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Application of headspace—solid phase microextraction and multivariate analysis for plant oils differentiation

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Abstract

Application of multivariate analysis (MVA)—principal component analysis (PCA) and cluster analysis—for the analysis of chromatographic and sensory data was investigated for volatiles of plant oils. Five oils—rapeseed, soybean, peanut, sunflower and olive oil—were compared. Volatile compounds of fresh oils and oils subjected to storage at 60 °C were isolated by HS-SPME sampling and analysed by GC/MS, and fast GC with FID detection. Based on developed methods and data treatment it was possible to distinguish between different oils and oils stored for various periods of time. PCA of chromatographic data was related to PCA sensory analysis and similarities in sample clustering were observed. Multivariate analysis facilitates comparison of chromatographic profiles of volatile compounds characteristic for various plant oils and for monitoring oil quality in storage.

Keywords: Plant oils; Rancidity; SPME; MVA; PCA; Chemometrics

1. Introduction

Oxidation of fatty acids in food results in the formation of volatile compounds among which many have an unpleasant odour and are responsible for flavour problems in the food industry. Alcohols, aldehydes, ketones, acids, hydrocarbons, furanones and lactones are major compounds formed as a result of this process (Grosch, 1982). Static headspace (Boyd, Nwosu, Young, & MacMillian, 1998; Frankel, 1993; Medina, Satué-Gracia, & Frankel, 1999) and dynamic headspace (Aparicio & Morales, 1994; Hartvigsen, Lund, Hansen, & Hølmer, 2000; Morales, Aparicio, & Rios, 1994) are normally used for isolation of products resulting from fatty acid oxidation. Despite the huge analytical potential of these techniques they suffer some drawbacks: the need for highly sophisticated and costly samplers for automated injections, long preparation time, and often, the need for sample heating to release volatiles. Heating accelerates further degradation of analysed compounds. Solid phase microextraction technique (SPME)—a solvent-free extraction technique (Pawliszyn, 1997) eliminates some of these disadvantages. SPME is based on an absorption or adsorption of analytes onto a polymer-coated silica fibre and their subsequent desorption in the hot injection port of a gas chromatograph. This technique proved to be an effective tool for detecting low levels of fat derived flavour compounds (Doleschall, Kemény, Recseg, & Kõvári, 2001, 2002; Jeleń, Obuchowska, Zawirska-Wojtasiak, & Wąsowicz, 2000; Marsili, 2000).

Application of chemometrics including principal component analysis (PCA) for processing chromatographic, as well as sensory data proved to be an efficient tool for classification, searching similarities and finding relationships (Angerosa, Di Giacinto, Vito, & Cumitini, 1996; Aparicio, Rocha, Delgadillo, & Morales, 2000; Bucci, Magri, Magri, Marini, & Marini, 2002; Héberger, Keszler, & Gude, 1999).

The purpose of this work was to develop a technique based on a volatile compound profiles comparison using multivariate analysis (MVA) for rapid differentiation of various plant oils and monitoring changes in their storage. Our goal was also to relate results obtained by

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principal component analysis (PCA) of chromatographic data to results of sensory analysis based also on PCA.

2. Materials and methods

2.1. Materials

Rapeseed (RS), soybean (SB), peanut (PN), sunflower (SF), and extra virgin olive oil (OO) were used for this study. All were purchased from a local grocery store. Table 1 shows the content (% w/w) of the fatty acids for all oils. A total of 100 ml of each oil was put into a 1000-ml flat-bottom flask with a glass cap and stored at 60 °C for 5 days. For determination of dynamics of volatile compounds formation rapeseed oil was stored for 10 days at 60 °C and sampled after 2, 4, 6, 8, 10 days of storage. All samples were stored at −20 °C until day 10 and then analysed. The divinylbenzene/carboxene/polydimethylsiloxane (DVB/CAR/PDMS) fibre (Supelco Inc., Bellefonte, PA, USA) was used for headspace sampling. This coating was chosen for volatiles isolation based on our previous experience (Jeleń et al., 2000). The fibre was conditioned prior to use in the gas chromatograph injection port at 270 °C for 4 h as recommended by the producer.

