Needle Trap Device and Solid Phase Microextraction Combined with Portable GC-MS for On-Site Applications

by

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A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Science
in
Chemistry

Waterloo, Ontario, Canada, 2011

Authors Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Jamie Warren

Abstract

Needle trap device (NTD) is a technique that is useful for a wide variety of applications involving the sample preparation of compounds with a wide range of chemico-physico properties, and varying volatilities. A newly designed NTD that improves the performance relative to previous NTD designs is simple to produce is developed. The NTD utilizes a side-hole needle with a modified tip to improve the sealing between the NTD and narrow neck liner of the GC injector, thereby increasing the desorption efficiency. The slurry packing method was applied, evaluated, and NTDs prepared by this method were compared to NTDs prepared using the vacuum aspiration method. NTD geometries including blunt tip with a side-hole needle, tapered tip with side-hole needle, dome tapered tip with side-hole, sliding tip with side-hole and blunt tip with no side-hole needle (expanded desorptive flow) were prepared and evaluated. Sampling performance and desorption efficiency were investigated using automated headspace extraction of benzene, toluene, ethylbenzene, *p*-xylene (BTEX), anthracene and pyrene. The tapered tip and sliding tip NTDs were found to have increased desorption efficiency.

SPME and NTDs are valuable sample preparation tools for on-site analysis. Combining both extraction techniques allows for the differentiation of free and particle-bound compounds in a sample matrix. Portable GC/MS instrumentation can achieve fast separation, identification, and quantitation of samples prepared by the above techniques on-site without the need for transport to the laboratory. This minimizes the effects of volatiles lost and sample degradation during storage time. Here, SPME and tapered tip NTDs combined with

portable GC/MS are used to investigate free and total emissions of BTEX and select PAHs from gasoline and diesel exhaust. Using the above optimized technologies, cigarette smoke in a smoking area where people were actively smoking and inside a smoker's car were also investigated. Target contaminants were found in the investigated matrices at ng/mL levels.

Acknowledgements

I would like to take this opportunity to give great thanks to all who have provided assistance, and support in the completion of this project. Firstly, I would like to thank my supervisor, Dr. Pawliszyn for accepting me into a great group, and providing the opportunity to work on this project. His instruction, guidance and encouragement have allowed for the completion of this work.

I would also like to express great thanks to my committee members, Dr. Tadeusz Gòrecki and Dr. Michael Chong, for their advice and time given to evaluate the work completed throughout this research project.

I would also like to thank fellow colleagues in the group. A dynamic group of students provided an atmosphere to participate in intellectual discussion that generated ideas and information that greatly assisted me throughout the project.

Dedication

I would like to dedicate this thesis to my family and friends for their encouragement and support.

"Life is 10% of what happens and 90% of how you react to it." John C. Maxwell

Table of contents

List of Figures

List of Tables

List of Abbreviations

BTEX	Benzene, toluene, ethylbenzene, xylene
CAR	Carboxen 1000
DVB	Divinylbenzene
FID	Flame ionization detector
GC	Gas chromatography
IMS	Ion mobility spectroscopy
LTM	Low thermal mass
NSH	No side hole
NTD	Needle trap device
MS	Mass spectrometry
PDMS	Polydimethylsiloxane
SPME	Solid-phase microextraction
TMS	Toroidal mass spectrometry
VOC	Volatile organic compound

Chapter 1. Introduction

1.1 On-site analysis

The increasing need for environmental monitoring, fast screening, and real-time decision making is rapidly moving analytical techniques to the field producing results directly on-site.[1] Such recent trends have led to development of new sampling and sample preparation techniques that are fast, solventless, and directly analyzed by analytical instrumentation.[2] Advancements in analytical instrumentation have miniaturized analytical instrumentation such as gas chromatographs coupled with different detectors including flame ionization detectors (FID) and mass spectrometers (MS).[3] Ion mobility spectroscopy (IMS) is commercially available in a hand held format.[4] Combination of on-site sample preparation with new portable instrumentation can complete on-site analysis to produce fast results, and support immediate decision making directly on-site.

On-site analysis has many advantages when compared with traditional analytical procedures. The on-site approach minimizes errors associated with storage and transport of samples to the laboratory; resulting in analytical data that is more accurate, precise and representative of the target system, and expedites and allows for immediate decision making.[5] The cost of analysis is also reduced by eliminating the need of repeated mobilization of personnel and equipment to the analysis site. Immediate results also allow analysts to make required modifications to their sampling and analysis procedure at the sampling site, reducing the number of samples required.

In the traditional analytical process, sampling and sample preparation are responsible for 80% of the total analysis time and often require multiple steps using toxic solvents.[6] Two sample preparation techniques recently developed that provide fast, solventless sampling, isolation, and pre-concentration, all integrated into one step are solid phase microextraction (SPME) and needle trap devices (NTDs). Combining these sample preparation technologies with portable instrumentation allows for quantitative sample analysis in real time. Applications of SPME and NTDs for on-site sample preparation with lab analysis have been described in the literature.[7-9] SPME has also been successfully coupled with field portable gas chromatographs (GC-FID and GC-MS) for different on-site applications including analysis of volatile organic compounds (VOCs)[1] and chemical warfare agents.[10]

1.2 Solid phase microextraction

1.2.1 Principles of solid phase microextraction

Developed in the early 1990's, SPME addressed the need to facilitate rapid sampling and sample preparation, both in the laboratory and on-site.[11] It is a solventless sample preparation technique with the advantage of combining sampling, isolation, and enrichment into one step.[12] The technique is based on extraction using a fused-silica fiber coated with a polymeric phase, such as liquid polydimethylsiloxane (PDMS) or solid divinylbenzene (DVB), housed in a modified syringe. When exposed to the sample matrix analytes partition between the extraction phase and the matrix. SPME has been used

routinely in combination with GC where analytes are removed via thermal desorption directly in the inlet port of the GC.

Combining SPME with GC-MS has been successfully applied to a wide variety of compounds, focusing on volatile and semi-volatile organic compounds from complex sample matrices. The SPME sampling approach has been popular for applications involving food[13,14] and environmental analysis including air,[15-17] water[18,19] and soil.[20,21]

The partitioning of analytes between the SPME fiber and the sample matrix is an equilibrium process. At equilibrium conditions, Eq. 1.1 describes the amount extracted according to the law of mass conservation:[22]

$$n = \frac{K_{fs} V_f V_s C_o}{K_{fs} V_f + V_s} \quad 1.1$$

where n is the number of moles extracted by the coating, K_{fs} is defined the distribution coefficient of the analyte between the fiber coating and sample matrix, V_f is the volume of the fiber coating, V_s is the sample volume, and C_o is the initial concentration of a given analyte in the sample. When Eq. 1.2 is valid, Eq. 1.1 can be further simplified to Eq. 1.3:

$$V_s >> K_{fs} V_f \quad 1.2$$

$$n = K_{fs} V_f C_0 \quad 1.3$$

Eq. 1.3 describes the effectiveness of SPME when implementing on-site analysis where the sample volume is typically unknown. The amount extracted is independent of sample volume; therefore, no defined volume of sample is required for collection. The SPME fiber can be exposed directly to the sample matrix and the amount of extracted analyte will correspond directly to the concentration in the sample.[23]

When completing on-site analysis, waiting for equilibrium conditions is not always feasible. Furthermore, when using porous solid coatings such as PDMS/DVB, competitive adsorption and displacement effects occur with long extraction times. This makes mass calibration and quantification challenging for solid SPME coatings. PDMS/DVB fibers, however, are reported to extract greater amounts of VOCs than the PDMS coating, particularly when short sampling time and pre-equilibrium conditions are used.[24] Thus, to take advantage of the high sensitivity of solid SPME coatings, calibration approaches relying on diffusion controlled extraction have been developed.[24-26]

SPME calibration methods are based on the fundamental principles governing the mass transfer of analytes in a multiphase system. Traditional calibration, equilibrium extraction, exhaustive extraction, diffusion based, and kinetic calibration methods have been extensively described in the literature.[27,28,23] For the purpose of this research, diffusion based calibration using the interface model was used; therefore, will be discussed briefly. Further information can be found in the related articles.[24-26]

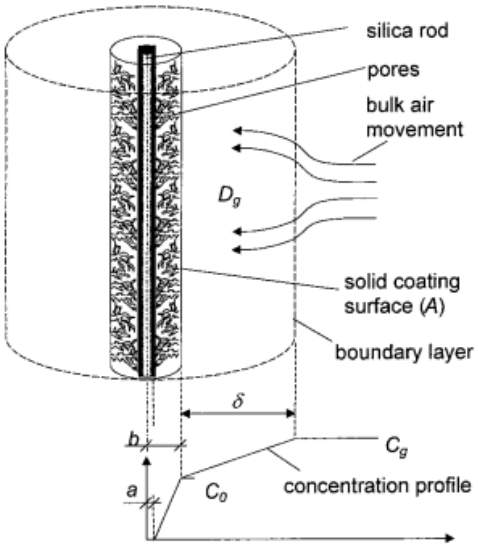


Figure 1. Schematic of rapid extraction with solid SPME fiber coating in a cross flow, the extraction is described by Eq. 1.4.

As shown in Fig. 1, the solid coating of an SPME fiber can be modeled as a long cylinder with length L, outside diameter b and inside diameter a. An interface (or boundary layer) with thickness δ exists between the idealized surface of the fiber and the bulk of air when the coating is exposed to moving air. Analytes are transported to the surface of the coating via molecular diffusion across the boundary layer. For short sampling times, the SPME solid coating can be treated as a perfect sink. Furthermore, the adsorption binding is considered instantaneous and the analyte concentration on the coating surface (C_o) is far from saturation and can be assumed negligible in typical air. The mass of extracted analyte can be determined from Eq. 1.4:

$$n(t) = \frac{2\pi D_g L}{\ln\left((b+\delta)/b\right)} C_g t \qquad 1.4$$

Where n is the mass of extracted analyte (ng) over sampling time t (s). D_g is the gas-phase molecular diffusion coefficient (cm^2/s), b is the outside radius of the fiber coating (cm). C_g is the analyte concentration in the bulk air (ng/mL) and is assumed constant for the short sampling time.

From Eq. 1.4 it can be seen that the mass extracted is proportional to the sampling time, D_g for each analyte, and bulk air concentration and inversely proportional to δ. Eq. 1.4 can be modified to calculate analyte concentration in the air (ng/mL) for short sampling to Eq. 1.5:

$$C_g = \frac{n ln((b+\delta)/b)}{2\pi D_g L t} \qquad 1.5$$

Analytes with a greater D_g will cross the interface and reach the surface of the fiber coating faster. Values of D_g can be estimated from physicochemical properties. A method developed by Fuller, Schettler, and Giddings has been reported to be the most accurate for non polar organic gases at low to moderate temperatures.[29]

$$D_g = \frac{0.001 T^{1.75} \sqrt{\frac{1}{M_{air}} + \frac{1}{M_{VOC}}}}{p\left[(\sum V_{air})^{1/3} + (\sum V_{VOC})^{1/3}\right]^2} \qquad 1.6$$

The effective thickness of the boundary layer can be estimated using eq. 1.6, derived from the heat-transfer theory of an SPME fiber in a cross flow Eq. 1.7:[23]

$$\delta = 9.52b/Re^{0.62}Sc^{0.38} \quad 1.7$$

Where Re is Reynolds number and SC is the Schmidt number.

1.3 Needle trap device

Introduced in 2001, NTD was developed in response to the demand for a more robust SPME system. Similar to SPME, NTD is a solventless, one-step sample preparation method. It offers increased robustness in comparison to SPME owing to the extraction sorbent packed inside a hypodermic needle rather than supported on a fragile silica fiber that is exposed to the analyte matrix during extraction. The concept of packing needles with sorbent, however, is not a new idea. In the 1970s Tenax-filled needles were used for sampling and analysis of airborne VOCs.[30] The major drawback to this design was the requirement of a dedicated carrier gas purge line and modified GC inlet to desorb the analytes. NTDs on the other hand, require no external gas lines and have potential for laboratory automation and on-site sampling compatibility with convenient coupling to analytical instrumentation without any custom modification.[31]

The NTD combines the idea of exhaustive sampling with the miniaturization and integration of SPME. The exhaustive nature of NTD simplifies the calibration and also allows particle trapping, which results in the extraction of total concentration as compared to free concentration obtained by SPME. Fig. 2 is a schematic of the original side-hole NTD. It consists of a hypodermic needle with a side-hole drilled about 3 cm from the tip. A piece of steel wire is coiled and pushed into the needle to a depth of the desired

particle packing length to act as a particle support. Sorbent particles of choice, such as divinylbenzene and/or Carboxen, are packed into the needle by a vacuum aspirator and gently compressed using a thin wire. Once the NTD has the desired amount of particles packed inside, they are supported. Conventionally epoxy glue has been used to support the particles at the tip of the needle, while the aspirator continues to operate to prevent the glue from sealing the NTD. The NTD can then be placed directly into the injector of a GC for thermal conditioning to remove impurities from the sorbent.

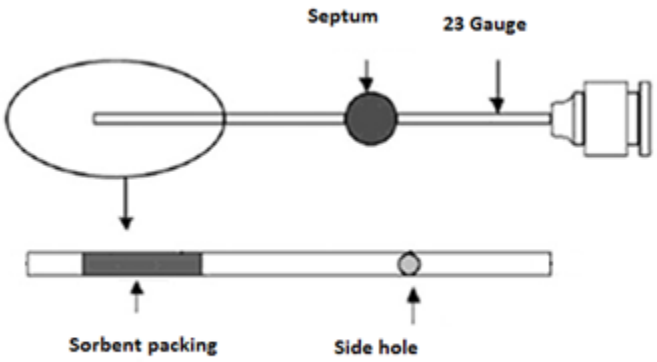


Figure 2. Schematic of a side-hole needle trap device. The side-hole is plugged using a septum during sampling and unplugged during desorption.

The amount of analyte extracted by the NTD is proportional to the sampling volume when the concentration of the analyte and sampling rate are constant. It is necessary however, to investigate the breakthrough volume of the NTD. The breakthrough volume is proportional to the length and density of the packing, affinity of the analyte to the sorbent, and concentration of the analyte. It is inversely proportional to the sampling rate.[32] Due to a limited surface area; the sorbent bed is easily saturated with

large sample volumes or high sample concentration,[31] which is often thought to be a limitation of NTD. However, compared to conventional exhaustive extraction techniques such as SPE and liquid-liquid extraction, using NTD, all extracted analytes are injected into the GC, eliminating dilution effects due to further sample preparation.[65]

Calibration of NTD is identical to other exhaustive sampling techniques. A known sample volume is required. The amount extracted is determined from a pre-determined instrument detector response calibration. The concentration in the sample can be calculated from Eq. 1.8:

$$C_o = \frac{n}{V_s} \qquad 1.8$$

Where n is the mass extracted, C_o is the concentration of the analyte, and V is the sample volume.

NTDs complete exhaustive sampling by drawing air through the sorbent tube via attachment of a syringe pump[33,34] or gas tight syringe.[35] This configuration has frequently been utilized for several applications. The use of NTDs for trace gas analysis in breath has been a popular application.[35,36] An on-site alveolar sampling method has been developed, providing sensitivity in the parts per trillion range.[35] The same group extended the above application of NTD to GC x GC characterization of breath samples.[36]

Applications for VOC analysis have also been developed using NTDs. Compounds such as BTEX[33,34,37] and mercury vapors[7] have been investigated in the laboratory. Mercury vapor sampling has been completed on-site coupled with in-lab analysis.[7]

One of the more interesting aspects of NTDs is the simple combination with SPME to distinguish free and total concentrations and, determine particle-bound analyte concentrations. On-site sample matrixes can be very complex, with a major fraction of analytes of interest being bound to particulate matter. Depending on the application or investigated analytes, differentiating between free and particle-bound analytes can yield important information.

Several applications have been completed comparing results obtained from SPME and NTD techniques. Results from Niri *et al.*[34] compare the analysis of mosquito coil smoke using SPME and NTD. The SPME method was found to exhibit high extraction efficiency for semi-volatile organic compounds, which can be explained by large partition coefficients between the gas phase and the SPME extraction phase. For more volatile compounds lower partition coefficients exist, leading to low amounts extracted and non-volatiles are fractionally bound to particulates causing lower amounts extracted. The NTD showed no specific selectivity for different analytes in the system. Differences, however, were found in comparison to SPME where NTD extracted the volatile components and non-volatile components efficiently. Using this data, the method was used distinguish free and total concentration.

An in-depth study on the validation of SPME and NTDs for particulate sampling has been completed by Li *et al.*[10] Using theoretical methodologies, lab and on-site experiments, the authors validated that SPME extracts only free portions of analyte in a sample matrix while NTD extracts total. Theoretical ideas described the extraction of particulates using SPME and NTD. The theory was validated experimentally using PAHs controlled in a standard particulate generator and those present in cigarette and barbeque smoke. To further validate that SPME did not extract particulates scanning electron microscope images were used.

There are several limitations yet to be explored using NTDs. Direct extraction from aqueous samples can introduce large amounts of water into the GC causing column degradation and detector problems. Second, the analysis of compounds with low thermal stability, desorption from the adsorbent is completed thermally in a hot GC injector which can lead to degradation of the unstable compounds.

