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Application of UV-HS-SPME/GC/FID/MS for analysis of volatile oxidation products in canola oil

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INTRODUCTION

The edible oils are one of the main and important diet compounds. The high interest is focused on oils with high amount of essential polyunsaturated fatty acids (olive or canola oil). It is connected with their health advantages. Canola oil which is popular in cooler regions of the Earth (North Europe, Asia, America) is worth consideration because of its nutrient value. The very good proportion equal 2:1 of linolenic and alpha-linolenic acids in this oil is almost ideal as far as nutrition is considered.
Due to the high amount of polyunsaturated acids canola oil is endangered by lipids changes in oxidation process by atmospheric oxygen which leads to decrease in biological activity and nutrition value. Therefore, early detection of oxidation process is very important.
In the presented investigations the UV irradiation was used as accelerator of oil oxidation process. After UV irradiation the formed volatile compounds were analyzed by the use of solid-phase microextraction (SPME) using DVB/CAR/PDMS fiber combined with gas chromatography coupled to flame ionization detector (GC/FID) and mass spectroscopy (GC/MS). The indicator of the oxidation process was the hexanal/2-*trans*-nonenal ratio.

MATERIALS AND METHODS

The analyses were carried out using AutoSystem XL (Perkin Elmer) gas chromatograph equipped with Flame Ionization Detector (FID) and Thermo Finingan gas chromatograph with Trace DSQ Mass Spectrometer. Chromatography conditions are listed in Table 2. To accelerate the oil oxidation process a photodegradation experiment was carried out using a photoreactor shown in Figure 1 (Cobrabid, Warsaw, Poland).

Tab. 1. The optimal parameters for extraction of volatile oxidation products by UV-HS-SPME.

Extraction parameter	HS-SPMEconditions
Stationary phase of the fiber	**DVB/CAR/PDMS, 50/30µm, 2 cm**
Sample volume	**8 ml in the 15 ml vial**
Equilibrium time	**10 min**
Extraction temperature	**30 °C**
Extraction time	**15 min**
Desorption temperature	**250 °C**
Sample agitation	**yes**

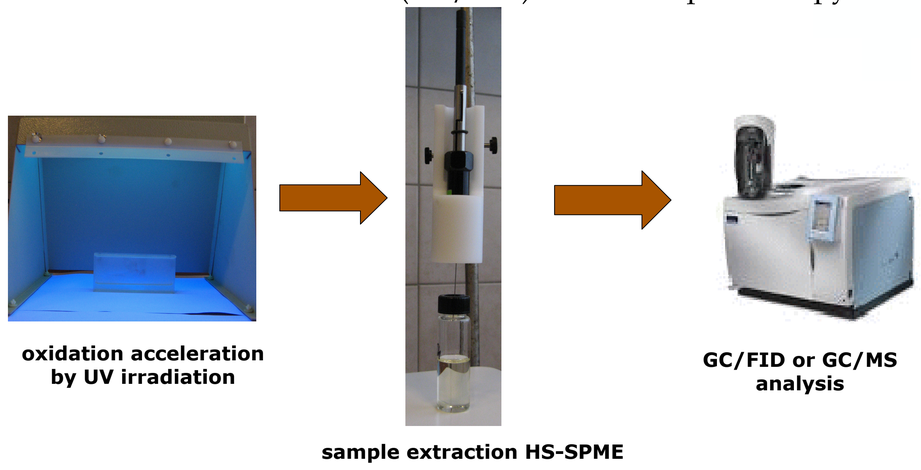

Fig. 1. The scheme of UV-HS-SPME/GC procedure

Tab. 2. The optimal conditions of GC/FID/MS analysis of volatiles in edible oils.

