Development of needle trap technology for on-site determinations: active and passive sampling

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Abstract

This study presents a thorough evaluation of new prototypes of extended tip needle trap devices (NT), as well as their application to *in situ* sampling of biological emissions and active/passive on-site sampling of indoor air. A new NT prototype was constructed with a side hole above the sorbent and an extended tip that fits inside the restriction of the narrow neck liner to increase desorption efficiency.New prototype needles were initially packed with divinylbenzene particles at SGE Analytical Science for the purpose of studying biogenic emissions of pine trees. Prior to their final application, they were evaluated in terms of robustness after multiple use ($n > 10$), as well as amount extracted of volatile organic compounds (VOCs). An ANOVA test for all the probes showed that at a 95 % level of confidence, there were not statistical differences observed among the 9 NTs tested. In addition, the needles were also packed in laboratory with synthesized highly cross linked PDMS as a frit to immobilize carboxen (Car) particles for spot sampling. For passive sampling, the needles were packed with Car particles embedded in PDMS in order to simplify calculations in passive mode. The use of NTs as spot samplers, as well as a passive sampler under controlled conditions in the laboratoryyielded a relative standard deviation of less than 15 %. Finally, a new, reusable and readily deployable pen-like diffusive sampler for needle traps (PDS-NT) was built and tested. Application of the PDS-NT in combination with NT-spot sampling towards the analysis of indoor air in a polymer synthesis laboratory showed good agreement between both techniques for the analyte studied, yielding averages of 0.03 ng/mL and 0.025 ng/mL of toluene, respectively.

Introduction

Recently, there has been increasing interest in air analysis among environmental scientists. Ideally, air samples should be analyzed on-site to avoid losing sample integrity[1]. In cases where on-site analysis is not possible, simple sampling/sample preparation techniques for field applications are required[2,3]. Sampler devices for field sampling should be simple and reliable, since sampling sites are generally located far from the laboratory. Consequently, the device should also comprise easy method deployment, one which allows operators with limited knowledge of the extraction mechanisms to easily operate the sampler. Moreover, the production of the device should be uncomplicated and inexpensive[4,5]. Additionally, during sample transportation and storage, any contamination, decomposition, and/or loss of the analytes should be negligible[5,6]. Finally, the device should be sensitive to the substances under study, unaffected by interfering matrix components, and not require in-laboratory sample pre-treatment[4,6]. Solid phase microextraction (SPME) and needle trap (NT) devices have been shown to be suitable techniques to address these concerns[7–9].

A NT is an extraction device that contains a sorbent packed inside of a needle, as shown in Figure 1. The NT method combines sampling, sample preparation, and sample introduction as SPME does. However, NT, as an active sampler, is an exhaustive technique that allows particle trapping. Hence, as shown in Equation 1,the total concentration of analyte can be easily obtained by controlling the sampled volume (v) and determining the amount extracted (n) in an analytical instrument [7,10].

Equation 1: $C_0 = n / V_s$

Several factors, such as pore size and shape, surface area, and particle size can affect the ability of the analyte to access and interact with the surface of the adsorbent. Therefore, these parameters must be contemplated and controlled when designing new needle trap devices [10,11]. Moreover, because of the special shape of the needle, sorbents used for NT must have the appropriate physical characteristics in size, hardness, and shape (spherical), as well as adequate mechanical and thermal stability[7,11]. The first practical and successful application of NT suitable for automation and on-site analysis was carried out using a 23 gauge stainless steel needle 40 mm long, containing 5 mm of quartz wool packing[12,13]. Since then, several groups have worked on the development of sorbent-packed needles or similar devices[7]. Some of the sorbents that have been used for the analysis of volatile organic compounds (VOCs) include carboxen (Car), divinylbenzene (DVB), Porapak Q™ , and Carbopack X™ [7,11,14]. The design of the NT geometry must guarantee several factors: exhaustive extraction (active sampling), negligible breakthrough during sampling, and efficient desorption [10,12,15,16].

Research performed by Warren *et al*., and Zhan *et al*. [11,17] demonstrated that in order to achieve complete desorption (non-carryover), an aid-gas should be directed through the needle trap packing, either through carrier gas or gas-tight assistance desorption[11]. Thus, if a good seal is created between the outer surface of the needle and the inner surface of the liner, the carrier gas is exclusively driven through the side-hole of the needle, passing through sorbent, then finally migrating alongside the extracted analytes by the needle tip. The sealing system on the first side-hole NTs relied entirely on the tapered shape of the needle's tip. However, inefficient desorption of analytes and carryover issues revealed the weaknesses of this design; basically, an effective and reliable hard-to-hard surface seal (metal needle and glass liner) was not achieved.

The needle/liner prototype herein described differs from the original design by relying on a metal/metal seal between the tip of the needle and the bore of the metal liner[17]. In this design, as shown in **Figure SI-1**, the outside diameter of the needle tip (O.D. 0.495mm) fits precisely on the bottom section of the GC-liner, which has a smaller diameter (I.D. 0.500 mm) than the upper part of the liner. A conical guiding system allows the smooth insertion of the needle tip into the smaller section of the liner. Since this design guarantees a better seal with the narrow neck liner[11,17], the carrier gas is forced to only go through the sorbent bed, as seen in **Figure 1**. In addition to addressing the sealing issues related to glass liners, metal liners proved to be more efficient in transferring heat evenly throughout the full length of the packing. Chemical deactivation of metal liners was performed in order to avoid the presence of active sites.

