EUROPEAN JOURNAL OF MATERIALS SCIENCE AND ENGINEERING
Volume 4, Issue 1, 2019: 3--10 | www.ejmse.tuiasi.ro | ISSN: 2537-4338

DOI: 10.36868/ejmse.2019.04.01.003

FTIR-SPECTROSCOPY STUDY OF MICROWAVE AND CONVENTIONAL HEATING ON THE DEGRADATION OF MARGARINE AND BUTTER

Fatos REXHEPI[1,*], Gresa KURTI[1], Flora FERATI[1], Shkumbin SHALA[2]

[1]Faculty of Food Technology, University of Mitrovica “Isa Boletini” Ukshin Kovaqica, Mitrovica, 40000, Kosovo.
[2]University of Business and Technology, Kalabria, 10 000 Prishtina, Kosovo.

Abstract

Our investigation consists to evaluate the effects that microwave heating (5 min at 1100 W) and conventional heating (18 min at 180 °C and 20 min at 250 °C) have on margarine and butter samples. The finally experimental results showed oxidations of margarine and butter samples during conventional heating which is in contrast with microwave heating for both treated samples used ratio of characteristic FTIR absorbances used as indicator of oxidation level. Significant increases in intensity of FTIR vibrations which corresponding with imine group in region from 1690-1640 cm^{-1} were compared after conventional oven heating, showing that there do not have any increase intensity in this region of spectra. Otherwise, microwave heating different impact has on evaporation of polar ingredients such as water in margarine samples compare with several butter which contain low level of water but evaporation is happened easy which is coming from different type of interaction of between microwave and water and this type of energy can’t be transfer all in water molecule and to initiate evaporation. Therefore, the degradation of margarine and butter samples can be accurately measured using FTIR spectroscopy as a green, sensitive and not expensive method of analysis.

Keywords: *FTIR spectroscopy, microwave oven, convective heating; margarine, butter.*

Introduction

Food cooking in our case margarine and butter, involve and other chemical and physical qualitative changes which is source from different chemical reactions which changes also and their nutritional value. Heating of food samples induces their water loss, but in most cases increases its lipid content and only some fat is lost. In General this effect depends from the type of heating condition [1, 2].

Conventional heating oven consists by surrounding hot air, which is heated by a source of electricity heat in comparison to microwave oven which working principle is by a power source which emitting microwaves that are absorbed by the heated food samples. The electromagnetic field generated inside the microwave oven produces rotation and collision of polar molecules such water and ions inside the food. Water and other polar molecules which will rotate very faster in food causing frictions that generate heat and increase temperature. Possibility of interaction between ionic compounds and other molecules and disrupting hydrogen bonds with water can be accelerated by the electromagnetic field interaction additional heat [3, 4].

Some researchers reports that food heated in microwave oven can provide a product comparable to conventional oven preparation also other authors monitor meat samples during conventional heating by FTIR spectroscopy they observed increase intensity which confirm

Corresponding author: fatos.rexhepi@umib.net

Maillard reaction to happened during conventional heating compared with microwave heating where this effect is reduced and this reaction is occur partially [5, 6]. But in contrast, other authors reported that the flavor and aroma of conventional oven heated samples are better and more acceptable as compared to microwave oven heated samples [7]. Some research confirms that microwave heating initiate oxidation of fat contents and transforms fatty acid in different isomers [8-11]. FTIR spectroscopy has been applied for quantitative and qualitative analysis and characterization of fat, protein and carbohydrates in different food samples [12-14].

Margarine and butter in general has a lot of difference because butter is from animal origin and margarine is vegetable oil mixed with water. Usually butter any additives aren't contains and margarine may contain an antioxidant, vitamins, coloring matter, and an emulsifier. Rule of emulsifiers in margarine is to dissolve oils in water but butter if contain water that is low percent and rule of emulsifiers in butter play natural protein [15]. Comparative study between microwave and conventional heating was reports before in olive oil samples using gas chromatography methods and they conclude higher degradation level during microwave heated than conventional heating. In the case of microwave heating they reports higher formation of radicals, triglyceride oligopolymers and polar compounds [16].