2.2. Volatile compounds analysis

Oil samples (10 ml) were put in a 20-ml headspace vial, fitted with a Teflon-lined septum. Volatiles were sampled for 15 min at 50 °C from the headspace of the vial. The fibre was then immediately inserted into the injection port of the gas chromatograph for 5 min at 260 °C. A Hewlett-Packard HP5890II gas chromatograph coupled to a 5971 MSD quadrupole mass spectrometer and a HP6890 gas chromatograph with flame ionisation detector (FID) were used. The HP5890 and HP6890 chromatographs were equipped with MDN-5 (30 m×0.25 mm i.d.×0.25 μm d_f, Supelco) and HP5 (10 m ×100 μm i.d.×0,4 μm, d_f, Hewlett-Packard) columns respectively. Operating conditions for GC/MS were: helium flow 0.6 ml min^{-1}, initial oven temperature 40 °C (3 min), then 8 °C min^{-1} to 200 °C and 20 °C min^{-1} to 280 °C (3 min). GC/MS samples were run at least in triplicate. Chromatograph operating conditions for GC/FID were: helium flow 1 ml min^{-1}, initial oven temperature 40 °C hold 1 min, then 20 °C min^{-1} to 280 °C (1 min). All samples were run at least in five repetitions. Volatile compounds were identified by comparison of their retention indices and mass spectra with authentic standards or, in some cases tentatively only by NBS 75K mass spectra library search and Kováts RI.

Table 1
The content (% w/w) of fatty acids of analysed plant oils

	RS rapeseed	SB soybean	PN peanut	SF sunflower	OO olive oil
C16:0	4.6	11.2	10.8	5.5	9.0
C18:0	1.7	3.9	3.7	2.9	3.2
C18:1	62.1	23.4	60.0	23.0	79.9
C18:2	19.8	53.8	22.6	67.3	6.3
C18:3	8.5	6.0	–	0.7	0.7
C20:0	0.6	1.1	1.6	0.3	0.5
C20:1	1.6	0.3	1.3	0.3	0.4
C22:0	0.3	0.3	–	–	–
C22:1	0.8	–	–	–	–

2.3. Sensory analysis

A 10-member panel, experienced in descriptive analysis did the odour profiling of samples in three sessions. The oil samples (10 ml) were kept in 100 ml closed vessels at room temperature. After about 30 min the vessels were removed and the panel members sniffed the samples.

Six odour attributes—acidic (ac), sweet (sw), green (gr), floral (fl), oxidised (ox) and hay (hy)—were scaled on linear 10-cm scales anchored on both sides for the intensity as "not desired" and "very desired", respectively. The odour attributes were chosen according to the "Basic Flavour Descriptive Language" from Givaudan Roure Flavor Ltd (Stampanoni, 1998). 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 three sessions. The data obtained were calculated from 30 replicates and after statistical interpretation by multivariate procedure presented as a graphic projection of Principal Component Analysis (PCA; Baryłko-Piekielna, Zawirska-Wojtasiak, Kornelson, & Rothe, 1992).

2.4. Oxidation measurements

Peroxide value (miliequivalent O_2 kg^{-1} lipids) was determined by the International Norm ISO 3960-1977(E). Anisidine value and total oxidation value (totox) were determined according to the International Norm ISO 6885:1988. All the analyses were performed in duplicate.

2.5. Statistical analysis

Integration reports obtained as a result of SPME-GC/FID were transformed by Chromstat (v. 2.4) software from Analyt GmBH (Germany). Two-dimensional principal component analysis score plots were created from the data. The software was based on the comparison between "skeletons of chromatograms". The PC1 was the axis, which contained the largest possible

amount of information and PC2 was perpendicular to PC1. The principal components were orthogonal and linear combinations of the original variables. PCA score plots were used to determine whether samples of various oils fresh and stored at 60 °C could be grouped into different classes. SPME-GC/MS data were subjected to cluster analysis and PCA using Statgraphic Plus v. 5.0, Professional Edition (Mangustics, Inc., USA) software.

