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Analytical Methods

The potential of different techniques for volatile compounds analysis coupled with PCA for the detection of the adulteration of olive oil with hazelnut oil

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Abstract

This paper investigates the effectiveness of three rapid methods of volatile compounds analysis with subsequent principal component analysis (PCA) treatment of data for differentiation between virgin olive oil samples adulterated with hazelnut oil. Tested methods included comparison of chromatograms of volatiles obtained using SPME-fast GC-FID, volatiles analysis by electronic nose based on MOS sensors (HS-Enose), and by direct coupling of SPME to MS (SPME-MS). Volatile compounds were analyzed also by SPME-GC/MS technique. Data obtained as a result of SPME-GC/MS was subjected to PCA. SPME-GC–MS analysis with subsequent PCA yielded good results, however being time consuming. The three methods of analysis of volatiles, with subsequent PCA treatment of data, allowed detection of olive oil adulteration with different contents of hazelnut oil ranging from 5 to 50% (v/v).

Keywords: Adulteration; Olive oil; Volatile compounds; Hazelnut oil

1. Introduction

Determination of food authenticity is one of the most crucial issues in food quality control. Due to high prices of extra virgin olive oil, this product is often subjected to adulteration with cheaper plant oils of poorer quality. Among the most frequent adulterations are those carried out with low-grades olive oils – pomace oil or refined oil and other cheaper plant oils such as hazelnut oil, sunflower oil and maize oil (Oliveros et al., 2002).

Determination of fraudulent addition of hazelnut oil to olive oil especially below 20% has always been very difficult to confirm, due to the similarity of the two oils in the composition of fatty acids, triacylglycerols and sterols (Mariani, Bellan, Lestini, & Aparicio, 2006; Sayago, García-González, Morales, & Aparicio, 2004; Zabras & Gordon, 2004). Analytical methods for monitoring olive oil adulteration with hazelnut oil include determination of filbertone ((*E*)-5-methylhept-2-en-4-one) by liquid chromatography–gas chromatography (LC–GC) and isotope dilution (Blanch, Caja, Leon, & Herraiz, 2000; Flores, Ruiz del Castillo, Herraiz, & Blanch, 2006), composition of sterols and triacylglycerols by GC and high-field ^{1}H NMR (AcKurt, Özdemir, Biringen, & Löker, 1999; Mariani et al., 2006), non-volatile marker components present in the polar fraction of hazelnut oils by RP-HPLC (Zabras & Gordon, 2004), vitamins (AcKurt et al., 1999) and tocopherols composition by RP-HPLC and specific tocopherols ratio (γ/β and β/δ) (Parcerisa, Casals, Boatella, Codony, & Rafecas, 2000). However, the amount and composition of sterols cannot detect levels of hazelnut oil below 30% (Cercaci, Rodriguez-Estada, & Lercker, 2003). Moreover, some parameters like content of triacylglycerols with 50 carbon atoms, the ratio of some triacylglycerols and composition of tocopherol require performing

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other analysis, particularly for oils adulterated with low percentages of hazelnut oil (Cercaci et al., 2003).

Profile of volatile compounds of oils, especially those obtained by cold pressing and unrefined could serve as a valuable tool in the identification of their origin and adulteration. Analysis of volatile compounds can be performed by GC/MS, based on their separation on analytical column and subsequent identification using mass spectrometry or other detector. The alternative approach to the analysis of volatiles is to mimic the human olfactory system analyzing unresolved mixture of volatiles present in headspace. This approach is exemplified by electronic nose technology. Of the electronic noses present on a market, two main types can be distinguished: sensor based and mass spectrometer based quasi-electronic nose. In recent years, a number of applications have been developed for the quality analysis of olive oil. Electronic nose have been applied to detect of rancidity (Aparicio, Rocha, Delgadillo, & Morales, 2000; Cosio, Ballabio, Benedetti, & Gigliotti, 2007), adulterants (Cosio, Ballabio, Benedetti, & Gigliotti, 2006; Oliveros et al., 2002) and determination of geographical origin (Cosio et al., 2006; Cimato et al., 2006; Taurino et al., 2002). The metal oxide semiconductors sensors are the most frequently used in studies on food products (Martin, Oliveros, Pavon, Pinto, & Cordero, 2001; Oliveros et al., 2002). More recently, another type of "electronic nose" system based on mass spectrometry has also been investigated (Peňa, Càrdenas, Gallego, & Valcàrcel, 2005). SPME-MS method is based on introduction of volatiles adsorbed onto a polymer-coated SPME fiber from sample into the injection port of gas chromatograph to effectively perform a desorption, however restriction non-coated capillary is mounted into GC instead of analytical column, so no separation of compounds is achieved and in the ionization chamber of MS an average spectrum of introduced headspace is obtained. Application of multivariate statistic analysis including principal component analysis (PCA) enables differentiation between samples. Multivariate analysis for processing chromatographic data has been shown to be an efficient tool for classification and searching similarities of oil samples and it shows promise for routine quality control of oils (Biswas, Heindselmen, Wohltjen, & Staff, 2004; Capote, Castro, & Luque, 2007; Mildner-Szkudlarz, Jeleń, Zawirska-Wojtasiak, & Wąsowicz, 2003).

The main objective of this work was to assess the potential of three methods to distinguish extra virgin olive oil mixed with hazelnut oil, based on volatile compounds, at four different levels: 5, 10, 25 and 50% (v/v). These methods included: (i) comparison of chromatographic "fingerprints" obtained by SPME-fast-GC (FID) analysis; (ii) sample headspace comparison using an electronic nose based on metal oxide (MOS) sensors (HS-Enose); (iii) sample headspace comparison using SPME-MS method. Another objective of this study was to relate result obtained by SPME-GC/MS to the tested three methods of volatiles comparison.

2. Materials and methods

2.1. Materials

Four extra virgin olive oils (EVOO) with certificate of origin, five cheaper olive oils (OO) and virgin hazelnut oil (H) were used for this study. All were purchased from a local grocery store. The adulterated samples were prepared at our laboratory. Virgin olive oil was mixed with hazelnut oil at four different levels of adulteration: 5, 10, 25 and 50% (v/v). The divinylbenzene/carboxene/polydimethylsiloxane (DVB/CAR/PDMS) fiber (Supelco Inc., Bellefonte, PA, USA) was used for headspace sampling. This coating was chosen for volatiles isolation based on our previous experience (Jeleń, Obuchowska, Zawirska-Wojtasiak, & Wąsowicz, 2000). The fiber was conditioned prior to use in the gas chromatograph injection port as recommended by the producer.