Mailard reaction is basic reaction what occur in most of food samples during thermal treatment which is reaction between carbonyl group from reducing sugars and ammino group from proteins or in general between carbonyl group and amino group. Mailard reaction has high impact in quality of heated food samples rather it is better investigated through subdividing in three stages: Early stage, Advanced stage, Final stage [17]. At early stage of Mailard reaction between sugar and amines synthesis product is Schiff's base and later rearrangement at compound known as Amadori compound.

Anyway, still have insufficient reports for applying FTIR-Spectroscopy to detect product formation from Mailard reaction in heated food samples and for this reason our research interest is applying FTIR as a rapid tool for detection of Mailard reaction products especially their early stages of formation and also using IR frequencies to found oxidation level of compounds after heating of samples.

The aim of this work was to apply FTIR-Spectroscopy to study thermal transformations of lipids that occur and understanding chemical interaction between composition components under the different time of heating during conventional and microwave heating for margarine and butter samples.

Materials and Methods

Samples Preparation

Margarine and Butter samples purchased from local market in Mitrovica, R Kosovo were used. Two commercial brands of each type were studied. The samples were then heated either in a conventional oven for 18 min at 180 °C and 20 min at 250 °C or in a microwave oven for 5 min at a frequency of 2,450 MHz and a power of 1,100 W. These combinations of time and temperature for each type of heating system were necessary to reach similar final temperatures.

FTIR Measurements

An Irrafinity-1 Shimadzu FT-IR spectrophotometer equipped with a deuterated triglycerine sulphate (DTGS) detector was used to acquire FTIR spectra. The FTIR spectra were obtain with a resolution of 4 cm^{-1} with a data point spacing of approximately 1.9 cm^{-1}, each spectrum was obtained in average from over 64 scans. Samples were deposited between two CaF_2 windows creating a thin film. All spectra were recorded from 4000 to 1000 cm^{-1} and processed using IR-Solution Software for Windows (Shimadzu). Spectra obtained using higher resolution gave similar characteristic FTIR data for all measured samples, but also and higher noise level and their scanning is too time consuming. After each measurements, the CaF_2 window was careful washed using acetone as a solvent and then dried in dry oven.

Assignment of bands was done by comparison with literature spectral data and with reference compounds spectra included in the software spectral library. Height and area of each band were measured and calculated by the essential FTIR-Shimadzu software.

Results and Discussion

Evaluation of FTIR Spectra

Samples were analyzed after each cycle of heating by FTIR spectroscopy. Both intensity and frequency of the bands were assessed to identify structural changes before and after heating. The band assignments and their respective mode of vibration are shown in Table 1. For better monitoration IR spectra we divided in two basic regions first is 4000-2500 cm^{-1} and 2000-1000 cm^{-1}. Analyzed sample (margarine and butter) spectra presented in Fig. 1 for margarine and Fig. 2 for butter comprised the characteristic broad bands due to O-H bond of the hydroxides: 3600 – 3200 cm^{-1}, from water molecules which is present only in margarine microwave heated samples not and conventional oven heated samples where thermal treatment was evaporated water from samples.

These can explain based on margarine contains emulsifier which role is to homogenize vegetable oil and water and butter usually any additives are used [15]. From this maybe evaporation of water from margarine with added additives composition is difficult to separate especially using microwave thermal treating which interact differently with dipole molecules such us water and definitely transferred microwave energy is insufficient to evaporate water molecules compare with conventional oven heating where transfer of energy in sample is different and water evaporation is possible.

In Fig. 2 is FTIR spectra of butter where all type of heating remove the water and any characteristic peak in this region is not present in this region and this mean butter don't contain moisture or it is in low level.

