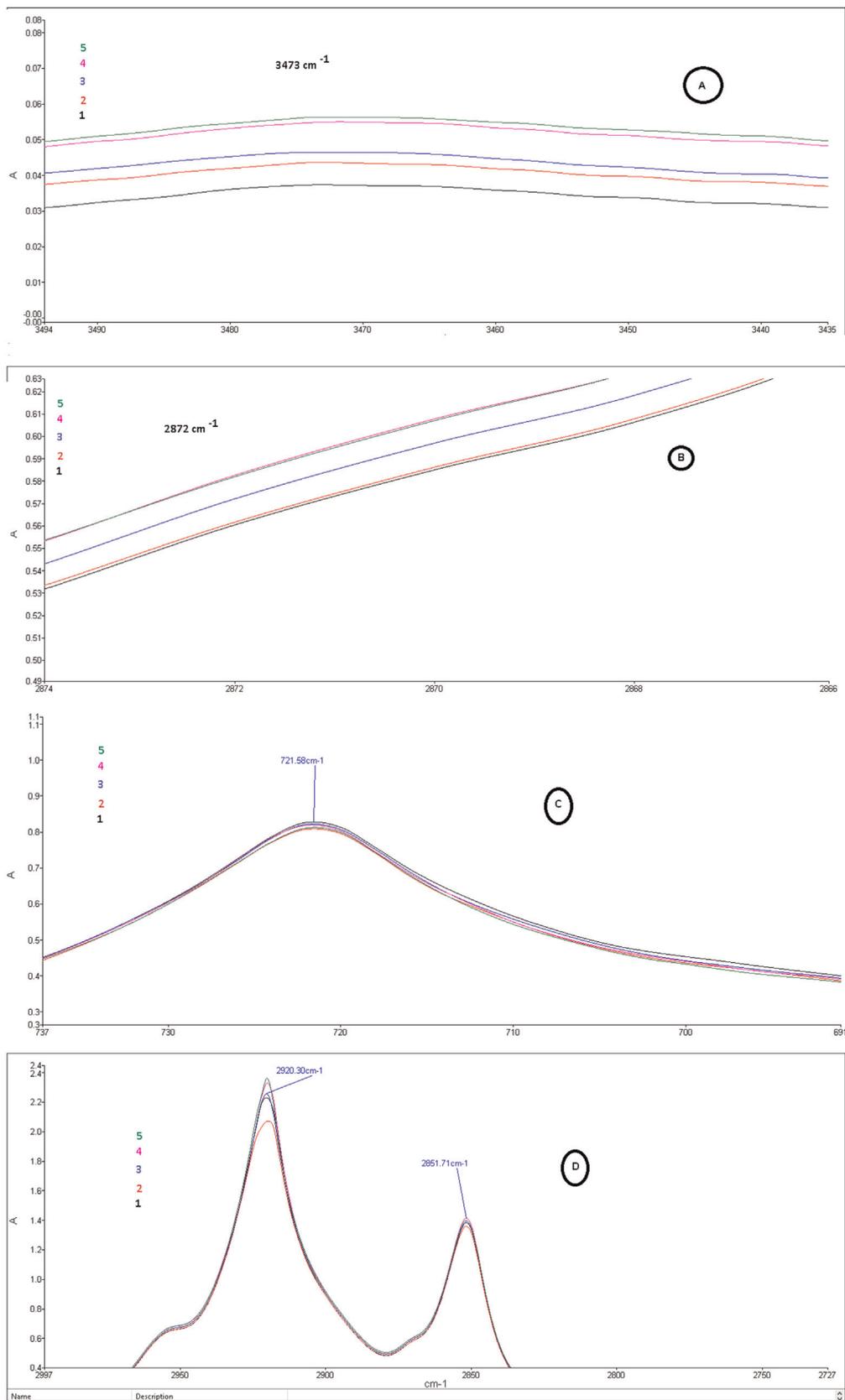


FTIR spectra of fresh and frying lard. FTIR, Fourier transform infrared.

and the out-of-plane bending vibration of *cis*-disubstituted olefins [35,36].

