Effect of Microwave Radiation on Dielectric Behavior of Two Vegetable Oils

Margareta Pecovska Gjorgjevich[1], Julijana Velevska[1] and Metodija Najdoski[2]

1. Faculty of Natural Sciences and Mathematics, Institute of Physics, "Sts. Cyril and Methodius" University, 1000 Skopje, Republic of Macedonia

2. Faculty of Natural Sciences and Mathematics, Institute of Chemistry, "Sts. Cyril and Methodius" University, 1000 Skopje, Republic of Macedonia

Abstract: The effect of microwave (MW) heating on the dielectric properties and oxidation processes of virgin olive oil and refined sunflower oil were determined by dielectric and UV- spectroscopy. Samples were heated in the microwave oven (850 W, 2.450 MHz) for 0 to 14 minutes. The results show degradation of dielectric characteristics, conductivity and oxidative stability of investigated oils, increasing with the exposure time. UV spectrum shows only one defined peak at 206 nm for olive oil confirming the dominant presence of monounsaturated fats and four peaks for sunflower oil (203 nm, 230 nm, 269 nm and 278 nm) dependent on polyunsaturated acid fats contents. Increasing of absorbance at all peak wave lengths indicates production of lipid oxidation, due to formation of conjugated monoenes and dienes and in small amounts due to trienes and secondary products like ketoaldehydes. Dielectric constant for olive oil is stable and almost unchangeable with MW radiation while sunflower oil's ε' oscillates around the origin value in greater rate. Dielectric loss ε'' decreases with increasing time of MW radiation and its maximum shifts towards higher frequencies for sunflower oil indicating shortening of the relaxation times, while for olive oil it is unchanged. Cole-Cole analysis show the presence of only one relaxation process in the oils. Conductivity of oils is increasing in similar way with increasing frequency following the Jonscher's power law and is not changed with MW exposure time. Olive oil has conductivity higher for four orders of magnitude than sunflower oil, which is connected to the high content of monounsaturated fats. The differences between sunflower and olive oil characteristics are discussed.

Key words: Vegetable oils, microwave radiation, dielectric properties, absorbance.

Nomenclature

MW:	Microwave
C:	Capacitance
G:	Conductance
B:	Susceptance
Y:	Admittance

Greek letters

ε:	Dielectric constant
δ:	Angle
σ:	Conductivity
λ:	Wavelenght

Corresponding author: Margareta Pecovska Gjorgjevich, Ph.D., research fields: dielectric materials, semiconductors and biophysics. E-mail: pecovska@pmf.ukim.mk.

1. Introduction

Vegetable oils biodegrade quickly and completely and exhibit very low or no toxicity compared to mineral oils because they do not contain halogens, polynuclear aromatics, volatile or semi-volatile organics [1]. These esters degrade almost 100% within. Very important characteristics are their environmental friendly behavior: renewable, non toxic and biodegradable. Natural oils show good oxidation stability. Their viscosity rapidly increases with the heating and they ultimately polymerize, which may form the basis of a "smart" self sealing system [2]. The thermal and chemical stability of natural esters is very high. Natural oils are considered as a replacement of

mineral oils, as a coolant and insulation, since the world's energy requirement is increasing and petroleum industry is reaching its frontiers in reserves. There is also an ecological issue, putting natural oils application before mineral oils. Dielectric properties such as relative permittivity (dielectric constant), dielectric dissipation (loss tangent) and breakdown voltage are influenced by thermal aging of oils and it is necessary to define oils dielectric behavior when submitted to this process. Also there is natural oil food industry which is growing using new methods of fabrication. The conventional heating of oils is now days in great deal replaced by microwave heating, because of saving energy, significant reduction in heating time, providing inner penetration and fast heat conduction and preserving the dielectric properties of material. In microwave ovens microwaves of 2.45 GHz (high frequency oscillating electric and magnetic fields) are produced and applied to cavity oven [4], where they are absorbed by the material, in this case natural oils. The rate absorbed microwave energy depends on the dielectric properties of the material, primarily two mechanisms: dipolar relaxation and ionic conduction.

