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Needle microextraction trap for on-site analysis of airborne volatile compounds at ultra-trace levels in gaseous samples

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RUNNIG TITLE: Needle traps for volatile compound analysis

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NONSTANDARD ABBREVIATIONS:

amu	atomic mass unit
ºC	degree Celsius
eV	electron volt
g	gram
G	gauge
h	hour
L	liter
m	meter
min	minute
mL	milliliter
mm	millimeter
µg	microgram
µm	micrometer
ng	nanogram
NT	needle trap
PTFE	polytetrafluoroethylene (Teflon)
SPME	solid phase microextraction
VOC	volatile organic compound

ABSTRACT

Different capillary needle trap (NT) configurations are studied and compared to evaluate the suitability of this methodology for screening in the analysis of volatile organic compounds (VOC's) in air samples at ultra-trace levels. 22 gauge needles with side holes give the best performance and results, resulting in good sampling flow reproducibility as well as fast and complete NT conditioning and cleaning. Two different types of sorbent are evaluated: a graphitized carbon (Carbopack X) and a polymeric sorbent (Tenax TA). Optimized experimental conditions were desorption in the GC injector at 300ºC, no make-up gas to help the transport of the desorbed compounds to the GC column, 1 min splitless time for injection/desorption, and leaving the NT in the hot injector for about 20 min. Cross-contamination is avoided when samples containing high VOC levels (above likely breakthrough values) are evaluated. Neither carryover nor contamination is detected for storage times up to 48 h at 4ºC. The method developed is applied to the analysis of indoor air, outdoor air and breath samples. The results obtained are equivalent to those obtained with other thermal desorption devices but have the advantage of using small sample volumes, being simpler, more economical and more robust than conventional methodologies used for VOC analysis in air samples.

1. Introduction

Given the ever greater interest in evaluating atmospheric pollutants for screening purposes at ultra-trace levels, continuous improvement of monitoring methods is required. Analysis of volatile organic compounds (VOC's) in air samples is extensively carried out by sorption on solid sorbents followed by thermal desorption and GC-MS determination (e.g., US-EPA method TO-17 [1]). This methodology, which requires highly skilled technicians, makes use of complex and relatively expensive thermal desorption units and needs two desorption steps, increasing the probability of artifact formation.

The development of economical and ecological small-scale sample preparation techniques that are able to meet requirements such as enhanced sensitivity and selectivity, robustness, and simple handling are desirable. In this respect, solvent-free extraction methods based on the partitioning of analytes between gaseous or liquid phase and a stationary phase have become increasingly important and have been widely applied in research over the last decade. As a sample preparation technique intended for VOC analysis, solid-phase microextraction (SPME) has been one of the most successful approaches [2]. However, conventional SPME has the disadvantages of the relative fragility of the exposed coated fused-silica rod and the low sorption capacity of the technique [3].

Although Raschdorf [4] developed the first device based on a needle filled with Tenax sorbent in the 1970's, needle trap (NT) extraction devices have only recently become popular due to their combination of the advantages of SPME (e.g. solventless, fast, sensitive, one-step sample preparation and injection method, small in size and convenient for designing portable devices that can be used in field analysis) with robustness, easier handling during sampling and desorption, and the fact that they permit a high degree of automation and on-line coupling to GC instruments [5]. NT devices can be divided into two different categories: (i) internally coated needles [6-8]; and (ii) needles packed with commercially available sorbents [3,9-21] or chemically synthesized polymers [22,23]. One commercial approach uses an add-on module packed with a sorbent material positioned between the needle and the syringe (in-tube extraction, ITEX and ITEX-2) [24]. The ITEX device has the drawback of requiring an external thermal desorption unit for the release of the compounds before moving to the GC injector. Other experimental approaches are less complex allowing the desorption process to be performed by inserting the needle into the GC injector port without the need of an external power source. These approaches drastically reduce the current sampling treatment times as well as the cost.

The use of NT extraction has the advantages of being solvent free and of having sampling and analysis times that are significantly shorter than most existing methods. Moreover, NT has great potential as a screening tool whenever fast analysis is needed. The main drawbacks of NT are: (i) relatively low sampling capacity, (ii) rapid breakthrough of the trap, (iii) possible dispersion of the elution zones of the analytes [25], and (iv) the poor sampling flow reproducibility from needle to needle [16].