Completing efficient desorption of NTDs has been a challenge and focus of development for many authors. Several desorption methods have been investigated to determine the optimum transfer of analytes from NTD sorbent bed to the column. Initial sorbent tubes produced in the 1970s required an additional carrier gas to desorb analytes from the trap. The NTDs produced by the Pawliszyn group were further evolved to use thermal desorption directly in the GC injector without the need of an external carrier gas supply. Original NTDs produced by the Pawliszyn group, operated on air-assisted desorption, whereby the NTD was placed into the hot GC injector and 10 μl of clean air

was delivered via a gas tight syringe.[38] The method was easy; however, sometimes split peaks were observed due to initial desorption caused by the hot injector, followed by desorption assisted by the introduction of air.[38]

Sample transfer has been conducted via internally expanded desorptive flow. NTDs without a side-hole were loaded with VOCs and injected into the hot injector for thermal desorption and sample transfer. The high desorption temperature produces a desorptive flow inside the NTD due to the expansion of air inside the needle. This method has worked well for BTEX and alkane (C6-C15) mixtures.[37] Here, the length and profile of the temperature variation within the injector are critical in determining the optimal sorbent bed length. Carryover was significant when part of the sorbent bed was located outside the optimal heated zone of the injector during use. The addition of water vapor expansion has been found to aid in the efficiency of this technique, which make it valuable for breath analysis where the sample is naturally wet.[35,36]

A more effective approach was developed by A. Wang *et al*. where a side-hole was placed above the sorbent particles.[39] Combining a side-hole NTD with a narrow neck GC injector liner; the side-hole directs a continual supply of carrier gas through the sorbent bed, transferring analytes onto the column. This method has been found the most efficient for desorption with no memory effects observed.[39]

1.4 Portable instrumentation

Portable instrumentation is required to complete on-site sample analysis. The idea of portable instrumentation is not new and has been a focus of development in analytical chemistry for over two decades.[4] When using portable instrumentation, several factors are important to consider: the entire analytical system should be small enough to fit in the environment of its application, affordable and operationally simple enough to match the skills of the end users. The instrument must also be robust to produce reliable data.[3]

In the late 1970s, Finnigan[40] and Hewlett Packard,[41] developed desktop sized ion trap and quadrupole type GC detectors. Since then, several well-known commercial vehicle portable GC/MS systems have been produced, including MM1 (Bruker-Franzen),[42] CAMS (Perkin Elmer),[43] and SpectraTrak (Viking Instruments)[44]. Since the 1990s miniature MS instruments have been considered for their potential use as detectors for on-site analysis.[3] In 1991, a portable GC/MS system that could be transported to the sampling site by two people was produced based on the Hewlett Packard MSD.[45] This led to the first hand-portable GC/MS prototype in 1998.[46] A major drawback to initial hand-portable GC/MS prototypes was they were not self contained or sustainable. External pumps had to be attached to the instrument at start up to achieve vacuum. Once vacuum was obtained it could only be sustained for a limited time.[3]

Currently, Torion has developed a self contained and sustainable instrument that uses a low thermal mass gas chromatograph/toroidal ion trap mass spectrometer (LTM GC/TMS). TMS requires less power, operates under higher pressure, and can obtain lower

limits of detection than portable quadrupole mass spectrometers. Furthermore, the miniaturized TMS combines many advantages of larger non-toroidal ion traps such as simplicity, pressure tolerance, and comparable ion storage volume. The miniature TMS operates at less than 1 V, compared to 15 V for the larger alternative portable ion trap.[10]

LTM GC refers to a miniaturized form of GC in which the convectively operated column oven is replaced with direct electrical resistive heating of the capillary column. LTM GC uses a conventional GC column that is intertwined with resistive heating and temperature-sensing wires and wrapped with aluminum foil for greater heating efficiency. The low thermal mass of this column heating arrangement allows much smaller instrumentation and operating power as well as faster heating and cooling of the column.[10]

1.5 Thesis objectives

SPME and NTDs have shown to be popular choices for on-site sample preparation. Both techniques provide fast, solventless sample preparation where the device can be directly inserted into a GC injector for thermal desorption. SPME is an equilibrium extraction technique that can be use to sample free concentration. NTD is an exhaustive extraction technique that extracts total concentration. Using both techniques to extract from a sample matrix in unison allows for the determination of free, total, and therefore, particle-bound concentrations. With on-site analysis typically requiring fast sample preparation beyond SPME equilibrium times, pre-equilibrium calibration methods have

been developed for SPME sampling allowing rapid sampling and simple quantification of results.

The aim of this project was to develop a new NTD design, and evaluate the performance against previous designs through sample analysis of BTEX and two PAH compounds. NTD designs including a no side-hole NTD using expanded desorptive flow as the mode of desorption, a blunt tip NTD with side-hole above the sorbent, a tapered tip NTD with side-hole above the sorbent (conical and dome geometries), and a sliding insert tip NTD with side-hole above the sorbent were evaluated. The slurry packing method was applied to NTD production to shorten production time and improve the reproducibility of packing.

The improved NTD and SPME were both coupled to a portable LTM GC/TMS. Both techniques were used to complete on-site analysis of BTEX and select PAHs. Free and total emissions of the selected analytes were investigated in gasoline exhaust from a small car and diesel exhaust from a dump truck. In addition, the technique was applied to determine the free and total concentration of BTEX and select PAHs inside a car and in an outdoor smoking area when two smokers were present.

Chapter 2. Development of improved need trap device

2.1 Introduction

The NTD complements several shortcomings of SPME. The extraction phase of the NTD is packed inside a metal needle making it resistant to mechanical damage. Relative to SPME, a larger volume of extraction phase can also be packed into the NTD. This provides powerful preconcentration potential, making it useful as either an exhaustive or equilibrium extraction technique.[47] A large availability of packing materials also provide the ability to customize NTDs to better suit target analytes. Work involving NTD development has been completed and involves sampling aerosols with quartz wool packing, and packed sorbents.[38] Single layer packed sorbents such as Carboxen (CAR), and divinylbenzene (DVB) have been used to sample benzene, toluene, ethylbenzene, and xylene (BTEX),[48,49] and particle-bound chemicals in mosquito coil smoke.[34] Multilayer sorbents combining three layers of sorbent with sequentially increasing adsorbent power have been used for analysis of a broad spectrum of VOCs and are commonly used in breath analysis.[35,36] Gold wire has been used as an extraction phase to sample atmospheric mercury.[7] NTDs have also been developed as an effective time-weighted averaging (TWA) sampling device.[50] A recent review of NTDs describes the fundamentals and further applications.[51]

There have been several designs of NTD developed since the inception of the NTD in 2000. Initial NTDs were blunt tip needles where the desorbed analytes could exit the needle through a flow of air injected through the NTD via syringe after injection into a GC

injector.[38] NTDs produced by Shinwa were constructed with a sharp tip and small hole located near the tip to allow desorbed analytes to exit the NTD.[47] This technique also required air from a syringe to remove desorbed analytes. A third design of NTD utilized a side-hole drilled above the sorbent. After injection into the injection port, carrier gas flows through the side of the needle carrying desorbed analytes from the sorbent onto the column.[48] Work has also been completed using a blunt tip NTD without a side-hole or assistance of external air from a syringe. The method takes advantage of a sweep of hot air that flows from the NTD as the cold air inside the needle expands from heating in the injector (expanded desorptive flow).[49] This method is more effective for "wet" samples where several nanograms of water are extracted with the analytes. The expansion of water inside the needle produces added pressure and displacement which assists in removing analytes from the trap.

In the majority of recent work completed utilizing NTD as a sample preparation method, the two most commonly used needle geometries were the blunt needle with a side-hole,[7,34,48,52] and blunt needle without a side-hole.[35,36,49] NTDs were packed with sorbent to suit the user's needs. Blunt needles without a side-hole have been used in sampling VOCs such as BTEX and breath biomarkers;[35,36] however, work has not been completed investigating the effectiveness of desorption on semi- and non-volatile compounds. The blunt NTD with a side-hole has the limitation of requiring a narrow neck liner to complete a successful injection. For the injection to produce sharp peaks with no carryover, a good seal is needed between the liner and the needle.[7] For the general NTD

designs a common packing method has been developed.[35,36,48,49,52] This method uses a vacuum aspirator pump and metal wire to pack particles inside the NTD. This method is time consuming and flow rates between packed needles are not reproducible.[36]

This report describes two new NTD geometries: one configuration, where the tip of a side-hole NTD was tapered in a conical shape to improve the seal between the NTD and the narrow neck liner; and a second sliding tip design, where a narrow tube was inserted inside the needle tube, which fits inside the restriction of the narrow neck liner. The conical shape tip fit tightly at the top of the narrow neck liner restriction. The sliding tip design allowed for a dual sealing system. A seal was made inside the restriction, as well as the top of the restriction where the original side-hole NTD seal was made. These modifications also held sorbent particles in place, removing the need to apply epoxy glue. The slurry packing method was applied to pack NTDs using a solvent slurry system rather than a vacuum aspirator. The slurry packing provides enough force that a metal wire is not required to mechanically pack sorbent particles inside the needle. Here, the new packing method is tested for packing time, flow rate reproducibility, and performance with regards to sampling efficiency and breakthrough volume of the NTD in comparison to the vacuum aspiration packing. Five different NTD designs (blunt no side-hole, blunt with side-hole, tapered with side-hole, SGE dome with side-hole, SGE slider with side-hole) were evaluated for desorption efficiency using a range of compounds with different volatilities: BTEX, anthracene, and pyrene.

2.2 Experimental

2.2.1 Chemicals and materials

Chemicals used: benzene, toluene, ethylbenzene, *o*-xylene, anthracene, and pyrene were purchased from Sigma-Aldrich (Ontario, Canada). DVB sorbent (HaySep Q, 60-80 mesh) was purchased from Restek (Bellefonte, PA, USA), Carboxen 1000 (60-80 mesh) was donated by Supelco (Bellefonte, PA, USA). Twenty two gauge hypodermic stainless steel needles (o.d. 0.71 mm, i.d. 0.39 mm) in lengths of 90 mm were purchased from Dyna Medical Corporation (London, ON, Canada). All 65 mm needles were produced by cutting the original Dyna medical needles. 100 μm o.d. stainless steel wires were purchased from Small Parts (Lexington, KY, USA). Epoxy glue was purchased from Henkel Canada (Oakville, Ontario, Canada). Narrow-neck liners and SGE tapered needles were donated by SGE Analytical Science (Austin, Texas, USA). Liners supplied from SGE were deactivated stainless steel liners. The narrow neck was produced by reducing the inner diameter of the liner. The liner was left with a flat surface for the restriction. ATAS liners purchased from ATAS GL (Veldhoven, The Netherlands) were glass liners with an hour glass shape restriction near the bottom of the liner. Schematics of the liners can be seen in Fig. 3. Required GC gases (helium, nitrogen, hydrogen, air) were purchased from Praxair (Kitchener, Ontario, Canada).

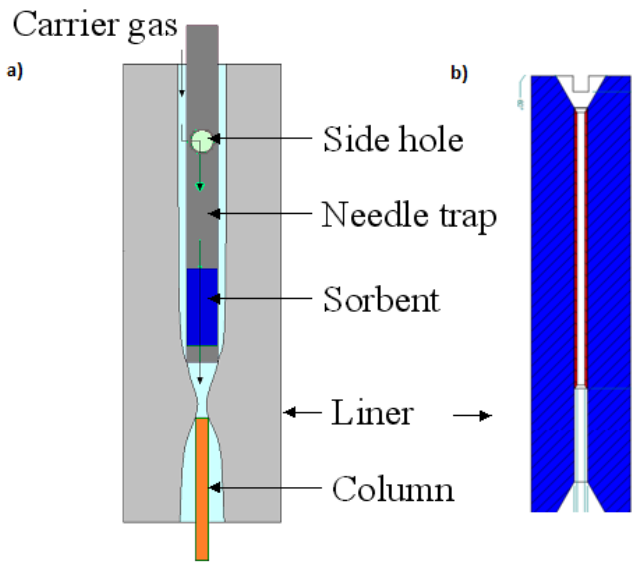


Figure 3. Schematic of different liner designs. a) Glass narrow neck liner with an hour glass shape restriction. b) SGE liner with a flat surface for the restriction.

2.2.2 Instrumentation

An ACME 6100 GC/FID from Young Lin Instruments (Republic of Korea) was operated with a capillary column installed RTX-5MS, 30m x 0.25mm, i.d. 0.25µm, Restek (Bellefonte, PA, USA). The GC injector from ATAS GL was equipped with a narrow neck liner (Veldhoven, The Netherlands). Manual analysis was completed using a bi-directional syringe pump (Kloehn Las Vegas, NV,USA). A Concept automated workstation, PAS Technology (Magdala, Germany) was used to automate sample extraction and introduction to the GC injector. Extractions of BTEX and PAH compounds were completed separately. Column temperature programming for BTEX compounds: begin 60^{o}C, ramp to 180^{o}C at a rate of 16^{o}C min^{-1}, hold for 1 min. For PAH analysis the column temperature programming was: begin 60^{o}C, ramp at a rate of 40^{o}Cmin^{-1} to 295^{o}C, hold for 4 min. The injector temperature was held at 260^{o}C with a column flow of 1.0 mL min^{-1}.

A GUARDION-7 portable gas chromatograph-mass spectrometer (GC-MS) (Torion North Forks, UT, USA) was used to evaluate the desorption characteristics of NTDs using a low thermal mass (LTM) injector that operates without a liner. A deactivated stainless steel insert wound with electrically heating wires was used to provide rapid, even heating. The GUARDION-7 operated at a flow rate of 0.2 mL min^{-1}, and had a MTX 5 capillary column 5 m; 0.1 mm i.d; 0.4 µm d_f from Restek (Bellefonte, PA, USA) installed. The experimentally optimized GC program was as follows: injector temperature; 270^{o}C, column flow; 0.2 mL min^{-1}, initial column temperature; 50^{o}C, hold for 5 seconds, ramp to 295^{o}C at a rate of 2^{o}C $second^{-1}$, hold for 5 seconds. The original injector was modified by Torion. The inner diameter of bottom end of the injector was reduced to provide a narrow neck restriction that could seal the NTD.

2.2.3 Preparation of chemical standards.

BTEX samples were prepared by spiking 10 mg of each BTEX component into 100 g of pump oil. The solution was left to equilibrate for a minimum of six hours in an agitator before sampling. Extractions were completed using 20 mL headspace vials containing 5 mL of pump oil solution. PAH samples were prepared by placing 20 mg of each solid PAH into a 20 mL headspace sample vial, 10, 20, and 40 mg samples were tested to determine if increasing the amount of solid would increase the amount extracted. No difference was found with either amount after 20 extractions.

2.2.4 Automated and manual sample preparation.

Automated sample extraction and desorption was completed using the CONCEPT workstation. Small volume sampling was completed using a 1 mL gas tight syringe by cycling the syringe up and down while the NTD needle was located in the sample vial and remained inside. The 20 mL extractions were completed by extracting from the headspace at 1 mL min^{-1} with a 5 s wait time after the syringe plunger was fully extended to ensure the pressure differential had equilibrated and the entire sample was extracted. The plunger was then depressed into the barrel of the syringe at approximately 30 mL min^{-1} recycling the headspace back into the vial. A wait time of five seconds was used after each depression of the syringe to ensure all the air escaped the NTD. BTEX sampling was completed at room temperature. PAH sampling was completed at 50^{o}C.

Manual sample extraction and desorption was completed using a bi-directional syringe pump. Extraction conditions were the same as above. The pump was programmed to complete 1 mL sampling cycles at 1 mL per minute to complete the 20 mL extraction. Using the bi-directional syringe pump, air recycled from the NTD was injected back into the sample via a secondary gas line.

2.2.5 Preparation of needle trap devices

The NTDs were evaluated using different needle trap geometries and two different packing methods. Fig. 4 shows a schematic diagram of the different NTD geometries evaluated. Sets of NTDs were packed using two different packing techniques: air

aspiration and slurry packing. All needles were packed with a dual layer sorbent as seen in Fig 5. Both layers were 1.2 cm in length. The first layer consisted of DVB 60-80 mesh followed by 1.2 cm of Carboxen 1000 60-80 mesh.

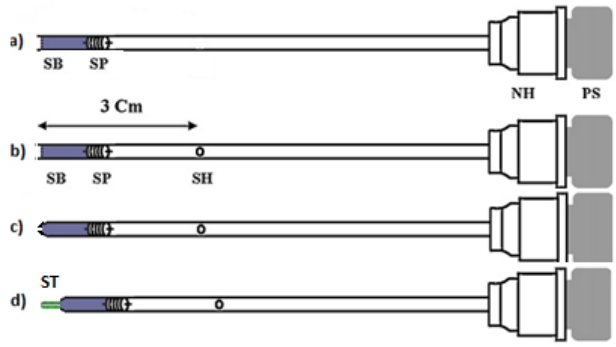


Figure 4. The design of different NTDs. a) NTD with a blunt tip and without a side-hole. b) NTD with a blunt tip and a side-hole. c) NTD with a tapered tip and a side-hole. d) NTD with sliding tip and a side-hole. SB: sorbent; SP: spiral plug; SH: side-hole; NH: needle head; PS: PTFE sealer.

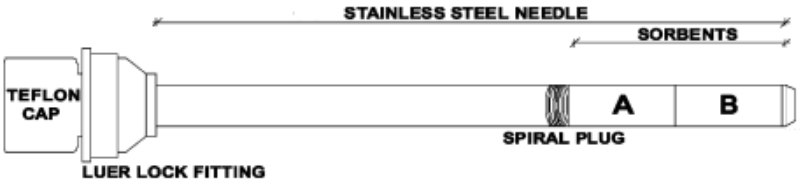


Figure 5. Schematic of NTD with dual layer packing. Carboxen 1000 60-80 mesh (A), and DVB 60-80 mesh (B).

The air aspiration technique is commonly used as the method to pack NTDs.[36, 51] The technique involves inserting a stainless steel spring plug inside the needle at a desired depth (2.5 cm from the tip) and compressing it by inserting wires from the front and back and pushing against the spring. The spring acts as a support for particles that are aspirated into the needle using a water vacuum. Particles are aspirated one by one into the needle. Once five particles are aspirated inside the needle, a steel wire is inserted into the tip to pack the particles firmly. This process is repeated until the desired length of packing is achieved. In this case, 1.2 cm of Carboxen 1000 sorbent was aspirated first, followed by 1.2 cm of DVB sorbent. For blunt tip needles, a small amount of five minute epoxy glue was used to secure the particles in place. As the glue dries, the NTD is connected to the vacuum aspirator to ensure the glue does not block the flow of air through the needle.