In this article we obtain the dielectric properties of two types of edible oils that are common in our region (south Europe-Balkan), refined sunflower oil and virgin olive oil. Their characteristics under conventional heating were discussed in our previous work [3]. In this work we submit investigated oils under microwave heating. The dielectric loss factor and electric polarity of natural esters are low, but specific heat is also low and that's the reason why they are heated very quickly [5].

2. Materials and Methods

Refined sunflower oil and extra virgin olive oil were obtained from commercial market. Their composition was: saturated fats 13%, monounsaturated 71.8% and polyunsaturated 6.5% in olive oil and 56.5 % saturated, 34% monounsaturated and 9.5% polyunsaturated fats

in the sample of sunflower oil.

Samples were submitted to MW heating in microwave oven (model LG Wavedom, 850 W effective power, 2,450 MHz frequency) for 0, 2, 4, 6, 8, 10, 12, 14 min. Oil temperature was determined after each microwave exposure period with thermocouple DT 200 with accuracy 0.1 K. Oil samples were cooled at room temperature 22 ± 1 °C for the analysis.

For the UV analysis the samples were dissolved in isooctan. Cary 3 Scan Spectrophotometer was used to determine absorbance at UV spectrum (200-320 nm) before and after the samples were submitted to MW radiation.

Dielectric measurements were made with Agilent 4192 A LF Impedance Analyzer and 16452 A Liquid Test Fixture (four contact probe). We measured capacitance of an empty cell C_0, capacitance of the cell filled with the investigated oil C_x, dielectric loss $D = \tan\delta$ conductance G and susceptance B of the samples in the frequency range from 100 Hz to 13 MHz.

The complex dielectric permittivity ε^* of the oils is given by [6]:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{1}$$

where ε' and ε'' are real and imaginary part of complex permittivity. The real part of the complex permittivity or dielectric constant ε' and the imaginary part ε'' are calculated from measured capacitance value and dielectric losses from the relations:

$$\varepsilon' = \frac{C_x}{C_0} = \frac{C_x \cdot d}{\varepsilon_0 S} \; ; \quad \varepsilon'' = \varepsilon' \tan\delta \tag{2}$$

where S is electrode area in cm^2, d is the thickness of the gate in cm, ε_0 is dielectric constant of the vacuum (8.85×10^{-12} F/m).

Frequency dependence of imaginary part of ε^* shows the changes which exhibit a maximum at $\omega\tau = 1$, where oscillating charges are coupled with the oscillating field and absorb a maximum electrical energy. If we observe dielectric dispersion with single relaxation time, the complex permittivity exhibits a symmetric Debye behavior with maximum at $\omega\tau = (\varepsilon_s/\varepsilon_\infty)^{1/2}$ (symmetrical semicircle with the

center on the *x*-axis is observed) and can be described with Debye equation:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} \quad (3)$$

where ε_s and ε_∞ are the low and high frequency values of dielectric constant.

If non Debye behavior is observed (distorted semicircle with center bellow the x-axis) we can describe this response using Cole-Cole equation [5]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (4)$$

The conductivity of the sample σ was calculated from following equations:

$$\sigma_{tot} = Y \cdot \frac{d}{S} = \sigma' + i\sigma'' \quad (Y = \sqrt{G^2 + B^2}) \quad (5)$$

$$\sigma' = \omega C \tan\delta \cdot \frac{d}{S} = \omega \varepsilon_0 \varepsilon'' \quad (6)$$

$$\sigma'' = G \cdot \frac{d}{S} \quad (7)$$

where σ' is *ac* conductivity of the dielectric material, connected to the dielectric loss due to relaxation processes, σ' is the bulk conductivity coming from Ohmic resistance without any relaxation processes, and σ is total conductivity of the sample (Y is admittance-complex conductance of the sample).

3. Results and Discussion

We followed the oxidative alteration of MW heated oils with UV absorbance changes. Different products absorb at different wavelength thus defining the changes in the oil during oxidation process. Temperature dependence from MW heating time, similar for both investigated oils is given in Fig. 1. The dependence saturates over 14 minutes heating and afterwards the temperature increases slowly with time exposure [5].

