

GLOBAL ANALYTICAL SOLUTIONS



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Elucidation of the Hoppy Aroma in Beers by Stir Bar and Headspace Sorptive Extraction followed by Thermal Desorption - CGC - MS/PFPD

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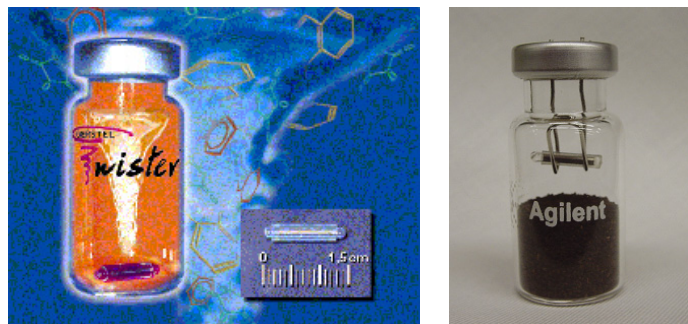
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INTRODUCTION

The elucidation of the “hoppy aroma note” in beer has always been a challenging task. The main reason without any doubt is the lack of sensitive and selective analytical methods. In the brewery industry, organoleptic panels very often identify a hoppy note in beers, but analytical evidence cannot support their observations. Two new sampling techniques, namely stir bar sorptive extraction (SBSE)[1] and headspace sorptive extraction (HSSE)[2] were evaluated for the enrichment of hop derived solutes in beers.

Both techniques offer an effective and easy-handling enrichment of important organic solutes from the aqueous or gaseous (headspace) matrix. The high amount of sorbent coated on the bars (24 μL on a 1 cm bar coated with a 0.5 μm dimethylpolysiloxane film) results in excellent sensitivities due to a more favourable phase ratio (PDMS/sample) than in solid phase micro-extraction (SPME) using 100 μm coated fibers.



SBSE (left) and HSSE (right) extraction using Twister

EXPERIMENTAL

Sample preparation. Sample extraction by SBSE is performed by placing a 10 mL beer sample in a 20 mL headspace vial, adding a stir bar (10 mm x 0.5 mm PDMS coating) and stirring at 700 rpm during 45

min. After extraction, the stir bar is rinsed with some distilled water to remove sugars from the surface, dipped on a filter paper and introduced in a glass thermal desorption tube (4 mm i.d. x 178 mm L).

For headspace sorptive extraction, a stir bar is placed above the sample in a small holder. Equilibration during 45 min is done at room temperature while the sample is stirred with a glass coated magnetic stir bar. After extraction, the stir bar is directly inserted in a thermal desorption tube.

Analysis. For thermal desorption a TDS-2 system (Gerstel GmbH) is used. The thermal desorption unit is mounted on a HP 6890 GC (Agilent Technologies, Wilmington, DE, USA) equipped with a CIS 4 PTV inlet. Following conditions were used :

Thermal desorption : 20°C - 60°C/min - 240°C (10 min); splitless mode ; 50 mL/min desorption flow.

PTV : -150°C (cryofocussing temp) - 600°C/min - 280°C (2 min) ; split mode (1/20).

Column : 30 m x 0.25 mm i.d. x 0.25 μm Stabilwax
Carrier : 1 mL/min helium

Oven Temp. : 40°C (1 min) - 5°C/min - 240°C (30 min).

Detection : 1:1 effluent splitting to HP 5973 MSD (scan) and OI PFPD detector.

SPME VERSUS HSSE

A comparison between SPME and HSSE was made by analysing a test mixture containing C6 - C 13 volatiles at 40 ppb in water (2).

Extraction was done under identical conditions using SPME with a 100 μm PDMS fiber and HSSE.

The results are shown in Figure 1 (SBSE and HSSE behave very similar, both result in increased recovery in comparison to SPME).

