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Sorbent-packed needle microextraction trap for synthetic musks determination in wastewater samples

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Abstract

A needle trap (NT) device filled with HF Bondesil-C18 as a sorbent material was evaluated for the dynamic headspace analysis of a family of nine synthetic musks compounds that include two nitro musks, six polycyclic musks (with galaxolide and tonalide as the most widespread used polycyclic musks) and the degradation product of galaxolide (galaxolidone) in wastewater samples. Different parameters affecting the adsorption capacity of the sorbent were studied (*e.g.* extraction mode, extraction temperature, salt concentration, preincubation time fill and ejection speed or fill volume). Furthermore, injection parameters used with the NT device (*e.g.* desorption mode, desorption temperature and time) were evaluated to optimize the desorption and transfer of the target compounds into the GC column. Method detection limits obtained with gas chromatography-tandem mass spectrometry (GC-MS/MS) detection were found in the low ng L^{-1} range, between 2.5- 10 ng L^{-1} , depending on the target compounds. Moreover, under optimized conditions, the method gave good levels of intra-day and inter-day repeatabilities in wastewater samples with relative standard deviations ($n=5$, 100 ng L^{-1}) less than 11 and 17%, respectively. The developed method was satisfactorily applied to the analysis of aqueous samples obtained from three wastewater treatment plants. All the polycyclic musks studied were detected in influent samples with cashmeran, galaxolide and tonalide as the most representative compounds. The analysis of effluent wastewater showed a decrease in the concentrations of all of the polycyclic musk detected in influent samples and an increase in the concentration of galaxolidone until a maximum value of 820 ng L^{-1} .

Keywords: Gas chromatography-tandem mass spectrometry; Needle trap; Synthetic musk fragrances; Thermal desorption; Wastewater samples

1. Introduction

Sample preparation is the cornerstone of chemical analysis. Preconcentration is a crucial step when synthetic musk fragrances often occurring in concentrations as low as $\mu\text{g L}^{-1}$ or ng L^{-1} are to be determined in environmental water samples. Some preconcentration techniques such as liquid-liquid extraction (LLE) [1-3], solid-phase extraction (SPE) [4-7], dispersive liquid-liquid extraction (DLLME) [8-10], solid phase microextraction (SPME) [11,12], single drop microextraction (SDME) [13,14], microextraction by packed sorbents (MEPs) [15,16] or dispersive micro solid-phase extraction (D- μ -SPE) [17] have been reported. Of all the extraction techniques mentioned, SPE is the most widely used in the environmental analytical field because it consumes minimal amount of organic solvents and a great diversity of sorbents is commercially available.

Nevertheless the development of economical and ecological small scale sample preparation techniques that are able to meet requirements such as enhanced sensitivity and selectivity, robustness and simple handling are desirable [18,19]. In this way, solvent-free extraction methods based on the partitioning of analytes between gaseous or liquid phase and stationary phase have become important and have been widely applied in research over the last decade, with SPME as one of the most successfully approaches [20,21].

Although Raschdorf [22] developed the first device based on a needle filled with Tenax sorbent in the 1970s, needle trap (NT) extraction devices have only recently become popular due to their

combination of advantages of SPME (e.g. solvent-free, fast, sensitive and one-step sample preparation and injection method) and SPE (e.g. sensitivity of the method can be increased by increasing the sample volume) with robustness, easier handling during sampling and desorption, and the fact that they permit a high degree of automation and on-line coupling to GC instruments [23-26]. The literature found up to now can be divided in two categories depending on the NT device used: a) internally coated needles [27-29] and b) needles packed with commercially available sorbents [26,30-36] or chemically synthesized polymers [37,38]. Regardless of the kind of NT used, the extraction by NT has the advantages of being solvent-free and of having sampling and analysis times that are significantly shorter than most existing methods.

In this study, two different needles packed with 20 mm or 30 mm of HF Bondesil-C18 sorbent were evaluated in order to determine the optimal configuration to extract the synthetic musks fragrances present in wastewater samples prior to analysis by GC-MS/MS. The different parameters affecting the adsorption capacity of the NT as well as the desorption and transferring of the target compounds into the GC were also studied. Once the most appropriate experimental conditions were found, the NT methodology was compared in terms of method validation parameters with other microextraction techniques and was successfully applied for the analysis of synthetic musk fragrances in wastewater samples.

2. Experimental part

2.1 Chemical Standards

The nitro musk fragrances 2,4,6-trinitro-1,3-dimethyl-5-tert-butylbenzene (MX, musk xylene) and 1,1,3,3,5-pentamethyl-4,6-dinitroindane (MM, musk moskene) were purchased as 100 $\mu\text{g mL}^{-1}$ solutions in acetonitrile from Sigma–Aldrich (Steinheim, Germany) and Riedel de Haën (Seelze, Germany), respectively. The six polycyclic musks studied were supplied by Promochem Iberia (Barcelona, Spain) and were the following: 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone

(DPMI, cashmeran), 4-acetyl-1,1-dimethyl-6-tert-butylindane (ADBI, celestolide), 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI, phantolide), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane (ATII, traseolide), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(g)-2-benzopyran (HHCB, galaxolide), 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN, tonalide). International Flavors & Fragrances Inc. (Barcelona, Spain) provided 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-[g]-2-benzopyran-1-one (HHCB-lactone, galaxolidone) and the deuterated analogue $^2\text{H}15$ -Musk xylene ($^2\text{H}15$ -MX, surrogate standard) was supplied as a $100 \mu\text{g mL}^{-1}$ solution in acetone by Symta (Madrid, Spain). Table 1 shows the boiling point and the octanol/water partition coefficient of each target compound.

Individual standard solutions of the synthetic musks were prepared in acetone at concentrations of $4,000 \mu\text{g mL}^{-1}$ for polycyclic musks and $1,000 \mu\text{g mL}^{-1}$ for HHCB-lactone. A standard mixture solution of $100 \mu\text{g mL}^{-1}$ was prepared in ethyl acetate. MX, $^2\text{H}15$ -MX and MM standards were supplied directly at a concentration of $100 \mu\text{g mL}^{-1}$ and used as received. Acetone and ethyl acetate were GC grade with purity $>99.9\%$ from Prolabo (VWR, Llinars del Vallès, Barcelona, Spain).

Ultrapure water was obtained using an ultrapure water purification system from Veolia waters (Sant Cugat del Vallés, Barcelona, Spain). Helium gas with a purity of 99.999% was used for the chromatographic analysis (Carburros Metálicos, Tarragona, Spain).

2.2 Sampling

Influent and effluent wastewater samples were collected from three urban wastewater treatment plants (WWTPs) located in Tarragona (WWTP A), Reus (WWTP B) and Vila-seca/Salou (WWTP C) between October and December 2013. The WWTPs receive urban sewage and industrial discharges from a population of about 130,000 inhabitants. The three WWTPs use activated sludge for biological treatment and the WWTP C also employs a tertiary treatment based on reverse osmosis (RO). All samples were collected by using pre-cleaned amber glass bottles and were filtered using a $1.2 \mu\text{m}$ glass fibre filter (Fisherbrand, Loughborough, UK) and a $0.22 \mu\text{m}$ nylon filter

(Scharlab, Barcelona, Spain). Samples were analysed within three days of their collection (stored at 4°C in the fridge).