Table 2. FTIR absorbance bands and their characteristic functional groups

Wavenumbers cm^{-1}	Characteristic group and mode of vibration
3300-3600	−O−H
3008	=C-H Stretching (cis)
2925	−CH(CH_2) Asymmetric stretching
2854	−CH(CH_2) Symmetric stretching
1745	−C=O (ester) Stretching
1690-1640	C=N Stretching (imine/oximes)
1463	−C−H (CH_2 and CH_3) Bending
1377	−C−H (CH_3) Symmetric bending
1237	Stretching vibration of the C−O ester groups
1163	Stretching vibration of the −C−O ester groups
1099	−C−O Stretching

For lipid characterization by FTIR Spectroscopy are stretching vibration of methylene gropu from 3000 to 2800 cm^{-1} region, represented in Table 2.

Both bands of methylene group were clearly observed in spectra after heating of margarine sample using the conventional electric oven and microwave whereas their intensity after microwave oven heating were significantly lower in comparison to the intensity after conventional oven heating in two different temperatures as can be observed in Fig. 1 (black lines refer to spectra of margarine sample heated in microwave oven). But is not same and with butter sample where intensity of both bands 2924 and 2854 cm^{-1} in case of microwave heated butter samples where their intensity are near with spectra intensity obtained from conventional heating in 250 °C and decreasing intensity of conventional heating in 180 °C observed in Fig. 2. This difference in those bands refers to lipids where butter it has animal origin compare with margarine which lipids are from vegetable origin.

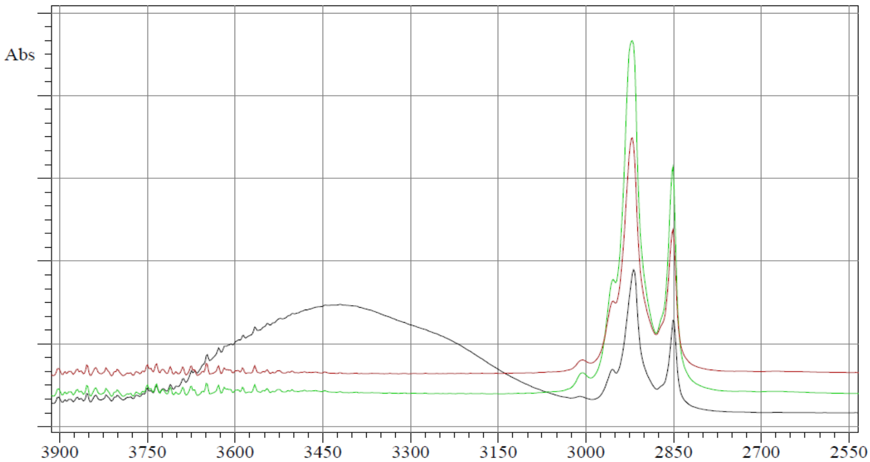

Fig. 1. FTIR Spectra (region 4000-2500cm-1) of margarine sample green line conventional heating 180 °C, red line 250 °C conventional heating, black line microwave heating

In general intensity peak of methylene group and carbonyl group (1745 cm^{-1}) after conventional thermal treating are higher compare with microwave treatment. At same relation reports other authors using FTIR in comparison microwave and conventional heating of meat and they explain this with possibility of occur Mailard reactions during conventional cooking compare with microwave cooking where this reaction partially happened based vibrational spectroscopy analysis [6].