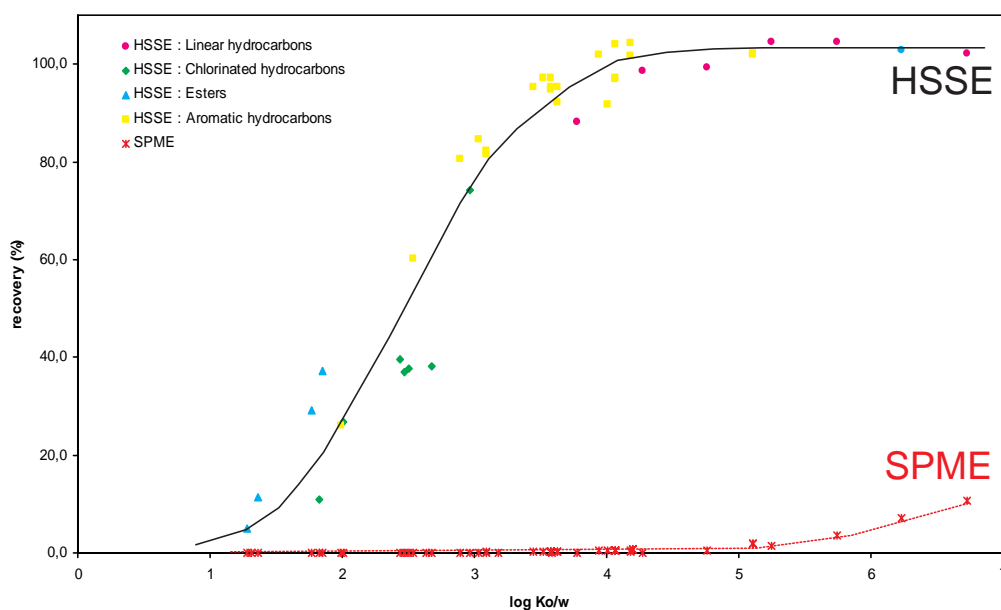


Figure 1. Analyte recoveries for HSSE and SPME versus their log $K_{o/w}$ -values for the test mixture. Recoveries are calculated with a liquid injection of the spike solution as reference.

The chromatograms obtained by parallel PFPD (S-mode) and MS detection for a beer after stir bar sorptive extraction are given below. A very complex profile is obtained. The enriched compounds range from acetaldehyde (peak 1) to palmitic acid (peak 2) and thus cover a wide volatility range. Also different sulphur compounds are detected.