3. Results and discussion

Gas chromatography coupled with mass spectrometry was used for the identification of volatile compounds of various oils. In Table 2, major compounds identified by SPME-GC/MS in both fresh oils and oils stored for 5 days at 60 °C are shown. Most of them had been reported in previous works whether using SPME (Doleschall et al., 2001, 2002; Jeleń et al., 2000) or dynamic headspace as sampling technique (Angerosa, Mostallino, Basti, & Vito, 2000; Morales, Rios, & Aparicio, 1997). Aldehydes were the most abundant group of volatiles associated with stored/rancid oils. Of them pentanal, E-2-pentenal, hexanal, E-2-hexenal, heptanal, E-2-heptenal, E-2-octenal dominated in these samples. In the oxidation process also alcohols were produced and formed an important fraction of volatiles. The most abundant ones were: 1-penten-3-ol, 1-pentanol, 1-hexanol, 1-octen-3-ol, 1-octanol. Fresh oils except virgin olive oil were characterised by a low number of volatile compounds. Some compounds such as propanal, pentanal, hexanal, octanal, 1-octen-3-ol, were reported before as the volatile oxidation products of vegetable oils (Snyder, Frankel, & Selke, 1985). Morales et al. (1997) stated that the hexanal/nonanal ratio could be used to distinguish between good-quality and oxidised olive oil. Solinas, Marsilio, and Angerosa (1987) indicated a relation between perceived rancidity and 2-pentanal, hexanal, 2-heptanal, octanal and nonanal. Various methods were used for isolation of oils volatiles: Guth and Grosch (1990) used aroma extract dilution analysis in investigation of rapeseed oil and identified hexanal, 2-heptanal, 2,4-heptadienal, 2-octenal, nonanal, 2,4-nonadienal and 2,4-decadienal, whereas Snyder (1995) using supercritical fluid extraction for compounds isolation identified hexanal, octanal, nonanal and 2,4-decadienal. Hexanal, (E)-2-pentanal, (Z)-2-pentenal, 3-hexenal, (E)-2-hexenal, (Z)-2-hexenal and 2,4-hexadienal were identified in olive oil using dynamic headspace sampling by Morales et al. (1994).

SPME-GC/MS data were subjected to hierarchical cluster analyses, i.e. the nearest neighbour method with the squared Euclidean distance measure based on presence/absence of a particular compound and PCA. Fig. 1 shows a dendrogram formed using the nearest neighbour method and the PCA projection of the same samples. In PCA analysis four components were extracted and accounted together for 82.43% of the variability in the original data. Components 1 and 2 accounted for 30.79 and 22.4% of variance. Both methods indicated a similar grouping, and clearly showed the differences between the oils. There were two groups characterised by samples with oxidised off-flavour and fresh samples of oil. The samples of OO and stored OO′ formed a distinct cluster, which was linked to the other clusters at large distance value indicating a significant difference.

GC/MS analysis with subsequent PCA or cluster data treatment yielded good results. The obvious advantage of using mass spectrometer for detection is the information of compounds identity. The main drawback, however, is the relatively high cost of such a detector and long analysis time using conventional capillary columns. Narrow bore columns (0.050–0.100 mm) produce peaks too narrow to be properly identified by older type

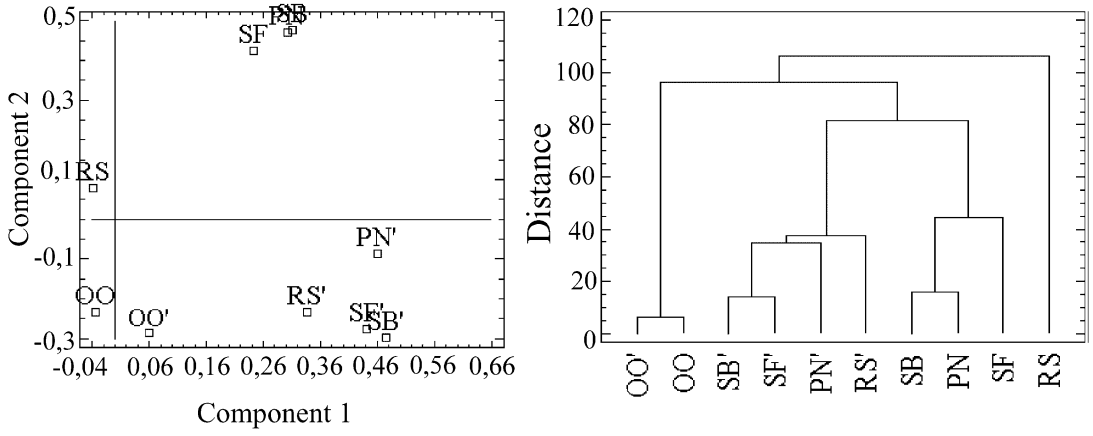

Fig. 1. PCA plot and dendrogram of plant oils fresh and subjected to storage at 60 °C for 5 days, grouped using the nearest neighbour method with squared Euclidean distances. Sample codes: fresh oils—(RS) rapeseed oil; (SB) soybean oil; (PN) peanut oil; (SF) sunflower oil; (OO) olive oil; stored oils—(RS′) rapeseed oil; (SB′) soybean oil; (PN′) peanut oil; (SF′) sunflower oil; (OO′) olive oil.