To prepare NTDs using the slurry packing method the stainless steel spring was inserted as stated above. Once the steel plug was inserted, the tip of the NTD was connected to solvent pump. 100 µL injections of ethanol particle slurry were injected into the solvent pump, which pumped the slurry into the needle. The pressure applied via the solvent pump supplies enough force to pack the sorbent particles, thus eliminating the need for a metal wire to mechanically pack the particles and substantially reducing the time required to pack the NTD. Once the required amount of particles was packed into the needle, it was connected to a vacuum aspirator or placed in the oven to dry. If preparing a blunt tip NTD, after drying it was connected to a vacuum aspirator for glue application.

A further modification of the side-hole needle was to taper the tip to provide a more efficient seal in the narrow-neck GC injector liner, thus improving desorption efficiency. In preparation of the tapered tip NTDs, the need for epoxy glue was eliminated due to the inner diameter of the taper being smaller than that of the particles. Tapered needles were produced in-house using a drill and a chrome vanadium pressure applicator. As the needle was spun in the drill, the pressure applicator was applied to the tip until the taper reached the desired dimensions (~200 µm I.D.). NTDs were conditioned for two hours at 285^{o}C to remove any impurities from the sorbent bed.

The sliding fit tip NTD featured in Fig. 6 was a further modification developed and evaluated to improve the side-hole NTD. A narrow tube was inserted into the tip of original NTD. The outer diameter of tube was 500 µm and fit tightly inside the restriction of the narrow neck liner. The inner diameter of the tube was 200 µm, which was sufficient to retain sorbent particles inside the NTD, and was 8 mm in length. The tube created a dual sealing system. The sliding tip formed a tight tolerance fit inside the narrow restriction. A second seal was achieved when the actual tip of the NTD tube impacted on the liner restriction.

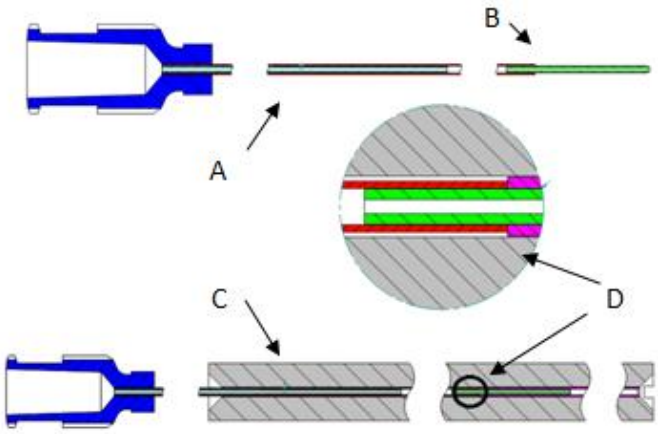


Figure 6. Schematic of sliding fit NTD and complementing liner. (A) NTD, (B) laser weld connecting sliding tip to NTD, (C) liner with restriction required for sliding tip, (D) tight tolerance fit between restriction and sliding tip.

2.2.6 Packing method evaluation

When preparing NTDs, three factors were taken into account: time, reproducibility of flow rate, and mass extracted at breakthrough. To evaluate the time taken to prepare NTDs, three NTDs were prepared in sequence via the vacuum aspirator method and three were prepared using the slurry packing method. The total time required to prepare the three NTDs was averaged to acquire the average time taken to prepare a NTD with each technique. To evaluate reproducibility of the packing method, reproducibility of flow rate due to packing density, and breakthrough volume were investigated. Reproducibility of flow rate was completed at flow rates near 60 mL min^{-1} and 20 mL min^{-1} under 1 bar constant pressure using both packing methods. To test the reproducibility of breakthrough volume, a fixed sampling rate of 1 mL min^{-1} and fixed concentration of BTEX

in pump oil were used. The sample volume extracted was increased until breakthrough was observed. The amount of analyte extracted was plotted against the corresponding sample volumes. As sample volume increased, the amount extracted increased proportionally until breakthrough was achieved. Breakthrough was determined using two methods. When the extracted amount of analyte was 10% less than expected, breakthrough was considered to have occurred. A second validation method combined two NTDs in sequence. After sampling, the second needle was desorbed. Breakthrough was considered achieved when the analyte could be detected on the second NTD.

2.2.7 Evaluation of desorption efficiency

Reusability is a necessity when using a single NTD for multiple analyses. To determine reusability, carryover after desorption was evaluated. To investigate the performance of the evaluated NTD geometries, BTEX, anthracene, and pyrene were loaded onto the NTD at a fixed sample volume of 20 mL and sampling rate of 1 mL min^{-1}. Needles were then desorbed at increasing time intervals from 15-300 s followed with carryover experiments. After an initial desorption a subsequent desorption for 300 s was completed to determine the amount of analyte remaining. Carryover was evaluated until undetectable analyte amounts were found on the subsequent desorption. The needle geometries were evaluated using NTDS packed with two different densities resulting in needle flow rates of 20 mL min^{-1} and 60 mL min^{-1}. BTEX was extracted from headspace of 5 mL of pump oil spiked with BTEX in a 20 mL headspace vial and PAHS were extracted from headspace of 20 mg of each solid sample placed in a 20 mL headspace vial.

2.2.7.1 Effect of column flow and liner design on desorption efficiency

To improve desorption over traditional NTDs, a side-hole was introduced to force hot carrier gas through the sorbent bed of the NTD during desorption. The volume of carrier gas flowing through the sorbent bed was determined by column flow and desorption time. Changing the column flow affects the linear velocity and volume of carrier gas moving through the NTD. Column flow rates of 1.0 and 2.0 mL min^{-1} were used to investigate the effects of column flow rate on desorption efficiency.

The liner design can also play a role in desorption of analytes from a NTD. Glass liners utilizing an hour-glass shape narrow neck design and stainless steel liners using a restriction tube producing a flat surface were evaluated to determine the effect of design on desorption efficiency.

2.2.7.2 Validation of automated sample preparation and desorption efficiency

The automated sampling and desorption procedures were validated by comparing results to those obtained by manual extractions and desorptions. Manual extractions were performed using a bi-directional syringe pump using the same sampling parameters as the workstation. Manual desorptions were performed by hand to validate the sealing of the NTD in the narrow neck liner using the autosampler.

2.3 Results and Discussion

2.3.1 Reproducibility of packing methods.

When completing work either in the laboratory or on-site, it is important to have a sample preparation tool that will perform reproducibly, both inter and intra-NTD and produce accurate results. If on-site extractions are completed with transport to the lab for analysis, multiple NTDs are needed. To take a representative sample of the target matrix, at least three replicates are needed if the matrix is homogeneous and more for heterogeneous matrices. Another factor to take into account is the time required to make the NTD. If multiple NTDs are made in-house, a faster packing method producing reproducible NTDs would be ideal. Results in Table 1 demonstrate that the slurry packing method produced NTDs with a more reproducible flow rate under 1 bar of pressure compared to NTDs produced by vacuum aspiration packing. The higher reproducibility obtained using the slurry packing method is attributed to less mechanical manipulation of the sorbent particles after being placed inside the NTD. Using the slurry packing method two or three sweeps of particle slurry are passed through the needle tube to fill the desired amount of sorbent particles, allowing the pressure created by the supporting fluid to pack the particles tightly. Packing using the aspiration mode requires a mechanical packing of the particles inside the needle tube using a metal wire after several particles are aspirated. The mechanical packing of the particles is more difficult to control and risks damaging the particle packing.

Table 1. Reproducibility of sorbent bed density for NTDs produced using different packing methods. (Density determined by flow rate under 1 bar pressure)

Packing Method	NTD Flow Rate (mL min^{-1})					Average	STD	%RSD
Slurry	62.4	64.8	67.3	64.2	63.2	64.4	1.9	2.9
Slurry	18.9	23.8	16.7	16.2	21.6	19.5	3.3	16.7
Aspiration	47.7	89.3	59.5	102.5	53.2	70.5	24.1	34.1
Aspiration	12.5	16.4	26.8	19.5	8.5	16.7	7.0	41.7

As mentioned above, the time required to pack the NTDs is important if multiple NTDs are required. The results in Table 1 demonstrate that the slurry packing method produced NTDs more reproducibly than vacuum aspiration. In Table 2, it is seen that the slurry packing method produced NTDs at twice the rate of the aspiration packing method making slurry packing more efficient than aspiration packing.

Table 2. Time required for NTD production using different packing methods.

Packing Method	Total Time (min)	Time/Needle (min)
Slurry	47	15.7
Aspiration	82	27.3

2.3.2 Effect of packing method and packing flow rate on breakthrough volume.

One question regarding the slurry packing method was whether suspending the particles in solvent would have any effect on the performance of the NTD. To answer this question, breakthrough experiments with 60 mL min^{-1} and 20 mL min^{-1} produced by both packing methods were completed using BTEX and PAHs. Results shown in Fig. 7 display

that within the experimental error; there is no significant difference in breakthrough volume between both packing methods.

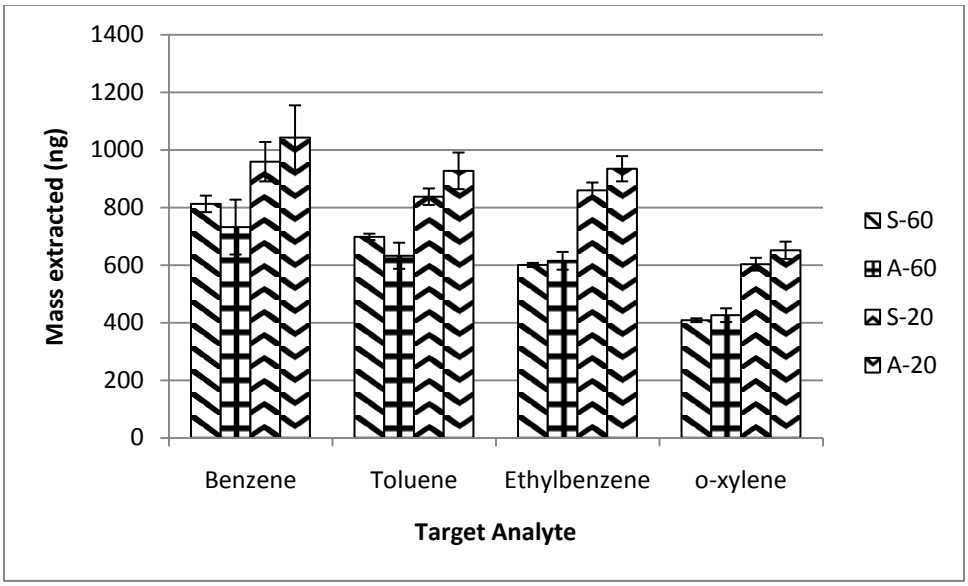


Figure 7. Comparison of the amount extracted at breakthrough for NTDs packed by vacuum aspiration and slurry packing methods with different packing densities. S-60: slurry packing, 60 mL min^{-1}, A-60: Vacuum aspiration, 60 mL min^{-1} , S-20: slurry packing 20 mL m L min^{-1}, S-20: Vacuum aspiration, 20 mL min^{-1}. n=5

Analyzing the effect of packing density measured by flow rate, it was found that benzene and toluene broke through near 125 mL extracted for 60 mL min^{-1}, 150 mL for 20 mL min^{-1}, ethylbenzene and *o*-xylene breakthrough was reached at approximately 150 mL extracted for 60 mL min^{-1}, and 180 mL for 20 mL min^{-1}. Sampling up to 250 mL for PAHs was completed. Both compounds showed linear uptake with no presence of breakthrough. The NTDs with increased packing density achieved an average of 17% increase in the amount extracted. This is an important factor to consider when sampling with NTDs. The more densely packed the NTD, the greater the breakthrough volume. The

drawback, however, when completing exhaustive extraction, is a lower sampling speed is required. Extracting with a syringe barrel at a high rate will create a large pressure differential between the atmosphere and the barrel due to the restriction of the sorbent. If the syringe barrel is retracted too quickly, the flow of target matrix will be much higher at the beginning of extraction. Flow through the sorbent will decrease as the pressure differential drops. This high rate at the beginning of extraction can lead to premature breakthrough.

2.3.3 Analysis of needle trap device geometry

2.3.3.1 Amount extracted

NTDs can be used as exhaustive samplers. The amount extracted is proportional to the volume of sample extracted, and the concentration of analyte:

$$n = cV \qquad 3.1$$

Where n is the amount, c is the concentration, and V is the volume of sample.

The geometry of each NTD was tested to determine if the design of the NTD had an effect on the amount extracted. Table 3 shows statistically that all three geometries of NTDs extract the same amount of analytes; therefore geometry of the NTD has minimal effect on the amount extracted.

Table 3. Linearity of amount extracted versus sample volume for ethylbenzene sampling with different NTD designs.

	Equation of Line	R^2
House tapered	y = 72.943x	0.9969
Blunt	y = 73.134x	0.9922
No side-hole	y = 71.101x	0.9917

2.3.3.2 Desorption efficiency

To evaluate the desorption efficiency of each NTD design, BTEX and PAHs were used. Initial experiments using BTEX yielded results of fast desorption times, as seen in Fig 8. The two side-hole designs tested had undetectable carryover after forty-five seconds. Using BTEX, desorption times were too short to determine a significant relationship between NTD design and desorption efficiency.

When evaluating the no side-hole (NSH) NTD, from Fig. 8 it is seen that after forty-five seconds of desorption, detectable carryover persists between 0.5 and 2%. After desorbing for three minutes the carryover remains. The carryover can be attributed to a function of the injector. The non side hole NTD operates on expanded desorptive flow.[10] When a NTD is inserted into a hot GC injector the cold dead volume inside the tube of the NTD is rapidly heated causing expansion and exits the tip of the NTD. The expansion sweeps analytes that were adsorbed to the sorbent onto to the column. There is a second mechanism that occurs due to the head pressure in the injector. After the initial sweep of air traveling out of the needle, the head pressure in the injector forces hot carrier gas to

enter the tip of the needle. Any analytes not completely desorbed by the initial expansion of air is carried along with hot carrier gas, contaminating the upper dead volume of the sealed NTD.

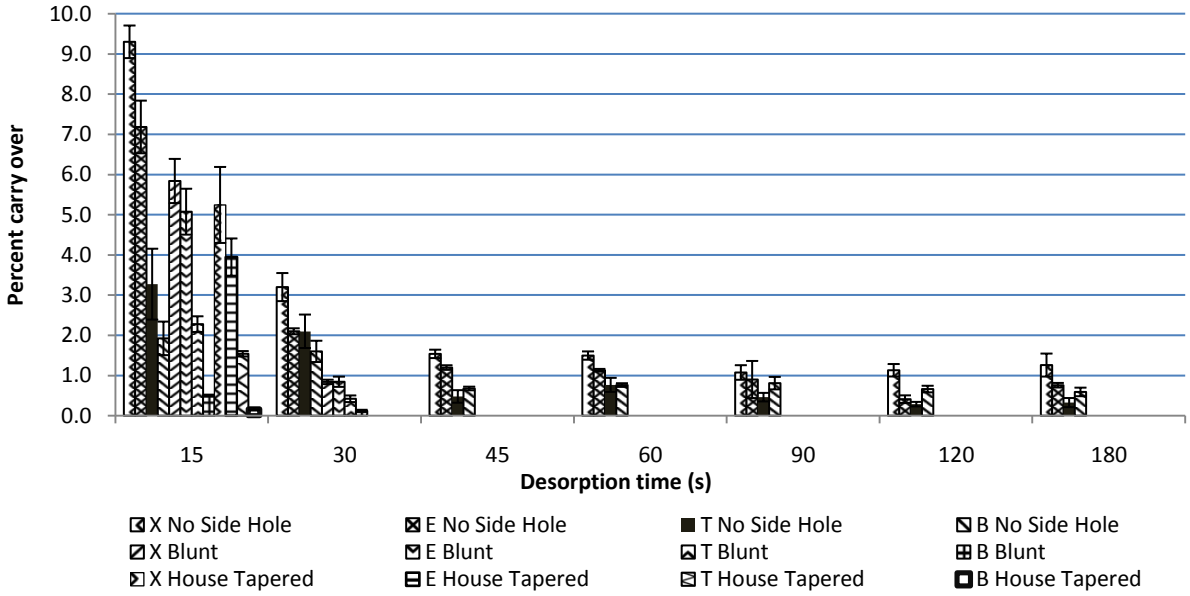
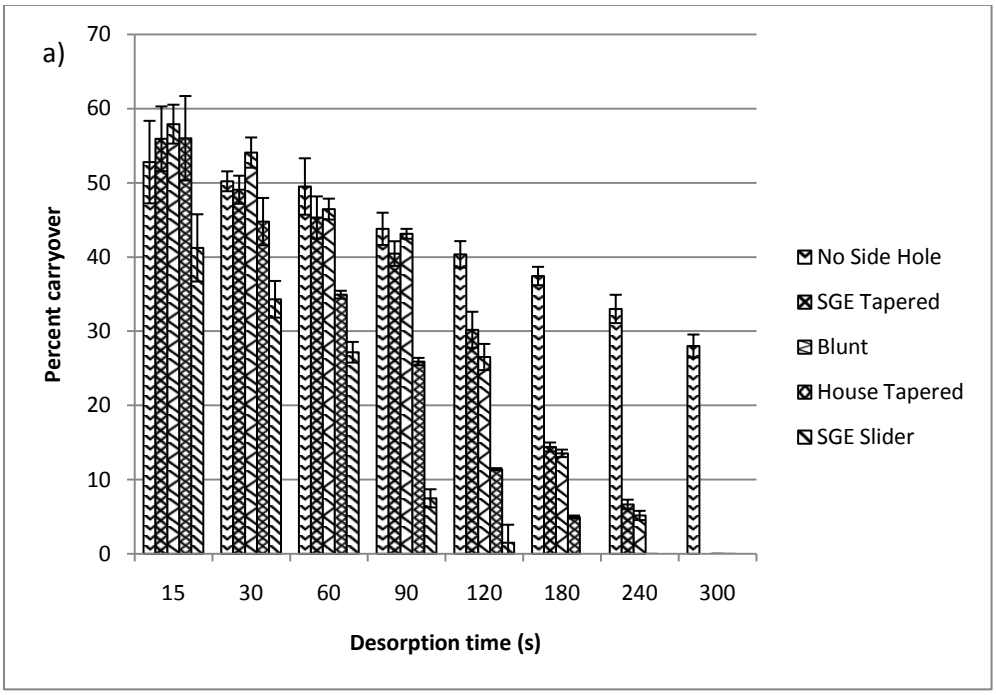


Figure 8. Carryover of BTEX from 15 to 180 s using autosampler. NTD flow rate under 1bar pressure 60 mL min^{-1}. (X) *p*-xylene, (E) ethylbenzene, (T) toluene, (B) benzene.