In this study, we experimented with different needle configurations and packing methods in order to determine the most appropriate configuration to overcome reproducibility problems. The different parameters affecting injection band broadening obtained with NT were also evaluated (e.g., injector temperature, liner id, splitless time, and conditioning time) to determine the desorption mechanism involved and to improve our understanding of these devices. Once the most appropriate experimental conditions were found, the NT methodology was successfully applied to the analysis of VOC's in environmental air and breath samples.

2. Experimental

2.1. Materials

Two different sorbent materials (Supelco, Bellefonte, PA, USA) were evaluated: a graphitized carbon (Carbopack X, 60/80 mesh, specific surface area of 240 $m^2 \cdot g^{-1}$ and a density of 0.44 $g \cdot mL^{-1}$) and a porous polymer (Tenax TA, 60/80 mesh, specific surface area of 35 $m^2 \cdot g^{-1}$ and a density of 2.5 $g \cdot mL^{-1}$). Reagents (purity >97%, Table 1) were supplied by Sigma-Aldrich (Steinheim, Germany).

22-gauge (22G) (od 0.71 mm, id 0.41 mm, 51 mm length) stainless steel (metal hub) needles with point style 2 and 5 were from Hamilton (Bonaduz, Switzerland). Gold wire of 100 μm diameter (Supelco) was used to prepare the spiral plugs and 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. Calibration standards 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. Stocks and standards were freshly prepared for each calibration.

2.2. Preparation of needle traps

For point style 2 needles, a spiral plug (five turns, prepared as described in Reference [6]) was positioned inside the needle 11 mm from the tip. The sorbent was then aspirated into the needle with the help of a vacuum pump until it reached the required position (~1 mm from the tip). A small amount of epoxy resin was applied to the tip of the needle to immobilize the sorbent particles. In order to prevent the glue from blocking the needle, dry air was passed through the NT until the epoxy was cured. Each NT was conditioned in the GC injector at 300ºC with a permanent helium flow to remove impurities. A conditioning time of at least 24 h was necessary to avoid the presence of some semi-volatile compounds from the epoxy glue in the blank test.

In the case of point style 5 needles (Figure 1), the use of epoxy resin was avoided. Although the diameter of the side hole is sufficiently small as to allow the sorbent particles to be fixed inside the needle, a small piece of spiral plug (~1.5 mm) was fixed in the tip of the needle to prevent sorbent particles from being fixed in the hole. The sorbent material was then introduced to the desired position with the help of a vacuum pump (~10 mm length). Next, a spiral plug was carefully introduced in the upper position of the needle until it reached the desired distance to fix the sorbent materials inside it. Using this needle configuration, NT's were conditioned in the GC injector at 300ºC for 2-3 hours with a permanent helium flow. 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. Furthermore, each needle was stored inside a closed vial.

2.3. NT sampling

Both manual and automatic sampling were used. For manual sampling, gas samples were passed through the NT's with the help of a gas-tight syringe (Hamilton). For automatic sampling, a vacuum pump (Air Cadet Vacuum Station, Barnant Co., Barrington, IL, USA) was used to pull the sample through the sorbent at a predetermined flow. Sampling was performed at 22±1ºC. The NT was then inserted into the injection port of the GC for thermal desorption and analysis. The push button syringe valve was kept open during the sampling step and the conditioning of the NT after thermal desorption. For the remainder of the time it was in the closed position.

2.4. GC analysis

Component separation was achieved by the use of a 30 m long Zebron-5ms column with 0.25 mm id and 0.25 μm film thickness (Phenomenex, Torrance, CA, USA). A Focus GC (Thermo Scientific, Waltham, MA, USA) with a mass spectrometer detector (DSQ II, Thermo Scientific) was used.

1 and 3 mm id straight liners (8.0 mm od, 105 mm length) were from Restek (Bellefonte, PA, USA). The injector (desorption) temperature was maintained at 300ºC to ensure complete and fast desorption of target VOCs [12,15] (see Figure 1 in Supplementary Materials). Temperatures above 300ºC were not appropriate due to the limited thermal stability of Tenax TA and the fact that some reactive compounds decompose at temperatures up to 300ºC (8-12% decomposition for β-pinene and α-pinene), increasing exponentially at temperatures over 300ºC [26,27].

