

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 desorption 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 then, 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 HPLC⁴ for the determination of chlorinated hydrocarbons⁵ and pesticides⁶. 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 amines⁷. 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 Kubinek¹². Another needle based device that uses a packed sorbent is the needle trap (NT) by Wang and Pawliszyn¹³ 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 dimethacrylate¹⁴. 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

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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 pollutants¹⁵,¹⁶ 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 carcinogens¹⁷.

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 %)

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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.

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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 desorber 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 procedure¹⁸ 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 $\mu\text{L/s}$ and 1000 μL , respectively. The desorption flow rate and extraction volume were held constant at 50 $\mu\text{L/S}$ 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 varied between 10 $\mu\text{L/s}$ and 150 $\mu\text{L/s}$ at otherwise constant method parameters (desorption volume: 1 mL; 15 extraction cycles; desorption flow rate: 50 $\mu\text{L/s}$). 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 $\mu\text{L/s}$, 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 $\mu\text{L/s}$ 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 $\mu\text{L/s}$ 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 $\mu\text{L/s}$, respectively. For desorption flow rates of 10 $\mu\text{L/s}$, a factor of 4 (DCM) to 26 times higher peak areas (ethylbenzene) than for 100 $\mu\text{L/s}$ 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

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HS-SPDE¹⁰ and with similar results reported in the literature.²⁰ Thus, in the parameter set of the optimized method a desorption flow rate of 10 $\mu\text{L/s}$ 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 hydrocarbons¹⁰ and alcohols²¹. 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 $\mu\text{g/L}$ 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

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found for HS-SPDE¹⁰. 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.

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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 hydrocarbons¹⁰. 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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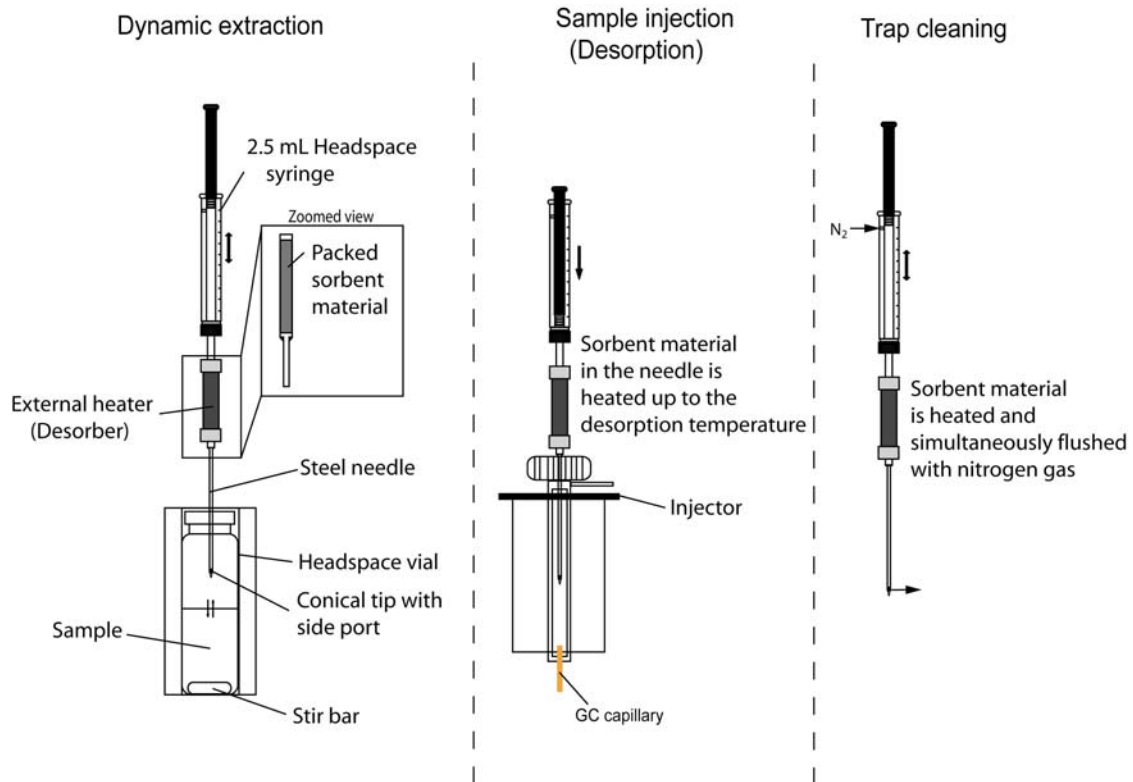


