Journal of Separation Science

Title: **Sorbent-Packed Needle Microextraction Trap for Benzene, Toluene, Ethylbenzene, and Xylenes Determination in Aqueous Samples**

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Keywords: needle trap, adsorption, BTEX, SPME

Abstract

A needle trap (NT) device filled with Carbopack X as a sorbent material is evaluated for the static headspace analysis of benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds in aqueous samples. Injection parameters used with the NT device (e.g., volume of carrier gas and time to open the split valve) are evaluated to determine the mechanism involved during the desorption and transferring of the target compounds into the gas chromatographic column. Furthermore, different parameters affecting the adsorption capacity of the sorbent are studied (e.g., sampling time and temperature, headspace/sample volume ratio, salting-out, and stirring). The evaluation of the method with aqueous samples shows that repeatability and recoveries with the NT device are equivalent to those obtained using solid-phase microextraction (SPME) with a carboxen/polydimethylsiloxane (CAR/PDMS) coating. Limits of detection obtained with Flame Ionization Detection (FID) are in the 10-25 $\mu g \cdot L^{-1}$ range, and in the range of hundredths of $\mu g \cdot L^{-1}$ with MS detection. The method developed is satisfactorily applied to the analysis of aqueous samples obtained from wastewater treatment plants.

1. Introduction

Volatile organic compounds (VOCs) are a broad group of organic compounds that can be found as contaminants in waters and air at very low concentrations. These compounds, which may have short- and long-term adverse health effects, are originated by a wide range of products such as gasoline, paints and lacquers, cleaning supplies, pesticides, building materials and furnishings, glues and adhesives, and photographic solutions. Given this situation, the development of simple, robust, fast, and cost-effective analytical methodologies for the accurate determination of VOCs at trace levels in different environmental and biological matrices is of considerable interest. Since its introduction in the 1950s [1], static headspace (HS) sampling has become a routine sampling technique for determining VOCs from aqueous and solid samples. However, the equipment needed is not cheap and its sensitivity may not be sufficient for samples at low levels of the target VOCs. Static HS sampling is suitable for the analysis of samples containing higher levels of VOCs such as applications in the high $\mu g \cdot L^{-1}$ to percent concentration ranges [2] and the detection limits achieved are usually not sufficiently low as to comply with some environmental regulations (e.g., the technique cannot be used to measure benzene concentrations below 0.5–1 $\mu g \cdot L^{-1}$ in waters [3]). Recent developments in GC/MS hardware have resulted in higher sensitivity and lower detection limits, thereby allowing static HS to be considered for drinking and surface water analyses.

Solid-phase microextration (SPME) is an attractive, solvent-free, fast and simple alternative to conventional HS sampling. HS-SPME has become a well-established method for the analysis of VOCs in water and air samples [4]. When static HS and HS-SPME methodologies are compared, HS-SPME shows lower detection limits (between 1 and 2 orders of magnitude lower), better sensitivity and selectivity, and reduced

analysis times than static HS [5,6]. On the other hand, HS yields better analytical precision [6]. Another disadvantage of SPME is the limited number of commercially available stationary phases and the limited robustness of the fibers.

Since the late 1970s, when Raschdorf [7] developed the first device based on a needle filled with Tenax sorbent, in-needle extraction devices have become increasingly popular as they combine the advantages of SPME with robustness, easier handling during sampling and desorption whilst at the same time permitting a high degree of automation and on-line coupling to GC instruments [4]. There are currently three different experimental approaches for the preparation of in-needle extraction devices: (i) a needle filled with a sorbent material, this common set-up is called needle trap (NT) or inside needle capillary adsorption trap (INCAT) [8-17]; (ii) the use of a needle that has a sorbent material coated on its inner surface [18-20]; and (iii) the use of a body packed with a sorbent material and positioned between the needle and the syringe (in-tube extraction, ITEX) [21]. The two first approaches are experimentally less complex and the desorption process is performed by inserting the needle into the GC injector port, which does not require any external power requirements. The third option is commercially available [22] but has the disadvantage that requires an external thermal desorption unit to allow the desorption of the retained compounds before being moved to the GC injector. A simpler option with ITEX devices is to use of a small volume of solvent to desorb the compounds. This, however, will not result in a solventless injection and so target compounds with boiling points below or near the boiling point of the solvent used cannot be analyzed in this manner.

Needle trap (NT) devices have been satisfactorily used for the determination of different VOCs in air samples [10-12,17,18,20], for the analysis of airborne particulate matter and aerosols [16] and for the determination of VOCs in breath samples [14,15].

