Multi-Cumulative Trapping HS-SPME to enhance the volatile profile of extra-virgin olive oil

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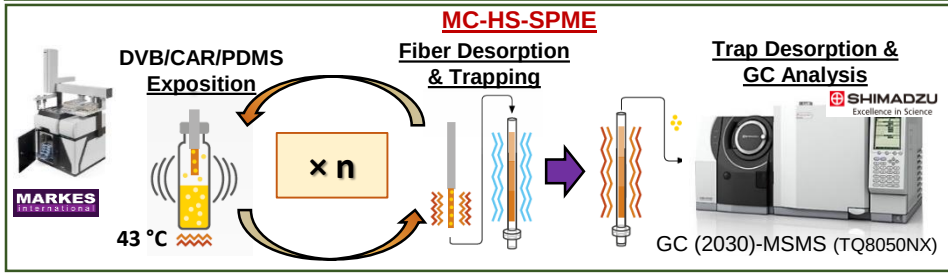
Introduction

This work explores the capability of multiple-cumulative trapping (MC) SPME on the characterization of the aroma profiling of olive oils, exploiting the automation capability of a novel headspace autosampler. The theory that underlays this extraction technique is based on the equilibrium among a three-phase system, i.e., sample-headspace-fiber. A compromise between sensitivity and extraction time is usually needed to optimize the sample throughput, mainly when a large number of samples are analyzed, as usually the case in cross-samples studies. Moreover, contrary to what is usually applied, the selection of the sample volume which does not saturate the headspace (i.e. even 10 times lower than the commonly used quantity), is of high relevance in order to maximize the information extractable. In this work, the fingerprinting of olive oil is explored to discriminate among extra virgin, virgin, and lampante oil, a challenging task of interest for quality and authenticity assessment. The different conditions were compared, considering the general information as pattern analysis, rather than intensity-wise.

Material and Methods



GC-qMS

GC: Column : SLB – 5ms 30 m x 0.25 mm x 0.5 µm; Oven : 30 °C (5.5 min) to 310°C at 10 °C/min; 250 °C to 300 °C at 25 °C/min; Carrier gas: He, 35 cm/s (Constant µ)
MS: Mass range: 35 – 500 m/z; MS ionization : EI 70 eV

GC×GC-qMS

^{1}D column: BPX-5MS 20 m × 0.18 mm × 0.18 µm
^{2}D column: BPX-50ms 5 m × 0.25 mm × 0.25 µm
Oven: 40°C (1 min); 4 °C/min to 280 °C (4 min)
Carier gas: He; Flow ^{1}D: 0.5 mL/min; ^{2}D 12 mL/min
Modulation period: 4.0 s; Flush time: 300 ms
2D Software: ChromSpace (SepSolve)

Table 1. *Sampling design for MC-SPME. In italic conditions applied for the cross-sample comparison.*

Sample amount (g)	Extraction time (min)	N cumulative extraction			Sample amount (g)	Extraction time (min)	N cumulative extraction		
0.1	*10*	*1*	*3*	*6*	1	10	1	3	6
	30	*1*	3	6		30	1	3	6
0.25	10	1	3	6	*1.5*	*10*	*1*	3	*6*
	30	1	3	6		30	1	3	6
0.5	10	1	3	6					
	30	1	3	6					

Results and Discussion

Sample volume study

The use of peak area intensity as indicator of the absolute concentration is widely applied in cross sample comparisons, but HS linearity condition needs to be verified. According to the theory, when the HS linearity condition is verified, multiple headspace extractions (MHE) from the same vial determine an exponential decline of the area recorded, which reflects in a log increase in MC-SPME.
Figure 1 shows the R^2 obtained with the linear and exponential models, when performing MC-SPME for 10 or 30 min with different sample volumes. The linear model fits better the cumulative curve when HS was saturated. Contrarily, the R^2 of the exponential model maximized with 0.1 g of sample.

