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Author: Juan M. Sanchez

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Effects of packing density, flow and humidity on the performance of needle trap devices

Juan M. Sanchez*

Department of Chemistry, University of Girona, Campus Montilivi s/n, 17071-Girona, Spain

* Corresponding author

Chemistry Department

Science Faculty

University of Girona

Campus Montilivi s/n

17071-Girona (Spain)

E-mail: juanma.sanchez@udg.edu

Phone: +34-972418276

FAX: +34-972418150

Abstract

Needle trap devices (NTDs) have become a promising alternative to solid-phase microextraction (SPME) due to their robustness and exhaustive sampling while maintaining all the advantages of SPME. This study investigates the compromise required in packing NTDs starting from the hypothesis that their diameter makes perfect packing impractical. The most limiting parameter of NTDs is the small amount of sorbent that can be fitted in the trap. On evaluating packing density, it is found that the densest packing cannot practically be achieved with NTDs. This poor packing leads to oscillations in the fluid flow profiles and so sampling flows up to 10-15 mL min^{-1} are recommended for this methodology. The limited amount of sorbent materials inside the needles makes breakthrough another limiting aspect of NTDs. However, one of the most significant advantages of these devices is that they have a large preconcentration factor, which results in method detection limits in the pptv range with sample volumes <100 mL. This methodology gives promising results in the analysis of water saturated samples as the limited amount of sorbents reduces water retention. Moreover, it is desirable for a small amount of water to be retained with NTDs as this improves the desorption of the retained compounds in the GC injector and allows sharper injection band-widths to be obtained.

Keywords: breakthrough; humidity; needle trap; packing density; flow profile

1. Introduction

Solid-phase microextraction (SPME) appeared in the 1990s as a fast and solvent-free microextraction alternative to traditional liquid-liquid extraction (LLE) and solid-phase extraction (SPE) methods [1]. Despite its widespread use, SPME has certain limitations, especially when dealing with complex matrices as is the case in biomedical analysis [2]. Moreover, carryover effects at trace levels occur easily in SPME methods because of the repeated use of the same fiber [2,3].

Needle trap devices (NTDs) are a relatively new sampling methodology that appeared in response to the demand for a more robust microextraction sampling technique than SPME [4,5]. Although the first device based on a needle filled with Tenax sorbent was introduced by Raschdorf in the late 1970s [6], NTDs started to be seriously considered by the scientific community at the end of the 1990s and beginning of 2000s [7-9]. Simply, NTDs consist of a blunt tipped needle packed with sorbents [5].

There is a significant difference between the two extraction methods. SPME is generally defined as a non-exhaustive sample preparation method that uses a tiny volume of extracting phase relative to the sample volume. Isolation of the analytes is based on achieving the equilibrium between the sample matrix and the extractive coating [10]. Thus, SPME requires small volumes of sample to extract large amounts of analytes and there is no limitation associated with breakthrough volume. However, the non-exhaustive nature of SPME results in complicated calibration processes as the standards have to be treated in the same way as the samples. NTD, on the other hand, is an exhaustive sampling method [10,11] that results in easier quantitation and maximum sensitivity but which has the sample volume limited by the breakthrough volume [10,11]. The limitation in sample volume does not represent a significant problem for conventional thermal desorption cartridges (usually 4 mm i.d.) where large amounts of sorbent are used, ranging from tens of milligrams to several hundred [12]. When small capillary traps with inner diameters between 1-2 mm have been used for thermal desorption (containing bed masses of between 1-15 mg), breakthrough volumes in the range of 0.5-3 L have been found for synthetic samples [13]. In the case of NTDs, the small inner diameter of conventional 22 gauge needles (22G, 0.41 mm i.d.) results in bed masses <1.5 mg [11,14,15]. In this case, breakthrough volumes ranging from tens to hundreds of mL have been found [11,14,16]. This shows that the design parameters of NTDs must be carefully optimized to prevent analyte loss during sampling.

Zhan and Pawliszyn [11] performed a first evaluation of the particle dimensions of NTDs and concluded that choosing a proper sorbent with a high retention factor is more significant than optimizing the particle size and packing density. They suggested 22G needles packed with 2 cm 60/80 mesh size particles as the most appropriate experimental option. In the present study, a further step is performed by assessing the effects of packing density, sampling flow and humidity on the extraction precision and efficiency in NTDs.

Theoretical considerations about the behavior of NTDs are important to understand and refine the design of these devices but these should be confirmed experimentally. Although preliminary attempts have been made to study NTDs theoretically [11,17], there is still a lack of information about the packing performance and the effect of sampling flow on efficiency as most studies have focused on practical aspects such as the configuration of the needles, sorbent selection and the desorption conditions required to obtain sharp injection bandwidths [9,14-16,18-22]. The present study aims to investigate the effects of 1) packing density, 2) flow and 3) humidity in extraction efficiency (e.g. detection limits, breakthrough and desorption) with the aim of improving our knowledge of how best to use this technique.

2. Experimental

2.1. Materials

All sorbent materials evaluated (Carboxen 1000, Carbopack X, Carbopack B, and Tenax TA) were obtained from Supelco (Bellefonte, PA, USA) with 60/80 mesh. Reagents (purity >97%, Table 1) were supplied by Sigma-Aldrich (Steinheim, Germany).

