

The development of the MVM (Multi-Volatile Method) in the whisky matrix

Mailie SAINT-HILAIRE, Kathy RIDGWAY, Anatune Ltd. Girton, Cambridgeshire (UK).

Introduction

Recently, a new method named the Multi Volatile Method (MVM) was developed by GERSTEL to analyze volatile compounds in aqueous matrix by Dynamic Headspace (DHS)-GC/MS. The method is designed to extract a wider range of compounds, in particular those with high volatility which can be hard to extract. There are two aspects of the MVM methodology. Firstly, the development of the Shincarbon X/Carbopack B+X trap to enable a better extraction for the highly volatile compounds. Secondly, the use of multi extraction and multi desorption methods. MVM uses a multi-extraction of the same sample with three traps which allow three different DHS extraction methods. Different desorption parameters can also be used for each trap. The final result of these three desorption is obtained in one chromatogram. Good results were obtained in the coffee matrix by GERSTEL¹.

Within this application note, we show how it is possible to develop the MVM in the whisky matrix by using only two traps: the Carboxen 1000/Carbopack B+X and the Tenax TA trap. The figure 1 below shows the instrument set up at Anatune.



Figure 1: DHS-GC/MS MVM with the TDU/CIS injector

One single DHS extraction consists of three or four steps (Figure 2). The first step consists in incubating the sample at a chosen temperature in order to extract the compounds of interest by creating an equilibrium between the liquid and the gas.

The second step is the trapping of the compounds. This action is enabled thanks to a double needle. After the piercing of the vial septum, a continuous flow of nitrogen enables the compounds to be extracted from the headspace to the trap. With the DHS it is possible to have as a third step, a dry step of the trap after sample trapping. The trap is dried thanks to the flow of nitrogen with the double needle in a 2 mL empty vial. After these steps, the trap is desorbed in the GC inlet thanks to a Thermal Desorption Unit (TDU)/Cooled Inlet System (CIS) injector.

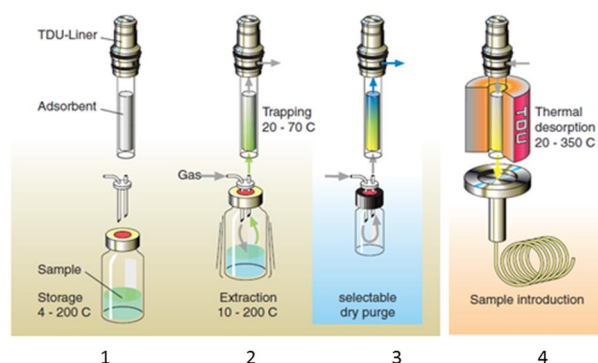


Figure 2: The steps for a single DHS method

Using MVM the extraction process is repeated and then subsequently the CIS temperature program transfers the analytes onto the analytical column. This is illustrated in Figure 3.

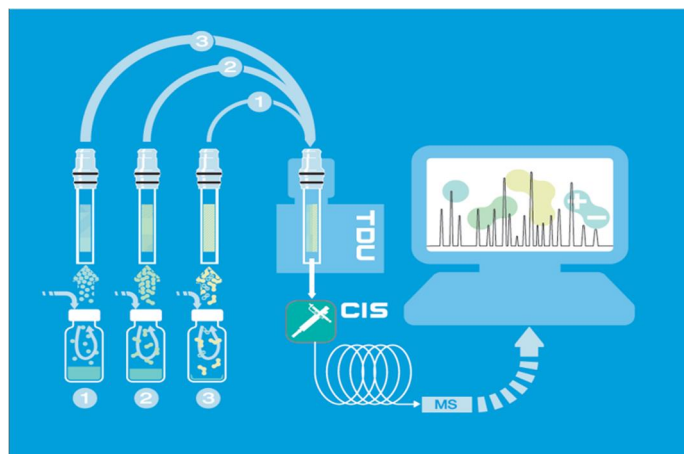


Figure 3: GERSTEL MVM Method with 3 Extractions

For the MVM developed at Anatune for whisky, only two traps were employed.

Instrumentation

Agilent GC 7890A with MS detector QQQ (used in MS one scan)
 Dual head Gerstel MPS 2 Left hand liquid syringe (not used), right hand syringe gripper.
 Agilent MSD Chemstation software (version B.07.01.1805)
 Maestro software integrated (version 1.4.30.11./3.5)

Method

Volume sample: 100 µL of whisky in a 10 mL headspace vial

DHS parameters:

For the **Carboxen 1000/ Carboxen B+X** (incubation temperature 55°C)
10 mL as trapping volume with a small drying phase

For the **Tenax TA** (incubation temperature 80°C)
750 mL as trapping volume with a large dry phase

GC-MS parameters:

TDU ramped from 30 C to 300 C (splitless desorption)

CIS ramped from -50 C to 250 C

Split ratio 33:1

Column: DB-WAX

MS: Single quadrupole-Full scan

MVM procedure:

The first DHS extraction is made with the Carboxen 1000/ Carboxen B+X adsorbent and then the second with the Tenax adsorbent. After these two extractions from the same headspace vial, the Tenax adsorbent is firstly desorbed in the TDU by keeping the CIS at 10 C. Afterwards, the Carboxen 1000/ Carboxen B+X is desorbed into the TDU by keeping the CIS at -50 C. The CIS temperature program enables focussing and transfers the analytes to the analytical column. The reverse desorption order gave better recovery of the highly volatile compounds, better separation and also better shapes peaks.