Published results suggest that NT is a more robust sampling device than a SPME fiber as the solvent particles are protected inside a steel needle [10] and that the technique has certain advantages for on-site sampling [12].

NT devices filled with Porapack Q [8,13] and Carbopack X [9] have been compared with SPME (using a PDMS-DVB coating) and purge-and-trap techniques in the analysis of BTEX in water samples. These studies concluded that the analytical characteristics of the NT devices are better than those of SPME and comparable with purge-and-trap techniques. Moreover, NT analysis is less expensive and sampling can be performed in the field. Needle traps with their inner surfaces coated with PDMS [19] and carbon [20] have also been used for the analysis of BTEX in aqueous samples. These studies also concluded that NT devices gave comparable results to static HS and for some compounds the detection limits were lower. Jochmann et al. [21] analyzed halogenated VOCs usually found as contaminants in groundwater and determined that the NT device is a highly suitable alternative to SPME due to its greater robustness, the longer extraction phase lifetimes and the lower detection limits.

This study is intended to show the feasibility of sampling BTEX in aqueous samples with a new NT device filled with Carbopack X. Two different SPME fibers were also evaluated and the results obtained with the NT device were compared with those obtained with the most appropriate SPME fiber for BTEX analysis. Different experimental parameters (e.g., sampling time, adsorption temperature, stirring, and injection conditions) were assayed with the NT device in order to find the most appropriate sampling and desorption conditions. Finally, the developed NT device was used in the analysis of aqueous samples from two wastewater treatment plants.

2. Experimental

2.1. Materials

Carbopack X (40/60 mesh) with a specific surface area of 250 $m^2 \cdot g^{-1}$ and a density of 0.41 $g \cdot mL^{-1}$ was obtained from Supelco (Bellefonte, PA, USA). Standards of benzene (99.8%), toluene (99.8%), ethylbenzene (99.8%), *o*-xylene (97%), and *p*-xylene (99.8%) were obtained from Sigma-Aldrich (Steinheim, Germany). HPLC gradient grade methanol was from Carlo-Erba Reagents (Milan, Italy). Milli-Q water from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA) was used. 20-gauge stainless steel (metal hub) needles (O.D. 0.91 mm, I.D. 0.60 mm, 51 mm length) with point style 2 were from Hamilton (Bonaduz, Switzerland). Small pieces of stainless steel screening (10 μm pore size, Supelco) were used to make the plugs and hold sorbent particles inside the needle. Vials, PTFE/silicone septum and caps were purchased from Supelco.

Methanolic stock solutions containing 100 $mg \cdot L^{-1}$ of each BTEX were prepared weekly and stored at 4ºC. Working samples were prepared daily by dilution of stock solutions in Milli-Q water.

Water samples were obtained from two wastewater treatment plants sited in Port de la Selva and Quart (Girona, Spain). Samples were obtained from influent, secondary treatment and effluent of the plants, and stored in glass bottles at -16ºC until the analysis.

2.2. Preparation of needle trap

The NT consisted of a 20-gauge needle and Carbopack X as a sorbent material. A small piece of stainless steel screen was cut and fixed inside the needle at approximately 35 mm from the end of the needle; the sorbent was then aspirated into the needle with the help of a vacuum pump until it reached the required position (at ~15 mm from the end

of the needle). Another small piece of stainless steel screen was used to immobilize the sorbent. The NT was conditioned in a GC injector at 300ºC for 3 hours with a permanent helium flow to remove impurities. Finally, the two ends were sealed with Teflon caps.

2.3. NT sampling

The sample solution was introduced in a closed screw-cap glass vial. The needle with the sorbent was inserted in the vial through a PTFE/silicone septum before placing it in a water-thermostated bath to perform static headspace extraction. Afterwards, the needle was removed from the vial and inserted into the injection port of the GC for thermal desorption and analysis.

2.4. SPME sampling

SPME was used as the benchmark method. Experiments were performed with a manual fiber holder with two different commercially available fiber coatings: a 100 µm polydimethylsiloxane (PDMS) and a 75 µm carboxen/polydimethylsiloxane (CAR/PDMS). The fiber holder and coatings were supplied by Supelco. Before use, each fiber was conditioned according to the manufacturer's instructions. Sample solution (5 mL) was introduced into a 15 mL screw-cap glass vial. The vial was closed and put over a magnetic stirrer (Variomag®) in a water-thermostated bath. Magnetic stirring (medium speed) was employed during the extraction using a PTFE-coated stir bar. The solution was allowed to equilibrate at a fixed temperature for 30 minutes before introducing the SPME fiber. After equilibration, the fiber was exposed to the headspace generated in the sample vial for 15 minutes. The fiber was then removed

from the vial and inserted into the injection port of the GC for thermal desorption and analysis.