22-gauge (22G) (o.d. 0.71 mm, i.d. 0.41 mm, 51 mm length) stainless steel (metal hub) needles with point style 5 were from Hamilton (Bonaduz, Switzerland). Gold wire of 100 μm diameter (Supelco) was used to prepare the spiral plugs and to hold sorbent particles inside the needles. Vials, PTFE/silicone septum and caps were purchased from Supelco.

Sample stocks were prepared by injecting 1-2 μL of single components into cleaned 10 L Tedlar gas-sampling bags (SKC, Eighty Four, PA, USA), diluting with nitrogen 5.0 (99.9990% purity, purified for hydrocarbons, oxygen and water vapor). To ensure complete volatilization, the mixture was equilibrated for 60 min at room temperature before use. Working solutions were prepared by taking a fixed volume of the stock gas mixture with gas tight syringes (Hamilton)

and diluting to 10 L with purified nitrogen in a clean Tedlar bag. Stock and working solutions were freshly prepared every day.

2.2. Preparation of traps

A three-bed microtrap was prepared by filling it with 2.5 mg of Carboxen 1000 and Carbopack X and 5.5 mg of Carbopack B, which were sequentially introduced in an 80 mm long, 1.35 mm ID Ni/Co alloy tube (Accu-Tube Corp., Englewood, CO, USA). A full description of the device and its preparation is given in previous studies [23,24].

In the case of NTDs, 22G needles were used. A small piece of spiral plug (~1.5 mm) was fixed in the tip of the needles to prevent sorbent particles from being fixed in the side hole (Figure 1). Different needles were filled with 10 mm length of one of the sorbent materials indicated in the materials section. A spiral plug was then introduced in the upper position of the needle to fix the sorbent material inside. Using this needle configuration, NTDs were conditioned in the GC injector at 300ºC for 2-3 hours with a permanent helium flow to remove impurities. Finally, the tip end was sealed with the help of a Teflon septum and the upper part of the needle was closed with a push button syringe valve (SGE Europe Ltd, Milton Keynes, UK) to prevent contamination during storage. All needles were stored inside closed vials. A more complete description of the preparation of the NTDs is giving in previous publications [15,16,18].

2.3. Packing density

The density of random packing spheres in a cylinder can be determined from random close packing (RCP) and random loose packing (RLP) models [25-28]. RCP models result in a maximum packing fraction of ~64%, whereas RLP models give densities of 55-60%. Therefore, if we assume that the sorbent materials used to fill NTDs are perfect spheres, the fraction of these materials inside the needle can reach a maximum packing fraction of ~60%.

The packing density depends on the diameter aspect ratio (β):

$$\beta = \frac{D}{d} \qquad \text{(eq. 1)}$$

where D is the inner diameter of the cylinder and d is the diameter of the sphere particles.

131

132 2.4. Sampling and desorption

133 Gas samples were passed through the traps with the help of a vacuum pump (Air Cadet
134 Vacuum Station, Barnant Co., Barrington, IL, USA) at fixed pressures to obtain predetermined
135 sampling flow rates. Sampling was performed at 22±1ºC.

136 Zhan and Pawliszyn [11] described the following equation to calculate the volume flow rate (Q)
137 in a needle trap:

$$Q = \left(\frac{k_p A}{\mu}\right)\left(\frac{\Delta p}{L}\right) \quad \text{(eq. 2)}$$

138 where k_p is the permeability of the sorbent bed, A is the cross sectional area of the needle, μ is
139 the viscosity of the fluid, Δp is the hydrostatic pressure drop and L the length of the packed
140 bed.

141 An AC current transformer was connected to the microtrap and a fast pulse was applied to the
142 trap to obtain a desorption temperature between 270 and 280ºC. Full details of the system
143 configuration are given in previous publications [23,24].

144 NTDs were desorbed in the GC injector at 280ºC in splitless mode. In these conditions the
145 compounds were transported to the GC column with the help of the desorptive flow produced
146 by the internal air expansion inside the needle at the hot desorption temperatures of the GC
147 injector [15,18,19]. The push button syringe valve was kept closed for 1 minute to ensure that
148 compounds were quantitatively moved to the GC column. The split valve of the GC injector
149 and the push button syringe valve in the top of the NTD were then opened. NTDs were
150 maintained in the hot injector for 1 more minute to clean and recondition the trap.

151

152 2.5. GC analysis

153 Component separation was achieved by the use of a 30 m long TR-Meta.VOC column with an
154 0.25 mm i.d. and 1.5 μm film thickness (Teknokroma, Barcelona, Spain). A Focus GC (Thermo
155 Scientific, Waltham, MA, USA) with a mass spectrometer detector (DSQ II, Thermo Scientific)
156 was used. The oven temperature program was 40ºC for 4 min, then ramped at 10ºC·min^{-1} to
157 270ºC and held for 1 min. Helium carrier gas was used after purification for water vapor,
158 hydrocarbons and oxygen. A constant inlet pressure of 31 kPa was used with the microtrap

and a constant inlet flow of 0.8 mL min^{-1} with NTDs. MS analyses were carried out in full-scan mode, with a scan range of 30-250 uma, electron impact ionization was applied at 70 eV, and the transfer line was maintained at 250ºC. Chromatographic data was acquired by means of Xcalibur software (v. 1.4, Thermo Electron).