This report also presents the evaluation of a new extended tip NT packed with DVB particles, including modifications to allow the use of Car particles, a reassessment of the new designs, and its application to on-site analysis in active and passive sampling modes. In addition, a new NT diffusive sampler is presented in this study. It has a similar mechanism to the one described by Gong *et al.* [10]. However, in contrast to the previous design, loading the NT on the holder is simpler and can be accomplished in a few seconds. Also, a clever clicking exposure system places the NT automatically in the sampling position when it is fixed in a pocket. Unlike previous works, a sampling chamber was successfully designed and built for the evaluation of the sampler device under a controlled environment. Moreover, the new PDS-NT can be used for either manual desorption with the holder, or automated unattended NT desorption [7].

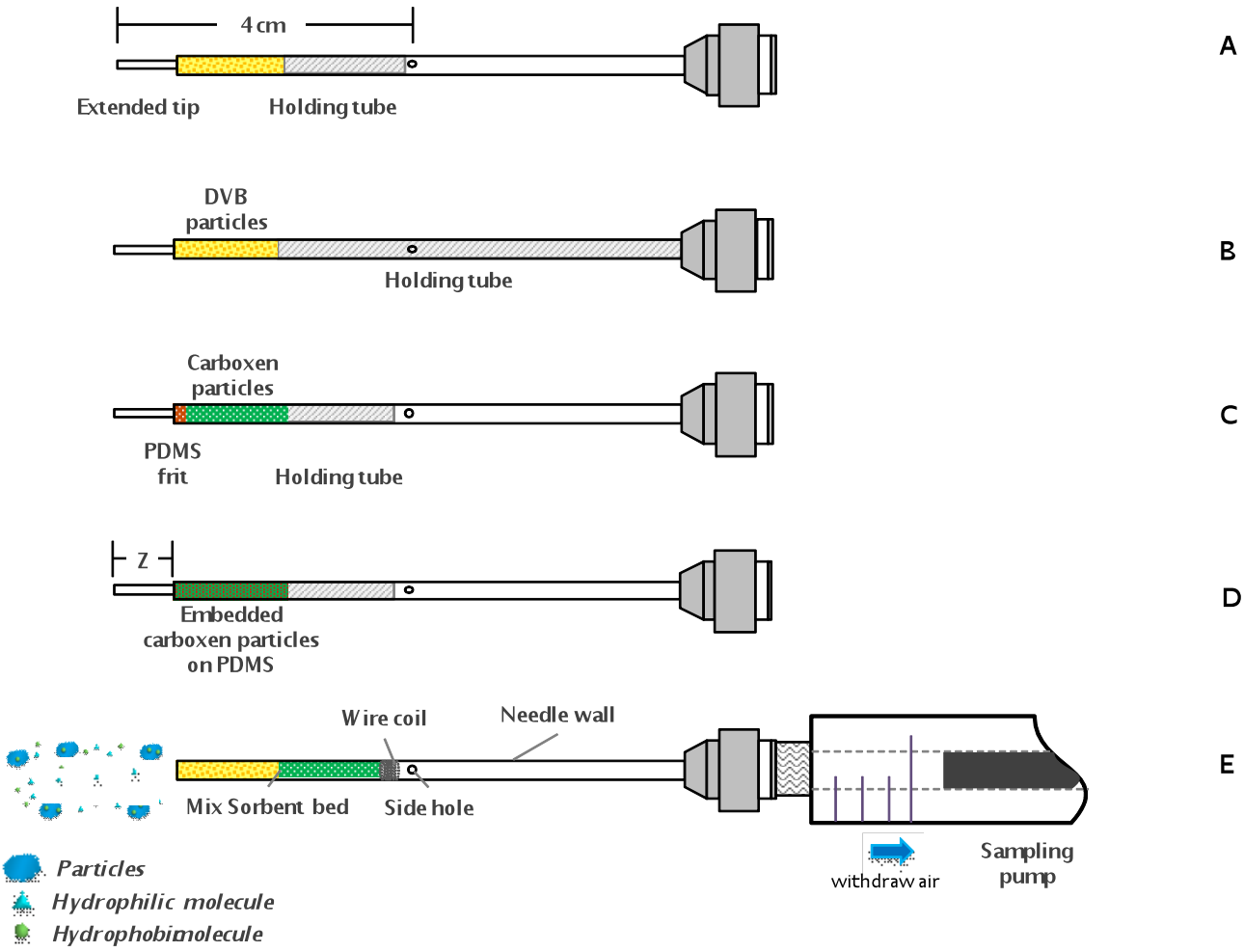

Figure 1 Schematic of the modified needle traps. A. Initial prototype packed with DVB particles; B. Modified prototype packed with DVB particles; C. New extended tip needle trap packed with PDMS frit and Car particles for active sampling; D. New extended tip needle trap packed with Car particles embedded on PDMS for passive sampling and E. Sampling with conventional blunt tip NT

Experimental

Materials and reagents

130 The details for chemicals and materials are described in the supporting information (section
131 1.1).
132
133
134 **Instrumentation**
135 Instruments and instrumental conditions used for the different analytical procedures are
136 described in the supporting information (section 1.2). Similarly, section 1.3 of the supporting
137 information provides a thorough explanation of the sampling chambers used for NT and PDS-NT
138 evaluation, as well as a description of the device used for *in situ* sampling.
139
140 **Procedures**
141 *Preparation of the custom made needle traps at UW*
142 A PDMS pre-polymer was added to the curing agent using a ratio of (10:1). The prepared 1%
143 SDS solution was added to a mixture of PDMS and curing agent (with a ratio of 1:2) and stirred
144 for 15 min to make a homogenized mixture. Glass capillaries with the same inner diameter as
145 NTs were tilled with a homogenized prepared mixture. The polymerization was allowed to
146 proceed at 80 ºC for 1 hour [18]. After the PDMS mixture was cured, the polymerized PDMS was
147 heated at 120 ºC for 3 hours in order to evaporate water and remove impurities. Both the amount
148 of water added to the mixture and the temperature of polymerization have an effect on the
149 porosity of synthesized PDMS; since temperature is the most effective parameter in obtaining
150 open pores, temperature was increased to 20 ºC higher than the boiling point of water in order to
151 obtain maximum porosity. To prepare the NT with Car embedded in PDMS, 5 μm Car particles
152 were added to a mixture consisting of the previously described ratios of PDMS pre-polymer,

curing agent, and 1% SDS solution, and stirred for 10 min. Next, glass capillaries were tilled with the mixture and heated at 80 ^{0}C for 1 hour. After curing, the oven temperature was increased to120 ºC, and the mixture containing polymerized Car embedded in PDMS was heated for 3 hours to remove the impurities.

