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ORIGINAL PAPER

# A Headspace–SPME–MS Method for Monitoring Rapeseed Oil Autoxidation

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**Abstract** Headspace SPME–MS was used to analyze volatile compounds from rapeseed oil subjected to an accelerated storage test consisting of 0–12 days of storage at 60 °C. The SPME–MS data was compared with the data obtained by solid phase microextraction–gas chromatography/mass spectrometry (SPME–GC/MS). The SPME–GC/MS method allowed detection of 37 volatile compounds, of which 28 were identified. Predominant ones were hexanal, 2,4-heptadienal, 2-heptenal and 1-pentene-3-ol. Volatile compounds were not separated in SPME–MS—a single peak reflecting the total amount of volatiles was obtained. An increase in the abundance of characteristic ions in this peak could be used to detect of compounds characteristic for rapeseed oil autoxidation. These compounds (with their characteristic ions) were hexanal (*m/z* 56), 1-pentene-3-ol and 1-octene-3-ol (*m/z* 57), 2-pentenal and 2-heptenal (*m/z* 83 and 84), and 2,4-heptadienal (ions *m/z* 81 and 110). The SPME–MS peak area was correlated with peroxide value at 0.9779 and with Totox at 0.9841. Principal component analysis (PCA) of fatty acid volatile oxidation products from a model rapeseed oil indicated that SPME–MS was able to differentiate samples containing hexanal at a concentration of 0.2, 0.4, 0.6, 0.8 and 1.0 mg/L with proportional amounts of other compounds. Further, samples that were subjected to 0, 2, 4, 6, 8, 10 and 12 days of storage at 60 °C were differentiated using SPME–MS–PCA. PCA showed similarities in clustering of the data obtained by SPME–MS and sensory analysis.

**Keywords** Autoxidation · HS–SPME–MS · Rapeseed oil · Volatile compounds

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## Introduction

Oxidation of lipids is one of the major causes of food deterioration, resulting in the formation of various compounds that impair product quality. Aldehydes, ketones, alcohols, alkanes and alkenes are some of the major volatile secondary lipid oxidation products. They affect flavor of oils and other food products containing fat. Rapeseed oil produced in Poland contains oleic acid (up to 68%), linoleic acid (approximately 20%), and a significant amount of linolenic acid (up to 9%). The presence of a relatively high percentage of linolenic acid in rapeseed oil, apart from linoleic and oleic acids, accelerates oxidation of this product.

For characterization of volatile lipid oxidation products gas chromatography coupled to mass spectrometry (GC–MS) is the method of choice. GC–MS provides sufficient separation power for the identification of compounds in fairly complex mixtures. Volatile lipid oxidation products in oils are used as freshness markers, a measure of the extent of oxidation and in the detection of regional origin or adulteration of oils. Sample preparation for the analysis of volatile secondary lipid oxidation products involves various approaches such as static headspace, thermal desorption and solid phase microextraction (SPME) [1]. Headspace SPME can be used either for a rapid profiling of volatile compounds for qualitative purposes or for quantitation of particular compounds.

In addition to a systematic analysis of lipid oxidation products, there is a need for a rapid differentiation of samples exhibiting different degrees of rancidity from fresh ones. Sensory analysis can be used for this purpose. Sensory profiling methods provide accurate information on the development of flavor notes in a product. However, sensory methods usually require a panel of well-trained assessors, and are time-consuming. Therefore, attempts have been made to mimic the human olfactory system response by developing electronic noses. These instruments discriminate samples based on the aroma profile, and their mode of operation is similar to human olfaction—an unresolved mixture of volatile compounds reaches the sensor array producing signals unique to the analyzed mixture. There is a vast body of literature describing technical aspects of electronic noses [2]. One group of electronic noses, or rather quasi-electronic noses, includes instruments in which a mass spectrometer (analyzer) plays a role of a sensor array [3]. When a mass spectrometer acquires ions, the abundance of each one can be expressed as a sensor response. When volatile compounds are introduced into the ionization chamber of a mass spectrometer without separation, a ''fingerprint'' of the aroma is obtained. Instrumental and methodological aspects of headspace–mass spectrometry (HS–MS) have been summarized by Pérès et al. [3]. MS-based electronic noses have been used for the characterization of off-flavors [4], and prediction of shelf life [5] of milk and the detection of olive oil adulterants [6]. They have also been used to monitor lipid oxidation processes in potato crisps [7] and infant formulas [8].

The aim of the study in this manuscript was to (1) explore the potential of headspace SPME coupled with mass spectrometry (HS–SPME–MS) as a tool for monitoring the oxidation process occurring in the refined rapeseed oil, and (2) to compare the data obtained using this technique with the data obtained using GC/MS, sensory profile analysis and the autoxidation indicators, such as peroxide value (PV) and Totox. All samples used in this study were subjected to storage at 60 °C for 0–12 days.