Table 2
Volatile compounds identified in various plant oils before and after 5 days storage at 60 °C using SPME-GC/MS[a]

t_R	Compound	RI	Oils stored for 5 days at 60 °C peak area [×10⁶]					Fresh oils peak area [×10⁶]				
			Olive oil	Soybean oil	Sunflower oil	Peanut oil	Rapeseed oil	Olive oil	Soybean oil	Sunflower oil	Peanut oil	Rapeseed oil
2.53	Butanal	593	–	–	28.5	10.6	–	–	–	0.2	0.1	–
2.69	Acetic acid[b]	641	25.8	16.0	12.6	6.8	–	23.1	–	–	–	–
3.15	E-2-butenal	665	1.7	6.4	2.9	0.7	10.6	–	–	–	–	–
3.32	1-Butanol[b]	670	–	1.0	1.0	1.2	–	–	–	0.4	–	–
3.60	1-Penten-3-ol	685	2.5	7.9	2.1	0.7	16.2	3.4	–	–	–	–
3.82	Pentanal[b]	705	3.6	9.9	11.7	54.9	5.4	3.3	6.0	1.5	2.5	–
4.05	2-Pentanol[b]	718	0.4	0.5	–	–	1.1	–	–	–	–	–
4.35	Unidentified	735	–	–	–	–	–	–	–	0.7	–	–
4.64	3-Methyl-1-butanol[b]	749	1.1	–	–	–	–	0.02	–	–	–	–
4.79	2-Methyl-1-butanol[b]	756	0.5	0.7	–	–	1.1	–	–	–	–	–
4.99	E-2-pentenal[b]	765	4.5	10.2	3.0	0.4	16.7	0.6	–	–	–	–
5.23	Toluene	773	0.6	–	–	–	–	0.5	–	–	–	–
5.31	1-Pentanol[b]	776	1.2	3.8	5.2	14.1	2.9	0.8	–	–	–	–
5.39	2-Penten-1-ol	781	–	–	–	–	–	0.6	–	–	–	–
5.53	Unidentified	786	1.2	1.9	–	–	2.1	–	–	–	–	–
5.65	Unidentified	790	4.9	–	–	–	–	–	–	–	–	–
5.75	1-Octene	794	–	0.7	0.5	1.8	0.8	0.5	–	0.3	0.7	–
5.97	*n*-Octane	800	–	–	–	–	–	5.4	0.07	0.3	–	0.1
6.02	Hexanal[b]	804	18.7	30.7	58.6	140	23.6	–	1.7	0.7	1.2	–
6.12	2-Octene	810	–	–	–	–	–	–	–	1.7	–	–
6.59	1-Methoxy-hexane	832	4.1	–	–	2.2	–	7.4	–	–	–	–
6.68	Unidentified	836	3.4	–	–	–	–	6.4	–		–	–
7.15	2-Methylethyl butanone	855	1.0	–	–	0.6	0.6	1.7	–	–	–	–
7.30	E-2-hexenal[b]	861	18.1	3.3	9.2	13.3	1.6	18.1	–	–	–	–
7.36	E-3-hexen-1-ol[b]	864	29.3	–	–	–	–	37.4	–	–	–	–
7.60	E-2-hexen-1-ol[b]	874	3.3	–	–	0.4	–	3.6	–	–	–	–
7.67	1-Hexanol[b]	878	10.7	1.5	1.2	1.3	–	13.1	–	–	–	–
8.15	Unidentified	894	2.1	0.8	1.7	2.9	0.6	1.2	–	–	0.9	–