2.5. GC analysis

Component separation was achieved by the use of a 30 m long non-polar 5% phenyl 95% dimethylpolysiloxane column with 0.25 mm ID and 0.25 μm film thickness (DB-5, J&W Scientific, Folsom, CA, USA for FID applications; and BPX5, SGE Analytical Science, UK for MS applications). For the evaluation of the SPME fibers and the NT device performance, a GC 8000 series (Fisons Instruments, Milano, Italy) with an FID at 250ºC was used. For the analysis of water samples, a Focus GC (Thermo Scientific, Waltham, MA, USA) with a mass spectrometer detector (DSQ II, Thermo Scientific) was used.

The oven temperature program was: (i) 40ºC held for 2 min, then ramped at 5ºC/min to 200ºC and held for 2 min for FID applications; (ii) 40ºC held for 2 min, then ramped at 15ºC/min to 250ºC and held for 2 min for MS analyses. Helium carrier gas was used, with a constant inlet low of 0.8 $mL \cdot min^{-1}$ (GC-MS) or constant inlet pressure of 15 psi (GC-FID), after purification for water vapor, hydrocarbons, and oxygen. MS analyses were carried out in full-scan mode, with scan range 40-200 amu, electron impact ionization was applied at 70 eV, and the transfer line was maintained at 230ºC.

The acquisition of chromatographic data was performed by means of (i) Xcalibur software in GC-MS (v. 1.4, Thermo Electron) and (ii) Chrom-Card for Windows in GC-FID (v. 3.1, CE Instruments, Milan, Italy).

3. Results and Discussion

3.1. NT design

A NT device with Carbopack X as the adsorbent material filling the inside of the stainless steel needle was developed. Other NT devices developed for the analysis of aqueous samples are based (i) on static HS [19,20], (ii) on dynamic HS (purge and trap) sampling [8,9,19-21] and (iii) directly by allowing aqueous samples to pass through the sorbent [13]. The use of water vapor [8] or allowing aqueous sample to pass through the sorbent [13] have been reported as helping to obtain clean and sharp chromatograms. However, these options have been rejected in this study due to their potential weaknesses [4,12] and the fact that it has been demonstrated that polar compounds (e.g., alcohols) cannot be quantitatively retained by carbon-based sorbents when considerable amounts of water are present in the sample [23].

The NT device prepared in this study did not allow the use of dynamic HS sampling as the trap's pneumatic restrictions were too great to allow a constant flow, at an appropriate flow rate, of a purge gas through the sorbent material. This resulted in an excess of pressure inside the vial and, consequently, inadequate sampling. Static (passive) HS was therefore selected as the sampling procedure for this study.

3.2. Evaluation of the NT injection/desorption parameters

3.2.1. Influence of the gas volume of carrier gas

When the in-house NT developed was evaluated applying injection conditions equivalent to those usually used with SPME, chromatograms showed a large early peak with severe tailing, which resulted in benzene and toluene not being detected because they co-elute in the tail of the early peak. This indicated that the experimental parameters to be used with the NT device cannot be equivalent to those applied with SPME injections.

Similarly to SPME, the needle trap device developed makes use of the GC injector for the thermal desorption of the compounds retained on the sorbent. The sample transfer into the GC column to produce sharp bands with minimum or no carryover is one of the limiting steps of these devices and the use of a small volume of a carrier gas to transfer the desorbed compounds to the GC column is the simplest approach [12,16]. When the NT was positioned in the injector and no volume of carrier gas (clean air) was used, peaks obtained showed small peak heights and excessive tailing. The use of small volumes of clean air (0.1 to 1.0 mL) resulted in a significant increase in the peak height for all BTEX compounds analyzed (Figure 1), but there was still considerable tailing. Excessive volumes of clean air (5 mL) yielded smaller peak heights as the gas volume introduced exceeded the total volume of the 3 mm ID liner (~1 mL) and a large amount of the sample was lost. A volume of 0.2 mL of carrier gas was selected for subsequent analyses.

3.2.2. Effect of the time to open the split valve after the thermal desorption of the analytes from the NT

As in the case of SPME, splitless injection is preferred with NT devices because this is also a solventless methodology. To facilitate desorbed analytes being removed rapidly from the injector, a high linear flow rate of the carrier gas around the fiber is required in SPME [24]. This is normally accomplished by using narrow liners with internal diameters (0.8 - 0.9 mm ID) as close as possible to the outer diameter of the fiber. This would also be the most adequate procedure with a needle trap. However, one of the drawbacks of using a 20-gauge needle is its outer diameter (0.91 mm), which required the use of a conventional 3 mm ID liner in the GC injector. The use of such a liner did not permit the production of linear flow rates that were high enough to obtain sharp

injection bands. The use of higher gauge needles (i.e., smaller OD) would allow the use of smaller ID liners (0.8 - 0.9 mm ID), which would help in obtaining sharper injection bands.