## Experimental Procedures

### Materials

Refined rapeseed oil was obtained from ZPT Warsaw directly after the refining process and bottling. Oil portions (100 g) were placed into 1,000 mL flat-bottom flasks closed with stoppers and kept for up to 12 days at 60 °C. Seven flasks were prepared and at each sampling day (day 0, 2, 4, 6, 8, 10, 12) one flask was taken out from the incubation chamber for analyses. All flasks were stored at (–27 °C) after the incubation and until they were analyzed. All reagents and chromatography standards were purchased from Sigma-Aldrich (Poznań, Poland).

### Isolation of Rapeseed Oil Volatile Compounds by SPME

Carboxene/divinylbenzene/PDMS 1 cm fiber (Supelco, Bellefonte, PA) was used to extract volatiles from oil. After thawing, 20 mL oil from each flask were placed in a 40 mL vial for SPME–GC/MS analyses (in duplicates) and for SPME–MS analyses (six replicates for each sample). Sampling for SPME–MS and SPME–GC/MS was performed from the same vial. Samples were extracted using an SPME device in a heating block at 50 °C for 15 min. for SPME–GC/MS and for 15 min. at 35 °C for SPME–MS. Selection of extraction temperature for SPME–GC/MS was based on our previous experience and extraction temperature for SPME–MS was chosen from the temperature range of 35–50 °C for the best reproducibility.

### Analysis of Volatile Compounds by SPME–MS

Samples were analyzed using a Hewlett Packard 5890II gas chromatograph with a split/splitless injector, coupled to a HP 5971 quadrupole mass spectrometer. For SPME–MS experiments, the column in GC–MS was replaced with an uncoated fused silica capillary (15 m × 0.200 μm, Supelco, Bellefonte, PA) and analyses were performed at 150 °C (isothermal conditions) using a helium flow of 0.6 mL/min. The MAStat software package (Analyt GmBH, Germany) was used for the principal components analysis (PCA) of SPME–MS data. The use of PCA was to represent the variations present in many variables using a smaller number of factors, i.e. to describe the interpoint distances (spread of variation) using as few dimensions (axes, principal components) as possible. This method was used to visualize trends in data and observe any possible clusters within analyzed samples.

### Analyses of Volatile Compounds by SPME–GC/MS

Analyses of volatile compounds were performed on the same instrument as in SPME–MS experiments. Compounds were resolved on a DB-5 column (25 m × 0.200-mm id. × 0.33 μm, Agilent Technologies, Palo Alto, CA, USA). Helium flow was 0.6 mL/min, and programmed temperature (40 °C for 3 min., 8 °C/min to 280 °C) was used for compounds resolution. Compounds were identified based on the comparison of their retention indices and mass

spectra with those of authentic standards, or they were identified tentatively based on the comparison of mass spectra using the NIST 05 mass spectral library, when standards were unavailable.

### Discrimination of Model Rancid Rapeseed Oil Samples by SPME–MS–PCA

To test the ability of SPME–MS–PCA to discriminate samples containing different amounts of oil oxidation products, a model text mixture of aldehydes and alcohols, known as fatty acid oxidation products, was prepared. It contained 21.5% (w/w) hexanal, 17.7% nonanal, 15.3% E-2-pentenal, 13.0% 1-octene-3-ol, 9.3% octanal, 5.5% E-2-octenal, 4.9% pentanal, 4.4% heptanal, 2,6% 1-pentanol, 2.0% E,E-2,4-decadienal, 1.5% E-2-hexenal, 1.4% E-2-decenal and 0.9% E-2-nonenal. Standards of these compounds were weighted directly into refined rapeseed oil to avoid the use of organic solvents that might affect the SPME process. This test mixture was then diluted with freshly refined rapeseed oil to obtain solutions containing 1, 2, 3, 4, or 5 ppm, and 0.2, 0.4, 0.6. 0.8 or 1.0 ppm of hexanal with proportional amounts of the other compounds.

### Sensory Profile Analysis of Oil Samples

Sensory profile analysis was performed by a ten-member panel, in three sessions. Samples were kept in 100-ml closed vessels at 35 °C for 30 min. to liberate volatile compounds. At this stage, samples were sniffed by all members of the sensory panel. The odor attributes were chosen based on our earlier experience with sensory profile analysis of vegetable oils [1]. The following odor descriptors were offered for examined oil samples: acidic (ac), sweet (sw), green (gr), floral (fl), oxidized (ox) and hay (hy). Panel members assigned the intensity of each odor descriptor on a 0–10 scale. Results from linear scales were converted into numerical values for data analysis. Mean, variance, and standard deviations were calculated for all attributes of each sample, for each session separately, and across all the three sessions. The data obtained were calculated from 30 replicates and after statistical interpretation using the multivariate procedure presented as a graphic projection of PCA.

