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# Mass Spectroscopic Evaluation of Virgin Olive Oils (VOOs) Fatty Acid Profile in terms of Cultivar, Geographical Origin, Extraction and Packaging Type

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ARTICLEINFO	ABSTRACT
Research Article	Ensuring the olive oil quality and authenticity has become a great importance for both traditional and emerging olive oil producing countries. The chemical composition in olive oil heavily varies depending on the olive cultivar and its growing region, the agronomic applications, the olive oil
Received : 16/01/2019 Accepted : 15/04/2019	production methods and the process and storage conditions. With the help of some analytical techniques and data evaluation methods, it is possible to grade olive oils in terms of their differences. This research examines particularly fatty acid composition of commercial olive oils (2017/2018 season) with mass detector coupled with gas chromatography (GC/MS). Results were evaluated for
<i>Keywords:</i> Grading Olive Oil Fatty Acid Profile GC/MS Mass Selective Detector	grading of them according to IOC regulations based on cultivar (ripe or unripe Ayvalik and Memecik), production (organic, stone mill, cold press, two or more centrifugation systems, filtered or unfiltered) and packing type (transparent or dark glass bottle and plastic bottle), and also their geographic origin (Ayvalik and Edremit towns, the Cunda Island, North Aegean region or South Aegean Region). According to overall data processing, virgin olive samples could be successfully distinguished in terms of theirs geographic origin and cultivar roots. Moreover, it was also explained that the effect of process and package type for grading of olive oils as 'extra virgin' or 'virgin'.

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#### Introduction

Virgin olive oils are extracted from fresh olive fruits (*Olea europaea* L.) using only mechanical and physical processes such as milling, olive paste mixing and centrifugation, and oil settling. It has high commercial interest due to its healthy and sensorial quality and highly prized for its contribution to the basic Mediterranean diet. Like elsewhere around the Mediterranean, olive oil is a very important foodstuff in Turkey and takes pride of place in Turkish cuisine. By the 2017/2018 season, 2 100 000 tonnes olive were cultivated and 1 640 000 tonnes of this were processed into the olive oil (TSI, 2019).

The International Olive Council (IOC, 2019) regulation defines three categories for olive oils based on their free acidity namely extra virgin, virgin and ordinary virgin olive oil. The acidity value of oils was influenced by several factors such as variety, method of harvesting, extraction process, packing and storage conditions (Tsimidou et al., 2005). Peroxide value,  $K_{232}$  and  $K_{270}$ specific absorbance and fatty acid composition are the other quality and purity parameters used for grading of olive oils. Overall quality of olive oil is also affected by many factors. These factors include the cultivar and extraction process (Di Giovacchino et al, 1994), the climatic conditions during the production year and the geographic production area (Vichi et al, 2003; Temime et al, 2006). Many analytical techniques can be used for measuring or detecting those parameters.

In the last decade, gas chromatography coupled to mass spectrometer (GC/MS) is increasingly used because of the power of MS in structural data studies (Ecker et al, 2012; Alves et al., 2016). Particularly, mass spectroscopy is mainly utilized for characterization (Lara-Ortega et al., 2018) of olive oil in terms of detecting adulterant (Lorenzo et al, 2002; Alves et al, 2013) or authenticates the specific compounds (Angerosa et al., 1996; Vaclavik et al., 2009), i.e. phenolic and secoiridoid aglycons, or geographic origin (Casale et al., 2012; Persuric et al., 2018).

Over the recent decades, the guarantee of olive oil quality and authenticity has become a great importance to consumers, suppliers, retailers, and regulators in both traditional and emerging olive oil producing countries, mainly due to the upgrading worldwide obtained popularity and the trade globalization of virgin olive oils (Bajoub et al., 2018). Mostly, in Turkey, olive oil is extracted via stone mill production, cold press or centrifugation systems. They can be filtered or unfiltered. Olive oils packed in transparent or dark plastic or glass bottles and different volumes of tin cans. This research examines particularly fatty acid composition of commercial high quality Ayvalik and Memecik olive oils with mass detector (MS) coupled with gas chromotography (GC). Results were evaluated for grading of them according to cultivar, production and packing type, and also their geographic origins. The commercial olive oil samples were collected at 2017-2018 harvest season and total free acidity, peroxide value and fatty acid profile with mass detection were discussed in detail.