Figure 1 Schematic overview of the different operation steps of the ITEX method. The left part shows the dynamic extraction of the sample headspace. In the middle part, the thermal desorption into the injector by heating the desorber is shown. In the right part, the trap is cleaned by flushing the heated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

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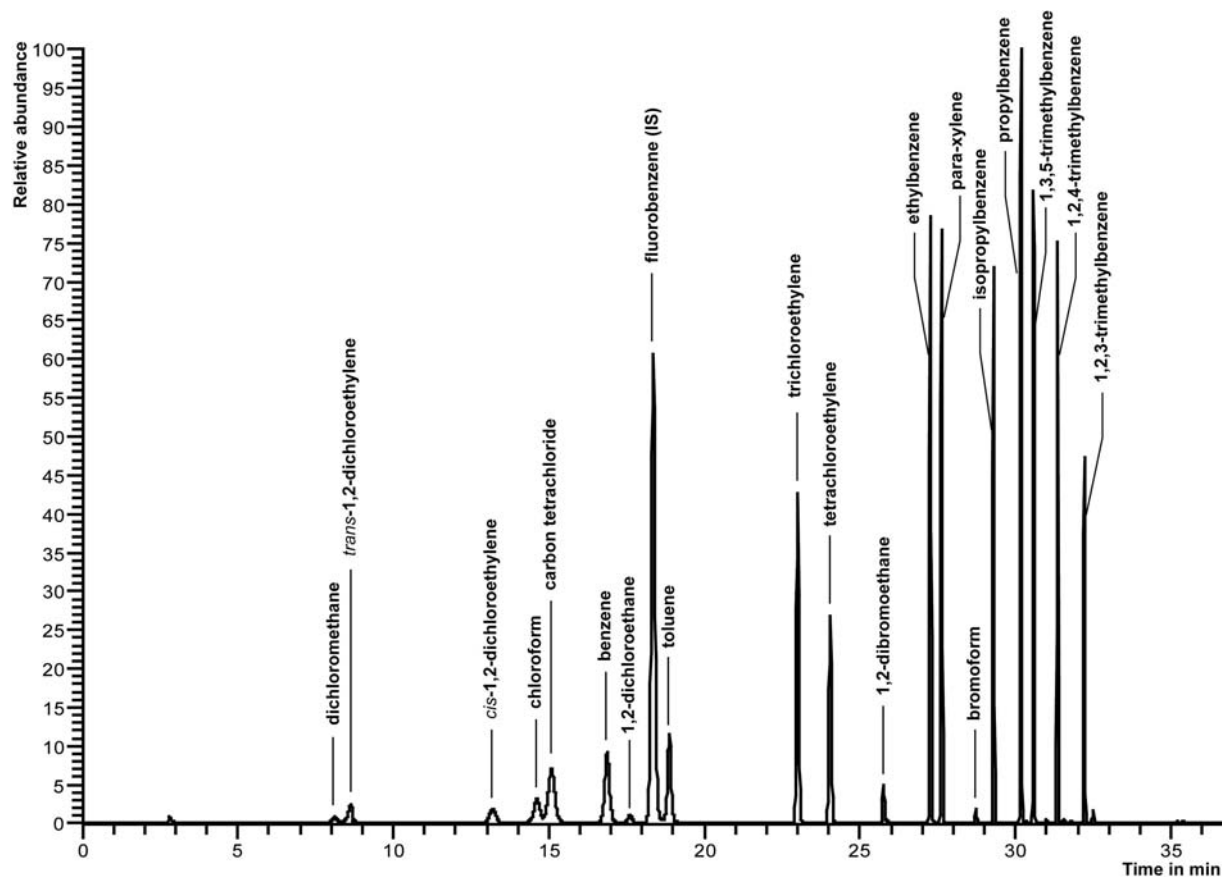