8.29	Unidentified	897	–	0.8	–	–	–	0.3	–	–	–	–
8.34	*n*-Nonane	890	–	1.8	–	–	–	–	–	–	–	–
8.42	1-Heptanal[b]	902	3.2	5.7	7.1	13.5	4.8	–	–	–	0.2	–
8.83	Pentanoic acid	922	1.9	1.4	0.7	8.8	0.9	–	–	–	–	–
9.38	3-Ethyl-1,5-octadiene	947	30.6	24.6	6.6	–	50.8	2.3	–	–	–	–
9.45	3-Ethyl-1,5-octadiene isomer	949	20.9	26.2	8.1	2.7	56.7	–	–	0.3	–	–
9.80	E-2-heptenal[b]	964	12.5	95.6	226	154	40.5	1.2	–	–	–	–
9.94	Unidentified	970	2.4	3.9	–	–	1.9	0.7	–	–	–	–
10.03	1-Heptanol[b]	974	7.6	–	1.7	4.3	2.9	3.9	–	–	–	–
10.23	1-Octen-3-ol[b]	983	2.5	26.1	71.2	33.6	14.3	–	–	–	–	–
10.43	Unidentified	991	5.5	3.9	3.7	13.1	2.4	2.8	–	–	–	–
10.62	*n*-Decane	1000	25.8	37.4	10.1	2.9	83.1	11.3	0.2	0.4	0.2	0.7
10.70	Hexanoic acid	1009	–	–	12.9	–	–	–	–	–	–	–
10.72	Octanal[b]	1010	–	8.0	12.0	25.7	10.1	–	–	–	–	–
10.78	Hexyl acetate	1014	159	–	–	–	–	118	–	–	–	–
10.96	E,E-2,4-heptadienal	1023	5.7	28.1	16.1	10.7	–	–	–	–	–	–
11.38	Unidentified	1047	–	0.9	–	2.4	1.3	0.5	–	–	0.9	–
11.71	Unidentified	1065	–	2.6	4.9	5.0	1.5	–	–	–	0.3	–
11.83	E-2-octenal[b]	1071	2.5	7.5	14.8	40.0	6.1	–	–	–	–	–
12.23	1-Octanol	1091	4.3	0.9	0.9	4.1	3.2	–	–	–	–	–
12.36	3,5-Octadien-2-one	1098	–	–	2.6	4.0	3.6	–	–	–	–	–
12.46	Unidentified	1103	–	2.2	–	–	1.9	–	–	–	–	–
12.72	*n*-Undecane[b]	1115	–	2.7	1.3	–	1.7	–	0.3	0.3	–	0.3
12.86	Nonanal[b]	1122	22.7	2.8	4.1	137	19.5	1.1	–	–	–	–
13.68	2,4-Dimethyl undecane	1160	0.7	–	–	–	–	0.4	–	–	–	–
14.02	E-2-nonenal[b]	1174	–	–	1.5	4.9	1.0	–	–	–	–	–
14.68	*n*-Dodecane	1200	5.2	0.3	–	9.5	0.2	2.5	–	–	–	–
15.05	Decanal	1227	0.4	–	–	0.8	0.6	–	–	–	–	–
15.92	E-2-decenal[b]	1279	0.9	–	0.8	11.8	1.6	–	–	–	–	–
16.55	E,E-2,4-decadienal[b]	1315	–	1.8	5.5	7.2	2.2	–	–	–	–	–
17.66	2-Undecenal	1375	–	–	–	3.9	–	–	–	–	–	–
18.19	*n*-Tetradecane[b]	1400	0.5	–	–	–	–	–	–	–	–	–

