Journal of Chromatography A, 1369 (2014) 18–25

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

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

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ARTICLE INFO

Article history:
Received 24 July 2014
Received in revised form
26 September 2014
Accepted 29 September 2014
Available online 5 October 2014

Keywords:
Breakthrough
Humidity
Needle trap
Packing density
Flow profile

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.

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 and 2 mm have been used for thermal desorption (containing bed masses of between 1 and 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

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http://dx.doi.org/10.1016/j.chroma.2014.09.081
0021-9673/

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

Compound name	b.p. (°C)	Characteristic masses[a]
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

[a] Mass used for quantification in bold.

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.

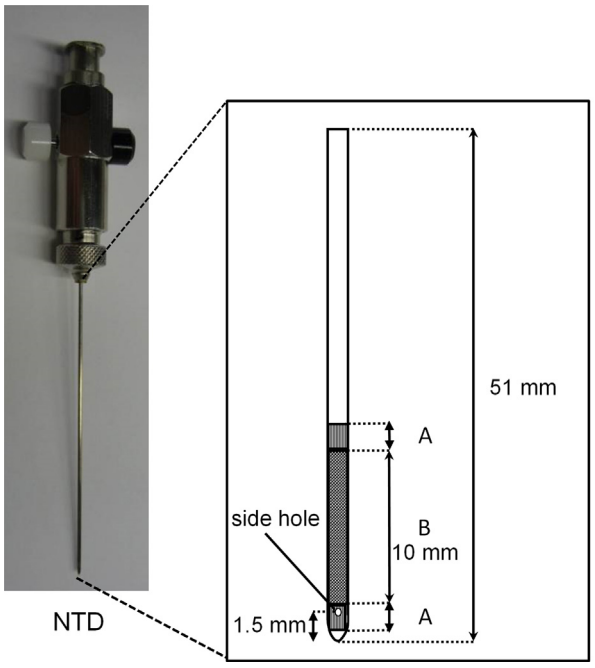

Fig. 1. Scheme of an NTD device. (A) Spiral plugs and (B) sorbent material.

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 i.d. 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 (Fig. 1). Different needles were filled with 10 mm length of one of the sorbent materials indicated in Section 2.1. 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 300 °C 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):

$$\beta = \frac{D}{d} \quad (1)$$

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