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High Flow Air Sampler for Rapid Analysis of Volatile and Semi-Volatile Organic Compounds

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A dissertation submitted to the faculty of
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Doctor of Philosophy

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ABSTRACT

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Volatile and semi-volatile organic compounds are ubiquitous, and some of them are hazardous. The ability to rapidly detect and identify trace levels of them in air has become increasingly important. The conventional device used today for sampling and concentrating them in air is thermal desorption tubes filled with specific sorbents, which can only collect air samples at flow rates of 100-200 mL/min. In order to detect low concentration (ppt level) VOC compounds, long sampling time (>2 h) and sensitive detection are required. At the same time, portable instrumentation for on-site analysis has been developing rapidly. The somewhat lower performance of portable instruments compared to benchtop systems requires the sampling of even greater sample volume in order to reach the same detection limits.

In this study, two high flow rate air sampling devices, i.e., a multi-capillary trap and a concentric packed trap, were developed to sample a large volume of air in a short time period. The multi-capillary trap was constructed by bundling analytical capillary gas chromatography columns together in parallel. As low as single digit ppt detection limits were reached in less than 25 min with this trap, and as high as 8.0 L/min flow rate was sampled. The simple and compact multi-capillary trap could be easily used with a conventional thermal desorption system to perform high flow rate sampling. A concentric packed high flow rate trap was also developed by packing sorbent layers concentrically around an empty tube. The concentric packed trap achieved a high flow rate (>10 L/min) because it had a high surface area and short sorbent bed. Also, its large sorbent amount (>1 g) provided large breakthrough volume (>100 L) required to achieve low detection limits.

An equilibrium distribution sampling system was developed by absorbing selected analytes in granular PDMS to provide calibration for on-site instrumentation. Furthermore, a needle trap device was coupled in tandem to both high flow rate air samplers to perform second-stage concentration of VOCs down to the ppt level. Concentration factors of 10^4 to 10^5 were achieved within 30 min using both systems, i.e., over 10 to 100 times more sample was collected compared to conventional TD systems.

Keywords: gas chromatography, air, sampling, high flow rate, detection limits, volatile organic compounds, thermal desorption, parts per trillion, rapid, concentric packed trap, multi-capillary trap

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
BTEX	Benzene, toluene and xylene
CI	Chemical ionization
CMS	Carbon molecular sieve
DOAS	Differential optical absorption spectroscopy
DVB	Divinylbenzene
EPA	Environmental Protection Agency
EDS	Equilibrium Distribution System
FID	Flame ionization detector
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
GPL	General population limit
HC	Hollow cathode
HF	High flow trap
HPLC	High-performance liquid chromatography
HSE	Health and Safety Executive
i.d.	Inner diameter
LOD	Limit of detection
MDHS	Methods for the determination of hazardous substances
MDL	Method detection limit
MS	Mass spectrometry

MSD	Mass spectrometer detector
MTBE	Methyl-*tert*-butyl ether
mw	Molecular weight
NATA	National-scale Air Toxics Assessment
NE	Not established
NIOSH	National Institute for Occupational Safety and Health
NT	Needle trap
o.d.	Outer diameter
OSHA	Occupational Safety and Health Administration
PDAS	Portable dynamic air sampler
PDMS	Polydimethylsiloxane
PFTBA	Perfluorotributylamine
PLOT	Porous layer open tubular
ppm	Parts per million
ppb	Parts per billion
ppt	Parts per trillion
PTR-MS	Proton transfer reaction mass spectrometry
RDX	Research department explosive
RSD	Relative standard derivation
S/N	Signal-to-noise ratio
SD	Source drift
SD	Standard derivation

SIM	Selected-ion monitoring
SPME	Solid phase microextraction
STEL	Short-term exposure limit
SVOC	Semivolatile organic compounds
TD	Thermal desorption
TNT	2,4,6-Trinitrotoluene
TOF	Time-of-flight
TWA	Time-weighted average
VOC	Volatile organic compound
VVOC	Very volatile organic compound
VX	O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate
WCOT	Wall-coated open tubular
WHO	World Health Organization

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Chapter 1 Introduction

1.1 Volatile organic compounds

Volatile organic compounds (VOCs) are gas-phase organic compounds that range in volatility from *n*-C_1 to *n*-C_{20} with boiling points lower than 400 °C; they can include most chemical functional groups.[1-2] The World Health Organization (WHO) divides VOCs into three categories: (1) very volatile (gaseous) organic compounds (VVOC), with b.p. from <0 °C to 50-100 °C (e.g., propane, butane, and methylene chloride); (2) volatile organic compounds (VOC), with b.p. from 50-100 °C to 240-260 °C (e.g., formaldehyde, *d*-limonene, and toluene); and (3) semi-volatile organic compounds (SVOC), with b.p. from 240-260 °C to 380-400 °C (e.g., pesticides, plasticizers, and fire retardants).[1]

Interest in VOCs is high because of their roles in industrial hygiene,[3] atmospheric chemistry,[4-6] chemical warfare,[7] and in-door and environmental pollution.[8,9] Levels of VOCs in air are usually between low ppt to low percent.[2] Various regulatory agencies, including EPA (Environmental Protection Agency), OSHA (Occupational Safety and Health Administration), NIOSH (National Institute for Occupational Safety and Health), and Health and Safety Executive (HSE) develop standard methods for monitoring VOCs in air both indoors and outside. Many documented standard methods have been published over the past decades, for example: EPA methods from TO-1 to TO-17, ASTM Standard D-6196-03, ISO 16017, and UK HSE MDHS 80.[10-15]

Most standard methods deal with VOCs in concentrations from ppb to ppm, not only because these levels have the most significant effect on human health and the environment, but VOCs are also technically challenging to quantitatively measure below the ppb level. However, in some cases, such as for the nerve agent VX, the short-term exposure limit (STEL, 15-min exposure limit) is very low, and the general population limit (GPL, long time safe level) is even lower (e.g., 910 ppt and 50 ppt, respectively).[16] Recently, the EPA published the 10^{-6} risk level (1 in 1 million to become ill) for the National-scale Air Toxics Assessment (NATA), which is in the range of 1 ppt for 1,3-butadiene to 576 ppt for dichloromethane as listed in Table 1.1.[17] At the same time, the EPA also published a supplement to EPA TO-15 for reducing the method detection limit (MDL) to lower than 500 ppt to reach the 10^{-6} risk level.[17] Finally, the ability to detect VOCs at the ppt level would help to determine health effects, sources of pollution, and spatial and seasonal variations.

VOC analysis generally includes three steps: (1) collecting the sample using a canister/bag, solid adsorbent or specially treated filter, followed by (2) enrichment of analytes in as small a volume as possible and (3) separation, identification and quantitation using gas chromatography (GC) with an appropriate detector (such as a mass spectrometer, MS). In limited situations, the first sampling step can be as simple as directing the sample into the separation system or detector. Figure 1.1 shows a general workflow scheme for collecting and analyzing VOC samples. In order to measure VOCs in low concentrations (sub ppb, v/v or mol/mol), either a high efficiency sampling/enrichment method or a sensitive detector is needed.

Table 1.1 NATA compound 10^{-6} risk levels.

Compound	Risk level /pptv	Compound	Risk level /pptv
Vinyl chloride	90	*trans*-1,3-Dichloropropene	44
1,1-Dichloroethene	50	1,1,2-Trichloroethane	11
Dichloromethane	576	1,2-Dibromoethane	1
Trichloromethane	8	Tetrachloroethene	NE
1,2-Dichloroethane	10	1,1,2,2-Tetrachloroethane	3
Benzene	41	Hexachlorobutadiene	5
Carbon tetrachloride	11	Acrylonitrile	5
1,2-Dichloropropane	NE	1,3-Butadiene	1
Trichloroethene	NE	Ethylene oxide	NE
cis-1,3-Dichloropropene	44		

NE = not established

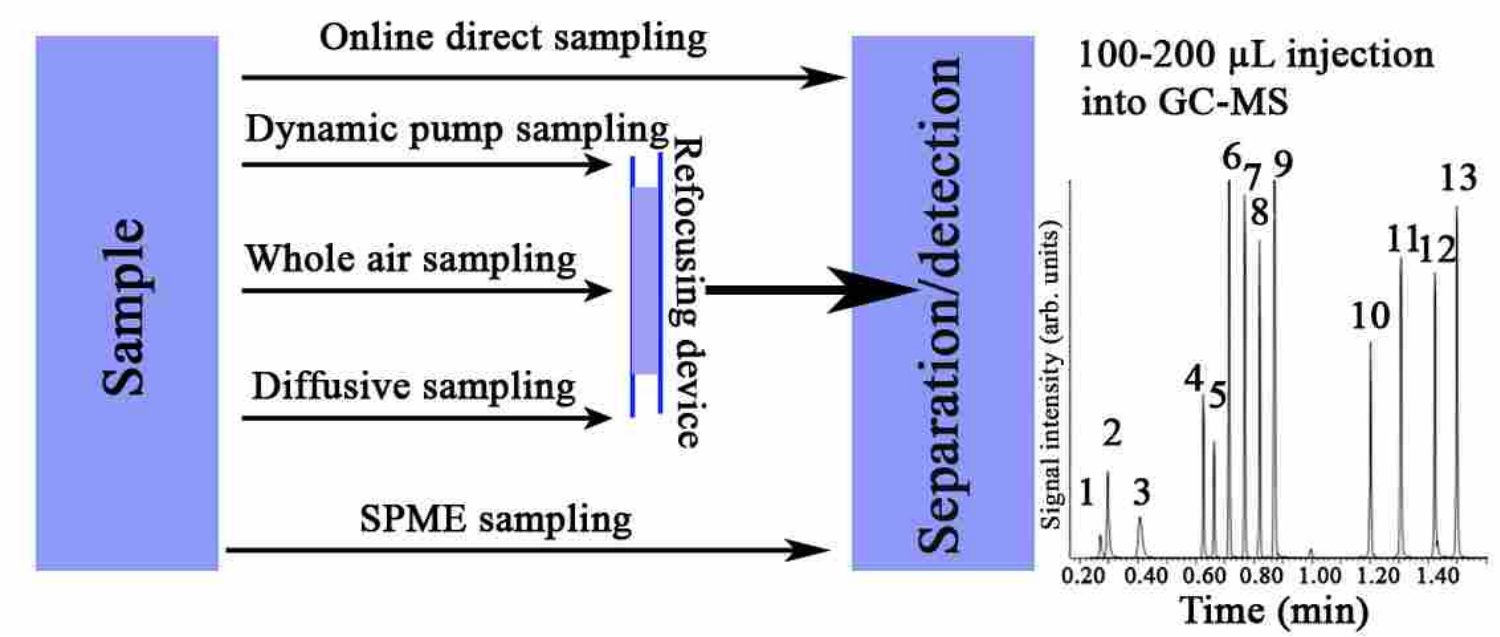

Figure 1.1. Typical workflow for VOC analysis.

In this chapter, I first describe the current techniques that are capable of detecting VOCs at the ppt level, with their pros and cons. Then high flow air sampling is introduced with its history and advantages compared to traditional techniques. Also, a new needle trap technique is described as a potential refocusing trap for on-site analysis where fast flow sampling is desirable.

1.2 Ultra-sensitive detection

Although sample enrichment is often used to achieve low detection limits, it adds extra steps to the sampling and analysis procedure. The preferred way to analyze samples at the ppt level is to collect the original sample and detect it directly with a sensitive detector. With a 100 ppt sample, detection of approximately 0.4 pg/mL would be required (assuming the molecular weight of the analyte is 100). Currently, there are only a few detectors or approaches that can achieve this goal.

1.2.1 Selected-ion monitoring mass spectrometry

Selected-ion monitoring mass spectrometry (SIM-MS) is the most popular approach for detection of low level VOCs. Compared to MS in the full scan mode (i.e., a full mass spectrum is scanned during analysis), the SIM mode records ion mass intensities at predetermined mass numbers.[18] However, if time-of-flight (TOF) MS is used, all ions can be monitored simultaneously across the mass range. Therefore, TOF-MS is significantly more powerful than scanning mass spectrometers (such as quadrupoles) because SIM-type detection limits are achieved while still monitoring all ions. The problem with TOF-MS is its relatively high cost and bulky high-vacuum system, which makes it almost impossible for on-site analysis.

The detection limits for benchtop MS instruments are usually between 0.01 ng to 0.1 ng in the full-scan mode. In the SIM mode, they can reach down to the pg range and push to near the ppt level. However, direct-analysis of VOCs at the ppt level is not very practical with most systems, and must be achieved using some type of pre-concentration step.

1.2.2 Proton transfer reaction mass spectrometry

Proton transfer reaction mass spectrometry (PTR-MS) is a technique invented in the 1990s based on chemical ionization (CI), flow drift tube and MS.[19,20] Trace level VOCs can be protonated by H_3O^+ and detected by MS at the ppt level while most other components in the air remain undetected. The PTR-MS technique is widely used to study atmospheric science,[21] plant emissions,[22] food science,[23] and medical applications.[24-26] For example, Lindinger used PTR-MS to perform on-line monitoring of C_9-alkylbenzene and its ^{13}C-isotope in ambient air with a detection limit of 2 to 5 ppt.[27] Online monitoring of anesthetic gases, sevoflurane and isoflurane, at a urological post-anesthesia care unit at low ppb concentration was performed using PTR-MS.[26]

PTR-MS experiments are performed in several steps as shown in Figure 1.2. First, ions from a hollow-cathode (HC) are directed into a short source drift (SD) region filled with water vapor. After passing the SD region, high concentration (>99.5%) of H_3O^+ ions are obtained.[20] Then, these H_3O^+ ions enter the drift tube section filled with air sample containing trace VOCs to be analyzed. There is no other buffer gas in the drift tube; therefore, the original concentration of trace VOCs is preserved. Inside the drift tube, the H_3O^+ ions undergo non-reactive collisions

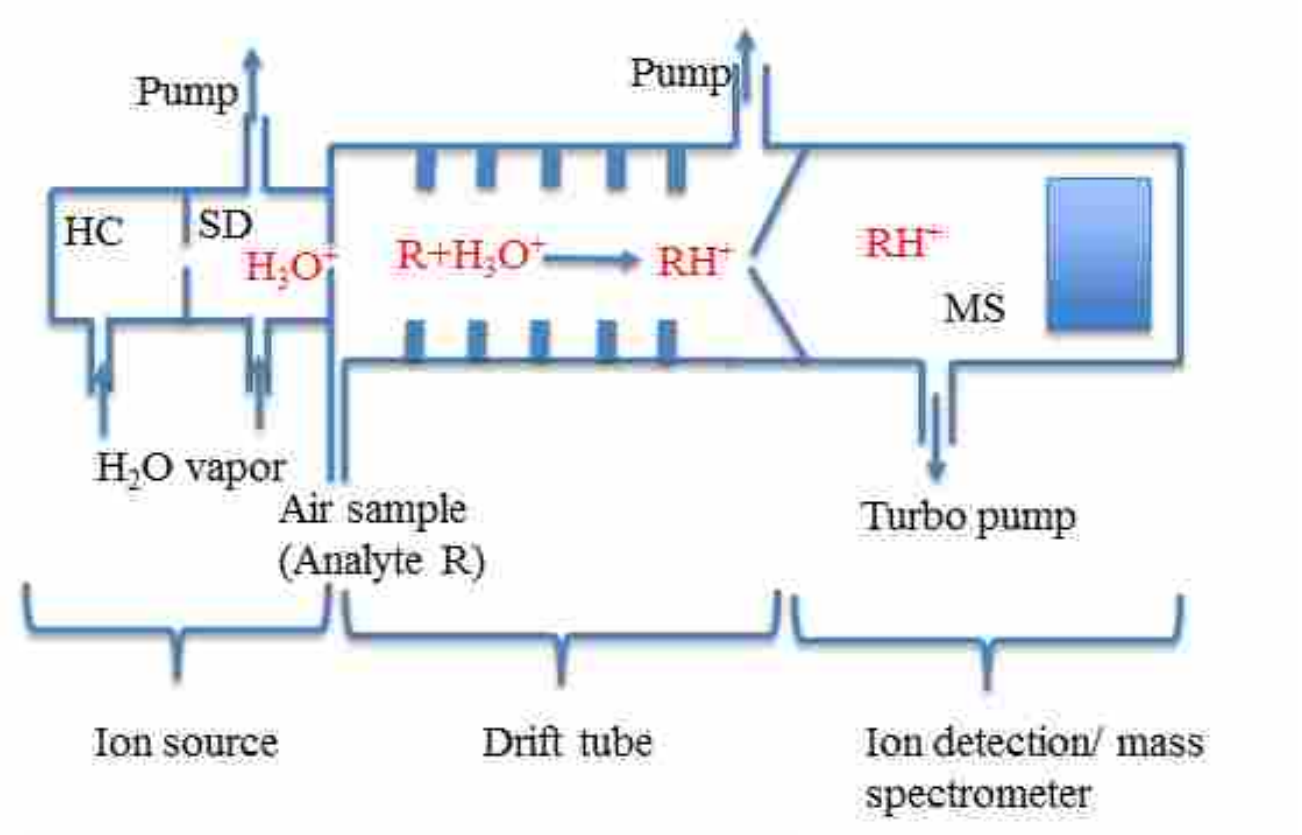

Figure 1.2 Schematic representation of a PTR-MS system.

with the most abundant components in the air (nitrogen, oxygen, and others with proton affinities lower than that of water, i.e.,7.2 ev); however, a small fraction reacts with trace VOCs in the air. PTR-MS is the best choice if it is desired to monitor a variety of gas species in a time interval of less than 1 min. It is more sensitive and faster than most other VOC detection techniques. PTR-MS instruments are also relatively compact, PTR-MS does not require a solvent, and only needs a limited amount of carrier gas. These make it an ideal candidate for on-site analysis and remote monitoring. Compared to thermal desorption methods, no heating is required for PTR-MS, making it suitable for detection of thermally labile compounds. However, PTR-MS is not an ideal technique for identification of complex unknown samples, since it can be difficult to interpret spectra from complex mixtures. In addition to PTR-MS, there are similar techniques, such as selected-ion flow tube mass spectrometry and atmospheric flow tube mass spectrometry that can be used to detect VOCs at the ppt level.[28,29]

1.2.3 Specific/selective detection

In addition to the more universal detectors, there are several sensitive detectors designed specifically for certain compounds of interest that can reach very low detection limits. Long-path differential optical absorption spectroscopy (DOAS) uses narrow molecular absorption bands in the UV and visible spectral regions to identify trace gases in the atmosphere.[30,31] DOAS can reach below 100 ppt without sample collection or preparation; however, DOAS is only applicable to molecules that absorb in a specific wavelength region, mostly aromatic hydrocarbons.[32] Selective carbon nanotube-based sensors and sensor arrays have been developed for trace vapor detection of nitroaromatic explosives.[33] Microwave (MW)-based sensing uses absorption-induced swelling of PDMS (polydimethylsiloxane) to detect

acetone at concentrations >265 ppt.[34] Silver nanocube aggregates within cylindrical pores can be employed as surface-enhanced Raman scattering substrates for trace level organic vapor detection with detection limits of 600 ppt for the explosives binder, N-methyl-4-nitroaniline.[35] A microcantilever was developed based on a specific peptide that can recognize and then detect 2,3-dinitrotoluene at 431 ppt.[36] Organic field effect transistors reported by Dudhe and others demonstrate excellent sensitivity of less than 70 ppt RDX (research department explosive) and less than 100 ppt 2,4,6-trinitrotoluene (TNT).[37] A secondary electrospray ionization triple quadrupole mass spectrometer was developed to detect nitrogen samples containing low concentrations (ppt-ppb range) of volatile organic compounds.[38]

These selective detection approaches are only applicable to targeted VOCs, for which they give excellent detection limits with relatively simple design and low cost. However, when detection of a range of analytes or unknown VOCs is desired, it is preferable to have a more universal detection system.