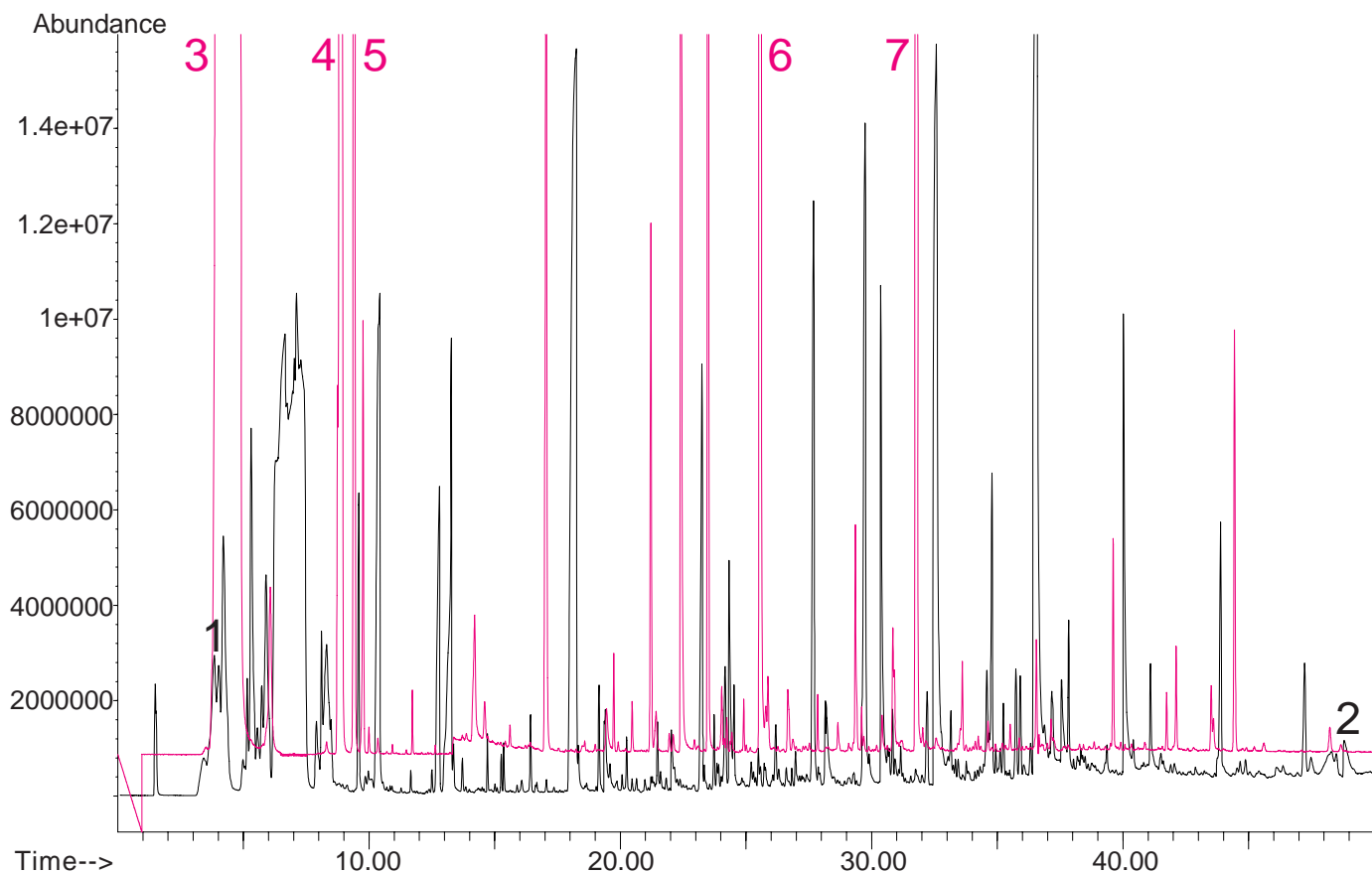


Figure 2. Analysis of a beer sample by SBSE - thermal desorption - GC-MS/PFPD. The sulphur trace is given in red (Peaks : 1.acetaldehyde, 2. palmitic acid, 3. dimethylsulphide,4. methylthioacetate, 5. dimethyldisulphide, 6. methional, 7. 2-(2-furfanyl)thiazole.).

Several hop derived solutes could be identified in different beers. In Figure 3, the extracted ion chromatogram (m/e 204) of the sesquiterpene fraction is shown.

In this fraction, important sesquiterpenes and sesquiterpenoids such as humulene (α -caryophyllene) and β -damascenone (1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one) are detected.