2.2. Volatile compounds analysis

2.2.1. SPME-GC/MS

Ten milliliter of oil sample were placed into 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 fiber 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 was used. The HP5890 chromatograph was equipped with MDN-5 column (30 m × 0.25 mm i.d. × 0.25 μm d_f, Supelco). Operating conditions for GC/MS were the following: 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). All samples were run in triplicate. Volatile compounds were identified by comparison of their retention indices and mass spectra with authentic standards, or, in some cases tentatively only by NBS 75 K mass spectra library search and Kováts retention indices (RI). Retention Indices were calculated for each compound using homologous series of C_5–C_{16} *n*-alkanes (Dool & Kratz, 1963). SPME-GC/MS data were subjected to cluster analysis and PCA using Statistica v. 7.1, (StatSoft, Inc.) software.

2.2.2. SPME-MS

A Hewlett-Packard HP5890II gas chromatograph coupled to a 5971 MSD quadrupole mass spectrometer was used. Twenty milliliter of oil sample was put in a 40 ml headspace vial, fitted with a teflon-lined septum. Volatiles were sampled for 15 min at 35 °C from the headspace of the vial. The fiber 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 was used. HP5890 chromatograph was equipped with uncoated fused silica, Supelco, Bellefonte (15 m × 0.20 μm

i.d.) column. Chromatograph operating conditions were as follows: helium flow 0.4 ml min^{-1}, oven temperature 150 °C (isotherm). All samples were run in 6 repetitions. Mass spectra were processed using in MsStat software (Analyt GmBH, Germany).

2.2.3. SPME-fast GC-FID

A HP6890 gas chromatograph with flame ionisation detector (FID) was used. Compounds were introduced using solid phase microextraction (SPME) device. Twenty milliliter of oil sample was put in a 40 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 fiber was then immediately inserted into the injection port of the gas chromatograph for 5 min at 260 °C. The HP6890 chromatograph was equipped with HP5 (10 m × 100 μm i.d. × 0.4 μm d_f, Hewlett-Packard) column. Chromatograph operating conditions were as follows: 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 in four repetitions. Data were processed using ChromStat software (Analyt GmBH, Germany).

2.2.4. HS-E nose

An Alpha MOS Electronic nose system, the Fox 4000 was used. The electronic nose used static headspace (HS-100) autosampler for sample introduction. Three sensor chambers, each containing 6 MOS sensors were used for the measurement of the odour characteristics of the samples. Static headspace was generated in a 10 ml vial using 2 g of oils, during 30 min at 35 °C. Five hundreds microliter of the gaseous phase were injected into the electronic nose. Sensor resistance was measured during 120 s at the rate of one acquisition every 0.5 s. All samples were run in three repetitions. Operation on the raw signals included signal pre-processing, selection of sensors providing the highest degree of sample differentiation and principal component analysis (PCA) of obtained data. Alpha Soft (v. 8.0) software was used for data processing.

2.3. Statistical analysis

Two-dimensional principal component analysis score plots (PCA) were created on the data. The principal components were orthogonal and linear combinations of the original variables. The principal components were classified depending on the level of information they produced. The PC1 was the axis, which contained the largest possible amount of information and PC2 was perpendicular to PC1. The two main aim of PCA were reduction the number of variables and elimination of redundancy. All models were validated using "leave-one-out" method.

In electronic nose the discrimination index gives the discrimination quality through an indication of the surfaces between groups. When groups are distinct, the discrimination index is positive and defined as $D_i = 100 \times [1 - (\text{surface (A)} + \text{surface (B)} + \cdots + \text{surface } (n)/\text{total surface})]$. When groups overlap each other, the discrimination index is negative and defined as $D_i = -(\Sigma \text{ intersection surface}/\text{total surface}) \times 100$ (Alpha M.O.S., 2002a).

Partial least squares analysis (PLS) was used to build a model that was able to predict the quantitative information. PLS algorithm was based on linear regression method. Partial least squares is a method for constructing predictive models when the factors are many and highly collinear. The goal of PLS was to predict Y from X and to describe their common structure.

3. Results and discussion

Gas chromatography coupled with mass spectrometry was used for the identification of volatile compounds of different olive oils, hazelnut oil and olive oil adulterated with hazelnut oil.

3.1. Volatile compounds of olive oils

Several volatile components that contribute to the aroma profile of different olive oils using SPME-GC/MS are listed in Table 1. Most of these components represented groups of characteristic volatiles produced through the lipoxygenase pathway. Those include 12 aldehydes, 9 alcohols, 7 ketones and 6 acids. For samples of extra virgin olive oil (EVOO) aldehydes were found in great quantities in comparison with other volatiles. These compounds contributed to nearly 68% of total amount of volatiles compared to cheaper olive oils (OO) where aldehydes represented average 38%. According to Montedoro, Bertuccioli, and Anichini (1978) content of aldehydes in black and green olives is 75 and 50%, respectively. Characteristic volatile aldehyde for EVOO was *E*-2-hexenal. Those components account for 54% and 2% of EVOO and OO total volatiles, respectively, and could be used to differentiate EVOO from cheaper olive oils. Also Cavalli, Fernandez, Cuvelier, and Loiseau (2004) analyzed by SPME-GC/MS samples of EVOO identified *E*-2 hexenal as predominant flavour component. For cheaper olive oils which were either refined or produced from pomace olive or adulterated the most abundant compounds were ketones and acids, which had a 7-fold and 11-fold, respectively greater content compared to EVOO.

Fig. 1 (Graph I) shows a PCA plot of different olive oils. Based on volatile compounds measured by SPME-GC/MS it was possible to distinguish between samples. Samples of EVOO, which formed one cluster, were well separated from other cheaper olive oils (OO). *E*-2-hexenal, hexanal, pentanal, acetic acid, 2-octanon, 2-heptanon were responsible for samples discrimination. For component 1 mainly contribute *E*-2-hexenal, hexanal, whereas for component 2 mostly pentanal, acetic acid, 2-octanon and 2-heptanon.