PAHs are less volatile than BTEX components. They require longer desorption times. The process of PAH desorption allows a relationship to be found between desorption time, carryover and NTD design. The evaluation in Fig. 9 shows the percentage carryover for five different needle designs packed to a density resulting in 60 mL min^{-1} under 1 bar of pressure. Over a five minute desorption assessment, the SGE slider tip was found to have the highest desorption efficiency. Undetectable amounts of anthracene and pyrene were determined after 180 seconds desorption. The house tapered (HT) NTD was

found to have the second highest desorption efficiency. Undetectable amounts of anthracene and pyrene were found at 240 and 300 second desorption times, respectively. Statistically, the SGE and blunt side-hole NTDs performed equally. Carryover of anthracene and pyrene were discovered after 300 seconds of desorption. Fig. 10 shows that the NTDs tapered in the lab were a conical shape where SGE NTDs were shaped like a dome at the tip. Using a glass narrow neck liner, the dome shape showed no improvement on desorption, whereas the conical shape did. This can be attributed to a more efficient seal between the conical geometry and the narrow neck liner. The geometry of the cone provides greater surface area contact between the liner and NTD reducing the possibility of carrier gas passing through the seal.



(a) Carryover of pyrene

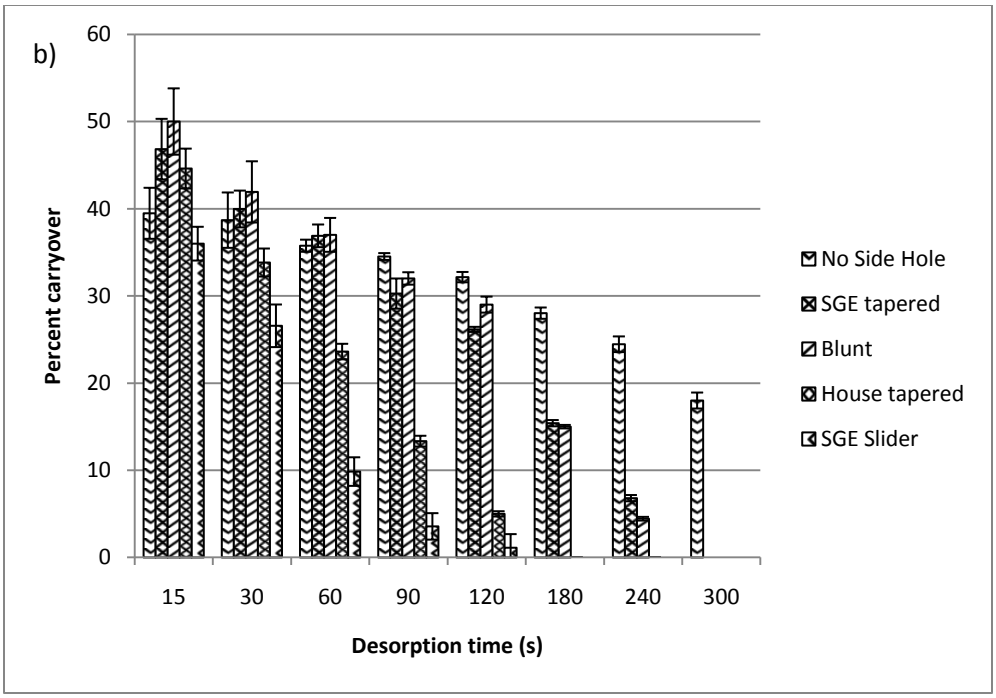


Figure 9. Carryover of pyrene (a) and anthracene (b) desorption time 15 to 300 s using autosampler. NTD flow rate 60 mL min^{-1} under 1 bar pressure.

Figure 10. Magnified image of NTD tips (10x). a. House tapered (HT) NTD. b. SGE tapered NTD. c. Blunt (B) tip NTD.

Examination of the results from Fig. 9a and b illustrate that when using the no side-hole NTDs, the initial sweep of analytes from the expanded desorptive flow NTD is as effective as the side-hole NTD for the first fifteen seconds of desorption. This would be expected as the initial expansion of air acts as a carrier gas removing desorbed analytes from the sorbent bed. The side-hole NTDs do not experience any added effect of the expansion. The heated expanding air escapes from the side-hole before the seal between the liner and NTD is made, rather than passing through the sorbent. The initial expansion of air is effective in removing approximately 50% of pyrene and 60% of anthracene. Increasing desorption time to five minutes removed an additional 20% of each analyte. Desorption profiles of anthracene for three needle geometries are presented in Fig. 11.

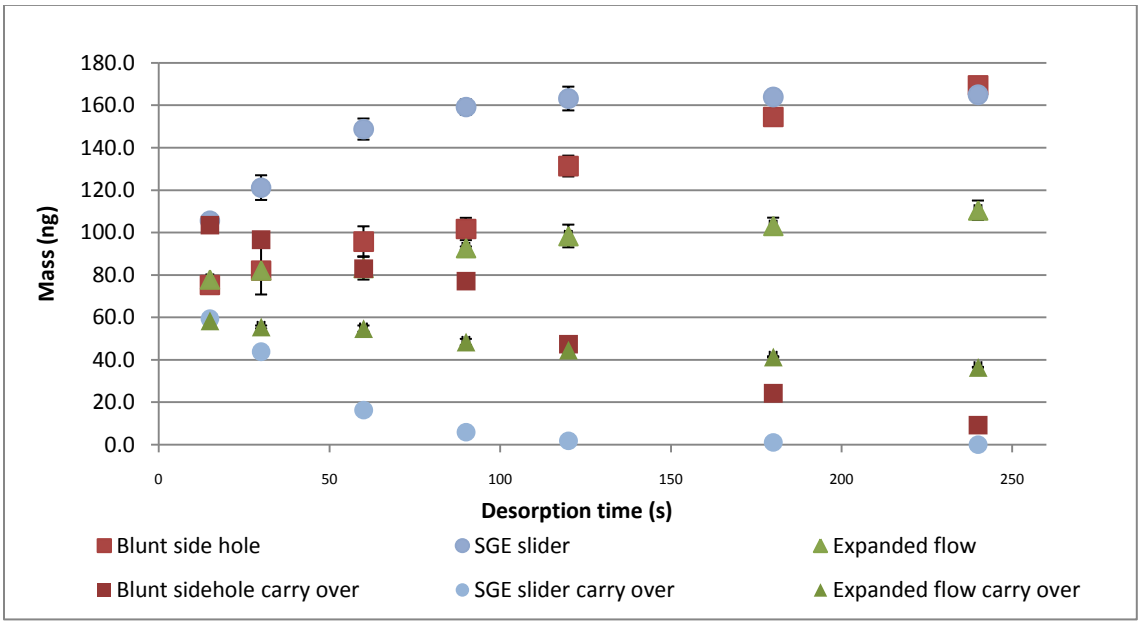
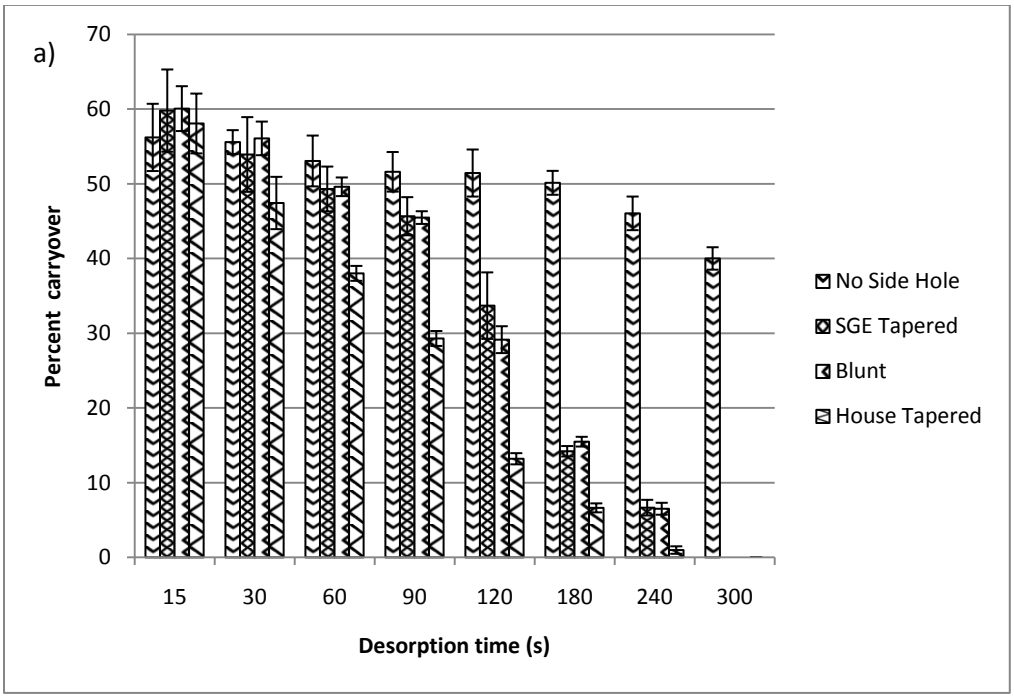


Figure 11. Desorption and carry over profile of anthracene for three different needle geometries.

Depending on the application, density of packing inside the NTD may vary. The density of the NTD packing was evaluated to determine the effect on desorption of analytes. NTDs with 20 and 60 mL min^{-1} flow rate were examined for the comparison. Using the side-hole NTDs there was no significant increase in amount of carryover resulting from more densely packed sorbent. For the NSH NTDs the packing density was found to increase the carryover of the NTD. When compared to the less densely packed NTDs, desorption of pyrene for 15 – 90 seconds showed an increase in carryover of 5%. Longer desorption times for pyrene showed an increase near 10%. For anthracene, a 10% increase in carryover was found for each point during the 5 minute desorption time. (see Fig. 12)



a) Carryover of pyrene

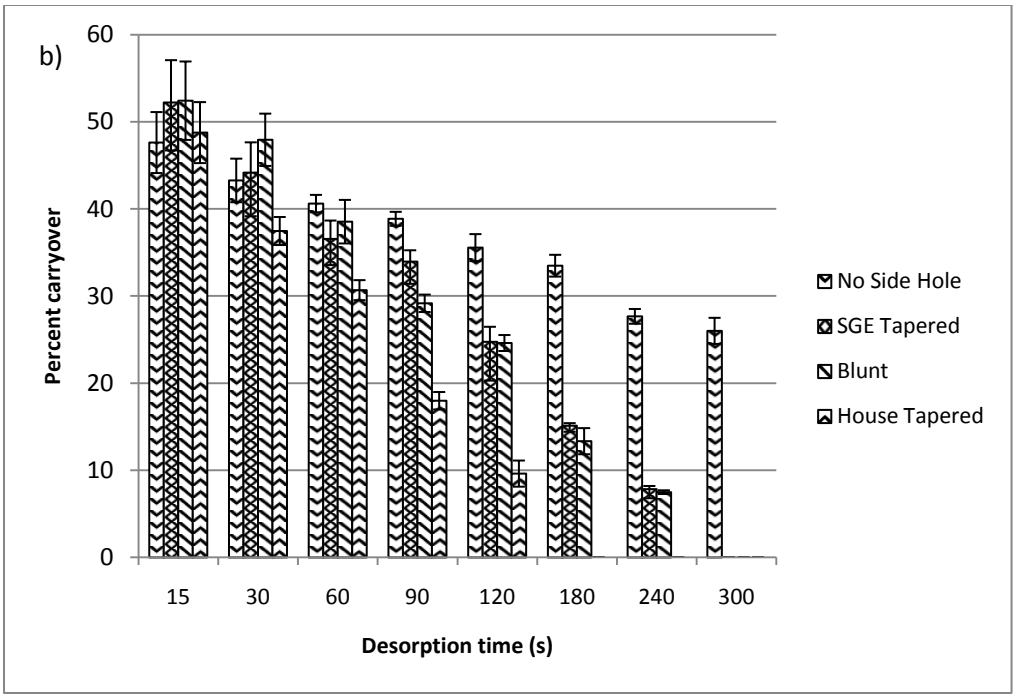


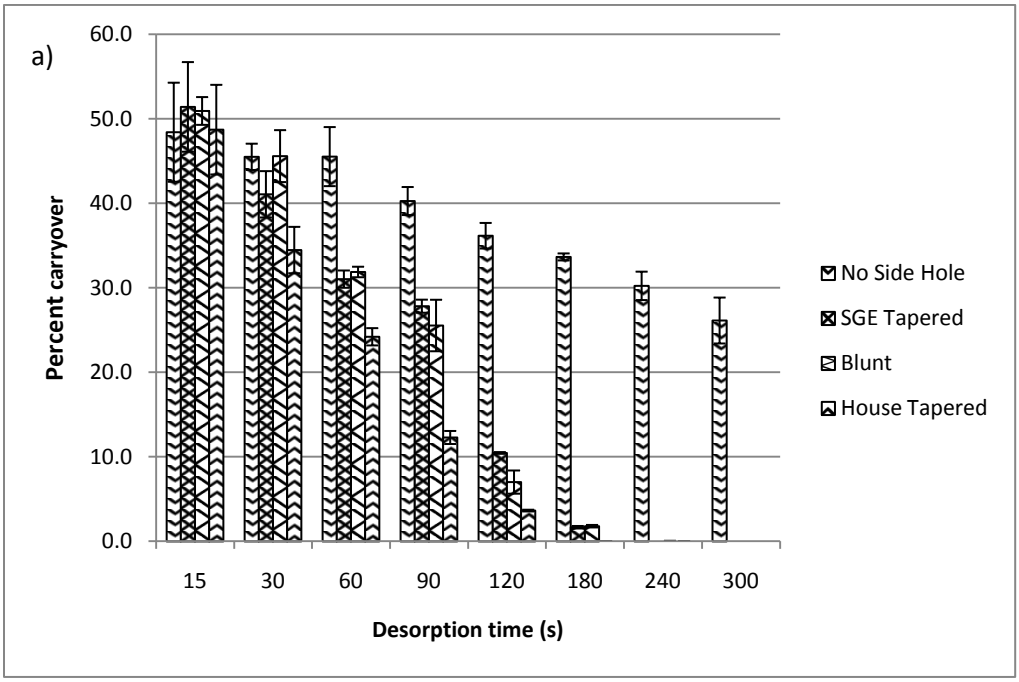
Figure 12. Carryover of pyrene (a) and anthracene (b) desorption time from 15 to 300 s using autosampler. NTD flow rate is 20 mL min^{-1} under 1 bar.

2.3.3.3 Column flow rate and liner designs

Increasing the column flow rate increases the linear velocity and volume of carrier gas flowing through the side-hole NTDs for a given time period. To evaluate the effect of column flow rate on desorption, carryover experiments were completed using the 60 mL min^{-1} NTDs and a column flow rate of 2.0 mL min^{-1}. Comparing results shown in Fig. 13 to results obtained using a 1 mL min^{-1} flow rate (see Fig. 9), it was found that an increase in column flow increases the desorption efficiency of NTDs with a side-hole. For both PAHs initial decrease in carryover of 10% were found. As desorption time increased, the decrease in carryover reached 20%. For all side-hole NTDs, the time required for both

NTDs to reach undetectable carryover was one minute faster for both PAH compounds than when compared to 1 mL min^{-1} column flow rate.

