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COMPARISON OF OXIDATIVE STABILITY OF DIFFERENT EDIBLE OILS*

Summary. The aim of the presented study was to compare oxidative stability of different edible oils originating from Poland, Finland and Spain. The UV irradiation was used as accelerator of the oil oxidation process. After UV irradiation, the formed volatile compounds were extracted by use of the headspace solid-phase microextraction HS-SPME (DVB/CAR/PDMS fibre) and analysed by gas chromatography coupled with flame ionization detector (GC/FID). The induction periods were determined on the basis of hexanal to 2-*trans*-nonenal ratio in analysed samples. At the end, the obtained results were compared with values of induction period obtained by Rancimat method and peroxide value. During the method development, the optimal parameters for extraction of volatiles were determined and the elements of the method validation was performed. The described method permits to detect typical oil oxidation products with satisfactory precision and repeatability.

Key words: edible oils, oxidative stability, UV irradiation, volatile compounds, gas chromatography, solid phase microextraction (SPME)

Introduction

Vegetable oils, like other food products, have a characteristic profile of volatile flavour substances, which create oil aroma. In the creation of aroma bouquet, both natural volatile compounds and derivative substances from extraction or press of oil processes, which are next dissolved in oil phase, take part (GROMADZKA and WARDENCKI 2007). Another group of compounds which also take part in smell formation are substances

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that are created during oil changes, e.g. in the lipooxygenase pathway or autooxidation process. Short chain hydrocarbons, ketones, aldehydes, alcohols, epoxides, esters and lactones may be formed giving a smell and taste of rancidity to food products (BELITZ et AL. 2009).

The presence of many polyunsaturated acids in the oils is the most endangered for lipids changes in oxidation process caused by atmospheric oxygen leading to the changes in volatile substances composition.

Among commonly used methods for the determination of oil oxidation stability there are peroxide value determination and the Rancimat test. Peroxide value enables to determine only the total amount of oxidation products. Additionally, it strongly depends on the analytical experience of the chemist and the measurements cannot be automated. In contrast, the Rancimat test is fully automated, but is usually performed at higher temperatures (100-120°C). Furthermore, the Rancimat test is an indirect method based on the measurement of water conductivity in which volatile oil oxidation compounds are absorbed.

The promising method to diagnose the volatile compounds can be the solid-phase microextraction technique connected with gas chromatography coupled to mass spectrometry or flame ionization detector (SPME/GC/MS or SPME/GC/FID). The indicator of the oxidation process can be the level of hexanal in sample or the hexanal / 2-*trans*--nonenal ratio (JIMENEZ et. AL. 2004). Hexanal is formed either during chemical oxidation process from linoleic acid, or during enzymatic metabolic process of the lipooxygenase pathway, whereas 2-*trans*-nonenal is formed only in auto-oxidation process of oleic acid (VICHI et AL. 2003).

The aim of the presented investigation was to verify the availability of using the SPME/GC/FID technique to assess quality and freshness of edible oils in a fast, precise and unequivocal way, by analysing only volatile oxidation compounds. The values of induction period of edible oils were determined graphically on the basis of the ratio of two characteristic oxidation compounds – hexanal and 2-*trans*-nonenal.

Material and methods

Samples and reagents

Edible oils used in the investigation were sunflower and rapeseed from Poland, Finland and Spain, purchased from a local store. Solvent used in sample preparation was hexane – GC grade from Merck and standard reagents: pentanal, purity > 87% (GC), hexanal, purity: > 97% (GC), heptanal, purity > 95% (GC), octanal, purity > 98% (GC), nonanal, purity > 95% (GC), decanal, purity > 95% (GC) decane, purity > 98% (GC), dodecane, purity > 98% (GC), *trans*-2-heptenal, purity > 96% (GC), all from Fluka and 2-*trans*-nonenal, purity 97%, from Aldrich.

To determine the peroxide value chloroform and acetic acid (purity 99.5%) from Chempur (Poland) as solvents and potassium iodide (Chempur – Poland), starch (Merck) and sodium thiosulfide (POCH) were used.