Cavalli et al. (2004), using SPME-GC/MS method, identified in virgin olive oil hexanal, *E*-2-hexenal, *E*-2-hexenol,

Table 1
Volatile compounds identified in different olive oils using SPME-GC/MS

Compound	RI	Peak area (TIC∗10^6)								
		EVOO 1	EVOO 2	EVOO 3	EVOO 4	OO 1	OO 2	OO 3	OO 4	OO 5
1. Acetic acid[A]	641	30.61[b]	0.97[b]	4.29[a]	0.90[c]	27.02[a]	30.37[a]	25.47[a]	18.72[a]	25.23[a]
2. Ethyl acetate	648	12.51[a]	0.61[b]	1.76[a]	0.44[c]	9.54[a]	–	5.03[a]	2.29[a]	–
3. 3-Methyl-1-butanal	654	3.81[c]	–	0.30[b]	0.52[d]	1.61[c]	–	–	–	–
4. 2-Methyl-1-butanal	662	4.02[a]	–	0.52[a]	0.60[b]	3.34[c]	–	–	–	–
5. 1-Butanol[A]	670	–	0.70[a]	–	–	–	–	–	–	1.07[b]
6. 1-Penten-3-ol	685	56.26[a]	0.99[a]	1.65[b]	3.71[a]	4.51[a]	–	–	–	–
7. 3-Pentanone	687	–	4.17[b]	2.27[b]	–	–	–	–	–	–
8. Propanoic acid	690	–	–	–	–	–	3.26[a]	–	2.36[b]	2.66[b]
9. 2-Pentanone	703	13.26[a]	1.87[a]	5.49[a]	0.68[b]	5.68[b]	–	–	–	–
10. Pentanal[A]	705	21.37[a]	1.61[b]	1.77[b]	1.99[b]	25.73[a]	63.42[b]	40.67[b]	17.23[a]	12.55[b]
11. 3-Methyl-1-butanol[A]	749	6.65[a]	0.54[b]	1.04[a]	0.44[b]	5.99[a]	–	1.77[b]	0.77[d]	–
12. 2-Methyl-1-butanol[A]	756	4.66[a]	0.70[e]	1.05[b]	0.35[b]	5.47[a]	–	1.78[b]	0.73[d]	–
13. *E*-2-pentenal[A]	765	6.24[a]	0.38[a]	0.63[b]	0.43[b]	3.07[b]	–	–	–	–
14. Toluene	773	–	–	–	–	5.32[a]	–	–	–	–
15. 1-Pentanol[A]	776	–	0.70[a]	1.14[a]	–	–	3.40[b]	4.71[b]	3.16[c]	2.44[b]
16. 2-Penten-1-ol	781	24.32[a]	1.39[b]	1.74[a]	0.76[b]	5.02[a]	–	–	–	–
17. Butanoic acid	786	–	–	–	–	2.86[a]	1.75[d]	3.15[a]	2.35[a]	1.13[d]
18. 2-Hexanone	792	–	–	–	–	–	7.54[a]	–	1.89[d]	2.39[c]
19. 1-Octene	794	4.92[b]	0.30[a]	0.49[a]	0.32[a]	3.92[a]	1.31[b]	3.04[a]	2.35[d]	1.40[d]
20. Hexanal[A]	804	117.39[b]	13.05[b]	11.92[b]	13.92[b]	81.61[a]	29.53[a]	25.59[b]	40.26[a]	22.66[b]
21. 2-Octene	810	12.85[c]	–	0.64[c]	4.02[a]	5.65[a]	–	–	2.68[d]	–
22. Hexane-1-methoxy	832	–	–	–	–	10.16[b]	–	2.52[a]	–	–
23. *E*-2-hexenal[A]	861	742.53[a]	78.57[a]	86.09[a]	128.47[a]	5.23[a]	1.39[a]	0.89[b]	16.18[b]	0.52[a]
24. *E*-3-hexen-1-ol[A]	864	–	–	13.60[a]	–	21.52[b]	–	1.99[a]	–	–
25. *E*-2-hexen-1-ol[A]	874	62.55[a]	32.92[b]	4.80[a]	7.95[a]	27.24[a]	0.42[b]	0.23[a]	4.69[b]	–
26. 1-Hexanol[A]	878	58.56[a]	18.35[b]	5.41[a]	3.75[b]	26.50[a]	1.03[b]	2.20[b]	2.11[c]	0.83[b]
27. Pentanoic acid	887	–	–	–	–		2.52[b]	1.44[a]	–	1.62[b]
28. 2-Heptanone	897	–	–	–	–	1.03[a]	31.48[a]	7.71[b]	7.17[a]	10.10[a]
29. *p*-Xylene	899	13.15[a]	1.51[c]	1.98[b]	1.08[d]	10.21[b]	30.64[d]	26.85[b]	2.88[a]	5.48[b]
30. 1-Heptanal[A]	902	3.19[a]	0.27[a]	0.36[b]	0.46[a]	4.10[a]	1.76[a]	2.08[c]	3.15[b]	2.90[b]
31. 3-Ethyl-1,5-octadiene	947	22.65[a]	0.92[a]	4.03[a]	0.65[b]	7.54[a]	–	–	0.98[b]	–
32. 3-Etyhl-1,5-octadiene isomer	949	27.65[a]	2.43[a]	4.50[a]	1.94[c]	10.17[a]	–	–	1.87[a]	–
33. *E*-2-heptenal[A]	964	4.09[a]	0.72[b]	0.53[c]	0.85[b]	3.51[a]	0.88[b]	0.75[c]	1.84[b]	0.47[d]
34. Unidentified	980	8.16[a]	0.61[a]	1.58[a]	0.52[d]	15.60[a]	8.16[a]	–	29.13[a]	4.21[a]
35. Unidentified	991	2.23[a]	0.26[b]	0.32[a]	0.30[c]	2.94[a]	0.94[b]	0.71[a]	1.25[a]	0.52[c]
36. Hexanoic acid	1001	–	0.59[c]	–	–	–	5.00[b]	4.09[b]	3.08[c]	3.20[b]
37. 2-Octanone	1003	–	–	–	–	–	32.15[a]	30.23[b]	13.02[a]	9.29[b]
38. Unidentified	1006	12.86[a]	0.72[b]	2.34[a]	0.36[c]	8.56[a]	–	–	–	–
39. Unidentified	1008	37.32[a]	2.40[b]	5.96[a]	1.65[b]	10.80[a]	–	–	–	–
40. Octanal[A]	1010	37.00[a]	0.73[b]	4.71[a]	1.17[b]	17.64[a]	1.51[b]	2.77[b]	4.53[a]	1.35[a]
41. Hexyl acetate	1014	16.25[a]	0.66[c]	2.09[a]	0.75[b]	6.91[b]	–	–	–	–
42. *E*, *E*-2,4-heptadienal	1023	–	–	–	–	–	–	–	–	–
43. Unidentified	1050	0.64[c]	0.21[e]	0.23[c]	–	1.21[a]	9.24[e]	8.51[b]	1.14[b]	0.84[a]
44. Heptanoic acid	1085	–	–	–	–		1.61[a]	1.17[a]	0.73[a]	0.67[b]
45. 1-Octanol	1091	–	–	–	–	1.38[a]	–	–	–	–
46. 2-Nonanone	1095	–	–	–	–	2.34[a]	6.32[b]	2.42[a]	4.95[b]	2.17[b]
47. Nonanal[A]	1122	20.18[b]	1.57[b]	1.57[c]	1.91[a]	8.76[b]	1.11[b]	1.90[b]	2.42[a]	1.09[b]
48. 2-Decanone	1193	–	–	–	–	0.26[b]	3.75[a]	1.84[b]	1.26[a]	0.93[b]
49. Decanal	1227	11.43[a]	0.36[e]	3.32[b]	0.55[a]	14.53[a]	0.37[c]	2.34[b]	1.86[b]	–
50. *E*-2-decenal[A]	1279	0.90[c]	0.22[b]	0.21[b]	0.44[b]	0.83[a]	0.41[c]	–	–	–