Sampling procedures

Detailed description of the sampling procedures used to evaluate needle traps, as well for on-site and *in situ* sampling are described on section 1.4 of the supplementary information.

Results and Discussion

Evaluation and application of a new extended tip NT packed with DVB particles

Initial assessment of the extended tip needles

Based on previous findings reported by Warren *et al*., and Zhan *et al*. [11,17], SGE manufactured a NT prototype to be evaluated by our group. The new NT consisted of a 22-gauge stainless steel needle with a side-hole 4 cm from the tip, and a sliding-fit tip inserted into the tip of the needle (**Figure SI-1**). Preliminary experiments revealed that the initial design lacked mechanical resistance, and the needles were easily blocked with the septum of the injection port (thoroughly described on Section 2.1 of the supplementary information). To overcome this issue, improvements on the welding of the tube to the needle hub, insertion of a particle-holding tube of a smaller diameter inside the NTs, and smoothing and blunting of the side-hole and extended tip were recommended to the manufacturer for further experiments.

Evaluation of modified extended tip needles packed with DVB particles

In order to evaluate potential differences in the collection capability of the improved prototype at different sampling rates, extraction of a fixed concentration from the gas generator-sampling chamber was carried out at 5 and 10 mL/min. To reduce the effect of systematic errors, and statistically evaluate the results obtained only according to the factor of interest, namely the response in terms of mass extracted by the different NTs, extractions were performed using a randomized block design. As can be seen in **Table SI-1**and **Figure SI-7**, no statistically significant difference was found in the amount extracted for the probe analytes at a 95% level of confidence when sampling at rates up to 5mL/min. Conversely, sampling at higher flow rates, such as 10 mL/min, found in **Table SI-2** and **Figure SI-8**, provided statistical differences in the amount of probes extracted among the different NTs tested. As well, lower amounts of analyte were extracted per each needle trap for higher flow rates. . These observations can be explained by differences on the packing characteristics of each NT. For example, NTs that provided reproducible adsorption capacity at different flow rates had packing which was compact enough to evade channeling phenomena. In contrast, for NTs that showed a significant reduction in the amount of probes collected at higher flow rates, the packing of the particles was not compacted enough, implying that increasing the sampling flow rate may promote channeling effects, consequently reducing the amount of probes adsorbed.

In summary, the modified prototype has shown to be statistically reproducible among the 9 different NTs evaluated as long as the sampling is performed at sampling rates lower than 5 mL/min. Additionally, it was found that after approximately 10 injections, the pre-punch septum should be replaced in order to avoid pieces of septum going inside the restriction of the liner. To test the durability of the liner, continuous testing of the same liner was conducted. The liner was checked every 20 injections with a gas duster and a small wire passing through the restriction in

order to remove small pieces of septum remaining from previous injections. Excessive tightening of the septum may lead blockages in the liner, which can cause high RSD values. Presently, the use of septum-less injection ports capable of preventing possible septum coring is being evaluated by our group. Finally, it was observed that after 5 injections, the Teflon slider (**Figure SI-9**) failed to properly seal the side-hole of the needle trap. This could be related to the intrinsic properties of Teflon, which expands after being exposed at 260 ºC for several injections. As such, leaks may occur during the sampling if the Teflon slider is not replaced, leading to a smaller amount of analytes being adsorbed onto the DVB particles. Lastly, it was found that the hole in the slider should not be bigger than 0.7 mm.

Application of NTs packed with DVB particles towards in situ sampling of plants

Volatile and semi-volatile compounds produced by plants are collectively known as biogenic volatile organic compounds (BVOC)[19]. They comprise a wide variety of organic substances, such as alcohols, terpenes, alkanes and esters. Owing to the fact that BVOCs are responsible for multiple interactions between plants and other organisms, and also play a key role in atmospheric chemistry, their identification, characterization and quantification are of great relevance[19].

Generally, *in situ* research is best suited to observe real conditions when compared to *in vitro* research[19]. As biological systems are very complex and readily react to any perturbation in the surrounding environment, *in situ* research can provide more accurate results than *in vitro* studies [20,21]. An ideal *in situ* sampling technique should be solvent-free, portable, and offer integration of the sampling, sample preparation and analysis steps. With NT, both *in situ* sampling and sample preparation are accomplished by placing the needle in the area surrounding the system under study[21]. Consequently, the plant tissue being analyzed is only minimally disturbed. *In situ*

222 analysis using SPME and NT is gaining ground in metabolomics studies[22] due to its unique
223 characteristics: on-site sampling, easy extraction, and analysis of whole extracted amounts.[23]
224 Until now, numerous applications for the analysis of BVOCs have been developed with SPME
225 and NT[1]. For instance, circadian BVOC emission profiles and phytoremediation properties of
226 plants were explored by Reyes-Garcés *et al*., Zini *et al*. and Sheehan *et al*., respectively[19,24,25].
227 However, just as observed in air quality studies, only a handful of these studies have included the
228 use of multiple devices.

