

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

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16

17 **Abstract**

18 This study presents a thorough evaluation of new prototypes of extended tip needle trap devices
19 (NT), as well as their application to *in situ* sampling of biological emissions and active/passive
20 on-site sampling of indoor air. A new NT prototype was constructed with a side hole above the
21 sorbent and an extended tip that fits inside the restriction of the narrow neck liner to increase
22 desorption efficiency. New prototype needles were initially packed with divinylbenzene particles
23 at SGE Analytical Science for the purpose of studying biogenic emissions of pine trees. Prior to
24 their final application, they were evaluated in terms of robustness after multiple use ($n > 10$), as
25 well as amount extracted of volatile organic compounds (VOCs). An ANOVA test for all the
26 probes showed that at a 95 % level of confidence, there were not statistical differences observed
27 among the 9 NTs tested. In addition, the needles were also packed in laboratory with synthesized
28 highly cross linked PDMS as a frit to immobilize carboxen (Car) particles for spot sampling. For
29 passive sampling, the needles were packed with Car particles embedded in PDMS in order to
30 simplify calculations in passive mode. The use of NTs as spot samplers, as well as a passive
31 sampler under controlled conditions in the laboratory yielded a relative standard deviation of less
32 than 15 %. Finally, a new, reusable and readily deployable pen-like diffusive sampler for needle
33 traps (PDS-NT) was built and tested. Application of the PDS-NT in combination with NT-spot
34 sampling towards the analysis of indoor air in a polymer synthesis laboratory showed good
35 agreement between both techniques for the analyte studied, yielding averages of 0.03 ng/mL and
36 0.025 ng/mL of toluene, respectively.

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38

39 **Introduction**

40 Recently, there has been increasing interest in air analysis among environmental scientists.
41 Ideally, air samples should be analyzed on-site to avoid losing sample integrity¹. In cases where
42 on-site analysis is not possible, simple sampling/sample preparation techniques for field
43 applications are required^{2,3}. Sampler devices for field sampling should be simple and reliable,
44 since sampling sites are generally located far from the laboratory. Consequently, the device
45 should also comprise easy method deployment, one which allows operators with limited
46 knowledge of the extraction mechanisms to easily operate the sampler. Moreover, the production
47 of the device should be uncomplicated and inexpensive^{4,5}. Additionally, during sample
48 transportation and storage, any contamination, decomposition, and/or loss of the analytes should
49 be negligible^{5,6}. Finally, the device should be sensitive to the substances under study, unaffected
50 by interfering matrix components, and not require in-laboratory sample pre-treatment^{4,6}. Solid
51 phase microextraction (SPME) and needle trap (NT) devices have been shown to be suitable
52 techniques to address these concerns⁷⁻⁹.

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

59 **Equation 1:** $C_0 = n/V_s$

60 Several factors, such as pore size and shape, surface area, and particle size can affect the
61 ability of the analyte to access and interact with the surface of the adsorbent. Therefore, these
62 parameters must be contemplated and controlled when designing new needle trap devices ^{10,11}.
63 Moreover, because of the special shape of the needle, sorbents used for NT must have the
64 appropriate physical characteristics in size, hardness, and shape (spherical), as well as adequate
65 mechanical and thermal stability^{7,11}. The first practical and successful application of NT suitable
66 for automation and on-site analysis was carried out using a 23 gauge stainless steel needle 40
67 mm long, containing 5 mm of quartz wool packing^{12,13}. Since then, several groups have worked
68 on the development of sorbent-packed needles or similar devices⁷. Some of the sorbents that
69 have been used for the analysis of volatile organic compounds (VOCs) include carboxen (Car),
70 divinylbenzene (DVB), Porapak QTM, and Carbopack XTM^{7,11,14}. The design of the NT geometry
71 must guarantee several factors: exhaustive extraction (active sampling), negligible breakthrough
72 during sampling, and efficient desorption ^{10,12,15,16}.