#### **Materials and Methods**

## Materials

The commercial olive oil samples analysed in this study was collected from local boutique stores on March after 2017/2018 harvest season (October-November). As shown at Table 1, olive cultivars (Ayvalik and Memecik), olive types (organic, ripe or unripe), theirs geographic origins (Ayvalik, Cunda and Edremit towns, North and South Aegean Regions), oil processing type (cold press, filtered or unfiltered) and packing material (transparent or dark glass bottle and plastic bottle) were different, their brands were kept secret, so, they were signed as A, B, C, D and E. Three random bottles for each brand package were used and each oil sample bottle was analysed in triplicate ( $3 \times 3 \times 16$ , n:144).

### Methods

Total free acidity (FFA, as percentage of oleic acid) and peroxide value (PV, as milliequivalents of active oxygen per kilogram of oil) parameters were determined. All analyses were measured in triplicate according to standard methods declared in the European Union Commission Regulation EEC 2568 (1991) and its later amendments.

The fatty acid methyl esters (FAMEs) were prepared according to the International Olive Council's method (COI/T.20/Doc. No. 24, 2001), and were analysed by the Agilent-Technologies GC equipped with 6890 N Network GC system containing an Agilent-Technologies 5975 inert XL Mass Selective Detector (MSD) and Agilent autosampler 7683-B injector (Agilent technologies, Little Falls, NY, USA). The FAMEs were separated on Agilent-Technologies capillary column HP-5 MS (5% phenyl

Table 1 Sample descriptions

methylsiloxane) with dimension of 30 m  $\times$  0.25 mm i.d.  $\times$ 0.25 µm film thickness. A sample volume of 1.0 µL was injected into the column using the split mode (split ratio 100:1). The carrier gas used was helium at a flow rate of 1.0 mL.min<sup>-1</sup>. Initial oven temperature was 60 °C, then, 3 °C/min to 200 °C for 20 min and finally 3 °C/min to 270 °C for 30 min. The scanning mass range varied from 50 to 550 m/z. All measurements were triplicated. This method was originated from Anwar et al. (2010) with small modifications. The GC-MS apparatus was linked to a PC running software for data acquisition and processing. Under the GC-MS conditions used, FAMEs eluted in order of increasing molecular weight and, for a given molecular weight, in order of decreasing saturation. The fatty acid composition was reported below as a relative percentage. The identification of unknown fatty acid methyl esters (FAMEs) was performed by comparing their relative and absolute retention times with those of pure standards of FAMEs. FAMEs were further identified by comparing their MS spectra with those from the NIST mass spectral library of the GC/MS system. All chemicals were chromatographic grade (Sigma-Aldrich, Madrid, Spain).

Statistical analysis was performed by SPSS (version 23, IBM SPSS Statistics Inc. Chicago, IL) statistical software and using One-way ANOVA method. Differences among all groups were determined by Duncan and LSD test. All statistical analyses were performed at least duplicate.

#### **Results and Discussion**

Even though the information was written on label of package, FFA and PV were again determined due to discuss this study results exactly and correctly. Obtained analyse results were given in Table 2. It was observed that FFA and PV were changed between 0.45-0.93% and 3.98-14.20 meq active O2/kg oil, respectively. It was declared by Council of Higher Education Thesis Center (2019) from Turkey, according to newly accessed studies, Ayvalik and Memecik virgin olive oils FFA content ranged from 0.2% to 0.9% and PV ranged from 3.0 to 23.4 during 2012-2016 harvest seasons (Cevik, 2014; Ucuncuoglu, 2018). Thus, our results were parallel with those works.

