Comparison among SPME, DHS and DHS with total vaporization sampling in wine volatile compounds profile by GC-MS

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Introduction

The use of different approaches of sample pre-treatment in flavour analysis gives nowadays a broad set of opportunity to investigate all the components in very complex matrices.
It is possible, using devices with a different extraction capability, to extract classes of compounds, starting from the most volatile ones to the "theoretical" non volatiles. The information provided can draw a new picture, containing also some redundant details, but really complete, where we can study the flavours interactions inside the matrix and evaluate the influence of non-volatile compounds to the volatility of the others.
Using weak to mild extract conditions, only the more volatile compounds will be sampled (SPME), but enforcing the extraction conditions, for example changing continuously the equilibrium from adsorbing material and head space, is it possible to remove molecules at lowest concentration. At the end, drying completely the sample, we can find into the head space non volatile compounds like sugars.
In this poster we compare the aromatic profile of a Tuscany Sangiovese wine, analyzed by SPME, with labelled internal standard and quantitative results against other extraction techniques, like Dynamic Head Space (DHS) where we purge the head space with nitrogen to renew the gaseous phase, and trapping this gas on a stationary phase, inside a tube. We can choose between different phases to be more or less selective. Another step ahead of this consists in a total vaporization experiment, using few microliters sample, dried completely and extracted in DHS. All these operations were performed automatically using an MPS2 autosampler.

Materials and methods

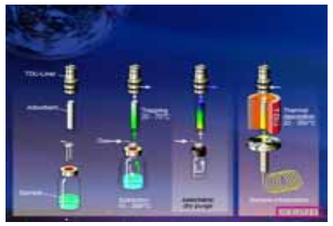
GC Agilent Technologies mod. 7890N
Inlet: CIS 4, in PTV mode, solvent vent
Column: HP-Innowax, 30 mt x 0.25 mm ID df: 0.25 µm
Oven: 40 °C for 1 min
then 2 °C/min to 60 degrees C for 0 min
then 3 °C/min to 150 degrees C for 0 min
then 10 °C/min to 200 degrees C for 0 min
then 25 °C/min to 260 degrees C for 6.6 min
Software: MSD Agilent Chemstation and Gerstel Maestro

MSD Agilent Technologies mod. 5975 C
Transfer line temp.: 280°C
Source temp.: 270°C
Acquisition mode: full scan

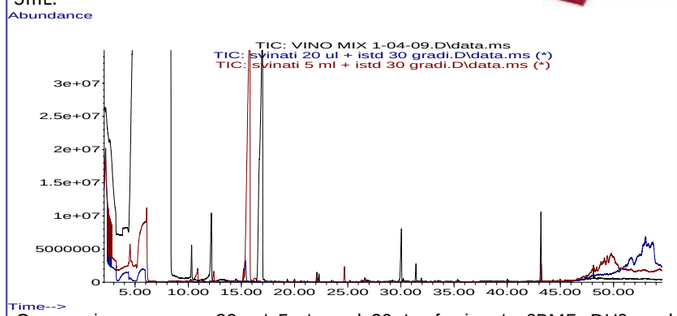
Autosampler
Gerstel MPS2 Autosampler, Liquid Injection, with Dynamic Head Space option and Thermal Desorption Unit (TDU)
Software: Gerstel Maestro

Experimental

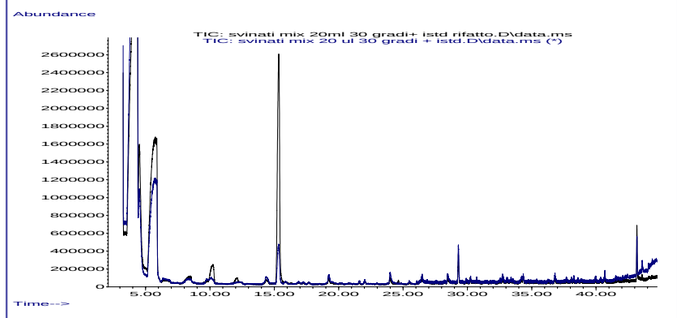
We verified the different profiles obtained on a 624 column, comparing the relative abundances and the presence/absence of particular ones, we also choose the Tenax phase inside the trapping tube, to avoid the ethanol overloading.



Nevertheless the use of Tenax, the presence of ethanol remains very strong into the chromatograms, covering with a very broad peak, a large part of the acquisition, hiding the signals, and interfering with the adsorption into the tube. The temperature to sample the volatile compounds is in our experiments 80°C, incubating into the MPS2 XL Autosampler oven, on 5mL.

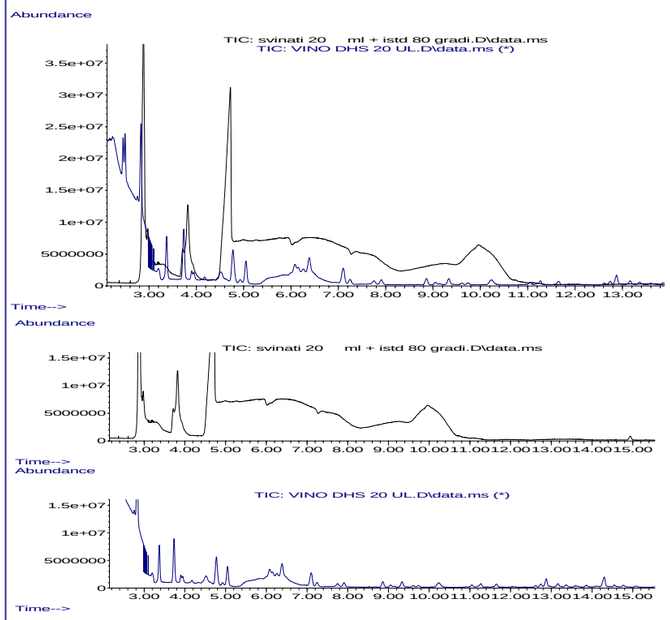


Comparison among 20 mL,5mL and 20uL of wine In SPME, DHS and DHS TV



Results and Conclusions

The dynamic head space extraction performed at 30°C give no differences comparing 20uL or 5 mL in terms of number of identified peaks. These conditions applied to a smaller amount of wine, 20uL for example, bring to the complete sample evaporation (Total Vaporization, TV), and the ethanol presence is not enough to disturb the adsorption process or the chromatographic separation.
The chromatogram overlay shows the impossibility to handle the first part of chromatograms using 5mL sample, while it is easy to analyze and to identify in the case of 20uL.



The hydrocarbons signals from C6 to C12, are highlighted and easy to identify inside the run, but the biggest improvement is the possibility to handle the first part of chromatogram, the first 15 minutes of a 60 minutes run on a 624 column, where the small molecules can be easily identified, like ethyl acetate, small chain alcohols and esters .

Conclusions: CThe use of TV lead to achieve better chromatogram in the first part of the run producing trace easiest to handle; changing purging volumes and split ratio in the GC injector, it is also possible to reveal molecules with low volatility and high polarity, such as phtalates. This versatility makes Total Vaporization a valid alternative to SPME