3. Results and discussion

3.1. Packing density with NTDs

$$\beta = \frac{D}{d}$$

As indicated in the experimental section, maximum packing fractions of ~60% are usually obtained for random packing of spheres in a cylinder. However, this percentage can only be obtained at infinite diameter aspect ratio (β) values [26]. From a practical point of view, it has been demonstrated that there is no significant diameter dependence for ratios of β>10-15 [29]. Thus, a close-to-perfect packing density can only be considered if a β~10 is obtained.

In the present study, some calculations have been performed to determine β values for the most common particles mesh sizes and needle gauges used with NTDs. The results obtained (Table 2) show that β values resulting in all configurations are well below the minimum value required to obtain perfect packing. Moreover, some studies [30,31] have demonstrated that for β<2.715 the densest packing only consist of spheres that are in contact with the internal surface of the cylinder container, which also represents a limitation in the fluid flow reproducibility, as will be shown in the next section.

The most conventional needle gauge used when preparing NTDs is 22G. If we consider a 22G needle, the particle diameter required to obtain perfect packing (β=10) is 0.041 mm, which would require 325 mesh particles (0.044 mm). On the other hand, if we select the most common particles size used, 60 mesh particles, the minimum diameter for the needle would be 2.5 mm (11G needles, 2.4 mm i.d.). Both situations have many experimental limitations for NTDs. In the first situation, 325 mesh particles, a large pressure drop would be generated that would require high pressure pumps for sampling at low sampling flows. Some experiments performed in our laboratory showed that it was necessary to reduce the sampling flow to <1

mL min^{-1} to obtain reproducible results using a NTD filled with 120 mesh particles in a 22G needle. In the second situation, 11G needles, the outer diameter of the needle (3.1 mm) makes it impossible to introduce the shaft of the needle in the required SPME GC injector (~0.75 mm i.d.) and would result in (i) the use of large diameter liners and (ii) a significant thermal resistance along the sorbent trap that would lead to excessive diffusion paths for appropriate injection bands in the GC column.

The effect of the needle gauge on the performance of NTDs can be seen in Figure 2. The increase in the needle diameter (i.e. smaller gauge, Figure 2a) results in broader peaks and reduced resolution (ethylbenzene and *p*-xylene cannot be separated when compounds are sorbed using a 20G needle). This is the due to the slower desorption of the compounds from the trap particles in the injector of the GC as a consequence of the large thermal resistance inside the needle, which results in long diffusion paths. The decrease in the needle diameter (Figure 2b) gives lower thermal resistance inside the needle and yields sharper peaks and increased resolution. The use of a 3 mm i.d. liner (Figures 2a and 2b) results in a large difference between the i.d. of the liner and the o.d. of the needles (0.71 mm for 22G needles and 0.91 mm for 20G). This results in a diffusion of the desorbed compounds in the internal volume of the liner around the needle and leads to excessive injection bands entering the GC column. This problem can be solved using a smaller i.d. liner (Figure 3c, 22G needle and 1 mm i.d. liner). The results obtained indicate that the needle gauge selection is significant for NTDs and it is required to use 22G or larger gauges in order to obtain sharp injection bands that allow the separation of VOCs in the GC column.

Another parameter affecting the packing of perfect spheres into a cylinder is the height of the packing structure. Stoyan and Yaskov [32] evaluated the packing of spheres into cylinders of minimal heights and found that packing density increases with the height of the packing structure until the maximum packing density is reached. Therefore, the height of the bed in NTDs is another parameter that affects the packing density in these devices.

It is clear from the results indicated that experimental restrictions impede perfect packing for NTDs making it necessary to accept a compromise for the needle gauge, particle size, and height of the sorbent bed. The most accepted parameters are 22G needles, 60/80 mesh size particles, and 1 to 3 cm bed height [11,14-16,20-22,33].

3.2. Fluid flow reproducibility with NTDs

220

$$Q = \left(\frac{k_p A}{\mu}\right)\left(\frac{\Delta p}{L}\right)$$

221 The fact that perfect packing cannot be achieved with NTDs has also a significant effect on the
222 fluid flow profile and reproducibility during sampling. According to equation 2, the volumetric
223 flow rate of each NTD is expected to be proportional to the permeability (k_p) of the sorbent
224 bed and cross-sectional area (A) and inversely proportional to the length of the sorbent bed (L)
225 [11]. Taking into account that small resistance to flow is required for efficient sampling and
226 desorption, large permeability is desired in NTDs. Zhan and Pawliszyn [11] found that NTDs
227 filled with smaller particles (i.e. large mesh sizes) gave smaller permeabilities (in the case of a 1
228 cm bed packed with Carboxen 1000, k_p values ranged from 3.31 to 1.49 for mesh sizes ranging
229 from 60/80 to 100/120), which was attributed to a smaller porosity of the sorbent bed due to
230 the fact that smaller particles can be more efficiently packed inside the needle. Moreover, they
231 found that carryover decreases with increased permeability (i.e., 60/80 mesh particles gave
232 lower carryover). The authors suggest that 60/80 mesh particles seem to be the most
233 adequate option since larger amounts of sorbent can be used without increasing the flow
234 restrictions despite the fact that the packing density is poorer.