SS	Brand	Label Information on Bottle	РМ	GI
1	А	Organic, Cold Press, GO: Aegean Region Originated, Cultivar: Ayvalik	Dark, Glass	No
2	B.1	GO: Ayvalik town (North Aegean Region), Cultivar: Ayvalik	Dark, Glass	No
3	C.1	Stone mill production, GO: Ayvalik town (North Aegean Region), Cultivar: Ayvalik	Dark, Glass	Yes
4	C.2	Unfiltered cold press, GO: Ayvalik town (North Aegean Region), Cultivar: Ayvalik	Dark, Glass	Yes
5	B.2	Green, unripe olive extract, GO: Edremit town (North Aegean Region), Cultivar: Ayvalik	Transparent, Glass	No
6	B.3	Ripe olive extract, GO: Edremit town (North Aegean Region), Cultivar: Ayvalik	Transparent, Glass	No
7	B.4	GO: Ayvalik town (North Aegean Region), Cultivar: Ayvalik	Dark, Glass	No
8	B.5	GO: Cunda Island from Balikesir (North Aegean Region), Cultivar: Ayvalik	Dark, Glass	No
9	B.6	GO: Edremit town (North Aegean Region), Cultivar: Ayvalik	Dark, Glass	No
10	<b>B</b> .7	GO: North Aegean Region, Cultivar: Ayvalik	Dark, Glass	No
11	B.8	GO: North Aegean Region, Cultivar: Ayvalik	Transparent, Glass	No
12	B.9	GO: South Aegean Region, Cultivar: Memecik	Transparent, Glass	No
13	C.3	No info about cultivar and region	Plastic	No
14	D	No info about cultivar and region	Plastic	No
15	E.1	Cold press, GO: South Aegean Region, Cultivar: Memecik	Transparent, Glass	No
16	E.2	Cold press, GO: North Aegean Region, Cultivar: Ayvalik	Transparent, Glass	No

SS: Sample Series, PM: Packaging Material, GI: Geographic Indication, GO: Geographic origin of virgin olive oil samples