The oven temperature program was 40ºC held for 2 min, then ramped at 15ºC·min^{-1} to 250ºC and held for 2 min. Helium carrier gas was used with a constant inlet flow of 0.8 mL·min^{-1} after purification for water vapor, hydrocarbons, and oxygen. MS analyses were carried out in full-scan mode, with a scan range of 40-200 amu, electron impact ionization was applied at 70 eV, and the transfer line was maintained at 230ºC. Chromatographic data was acquired by means of Xcalibur software (v. 1.4, Thermo Electron).

3. Results and discussion

3.1. Sorbent packing and needle configuration

The type of end plug used for fixing the sorbent material inside the needle was evaluated. The simplest and most conventional approach is based on the use of a narrow metal spiral plug in the shaft of the needle and epoxy resin at the tip of the needle [6,11-13,15,16,18,19]. We evaluated conventional open end needles (point style 2) by using this configuration.

It was found that needle-to-needle sampling flow reproducibility was poor (ranging from 0, total blockage of the needle, to 40 mL·min^{-1}; n=5, RSD=116%, see Figure 2 in Supplementary Materials). A similar limitation has previously been described as an important drawback of this configuration although blockage was not reported [16]. Our results confirm that the amount of epoxy resin used to fix the sorbent was the main parameter affecting the sampling flow variability from needle to needle. Unfortunately, the amount of epoxy resin used could not be measured and the quantity of resin applied was based on the skills of the operator. One solution proposed by some laboratories is to reject those NT's that do not yield a minimum prefixed sampling flow, but this practice results in a considerable number of discarded needles.

A further difficulty with the use of epoxy resins is that they are an important source of volatile impurities when trace analysis is the goal. Eom and al. [13] indicated that a conditioning time of 30 min was enough to clean the trap from impurities using a flame ionization detector. However, we found that a significant amount of impurities from the epoxy resin remained in the chromatograms after this conditioning time using an MS detector (Figure 2a). A minimum conditioning time of 24 hours was necessary to eliminate the main portion of contaminants from the epoxy resin (which was also described by Mieth el al. [15,16]), but there were still some semi-volatile impurities detected in the blank chromatograms.

A different needle configuration with a closed conical tip and a small side hole (point style 5) was also evaluated. This configuration avoided the need for epoxy resin as the side hole was small enough to maintain the sorbent particles inside the needle. In preliminary experiments, an amount of the sorbent was inserted directly into the needle and the upper end was then closed with a metal spiral plug. However, it was found that a particle of sorbent material was sometimes placed in the side hole, which led to partial blocking and flow reproducibility problems. To solve this problem, a small piece of spiral plug (~1.5 mm) was located in the tip of the needle, preventing sorbent particles from coming into contact with the side hole (Figure 1). This configuration (without using epoxy resin) had two important advantages: firstly, it allowed faster conditioning of the sorbent materials (2-3 hours were enough, Figure 2b) without detection of impurities in the blank chromatograms, and secondly, no blocking of the needles took place and more reproducible needle-to-needle flows were obtained (flows ranged from 30 to 50 $mL \cdot min^{-1}$; n=5, RSD=25%, see Figure 2 in Supplementary Materials).

It is clear from these results that the use of epoxy resins to fix the sorbent results in important drawbacks in the performance of the NT's and should be avoided for ultra-trace analysis and MS detection. Point style 5 needles with a side hole are recommended.

One of the great advantages of NT devices is that thermal desorption is directly performed inside the GC injector without the need of resistively heated devices. This means that the injection mechanism involved is equivalent to that described for SPME [28] so it is important to achieve high linear flows around the needle to help remove desorbed analytes from the injector rapidly. This can be accomplished by reducing the diameter of the injector inset (i.e., smaller liner id). The comparison of the results obtained with 3 and 1 mm id liners showed a significant improvement of bandwidths and chromatographic resolution when the liner diameter was decreased (see Figure 3 in Supplementary Materials). The expanded desorptive flow produced at the hot temperature of the GC injector (300ºC) was sufficient to produce an adequate

linear flow inside the liner and move the analytes to the GC column as a narrow band, as was also described by Eom and Pawliszyn [13]. The attachment of the NT to a clean gastight syringe with a plunger positioned at 50 μL clean air to help the transfer of the desorbed analytes [17] was evaluated but did not improve the chromatographic results significantly.