[a] t_R, retention time; RI, Kováts retention index; SPME extraction at 50 °C for 15 min.
[b] Identity of compounds by comparison of their mass spectra and t_R with standards, rest of compounds identified tentatively using NBS 75K mass spectra library search.

quadrupole mass spectrometers. To simplify procedure we decided to couple fast GC/FID with PCA data treatment to differentiate between samples.

Fig. 2 shows chromatograms of volatile compounds isolated from fresh (left column) and stored (right column) plant oils, using HS-SPME-GC/FID. Compared to GC/MS runs of over 25 min the separation of volatile compounds was achieved within 8 min, using fast GC/FID. Integration reports obtained as a result of SPME-GC/FID of plant oils without particular compounds

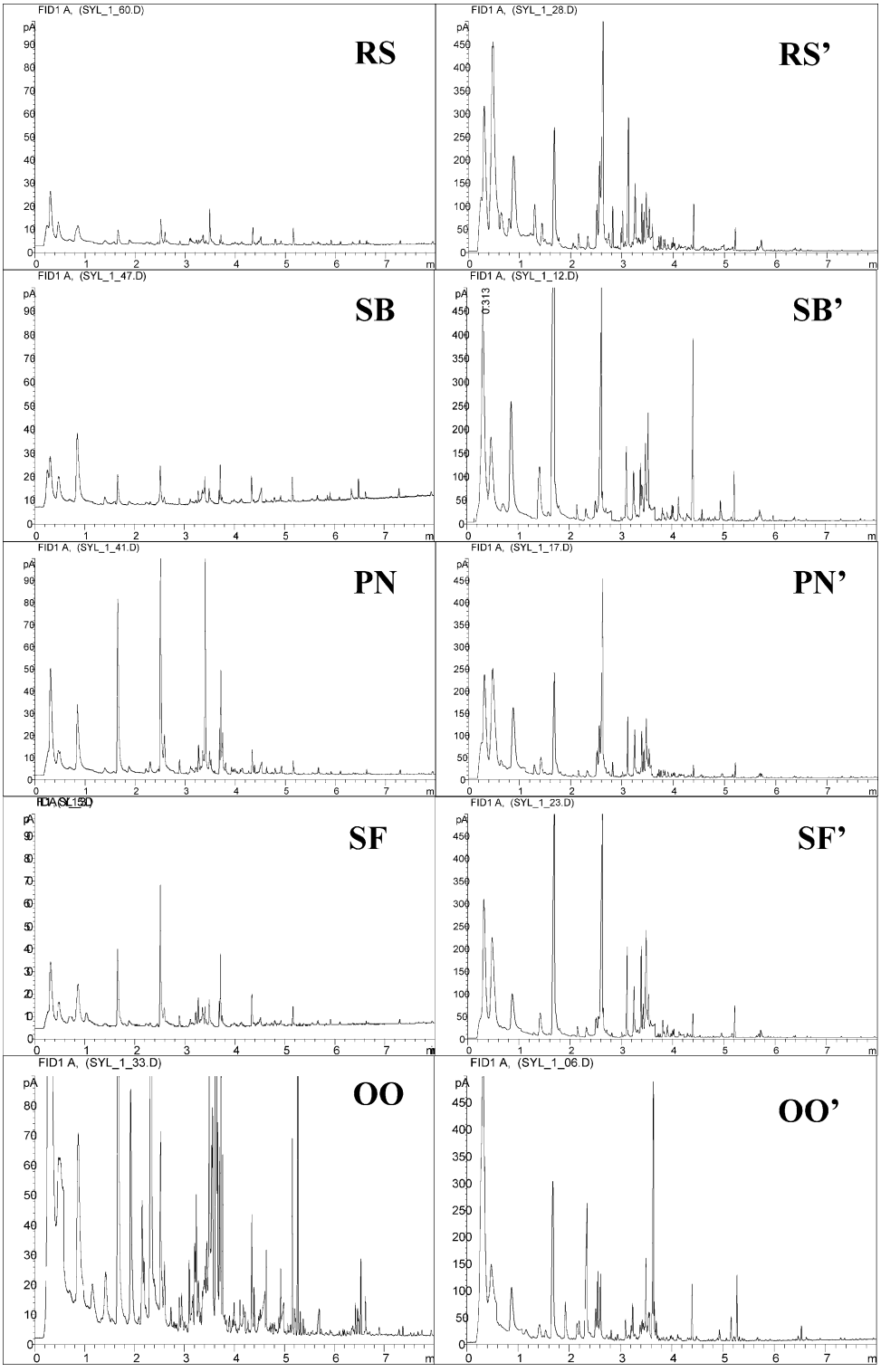

Fig. 2. Chromatograms of volatile compounds isolated from fresh oils and oils stored at 60 °C for 5-day-old oils using HS-SPME-GC/FID. Sample codes are the same as for Fig. 1.

identification, were subjected to PCA computed using the normalised data.

Fig. 3 shows the comparison of PCA sensory data with PCA treatment of chromatographical data of oils volatiles. Samples were subjected to PCA based on odour profiling analysis to find discrimination according to their sensory quality (Graph I). All analysed plant oils were compared with each other in relation to all used odour attributes. Oxidised (ox), hay (hy), acidic (ac) and sweet (sw) were the major odour attributes responsible for the differentiation. Three oils rapeseed (RS), peanut (PN) and sunflower (SF) were similar and almost odourless, characterised only by a weak sweet (sw) odour. Soybean oil (SB) was characterised by sweet (sw) and hay (hy) odours. Stored oils rapeseed, olive, soybean and sunflower RS′, OO′, SB′, SF′ were characterised by an undesired sensory quality with oxidised (ox); acidic (ac) attributes being predominant. Stored peanut oil was characterised by hay and flowery notes in addition to oxidised one. Fresh olive oil was perceived as the most aromatic of investigated fresh oils and described with the dominant acidic, green notes.

Graph II on Fig. 3 shows PCA plot of volatile compounds for fresh and stored oils. That plot indicates a significant separation of samples with oxidised off-flavours from fresh control samples of oil. Samples of oils with lower content of volatile compounds were located near fresh samples. Oils with higher flavour compounds content were more distant from fresh samples. Stored rapeseed (RS′) and peanut (PN′) oils were characterised by the longest distance from other oils both stored and fresh, indicating that these two oils oxidised more rapidly than the others. The significant correlation of 0.95 ($P < 0.1$) between total volatile compounds of plant oils before and after storage and total oxidation value was found. Compared to stored samples fresh oils except olive oil formed one cluster when projected on the same PCA graph (Graph II). Based on GC/MS experiment E-2-heptenal, 3-ethyl-1,5-octadiene isomer, 1-octen-3-ol, nonanal, E-2-octenal, octanal, E-2-pentenal, 1-octanol, E-2-hexenal, and E-2-butenal, 1-penten-3-ol, 1-pentanol, *n*-octane, 1-heptanal, were the main volatile components responsible for differences between fresh and stored oil samples.