Photoreaction conditions

A photoreactor (COBRABiD, Warsaw, Poland) with two ultraviolet low-pressure mercury lamps (6 W each) with maximum emission at 254 nm was used in the study. The photoreactor has two possible modes of work (6 W, 12 W). In this case all experiments were carried out with a power of 12 W, so both lamps were turned on. Samples containing 10 ml of oil were poured to quartz closed cells. Later the cells were placed into the photoreactor for ultraviolet irradiation at different irradiation times (0-72 h).

Headspace solid-phase microextraction (HS-SPME) conditions

The oil samples (8 ml) were placed in 15 ml vials and closed by an aluminium cap with a PTFE/Silicone-faced septum. Before extraction, stabilization of the headspace in the vial was conducted by equilibration for 10 min at 30°C. On the basis of literature review (JELEŃ et AL. 2000) a combined SPME fiber, coated with divinylbenzene/carboxen/polydimethylosiloxane (DVB/CAR/PDMS, 2 cm long, with 50/30 μm coating thickness, Supelco, Bellefonte, PA, USA) stationary phase, was chosen as most appropriate for the extraction of volatile compounds from the oil matrix. The extraction was carried out by inserting the fiber into the headspace of the oil sample for 15 min at 30°C with a magnetic stirring. After the exposure, the fiber was thermally desorbed for 4 min into the GC injector at 250°C.

Gas chromatography conditions

The analyses were carried out on an Autosystem XL (Perkin-Elmer, USA) gas chromatograph equipped with Flame Ionization Detector. The injection was made for 4 min in the splitless mode. The temperatures of the injector and detector were 250°C. The separation was carried out on a SPB-20 column (Supelco, Bellefonte, PA, USA) with 20% poly(diphenyl) and 80% poly(dimethylsiloxane) (30 m × 0.25 mm × 1 μm) with an oven temperature program as follows: initial temperature was 50°C held for 1 min, then ramped at 6°C/min to 100°C, again ramped at 15°C/min to 250°C and held for 2 min. The total time of the analysis was 22 min. The carrier gas was helium with a flow rate of 1 ml/min.

To identify the oil oxidation volatiles their retention times were compared with retention times of standards. All samples were analysed at least in triplicate.

Peroxide value

Peroxide value was determined according to Polish Standard PN-EN ISO 3960:2005 in fresh oils and in oils after different times of UV irradiation (oxidation acceleration: 0-24 h). Each value was determined in triplet and as a final result the average was calculated.

Rancimat test

Edible oils oxidation stability was assessed by Rancimat test according to Polish Standard PN-EN ISO 6886:1997. The investigation was carried out automatically at 120°C with oxygen flow of 20 dm^3/h. The sample mass was 2.5 g.

Results and discussion

GC analysis

During the step of sample preparation edible oils were irradiated from 0 until 24 h. The UV irradiation was used to accelerate the oxidation process in real edible oils samples (SZUKALSKA 2003, HĘŚ et AL. 2001, GROMADZKA et AL. 2008). After UV irradiation the volatile oxidation products were extracted with the use of HS-SPME method (GROMADZKA i WARDENCKI 2008 a, GROMADZKA i WARDENCKI 2008 b) and then samples were analysed using GC/FID (Fig. 1). Generally, the concentration level of the detected compounds increased during the photo-induced process. Similar behaviour was observed during other investigation on influence of temperature for the presence of oil volatiles (JELEŃ et AL. 2000, 2007, MILDNER-SZKUDLARZ et AL. 2003). The longer oil was irradiated the higher peak were observed on chromatogram and the higher concentration level of selected volatile compounds was detected. The main task was to detect the level of two oxidation marker compounds – hexanal and 2-*trans*-nonenal. They were identified on the basis of retention time of standard compounds.

