Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1072 (2005) 127–135
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Sampling and determination of volatile organic compounds with needle trap devices

Aiping Wang, Fang Fang, Janusz Pawliszyn*

Department of Chemistry, University of Waterloo, Waterloo, Ont., Canada N2L 3G1

Available online 8 January 2005

Abstract

In this study, a sorbent was immobilized inside a needle resulting in the development of a needle trap (NT) device. This device was applied to extract organic components from gaseous samples and to introduce an enriched mixture into a conventional gas chromatography (GC) injector. Construction of this simple and integrated sampling/extraction/sample introduction device was optimized by considering different ways to immobilize a sorbent in the needle, packing single and multiple-layer sorbent beds, and applying different desorption strategies into the GC injector. A carrier gas system was modified to minimize the carryover for the needle trap with a sealed tip (NT-1), and a narrow-neck liner was used for the blunt-tip needle trap (NT-2). Breakthrough in the device was investigated by connecting two NT-2 devices in series. The needle trap performed very well as an exhaustive spot sampler, as well as in a time-weighted average (TWA) operation. The linear velocity of the mobile phase has no influence on the sampling rate of the needle trap. Validation results against the standard NIOSH 1501 method using charcoal tubes for indoor air surveys demonstrated good accuracy for the NT approach. The reproducibility of the NT-2 was about 1% for benzene. The detection limits for FID detection and for 25 ml gas sample were 0.23 ng/l, 2.10 ng/l and 1.12 ng/l for benzene, ethylbenzene and *o*-xylene, respectively.

Keywords: Needle trap devices; Exhaustive extraction; Time weighted average sampling; Volatile organic compounds; Gas chromatography

1. Introduction

There is increasing interest in the accurate determination of volatile organic compounds (VOCs) at trace levels in ambient air. VOCs are emitted from a variety of sources including fabrics, upholstery, carpets, adhesives, paint, cleaning materials and exhaust fumes from vehicles. Other sources include fuels and lubricants. Although the contribution from any one product may not be significant, the cumulative effect of the emissions from these products is becoming a major concern. Exposure to VOCs might cause eye, nose and throat irritation in addition to damage to the liver, kidney and central nervous system. Some VOCs are suspected and confirmed carcinogens in humans [1–5]. VOCs also affect the global environment by accelerating the global greenhouse effect [6].

Determination of VOCs is typically performed with passive badges, canisters and sorbent traps, followed by separation using gas chromatography with flame ionisation detection (GC–FID) or with mass spectrometry (GC–MS) [7–11]. Compared to passive badges and sorbent traps, the TO-15 method using canisters is useful for a wide range of volatiles. However, the cost of canister sampling methods is higher due to the need for the specialized equipment. The sorbent trap technique provides many advantages over canister sampling. However, it requires considerable sampling expertise, and sample preparation with the use of organic solvents is time-consuming. Therefore, the need for a faster, simpler, and cost-effective sampler has been identified, as well as a more robust field sampling technique.

Solid-phase microextraction (SPME) was developed in the late 1990s and is a successful small size extraction technique, in which the extraction phase is coated on a fiber [11]. To perform sampling, the fiber is exposed to the sample, and analytes are partitioned between the coating and the sample matrix. Desorption is done by directly exposing the fiber to a GC injector or HPLC. SPME is used for sampling VOCs, formaldehyde and volatile organic sulfur compounds in air in addition to passive time-weighted average (TWA) sampling of airborne VOCs [11–17]. Compared to conventional

* Corresponding author. Tel.: +1 519 888 4641; fax: +1 519 746 0435.
E-mail address: janusz@uwaterloo.ca (J. Pawliszyn).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.12.064

sampling methods, the advantage of this solvent-free technology is that it integrates sampling and sample preparation into one step, thus decreasing the analysis time and simplifying the analysis procedure. Moreover, it does not use solvents for desorption of the concentrated analytes, therefore, reducing the risk of technicians' exposure to toxic substances and the pollution to the environment. SPME reduces the cost of analysis because it is reusable. In addition, a number of micro extraction techniques based on coated needles or capillaries have been described as well [18–21]. They are operated on similar principles as SPME. In these approaches, partitioning between sample matrix and needle or capillary coatings is achieved during the sampling.

Recently, a NT device packed with quartz wool was developed to trap particulate matter and aerosols in air [22]. The NT device combines the concept of active sampling and SPME. For extraction, the sample is drawn, and the analytes are concentrated by the quartz wool. Desorption is performed by inserting the needle into the GC injector port and injecting 10 μl of clean air in the syringe to the injector, which aids the introduction of the desorbed analytes to the column. This device shares the advantages of SPME described above. Specifically, the in-needle trap device is robust because the needle protects the quartz wool. However, this device is limited by memory effect and limited reusability.

In this manuscript, the concept of the in-needle trap was applied to develop a sorbent packed NT device. Also, different approaches were carefully evaluated for the transfer of enriched components in to the analytical instrument. In addition, applications of the NT device for exhaustive extraction and passive TWA sampling are discussed.