RI, Kováts retention index.SPME extraction at 50 °C for 15 min.
[A] Identity of compounds by comparison of their mass spectra with standards, rest of compounds identified tentatively using NBS 75 K mass spectra library search.
[a] (RSD) < 5%.
[b] 5 < (RSD) < 15%.
[c] 15 < (RSD) < 25%.
[d] 25 < (RSD) < 50%.
[e] (RSD) > 50%, $n = 3$.

Z-3-hexenol and hexanol. According to Montedoro et al. (1978) hexanal, *E*-2-hexenal, 1-hexanol and 3-methyl-1-butanol are the main volatile compounds of virgin olive oil. However, Solinas, Angerosa, and Camera (1988) stated that octanal, nonanal and 2-hexenal are characteristic volatiles of virgin olive oil.

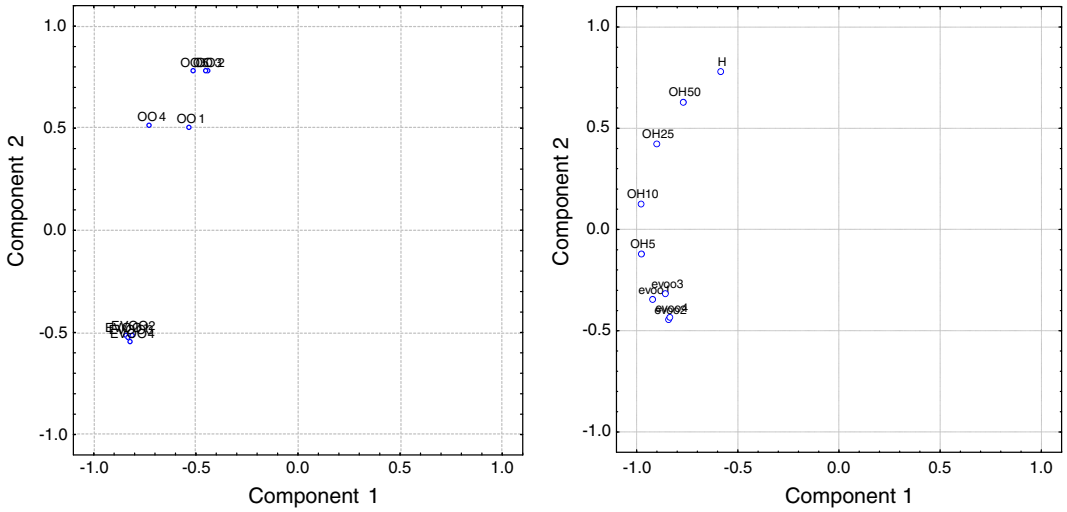

Fig. 1. PCA score plot based on SPME-GC/MS analysis. Graph I – PCA score plot of different olive oil samples. Sample codes: EVOO 1–EVOO 4, extra virgin olive oils, OO 1–OO 5, cheaper olive oils. Graph II – PCA score plot of hazelnut oil, EVOO 1–EVOO 4 and EVOO 1 with different levels of adulteration. Sample codes: H, hazelnut oil; EVOO 1–EVOO 4, extra virgin olive oils; OH 5, OH 10, OH 25 and OH 50, EVOO 1 with addition of 5, 10, 25 and 50% (v/v) of hazelnut oil, respectively.

3.2. Volatile compounds of hazelnut oil and EVOO adulterated with hazelnut oil

In Table 2, major compounds identified in hazelnut oil and EVOO 1 adulterated with hazelnut oil have been shown. Some of volatiles, such as acetic acid, 3-methyl-butanal, 2-methyl-butanal, pentanal, 1-octene, hexanal, 2-octene, 1-heptanal, *E*-2-heptenal, octanal, nonanal, decanal, *E*-2-decenal were present in both of oils but the amount in which these volatiles were present varied. In contrast, lots of volatile compounds appeared only in hazelnut oil so its presence might be used to determine potential adulteration of olive oil samples. Certainly furfural, 2-furanmethanol, 2,6-dimethyl pyrazine and 5-methyl-2-furancarboxaldehyde, which contributed to nearly 23% of total amount of volatiles, were only detect in hazelnut oil. Among acids hexanoic and octanoic acids were only detectable by SPME in the investigated samples of hazelnut oil. Moreover, acetic acid had 14-fold greater content compared to EVOO 1. Hazelnut oil produced also lots of aldehydes, ketones and alcohols, which formed an important fraction of volatile compounds. However, aldehydes represented average 32% compared to EVOO 1 where these components represented nearly 70% of total volatiles. According to producer the production of hazelnut oil was as follows: hazelnut fruits were crushed under a big millstone to obtain a paste, which was then cooked for one hour in cast iron frying pans. Afterwards the gilt paste was poured into pressing machines from where fruited oil was flowing out. From 2.5 kg of skinned hazelnuts one liter of hazelnut oil is obtained. This manufacturing process clarifies appearance of Maillard reaction products such as furfural, 2-furanmethanol, 2,6-dimethyl-pyrazine and 5-methyl-2-furancarboxaldehyde. The best known compound is furfural obtained on the decomposition of 3-deoxyosones formed from 1-deoxyketose by conversion, enolization, water elimination and hydrolysis (Belitz, Grosch, & Schieberle, 2004). However, that heat treatment of hazelnut fruit did not induce changes in the chemical composition of unsaturated fatty acids compared to roasting or refining process which cause appearance of trans fatty acids (data not shown). According to Kirbaşlar and Erkmen (2003) roasting of hazelnuts for 20 min at 135 °C caused significantly decrease of linoleic acid content. Roasting is the main process of hazelnut manufacturing and it is usually utilized for inducing development of the colour, taste and flavour of hazelnuts. The typical volatile compound formed during roasting is hydroxymethylfurfural (Fallico, Arena, & Zappalá, 2003). Furfural, 2-furanmethanol, 2,6-dimethyl-pyrazine, 5-methyl-2-furancarboxaldehyde and 1-heptanol identified in hazelnut oil were found in samples of olive oil to which adulterant was added in 5% (v/v). Among the ketones, which were characteristic to hazelnut oil, 2-heptanone was identified in samples of olive oil with 5% (v/v) of adulteration, while 2-decanone was detected in samples to which adulterant was added in 50%. *E*-2-octenal also was identified in samples of olive oil with 5% (v/v) of hazelnut oil.