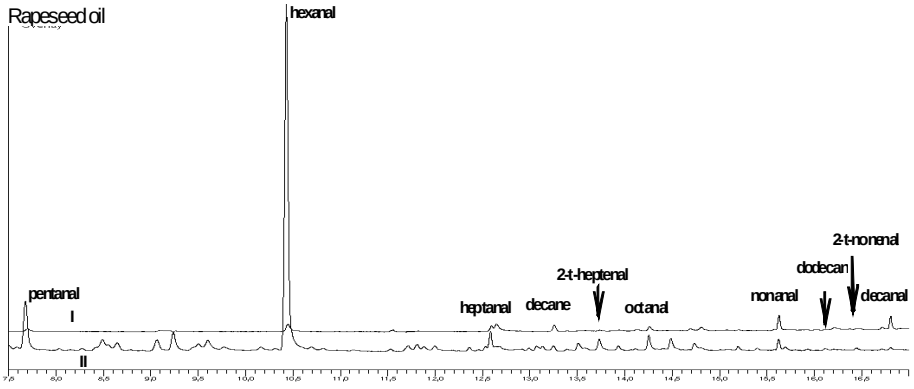

Fig. 1. The chromatogram of rapeseed oil sample before UV irradiation (I) and after 72 h of UV irradiation (II) extracted with the solid-phase microextraction technique connected with gas chromatography HS-SPME/GC/FID (2 cm long DVB/CAR/PDMS fibre with 50/30 µm thickness of stationary phase; SPB-20 capillary column, 30 m × 0.25 mm × 1 µm, Supelco, Bellefonte, PA, USA)
Rys. 1. Chromatogram próbki oleju rzepakowego przed procesem naświetlania promieniowaniem UV (I) i po 72 h naświetlania (II); związki lotne ekstrahowano za pomocą mikroekstrakcji do fazy stacjonarnej połączonej z chromatografią gazową HS-SPME/GC/FID (włókno z fazą stacjonarną DVB/CAR/PDMS – długość 2 cm, grubość filmu 50/30 µm; kolumna kapilarna SPB-20, 30 m × 0,25 mm × 1 µm, Supelco, Bellefonte, PA, USA)

After the detection, the ratio of these compounds after different irradiation time was calculated and as a result, an oxidation curve was drawn (Figs. 2, 3). The induction period of edible oils was determined graphically on the basis of these curves. The obtained oxidation curves have similar course like the curves expressing peroxide values.

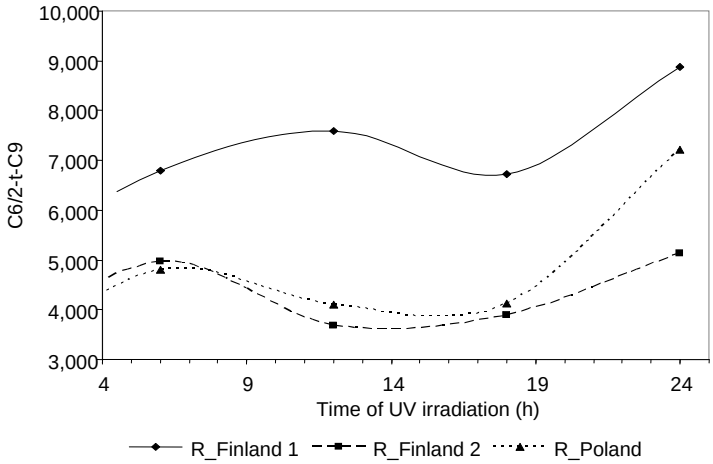

Fig. 2. Oxidation curves of three rapeseed oil samples achieved after calculation the ratio of hexanal to 2-*trans*-nonenal after different time of UV irradiation; compounds detected with the use of the solid-phase microextraction technique connected with gas chromatography HS-SPME/GC/FID (2 cm long DVB/CAR/PDMS fibre with 50/30 µm thickness of stationary phase; SPB-20 capillary column, 30 m × 0,25 mm × 1 µm, Supelco, Bellefonte, PA, USA)
Rys. 2. Krzywe utleniania trzech próbek oleju rzepakowego otrzymane na podstawie stosunku powierzchni pików heksanalu do 2-*trans*-nonenalu w różnych czasach naświetlania próbki; związki lotne wykryto za pomocą mikroekstrakcji do fazy stacjonarnej połączonej z chromatografią gazową HS-SPME/GC/FID (włókno z fazą stacjonarną DVB/CAR/PDMS – długość 2 cm, grubość filmu 50/30 µm; kolumna kapilarna SPB-20, 30 m × 0,25 mm × 1 µm, Supelco, Bellefonte, PA, USA)