2. Experimental

2.1. Chemicals and materials

The *n*-alkanes (*n*-octane, *n*-nonane, *n*-decane and *n*-undecane) and BTEX (benzene, toluene, ethylbenzene and *o*-xylene) were obtained from Sigma-Aldrich (Mississauga, Canada). Needles and syringes were obtained from Hamilton (Reno, NV, USA). SPME fibre coatings, narrow-neck liners and gas-sampling bulb (1L) were purchased from Supelco (Mississauga, Canada). Segmental needle trap filled with polydimethylsiloxane (PDMS), divinylbenzene (DVB) and Carboxen particles was from Restek (Bellefonte, PA, USA). The timer was purchased from VWR (Mississauga, Canada). Ultra pure hydrogen, nitrogen and helium were purchased from Praxair (Waterloo, Canada). The 5-min epoxy glue was purchased from Henkel Canada (Brampton, Canada).

2.2. Standard gas generator and sampling chamber

US National Institute of Standards and Technology (NIST) traceable certified permeation tubes (Kin-Tek, La Marque, TX, USA) placed inside a glass cylinder were used to generate *n*-alkanes and BTEX. Ultra pure air at 50 psig (1 psig = 6894.76 Pa above atmospheric pressure) was used to sweep the permeation tubes in order to dilute the gases. A wide range of concentrations of *n*-alkanes and BTEX were obtained by adjusting both the air flow-rate and the temperature of the glass cylinder. Sampling chambers were installed downstream from the standard gas generators.

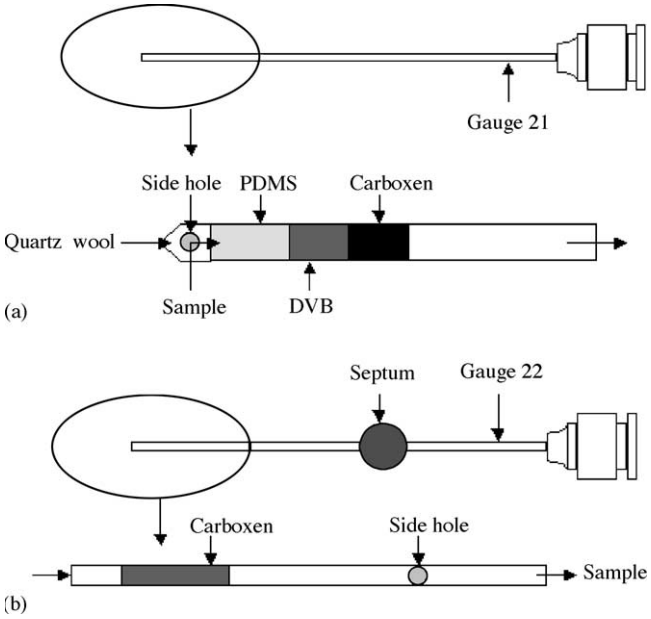

Fig. 1. Schematic of the NT-1 packed with PDMS, DVB and CARBOXEN particles (a) and the NT-2 filled with Carboxen 1000 (b).

2.3. Needle trap

Two types of needle traps (NT) are introduced in this paper. Fig. 1a illustrates the NT device with a sealed tip (NT-1) in which sorbents were packed layer by layer with PDMS particles, DVB particles and Carboxen particles. The thickness of each layer was 3 mm, 2 mm and 2 mm, respectively. Quartz wool was packed between the tip of the needle and the side port because it was difficult to remove the analytes that were extracted by the sorbent near the tip of the needle.

Fig. 1b illustrates the second type of NT device with a blunt tip (NT-2) presented herein, in which the sorbent (Carboxen 1000) was packed near the tip of the needle. The needle size was gauge 22. If the needle was bigger poor resolution was often observed. If it was smaller, the needle was easy to be blocked. The distance between the sorbent and the tip of the needle varied according to its application. If the NT was utilized for passive TWA sampling, the distance could not be zero. For exhaustive sampling, the sorbent could be packed to the tip of the needle. The side hole (I.D.: 0.016 in.; 1 in. = 2.54 cm) was drilled, and positioned 3 cm from the tip of the needle. To immobilize the sorbent, the mixture of the 5-min epoxy glue and the sorbent was packed into the needle. Before the glue cured, a syringe was connected to the needle trap, and the syringe was pushed and pulled to prevent the

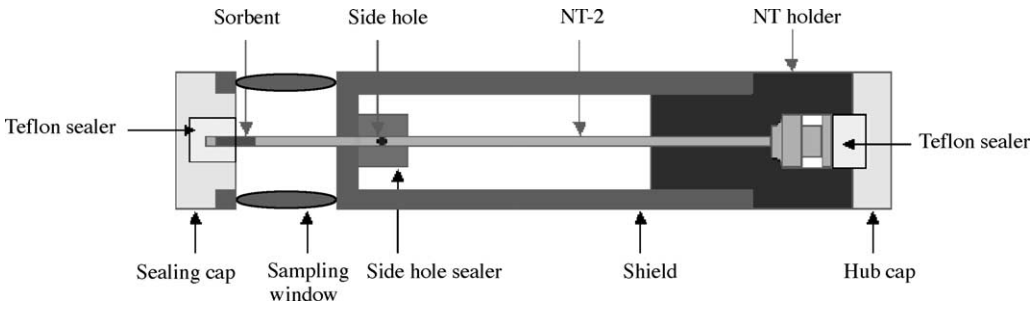

Fig. 2. Schematic of the NT-2 field sampler.

sorbent from blocking the needle trap. After the glue completely cured, the needle trap was conditioned in a GC injector at 300 °C for 5 h to remove impurities, and the NT device was ready for use. During sampling, the needle was exposed to the sample, and the side hole was sealed with a septum. Active sampling required that the needle be connected with a pump or syringe.