229 In real applications, numerous fibers/NTs are required in order to obtain a better spectrum of
230 the emissions being studied[19]. For that reason, the application of multiple NTs used in the
231 identification and quantification of BVOCs emitted by a pine tree is also presented in this article.
232 The selection of NT packed with DVB was based on previous studies conducted in BVOCs
233 analysis[19]. The BVOCs emission profiles of a pine tree branch were evaluated in a time span of
234 12 hours during the second week of July, 2013. A typical chromatographic profile after *in situ*
235 sampling and peak identity are presented in **Figure SI-19** and **Table SI-6**. Three major
236 compounds found at any time of the day were selected for quantitation: limonene, α-pinene and
237 β-pinene. **Table 1** presents the concentrations determined for each compound every 3 hours,
238 starting from 8 am to 8 pm. Error bars represent the standard deviation of the mean calculated
239 with three independent NTs packed with DVB.

240 In summary, 18 compounds were completely identified by their linear retention indices and
241 comparison of mass spectra with those found in the NIST database and literature. The
242 concentration of the target analytes showed a similar trend over the duration of the experiment:
243 the highest concentrations for the target compounds were obtained at 2 pm with 0.75, 2.87 and
244 11.63 ng/mL for β-pinene, limonene and α-pinene, respectively. All the concentrations were in

the range of hundreds of nanograms per liter, which are within the typical range for forest atmospheric environments. Good inter-NT repeatability for 3 NTs was found, with RSD values between 2 to 10 % in all the cases. The circadian variations observed in the concentrations of the target analytes can be a reflex from the variations of temperature and illumination conditions during the sampling cycle. Similar trends have been previously reported for isoprene in the analysis of *Eucalyptus citriodora,* and eucalyptol in the analysis of *Brugmansia suaveolens* flowers[19,21].

Table 1. Evaluation of the concentration of α-pinene, β-pinene and limonene emitted at different hours by a pine tree at University of Waterloo. Spot sampling using three NT packed with 2 cm DVB (V= 5mL, Avg. T=26.1ºC)

Time	α-pinene (ng/mL)			β-pinene (ng/mL)			Limonene (ng/mL)		
	NT_1	NT_2	NT_3	NT_1	NT_2	NT_3	NT_1	NT_2	NT_3
8 am	6.6	6.4	6.2	0.3	0.3	0.2	1.8	1.7	1.4
11 am	7.5	7.4	7.7	0.5	0.4	0.6	2.2	2.4	2.3
2 pm	12	11.5	11.4	0.6	0.7	0.8	3.0	2.7	2.9
5 pm	6.7	7.1	6.5	0.5	0.3	0.5	2.1	2.0	1.9
8pm	3.6	4.2	4.3	0.3	0.2	0.3	1.4	1.2	1.3

Development, evaluationand application of extended tip NT packed with Car particles

Development and evaluation of PDMS frit-Car needle traps towards active sampling

The main limitation of the modified extended tip-NTs packed with bare Car, compared to DVB, is that the particles do not “stick- together” due to their spherical shape and surface properties, eventually blocking the sliding-fit tubing. As a result, the flow is completely

restricted and no analytes are collected by the NT (data not presented). With the objective of broadening the applicability of the new extended tip-needles, our laboratory manufactured a novel type of NT that allows the use of Car as a packing material. The new NT consists of a small PDMS frit (2 mm thickness) that is fitted prior to the Car particles being added, as shown in **Figure 1.**

In total, 6 needles were packed with 2mm of PDMS frit and 2cm Car particles (60-80 mesh). For each of the NTs, 2 h (300 ºC) conditioning was carried out, and for all of them, a blank was performed in order to evaluate possible residual contamination. Extractions from the gas-generator chamber were performed at a 5 ml/min sampling flow rate. All the experiments were randomized for different needles and performed in triplicate. As shown in **Table 2** (please also refer to **Figure SI-7**), the relative standard deviation for the intra-needle trap repeatability of the 6 needle traps is satisfactory, since values were lower than 8% in all cases for the two analytes evaluated (toluene and ethylbenzene). Similarly, NTs proved to be statistically similar ($F_{NT} < F_{crit}$) for both compounds, and inter-needle trap RSDs lower than 5.3% were obtained.

Table 2. Intra-needle trap repeatability expressed as RSD (%) for each needle trap (n=3) using a 5 mL/min sampling volume, and statistical comparisons of 6 in-house needle traps packed with 2 mm of synthesized PDMS and 2 cm of Car particles. F_{NT} is the F-ratio for the different treatments evaluated (different needle traps) and F_{crit} is the critical value of F for 18 experiments at a 95% level of confidence. RSD* is the relative standard deviation (%) for the inter-needle trap repeatability of 6 NTs (n=3) using a sampling volume of 5 mL/min.

Compound	Intra-needle trap						Inter-needle trap		
	NT_1	NT_2	NT_3	NT_4	NT_5	NT_6	F_{NT}	F_{crit}	RSD*
Toluene	0.9	4.8	2.8	5.2	4.5	4.9	2.8	3.6	3.3
Ethylbenzene	1.8	3.8	3.2	7.8	6.4	0.4	1.5		5.3

In order to evaluate the effect of the sampling rate on the amount of analyte extracted, one of the needle traps was selected to sample at flow rates of 2, 5, and 10 mL/min. As can be seen in **Figure SI-10**, results indicate that a slightly higher amount of ethyl benzene was extracted at the lowest tested flow rate, while the same trend was not observed for toluene. However, as presented on **Table SI-3**, at a 95% level of confidence, no statistically significant difference was observed among the three different flows evaluated. It is important to highlight that variations in the packing of NTs may cause channeling through the bed, which can significantly decrease the amount of analyte extracted at higher flow rates. Such phenomena seems to be more prone in less volatile compounds, but further experiments using analytes with a broader range of vapour pressures are required to validate this observation.