It is noticeable from Fig. 13 that the increase in flow rate had no significant effect on the non side-hole NTD. Again this verifies that desorption is completed by the internally expanded desorptive flow and not affected by column flow.



a) Carryover of pyrene

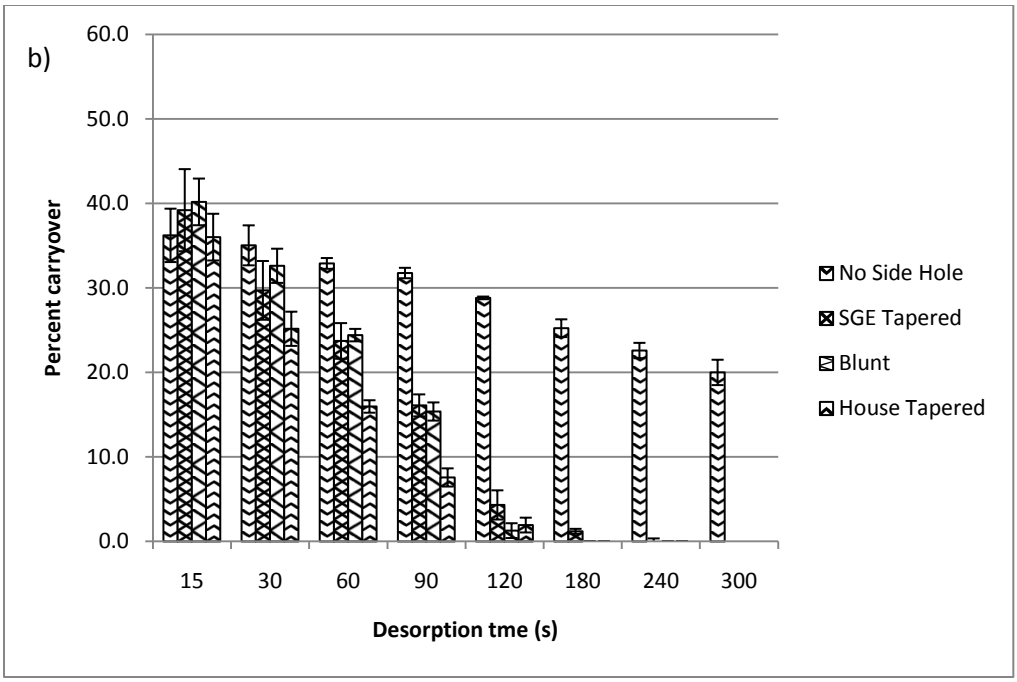
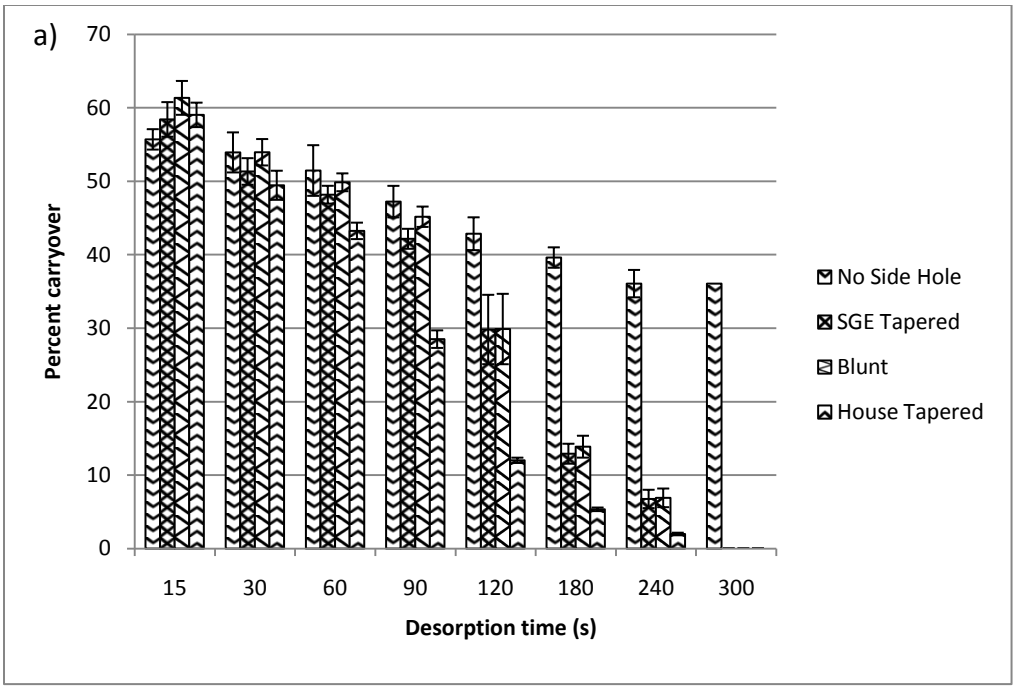


Figure 13. Carryover of pyrene (a) and anthracene (b) desorption time from 15 to 300 s using autosampler. NTD flow rate 60 mL min^{-1} under 1 bar. Column flow rate is 2.0 mL min^{-1}.

Evaluation of liner design compares the sealing efficiency of the hour-glass shape narrow neck glass liner (see Fig. 10) to that of the flat restriction stainless steel SGE liner (see Fig. 14). No significant differences were found between the liner designs. The blunt and SGE tapered needles sit on top of the restriction of each liner. If pressure is not uniform the seal will not be efficient. The conical tip fits slightly inside the restriction of both liners forming a more efficient seal in the liner.



a) Carryover of pyrene

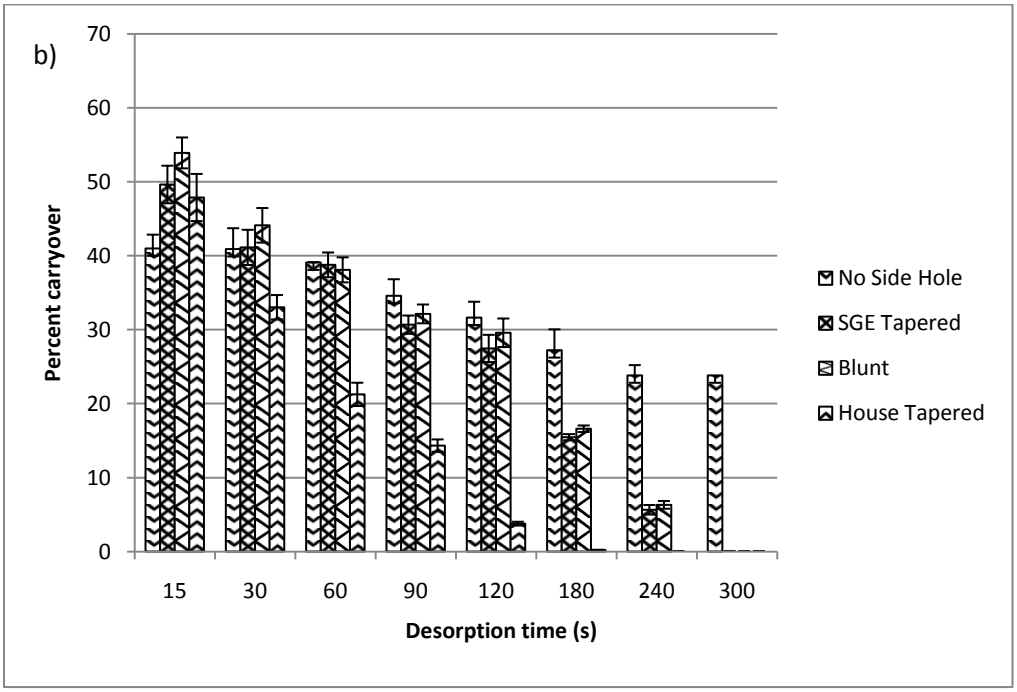
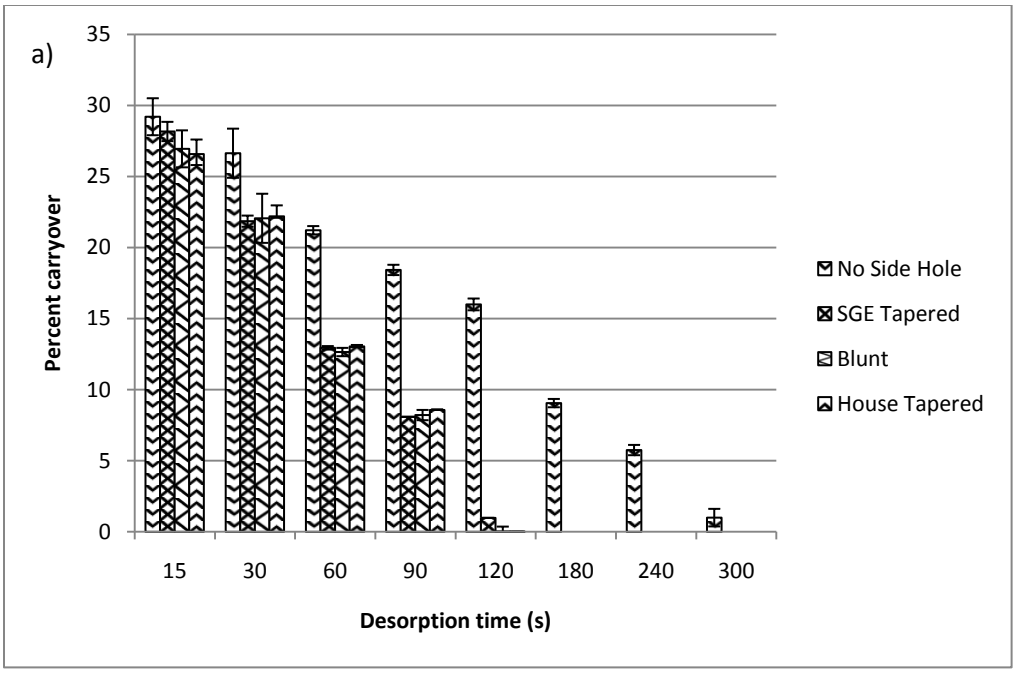


Figure 14. Carryover of pyrene (a) and anthracene (b) desorption time from 15 to 300 s using autosampler and SGE narrow neck liner. NTD flow rate is 60 mL min^{-1} under 1 bar. SGE liner.

Carryover experiments were completed using the Torion GUARDION-7 GC/TMS instrument to evaluate both performance of the NTDs and a modified injection port that was developed by Torion for this device. Carryover results using the GUARDION-7 show a large decrease in carryover when compared to the ATAS and SGE injectors. Analysis of data in Fig. 15 demonstrates that the three designs of side-hole NTD statistically performed equivalently. For each side-hole NTD carryover for anthracene was undetectable at 120 seconds, whereas carryover for pyrene was less than 0.5%. The LTM injector evenly heats the whole injector creating a larger hot zone than that of the standard injector. This larger zone allows for efficient desorption.

Data from the NSH NTD show that anthracene carryover was no longer detectable at 300 seconds and pyrene carryover was less than 1%. Several factors are considered to result in the increased desorption efficiency for the NSH NTDs. The NTDs prepared for the GUARDION-7 were shorter in length than those prepared for the ATAS injector, leaving only a short length of needle tube exposed to the atmosphere. The longer needles used for the ATAS injector have a longer length exposed to the atmosphere to allow room for the auto sampler assembly. The cold air in the dead volume of the NTD provides a cushion effect on the expanded desorptive flow reducing the linear velocity. The short NTDs have less cushioning effect, therefore, creating a more efficient desorption. A second factor is a more evenly heated LTM injector in the GUARDION-7 compared to oven heated GC injectors. The uniform heating heats the whole NTD evenly reducing any cold sections above the sorbent, improving the performance of the expansion gas.



a) Carryover of pyrene

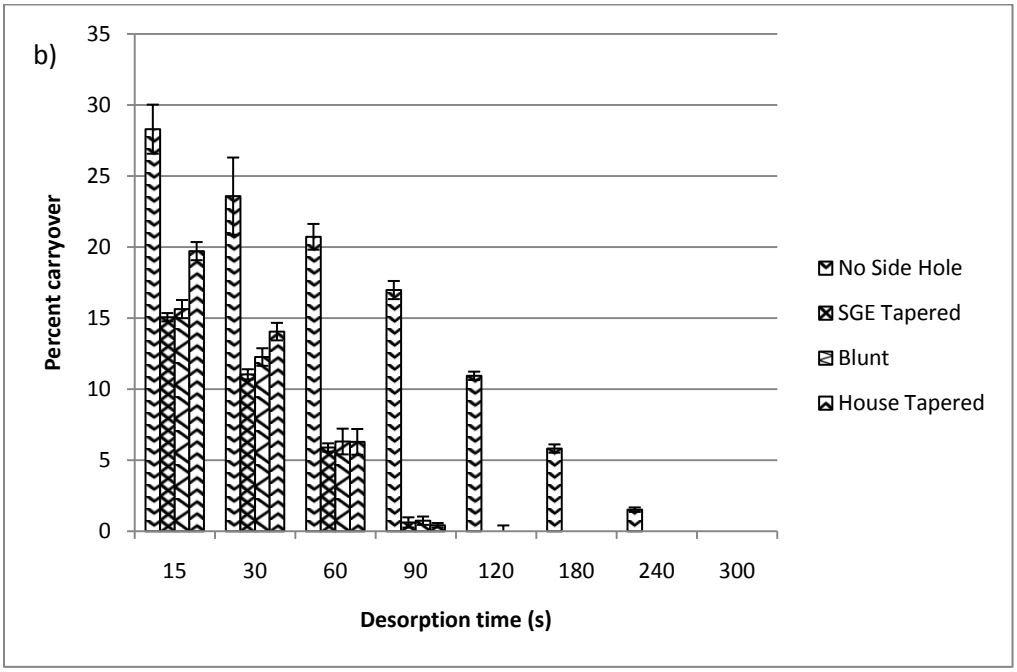


Figure 15. Carryover of pyrene (a) and anthracene (b) desorption time from 15 to 300 s using GUARDION-7. NTD flow rate is 60 mL min^{-1} under 1 bar.

2.3.3.4 Validation of automated sample extraction

Automated sample extraction is completed by the cycling of a gas tight syringe. The cycle of filtered air back through the sorbent bed has potential to remove adsorbed analytes. To verify that there is no sample loss during the cycle, a bi-directional syringe pump was used. Here, analyte gas flows through the sorbent bed in only one direction. The recycled gas flows through a secondary line. Fig. 16 shows that the automated extraction of ethylbenzene and pyrene are statistically equivalent to the manual extracted counterparts. The binding of the analytes to the sorbent bed is strong enough that passing a small volume of gas through the sorbent bed will not cause analyte loss.

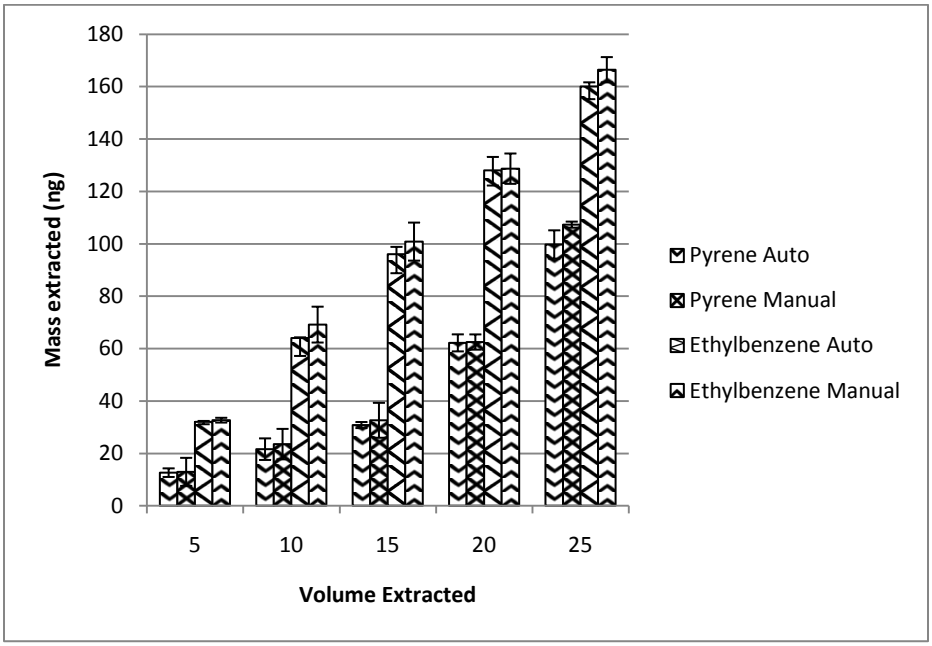
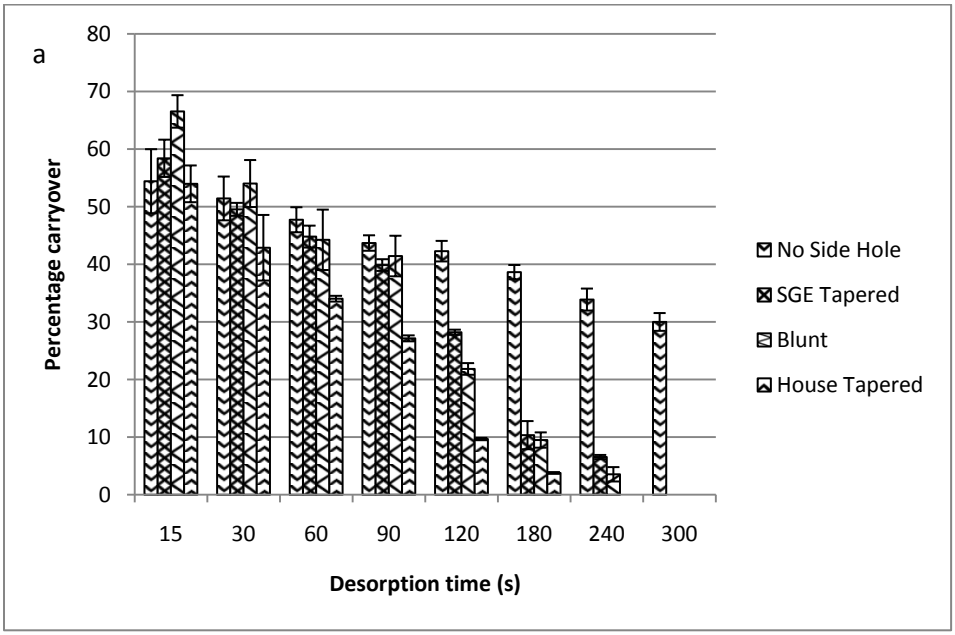


Figure 16. Amount of pyrene and ethylbenzene extracted using automated and manual sample extraction.