Figure 2 Full-scan chromatogram of the 19 chlorinated volatile hydrocarbons and BTEX target compounds with a combination of reconstructed ion chromatograms of a 5 $\mu\text{g/L}$ standard solution under optimized conditions. Quantifier m/z and retention times are given in Table 2. Internal standard (IS)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

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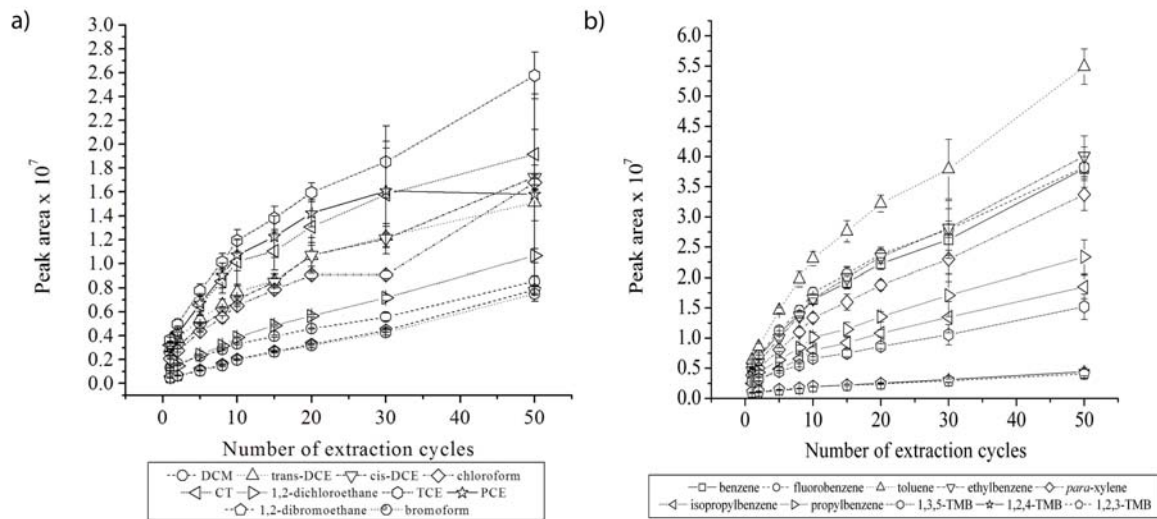


Figure 3 Extraction profiles for the investigated compounds at 30 °C for a) chlorinated hydrocarbons and b) aromatic hydrocarbons as a function of extraction time (i.e., extraction cycles). Triplicate measurements were done for each point; error bars indicate the standard deviation.