1.3 Sample enrichment

Due to the limited sensitivity of most detectors, increasing the concentration before analysis is usually necessary for low concentration detection. Concentrating/enriching/pre-concentrating means increasing the concentration of the original sample via a trapping and releasing process. For example, a VOC sample of 100 ppt (i.e., 0.41 ng/L, assuming that the average molecular weight of the analyte is 100) would require an analytical system with a detection limit of 0.4 ng/L or 0.4 pg/mL. By passing 1 L of the original sample through a trap filled with a sorbent, analytes can be retained and then released by heat in a volume of 1 mL (concentration factor of

1000). The trap acts as a pre-concentrator with a concentration factor of 1000, making it much easier to reach the required detection limit.

There are different approaches for sampling and enrichment: sorbent or cryogenic, passive (diffusive) or active (pumping), and equilibrium or exhaustive. Sorbent sampling utilizes sorbent materials to retain chemicals by adsorption or absorption; while cryogenic sampling retains chemicals through condensation or deposition (i.e., desublimation). Sometimes sorbent and cryogenic trapping are used together to increase trapping efficiency. Active sampling relies on a pump (manual or battery powered) to withdraw sample through the trap; while passive sampling depends only on diffusion of analytes from the surroundings. The major difference between equilibrium and exhaustive sampling is that exhaustive sampling completely retains all analytes of interest while equilibrium sampling extracts only some portions of them. After a sample is collected in/on an appropriate sorbent, thermal desorption or solvent extraction is usually used to release the sample prior to GC analysis. Liquid extraction typically leads to poor detection limits because a large amount of solvent is needed and only a small portion can be injected for detection. On the other hand, thermal desorption relies on heat to release the sample into a small volume of gas; all or most of the desorbed sample can be injected for better detection limits. The most popular sampling devices, (i.e, thermal desorption tubes, canister/Tedlar® bags combined with thermal desorption tubes, and solid phase micro-extraction fibers), are described in the following sections.

1.3.1 Thermal desorption

Thermal desorption (TD) tubes can be used for exhaustive active sampling or equilibrium

diffusive sampling. The exhaustive active mode is most popular and reliable for quantitative sampling at low concentrations; therefore, this work focuses on active sampling. One of the early TD tube applications was reported in the 1970s; a chromatographic sorbent was packed into an enriching glass tube/column for sampling air for *bis*-chloromethyl ether.[39-41] The tube was then directly connected to a gas chromatograph-mass spectrometer (GC-MS) system and heated for desorption and analysis. A detection limit in the low ppb range was achieved with over 1000 times enrichment compared with direct air analysis.

Over the years, multiple enhancements have been made to the TD technique (Figure 1.3). First, instead of coupling the tube directly to the detection system, another tube called a refocusing tube (a smaller size trap) was added. By using a second stage trap, the sample band released from the sampling (first stage) tube is trapped and released in a narrower band for better detection and quantitation. Also, cryogen-trapping/back-flushing can be used with the second trap to further improve the performance (i.e., narrower bands and better resolution). Finally, advancements in materials science have greatly improved the adsorbent materials that are used for thermal desorption, including polymeric materials (e.g., Tenax and XAD resins), graphitized carbon materials (e.g., Carbotraps), and carbon molecular sieves (e.g., Carboxens).[42,43] Each has different trapping strengths, artifact levels, and mechanical strengths. Sorbent selection and optimization are steps in VOC analysis method devlopment.[42]

Today, a standard TD system includes two major components as shown in Figure 1.3. First, the TD tubes used in most standard methods are: (a) 89 mm (3.5 in.) long with an o.d. of ¼ in. (6.4 mm), (b) 6 mm long with an i.d. of 5 mm (stainless steel), or (c) 6 mm long with i.d. of 4 mm

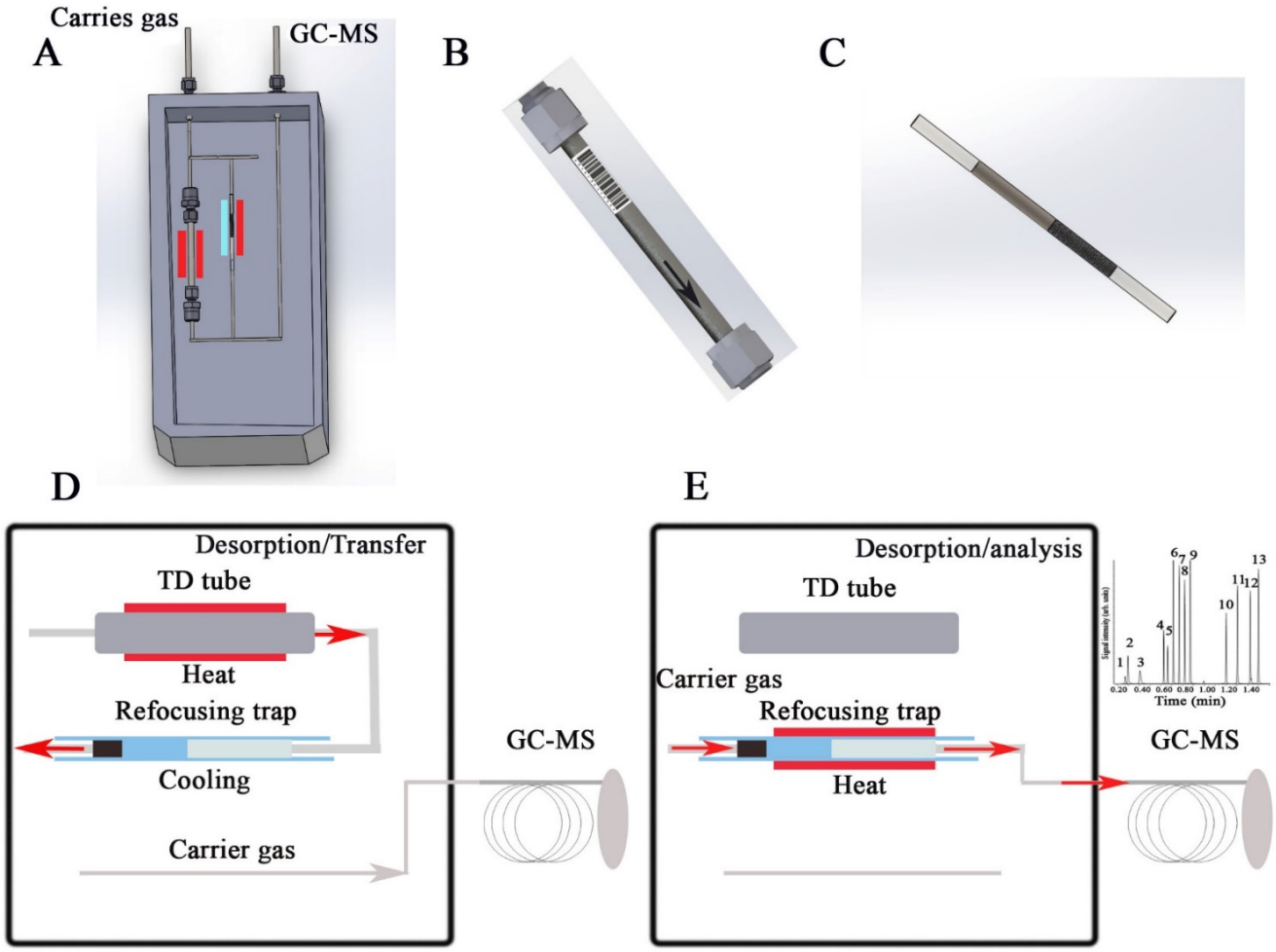

Figure 1.3 Typical thermal desorption system: (A) simplified schematic view of a thermal desorber, (B) ¼ in. thermal desorption tube, (C) refocusing tube, (D) sample tube desorption and transfer, (E) refocusing tube desorption and analysis.

(glass). The tube is usually packed with up to 3 to 4 layers of different sorbents, with a total maximum length of 60 mm and a total weight of 100 to 600 mg. The tube can be used for active sampling with a pump or for passive sampling by diffusion. The second TD component is the thermal desorber, which usually utilizes a heater for transferring the sample from the initial TD tube to a micro-concentrator/refocusing tube to further concentrate the sample, a cooling system (usually a Peltier cooler or liquid nitrogen) to cool the refocusing device, and a pneumatic system to direct the gas flow from the first-stage tube to the second-stage concentrator, and finally to the GC system. The refocusing tube (micro-concentrator) is usually 0.75 mm i.d., filled with 1 or 2 layers of sorbent. After the sample is collected in the TD tube, it is placed in the desorber for further processing and analysis. Inside the desorber, the TD tube is heated while the refocusing tube is cooled to transfer the sample to the refocusing tube using the carrier gas as shown in Figure 1.3D. After desorption is complete, the refocusing tube is ramped to a high temperature, and the sample is swept into the GC system in the reverse direction (back flush) for separation and detection (Figure 1.3E). Another accessory, called a sample tray or carousel is typically included in modern stand-alone thermal desorbers for continuous automatic TD analysis. Commercial thermal desorber units are available from Markes, PerkinElmer, Shimadzu, and others, for most GC systems.

The parameters for TD sampling and analysis, including sorbent type/amount, sampling/desorption temperature, flow rate, breakthrough/retention/ safe-sampling volume, and split ratio, all affect the performance of the system. One of the most important factors is breakthrough/retention/safe-sampling volume, which defines the volume of sample that can be quantitatively sampled to provide the desired or specified detection limits. By definition,

breakthrough/retention volume is the sample volume passed through the TD tube until the outlet concentration becomes equal to 5% of the inlet. The sampling volume is defined as 2/3 of the breakthrough volume. The breakthrough volume mainly depends on the type and amount of sorbent, the analytes in the sample and the environmental conditions (mainly temperature and humidity). To reach a low detection limit, it is crucial to choose the right configuration with the right breakthrough volume. For example, in order to deliver 1 ng to the detector, it is necessary to have a breakthrough volume larger than 100 L for a sample concentration of 0.01 ng/L.

Humidity level is an important aspect of VOC sampling and analysis, and greatly affects most sample enrichment techniques. High levels of water vapor lead to compromised results or even component damage (mostly the GC column). For TD methods, humidity can affect the breakthrough volume of the sorbent; as high as 90% reduction in breakthrough volume can occur and lead to inaccurate results if not removed prior to analysis.[44] Most weak and medium sorbents (polymeric materials and graphitized carbon) are hydrophobic, and can tolerate as high as 80% relative humidity.[44,45] However, carbon molecular sieve (CMS), a relatively strong sorbent, can trap large amounts of water vapor.[45,46] In order to minimize the effect of high humidity, many approaches have been used, including utilizing small sample volume and sorbent, warming the tube and, most popular, adding a dry purge step prior to analysis.[45] During dry purging, a flow of pure dry air or nitrogen is passed through the primary and/or refocusing trap in the sampling direction prior to desorption.

A carefully designed TD system can easily achieve sub-ppb detection limits. Recent publications show below ppb detection limits for various analytes under different conditions. Le Calve et al.

reported two thermal desorption systems to analyze BTEX with detection limits ranging from 7 to 85 ppt; the temperature of the second stage trap was kept at -30 °C for better focusing.[47] An automated system was developed to collect and analyze VOCs, which utilized trap sizes of 10 in. x 1/8 in. (1st stage) and 10 in. x 0.042 in. (2nd stage, cooled to -30 °C when sampling); the detection limits were less than 100 ppt for the 41 tested VOCs.[48] Borrull et al. compared the performance of solvent extraction and TD for determining levels of 90 VOCs. The TD system showed better repeatability and recovery, and lower limits of detection and quantification for all target compounds.[49] The method quantification limits for a sampling volume of 1200 mL during a sampling campaign were between 0.03 and 1.67 ng/m^3 (below 1 ppt) using TD with GC-SIM-MS.[50]

For sub-ppm sampling, TD promises: (1) fast and accurate quantitation, (2) reliable and reproducible results, (3) applicability for on-site/field analysis, (4) low detection limits, and (5) easy calibration and automation. On the other hand, TD has the following limitations: (1) high initial cost, (2) need for power to operate, and (3) limited applicability for very volatile and thermally labile compounds.

1.3.2 Whole-air sampling/enrichment

The simplest and most straightforward way to sample air is by collecting it in a container, called "whole-air sampling." The collected sample can then be analyzed by direct injection into GC or GC-MS, or more commonly, with an intermediate pre-concentration step. The most popular containers used in whole-air sampling are stainless-steel containers (canisters) and polymer bags (Tedlar bags).[3] Air sampling bags are usually inexpensive and range from 500 mL to 100 L,

while canisters are considerably more expensive and are usually between 0.4 to 15 L. Canisters were first introduced by Hutton and Rasmussen to use with a cryogenic pre-concentrator for analyzing chlorinated hydrocarbons and reduced sulfur compounds at ppt levels.[51] Air bags are typically used once for a short period of time as compounds may not remain stable for more than 24-48 h. Air sampling bags can be permeable to certain compounds and water vapor, which leads to inaccurate results.[3,52] In contrast, canisters are usually passivated using chemical treatments to make their surfaces inert, and they can store samples up to 30 days and be re-used after cleaning.[53]

For whole-air sampling, the sample can be pulled (under sub-atmospheric pressure) or pushed (pressurized with a pump) into the canisters. The push mode collects more air volume with the potential of introducing contamination from the pump. Either mode can perform grab sampling or integrated sampling. For grab sampling, samples are taken during a short time period to measure VOC concentrations at specific times. For integrated sampling, a flow regulator is used to meter sample over a few hours/days for measuring the time-weighted average (TWA) concentration.

For whole-air sampling, sample is collected at the sampling site and then transported back to the laboratory for analysis. There is no sample enrichment in the sampling step; therefore, an additional pre-concentration step is necessary to improve the detection limits.
Both sorbent and cryogenic trapping can be used for enrichment.[52] In EPA Method TO-14A, another focusing step is added via cooling the GC oven to -50 $^{\circ}$C.[54] VOCs are then cryogenically

focused on the head of the column to achieve good chromatographic performance and good sensitivity.

A typical canister sampling system is schematically illustrated in Figure 1.4. During sampling, the canister is connected to the sample collection system in the field for sub-atmospheric pressure or pressurized sampling. This is followed by transferring the canister to the analytical laboratory for analysis, where it is connected to the analysis system, and sample is directed from the canister through a dryer into a cryogenic or sorbent trapping unit via a six-port valve. Finally, the trapped analytes are released by heat into a GC-MS system for analysis.

As described in EPA 14A, the canister method has sub-ppbv detection limits for a 300-500 mL whole air sample.[54] The detection limits mainly depend on how good the sample is preserved, the enrichment factor for the concentration/analysis step, and the sensitivity of the detector. An appropriate canister passivation technique is needed to ensure good sample integrity and to achieve good sensitivity. Summa canisters achieve inertness from a chrome-nickel oxide layer coating, while fused-silica-lined canisters have a thin fused silica coating.[53] Sorbent trapping and cryogenic trapping are commonly used to improve method detection limits. Tolnai et al. used a three-adsorbent trap cooled at -80 $^{\circ}$C to enrich the sample from a canister; 52 VOCs were measured at levels as low as 10-100 ppt.[55]

High humidity can affect the whole-air sampling approach. If sample is pressurized inside the canister, condensation may occur, which may affect the humidity level after sample is released from the canister, and analytes may be lost in the aqueous phase.[56] An in-line permeable

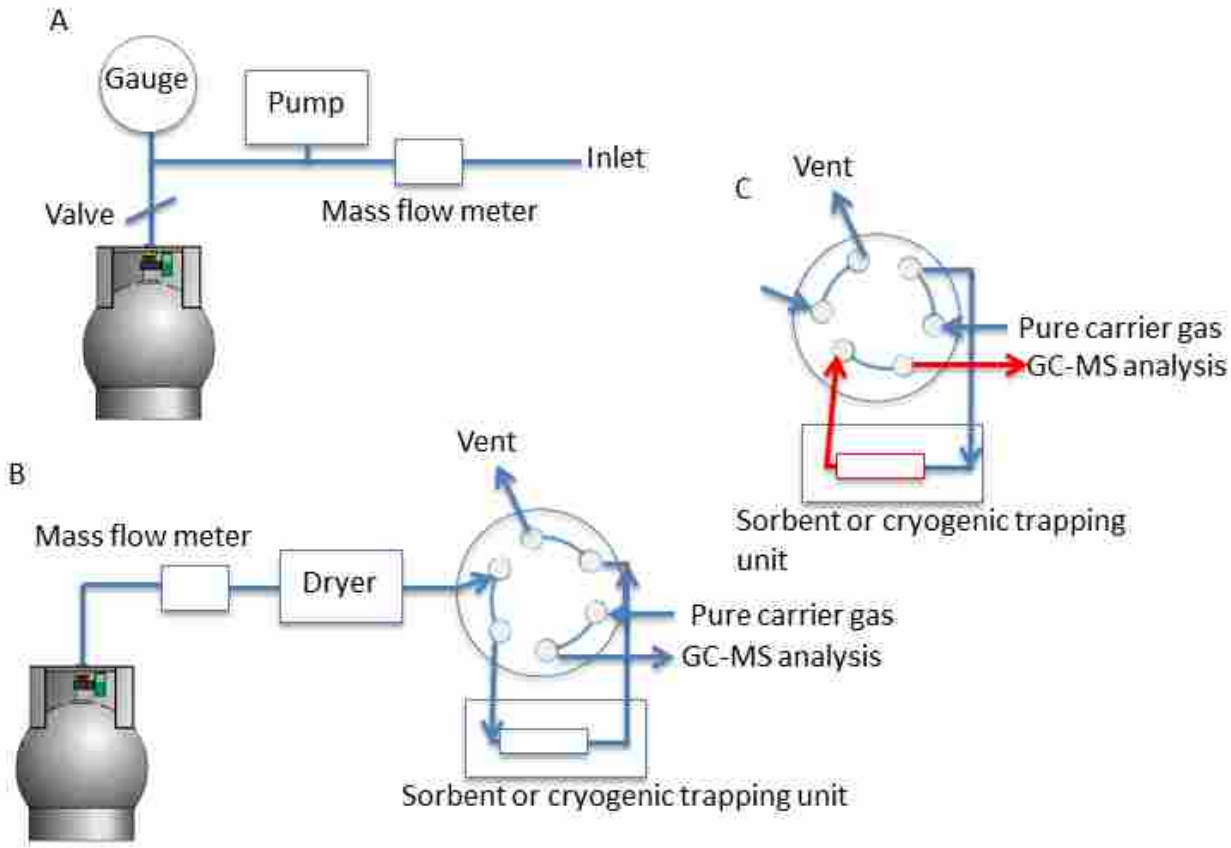

Figure 1.4 Simplified canister sampling and analysis system: (A) subatmospheric pressure or pressurized canister sampling, (B) sample transfer from canister to focusing trap, (C) desorption from trap to GC-MS.

membrane dryer such as a Nafion® dryer or a dry purge are often used prior to GC-MS analysis. The former eliminates both water and polar organic compounds before they reach the refocusing trap, while the dry purge (i.e., dry carrier gas) eliminates water vapor and very volatile compounds such as C_2 hydrocarbons.