One way to create high linear flow rates in the injector port with 20-gauge needles and 3 mm ID liners is to open the split valve rapidly after the desorption of the analytes. When done in this way, it is necessary to guarantee that all target compounds are quantitatively desorbed from the sorbent material before opening the split valve. BTEX compounds have boiling points ranging from 80.1ºC (benzene) to 139.1ºC (*m*-xylene). Their quantitative desorption from SPME fibers requires just a few seconds (e.g., naphtalene, b.p. 80ºC, is completely desorbed from PDMS fibers in ~12 seconds [25]; some studies performed in our laboratory suggest the complete desorption of BTEX compounds from a CAR/PDMS fiber is performed in less than 10 seconds). In the case of the carbon-based sorbent used in the NT, quantitative thermal desorption of BTEX is considerably faster and requires less than one second at desorption temperatures above 250ºC [26]. The evaluation of different times to open the split valve after injection (Figure 2) showed that reduced tailings and peak widths were obtained for all BTEX when the split valve was opened after 1-2 seconds of injection. Larger times resulted in increased peak widths and tailing for all the compounds evaluated. A splitless time of two seconds was selected for subsequent analyses.

3.2.3. Influence of the desorption temperature and time

The desorption temperature and time were investigated for the analysis of BTEX. When the injector temperature was ≥ 250ºC and the NT was maintained in the injector for 2 minutes, desorption was complete and no carryover was observed with the NT device developed.

3.3. Evaluation of the extraction conditions for the NT device

3.3.1. Sampling time

The use of static (passive) HS sampling requires the effect of sampling time and adsorption temperature to be evaluated. Static sampling is favored by an increase in the sampling time to help VOCs to diffuse through the sorbent. As can be seen in Figure 3, the amount of compounds retained by the Carbopack X sorbent increased as the sampling time was lengthened up to 50 minutes. At the sampling temperature evaluated (30±1ºC), equilibrium was reached at 50 minutes, and only benzene showed a slight increase in its sorption when sampling was at 60 minutes.

3.3.2. Extraction temperature

Another important parameter to be taken into account is the extraction temperature. Figure 4 shows the results obtained in the extraction capacity of BTEX at different extraction temperatures for the NT developed and their comparison with the results obtained for two commercial SPME fibers.

Extraction with a PDMS fiber is based on an absorption mechanism, which is an exothermic process whereby an increase in temperature leads to a decrease in partition coefficients [5]. This results in a decrease in the absorption capacity with the PDMS fiber at increased temperatures (Figure 4a) and practically no absorption at temperatures above 90ºC (<5% absorption for all BTEX compared to values obtained at 30ºC). For this reason, absorption at room temperature is recommended for the analysis of BTEX with this coating [5].

The results obtained with carbon-based sorbents, such as the CAR/PDMS fiber in SPME (Figure 4b) and the Carbopack X sorbent with the NT (Figure 4c), showed

equivalent behaviors for both devices, which are significantly different from those obtained with the PDMS fiber. Compounds are retained by an adsorption mechanism with carbon-based sorbents. In this situation, an increase in the extraction temperature enhances the amount of analytes present in the headspace of the sampling vials, which favors the adsorption by the sorbent. At the same time, increasing the temperature improves the desorption of VOCs from the sorbent surface, which might decrease the amount of compounds being retained. The results obtained showed an increase in the adsorption of all BTEX compounds when the temperature was increased until a maximum was reached, and then the adsorption decreased. For the most volatile compound (benzene), maximum adsorption was reached at low temperatures (around 40ºC for the NT device and 50ºC for the CAR/PDMS SPME fiber). For the intermediate volatile (toluene), the desorption process had no significant effect with temperature values of up to 70ºC. For the less volatile compounds (xylenes), adsorption did not decrease until temperatures were above 70ºC. A compromise temperature had to be chosen for the analysis of VOCs with different volatility ranges when carbon-based sorbents were used in order to obtain the most appropriate extraction percentages for all compounds. This was set at 50ºC for subsequent analyses to ensure that the most volatile compounds were appropriately extracted.