### Totox Value Determination

The Totox value was calculated from PV and anisidine value (AV) which were determined according to methods PN:ISO 3960:1996 and PN-93 A-86926, respectively. The Totox value, which describes the degree of fat oxidation, was calculated according to equation: Totox = 2PV (mequiv $O_2$ $kg^{-1}$) + AV.

## Results and Discussion

### Volatile Compounds of Rapeseed Oil Subjected to Accelerated Storage Test

Gas chromatography–mass spectrometry data of major volatile compounds isolated from rapeseed oil using SPME are summarized in Table 1. Two compounds were detected at day 0—hexanal and 6-methyl-5-hepten-2-one, whereas the number of compounds after 12 days of storage reached 37, of which 28 were identified either based on spectral comparison with authentic standards or tentatively, comparing their spectra with those of the NIST library. The majority of them were aldehydes: five alkanals, seven alkenals and two dienals. Also three acids were detected, four alcohols and four ketones. These compounds represented groups of characteristic fatty acid secondary oxidation products, resulting mostly from autoxidation of oleic, linoleic and linolenic acids. When total peak areas were considered, a tenfold increase was recorded between day 2 and 4. The rate of increase was smaller after 4 days. Based on peak areas, the most abundant volatile compounds were hexanal, 2,4-heptadienal, E-2-heptenal, E-2-pentenal, 1-pentene-3-ol and unidentified isomers of a compound eluting at RI 947 and 949. These compounds contributed to nearly 63% of volatiles (calculated as compounds adsorbed on a SPME fiber) and can be indicative compounds in the process of autoxidation of rapeseed oil kept at elevated temperature. There was a correlation of 0.97 and 0.99 ($p < 0.01$) between the appearance of rancid flavor (estimated by sensory profile analysis) and the presence of 1-pentene-3-ol and E-2-pentenal, respectively. Reports have shown evidence of 1-pentene-3-ol and E-2-pentenal being associated with the appearance of rancid flavor in olives [9]. Studies have also been reported a correlation between degree of oxidation and the presence of nonanal, 2-pentylfuran, (E)-2-propenal and 2,4-heptadienal isomers in olive oil subjected to an accelerated storage test at 60 °C [10]. Since hexanal is present even in fresh olive oil, use of hexanal as a freshness marker of olive oil may not be appropriate [11]. However, it is often used as an autoxidation process indicator in refined oils [12, 13]. Van Ruth et al. [14] have examined volatile compounds of sunflower and flax oil and stated that degree of oxidation is better reflected by the total profile of volatiles rather than the presence of a selected compound such as hexanal or propanal. E-2-heptenal was detected on the

**Table 1** Main volatile compounds detected by SPME–GC/MS from rapeseed oil subjected to accelerated storage test at 60 °C for a period of 12 days