Peroxide value (PV)

In parallel with HS-SPME/GC analysis, in order to compare calculated induction period, traditional analysis concerning peroxide value (PV) determination and Rancimat test was also carried out. For the determination of PV edible oils were oxidized in the same manner as in HS-SPME/GC analysis (oils were irradiated by UV light in different times) (Figs. 4, 5).

Determination of induction period

The induction period was determined graphically according to the manner described in Polish Standard PN-EN ISO 6886:1997. On the obtained graph a curve should be drawn which is parallel to the base line and which get thorough the point after 1 h of measurement. Then another curve was drawn which was the tangent to an oxidation curve in its rising area. The time determined by the point where these two curves are crossing is the induction period. The procedure for the determination of induction period is presented on Figure 6.

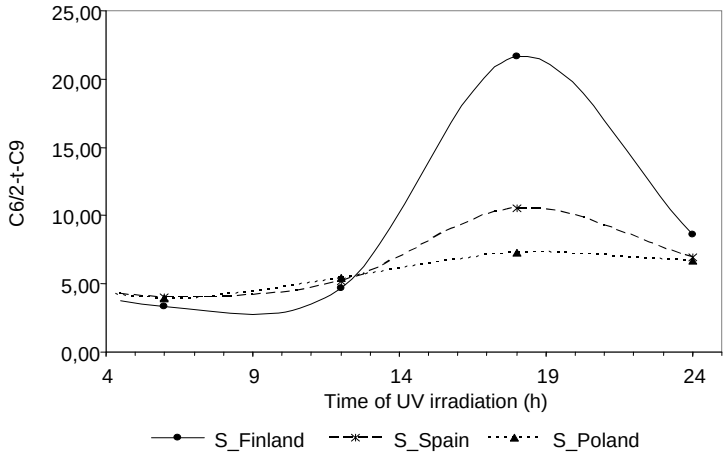

Fig. 3. Oxidation curves of three sunflower oil samples achieved after calculation the ratio of hexanal to 2-*trans*-nonenal in different time of UV irradiation; compounds detected with the use of the solid-phase microextraction technique connected with gas chromatography HS-SPME/GC/FID (2 cm long DVB/CAR/PDMS fibre with 50/30 µm thickness of stationary phase; SPB-20 capillary column, 30 m × 0.25 mm × 1 µm, Supelco, Bellefonte, PA, USA)

Rys. 3. Krzywe utleniania trzech próbek oleju słonecznikowego otrzymane na podstawie stosunku powierzchni pików heksanalu do 2-*trans*--nonenalu w różnych czasach naświetlania próbki; związki lotne wykryto za pomocą mikroekstrakcji do fazy stacjonarnej połączonej z chromatografią gazową HS-SPME/GC/FID (włókno z fazą stacjonarną DVB/CAR/PDMS – długość 2 cm, grubość filmu 50/30 µm; kolumna kapilarna SPB-20, 30 m × 0,25 mm × 1 µm, Supelco, Bellefonte, PA, USA)