Development and evaluation of needle traps packed with Car particles embedded in PDMS for passive sampling

Indoor air quality is a vital issue in occupational health. Factors such as ventilation system deficiencies, microbiological contamination, and off-gassing from building materials can cause poor indoor air quality[1]. Since an average person in a developed country spends up to 90% of their time indoors, there has been a growing concern over the past decades in regards to indoor pollutants, including the type of methods currently being used in their analysis[1,5,15]. SPME and NTs have become attractive techniques for indoor air sampling due to their accuracy, cost, simplicity and speed[1,7]. In addition, both microextraction techniques can be indistinctively used for either active or passive sampling[1,7,11,25].

The basic principle of passive sampling is the free circulation of analyte molecules from the sampled medium to the sampling device as a result of the difference in chemical potential

between them[5]. Passive sampling can be performed using NTs if a strong sorbent is packed at a defined distance Z from the needle opening of a fixed area A; thus, a diminutive tube-type diffusive sampler is created [7]. As shown in **Figure SI-11**, during the process of diffusion, there exists a linear concentration gradient across Z. Therefore, by using Fick's law of diffusion, it is possible to determine the amount of analyte loaded on the sorbent, n, during the sampling time, t[26,27]. The equations that describe the analyte uptake on the NT were summarized in **Table SI-4** and have been explained in detail in the literature [1,5,6,28]. In addition, three main conjectures should be achieved during passive sampling with NT. First, the device should respond proportionally to the changing analyte concentration at the face of the needle[26,27]. Secondly, the concentration of the gas system must be equal to the analyte concentration at the face of the opening[26,27]. And third, the sorbent should be a zero sink for the target analytes[26,27]. Such conditions were evaluated by Gong *et al*., and their results demonstrated the suitability of NT for passive sampling [10].

Owing to the flexibility of selecting a wide range of sampling times in passive mode (from less than 1 min to days), several applications designed to test a broad range of analytes have been developed to date using SPME and NT devices[11,17,25,29,30]. However, up to date studies were only performed using blunt tip NTs [7,11,17]. In this work, we proposed for the first time the application of the extended tip NT packed with Car particles embedded into PDMS (see **Figure 1**) for sampling of volatile compounds in passive mode. It should be noted that this configuration is different from the one used for active sampling. First, the NT design with Car particles was not used for passive sampling; by adding a PDMS frit, Fick's law could not be applied in a straightforward manner towards the calculation of the concentration (as presented in **Table SI-4**). In such scenario, permeation of the analytes through the PDMS frit and diffusion through the

open tubular path must be considered together with the aim of calculating the concentration on the sample. As expected, the initial configuration added more complexity to the calculations and higher inter-needle trap variability in passive mode. Conversely, by loading the particles onto the PDMS, it is assumed that PDMS acts only as glue, similar to SPME[1], and adsorption occurs mainly on Car particles. As such, the amount of sample collected would depend on the diffusion of the analytes from the entrance of the NT to the face of the sorbent (Z), the diffusion coefficient of the target analyte (D_g), the area of the cross-section of the diffusion barrier (A) and the concentration of the analyte at the needle opening (C_F).

In order to validate these assumptions, passive sampling was performed from a sampling chamber with a known concentration of benzene and toluene and with an electronic control of temperature and humidity. Samples were collected at 15, 30 and 60 min, and all the experiments were performed in triplicate for each NT. As can be seen in **Table 3 and Table SI-5**, the inter-needle trap repeatability, expressed as RSD, was <15 % for both probes. Moreover, an average absolute deviation of 9% from the theoretical amount extracted was observed. Such differences can be due to different factors. First, when calculating the theoretical amount extracted, the diffusion path Z was assumed to be exactly 1.00 cm. However, as shown in **Figure SI-12**, assessment of the sampling rate for the three probes (benzene, toluene and ethylbenzene, keeping all the parameters constant but for different diffusion paths) showed that variations as slight as 0.01 cm in Z might understate the actual value by approximately 7 %. Therefore, differences observed in relation to the theoretical value can be partially due to the inaccurate determination of the diffusion path.

Next, the diffusion coefficients of the analytes were estimated by the method proposed by Fuller, Schettler, and Giddings (FSG, please refer to Equation 1 in the supplementary

355 information)[31]. As can be found on the literature[31], such estimation is based on the number of
356 atoms present on a given molecule rather than other physicochemical factors such as structure
357 conformation or polarity. Expectedly, a common criticism of SPME/NT is a lack of published
358 experimental sampling rate values[32]. As a result, our group is currently working on a new
359 strategy towards the experimental determination of sampling rates of analytes using a recently
360 developed in-vial standard gas generator [16]. In this sense, since most of the variables involved in
361 passive sampling can be controlled or calculated (such as sampling time, diffusion path, cross
362 sectional area, and vial concentration), the vial approach could be further pursued with the aim of
363 building a comprehensive database of experimental diffusion coefficients of VOCs.