UV spectra changes indicate that MW heating produces lipid oxidation. Four characteristic peaks for sunflower oil, at ~203 nm, 230 nm 269 nm and 278 nm, were observed. Their changes with different MW exposure times are shown in Fig. 2. The former two peaks are related to the primary products of oxidation in
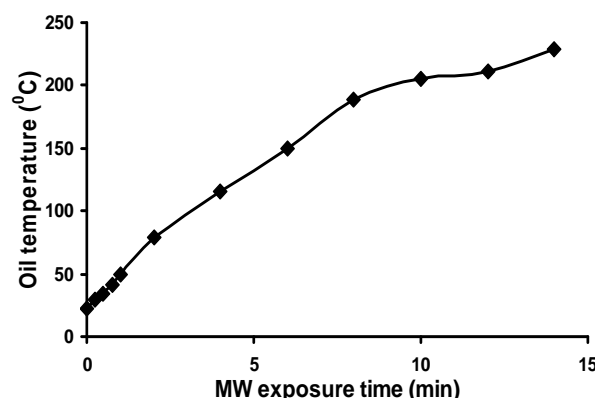

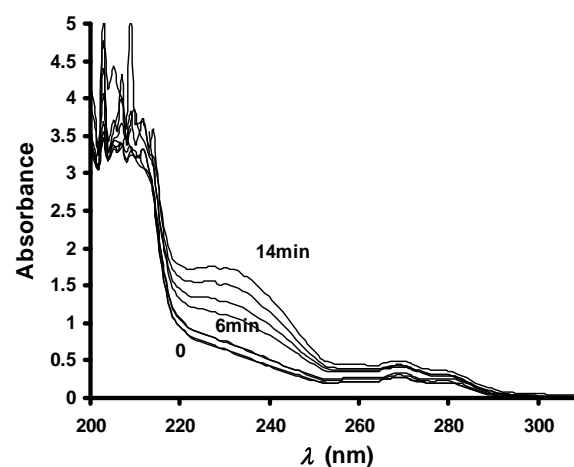Fig. 1   Oil temperature (°C) *vs* MW exposure time (min).

Fig. 2   UV spectra for sunflower oils submitted to different MW exposure times.

the oil, trienes and secondary products, ketoaldehydes (265-280 nm), and the first two to primary compounds of oxidation-monoenes at 203 nm and dienes at 230 nm [6].

Fig. 3 shows relative increasing of the absorbance with increasing MW exposure time. The increasing is with low rate for all detected peaks, except for 230 nm peak. This peak is connected to the oxidation of double unsaturated fatty acids. For MW exposure time over 6 minutes this peak is rapidly increasing. The position of the peaks is not changed with MW heating.

From the next figure, Fig. 4, it can be seen that different behavior of olive oil in the UV region for different MW exposures. The main peak is at 206 nm showing the products of oxidation of monounsaturated fatty acid- monoenes. The peaks at 230 nm and 269 nm

are very wide and almost unrecognizable. The presence of only one peak at 206 nm confirms the information about the content of the olive oil with almost 72% of monounsaturated fats and only 6.5% of polyunsaturated fats. Absorbance connected to the secondary products of oxidation is missing in the spectra.

Variation of relative absorbance for all three peaks is observed for olive oil also, Fig. 5. The changes are weak and very similar for all exposure times. Absorbance of monoenes and dienes is more pronounced but it is lowering with exposure time. The peaks don't change their positions with MW heating, also.

The oxidation is linearly progressive for sunflower oil, while it's almost constant and very low for olive oil. For absorption at 230 nm we observe decreasing with increasing exposure time. Since olive oil is virgin and with no additives, its structure is stable and shows no changes with the MW treatment. This is not observed for sunflower oil which is refined and submitted to several processes that influence its purity and stability. Its double unsaturated fats degradation is for one order of magnitude higher from other oxidation processes that take place in the oil.

