GC-MS and 2DGC-MS/TOF volatile profile of monovarietal extra virgin olive oils

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Extravirgin olive oil (EVOO) is worldwide appreciated also for its taste and aroma that is characterized by various volatile compounds: aldehydes, alcohols, esters, hydrocarbons, ketones, furans and other unidentified volatile compounds [1,2]. Both positive attributes and sensory defects in olive oil can be associated with volatile organic compounds (VOCs).

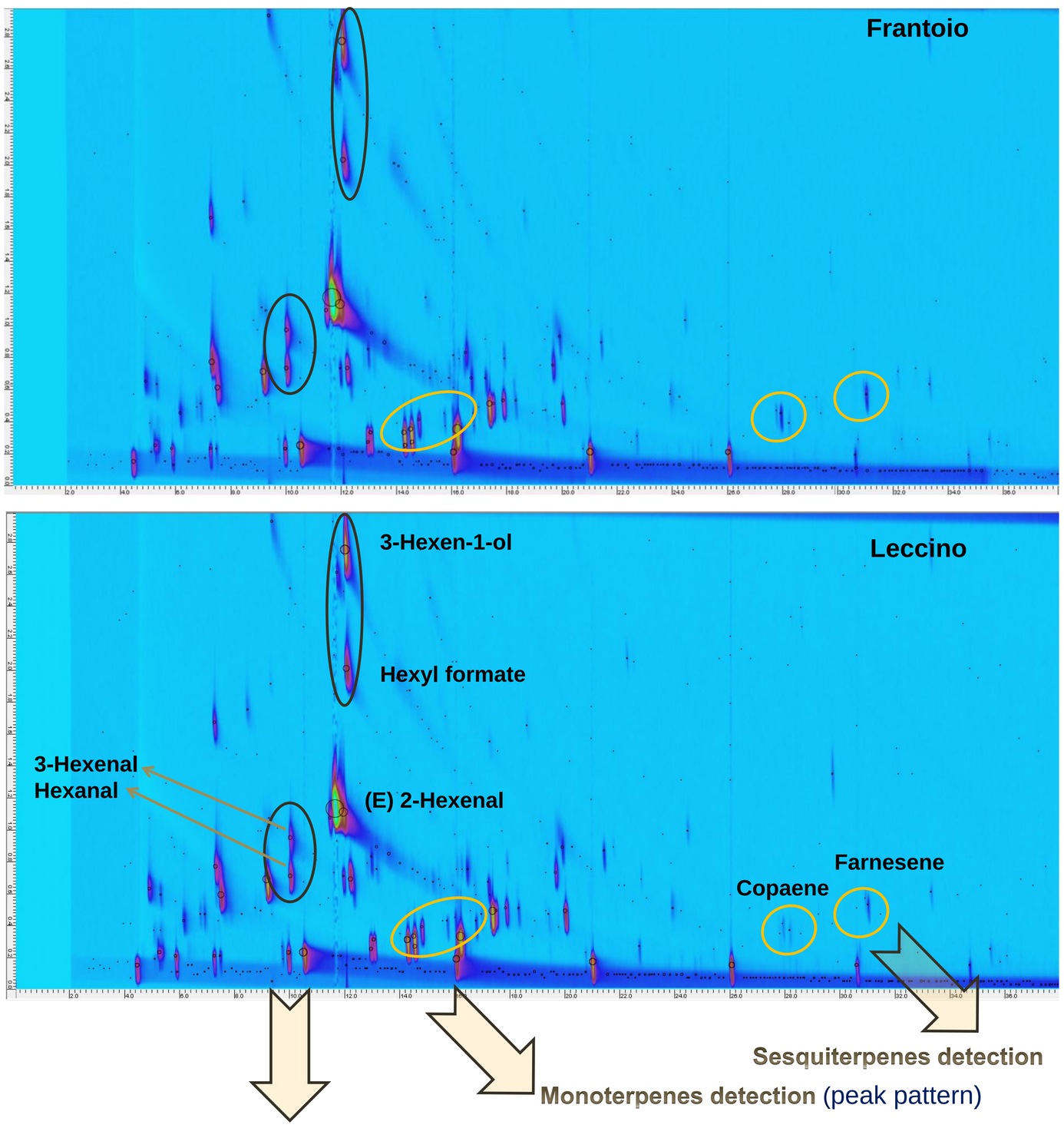
The unique and delicate EVOO flavor depends on the interaction of hundreds of compounds and the GC-MS (Gas Chromatography-Mass Spectrometry) technique applied to VOCs allows for their characterization and quantification, as relative abundance, in food samples.

SPME (solid-phase microextraction) technique is very efficient and able to evaluate most of the VOCs related to the EVOO flavor and off-flavor [3,4]. SPME seems particularly appealing since it also eliminates problems associated with chemically and thermally unstable samples where generation of artifacts can be problematic as in the case of oil. **We selected the DVB/CAR/PDMS fiber since it proved to be the most universal assembly for sufficient isolation of compounds with different physico-chemical properties** [5].

Two monovarietal EVOOs (Frantoio and Leccino cvs.) were analyzed by GC-MS and 2DGC-MS/TOF.
Biophenols characterization was also performed by HPLC-DAD-MS technique.

An Agilent 7890a GC equipped with a 5975C MSD was used and comprehensive GC×GC analyses were carried out on an Agilent GC 7890B, with an Agilent flow modulator system, coupled to an TOF-DS Markes detector. The analytes separation was achieved with a HP-5MS UI column (0.18x0.18mm, 20 m) coupled with a InnoWAX column 0.23x0.32 mm, 5 m. A tentative compounds identification was performed by comparing Mass spectra of each peak with those reported in mass spectral databases.