$Table 2$ Detected quality and builty barameters of commercial only ons of $\times 0.0$	Table 2 Detected quality and purity parameters of	commercial	olive oils	(P < 0.01)
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S	FFA	PV	C16:1	C17:1	C18:1	C20:1
1	$0.9{\pm}0.0^{AB}$	$6.5 \pm 0.5^{CD}$	$0.6 \pm 0.0^{B}$	nd	75.0±0.1 <sup>C</sup>	$0.3 \pm 0.0^{A}$
2	$0.5{\pm}0.0^{I}$	$5.0\pm0.7^{\rm EF}$	$0.6 \pm 0.0^{B}$	$0.1 \pm 0.0^{BC}$	$73.6 \pm 0.2^{\text{DEF}}$	$0.2{\pm}0.0^{\mathrm{ABC}}$
3	$0.8{\pm}0.0^{\mathrm{BC}}$	$7.5 \pm 0.3^{CD}$	$0.7 \pm 0.1^{A}$	$0.1 \pm 0.0^{AB}$	$72.9 \pm 0.1^{FG}$	$0.2\pm0.0^{\mathrm{ABC}}$
4	$0.7{\pm}0.0^{\text{CD}}$	13.0±0.9 <sup>A</sup>	$0.5 \pm 0.1^{BC}$	$0.1 \pm 0.0^{AB}$	$72.7 \pm 0.2^{FG}$	$0.2{\pm}0.0^{\mathrm{ABC}}$
5	$0.6 \pm 0.0^{FG}$	$5.5 \pm 0.7^{DE}$	$0.5\pm0.0^{\mathrm{BCD}}$	$0.2{\pm}0.0^{A}$	$73.4 \pm 0.0^{\text{EFG}}$	$0.3{\pm}0.0^{AB}$
6	$0.6 \pm 0.0^{\text{EF}}$	$4.5 \pm 0.4^{\text{EF}}$	$0.5\pm0.0^{\mathrm{BCD}}$	$0.2{\pm}0.0^{A}$	$73.4\pm0.0^{\mathrm{EFG}}$	$0.3{\pm}0.0^{AB}$
7	$0.6 \pm 0.0^{FG}$	$4.0 \pm 0.7^{FG}$	$0.4{\pm}0.1^{DE}$	$0.1{\pm}0.0^{\rm D}$	72.4±1.1 <sup>G</sup>	$0.2{\pm}0.0^{\rm BC}$
8	$0.6 \pm 0.0^{FG}$	$7.5 \pm 0.4^{\circ}$	$0.5\pm0.0^{\mathrm{BCD}}$	$0.1\pm0.0^{\mathrm{ABC}}$	$74.3 \pm 1.5^{\text{CDE}}$	$0.3{\pm}0.1^{AB}$
9	$0.6 \pm 0.0^{FG}$	$4.0\pm0.3^{G}$	$0.4{\pm}0.0^{\mathrm{DE}}$	$0.1 \pm 0.0^{CD}$	$74.1 \pm 0.1^{\text{CDE}}$	$0.2{\pm}0.0^{\circ}$
10	$0.6{\pm}0.0^{ m FG}$	$4.5 \pm 0.4^{\text{EF}}$	$0.4{\pm}0.0^{\mathrm{EF}}$	nd	$74.5 \pm 0.7^{\text{CDE}}$	$0.2{\pm}0.0^{\circ}$
11	$0.5{\pm}0.0^{ m HI}$	$4.0{\pm}0.7^{\rm FG}$	$0.4{\pm}0.1^{E}$	$0.1{\pm}0.0^{\rm D}$	$76.3 \pm 0.8^{B}$	$0.1{\pm}0.0^{ m D}$
12	$0.7{\pm}0.0^{ ext{DE}}$	$7.5 \pm 0.7^{\circ}$	$0.3 \pm 0.1^{FG}$	nd	$76.8 \pm 0.4^{B}$	$0.1{\pm}0.0^{\rm D}$
13	$0.8{\pm}0.0^{\mathrm{BC}}$	$7.0{\pm}0.7^{\circ}$	$0.3{\pm}0.0^{G}$	nd	$78.1 \pm 0.4^{A}$	nd
14	$0.9{\pm}0.0^{\rm A}$	$10.0\pm0.3^{B}$	$0.3 \pm 0.0^{FG}$	nd	$78.0{\pm}0.5^{\text{A}}$	nd
15	$0.5 {\pm} 0.00^{I}$	$4.0 \pm 0.7^{FG}$	$0.3 \pm 0.0^{FG}$	nd	$78.0{\pm}0.5^{\rm A}$	nd
16	$0.7{\pm}0.0^{\mathrm{EF}}$	$7.0{\pm}0.7^{\circ}$	$0.7\pm0.3^{\text{CDE}}$	nd	$74.6 \pm 0.4^{CD}$	nd
S	C18:3 & C18:2	C16:0	C18:0	C20:0	C22:0	
1	$7.6 \pm 0.2^{E}$	12.1±0.1 <sup>G</sup>	$3.2 \pm 0.0^{A}$	$0.5{\pm}0.0^{ m A}$	$0.0{\pm}0.0^{\rm C}$	
2	$8.5{\pm}0.2^{D}$	$13.0\pm0.1^{DE}$	$2.9 \pm 0.1^{BCD}$	$0.4{\pm}0.0^{\mathrm{ABC}}$	$0.2{\pm}0.0^{ m A}$	
3	$7.4 \pm 0.2^{\text{EF}}$	$14.3 \pm 0.2^{A}$	$3.1 \pm 0.1^{AB}$	$0.4{\pm}0.0^{\mathrm{ABC}}$	$0.1{\pm}0.0^{B}$	
4	$9.1 \pm 0.0^{B}$	13.6±0.0 <sup>C</sup>	$2.8 \pm 0.1^{DE}$	$0.4{\pm}0.0^{ m BC}$	$0.1{\pm}0.0^{B}$	
5	$9.0 \pm 0.1^{BC}$	$12.5 \pm 0.0^{F}$	$3.1 \pm 0.1^{AB}$	$0.5{\pm}0.0^{ m AB}$	$0.1{\pm}0.0^{B}$	
6	$9.0\pm0.1^{BC}$	$12.5 \pm 0.0^{F}$	$3.1 \pm 0.1^{AB}$	$0.5{\pm}0.0^{ m AB}$	$0.1{\pm}0.0^{B}$	
7	$9.5 \pm 0.4^{A}$	$13.0\pm0.1^{DE}$	$3.1 \pm 0.2^{ABC}$	$0.4{\pm}0.1^{BC}$	$0.2{\pm}0.0^{A}$	
8	$8.9 \pm 0.1^{BC}$	$13.2 \pm 0.0^{D}$	$2.0 \pm 1.5^{\text{EF}}$	$0.3 \pm 0.1^{DE}$	nd	
9	$8.6 \pm 0.0^{CD}$	$13.0\pm0.0^{DE}$	$2.8 \pm 0.0^{DE}$	$0.4 \pm 0.01^{BCD}$	nd	
10	$8.4{\pm}0.4^{ m D}$	$13.1\pm0.2$ DE	$2.9 \pm 0.1^{CD}$	$0.4{\pm}0.0^{CD}$	nd	
11	$7.1 \pm 0.3^{FG}$	$12.9 \pm 0.1^{E}$	$2.6 \pm 0.1^{\text{EF}}$	$0.3 \pm 0.1^{\text{EF}}$	nd	
12	$7.4 \pm 0.2^{\text{EF}}$	12.6±0.2 <sup>F</sup>	$2.5 \pm 0.1^{FG}$	$0.2 \pm 0.0^{\text{EF}}$	nd	
13	$7.0{\pm}0.2^{G}$	$12.2 \pm 0.1^{G}$	$2.3 \pm 0.2^{G}$	$0.2{\pm}0.0^{\rm F}$	nd	
14	$7.0{\pm}0.2^{G}$	$12.1 \pm 0.1^{G}$	$2.4 \pm 0.1^{FG}$	$0.2 \pm 0.0^{\text{EF}}$	nd	
15	$7.0{\pm}0.2^{G}$	$12.1 \pm 0.1^{G}$	$2.4 \pm 0.1^{FG}$	$0.2 \pm 0.0^{\text{EF}}$	nd	
16	$8.8\pm0.2^{\mathrm{BCD}}$	14.5±0.7 <sup>B</sup>	$1.6\pm0.1^{I}$	nd	nd	