The effect of MW heating was observed in dielectric behavior of oils, too. Fig. 6 shows the frequency dependent changes in ε' at different MW exposures for both oils.

The difference between the two oils is evident. Olive oil has very similar behavior of dielectric constant for all MW exposures, around 3.02-3.08 while for untreated sunflower oil ε' has value of 3.18, decreases until 6 minutes, than increases (8 minutes) and goes back to origin value for longer MW exposure times. The dispersion of the curve moves to higher frequencies for sunflower oil, but not for olive oil.

Same conclusions can be extracted from the dielectric loss spectra, for both oils (Fig. 7). The losses influenced by the degree of polarization of the oil for untreated sunflower oil are high (~0.05), they decrease
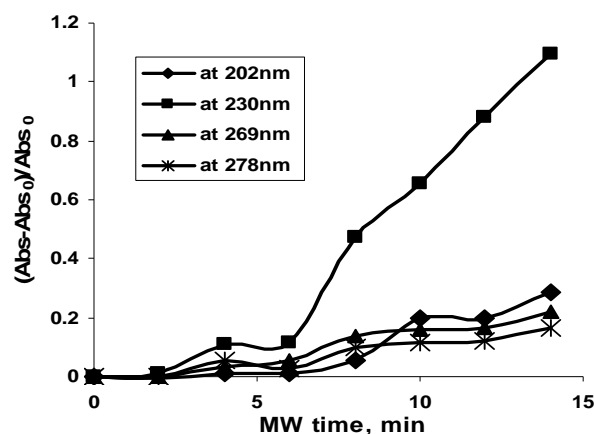

Fig. 3 MW exposure time dependent absorbance at peak wavelengths (given in the legend) for sunflower oils, where Abs_0 is for untreated sample and Abs for sample treated for given time of MW exposure.
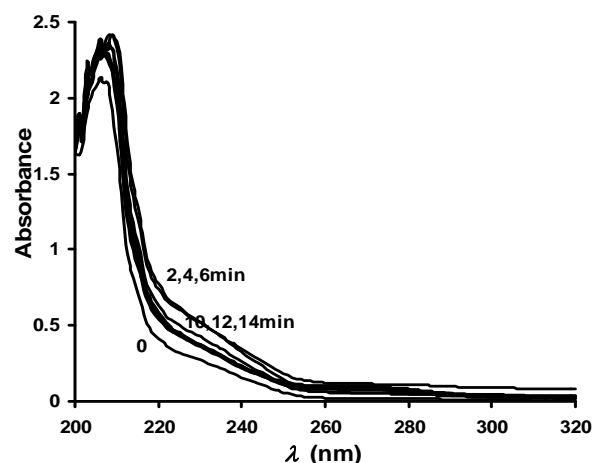

Fig.4 UV spectra for olive oils submitted to different MW exposure times.
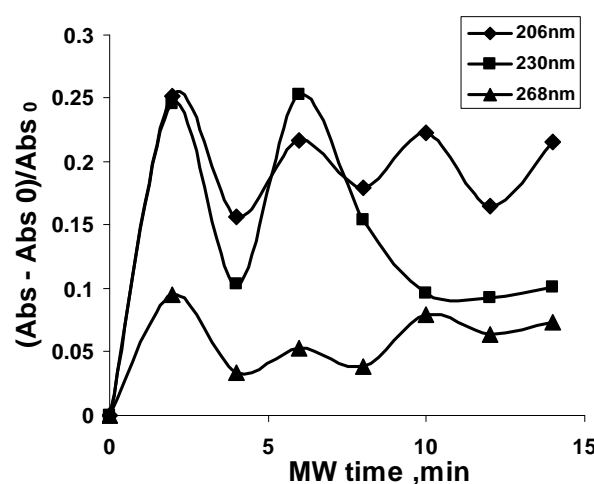

