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ITEX Application Note # 01

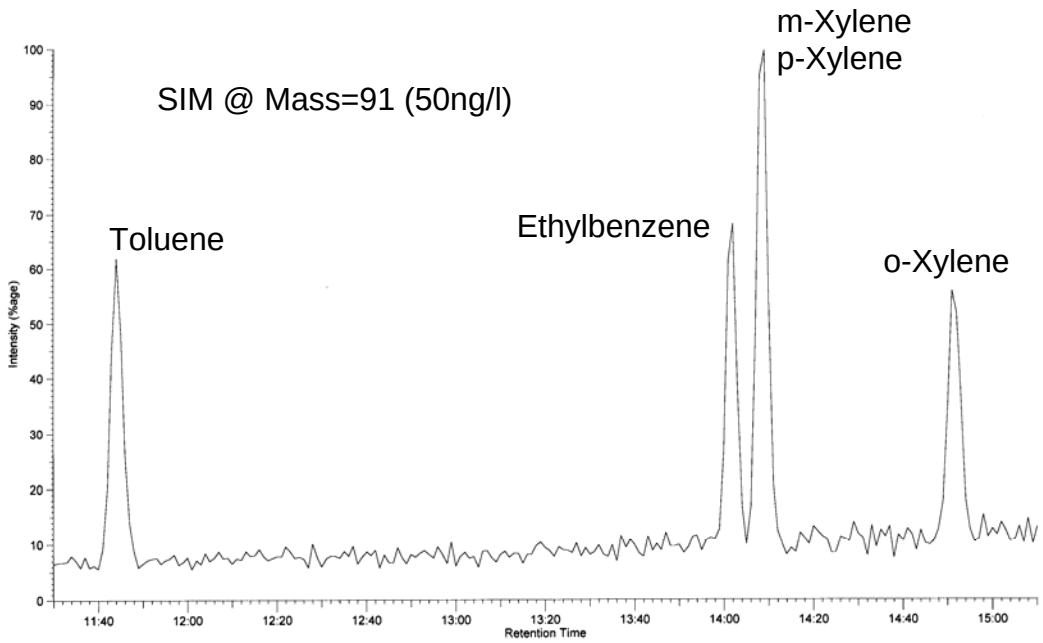
Author: Natascha Meggiolaro, Labor Veritas, Engimattstrasse 11, CH-8027 Zuerich, Switzerland
Keyword: **VOC, BTEX, EPA Method 502.2, ITEX**
Pages: 1

BTEX and VOC Compounds according to EPA Method 502.2 are analysed using ITEX sample preparation technique. Total sample preparation time of less than 15 minutes allows a high sample throughput.

Sample Preparation:
10ml water are filled in 20ml Headspace sample vials. 3g Sodium chloride and 1µl of the internal standard IS VOC (50ppb Fluorobenzene in Ethanol) is added. After sample conditioning at 60°C during 10 minutes 20 strokes of the headspace are pumped through the ITEX-trap with a velocity of 100µl/sec. The resulting sensitivity is sufficient to obtain the requested detection limit for drinking water of 0.05µg/l.

ITEX Conditions:
Sample Conditioning @ 60°C, 10 min.
Extraction Strokes: 20 x 1ml
Desorption @ 230°C with 1.3ml Headspace 20µl/sec.
Trap material: Tenax TA 80/100mesh

Chromatography:
Column: Rtx-502.2, 60m x 0.32mm,1.8µm film
Carrier Gas: Helium 20psi
Temperature Program: 40°C (2 min.) to 240°C (2 min.) at 10°C/min.
Precolumn: 1m x 0.32mm deactivated with DPTMDS
Injector: Gerstel KAS3 with septa @ 150°C isothermal
GC: Varian 3300
Detector: Varian Saturn 4D GC/MS/MS



Chromatogram1 shows BTEX Compounds at a concentration of 50ng/l using 20 Extraction strokes

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ITEX Application Note # 02

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Research Institute for Chromatography, Pres. Kennedypark 26, 8500 Kortrijk, Belgium
Keyword: **Allergens, cosmetics, headspace sampling, ITEX**
Pages: 7

Analysis of Suspected Flavor and Fragrance Allergens in Lotion Samples. A comparison between Static Headspace, SPME, HSSE and ITEX Headspace Sampling

Abstract

Suspected flavor and fragrance allergens were determined in an alcohol/water based lotion using ITEX headspace sampling. The dynamic headspace sampling was compared to static headspace, SPME and headspace sorptive extraction.

Introduction

According to recent EU regulation [1], 27 suspected allergen compounds should be monitored in cosmetic products. Depending on the sample matrix and solute concentrations, different sample preparation methods are developed and applied [2]. For the determination of suspected allergens in cosmetic products, one of the major problems is related to the presence of detergents that contaminate the analytical system if the samples are introduced without selective sample preparation. Selective extraction or selective sample introduction is however not easy since the target compounds cover a broad volatility range (from limonene to benzyl benzoate) and polarity range (from relatively polar benzyl alcohol, K_{ow}=1.1, to apolar benzyl benzoate, K_{ow} =4.0). Liquid sample introduction with selective retention of non-volatiles in a PTV liner [3] or sorptive extraction using a PDMS coated stir bar [2] have been used for this application. Sampling from the headspace, using static headspace, dynamic headspace, SPME or headspace sorptive extraction (HSSE) can also be considered as these techniques avoid contamination of the analytical system by high molecular weight material such as detergents. The method of choice should however give ppm sensitivity, on one hand, and avoid discrimination of the target solutes based on relative volatility or polarity, on the other hand. In this application note, the use of dynamic headspace extraction using ITEX is demonstrated. The technique is compared to classical static headspace, solid phase micro-extraction (SPME) and to headspace sorptive extraction, using a polydimethyl siloxane (PDMS) coated stir bar in the headspace of the sample. The latter two techniques are similar in concept, only the total amount of sorptive PDMS phase is different [2,4].

Sample Preparation

As typical sample an alcohol/water based lotion was analysed. The lotion is used in wet wipes and contains besides different detergents also a fragrance.
For each method, 100 mg sample was placed in a 20 mL headspace vial. Two internal standards (1,4-dibromobenzene and 4,4'-dibromobiphenyl) were added at 10 ppm level, according to the reference method for the determination of allergens in perfumes described by Chaintreau et al [5].

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Static HS conditions

Sample Conditioning @ 80°C, 15 min
HS needle: 2.5 mL, 90°C
Injection: 1 mL; 350 µL/s; 1/10 split ratio

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

SPME conditions

Fiber: 100 µm PDMS
Sample Conditioning @ 80°C, 15 min
Desorption @ 250°C, 2 min

Headspace Sorbtive Stirbar Extraction conditions

Sample Conditioning @ 80°C, 15 min
HSSE sampling in headspace: 10 mm x 0.5 mm df TwisterTM
Desorption @ 250°C during 10 min in splitless mode
Cryo-focussing @
Injection: -100°C @ 600°C/min to 250°C, 1/10 split ratio

GC conditions

All analyses were performed on an Agilent 6890 GC – 5975 MSD combination.

Column: 30 m x 0.25 mm i.d. x 0.25 µm df HP-5MS (Agilent)
Carrier gas: helium, 168 kPa constant pressure at inlet (column outlet pressure: 28 kPa using AUX EPC and QuickSwap connector) (*)
Inlet: split, 250°C, 1/10 split ratio
Oven temperature program: 50°C, 1 min, 8°C/min to 270°C.
MSD transfer line: 250°C (17 cm x 110 µm i.d. restrictor, 28 kPa)
Detection: MS in scan mode , scan range: 40-350 amu

(*)under these conditions, alpha isomethyl ionone elutes at 15.5 min. These settings were used to performe the analyses under retention time locked conditions [2].

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ITEX Application Note # 02

Results

In Figure 1, the total ion chromatogram obtained for the lotion sample using classical static headspace sampling is given. The internal standards, added at the same concentration level, are detected at 10.3 min and 23.1 min respectively. The response for the first internal standard is higher in comparison to the second internal standard, corresponding to their relative volatility.
In this sample, some allergens could be detected. Linalool (peak 1) and hexyl cinnamaldehyde (peak 6) are easily detected. Other allergens are only detected as traces and confirmation of their presence by mass spectral comparison with a library spectrum is difficult.

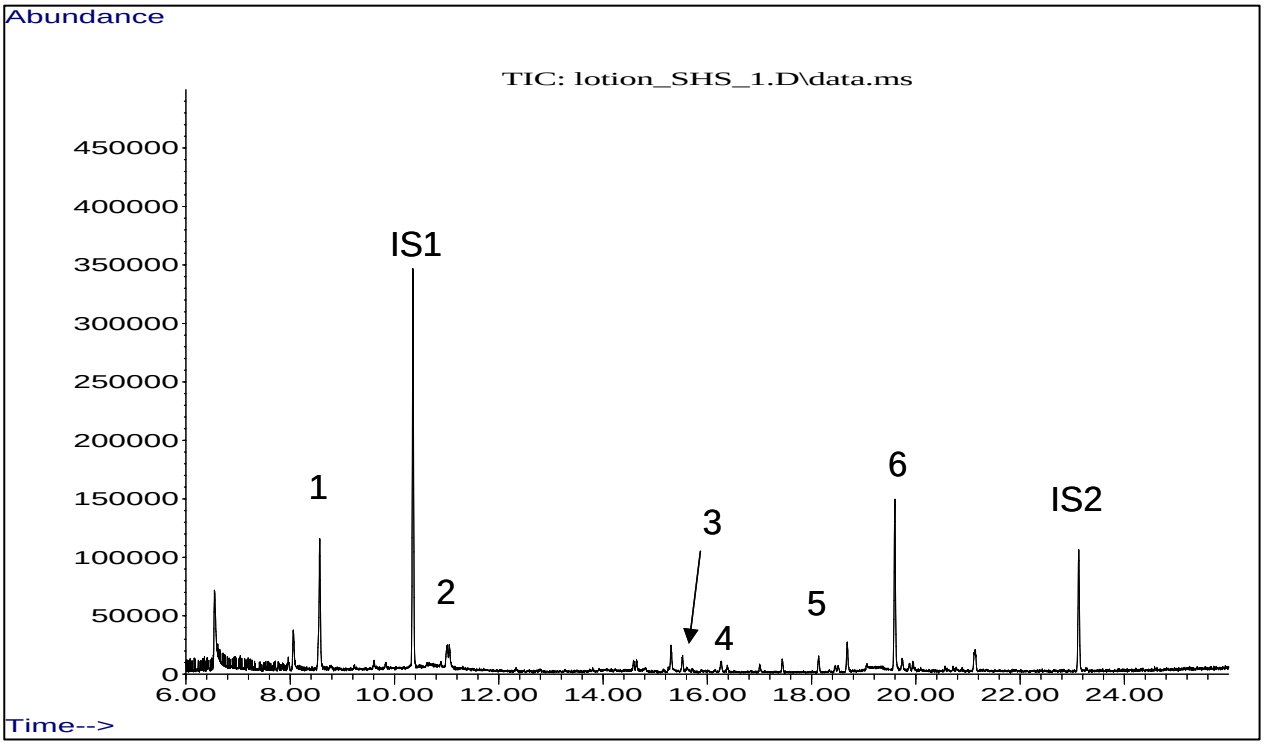

Figure 1: static headspace

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The chromatogram obtained by ITEX headspace sampling is shown in Figure 2. A much higher sensitivity is obtained in comparison to static headspace and several flavor and fragrance solutes could be detected. It is very interesting to observe that the response for the two internal standards is nearly equal, corresponding to there equal concentration in the sample. In this analysis, 6 allergens are detected and their presence could easily be confirmed by the mass spectra. Following allergens are present: 1. linalool, 2. citronellol, 3. alpha isomethyl ionone, 4. lilial, 5. amyl cinnamaldehyde and 6. hexyl cinnamaldehyde.