2.3 Preparation of the Needle Trap

Hamilton (Bonaduz, Switzerland) 22 gauge stainless steel (metal hub) needles (O.D.= 0.718 mm, I.D.= 0.413 mm and 51 mm length) with point style 5 (Fig.1) were filled with HF Bondesil-C18 sorbent (120 µm) from Agilent Technologies (Palo Alto, USA). Stainless steel wire (AISI 316L, GoodFellow, Huntingdon, UK) of 100 µm diameter was used to prepare spiral plugs to hold sorbent particles inside the needles. First, a small piece of spiral plug (five turns, ~1.5 mm) was fixed in the tip of the needle to prevent sorbent particles from being fixed in the side hole of the needle. Then, 20 mm or 30 mm of C18 sorbent particles were positioned inside the needle. Finally, another spiral plug was carefully introduced in the upper position of the needle until it reached the end of the sorbent layer to fix the sorbent particles. Using this needle configuration, needle traps were conditioned in the GC injector at 230°C for 30 min to eliminate any contaminations from the manufacturing process or shipping. Each needle was stored inside a closed vial until analysis.

2.4 Needle Trap Extraction

A CombiPAL autosampler (CTC Analytics, Zwingen, Switzerland) equipped with a single Magnet Mixer, a 100 µL Hamilton syringe and controlled by the Cyclo Composer Macro Editor 1.4 Software was used for the fully automated needle trap (NT) microextraction. The general microextraction procedure was as follows: 10 mL of sample or standard solution was introduced into a 20 mL HS glass vial and immediately sealed with a Teflon septum. When the temperature of the heat/stir accessory reached 60°C, the vial was automatically transported there and the headspace was allow to

equilibrate with the sample at the extraction temperature for 15 min. The needle with 30 mm of HF Bondesil-C18 sorbent was inserted in the vial to perform the HS dynamic extraction. 500 μL of headspace vapours were then percolated by pumping up through the sorbent 5 cycles of 100 μL at 10 $\mu\text{L s}^{-1}$ fill and 30 $\mu\text{L s}^{-1}$ ejection speeds. Afterward, the desorption was conducted at 230°C for 3 min and the compounds were subsequently analysed by GC-MS/MS.

2.5 Gas chromatography- tandem mass spectrometry

The GC-MS/MS analyses were performed on a Varian 3800 gas chromatograph (Varian, Walnut Creek, CA, USA) connected to a Varian 4000 ion trap detector. The GC was equipped with a 1079 programmable temperature injector and a 0.8 mm i.d. insert liner (Varian) and a CombiPal autosampler (CTC Analytics, Zwingen, Switzerland). A fused silica capillary column (3 m x 0.25 mm i.d.) from Micron Phenomenex (Torrance, CA, USA) was used as a guard column. The chromatographic separation was done in a midpolarity phase capillary analytical column with 50% diphenyl/ 50%dimethylpolysiloxane (30 m x 0.25 mm i.d.; 0.25 μm film thickness) from Micron Phenomenex. The oven temperature was programmed as follows: 70°C hold for 3 min, raised at 40°C min^{-1} to 180°C, then 5°C min^{-1} to 220°C and finally 20°C min^{-1} to 280°C (hold 3.25 min). The carrier gas employed was helium with purity of 99.999%, at a constant flow of 1 mL min^{-1} . During the thermal desorption the injector was operated in splitless mode at 230°C. Temperatures of transfer line, manifold and trap temperatures were 280°C, 50°C and 200°C, respectively. A filament-multiplier delay of 3 min was established in order to increase filament's service life. The mass spectrometer analysed the substances after electron impact ionization in tandem mass spectrometry mode (MS/MS).

3. Results and discussion

3.1 GC-MS/MS Optimization

A mixed solution of $10 \mu\text{g mL}^{-1}$ of the target musk fragrances and $1 \mu\text{g mL}^{-1}$ of $^2\text{H15-MX}$ as surrogate standard (SS) was prepared in ethyl acetate and $1 \mu\text{L}$ of this solution was directly injected into the GC-MS, using electron ionization fragmentation in full scan mode. All compounds were separated in just 17 min using the chromatographic conditions described in Section 2.4. Under optimum chromatographic conditions, the chromatogram (Fig. 2a) also shows the separation of two galaxolide stereoisomers (4S, 7S; 4S, 7R). The galaxolide was quantified by integrating the 4S and 7R/S peaks together due to the fact that both stereoisomers are responsible for the musky odour [39]. In order to achieve maximum sensitivity/selectivity of the compounds, the MS/MS method was carried out by selecting appropriate precursor/product ions and the MS/MS parameters optimized in a previous paper [14]. The three product ions selected for a correct identification of the target analytes as well as the retention time and the parent ion of each analyte are summarized in Table 1. Each compound was acquired separately in one segment, except, HHCB and AHTN and the target nitro musks ($^2\text{H15-MX}$, MX and MM).

3.2 Needle Trap Optimization

To optimize needle trap (NT) microextraction conditions, two different NT were tested, the first one contained 20 mm of HF Bondesil-C18 sorbent while the second one was filled with 30 mm of the same sorbent. HFBondesil-C18 sorbent was selected as extraction sorbent due to its ability to extract a wide range of non polar compounds, including synthetic musk fragrances, by establishing non polar interactions [4,6,16]. More selective SPE sorbents previously used to extract synthetic musk fragrances from environmental samples, as Oasis HLB [5] or Bond Elut Nexus [7], were discharged because are not commercially available at higher particle size (100-250 μm). The particle size would affect the packing density and consequently affect the capacity, the extraction efficiency and desorption efficiency of the NT device. As has been demonstrated by Zhan and Pawliszyn [40], NTs packed with small particles possess higher extraction capacity and efficiency but much higher resistances to flow as well. In addition, the use of low particle size sorbents could make pneumatic restrictions and generation of bubbles and important factor to take into account.

The main parameters that affect the sorption and desorption process in NT microextraction were optimized for each needle in order to maximize the chromatographic peak area of the compounds by analysing a standard mixed solution of 1 $\mu\text{g L}^{-1}$ of all the target musks and the SS ²H15-MX in 10 mL of ultrapure water. To obtain the best conditions for each needle, such variables as extraction mode, extraction temperature, salt concentration, preincubation time, fill and ejection speed, fill volume and desorption parameters (temperature and time) were optimized because these factors were expected to be the most influential in the extraction process. Taking into account our previous experience in the determination of synthetic musk fragrances in wastewater samples by SDME and previous literature on synthetic musks [12,14,41,42], the initial experimental conditions selected were as follows: 300 g L^{-1} NaCl, 80°C extraction temperature, 5 min preincubation time, 200 μL fill

volume (2 cycles x 100 μL), 30 $\mu\text{L s}^{-1}$ fill and ejection speed, 3 min of desorption time at 230°C. In the same way, sample volume and stirring rate were fixed at 10 mL (20 mL HS vials) and 750 rpm, respectively.