Whole-air sampling is a good approach for sub-ppb level sampling. Compared to TD methods, there are some advantages with whole-air sampling: (1) a single collected sample can be analyzed multiple times, (2) there is no breakthrough of target compounds and no need for thermal or solvent desorption from the sampler, (3) long storage time is possible, (4) integrated sampling for long-term average concentration is convenient, (5) remote or automatic sampling is possible, (6) a wide range of VOCs can be collected, and (7) no field calibration is needed. On the other hand, it can be plagued with problems such as: sample instability/degradation during storage, potential contamination from collection/storage/cleaning, need for cleaning before each sampling event, limited volume (i.e., canister volume) and bulky sampling device.

1.3.3 Solid phase micro-extraction (SPME)

Solid phase microextraction (SPME) is a novel sampling technique in which a fiber is used to perform sampling and pre-concentration in a single step. SPME is an equilibrium-based method using a fiber coated with a sorptive film to enrich sample from its surrounding environment. Pawliszyn et al. first reported the SPME method in the 1990s for sampling liquid samples.[57] They later applied this technique to extract VOCs from air, followed by analysis using a GC-MS system.[58]

The SPME device is comprised of a coated fused-silica fiber and a modified syringe holder. The SPME method involves the following steps. First, the fiber is extended and exposed to a sample vapor matrix, during which analytes partition between the gas phase and the fiber coating until equilibrium is reached. After the sample is enriched in the fiber film, the fiber is retracted back into the needle of the syringe holder for storage. Finally, the SPME syringe needle is inserted into a heated GC port where analytes are thermally released from the extended fiber for analysis.[57] In addition to sampling as described above, time-averaged sampling can be done by extended exposure of the fiber to the sample.[59]

Compared to TD and whole-air sampling, quantitation with SPME is challenging as both the volume sampled and the percentage of sample trapped is unknown. Because the amount trapped on the SPME fiber is proportional to the initial concentration in the sample, the sample concentration can be calculated from a calibration curve prepared from gas standards under similar conditions. Also a semi-empirical equation can be used to determine the partition coefficient as well as sample concentration.[60]

Unlike TD and whole-air sampling, the SPME technique enriches the VOC concentration only during the sampling step; no further enrichment is involved during the analysis. There have been many attempts to improve the enrichment factor/detection limit in SPME air sampling, all related to the partition coefficient. First, film type, length and thickness have major effects on the partition coefficient. Different films have been developed, including polymeric films (e.g., PDMS/DVB), similar to those used in TD, graphitized carbon materials (e.g., Carbotrap materials), carbon molecular sieves (e.g., Carboxens), and sol-gel based coatings, as well as

reactive chemicals for trapping specific analytes such as formaldehyde.[61-63] Choosing the best film (high partition coefficient for the target analytes) and greater fiber coating can increase the enrichment factor.[64] Second, a lower fiber temperature leads to a higher partition coefficient.[65] Therefore, a lower temperature leads to better detection. Finally, dynamic sampling (i.e., pumping air sample over the SPME fiber instead of sampling a static air sample) and equilibrium sampling (i.e., waiting until equilibrium is fully reached) maximize the enrichment factor.[66-68] Generally, SPME is applicable to the ppb to ppm range; with carefully selected conditions, this method can achieve ppt detection limits for some analytes.[58,69] Humidity also plays an important role in SPME VOC sampling. Generally, high humidity leads to lower extraction efficiency as water molecules occupy available sorption sites.[70] However, short-term sampling (far before equilibrium) is less affected by humidity as these sites are not saturated.

Compared to other methods, SPME is a simple approach to detect low-level VOCs in the air. First, SPME is convenient, small/compact and relatively inexpensive, with no additional accessories. Also, it is environmentally friendly, and it has good linear response over a wide concentration range. There are some shortcomings of SPME sampling: quantitative measurements are difficult to obtain, standard gas calibration is required and matrix effects may affect the results. Compared to other sampling methods, enrichment factors are generally lower and lead to higher detection limits. Finally, SPME is more sensitive to environmental conditions; temperature, sample matrix and other factors affect the trapping efficiency.

1.3.4 Other sampling techniques

In addition to the methods described above, there are a variety of other less popular enrichment

techniques to detect low level VOCs, such as cooled membrane,[71] needle trap,[72] membrane introduction mass spectrometry[73] and passive air sampling.[2] The key to achieving low detection limits is having a high enrichment factor. High capacity and high affinity/partition coefficient are essential to achieving a high enrichment factor.

1.4 High flow rate air sampling

1.4.1 General considerations

Although mainstream methods like thermal desorption can detect low level VOCs, it usually requires extremely long sampling time. For example, the STEL (short-term exposure limit) level for VX (a nerve agent) is 10 ng/m^3.[74] Assuming that reliable detection requires trapping and desorption of 1 ng of analyte, then a conventional TD tube sampling at 150 mL/min would take up to approximately 700 min and 100 L to detect the STEL level of VX, which is not safe or convenient. Even if the target analyte is present at a much higher level, 150 mL/min is still usually not fast enough to grab the sample and get away from a dangerous location. Another issue with current approaches is that most of the methods are not suitable for on-site analysis because of the complex desorption/analysis system. Also, many TD and canister methods require liquid nitrogen for cryogenic cooling, which is usually not available for on-site analysis.

An alternative approach to solve the problem of detecting low concentration VOCs is high/fast flow rate sampling, because the amount the sampler collects is directly proportional to the flow rate and the time. As time becomes limited in certain applications because of the need for fast response, in order to detect trace levels of analytes, increasing the sample flow rate is the only option. Therefore, there is a need to sample VOCs at very high flow rate to collect analytes from

a large volume for detection without an ultra-sensitive detector. Instead of providing the detector with 0.5 ng of sample by TD sampling for 2 h at 150 mL/min, 4.2 ng can be collected by sampling the same sample at 10 L/min for 15 min.

There are some challenges associated with high flow rate air sampling. For active air sampling, a hand-portable air pump is usually used. Such pumps have a limited maximum back-pressure, on the order of 10-20 in. water (0.36 to 0.72 psi). Since the back-pressure is directly proportional to the flow rate, at a higher sampling flow rate, the back-pressure would increase accordingly. Exhaustive trapping under high flow rate conditions is very difficult, as it involves forcing the sample to pass through a long, densely packed sorbent, which produces a very high back-pressure. In contrast, equilibrium-based high flow sampling is much easier with respect to back-pressure. In addition, high flow rate sampling and large sample volume requires large breakthrough volume. A large breakthrough volume would require a large amount of sorbent, which would cause problems in the desorption step. Choosing the right sorbent type and amount to provide large breakthrough volume for analytes of interest and reasonable desorption volume is crucial.

Currently, there are no commercially available systems that sample at flow rates of L/min, and only limited research has been reported for both equilibrium and exhaustive modes. There is currently no working system for exhaustive trapping of a wide range of VOCs at flow rates of L/min (some research indicates that certain systems work for specific analytes).

1.4.2 Equilibrium-based high flow sampling

With the growth of SPME sampling, some researchers tried to operate active SPME air sampling at high flow rate. Koziel et al. and Augusto et al. developed a portable dynamic air sampler (PDAS) to use with SPME.[70,75] In their design, the PDAS generated a flow stream in which an unmodified SPME fiber was inserted perpendicular to the flow for sampling VOCs. Greater adsorbed VOC mass compared to conventional SPME extraction in static air, and detection limits of low ppb in only 30 s were achieved with this technology. Hook et al. reported that a high flow rate SPME device operated at a flow rate of 2.16 L/min using a PDAS was employed to detect the chemical warfare agent sarin.[76] The average linear sampling velocity was 21 cm/s, which is higher than the threshold sampling velocity (10 cm/s) that is needed to ensure that the mass uptake rate remains nearly constant.[70] Another group developed a novel high flow air sampling system by coating a solid sorbent onto a 100 mm x 0.127 mm o.d. nickel alloy wire which served as the sampling device as well as resistively-heated wire for desorption. The coated wire was further wound in a helical fashion with a constant pitch around an inner borosilicate glass tube to maximize contact between the flowing air and the wire.[77] High air sampling flow rates up to 4-5 L/min were achieved.

When using SPME for high flow sampling, instead of being limited by the back-pressure, there is an extraction efficiency limitation (i.e., the amount of analyte that can be sorbed by the SPME) which depends on the linear velocity of air passed over the SPME film, and a capacity limitation (i.e., the amount that can be retained on the fiber as a result of the sorbent amount). In addition, an equilibrium-based high flow trap is also more difficult to use for quantitation and for low concentration samples.

1.4.3 Exhaustive-based high flow sampling

Exhaustive trapping at flow rates of L/min is very difficult to accomplish. The two major problems are high back-pressure and short trapping time/path length at high linear velocity. One way to achieve high flow exhaustive sampling is by bundling multiple wall-coated capillaries together. There have been a number of studies that describe the use of a multi-capillary sampler,[78,79] including one from our group;[80] sampling rates as high as 16.7 L/min were achieved.[78] One of these devices consisted of 120 capillaries.[81] However, there are several problems associated with the multi-capillary high flow trap approach. First, with a thin layer coating on the walls of the capillaries, the interaction (breakthrough volume) for volatile compounds is usually not very good. While multiple bed packings can be used in packed traps to increase interaction; using multiple coatings in capillaries is relatively difficult. Second, large i.d. (530 μm) capillaries are usually used in high flow rate samplers,[80] which makes it difficult for semi-volatile compounds to migrate from the center of the capillaries to the coated capillary walls (poor mass transfer).[82] For example, the minimum length of an open tubular trap, which would allow 99% of an analyte, methyl salicylate, to diffuse to the wall is 9.5 cm for a flow rate of 100 mL/min. Based on the following equation,[82]

$$L = \frac{1.2 \times u \times r^2}{D} \quad (1.1)$$

where L is the length of the capillary, u is the linear velocity, r is the internal radius and D is the diffusion coefficient of the analyte, the length is directly proportional to the square of the radius. Longer capillaries would increase the back-pressure (i.e., the back-pressure from forty 530 μm i.d. x 20 cm capillaries is higher than 20 in. water). Finally, it is a technical challenge to bind multiple capillaries together, connect the assembly to a metal fitting, and then maintain a good seal during cycling from 5 °C to 350 °C.

1.5 Needle trap and refocusing/second stage trap

The needle trap is an extraction device that contains sorbent materials inside a needle, in which analytes are sorbed, similar to TD.[83] The needle trap is a good candidate for green chemistry, as it is usually solvent-less, compact, and can be desorbed simply inside a heated injector.

A typical needle trap device for air sampling usually includes three parts: an empty needle with openings at each end, one to three sorbent layers with each weighing approximately 1 mg, and two retaining obstacles at each end of the packed bed to keep the sorbent in place as shown in Figure 1.5A. The needle trap device was first reported in the 1970s for fragrance detection.[84] The principle of needle trap VOC sampling is fairly simple. Using a pump or syringe to create a pressure difference between the two ends of the needle trap, air sample with VOCs is forced to flow through the needle while the sorbents extract the VOCs. The needle trap is then thermally desorbed in the GC injection port with carrier gas. A clever design from Pawliszyn's group simplified the desorption process; a modified gooseneck liner was used to divert the carrier gas temporarily through the sorbent bed for desorption (Figure 1.5B).[85] With this design, the flow through the column is held constant and no additional flow control system is needed. The sorbent materials used in the needle trap are similar to those used in TD, including polymeric materials (e.g., Tenax and XAD resins), graphitized carbon materials (e.g., Carbotraps), and carbon molecular sieves (e.g., Carboxens).

The needle trap can be used for exhaustive active sampling, passive equilibrium sampling or active equilibrium sampling. Various applications have been reported using a needle trap as air

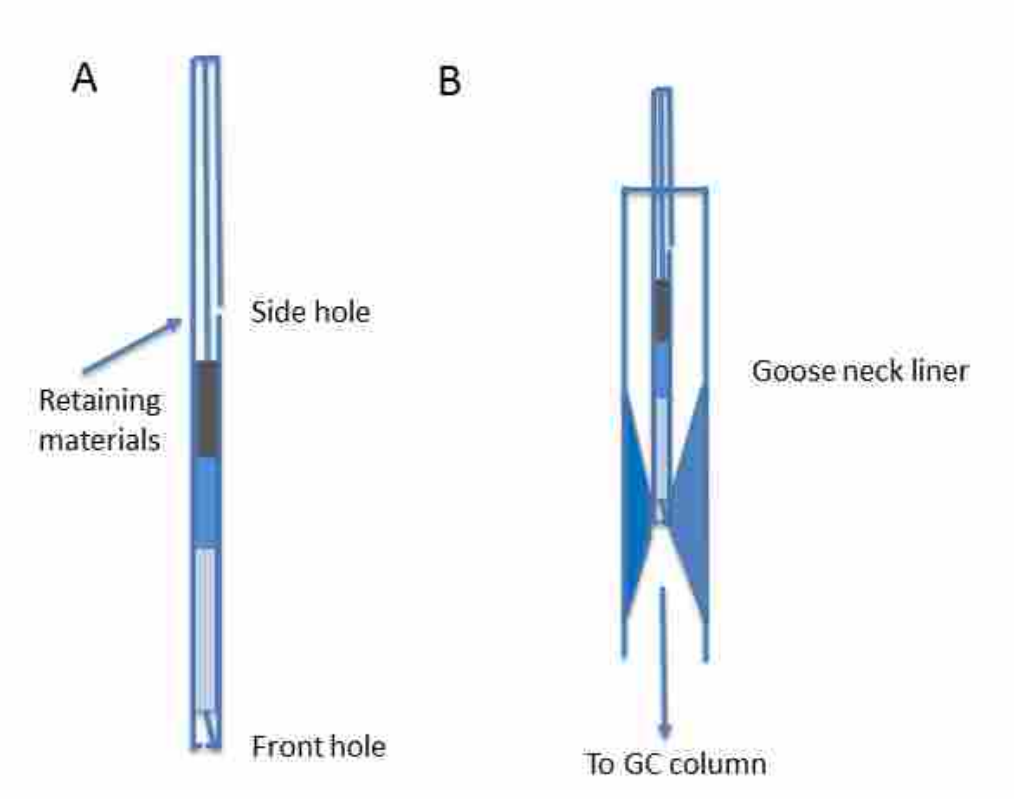

Figure 1.5. (A) Needle trap with a side hole and three adsorbent materials, (B) Desorption of sample from a needle trap inside a goose-neck liner in the GC injector.

sampling device. Mieth et al. used a multi-bed needle trap to perform on-site sampling and pre-concentration of volatile breath biomarkers.[86] LODs (limits of detection) of parts per trillion to parts per billion were achieved for various VOCs without cryofocusing. Good linearity was observed with calibration curve R values > 0.98. The use of a needle trap device for time-weighted average (TWA) diffusive sampling of BTEX was reported.[87]

As described in the previous sampling/enrichment section, desorption band widths from TD tubes usually range from a few seconds to a few minutes, while GC requires an injection band width that is less than 2 s.[88] In order to solve this problem, a two-stage desorption approach is usually used. Instead of desorbing analytes directly into the injection port, the analytes are first transferred to a second-stage trap to be refocused into a narrower band. After the first-stage trap is completely desorbed, analytes in the second-stage are introduced by rapid heating into the GC within a narrow band. The current industry standard for the second-stage trap is a 1/8 in. micro concentrator, which is used to transfer sample from a primary trap to the GC-MS or other detection system.

The commercial second-stage micro concentrator is usually connected to the GC system with a modified injector, and an additional heating/cooling system is used. However, this is not convenient, especially for on-site analysis. The simplicity of the needle trap design and its compatibility with a standard injector make it an ideal candidate for the refocusing trap. One limitation for using the needle trap as a refocusing trap is, at least at this point in time, the availability of only manual operation compared to full automation already developed for

conventional 1/8 in. micro concentrator systems. However, in recent years, researchers have successfully used the needle trap in automated VOC analysis systems.[89,90]

1.6 On-site analysis and portable instruments

On-site analysis is defined as analysis of sample on the spot in its original environment instead of transferring it back to the laboratory for analysis. There are many applications for which on-site analysis is beneficial. For example, one can envision events where timely response is critical, such as in the battle field where immediate knowledge is required to make the next move, or in a fire situation where precautious must be taken for hazardous chemicals and other potential threats.[91] For other events, it may be impossible to perform the analysis at another location. For forensics applications, it is often unrealistic and expensive to transfer the sample back to the laboratory for analysis; on-site analysis provides the most reliable and immediate analytical result. Compared to transferring analytes back to the laboratory for analysis, on-site analysis can provide timely results while preserving good sample integrity.

In recent years, various portable GC and GC-MS instruments have been developed, which make on-site analysis possible and popular.[92,93] Portable GC-MS is the most widely used technique to perform on-site analysis of VOCs because of its ability to quickly identify and quantitate unknown VOCs. Various commercial systems have been developed: HAPSITE™ from INFICON, TRIDION™ from Torion/PerkinElmer, GARDION™ from Smiths Detection and GRIFFIN™ from FLIR. All of these systems can accommodate various methods to introduce samples for analysis, including direct liquid injection, SPME, gas sampling, and thermal desorption. Concentration levels as low as ppt have been reached for some compounds.