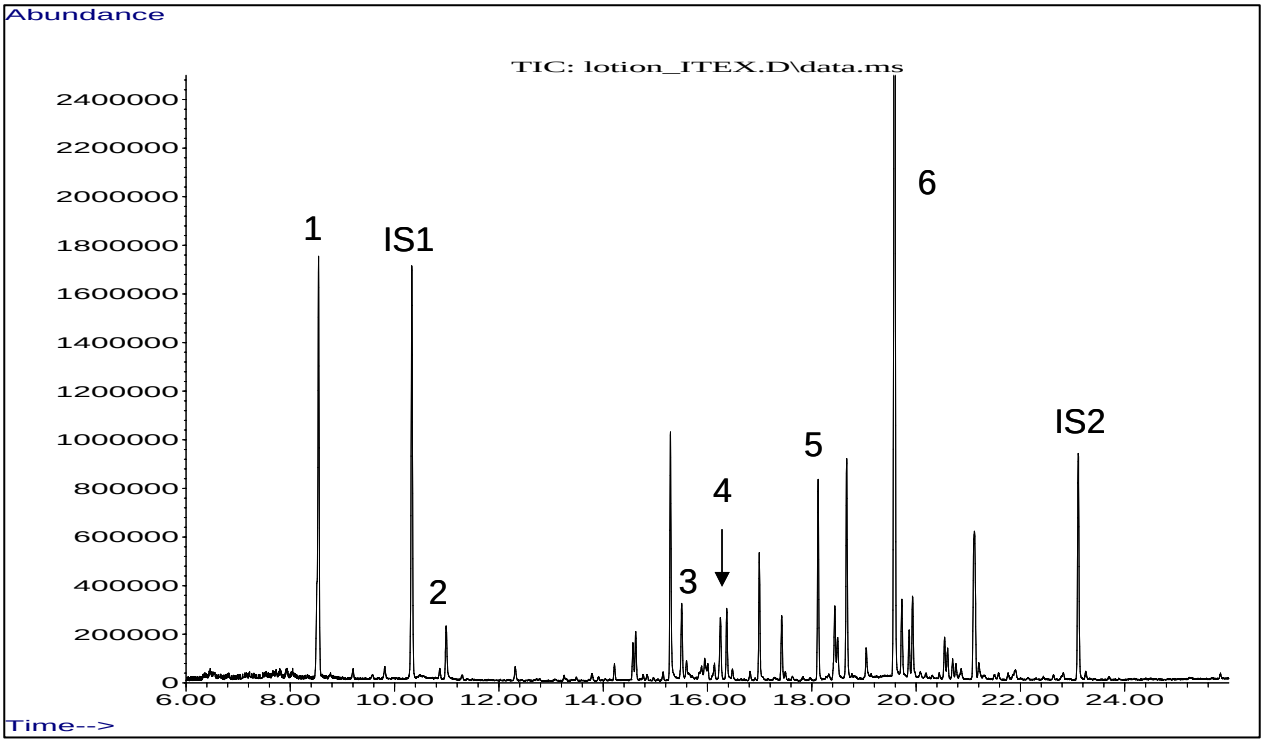

Figure 2: ITEX

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The chromatogram obtained by SPME headspace sampling is shown in Figure 3. Excellent enrichment is obtained and all 6 allergens could easily be detected. However, it is interesting to observe that the response of the second internal standard is much higher than for the first eluting internal standard. This difference can be explained due to the higher partitioning coefficient between PDMS and air for the higher molecular weight, later eluting compound. From the whole chromatogram it is clear that the less volatile compounds, having higher $K_{PDMS/air}$ coefficients, are more enriched in comparison to more volatile solutes. The responses of the target solutes largely vary in function of the $K_{PDMS/air}$ coefficients. This corresponds well with theoretical predictions [6].

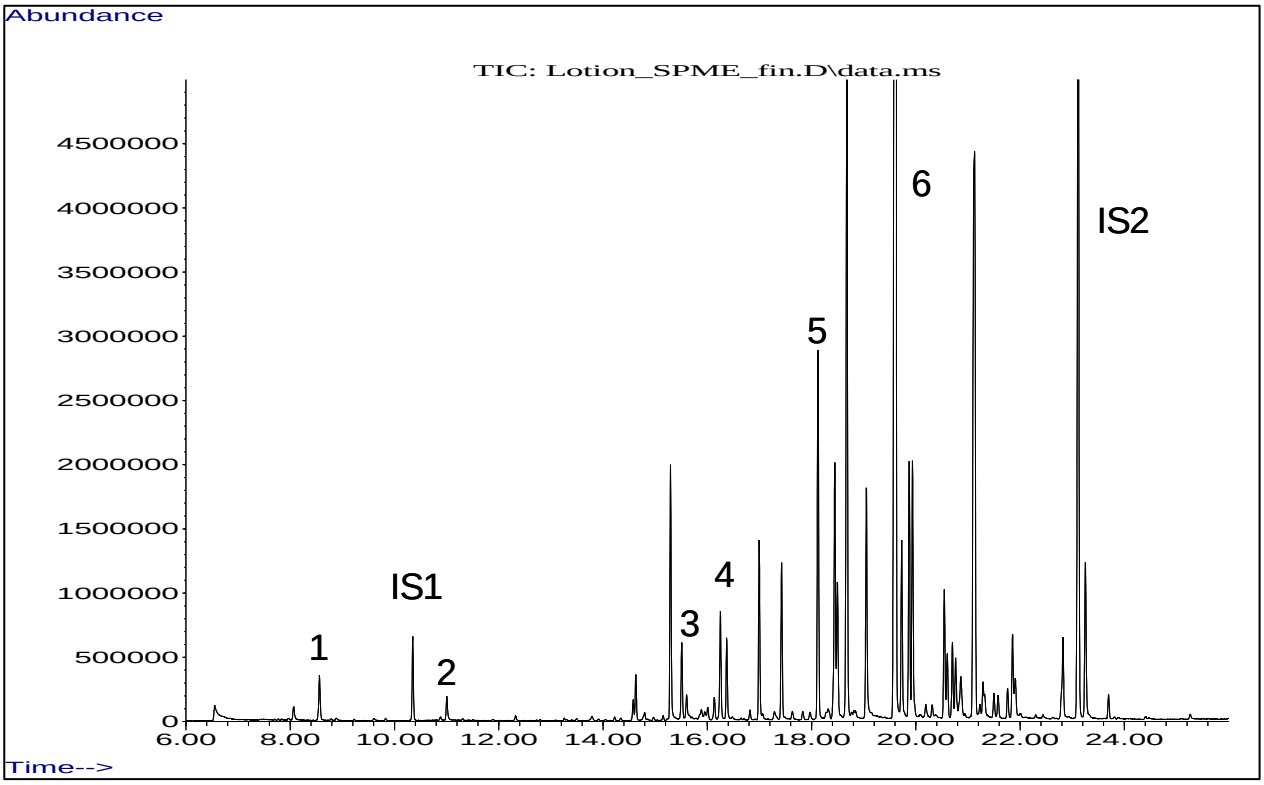

Figure 3: SPME

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The chromatogram obtained by headspace sorptive extraction sampling on a 1 cm stir bar coated with 0.5 mm PDMS is shown in Figure 4. As in SPME, excellent enrichment is obtained, but now the response of two internal standards is nearly equal, corresponding to there equal concentration in the sample. Since more PDMS material is available, quantitative recovery is obtained at lower $K_{PDMS/air}$ coefficients and the profile is very similar to the profile obtained by ITEX sampling. In this analysis, 6 allergens are also detected and their presence could easily be confirmed by the mass spectra.

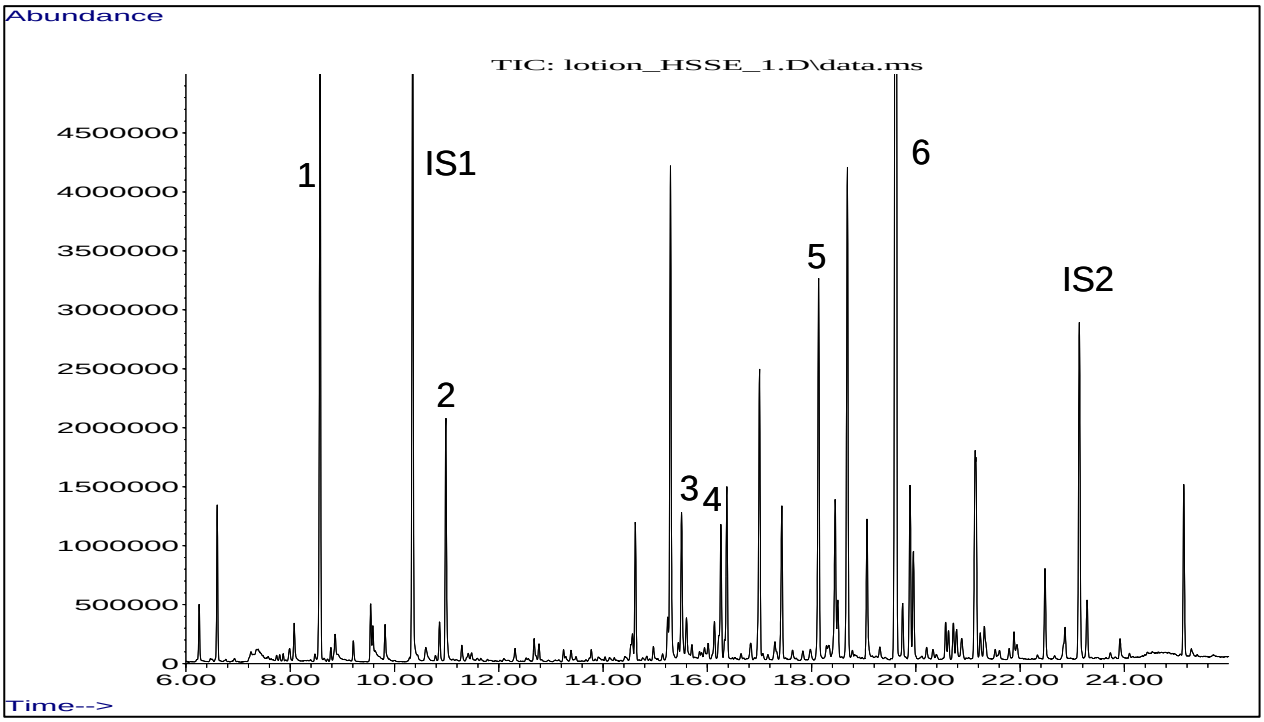

Figure 4: HSSE (Twister™)

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ITEX Application Note # 02

Conclusion

For the determination of flavour and fragrance allergens in cosmetics, ITEX headspace sampling results in much higher sensitivity than static headspace. The obtained profile is similar to the profile obtained by headspace sorptive sampling (using a Twister™ stir bar in headspace). In comparison to SPME, the relative response of the solutes is less dependent on the individual $K_{PDMS/air}$ coefficients of the target solutes.
The sensitivity of the ITEX determination can be increased if the number of extraction strokes would be increased.

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ITEX Application Note # 03

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Keyword: **Arson Detection using ITEX Headspace Sampling**
Pages: 4

Arson Detection using ITEX Headspace Sampling

Abstract

The analysis of residues of fire accelerants in fire debris samples can be used for arson detection. The analysis can be performed by ITEX sampling, followed by GC-MS analysis. In comparison to static headspace, the sensitivity is increased by a factor of 10 using ITEX enrichment.

Introduction

The detection of residues of fuels (gasoline, naphtha, kerosene) or organic solvents such as paint thinner in fire debris samples is an important application in forensic analysis. The target compounds include C5-C12 hydrocarbons, aromatic hydrocarbons, ethers and alcohols (methanol).
Different methods are used for this analysis including static and dynamic headspace, solid phase micro-extraction, etc. Using static headspace, the sensitivity of the method is often not high enough to detect traces of solvent residues. Higher sensitivity can be obtained using dynamic headspace with enrichment of the volatile organic compounds that are characteristic for fire accelerators. These solutes can be enriched on a Tenax trap. Consequently the solutes are desorbed from the trap and analyzed by GC-MS. Enrichment of VOCs from the headspace of solid or liquid samples 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.

Sample Preparation

Typically 1-5 g material is placed in a 20 mL headspace vial and the samples are analyzed as such. Materials introduced are not homogeneous and therefore often multiple samples are analyzed.
For the example showed below, two fire debris samples were taken from a burned wooden floor. Sample A was taken at the place were the fire started and sample B was taken at an area away from the original fire location. From both samples similar amounts were introduced in a 20 mL headspace vial and the vial was sealed.