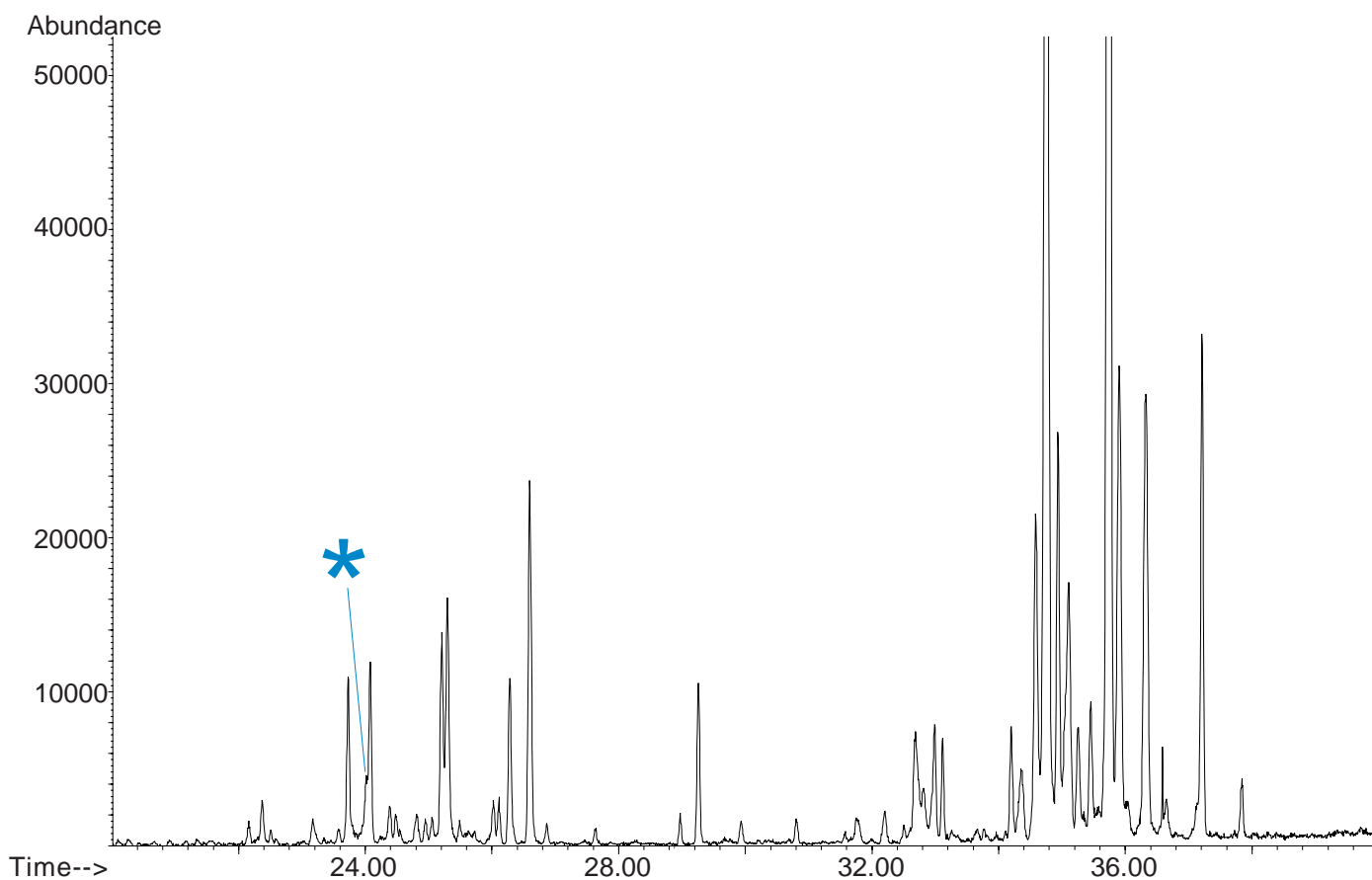
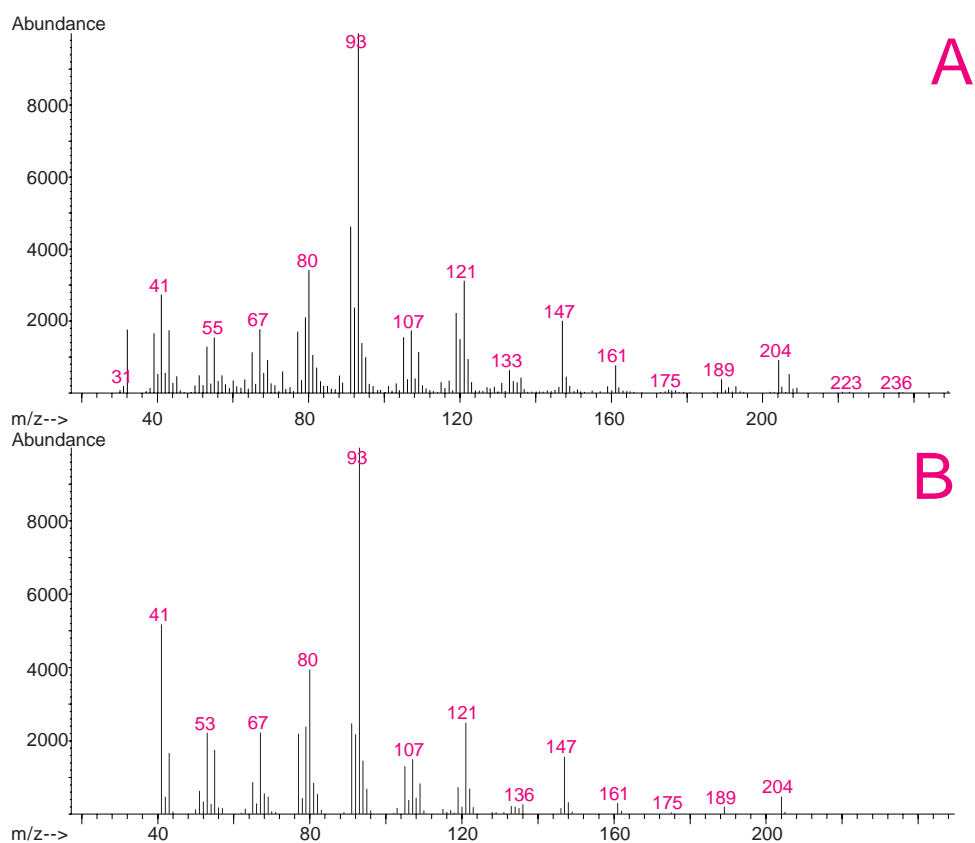