73 Research performed by Warren *et al.*, and Zhan *et al.* ^{11,17} demonstrated that in order to achieve
74 complete desorption (non-carryover), an aid-gas should be directed through the needle trap
75 packing, either through carrier gas or gas-tight assistance desorption¹¹. Thus, if a good seal is
76 created between the outer surface of the needle and the inner surface of the liner, the carrier gas
77 is exclusively driven through the side-hole of the needle, passing through sorbent, then finally
78 migrating alongside the extracted analytes by the needle tip. The sealing system on the first side-
79 hole NTs relied entirely on the tapered shape of the needle's tip. However, inefficient desorption
80 of analytes and carryover issues revealed the weaknesses of this design; basically, an effective
81 and reliable hard-to-hard surface seal (metal needle and glass liner) was not achieved.

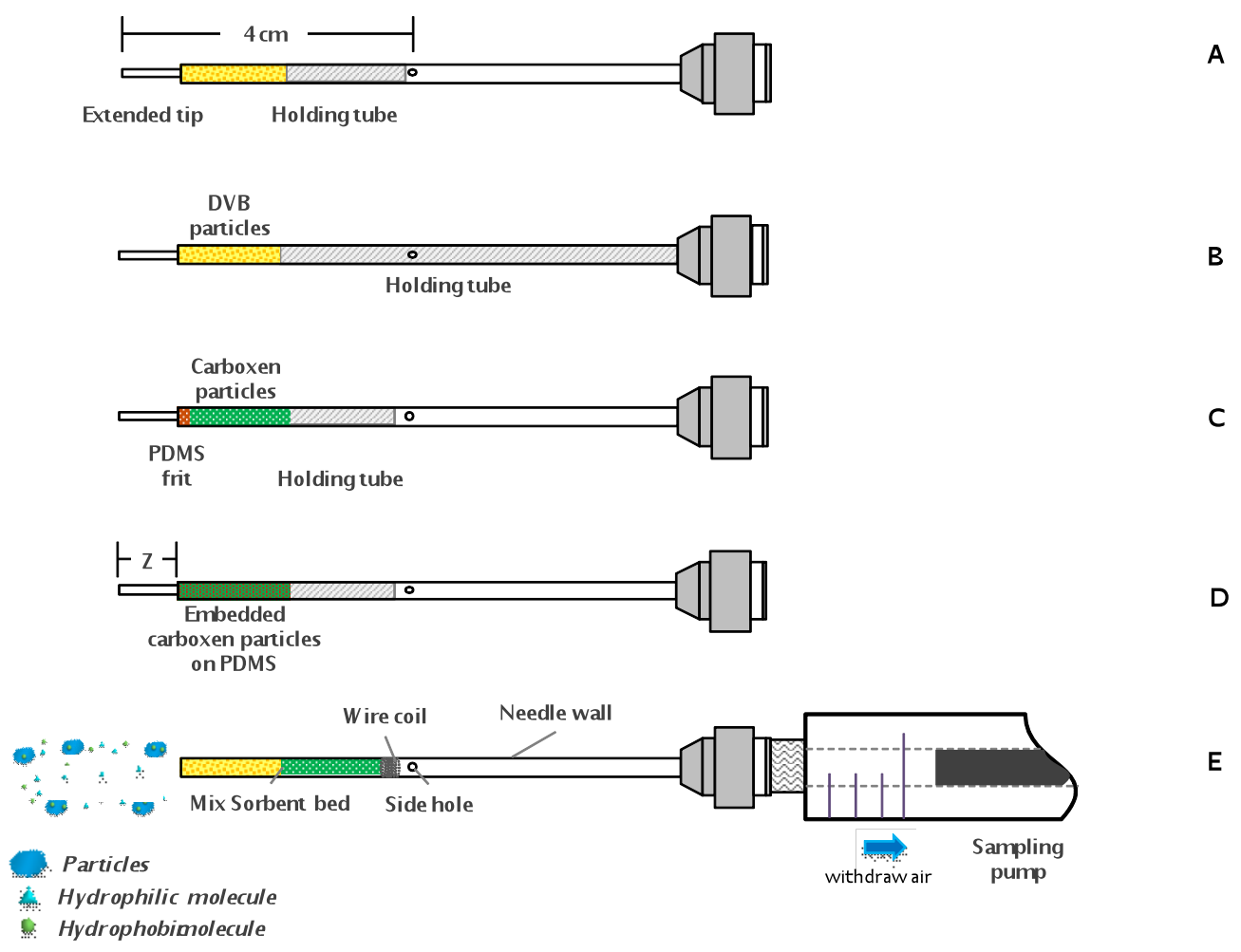
82 The needle/liner prototype herein described differs from the original design by relying on a
83 metal/metal seal between the tip of the needle and the bore of the metal liner¹⁷. In this design, as
84 shown in **Figure SI-1**, the outside diameter of the needle tip (O.D. 0.495mm) fits precisely on
85 the bottom section of the GC-liner, which has a smaller diameter (I.D. 0.500 mm) than the upper
86 part of the liner. A conical guiding system allows the smooth insertion of the needle tip into the
87 smaller section of the liner. Since this design guarantees a better seal with the narrow neck
88 liner^{11,17}, the carrier gas is forced to only go through the sorbent bed, as seen in **Figure 1**. In
89 addition to addressing the sealing issues related to glass liners, metal liners proved to be more
90 efficient in transferring heat evenly throughout the full length of the packing. Chemical
91 deactivation of metal liners was performed in order to avoid the presence of active sites.