235 The model proposed by Zhan and Pawliszyn [11] assumes that the flow rate is constant
236 throughout the packed bed. However, this is not the case with NTDs. In designing fixed-bed
237 processes in unstructured fixed beds, it is necessary to take into account, firstly, the fact that
238 the void fraction in the vicinity of the tube walls approaches unity and fluid flow through a
239 packed bed is always characterized by a channeling effect at the wall and, secondly, that for
240 packing of round spheres, the velocity profiles are always characterized by oscillations of up to
241 a distance of two particle diameters from the tube wall [34].

242 The mean porosity (i.e., the void volume divided by the total volume) and the radial porosity
243 are the most common packed bed parameters used to compare numerical simulations with
244 experimental data [35]. The radial porosity is a characteristic structural feature of confined
245 packed beds, which occurs because of the influence of container beds and is characterized as a
246 volumetric property of a packing system [36]. The radial porosity distribution (radial porosity
247 profile) is the variation of the local radial porosity as a function of the radial direction.
248 Distribution values present oscillations with higher values close to the walls of the container
249 due to near-wall packing effects on the velocity profile [27,36]. These oscillations decrease as
250 the distance from the wall increases. Some studies [34,36] have evaluated the fluid flow profile

in packed beds and found that fluid flow between particles in packed beds is characterized by a random packing geometry, high turbulence and strong velocity fluctuations. The oscillations in the velocity profile cannot be eliminated but are reduced and become more reproducible as the diameter aspect ratio (β) increases. A β>10 is suggested to reach the minimum variation and maximum reproducibility in the velocity profile given that, as indicated in the previous section, there are no significant variations in the packing density under these conditions. This means that the flow profile is more reproducible when a close-to-perfect packing density is obtained, which is not the case with NTDs.

As can be seen in Table 2, β<2.715 are obtained for the most common types of mesh sizes and needle gauges used in conventional NTDs, which means that all the spheres particles are in contact with the internal surface of the needle [30,31]. These conditions result in large oscillations in the velocity profiles due to the wall packing effects. Different studies have found deviations of up to 60-70% [20,37] when comparing inter-needle extraction efficiencies, whereas intra-needle variations have been found to be <15%. Alonso et al. [15] found variations ~50% in the maximum flow reproducibility for different NTDs and excessive deviations (up to 40%) in the extraction efficiency at high sampling flow rates (53 mL min^{-1}). These variations can be explained by non-structured packing with significantly different packing densities from one NTD to another. This results in large and non-reproducible flow profile oscillations when excessive sampling flow rates are used in non-structured packed materials.

The most appropriate option to minimize this variability is to decrease flow profile oscillations by reducing the sampling flow along the sorbent bed. Alonso et al. [15] demonstrated that a decrease in the sampling flow resulted in a significant improvement in the precision of the extraction efficiency results obtained with different NTDs. Precision values were excessive (in the range 5-47%) at sampling flows >30 mL min^{-1} but were acceptable (<14%) when sampling flows were reduced to <15 mL min^{-1}. In line with this finding, the instruction manual of NeedlEx commercial NTDs recommends using sampling flows up to 10 mL min^{-1}. In the present study, sampling flows in the range of 5 to 30 mL min^{-1} were evaluated. Excessive variation coefficients in the extraction efficiency (up to 40%) were obtained when sampling at 20 and 30 mL·min^{-1}, whereas variation coefficients <11% were obtained for all the compounds and NTD configurations prepared when sampling at 5 and 10 ml·min^{-1}.

In order to evaluate and confirm the effect of packing density on flow reproducibility and precision, a microtrap with 1.35 mm i.d. and filled with a bed containing 60/80 mesh particles

(β=5.4-9.3), as described by Sanchez and Sacks [23,38], was prepared. Sampling flows ranging from 10 to 80 mL min^{-1} (maximum flow achieved taking into account the pressure drop generated in the microtrap) were evaluated. It was found that the precision of the extraction efficiency was acceptable (<15%) at all the flows evaluated. In the case of commercial thermal desorption traps, where conventional desorption tubes have a 4 mm i.d. (i.e., β=16-23 for 60/80 mesh size particles), flows of up to 200 mL min^{-1} can be used for the determination of VOCs without loss of precision [39,40].

These results confirm that flow profiles with fewer oscillations and which are more reproducible are obtained when perfect packings are used. However, as this is not feasible in NTDs, sampling flow should be limited to 10-15 mL min^{-1} to achieve a good level of precision.

3.3. Detection limits with NTDs

The limitation in sampling flows restricts the sample volumes that can be used practically when working with NTDs (i.e., up to 100 mL) so these devices will only be a good choice if their concentration factors are sufficiently large as to allow low method detection limits (MDLs) to be obtained.