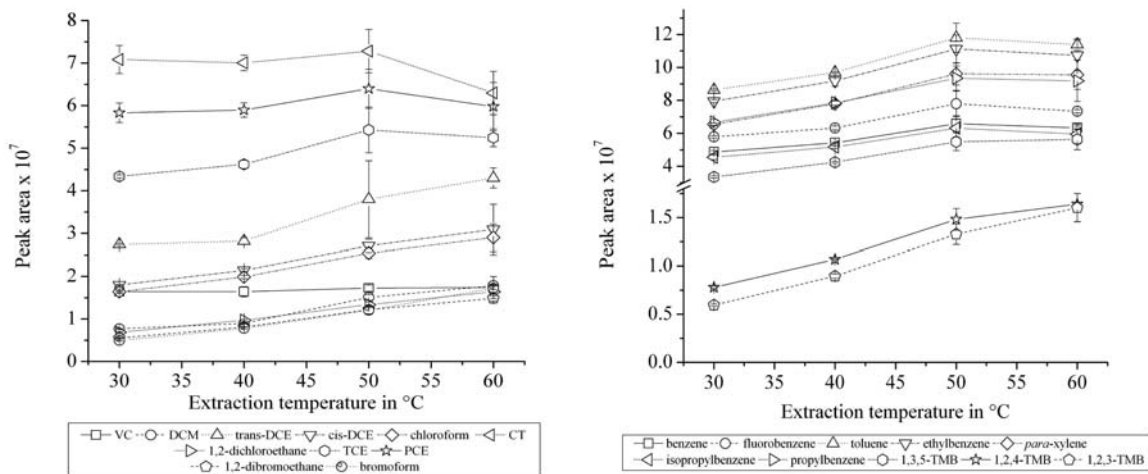


Figure 4 Dependency of extraction yield on extraction temperature for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

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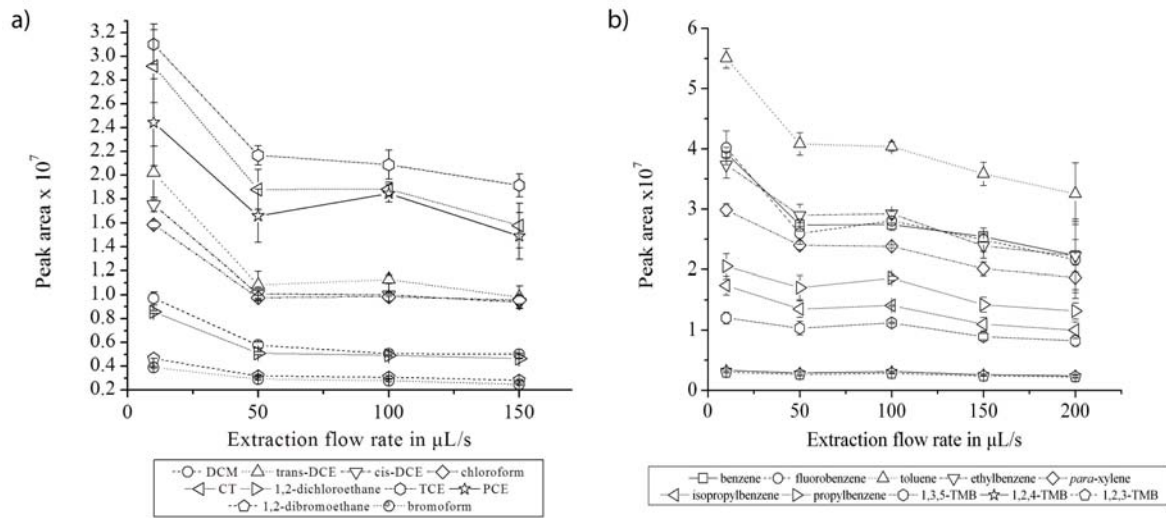


Figure 5 Dependency of the extraction yield on extraction flow rate for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