3.2. Sampling flow

The amount of gas sample to be collected depends on (i) the concentration factor that can be achieved with the proposed methodology and (ii) the level at which the target VOC's are present in the sample. One of the main advantages of the NT methodology is that the LOD's obtained with capillary traps are significantly smaller than those of conventional desorption methods. Previous analyses performed in our laboratory with the 22G NT's showed that sample volumes around 1 L were required to reach LOD's of target VOC's at low ng·m^{-3} range (see last column in Table 1). On the other hand, sample volumes as small as 10 mL were enough to detect VOC's at levels one order of magnitude below regulated values in environmental samples (e.g., 5 μg·m^{-3} for benzene in atmospheric air in Europe [29]). As the time needed to collect a pre-established volume of gas depends on the sampling flow, a high rate of flow is preferred for environmental analysis to decrease the total determination time. The effect of the sampling flow on the sorption capacity of the NT's was then evaluated.

Reproducibility of the adsorption capacity at different sampling flows was assessed with NT's packed either with Carbopack X or Tenax TA. Automatic sampling was performed by connecting the NT to a vacuum pump and varying the vacuum pressure to reach prefixed and constant sampling flows in the range of 5 to 55 mL·min^{-1}. It was found that flow rates ≤15 mL·min^{-1} were required to obtain repeatability values below 15% for all the compounds evaluated with the two sorbents (Table 2). NT's have a small id (0.41 mm in the case of 22G needles), which results in high linear sampling flows inside traps. This may lead to non-quantitative retention of the most volatile compounds as the elution zones of the analytes could be slightly dispersed resulting in incomplete sorption at excessive linear flows. Note that a 20 mL·min^{-1} sampling flow corresponds to an average linear velocity of air sample inside a 22G NT of ~250 cm·s^{-1}, which corresponds to a residence time of analytes in 10-mm trap of 0.004 s. Under these conditions, it is possible that a portion of the molecules of analytes are unlikely to have sufficient time to reach the sorbent surface, and partial breakthrough may take place.

Manual sampling using gas tight syringes was also evaluated. It showed two main limitations: firstly, the pneumatic restrictions of the 22G NT's only allowed small volumes to be obtained manually, which makes it impractical for the analysis of non-contaminated samples when large volumes are required; secondly, it was complicated to maintain a constant and reproducible flow during sampling, which led to poor sampling reproducibility. It was necessary to move the piston of the syringe slowly and constantly for 4 s until reaching the 1 mL mark to get a sampling flow of 15 $mL \cdot min^{-1}$. Operators often change this procedure to a faster movement of the piston until reaching the fixed volume. They then wait for 4 s to obtain equilibration. Comparison of manual and automatic sampling showed that automatic sampling always gave better reproducibility. Moreover, peak areas tend to be higher with automatic sampling, which indicates that the sample volume passed through the sorbent was usually smaller than expected when manual sampling is applied and no strict protocol is used. It is clear that automatic sampling is required when using capillary traps. Automatic sampling at ≤15 $mL \cdot min^{-1}$ was used for the analysis of samples in the following experiments.

3.3. Storage stability

In order to evaluate the applicability of the NT methodology in the field, 5 mL of standards containing all target VOC's at concentrations ~20 $\mu g \cdot m^{-3}$ for each analyte (~0.1 ng each compound) were passed through different traps using both sorbents, and stored for 24 and 48 h periods at 4ºC. Recoveries ranging from 91 to 110% were obtained for the two sorbents, confirming the stability of the target VOC's in these conditions.

Needle traps were maintained in the hot injector for a minimum of 20 min after the split valve was opened to avoid cross-contamination. The absence of cross-contamination was confirmed by passing 5 mL of purified nitrogen through different NT's immediately after the analysis of a few samples. These traps were stored separately at 4ºC for 72 h. Posterior analysis showed clean chromatograms, confirming the applicability of the proposed methodology for environmental analysis.