ITEX conditions

Sample Conditioning @ 80°C, 10 min
Extraction Strokes: 20 x 1 mL; 50 µL/s
Desorption @ 250°C with 1 mL headspace; 50 µL/s
Trap Material Tenax TA 80/100 mesh

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ITEX Application Note # 03

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, 170 kPa constant pressure at inlet (column outlet pressure: 28 kPa using AUX EPC and QuickSwap connector)
Inlet: split, 1/10 split ratio
Oven temperature program: 35°C, 2 min, 8°C/min to 190°C, 20°C/min to 250°C, 2 min.
Detection: MS in scan mode (33-300 amu)

Results

The total ion chromatogram obtained for sample A (suspected sample) is given in Figure 1. The most abundant peaks are identified as alpha-pinene (12.5 min), camphene (12.9 min), and limonene (14.8 min). These compounds are typical pyrolysis products from wood and are no indicators for fire accelerants.

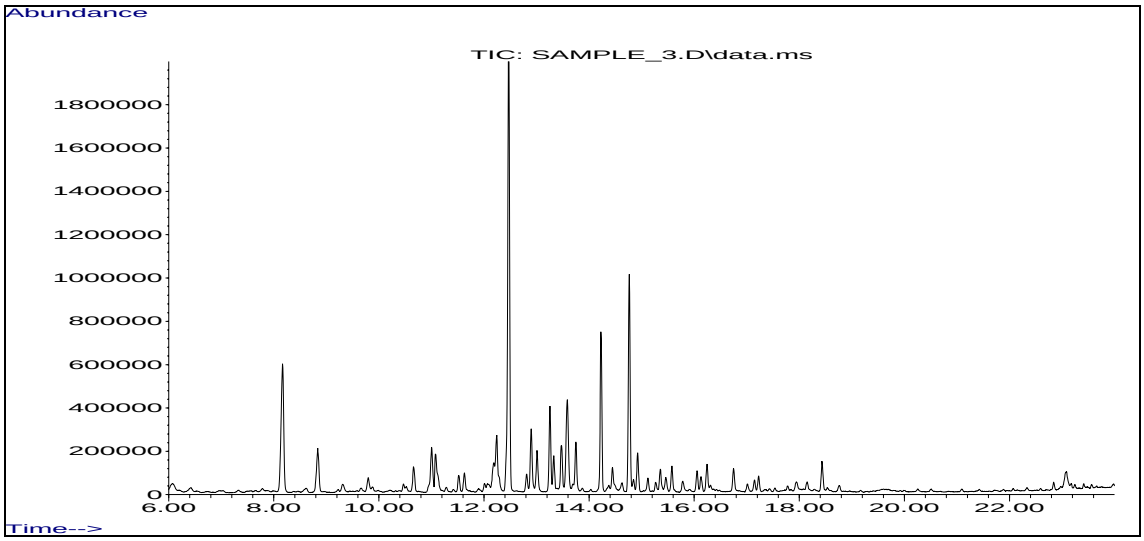

Figure 1

The total ion chromatogram obtained for sample B (believed to be blank) is given in Figure 2. The chromatogram is similar and the major peaks correspond also to the peaks detected in sample A (pyrolysis products of wood).

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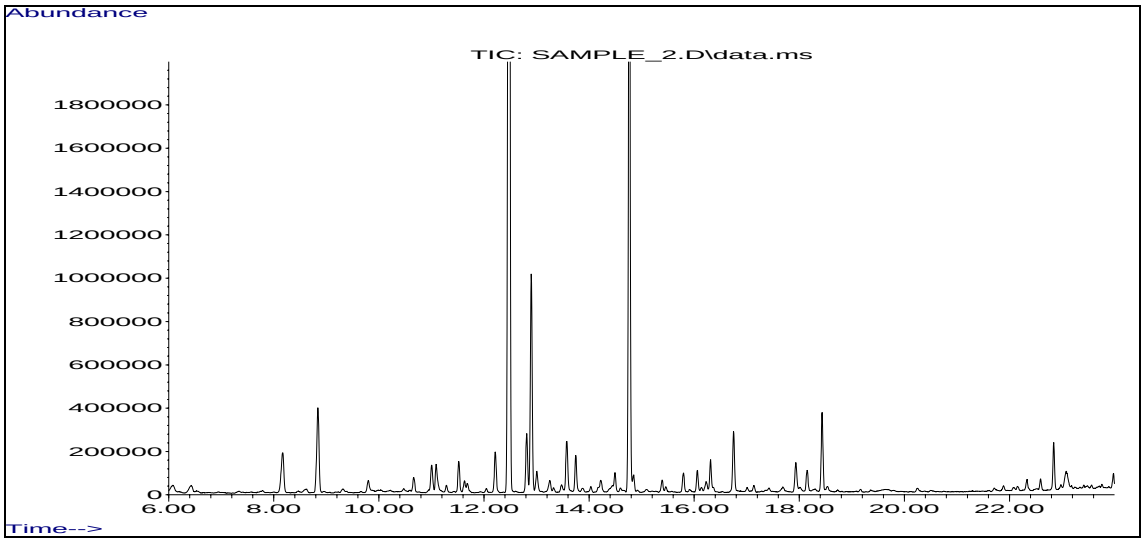

Figure 2

Using extracted ion chromatograms, it is however possible to differentiate both samples. The chromatograms below show the extracted ion chromatograms for m/e 120 (C3-aromatics) and m/e 134 (C4-aromatics) for respectively sample A (Figure 3) and sample B (Figure 4).

It is clear that in sample A, a typical profile of aromatic hydrocarbons is observed, while in sample B only one main peak is detected. This peak was identified as p.cymene and is also a pyrolysis product of wood. The profile of the aromatic hydrocarbons detected in sample A, on the other hand, corresponds to gasoline.

This could be confirmed by analyzing a blank sample spiked with a small amount of gasoline. In Figure 5, the profiles of the C3-aromatics in the spiked sample and in sample A are compared. It is clear that a good correspondence is obtained and that sample A contains traces of a fire accelerant, in this case gasoline.

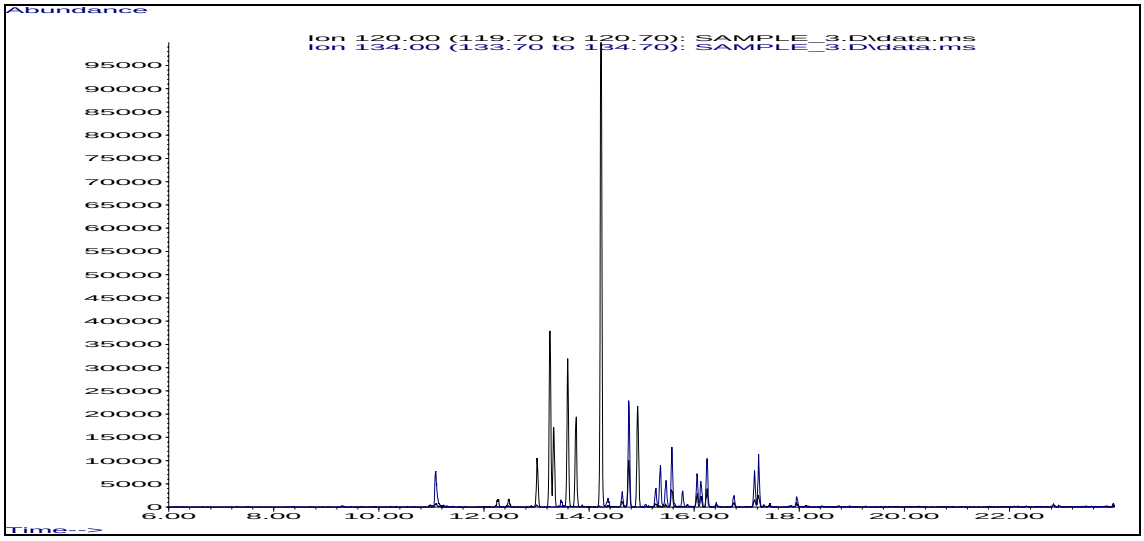

Figure 3

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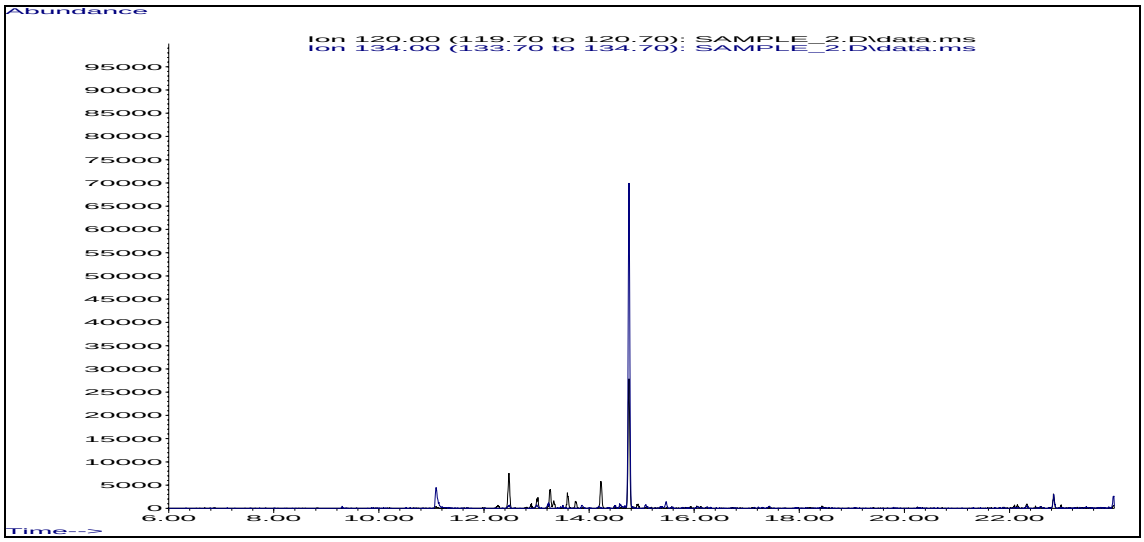

Figure 4

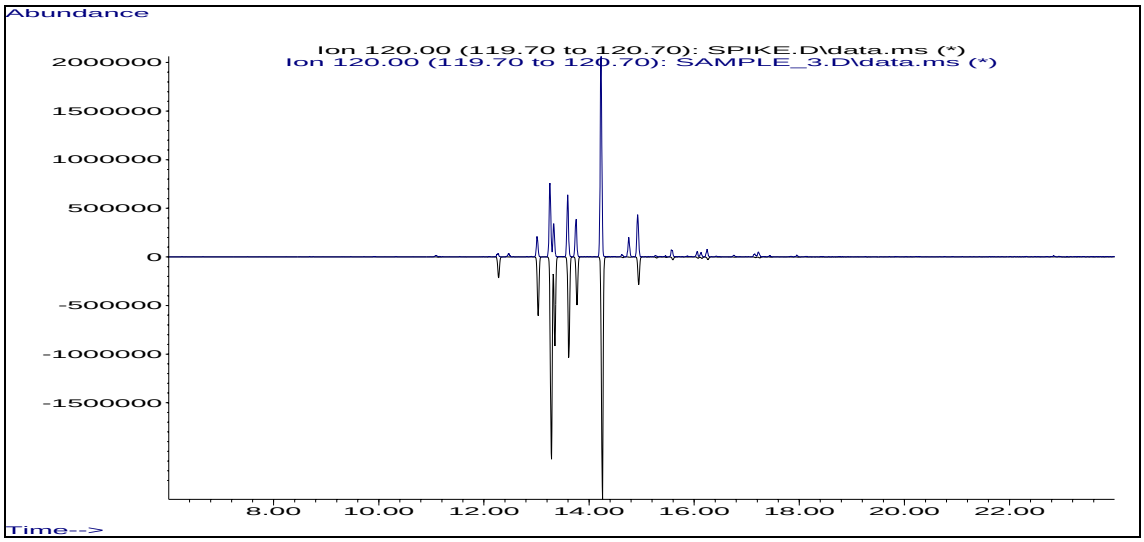

Figure 5: top: sample A (suspected sample); bottom: blank sample spiked with gasoline (reference)

Conclusion

Headspace sampling with enrichment of VOCs using the ITEX option was used for the detection of fire accelerants in fire debris samples. Excellent sensitivities are obtained, allowing detailed profiling of samples. In comparison to static headspace, the sensitivity of the ITEX-GC-MS was increased by a factor of 10, while no discrimination was observed in function of the boiling point of the solutes in the range from C5 to C15.

