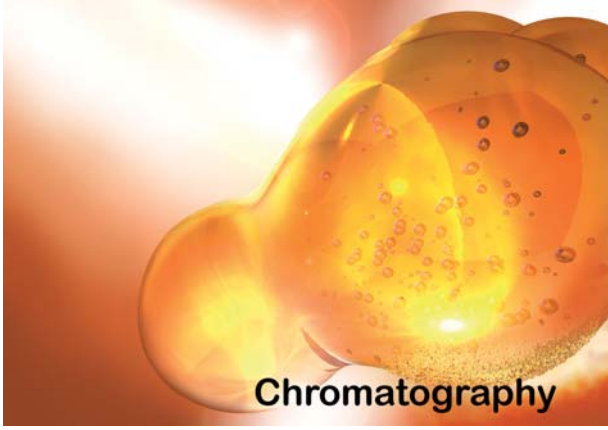
Application Note



Determination of 2,4,6 Trichloroanisole in cork and wine with HS-SPME/GCMS
- standard
- fast

Cork stoppers used for wine bottles can effect the taste of the wine. The main contaminant is the well known 2,4,6-Trichloroanisole. This is an off-flavor which is believed to be produced by methylation of phenols of the cork tree and final bleaching of the cork. Human nose and taste can trace back down to about 5-10 ng/L (5-10 ppt). For the quality control of cork stoppers therefore an enrichment technique like solid phase microextraction (SPME) is needed. Then the analysis with GC-ECD or GCMS is performed. Here the result obtained with GCMS are reported.
Before the headspace SPME is done a liquid extraction was performed with the corks. For this the cork stoppers were put into a 2 L ethanol water solution (12 %) for 24 hours at room temperature. Then an aliquot of 10 ml were put into a 20 ml headspace vial saturated with 3 g NaCl. The latter increases the effectivity of the adsorption of the TCA onto the fiber. As an internal standard a deuterized TCA is added ($^2H_5$-2,4,6-TCA). With these vials the automatized headspace-SPME experiments were performed using a polydimethylsiloxane fiber (PDMS, Supelco). The instrument used was a GCMS-QP2010 with an AOC-5000 autosampler. In figure 1 the incubator of the AOC-5000 is shown when the headspace vial is placed into it.

Fig. 1: 20 ml Headspace vial placed into incubator of the AOC-5000

For the method optimization in a first step a liquid standard was injected. In the second step the liquid extract prepared a stated above was spiked with TCA. To have maximum intensity the MS was run in selected ion monitoring (SIM).

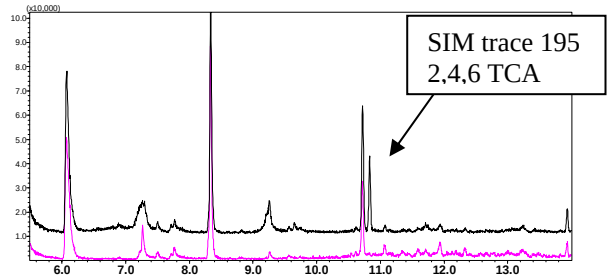


Fig. 2: Top: SIM [1)] data of mass trace 195 relative to an extract spiked with 17 ppt TCA compared with an unspiked extract.

In figure 2 the SIM data of an extract spiked with 17 ppt compared to the blank extract is shown clearly indicating the 195 amu trace relative to the 2,4,6, TCA which was used as the quantifier ion. Qualifier ions used were 210 and 212.
The SPME parameters were: Extraction temperature and time 50 °C 30 min, desorption at 220 °C for 2 min.
The analysis conditions used for the GCMS were: Injection splitless 2 min with high pressure pulse at 200 Kpa, Column: TRB 5 25 m, 0.25 mm, 0.25 µm, 50 °C 2 min, 12 °C/min 138 °C 3 min 20 °C/min 260 ° 2 min linear velocity of the carrier gas 48.2 cm/s, interface temperature: 270ºC.
As a quantifier ion for the D-TCA the mass trace of 215 was used. Figure 3 shows the zoomed mass trace of 195 and 215 relativ to a standard of 0.7 ppt. The peak of the 2,4,6 TCA is still clearly visible. The calibration curve is also shown in that figure.