However, compared to laboratory benchtop instruments, portable instruments have some limitations, including some compromise in sensitivity, frequent maintenance and calibration, and reliance on battery life. These problems are challenging when dealing with trace analyte detection, as small amounts of analytes are available and signal-to-noise ratio is low. One way to compensate for the compromised performance of portable instruments is by introducing more sample or using better sample collection methods. Generally, more analyte amount provides better signal-to-noise ratio as well as more stable signal. Therefore, for VOC analysis, a high flow air sampler would greatly improve the performance of portable instrumentation by increasing the amount of analytes collected. Compared to conventional TD tubes, more than 10-50 times greater flow rate for collecting samples would lead to more than one order of magnitude improvement in detection limits.

1.7 Conclusions

In this chapter, current enrichment techniques and detectors that are used to reach very low detection limits (ppt range) were reviewed. The current status of high flow air sampling, needle trap, and on-site analysis were summarized. It is clear that using current techniques for sampling VOCs at ppt levels is far from ideal. High flow rate sampling is a good option for low level and fast VOC detection, which is especially important for on-site analysis because of the lower sensitivity of portable instruments.

In the following chapters, I describe work performed on high flow air sampling, first using a multi-capillary sorbent trap (Chapter 2), followed by an alternative trap based on a concentric packing design (Chapter 3). Chapter 4 describes a novel approach for generating an internal

standard for a high flow air sampling system. Finally, Chapter 5 provides suggestions for further investigation of high flow trap systems and their applications.

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Chapter 2 Multi-capillary High Flow Rate Trap

2.1 Introduction

As described in Chapter 1, the ability to detect VOCs at ppt (parts per trillion) levels is important in certain applications. With current technologies, long time period (hours with a thermal desorption system), complex system, and off-site analysis (whole air sampling or proton transfer reaction-mass spectrometry) are required to detect ppt levels of VOCs. The idea of high/fast flow rate sampling is reasonable to achieve low detection limits (<100 ppt) with GC-MS in a short period of time as described in Chapter 1. By combining the advantages of a high flow rate air sampler and a needle trap, the goal was to reach a 5-10 L/min air sample collection rate and low ppt detection limits without cryogenic cooling for both laboratory and on-site portable instruments. The approach I explored was to use a multi-capillary bundle (i.e., a parallel assembly of analytical capillary GC columns) for high flow rate sampling of low level VOCs.

In this chapter, I describe efforts to develop a multi-capillary high flow rate air sampling trap. Several different open tubular columns were evaluated for constructing the high flow rate trap. By varying the coating material and capillary length, retention and desorption efficiencies for various VOCs were evaluated. Several high flow traps were constructed with bundled capillaries and tested with two-stage analysis using a needle trap.

2.2 Materials and methods

2.2.1 Chemicals and materials

All chemicals used were from Fisher Scientific (Pittsburgh, PA, USA) and Sigma Aldrich (St. Louis, MO, USA). A 110 ppb gas mixture containing benzene, ethylbenzene, methyl-*tert*-butyl

ether (MTBE), toluene, *m*-xylene, *o*-xylene and *p*-xylene was purchased from Air Liquide (Houston, TX, USA) and used in this work.

2.2.2 Instrumentation

Dynamic vapor generation. A challenge for testing the high flow trap is preparing a large amount of low concentration (ppt to ppb) gas standards, sufficient for 5-10 L/min testing for hundreds of hours. There were three key experiments that relied on these gas standards: breakthrough volume measurements, desorption testing and quantitative measurements. There are various ways to prepare gas standards; the most accurate and widely used method is micrograviметric preparation, which involves carefully weighing the components.[1,2] Due to high cost and time-consuming procedures, micrograviметric preparation was not suitable for this work. Therefore, the first approach that was evaluated was a custom-made device called a dynamic vapor generator, which vaporizes analytes from a syringe pump into a gas stream and then further dilutes their concentrations down to the desired level. As shown in Figure 2.1, an analyte test sample (a pure target analyte or a dilute solution for lower vapor concentration) was prepared and introduced into the syringe of a syringe pump (Harvard Apparatus, Hollison, MA). The syringe pump pushed the solution into an injector (Agilent 5890 GC), which was heated at 250 $^{\circ}$C. Carrier gas (N_2, 100-200 mL/min), controlled by a mass flow controller (Brooks 5850E, Hatfield, PA), was passed through a hydrocarbon filter (Restek, Bellefonte, PA) and mixed with the vaporized analytes to form a standard gas stream of high ppb to ppm concentration. This gas

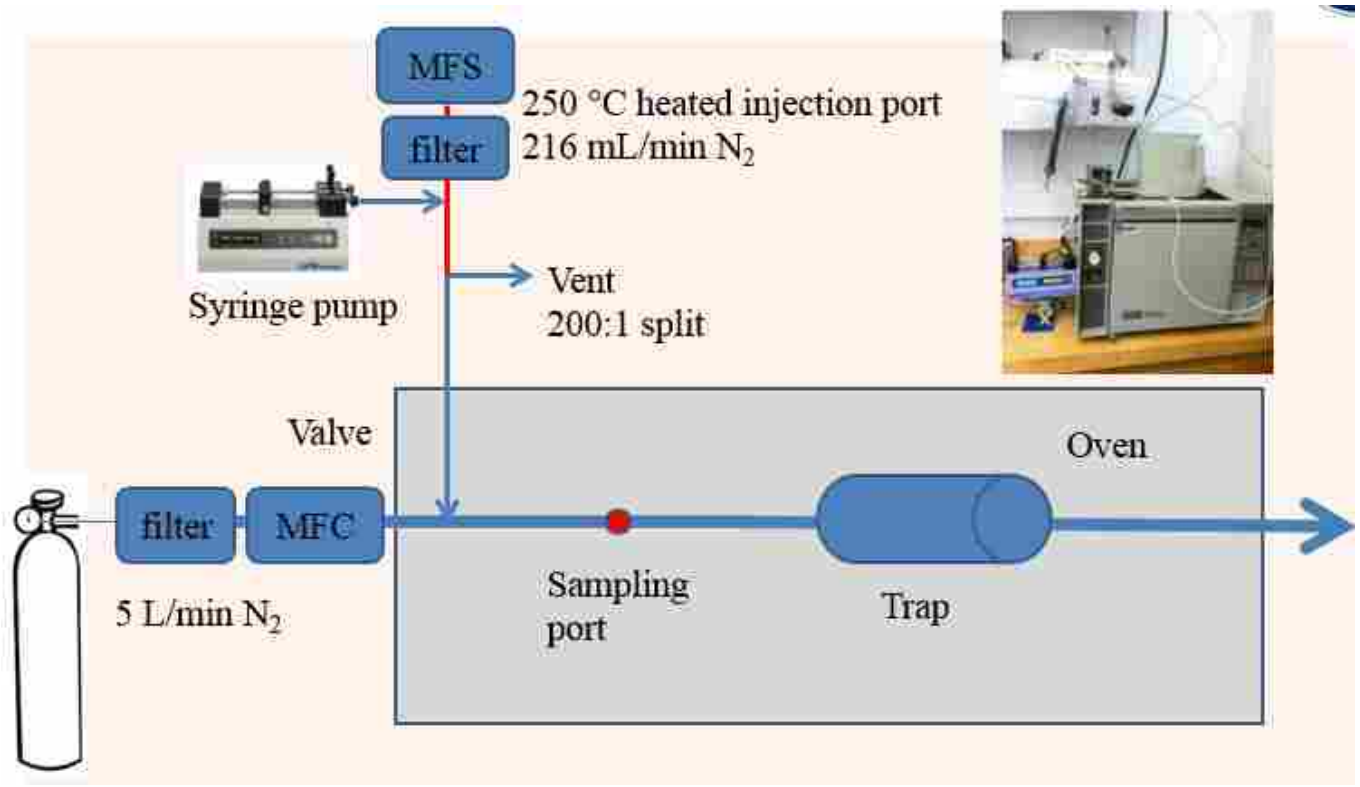


Figure 2.1 Schematic of the dynamic vapor generator.

stream was reduced by a split valve and then further diluted down to the ppt range using a high flow (5-10 L/min) nitrogen stream. The resultant gas stream gave a concentration of low ppt to ppb with a flow rate of 1-10 L/min, determined by the flow rate, split ratio, solution concentration and pump speed. Ideally, this stream could be used for breakthrough volume, desorption volume, and quantitation measurements.

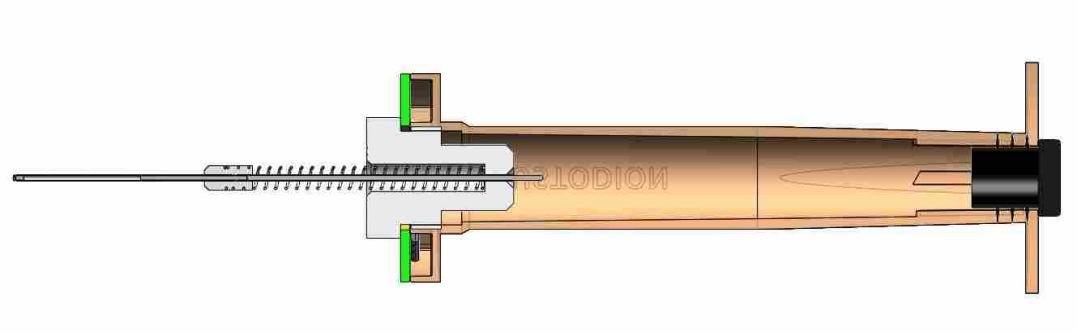
An alternative way to generate a standard mixture is a combination of microgravimetric preparation and dynamic dilution. A low ppt VOC standard flow stream was generated by dynamically diluting a high concentration commercial standard (ppb to ppm range, prepared using a microgravimetric method) with clean nitrogen gas. This method provided a consistent high flow VOC stream, especially at low ppt levels. A 110 ppb of BTEX and MTBE [benzene, ethylbenzene, methyl-*tert*-butyl ether (MTBE), toluene, *m*-xylene, *o*-xylene, and *p*-xylene] was used in this work. An approximately 20 cm long empty capillary (Polymicro Technologies, Phoenix, AZ) with 75 μm i.d., was used to restrict the flow rate from the standard gas tank to between 0.5 to 60 mL/min as controlled by a regulator. This high concentration flow was then mixed into a nitrogen gas stream through a tee to generate a desired sample stream of 0.2 to 10 L/min. At least 1-h equilibrium time was provided before each sampling event and the system was maintained at room temperature.

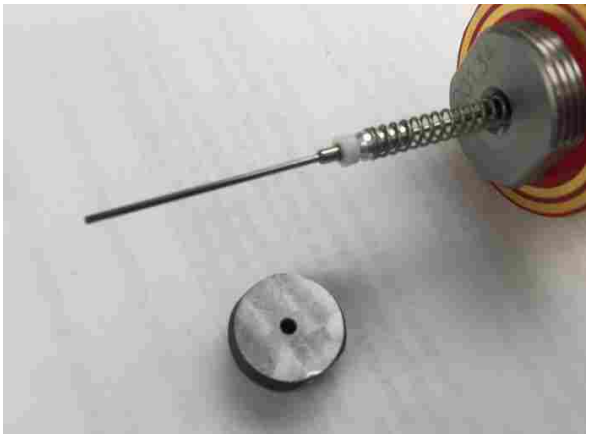
Gas chromatographic instrumentation. Breakthrough experiments with frontal chromatography and desorption volume measurements were performed using an Agilent 7820A GC-FID system (Santa Clara, CA, USA). All needle trap analyses were performed using an Agilent 5890 GC system coupled to an Agilent 5972 MSD. The GC-MS system contained a fused silica capillary

column (10 m × 100 μm i.d. × 0.1 μm film of Rxi-5ms) from Restek (Bellefonte, PA). A custom-made quartz liner as shown in Figure 2.2 was used with a split/splitless injector for all needle trap injections. Helium was used as carrier gas for all GC analyses.

Typical chromatographic operating parameters included 300 °C inlet temperature, 10 s splitless injection (15:1 split ratio after 10 s), 45 psi constant pressure, 310 °C transfer line temperature between the GC and MSD, and temperature program with initial temperature of 35 °C for 1 min, and then ramp to 250 °C at 30 °C/min, with a final hold time of 1 min. The FID operating conditions were: 250 °C, 450 mL/min air, 40 mL/min hydrogen, 15 psi make-up helium flow, and 5 Hz data rate. The MSD operating parameters for all experiments were: 164 °C EI source temperature, 35–350 m/z mass range, 35 μA emission current and full scan mode. All data were collected using Agilent Chemstation, and the processed data were exported as peak areas to Microsoft Excel (Redmond, WA, USA) for final processing; quantitation was based on integrated peak areas.

Needle trap and accessories. Both custom-made and commercial (Torion Technologies, American Fork, UT) needle traps were used. They were fabricated by packing 1 mg of Tenax TA, 1.6 mg of Carboxen 1006 and 1.5 mg of Carboxen 1003 into a customized 19- gauge needle from SGE (Victoria, Australia). The needle had two inlets/outlets: one at the free needle end and the other on the side of the needle above the sorbent. A sliding Teflon cylinder attached to a spring manually covered the side hole for sample preservation. Desorption of the needle trap was achieved using a goose-neck liner inside a GC injector to temporarily force the carrier gas to flow through the needle bed.[3] A Merlin nut was modified to accommodate the needle trap inside





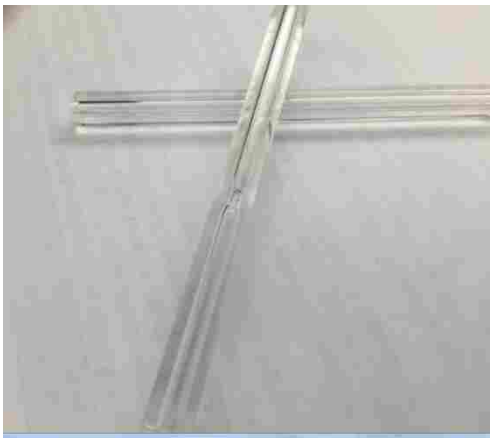


Figure 2.2 Needle trap, modified Merlin nut, and gooseneck liner.

the Agilent GC system. The needle trap and its accessories are shown in Figure 2.2; the Teflon cap is pushed away from the side hole by the injector cap as the needle is inserted into the GC injection port, or during sampling.

2.2.3 Preparation of bundled capillary traps

Five different types of capillary GC columns were used for fabricating the high flow trap, including a 30 m x 0.53 mm i.d. Carboxen 1006 PLOT column from Supelco (Bellefonte, PA), a 60 m x 0.53 mm i.d. x 7 μm d_f RXT-1 column, a 30 m x 0.53 mm i.d. x 20 μm d_f RT-Q-BOND PLOT column, a 30 m x 0.53 mm i.d. x 20 μm d_f RT-QS-BOND PLOT column, and a 30 m x 0.53 mm i.d. x 0.15 μm d_f Rxi-5HT column from Restek (Bellefonte, PA). These capillaries were cut into lengths of 8.9 cm (3.5 in.), 19.1 cm (7.5 in.) and 57.0 cm to be used as single capillary traps or bound together in multi-capillary traps.

Binding of multiple capillaries together to form a high flow trap was achieved by the following steps. First, the open tubular column was cut into the pre-determined lengths of the traps (8.9 to 57.0 cm) using a column cutter. Then, the capillaries were inserted into a 3.0 cm long ¼ in. o.d. tube to determine the maximum number of capillaries that would fit in this tubing size. High temperature heat-conductive epoxy (H70E, Epoxy Technology, Billerica, MA) was applied to the outside of each capillary approximately 0.5 cm from the ends. Two 3.0 cm ¼ in. o.d. tubes were placed at both ends of the capillary bundle to keep the capillaries in place and to provide easy coupling to a Swagelok fitting. Additional epoxy was used to fill the gaps between the capillaries in the middle section after the epoxy on both ends was cured (approximate 12 h). Finally, the epoxy was fully cured in an oven at a temperature of 150 ˚C for 1 h under an inert

gas. Figure 2.3 shows several traps prepared according to this procedure. Modifications were made to the multi-capillary traps used in the two-stage quantitation experiments as described in Section 2.3.4

2.2.4 Methods

Breakthrough and desorption volume measurements. The breakthrough volume is defined as the volume passed through the sorbent tube until the outlet analyte concentration reaches 5% of the inlet concentration as discussed in Chapter 1. The most straightforward method to measure the breakthrough volume is by using frontal chromatography. A continuous vapor sample is introduced into the trap device, and the signal at the outlet is monitored with a flame ionization detector (FID). A system was constructed to test the breakthrough volume for various trap devices, and a 2-position, 6-port valve (VICI, Houston, TX) was used to switch between the sampling mode (for breakthrough measurements) and the desorption mode. As shown in Figure 2.4, in the sampling mode, one end of the trap was fed continuously with sample, while the other end was monitored with an FID. After sampling, the valve was switched to the desorption mode, and the flow direction was reversed. The new inlet of the trap was connected to a source of clean carrier gas while the other end was monitored with an FID. With this design, it was possible to feed the trap in one direction to measure the breakthrough volume and then desorb it in the reverse direction for desorption volume measurement. During high flow rate breakthrough volume measurements, as the FID cannot handle a very high flow rate directly, a split valve and a tee were used to divert to waste the extra gas from the outlet of the trap to maintain a stable flow rate of approximately 20 mL/min to the FID. For the desorption experiments, after the trap was loaded with 10 min of sample, the carrier gas flow rate was set at 20 mL/min and the oven

Figure 2.3 Multi-capillary traps with various lengths.