Olive oil (extra virgin) used in this study was a non-refined one; therefore it had an abundant fraction of volatiles. This caused the distant location of olive oil from the remaining ones. Due to the presence of natural antioxidants, the olive oil profile of volatile compounds did not change to the extent observed in other oils. This was reflected in the close distance between stored and fresh olive oils on Graph II. Similar relations were observed on the sensory PCA plot (Graph I). It was also in agreement with small differences between total oxidation value of fresh and stored olive oil samples (Table 3). Solinas, Angerosa, and Camera (1988) also showed highest flavour stability of olive oil compared with other oils.

To focus on the differences between fresh oils, a PCA projection of these samples were shown in Graph III. The score plot by the first two principal components showed that the five fresh plant oils were well differentiated and the type of oil was associated with specific headspace volatiles. When the first four PCs were applied, samples of oils were not well differentiated (data not shown), so further analyses were based only on the first two components. Two distinct groups were formed by the rapeseed (RS) and soybean (SB) and by the peanut (PN) and sunflower (SF), whereas samples of olive oil (OO) were clearly separated from these groups. OO with the longest distance from other vegetable oils had a different peak pattern and the highest total oxidation value (Table 3). Correlation value between total volatile compounds of fresh oils and total oxidation value was 0.84.

In a similar investigation Marsili (1999, 2000) using SPME-MS-PCA studied off-odours in milk and obtained a distinct separation of samples with microbial

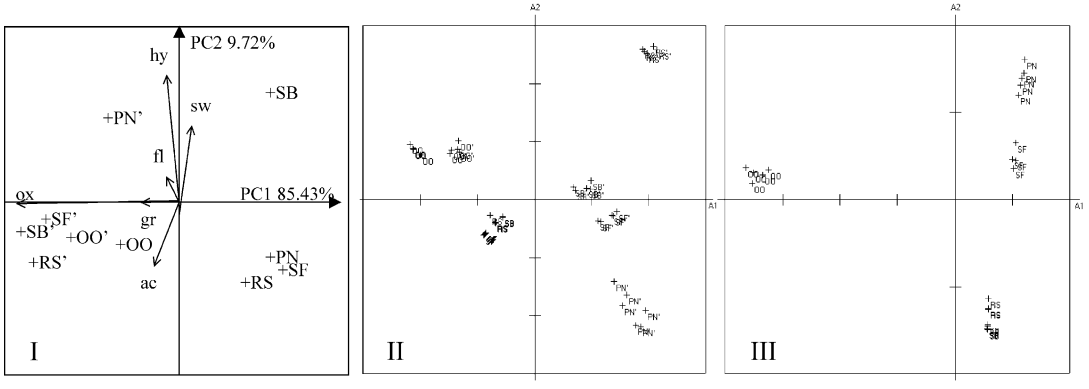

Fig. 3. PCA score plots of plant oils fresh and stored at 60 °C for 5 days. Graph I—PCA of sensory data; Graph II—PCA data of volatile compounds analysed by HS-SPME-GC/FID in fresh and stored oils; Graph III—PCA data of volatile compounds of fresh oils. Sample codes: fresh oils—(RS) rapeseed oil; (SB) soybean oil; (PN) peanut oil; (SF) sunflower oil; (OO) olive oil; stored oils—(RS′) rapeseed oil; (SB′) soybean oil; (PN′) peanut oil; (SF′) sunflower oil; (OO′) olive oil. Descriptors: (ac) acidic; (sw) sweet; (gr) green; (fl) floral; (ox) oxidised; (hy) hay.