3.3.3. Headspace/sample volume ratio

The compounds evaluated in this study are highly volatile, and, as such, tend to accumulate in the headspace, resulting in a substantial loss of sensitivity when the headspace volume is excessive [24]. The evaluation of the headspace/sample volume ratio used during the extraction process with the NT showed that a decrease in this ratio yielded higher amounts of analytes being adsorbed (20% at 2:1 ratio, 38 % at 1:2 ratio,

and 100% at 1:5 ratio, percentages normalized at the maximum extraction obtained). Decreased headspace/sample volume ratio results in higher concentrations of molecules in the headspace phase. Therefore, when static (passive) headspace sampling of BTEX with NT devices is performed, a headspace/sample volume ratio around 0.2 is recommended (lower ratios make it more difficult to position the needle in the headspace volume of the vial without coming into contact with the aqueous solution).

3.3.3. Salting-out and stirring effects

Salting-out effects were also evaluated by analyzing samples saturated with sodium chloride. No significant differences were found in the recoveries between aqueous samples without the addition of sodium chloride (n=3) and those saturated with this salt (n=3) for toluene (P=0.137), *p*-xylene (P=0.157) and *o*-xylene (P=0.122). Benzene gave slightly significant lower recoveries in the saturated samples (P=0.032). Similar behavior has also been described for the HS-SPME analysis of these compounds [6]. Consequently, no salt was added for subsequent experiments.

Stirring of the aqueous solutions is also not recommended as the results obtained showed that there were no significant differences in the recoveries for toluene (P=0.148), *p*-xylene (P=0.169) and *o*-xylene (P=0.332). Benzene gave significantly lower recoveries (P=0.014) with the stirring of the aqueous sample.

3.4. Validation of the NT methodology

Linearity ranges and detection limits (LODs) for the NT device were evaluated. Linearity in the 50-300 $\mu g \cdot L^{-1}$ range was confirmed for all BTEX from the residual plots obtained by the calibration curves. LODs were experimentally determined by analyzing samples (n=6) at reduced concentrations. The calculated standard deviations

for each compound was taken as the standard deviation of the blank. IUPAC 3σ criteria were used to determine LODs, which were 25 $\mu g \cdot L^{-1}$ for benzene and 10 $\mu g \cdot L^{-1}$ for the other compounds (FID detection). These values are about one order of magnitude higher than those obtained with HS-SPME sampling (1 $\mu g \cdot L^{-1}$ for benzene and 0.5-0.3 $\mu g \cdot L^{-1}$ for the other VOCs), although the use of dynamic HS sampling instead of static HS would considerably decrease the LODs obtained with a NT. Unfortunately, the NT device developed cannot be used with dynamic HS and further attempts to prepare a NT that will allow this sampling methodology are being tested in our laboratory.

The NT methodology was evaluated by analyzing fortified water samples at 100 $\mu g \cdot L^{-1}$ for each compound (Table 1). Recoveries obtained are in agreement with the "single laboratory validation guidelines" of the AOAC [27] that set an acceptable recovery range of between 70-125% at this concentration level. Repeatability values ranged from 1 to 8%, which are of the same order as those obtained with HS-SPME (6-10%). These values are all in agreement with the theoretical values determined from the Horwitz curve at this concentration level (16% for 1 $mg \cdot L^{-1}$) [28-30] and with the recommended limits proposed by AOAC (~15%) [27].

3.5. Analysis of wastewater samples

The NT method developed was applied to the analysis of samples obtained from a wastewater treatment plant. The analysis of these samples was performed using MS detection to allow the quantification of the compounds given that they appear at concentrations below the LODs obtained with FID in many samples. LODs obtained with MS detection in analyzing environmental aqueous samples were in the range of hundredths of $\mu g \cdot L^{-1}$. Figure 5 shows the results obtained in the analysis of an influent

sample. Here, benzene was not detected (peak #1) and all other compounds were detected at concentrations from 0.1-0.5 $\mu g \cdot L^{-1}$.

3.6. Comparison between NT and HS-SPME

A PDMS/CAR fiber was used for comparison with the NT device as this fiber has been considered to be the most appropriate in the analysis of BTEX compounds [31,32]. As indicated in the "extraction temperature" section a compromise extraction temperature of 50ºC is appropriate with this fiber (Figure 4b).

SPME results have shown two advantages with respect to the NT developed. First, a shorter extraction time is needed with HS-SPME (i.e., 10 minutes were enough to reach equilibrium). Second, LODs are around one order of magnitude lower. Figure 6 shows the HS-SPME GC-FID analysis of water samples from a wastewater treatment plant. As can be seen, the use of a CAR/PDMS fiber allowed the detection of BTEX in the influent sample. Benzene and toluene were not detected after the secondary treatment and no BTEX were detected in the effluent. Many other unknown VOCs were detected in the samples, some of which were not completely eliminated after the tertiary treatment. However, the use of FID detection did not allow the identification of these compounds.