92
93 This report also presents the evaluation of a new extended tip NT packed with DVB particles,
94 including modifications to allow the use of Car particles, a reassessment of the new designs, and
95 its application to on-site analysis in active and passive sampling modes. In addition, a new NT
96 diffusive sampler is presented in this study. It has a similar mechanism to the one described by
97 Gong *et al.*¹⁰. However, in contrast to the previous design, loading the NT on the holder is
98 simpler and can be accomplished in a few seconds. Also, a clever clicking exposure system
99 places the NT automatically in the sampling position when it is fixed in a pocket. Unlike
100 previous works, a sampling chamber was successfully designed and built for the evaluation of
101 the sampler device under a controlled environment. Moreover, the new PDS-NT can be used for
102 either manual desorption with the holder, or automated unattended NT desorption⁷.

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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

127

128 **Experimental**

129 **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 °C for 1 hour¹⁸. After the PDMS mixture was cured, the polymerized PDMS was
147 heated at 120 °C 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 °C 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,

153 curing agent, and 1% SDS solution, and stirred for 10 min. Next, glass capillaries were tilled
154 with the mixture and heated at 80 °C for 1 hour. After curing, the oven temperature was
155 increased to 120 °C, and the mixture containing polymerized Car embedded in PDMS was heated
156 for 3 hours to remove the impurities.

157 *Sampling procedures*

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

160

161 **Results and Discussion**

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

163 *Initial assessment of the extended tip needles*

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

173

174 *Evaluation of modified extended tip needles packed with DVB particles*

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

192
193 In summary, the modified prototype has shown to be statistically reproducible among the 9
194 different NTs evaluated as long as the sampling is performed at sampling rates lower than 5
195 mL/min. Additionally, it was found that after approximately 10 injections, the pre-punch septum
196 should be replaced in order to avoid pieces of septum going inside the restriction of the liner. To
197 test the durability of the liner, continuous testing of the same liner was conducted. The liner was
198 checked every 20 injections with a gas duster and a small wire passing through the restriction in

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

208

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

210 Volatile and semi-volatile compounds produced by plants are collectively known as biogenic
211 volatile organic compounds (BVOC)¹⁹. They comprise a wide variety of organic substances, such
212 as alcohols, terpenes, alkanes and esters. Owing to the fact that BVOCs are responsible for
213 multiple interactions between plants and other organisms, and also play a key role in atmospheric
214 chemistry, their identification, characterization and quantification are of great relevance¹⁹.