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ITEX Application Note # 04

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Keyword: **Volatile Organic Compounds, alcohols, dimethyl sulphide, diacetyl, beer, headspace, ITEX**
Pages: 4

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 is 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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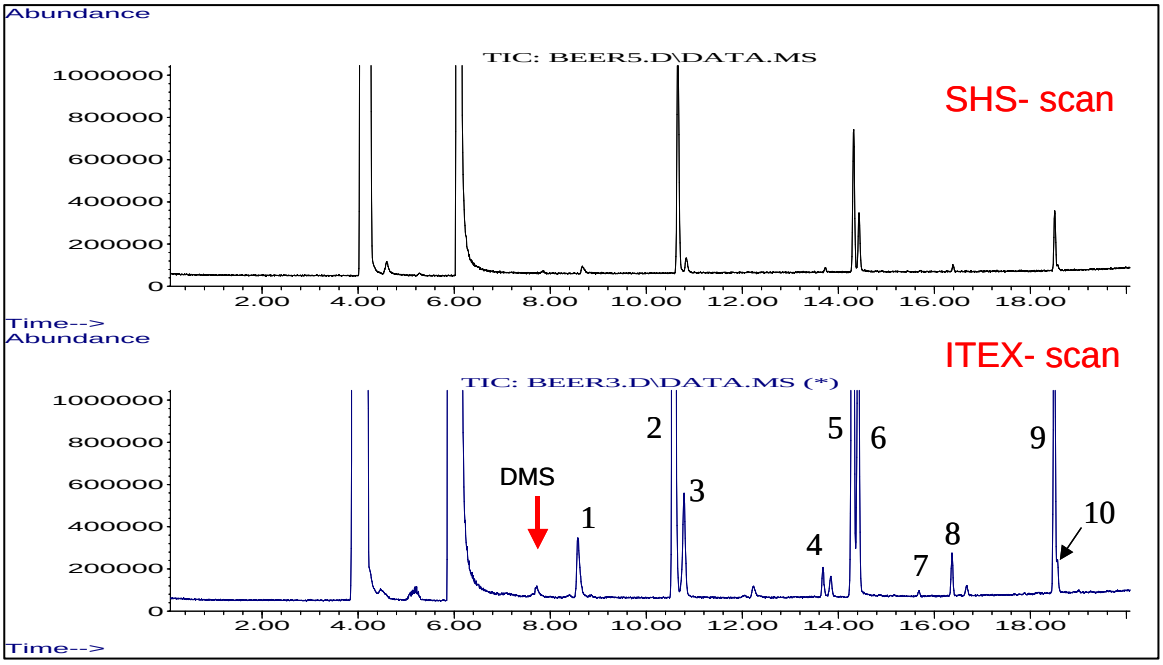

Figure 1

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.

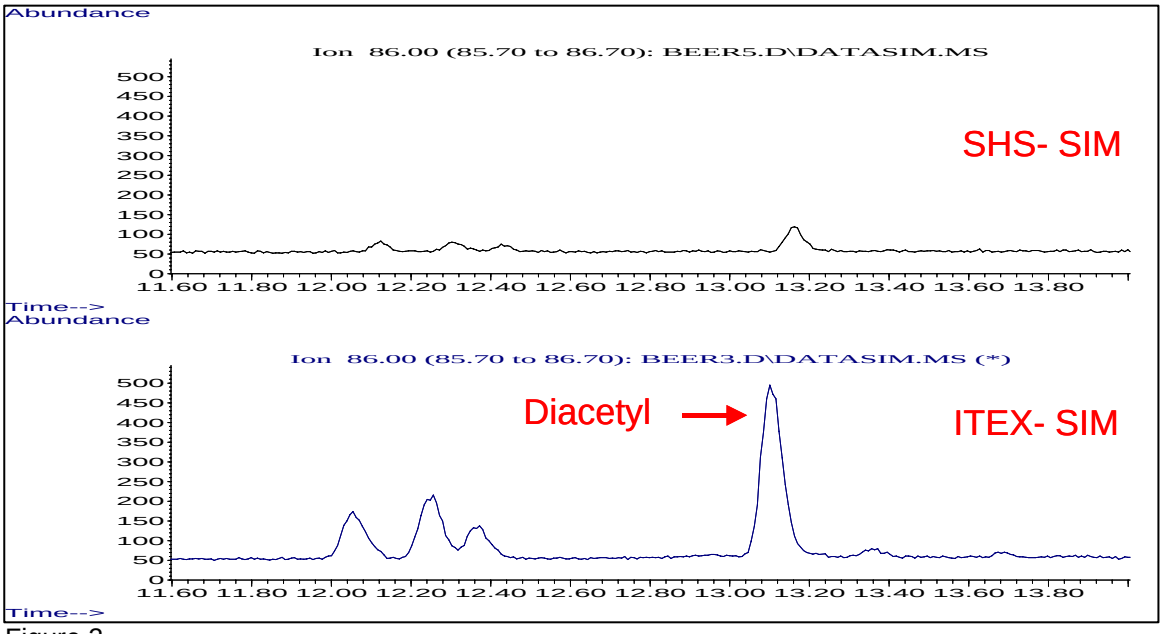

Figure 2

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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.

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ITEX Application Note # 05

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Determination of Volatile Organic Compounds in Drinking and Surface Water with In-Tube-Extraction comprehensive GC/time-of-flight mass spectrometry

Abstract

A series of volatile organic compounds (VOCs) in drinking water are determined using In-Tube Extraction comprehensive GC/time-of-flight mass spectrometry (ITEX GCxGC/TOF-MS). A method for determining these compounds has been established and detection limits for a selected number of VOCs are depicted. Detection limits were below 20 ng/L for all compounds. A comparison with 'classical' Purge & Trap GC/MS is made. Repeatablility experiments revealed an RSD of less than 20% for all the compounds, well within the demands of the Flemish decree on drinking water.

Introduction and Discussion

Antwerpse Waterwerken (AWW) is one of the largest drinking water companies in the Benelux, producing yearly 160 million m3 of drinking water. Therefore, the daily control of both drinking water and surface water (out of which the drinking water is produced) is an important task. Several parameters are determined under the international standard ISO 17025 in order to keep the quality as high as possible. One of these parameters are the compounds, mentioned in EPA 524.2, i.e. a series of volatile organic compounds.

These compounds are giving a serious threat to human safety. Hence, measuring of a series of VOCs (benzene, 1,2-dichloorethane, tetrachloroethene, trichloroethene, bromodichloromethane and the total concentrations of trihalomethanes and trichlorobenzenes) is demanded by the Flemish government in a decree of 2003. In this decree detection limits are mentioned which have to be reached by the controlling laboratory and are typically 10% of the norm value. Therefore, demanded detection limits are usually above 1 µg/L and do not pose any problem to most analysis methods. However, for 1,2-dichloroethane, being one of the more "difficult" VOCs to analyze, the detection limit should be below 0.3 µg/L in drinking water.

Presently, VOCs in drinking water are measured using two methods: Purge & Trap GC/MS and Headspace GC/MS. The former method is sensitive, but has a number of large drawbacks (e.g. memory effects), while the latter is at least ten times less sensitive. By CTC Analytics a new technique has been introduced, namely In-Tube Extraction Sample Preparation (ITEX®). The principle of this technique is showed in Figure 1. This method gives both easiness to use and sensitivity.

Another problem, which is often encountered, is the occurrence of interferences. Hence, wrong assignments can occur which gives a serious reduction in the quality of the measurement. High chromatographic resolution, as obtained by comprehensive GC/time-of-flight mass spectrometry does give a solution to this problem. Moreover, lower detection limits can be obtained. Using these conditions extremely low detection limits were obtained (see Table 1). A comparison is made with Purge & Trap GC/ion trap mass spectrometry. Repeatability experiments revealed RSDs of less than 20%, as can be seen in Table 1. A typical chromatogram of a 0.2 µg/L is depicted in Figure 2.

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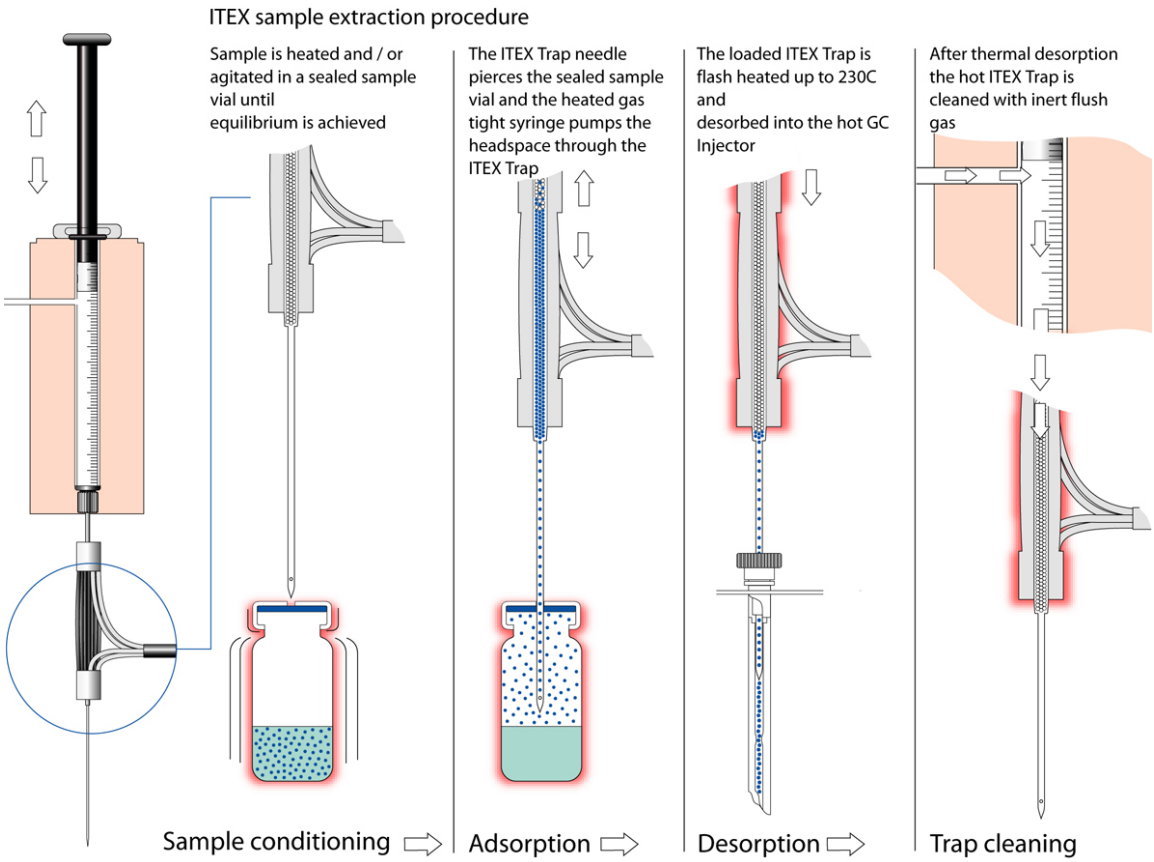

Figure 1: Working principle of ITEX ®

Experimental

ITEX (in combination with CTC CombiPAL)
- Trap Material Tenax TA 80/100mesh
- Extraction speed: 100 µL/s
- Total pumping strokes: 50 x 1 mL
- Temperature Pumping Syringe/sample incubation: 60°C (10 min)
- Desorption: 200°C (15 s; splitless)

Comprehensive GC (Agilent 6890 / LECO modulator)
- 1st column: HP-5ms SV (30 m; 250 µm id; 0.5µm)
- 2nd column: VF-17ms (2m; 100 µm id; 0.2 µm)
- Carrier gas: Helium
- Injector temperature: 250°C
- 1st oven temperature program: 40°C (2min) to 200°C at 4°C/min
- 2nd oven temperature is 5°C offset from 1st oven temperature
- Transferline temperature: 250°C
- Modulation time: 5.5 s

Mass Spectrometry (LECO Pegasus 4D TOF)
- Mass range: 45-300 amu
- Acquisition rate: 100 spectra/s
- Detector voltage: 1750 V
- Ion source temperature: 200°C