Firstly the extraction mode was optimized. As musk fragrances are semi-volatile compounds two extraction modes were tested, immersion [43] and headspace [26,30]. The results showed that immersion mode provided higher peak areas than those obtained by headspace mode for all of the target compounds using both 20 mm and 30 mm NTs (data not shown). However, due to the trap's pneumatic restrictions and the bubble formation it was impossible to ensure a constant flow rate of the sample inside the needle and the exact sample volume that pass through the sorbent, obtaining non reproducible results. So, headspace mode was selected to optimize the NT microextraction. In the same way NT desorption with organic solvent was discarded and replaced by thermal desorption.

Then the extraction temperature was studied by comparison of the peak areas obtained at 30°C, 45°C, 60°C, 80°C and 100°C. The other extraction conditions were the same as described previously. Independently of the NT used, a progressive increase in the peak areas was observed for all of the polycyclic musks up to an optimum extraction temperature of 60°C after which there was a decrease when the extraction temperature was extended up to 100°C (Fig.3.). While nitro musks compounds reached the highest peak areas at 80°C with slightly better peak areas than those obtained at 60°C. However, as a compromise 60°C was chosen as the optimum extraction temperature.

To study the influence of adding salt on the efficiency of NT microextraction, the ionic strength of the ultrapure water solutions was modified by adding NaCl in the range of 0-360 g L^{-1} . 300 g L^{-1} was selected as the optimal salt concentration because maximal peak areas were obtained for most of the target compounds (data not shown). DPMI and HHCB-lactone showed maximal peak areas at 200 g L^{-1} NaCl but only a slight decrease in those analytical signals was observed at 300 g L^{-1} NaCl. It is clear that the addition of NaCl increased the ionic strength and thus promotes the transport of the analytes to the headspace and hence to the NT [44]. Therefore, it is to be expected that this will drive additional analytes into the headspace or gaseous phase and NT.

Regarding the preincubation time, 5, 15 and 30 min were also studied in order to enhance the efficiency of the NT efficiency. The best results were obtained working with 30 min (data not shown). However due to the fact that no statistical differences were observed between 15 and 30 min (differences <10% of peak areas), 15 min of preincubation time was selected as optimum in order to reduce the analyses time.

Fill and ejection speed were studied in the range of $1 \mu\text{L s}^{-1}$ to $100 \mu\text{L s}^{-1}$ with a $100 \mu\text{L}$ Hamilton syringe. Higher fill/ejection speeds were discarded for pneumatic restrictions of the NT that can lead in repeatability problems [23]. Theoretically, lower fill speeds increase the sampling time to help musks to diffuse through the sorbent, so the extraction efficiency of the NT should be better working at low fill speeds than working at high fill speeds [23]. Experimental results (Fig. 4) showed that the highest peak areas and therefore the best extraction efficiency was achieved working at $1 \mu\text{L s}^{-1}$ fill and $30 \mu\text{L s}^{-1}$ ejection speeds for all of the target analytes independently of the NT used. However, since no statistical differences were observed between working at $1 \mu\text{L s}^{-1}$ or $10 \mu\text{L s}^{-1}$ fill speeds and not to lengthen the extraction time, $10 \mu\text{L s}^{-1}$ fill speed was chosen as optimal.

Then, fill volume was optimized under optimal conditions for both 20 mm and 30 mm sorbent NTs. The range of volumes studied was between $100 \mu\text{L}$ to $1000 \mu\text{L}$ and were percolated by drawing and discarding between 1 and 10 cycles of $100 \mu\text{L}$. In concordance with the results obtained by *Eom et al.* [45] and *Alonso et al.* [46] for the determination by NT microextraction of BTEX (benzene, toluene, ethylbenzene and *p*-xylene) and volatile organic compounds in water and blood, respectively, increasing sampling volume, the extracted amount of analyte was increased: this occurred because sampling more headspace induced the transfer of more target analytes from the solution to the headspace, resulting in higher trapping efficiency. The results show that working with a 20 mm sorbent NT a proportional increase of the response of all of the target compounds up to $300 \mu\text{L}$ was observed (data not shown). At higher fill volumes the analytical signal remains constant. Whereas the 30 mm sorbent NT reached the highest peak areas at $500 \mu\text{L}$ or $750 \mu\text{L}$ depending on

the target compounds. Due to the compounds that reached the highest peak areas at 500 μL are the less sensitive ones (nitro musk), 500 μL was chosen to work with a 30 mm sorbent NT.

Finally desorption parameters as desorption time and temperature were tested. Working with a 20 mm sorbent NT the highest peak areas were obtained at holding for 1 min the NT at 230 $^{\circ}\text{C}$ while not statistical differences were observed increasing the desorption time to 3 or 5 min, and carryover problems were not detected. Moreover, with a 30 mm NT the best peak areas were reached at 3 min desorption time and 230 $^{\circ}\text{C}$ desorption temperature. Not statistical differences were observed for the vast majority of the target compounds between 1 or 3 min of desorption time but carryover problems were detected for HHCB and AHTN working at 1 min desorption time.

Under the optimized conditions described at Table 2, as can be seen in Fig.5, the 30 mm sorbent NT presented higher peak areas for all the target analytes, so this was the NT selected to validate the method.

3.3 Method Validation

As NT microextraction may be strongly influenced by the sample matrix, before validating the method, the matrix effect was studied by statistically comparing the slopes of the calibration curves for influent and effluent WWTPs samples with that obtained with ultrapure water. As expected, the matrix effect was observed in both kinds of water, especially in influent samples. The feasibility of the microextraction procedure must be demonstrated with real samples spiked at different concentrations.

The method was then analytically validated with an influent and an effluent sample from WWTP A i by establishing the linear ranges, method detection limits (MDL), method quantification limits (MQL), intra-day and inter-day repeatabilities (expressed as relative standard deviation (RSD)). Procedural blanks of the conditioned NT were performed before NT microextraction in order to prevent carryover effects and ensure the repeatability of the analytical method.

The WWTP A samples used to validate the method were analysed ($n=5$), and the peaks of t HHCB and AHTN appeared in the chromatogram of the influent sample, while in the effluent sample peaks of HHCB, AHTN and also HHCB-lactone were found. The averaged peak area of each detected compound was subtracted from the corresponding peak area of each spiked sample.

The linear range of the method was obtained by analysing the WWTP A samples spiked with all of the target analytes at concentrations between 2.5 ng L^{-1} and $5,000 \text{ ng L}^{-1}$ while the SS concentration remained constant at $1,000 \text{ ng L}^{-1}$. The method was linear in all ranges between MQL and $5,000 \text{ ng L}^{-1}$ for all of the target analytes and matrices. In addition, the presence of the SS enabled us to improve the determination coefficients (r^2) of the calibration curves to values higher than 0.997 for all the target compounds. MQLs were the lowest point of the calibration curve and MDLs were evaluated by spiking WWTP A influent or effluent samples in order to obtain a signal-to-noise ratio higher than three, for the compounds that did not appear in these samples. MDLs for HHCB, AHTN and HHCB-lactone were estimated as the concentration that gave a signal average of plus three times the standard deviation of the influent or effluent sample signal ($n=10$). These limits are shown in Table 3. Thus, MQLs ranged from 5 ng L^{-1} to 25 ng L^{-1} and MDLs ranged from 2.5 ng L^{-1} to 12 ng L^{-1} depending of the compound and matrix studied. These limits are better than those reported in the literature, which reports MDLs between 5 ng L^{-1} and 63 ng L^{-1} for influent and effluent waters working with microextraction by packed sorbents [16], dispersive liquid-liquid microextraction [9,10] or ultrasound-assisted emulsification-microextraction [8] as extraction technique. However, slightly better MDLs (from 0.25 ng L^{-1} to 9 ng L^{-1}) were obtained working with solid phase microextraction as preconcentration technique [41,47].