Figure 3. Analysis of beer by SBSE - thermal desorption - GC-MS/PFPD.

Extracted Ion Chromatogram (top) at m/e 204 (sesquiterpenes) and Identification of humulene (A: sample spectrum, B: library spectrum).



The power of parallel sulphur detection using a PFPD detector and MS detection is clearly demonstrated by the identification of various sulphur compounds. Figure 4 shows an overlay of PFPD chromatogram with the TIC from the MS detector. The important sulphur peak (red trace) is only a very small peak in the TIC trace, but it could be identified as dimethyldisulphide.

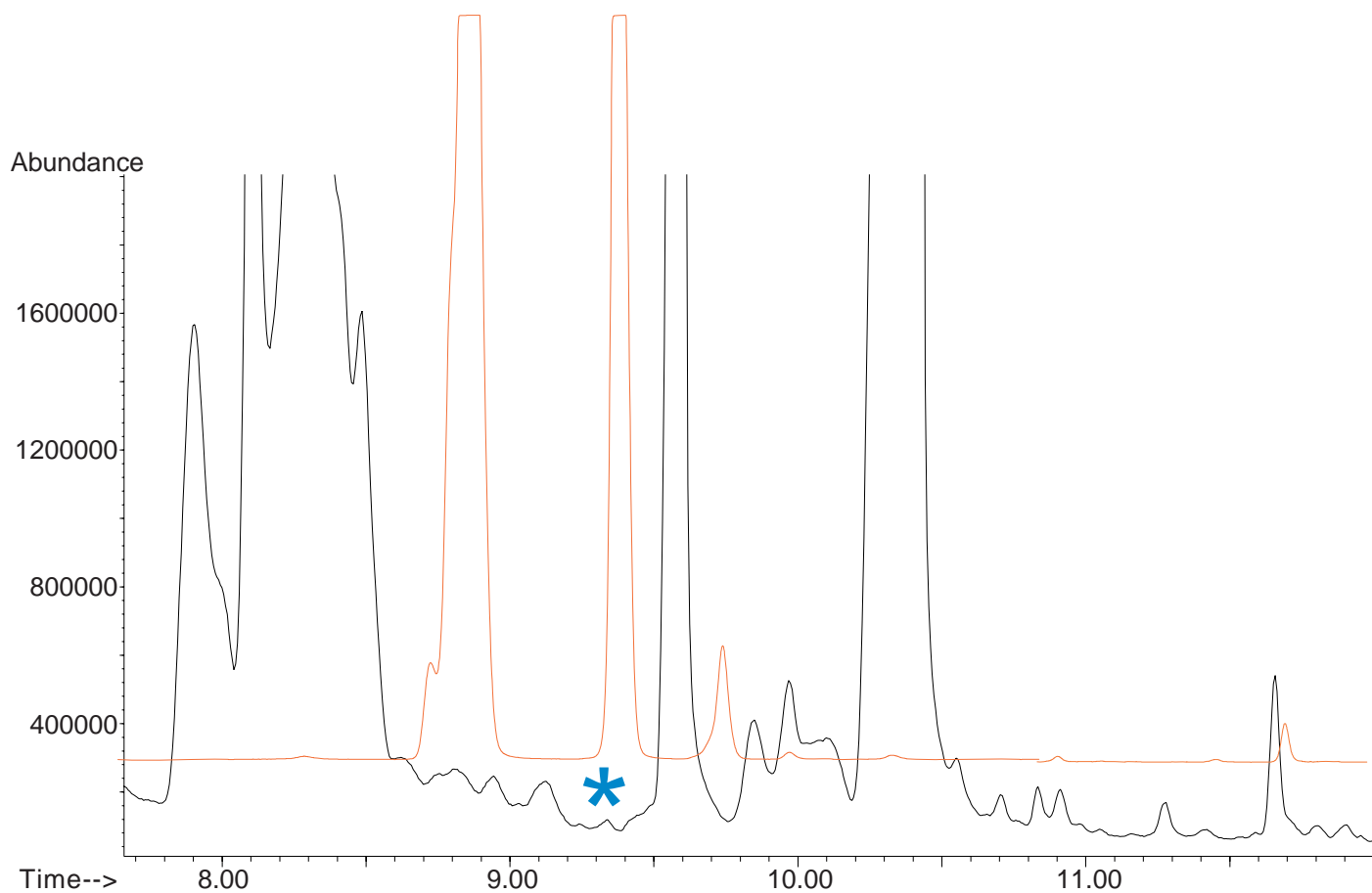
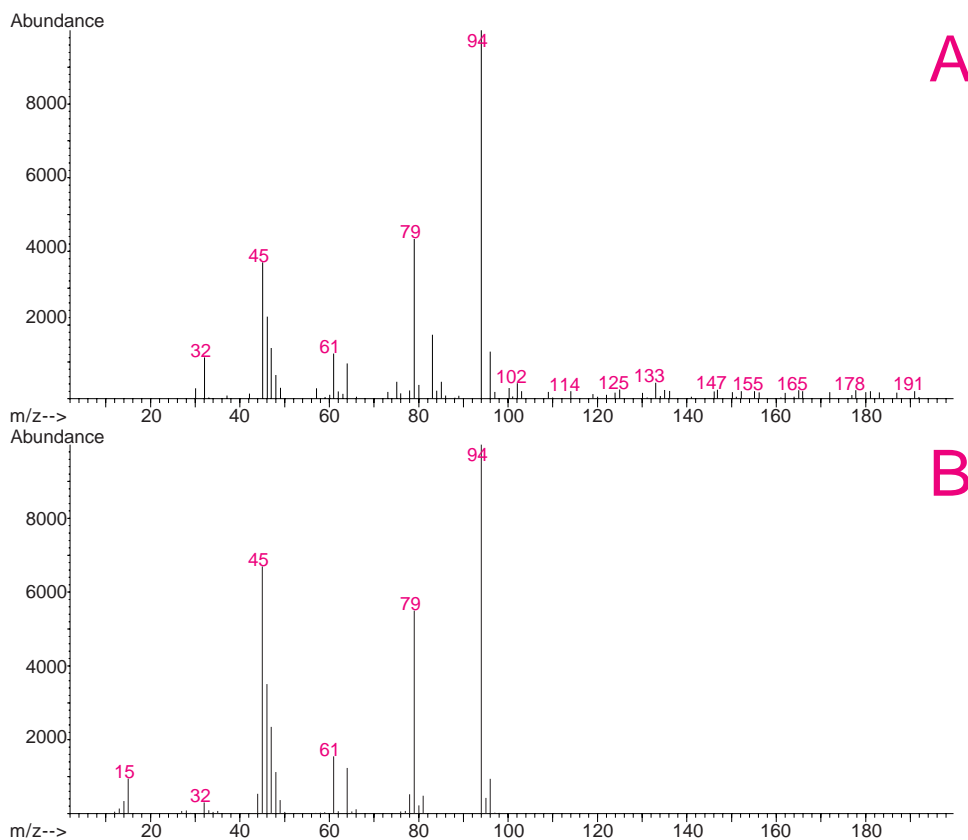