nd: not detected

Table 3 Some of quality and purity parameter of olive oils (IOC, 2019)

Parameters		Extra virgin olive oil	Virgin olive oil
Quality	FFA (% oleic acid)	$\leq 0.8$	$\leq 2.0$
criteria	PV (meq active O <sub>2</sub> /kg oil)	$\leq 20$	$\leq 20$
	Lignoceric acid (C24:0)	$\leq 0.2$	$\leq 0.2$
	Behenic acid (C22:0)	$\leq 0.2$	$\leq 0.2$
	Arachidic acid (C20:0)	$\leq 0.6$	$\leq 0.6$
	Stearic acid (C18:0)	0.5 - 5.0	0.5 - 5.0
	Heptadecanoic acid (C17:0)	$\leq 0.3$	$\leq 0.3$
	Palmitic acid (C16:0)	7.5 - 20.0	7.5 - 20.0
Durity	Myristic acid (C14:0)	$\leq 0.05$	$\leq 0.05$
runny	Eicosenoic acid (C20:1)	$\leq 0.4$	$\leq 0.4$
cinteria	Oleic acid (cis-C18:1)	55.0 - 83.0	55.0 - 83.0
	Heptadecenoic acid (C17:1)	$\leq 0.3$	$\leq 0.3$
	Palmitoleic acid (C16:1)	0.3 - 3.5	0.3 - 3.5
	Linolenic acid (C18:3)	≤ 1.5	≤ 1.5
	Linoleic acid (C18:2)	3.5-21.0	3.5-21.0
	Trans fatty acid content (%) (trans-C18:1)	$\leq 0.05$	$\leq 0.05$
	Trans fatty acid content (%) (trans-C18:2 + trans-C18:3)	$\leq 0.05$	$\leq 0.05$

According to FFA values, Sample 1 (the organic one) and Sample 14 (plastic and transparent packed) were not qualified as "extra virgin". The increments of FFA might be caused approximately five month (between October and March) shelf life. On the other hand, all samples had lower PV values than 20 meq active  $O_2/kg$  oil. Therefore, it can

be classified every sample as "virgin" according IOC (2019) described in Table 3. As also shown at Table 2, there was a good classification (P<0.01) between cold press virgin olive oils which were collected South Aegean region (Memecik cultivar, Sample 15) and North Aegean region (Ayvalik cultivar, Sample 16) both FFA and PV.