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Compound	Repeatability (%)	Recovery (%)	LOD ITEX (ng/L	LOD P&T (ng/L)
Chloroform	9.1	103	2.6	40
1,2-Dichloroethane	11.6	109	3.0	46
1,3-Dichloro-*trans*-propene	8.7	91	2.8	54
Chlorobenzene	4.9	116	1.0	42
1,2,3-Trichloropropane	4.5	96	2.0	33
Butylbenzene	10.1	106	2.5	58
1,2-Dibromo-3-chloropropane	9.8	91	9.7	80
Naphtalene	12.1	89	1.4	57

Table 1: Quality parameters for a selected number of VOCs

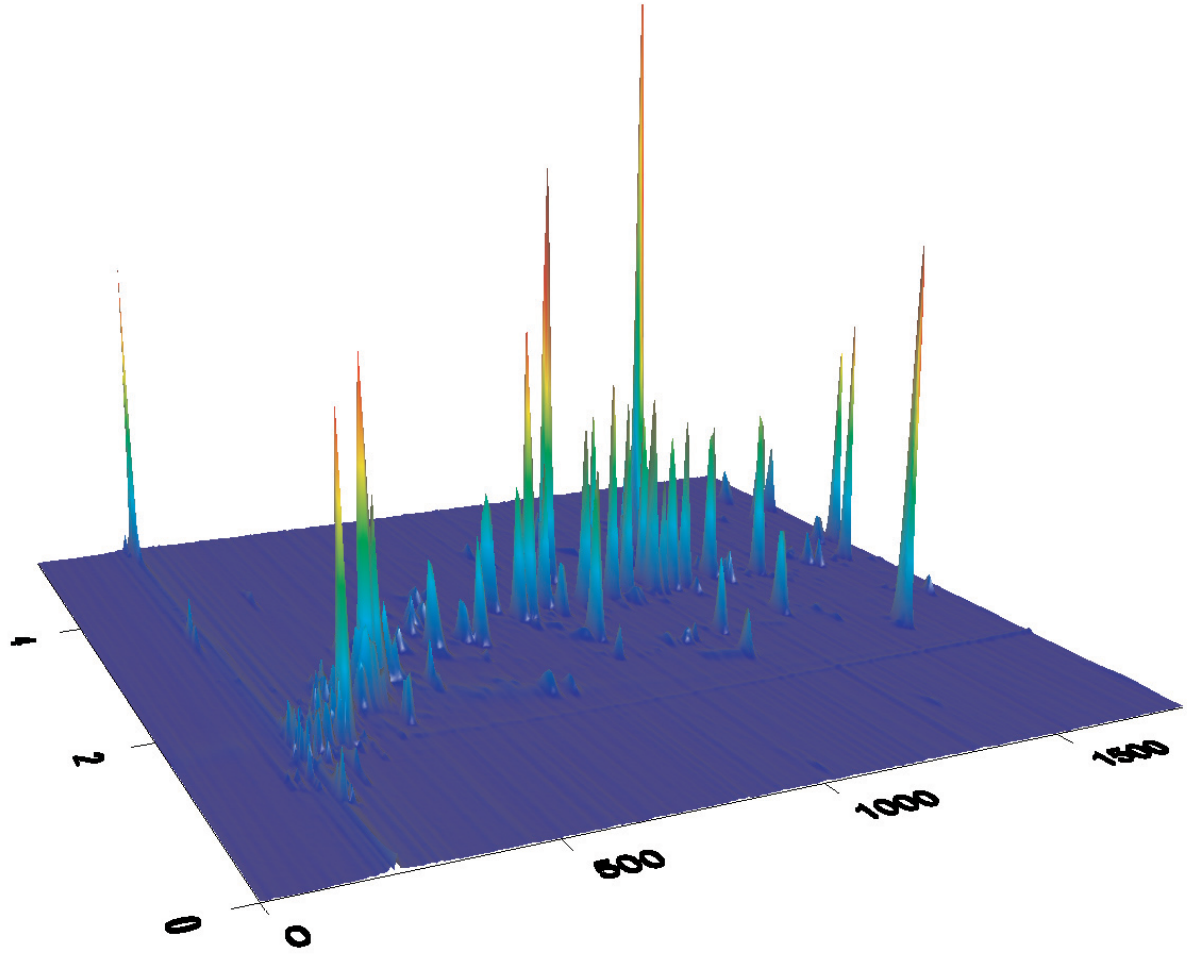

Figure 2: 3D-plot of a mixture of VOCs (concentration: 0.2 µg/L)

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ITEX Application Note # 06

In-tube Extraction (ITEX) for Extraction of Volatile Organic Hydrocarbons from Groundwater

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Summary

A full automated in-tube extraction (ITEX) method was evaluated and optimized for the determination of twenty common groundwater contaminants such as halogenated volatiles and monoaromatic compounds. ITEX applies an 2.5 mL headspace syringe with filled needle body (here Tenax TA). The analytes were extracted from sample headspace by dynamic extraction. The needle body is surrounded by a headable desorber , which is heated for analyte desorption into the injection port of an GC/MS. Method related parameters such as extraction temperature, number of extraction cycles, extraction and desprtion volume as well as extraction and desorption flow rates were determined in detail. The linear dynamic range of the ITEX method was over six orders of magnitude between 0.028 – 1218 µg/L with linear correlation coefficients between 0.990 and 0.998 for the investigated compounds. Method detection limits for monoaromatic compounds were between 28 ng/L (ethylbenzene) and 68 ng/L (1,2,4-trimethylbenzene). For halogenated volatile organic compounds MDLs between 48 ng/L (chloroform) and 799 ng/L (dichloromethane) were obtained. The precision of the method without internal standard was between 3.1 % (chloroform ethylbenzene) and 7.4 % (1,2,3-TMB).

Introduction

Around 15 years ago solid-phase microextraction (SPME) was introduced as solventless equilibrium microextraction method [1]. Since than, other related microextraction methods such as stir bar sorptive extraction (SBSE), liquid-phase microextraction (LPME) and several in-tube or in-needle extraction techniques were developed to overcome some fiber related drawbacks such as fiber fragility, diminished lifetimes of polar coating materials and low sorption capacities [2]. In-tube or in-needle extraction techniques roughly can be divided in methods that either apply a coating on the inner surface or a sorbent material packed inside a tube or a needle.

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Methods with sorbent packings, such as in-tube extraction (ITEX) offers the advantage that a variety of commercial available sorbent materials and higher amounts of sorbent material can be used to obtain higher extraction yields than possible with coated extraction phases. Early approaches used gas chromatography capillary columns such as so called open tubular traps (OTT) [3]. A very similar method is known as in-tube SPME, which was originally developed in combination with HPLC [4] for the determination of chlorinated hydrocarbons[5] and pesticides [6]. A shorter capillary with a sol-gel coating (sol-gel CME) was used by Bigham et al. for determination of compounds such as PAHs, aldehydes and ketones as well as for more polar compounds such as phenols, alcohols and amines [7]. Other in-tube techniques such as in-capillary extraction (INCAT) [8] or solid-phase dynamic extraction (SPDE) [9-11] use a needle as support for the extraction phase. These needle based methods have the advantage that thermal desorption can be carried out directly in the injection port of a gas chromatograph and the whole process can easily be implemented in an auto-sampler. To achieve higher extraction yields, efforts were made to increase the amount of extraction phase by applying packed sorbent materials. A method to determine BTEX compounds that applies a sorbent bed was developed by Berezkin and Kubinek [12]. Another needle based device that uses a packed sorbent is the needle trap (NT) by Wang and Pawliszyn [13] and similar needle extraction device for GC/MS analysis of VOCs (toluene, ethyl acetate) was presented by Saito and co-workers, by using a copolymer bed of methacrylic acid and ethylene glycol dimethacrylate [14]. The here presented ITEX method enhances the advantages of previous needle-based methods by applying a stainless steel needle that is divided into two parts. As shown in the schematic illustration of the ITEX procedure in Figure 1, the lower part consists of an ordinary needle canula with a hole on the side for septum penetration. The upper part with a bigger diameter contains the sorbent material. Additionally, the upper part of the ITEX needle is surrounded by a heater for thermal desorption after. Compared with other in-needle techniques the thermal desorption occurs outside the GC injector, which makes the method independent from the injector temperature profile and offers a gradient free desorption. After thermal desorption, the sorbent

material is flushed with nitrogen at an elevated temperature for cleaning. In this study, Tenax TA® was used as packing material for extraction of the target analytes. The ability to apply relatively high amounts of a variety of packing materials, e.g. as used in purge&trap, is a special advantage of the method and opens a wide range of applications to various compound classes with different polarities.

In this work, ITEX was evaluated for the determination of nineteen priority groundwater pollutants [15, 16] such as volatile halogenated hydrocarbons (dichloromethane (DCM), chloroform, carbon tetrachloride (CT), bromoform, 1,2-dichloroethane, 1,2-dibromoethane, *cis*-1,2-dichloroethylene (*cis*-DCE), *trans*-1,2-dichloroethylene (*trans*-DCE), trichloroethylene (TCE), tetrachloroethylene (PCE)) and BTEX compounds (toluene, ethylbenzene, propylbenzene, 1,2,4-trimethylbenzene (1,2,4-TMB), benzene, 1,3,5-trimethylbenzene (1,3,5-TMB), 1,2,3-trimethylbenzene (1,2,3-TMB), *para*-xylene). All these compounds have adverse effects to environmental systems and human health and most of the components are known or probable human carcinogens [17].

The main objective was to evaluate a sensitive, robust method that applies a solid sorbent material as extraction phase, with the ability to use the wide range of sorbent materials that were available for purge and trap and air sampling. To this end, in this work the evaluation of (i) the most important extraction and desorption parameters, as well as the (ii) determination of validation parameters such as method detection limits and precisions for volatile organic compounds was carried out.

Experimental

Reagents

Methanol (99.9 %) from Merck (Darmstadt, Germany) was used to prepare stock solutions. As solvent for the preparation of standard solutions, Milli-Q water from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA) was used. Trichloroethylene (99.5 %), dichloromethane (≥99.9 %)

and toluene (99.9 %) were obtained from Merck (Darmstadt, Germany). *Cis*-1,2-dichloroethylene (97 %), *trans*-1,2-dichloroethylene (98 %), tetrachloroethylene (99.9+ %), bromoform (99+ %), 1,2-dichloroethane (99.8%), 1,2-dibromomethane (99 %), carbon tetrachloride (99+ %), isopropylbenzene (99 %), *para*-xylene (99 %), ethylbenzene (99.8 %), propylbenzene (98 %), 1,2,4-trimethylbenzene (98 %) were purchased from Aldrich (Steinheim, Germany) and chloroform (99.5 %), benzene (99.5 %), 1,3,5-trimethylbenzene (99 %), 1,2,3-trimethylbenzene (90-95 %) from Fluka (Buchs, Switzerland). Fluorobenzene (99 %) from Aldrich (Steinheim, Germany) was used as internal standard. Sodium chloride (>99.5%) purchased from Fluka (Buchs, Switzerland) was used to vary the ionic strength of the water samples. Sodium chloride was pulverized for a faster dissolution in a mortar and heated over night at 180°C in an incubator to remove organic residues.

GC/MS Equipment and Method

All samples were measured using a TraceGC 2000 (ThermoFinnigan, Milano, Italy) gaschromatograph coupled with a TraceDSQ (ThermoFinnigan, Austin TX, US) single quadrupole mass spectrometer. ITEX was performed with a CTC-CombiPAL autosampler supplied by Chromtech (Idstein, Germany). Data acquisition, processing and evaluation were carried out using the standard software Xcalibur Data System Version 1.3 (ThermoFinnigan, Austin TX, US). The analytes were separated on a RTX-VMS capillary column (60 m x 0.32 mm ID, 1.8 µm film thickness, Restek Corp., Bellefonte PA, US). To obtain sharper peaks, especially for the early eluting chlorinated hydrocarbons, 1 m of a 0.53 i.d. deactivated capillary column was used as retention gap between the injector and the analytical column. The temperature program used to obtain separation of the target compounds was as follows: 14 min at 40 °C, 4 °C/min to 100 °C, hold for 2 min, 10°C/min to 170 °C and hold for 5 min. The total runtime of the GC program was 36 minutes and the temperatures for the transfer line and the ion source were set to 250 °C and 220 °C, respectively.