Fig. 5 MW exposure time dependent absorbance at peak wavelengths (given in the legend) for olive oils.
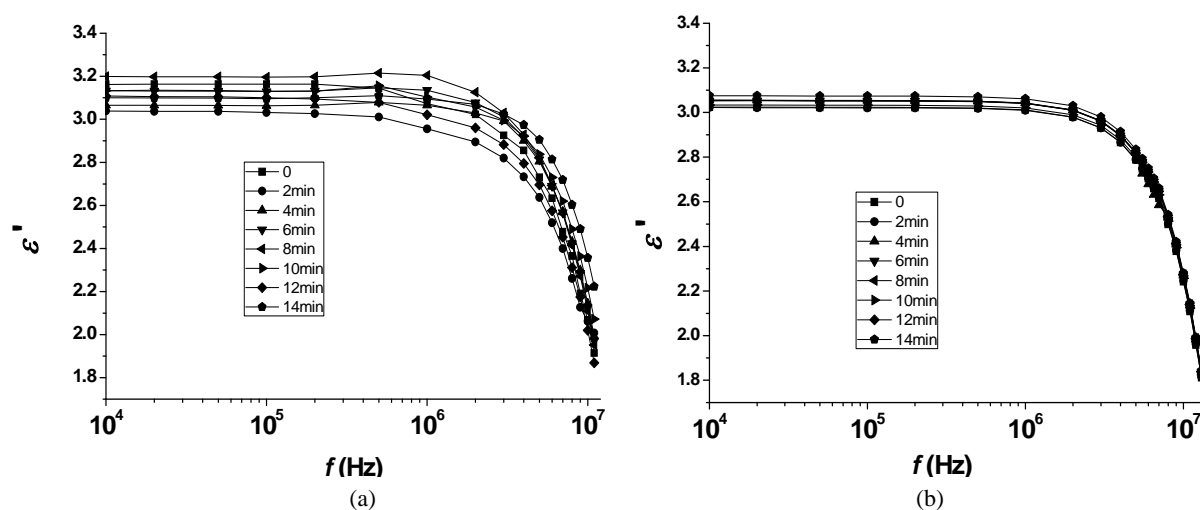
Fig. 6 Frequency dependence of the real part of dielectric constant for different MW exposure: (a) sunflower oil; (b) olive oil.

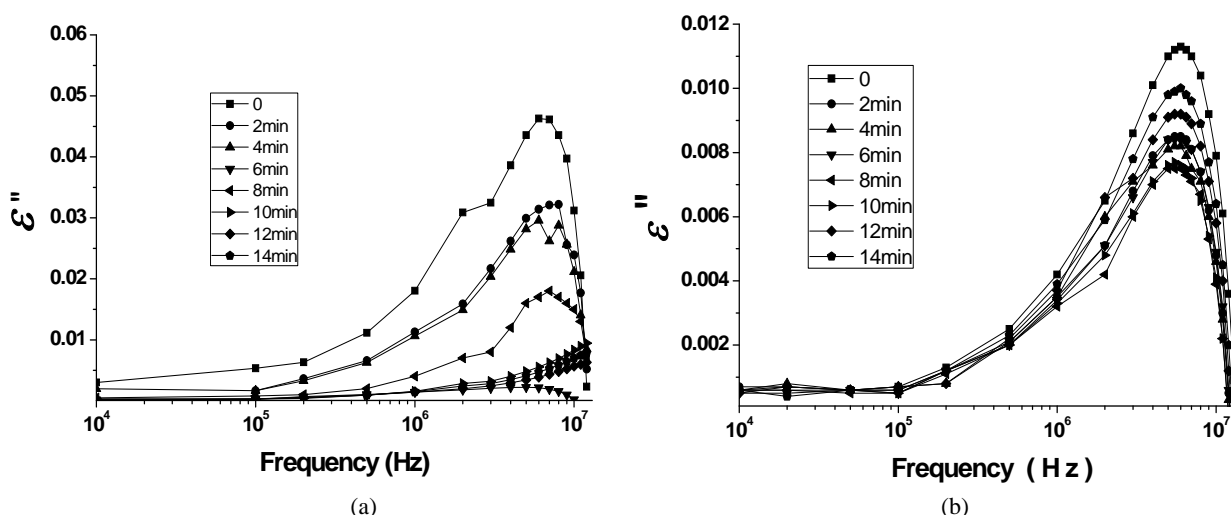**Fig. 7 Frequency dependence of dielectric loss for different MW exposures, (a) sunflower oil, (b) olive oil.**