| Compound | RI | Storage time at 60 °C (days) Peak area (TIC units × $10^6$) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 2 | 4 | 6 | 8 | 10 | 12 |
| Acetic acid[g] | 641 | – | – | – | 3.30[b] | 8.53[a] | 12.33[b] | 11.74[a] |
| 2-Butenal | 665 | – | – | 1.11[b] | 2.66[b] | 6.29[a] | 7.67[b] | 9.83[b] |
| 1-Pentene-3-ol | 685 | – | – | 6.09[a] | 13.24[b] | 23.72[a] | 28.54[a] | 30.08[b] |
| Pentanal[f,g] | 705 | – | 0.93[d] | 6.86[a] | 5.52[a] | 10.82[b] | 12.82[a] | 15.34[a] |
| Propanoic acid | 735 | – | – | – | 1.39[a] | 4.29[a] | 5.56[a] | 5.34[b] |
| E-2-pentenal[g] | 765 | – | – | 1.79[a] | 5.21[a] | 14.51[a] | 18.93[a] | 23.63[a] |
| 2-Penten-1-ol | 781 | – | – | – | – | 1.1[a] | 1.88[a] | 2.42[a] |
| Unidentified | 786 | – | – | 0.24[c] | 0.49[c] | 0.94[d] | 1.51[d] | 3.20[b] |
| Hexanal[g] | 804 | 0.61[a] | 0.80[d] | 1.66[d] | 4.53[d] | 19.68[d] | 28.06[d] | 45.64[b] |
| Unidentified | 836 | – | – | – | 0.23[b] | 0.98[b] | 1.69[d] | 3.20[b] |
| Unidentified | 855 | – | – | – | 0.23[a] | 0.37[a] | 0.50[a] | 0.62[b] |
| E-2-hexenal[g] | 861 | – | – | – | 0.33[b] | 1.07[c] | 1.94[a] | 2.67[b] |
| 1-Hexanol[g] | 878 | – | – | – | – | 0.51[a] | 0.67[b] | 0.89[b] |
| Unidentified | 887 | – | – | – | – | 0.42[b] | 0.57[b] | 0.88[b] |
| 2-Heptanone | 897 | – | – | – | 0.12[b] | 0.37[b] | 0.57[b] | 0.84[b] |
| p-Xylene | 899 | – | – | 1.81[b] | 0.65[a] | 1.76[a] | 0.72[a] | 2.35[a] |
| Heptanal[g] | 902 | – | – | 0.14[a] | 0.64[c] | 1.43[a] | 2.54[b] | 3.83[c] |
| Unidentified | 922 | – | – | 0.29[a] | 0.69[a] | 1.63[a] | 2.24[a] | 2.88[b] |
| Unidentified | 947 | – | – | 2.94[a] | 9.62[a] | 21.48[a] | 29.08[a] | 35.59[a] |
| Unidentified | 949 | – | – | 1.95[a] | 6.57[a] | 16.66[a] | 23.99[a] | 31.75[a] |
| E-2-heptenal[g] | 964 | – | 0.52[b] | 1.68[a] | 4.84[a] | 12.60[a] | 22.94[a] | 32.61[a] |
| Unidentified | 970 | – | – | – | – | 0.44[c] | 1.04[a] | 1.43[b] |
| 1-Heptanol[g] | 974 | – | – | – | – | 0.25[a] | 0.58[b] | 0.95[c] |
| 1-Octene-3-ol[g] | 983 | – | – | – | 1.81[a] | 4.93[a] | 9.09[b] | 12.72[a] |
| 6-Methyl 5-hepten-2-one | 991 | 0.36[b] | 0.34[a] | 0.43[a] | 0.70[a] | 1.45[b] | 2.87[b] | 5.64[b] |
| Hexanoic acid | 1001 | – | – | – | – | – | – | 1.20[a] |
| 2-Octanone | 1003 | – | – | – | – | 0.56[d] | 1.19[b] | 1.35[b] |
| 2,4-Heptadienal | 1007 | – | – | 1.29[a] | 4.62[a] | 10.59[a] | 18.33[a] | 25.53[a] |
| Octanal[g] | 1010 | – | – | – | 0.16[b] | 0.78[d] | 1.44[d] | 2.08[c] |
| 2,4-Heptadienal isomer | 1023 | – | – | 0.72[c] | 2.86[a] | 8.27[a] | 16.27[a] | 25.31[a] |
| Unidentified | 1065 | – | – | – | – | 0.25[a] | 0.64[a] | 1.02[b] |
| E-2-octenal[g] | 1071 | – | – | – | 0.46[a] | 1.61[b] | 3.69[b] | 7.55[b] |
| 3,5-Octadien-2-one | 1098 | – | – | 0.20[e] | 0.58[a] | 1.12[a] | 1.95[a] | 2.58[b] |
| Nonanal[g] | 1122 | – | – | 0.11[b] | 0.23[d] | 0.90[d] | 2.25[c] | 3.26[d] |
| E-2-nonenal[g] | 1174 | – | – | – | – | 0.19[b] | 0.60[c] | 0.75[d] |
| E-2-decenal[g] | 1279 | – | – | – | – | – | – | 0.67[d] |
| E,E-2,4-decadienal[g] | 1315 | – | – | – | – | – | 0.58[d] | 0.83[a] |
| Total volatiles | | 0.97 | 2.59 | 29.31 | 71.68 | 180.50 | 265.27 | 358.20 |

*RI* retention indices on DB-5 type column

[a–e] Relative standard deviations: [a]RSD < 5%, [b]5 < RSD < 15%, [c]15 < RSD < 25%,[d]25 < RSD < 50%, [e]RSD > 50%

[f] Heptane coeluting with pentanal

[g] Identification of compounds based on a comparison of their mass spectra and retention times with those of authentic standards, other compounds identified tentatively based on mass spectra library search