The initial GC oven temperature was held at 40 °C to trap the analytes before separation in order to prevent peak broadening. The GC was equipped with a programmable temperature vaporiser BEST PTV (ThermoQuest, Austin TX, US) that was used in the splitless mode at an injection port base temperature of 170 °C and a splitless time of 2 min. The PTV was programmed such that during the injection phase the column flow was set to 1 mL/min to minimize the pressure during injection of the gas volume. After 2 min it was set to a constant column flow of 1.5 mL/min for the rest of the chromatographic separation. A 1 mm I.D. deactivated silcosteel liner (Restek Corp., Bellefonte PA, US) was used. As carrier gas Helium 5.0 (AirLiquide, Düsseldorf, Germany) was used. The MS was in the electron impact ionization mode (EI) at 70 eV. Full-scan mode (m/z = 49-300) was used for all measurements, including the real samples. A chromatogram of a 5 µg/L standard obtained under optimized conditions is shown in Figure 2.

Equipment and Procedure

The autosampler was equipped with a single magnet mixer (Chromtech, Idstein, Germany) and a temperature controlled tray holder (Chromtech, Idstein, Germany). The samples were placed in the thermostated tray holder (45 °C). Before extraction the sample was stirred for 15 min in the single magnet mixer at an incubation temperature of 50 °C to establish equilibrium distribution of the analytes between aqueous and gas phase in the vial before extraction. The extraction volume of the gas phase was set to 1000 µL and 20 extraction cycles were used for the optimized method. The extraction flow rate during the extraction was set to 100 µL/s. For thermal desorption, the desober was heated up to 170 °C and 700 µL of the sample were transferred by a desorption flow rate of 10 µL/s into the hot injector. After desorption, the ITEX device was flushed with nitrogen gas at a desorber temperature of 210 °C for 20 min.

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Stock Solutions and Standard Mixture

Mixed methanolic stock solutions with a concentration of 2000 mg/L were prepared weekly and were stored at 4 °C in the dark refrigerator. Standard solutions were prepared before each experiment from these primary stock solutions in Milli-Q water. Lower concentrated solutions for calibrations, MDL determination and optimization were prepared likewise by volumetric dilution to the required concentration levels. During evaluation of optimized parameters, all measurements have been carried out in triplicates using 100 µg/L standard solution mixtures.

Preparation of Stock and Standard Solutions

Twenty-mL screw cap headspace vials (BGBAnalytik, Anwil, Switzerland) were filled with 0.52 g (5 % (w/w)) sodium chloride, 8 mm glass coated stir bars (FisherScientific, Ulm, Germany) and 10 mL of standard solution mixture were transferred immediately with a 10 mL gastight Hamilton syringe (BGBAnalytik, Anwil, Switzerland) into the vials that were sealed immediately with PTFE coated silicone septa and magnetic screw caps. It was necessary to shake the vials for at least ten minutes in order to ensure complete dissolution of the salt.

Method detection limits, Precision

Method detection limits (MDLs) were determined according to the U.S. Environmental Protection Agency procedure [18] by using the optimized conditions indicated in the experimental section. To this end, seven replicates were measured at an approximate signal to noise ratio of 5:1, and standard deviations for these were calculated. For each compound, six point calibrations curves bracketing the test level were used for quantification. Finally, MDLs were calculated by multiplying the standard deviation s_d with the student *t*-factor for the corresponding degree of freedom ($f = 6$). The precision was determined at the fortification level concentration used for MDL determination as well as at the end of the determined linear range.

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Results and Discussion

Evaluation of Extraction and Desorption Parameters for ITEX

The optimization of polymer based microextraction methods include various extraction and desorption parameters. Such parameters are the extraction temperature and time as well as the influence of the ionic strength and the desorption temperature. To obtain highest extraction yields for dynamic in-needle extraction methods additional parameters concerning the dynamic headspace extraction process have to be optimized, i.e., desorption flow rate, desorption volume, extraction flow rate as well as the extraction volume.

Number of Extraction Cycles

As shown in Figure 3, one to fifty extraction cycles corresponding to extraction times of 0.66 to 33.3 min were investigated. During the extraction process the temperature was held at 30 °C and before extraction the samples were equilibrated for 2 h in the 25 °C heated tray to establish equilibrium before starting the extraction. The extraction flow rate and volume were set to 40 µL/s and 1000 µL, respectively. The desorption flow rate and extraction volume were held constant at 50 µL/S and 700 µL, respectively. Figure 3 shows that a state of equilibrium could not be observed for most of the investigated compounds after 50 cycles. Only for PCE equilibrium was established after 30 cycles (20 min). However, as an adequate extraction time, a fixed value of 20 extraction cycles was chosen for the optimized method.

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Extraction Temperature and Ionic Strength

The effect of extraction temperature on extraction efficiency was studied within a range between 30 °C and 60 °C. For this evaluation, the extraction flow rate was held constant at 50 µL/s and the extraction volume for each extraction cycle at 1000 µL. Twenty extraction cycles corresponding to an extraction time of 13.3 min and a total extraction volume of 20 mL were carried out. The desorption volume was set to 700 µL and a desorption flow rate of 10 µL/s was used. As shown in Figure 4, most BTEX compounds show optimum extraction yields at 50 °C with a slight decrease at 60 °C. Only the trimethylbenzene isomers showed highest extraction yields at 60°C. For the halogenated compounds an increase up to 60°C was observed for most compounds, only CT, TCE and PCE showed a slight decrease at the highest temperature. However, the extraction yields for BTEX as well as chlorinated hydrocarbons increase between 30°C to 50°C on average by a factor of 1.6 and for the optimized method an extraction temperature of 50 °C was used.

Compared with extraction temperature profiles for HS-SPME [19] the optimum extraction temperature was about 20 °C higher both for HS-ITEX as well as for HS-SPDE [10]. This may be rationalized as follows. In HS-SPME, the entire extraction phase is immersed completely into the heated headspace of the sample during extraction while in HS-SPDE the tip of the needle with a short part of extraction phase and in HS-ITEX only the needle is in direct contact with the heated headspace, and the lower temperature of the extraction chamber of SPDE and ITEX allows a more efficient extraction due to the exothermic nature of the gas phase to solid sorption processes. Thus, higher temperatures for promoting the air-water partitioning (endothermic processes) can be applied in ITEX without compromising the extraction yields by lowering the air-sorbent partitioning coefficients.

According to the results obtained in a previous study [10]a salt concentration of 5 % (w/w) NaCl (0.52 g) was used for the final method.

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Extraction Flow Rate and Volume

Figure 5 shows the effect of the extraction flow rate on the extraction yields (signified by peak areas) of the investigated compounds. The extraction flow rate was has been varied between 10 µL/s and 150 µL/s at otherwise constant method parameters (desorption volume: 1 mL; 15 extraction cycles; desorption flow rate: 50 µL/s). Under these conditions the corresponding extraction times were between 3.3 and 50 minutes. The peak areas increased by a factor of 1.3 for 1,3,5-TMB to 2.6 for DCM. With decreasing extraction flow rate an increase in the extraction yield occurred indicating a higher degree of non-equilibrium sorption due to rate limiting diffusion into the extraction phase at higher extraction flow rates. Variations of the extraction volume were examined in a range from 500 – 2500 µL at an extraction flow rate of 50 µL/s, an incubation temperature of 30 °C and at 15 extraction cycles. As shown in Figure 6 an almost linear increase of extraction yields with extraction volume occurred, the maximum increase depended on the analytes and ranged from a factor of 1.8 (*trans*-DCE) to 4.8 (bromoform). An extraction flow rate of 50 µL/s was used for the optimized method with a constant extraction volume of 1 mL.

Conditions for the Desorption Step: Temperature, Flow Rate, Volume

As presented in Figure 7 the desorption flow rate showed a strong influence on the extraction yield. The desorption flow rate was varied from 10 - 500 µL/s at a constant desorption volume of 1 mL, which correlates to desorption times between 1 s and 100 s. During the evaluation of this parameter, the extraction volume as well as the extraction flow rate were kept constant at 1000 µL and 50 µL/s, respectively. For desorption flow rates of 10 µL/s, a factor of 4 (DCM) to 26 times higher peak areas (ethylbenzene) than for 100µL/s were obtained indicating a rate limiting diffusion of the analytes from the coating into the nitrogen gas stream during the desorption step. These results agree with results for

HS-SPDE [10] and with similar results reported in the literature. [20] Thus, in the parameter set of the optimized method a desorption flow rate of 10 µL/s was used.

A fixed desorption temperature of 170 °C was used during the evaluation of other method parameters as well as in of the optimized method. Although higher desorption temperatures might increase desorption rates, this temperature was chosen to assure a prolonged lifetime of the extraction phase and thus unchanged properties of the fiber over extended use times.

The effect of the desorption volume on peak areas was investigated between 500 µL and 1000 µL, but no significant influence on the extraction yield was observed (Figure 8). This observation is in agreement with results obtained for solid-phase dynamic extraction of chlorinated hydrocarbons [10] and alcohols[21]. In this study only a slight peak area increase was observed for desorption volumes of 700 µL compared with 500 µL. For some compounds such as *trans*-DCE and benzene a decrease in the peak area can be observed when using 1000 µL. At a desorption flow rate of 500 µL the standard deviation for some compounds, e.g. carbon tetrachloride is relatively high. A desorption volume of 700 µL was used in the parameter set of the optimized method.

Validation of the Method

The linear dynamic range of the ITEX method was investigated over six orders of magnitude between 0.028 – 1218 µg/L and linear correlation coefficients between 0.990 and 0.998 were obtained.

Method detection limits (MDLs) were determined as described in the experimental part according to the U.S. Environmental Protection Agency procedure. [18] Method detection limits for all target compounds were determined with and without fluorobenzene as internal standard.

By using fluorobenzene as internal standard higher MDLs (Table 1) as well as lower precisions especially for the chlorinated compounds were obtained. This observation is in agreement with results

found for HS-SPDE[10]. Especially for the chlorinated compounds (e.g., EDB), fluorobenzene is not an ideal internal standard. DCM and *trans*-DCE deviate from this trend. These two very volatile and early eluting compounds are very susceptible to the desorption parameters. We expect improved precisions and MDLs for such compounds by using a cryofocus unit .

The method detection limits for the BTEX compounds without internal standard ranged between 28 ng/L for ethylbenzene and 68 ng/L for 1,2,3-TMB. MDLs for chlorinated hydrocarbons without internal standard were between 48 ng/L for chloroform and 799 ng/L for dichloromethane.

All MDL values given refer to concentrations of the analytes in the water phase.

In Table 2 a comparison between the HS-ITEX-GC/MS method, a HS-SPDE-GC/MS method and other extraction methods such as HS-SPME and P&T is shown. When comparing the obtained data one needs to take into account that different extraction phases and different methods for MDL determination were used. It can be seen from Table 2 that with mixed extraction phases such as Carboxen/polydimethylsiloxane (CAR/PDMS) lower MDLs can be obtained than with pure partitioning phases as polydimethylsiloxane (PDMS). This trend can also be observed for benzene, determined by the HS-SPDE/MS method compared with the HS-SPDE method evaluated by Ridgway et al. . [11] Here a 30 times lower method detection limit was found with the PDMS/AC coating compared with PDMS in their study. Another important point is that MDLs for an enrichment method obtained using an electron capture detector (ECD) are not comparable with data obtained by an MS because of the much higher sensitivity of the former one for polyhalogenated compounds. The HS-SPDE-GC/MS method showed a factor of 2 to 30 times lower MDLs than the HS-ITEX-GC/MS method by using a PDMS/AC extraction phase. However, the method showed one order of magnitude lower detection limits than the comparable HS-SPME/MS method by Wypych et al. [22], which used the same MDL determination method as used in this study. Compared with a P&T-GC/MS method by Martinez et al. [23] two to three orders of magnitude higher MDLs were obtained by HS-SPDE/MS.