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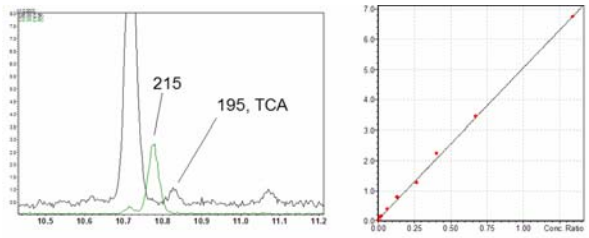

Fig. 3: Left - Mass Trace of SIM ions 195 and 215 (internal Std) of a standard sample of 0.7 ppt TCA.
Right- Calibration curve of the 2,4,6,TCA with d-TCA as an internal standard. Concentration range: 0.54 to 53.8 ppt.

The correlation coefficient of the calibration curve has a value of 0.99994 indicating the good linearity and precision of the automated SPME method over the concentration range applied. The quantitation limit of the method was determined to be about 0.7 ppt.
After recording the calibration standards the method was applied to real cork samples.

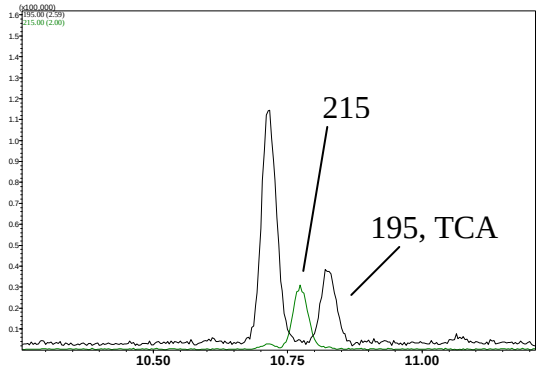

Fig 4: SIM [1)] data recorded with a real cork sample. The determined concentration of 2,4,6 TCA is 6 ppt.

In figure 4 the SIM data are shown together with the determined concentration based on the calibration curve. The amount of 2,4,6, TCA for that cork sample was determined to be 6 ppt.

Fast GC/GCMS using narrow bore columns has been applied in many different fields. Mainly liquid hot split injections were performed. In fast GCMS several condition has to be met. The details are described elsewhere [1]. The main issues are rapid transfer of sample onto the column, constant linear velocity mode of the carrier gas, high linear temperature ramps and a fast detector which is in quadrupole MS a high number of data points (scan/sim) per second in combination with a high scanning speed (50Hz, 10000 amu/s for the GCMS-QP2010, respectively). Regarding the SPME the first point means that the desorption process must be fast enough. This was confirmed by comparing the peak width of a liquid injection with the one observed with SPME. Both peak width were about 0.6 s at half height. In figure 5 the data relative to a red wine sample spiked with 5 ppt 2,4,6 TCA is shown together with the blank red wine measured this time in scan mode (20 scans/s 100-300 amu). The injection was done in the splitless mode. Average linear velocity of the carrier gas was 40 cm/s with 50 °C or 1 min and 40 °C/min to 250 °C. The column was an RTX.-5 10m, 0.1 mm, 0.1 μm.

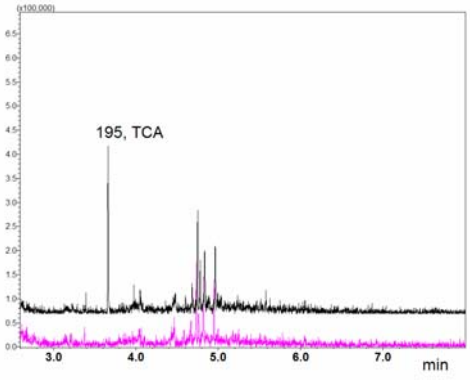

Fig 5: Trace of mass 195 of a fast GCMS full scan data recoded with a red wine spiked with 5 ppt 2,4,6 TCA. The bottom data is relative to a blank wine

A clearly visible peak of the trace 195 derived from the scan is observed indicating that the sensitivity is drastically increased in fast HS-SPME/GCMS.

Literature

[1] Shimadzu Application book Chromatography-Vol 2: fast GC&GCMS, by L. Mondello and H.-U. Baier

Acknowledgement:
[1)] Data were measured and kindly given by S. Moutinho CTCOR, Porto, Portugal