Results

In order to check the reproducibility of the method, 10 µL of a mix of two internal standards were added to the 100 µL of sample. The first internal standard was butyl acrylate and was used to check the extraction with the first trap. The second internal standard was benzyl 2,3,4,5,6 d-5 alcohol and was used to check the extraction with the second trap.

Good reproducibility was achieved (Table 1). Figure 4 shows the overlaid chromatograms of 5 replicates of whisky with the addition of the internal standards.

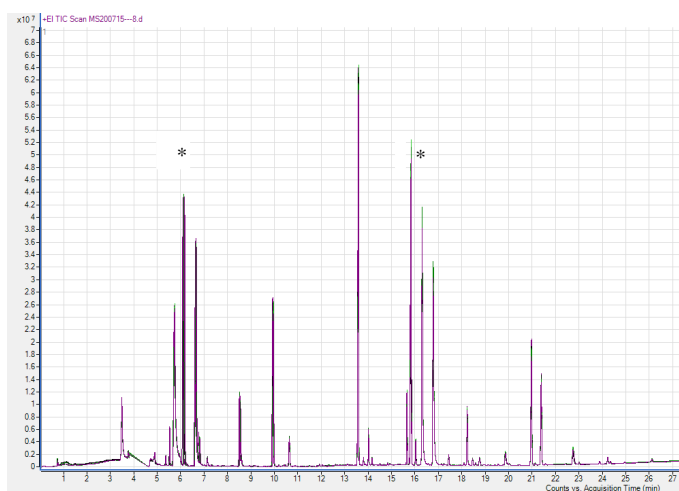


Figure 4: Reproducibility of the MVM in the whisky matrix (n=5)
*internal standards

Table 1 shows the reproducibility of the internal standards and selected compounds determined in the whisky (both high and low concentrations).

Compounds	Retention time (min)	RSD (%)
1-propanol, 2-methyl*	5.35	8.17
Butyl acrylate*	6.14	2.30
Ethyl octanoate	9.95	3.86
Ethyl decanoate	12.59	2.69
Benzyl 2,3,4,5,6 d-5 alcohol*	16.31	4.71
Ethyl oleate*	24.23	5.49

Table 1: Reproducibility for selected compounds in whisky (n=5) in 10 mL vials

*compounds in very low concentrations in the whisky

Discussion

- *Benefit of the MVM method compared to a DHS single extraction*

In order to demonstrate the benefit of MVM, two single DHS extractions were made in 10 mL vials containing 50 µL of sample. As summarized in Figure 5: the single DHS extraction with the Tenax TA trap and the MVM extraction with the two traps. The single DHS extraction for the Tenax TA trap used exactly the same parameters as the second method used for MVM.

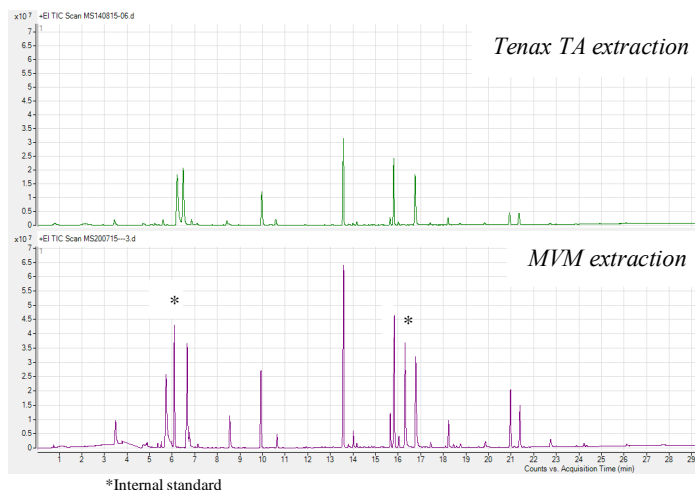


Figure 5: Comparison between a single DHS Tenax extraction and an MVM extraction

Better recoveries and extraction were achieved with the MVM extraction compare to a single DHS extraction.

- *Benefit of using the Shincarbon X/Carboxen B+X trap*

Following the optimization using the Carboxen trap, the Shincarbon X/Carboxen B+X trap (as using in the initial work by GERSTEL) was evaluated. The Shincarbon X/Carboxen B+X trap is reported to give better extraction of t higher volatiles compounds. In whisky, this included the ethane, ethoxy and the acetaldehyde which are harder to extract with other traps.

Reference:

1. J. Chrom A, Volume 1371, 5 December 2014, Pages 65-73
Nobuo Ochiai, Jun Tsunokawa, Kikuo Sasamoto, Andreas Hoffmann
Multi-volatile method for aroma analysis using sequential dynamic headspace sampling with an application to brewed coffee