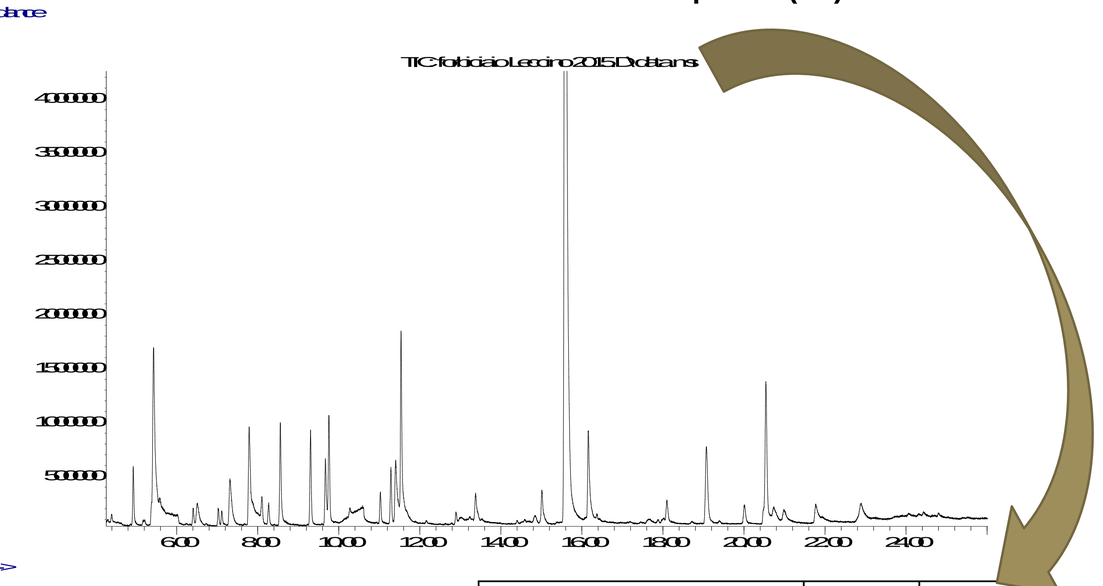
HS-SPME and GC×GC-MS fingerprint analysis are ideal tools to analyze complex volatile matrices, and provide a sensitive method for the direct comparison and chemical visualization of food volatile components. HS-SPME GC×GC-TOF-MS analysis of the complex volatile fraction of EVOO was submitted to advanced fingerprinting analysis of 2D chromatographic data.
GC×GC-MS is currently adopted as separation technique not only because of its high separation power and sensitivity but also for its ability to produce more widely distributed and rationalized peak patterns for chemically correlated group of analytes.



HS-SPME-2DGC-MS/TOF: 238 blobs were detected and, after subtracting base line blobs corresponding to fiber blending or background interferences, 113 blobs/compounds were identified.

Very similar VOCs profiles were detected for the two EVOOs with both techniques.
A larger number of compounds were detected with 2D-GC. In particular the patterns of monoterpenes and sesquiterpenes, which are important as indicator of EVOOs geographical proveniences, are markedly evidenced in GCxGC profiles.

Zoom of HS-SPME-GC-MS profile (1D)



The complete list of all the identified compounds for EVOOs is reported in **Table.** The relative proportions of the constituents (% distribution of VOCs) are reported **(1D-GC-MS).**
*Total area: sum of TIC responses of identified VOCs

(HPLC DATA) mg/L	frantoio	leccino
OH-Tyrosol	11.2	6.1
Tyrosol	13.3	4.7
Elenolic Acid	54.2	16.1
EA derivatives	10.2	8.7
deacetoxy oleuropein aglycone	41.1	165.3
Secoiridoid derivatives	48.5	37.1
Lignan derivatives	84.0	45.4
Oleuropein aglycone	47.3	21.5
oleocanthal	36.6	55.6
Total Polyphenols	346.3	360.5

compound	frobiciaio frantoio % of total Area	forbiciaio leccino % of total Area
Octane	0,71	1,24
Acetone	0,00	0,00
Ethyl Acetate	0,48	0,44
Butanal, 2-methyl-	0,28	0,45
Butanal, 3-methyl-	0,20	0,32
Ethanol	1,30	2,32
3-Pentanone	1,49	2,79
Pentanal	0,00	0,00
3-Ethyl-1,5-octadiene	1,97	2,27
1-Penten-3-one	2,21	1,79
Hexanal	0,00	0,00
1-Penten-3-ol	0,70	0,97
1-Butanol, 3-methyl-	1,33	0,47
2-Hexenal, (E)-	76,81	69,37
.beta.-Ocimene	0,09	0,11
Acetic acid, hexyl ester	0,05	0,00
2-Penten-1-ol, (E)-	0,11	0,13
2-Penten-1-ol, (Z)-	0,64	0,58
3-Hexen-1-ol, acetate	0,15	0,00
1-Hexanol	1,87	3,12
3-Hexen-1-ol, (Z)-	0,68	0,77
2-Hexen-1-ol, (E)-	3,12	5,32
2,4-Hexadienal, (E,Z)-	0,47	1,33
2,4-Hexadienal (E,E)-	0,76	1,20
Acetic acid	1,47	1,63
2,4-Heptadienal, (E,E)-	0,00	0,00
3-Ethyl-1,5-octadiene (isomer)	2,40	2,55
2-Pentenal, (E)-	0,32	0,31
2-Heptanone	0,06	0,07
Heptanal	0,01	0,03
2-octanone	0,04	0,06
octanal	0,06	0,21
2-hexenyl-acetate	0,12	0,03
E-3-Hexenol	0,09	0,11
Benzaldehyde	0,01	0,02

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