Both methodologies, NT and SPME, were successfully applied in the analysis of the wastewater samples and the same qualitative behavior was observed: a decrease in the levels of BTEX after the different treatments, and no BTEX were detected in the effluents. The NT methodology was only able to quantify some BTEX in the influent samples, but it was not possible to determine their levels in the other two sampling points of the plants. The SPME methodology allowed some of the compounds to be quantified after the secondary treatment.

4. Conclusions

A new needle trap device filled with Carbopack X as a sorbent material has been developed and successfully applied to the analysis of aqueous samples from wastewater treatment plants in this study. Comparison with HS-SPME reveals NT still presents some disadvantages over conventional HS-SPME. However, it should be noted that SPME is a well-established analytical methodology whereas NT still requires considerable development. The good results obtained with the NT developed in this study would seem to indicate that NT could be a useful, robust and economic alternative to conventional HS or HS-SPME.

One advantage of NT devices is their robustness in comparison with SPME. The NT developed has been applied in more than 200 analyses without any loss in resolution and reproducibility being detected. Moreover, other similar micro-traps developed in our laboratory [23,26] have been used for more than 1000 analyses without any analytical difficulties. More exhaustive work is needed to develop NT devices that allow dynamic HS sampling.

Acknowledgements

We gratefully acknowledge the financial support of the MICINN (project # CTM2008-06847-C02-02/TECNO). M. Alonso acknowledges the Spanish Ministry of Education for her research grant (FPU program, # AP2008-01628).

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Table 1. Recoveries obtained with the CAR/PDMS fiber and the NT device in the analysis of fortified water samples (GC-FID analysis).

Compound	benzene	toluene	*p*-xylene	*o*-xylene
	SPME (samples fortified at 30 μg·L^{-1} each compound)			
n	4	4	4	4
Recovery (%)	103	116	123	125
Repeteability (%)	10	6	7	7
	NT (samples fortified at 100 μg·L^{-1} each compound)			
n	3	3	3	3
Recovery (%)	95	108	93	89
Repeteability (%)	7	1	8	8

Figure Captions

Figure 1. Influence of the gas volume of carrier gas used to transfer the desorbed compounds from the NT device to the GC column. Experimental conditions: 500 $\mu g \cdot L^{-1}$ standards, 15 minutes sampling at 30ºC, 3 mm ID liner.

Figure 2. Effect of the time to open the split valve after the thermal desorption of the analytes from the NT. Experimental conditions as in Figure 1.

Figure 3. Sampling heating time profiles for BTEX analysis by static HS-NT. Experimental conditions as in Figure 1, 0.2 mL carrier gas volume to transfer the compounds, 2 seconds to open the split valve, adsorption temperature = 50ºC.

Figure 4. Influence of the extraction temperature on the sensitivity of the analysis (values normalized at the peak areas obtained at 30ºC) . (a) SPME analysis with PDMS fiber, (b) SPME analysis with CAR/PDMS fiber, and (c) NT device.
Experimental conditions for SPME analysis: 10 minute extraction, standard at 50 $\mu g \cdot L^{-1}$, 3 replicates at each temperature.
Experimental conditions for NT device: 50 minutes adsorption, standard at 500 $\mu g \cdot L^{-1}$, 3 replicates at each temperature.

Figure 5. Static HS-NT GC-MS analysis of an influent sample from a wastewater treatment plant in Quart (Girona, Spain). 1: benzene, 2: toluene, 3: ethylbenzene, 4: *m-, p*--xylene, 5: *o*-xylene.

Figure 6. HS-SPME GC-FID analysis of samples from a wastewater treatment plant in Port de la Selva (Girona, Spain). (a) influent, (b) after secondary treatment and (c) after tertiary treatment. 1: benzene, 2: toluene, 3: ethylbenzene, 4: *m*-, *p*-xylene, 5: *o*-xylene. Experimental conditions: CAR/PDMS fiber, absorption at 50ºC for 15 minutes.