Intra-day and inter-day repeatability were obtained with five replicates of influent and effluent sample spiked at 100 ng L^{-1} (see Table 3). Intra-day repeatability (%RSD, $n=5$) was always less than 11% for both influent and effluent samples. Inter-day repeatability was always less than 17% or 15% (%RSD, $n=5$) for influent and effluent samples, respectively.

3.4 Needle trap extraction versus ionic liquid-based headspace single drop microextraction

The NT methodology was compared in terms of method validation parameters with an ionic liquid-based headspace single drop microextraction (IL-HS-SDME) methodology, which was successfully applied by our research group for the determination of musk fragrances in wastewater samples[14]. Both microextraction techniques are considered environmentally friendly because of the use of 1 μL of an ionic liquid as extraction solvent instead of an organic solvent in the case of the IL-HS-SDME or because it is a solventless technique as NT. In addition both extraction procedures were fully automated by a CombiPal autosampler to ensure the repeatability of the methodology when dispensing a drop of ionic liquid (IL-HS-SPME) or to control the fill/ejection speed (NT).

Method validation parameters were obtained by the analysis of 10 mL influent and effluent samples spiked at different concentrations by using GC-MS/MS as separation and detection technique. The results showed that better MDLs were obtained with NT microextraction with values between 2.5 ng L^{-1} and 12 ng L^{-1} , while IL-HS-SDME MDLs ranging between 10 ng L^{-1} -30 ng L^{-1} . The main reason of the increase of the MDLs when working with IL-HS-SDME is that because of the low volatility of the ionic liquids, residues could be accumulated in the glass wool placed inside the GC liner. In the same way, higher MQLs were obtained with IL-HS-SDME (50 ng L^{-1} -100 ng L^{-1}). Both methods were linear between the MQLs and 5,000 ng mL^{-1} with NT microextraction and up to 10,000 ng mL^{-1} with IL-HS-SDME. On the other hand, slightly better repeatability results were obtained with IL-HS-SDME, with intra-day repeatability values between 2-6% and inter-day repeatabilities ranging between 5-11%.

Summarizing, both methodologies were successfully applied for the determination of musk fragrances in wastewater samples but the validation results as well as daily work have led me to conclude that the NT microextraction is preferable to IL-HS-SDME.

Furthermore, NT microextraction validation values can also be compared with those obtained by Moeder *et. al.* [15] working with MEPs as extraction technique. MEPs is a microextraction technique that can be considered as a miniaturized solid-phase extraction in which the sorbent (1 mg) is inserted between the needle and the barrel as a cartridge but not in the needle. Moeder *et. al.* [15] obtained MDLs of 42 ng L⁻¹ and 37 ng L⁻¹ for HHCB and AHTN, respectively, while working with NT as extraction technique slightly better MDLs, between 2.5 and 3.5 ng L⁻¹ for HHCB and AHTN, were obtained. These values can be explained by the differences in sorbent position. NT design allows working in headspace mode and thermal desorption, and that makes this technique ideal for the extraction of volatile organic compounds from air or wastewater samples. On the other hand, MEPs bin is ideal for work in immersion mode and desorption with organic solvents and is normally used to extract polar compounds from environmental or biological samples [48].

3.5 Method application

To demonstrate the applicability of the NT-GC-MS/MS, influent and effluent wastewater samples from three WWTPs (A, B, C) on different dates were analysed ($n=8$). All the polycyclic musk compounds were detected in some of the influent samples from WWTP A and WWTP B, with HHCB (20 ng L⁻¹-1,160 ng L⁻¹) and AHTN (<MQL-430 ng L⁻¹) as the only compounds present in all the samples analysed (Table 4). For instance, Fig. 2b shows MRM chromatograms of the influent from WWTP B for the sample spiked with 1,000 ng L⁻¹ of musk fragrances a), and the unspiked sample b). As expected, the concentrations of polycyclic musk found in effluent WWTP A and B samples were lower than those detected in influent samples and with DPME (n.d.-180 ng L⁻¹), HHCB (10 ng L⁻¹-550 ng L⁻¹) and AHTN (<MQL-240 ng L⁻¹) as the compounds that showed the highest concentrations. None of the samples contained detectable traces of nitro musk compounds. HHCB-lactone was only detected in effluent WWTP A and B samples as a result of the degradation of HHCB to HHCB-lactone during the WWTP treatment [49,50].

In the same way, HHCB ($70 \text{ ng L}^{-1} - 240 \text{ ng L}^{-1}$) and AHTN ($<\text{MQL}-50 \text{ ng L}^{-1}$) are the only compounds present in all the influent samples of RO taken from WWTP C. The remaining polycyclic musk as well as HHCB-lactone were detected in some of the samples in minor concentrations. In effluent RO samples all targets musks were detected at values below the MQL or were not detected.

Previous works [4,7,51,52] that have focused on the determination of synthetic musk fragrances in wastewater samples confirms the finding of the present study, i.e. that the most abundant fragrances found in wastewater samples are the polycyclic musks HHCB and AHTN, although other polycyclic musks as DPMI, ADBI or AHMI can also be present in minor concentrations.

4. Conclusions

In this study, a NT microextraction followed by GC-MS/MS procedure was developed for determining nine musk fragrances in water samples. The NT-GC-MS/MS method was shown to be completely automated, simple and environmentally friendly. It also provided low ng L^{-1} MDLs and satisfactory precision (RSD between 3 and 11%) for wastewater samples.

The following main parameters involved in the NT microextraction were evaluated and optimized: sorbent-packed needle trap, extraction mode, extraction temperature, salt concentration, preincubation time, fill and ejection speed, fill volume and desorption parameters (temperature and time). Two sorbent-packed needle traps were tested (20 mm HF Bondesil-C18 sorbent and 30 mm HF Bondesil-C18 sorbent), and the best conditions were found to be the following: 30 mm HF Bondesil-C18 sorbent needle trap, 10 mL sample volume placed in a 20 mL HS vial and stirred at

750 rpm, 30% NaCl addition, an extraction temperature of 60°C, preincubation 15 min, 10 $\mu\text{L s}^{-1}$ / 30 $\mu\text{L s}^{-1}$ fill and ejection speed, 500 μL fill volume and 3 min desorption time (230°C).

The applicability of the method was also tested with water samples from influent and effluent WWTPs. The most abundant compounds were found to be DPMI, HHCB and AHTN while the remaining polycyclic musk fragrances were present at lower concentrations. None of the samples analysed contained detectable traces of nitro musk compounds and HHCB-lactone was only detected in effluent samples as a degradation product of HHCB.

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FIGURE CAPTION

Fig. 1: Sorbent-packed needle trap device. A: Spiral plugs, B: sorbent material.

Fig. 2: MRM chromatograms of a influent wastewater sample from WWTP B. a) Sample spiked with $1 \mu\text{g L}^{-1}$ of musk fragrances; b) Unspiked sample.