3.4. Quality parameters

The quality parameters of the methodology are set out in Table 1. The linearity of the proposed methodology was evaluated by preparing a calibration standard at 2.2-2.6 $\mu g \cdot m^{-3}$ for each component and sampling it at different times (n=7) at a constant sampling flow of 15 $mL \cdot min^{-1}$ (ranging from 5 to 60

min). Higher masses were not used since analyses of 1 L samples of non-contaminated environments were expected to be within the selected range [30]. Evaluation of the residual plots showed that the method was linear for all target VOC's in the range evaluated for both sorbents. LOD and LOQ were experimentally determined by preparing standards at reduced concentrations and analyzing them until S/N ~3 (LOD) and ~10 (LOQ) were found in the chromatograms. Table 1 shows the limit values obtained for Tenax TA and the corresponding concentration detection limit when a sampling volume of 1 L is assumed (values obtained using Carbopack X as a sorbent were in the same concentration range). It should be noted that LOD's for benzene with a 1 L sample volume (units of $ng \cdot m^{-3}$) are three orders of magnitude lower than the limit value regulated in ambient air by the European Union for the protection of human health (5 $\mu g \cdot m^{-3}$ [29]) and so sample volumes of 10 mL will be sufficient to detect this compound below these regulated levels.

Intra-day precision was measured for five different traps (three containing Tenax TA and two with Carbopack X) analyzing replicates (n=3) at the lowest and highest masses of the linear ranges indicated. It was found that RSD values ranged from 1.0 to 12.1% (see Table 1 in Supplementary Materials).

3.10. Analysis of breath and environmental samples

We applied the developed NT method to the analysis of VOC's in breath, indoor air and outdoor air samples (Figure 3). The results did not show significant differences to those obtained in the evaluation of the same samples applying other thermal desorption methods [30,31] so confirming the utility of the NT methodology.

Figure 3a corresponds to a smoker's breath sample (mixed expiratory breath) after ~30 min of smoking a cigarette. It was possible to detect the presence of 2,5-dimethylfuran (peak #2, 0.21 $\mu g \cdot m^{-3}$), which was confirmed in a previous study [31] as a selective breath biomarker of smoking status. In this case, the sample volume was 847 mL.

For clinical purposes alveolar rather than mixed expiratory breath sampling is required for the determination of blood-borne biomarkers, which requires volumes of breath samples ≤20 mL [32]. We evaluated the use of alveolar breath sampling for this application but found it to be inadequate. 15 mL of alveolar breath were collected with the help of a capnometer [32] from different smoking volunteers ~60 min after smoking a cigarette. The presence of 2,5-dimethylfuran was not detected in any of the alveolar samples but was detected in mixed expiratory breath samples collected at the same moment using ~850

mL of mixed breath. The low levels of 2,5-dimethylfuran in a smoker's breath require the use of large sample volumes to be able to detect the compound a few minutes after smoking. Taking into account the LOD for this compound with the NT using a sample volume of 10 mL (~1 $\mu g \cdot m^{-3}$), it is impossible to detect the compound's presence in mixed expiratory breath ~30 min after smoking [31], which substantially reduces its utility as a breath biomarker of smoking status. Therefore, a large volume of breath is needed for the analysis of exogenous contaminants in breath at ultra-trace levels, which makes it necessary to use mixed expiratory breath.

The NT methodology also gave successful results for environmental samples. The analysis of a pedestrian outdoor area (Figure 3b, 220 mL sample) showed reduced levels of those compounds that are strongly associated to air contamination by car exhausts, such as benzene (peak #1, 0.52 $\mu g \cdot m^{-3}$). NT's were also used for the evaluation of contamination by environmental tobacco smoke by analyzing 2,5-dimethylfuran, which has also been shown to be an appropriate marker for this purpose [30]. A minimum sample volume of 500 mL was required to be able to detect the presence of 2,5-dimethylfuran in those premises where only one smoker was present in the room before sampling. Five indoor non-smoking areas and three outdoor areas were analyzed without 2,5-dimethylfuran being detected. On the other hand, this marker was detected in the three indoor smoking areas which were analyzed.