Figure 1

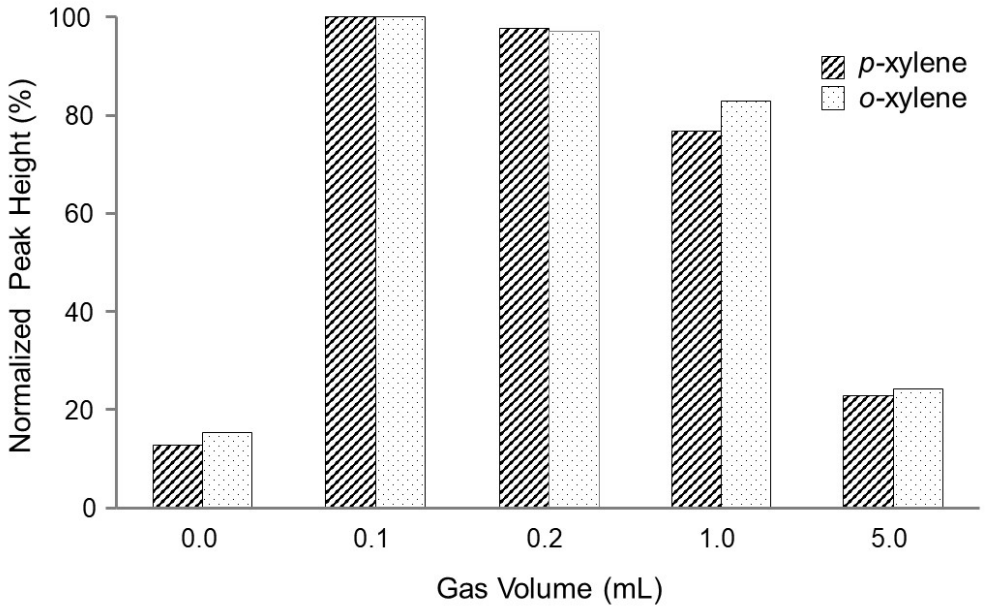

Figure 2

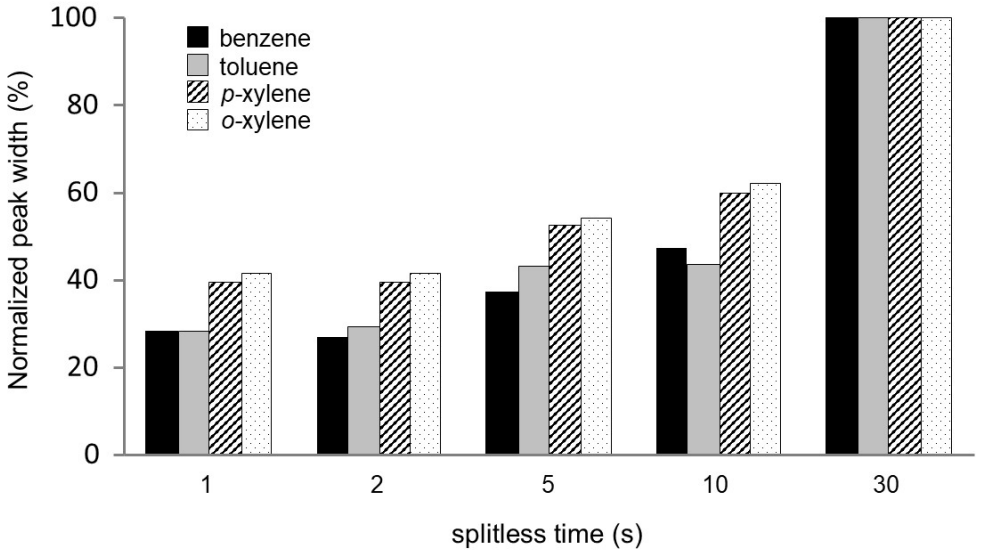

Figure 3