364 Finally, an additional source of error could be related to the adsorption of analytes onto the
365 needle walls. Several studies found that the likelihood of adsorption onto the needle walls is not
366 easily predictable, and seems to depend on the concentration to which the device is exposed[26,33].
367 In addition, at long exposure times, the amount of analytes collected on the sorbent would be
368 considerably higher than the amount adsorbed onto needle walls, and consequently, under these
369 conditions, the needle adsorption effect on uptake rates would be negligible. It has also been
370 observed that if the sampling temperature increases, the adsorption of the compound on the
371 needle diminishes, and the experimental value of the sampling rates is closer to the theoretical
372 value. Other authors have also suggested that matter of adsorption onto the needle walls is not a
373 major issue, as it is only observed in less volatile compounds[26,34]. Chen and Hsiech reported that
374 the experimental sampling rates of dichloromethane at very short sampling times were higher
375 than rates obtained with long sampling exposures[33]. However, similarly to observations reported
376 by Chen and Pawliszyn, the values become constant as the sampling time increases[3]. In order to
377 eliminate the effect of needle adsorption, Chen *et al*. proposed the use of deactivated needles for

TWA samplers, such as Silicosteel-coated needles[1,26]. Further evaluation of needle deactivation would need to be carried-out for this prototype prior to its commercialization as a passive sampler.

In summary, the results herein presented demonstrate that the new extended tip needle trap packed with Car particles loaded on PDMS, and with a Z of approximately 1 cm, could be successfully used as a passive sampler if the diffusion path, diffusion coefficient, and needle deactivation are properly controlled/determined.

Table 3. Comparison of the amount of benzene collected in passive sampling mode (Z ~1.0 cm) by 2 different NTs packed with a PDMS frit of 0.2 cm and 1 cm of Car *versus* theoretical amounts determined using Fick's law.

Sample collection time (min)	Theoretical amount extracted (ng)	Experimental amount extracted (ng)		Inter-needle trap repeatability (%)		Experimental error (%)	
		NT_1	NT_2	RSD_1	RSD_2	CV_1	CV_2
15	6.6	6.0	6.3	10	8	9	5
30	13.2	12.2	14.5	15	14	7	9
60	26.5	23.0	30.0	13	5	12	13

Development of a new pen-like diffusive sampler (PDS)

Design of the PDS

Several field samplers have been developed to date for microextraction devices. However, the majority of these devices do not integrate critical factors of passive samplers such as a)preservation of the samples, and b) ease of deployment, storage, and transportation [2,4]. The field sampler developed by Chen and Pawliszyn[3] was designed to be used interchangeably with

commercial SPME fiber assemblies, making this sampler more universal. Moreover, this device achieved three of the four design requirements of a field sampler, namely proper sealing of the needle, needle protection, and a user-friendly interface. However, despite its small size and ease of use, this assembly was not suitable for use in a multiple device exchanger[16,26]. Recently, Zare *et al*. developed a SPME pen-shaped holder for passive sampling of anesthetics in operating rooms[30]. However, a serious drawback of this device is that storage features, such as a Teflon cap, were not included in its design. Research has shown that Teflon is an appropriate sealing material with negligible memory effects, and that it appropriately isolates the sorbent from the ambient environment, thus avoiding contamination while protecting sample integrity[2,3]. The effectiveness of the Teflon cap was also demonstrated when used with highly efficient sorbents such as Car, since it can retain VOCs for up to two weeks without significant losses[3]. Cross contamination may only be an issue when Teflon caps are used repeatedly. Nonetheless, simple solutions, such as Teflon cap conditioning at high temperatures, can diminish the potential for cross contamination[3].

Up to date, only two portable personal diffusive samplers have been developed for NT. The first is the badge-like sampler (**Figure SI-13**, inset A), which consists of two components, a sampler holder and a NT. The sampler holder is a metal plate with four Teflon chips. A hole in the center of each chip allows sealing of the side hole and tip of the needle, so as to preserve sample integrity. An advantage of this device is that it could be fixed either to the front pocket of the operator or under a shirt collar during the sampling process[10]. Conversely, the pen-like device (**Figure SI-13**, inset B) is lighter and more user-friendly than the former[10]. However, because of its design, it is complicated to load the NTD into the holder, as well as in the tray of the

autosampler. This device operates in two positions, the sealing position and the sampling position. When the button at the end of the pen is pressed, the tip of the needle is sealed by a Teflon cap found in the tip of the pen. Alternatively, when the needle is retracted by pressing the button, the tip of the needle is exposed to air that moves in and out through the elliptical windows on each side of the pen. **Figure SI-14** and **Figure 2** summarize the main features of the new pen-like diffusive sampler (PDS). One of the most important characteristics of the new device is its versatility: most commercial needle traps can be installed. Because of the plug-screw system designed for the top of the needle, it can be easily fitted to the upper part of the holder. This feature allows the analyst to do a manual injection whenever a needle trap with a side-hole is used[11,17]. Another remarkable characteristic is the automatic exposure system. By placing the PDS on a shirt pocket (**Figure2**), the needle is moved automatically to the sampling position. Finally, the screw-type Teflon tip not only guarantees sample preservation during its transportation/storage, but it can also be easily disassembled for cleaning purposes[3].