Extraction parameter	HS-SPME/GC-FID	HS-SPME/GC-MS
Capillary columns	SPB-20 (Supelco) 30mx0,25mmx1 µm (20% diphenyl / 80% dimethylsiloxane)	Stabilwax DA (Restek) 30mx0,32mmx 0,5µm (20% diphenyl / 80% dimetylosiloxane)
GC oven temperature program	50°C (1 min), 6°C/min to 100°C, 15°C/min to 250°C (2 min)	40°C (4 min), 5°C/min to 80°C, 10°C/min to 220°C (10 min)
Split mode	split less	
Carrier gas	helium with a flow rate of 1 ml/min	
Injector/detector temperature	250 °C / 250 °C	250 °C / 240 °C
Photoreactor	2 ultraviolet low-pressure mercury lamps (12 W), maximum emission at 254 nm	

RESULTS

In the presented investigation the UV irradiation was used as accelerator of the oil oxidation process. After UV irradiation the formed volatile compounds were analyzed by the use of the static headspace HSA or solid-phase microextraction SPME (DVB/CAR/PDMS fibre) techniques combined with gas chromatography. During the process of methods development, the optimal parameters for extractions of volatile compounds were determined (Tab. 1.).
The volatile compounds were identified on the basis of retention time of standards. The model chromatograms are shown in Figure 3 and Figure 4.
The induction period of canola oil was set on the basis of the hexanal/2-trans-nonenal relation (Fig. 2. and Tab. 3). It is a period at which the testing oil remains oxidatively stable.

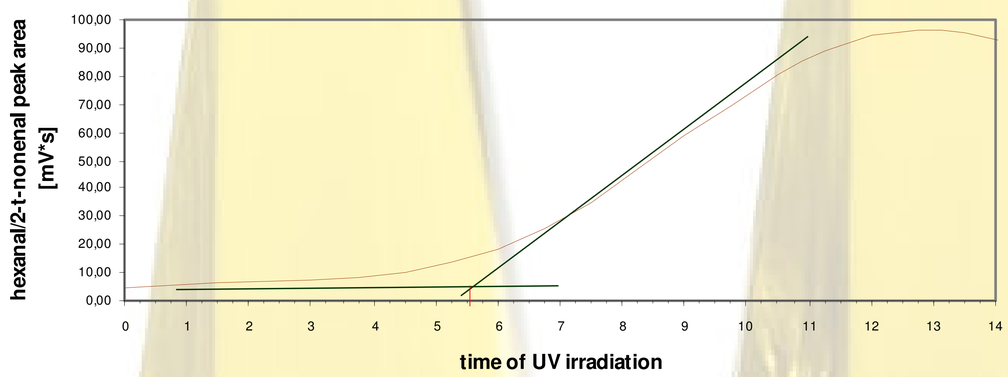

Fig.2. Dependence of hexanal to *t*-2-nonenal ratio in UV irradiation process. Determination of induction period.

Tab. 3. The comparison of the induction period of different canola oils determined by UV-HS-SPME/GC and Rancimat test.

No	Country	Rancimat test	UV-HS-SPME	SPME/Rancimat
1	Poland	2.41	6.00	2.49
2	Finland	4.32	14.75	3.41
3	Finland	4.46	16.00	3.59
4	Poland	4.70	16.80	3.57
5	France	4.85	11.90	2.45
6	Poland	4.96	15.50	3.13
7	Poland	5.54	14.80	2.67
8	Poland	5.44	11.70	2.15
9	Poland	5.55	15.75	2.84