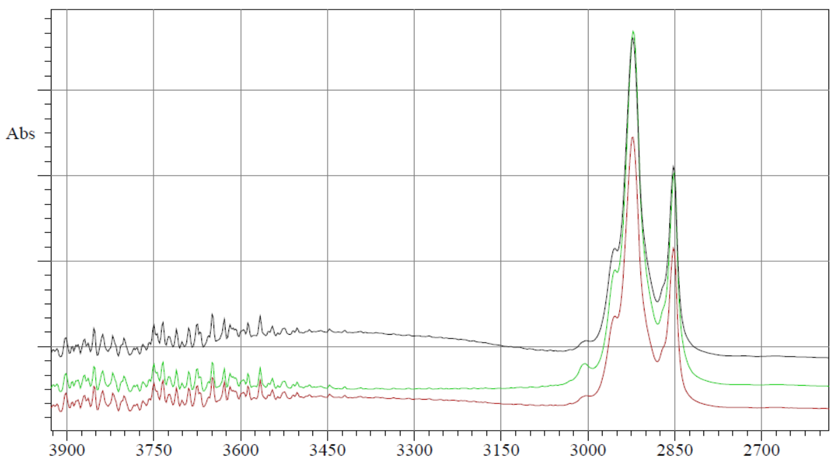

Fig. 2. FTIR Spectra (region 2500-4000 cm^{-1}) of butter sample black line conventional heating 250 °C, red line 180 °C, green line microwave heating

But this is not sufficient confirmation of Mailard products because Schiff's base consists of new double bond formation C=N known as imines. Change in the intensity of carbonyl and methylene group at same time it is insufficient information to confirm product from Mailard reaction.

In Fig. 3 as can be seen margarine sample during microwave heating FTIR spectra shows characteristic absorptions in the region from 1650-1680 cm^{-1} which is characteristic for most of imines compounds or Schiff's base known in early stages of Mailard reaction which is presented in Fig. 4 and intensity in this region is lower for same samples heated with conventional heating.

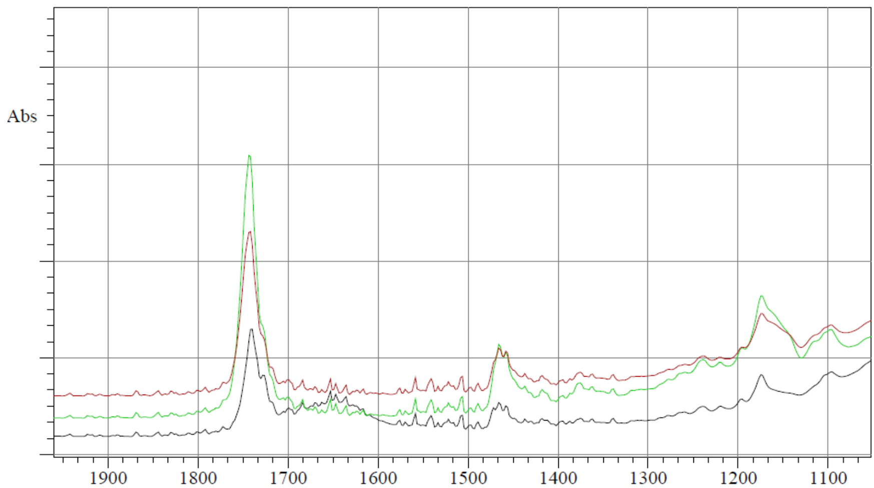

Fig. 3. FTIR Spectra (region 1000-2000 cm-1) of margarine sample green line conventional heating 180 °C, red line 250 °C conventional heating, black line microwave heating

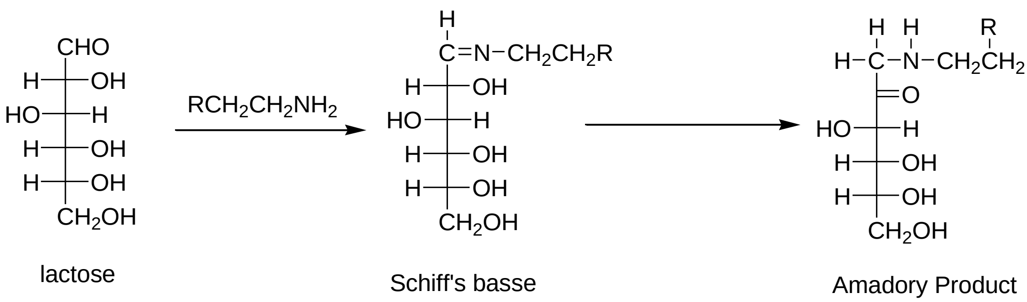

Fig. 4. Early stage of Mailard reaction until Amadory Product

But after same treatment procedure applied and butter samples FTIR spectra in same region doesn't present significant changes between which mean butter samples it isn't going in same trend of Mailard reactions and in this conditions of heating is not detected Schiff basis (imine functional group) present in Fig. 5.