215 Generally, *in situ* research is best suited to observe real conditions when compared to *in vitro*
216 research¹⁹. As biological systems are very complex and readily react to any perturbation in the
217 surrounding environment, *in situ* research can provide more accurate results than *in vitro* studies
218 ^{20,21}. An ideal *in situ* sampling technique should be solvent-free, portable, and offer integration of
219 the sampling, sample preparation and analysis steps. With NT, both *in situ* sampling and sample
220 preparation are accomplished by placing the needle in the area surrounding the system under
221 study²¹. Consequently, the plant tissue being analyzed is only minimally disturbed. *In situ*

222 analysis using SPME and NT is gaining ground in metabolomics studies²² 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 NT¹. 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 studied¹⁹. 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 analysis¹⁹. 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

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

252

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

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

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257

258 **Development, evaluation and application of extended tip NT packed with Car particles**

259

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

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

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

269 In total, 6 needles were packed with 2mm of PDMS frit and 2cm Car particles (60-80 mesh).
 270 For each of the NTs, 2 h (300 °C) conditioning was carried out, and for all of them, a blank was
 271 performed in order to evaluate possible residual contamination. Extractions from the gas-
 272 generator chamber were performed at a 5 ml/min sampling flow rate. All the experiments were
 273 randomized for different needles and performed in triplicate. As shown in **Table 2** (please also
 274 refer to **Figure SI-7**), the relative standard deviation for the intra-needle trap repeatability of the
 275 6 needle traps is satisfactory, since values were lower than 8% in all cases for the two analytes
 276 evaluated (toluene and ethylbenzene). Similarly, NTs proved to be statistically similar ($F_{NT} <$
 277 F_{crit}) for both compounds, and inter-needle trap RSDs lower than 5.3% were obtained.

278 **Table 2.** Intra-needle trap repeatability expressed as RSD (%) for each needle trap (n=3) using
 279 a 5 mL/min sampling volume, and statistical comparisons of 6 in-house needle traps packed with
 280 2 mm of synthesized PDMS and 2 cm of Car particles. F_{NT} is the F-ratio for the different
 281 treatments evaluated (different needle traps) and F_{crit} is the critical value of F for 18 experiments
 282 at a 95% level of confidence. RSD* is the relative standard deviation (%) for the inter-needle
 283 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

284

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

295

296

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

299 Indoor air quality is a vital issue in occupational health. Factors such as ventilation system
300 deficiencies, microbiological contamination, and off-gassing from building materials can cause
301 poor indoor air quality¹. Since an average person in a developed country spends up to 90% of
302 their time indoors, there has been a growing concern over the past decades in regards to indoor
303 pollutants, including the type of methods currently being used in their analysis^{1,5,15}. SPME and
304 NTs have become attractive techniques for indoor air sampling due to their accuracy, cost,
305 simplicity and speed^{1,7}. In addition, both microextraction techniques can be indistinctively used
306 for either active or passive sampling^{1,7,11,25}.

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

309 between them⁵. Passive sampling can be performed using NTs if a strong sorbent is packed at a
310 defined distance Z from the needle opening of a fixed area A ; thus, a diminutive tube-type
311 diffusive sampler is created⁷. As shown in **Figure SI-11**, during the process of diffusion, there
312 exists a linear concentration gradient across Z . Therefore, by using Fick's law of diffusion, it is
313 possible to determine the amount of analyte loaded on the sorbent, n , during the sampling time,
314 $t^{26,27}$. The equations that describe the analyte uptake on the NT were summarized in **Table SI-4**
315 and have been explained in detail in the literature^{1,5,6,28}. In addition, three main conjectures
316 should be achieved during passive sampling with NT. First, the device should respond
317 proportionally to the changing analyte concentration at the face of the needle^{26,27}. Secondly, the
318 concentration of the gas system must be equal to the analyte concentration at the face of the
319 opening^{26,27}. And third, the sorbent should be a zero sink for the target analytes^{26,27}. Such
320 conditions were evaluated by Gong *et al.*, and their results demonstrated the suitability of NT for
321 passive sampling¹⁰.

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

332 open tubular path must be considered together with the aim of calculating the concentration on
333 the sample. As expected, the initial configuration added more complexity to the calculations and
334 higher inter-needle trap variability in passive mode. Conversely, by loading the particles onto the
335 PDMS, it is assumed that PDMS acts only as glue, similar to SPME¹, and adsorption occurs
336 mainly on Car particles. As such, the amount of sample collected would depend on the diffusion
337 of the analytes from the entrance of the NT to the face of the sorbent (Z), the diffusion
338 coefficient of the target analyte (D_g), the area of the cross-section of the diffusion barrier (A) and
339 the concentration of the analyte at the needle opening (C_F).