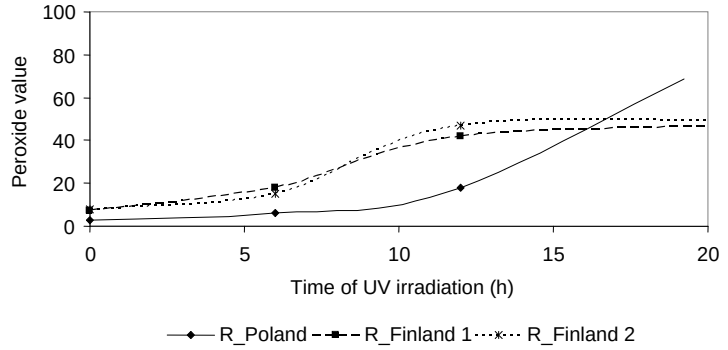

Fig. 4. Oxidation curves of three rapeseed oil samples achieved after calculation the peroxide value in different time of UV irradiation

Rys. 4. Krzywe utleniania trzech próbek oleju rzepakowego otrzymane po oznaczeniu liczby nadtlenkowej w różnych czasach naświetlania próbki

Gromadzka J., Wardencki W., 2009. Comparison of oxidative stability of different edible oils. Nauka Przyr. Technol. 3, 4, #138.

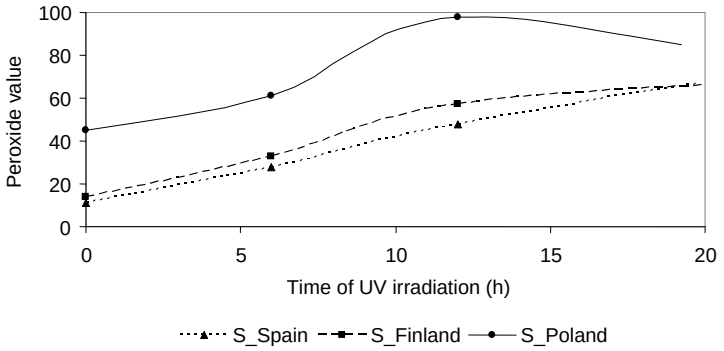

Fig. 5. Oxidation curves of three sunflower oil samples achieved after calculation the peroxide value in different time of UV irradiation
Rys. 5. Krzywe utleniania trzech próbek oleju słonecznikowego otrzymane po oznaczeniu liczby nadtlenkowej w różnych czasach naświetlania próbki

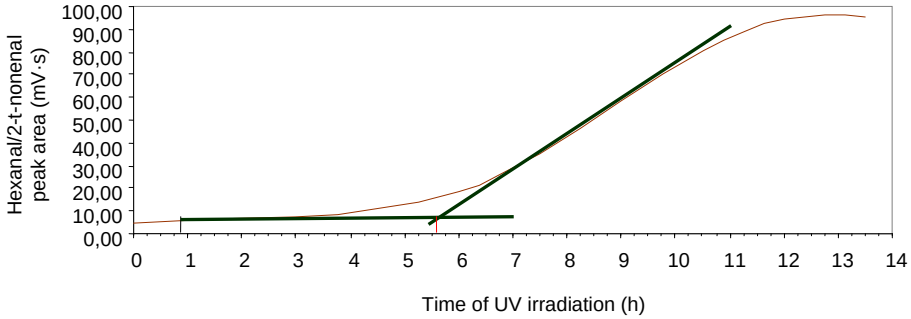

Fig. 6. The example of the graphical determination of the induction period of oil sample on the basis of oxidation curve
Rys. 6. Przykład graficznego wyznaczenia okresu indukcji dla próbki oleju na podstawie krzywej utleniania

Comparison of the induction period determined by SPME/GC, PV and Rancimat test

The selected oil samples were analysed in order to compare the developed method, based on solid phase microextraction coupled to gas chromatograph, with traditional techniques of oils stability determination. Then, the induction period for each oil was determined by three different methods. The results of this experiment are presented in Table 1. The highest values of induction period were observed after SPME technique. It is difficult to observe a correlation between peroxide value and values in Rancimat method, although a good correlation between Rancimat and SPME can be seen (the last column in Table 1). The values of induction period from SPME determination are three to five times higher than those from Rancimat but they show a similar tendency. The reason of such a behaviour could be the temperature of oil oxidation – in Rancimat oil is