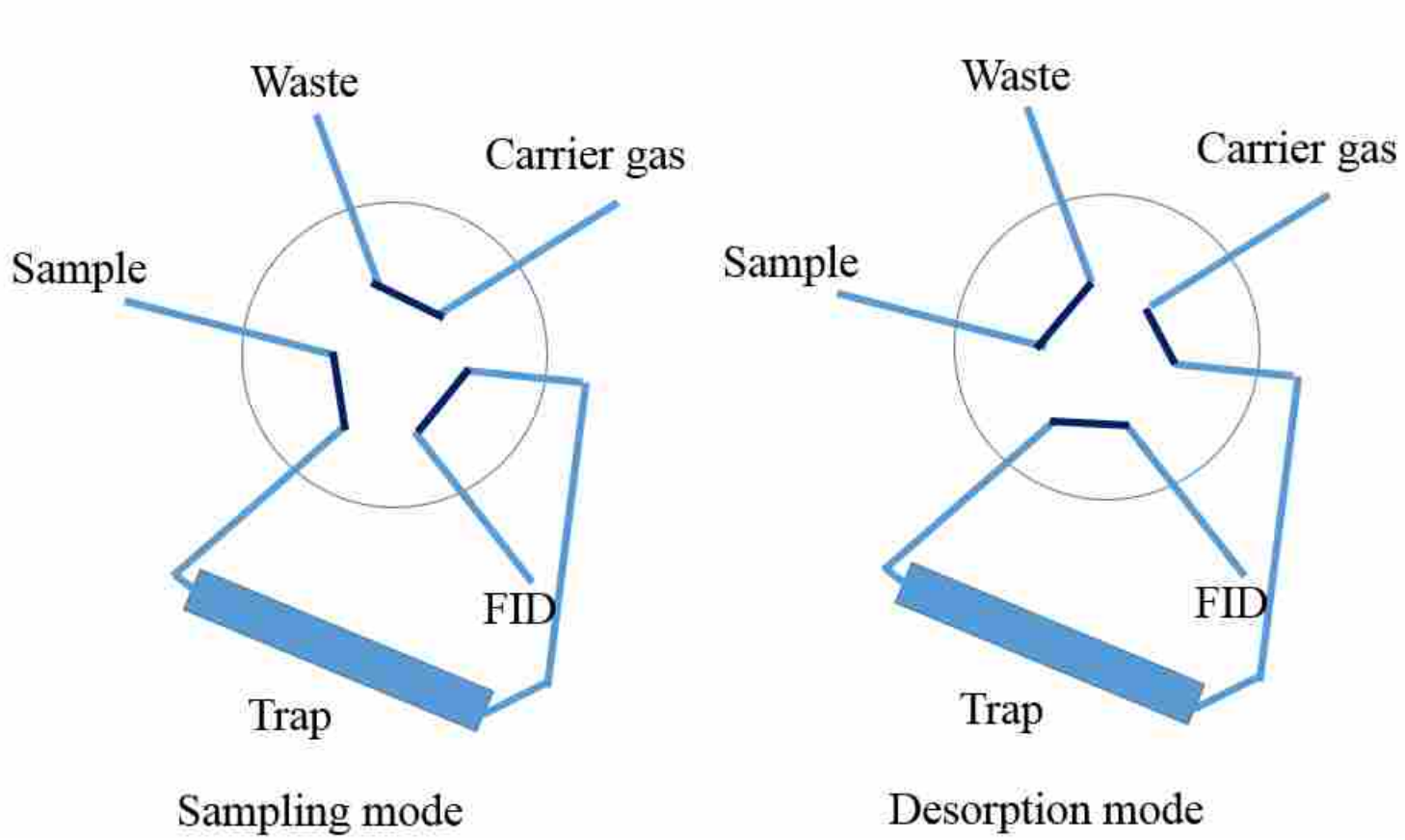


Figure 2.4 Six-port valve for switching between sampling and desorption modes.

temperature was raised to 250 to 300 ˚C. Both breakthrough volumes and desorption volumes were determined from the recorded chromatograms. All breakthrough and desorption tests were conducted using an Agilent 6890 GC-FID system.

Two-stage high flow trap to needle trap sampling. Two-stage analysis of VOCs using a high flow trap followed by a needle trap was performed in three steps. First, the high flow trap was used to collect the sample, i.e., sample was pulled through the trap using a portable suction pump (SKC, Eighty Four, PA) or pushed through the trap with a pressurized home-generated standard stream. Then, the high flow trap containing the collected sample was connected to a home-built thermal desorber. The thermal desorber included the high flow trap connections to an upstream flow of 20 mL/min nitrogen carrier gas controlled by a mass flow controller (Brooks 5850E, Hatfield, PA), and to a downstream needle trap. A 6.0 cm long, ¼ in. o.d., deactivated stainless steel tube from VICI (Houston, TX) was used to connect the high flow trap to the needle trap, and to cool the hot desorption stream from the high flow trap. A GC septum with a finger-tightened nut was used as a sampling port for the needle trap. The thermal desorber was pre-heated to 300 ˚C using a heating cartridge (Omega, Stamford, CT), and the desorption process required 10 min. Finally, the needle trap was disconnected and inserted into the heated GC injection port at 300 ˚C for 30 s for complete desorption. For the initial desorption test, a GC oven was used as heating source and another approximately 20 cm, ¼ in. o.d., stainless steel tube was used as transfer line.

2.3 Results and discussion

2.3.1. Trap design

In order to perform high flow rate air sampling, the back pressure/restriction from the trap itself should be minimized. The back pressure of the capillary bundle depends on the capillary i.d., capillary length, and flow rate as well as on other environmental conditions.

Capillary internal diameter. From the well-known Hagen–Poiseuille equation, the flow rate from the outlet of a single capillary can be calculated from the inlet and outlet pressures, capillary dimensions and temperature.[4] Commercial portable air sampling pumps are usually restricted to a back pressure under 20 in. of water (0.72 psi). For 530 μm i.d. capillaries, 14, 30 or 158 capillaries with lengths of 8.9 cm (3.5 in.), which is the same as a standard thermal desorption unit, 19.0 cm (7.5 in.) and 100.0 cm (39.4 in.), respectively, would be required to obtain 5.0 L/min sampling rate. If the i.d. of the capillaries was decreased to 320 μm, this would dramatically increase the number of capillaries needed to 106, 227 and 1,192, respectively. Therefore, 530 μm i.d. is appropriate for constructing a high flow multi-capillary trap from the perspective of back pressure.

Capillary length. The capillary length affects two aspects of the capillary trap, the back pressure and the trapping length; a longer capillary would provide longer trapping distance, (i.e., capacity) but increase the back pressure. In order to trap the analyte on the capillary wall, the analyte must diffuse from somewhere in the flowing stream to the wall. Therefore, the capillary trap should be long enough to allow the analyte to migrate from the center of the capillary to the wall before exiting the capillary. According to well-established theory in the aerosol denuder field, [5-6] the fractional penetration, P, of vapor passing through the capillary without hitting the wall can be expressed as

$$P = 0.819\pi e^{-3.66\mu} \quad (2.1)$$

where $\mu = DL\pi/Q$, L is the length of the capillary, Q is the volumetric flow rate of the fluid, and D is the diffusion coefficient of the analyte in the mobile phase (air). To trap 99% of the analytes (P <1%), the capillary must be longer than a certain length. At a flow rate of 1.0 mL/min (single capillary flow rate), only 0.068 cm for benzene, 0.075 cm for toluene, 0.103 cm for octane, and 0.128 cm for diethyl phthalate are required. However, at 100 mL/min, these lengths increase to 6.8 cm for benzene, 7.5 cm for toluene, 10.3 cm for octane and 12.8 cm for diethyl phthalate.

Based on these results, multi-capillary traps with the following two configurations were constructed: (1) 8.9 cm x 530 µm i.d. capillaries with 1/4 in. fittings (33 capillaries), which is the same size as standard TD tubes, and (2) 19 cm x 530 µm i.d. capillaries with 1/4 in. i.d. fittings (33 capillaries).

Capillary coating. The coating inside the capillary greatly affects the trapping capacity. Five commercially available capillary GC column types were selected for this work, including Carboxen 1006 PLOT (carbonaceous material) from Supelco, RT-QS-BOND (20 µm divinylbenzene incorporating low 4-vinylpyridine), RT-Q-BOND (20 µm divinylbenzene), Rxi-5HT (0.15 µm diphenyldimethylpolysiloxane), and MXT-1 (7 µm 100% polydimethylsiloxane). The first three were porous layer open tubular (PLOT) columns, while the last two were wall-coated open tubular (WCOT) columns, The MXT-1 column was stainless steel, while the others were fused silica.

Flow rate measurements. In order to confirm the calculations, measurements were carried out to measure the flow rates of various single capillaries, as well as bundled capillaries, under different conditions. First, a pressure was applied at the end of a single capillary, and the flow rate was measured at the outlet. With approximately 20 in. water pressure (4.98 Kpa), a 8.9 cm x 530 μm i.d. capillary produced 316 mL/min compared to a calculated value of 318 mL/min at 0.85 atm local pressure, while a 19.0 cm x 530 μm i.d. capillary produced 181 mL/min compared to a calculated value of 149 mL/min. When one end of a bundled capillary trap (33 capillaries of 8.9 cm x 530 μm i.d.) was pressurized to approximately 0.70 psi (4.83 Kpa) pressure, and the individual flow rates from 10 single capillaries were measured at their outlets, the average flow rate was 255 mL/min, with an RSD value of 4.8%, which indicated that the flow was fairly evenly distributed between the capillaries. With a completely sealed bundled capillary trap at both ends (33 capillaries of 8.9 cm x 530 μm i.d.), and 0.72 psi (4.96 Kpa), approximately 6.5 L/min flow rate was obtained. The hand portable pump that was used was capable of a maximum flow rate of 8.0 L/min using the bundled capillary trap. These flow measurement results confirm the previous calculations, that the 8.9 cm and 19.0 cm long 530 μm i.d. bundled capillaries should provide sufficient trapping length and minimum back pressure.

2.3.2. Breakthrough volume measurements for single capillaries

Experiments were conducted to measure the breakthrough times/volumes for different capillaries under different conditions. The capillaries used were: 8.9/19.0 cm Carboxen 1006, 8.9/19.0 cm Restek Rxi-5HT, 8.9/19.0 cm Restek RT-Q-BOND, 8.9/19.0 cm Restek RT-QS-BOND, 19.0/57.1 cm Restek MXT-1 and an empty 19.0 cm capillary tube, all of them with i.d. of 530 μm. Three different analytes (methylene chloride, toluene and methyl salicylate) were tested at

four different concentrations (1.5 ppm, 3.0 ppm, 7.5 ppm and 15 ppm). The trapping temperatures were room temperature (approximately 22 ˚C) and 40 ˚C, the flow rate through a single capillary was approximately 140 mL/min, and the results reported were an average of three measurements.

For the most volatile compound tested, methylene chloride, breakthrough occurred very rapidly (in less than 0.5 min) for most capillaries. The 19.0 cm Carboxen 1006 column retained the analyte for 3.7 min at room temperature and 1.67 min at 40 ˚C, while the 19.0 cm RT-QS-BOND column allowed breakthrough at 0.49 min at room temperature. For toluene, as shown in Table 2.1, three types of capillaries gave noticeable retention. As expected, Carboxen 1006 was the highest (128.5 min at room temperature for 19.0 cm), followed by RT-QS-BOND and RT-Q-BOND. For methyl salicylate, most of the capillaries trapped the analyte very well, as indicated in Table 2.2. For reference, the breakthrough time from the empty tube was 0.6 min, and the Rxi-5HT column gave a similar result, which indicated that they were not suitable for trapping this analyte. With a thicker film coating, the MXT-1 column trapped the analyte for 1.6 min with a 19.0 cm capillary. All of the PLOT columns provided relatively large breakthrough times (>15 min).

From the above results, several conclusions can be made. First, the coating type was the dominating factor affecting retention, as expected, Carboxen 1006 provided the longest breakthrough times in all of the tests, followed by RT-QS-BOND, RT-Q-BOND, MXT-1 and Rxi-5HT. In addition, the trap length was directly related to the breakthrough time. Generally, breakthrough time was reduced to approximately 1/4 to 1/3 as the length was cut in half. As

Table 2.1 Breakthrough times for single capillaries with toluene.

Column		1.5 ppm Toluene			
Name	Length/cm	Room temperature		40 ˚C	
		Time/min	RSD/%	Time/min	RSD/%
Carboxen 1006	8.9	29.6	4.0	26.3	2.2
	19.0	128.5	6.6	95.5	14.1
RT-Q-BOND	8.9	1.1	5.4	na	na
	19.0	5.2	9.4	1.6	3.5
RT-QS-BOND	8.9	1.1	14.3	na	na
	19.0	6.5	10.5	2.0	4.0

19.0 cm Carboxen 1006		
Concentration/ppm	Time/min	RSD/%
1.5	128.5	6.6
3.0	66.8	7.9
7.5	31.7	5.0
15.0	16.6	4.7

na: not available

Table 2.2 Breakthrough times for single capillaries with methyl salicylate.

Column		1.5 ppm methyl salicylate			
		Room temperature		40 ℃	
Name	length/cm	Time/min	RSD/%	Time/min	RSD/%
Carboxen 1006	8.9	55.3	6.2	52.7	2.9
	19.0	169.3	3.0	141.0	2.5
Rxi-5HT	8.9	na	na	na	na
	19.0	0.6	12.2	0.5	6.8
RT-Q-BOND	8.9	28.5	1.8	18.0	2.8
	19.0	92.0	3.3	52.3	2.4
RT-QS-BOND	8.9	35.7	9.0	21.2	12.1
	19.0	69.5	2.2	49.7	5.5
MXT-1	19.0	1.6	3.5	0.8	1.5
	22.5	4.0	2.1	na	na
Empty tube	19.0	0.6	5.7	0.4	8.0

57 cm MXT-1		
Concentration/ppm	Time/min	RSD/%
1.5	4.1	2.1
3.0	3.6	8.4
7.5	3.2	1.8
15.0	2.8	5.4

expected, higher temperature also decreased the breakthrough time. It was interesting that the PLOT columns and WCOT columns behaved differently with different analyte concentrations. As the concentration increased, the breakthrough time for toluene in the Carboxen 1006 column decreased proportionally, while in the MXT-1 column, it decreased much less significantly. This behavior is most likely because analytes are retained by partition in the WCOT columns before the stationary phase becomes saturated (overloading). The time required for saturating the coating in WCOT columns decreases gradually with an increase in analyte concentration, which leads to short breakthrough time. For the PLOT columns, retention of analytes was achieved by adsorption, which heavily depends on active sites on the sorbent. Therefore, breakthrough volumes were clearly related to analyte amounts in the gas stream. These tests were performed using relatively high analyte concentrations for easy detection. In theory, for low concentrations, the sample should not overload the columns, which would lead to large breakthrough volumes. From the results obtained, the following capillaries were selected to construct the bundled capillary high flow traps: 8.9 cm Carboxen 1006, 19.0 cm Carboxen 1006, and 19.0 cm RT-QS-BOND.

2.3.3. Breakthrough and desorption volume measurements for bundled capillary traps

The three bundled capillary traps were first challenged with the same three analytes at high flow rate, approximately 5.0 L/min (~70 ppb). Breakthrough plots were recorded, and breakthrough volumes and times were measured as listed in Table 2.3.

Table 2.3. Breakthrough and desorption times for bundled capillaries.

	Analytes	3.5 Carboxen 1006/min(RSD/%)	7.5 Carboxen 1006/min(RSD/%)	7.5 RT-QS BOND/min(RSD/%)
Breakthrough	Methylene chloride	2(10.9)	3(25.7)	na
	Toluene	26(11.8)	60(5.6)	6(15.6)
	Methyl salicylate	18(20.2)	100+	60+
Desorption	Methylene chloride	12(5.2)		
	Toluene	18(3.5)		<10
	Methyl salicylate	30(2.2)		<10

The 8.9 cm Carboxen 1006 bundled trap gave a breakthrough volume of approximately 10 L for dichloromethane, 130 L for toluene, and 90 L for methyl salicylate. By increasing the length to 19.0 cm, the breakthrough volume increased to approximately 15 L for dichloromethane, 300 L for toluene, and over 500 L for methyl salicylate. On the other hand, for the 19.0 cm RT-QS BOND trap, the breakthrough volume was 34 L for toluene, over 300 L for methyl salicylate, and almost no retention for dichloromethane. It is interesting that the 8.9 cm Carboxen trap gave a lower breakthrough volume for methyl salicylate than toluene, even though the latter was less volatile. Either toluene was able to migrate to the capillary wall faster than methyl salicylate, or it has a higher affinity for the stationary phase coating.

After trapping the analytes in the bundled capillary trap, it was important to determine how fast they could be desorbed. Experiments were designed to first load a trap with 10 min of sample at 5.0 L/min (~700 nmol) and then desorb the trap inside a GC oven at 300 ˚C with a desorption flow rate of 20 mL/min. An FID was used to monitor the signal at the outlet, and the resultant plot was used to determine the desorption volume.

As shown in Table 2.3, the 19.0 cm RT-QS-BOND trap was desorbed in less than 10 min (the oven required approximately 3-4 min to reach the desired temperature). The 8.9 cm and 19.0 cm Carboxen 1006 bundled capillaries gave the expected results; methylene chloride was desorbed in 12 min, toluene was desorbed in 18 min and the least volatile methyl salicylate was desorbed in approximately 30 min.

Among the three selected bundled capillary traps, as expected, the 19.0 cm Carboxen 1006 trap gave the best performance by exhibiting over 100 L breakthrough volume for toluene and methyl salicylate and 15 L for methylene chloride. Desorption of methyl salicylate was difficult, taking 30 min to complete. The RT-QS-BOND trap gave smaller breakthrough volumes. After considering both breakthrough and desorption volumes, the 8.9 cm Carboxen 1006 trap was selected for further experiments. In addition to providing low back pressure, and large breakthrough volume, the 8.9 cm trap also had the same form factor as the traditional thermal desorption tube, and could potentially be used interchangeable with traditional thermal desorption systems.

2.3.4. Two-stage quantitative analysis

The back pressure, breakthrough volume and desorption volume measurements provided the necessary background information for utilizing the multi-capillary trap as the primary sample collection device for two-stage VOC analysis. Several modifications were made to the multi-capillary trap for better quantitation. First, polyimide (Supelco, Bellefonte, PA) was used instead of epoxy for gluing the capillaries together. Also, a ¼ in. steel stainless tube was used to completely enclose the capillaries comprising the multi-capillary trap, which made the trap more robust. Instead of using a GC oven as a heating source, a home-made thermal desorber (see Section 2.2.4) was used to transfer the retained analytes from the high flow trap to the needle trap. The thermal desorption temperature was 300 °C and the desorption flow rate was 20 mL/min. A 110 ppb gas standard of BTEX and MTBE [benzene, ethylbenzene, methyl-*tert*-butyl ether (MTBE), toluene, *m*-xylene, *o*-xylene, and *p*-xylene] was used to generate a ppt

concentration gas sample. By mixing a 9.5 mL/min BTEX standard stream with 5.0 L/min nitrogen gas, a sample stream of 5.0 L/min (209 ppt) was obtained.

One of the most critical parameters for analyte transfer between the high flow rate trap and the needle trap is the total desorption time/volume. Ideally, the desorption volume should be sufficient to completely desorb the analytes of interest from the primary trap, but not exceed the breakthrough volume of the second-stage needle trap. A set of experiments were carried out to determine the effect of desorption time/volume on analytes recovered.