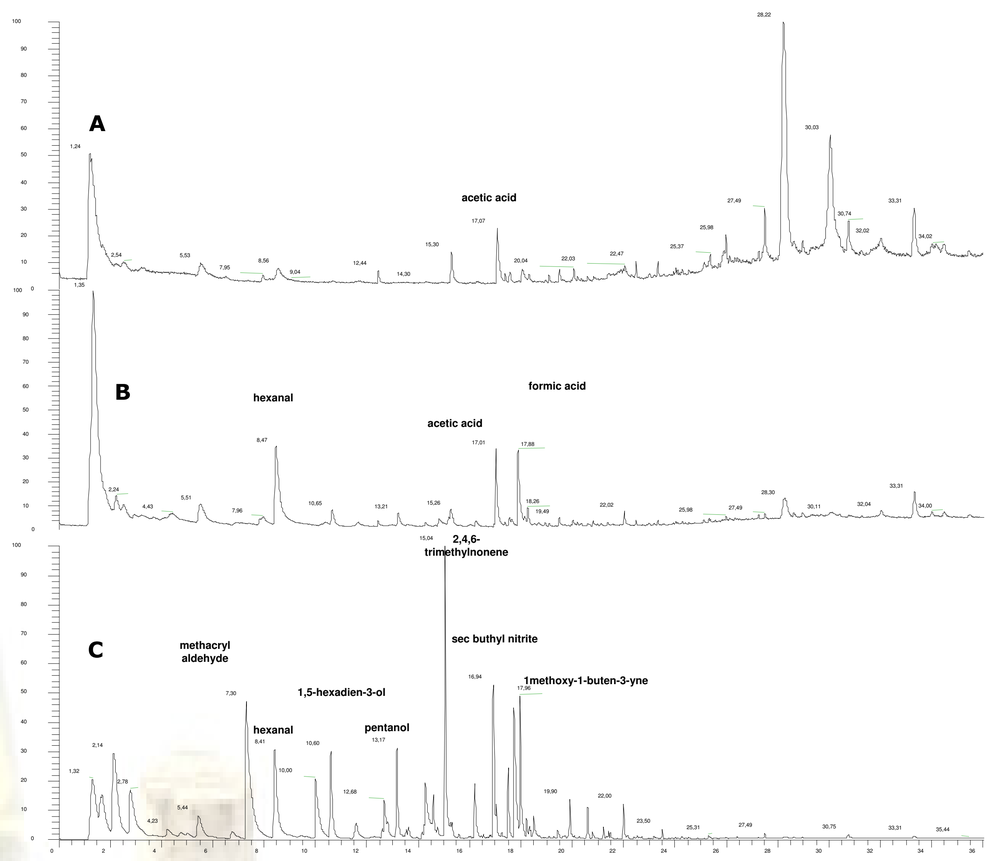

Fig.3. GC-MS chromatograms of canola oil without oxidation (A), after 12 h of UV irradiation (B) and after 12 h at elevated temperature (C) in optimized conditions (Tab.2.)

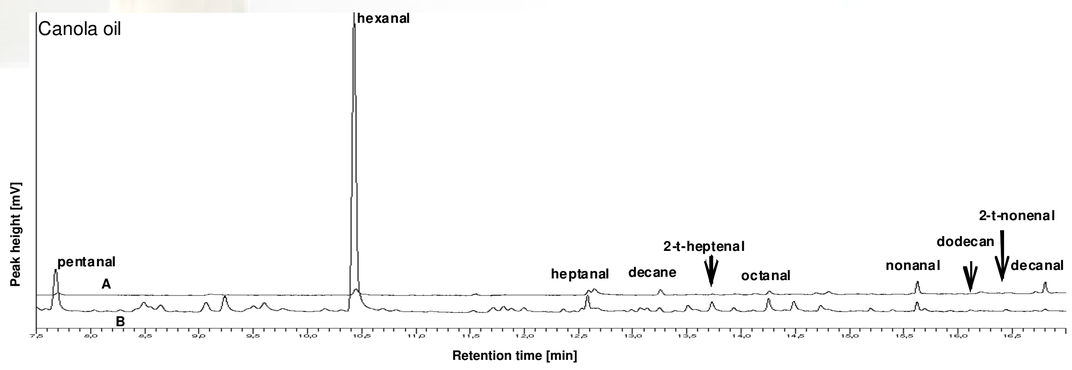

Fig.4. GC-FID chromatograms of canola oil without oxidation (A) and after 12 h of UV irradiation (B) in optimized conditions (Tab. 2.)

CONCLUSIONS

- The proposed method is fast and repeatable fulfilling the requirements of this type of analysis.
- It allows for analysis of oil rancidity in qualitatively and quantitatively way.
- Volatile compounds which were identified are characteristic for oil oxidation products.
- The UV irradiation as a method of oils oxidation acceleration was used for the first time in connection with SPME and gas chromatography.
- This method is sensitive and precise, giving the possibility for tracing oil oxidation process.
- This method could be also applied for oils identification, classification and detection of adulteration.

ACKNOWLEDGEMENTS

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