2.4. Needle trap field sampler

It is necessary to develop a portable sampling device for convenient on-site application. Fig. 2 shows the schematic of the needle trap field sampler. The field sampler includes five parts: the hubcap, the shield, the NT holder, the sealing cap, and the NT device. The material of the shield and the NT holder is aluminium, and that of the hubcap and the sealing cap is brass. In the hubcap and the sealing cap, there are PTFE parts inserted, which are used to seal the opening of the needle and the hub. PTFE was chosen to seal the NT device because it is soft and it can seal the needle trap very well. Another advantage of this material is that it does not sorb organic compounds well compared to PDMS. The PTFE parts are easily replaceable if they are worn out. In addition, since the PTFE parts are inserted into the caps tightly, they are not easy to be lost. Passive TWA sampling was performed by retracting the needle and exposing the opening of the needle to the sampling window. To perform exhaustive extraction, the NT device was removed from the field sampler holder and connected to a syringe or a pump. After sampling, the NT device was disconnected from the syringe and inserted into the field sampler for storage. During desorption of the analytes, the sealing cap and the shield were removed and the needle was inserted into the GC injector port.

2.5. Instrumentation

A Varian GC–FID system was used for separation and determination of the target compounds extracted by the NT device. A narrow-neck liner (I.D. 0.8 mm) was connected to a RXT-5 column (30 m × 0.25 mm I.D., 1.0 μm film thickness). The flow-rate of the carrier gas was 1.8 ml/min. Table 1 lists the GC parameters for the determination of BTEX and *n*-alkanes.

3. Results and discussion

3.1. Desorption

3.1.1. Different ways of packing sorbent

Desorption is a limiting step in the operation of a needle trap. The preparation of the needle trap (NT-2) packed with a single layer sorbent was very simple, but one type of sorbent does not cover a wide range of volatiles. In addition, when a single type sorbent is used, broad peaks are more likely, especially for the higher-boiling-point compounds.

Another way of packing sorbent in the needle involved the use of sorbents with different adsorption/absorption strengths. Fig. 1a illustrates the needle trap packed with multiple segments of sorbents. The adsorption (DVB and Carboxen) or absorption (PDMS) strengths of the sorbents were graded; Carboxen was the strongest and PDMS was the weakest. For extraction, the sample flowed from the left of the needle to the right through the sorbents, and the higher-boiling-point compounds were extracted by the weaker sorbents [23–25]. When sample desorption occurred, the flow was reversed, and the highest-boiling-point compounds were desorbed into the carrier gas.

3.1.2. NT-2 Field sampler

To test the storage ability of the NT-2 field sampler, benzene was extracted by active sampling from the standard gas generator using the NT-2 device and a syringe with a sample volume of 10 ml, followed immediately by GC analysis. This experiment was repeated six times, and the relative standard deviation (RSD) was 4%. In addition, the above experiment was repeated, but the NT-2 device was stored inside the NT-2

Table 1
GC parameters for the determination of BTEX and *n*-alkanes

Analytes	BTEX	*n*-Alkanes
Injector (°C)	300	300
Initial column temperature (°C)	50[a]	35[b]
Final column temperature (°C)	120	250
Heating rate (°C/min)	20	20
Detector (°C)	300	300

[a] For 1 min.
[b] For 2 min.

field sampler for 24 h. The results show that there was no significant difference between the initial mass of benzene and after 24 h of storage, which means that volatile samples can be stored in the field sampler for at least 1 day without loss. A 6% loss of benzene enriched on the Carboxen sorbent was observed after 4 days of storage in the field sampler.

3.1.3. Direct syringe desorption

For direct syringe desorption, sampling was performed by drawing a known volume of *n*-alkanes from the standard gas generator through the NT-1 device with a syringe. A volume of 1.5 ml of after-extraction air was kept in the plunger and the rest of it was pushed out of the syringe. Following sampling, the needle was inserted into the GC injector immediately and the air in the plunger was injected to aid desorption of the analytes. To observe the carryover, the needle was re-introduced into the GC injector once the NT-1 was withdrawn from the injector. Carryover was determined by the percentage of the target compounds identified in the second desorption of the NT-1 device. Although this desorption method was simple, the carryover of *n*-alkanes was very high (20–25%). In addition, the resulting chromatograms exhibited problems of peak broadening caused by slow desorption and peak split caused by two desorptions occurring during one injection. When the needle was introduced into the injector port, the air inside the needle expanded significantly due to the high temperature in the port. The expanded air went through the needle and swept part of the analytes into the GC column, which was the first desorption. The plunger was pushed to force the air in the syringe to flow through the sorbent and into the GC column, which was the second desorption. In order to solve these problems, the following two different desorption modes were introduced.