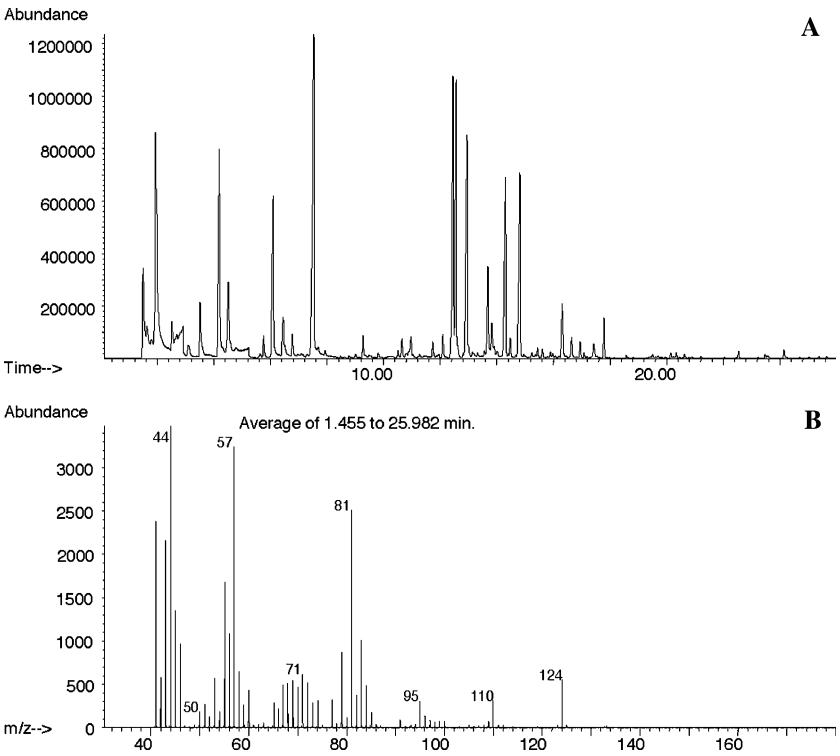


**Fig. 1** **a** Total ion chromatogram of volatile compounds isolated from refined rapeseed oil stored at 60 °C for 12 days. The chromatogram was obtained using a 25-m DB-5 capillary column. **b** An average mass spectrum of separated compounds

second day of sample storage at 60 °C, which confirms data on its appearance in the initial stage of fatty acid (linoleic acid) oxidation [15].

## SPME–MS Data Comparison with SPME–GC–MS

Figure 1 shows a chromatogram of compounds isolated using SPME from rapeseed oil after 12-day incubation at 60 °C and resolved on a DB-5 column. It also shows an average mass spectrum acquired throughout the entire run from 1.45 to 29.58 min. The average spectrum represents all volatile compounds resolved on the column used and obviously does not carry information on an identity of any single compound. Similar results were obtained when the analytical column was replaced with an uncoated fused silica restriction capillary. Because of the lack of stationary phase for interaction in the uncoated capillary, no compounds were resolved and all compounds were eluted as a single peak (Fig. 2). The average spectrum taken across this peak represents all volatile compounds, which reached the ionization chamber simultaneously. It was similar to the average spectrum presented on Fig. 1 and it did not provide information on any single compound, either. However, it reflected the spectrum of the headspace extracted from rapeseed oil by SPME fiber.

Contrary to the average spectrum of the SPME–GC/MS, the SPME–MS run yielded a spectrum with much higher intensity in a shorter run time (2-min). When peak areas of SPME–MS analyses were compared with total volatiles resulting from the addition of GC/MS peak areas, a significant correlation (0.9928) was found. Throughout the 12-day incubation period, the amount of volatile compounds, expressed as a sum of peak areas from SPME–GC/MS analysis, increased significantly (Table 1).

In the spectrum in Fig. 2 several clusters can be observed, grouped around ions *m/z* 44, 57, 70 and 81. Uniqueness of ions forming these clusters was evaluated by the examination of extracted ion chromatograms (EIC) of GC/MS data. This approach made it possible to select ions, which were the most abundant and the most unique for detected volatile oxidation products. However, it must be remembered that assumptions stated in the following paragraph were made for the rapeseed oil and that deducing the presence of specific compounds based on a single ion in the SPME–MS peak is not always feasible.

When analyzing EICs of the GC/MS data, the following conclusions may be drawn on the usefulness of particular ions to monitor oxidation of rapeseed oil. Although it is a significant ion in the hexanal mass spectrum, the dominating ion of *m/z* 44 cannot be used for this purpose because of the possible presence of traces of $CO_2$ in the carrier gas. Furthermore, ions 41, 42 and 43 are non-specific and present in almost all compounds, and *m/z* 45 is found in acetic and propanoic acids and in hexanol. The next cluster grouped around ion *m/z* 57, apart from non-specific ions *m/z* 53 and 55 has several ions that can be used to detect specific compounds: ion *m/z* 60 is specific