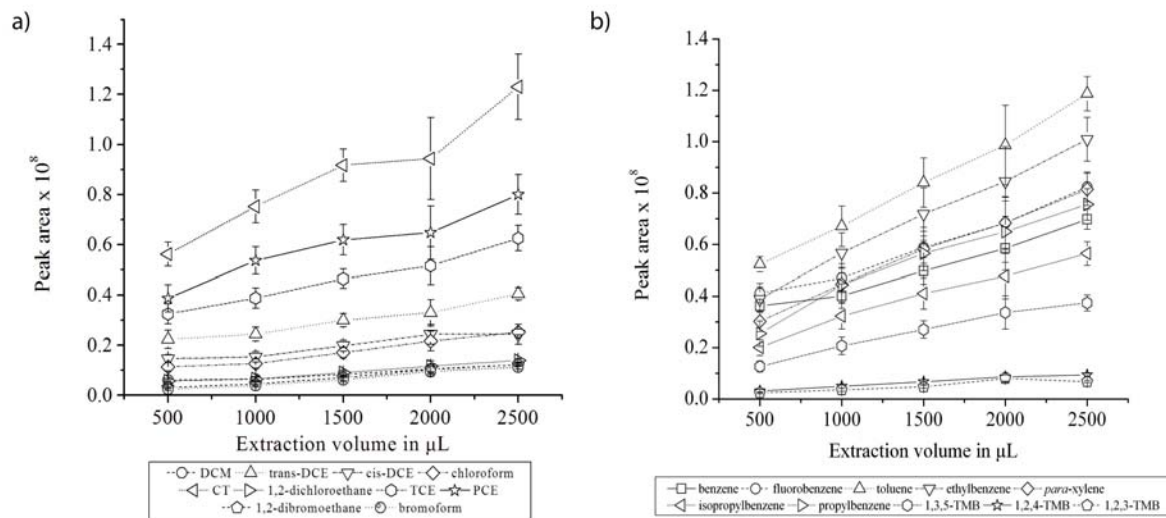


Figure 6 Dependency of extraction yield on extraction volume for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

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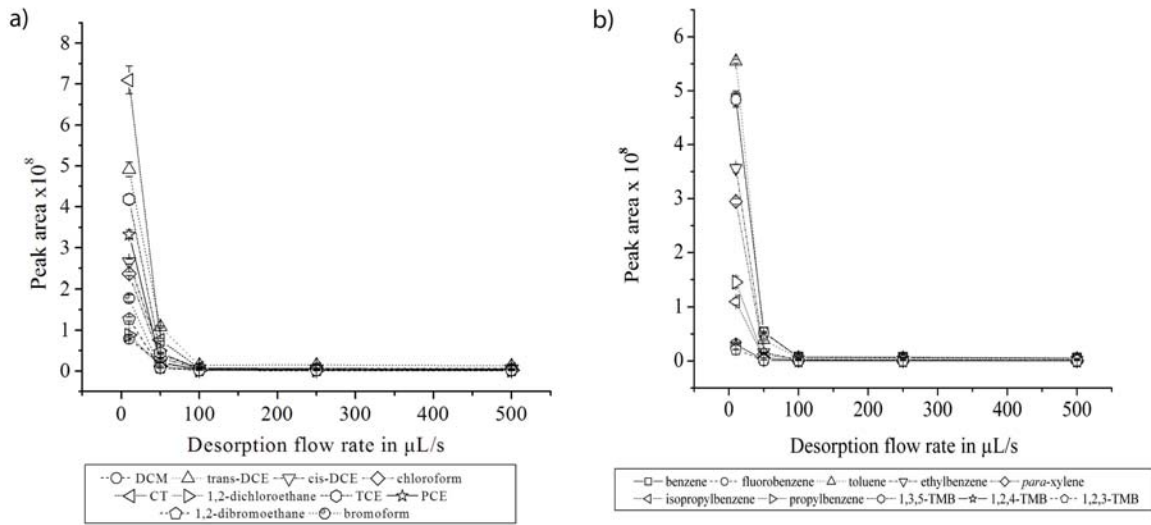


Figure 7 Dependency of peak areas on desorption flow rate for a) chlorinated hydrocarbons and b) monoaromatic hydrocarbons. Triplicate measurements were carried out for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