3.1.4. Desorption of the NT-1 device by diverting the carrier gas

To improve desorption, a new carrier gas line system was constructed to use with the NT-1 device (Fig. 3). In this system, the carrier gas line was split into two lines by a T valve, which controlled the state of the two lines. The first carrier gas line was connected to the needle of the NT-1 device, and the second carrier gas line was directly connected to the injector port. During standby, the second gas line was opened to provide carrier gas to the GC system. After sampling, the needle trap was connected to the first carrier gas line. The needle was inserted into the GC injector and the valve was quickly switched to open the first line. The desorbed analytes were swept by the carrier gas from the first line into the GC insert. The needle was then removed from the GC injector, and the second gas line was opened immediately. The carryover of C_8–C_{11} by PDMS-DVB-Carboxen segmental NT-1 device with a sealed tip was less than 1%, which was caused by the analytes trapped in a dead volume filled with the quartz wool near the tip of the needle. Chromatograms obtained by the segmental NT-1 device and the new carrier gas line system did not exhibit problems of peak broadening, peak tailing or peak-splitting.

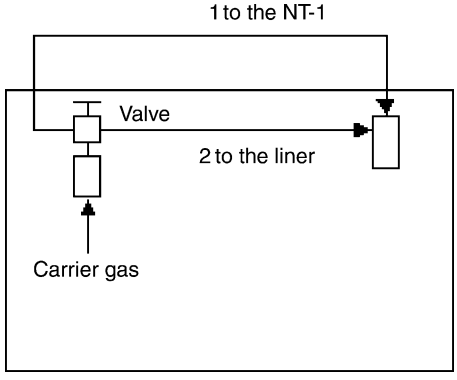

Fig. 3. Schematic of the new carrier system for desorption of the extracted analytes by the NT-1. The carrier gas line (1) was connected to the NT-1 and the line (2) was connected to the GC injection port.

3.1.5. Desorption of the NT-2 device with the narrow neck insert

For NT-2, a GC injector with a narrow-neck liner was used to desorb the analytes enriched by the NT-2 device (Fig. 4). For desorption, the hub of the needle was sealed and the

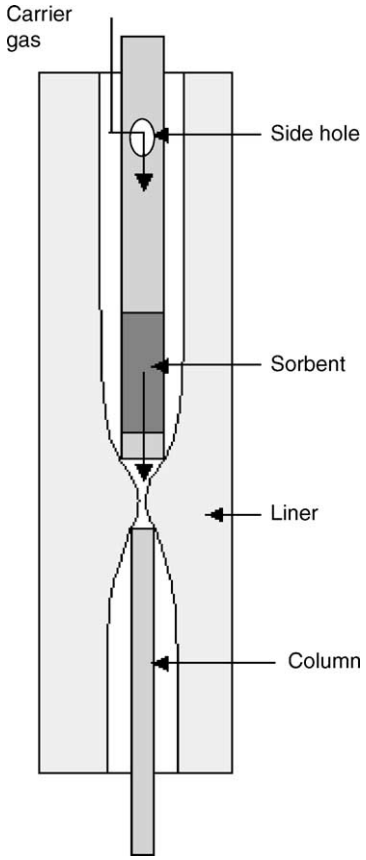

Fig. 4. Diagram of the coupling of the NT-2 with the narrow-neck glass liner. The carrier gas enters the needle through the side hole, flows through the sorbent and facilitates the introduction of the desorbed analytes into the GC column.

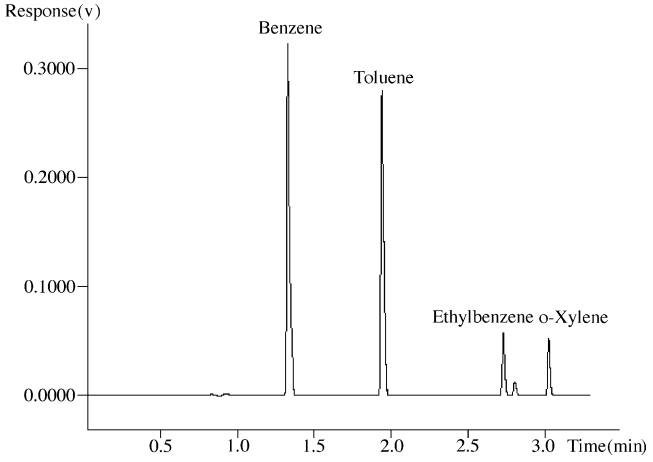

Fig. 5. Separation of BTEX obtained with the NT-2.

septum was removed to open the side hole. The needle was inserted down to the narrow part of the liner so that the liner sealed the needle tip. Fig. 4 illustrates the coupling of the NT-2 device with the narrow-neck liner during the desorption position. The carrier gas entered the needle through the side hole, passed through the sorbent and aided the delivery of the desorbed analytes into the GC column. Following desorption, the NT-2 device was removed from the injector, and the system was then ready for another sampling. This desorption method was convenient, and no memory effect was observed, which was simpler than the method associated with modification of the carrier gas line. Fig. 5 shows the chromatogram of BTEX obtained by the NT-2 device.

