Validation of a method of trace analysis of Haloanisoles in wine by Solid Phase Micro Extraction (SPME)

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Introduction

Haloanisoles are well known as being the main cause for "corkiness" in wine. This paper describes: the applicability of a new simple approach in extraction of these compounds from aqueous samples, and identification of Haloanisoles like: TCA (2,4,6-Trichloroanisole), TeCA (2,3,4,6-Tétrachloroanisole), TBA (2,4,6-Tribromoanisole) and PCA (Pentachloroanisole).
Some studies have concluded that TCA is the main responsible factor for "corkiness" flavour, although other chemical compounds also contribute. Under specific conditions, TCA can be formed in cork banks used in the production of cork stoppers. The leaching of this compound from cork stoppers to the wine results in an unpleasant taste and odour. TCA in wine, results in what is commonly called "corked" wine.
About 10 years ago, C. Arthur and J. Pawliszyn developed a technique called Solid Phase Micro Extraction (SPME). The principle of extraction by SPME is based on chemical compound adsorption on a fused silica fiber coated with a polymeric phase.

Experimental Conditions

Development of the method
The analytical system consisted of a gas chromatograph and a mass selective detector (Varian Saturn 2100T GC/MS/MS).
Corks were macerated in a wine or soaked solution for 24h. Extracted samples were prepared by mixing 5mL of wine (or soaked solution), 5mL of HPLC water (pH = 3), 3 g of NaCL and 50µL of an internal standard (TCA-d5) in a 20 mL vial.
Adsorption was performed at 40°C for 30 minutes within the headspace vial. The thermal desorption was performed at a temperature of 260°C for 10 minutes.
The internal standard (TCA-d5) allowed for the chromatograms to quantify the content of each of these molecules: TCA, TeCA, TBA and PCA (cf figure 1).

Validation of the method
In order to validate this method of analysis, several parameters were tested such as: linearity, repeatability, reproducibility and accuracy. These criteria were validated according to the statistical tests of the standard AFNOR NF V03-110 and the IOV (International Organization of the vineyard and the wine).

Results and discussion

The SPME fiber was exposed to either the headspace or the liquid matrix. The analytes share between the fiber's coating and the sample. After an equilibrium was reached, the fiber was withdrawn into the needle.
In the desorption process, the needle was inserted into the injection port of the analytical instrument, the fiber was exposed, and the target analytes were desorbed to the instrument for analysis.
The internal standard (TCA-d5) allowed for the chromatograms to quantify the content of each of these molecules: TCA, TeCA, TBA and PCA. Repeatability and reproducibility parameters were validated, as well as accuracy, by comparison with inter-laboratory essays. Parameters such as specificity and LOQ will have to be further tested before having this method accredited by Cofrac.

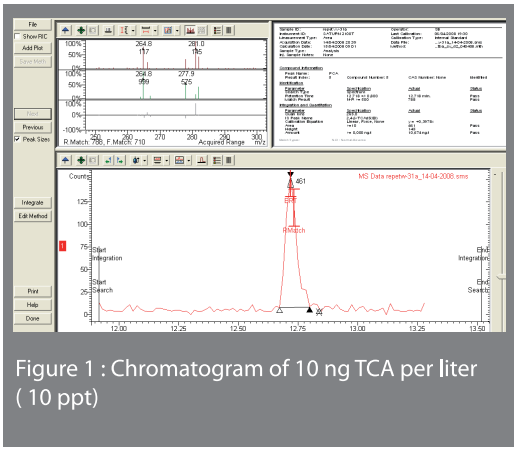

Figure 1 : Chromatogram of 10 ng TCA per liter (10 ppt)

Results and conclusion

SPME is an extremely powerful technique for the determination of Haloanisoles in wine. The combination of its ease of use, accuracy, speed, and sensitivity makes it very useful for trace analysis of aqueous samples.
No sample preparation is necessary, and the Solid Phase Micro extraction (SPME) is a solvent-free sample preparation technique.
In addition, the entire methodology is "environmentally friendly", due to the absence of organic solvents throughout the analysis.