Intensity changed in frequency 1653 cm^{-1} is present in Fig. 6 and as can be seen margarine samples is not involved in Mailard reaction during all conventional heating but its intensity rapid increased at the microwave heating which can be from imine formation compounds (present in Mailard reaction in Fig. 4) which is not in case a butter samples where in conventional heating it has intensity increasing but is going very slowly and after microwave heating doesn't have any significant changes.

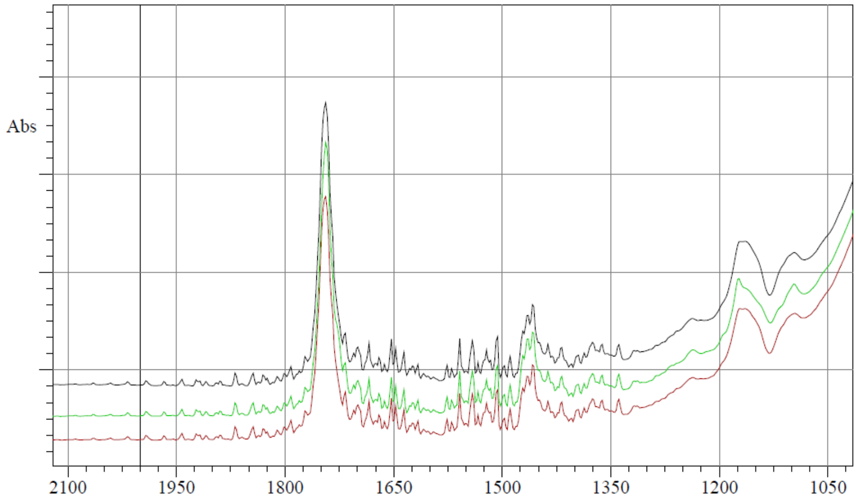

Fig. 5. FTIR Spectra (region 1000-2000 cm^{-1}) of butter sample black line conventional heating 250 °C, red line 180 °C, green line microwave heating

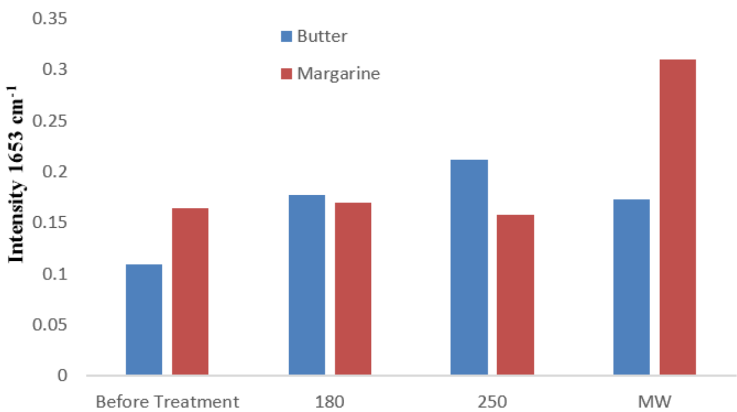

Fig. 6. Intensity changes of peak 1653 cm^{-1} for both samples in different heating conditions