The injector temperature influences desorption efficiency, and it increases with the increasing affinity of the analytes to the sorbent. For the sorbent Tenax, desorption temperature of BTEX is 250 °C which is lower than that of Carboxen 1000 (300 °C) because the affinity of Tenax to BTEX is lower. In this study, the desorption efficiency of the NT-2 device packed with Carboxen 1000 was investigated with the analysis of BTEX. When the injector temperature was higher than 300 °C, desorption was complete, and no carryover was observed. If the injector temperature was lower than 300 °C, the analytes could not be completely desorbed, thus resulting in carryover. Furthermore, the carryover increased with the decreasing desorption temperature. It was observed that the carryover reached 25% when the injector temperature was 250 °C. Desorption efficiency also depends on desorption time that is the time the NT in the injector. Table 2 presents the effect of the different desorption time on desorption efficiency for BTEX by the NT-2 device packed with Carboxen 1000 when the injector temperature was set at 300 °C. The appropriate desorption time for this NT-2 device was 1.5 min and no carryover was observed. If the desorption time was less than 1.5 min, carryover was detected. In addition, the sealing between the needle and the narrow-neck liner was important for complete desorption. Good sealing caused more carrier gas to pass through the needle and ensured complete desorption of the analytes, while poor sealing caused a carryover effect. To ensure good sealing, the tip of the needle should be well squared and fit the liner.

Table 2
Carryover of BEX for different desorption time

Desorption time	Carryover (B, %)	Carryover (E, %)	Carryover (X, %)
30 s	0.40	1.10	1.60
1 min	0.10	0.20	0.20
1.5 min	n.d.[a]	n.d.	n.d.

[a] Not detected.

The capacity of the needle trap was enhanced with the increasing sorbent length, but it was limited by the uneven temperature distribution of the injector heat zone. To obtain the high capacity of the NT-2 device and ensure complete desorption, the temperature distribution of the heating zone of the 1093/1094 injector of GC 3400 was tested by inserting a thermocouple into the injector. It was observed that the heating zone in which the temperature was above 300 °C was 1.3 cm long away from the narrow part of the liner. For exhaustive extraction, the length of the sorbent could not be more than 1.1 mm. However, the sorbent length could be more than 16 mm because the sample extracted was located on the tip of the sorbent for TWA sampling.

Sometimes chromatograms obtained by needle trap with Carboxen 1000 exhibited peak-tailing and peak-broadening problems, which could be solved by decreasing the initial oven temperature with carbon dioxide. Various initial column temperatures (35 °C, 0 °C, and −15 °C) were used to test the influence of the initial oven temperature on the peak shape of *n*-alkanes. The results suggest that a lower initial column temperature results in better peak shape. Rather, when the initial oven temperature was low, the analyte re-focused at the head of the column, thus leading to a narrow band.

Compared to the method in which the diverting carrier gas flow is used, use of the narrow-neck liner with the NT-2 device as desorption method is more convenient because it does not require modifying the gas line, the sampling procedure is simplified, and carryover is also eliminated.

3.2. Applications

3.2.1. Exhaustive sampling

One of the main advantages of the NT method is that it can be used in an exhaustive extraction mode. Exhaustive mode means that analytes are completely extracted by the sorbent inside the needle before breakthrough occurs. The amount of the analytes extracted by the NT device is proportional to the sampling volume when the concentration of the analyte and the sampling rate is constant.

To perform the exhaustive extraction, the NT device was exposed to the *n*-alkanes gas from the standard gas generator, and the sample was drawn with a syringe. The enriched analytes on the sorbent were thermally desorbed and separated in the GC. The results of the exhaustive extraction volume profile of the NT-1 device packed with PDMS-DVB-Carboxen

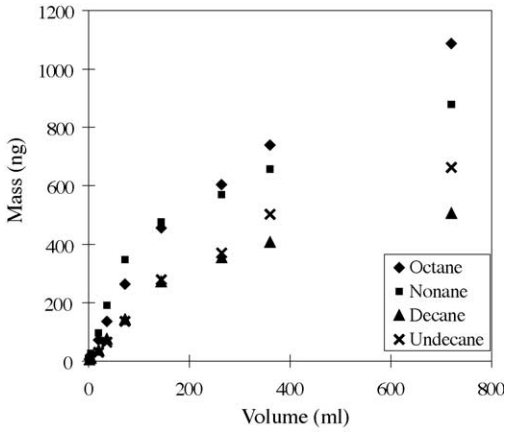

Fig. 6. Extraction volume profiles for exhaustive extraction by the segmental NT-1. Before breakthrough occurred, the linearity of the mass vs. volume was good.

are presented in Fig. 6. Before breakthrough occurred, the response of the analytes and the volume exhibited strong linearity (R^2 was between 0.9968 and 0.9986). After breakthrough occurred, the response versus the sampling volume was not linear. The concentrations of C_8–C_{11} obtained by exhaustive extraction using the segmental NT-1 were 3.65 ng/ml, 4.87 ng/ml, 1.97 ng/ml and 1.90 ng/ml, respectively. For the NT-2 device, benzene and xylene were used as analytes and the concentrations of benzene and xylene were 3.74 ng/ml and 0.32 ng/ml.

The reproducibility of the NT-1 device for *n*-alkanes (C_8–C_{11}) with a sampling rate of 5 ml/min and a sampling volume of 9 ml ranged from 3% to 5%, which indicates very good reproducibility despite the fact that it is a manual operation system. The reproducibility of the NT-2 device for exhaustive sampling of benzene was 1% with a sampling rate of 10 ml/min and a sample volume of 10 ml.