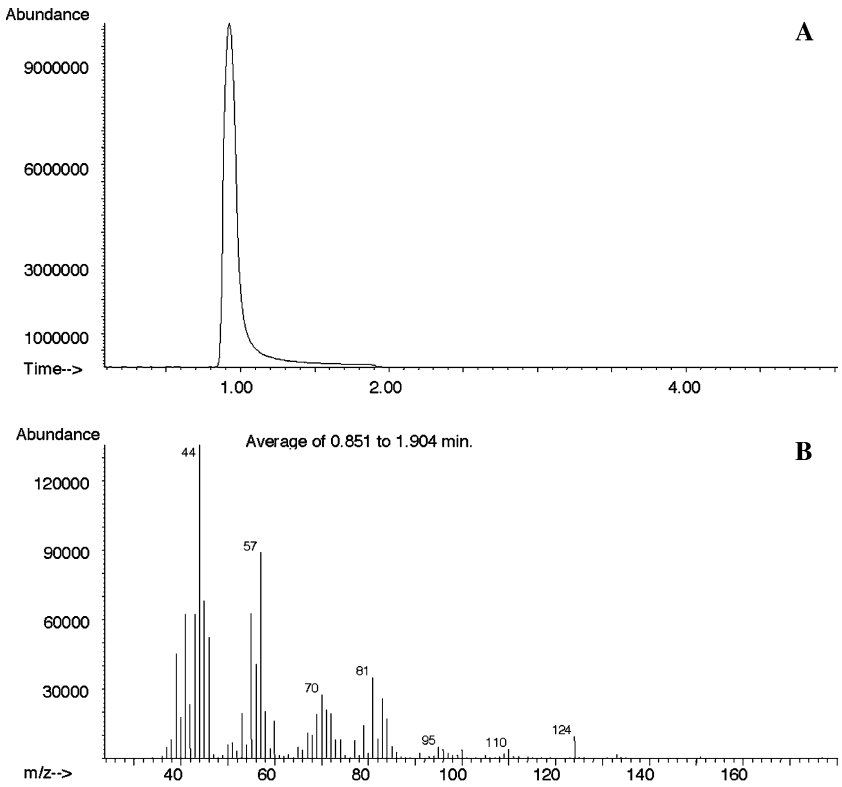


**Fig. 2** **a** Total ion chromatogram of volatile compounds isolated from refined rapeseed oil stored at 60 °C for 12 days. Analysis was performed on a 5-m uncoated fused silica capillary (**a**). **b** An average mass spectrum of unseparated compounds

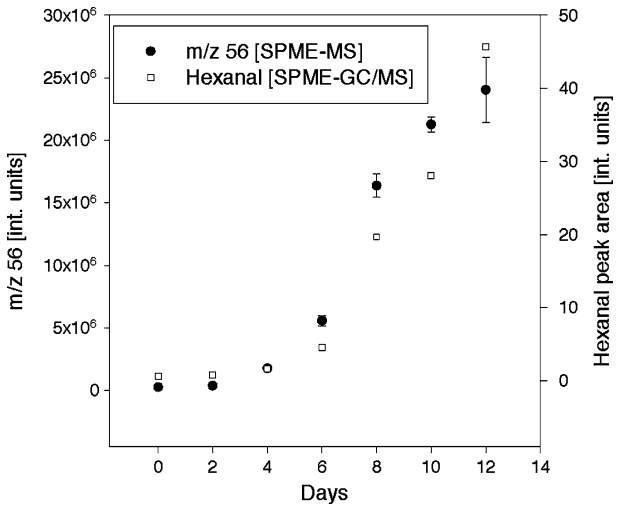


**Fig. 3** Changes in hexanal content (measured by SPME–GC/MS), and *m/z* 56 peak intensity (measured by SPME–MS), of rapeseed oil during 12-day storage at 60 °C. Peak areas are expressed as integrator units (Int. units)

for free fatty acids: acetic, hexanoic and traces of butanoic and pentanoic acids present in analyzed samples. Ion *m/z* 56 is the second most abundant ion in the hexanal spectrum. It is also present in significant abundance in 2-heptenal, and to a lesser extent in 2-pentenal and nonanal. Therefore, changes of its intensity in the SPME–MS spectrum can be correlated with changes of hexanal content in oil as detected using SPME GC/MS (Fig. 3). The correlation between an increase of the hexanal peak area in SPME–GC/MS analysis and an increase of ion *m/z* 56 abundance was expressed with a correlation coefficient of 0.9625. Ion *m/z* 57 was predominant in 1-pentene-3-ol and 1-octene-3-ol, and also abundant in hexanal and 2-heptenal. The correlation between the presence of 1-pentene-3-ol and ion *m/z* 57 was 0.9783. Ions in the cluster around *m/z* 70 were present in the majority of compounds. Ions *m/z* 83 and 84 were predominant for 2-pentenal and 2-heptenal, while *m/z* 81 was characteristic for isomers of 2,4-heptadienal and isomers of unidentified compounds eluted at RI 947 and RI 949. Ion *m/z* 110 reflects the presence of 2,4-heptadienal. It was a very specific ion in the SPME–MS spectrum, and almost undetectable in other compounds. The correlation between its level and the intensity of ion *m/z* 110 was 0.9972. The same correlation coefficient was found for ion 81.