Figure 4. Overlay (top) of S-trace (PFPD) and TIC. The peak marked with an asterisk is identified as dimethyldisulphide by GC-MS (A: sample spectrum, B: library spectrum).



Moreover, by using the PFPD detector in the sulphur mode, off-flavour compounds, such as the “sunstruck” flavour that originates from the bitter acids, could be detected and quantified at ppt level. This is shown in Figure 5. A fresh beer sample was analysed directly after opening the bottle (red trace). An aliquot of the sample was then exposed to UV light and analysed under the same conditions (black trace). At 10 min, a peak appears in the PFPD sulphur chromatogram of the beer sample exposed to light. This compound was identified as 3-methyl-but-2-ene-thiol and is known to be responsible for the “sunstruck” flavor of beer.

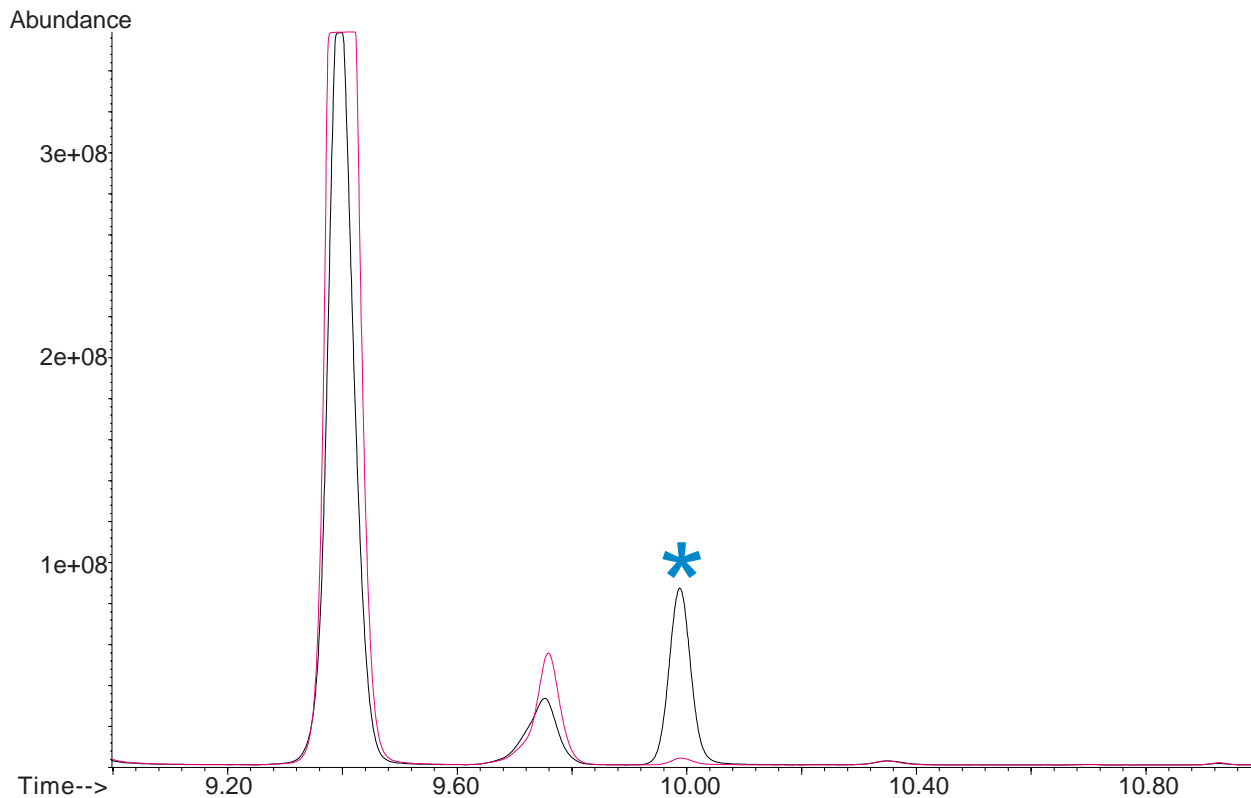