2.3.3.5 Validation of automated sample desorption

Automated desorption of the NTD was validated relative to manual desorption to determine if the sealing using the autosampler was the same as by hand. It was found that the autosampler created a seal in the narrow neck liner to the same efficiency as that of a manual desorption pressing the NTD down by hand as supported by desorption data; see Fig. 17. Validation of the automated sample preparation method demonstrates that NTDs can produce simple reliable sample analysis with simple calibration of results.



a) Carryover of pyrene

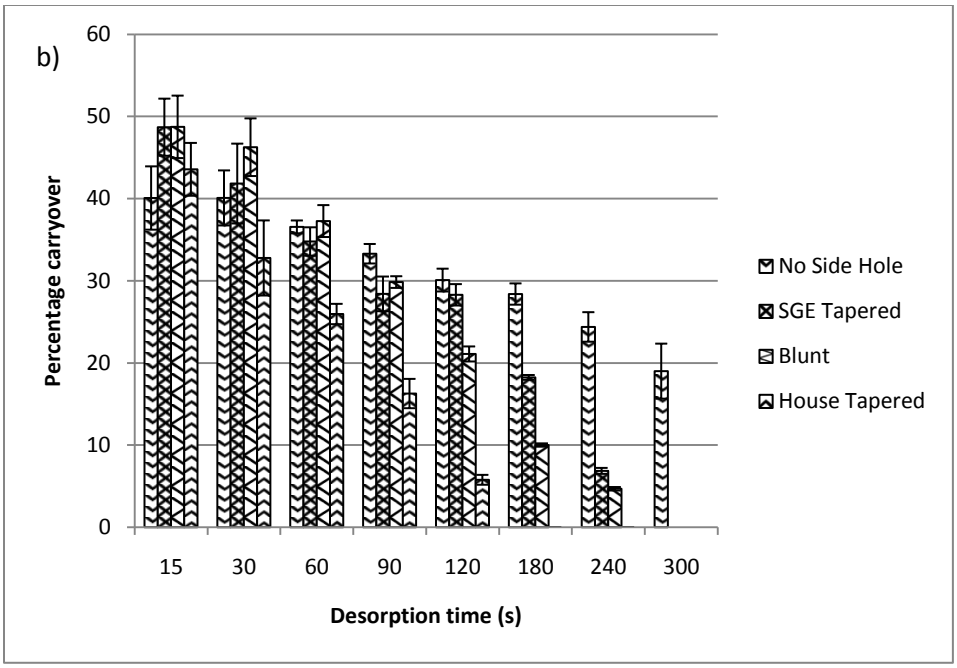


Figure 17. Carryover of pyrene (a) and anthracene (b) with a desorption time from 15 to 300 s using manual desorption. NTD flow rate is 60 mL min^{-1} under 1 bar. Column flow rate is 1.0 mL min^{-1} using narrow neck glass liner.

2.4 Conclusions

Automated sample preparation has been evaluated and validated relative to manual sample preparation. The slurry packing method was applied to NTDs, and two new designs of NTD have been developed to improve the desorption efficiency of manual and automated sample preparation. The new NTD design has been used to successfully desorb volatile compounds such as BTEX and improve desorption of semi-volatile compounds including anthracene and pyrene. Tapering the tip of the NTD or introducing the sliding tip improved the seal inside the narrow neck liner more efficiently than traditional methods forcing carrier gas through the sorbent bed. When sampling VOCs,

NTDs without a side-hole can be used for single injections; however, if required for multiple use, a conditioning step to ensure the analytes are removed from the NTD is required. The slurry packing method reduced the time required to produce NTDs and improved NTD reproducibility. Here we see that NTDs are a solventless, exhaustive sample preparation technique that can be automated in lab and used manually to complete fast exhaustive sample preparation.

Chapter 3. Determination of free and total concentration using SPME and NTDs for on-Site analysis

3.1 Introduction

Needle trap devices (NTDs) complement SPME with the ability to exhaustively extract analytes from a sample matrix.[31] NTDs contain a polymeric extraction phase (sorbent particles) packed inside of a needle. A gas tight syringe or syringe pump can be connected to the NTD to extract air from a sample matrix. Analytes and particles are extracted from the sample as air is drawn through the sorbent bed. NTDs have been previously used for particulate, BTEX, and breath sampling.[9,35,36,49] Most work completed using NTDs has focused on VOCs; however, recent work has evaluated NTDs for sample preparation of semi-volatile poly aromatic hydrocarbons (PAHs).[9,58] Both SPME and NTDs provide solventless, one step sample preparation with direct thermal desorption into chemical analyzers that are ideal for on-site sampling.[32,53]

Using a porous SPME fiber with a pre-equilibrium extraction approach as described by Koziel *et al*.[25,26] to extract free concentrations and NTDs as an exhaustive extraction technique to extract total concentrations, these techniques can be combined to characterize free and particle-bound compound concentrations in a sample matrix. Coupling SPME and NTD with a portable GC-MS, separation and identification of components in complex matrices can be completed on-site. Characterizing free and total concentrations of components in a sample matrix are important from an environmental

pollution perspective. Free and particle-bound pollutants in the atmosphere distribute differently in the environment, and can enter organisms through multiple pathways.[55]

In urban areas, the largest source of inhaled particles are from emissions of diesel- and gasoline-powered motor vehicles.[55,56] PAHs are not regulated in exhaust emissions;[57] however, they are considered to be one of the most pervasive classes of potential environmental carcinogens.[58,59] In tobacco smoke, approximately 4800 components have been identified. Of these, 400 have been quantified, 200 are known to be toxic to humans and animals and 80 are known, probable, or possible human carcinogens including BTEX and PAHs[60-65]. Both exhaust emissions and cigarette smoke generate pollution through combustion processes.

The purpose of this study was to combine SPME and NTDs as sample preparation techniques and couple them with portable GC-TMS to complete on-site analysis of free and total concentrations of BTEX and PAHs. Target areas included those contaminated by cigarette smoke and the emissions from diesel and gasoline exhaust. Custom devices were made for exhaust and smoke sampling using SPME and NTDs which allowed measuring of gas flow rate and temperature monitoring during sampling. Pre-equilibrium SPME extraction and exhaustive NTD extraction allowed for the determination of free and total concentration of the target compounds in the investigated sample matrices. Gasoline exhaust analysis from an automobile with an operating emissions control system was completed during a cold start at 0^{o}C and during operational temperatures. Diesel exhaust

was analyzed at operational temperatures. Cigarette smoke analysis was completed in an outdoor smoking area and inside a smoker's car.

3.2 Experimental

3.2.1 Chemicals and materials

Benzene, toluene, ethylbenzene, *o*-xylene, *p*-xylene, naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, pyrene, benzo(a)anthracene, 2, and 20 mL sample vials were purchased from Sigma-Aldrich (Oakville, Ontario, Canada). DVB sorbent (HaySep Q, 60-80 mesh) was purchased from Restek (Bellefonte, PA, USA), Carboxen 1000 (60-80 mesh) was donated by Supelco (Bellefonte, PA, USA), and PDMS/DVB/CAR SPME fibers were purchased from Supelco (Bellefonte, PA, USA). Twenty two gauge hypodermic stainless steel needles (O.D. 0.71 mm, I.D. 0.39 mm) were purchased from Dyna Medical Corporation (London, ON, Canada). 100 µm o.d. stainless steel wire was purchased from Small Parts (Lexington, KY, USA). A manual sampling pump, AP-20 was purchased from Komyo Ricagaku (Kanagawa, Japan). Helium carrier gas was purchased from Praxair (Kitchener, Ontario, Canada).

3.2.2 Instrumentation

A portable GUARDION-7 gas chromatograph equipped with a toroidal mass spectrometer, manufactured by Torion, (American Forks, UT, USA) was used for on-site separation and detection of target compounds. The GUARDION-7 was equipped with a modified inlet to create a restriction to allow the use of side-hole NTDs. The instrument

utilized a low thermal mass GC column assembly fabricated by RVM Scientific (California, USA) with a MTX 5 capillary column 5 m; 0.1 mm; 0.4 µm d_f from Restek (Bellefonte, PA, USA). The experimentally optimized GC program was as follows: injector temperature; 270^{o}C, column flow; 0.2 mL min^{-1}, initial column temperature 50^{o}C, hold for 5 seconds, ramp to 295^{o}C at a rate of 1^{o}C second^{-1}, hold for 5 seconds. The MS system was operated in EI mode at 70 eV using a mass range of 45 – 350 kDa.

3.2.3 Preparation of standards

Calibration of SPME and NTD for amounts of BTEX and PAHs extracted were completed via liquid injections. Solutions of 0.5, 1, 10, 50, and 100 ppm in methanol were prepared from serial dilution of a 100 ppm stock solution. The stock solutions were prepared by adding the appropriate volume of BTEX compounds and weighing the appropriate amount of each PAH in a 100 mL volumetric flask and filling with methanol.

100 µg/g BTEX in pump oil was prepared by spiking 10 mg of each BTEX compound into 100 g pump oil.

3.2.4 Preparation of needle trap devices

All NTDs were cut to 65 mm, utilized a tapered tip, and had a side-hole above the sorbent. NTDs were packed with a sandwich sorbent: 1 cm of DVB 60-80 mesh sorbent at the tip, followed by 1 cm of Carboxen 1000 60-80 mesh sorbent. These were prepared as follows.

NTDs were packed using a slurry packing method. A stainless steel spring was inserted into the barrel of the needle at a desired depth, 2.2 cm from the tip, and locked in that position by inserting wires into both ends of the needle and compressing the spring. This spring holds the sorbent inside the needle for packing and sampling. After inserting the steel spring, the tip of the NTD was connected to solvent pump. Small amounts of particle slurry suspended in ethanol were injected into the solvent pump and pumped into the needle. The pressure applied from the solvent pump supplied force to pack the sorbent particles. Once the desired particle amount was packed into the needle, it was connected to a helium line to dry. Needles were then tapered using a drill and a chrome vanadium pressure applicator. As the needle was spun in the drill, the pressure applicator was applied to the tip until the taper reached the desired internal diameter of 0.1 mm. NTDs were conditioned for two hours at 285^{o}C to remove any impurities from the sorbent bed. After NTD conditioning, the side-hole, tip, and luer lock end of the needle were sealed using Teflon caps.

3.2.5 Optimization of sampling procedures

The PDMS/DVB/CAR fiber coating and DVB/CAR NTD packing were selected for fast sampling of target compounds on-site. During short extraction times, solid coatings act as a perfect sink where adsorption binding is essentially irreversible and instantaneous.[32] With precise control of sampling time and monitoring of convection, extraction can be calibrated based on diffusion coefficients, rather than by distribution constants. Extraction times of 30, 60, 120, 180, 300 seconds were evaluated on-site.

As exhaustive extraction devices, the amount of analyte extracted using NTD is proportional to the sampling volume as long as breakthrough does not occur. This way, one can increase the sensitivity of a NTD method simply by increasing the sample volume. Sample volumes of 10, 20, 50, and 100 mL were investigated on-site. Breakthrough was investigated while completing on-site analysis using two NTDs in line. The rear NTD was desorbed, if no analyte was found, breakthrough was considered insignificant.

3.2.6 Reusability of SPME and NTDs for on-site sampling.

To evaluate the reusability of SPME fibers and NTDs, extractions from the headspace of BTEX in pump oil solution were completed. 5 ml of BTEX solution was put in a 20 mL sample vial at 25^{o}C. A 5 minute extraction time was used for SPME and 20 mL extraction volumes were used for NTD. After completing 5, 10, 15, 20, and 25 extractions of cigarette smoke or exhaust emissions, subsequent extractions from the BTEX sample were completed. SPME fibers were evaluated for reproducibility and capacity. NTDs were evaluated to determine the effect of particle contamination on amount extracted and breakthrough volume.

3.2.7 Analysis of exhaust emissions

Car and diesel exhaust were analyzed for BTEX and PAHs. Sampling was completed using a custom device seen in Fig. 18. The device allowed for SPME and NTD extraction along with flow rate and temperature measurement.[44] Both diesel and gasoline exhaust

extraction conditions were the same. SPME extraction time was 1 minute. NTD sample volume was 20 mL.

Figure 18. On-site sampling of gasoline exhaust. (A) GUARDION-7, (B) custom exhaust sampling device, (C) NTD vacuum syringe, (D) SPME sampler, (E) thermometer, (F) flow meter.

The subject car for gasoline analysis had an operating emissions cleaning system that passed emissions testing. Analyses of emissions were completed immediately after ignition of the engine and after the engine had reached optimal operational temperatures according to the temperature gauge on the dash.

To complete diesel exhaust analysis, a diesel dump truck was used for the sampling. To evaluate the emissions from the vehicle, sampling was completed only when the vehicle was at optimal operational temperatures.

3.2.8 Analysis of cigarette smoke

To complete cigarette smoke analysis, SPME and NTD sampling was completed with the assistance of a portable dynamic air sampling device described by Augusto *et al.*[33] As shown in Fig. 19, the device consisted of a fan to supply a constant flow through a tube. This allowed monitoring of temperature and flow for diffusion based calibration. Sampling was completed in three different scenarios: an outdoor environment where people were actively smoking, inside a smoker's car prior to smoking, and inside a smoker's car while two smokers were smoking. The SPME extraction time for the outdoor analysis was 1 minute. To complete NTD sampling, a 50 mL sample volume was used. Extractions were completed in the vicinity of the smokers, where the direct exhalation of smoke from the smokers could be sampled.

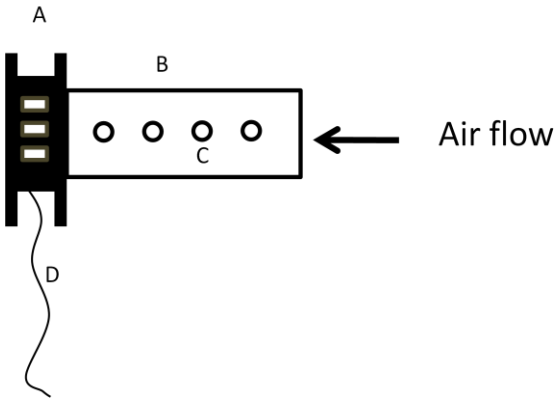


Figure 19. Schematic of portable dynamic sampler for SPME and NTD. (A) Fan, (B) aluminum tube, (C) sampling ports, (D) power cord to battery.

To complete sampling inside a smoker's car, initial extractions were completed approximately 18 hours after a smoker was present. This produced an environment of residual smoke, in which any passenger would be exposed to, if traveling in the car. Extractions were then completed while smokers were actively smoking inside the car. To complete these extractions, the SPME extraction time was 1 minute and NTD sample volume was 20 mL. A blank from a "clean" car where no one has been known to smoke in was sampled to provide a blank for extractions inside the smoker's car.

3.3 Results and Discussion

3.3.1 SPME and NTD optimization

3.3.1.1 Optimization of extraction SPME extraction time

For on-site analysis, the major variable that can be controlled when completing SPME extraction is time. SPME extractions were completed for 30, 60, 120, 180, and 300 seconds in gasoline exhaust and outdoor cigarette smoke to verify linearity of the extraction and determine an optimum sampling time. Of the BTEX components, benzene was the first to encounter displacement. Benzene and naphthalene were chosen to evaluate the linearity of the pre-equilibrium extraction. From Fig. 20 a and b, the results show that for benzene the SPME coating performed as a zero sink, with linear uptake for extraction times under 2 minutes. For naphthalene, the extraction remained linear for 5 minutes. Displacement of benzene was seen after 2 minutes. The linear regressions for benzene extraction from exhaust and smoke were 0.995 and 0.998, respectively. Linear regressions for naphthalene in exhaust and smoke were 0.995 and 0.990, respectively. A 1

minute sampling time was chosen to ensure extraction remained linear. Under these conditions, quantitation was completed using the model of diffusion through a boundary layer rather than using distribution constants. This eliminated the need for calibration curves and required a sampling time much shorter than that compared to equilibrium extraction. With no calibration curves, well monitored flow rates and temperature were crucial to complete quantitative analysis described by Koziel *et al.*[32]

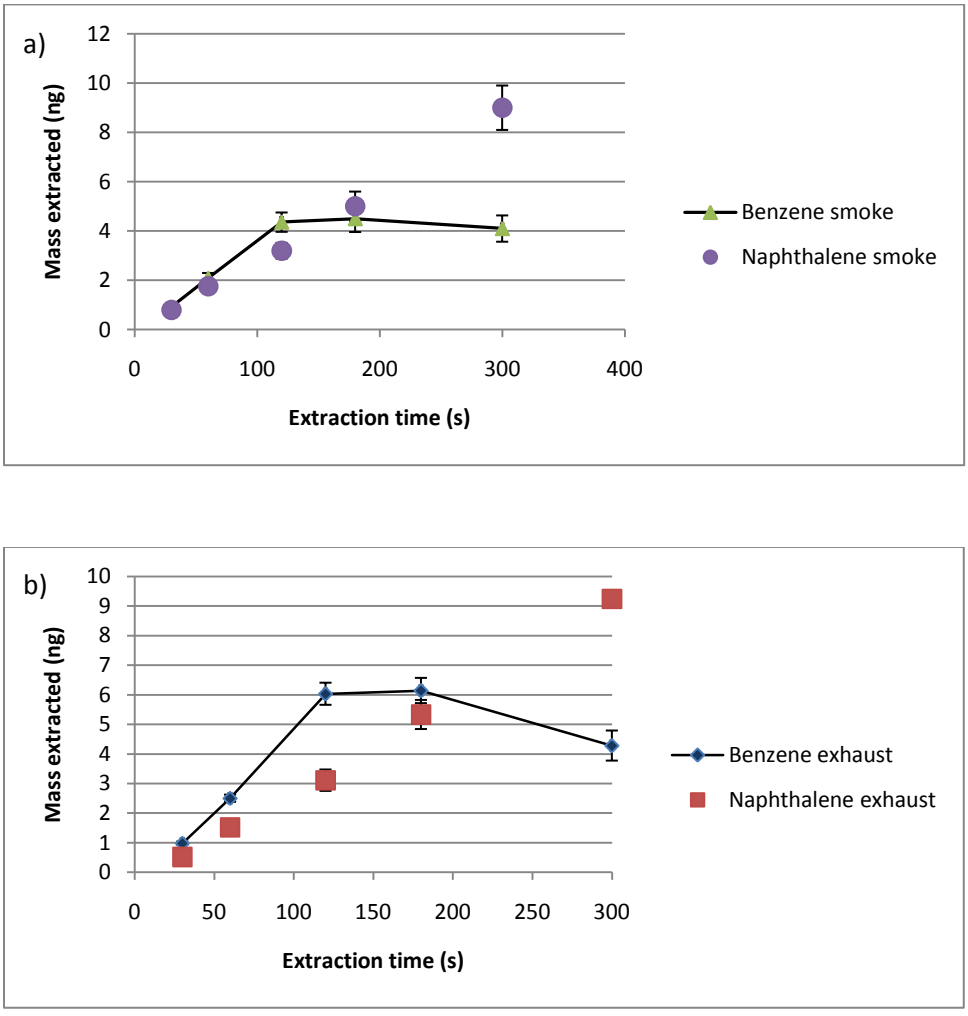


Figure 20. The effect of sampling time on competitive adsorption and linearity of pre-equilibrium extraction for benzene and naphthalene for a) cigarette smoke in an outdoor environment and b) car exhaust.