## SPME-MS versus Totox

The Totox value as a sum of peroxide and AVs reflects oxidation changes in fats and oils. Peroxide value measures the amount of peroxides formed from fatty acids in the process of autoxidation in the initial steps, whereas anisidin value indicates the presence of secondary oxidation

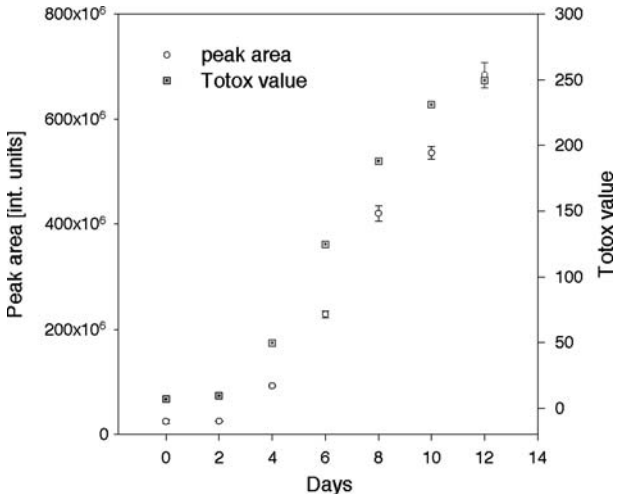


**Fig. 4** Changes in total ion chromatogram peak area obtained from SPME–MS analyses and Totox value changes during 12-day storage of rapeseed oil at 60 °C. Peak areas are expressed as integrator units (Int. units)

products. On the other hand measurement of volatile compounds resulting from the autooxidation of oils is a reliable method to measure their rancidity. Figure 4 shows an increase of SPME–MS peak area and the Totox value during the 12-day accelerated storage test. The correlation coefficient between these two parameters was 0.9841, whereas the correlation between SPME–MS peak area and PV was 0.9779. Shen et al. [16] analyzed corn, soybean and rapeseed oils stored at 60 °C for 0, 3, 6, 9 and 12 days and found correlations between 0.91 and 0.99 ($p \leq 0.05$) for PV and the signal generated by gas sensors.

## Discrimination of Autoxidized Rapeseed Oil Samples by SPME–MS

As it was shown, information obtained from SPME–MS could be used to observe autoxidation of rapeseed oil. A majority of papers on this technique show its potential applications in sample discrimination based on the degree of oxidation. PCA was used for the analysis of SPME–MS results [4, 8] while LDA or PLS was used for predictive purposes [6, 7]. The ability of SPME–MS to discriminate between oil samples of different rancidity levels was tested in using the model rancid oil samples and PCA. The results for the model rancid oil samples containing hexanal at concentrations ranging from 1 to 5 mg/L are shown in Fig. 5, graph A. Concentrations on the graph represent hexanal, which comprised 21.5% (w/w) of the total amount of oxidation products in the model sample. All samples were separated from 0 sample and separated from each other. Graph B of Fig. 5 presents discrimination of model standard samples at much lower hexanal concentrations ranging from 0.2 to 1.0 mg/L in 0.2 mg/L increments. In

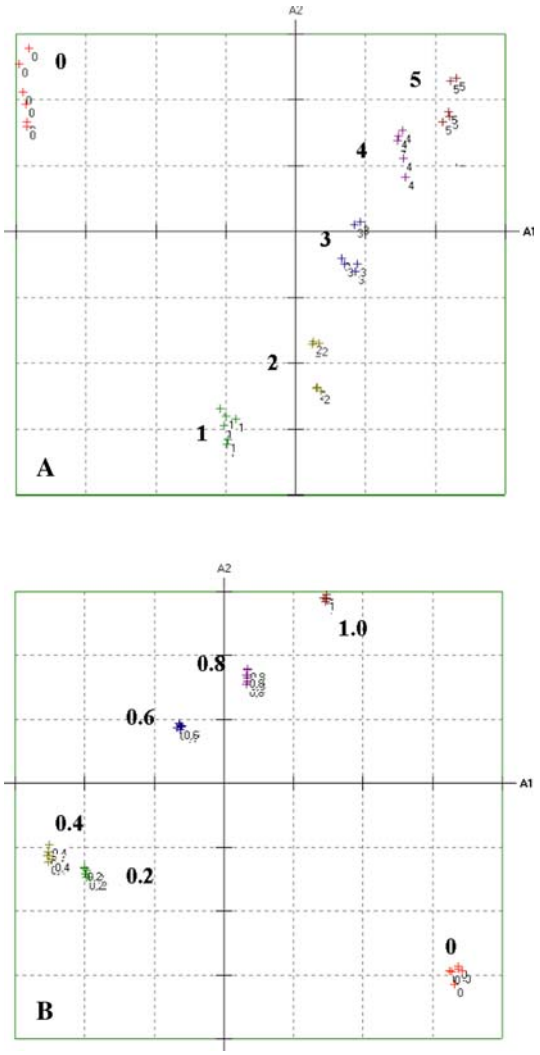


**Fig. 5** Principal component analysis (*PCA*) plots of data from SPME–MS analysis of model rapeseed oil samples containing different levels of oil oxidation products in the range of 1–5 mg/L (**a**) and 0.2–1.0 mg/L (**b**). A1 and A2 axes are the first two principal components

this case also, all samples were well-separated from 0 sample and from each other. When PCA was applied to the data obtained in the accelerated storage experiment, all samples were separated from each other, forming clusters with a very small variation between samples replicates (Fig. 6).