with the exposure time and stay at ~0.01 for longer times indicating high deterioration of the oil in the interval until 10 minutes and slow repairing afterward. The lowering of the losses for olive oil is less pronounced, but with similar behavior, from ~0.012 for untreated sample to 0.007 for the sample with 8-10 minute exposure, and increasing with increasing exposure time, reaching slowly the origin value. The losses at beginning are differing (higher for sunflower oil), but with increasing MW exposure time, they become similar.

From the position of the loss peak we can define the time of one or more relaxation processes in the oil.

We observe shift of the peak to higher frequencies for sunflower oil with the MW heating, while the peak position is not changed for olive oil. It is placed at 5.5MHz which corresponds to relaxation time of 2.89 $\times 10^{-8}$ s ($\tau = 1/2\pi f$, f, angular frequency of the applied electric field). The relaxation time for sunflower oil moves from 2.89×10^{-8}s for untreated sample to lower values with the longer heating times. For times over 10 minutes, the peak is moved out of range of frequencies we measured, which puts the relaxation time bellow 10^{-8} s. Cole-Cole diagram (not given here) gives one distorted semicircle confirming one relaxation process with non-Debye behavior. The

height of loss peak depends on the size of side chain [7]. Lowering the peak with increasing MW time exposure for sunflower oil reveals the shortening of the chain in this edible oil, while in the same time, no significant changes are observed for olive oil. Another characteristics indicated by the height of the loss peak is the strength of dispersion which reflects the large dipole moment [8].

Fig. 8 shows frequency dependence of conductivity for both oils. The conductivity dependence from MW exposure is not similar to dielectric losses, because both susceptance B and conductance G are taken in consideration. So while conductance (ac conductivity) is connected to dielectric losses and lowers after the maximum value, in the same time susceptance increases and influences the linear change of the complex conductivity. The shape of the conductivity curves for both oils is similar and no changes were observed with MW radiation. The part of the curves in low frequency region where polarization effect takes place is omitted. The dependence of the conductivity is fitted to so-called universal dynamic response or Jonscher power low $\sigma_\omega = \sigma_0 + A\omega^n$, where $\omega = 2\pi f$ is radial frequency and n is exponential factor within values $0.6 < n < 1$ [9, 10].

For investigated samples the values for n and A are obtained from nonlinear least square fitting, n = 0.95, A = 1.3 × 10-16, for sunflower, and n = 0.98, A = 2 × 10-12, for olive oil. dc = 0 was obtained from the intercept of the curve with y-axis, 2.24 × 10-12 S/cm for untreated sample until 2.28 × 10-12 S/cm for olive oil exposed for 14 minutes and 5.34 × 10-16 S/cm to 5.37 × 10-16 S/cm for sunflower oil. Sunflower oil conductivity is lower than olive oil conductivity for almost four orders of magnitude, perhaps owing to the lower presence of monounsaturated fats, longer (heavier reorient) molecule and to presence of the additives such as antioxidant or metal deactivators, whose assignment is to improve the performance and oxidation stability, from the industrial processes involved.
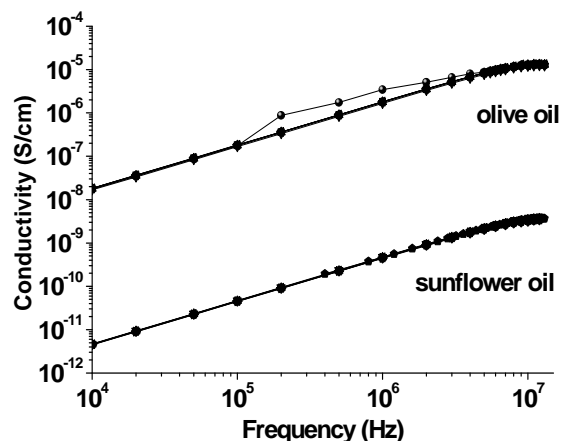

Fig. 8   Conductivity spectra of sunflower and olive oil for different MW exposures.