SPME-GC/MS data were subjected to PCA analysis. Fig. 1 (Graph II) shows a PCA plot of four EVOO, hazelnut oil, and EVOO 1 with different levels of adulteration. EVOO 1 with addition of 5, 10, 25 and 50% (v/v) of hazelnut oil has been marked as OH 5, OH 10, OH 25 and OH 50. The PCA provided good separation of samples with 73.93% of the variation accounted for PC1 and 20.21% accounted for PC2. SPME-GC/MS-PCA analysis clearly showed the differences between the samples. It was possible to distinguish pure samples of EVOO which formed separated cluster from samples of EVOO 1 with 5% (v/v) of

Table 2
Volatile compounds identified in hazelnut oil and olive oil with different levels of adulteration using SPME-GC/MS

Compound	RI	Peak area (TIC∗10^6)					
		Hazelnut oil	EVOO1	Percentages of hazelnut oil (% v/v)			
				5	10	25	50
1. Butanal	593	19.28[a]	–	–	16.26[b]	16.36[a]	18.15[a]
2. Acetic acid[A]	641	442.64[a]	30.61[b]	56.73[b]	92.02[b]	143.32[b]	254.97[a]
3. Ethyl acetate	648	–	12.51[a]	12.59[b]	–	–	–
4. 3-Methyl-1-butanal	654	18.33[b]	3.81[c]	3.12[c]	3.67[c]	5.48[c]	10.00[b]
5. 2-Methyl-1-butanal	662	88.46[a]	4.02[a]	4.06[b]	7.66[b]	23.31[a]	21.86[a]
6. 1-Penten-3-ol	685	–	56.26[a]	53.10[a]	53.46[b]	46.01[a]	36.19[a]
7. 2-Pentanone	703	–	13.26[a]	11.96[b]	12.50[b]	11.00[b]	7.61[b]
8. Pentanal[A]	705	37.34[a]	21.37[a]	15.21[a]	50.03[a]	41.72[a]	47.65[a]
9. 3-Methyl-1-butanol[A]	749	–	6.65[a]	5.79[a]	6.06[b]	5.53[a]	5.30[a]
10. 2-Methyl-1-butanol[A]	756	–	4.66[a]	3.95[a]	4.94[b]	6.16[a]	8.17[b]
11. *E*-2-pentenal[A]	765	–	6.24[a]	4.53[b]	5.25[b]	5.76[a]	4.99[b]
12. 2-Penten-1-ol	781	–	24.32[a]	18.91[b]	20.98[b]	18.19[a]	21.14[c]
13. 1-Octene	794	6.92[b]	4.92[b]	3.74[c]	5.30[a]	7.51[a]	6.93[a]
14. Hexanal[A]	804	122.92[b]	117.39[b]	103.97[b]	103.41[b]	98.59[b]	112.70[b]
15. 2-Octene	810	25.42[b]	12.85[c]	12.44[b]	8.22[a]	11.39[b]	16.98[a]
16. Unidentified	832	43.14[a]	–	2.97[b]	5.83[b]	11.15[a]	21.44[a]
17. Furfural	852	149.50[a]	–	6.44[b]	15.52[b]	34.05[a]	71.57[a]
18. 2-Furanmethanol	859	107.04[a]	–	–	–	–	–
19. *E*-2-hexenal[A]	861	–	742.53[a]	700.78[b]	680.90[a]	545.12[a]	410.78[a]
20. *E*-2-hexen-1-ol[A]	874	–	62.55[a]	57.37[a]	60.26[b]	48.99[a]	41.13[a]
21. 1-Hexanol[A]	878	–	58.56[a]	52.11[a]	53.95[b]	41.33[a]	31.96[a]
22. 2-Heptanone	897	6.44[b]	–	0.76[b]	1.07[a]	1.79[a]	4.04[a]
23. *p*-Xylene	899	–	13.15[a]	6.81[b]	26.07[b]	16.23[b]	18.17[b]
24. 1-Heptanal[A]	902	12.07[b]	3.19[a]	3.10[b]	3.68[b]	4.23[c]	7.15[b]
25. Unidentified	907	21.69[a]	–	–	–	–	–
26. Pyrazine-2,6-dimethyl	913	22.59[a]	–	5.57[a]	8.66[b]	8.35[a]	13.00[a]
27. Unidentified	935	23.24[d]	–	–	5.53[b]	5.62[a]	9.62[a]
28. 3-Ethyl-1,5-octadiene	947	–	22.65[a]	20.01[a]	20.70[b]	16.26[a]	11.54[c]
29. 3-Ethyl-1,5-octadiene isomer	949	–	27.65[a]	24.44[a]	25.62[b]	19.82[a]	14.75[a]
30. *E*-2-heptenal[A]	964	10.85[b]	4.09[a]	4.52[b]	5.10[b]	5.42[a]	7.27[a]
31. Unidentified	970		8.16[a]	–	–	–	–
32. 2-Furancarboxaldehyde-5-methyl	975	25.33[a]	–	8.23[a]	10.84[a]	10.97[a]	15.40[a]
33. 1-Heptanol	981	2.14[b]	–	0.9[b]	1.04[c]	1.23[a]	1.52[a]
34. Unidentified	991	–	2.23[a]	1.76[b]	1.76[b]	1.49[a]	1.27[b]
35. Hexanoic acid	1001	5.65[b]	–	1.39[b]	2,8[b]	3.08[b]	5.80[b]
36. Unidentified	1006	–	12.86[a]	11,76[a]	12.45[b]	11.30[a]	5.58[a]
37. Unidentifiedy	1008	–	37.32[a]	33.20[a]	32.23[b]	24.87[a]	18.05[a]
38. Octanal[A]	1010	20.62[b]	37.00[a]	33.30[a]	33.80[b]	27.47[a]	24.33[a]
39. Hexyl acetate	1014	–	16.25[a]	14.38[b]	14.52[b]	11.75[a]	10.98[b]
40. *E*-2-octenal	1071	2.76[a]	–	0.59[a]	0.88[b]	0.86[b]	1.32[c]
41. 1-Octanol	1091	4.19[b]	–	–	0.88[b]	2.26[a]	2.59[c]
42. 2-Nonanone	1095	5.08[b]	–	–	–	–	–
43. Nonanal[A]	1122	12.95[b]	20.18[b]	17.83[b]	17.47[b]	13.78[c]	13.33[b]
44. *E*-2-nonenal	1174	0.72[d]	–	–	0.43[a]	0.35[b]	0.38[d]
45. Octanoic acid	1184	1.41[e]	–	–	–	–	–
46. 2-Decanone	1193	1.00[b]	–	–	–	–	0.49[c]
47. Decanal	1227	0.45[a]	11.43[a]	9.83[a]	9.07[a]	5.92[b]	4.20[c]
48. *E*-2-decenal[A]	1279	3.95[b]	0.90[c]	0.96[b]	2.16[e]	0.79[b]	1.41[b]
49. *E*,*E*-2,4-decadienal	1315	0.80[c]	–	–	–	–	–
50. *E*-2-undecenal	1375	0.54[c]	–	–	–	–	–