Fig. 3: Effect of the extraction temperature on the chromatographic peak areas obtained with NT microextraction ($1 \mu\text{g L}^{-1}$, $n=3$). Experimental conditions: 30 mm HF Bondesil-C18 sorbent NT, 10 mL sample volume poured in a 20 mL HS vial stirred at 750 rpm, 30% NaCl addition, preincubation time of 5 min, 200 μL fill volume, 30 $\mu\text{L s}^{-1}$ fill and ejection speed and 3 min desorption time (230°C).

Fig. 4: Effect of the fill speed on the chromatographic peak areas obtained with NT microextraction ($1 \mu\text{g L}^{-1}$, $n=3$). Experimental conditions: 30 mm HF Bondesil-C18 sorbent NT, 10 mL sample volume poured in a 20 mL HS vial stirred at 750 rpm, 30% NaCl addition, an extraction temperature of 60°C, preincubation time 15 min, 200 μL fill volume, 30 $\mu\text{L s}^{-1}$ ejection speed and 3 min desorption time (230°C).

Fig. 5: Comparison of the chromatographic peak areas obtained with the 2 sorbent-packed needle traps in the optimal NT microextraction conditions for extracting the target musk fragrances from 10 mL water samples spiked at $1 \mu\text{g L}^{-1}$ ($n=3$).

Table 2

NT microextraction optimum conditions for each HF Bondesil-C18 needle studied.

Process	Parameters	20mm sorbent NT	30mm sorbent NT
	Mode	Headspace	Headspace
	Temperature (°C)	60	60
	NaCl (g L ⁻¹)	30	30
Extraction	Preincubation time (min)	15	15
	Fill/ ejection speed (μL s ⁻¹)	10/ 30	10 /30
	Fill volume (μL)	200 (2 cycles×100μL)	500 (3cycles×100μL)
Desorption	Mode	Temperature	Temperature
	Temperature (°C)	230	230
	Time (min)	1	3

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Table 3

Method linear ranges, MDLs, MQLs, intra-day repeatabilities and inter-day repeatabilities.

Compound	Influent				Effluent			
	Linear range ^a	MDLs	RSD ^b	RSD ^c	Linear range ^a	MDLs	RSD ^b	RSD ^c
	(ng L ⁻¹)	(ng L ⁻¹)	(%)	(%)	(ng L ⁻¹)	(ng L ⁻¹)	(%)	(%)
DPMI	10-5,000	3.5	7	11	7.5-5,000	2.5	6	7
ADBI	7.5-5,000	3	8	15	5-5,000	2.5	6	14
AHMI	7.5-5,000	2.5	6	16	5-5,000	2.5	5	9
ATHI	20-5,000	5	11	11	5-5,000	2.5	8	11
HHCB	7.5-5,000	3*	10	13	7.5-5,000	2.5*	3	7
AHTN	7.5-5,000	3.5*	8	17	7.5-5,000	2.5*	5	10
MX	20-5,000	10	7	12	20-5,000	10	5	14
MM	25-5,000	12	6	13	20-5,000	10	9	15
HHCB-lactone	20-5,000	10	10	13	10-5,000	5*	8	11

aMQL (ng L⁻¹): were fixed as the lowest calibration level.

bIntra-day repeatability (% RSD): n=5, 100ng L⁻¹.

cInter-day repeatability (% RSD): n=5, 100ng L⁻¹.

*Estimated.

Table 4

Concentrations of the target musks found in wastewater samples (n=8) in ng L⁻¹.

Compounds	WWTP C		WWTP C		WWTP C	
	Influent	Effluent	Influent	Effluent	Influent RO	Effluent RO
DPMI	260–630	<MQL-10	<MQL-880	n.d.-180	n.d.-<MQL	n.d.-<MQL
ADBI	n.d.-30	n.d.-<MQL	<MQL-40	n.d.-<MQL	n.d.-30	n.d.-<MQL
AHMI	n.d.-20	n.d.-<MQL	<MQL-110	n.d.-<MQL	n.d.-40	n.d.-<MQL
ATII	n.d.-70	n.d.-<MQL	<MQL-180	n.d.-30	n.d.-90	n.d.-<MQL
HHCB	560–600	160–210	20–1,160	10–550	70–240	<MQL
AHTN	130–260	40–70	<MQL-430	<MQL-240	<MQL-50	<MQL
MX	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MM	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HHCB-Lactone	n.d.	<MQL-820	n.d.	<MQL-290	n.d.-270	n.d.

n.d.; not detected.

<MQL; values under the method quantification limit.

Highlights of the manuscript: “Sorbent-packed needle microextraction trap for synthetic musks determination in wastewater samples”.

- First time NT microextraction implemented for synthetic musks in wastewater samples.
- The developed method is simple, quick, full automated, cheap and environmentally friendly.
- Method detection and quantification limits at low ng L^{-1} were obtained.
- Galaxolide and tonalide were found in all the wastewater samples analysed.