The precision was determined as relative standard deviation at around five times higher concentrations than the method detection limit for (n=7) measurements. Good precisions between 3.1 % (ethylbenzene) and 7.4 % (1,2,3-TMB) were obtained for most of the compounds. The first two eluting compounds dichloromethane and *trans*-DCE show very high relative standard deviations of 50 % and 31 %. These poor precisions can be explained by the low response factor of these compounds in a quadropol MS detector as well as the broad shape of their peaks caused by not optimal desorption conditions (lack of cryo focusing). The precisions for the other analytes were comparable to those obtained for the SPDE-GC/MS method for chlorinated hydrocarbons[10]. The precisions for high concentrations of analytes were determined by calculating the relative standard deviations (n=3) at the highest concentration level of the linear range. The obtained precisions without internal standard were in the range 1.0 % (DCA) to 18 % (DCM). Except the low precisions for dichloromethane and *trans*-DCE the precisions are comparable with other microextraction methods. [22]

Conclusions

The here reported results show that the ITEX-GC/MS method is suitable for the trace determination of volatile organic compounds in aqueous matrices. The effects of the governing parameters for the method optimization of ITEX is very similar to other in needle extraction techniques such as SPDE. The ITEX method is a very suitable alternative to solid-phase microextraction (SPME) because it provides lower fragility and longer extraction phase lifetimes as well as lower MDLs. A special advantage to the otherwise similar SPDE method is the external desorber around the needle body, which makes the ITEX method independent of the injector temperature profile.

Further investigations with other extraction phases such as Carboxen would most likely lead to lower method detection limits.

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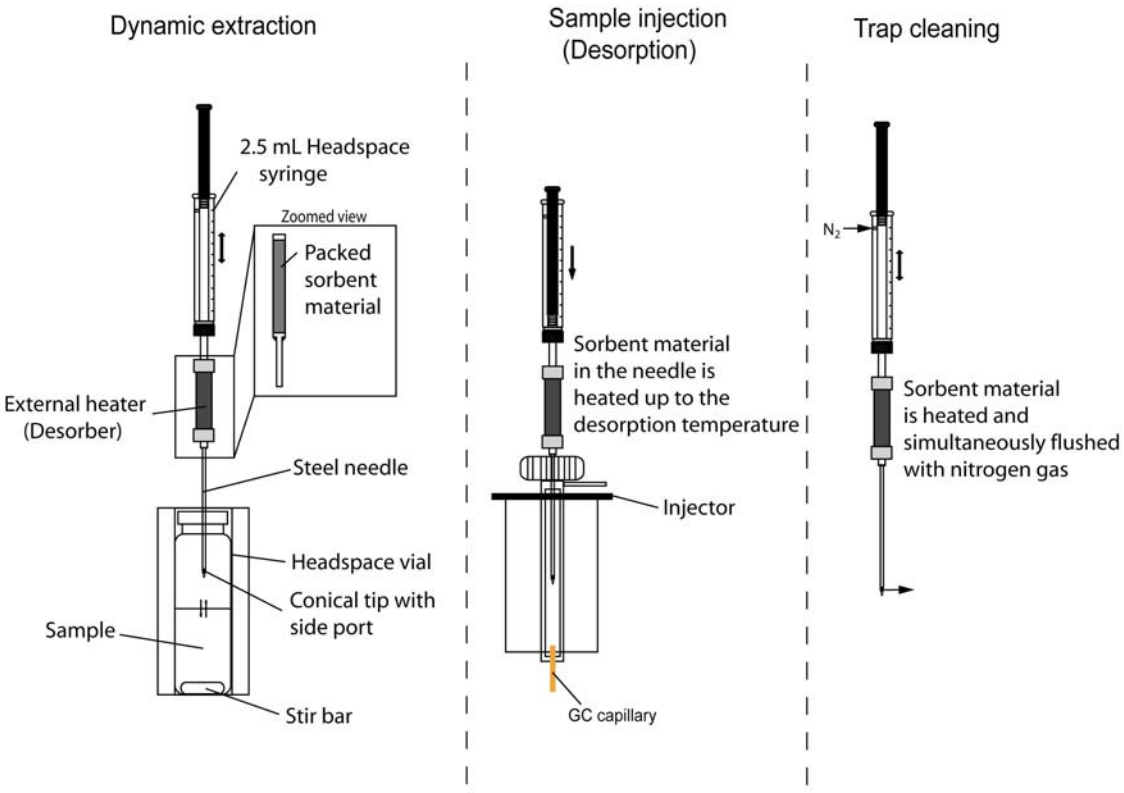

Figure 1 Schematic overview of the different operation steps of the ITEX method. The left part shows the dynamic extraction of the sample headspace. In the middle part, the thermal desorption into the injector by heating the desorber is shown. In the right part, the trap is cleaned by flushing the heated trap

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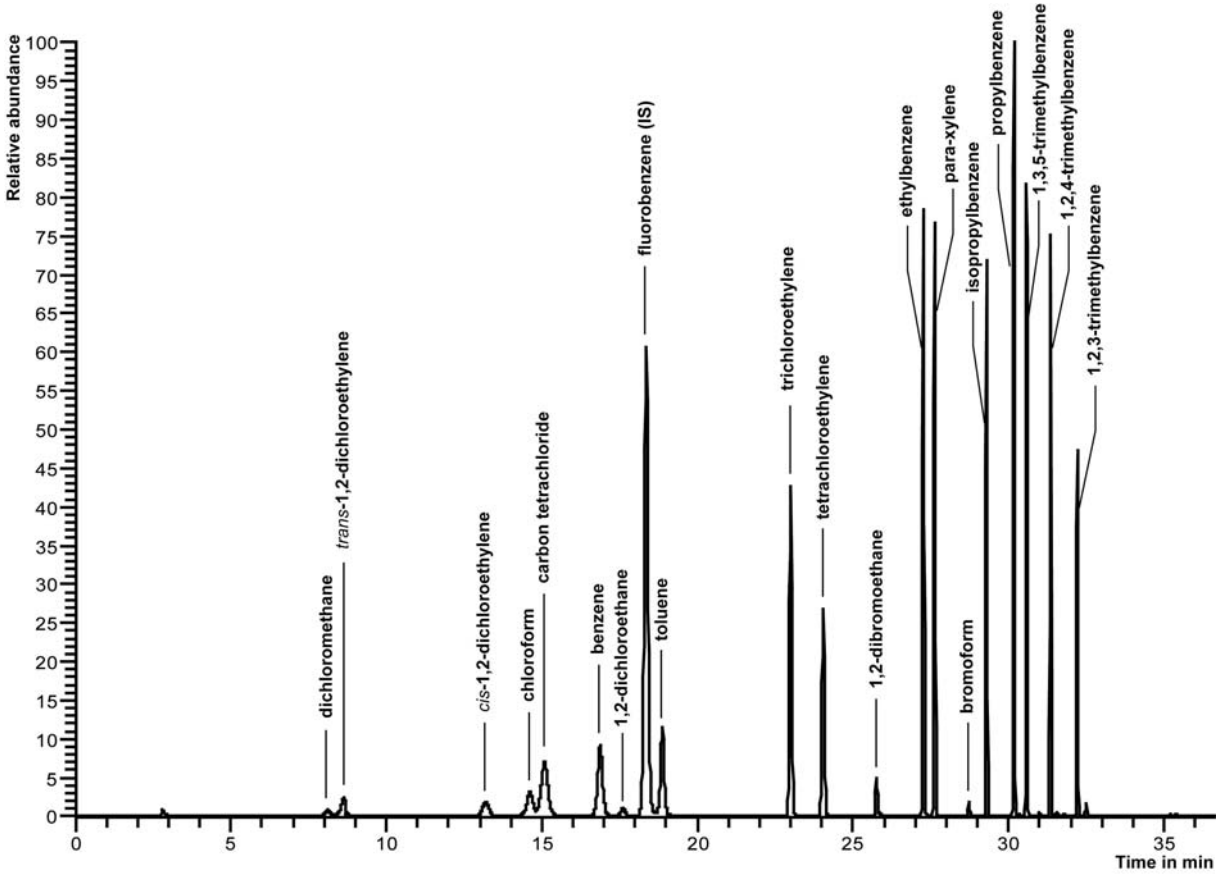

Figure 2 Full-scan chromatogram of the 19 chlorinated volatile hydrocarbons and BTEX target compounds with a combination of reconstructed ion chromatograms of a 5 µg/L standard solution under optimized conditions. Quantifier m/z and retention times are given in Table 2. Internal standard (IS) fluorobenzene with a retention time of 18.35 min (m/z = 96 and 70).

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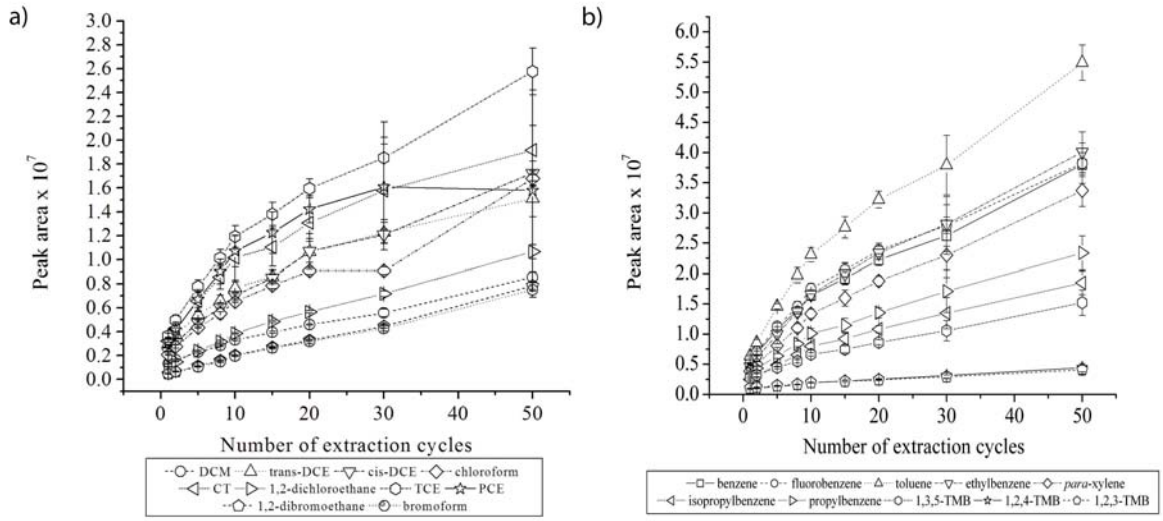

Figure 3 Extraction profiles for the investigated compounds at 30 °C for a) chlorinated hydrocarbons and b) aromatic hydrocarbons as a function of extraction time (i.e., extraction cycles) . Triplicate measurements were done for each point; error bars indicate the standard deviation.

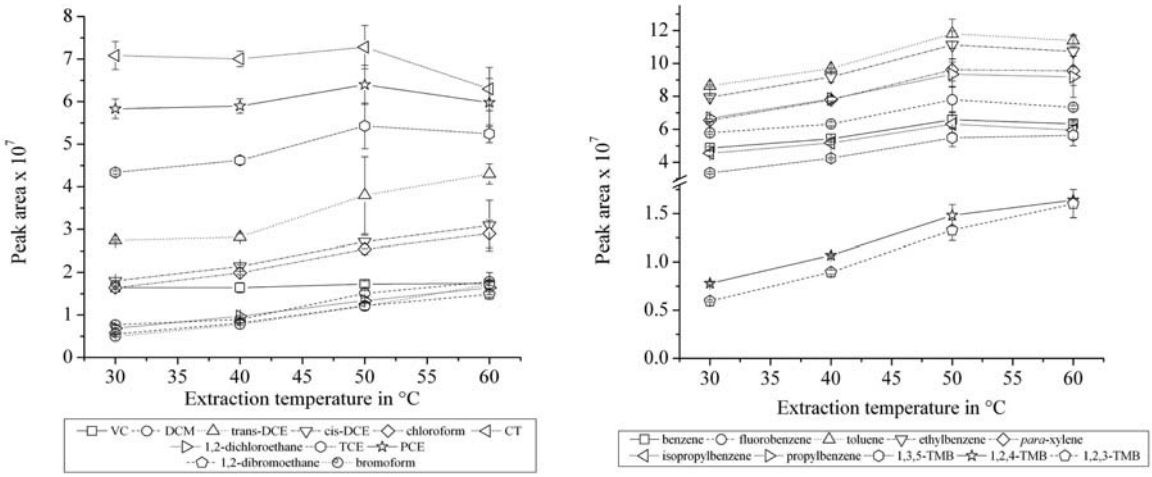

Figure 4 Dependency of extraction yield on extraction temperature for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