RI, Kováts retention index.
SPME extraction at 50 °C for 15 min.
[A] Identity of compounds by comparison of their mass spectra with standards, rest of compounds identified tentatively using NBS 75 K mass spectra library search.
[a] (RSD) < 5%.
[b] 5 < (RSD) < 15%.
[c] 15 < (RSD) < 25%.
[d] 25 < (RSD) < 50%.
[e] (RSD) > 50%, $n = 3$.

hazelnut oil (OH 5). Considering the map of the PCA performed on the data sets obtained from SPME-GC/MS analysis, all EVOO and OH 5 exhibited negative scores according to PC1 and PC2, whereas samples of OH 10, OH 25, OH 50 and pure hazelnut oil labeled H showed negative score values according to PC1 and positive scores according to PC2. Hazelnut oil, with the longest Euclidean distance from other samples, both EVOO and olive adulterated, showed different chromatographic profiles. Acetic acid, furfural, *E*-2-hexenal, 2-furanmethanol and 2-methyl-1-butanal, were responsible for samples discrimination. For component 1 mostly contribute *E*-2-hexenal whereas for component 2 mainly acetic acid, furfural, 2-furanmethanol and 2-methyl-1-butanal.

Caja, Ruiz del Castillo, Alvarez, Herraiz, and Blanch (2000) using simultaneous distillation-solvent extraction followed by gas chromatographic-mass spectrometric analysis detected furfural, *E*-5-methyl-hept-2-en-4-one, pyrazine, phenylacetaldehyde, sabinene, octanol, decanal, 2-acetyl pyrrole and terpineol as characteristic volatile compounds of hazelnut oil. Filberton had been identified as a chiral marker for detecting adulterations of virgin olive oil with hazelnut oil (Blanch et al., 2000; Flores, Ruiz del Castillo, Blanch, & Herraiz, 2006). Blanch, Caja, Ruiz del Castillo, and Herraiz (1998) and Flores et al. (2006) stated that RPLC-GC technique was the most satisfactory for determination of filbertone.

3.3. Discrimination of hazelnut oil and EVOO adulterated with hazelnut oil using SPME-fast GC-FID and SPME-MS

To obtain data on volatiles in headspace of investigated oils simplified procedures were used to differentiate between EVOO 1 and oils to which different levels of hazelnut oil were added. In SPME-MS only one peak was formed eluting completely in less than 2 min. The MsStat software employed in SPME-MS method utilized results obtained from average spectra of headspace in a mass range from 33 to 333. In SPME-fast GC-FID narrowbore column (0.100 mm) was used and separation of volatiles was achieved within 10 min. The ChromStat software used in SPME-fast GC-FID method was based on the comparison between "skeletons of chromatograms", like the area versus time results recorded in the integration report files. Data were normalized; it means that each peak was divided by total area. The normalization option enabled to reduce deviations coming from changes in the in concentration of products.

Fig. 2 shows PCA plots of headspace phase of analyzed samples based on SPME-fast GC-FID (Graph I) and SPME-MS (Graph II). Based on elaborated methods it was possible to differentiate between samples. SPME-fast GC-FID and SPME-MS were able to discriminate between samples even with the smallest addition of hazelnut oil and can be used for detecting of such adulterant in extra virgin olive oil with addition of as little as 5% (v/v). In both methods all pure samples of EVOO formed one cluster distinct from other samples. SPME-fast GC-FID and SPME-MS gave similar, however not the same samples plot. SPME-fast GC-FID grouped samples with 5, 10 and 25% (v/v) of adulteration in one cluster distant from both pure hazelnut oil and samples of EVOO. Those samples exhibited positive scores according to PC1 and negative scores according to the PC2. Second cluster formed all samples of EVOO which had positive scores according to PC2 and negative to PC1, whereas samples of OH 50 and H, which formed 3rd distinct group, presented positive value according to PC1 and PC2. Regarding the map obtained from SPME-MS also three groups can be observed. Also all EVOO samples formed one cluster, 2nd cluster was formed by samples with 5 and 10% (v/v) of adulteration, whereas 3rd bunch was created by samples with 25, 50% (v/v) and hazelnut oil.

The significant correlation of 0.924 between a sum of peak area of SPME-MS analyses and total volatile

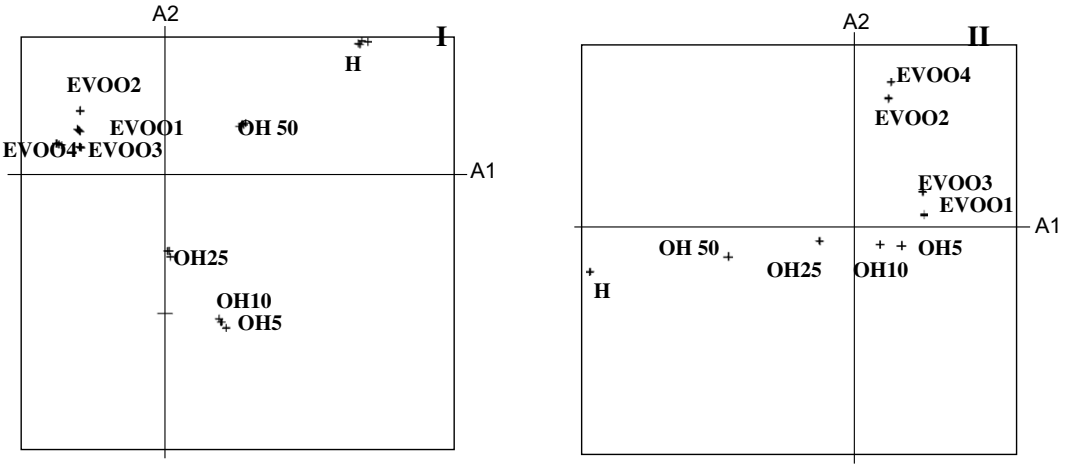

Fig. 2. PCA scores plots of hazelnut oil, EVOO 1–EVOO4 and EVOO 1 adulterated with various amount of hazelnut oil based on elaborated methods. Graph I – SPME-fast GC-FID, Graph II – SPME-MS. Sample codes: H, hazelnut oil; EVOO 1–EVOO 4, extra virgin olive oils; OH 5, OH 10, OH 25 and OH 50, EVOO 1 with addition of 5, 10, 25 and 50% (v/v) of hazelnut oil, respectively.