In our samples, we observed that the absence of a small shoulder, at  $1711\text{ cm}^{-1}$ , assigned to free fatty acids, and

Figure 4



Modifications of FTIR spectra of frying lard over time (1–fresh lard, 2–after 10 min frying, 3–after 20 min frying, 4–after 30 min frying, and 5–after 40 min frying). FTIR, Fourier transform infrared.

the absence of a band at around  $1648\text{ cm}^{-1}$ , assigned to disubstituted *cis*-olefins, can provide us with more information on the composition of lard.

Figure 3 shows the FTIR spectra of fresh and frying lard, while in Fig. 4, the FTIR spectra of frying lard over time are presented (1–fresh lard, 2–after 10 min frying, 3–after 20 min frying, 4–after 30 min frying, and 5–after 40 min frying). In the small boxes the modifications of intensities during the oxidative process are presented.

At first glance, there is no difference between the spectra. However, at closer examination, there are some differences.

Next, we will present only some of the most important changes:

- (1) Differences are observed at around  $3472$  and  $966\text{ cm}^{-1}$ . The peak intensities showed a slight increase; the time course of oxidation can be monitored by following the growth of the ROOH absorption band, which shifts progressively to lower wavenumbers as oxidation proceeds, making it necessary to use a peak find algorithm [37,38], boxes A in Fig. 4.
- (2) The band at  $2852\text{ cm}^{-1}$  and the shoulder at  $2952\text{ cm}^{-1}$  show an increase in their intensity during oxidation, boxes D in Fig. 4.
- (3) A shoulder at  $2872\text{ cm}^{-1}$  is also formed, associated with the production of the  $\text{CH}_3$  group.
- (4) It is also interesting to follow the spectral changes in the C=O region ( $1746\text{ cm}^{-1}$ ). Here, the study shows a widening of the band for the heated samples.

This observation is due to the production of saturated aldehyde functional groups or other secondary oxidation products that cause an absorbance at  $1728\text{ cm}^{-1}$ , which overlaps with the stretching vibration at  $1746\text{ cm}^{-1}$  of the ester carbonyl functional group of the triglycerides. When new carbonyls are formed from the initial aldehyde and ketone compounds, the maximum absorbance is in the region between  $1700$  and  $1726\text{ cm}^{-1}$ , resulting in a broadening of the  $1743\text{ cm}^{-1}$  band to lower wavenumbers [28], boxes B in Fig. 4.

- (1) A slight decrease in the intensity observed for the band at  $721\text{ cm}^{-1}$  implies the loss of *cis* double bonds during oxidation, boxes C in Fig. 4. This was confirmed by the decrease in intensity at  $3006\text{ cm}^{-1}$ , assigned to the stretching vibration of the *cis*-double bonds in  $\text{C}=\text{CH}$ , as mentioned before.

- (2) Moreover, a characteristic increase in intensity was observed at about  $3500\text{ cm}^{-1}$ , corresponding to the formation of peroxides.
- (3) Very small changes at  $1744\text{ cm}^{-1}$  may correspond to the formation of carbonyl compounds during oxidation [39,40].
- (4) It can be noticed that the bands corresponding to *cis-trans* isomerization ( $3008$ ,  $970$ , and  $720\text{ cm}^{-1}$ ) and, respectively, for oxidation reactions ( $3539$ ,  $1732$ , and  $1699\text{ cm}^{-1}$ ) present the same type of increasing or decreasing evolution, which can be explained by a similar rate-determining step, as stated before [19].
- (5) Lard had approximately equal proportions of saturated acyl groups and the oleic acyl group, which was reflected in the lard spectra, at peaks of  $1119$  and  $1100\text{ cm}^{-1}$ , but a slight increase in the value  $A_{1119}/A_{1110}$  from  $1.02$  to  $1.05$  was observed.

## Conclusion

FTIR spectroscopy has been found to be a versatile technique for evaluating the oxidative stability of lard and for providing information on the oxidation degree of a sample in a simple, fast and accurate way. Next, we will try to carry out similar studies for different animal fats (chicken, lamb, and cow) and different oils (olive, sunflower, and rapeseed).

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Nil.

## Conflicts of interest

There are no conflicts of interest.

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