Sample 11 and 12 was packed in a transparent glass bottle, but their origin and cultivar were different. Sample 12 (Memecik cultivar) had significant difference (P<0.01) from Sample 11 (Ayvalik cultivar) and higher FFA and PV than Sample 11. Plastic bottled olive oils (Sample 13 and 14) and unfiltered olive oil (Sample 4) had much more high values in terms of both FFA and PV. B brand samples, namely 7-10, were packed dark glass bottle, were the same cultivar (Ayvalik), but their geographic origin were different. According to FFA statistics, they could not be classified (P>0.05); however, the highest PV was found at Sample 8 originated from Cunda Island. There was no significant difference (P>0.05) between Sample 5 and 6 (unripe and ripe type of olive) in terms of both FFA and PV.

Fatty acids are the main constituents of olive oil forming part of TAGs molecules. Olive oil is mostly characterized by the predominance of monounsaturated (in particular, oleic acid), the low percentage of saturated and a very low percentage of polyunsaturated fatty acids. As shown at Table 2, detected FAMEs were palmitoleic acid (C16:1), palmitic acid (C16:0), margoleic acid (C17:1), margaric acid (C17:0), linoleic acid (C18:2), linolenic acid (C18:3), oleic acid (C18:1-cis), stearic acid (C18:0), eicosenoic acid (C20:1), arachidic acid (C20:0), behenic acid (C22:0), respectively. The polyunsaturated fatty acids ( $\Sigma$ PUFA, linoleic acid and linolenic acids) were given as sum of theirs contents in Table 2. A former study (Dıraman & H1ş1l, 2003) explained that HP-5 column with GC-FID can discriminate major fatty acids but cannot give C18:2 & C18:3 fatty acids separately and *trans*-forms of fatty acids. That's why C18:2 and C18:3 fatty acids percentages were given as "total amount" in this paper. Detected fatty acid methyl esters, except for C17:0, were significantly altered (P<0.01) between samples. Among all of the samples analysed, the values of the each fatty acid content fell within the ranges established for "virgin olive oil". The virgin olive oils extracted from Ayvalik cultivar contained 13.0% C16:0; 0.5% C16:1; 2.7% C18:0; 74.5% C18:1; 8.3% ∑PUFA; 0.4% C20:0; 0.1% C20:1 and 0.1% C22:0, respectively. The virgin olive oils extracted from Memecik cultivar contained 12.4% C16:0; 0.3% C16:1; 2.5% C18:0; 77.4% C18:1; 7.2% \Second PUFA; 0.2% C20:1 and 0.2% C22:0, respectively. There were several results about fatty acid composition of Turkish monoculture olive oils but they were mostly detected by GC and flame ionization detector (FID). A recent published research explained that the fatty acid profile differences of Ayvalik virgin olive oils based on geographical origin and harvest years. It was expressed that values varied over the three harvest years due to atmospheric conditions and particularly, C18:0, C18:1 and C18:2 values were different among origins (p<0.05) (Ucuncuoglu, 2018). Another research determined the fatty acid profile of Ayvalik olive oils that C16:0, C16:1, C18:0, C18:1, C18:2 were found 14%, 0.02%, 2%, 68% and 11%, respectively (Goldeli, 2015). On the other hand, "mass detection" enabled identification of structural isomers of C16:1 and C18:1, in particular. Such information about positional isomers of fatty acid differentiation in C16 and C18 provides a better understanding of the olive oil chemical composition (Laroussi-Mezghani et al., 2016). A typical fatty acid chromatogram was given in Figure 1 obtained by HP5-MS capillary column. There could be