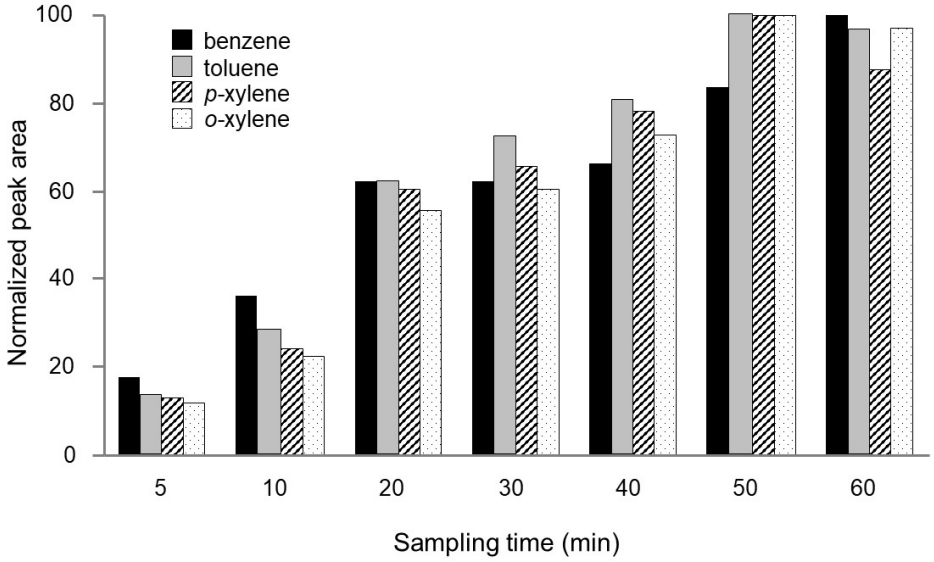

Figure 4

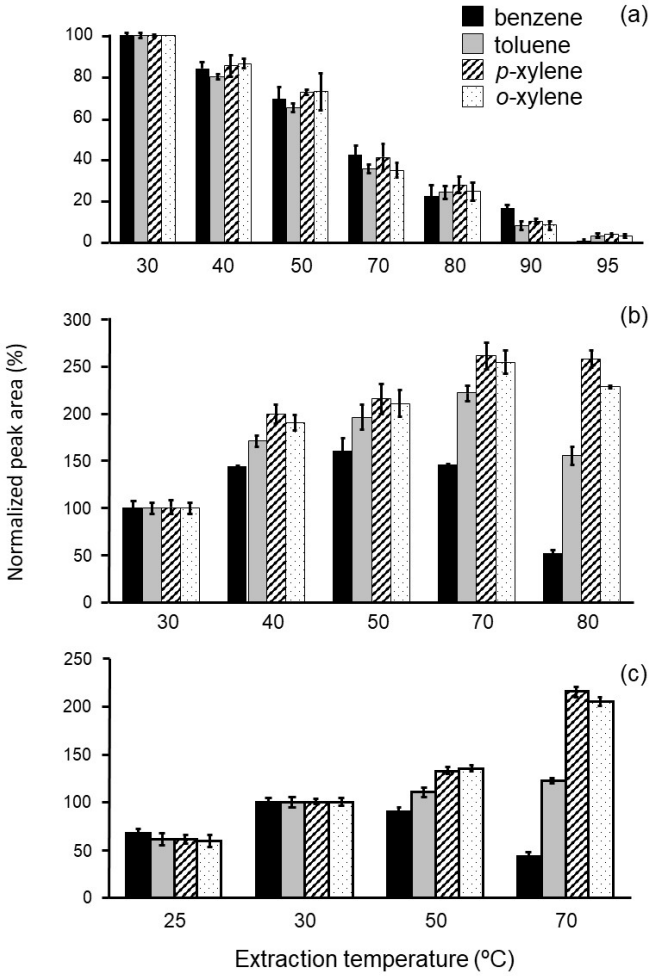

Figure 5

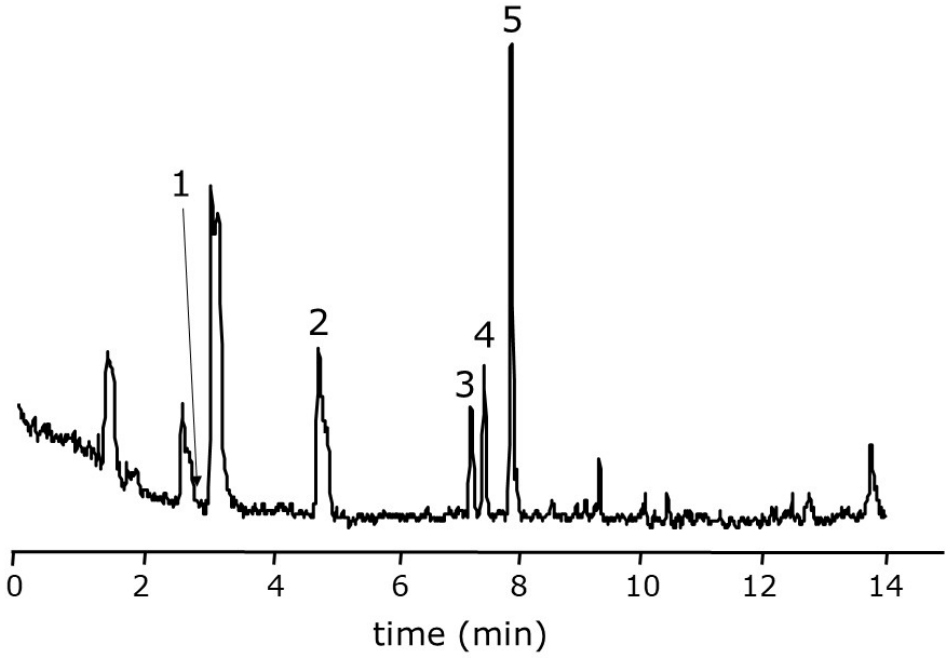

Figure 6