The limit of detection (LOD) for the NT method was determined by exhaustive sampling of BTEX using the NT-2 device with a sampling speed of 20 ml/min and a sampling volume of 25 ml. The NT-2 device was exposed to the standard gas that was diluted by pure nitrogen in a 1-l gas-sampling bulb. The LOD was 0.23 ng/l, 2.10 ng/l and 1.12 ng/l for benzene, ethylbenzene and *o*-xylene, respectively. In this experiment, the volume of the gas-sampling bulb limited the sensitivity of the NT-2 device. A greater volume of sample can be drawn during field sampling, however, therefore, allowing for a greater method sensitivity.

3.2.2. Breakthrough investigation

For the NT device, it is very important to investigate the breakthrough volumes when it is being used in the exhaustive extraction mode. In this study, the breakthrough volume was proportional to the quantity of the sorbent, the affinity of the sorbent to the analyte and the concentration of the analyte. It was inversely proportional to the sampling rate. In addition, the breakthrough volume decreased when the sorbent inside the needle trap was loosely packed.

In this study, two methods were introduced to test the breakthrough volume. First, the NT-1 device packed with PDMS-DVB-Carboxen was introduced into the sampling chamber to extract the analytes. After obtaining the desired sample volume, 1.5 ml of after-extraction air remained in the syringe. The needle trap was disconnected from the syringe, and another clean needle was connected to the syringe. The 1.5 ml of air was then immediately introduced into the GC injector to check analytes in the air. Sampling volume was increased until the analytes in the 1.5 ml of air were detected. The sampling volume equaled the breakthrough volume. The breakthrough volume of the NT-1 device was 72 ml for octane and nonane and 140 ml for decane and undecane. The lower breakthrough volume of octane and nonane might be due to the fact that the weaker affinity to the sorbent.

The second breakthrough investigation method involved connecting two NT-2 devices packed with Carboxen 1000 in series with a universal GC column connector. The hub of the front NT-2 device was cut so that it could be coupled to the back NT-2 device. To test for breakthrough, the two-section NT-2 devices were connected to the sampling pump, and the front NT-2 device was exposed to the sample. The sample was drawn through the two NT-2 devices at a sampling rate of 4.8 ml/min, followed by desorption of the analytes enriched by the two NT-2 devices in the GC. The sampling volume was increased until the analytes extracted by the back NT device could be detected by GC–FID. It was observed that the breakthrough volume of benzene, ethylbenzene and *o*-xylene was more than 1000 ml, and the mass of benzene extracted by the sorbent was more than 4 μg. The breakthrough volume of the NT-2 device packed with Carboxen 1000 was greater than that of the NT-1 device packed with PDMS-DVB-Carboxen because the affinity of Carboxen 1000 to the analytes is stronger. This two-section NT-2 method was more accurate than the first method to test breakthrough volume.

3.2.3. NT-2 device for passive TWA sampling

For TWA passive sampling, the sorbent of the passive sampler should be a zero sink for the target analytes. The zero sink effect of the sorbent inside the NT-2 device was tested by intermittent and continuous exposure to the standard BTEX gases. For the intermittent mode, the NT-2 device packed with Carboxen 1000 was inserted into the sampling chamber to extract BTEX for 15 min, and it was then exposed to pure nitrogen for 15 min. The NT-2 device was then exposed to BTEX for 15 min and then to nitrogen for 15 min, etc. The total exposure time to BTEX was 45 min and the total exposure time to pure nitrogen was 30 min. For the continuous mode, the NT-2 device was continuously exposed to BTEX for 45 min without being exposed to pure nitrogen. It was found that there was no significant difference between the masses loaded by these two different exposure modes, thus the sorbent Carboxen 1000 is a zero sink for BTEX.

A successful TWA sampling device also requires that the bulk analyte concentration equals to the analyte concentration at the tip of the needle. To facilitate this requirement the NT-2

Table 3
Relationship between face velocity and sampling rate

Face velocity (cm/min)	Sampling rate (ml/min)
1.2	0.00064
4.1	0.00063
14.4	0.00065
138.4	0.00062

device does not require a large sample linear velocity because the cross-section area is very small [26]. To validate the above assumption and to investigate the sampling rate versus the linear velocity of the NT-2 device, the NT-2 device packed with Carboxen 1000 was exposed to the standard BTEX gases with different linear velocities, ranging from 1.2 cm/min to 138.4 cm/min. The results are presented in Table 3, and it is evident that the sample linear velocity does not affect the mass loaded in the sorbent.

SPME was demonstrated to be a very successful passive TWA sampler when the fiber was retracted inside the needle during sampling [26,27]. The theoretical application of a NT device as a TWA sampler is analogous to the use of SPME [26]. Based on this theory, the following two equations were obtained.

$$R_1 = D\left(\frac{A}{Z}\right) \quad (1)$$

Sampling rate R_1 is theoretical and can be calculated. It depends on the diffusion coefficient of the analyte, D; the diffusion path length, Z; and the cross-section area of the needle, A.

$$R_2 = \frac{n}{C_f t} \quad (2)$$

Eq. (2) shows that the rate of the analyte mass n/t extracted by the sorbent depends on the sampling rate R_2, which could be obtained by an experiment, and the bulk analyte concentration C_f. Theoretical R_1 should equal the experimental R_2 in an ideal situation, and R_1 is constant for a given analyte and needle trap device at a specified temperature.