One of the most promising applications of NTDs is the analysis of VOCs in breath samples [22,33], where acetone, isoprene, ethanol, and methanol, which can be detected at ranges from few ppmv to ppbv, are the main components. The levels of other VOCs in breath samples are in the ppbv-pptv range [22,41,42]. In the case of environmental analysis, levels of VOCs in non-contaminated indoor and atmospheric samples are usually in the $\mu g \cdot m^{-3}$ to $ng \cdot m^{-3}$ (i.e., ppbv to pptv). Therefore, MDLs should be in the pptv range for NTDs and these limits should be reached with sample volumes of up to 100 mL.

One of the main advantages of NTDs is their large concentration factor. The MDLs obtained with NTDs in the present study are in the range of 0.002-0.015 ng, which agrees with the values obtained in other studies [4,15]. This means that MDLs in the pptv range can be achieved with sample volumes of <50 mL (e.g., MDL=60-450 pptv range with sample volumes of 10 mL, and 10-75 pptv with 50 mL samples). This confirms that, unlike conventional thermal desorption systems, NTDs can reach very low detection limits with small sample volumes. This fact also significantly reduces breakthrough limitations.

315 3.4. Breakthrough

316 The packed mass amount in conventional NTDs is ~0.5 mg for a packing length of 1 cm [11].
317 Taking into account that the maximum recommended length for NTD packing is 3 cm, the
318 maximum expected amount of sorbent is ~1.5 mg, which results in the breakthrough volume
319 (BV) being one of the most significant parameters to take into account with NTDs.

320 Calculation of practical BVs is complex as it depends on multiple variables, such as the type and
321 amount of sorbent material chosen, the composition and concentration of the sample, and the
322 effect of other parameters, such as relative humidity, on the sorption process. Lu and Zellers
323 [43] evaluated BVs for different sorbent materials with small amounts of sorbent beds (ranging
324 from 1-12 mg) and found BVs ranging from 0.2 to 4 L, with significant differences depending on
325 the sorbent evaluated, with carbon molecular sieves being the sorbents with the largest BVs.
326 The results obtained by these authors indicate that sorbent bed masses <1 mg result in BVs <1
327 L at target concentrations between 0.1-1 ppmv.

328 Different studies have evaluated BVs with NTDs in dry and humid samples with concentrations
329 of target compounds in the ppbv level. Zhan and Pawliszyn [11] evaluated synthetic dry
330 standard mixtures in the 0.2-1.7 ppbv range and found BVs ranging from 286 to 958 mL with
331 divinylbenzene (DVB) packed NTDs (1 cm), and from 55 to 191 mL with Tenax GC. Mieth et al.
332 [22] evaluated spiked breath samples (~80 ppbv for each target compound) using a triple-bed
333 containing Tenax, Carbopack X and Carboxen 1000 (1 cm each) and did not find breakthrough
334 with sampling volumes up to 40 mL. Trefz et al. [16] compared two types of NTDs, a copolymer
335 of methacrylic acid and ethylene glycol dimethacrylate (polymer NTD) and a three-bed NTD (1
336 cm each bed) filled with DVB, Carbopack X and Carboxen 1000. They evaluated synthetic dry
337 mixtures and spiked breath samples containing ~100 ppbv for each compound. Polymer NTD
338 gave lower BVs with humid samples than with dry samples, especially for highly volatile
339 compounds (<20 mL). The three-bed NTD did not show breakthrough in either dry or humid
340 samples with volumes up to 60 mL, except for some aldehydes. Dobrzynska and Beszewski [21]
341 used triple-bed NTDs with different sorbent combinations (maximum bed lengths of 3 cm) for
342 the analysis of chlorinated volatile compounds. The best results were obtained with an NTD
343 filled with Tenax, Carbopack X and Carboxen 1000. When synthetic dry mixtures containing
344 ~25 ppbv for each target compound were evaluated, BVs of >150 mL were found for
345 trichloromethane and dichloromethane and ~50 mL for tetrachloromethane.

346 In the present study, two 22G NTDs, one filled with 1 cm of Carbopack X and the other filled
347 with 1 cm of Tenax TA, were evaluated in the analysis of a synthetic mixture containing VOCs

in the 4-6 ppbv range. BVs of >20 mL (Figure 3a) were obtained for the target VOCs with both NTDs. When the same mixture was analyzed with a microtrap (1.35 mm i.d.) containing a three-bed sorbent (2.5 mg Carboxen 1000, 2.5 mg Carbopack X and 5 mg Carbopack B), BVs >1500 mL were achieved (Figure 3b). These results confirm the significance of BV when using NTDs due to the small amount of sorbent inside the needles.

Table 3 shows the ng of toluene that yield breakthrough for the different studies cited. As can be seen, the levels of toluene at BVs are in the range of 0.25-22 ng, depending on the configuration of the NTD. These levels are well above the reported detection limits of NTDs (<0.05 ng), which confirms that sample volumes in the range ~100 mL can be analyzed without significant BV limitations.

3.5. Relative humidity of the samples

Water uptake when high relative humidity (RH) samples are analyzed presents a series of additional problems with thermal desorption systems: (i) the formation of ice plugs during the capillary cryofocusing, (ii) the reduction of adsorption efficiency for some compounds during sampling, and (iii) the possible loss and chemical transformation of VOCs in the water/ice matrix [44]. Breath samples are particularly affected by these issues as they are water saturated. Given that NTDs do not use a second cryogenic trap to focalize the retained compounds, ice plugs do not form with these devices.