4. Conclusions

Two types of vegetable oils, refined sunflower oil and virgin olive oil, were subjected to microwave heating at 2.450 MHz and 850 W with different exposure times from 2 minutes until 14 minutes. The changes were observed in UV and dielectric spectra. Olive oil has higher content of monounsaturated fats (71.8%) than sunflower oil (34%) which is confirmed with the absorbance results. Absorbance spectra of olive oil show only one well defined peak at 206 nm connected to oxidation of monounsaturated fats, while wide plateau is observed at 230 nm indicating presence of polyunsaturated fats in small amounts. Absorbance of sunflower oil defines four peaks, at 202 nm connected to monoenes, at 230 nm to dienes, at 269 nm to trienes and at 278 nm to ketoaldehydes.

Observed changes of all peaks with MW exposure times show that oxidation of unsaturated fat acids takes place. This oxidation is increasing almost linearly with the increasing MW exposure time for all constituents of sunflower oil, but most pronounced is at 230 nm.

Oxidation process for olive oil is different. Fat acid oxidation is almost constant for all MW exposure time. Only dienes oxidation is lowering with increasing MW heating time. The oxidation happens at the beginning in first two minutes and the rate is unchangeable with the increasing MW exposure time.

Dielectric properties of olive oil are better than sunflower's ones. MW heating makes no changes to olive oil dielectric constant, but lowers gradually its dielectric losses. Sunflower oil changes of dielectric constant are more pronounced, but still around the initial value for untreated sample. In the same time its dielectric losses are decreasing and deforming which can be connected to the refining process of production and higher value of saturated fats content (56.5%).

Relaxation times for both oils were calculated from the position frequency of dielectric loss peaks. It was estimated to 2.89×10^{-8} s for both oils. τ remains the same after MW treatment for olive oil and decreases with increasing of MW exposure time for sunflower oil.

The conductivity obeys no changes with MW heating and undergoes Jonscher power law $\sigma = A \cdot \omega^n$ for both oils with four orders of higher value for olive oil than sunflower oil.

Although both oils present good dielectric and UV characteristics when subjected to MW heating, olive oil shows itself as better candidate for MW radiation use, because of lower deterioration during MW heating and stable characteristics during this process.

References

[1]   S. Howell, Promising Industrial Application for Soyabean Oil in the US, National Biodiesel Board, Jefferson City/MO, 1988.

[2]   Z.H. Shah, Q.A. Tahir, Dielectric properties of vegetable oils, Journal of Scientific Research 3 (3) (2011) 481-492.

[3]   M.P. Gjorgjevich, A. Andonovski, J. Velevska, Measuring frequency and temperature dependent permittivity of vegetable oils, Physica Macedonica 59 (2010) 77-90.

[4]   R. Malheiro, S. Casal, E. Ramalhosa, J.A. Pereira, Advances in Introduction and Microwave Heating of Mineral and Organic Materials, (Ed) In-tech, Chapter 26: Microwave heating: A time saving technology or a way to induce vegetable oils oxidation, pp. 597-614.

[5]   P. Fellows, Food Processing Technology-Principles and Practice, VCH, Cambridge, 1989, pp. 343-356.

[6]   C.P. Smyth, Dielectric Behaviour and Structure, McGraw-Hill, New York, 1955.

[7]   P. Rovellini, N. Cortesi, E. Fedeli, Ossidazioni dei lipidi, Nota 1. La Rivista Italiana delle Sostanze Grasse 74 (5) (1997) 181-189.

[8]   A. Javed, M. Akram, M.I. Shafiq, Dielectric properties of cholesterol derivates, Romanian Journal of Physics 51 (7-8) (2006) 819-826.

[9]   A.K. Jonscher, Dielectric Relaxation in Solids, Ed., Chelsey Dielectric Press, London, 1983.

[10] A.K. Jonscher, A new understanding of the dielectric relaxation of solids, Journal of Material Science 16 (1981) 2037.