The multi-capillary trap was used to sample the 209 ppt BTEX sample stream for 10 min and then it was connected to the thermal desorber for desorption at 20 mL/min at 300 ˚C. Different desorption times/volumes (1, 2, 3, 5, 7, 10, and 20 min) were evaluated by using the needle trap to collect the eluent. Then the analytes recovered from the needle trap were plotted vs. desorption time. As shown in Figure 2.5, the most volatile compound (i.e., MTBE) eluted in the first 3 mins as expected. Due to the limited retention of volatile compounds by the needle trap, the recovered amount of MTBE dropped dramatically after 3 min to as low as 20%. Similar patterns were also observed for the other five compounds; benzene reached its maximum two-step recovery at 5 min, toluene and ethylbenzene reached their maxima at 7 min, and the xylenes reached their maxima at 10 min. It should be mentioned that the desorption of analytes from the high flow trap and their retention in the needle trap were dynamic processes occurring at the same time. During these dynamic processes, before recovery reached its maximum, the needle trap adsorbed more of the analytes from the high flow trap than escaped out its outlet. After that, additional analyte amounts eluted, which led to decreased recovery. In theory, this problem can

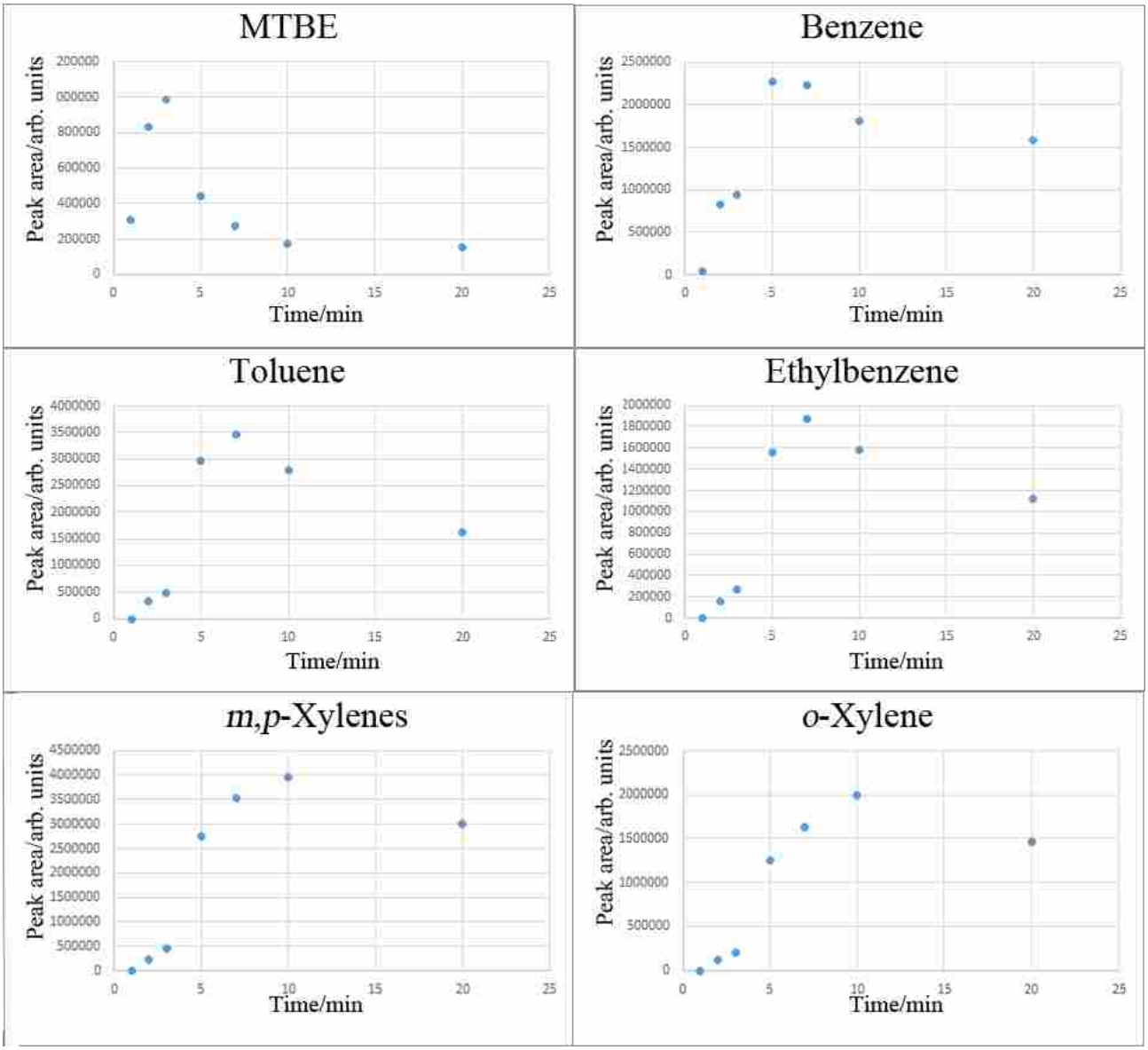


Figure 2.5 Recoveries of different BTEX standards as a function of desorption time.

be solved by decreasing the multi-capillary trap desorption volume (e.g., increasing the desorption temperature or using a weaker sorbent), and by increasing the breakthrough volume of the needle trap (e.g., cooling down the needle trap temperature or using a stronger sorbent. A 7 min desorption time, without any other modifications, resulted in the best recoveries of the analytes of interest. Therefore, in the following experiments, the following conditions were used: 10 min high flow trap sampling at 5.0 L/min, 7 min desorption at 20 mL/min with the needle trap at room temperature, and 30 s needle trap desorption time inside the 310 ˚C GC injector.

Using these conditions, the reproducibility of the high flow trap was good, with a relative standard derivation (RSD) below 10%, as listed in Table 2.4. For comparison, a needle trap experiment was performed with a 20 mL/min (52 ppb) BTEX standard steam, which resulted in an RSD below 5%. The needle trap and high flow trap experiments were designed to ensure that, in theory, there would be the same mass of analytes in the needle trap for sampling 10 min using both techniques. Using the results from Table 2.4, another important parameter of the high flow trap, i.e., the recovery ratio, can be calculated. For the two-stage analysis, the overall recovery should be the product of the recovery ratios from each stage. Therefore, the recovery ratio of the high flow trap can be calculated by dividing the overall recovered amounts from the trapping system by the recovered amounts from the needle trap. The recovery ratios were calculated to be, 22.46% for MTBE, above 90% for benzene and toluene, and around 50% for the rest of the compounds. The recovery ratio results were similar to the desorption time result; i.e., a 7 min desorption time was a compromise between the volatile compounds and less volatile ones and, therefore, gave the best recovery ratios for the compounds in the middle. A higher recovery ratio

Table 2.4 Comparison of high flow trap (HF) and needle trap (NT) sampling (peak area $x10^{-3}$).

	MTBE	Benzene	Toluene	Ethylbenzene	*m,p*-Xylenes	*o*-Xylene
HF	250	2100	3400	1900	3700	1700
	270	2100	3300	1800	3200	1400
	300	2400	3600	1900	3300	1500
NT	1200	2300	3900	3900	7100	3300
	1200	2200	3700	3600	6600	3100
	1200	2200	3700	3700	6700	3200
NT RSD/%	1.69	3.50	3.60	4.20	3.41	3.19
HF RSD/%	9.84	6.95	4.28	3.83	8.33	9.92
Recovery/%	22.46	97.48	90.45	49.01	50.14	48.51
Recovery RSD/%	9.99	7.78	5.59	5.68	9.00	10.41

would be obtained for the more volatile compounds or less volatile ones, if reduced or increased desorption times were used, respectively.

2.3.5. BTEX calibration curve and quantitation

A calibration curve is usually constructed in gas chromatography using liquid sample injection; however, it would be most ideally generated from gas standards. Calibration curves were generated for BTEX compounds (MTBE was not included here because of its low recovery and from possible breakthrough) using the high flow trap. The same 110 ppb BTEX standard gas was used, and a concentration range from 110 ppt to 763 ppt was obtained by varying the mixing ratio of the 110 ppb standard with clean nitrogen gas to provide a total flow rate of 5.0 L/min. The BTEX standard flow rates were set at 5.0, 9.5, and 34.7 mL/min to yield concentrations of 110.0, 209.0, and 763.4 ppt at 5.0 L/min. Each concentration was measured three times and plotted, and a blank value was obtained from 10 min sampling of pure nitrogen. The results are shown in Figure 2.6; good linear relationships were observed for all five compounds, with R^2 values from 0.9997 to 1. If the detection limit was defined as three times the noise level (to simplify the problem, the area from the blank sample covering the same time window as the peak of interest in the sample was used as the noise level), the detection limits for these compounds could be calculated from the calibration curves. The results gave detection limits of 125 ppt for benzene, 5.1 ppt for toluene and below 1 ppt for the others. The relatively high detection limit for benzene was caused by high background from the Carboxen capillary as well as from the polyimide glue that was used.

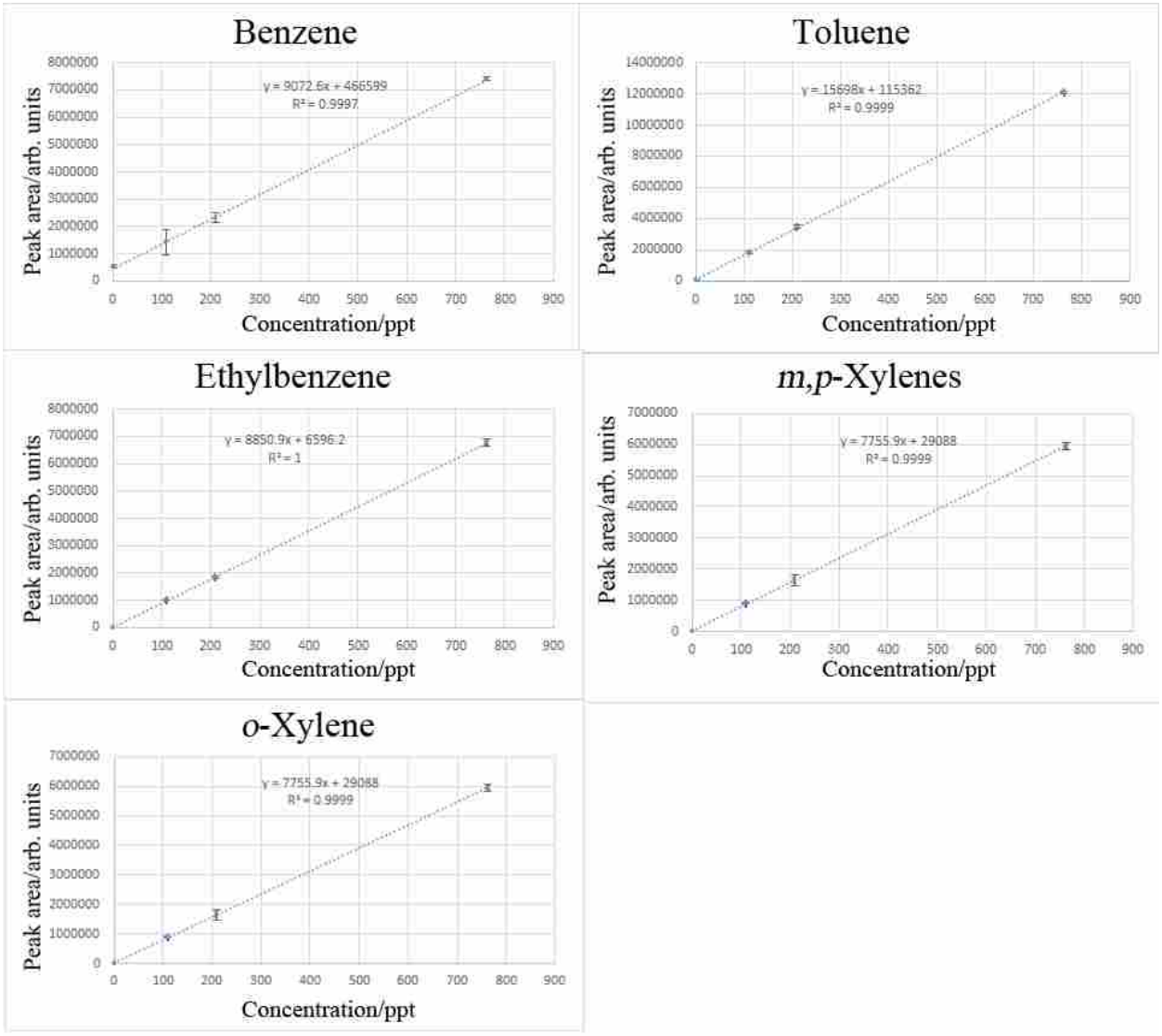


Figure 2.6 Calibration curves generated using high flow gas standards for BTEX compounds (error bars are include for at least duplicate measurements).

2.4 Conclusions

A multi-capillary high flow air sampling system was developed that was capable of detecting ppt levels of VOCs in less than 25 min using GC-MS for analysis. The advantages of this system include (1) high concentration factors of 10^4 to 10^5 (from 50-100 L to 1-2 mL), (2) low detection limits, (3) potential for enhancing on-site analysis, (4) relatively fast desorption, and (5) easily manufacturable and compatible with existing TD systems.

However, there are still problems to resolve and intrinsic disadvantages with this multi-capillary high flow rate sampling system. First, the use of epoxy or polyimide as binding material is problematic, causing both high artifact levels and loss during sorption/desorption steps. Also, the relatively weak and limited amount of sorbent led to limited breakthrough volume, especially for volatile compounds. Further optimization of the sample transfer process should be pursued to improve the recovery ratios for various compounds. Overall, this high flow VOC air sampling system demonstrates a significant advancement for low level VOC analysis, and should be useful for portable systems as well as for conventional use in the laboratory.

2.5 References

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Chapter 3 Concentrically Packed High Flow Rate Air Sampler

3.1 Introduction

In Chapter 2, the development of a multi-capillary high flow trap for sampling trace compounds in air was described. In order to increase the capacity for high flow-rate sampling, an alternative trapping system was explored after considering the differences between capillary gas chromatography (GC) columns and packed GC columns from the perspective of air sampling. In the history of GC, packed columns were used before open tubular (capillary) columns.[1,2] It wasn't until the 1980s, that capillary columns became popular, because of superior efficiency/resolution/separation power and the introduction of flexible fused-silica tubing. However, compared to capillary columns, packed columns still provide better sample capacity and sensitivity. In sorbent air sampling, similar principles also apply; open tubular designed traps will most likely give faster desorption, but packed traps will give greater breakthrough volumes (sample capacity) and lower detection limits.

In this chapter, efforts to develop a uniquely designed high flow packed trap are described. The objective of this work was to construct and evaluate an air sampling trap for VOCs that could sample at 5-10 L/min flow rate for 10-15 min, be used for both laboratory and on-site portable instruments, and is capable of detecting VOCs at 100 ppt levels. A needle trap or similar device would be used to transfer sample from the high flow trap to the GC-MS instrument with little or no modification of the GC injector.

With the novel design described in this work, the following advantages were expected: (a) very high flow rate (5-15 L/min) because of the low back pressure caused by the large cross section, (b) smaller desorption volume/time from the concentric packed sorbents, (c) easy interface with the GC-MS system with no modification to the injection port, and (d) high breakthrough volume for the interested VOCs. The system was evaluated for sampling and detection of ppt concentration VOCs in both laboratory and outdoor air within 15 min.

3.2 Experimental

3.2.1 Chemicals and materials

Methylene chloride (HPLC grade, 99.9%) was obtained from Mallinckrodt (St. Louis, MO, USA); toluene (HPLC, 99.8%) and methyl salicylate (99%) were from Fisher Scientific (Pittsburgh, PA, USA); and all other chemicals were from Sigma Aldrich (St. Louis, MO, USA). Two gas standard cylinders were purchased from Air Liquide (Houston, TX, USA) and used in this work. The first was 1.0 ppm concentration (mol/mol) of acrylonitrile (1.07), benzene (1.07), α-chloromethylbenzene (1.06), 1,2-dibromoethane (1.06), *n*-hexane (1.06) and *n*-nonane (1.07). The other was a 110 ppb gas mixture containing benzene, ethylbenzene, methyl-*tert*-butyl ether (MTBE), toluene, *m*-xylene, *o*-xylene and *p*-xylene.

3.2.2 Design and fabrication of the concentric packed trap

For all VOC air sampling devices, the objective is to concentrate VOCs from a large volume (0.1-100 L) to a small volume 10-1000 μL (with a concentration factor equal to the original volume divided by the final volume). For sorbent sampling, this means concentrating analytes in a small amount of sorbent and releasing them in a small volume of desorption gas. A

conventional thermal desorption tube is typically a 89 mm (3.5 in.) long, ¼ in. (6.4 mm) o.d., and 5 mm i.d. stainless steel tube.[3]

A straightforward way to achieve high flow rate sampling is to increase the thermal desorption tube diameter. However, there are challenges associated with this approach. First, a larger tube diameter would lead to larger desorption and dead volumes. Furthermore, analytes would be distributed in more sorbent, which would lead to a wide desorption band. There would be more possibility for unswept dead space, which would lead to carry-over from one sample to the next. Theoretically, a cone shaped sample tube would help to minimize the desorption volume, maintain large breakthrough volume and decrease backpressure. During the sampling process, analytes would first be retained at the beginning of the sorbent tube. During desorption, the flow direction is reversed, and analytes elute out of the sampling tube from the inlet end in minimum desorption volume. A cone shape is difficult to desorb evenly, and the larger diameter end may create a diffusive ingress problem, therefore, an alternative concentrically packed tube approach was selected for this work.