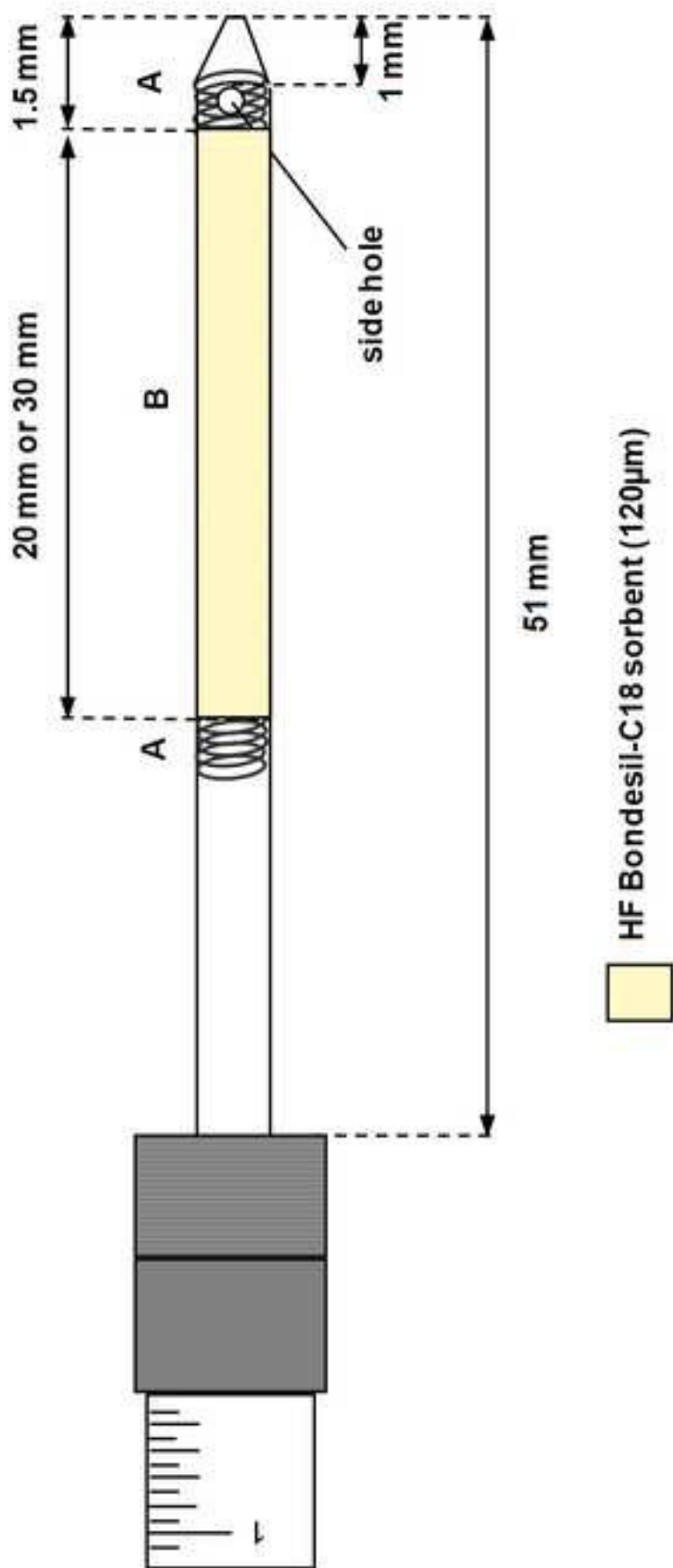
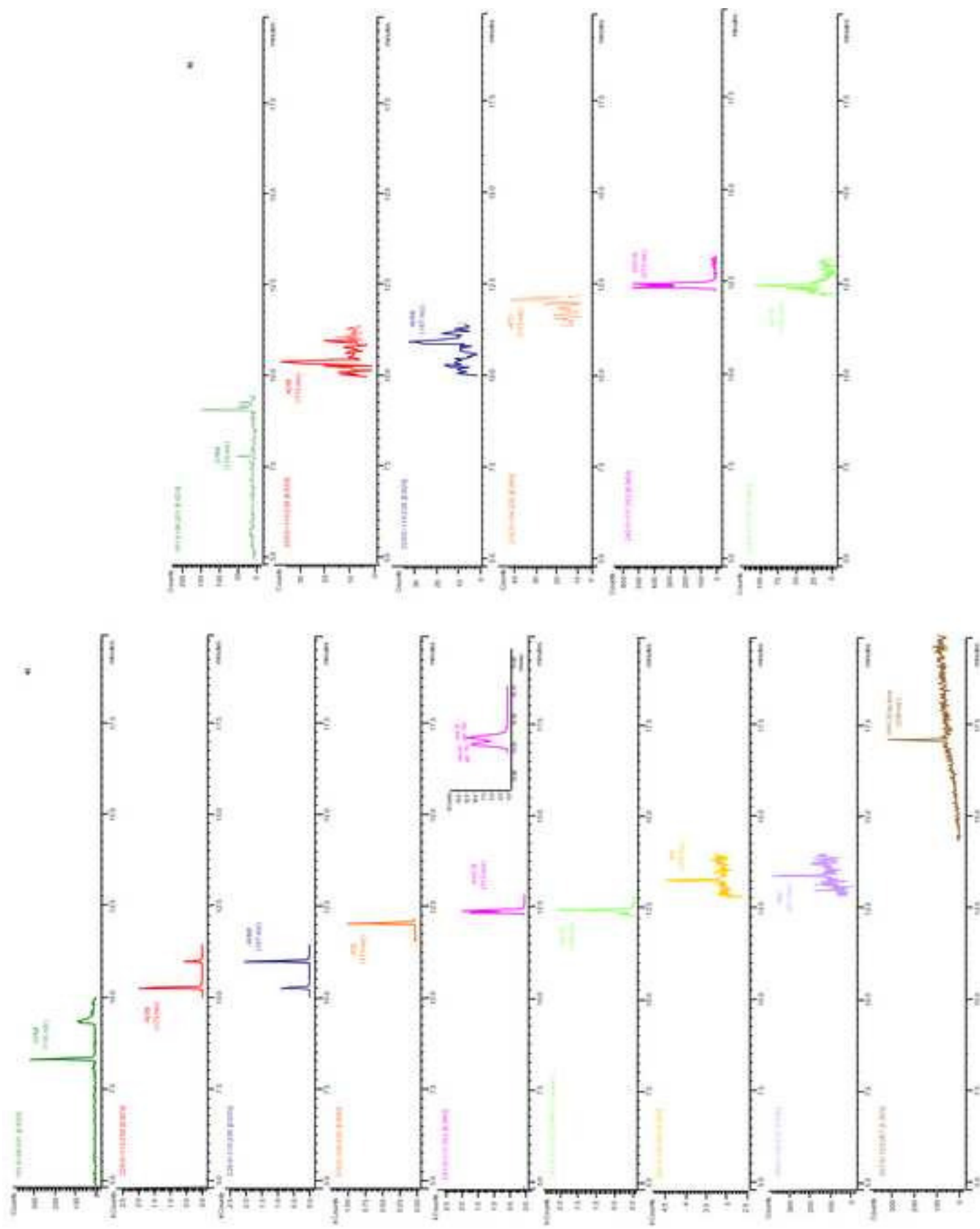