3.3.1.2 Optimization of NTD extraction volume

The amount extracted by NTD is proportional to the sample volume prior to breakthrough. When choosing a sample volume, breakthrough must not have occurred for data to remain quantitative.[25] Evaluation of breakthrough in the laboratory can be useful to determine sampling volumes that may be applicable to on-site analysis; however, in complex sample matrices there are many unknown compounds which can saturate the sorbent and are difficult to account for. For this reason, sample volume was optimized during the on-site analysis. For both exhaust and cigarette smoke 10, 20, 50, and 100 mL sample volumes were tested. A manual syringe pump and two NTDs connected in series were used for the breakthrough investigation.

Fig. 21 plots the amount of benzene and naphthalene extracted with increasing sample volume for exhaust emissions and cigarette smoke analysis. In both matrices breakthrough of naphthalene was not present until 100 mL sample volume. For the exhaust analysis, 50 mL extraction volume introduced volatile components including benzene into the second NTD. 20 mL was chosen to ensure no breakthrough would occur. For cigarette smoke sampling in an outdoor environment, 50 mL sample volume was used with no breakthrough. Inside the smoker's car, considering the increase in concentration due to an enclosed system, 20 mL sample volume was used. Two NTDs in line were used to verify that no breakthrough did occur.

After every 5 extractions, the NTDs were tested for breakthrough at the 20 mL sample volume to verify if sorbent degradation or particle contamination were causing premature breakthrough.

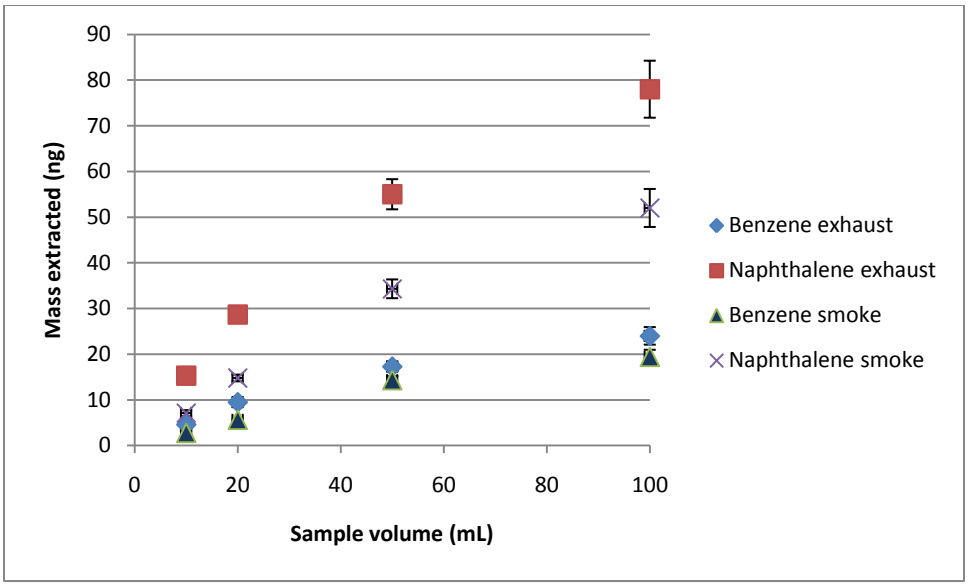


Figure 21. Mass extracted of benzene and toluene from cigarette smoke in an outdoor environment and car exhaust with increasing NTD extraction volumes.

3.3.1.2 Optimization of desorption conditions

Desorption time and temperature were optimized for SPME and NTD. Desorption temperatures of 260, 270, and 280^{o}C were tested for both devices. Desorption times of 1, 2 and 3 minutes were evaluated for each temperature. At 260^{o}C carry over was present for both devices after 3 minutes desorption. 280^{o}C was above the maximum operating temperature of the DVB used for the SPME and NTD extraction phase. This caused degradation of the DVB sorbent. At 270^{o}C there was undetectable carry over after 3 minutes desorption and no degradation of the sorbent was detected.

3.3.2 NTD and SPME reusability

Extraction using porous sorbent materials can be effected by displacement due to saturation and competitive binding. When multiple extractions of dirty samples using a porous sorbent is necessary, interferences such as particulates can contaminate the extraction phase, reducing the sorbent capacity. After multiple extractions, premature displacement may occur if sorbent capacity is reduced. If displacement occurs results are no longer quantitative.

Using a porous sorbent, the point of displacement for extraction is reproducible when extraction conditions remain the same. If this point remains constant for multiple extractions of dirty samples it can be said that extraction sites are not being contaminated and analysis will remain quantitative.

The NTD technique extracts particulates from the air, which eventually contaminate the sorbent bed. A consistent response in amount extracted for a specified sample volume and concentration, as well as the determination of the effect of contamination on breakthrough volume required evaluation. If particulate contamination affects the amount extracted, NTDs cannot be applicable for multiple uses. If the contamination reduces breakthrough volume a sample volume well below breakthrough should be selected and reduction of breakthrough volume monitored with use.

To verify if particulate contamination had any effect on performance of SPME or NTD, extractions of gasoline exhaust emissions followed by headspace extractions from 5

mL BTEX pump oil solution in a 20 mL sample vial were completed. A 1 minute SPME extraction time and 20 mL NTD sample volume were used. Fig. 22 and 23 demonstrate that after 25 extractions of particulate contamination from the exhaust extraction, both sample preparation devices continued to perform reproducibly.

Fig. 24 illustrates the effect of particle sampling on the breakthrough volume of NTDs. As particles were trapped on the sorbent bed of the NTD, the capacity decreased. To verify that the NTD was not losing capacity due to other factors, such as sorbent degradation, a second breakthrough experiment was completed extracting from the particle free headspace of a BTEX solution and desorbing in a GC using the conditions described in sections 3.3.1.2 and 3.3.1.3. Multiple extractions from BTEX headspace did not affect the breakthrough volume.

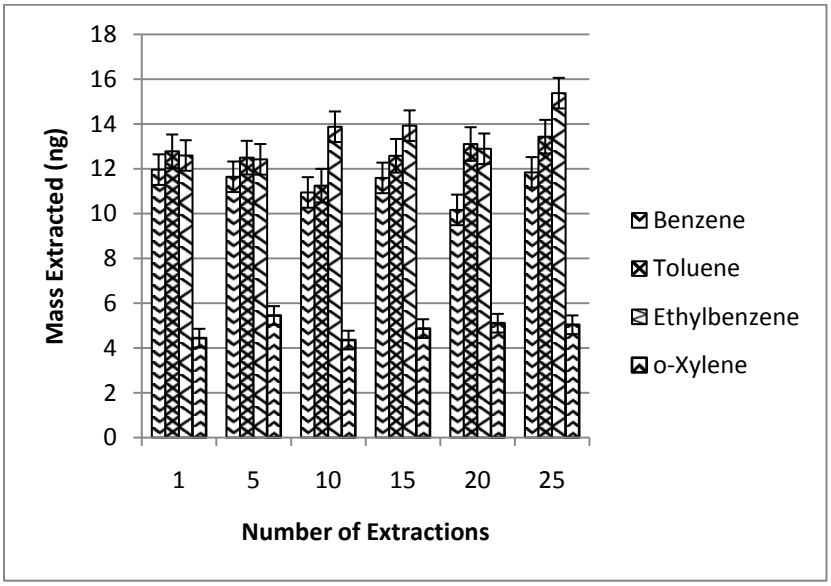


Figure 22. Reproducibility of BTEX extractions from headspace of pump oil solution using SPME.

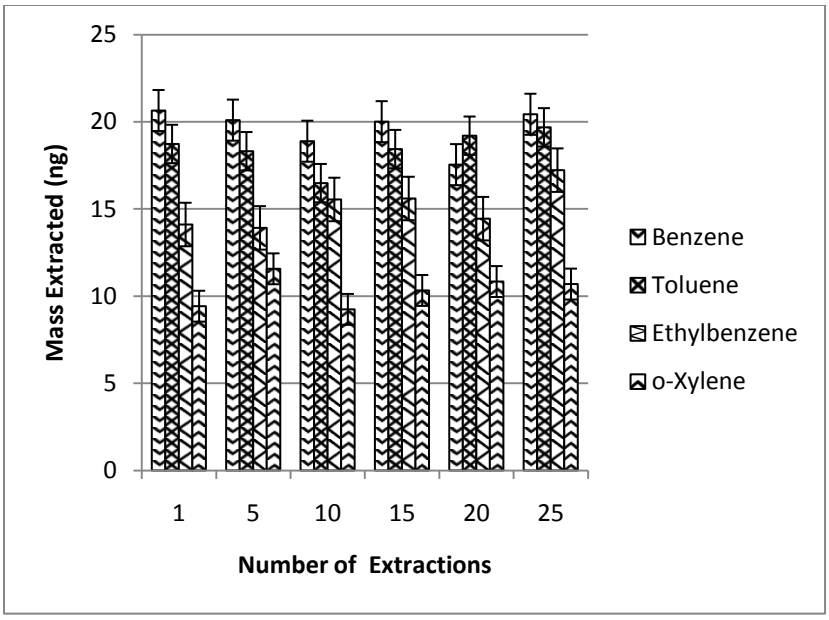


Figure 23. Reproducibility of BTEX extraction from headspace of pump oil solution using NTD.

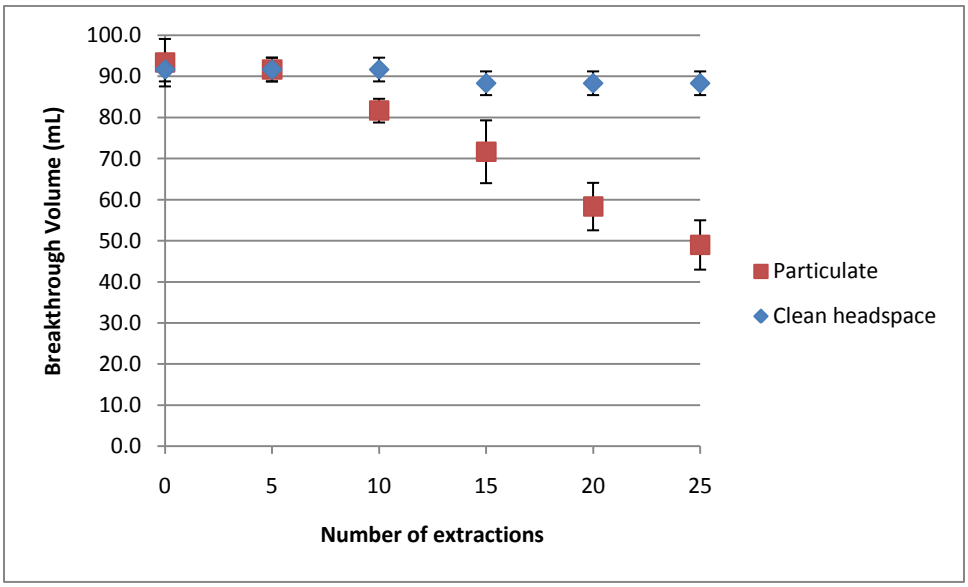


Figure 24. The effect of sampling from particulate contaminated air on NTD breakthrough volume.

3.3.3 Analysis of car exhaust

Fig. 25 a and b describe the emissions of BTEX and PAHs produced immediately after ignition of the car engine and how these concentrations change when the engine is running at optimal operating temperature. The combination of SPME and NTDs produce results differentiating between free and total concentrations of the compounds present in the emissions. Evaluation of BTEX components show that with the exception of *p*-xylene, for both cold and warm engine exhaust free and total concentrations were equivalent within the 10% experimental error. Fig. 25 b also demonstrates that naphthalene and acenaphthylene emission were much higher than the other PAH counterparts. Of the seven PAH compounds detected in the emissions, the total concentration of each analyte was higher than that of the free concentration signifying particle-binding. The percentage of target analytes bound to particulates can be seen in Table 4. It was also seen that the emissions of naphthalene and acenaphthylene were much higher than the other PAH counterparts. Target PAHs acenaphthylene and larger were not found in the warm gasoline exhaust emissions.

As the temperature of the exhaust increases, the emission levels of all compounds and the percentage of particle-bound compounds decreased. As the engine reaches optimal temperatures a more complete combustion occurs. Also the catalytic emissions control system is only efficient at warm temperatures.

Table 4. Percent particle bound for cold and warm gasoline emissions.

Compounds	Cold exhaust	Warm exhaust
Benzene	11	10
Toluene	4.0	6.0
o-xylene	5.0	6.0
Ethylbenzene	9.0	3.0
p-xylene	0.80	0.90
naphthalene	88	38
Acenaphthylene	63	n/d*
Acenaphthene	82	n/d
anthracene	100	n/d
phenanthrene	62	n/d
pyrene	n/d	n/d

Relative error +/- 10%, n/d*: not detected

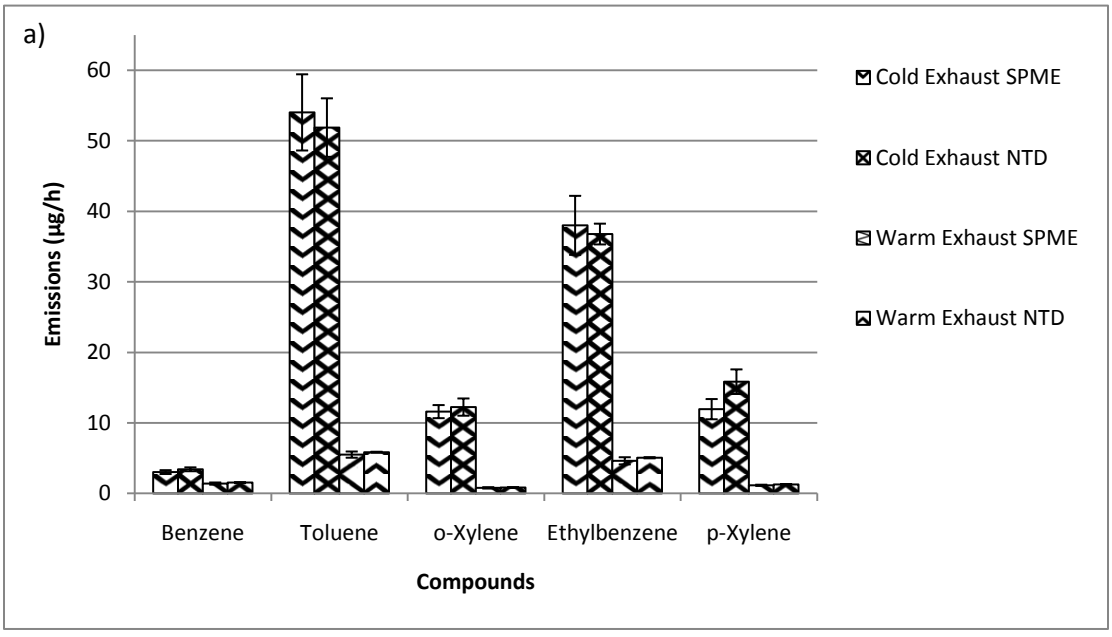


Figure 25. a) Emission of BTEX compounds from cold and warm gasoline exhaust extracted by NTD and SPME.

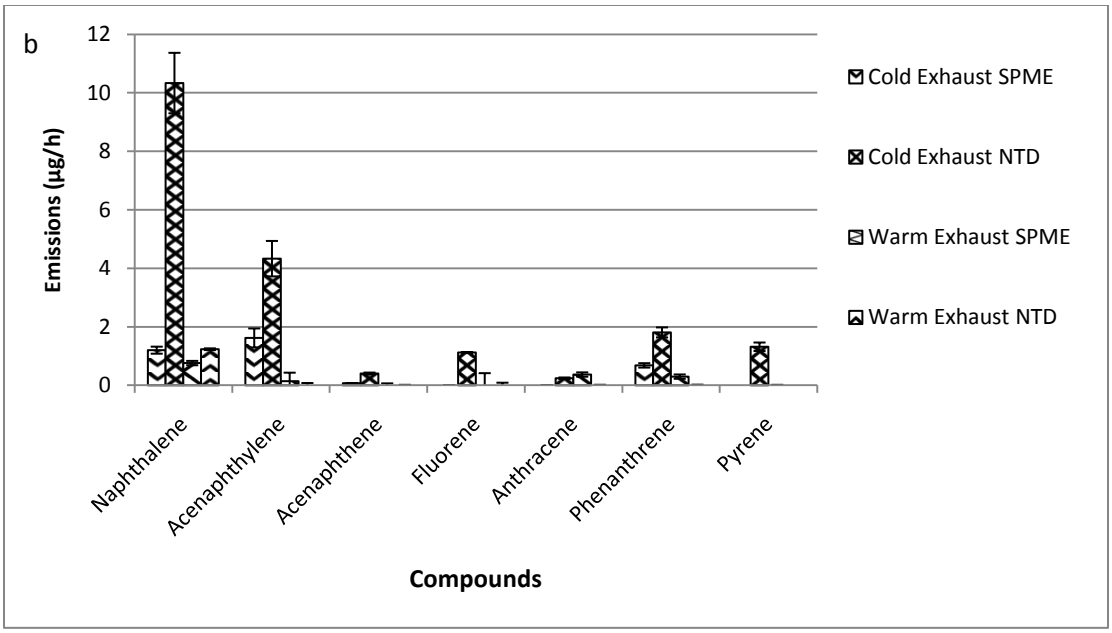


Figure 25. a) Emission of BTEX compounds from cold and warm gasoline exhaust extracted by NTD and SPME. b) Emissions of PAH compounds from cold and warm gasoline exhaust extracted using NTD and SPME.