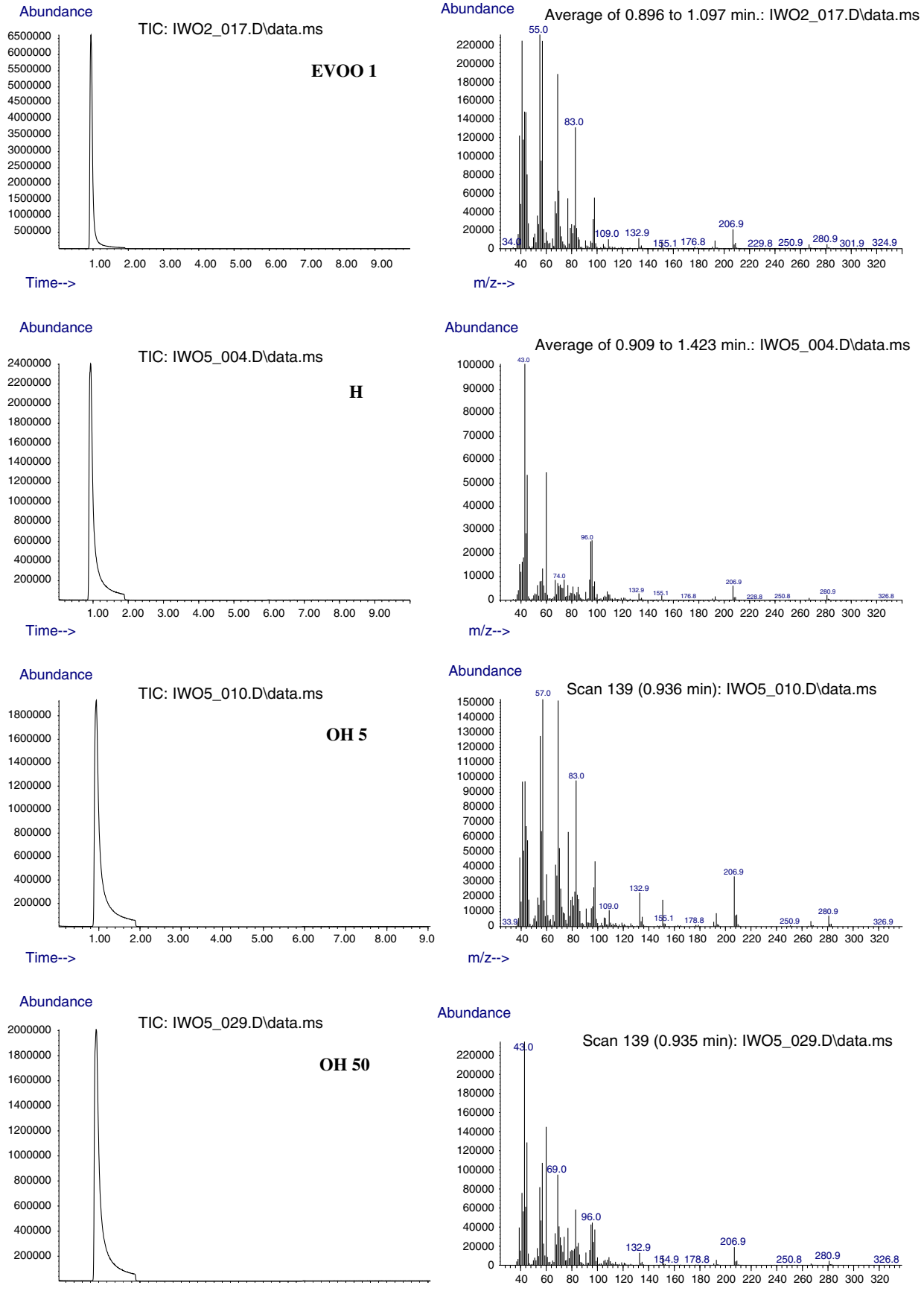

Fig. 3. Total ion chromatogram (left column) and average mass spectrum (right column) of volatile compounds isolated from EVOO 1 (Graph I), hazelnut oil (Graph II), OH 5 (Graph III) and OH 50 (Graph IV) obtained using SPME-MS technique.

compounds of SPME-fast GC-FID was found. The best repeatability ensured SPME-MS analyses (from 0.788% to 3.333%) compared to SPME-fast GC-FID which characterized higher RSD from 1.482% to 4.988%.

3.4. SPME-GC/MS data comparison with SPME-MS

The obvious advantage of SPME-GC/MS with PCA analysis for detection of volatiles is the information of compounds identity, but the main drawback is the relatively long analysis time using conventional capillary column, needed for compounds separation and tedious data preprocessing in preparation for PCA analysis. In SPME-MS only one peak was formed eluting completely in less than 2 min, due to the lack of phase in the column. Therefore, no separation of compounds is achieved and in the ionization chamber of MS an average spectrum of introduced headspace is obtained. Fig. 3 shows chromatogram and average spectrum of hazelnut oil, pure EVOO 1 and EVOO 1 with 5% and 50% (v/v) (OH 5 and OH 50, respectively) of adulteration obtained using SPME-MS technique. Several groups of ions can be observed which grouped around ion *m*/*z* 43, 55, 70, 83 for EVOO1 and *m*/*z* 43, 60, 74, 96 for hazelnut oil. Changes of specific ions intensity in the SPME-MS spectrum could be very cautiously correlated with the changes of particular components content in pure and adulterated oils detected using SPME GC/MS. For example ion of *m*/*z* 60 is characteristic for acetic, hexanoic and octanoic acids. Correlation between increases of sum of acids peak areas in SPME-GC/MS and an increase of ion *m*/*z* 60 in SPME-MS was 0.998. For furfural which was a characteristic volatile of hazelnut oil and which was responsible for discrimination of adulterated samples the dominating ion was *m*/*z* 96. Its intensity was well correlated (0.995) with the amount of furfural measured by SPME-GC/MS. We also found good correlation (0.960 and 0.983) between intensities of ion *m*/*z* 108 and 110 and increase of 2,6-dimethyl-pyrazine, and 5-methyl-2-furancarboxaldehyde, respectively. This method is promising for a routine quality control, because allows rapid sample differentiation without detailed knowledge of composition of headspace phase of analyzed samples.