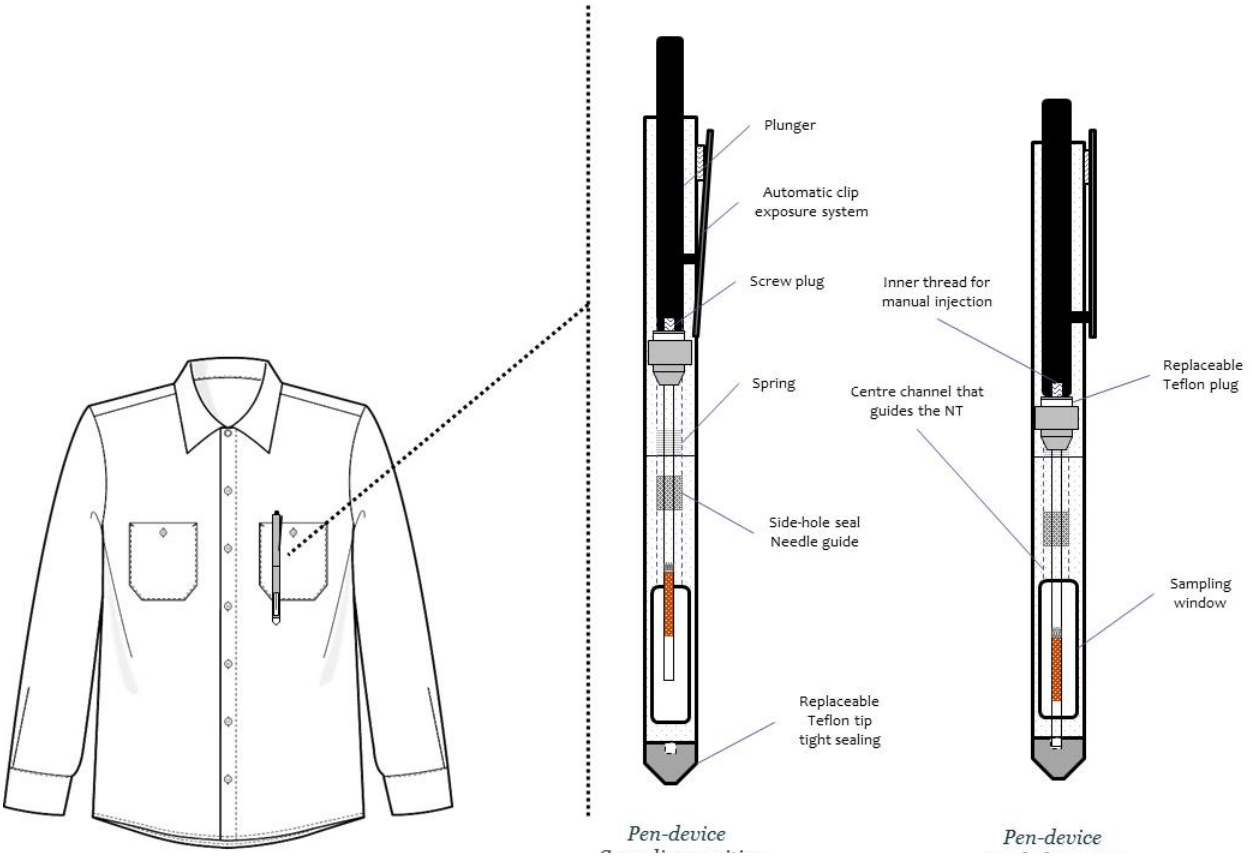

Figure 2 Schematic of the sampling and sealed positions of the PDS-NT.

Effect of the holder on the uptake rate

Two critical parameters of the pen-like diffusive sampler (PDS) were evaluated, specifically storage stability for up to 24 hours at room temperature, and possible effects of the sampler device on the uptake rate of the analytes. The former was evaluated by comparing the amount of BTX collected by a needle trap with and without the sampling holder. These compounds were selected based on data provided by *Gong et al*.[10], who demonstrated that a NT device packed with Carboxen1000 is a successful diffusive sampler for monitoring TWA concentrations of BTEX under low relative humidity[10]. **Figure SI-15** presents the comparison of the two independent needle traps versus the same needle trap installed in the holder. As can be seen, no statistically significant differences were found for any of the needle traps. Thus, based on these experimental findings, it is possible to use the PDS with no concerns regarding possible holder effects on analyte uptake rates. It should be highlighted that the initial experiments herein described using the PDS were performed using blunt needles; however, final application to the evaluation of indoor air analysis was performed using the previously tested extended tip needle traps.

Evaluation of storage stability

Storage stability is critical for field TWA sampling. If storage is unstable, analytes adsorbed inside the sampler may be lost, introducing experimental error. The storage stability of the PDS containing a NTD packed with Carboxen1000 was evaluated. First, the PDS-NTD was used to passively sample BTX from the standard gas system, then instantaneously injected into the

GC/FID. Next, the same device was used to sample passively, and immediately after, the button on top of the PDS was pressed to seal the needle with the pen's tip (made of Teflon). Subsequently, the pen was wrapped with aluminum foil to prevent cross contamination, and stored for 24 h at 23.5°C; after a 24 hour period, the NT was injected into the GC/FID. The results from the analysis, presented on **Figure SI-16**, showed no significant losses after 24 hours of storage at room temperature. These results agreed with those reported by Gong *et al*.[10]

Comparison of two PDS-NT holders

Two PDS-NT were built at the University of Waterloo machine shop. Two needle traps found to be statistically similar in terms of the amount of BTX collected were selected for the evaluation of these PDS devices. As shown in **Figure SI-17**, statistical differences were not found when comparing the two independent PDS devices (n=5). Inter-PDS repeatability was below 9 % for all compounds. Therefore, it can be concluded that two independent PDS-NT devices have the same performance under the controlled conditions here described. In order to have a complete acceptance of the PDS-NT, other environmental conditions that critically affect diffusive passive samplers, such as temperature and humidity, should be studied[10,30]. Several studies have shown that these environmental parameters might affect the uptake rate of the analyte, depending on its molecular weight and polarity[10,30]. Consequently, a broader range of VOCs should be evaluated using the PDS-NT.

