Vacuum-assisted headspace SPME: A powerful tool for extra virgin olive oil profiling enhancement

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Introduction

Vacuum is a new experimental parameter to control and exploit during headspace microextraction (HS-SPME) method optimization and has been proved to be a powerful alternative to accelerate the extraction kinetics of analytes with a low affinity for the headspace [1]. The effect of this additional parameter was explored for the first time on a fatty matrix, namely olive oil. Extra virgin olive oil has a complex volatile aroma profile, which depends on several parameters (e.g., cultivar, geographical origin, processing practices, storage). Past and current research efforts focus on unravelling the composition of this informative volatile fraction, so as to understand correlations with quality attributes. In the present work, the effects of extraction temperature and sampling time were investigated using traditional one variable at a time approach. The results showed a great improvement in the extraction of semi-volatile compounds using Vac-HS-SPME leading to an enhancement in the information gained by the olive oil aroma fingerprint [2].

Material and Methods

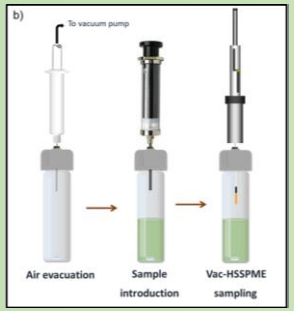

***Figure 1**: VAC-SPME procedure [1]*

Sample Preparation

1.5 g of olive oil in 20 mL vial added after removing air (1 min) by a gastight syringe
Stirred at 250 rpm; DVB/CAR/PDMS, 50/30 µm (1 cm)

Experimental Design

- **Single variable** study at 30 ° C and 43 °C at 10, 20, 30 and 40 min
- **Two variables** (k= 2) rotatable central composite experimental design (**CCD**):
  Temperature (30 – 55 °C); Extr. time (10–30 min); Central point: T= 43 °C; t= 20 min

Chromatography

GC : Column : SLB – 5ms 30 m x 0.25 mm x 0.5 µm; Oven : 35 °C (2 min) to 250 °C at 3 °C/min; 250 °C to 300 °C at 25 °C/min; Carrier gas: He, 1 mL/min (Constant flow)

MS : Mass range : 35 – 500 m/z ;
Frequency : 3.1 scans/sec ; Source T = 230 °C;
Quad T = 150 °C ; MS ionization : EI 70 eV

***Table 1**: Selected compounds for data elaboration*

#	Name	#	Name
V1	Acetic acid	V7	Octanal
V2	Penten-3-one	V8	Hex-(3Z)-enyl acetate
V3	Hexanal	V9	β-Ocimene
V4	1-Hexanol	V10	Nonanal
V5	2(E)-Heptenal	V11	Methyl salicylate
V6	Benzaldehyde	V12	α-Farnesene

Results and Discussion

Single variable study

33 compounds were selected over the entire chromatographic run to show the effect of Vac-HSSPME. For space reason only the effect on 12 compounds (**Table 1)** is shown here. It can be observed as the Vac-HS-SPME sampling increased the general profile (**Figure 2**, colour turning toward red and **Figure 3**). **Figure 4** shows the extraction kinetics of two compounds under reduced and atmospheric pressures.

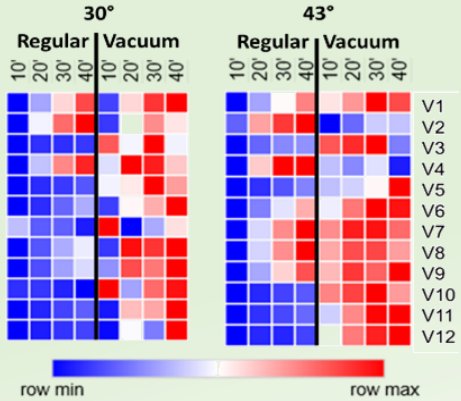

***Figure 2**: Extraction response obtained using regular and Vac-HS-SPME at 30 and 43 °C for different extraction time, namely 10, 20, 30 and 40 min.*

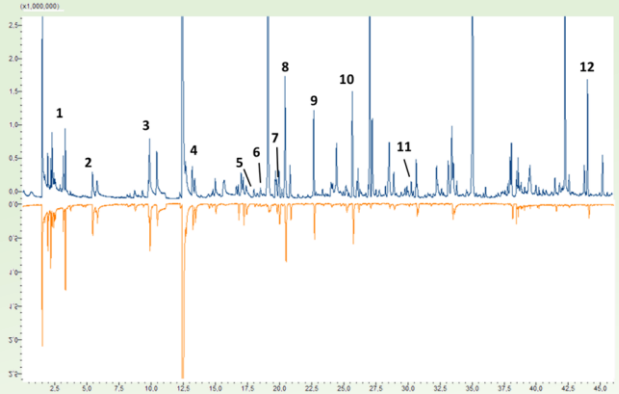

***Figure 3**: Total ion chromatogram obtained using regular (yellow, lower chromatogram) and Vac-HS-SPME (blue, upper chromatogram) at 43 °C for 10 min. Compound identification as for Table 1.*

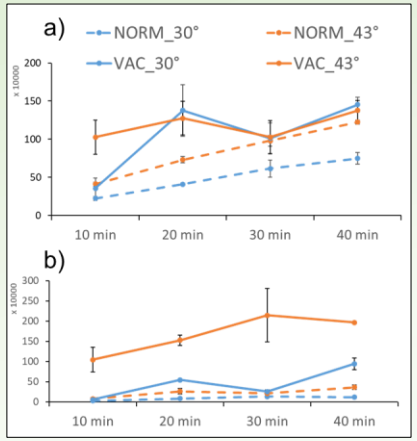

***Figure 4**: Extraction time profile, a) β-Ocimene and b) α-Farnesene*

Two variable rotable CCD

A (k= 2) rotatable central composite experimental design CCD was then applied to study the interaction between temperature and time in Regular-HS-SPME and VAC-HS-SPME.

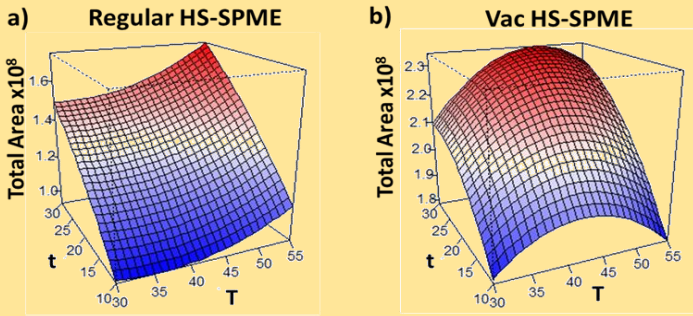

***Figure 5**: Response surface for the total chromatographic area from CCD for a) regular HS-SPME and b) Vac-HS-SPME sampling.*

Although the surface response for each compound has its own peculiarity, overall, the total peak area showed a significant improvement when vacuum is used. As expected, the maximum was reached at milder temperature and shorter time, namely ~45 °C for ~25 min (**Figure 5b**). Instead, at regular pressure, conditions are still far from a maximum even at the highest tested temperature and time (**Figure 5a**).

References:
[1] E. Psillakis, Analytica Chimica Acta, 986 (2017) 12
[2] S. Mascrez, E. Psillakis, G. Purcaro, Analytical Chimica Acta 1103 (2020) 106-114