Table 1. Comparison of the induction periods of six edible oils determined in different ways with the use of different techniques
Tabela 1. Porównanie okresów indukcji sześciu olejów roślinnych wyznaczonych różnymi sposobami z zastosowaniem różnych technik

Oil type	Country of oil origin	Rancimat	SPME	PV	PV/ SPME	PV/ Rancimat	SPME/ Rancimat
Rapeseed	Finland	4.3	15.2	4.9	0.3	1.1	3.5
	Finland	4.5	16.3	5.7	0.4	1.3	3.6
	Poland	4.7	17.2	10.0	0.6	2.1	3.7
Sunflower	Poland	1.8	9.0	5.3	0.6	2.9	5.0
	Spain	2.8	12.6	3.2	0.3	1.2	4.6
	Finland	2.5	12.8	4.6	0.4	1.9	5.2

kept under 120°C and in the case of SPME the highest temperature is 30°C. Furthermore, the conditions created by ultraviolet irradiation are more similar to natural ones under which oil is stored at home kitchen. The differences in oils type could be also easily seen from the correlation between the result of Rancimat and SPME technique. For each oil type there is different coefficient determined on the basis of these two mentioned techniques. It is because in SPME technique only two characteristic marker compounds are analysed, which are created during oxidation process of fatty acids. Because each type of edible oils has a characteristic composition of fatty acid, therefore the particular types of oils have a different coefficients for recalculating induction period from SPME technique to values obtained by Rancimat method.

Comparing the determined induction periods (in Table 1), it can be seen that rapeseed oils have very similar stability not depending on the region of Europe (north or east). A little bit different situation is with sunflower oils. In this case oils from Spain and Finland have similar stability which is better than those from Poland. But it is hard to decide which oil is better because they were achieved from local stores so there is no information how long they were stored at the shelves before taking them into analysis. But the results allow to compare different techniques used for assessing oil oxidation stability. The good correlation between Rancimat method (recommended by Polish and International Standards) and HS-SPME/GC (new method which determine only selected oxidation products) could be seen.

Conclusions

The applied HS-SPME/GC method allows to analyse the oils samples during oxidation process. By calculating the ratio of hexanal to 2-trans-nonenal it is possible to draw a characteristic oxidation curve for the investigated oil samples and then to determine graphically induction period for them. The ultraviolet irradiation, as a factor of oxidation process acceleration, complies with natural kitchen conditions under which oil is usually stored in shops and households. The good correlation between HS-SPME/GC and Rancimat method in determination of induction period was observed.

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PORÓWNANIE STABILNOŚCI OKSYDATYWNEJ RÓŻNYCH OLEJÓW ROŚLINNYCH

Streszczenie. Celem prezentowanych badań było porównanie stabilności oksydacyjnej olejów roślinnych z Polski, Finlandii i Hiszpanii. Na etapie przyspieszania utleniania zastosowano promieniowanie ultrafioletowe (UV). Po naświetlaniu olejów powstałe związki lotne ekstrahowano z fazy nadpowierzchniowej za pomocą techniki mikroekstrakcji do fazy stacjonarnej (HS-SPME) i analizowano z zastosowaniem chromatografu gazowego z detektorem płomieniowo-jonizacyjnym (GC/FID). Okres indukcji wyznaczono na podstawie stosunku stężeń heksanalu do 2-*trans*--nonenalu w badanych próbkach. Ostatnim etapem było porównanie uzyskanych wyników z okresami indukcji wyznaczonymi dla tych samych olejów metodą Rancimat i liczby nadtlenko-

wej. Podczas opracowywania metody określono optymalne parametry procesu ekstrakcji związków lotnych i przeprowadzono elementy walidacji metody. Opisana metoda umożliwia wykrywanie produktów utleniania olejów roślinnych z zadowalającą precyzją i powtarzalnością.

Słowa kluczowe: oleje roślinne, stabilność oksydacyjna, promieniowanie ultrafioletowe, związki lotne, kapilarna chromatografia gazowa, mikroekstrakcja do fazy stacjonarnej (SPME)

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