340 In order to validate these assumptions, passive sampling was performed from a sampling
341 chamber with a known concentration of benzene and toluene and with an electronic control of
342 temperature and humidity. Samples were collected at 15, 30 and 60 min, and all the experiments
343 were performed in triplicate for each NT. As can be seen in **Table 3 and Table SI-5**, the inter-
344 needle trap repeatability, expressed as RSD, was <15 % for both probes. Moreover, an average
345 absolute deviation of 9% from the theoretical amount extracted was observed. Such differences
346 can be due to different factors. First, when calculating the theoretical amount extracted, the
347 diffusion path Z was assumed to be exactly 1.00 cm. However, as shown in **Figure SI-12**,
348 assessment of the sampling rate for the three probes (benzene, toluene and ethylbenzene, keeping
349 all the parameters constant but for different diffusion paths) showed that variations as slight as
350 0.01 cm in Z might understate the actual value by approximately 7 %. Therefore, differences
351 observed in relation to the theoretical value can be partially due to the inaccurate determination
352 of the diffusion path.

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

355 information)³¹. As can be found on the literature³¹, 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 values³². 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 generator¹⁶. 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 Hsieh reported that
374 the experimental sampling rates of dichloromethane at very short sampling times were higher
375 than rates obtained with long sampling exposures³³. However, similarly to observations reported
376 by Chen and Pawliszyn, the values become constant as the sampling time increases³. In order to
377 eliminate the effect of needle adsorption, Chen *et al.* proposed the use of deactivated needles for

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

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

385

386 **Table 3.** Comparison of the amount of benzene collected in passive sampling mode (Z ~1.0
 387 cm) by 2 different NTs packed with a PDMS frit of 0.2 cm and 1 cm of Car *versus* theoretical
 388 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

389

390

391

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

393 *Design of the PDS*

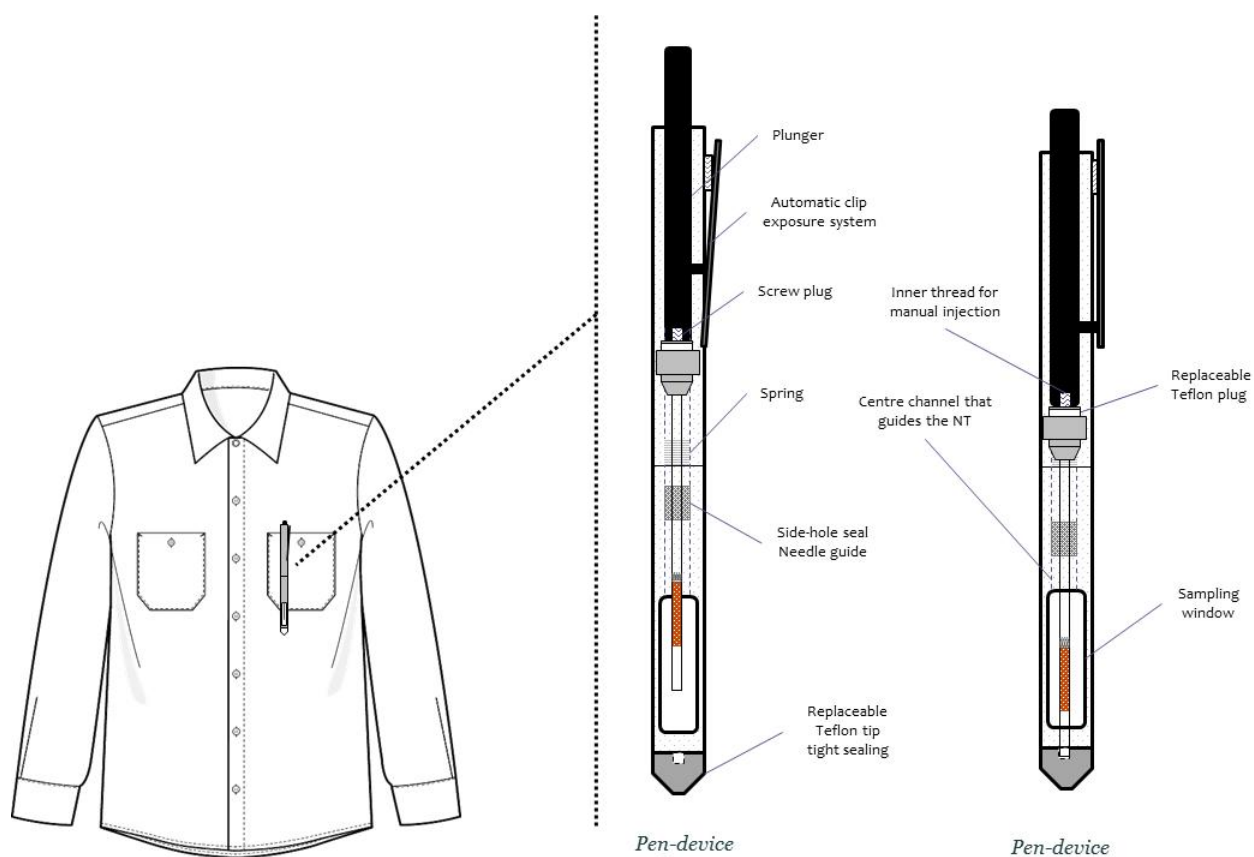
394 Several field samplers have been developed to date for microextraction devices. However, the
 395 majority of these devices do not integrate critical factors of passive samplers such as
 396 a) preservation of the samples, and b) ease of deployment, storage, and transportation^{2,4}. The
 397 field sampler developed by Chen and Pawliszyn³ was designed to be used interchangeably with