Several other authors has already reports about oxidation of lipid during microwave thermal treating [8-10], and monitoration of heated milk after microwave heating causes significant increase of the oxidation products [11]. The absorbance ratio at 3008 cm^{-1} and 2854 cm^{-1} was suggested as a marker of oxidation for docosahexaenoic acid and applied for estimation of degree of unsaturation [18]. In this study this absorbance ratio was applied to monitor oxidation of more complex matrix like plant edible oils. The matrix could influence the specific bands due to interference, signal overlapping or different oxidation rate. The effects were expected to be more pronounced in the case of edible oils. Moreover, stretching vibration of cis-double bonds =C-H and methylene vibrations CH_2 groups are in significant correlation. From a practical point of view, if the band 2850 cm^{-1} shifts or change in intensity and at the same moment band at 3008 cm^{-1} shift or change the intensity it very clear unsaturated bonds converted in saturated bonds or vice versa. Careful their observations can be seen they are strongly in correlations example when first increase second decreasing and vice versa. This ratio can be considered as an indicator of oxidation [19]. This was observed in heated samples of margarine and butter and results can see in Fig. 7.

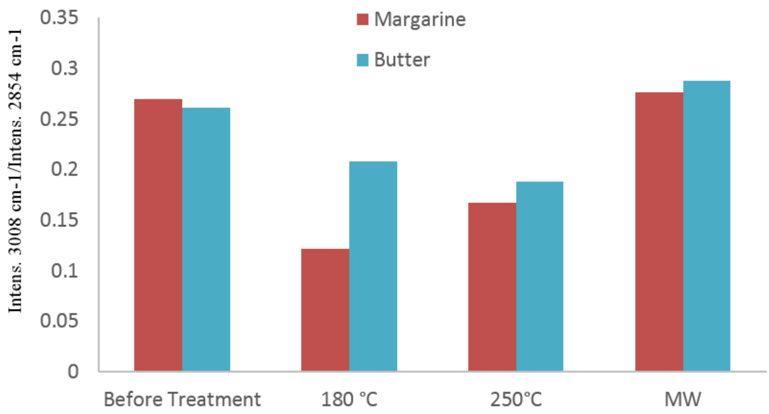

Fig. 7. Ratio of FTIR absorbance in wavenumber 3008 cm^{-1} / 2854 cm^{-1} of margarine and butter samples

From Fig.7 can explain changes of two samples during different type of heating. Before heating both samples are in similar level of this frequency ratio but during conventional heating in both applied temperatures decreased ratio of margarines more than butter samples which is easy to understand high level of oxidation margarines during conventional heating or unsaturated double bonds oxidized and converts in saturated compounds. This confirm higher thermal stability of butter samples compare with margarines during conventional heating but all of this if we compare with microwave heating which is approximately in same ratio level for both treated samples which confirm that microwave heating do not have any impact in oxidation of lipids in margarine and butter samples.

Conclussion

At microwave heating only in margarine samples was detected several peaks which corresponds with different imine compounds also this type of heating it isn't enough sufficient to evaporate water from margarine samples where is responsible interaction between polar molecule of water and microwave heating. During microwave heating both of samples are same resistant with respect to oxidation compare with conventional heating where oxidation level advanced more in margarine samples than butter. In general margarine is easy decomposed compare with butter where thermal stability is higher this should be from their different origin of product.

References

[1] A.P. Hearty, S.N. McCarthy, J.M. Kearney and M.J. Gibney, *Relationship between attitudes towards healthy eating and dietary behaviour, lifestyle and demographic factors in a representative sample of Irish adults*, **Appetite**, **48,** 2007, pp. 1–11.

[2] K. Sveinsdóttir, E. Martinsdóttir, D. Green-Petersen, G. Hyldig, R. Schelvis and C. Delahunty, *Sensory characteristics of different cod products related to consumer preferences and attitudes*, **Food Quality and Preference**, **20**, 2009, pp. 120–132.

[3] T. Ohlsson, *Domestic Use of Microwave Ovens*, In: R. Macrae, R. K. Robinson and M. J. Sadler, Eds., *Encyclopaedia of Food Science Food Technology and Nutrition*, **Academic Press, London**, 1993, pp. 1232-1237.