With conventional sorbent tubes, different options are used to reduce the water problem, including the use of desiccants, dry purging or heating the adsorbent during sampling [44,45]. However, these can lead to losses and sample contamination. It has been demonstrated that there are significant losses of analytes during dry purging with NTDs [22]. Heating of the sorbent during sampling also results in significant losses of the most volatile compounds [46]. Helming and Vierling [44] suggested that procedures to reduce water uptake in multibed sorbents should be focused on reducing sample volumes to the smallest possible value.

The selection of the sorbent affects the amount of water retained. Graphitized carbons and porous polymer sorbents are considered hydrophobic and their water retention is very limited. Only strong adsorbents (i.e., carbon molecular sieves) can retain significant amounts of water [44,47]. Some newly developed polymeric materials based on a copolymer of methacrylic acid and ethylene glycol dimethacrylate have also shown low retention capacities for highly volatile compounds when high RH samples were evaluated [16]. Therefore, the selection of the

sorbent materials is a significant factor to take into account when high RH matrices are to be analyzed.

Table 4 shows the calculations for the maximum amount of water that could be retained by NTDs taking into account different sampling volumes (up to 100 mL) and sample temperatures. 22 and 25ºC were chosen as representative for atmospheric sampling and laboratory controlled experiments, and 35ºC was used as mean breath temperature is 34.9-35ºC [48,49]. As can be seen, the reduced volume of sample used with NTDs without breakthrough problems (up to ~100 mL) results in maximum theoretical volumes of water <4 μL (for 100 mL of 100% RH sample at 35ºC). This results in expansion gas volumes of up to 7.6 mL (4.5 psig inlet pressure) and 5.9 mL (10 psig inlet pressure) for 100 mL samples. These values would be excessive for commercial SPME liners, which have total volumes between 16-22 μL, depending on their lengths. In the case of conventional splitless liners (e.g., 4 mm i.d.), volumes range from 465-622 μL, which indicates that sampling volumes up to 10 mL could also be managed if the maximum amount of water is retained by the trap.

Water volumes close to the maximum water uptake indicated in Table 4 could only be retained using single-bed traps containing a highly hydrophobic sorbent material, such as activated carbons or carbon molecular sieves, but to reach these volumes it is necessary to collect large volumes of samples (several liters). Helmig and Vierling [44] determined the maximum water adsorption capacity for different commercial sorbent materials. They found that the highest water sorption was obtained with carbon molecular sieves, with a maximum water adsorption of up to 400 mg water per gram of sorbent for the most hydrophilic sorbent tested (Carbosieve SIII). This means that for a 3 cm length (~1.5 mg) NTD filled with this sorbent, the maximum amount of water that could be retained would be ~0.6 μL.

In the case of multi-bed sorbents, water uptake is always determined by the most hydrophilic sorbent layer [44]. It has been found that three-bed NTDs containing small amounts (1 cm length) of a hydrophilic carbon molecular sieve (i.e. Carboxen 1000) and two hydrophobic sorbents did not give a significant water uptake in the analysis of water saturated breath samples [16,22]. With this NTD configuration, the maximum expected uptake of water, which has not been measured, is <0.2 μL for several liters of sample.

NTDs present two significant advantages over conventional sorbent desorption tubes for the analysis of water saturated samples. Firstly, the small amount of sorbents significantly decreases the amount of water that can be retained by the NTD reducing the probability of

412 artifacts in water saturated samples. Secondly, a small amount of water is recommended with
413 NTDs as the water-vapor flow produced during the expansion of water molecules helps to
414 purge the desorbed compounds out of the needle into the column, facilitating the production
415 of sharp injection band-widths [9]. This factor is significant because it permits the use of
416 expanded desorptive flow, which is the simplest desorption process with NTDs [15,18,19], and
417 may avoid the requirement for an external gas supply during the desorption, which has led to
418 peak tailing and splitting when >1 mL inert gas has been used [50-52].

419 Although the presence of significant amounts of water in the samples does not have a
420 significant effect on the extraction/desorption efficiency of VOCs with NTDs [16,22], the
421 presence of different amounts of water may affect the structure of the compounds in the
422 vapor phase and can modify the adsorption mechanism of highly polar compounds on carbon
423 based sorbents [53]. In the present study, two samples were prepared containing all the
424 compounds listed in Table 1, the first sample was prepared with dry nitrogen and the second
425 with water saturated nitrogen to simulate 100% RH conditions. Each sample was analyzed in
426 triplicate using an NTD filled with a dual bed containing 1 cm of Carboxen 1000 and 1 cm
427 Carbopack X. The results obtained show that there were no significant differences (t-test,
428 p>0.05) in the concentrations detected between the dry and humid samples for the majority of
429 the compounds analyzed. Only the most highly polar compounds (alcohols) gave significant
430 differences between the two types of samples. Methanol, the most polar compound tested
431 gave a 24% reduction in the concentration detected with the 100% RH sample. Ethanol yielded
432 a 12% reduction with the humid sample. 1-Propanol gave a reduction of <5% and 2-Butanol did
433 not give significant differences (p=0.11). These results indicate that the concentrations
434 detected decreased as the hydrophilicity of the compound increases, which seems to indicate
435 that highly polar compounds can form aggregates with water molecules that are not adsorbed
436 by carbon-based sorbent materials. Thus, the use of NTDs for the analysis of highly polar
437 alcohols requires the preparation of standards at the same RH conditions.