Another application of the NT methodology is to evaluate occupational environments. Different indoor environments of the Science Faculty of the University of Girona were analyzed. The analysis of the air quality of most contaminated spaces, such as chemistry laboratories, required sample volumes ≤30 mL to be able to detect a large presence of contaminants. As can be seen in Figure 3c, organic laboratories showed high levels of those solvents which were routinely used (acetone, dichloromethane, hexane, and ethylacetate). In the case of an analytical laboratory, only acetone was routinely detected at excessive levels due to its common use in glass drying (Figure 3d).

4. Concluding remarks

The results obtained in the present study and the simplicity of the needle traps suggest that this methodology is a powerful and robust alternative to conventional thermal desorption and SPME methods for the fast screening analysis of VOC's in air samples. Moreover, the fact that there is no need for specific additional instrumentation (e.g., holders, desorption units and cryogenic focusing devices) results in this being a simple and relatively inexpensive tool.

As can be seen from the results obtained, one of the great advantages of NT devices is that their high efficiency and sensitivity makes it possible to obtain detectable levels of target VOC's in small amounts of non-contaminated samples. Sample volumes of around 1 L were required to detect VOC's present at ultra-trace levels (LOD's ranging from 2 to 10 $ng \cdot m^{-3}$ for 1 L samples). In the case of routine environmental analysis, volumes below 50 mL were enough to detect the presence of contaminating VOC's at regulated levels. It is important to emphasize the high sensitivity of the developed NT technique. Commercial desorption devices require sample volumes of more than 10 L to achieve equivalent LOD's.

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Conflict of interest

Authors declare no conflict of interest.

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Table 1. Volatile compounds evaluated and their quality parameters obtained with the proposed NT methodology

Peak	Compound name	b,p, (ºC)	Characteristic masses*	r.t. (min)	Quality parameters		
					Slope (sd_{slope}) ($\cdot 10^6$)	r	LOD (n
1	benzene	80.1	**78**	2.6	49 (4)	0.991	0.004
2	2,5-dimethylfuran	92-94	95, **96**	3.2	29 (2)	0.993	0.010
3	toluene	110.6	**91**, 92	4.7	89 (7)	0.991	0.002
4	ethylbenzene	136.2	**91**, 106	7.1	82 (8)	0.988	0.002
5	*p*-xylene	138.3	**91**, 105, 106	7.4	118 (9)	0.991	0.002
6	*o*-xylene	143-145	**91**, 105, 106	7.8	110 (10)	0.976	0.002
7	styrene	145-146	103, **104**	7.8	190 (10)	0.990	nd
8	benzaldehyde	178-179	**106**	9.2	490 (50)	0.987	nd
9	2-ethyltoluene	164-165	**105**, 120	9.3	150 (20)	0.968	0.004
10	acetophenone	202	**105**, 120	10.6	920 (70)	0.992	0.003

* mass used for quantification in bold

nd: not determined.

Table 2. Repeatability (variation coefficient, %) obtained with both sorbent materials for the analysis of a standard mixture with all target compounds at different sampling flow rates. One-minute automatic sampling.

	Sampling flow ($mL \cdot min^{-1}$)					
	5 (n=6)	15 (n=3)	34 (n=2)	53 (n=3)	5 (n=3)	15 (n=3)
	Tenax TA				Carbopack X	
benzene	6.1	4.3	26.6	18.6	3.2	1.1
2,5-dimethylfuran	8.5	1.4	25.5	13.7	6.1	5.7
toluene	10.5	4.0	27.5	14.5	3.4	10.5
ethylbenzene	7.8	3.2	38.6	31.7	4.0	8.7
p-xylene	6.6	4.8	40.9	4.4	4.7	6.0
o-xylene	7.5	1.3	43.4	17.1	1.7	8.5
styrene	9.0	2.3	38.1	9.5	7.2	4.9
ethyltoluene	8.3	4.4	46.6	36.2	4.9	11.1
acetophenone	10.2	7.1	61.6	17.0	11.2	10.4

Figure Captions

Figure 1. Scheme of an NT device. A: spiral plugs, B: sorbent material, C: Luer-lock-Luer-tip-valve.

Figure 2. Blank chromatograms obtained after the preparation and conditioning of the two type of NT's: (a) point 2 type NT with epoxy resin (after 24 h conditioning at 300ºC) and (b) point 5 type NT without epoxy resin (after 2 h conditioning at 300ºC).