[4] C. R. Buffler, *Microwave Cooking and Processing: Engineering Fundamentals for the Food Scientist*, **Van Nostrand Reinhold, New York**, 1993.

[5] L. Fulton and C. Davis, *Roasting and Braising Beef Roasts in Microwave Ovens*, **Journal of the American Dietetic Association, 83 (5)**, 1983, p. 560.

[6] E. Calabrò and S. Magazù, *Comparison between Conventional Convective Heating and Microwave Heating: An FTIR Spectroscopy Study of the Effects of Microwave Oven Cooking of Bovine Breast Meat*, **Journal of Electromagnetic Analysis and Applications**, **4**, 2012, pp. 433-439.

[7] V. D. Pawar, F. A. Khan and B. S. Agarkar, *Effect of Fat/Whey Protein Concentrate Levels and Cooking Methods on Textural Characteristics of Chevon Patties*, **Journal of Food Science and Technology**, **39(4)**, 2002, pp. 429-431.

[8] T. Albi, A. Lanzon, A. Guinda, M. C. Pérez-Camino and M. Leon, *Microwave and Conventional Heating Effects on Some Physical and Chemical Parameters of Edible Fats*, **Journal of Agricultural and Food Chemistry**, **45(8)**, 1997, pp. 3000-3003.

[9] H. Yoshida, N. Hirooka and G. Kajimoto, *Microwave Heating Effects on Relative Stabilities of Tocopherols in Oils,* **Journal of Food Science**, **56(4)**, 1991, pp. 1042-1046.

[10] H. Yoshida and G. Kajimoto, *Microwave Heating Affects Composition and Oxidative Stability of Sesame (Sesamum indicum) Oil*, **Journal of Food Science**, **59(3)**, 1994, pp. 613-616.

[11] S. M. Herzallah, *Influence of Microwaving and Conventional Heating of Milk on Cholesterol Contents and Cholesterol Oxides Formation*, **Pakistan Journal of Nutrition**, **4 (2)**, 2005, pp. 85-88.

[12] F. R. Van de Voort, *Fourier Transform Infrared Spectroscopy Applied to Food Analysis*, **Food Research International**, **25(5)**, 1992, pp. 397-403.

[13] K. F. Ng-Kwai-Hang, J. E. Moxley and F. R. van de Voort, *Factors Affecting Differences in Milk Fat Test Obtained by Babcock, Rose-Gottlieb and Infrared Methods and in Protein Test From Infrared Milk Analysis*, **Journal of Dairy Science**, **71(2)**, 1988, pp. 290- 298.

[14] J. M. Olinger and P. R. Griffiths, *Effects of Sample Dilution and Particle Size/Morphology on Diffuse Reflection Spectra of Carbohydrate Systems in the Near and Mid-Infrared. Part 1: Single Analytes*, **Applied Spectroscopy**, **47(6),** 1993, pp. 687-694.

[15] P. Walstra, J.T.M. Wouters and T.J. Geurts, **Dairy Science and Technology**, Taylor Francis Group, Boca Raton, London, New York, 2006.

[16] F. Caponio, A. Pasqualone and T. Gomes, *Effects of conventional and microwave heating on the degradation of olive oil*, **Eur Food Res Technol, 215**, 2002, pp. 114–117.

[17] J. Mauron, *The Maillard reaction in food: a critical review from the nutritional standpoint*, **Progress in Food Nutrition Sciences**, **5**, 1981, pp. 5-35.

[18] M.H.H. Roby, V.C. De Castro, B.N. Targino, P.H. Alves Da Silva, C. Mangavel, F. Chretien, C. Humeau and S. Desobry, *Oxidative stability of DHA phenolic ester*, **Food Chemistry**, **169**, 2015, p. 41.

[19] M.D. Guillen and N. Cabo, *Fourier transform infrared spectra data versus peroxide and anisidine values to determine oxidative stability of edible oils,* **Food Chemistry, 77**, 2002, p. 503.

Received: September 6, 2018
Accepted: December 10, 2018