398 commercial SPME fiber assemblies, making this sampler more universal. Moreover, this device
399 achieved three of the four design requirements of a field sampler, namely proper sealing of the
400 needle, needle protection, and a user-friendly interface. However, despite its small size and ease
401 of use, this assembly was not suitable for use in a multiple device exchanger^{16,26}. Recently, Zare
402 *et al.* developed a SPME pen-shaped holder for passive sampling of anesthetics in operating
403 rooms³⁰. However, a serious drawback of this device is that storage features, such as a Teflon
404 cap, were not included in its design. Research has shown that Teflon is an appropriate sealing
405 material with negligible memory effects, and that it appropriately isolates the sorbent from the
406 ambient environment, thus avoiding contamination while protecting sample integrity^{2,3}. The
407 effectiveness of the Teflon cap was also demonstrated when used with highly efficient sorbents
408 such as Car, since it can retain VOCs for up to two weeks without significant losses³. Cross
409 contamination may only be an issue when Teflon caps are used repeatedly. Nonetheless, simple
410 solutions, such as Teflon cap conditioning at high temperatures, can diminish the potential for
411 cross contamination³.

412

413 Up to date, only two portable personal diffusive samplers have been developed for NT. The
414 first is the badge-like sampler (**Figure SI-13**, inset A), which consists of two components, a
415 sampler holder and a NT. The sampler holder is a metal plate with four Teflon chips. A hole in
416 the center of each chip allows sealing of the side hole and tip of the needle, so as to preserve
417 sample integrity. An advantage of this device is that it could be fixed either to the front pocket of
418 the operator or under a shirt collar during the sampling process¹⁰. Conversely, the pen-like device
419 (**Figure SI-13**, inset B) is lighter and more user-friendly than the former¹⁰. However, because of
420 its design, it is complicated to load the NTD into the holder, as well as in the tray of the

421 autosampler. This device operates in two positions, the sealing position and the sampling
422 position. When the button at the end of the pen is pressed, the tip of the needle is sealed by a
423 Teflon cap found in the tip of the pen. Alternatively, when the needle is retracted by pressing the
424 button, the tip of the needle is exposed to air that moves in and out through the elliptical
425 windows on each side of the pen. **Figure SI-14** and **Figure 2** summarize the main features of the
426 new pen-like diffusive sampler (PDS). One of the most important characteristics of the new
427 device is its versatility: most commercial needle traps can be installed. Because of the plug-
428 screw system designed for the top of the needle, it can be easily fitted to the upper part of the
429 holder. This feature allows the analyst to do a manual injection whenever a needle trap with a
430 side-hole is used^{11,17}. Another remarkable characteristic is the automatic exposure system. By
431 placing the PDS on a shirt pocket (**Figure2**), the needle is moved automatically to the sampling
432 position. Finally, the screw-type Teflon tip not only guarantees sample preservation during its
433 transportation/storage, but it can also be easily disassembled for cleaning purposes³.
434