The concentric packing design uses a similar idea as the cone design, i.e., an asymmetrical sorbent packing to reduce back pressure and desorption volume. Instead of packing sorbent along a tube vertically, the concentric design arranges sorbent materials along an empty center channel concentrically layer by layer. As shown in Figure 3.1, an empty center tube (1.52 mm, 0.06 in. i.d.) capped at one end and constructed of stainless steel mesh is placed in the center of the assembly. Then a mesh layer is placed concentrically 4.0 mm (0.157 in.) from the center tube. A third larger diameter mesh layer is placed in a similar manner. With the center channel

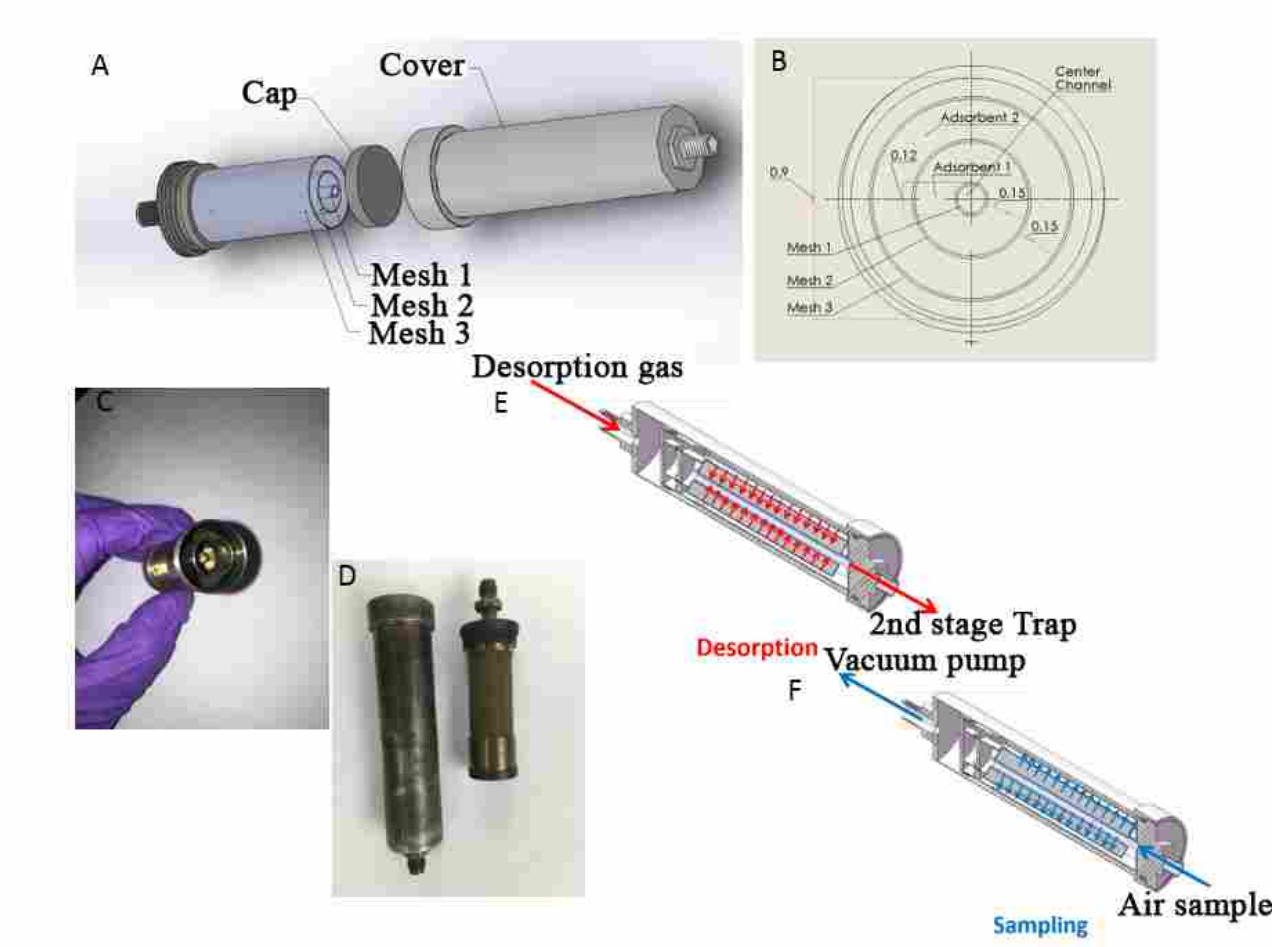

Figure 3.1 Concentric packed sampler design, construction and work flow. (A) complete assembly, (B) detailed design, (C) prototype with mesh layers, (D) prototype, (E) sampling mode, (F) desorption mode.

and two mesh layers assembled, two separate compartments are created, which can be packed with sorbent materials. I designed and manufactured three versions of the mesh layers, with lengths of 12.7 mm (0.5 in.), 38.1 mm (1.5 in.) and 63.5 mm (2.5 in.) for testing. After packing with sorbent, the end of the sampling tube is sealed with a cap. Finally, another cover is used to contain the whole unit for desorption as shown in Figure 3.1D.

During sampling, a portable vacuum pump is connected to the end fitting on the cover of the completely assembled sampling device. Air is pulled through the trap from the middle channel and VOCs are retained in the sorbent layers. After sampling, the air sampler is connected to a heated desorption system. During desorption, carrier gas is purged through the sampler from the cover fitting to the center channel, where the second-stage sorbent tube is connected.

Conventional thermal desorption systems typically employ a micro-concentrator as a second-stage trap to interface with the GC-MS detection system. A needle trap device was used here to transfer sample from the high flow trap to the GC-MS. The needle trap device contains a needle filled with sorbent material to extract analytes from liquid or gaseous matrices. It is a simple, robust and solvent-less tool for exhaustive sampling of VOCs. Descriptions and applications of the needle trap can be found in several reviews.[4,5] Since the needle trap is small enough to insert directly in a conventional GC injector equipped with a special liner, it is ideal for collecting analytes from the high flow trap and transferring them to the GC-MS system.

3.2.3 Instrumentation and methods

The dynamic vapor generation system, gas chromatographic instrumentation, and needle trap

device used in this study were described in Section 2.2.2. Sample introduction into the GC-MS system was accomplished using direct, gas sampling injection, solid phase microextraction, or needle trap depending on the experiments. A custom-made quartz liner was used with a split/splitless injector for all needle trap injections; a 0.75 mm i.d. liner was used for SPME; a 4 mm i.d. liner was used for direct gas sample injection (Restek, Bellefonte, PA). The methods used for breakthrough volumes, desorption volume, flow rates and back pressure were described in Section 2.2.4.

3.2.4 Thermal desorber

A thermal desorber unit was designed and constructed for this work to transfer sample from the high flow trap to the needle trap, which was then inserted into the GC-MS system for analysis. A conventional thermal desorber can only handle traps that are ¼ in. o.d., and none are compatible with a needle trap. Therefore, a thermal desorber was constructed that could accommodate a high flow trap with 2.29 cm (0.9 in.) o.d., and that could be interfaced with the needle trap as shown in Figure 3.2. The thermal desorber heats the first-stage trap to release the trapped VOCs, and directs them to a chilled second-stage trap for refocusing. The key criterion for thermal desorption is to heat the primary trap (high flow trap) in a short time period while keeping the second trap cool (needle trap) for a longer time. Instead of using resistance heating techniques to heat the trap directly, heat from two pre-heated hot metal plates were used to achieve fast heating and to avoid over-heating. Two aluminum blocks were heated to 300 ˚C before the primary trap was placed in contact with them. Then, they were clamped around the primary trap. Measurements showed that approximately 1 min was required to reach 200 ˚C and 2 min were required to reach 250-300 ˚C. In order to keep the needle trap cool while connected to the hot

Figure 3.2 Photographs of the laboratory prototype thermal desorber. (A) pre-heated block, (B) high flow desorber with cooling tube for volatiles, (C) high flow desorber with needle trap attached for semi-volatiles.

primary trap, a short deactivated metal tube was used to separate the needle trap from the high flow trap. Obviously, this laboratory prototype system would have to be engineered differently for on-site analysis. A small fan could be used to cool down the needle trap. Based on measurements, the temperature of the needle rose from 23 ˚C to 50 ˚C after 10 min desorption time. With this simple in-house thermal desorber, desorption of the high flow trap could be performed in less than 10 min with relatively simple equipment.

3.3 Results and discussion

3.3.1 Flow rate and back pressure

A portable pump and differential pressure gauge were used to determine the maximum flow rate and back pressure that the concentric sampling device can handle. During manufacturing of the device, three different versions of traps were made by varying the length of the metal mesh (i.e., 12.7 mm, 38.1 mm and 63.5 mm) to test the effect of length on back pressure. Three types of sorbents were also evaluated: Tenax TA (60/80 mesh), Carboxen 1016 (60/80 mesh), and Carboxen 569 (20/40 mesh). The results are given in Table 3.1. All four device lengths were able to sample above 6.0 L/min, and the highest flow rate achieved was 11.5 L/min. From the results in Table 3.1, it is obvious that the flow rate without the enclosure was much larger, approximately twice. For different sorbents, the difference in back pressure was not significant, although the larger particle sorbent (20/40 mesh Carboxen 569) gave slightly lower back pressure. It was interesting to find that the longer traps did not significantly reduce the back pressure (all back pressure tests were made with the enclosure). One explanation is that the backpressure arising from the packed layers was insignificant compared to that from the tubing

Table 3.1 Observed aximum flow rates and back pressures for various sampling device lengths.

	Maximum flow rate/L/min			
	12.7 mm trap			38.1 mm trap
Packing material	Carboxen 1016 60/80 mesh	Carboxen 569 20/40 mesh	Tenax TA 60/80 mesh	Tenax TA 60/80 mesh
With enclosure	6.5	7.0	6.5	7.0
Without enclosure	10.0	11.5	10.0	11.5
Flow rate/L/min	Back Pressure/in. water			
5.0	17.5	15.2	15.5	14.3
5.5	20.0	17.5	18.0	16.7
6.0	21.0	20.0	20.5	19.7
6.5	21.5	21.0	21.0	20.2
7.0	n/a	n/a	n/a	21.0*

*Unable to reach stable flow

and fitting. Even the shortest (12.7 mm) trap can be used for very high flow rate sampling because the back-pressure was essentially negligible.

3.3.2 Breakthrough measurements

After verifying acceptable backpressure, another important consideration of high flow sampling is breakthrough volume. At specific conditions (temperature, humidity, and total flow rate), breakthrough volume depends on the amount of sorbent and the flow distribution through the sorbent (i.e., whether or not sample flow is uniformly distributed through the sorbent). Assuming that flow rate is uniform, a large amount of sorbent (2-5 g) should lead to large breakthrough volume. The easiest way to determine this was to measure and compare the breakthrough volumes of different trap lengths. Breakthrough volume is defined as the volume of gaseous test sample passed through the trap until the outlet concentration from the trap reaches 5% of the inlet.[6] The most straightforward way to measure breakthrough volume is by monitoring the signal introduced continuously into the trap with its outlet connected to a GC detector (i.e., frontal chromatography). Breakthrough is defined as when the signal reaches 5% of the height of the analyte measured directly from the test sample stream. Another popular approach is by adding a second (backup) trap in tandem; breakthrough is defined as trapping of 5% of the test analyte in the backup trap compared to the first trap. The first approach was selected for this study as it is simple and easy to conduct.

Two trap lengths (12.7 and 38.1 mm) were filled with different amounts of sorbents, and challenged with VOC standards to measure breakthrough volumes. Four different types of air

samplers were prepared with different amounts of the same sorbent material (Carboxen 1016, 60/80 mesh): (1) 38.1 mm length with sorbent material in both channels (5.09 g), (2) 12.7 mm length with sorbent material in both channels (2.33 g), (3) 12.7 mm length with sorbent material only in the inner channel (0.82 g); and (4) 12.7 mm length with sorbent material only in the outer channel (1.51 g). A benzene-containing sample stream at a flow rate of 5.0 L/min and concentration of ~70 ppb was generated to challenge the different air samplers. An FID (flame ionization detector) was used to monitor the signal from the outlet; FID signal vs. time plots were used to determine breakthrough volumes as shown in Figure 3.3. The breakthrough volume for the 38.1 mm sampler filled with sorbent in both channels was very large, i.e., 1,150 L (5 L/min x 230 min). Since Carboxen 1016 is a medium strength sorbent, a higher breakthrough volume could be achieved if a stronger sorbent was used. When the length was decreased to 12.7 mm, the breakthrough volume also dropped to approximately 475 L. A decrease in trap size (sorbent amount) from 38.1 mm (5.09 g) to 12.7 mm (2.33 g) resulted in a proportional breakthrough volume drop from 1,150 L to 475 L, proving that the sample stream passed through the sorbent bed similarly for both traps. The two samplers with only one filled channel gave similar, but lower than expected, breakthrough volumes (~50 L). A possible explanation can be attributed to the relatively thin sorbent bed. With only one thin layer, there is not enough pressure built up in the center channel to provide uniform flow across the sorbent bed.

The breakthrough volumes from our studies were compared to other published results. According to data from Scientific Instrument Services, Tenax TA has a breakthrough volume of 70 L/g.[7] It is believed that Carboxen 1016 has similar trapping strength (breakthrough volume)

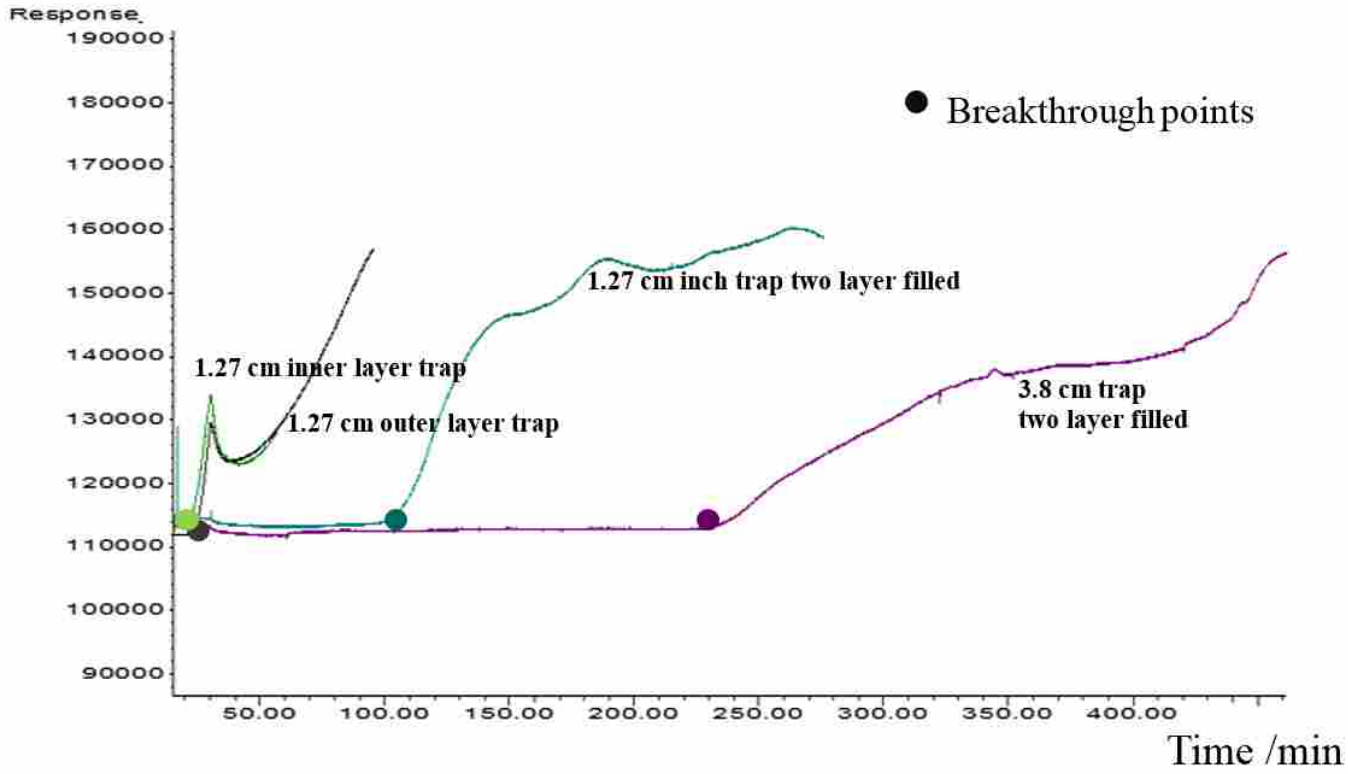

Figure 3.3. Breakthrough volume results for four concentric air sampler configurations (two lengths, different sorbent amounts, and each curve measured once).

as Tenax TA, and sometimes is used to replace Tenax TA because it generates fewer artifacts. As the breakthrough volumes per gram of sorbent (204 to 225 L/g) obtained in this work using Carboxen 1016 is much higher than that for Tenax TA, it appears that most of the trap is utilized with relatively uniform flow across the sorbent bed.

Similar experiments were conducted to measure the breakthrough volumes for other compounds under different conditions. It was found that at room temperature (~22 ˚C), a 12.7 mm trap filled with Carboxen 1016 gave 99.0 L breakthrough volume for pentane and 1,298.0 L for toluene; at 40 ˚C, the breakthrough volume for pentane dropped to 44.0 L. When the temperature was increased to 50 ˚C, the breakthrough volume was 33.0 L for pentane and 418.0 L for toluene. As expected, higher temperature dramatically decreases the breakthrough volume; therefore, a stronger sorbent is needed for elevated temperature conditions.

An alternative approach was also used to determine the breakthrough volume. Basically, by sampling the sample stream for different periods of time, the recovered amounts should be directly proportional to the times sampled before breakthrough.

A 5.0 L/min sample stream containing 40.7 ppt BTEX standards (mixing 1.85 mL/min of 110 ppb BTEX standard with 5.0 L/min nitrogen gas) was sampled for 5, 10, 20, 40, and 80 min, using a 10 min nitrogen gas sampling as a blank. As each sampling period was two times longer than the previous one, the trapped analyte amounts should also double each time before breakthrough. Breakthrough was indicated when the trapped amount was less than 1.7 times the previous analysis (the peak area from the blank analysis was subtracted from both for calculating

the ratio of the two analyses). As listed in Table 3.2, the three least volatile compounds did not reach breakthrough even after 80 min, and toluene reached breakthrough after 40 min. The result for benzene is somewhat confusing as the Tenax TA sorbent also generates benzene; it is likely that benzene reaches breakthrough after 40 min.

3.3.3 Analyte leakage and desorption measurements

An experiment was conducted to detect any possible analyte leakage around/through the sorbent bed in the high flow trap. In this experiment, a 5.0 L/min (~3.3 ppb) toluene gas standard was introduced for 1 min into a 12.7 mm trap filled with Carboxen 1016, with the exit end connected to a 5.0 L air bag (Restek, Bellefonte, PA). The contents in the air bag were analyzed using a GC-MS system. The result was compared to 5.0 L sampling of the original sample stream; less than 1% (almost negligible) of the analytes was found in the eluent (i.e., air bag) compared to the original sample.

Desorption volume measurements were carried out initially with a GC oven as a heating source; 6-8 min were required to reach 250 ˚C-300 ˚C. Four analytes were used: pentane (b.p. 36 ˚C), toluene (b.p. 111 ˚C), methyl salicylate (b.p. 220 ˚C) and diethyl phthalate (b.p. 295 ˚C). Desorption flow rates from 4 mL/min to 100 mL/min were evaluated. It was found that the desorption time was directly proportional to the desorption flow rate, as expected. With 20 mL/min desorption flow rate and 250 ˚C desorption temperature, pentane could be desorbed in 8 min (160 mL), while toluene and methyl salicylate required approximately 10 min (200 mL). The desorption volume for diethyl phthalate could not be determined under these conditions because the sorbent strength was too high.