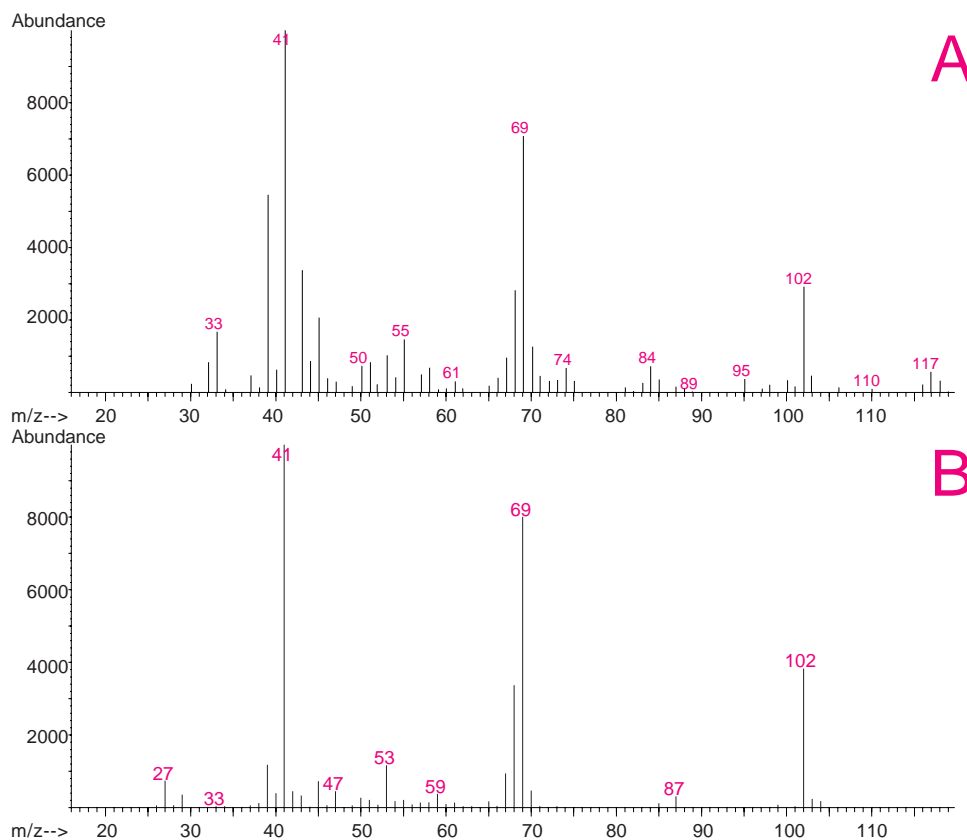


Figure 5. Analysis of fresh and irradiated beer by SBSE - thermal desorption - GC-PFPD. GC-PFPD chromatograms (top) of fresh beer (red) and irradiated beer (black), identification of “sunstruck flavor” compound (A: sample spectrum, B: library spectrum).



CONCLUSIONS

Stir bar sorptive extraction is a powerful technique for the extraction and analysis of aroma compounds in beer. The system can be used for quality control and for trace analysis of important compounds such as 3-methyl-but-2-ene-thiol (“sunstruck” flavor).

REFERENCES

- [1] Baltussen, E., Sandra, P., David, F., and Cramers, C., *J. Microcolumn Separations*, 1999, 11, 737.
- [2] Tienpont, B., David, F., Bicchi, C., and Sandra, P., *J. Microcolumn Separations*, 2000, 12, 577.



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