

## ITEX Application Note # 04

Author: Frank David and Christophe Devos, Research Institute for Chromatography, Pres. Kennedypark  
26, 8500 Kortrijk, Belgium

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### **Analysis of Volatile Organic Compounds in Beer using ITEX Headspace Sampling**

#### Abstract

Using ITEX in combination with GC-MS, different classes of volatile compounds could be measured in the headspace of beer samples using one single run. Alcohols, esters and dimethyl sulfide are monitored at ppm level using ITEX in combination with GC-MS operated in scan mode. Trace levels of diketones, such as diacetyl, are monitored simultaneously at ppb level using MS in SIM mode.

#### Introduction

In quality control of beer samples, several volatile organic compounds are monitored. These compounds include C3-C5 alcohols, C2-C5 esters, dimethyl sulfide and 1,2-diketones (diacetyl). These compounds are present at different concentration levels ranging from tens of ppm (alcohols) to ppb level (diacetyl, 2,3-pentanedione).

Beer samples are normally analyzed by static headspace in combination with GC. In order to cover all solutes and concentration levels, often several runs are needed per sample. Alternatively, the analysis is performed using effluent splitting to three detectors: FID for alcohols and esters, selective sulfur detection (FPD, PFPD) for dimethyl sulfide and ECD for diketones. The three detectors allow sufficient sensitivity and selectivity, but this set-up is rather complicated and problems with splitters and robustness are often encountered. Using mass spectroscopic detection, all solutes can be detected, either using scan or SIM mode. Recently, simultaneous scan and SIM acquisition have been made possible on benchtop GC-MS systems. However, for some solutes, the sensitivity of mass spectroscopic detection is at the limit, especially in combination with static headspace. Dynamic headspace and even purge and trap sampling have been used to obtain higher sensitivities. Also solid phase micro-extraction can be used, but in general SPME fibers will show different affinities for the solutes and calibration is more difficult.

Enrichment of VOCs from the headspace of the beer can be done fully automated using the in-tube extraction (ITEX) option on the CTC Combipal sampler. Enrichment is done in a Tenax packed modified syringe. After enrichment, thermal desorption is performed by flash heating the syringe needle and injection in a hot GC inlet, followed by GC-MS analysis in simultaneous scan/SIM mode.

#### Sample Preparation

Typically 10 mL beer sample is placed in a 20 mL headspace vial and the samples are analyzed as such. For the example below, a Belgian pils beer was selected. A comparison was made between classical static headspace and ITEX sampling.

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### SHS conditions

Sample Conditioning @ 80°C, 15 min  
HS needle: 2.5 mL, 90°C  
Injection: 1 mL; 500 µL/s

### ITEX conditions

Sample Conditioning @ 80°C, 15 min  
Extraction Strokes: 10 x 1 mL; 50 µL/s  
Desorption @ 250°C with 1 mL headspace; 50 µL/s  
Trap Material Tenax TA 80/100mesh

### GC conditions

The analysis was performed on an Agilent 6890 GC – 5975 MSD combination.

Column: 20 m x 0.18 mm i.d. x 1 µm df DB-VRX (Agilent)  
Carrier gas: helium, 200 kPa constant pressure at inlet (column outlet pressure: 28 kPa using AUX EPC and QuickSwap connector)  
Inlet: split, 1/25 split ratio  
Oven temperature program: 40°C, 5 min, 10°C/min to 250°C, 10 min.  
MSD transfer line: 250°C (17 cm x 110 µm i.d. restrictor, 28 kPa)  
Detection: MS in scan/SIM mode  
Scan: 29-400 amu  
SIM: ions monitored: 43, 57, 86, 100 (50 ms dwell times)

### Results

In Figure 1, the total ion chromatograms obtained for a beer sample using classical static headspace sampling (upper trace) and ITEX sampling (lower trace) are compared. Both chromatograms represent the datafiles obtained in scan acquisition mode.

Ethanol, the most abundant peak, elutes at 6 min. The peak at 4 min corresponds to the air peak (MS scan from m/e 29).

It is clear that more peaks are detected using the ITEX sampling. Following peaks could be identified using the mass spectra: 1. 1-propanol; 2. ethyl acetate; 3. 2-methyl-1-propanol; 4. ethyl propanoate; 5. 3-methyl-1-butanol; 6. 2-methyl-1-butanol; 7. 2-methyl propyl acetate; 8. ethyl butyrate; 9. 3-methyl butyl acetate; 10. 2-methyl butyl acetate.

Also dimethyl sulphide (DMS) could be detected at 7.7 min. Using an extracted ion chromatogram, the peak can be quantified without problem in the beer sample. The signal-to-noise, measured on ion m/e 62 was 70. The concentration of DMS in this sample was in the order of 10 ppb.

In the chromatogram obtained by static headspace, dimethyl sulfide was difficult to detect. Only in an extracted ion trace, a small peak with signal to noise of 5 could be detected, but no library search confirmation was obtained. The sensitivity was thus increased by a factor of more than 10 for this compound using ITEX sampling.