438

439 ## 4. Conclusions

440 A careful evaluation of the design parameters of NTDs shows that perfect packing is not
441 possible with these devices. The design requirements (mesh size of the particles and needle
442 gauge) to obtain perfect and reproducible packing are not possible if NTDs have to be injected
443 and desorbed directly in a conventional GC injector, as with SPME. It is therefore necessary to
444 adopt compromise needle gauge, particle mesh size and bed height characteristics. The results

found in different studies indicate that the most accepted parameters are 22G needles, 60/80 mesh particles and up to 3 cm bed height.

The fact that non-perfect packing has to be used with NTDs results in a significant oscillation and variation of the fluid flow profiles inside the NTD at large sampling flows. Therefore, the sampling flow must be reduced to up to 10-15 mL min^{-1} to obtain good precision in the results.

The high sensitivity resulting from the use of NTDs allows detection limits in the pptv range to be achieved with sampling volumes <50 mL, demonstrating that NTDs are reliable for the analysis of non-contaminated air samples.

Another advantage of NTDs is the good results obtained in the analysis of water saturated gas samples due to the small amount of hydrophilic sorbents used in the design. The low amount of water that can be retained does not represent a significant instrumental problem and gives the advantage of helping to obtain sharp injection band-widths due to the large expansion volume of the water molecules during desportion of the trapped compounds.

These findings confirm that NTDs are an efficient and robust alternative to SPME and that this is especially true in the case of breath sampling, as is illustrated by the advantages shown by NTDs in the analysis of water saturated samples. The main limitation to be taken into account is that sampling flows should not exceed 10 mL min^{-1}.

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601 Figure Captions

602

603 Figure 1. Scheme of an NTD device. A: spiral plugs, B: sorbent material.

604 Figure 2. Peak shape and chromatographic resolution obtained for VOC's using different liner
605 dimensions and NTD gauges. (a) 3 mm i.d. liner and 20G needle (0.91 mm o.d.), (b) 3 mm i.d.
606 liner and 22 G needle (0.71 mm o.d.), and (c) 1 mm i.d. liner and 22 G needle

607 VOC's analyzed: toluene (peak #1), ethylbenzene (#2), *p*-xylene (#3), and *o*-xylene (#4).
608 Experimental conditions: Carbopack X sorbent, injector temperature: 280ºC.

609 Figure 3. Breakthrough curves obtained in the analysis of a synthetic mixture containing VOCs
610 in the 4-6 ppbv range. (a) NTD filled with 1 cm of Tenax TA, (b) three-bed micro-trap.

611

611 Table 1. Volatile compounds evaluated with the micro-trap and NTD methodologies

Compound name	b.p. (ºC)	Characteristic masses*
acetone	56.2	58, 43
methanol	64.7	31, 32
hexane	69	57, 69, 85
ethanol	78.4	45, 31, 46
benzene	80.1	78
1-propanol	97	42, 31, 59
2-propanol	98	53, 31, 41
toluene	110.6	91, 92
ethylbenzene	136.2	91, 106
p-xylene	138.3	91, 105, 106
o-xylene	143-145	91, 105, 106

612 * mass used for quantification in bold

613

Table 2. Diameter aspect ratios ($\beta=D/d$, where D is the diameter of the needle container and d is the diameter of the particles) calculated for the most common particle mesh sizes and needle gauges used in NTD configurations

Particle mesh size	Needle gauge	
	22G (0.413 mm i.d.)	*23G (0.337 mm i.d.)*
60/80	1.61/2.33	1.35/1.90
80/100	2.33/2.77	1.90/2.26
100/120	2.77/3.30	2.26/2.70

618 Table 3. Levels of toluene (ng) at which breakthrough was observed in different studies using
619 NTDs

BV (mL)	Sorbent bed [a]	ng of toluene at BV	Reference
55	*Single-bed NTD* 10 mm Tenax GC (60/80)	0.25	[11]
>60	*Triple-bed NTD* 10 mm Carboxen 1000 10 mm Carbopack X 10 mm DVB	>22	[16]
>40	*Triple-bed NTD* 10 mm Carboxen 1000 (60/80) 10 mm Carbopack X (60/80) 10 mm Tenax (35/60)	>12	[22]
>20	*Single bed NTD* 10 mm Carbopack X (60/80)	>0.26	Present study
>1500	*Triple-bed (microtrap)* 2.5 mg Carboxen 1000 (60/80) 2.5 mg Carbopack X (60/80) 5 mg Carbopack B (60/80)	>26	Present study

620 [a] Values in brackets refer to the mesh size of the particles used

621

Table 4. Maximum volumes of water that could be retained when sampling 100% RH samples at three different sample temperatures (22ºC, 25ºC and 35ºC). The last section shows the gas volume generated in the GC injector for the calculated volume of water at two different inlet pressures.