Figure 3. Chromatograms of (a) the breath of a smoker, (b) outdoor air from a pedestrian area, (c) organic chemistry laboratory air, and (d) analytical chemistry laboratory air. Peak numbers correspond to the component numbers in Table 1. Compounds detected in (c) and (d): A, acetone; D, dichloromethane; H, hexane; and E, ethylacetate.
Experimental conditions: 850 mL samples (a, b) and 50 mL sample (c), Tenax TA sorbent, desorption at 300ºC, 60 s splitless, and 20 min conditioning time.

Figure 1

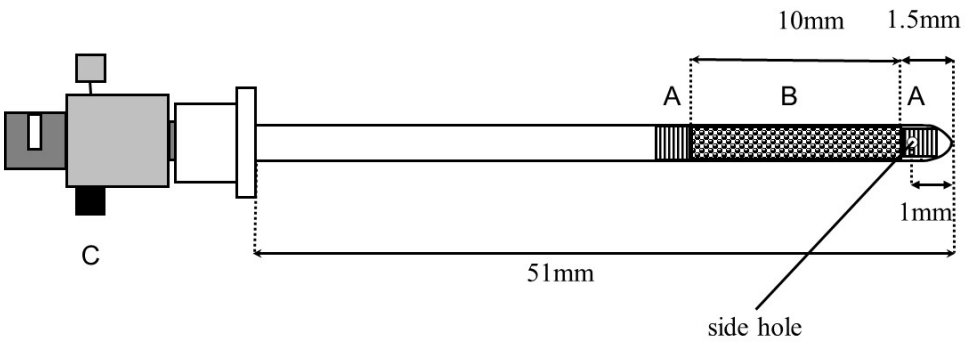

Figure 2

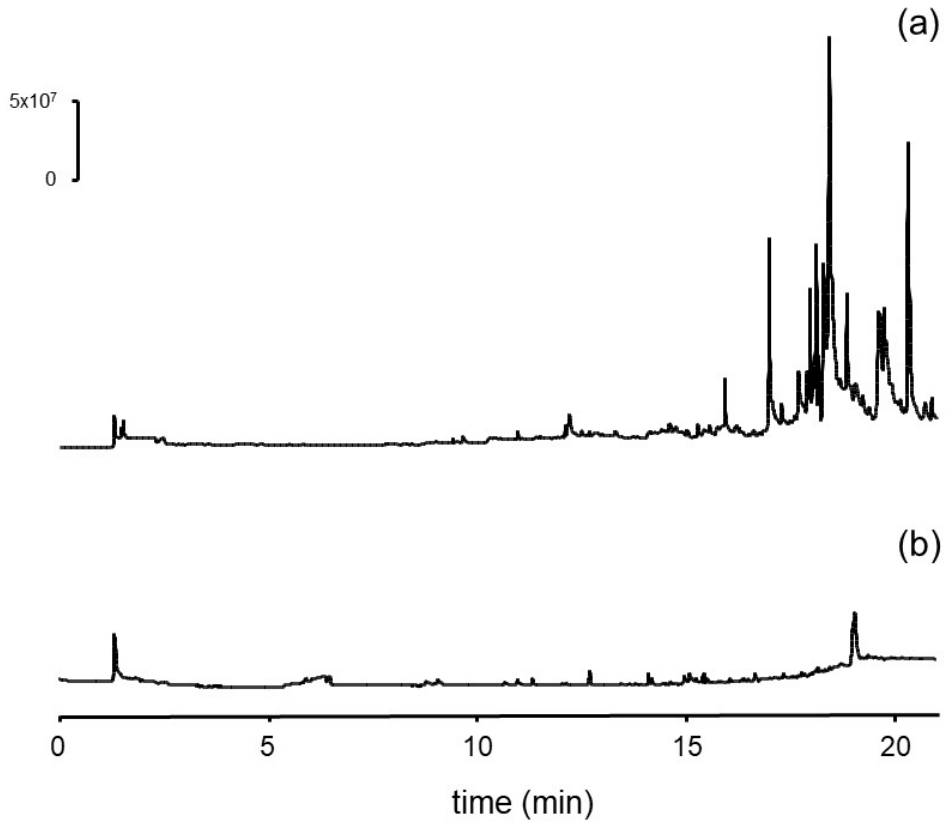

Figure 3