455

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

457

458 *Effect of the holder on the uptake rate*

459 Two critical parameters of the pen-like diffusive sampler (PDS) were evaluated, specifically
460 storage stability for up to 24 hours at room temperature, and possible effects of the sampler
461 device on the uptake rate of the analytes. The former was evaluated by comparing the amount of
462 BTX collected by a needle trap with and without the sampling holder. These compounds were
463 selected based on data provided by *Gong et al.*¹⁰, who demonstrated that a NT device packed
464 with Carboxen1000 is a successful diffusive sampler for monitoring TWA concentrations of
465 BTEX under low relative humidity¹⁰. **Figure SI-15** presents the comparison of the two
466 independent needle traps versus the same needle trap installed in the holder. As can be seen, no
467 statistically significant differences were found for any of the needle traps. Thus, based on these
468 experimental findings, it is possible to use the PDS with no concerns regarding possible holder
469 effects on analyte uptake rates. It should be highlighted that the initial experiments herein
470 described using the PDS were performed using blunt needles; however, final application to the
471 evaluation of indoor air analysis was performed using the previously tested extended tip needle
472 traps.

473

474 *Evaluation of storage stability*

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

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

485

486 *Comparison of two PDS-NT holders*

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

498

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

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

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

523 toxic compounds such as benzene, which have lower thresholds (0.32 ng/L TLV and 8 ng/L
524 STEL)^{7,26}.

525

526

527

528 **Conclusions**

529 Considering the increasing efforts made by the scientific community towards the development
530 of new on-site sampling technologies, the present work seeks to showcase the most recent
531 advances of NT technology. Here, an easy to deploy, reusable needle trap pen-like diffusive
532 sampler (PDS-NT) was presented. Unlike previous designs, a clicking exposure system positions
533 the NT automatically in the sampling position when placed in a fixed position; for testing
534 purposes, a pocket was used. In addition, the loading of the NT on the pen is simpler, and the
535 device can be used for both manual or automated unattended NT desorption. The designed PDS-
536 NT is meant to be paired with products from different manufacturers. As well, in-house or
537 commercially available devices such those produced by SGE or Shinwa can be easily installed⁷⁻
538 ^{9,24}. This study demonstrated that the new PDS-NT is effective for air analysis of benzene,
539 toluene, and o-xylene (BTX). No effects based on pen geometry were observed in regards to the
540 uptake of analytes. Good storage stability of the target analytes was observed for up to 24 hours.
541 Comparison of two independent PDS-NT devices showed that there were no statistically
542 significant differences between them. Finally, the application of the PDS-NT (NT containing
543 PDMS loaded with Car) towards on-site analysis showed good agreement with the results
544 obtained by active sampling using PDMS frit-Car NTs. However, further testing under different
545 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.

548

549

550

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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

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634 For Table of Contents Only

The diagram illustrates three sampling methods:

- in situ plant sampling:** Shows three chemical structures of terpenes (monoterpene, sesquiterpene, and diterpene) and a sampling tube containing DVB particles.
- on-site VOCs active sampling:** Shows a sampling tube containing PDM S frit + carboxen particles.
- on-site VOCs passive sampling:** Shows a sampling tube containing Embedded carboxen particles on PDM S, with a Z-factor label.

Chemical structures shown include:

- Terpenes: CC1=CC(C)C(C)C1, CC1=CC(C)C(C)C(C)C1, CC1=CC(C)C(C)C(C)C(C)C1
- VOCs: CC1=CC=C(C)C=C1 (Toluene), CC1=CC=C(C)C=C1 (Ethylbenzene)

636 Needle trap-Personal diffusive sampler (PDS)

637