accessed really limited paper about fatty acid profile using Mass Selective Detector in virgin olive oils and none of them about commercial virgin olive oils. For example, fourteen fatty acid methyl esters were detected in Croatian olive oil samples by use of GC-MS. C16:0, C16:1, C17:0, C17:1, C18:0, C18:1, C18:1, C18:2, C18:3, C20:0, C20:1, C22:0, C24:0 fatty acids were confirmed in this study with -cis and -trans positional structure (Peršurić et al., 2018). Sample 12 and Sample 15 were distinguished in terms of C16:0, C18:1 and polyunsaturated fatty acid content. These samples were originated same cultivar (Memecik) and packed same type in transparent glass bottle; however, one of them was produced using cold press technique. Therefore, it would be deduced that C16:0, C18:1 and  $\sum$ PUFA content were affected by oil production method. When the geographically indicated olive oils (Sample 3 and 4) compared, it was observed that C16:0, C18:0, C16:1 and  $\Sigma$ PUFA values were significantly (*p*<0.01) different. It could be checked that their cultivar (Ayvalik), geographic origin (Ayvalik town) were same; but, their production methods were different (stone mill production and unfiltered). Sample 15 and Sample 16 were distinguished in terms of all detected FAMEs. These samples were genetically originated different olive cultivar (Memecik and Ayvalik). On the other hand, their package and production type were same (transparent glass bottle and cold press). Sample 15 contained 78% oleic acid and 7%  $\Sigma$ PUFA. Since, Sample 16 contained 74.6% oleic acid and 8.8%  $\Sigma$ PUFA. If the B brand olive oils (Sample 2, 7, 8 and 9), bottled at dark glass and extracted same cultivar (Ayvalik), were compared based on olives geographic origin, it could be detected that Sample 7 (Ayvalik town) was significantly different (P<0.01) in terms of both lower oleic acid (72.4%) and higher  $\sum PUFA$  (9.5%) content. On the other hand, Ayvalik (Sample 7) and Edremit (Sample 9) town olive oil were clearly separated in terms of C18:0, and at the same time, Ayvalik (Sample 7) and Cunda Island (Sample 8) olive oil were also separated in terms of C20:0. If the B brand virgin olive oils (Sample 11 and 12), bottled in transparent glass, were compared based on olives cultivar, it could be observed that olives oils had different class statistically (P<0.01) in terms of both C16:0 and C16:1 content. Same results were obtained Sample 15 and 16. There was no significant difference (P>0.05) between Sample 5 and 6 in terms of their fatty acid profile. Theirs cultivar, extraction and packing type was same; but, harvest time was different (unripe-green and ripe olives). The organic olive oil, namely Sample 1, was clearly separated (P<0.01) from the other samples in terms of all fatty acid contents except for C16:1. Combined analytical technique and chemometrics were preferred in previous studies to discriminate virgin olive oils quality in terms of cultivar (Aranda et al., 2004; Agozzino et al., 2010; Ruiz-Samblas et al., 2011), growing area (Dıraman et al., 2010, 2011; Riccio et al., 2011).

#### Conclusion

Presented paper showed that the fatty acid profile of virgin olive oils has different quality (organic, package types, extraction types, cultivar and geographic origin) with mass selective detection coupled gas chromatography. Statistical analysis proved that C16:0, C18:1 and  $\Sigma$ PUFA

content were appropriate for grading the variation of commercial olive oil brands. It was determined that free acidity and peroxide value were changed between 0.45-0.93% and 3.98-14.20 meq active O2/kg oil. The oils extracted from Ayvalik cultivar contained 16.2% total saturated fatty acid ( $\Sigma$ SFA), 75.3% total monounsaturated fatty acids ( $\Sigma$ MUFA) and 8.3% total polyunsaturated fatty acids ( $\Sigma$ PUFA). On the other hand, the oils extracted from Memecik cultivar contained 15.1% SFA, 77.8%  $\sum$ MUFA and 7.2% PUFA. There were no *trans*- fatty acid form was detected with HP-5 capillary column in virgin olive oils. Mediterranean and European countries, which are major suppliers of olive oils on the world market, have adopted common regulations to protect olive oil growers and consumers from food adulterations and fraud. The authenticity of virgin olive oils covers many aspects, including genetic variety, geographical origin and quality grade. In this research, analytical profiling of fatty acids using GC-MS technique was tested in grading commercial olive oil's category. Statistical analysis showed a good classification power for virgin olive oils' geographical origin and cultivar.



Figure 1 A typical chromatogram for virgin olive oil obtained by HP5-MS capillary column

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