Application of *PDMS-Car* NTs towards the evaluation of indoor air contaminants in active and passive sampling mode

Indoor air was analyzed at a polymer synthesis laboratory at the University of Waterloo. Several samples were collected in the span of a workday (8 h) to determine variations in the air contamination profile within this time limit. Active sampling through a 2 cm DVB NT was carried out every hour to observe intra-day variations. Passive sampling over a period of 8 hours, using two PDS-NT packed with 1cm Car, were used to determine the average concentration of toluene to which workers were exposed. The sampling devices were located at approximately 2.5 meters from the rotary evaporator in order to account for the average exposure of a worker in the laboratory. As can be seen in **Figure SI-18**, good agreement was observed between passive and active techniques. According to laboratory workers, the increase in the concentration of toluene, observed at two different times during the day, at 10:30 am and 2:30 pm, correlated to the use of a rotary evaporator.

The active-NT concentration can be considered a time-weighted average sample obtained over a short sampling period (approximately 20 min sampling), only allowing the analyst to obtain results for a specific fragment of the day rather than the entire day variation. This explains why the average of the concentrations calculated using the active NTD (0.025 ng/mL) was slightly lower than the one obtained with NT in passive sampling mode (0.030 ± 0.01ng/mL, n=2). It is important to emphasize that toluene was not found to be present in concentrations higher than the regulatory quantities established by the National Institute for Occupational Safety and Health (NIOSH) at all times. For instance, the highest concentration of toluene found during the sampling was 0.078ng/mL, whereas the established 10-hour Threshold Limit Value (TLV) and the short-time exposure limit (STEL) of toluene are 377 and 565 ng/mL, respectively. The results presented in this study highlight the applicability of these techniques in the monitoring of more

toxic compounds such as benzene, which have lower thresholds (0.32 ng/L TLV and 8 ng/L STEL)[7,26].

Conclusions

Considering the increasing efforts made by the scientific community towards the development of new on-site sampling technologies, the present work seeks to showcase the most recent advances of NT technology. Here, an easy to deploy, reusable needle trap pen-like diffusive sampler (PDS-NT) was presented. Unlike previous designs, a clicking exposure system positions the NT automatically in the sampling position when placed in a fixed position; for testing purposes, a pocket was used. In addition, the loading of the NT on the pen is simpler, and the device can be used for both manual or automated unattended NT desorption. The designed PDS-NT is meant to be paired with products from different manufacturers. As well, in-house or commercially available devices such those produced by SGE or Shinwa can be easily installed[7–9,24]. This study demonstrated that the new PDS-NT is effective for air analysis of benzene, toluene, and o-xylene (BTX). No effects based on pen geometry were observed in regards to the uptake of analytes. Good storage stability of the target analytes was observed for up to 24 hours. Comparison of two independent PDS-NT devices showed that there were no statistically significant differences between them. Finally, the application of the PDS-NT (NT containing PDMS loaded with Car) towards on-site analysis showed good agreement with the results obtained by active sampling using PDMS frit-Car NTs. However, further testing under different environmental conditions needs to be undertaken in order to monitor a greater range of VOCs. It

546 can be predicted that the PDS-NT will be useful and convenient for monitoring both personal
547 exposure in the occupational environment and ambient air quality.
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562 **Associated content**

563 *Supporting Information*
564
565 Additional information as noted in the text. This material is available free of charge via the
566 Internet at http://pubs.acs.org.
567
568 **References**

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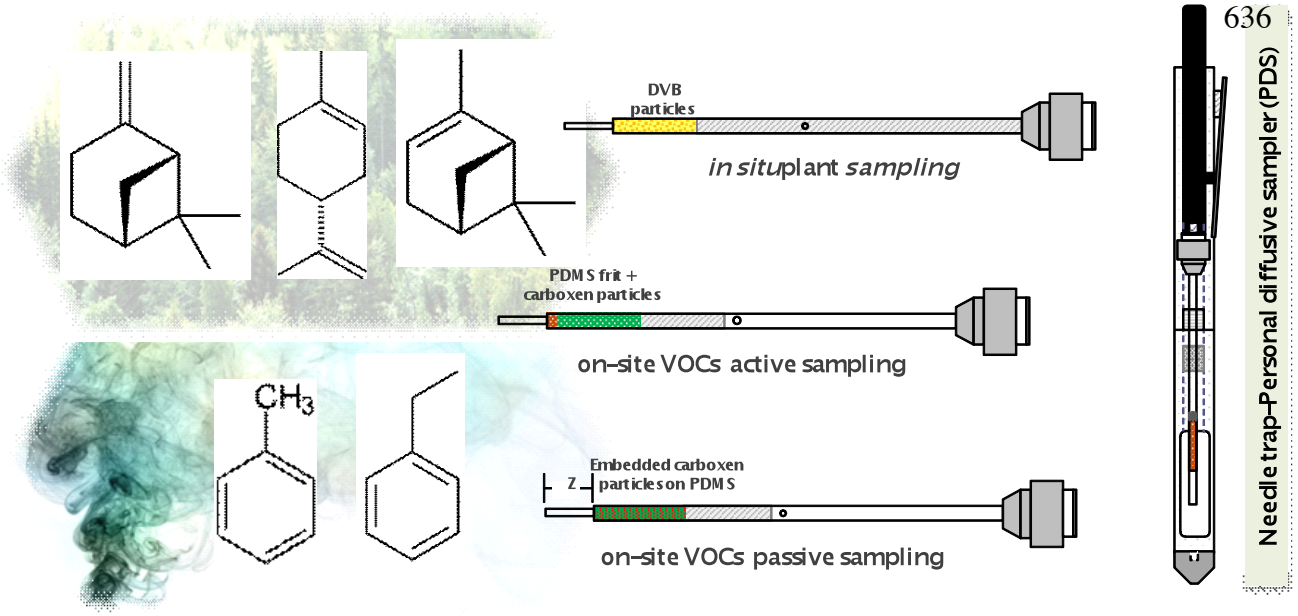

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