3.3.4 Analysis of diesel exhaust

Diesel exhaust emissions were evaluated only at optimal operational temperatures. Fig. 26 illustrates the emissions produced by a diesel dump truck. Emissions of components found in the diesel exhaust were significantly higher than those from the gasoline engine at operational temperatures. Again, in diesel exhaust the free and total concentration of BTEX components were equivalent within the experimental error. Six PAHs were detected in the diesel exhaust. The emission levels for all analytes, with the exception of pyrene, were above 20 µg/hour. The free and total emissions of phenanthrene in the diesel exhaust were significantly higher than any other compound.

The percent of bound target compounds can be seen in Table 5. Here it is seen, with the exception of phenanthrene and pyrene the amount of binding less than 45%. In recent years, diesel vehicles have been equipped with more advanced emission control and particle filtering systems.[36] PAHs with 3 rings or less, are thought to make up about 47% of total PAH emissions. [36] From Fig. 26 we see that the PAHs with 3 rings or less do have higher emission levels than pyrene, which contains 4 rings. A reason why these low molecular weight PAHs bypass emission control systems is thought to be that these PAHs may be in a vapor phase in hot engine exhaust, which after passing by the control systems, begin to cool, and nucleate to form fresh particles.[43] At the point of sampling, the temperature of diesel exhaust was 52^{o}C, allowing compounds to remain in the gaseous and vapor phase rather than bind to particulates.

Table 5. Percentage of target analytes bound to particulates in diesel emissions.

Compound	Diesel exhaust
Benzene	7.0
Toluene	1.0
o-Xylene	14
Ethylbenzene	4.0
p-Xylene	13
Naphthalene	13
Acenaphthylene	43
Acenaphthene	19
Anthracene	35
Phenanthrene	65
Pyrene	73

Relative error +/- 10%

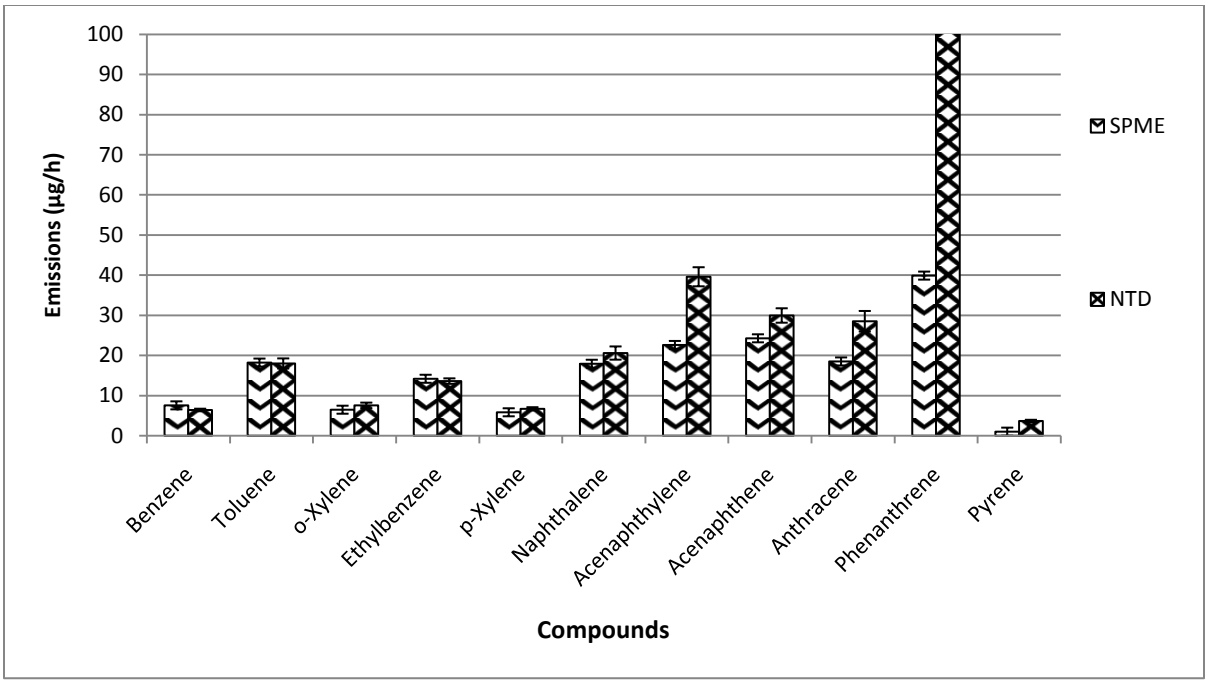


Figure 26. Evaluation of BTEX and PAH compound emissions in diesel exhaust using NTD and SPME.

3.3.5 Analysis of cigarette smoke

Figs. 27-29 illustrate the concentrations of BTEX and PAH components found in three different smoking environments. The concentrations of components found in the atmosphere in the vicinity of a smoking area were investigated. Smoking sections are commonly being removed from areas near doors of public buildings such as office buildings and especially hospitals due to the exposure of patients and visitors to cigarette smoke as well as the smoke entering the buildings. Fig. 27 separates the target compounds into free and total concentration and Table 6 contains the percentage of target analytes bound to particulates in outdoor smoke analysis and inside a smoker's car analysis.

Cigarette smoke is a more complex matrix than car exhaust. The uncontrolled combustion of the tobacco and paper is inefficient, producing a larger amount of particulates to which compounds can bind. Benzene and toluene were the only compounds found to have equivalent free and total concentrations in the outdoor smoke analysis. Here, nicotine was also evaluated. In the outdoor environment, 33% of total nicotine was found in the free form and inside 68% was found in the free form. Most of the ratios of free and total in the outdoor cigarette smoke are small. Two reasons for this are that the sampling devices were aimed at the mainstream smoke, exhaled from a smoking person. Here a large portion of free compounds have diffused into the lungs.[39] Also the atmospheric temperature was 10^{o}C. The lower temperatures will favor particulate binding.

Table 6. Percentage of target compounds bound to particulates for cigarette smoke analysis in an outdoor environment and inside a smoker's car

Compounds	Outdoor smoke	Inside car smoke
Benzene	10	1.0
Toluene	4.0	4.0
o-Xylene	83	9.0
Ethylbenzene	56	26
p-Xylene	43	2.0
Naphthalene	62	35
Nicotine	67	32
Acenaphthylene	62	45
Acenaphthene	23	26
Fluorene	90	54
Anthracene	23	41
Phenanthrene	28	36
Pyrene	92	99
Benzo(a)anthracene	n/d*	100

Relative error +/- 0.1, n/d*: not detected.

Residue from cigarette smoke is known to linger in an area long after smoking has taken place. Residue concentrations were evaluated inside a smoker's car 18 hours after someone had smoked. Fig. 28 illustrates the residues of BTEX and naphthalene found inside the car. The total concentrations in the atmosphere were equivalent to free concentrations. To test if these compounds were residue from smoke and not contaminants from exhaust emissions or gas spills, analysis of ambient air in a "clean" car where no one has been known to smoke was completed. No BTEX or PAH compounds were recovered from the "clean" car.

Profiles of free and total concentrations inside a smoker's car during smoking can be seen in Fig. 29. Inside the smoker's car, concentrations of analytes found were 3-5 times higher than outside. Also, with the exception of anthracene, free analyte concentrations were more prevalent than those in the outside smoke analysis. A reason for this deviation was that inside the car is a closed environment, there are less dilution effects from the atmosphere which can affect the distribution of free and particle-bound compounds.

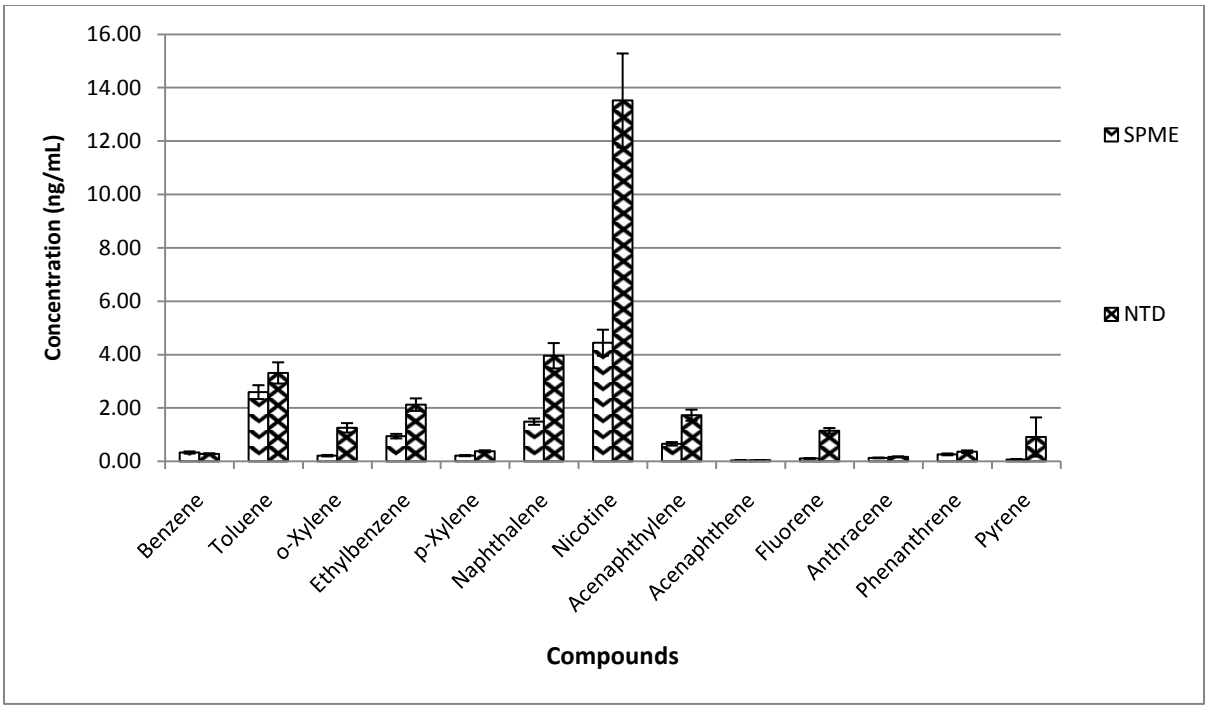


Figure 27. Free and total concentrations of BTEX and PAHs present in the atmosphere in the vicinity of a smoking area in an outdoor environment.

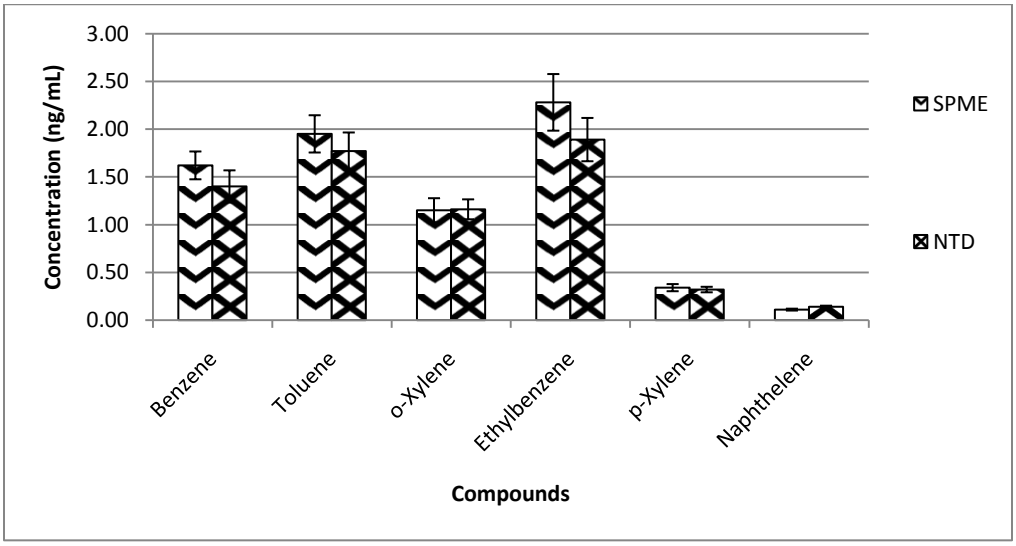


Figure 28. Free and total concentration of BTEX and naphthalene found from residual analysis of a smoker's car one day after smoking inside.

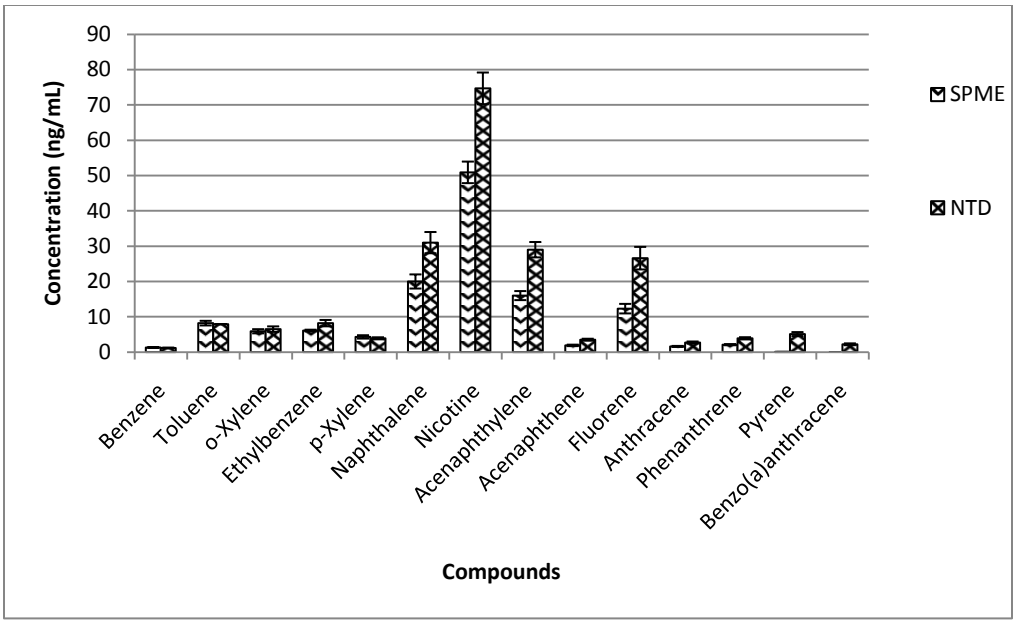


Figure 29. Free and total concentration of BTEX and PAHs inside a smoker's car while people are present smoking.

An estimate of method detection limits using diffusion based SPME extraction and exhaustive NTD extraction were completed by laboratory air sample analysis and can be seen in Table 7.

Table 7. Method detection limits for SPME and NTD extraction.

	Detection Limits (ng/mL)			
Compounds	SPME	RSD	NTD	RSD
Benzene	0.3	8	0.2	11
Toluene	0.4	8	0.4	8.00
o-Xylene	0.1	10	0.1	12
Ethylbenzene	0.4	4	0.5	11
p-Xylene	0.2	11	0.2	7.5
Naphthalene	0.1	10	0.1	9.7
Nicotine	0.1	6	0.2	6
Acenaphthylene	0.1	8	0.2	7.5
Acenaphthene	0.8	11	0.2	8
Fluorene	0.2	11	0.1	12
Anthracene	0.7	9.5	0.1	11
Phenanthrene	0.2	8	0.3	8
Pyrene	0.1	9.5	0.3	11
Benzo(a)anthracene	n/d*	n/d	0.5	12

n/d*: not detected

3.4 Conclusions

This study demonstrated the ability to determine free and total concentrations of compounds in a gaseous sample matrix without the preparation of calibration curves using SPME and NTDs coupled to a portable GC/MS. Free and particle-bound compounds enter the atmosphere from multiple sources where the public are susceptible to both components of the pollution. This fast, solventless method can be used for environmental monitoring; such as levels of cigarette smoke contaminants near entrances to buildings or other public areas. These techniques could also be used as an efficient method for emission screening and profiling of vehicles.

Future work using SPME and NTD to investigate atmospheric contaminants on-site could include monitoring exhaust emissions produced in different areas such as construction sites and traffic tunnels. Further investigations could include profiles of emission pollutants and how they distribute in the atmosphere. Future development in NTD technology would include employing a particle filter to remove particles before contaminating the sorbent bed.

Chapter 4. Summary

A new NTD and packing method was developed to improve the performance of this sample preparation technique. The extraction and desorption performance of the new NTD were characterized by automated sampling and manually sampling BTEX, anthracene and pyrene. The new tapered and sliding tip NTD designs exhibited equal extraction performance and improved desorption efficiency when compared to previous NTDs used in the literature. NTDs packed via slurry packing demonstrated better reproducibility and shorter production time when compared to NTDs packed by vacuum aspiration.

NTD and SPME were combined with a portable GC/MS instrument to complete on-site analysis. These techniques were applied for analysis of exhaust emissions and cigarette smoke pollutants. The total concentration obtained from NTD sampling was compared to free concentration obtained by rapid SPME sampling. The results show that for volatile compounds such as BTEX, the total concentrations are closely related to the free concentration. On the other hand, for semi-volatile compounds such as the target PAHs, differences were found between free and total concentration signifying particulate-binding and that NTD is useful for sampling gaseous matrices containing particulates.

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