In this study, the NT-2 device with a diffusion length 5 mm was exposed to BTEX in the sampling chamber with a diffusive sampling time ranging from 60 min to 1000 min, followed by desorption and separation by GC–FID. Fig. 7 illustrates the extraction time profiles of the NT-2 device for TWA sampling of BTEX. The amount of the enriched analytes and

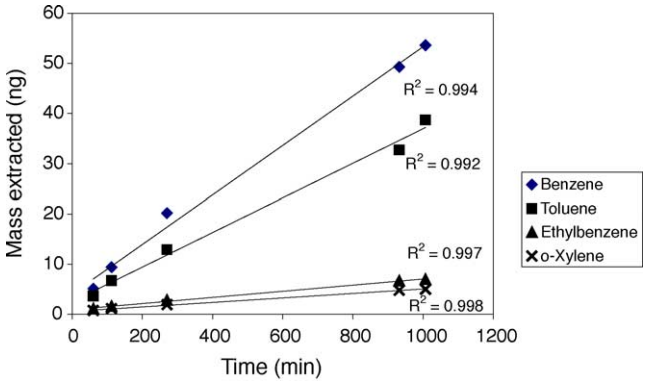

Fig. 7. The extraction time profiles of NT-2 with diffusion length of 5 mm for passive TWA sampling of BTEX.

sampling time exhibit good linearity (R^2 is 0.992–0.998). To ensure precision, the NT-2 device was used to passively sample BTEX for 40 min, and the experiment was repeated seven times. The reproducibility of the method was 2–9% for BTEX. The RSD of xylene (9%) was greater than that of benzene (2%) because the concentration of xylene was much lower. Good agreement between experimental R_1 and theoretical R_2 was observed, as noted in Table 4. These results demonstrate that the NT-2 device with a diffusion length of 5 mm could be used as a TWA sampler. No external calibration is necessary as long as diffusion for target analyte is known. The NT-2 device could not only be utilized to determine unknown concentration but also could be applied to test unknown diffusion coefficients of analytes. The same device could also be used in an exhaustive mode although the capacity of the NT-2 device ($z = 5$ mm) was smaller than that of the NT-2 device with $z = 0$, due to the smaller sorbent mass inside the needle.

3.2.4. Validation

The NT device was validated against NIOSH 1501 methods [28] for both exhaustive extraction and TWA sampling. The NT-1 device was used to take an air sample, in the exhaustive mode, in the hallway of the C2 building at the University of Waterloo, after one basement room was painted. The results in Table 5 show that the charcoal tube (NIOSH method) could not detect the toluene while the NT-1 device could detect it. The results are based on the assumption that the NT-1 device did not reach breakthrough because toluene

Table 4
Results of the NT-2 as a TWA sampler

Compounds	Concentration (ng/ml)	Sampling rate (ng/s)	R_1[a] (ml/s)	R_2[b] (ml/s)	R^2
Benzene	3.05	0.00082	0.00027	0.00024	0.994
Toluene	2.33	0.00057	0.00025	0.00022	0.992
Ethylbenzene	0.41	0.00010	0.00025	0.00020	0.997
o-Xylene	0.36	0.00008	0.00021	0.00019	0.998

[a] R_1 is experimental.
[b] R_2 is theoretical.

Table 5
Concentration of the toluene in the laboratory fume hood determined by the NIOSH method and the NT-1 method

Sampling time	Sampling place	NIOSH method		NT-1 method (ng/ml)
		Front	Backup	
10 h after painting	Hallway (10 m away from the painted room)	n.d[a].	n.d.	0.570
Third day after painting	Hallway (1 m away from the painted room)	n.d.	n.d.	0.065

The sampling rate of the charcoal tube was 0.13 l/min and the sampling volume of the segmental NT-1 was 10 ml.
[a] Not detected.

Table 6
Concentration of toluene in the hallway near the painted room determined by the NIOSH method and the NT-1

Item	Place	NIOSH		NT-1	
		Front (ng/ml)	Back (ng/ml)	Front (ng/ml)	Back (ng/ml)
Sample 1	Laboratory fume hood	15.7	n.d.[a]	14.6	n.d.
Sample 2	Laboratory fume hood	16.3	n.d.	16.2	n.d.
Sample 3	Laboratory fume hood	13.7	n.d.	15.4	n.d.
Average		15.2	n.a.[b]	15.4	n.a.
RSD (%)		8.9	n.a.	5.2	n.a.

The sampling flow-rate of the charcoal tube was 0.12 l/min and the sampling volume of the NT-1 was 3 ml.
[a] Not detected.
[b] Not applicable.

concentration in the air was very low. For high analyte concentration, it is important to ensure that the sampling volume is smaller compared to breakthrough volume. A two-section NT-1 device was required to guard against breakthrough, similar to the two-section charcoal tube used in the NIOSH method 1501. Sampling of toluene using the two-section NT-1 was carried out in a fume hood where the cap of a toluene bottle was loosened to increase the toluene concentration in the fume hood air. The results are presented in Table 6. The average toluene concentration obtained by the NT-1 method was 15.4 ng/ml, which is in good agreement with the average toluene concentration obtained by the NIOSH method (15.2 ng/ml). This result suggests that the two-section NT-1 is also practical for sampling VOCs at high concentrations.