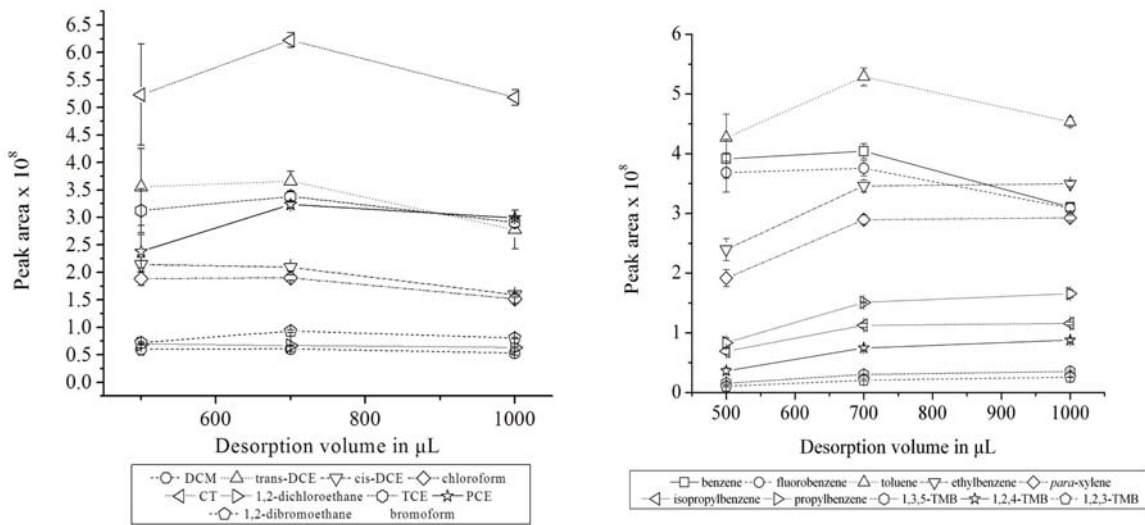


Figure 8 The diagrams show the dependency of desorption volume on extraction yield for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

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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	<u>84</u> , 49	8.13	0.799 - 618	0.991	799	413	50	18
<i>trans</i> -DCE	<u>96</u> , 61	8.63	0.365 - 523	0.993	365	261	31	3.9
<i>cis</i> -DCE	<u>96</u> , 61	13.20	0.061 - 521	0.992	61	116	4.6	1.2
chloroform	<u>83</u> , 119	14.64	0.048 - 611	0.993	48	242	3.1	3.2
CT	<u>117</u> , 119	15.11	0.072 - 676	0.992	72	124	4.3	1.4
benzene	<u>78</u> , 51	16.88	0.036 - 360	0.992	36	44	4.0	1.3
DCA	<u>62</u> , 98	17.61	0.071 - 510	0.990	71	157	5.6	1.0
TCE	<u>130</u> , 95	18.83	0.049 - 602	0.990	49	71	3.2	2.0
toluene	<u>92</u> , 91	23.00	0.035 - 364	0.998	35	19	3.8	2.4
PCE	166, <u>131</u>	24.04	0.057 - 683	0.992	57	67	3.3	3.1
EDB	<u>107</u> , 188	25.76	0.081 - 920	0.991	81	327	3.6	3.4
ethylbenzene	<u>106</u> , 91	27.25	0.028 - 360	0.998	28	24	3.1	1.9
<i>para</i> -xylene	<u>106</u> , 91	27.62	0.029 - 360	0.998	29	24	3.2	2.0
bromoform	<u>173</u> , 252	28.67	0.129 - 1218	0.992	129	418	4.3	4.2
isopropylbenzene	<u>105</u> , 120	29.30	0.041 - 362	0.990	41	50	4.4	2.7
propylbenzene	<u>91</u> , 120	30.14	0.048 - 361	0.992	48	62	5.5	2.1
1,3,5-TMB	<u>120</u> , 105	30.57	0.180 - 369	0.992	47	71	5.7	1.8
1,2,4-TMB	<u>120</u> , 119	31.35	0.047 - 359	0.991	47	67	5.2	2.0
1,2,3-TMB	<u>120</u> , 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
<i>trans</i> -DCE	365	12							
<i>cis</i> -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 ($S/N \geq 3/1$)

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

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