Table 3
Peroxide value, anisidine value and total oxidation value of plant oils before and after storage at 60 °C

Oils	Peroxide value (PV) [meqO_2 kg^{-1} lipids]	Anisidine value (p-AV)	Total oxidation value (2×PV + p-AV)
Fresh oils/oils stored for 5 days at 60 °C			
Rapeseed oil	0.54/9.95	0.46/11.54	1.54/31.44
Soybean oil	1.88/7.05	1.57/6.69	5.33/20.79
Peanut oil	4.10/11.40	1.90/7.34	10.11/29.62
Sunflower oil	3.00/9.17	1.60/7.15	7.58/25.04
Olive oil	5.30/4.37	4.36/7.63	14.96/16.37
Rapeseed oil stored over a period of up to 10 days at 60 °C			
Fresh oil	0.54	0.46	1.54
2 days	4.74	0.74	10.22
4 days	12.80	2.53	26.89
6 days	14.93	14.13	43.99
8 days	16.00	17.27	49.27
10 day	14.20	24.90	53.30

contamination from other samples with off-flavour, caused by progressive oxidation. Angerosa et al. (1996) using dynamic headspace sampling and artificial neural network to examine oil quality in order to predict panel test score obtained 96% correct answers and suggested that sensory evaluation could be replaced by those techniques. Correlation values from 0.76 to 0.99 ($P<0.05$) between electronic nose intensities of different sensors and sensory analysis of canola, soybean and corn oil were found (Shen, Moizuddin, Wilson, Duvick, White, & Pollak, 2001).

PCA was able to discriminate between samples of rapeseed oil stored over a period of 10 days at 60 °C (Fig. 4). In PCA plot (Graph I), data from fresh samples were separated from samples stored for 2 days, indicating the possibility of discrimination of samples in early state of oxidation based on volatile compounds. Two distinct groups were formed by the fresh samples (0) and the ones stored for 2 days at 60 °C and by the samples stored for 4 and 6 days, while samples stored during 8 and 10 days were well-differentiated from the other groups. Total volatile compounds well correlated with total oxidation value (0.66, $P<0.1$), indicating that these methods were capable of measuring changes in oxidative state of oils. Aparicio et al. (2000) studied the rancid defect in virgin olive oil and stated that the multidimensional scaling (MDS) was able to differentiate percentages of the rancidity of standard oils. The PCA plot of sensory evaluation also indicated considerable grouping of samples with oxidised off-odour from fresh samples (graph II). Oxidised (ox); acidic (ac); green (gr) and hay (hy) were the major odour attributes responsible for the differentiation. Fresh rapeseed oil (0) and oil stored for 2 days at 60 °C (2) were very similar and odourless. The most undesired sample was sample 10, which was characterised by: oxidised (ox); hay (hy) and acidic (ac) off-odour. The same attributes described samples 6 and 8 but their intensities were lower.

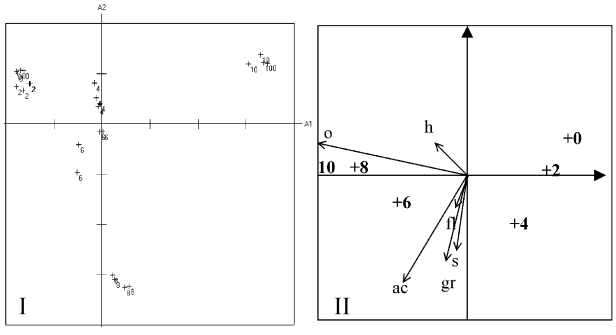

Fig. 4. PCA score plots of rapeseed oil stored at 60 °C up to 10 days. Graph I—PCA of volatile compounds, Graph II—PCA of sensory data. Sample codes: (0) rapeseed oil, fresh; (2) oil stored for 2 days at 60 °C; (4) oil stored for 4 days at 60 °C; (6) oil stored for 6 days at 60 °C; (8) oil stored for 8 days at 60 °C; (10) oil stored for 10 days at 60 °C. Descriptors: (ac) acidic; (sw) sweet; (gr) green; (fl) floral; (ox) oxidised; (hy) hay.

4. Conclusion

In conclusion, solid phase microextraction (SPME), gas chromatography (GC) and principal component analysis (PCA) can be a useful tool for rapid differentiation of plant oils based on the comparison of volatile compound profiles. Results of PCA analysis of volatiles can be related to profile sensory evaluation and classical "wet chemistry" methods. As the procedure of sensory assessment of samples requires a panel of several people and the procedure is long and laborious, in certain cases developed HS-SPME-GC/FID-PCA method can replace sensory evaluation. Satisfactory results were achieved using a flame ionisation detector, which is used routinely in oil processing plants, therefore the described method could be implemented in industrial laboratories for rapid screening of oil quality in production and storage. Profiling volatile compounds could also be used for the identity checking of oils. The absence of solvents, robustness and speed make solid

phase microextraction in conjunction with fast chromatography and PCA data treatment an attractive method for monitoring plant oil quality.

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