The NT-2 device packed with Carboxen (diffusion length, 2.5 mm) was used as a TWA sampler against a charcoal tube (NIOSH method) to extract benzene and toluene from the standard gas generator. For the charcoal tube, the sampling time was 1497 min, and the sampling rate was 160 ml/min. The concentrations of benzene and toluene obtained were 3.05 ng/ml and 0.97 ng/ml, respectively, which was in good agreement with the concentrations obtained by the charcoal tube method (2.96 ng/ml and 1.00 ng/ml, respectively).

Compared to the conventional methods for VOC sampling, the NT method does not require sample preparation and the determination of the desorption efficiency of the NT device is simpler, which reduces the analysis time to a few hours. The NT device is reusable, and therefore, decreases analysis costs. In addition, the NT device is a solvent-free technology, which minimizes the environment and human health impacts associated with solvents.

4. Conclusion

A needle trap device is a very convenient method to sample and analyze VOCs because it can be inexpensive, re-usable, and easy to operate. A blunt tip needle packed with immobilized sorbent (NT-2) appears to be the best approach because it does not require the diversion of the carrier gas, compared to needles with a sealed tip. The narrow neck inserts used with blunt tip needles are commercially available. The NT-2 device not only can be used in an exhaustive sampling mode but also can be used as a passive TWA sampler. In addition to using an NT device for the extraction of dissolved VOCs, possible applications include rapid screening for fire smoke, spray fog, etc. which, with the use of new sample introduction approaches described in this report, should be more effective compared to previous work [18]. Possible limitations associated with aqueous sampling or low thermal stability or non-volatile analytes exist, however, coupling with HPLC or CE might overcome these limitations.

Acknowledgement

The authors thank the Natural Sciences and Engineering Research Council of Canada for financial support.

References

[1] Threshold Limit Values for Chemical and Physical Agents, America Conference of Governmental Industrial Hugienists, 1996.
[2] N.C. Hawkins, S.K. Norwood, J.C. Rock, A Strategy for Occupational Exposure Assessment, America Industrial Hygiene Association, 1991.

[3] G.L. Gist, J.R. Burg, J. Expo. Anal. Environ. Epidemiol. 5 (1995) 197.
[4] G.B. Hamar, M.A. McGeekin, B.L. Phifer, D.L. Ashley, J. Expo. Anal. Environ. Epidemiol. 6 (1996) 247.
[5] N.H. Proctor, J.P. Hughes, M.L. Fischman, Chemical Hazards of the Workplace, J.B. Lippincott, Philadelphia, PA, 1998.
[6] S.M. Hays, R.V. Gobbell, N.R. Ganick, Indoor Air Quality Solutions and Strategies, McGraw-Hill, New York, 1995 (Chapter 2).
[7] J. Dewulf, H. Van Langenhove, J. Chromatogr. A 843 (1999) 163.
[8] J. Dewulf, H. Van Langenhove, Atmos. Environ. 31 (1997) 3291.
[9] C. Peng, S.J. Batterman, Environ. Monit. 2 (2000) 313.
[10] M. Van Winkle, P. Scheef, Indoor Air 11 (2000) 49.
[11] C. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[12] P.A. Martos, J. Pawliszyn, Anal. Chem. 69 (1997) 206.
[13] P.A. Martos, J. Pawliszyn, Anal. Chem. 69 (1997) 402.
[14] P.A. Martos, J. Pawliszyn, Anal. Chem. 70 (1998) 2301.
[15] W. Wardencki, J. Namiesnik, Chem. Anal. 44 (1999) 485.
[16] P.A. Martos, J. Pawliszyn, Anal. Chem. 71 (1999) 1513.
[17] F. Augusto, J. Koziel, J. Pawliszyn, Anal. Chem. 73 (2001) 481.
[18] M.E. McComb, R.D. Oleschuk, E. Giller, H.D. Gesser, Talanta 44 (1997) 2137.
[19] S. Shojania, R.D. Oleschuk, M.E. McComb, H.D. Gesser, A. Chow, Talanta 50 (1999) 193.
[20] F. Musshoff, D.W. Lachenmeier, L. Kroener, B. Madea, J. Chromatogr. A 958 (2002) 231.
[21] S. Bigham, J. Medlar, A. Kabir, C. Shende, A. Alli, A. Malik, Anal. Chem. 74 (2002) 752.
[22] J.A. Koziel, M. Odziemkowski, J. Pawliszyn, Anal. Chem. 73 (2001) 47.
[23] J.M. Sanchez, R.D. Sacks, Anal. Chem. 75 (2003) 2231.
[24] C. Lu, E. Zellers, Anal. Chem. 73 (2001) 3449.
[25] C. Lu, E. Zellers, Analyst 127 (2002) 1061.
[26] Y. Chen, J. Pawliszyn, Anal. Chem. 75 (2003) 2004.
[27] J. Koziel, M. Jia, A. Khaled, J. Noah, J. Pawliszyn, Anal. Chim. Acta 400 (1999) 153.
[28] NIOSH Manual of Analytical Method, fourth ed., National Institute for Occupational Safety and Health, US Department of Health and Human Service, Cincinnati, OH, 1994.