Figure 1



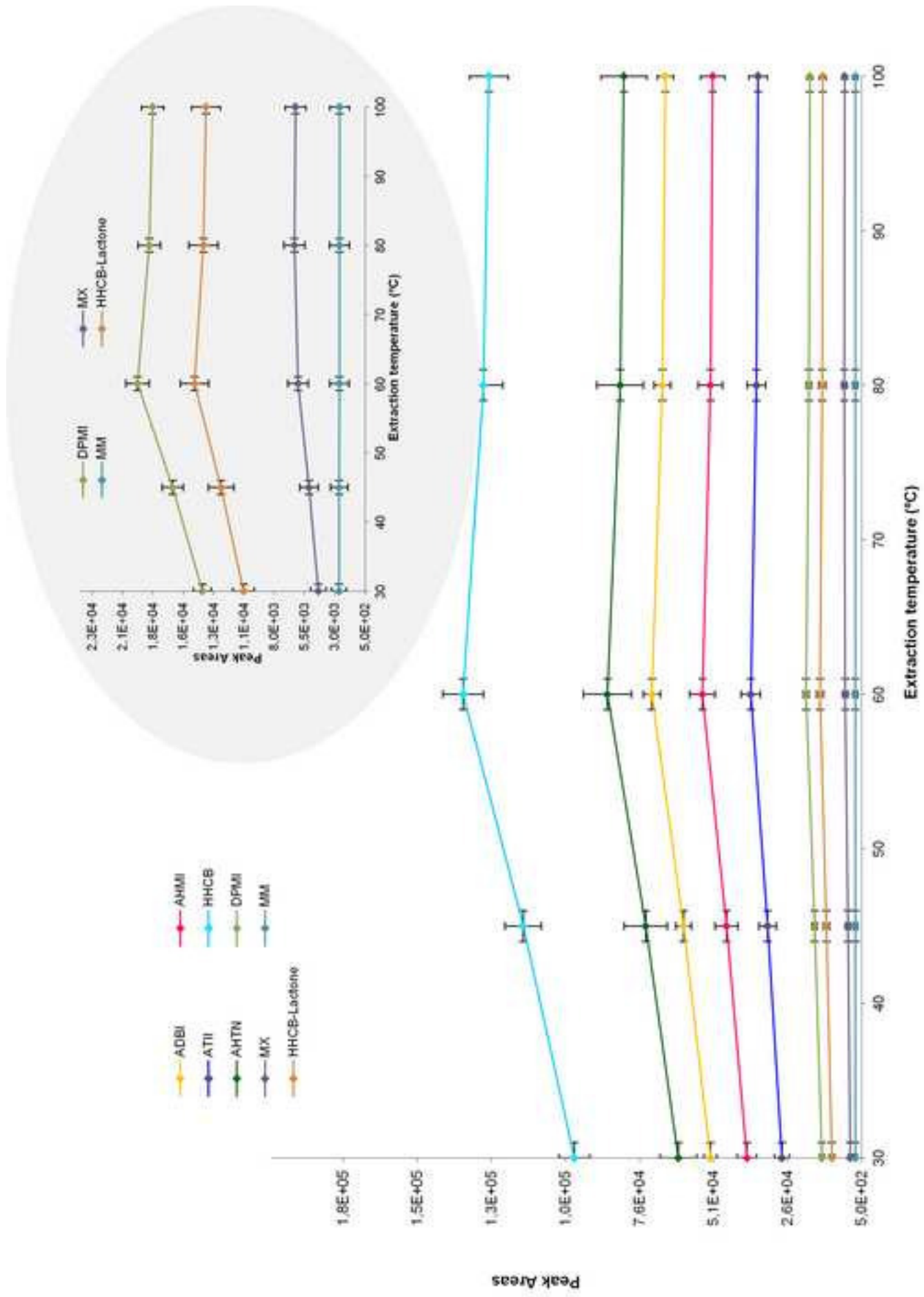


Figure 3

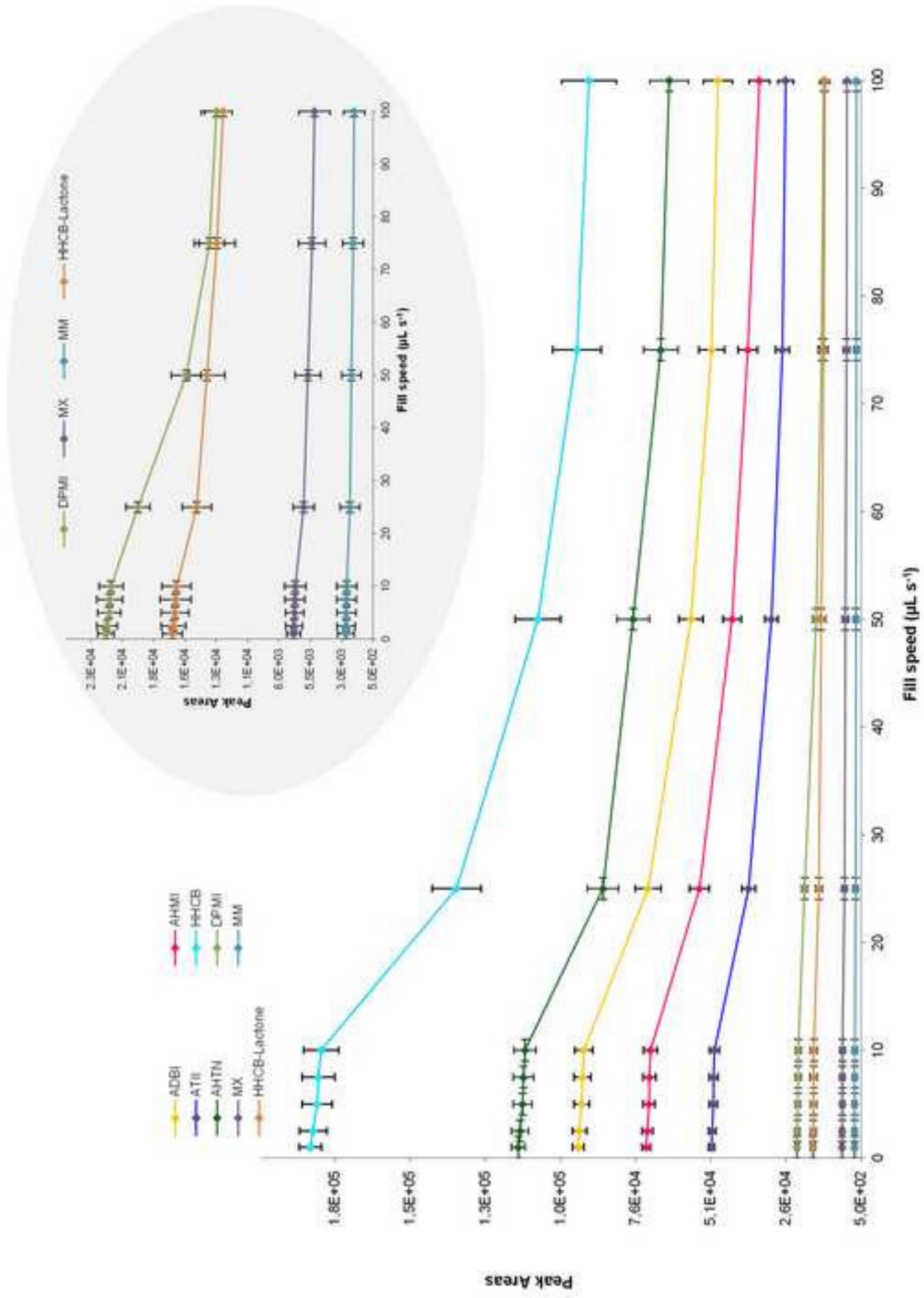


Figure 4

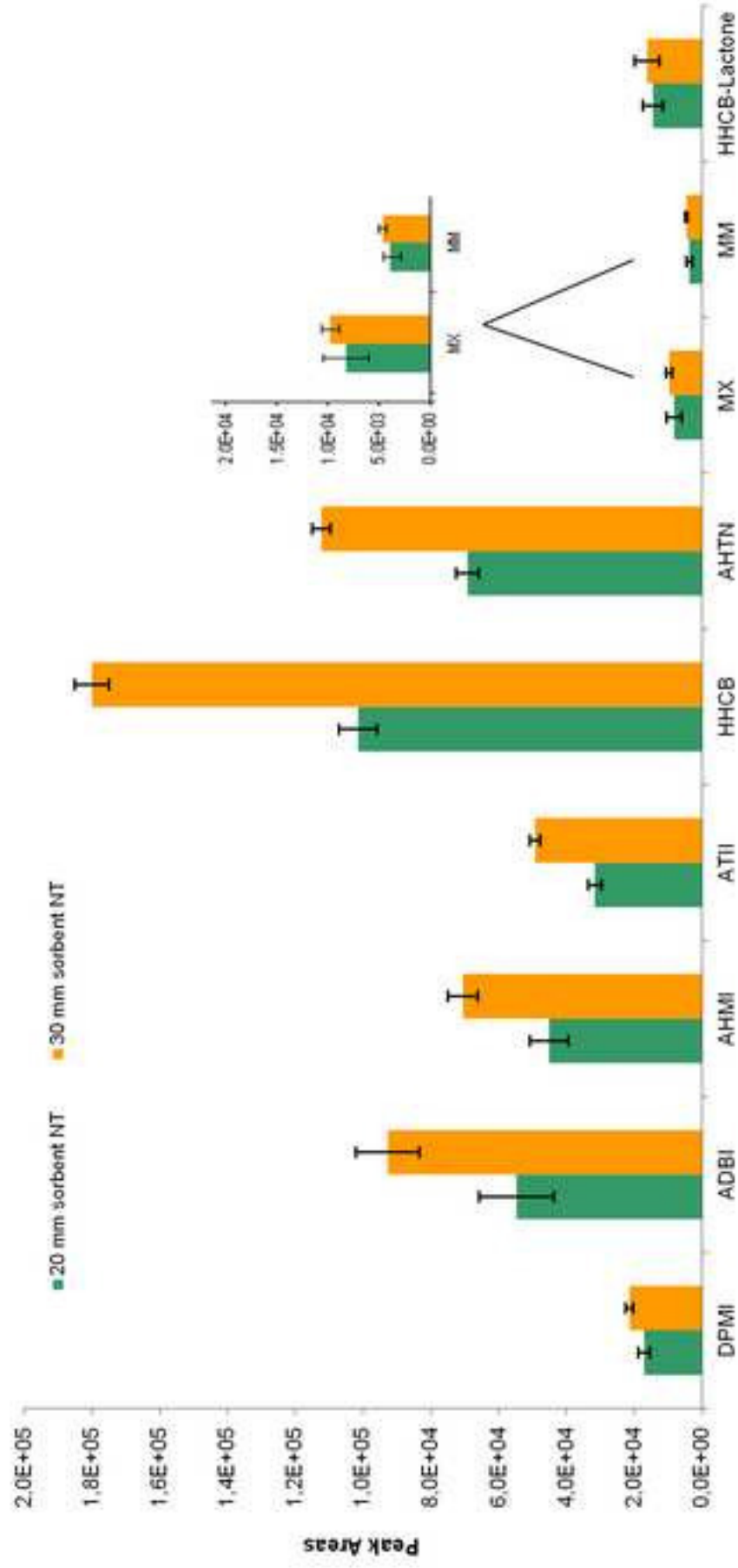
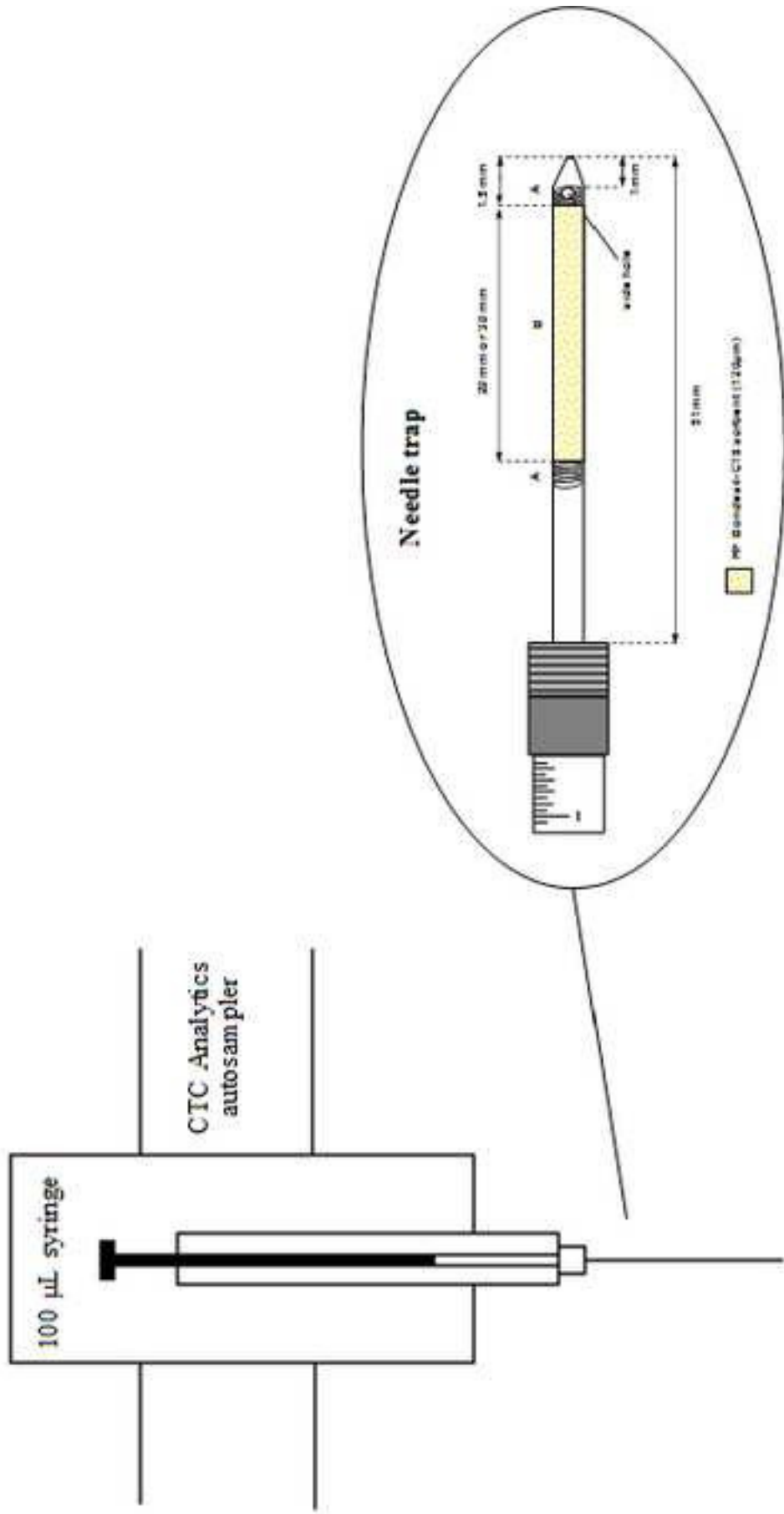


Figure 5



Wastewater samples

Table 1 Boiling point, log K_{ow} , retention times (t_R) and parent and products ions of the target compounds.

No.	Compound	Boiling point ($^{\circ}$ C)	Log K_{ow} ^a	t_R (min)	Parent ion (m/z)	Product ions (m/z) ^c
1	Cashmeran (DPMI)	286.1	5.9	8.33	191	107, 135 , 173
2	Celestolide (ADBI)	309	5.4	10.24	229	131, 173 , 187
3	Phantolide (AHMI)	336.6	5.9	10.98	229	131, 145, 187
4	Traseolide (ATII)	350	6.3	12.02	215	131, 171, 173
5	Galaxolide (HHCB)	326	5.9	12.31	243	171, 213
6	Tonalide (AHTN)	356.8	6.3	12.36	243	145 , 159, 187
7	Musk xylene (MX)	392.3	3.8	13.24	282	265 , 266, 281
8	Musk moskene (MM)	351.1	5.2	13.35	263	187, 201, 211
9	Galaxolidone (HHCB-Lactone)	*	*	16.93	257	183, 201, 239
10	² H15-Musk xylene (² H15-MX) ^b	*	*	13.10	294	170, 276 , 295

*Information not found at the bibliography.

^aLog K_{ow} values predicted from SRC- K_{ow} Win software.

^bSurrogate standard (SS).

^cQuantification ions (m/z) are shown in bold type.