Sample volume (mL)	Maximum volume of water (μL) retained at 100% RH [a]			Gas volume (μL) generated in the GC injector by solvent expansion [b]					
				Inlet pressure 4.5 psig			Inlet pressure 10 psig		
	22ºC	25ºC	35ºC	22ºC	25ºC	35ºC	22ºC	25ºC	35ºC
10	0.1942	0.2309	0.3975	373	444	764	290	345	594
50	0.9708	1.1548	1.9876	1867	2221	3822	1451	1726	2971
100	1.9417	2.3095	3.9752	3734	4441	7645	2902	3452	5942

[a] Values of saturated water density are 19.417, 23.095 and 39.752 $g \cdot m^{-3}$ for sample temperatures of 22ºC, 25ºC and 35ºC respectively

[b] Gas expansion volumes calculated for an injector temperature of 280ºC

Highlights

- The densest packing is not possible with needle trap devices
- Sampling flow has to be restricted to <10-15 mL min^{-1}
- NTDs can reach detection limits in the pptv range with 50 mL samples
- Water saturated samples do not restrict the use of NTDs

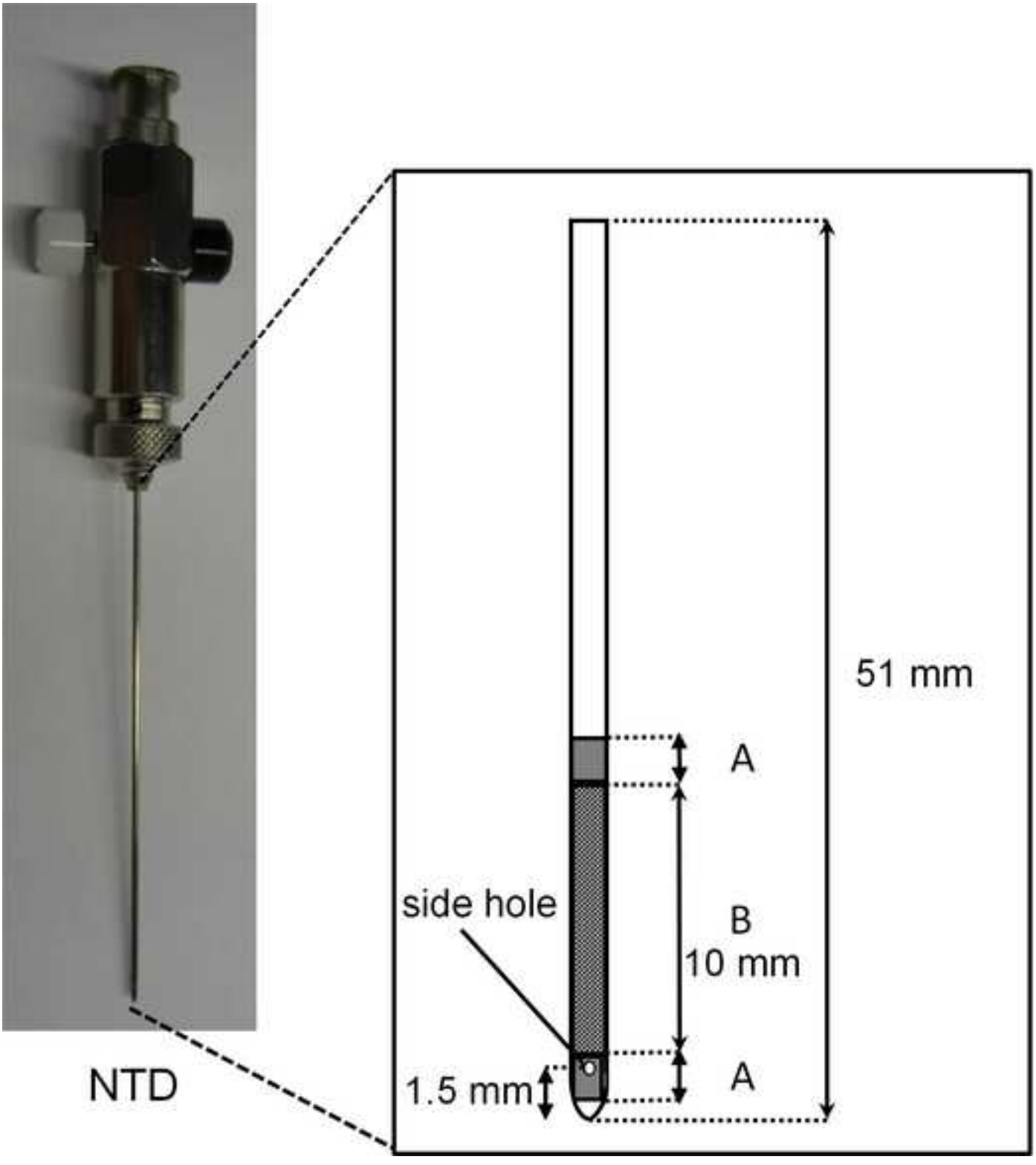

Figure 2