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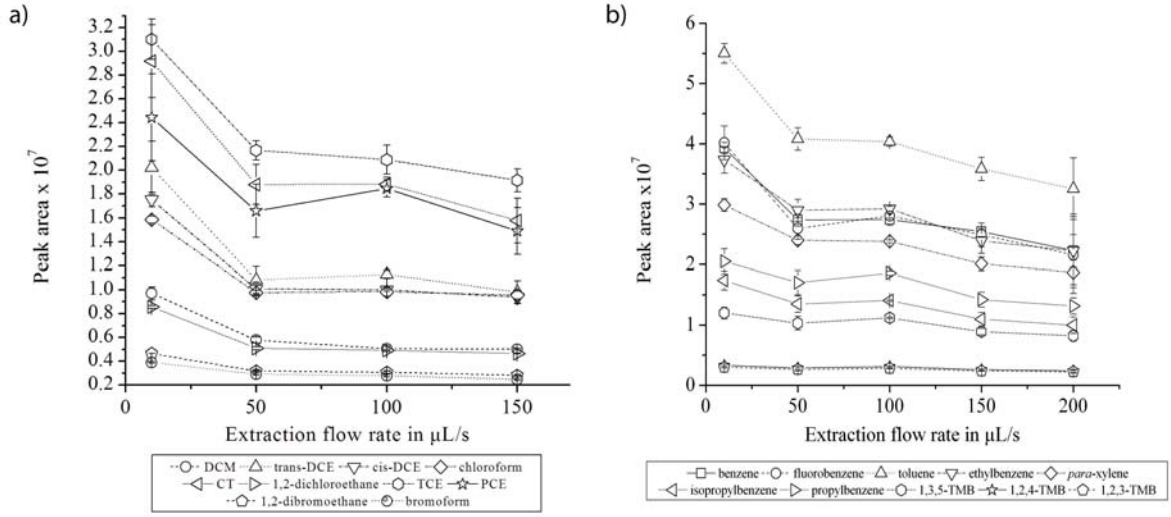

Figure 5 Dependency the extraction yield on extraction flow rate for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

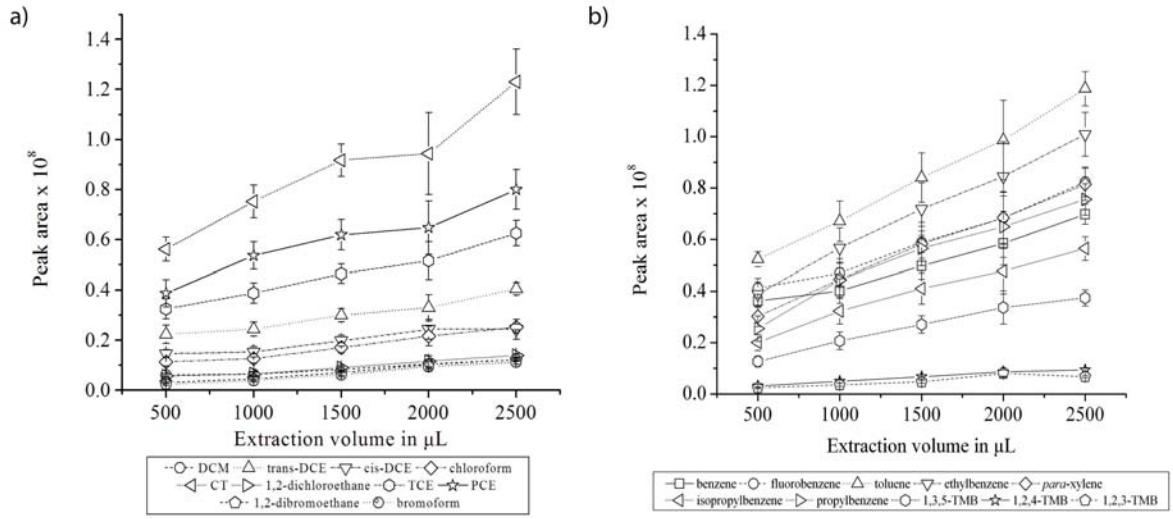

Figure 6 Dependency of extraction yield on extraction volume for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

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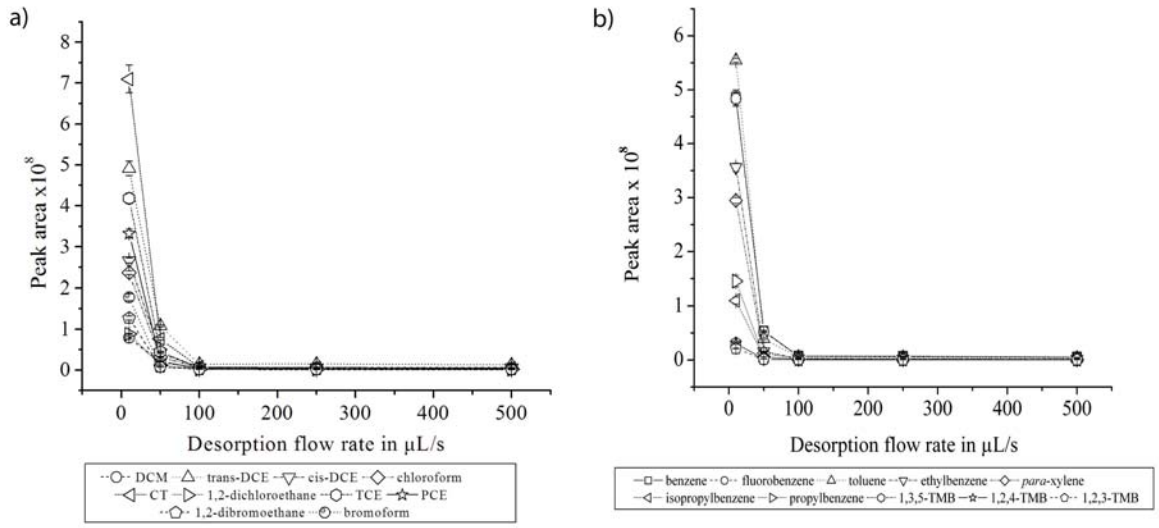

Figure 7 Dependency of peak areas on desorption flow rate for a)chlorinated hydrocarbons and b) monoaromatic hydrocarbons. Triplicate measurements were carried out for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

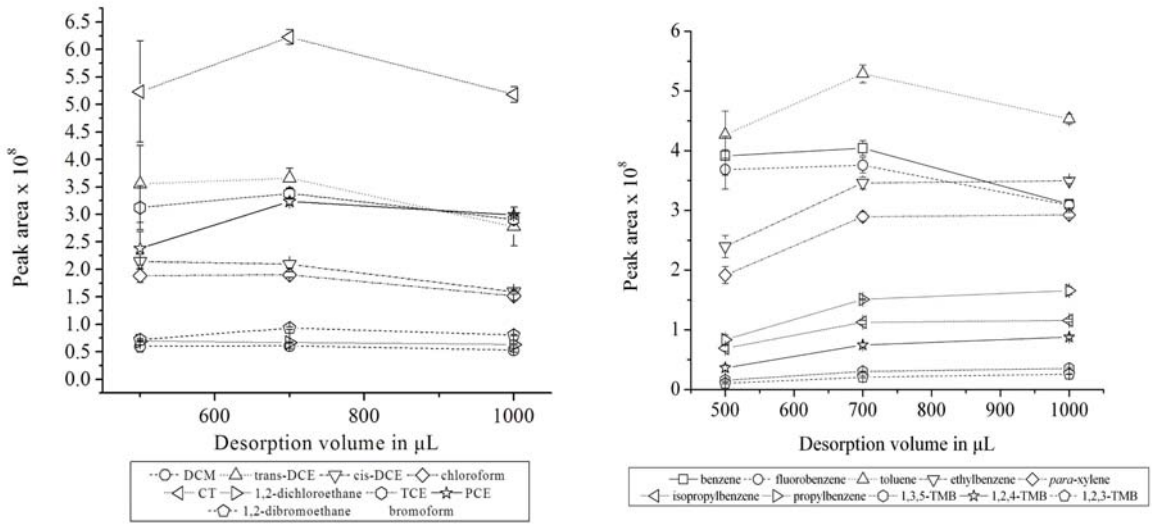

Figure 8 The diagrams show the dependency of desorption volume on extraction yield for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

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Table 1 Validation data of the ITEX-GC/MS method

Compounds in elution order	Target ions used for quantification (m/z)[a)]	Retention times (min)	Linear dynamic range (µg/L) without IS	R^2	MDL (ng/L) without IS [b)]	MDL (ng/L) with IS [b)]	Precision without IS (%)[c)]	Precision without IS (%)[d)]
DCM	84, 49	8.13	0.799 - 618	0.991	799	413	50	18
trans-DCE	96, 61	8.63	0.365 - 523	0.993	365	261	31	3.9
cis-DCE	96, 61	13.20	0.061 - 521	0.992	61	116	4.6	1.2
chloroform	83, 119	14.64	0.048 - 611	0.993	48	242	3.1	3.2
CT	117, 119	15.11	0.072 - 676	0.992	72	124	4.3	1.4
benzene	78, 51	16.88	0.036 - 360	0.992	36	44	4.0	1.3
DCA	62, 98	17.61	0.071 - 510	0.990	71	157	5.6	1.0
TCE	130, 95	18.83	0.049 - 602	0.990	49	71	3.2	2.0
toluene	92, 91	23.00	0.035 - 364	0.998	35	19	3.8	2.4
PCE	166, 131	24.04	0.057 - 683	0.992	57	67	3.3	3.1
EDB	107, 188	25.76	0.081 - 920	0.991	81	327	3.6	3.4
ethylbenzene	106, 91	27.25	0.028 - 360	0.998	28	24	3.1	1.9
para-xylene	106, 91	27.62	0.029 - 360	0.998	29	24	3.2	2.0
bromoform	173, 252	28.67	0.129 - 1218	0.992	129	418	4.3	4.2
isopropylbenzene	105, 120	29.30	0.041 - 362	0.990	41	50	4.4	2.7
propylbenzene	91, 120	30.14	0.048 - 361	0.992	48	62	5.5	2.1
1,3,5-TMB	120, 105	30.57	0.180 - 369	0.992	47	71	5.7	1.8
1,2,4-TMB	120, 119	31.35	0.047 - 359	0.991	47	67	5.2	2.0
1,2,3-TMB	120, 77	32.24	0.068 - 369	0.991	68	75	7.4	2.6

[a)] Base peak used for quantification is underlined.
[b)] (n = 7, fortification level 0.4 µg/L)
[c)] RSD at fortification level (n=7)
[d)] Relative standard deviation (n=3) at highest calibration level
IS: internal standard fluorobenzene with a retention time of 18.35 min (m/z = 9)

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Table 2 Comparison between MDLs of HS-ITEX-GC/MS and other micro enrichment methods. Note that different extraction phases as well as different MDL determination methods were used.

Method	**ITEX-GC/MS**	**SPDE-GC/MS**		**HS-SPME-GC/MS**				**HS-SPME-GC/ECD**	**P&T-GC/MS**
Extraction phase	**Tenax TA** [b]	**PDMS/AC** [b] [10]	**PDMS** [11]	**CAR/PDMS** [a] [24]	**PDMS** [b] [22]	**PDMS** [25]	**PDMS** [26]	**CAR/PDMS** [a] [19]	**Tenax** [a] [23]
DCM	799	119		1237					62
trans-DCE	365	12							
cis-DCE	61	12		38					
Chloroform	48	176		15	670	2960	1332	1.4	2
CT	72	19		632	450	2754	162		2
Benzene	36	13	400	8.8	200	528			2
DCA	71							3.7	2
TCE	49	13		73	280		730	1..3	10
Toluene	35		480	8.7		174			7
PCE	57	28		16			16.2	0.08	14
EDB	81			22					
Ethylbenzene	28			8.6					14
para-xylene	29								
Bromoform	129	22					86.7	0.3	27
isopropylbenzene	41								58
propylbenzene	48								
1,3,5-TMB	180			8.8					
1,2,4-TMB	47			8.8					
1,2,3-TMB	68								

[a] Signal to Noise ratio (S/N ≥ 3/1)

[b] MDL = $s_d \times t_{(0.99,\, f=6)}$

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