## Comparison of SPME-MS and Sensory Profile Method for Discrimination of Rapeseed Oil Samples

Similarities were observed in the cluster formation in PCA graph for SPME–MS and sensory profile data. Figure 6 revealed that the 2-day oil sample was clustered with control sample and located in the same quarter of the PCA graph. Next cluster was formed by samples acquired

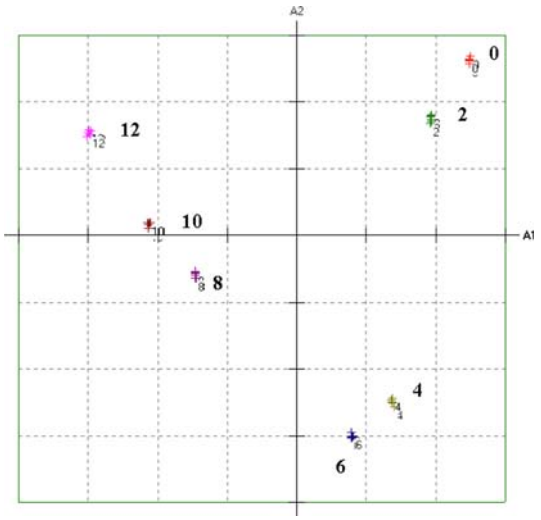


**Fig. 6** Principal component analysis plot of data from SPME–MS analysis of rapeseed oil samples subjected to storage at 60 °C for 12 days. Volatiles were measured at day 0, 2, 4, 6, 8, 10 and 12. A1 and A2 axes are the first two principal components

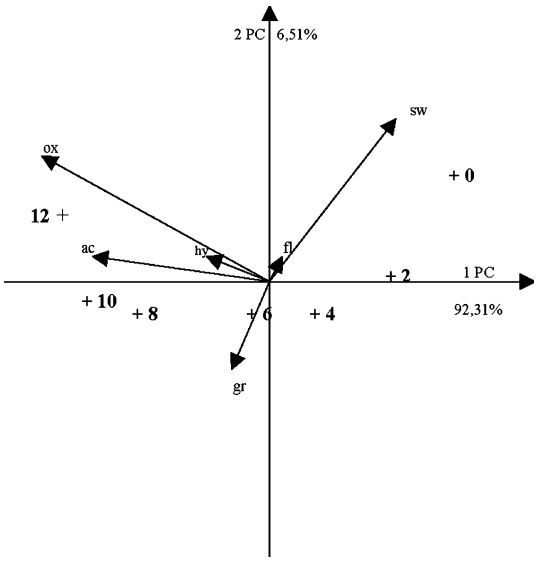


**Fig. 7** Principal component analysis plot of data from sensory profile analysis of rapeseed oil samples subjected to storage at 60 °C for 12 days. Samples were tested at day 0, 2, 4, 6, 8, 10, 12. Odor descriptors: acidic (*ac*), sweet (*sw*), green (*gr*), floral (*fl*), oxidised (*ox*) and hay (*hy*). PC1 and PC2 axes are the first two principal components

on day 4 and 6, whereas 8, 10 and 12-day samples formed a cluster separated by the A2 axis. A similar clustering was observed for sensory analysis data (Fig. 7). Sample 0 was described with the sweet attribute and the location of samples on the PCA plot indicated their gradual change in dominating odor notes from green, to acidic and oxidative. Similar grouping of samples on a PCA graph for SPME-MS data and sensory analyses, clearly shows the ability of SPME–MS in discriminating oil samples with varying rancidity.

The data indicated that SPME–MS could be an efficient tool to differentiate refined rapeseed oils of different rancidity. Two different types of information can be gathered from SPME–MS data: the peak area, and an ''average'' mass spectrum of headspace of the sample. An increase in peak areas for oil samples during the accelerated storage test correlated well with lipid oxidation indicators, such as PV (0.9779) or Totox (0.9841), indicating that these parameters were correlated with the total amount of volatile compounds produced during the autoxidation of rapeseed oil. Comparing the ''average spectra'' obtained from SPME–MS analyses with the data obtained from GC/MS analyses of the same samples indicated that intensities of some ions in the SPME–MS peak (*m/z* 56, 57, 83, 84, 81 and 110) reflected changes in the content of oxidation products, and could serve as indicators of the oxidation process in rapeseed oil. These oxidation products were hexanal (*m/z* 56), 1-pentene-3-ol and 1-octene-3-ol (*m/z* 57), 2-pentenal and 2-heptenal (*m/z* 83 and 84), and 2,4-heptadienal (ions *m/z* 81 and 110). However it should be noted that there was no single ion solely indicative of a presence of a single oxidation product in an oxidized rapeseed oil. A comparison of the SPME–MS data with the sensory profile data using PCA indicated similarities in clustering of the data obtained by these two methods. This result opens prospects for exploring SPME–MS as an ''electronic nose'' tool for monitoring autoxidation of rapeseed oil.

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