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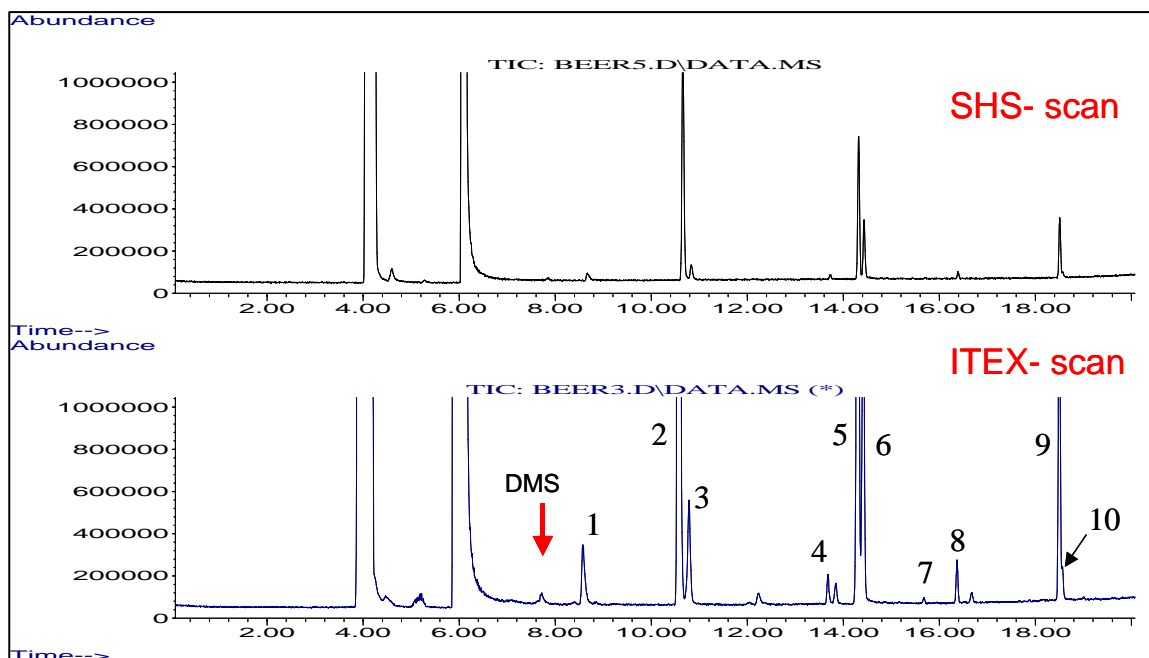


Figure 1

The extracted ion chromatograms for ion  $m/e$  86 obtained by GC-MS in SIM mode are compared in Figure 2. Diacetyl elutes at 13.1 min. The peak can be detected in the chromatogram obtained by static headspace only as a trace ( $S/N = 8$ ). Using ITEX, the peak can be detected more easily and confirmation of the identity through the relative ratios of target and qualifier ions is possible. The  $S/N$  value obtained by ITEX was 44 or 6 times higher than with static headspace. The concentration of diacetyl in this beer sample was also in the order of 10 ppb.

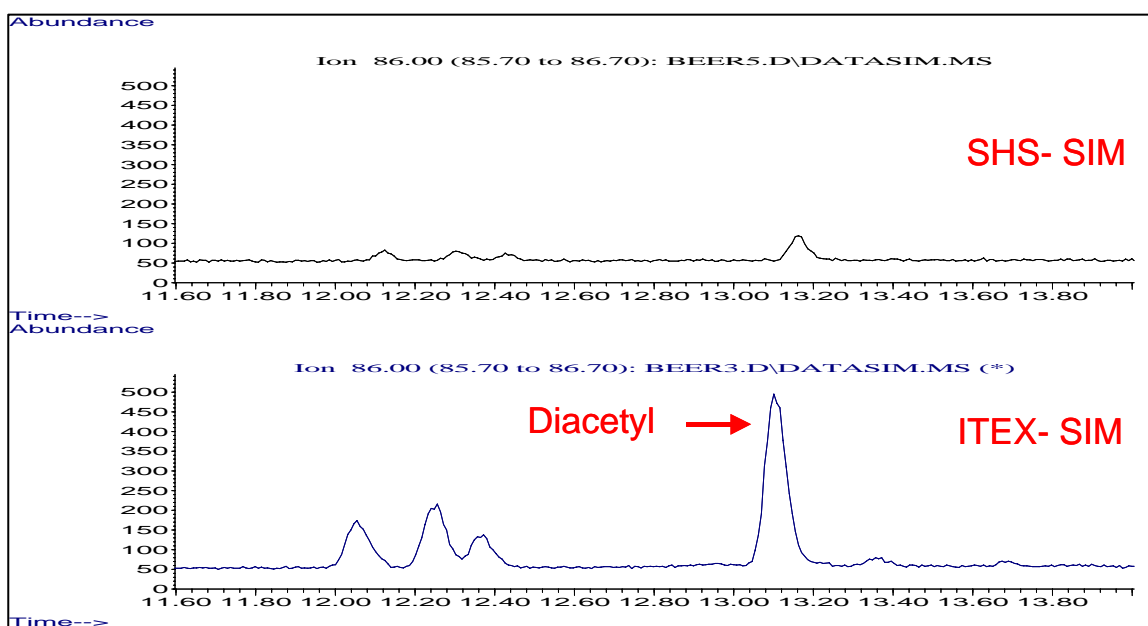


Figure 2

CTC Analytics AG  
Industriestrasse 20  
CH-4222 Zwingen  
Switzerland

Phone +41 61 765 81 00  
FAX +41 61 765 81 99  
email [info@ctc.ch](mailto:info@ctc.ch)  
Web [www.ctc.ch](http://www.ctc.ch)

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### Conclusion

Using ITEX headspace sampling in combination with GC-MS operated in simultaneous scan/SIM mode, different important volatile organic compounds present in beer can be monitored in a single run. Volatile alcohols and esters and dimethyl sulfide can be measured using scan mode. Diacetyl is monitored in SIM. In comparison to classical static headspace, ITEX offers a gain in sensitivity of a factor 5 to 10 using 10 pumping strokes only to shorten the sample preparation time. If a lower detection limit is required can the number of pump strokes be increased.