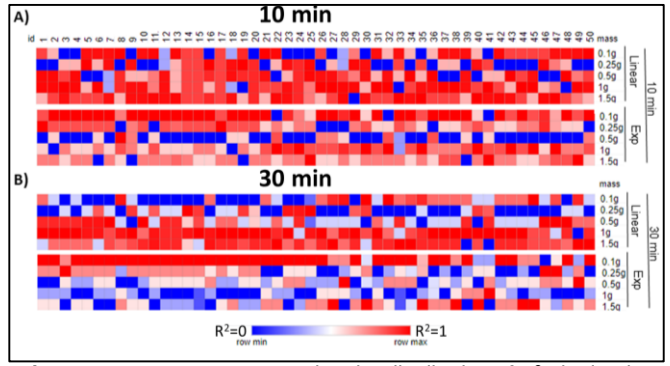


Figure 1: *Heat-maps representing the distribution of R^2 obtained applying a linear or an exponential model in the MC-SPME.*

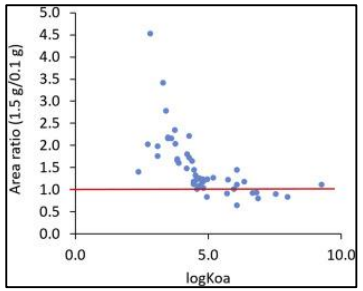


Figure 2: *Change in extraction efficiency as a function of the log K_{oa} extracting for 30 min at 43 °C.*

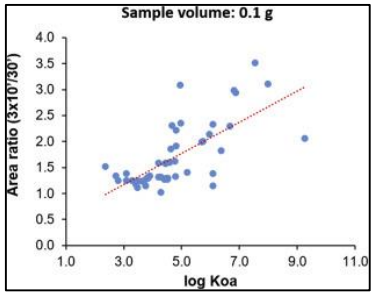


Figure 3: *Peak area ratio between performing 3 x 10-min-MC-SPME and 1 x 30-min versus log K_{oa}.*

The increase of the sample volume improved the extraction of high volatile compounds, contrarily, low volatile compounds are almost not affected (**Figure 2**). On the other hand, performing multiple-10 min extraction improved the sensitivity of the low volatile compounds compared to a single longer extraction (**Figure 3**).

Cross-sample comparison

Saturation of the HS hinders differences in the total concentration among samples, leading to a less informative fingerprint. The MC-HS-SPME approach improves the cross-sample comparison amplifying the differences and enhancing the sensitivity. 12 samples (6 EVO, 2 VO, and 4 LO) were tested under the italics conditions in **Table 1**.

The MC-HS-SPME improved the clustering using both 1.5 g or 0.1 g of samples. The clustering capability is maximized performing 3 x 10 min MC-SPME of 0.1 g, also compared to 1 x 30 min SPME, allowing a perfect discrimination between EVO, VO and LO (**Figure 4**). The use of GC×GC-MS allowed to improve the separation power facilitating the identification of the compounds of interest, saving the discrimination capability (**Figure 5**).

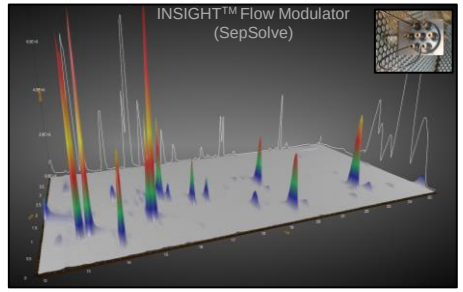


Figure 5: *expansion of EVO by GC×GC-MS.*

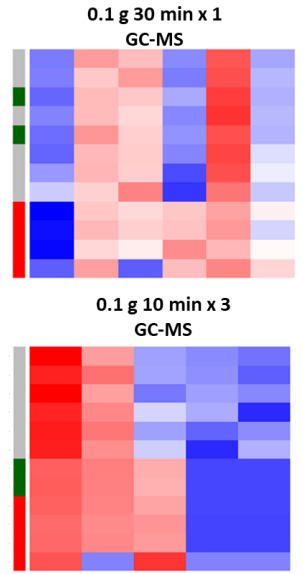


Figure 4: *Heat-maps of olive oil samples using the RF selected features for single extraction for 30 min with 0.1 g of sample; 3-cumulative 10 min-extractions with 0.1 g of sample by GC-MS and by GCxGC-MS.*

References:
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