3.5. Discrimination of hazelnut oil and EVOO adulterated with hazelnut oil using HS-Enose

Fig. 4 (Graph I) shows PCA plots of electronic nose data. For HS-Enose technique optimization of sensors was done. After sensor optimization, 9 sensors out of 18 were used to discriminate between samples (LY/LG, LY/G, LY/AA, P10/1, P10/2, PA2, P30/1, P40/2, and T30/1). According to the manufacturer LY/LG sensors are sensitive to fluorine, chlorine, nitrogen oxide and ozone and are used to detect oxidizing gases. Sensors LY/G are used for gas monitoring and are sensitive to ammonia, amines, carbon monoxides. Sensors LY/AA have been used for rancidity odor detect and are sensitive to alcohol. Sensors P10/1, P10/2 and P30/1 are sensitive to hydrocarbons and methane whereas sensors PA2 to amines. Sensors P40/2 are sensitive to chlorine whereas T30/1 are used for organic compounds detect (Alpha M.O.S., 2002b).

In PCA projection treatment of HS-Enose data a discrimination index of 96% was achieved for the examined samples. Sensors of HS-Enose were characterised by good repeatability generally from 0.037% to 17.721%. Likewise in SPME-fast GC-FID three clusters were observed. From the obtained result it appeared that all EVOO, which

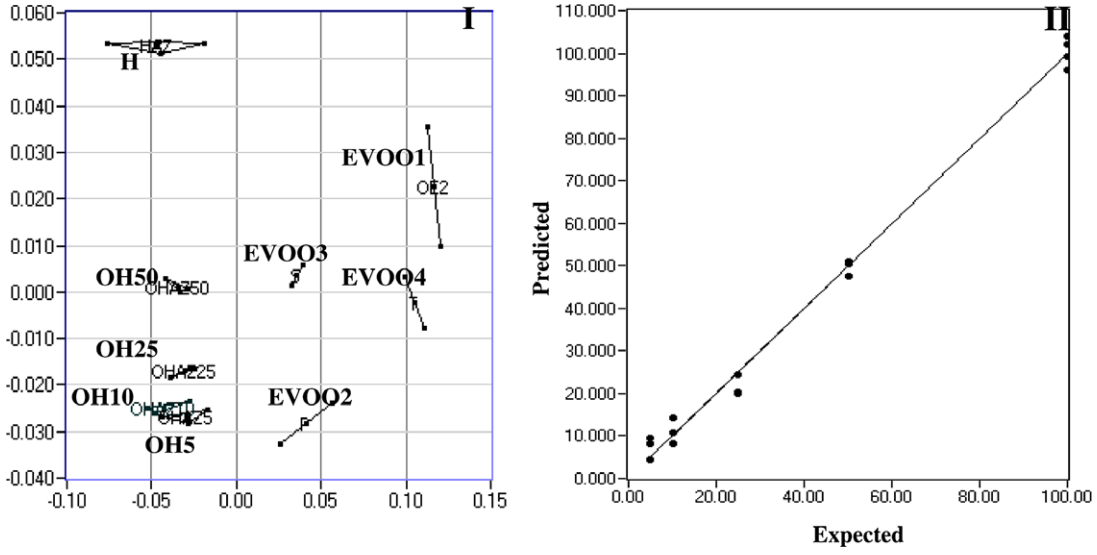

Fig. 4. PCA scores plots of hazelnut oil, EVOO 1–EVOO4 and EVOO 1 adulterated with various amount of hazelnut oil (Graph I) and PLS plot of predicted adulteration (Graph II) based on HS-E nose. Sample codes: H, hazelnut oil; EVOO 1–EVOO 4, extra virgin olive oils; OH 5, OH 10, OH 25 and OH 50, EVOO 1 with addition of 5, 10, 25 and 50% (v/v) of hazelnut oil, respectively.

formed one cluster were separated from remaining samples lengthways PC2. Next cluster was formed by samples of OH 5, OH 10 and OH 25, whereas samples OH 50 and H created 3rd group separated by PC1. The longest Euclidian distances, on average 0.142 were between groups of EVOO and H. The Euclidian distances between groups of EVOO and OH 5, OH 10 and OH 50 were very similar (0.121, 0.122 and 0.122, respectively).

Fig. 4 (Graph II) shows a plot of predicted adulteration versus actual (expected) adulteration based on electronic nose data samples of EVOO 1 adulterated with 5, 10, 25 and 50% (v/v) of hazelnut oil. PLS model predicted adulteration with well correlation coefficient of 0.997 and with an accuracy ±2.85%.

Peña et al. (2005) proposed using SH/MS technique for the detection of adulteration of refined and virgin olive oil with hazelnut oil. Proposed method allowed detection of adulteration in olive oil at the levels of 7% and 15%. Oliveros et al. (2002) used electronic nose based on 12 metal oxide semiconductor sensors to detect adulteration of virgin olive oil with sunflower oil and olive-pomace oil at five levels: 5, 10, 20, 40 and 60% (v/v). Excellent result was obtained in the differentiation of adulterated and non-adulterated samples of olive oils and it was even possible to identify the type of oil used in the adulteration. Lorenzo, Pavon, Laespada, Pinto, and Cordero (2002) proposed using SH/MS technique for the detection of adulterants in virgin olive oil. Authors mixed olive oil samples with 5%, 10%, 20%, 40% and 60% of sunflower and olive-pomace oil. Application of LDA analysis was sufficient to discriminate the adulterated from non-adulterated samples of olive oils and to discriminate the type of adulteration. Results achieved by Sayago et al. (2007) pointed out the possibilities of spectrofluorimetric method joined to multivariate analysis to detect the presence of refined hazelnut oils in refined olive oils at percentage higher than 9%. García-González, Mannina, D'Imperio, Segre, and Aparicio (2004) proposed using ^{1}H NMR and ^{13}C NMR coupled with artificial neural network to detect adulteration of olive oil with hazelnut oil. The detection limit of recommended method was around 8%.

4. Conclusion

In conclusion, three tested methods for fast analysis of volatile compounds in EVOO adulterated with hazelnut oil allowed discrimination of samples, which were characterized by different levels of adulterant. Samples of EVOO to which as little as 5% (v/v) of hazelnut oil was added were distinguishable from remaining ones using all three methods – SPME-fast GC (FID), SPME-MS and HS-E-nose. Contrary to SPME-GC/MS remaining tested methods of volatiles analysis are much faster (especially SPME-MS). Although to fully validate the usefulness of tested methods for detection of adulteration of olive oil with hazelnut oil large sets of data should be processed our experiment indicates potential of these methods for their use as a tool in olive oil quality assessment.

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