Table 3.2 Breakthrough volume measurements (n=3) from sampling experiments for different time period (peak are

Time/min	Benzene	RSD/%	Ratio	Toluene	RSD/%	Ratio	Ethylbenzene	RSD/%	Ratio
Blank	143	35.8		18	36.8		3	29.3	
5	260	19.0		254	14.5		227	9.8	
10	219	19.1	0.655	426	7.4	1.729	409	8.0	1.817
20	305	16.7	2.117	790	12.8	1.891	780	11.2	1.911
40	449	15.7	1.883	1510	2.5	1.933	1578	2.0	2.027
80	456	8.5	1.022	2451	5.9	1.63	2925	1.3	1.855
	m,p-Xylenes	RSD/%	Ratio	*o*-Xylene	RSD/%	Ratio			
Blank	12	38.3		15	26.0				
5	227	9.8		214	8.8				
10	759	8.7	3.479	359	10.2	1.723			
20	1413	10.5	1.876	663	14.1	1.885			
40	2811	2.5	1.998	1293	3.7	1.972			
80	5185	1.4	1.848	2339	2.7	1.818			

3.3.4 Quantitative measurements

With the home-built vapor generator, a series of toluene standards with concentrations from approximately 10 ppt to 5 ppm were generated. These gas streams were sampled and analyzed using the GC-FID system for various conditions using several sampling devices: 500 μL gas-injection; 30 s, 10 min, and 30 min solid phase microextraction sampling (SPME, 100 μM PDMS fiber from Supelco, State College, PA, USA); 10 min needle trap sampling at 33 mL/min and 78 mL/min; 30 min needle trap sampling at 78 mL/min, 10 min high flow trap sampling at 5 L/min; 20 min high flow trap sampling at 5 L/min and 65 min high flow trap sampling at 5 L/min. The resultant peak areas were recorded and plotted in Figure 3.4. The bold line in the figure indicates the peak area equivalent to approximately 5 ng. Figure 3.4 shows good linearity within each technique, which indicates that the concentrations generated were reasonable. With these results, it is possible to determine the detection limits of each technique; gas tight syringe sampling was found to be applicable down to approximately 100 ppb, various SPME and needle trap methods can go down to 100 ppt levels, and the high flow trap was able to detect 10 ppt levels.

There are several issues that must be addressed before more quantitative results can be obtained. First, the reproducibly of the vapor generator below 100 ppt was not very good, which may be due to the extremely slow syringe pump speed and very low flow rate from the initial sample stream (~1 mL/min). Other issues include slow heating by the oven for desorption, and long transfer line which causes sample loss and poor reproducibility.

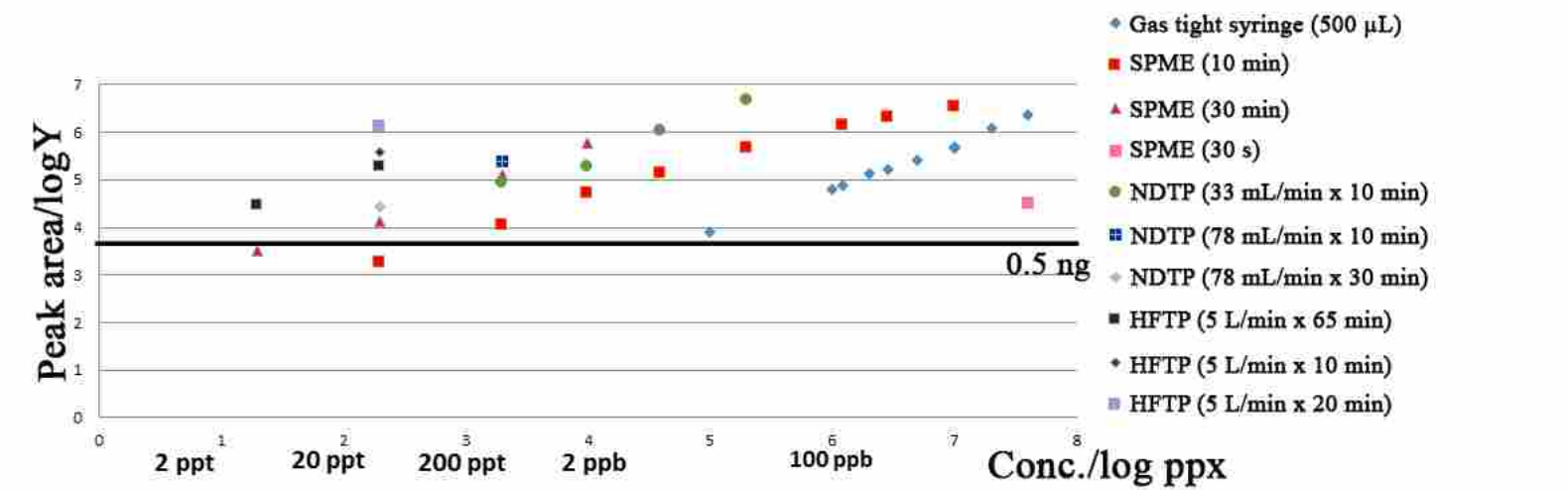

Figure 3.4 Semi-quantitative results for various sampling techniques.

With the new thermal desorber, six 1 ppm standards (acrylonitrile, benzene, *α*-chloromethylbenzene, 1,2-dibromoethane, *n*-hexane, and *n*-nonane) were used to perform quantitative measurements. After initial results were obtained using these six compounds, it was found that Tenax TA provided better trapping recovery for some compounds, especially the least volatile one (i.e., α-chloromethylbenzene) compared to the other sorbent. Therefore, all of the following experiments were performed with a 12.7 mm high flow trap filled with Tenax TA. All experiments were performed using GC-MS in the selected-ion-monitoring mode. A sample concentration of 100 ppt was prepared by mixing 0.5 mL/min of a 1 ppm standard with 5 L/min nitrogen.

Before measuring analyte-containing samples, background measurements were made for the high flow trap by comparing 10 min of 110 ppt standard sampling at 5 L/min, 10 min of pure nitrogen sampling at 5 L/min and a high flow trap blank without sampling. The results showed a very clean background (less than 5%) for all five compounds except benzene, which exhibited approximately 50% background in the blanks compared to the standard sample. The high background level of benzene most likely originated from the Tenax TA sorbent, which releases benzene at elevated temperatures.[8]

The performance of the high flow trap compared to the needle trap was accomplished by sampling a 100 ppt sample for 10 min with the high flow trap at 5 L/min, and sampling a 25 ppb sample for 10 min with the needle trap at 20 mL/min. Because both 100 ppt and 25 ppb samples were diluted from the same 0.5 mL/min sample, in theory, they should contain the same mass of analytes. The results are given in Table 3.3; the needle trap

Table 3.3 Comparison of high flow trap (HF) and needle trap (NT) sampling (peak area x10^{-3}).

	Acrylonitrile	*n*-Hexane	Benzene	1,2-Dibromoethane	*n*-Nonane	*α*-Chloromethyl benzene
NT	74	120	611	871	872	851
	91	147	680	901	921	885
	51	66	476	729	708	702
	51	64	491	753	735	746
	62	85	516	779	754	765
HF	32	23	352	555	817	491
	30	28	376	540	715	419
	130	132	675	1073	1583	869
	19	21	272	526	668	455
	23	30	348	499	567	338
RSD NT/%	26	37	16	9	12	10
RSD HF/%	100	102	39	38	47	40
RSD HF[a]/%	24	16	13	5	15	15
Recovery[b]/%	39	26	61	66	87	54

[a] Relative standard derivation calculation without the abnormal high flow trap data point (third).
[b] Ratio of peak areas from the high flow trap and the needle trap (the abnormal data point from the high flow trap was omitted).

gave RSD values from 9% to 37%, while the RSD values for the high flow trap were much higher at 38% to 102%. However, one of the data points from the high flow trap result was almost six times higher than the others. If the RSD is calculated without that abnormal data point, the high flow trap RSD values ranged from 5% to 24%, which are close to these for the needle trap. Another important parameter to calculate is the recovery ratio; for the two-stage analysis, the overall recovery should be the product of the recovery ratios from each stage. Therefore, the recovery ratio of the high flow trap can be calculated by dividing the recovered amounts from the high flow system (overall recovered amounts) by the recovered amounts from the needle trap. Based on the results from Table 3.2, the recovery ratios for benzene, 1,2-dibromethane, *n*-nonane and α-choromethyl benzene were within 54% to 87%, while those for the two volatile compounds were less than 40%.

One possible reason for lower recovery/sample loss of volatile compounds is that breakthrough occurred during transfer of the hot desorption sample stream from the high flow trap to the needle trap. Therefore, another set of experiments was conducted by cooling down the needle trap with an ice bag (Table 3.4). It is obvious that cooling down the needle trap during sample transfer greatly improved the recovery ratios for the volatile compounds: 57% to 78% for acrylonitrile, 43% to 75% for *n*-hexane, and 69% to 113% for benzene. For 1,2-dibromoethane and *n*-nonane, no significant difference was found. However, for the least volatile compound, α-chloromethyl benzene, the recovery ratio dropped from 66% to 57%, which may be caused by inevitable cooling of the transfer line. The ice bag used was close to the deactivated transfer line, which was between the high flow trap and needle trap. The ice bag may have introduced a cold spot in the transfer line, and less volatile compounds may have been retained at this cold spot.

Table 3.4 Effect of needle trap (NT) temperature on high flow trap (HF) desorption recovery (peak area x 10^{-3}).

	Acrylonitrile	*n*-Hexane	Benzene	1,2-Dibromoethane	*n*-Nonane	α-Chloromethyl benzene
HF (cold NT)	52	67	682	634	825	443
	40	46	501	597	686	426
	36	50	497	577	657	401
HF (normal NT temp)	46	35	387	660	958	601
	22	29	293	577	649	466
	25	29	347	531	668	399
NT	51	66	476	729	708	702
	51	64	491	753	735	746
	62	85	516	779	754	765
Recovery 1 (cold NT)/%	78	75	113	80	99	57
Recovery 2 (normal NT temp)/%	57	43	69	78	104	66
Recovery 1 RSD/%	22.7	26.13	19.31	5.83	12.82	6.64
Recovery 2 RSD/%	43.7	19.7	14.4	11.6	23.1	21.5

One challenge with this set of experiments was the less than ideal reproducibility of the standard sample stream, especially between different days. Due to the relatively high concentration of the original sample (1 ppm), the flow rate from the standard was set to around 0.5 mL/min, which could be easily affected by the high flow rate stream (5 L/min) and other conditions. Therefore, in order to obtain more reproducible results a lower concentration standard (110 ppb) was used in the following experiments, so that the sample stream from the standard was between 2 to 60 mL/min.

To verify the results obtained using the home-built thermal desorber, a 9 mL/min new 110 ppb standard mixture was diluted to 200 ppt (5 L/min) for high flow trap sampling and 49.5 ppb (20 mL/min) for needle trap sampling. Both traps were sampled for 10 min, and the results were summarized in Table 3.5. As can be seen, with the new standard, both needle trap and high flow trap gave very reproducible results, <15%. The recovery ratio from the high flow stage was not very good for volatiles; only 4% MTBE and 27% benzene were recovered compared to the needle trap. The recovery ratios for other less volatile compounds were much better at 42-46%.

3.3.5 Flow rate effect on recovery

After obtaining relatively low recovery ratios from quantitative measurement experiments, the possible reasons for sample loss were investigated. The major issue considered was the decrease in residence time that the analytes experience in the sorbent bed. If the flow rate is so large that analytes do not have enough time to interact with the sorbent materials, they will not be retained. According to the modified Wheeler Model reported by Zeller et al., breakthrough volume usually

Table 3.5 Quantitative results from seven 110 ppb standard compounds (peak area x 10^{-3}).

	MTBE	Benzene	Toluene	Ethylbenzene	*m,p*-Xylenes	*o*-Xylene
NT	1200	2300	3900	3900	7000	3300
NT	1200	2200	3600	3600	6600	3100
NT	1100	1900	3700	3700	6700	3200
HF	51	690	1500	1700	3000	1400
HF	42	570	1500	1500	2700	1300
HF	45	550	1700	1800	3300	1600
HF	44	530	1700	1800	3300	1500
NT RSD/%	5.00	11.00	3.00	4.20	3.40	3.20
HF RSD/%	9.00	12.00	8.00	9.00	8.40	8.20
Recovery/%	4	27	42	46	46	45
Recovery RSD/%	10.1	16.4	8.9	9.9	9.1	8.8

does not depend on the flow rate unless the flow rate is so fast that it exceeds the "safe" bed residence time, τ_{safe}.[9-11] In order to assess the effect of high flow on analyte recovery, the amounts of BTEX analytes recovered as a function of flow rate were compared. By mixing a 2.12 mL/min BTEX standard stream with 0, 0.02, 0.2, 2, 5, and 10 L/min nitrogen gas stream, sample streams of 2.12 mL/min (110 ppb) to 10 L/min (23.3 ppt) were obtained. By doing this, all resultant flow streams contained approximately 0.1 nmol of each standard analyte if the gas stream was sampled for 10 min. A comparison between the recovered analytes from these experiments would indicate whether or not the flow rate affected the trapping and recovery efficiencies.

As shown in Figure 3.5, from plots of recovered amount vs. flow rate for each analyte, the measured mass of the most volatile compound, MTBE, dropped dramatically at high flow rates; as little as only 11% was recovered at 10 L/min compared to 0.02 mL/min. For the other 5 compounds, the drop is relatively small; less than 20% for four of the compounds and a little over 20% for benzene. It is interesting that the recovery increased between 5 to 10 L/min, which may be due to variation in instrument response and other factors. When the residence times were calculated for the different flow rates, it was found that the residence time for the lowest flow rate was 12 s and for the highest flow rate of 10.0 L/min was 24.5 ms. The resultant residence times were all higher than the safe residence time reported in the literature.[11] One explanation, for the their low recovery is that as the flow rate increases, the analytes travel farther into the sorbent bed and become more widely distributed, which leads to loss during desorption. It was concluded that increased flow rate did not significantly decrease the capture of analytes, except

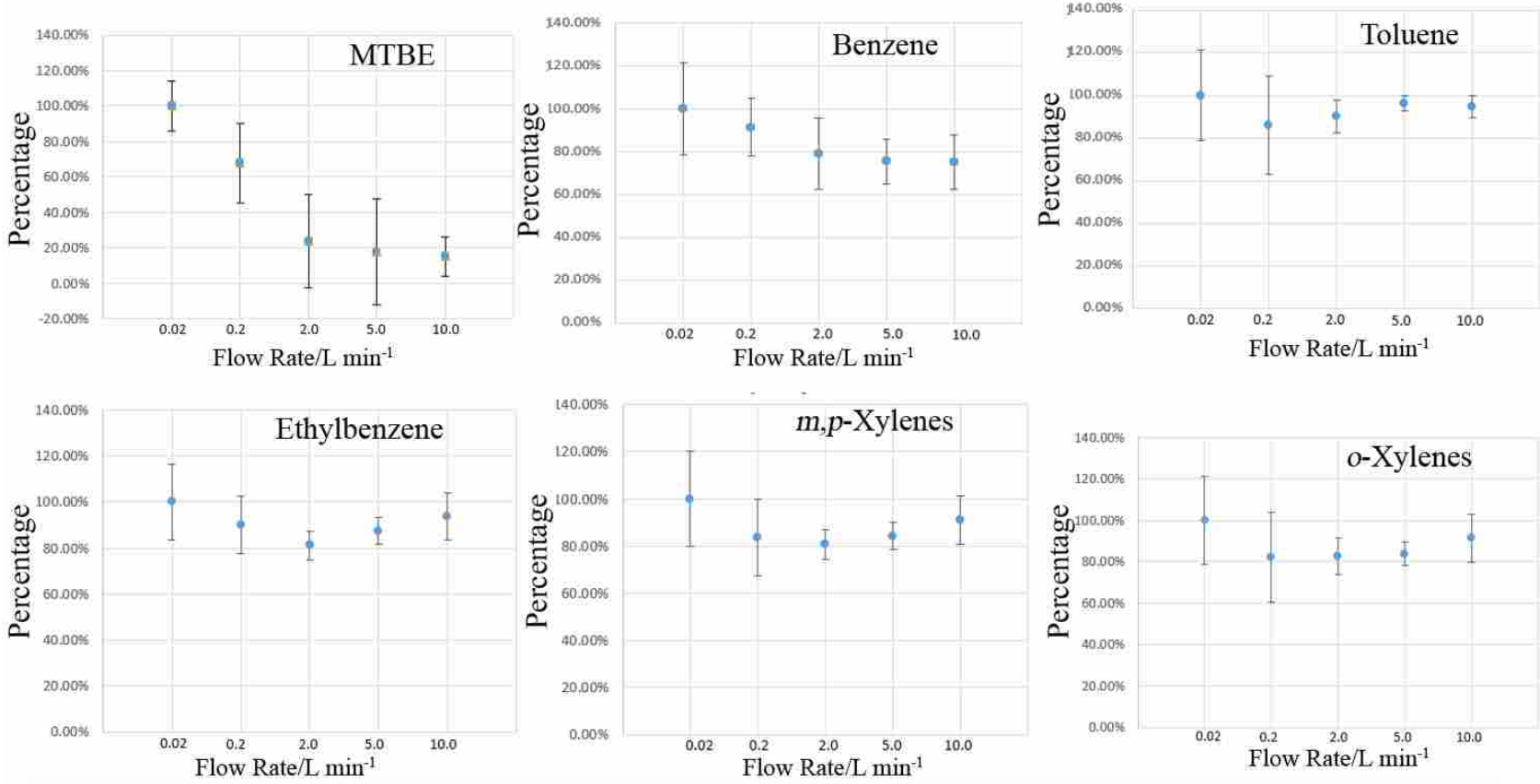

Figure 3.5 Flow rate effect on trapping and recovery efficiency (n=3).

for the most volatile compound, *t*-butyl methyl ether. The other analytes had enough residence time and breakthrough volume in the high flow trap. The less than ideal recovery ratios obtained in the experiments were most likely caused by sample loss during sample transfer from the high flow trap to the needle trap.

3.3.6 VOC air sampling and BTEX quantitative analysis

There are different approaches to quantitate the results from air sampling measurements. A calibration curve is usually constructed via liquid injection, but ideally from gas standards. Calibration curves were generated for BTEX compounds using the high flow concentric trap. The same 110 ppb BTEX standard gas was used, and a concentration range from 40.7 ppt to 1370 ppt (1.37 ppb) was obtained by varying the mixing ratio of the 110 ppb standard with clean nitrogen gas to provide a total flow rate of 5 L/min. The BTEX standard flow rates were set at 1.85, 9.40, 18.20, and 62.50 mL/min to yield concentrations of 41, 207, 400, and 1370 ppt at 5.0 L/min. Each concentration was measured three times and plotted; a blank value was obtained from 10 min sampling of pure nitrogen. The results are shown in Figure 3.6 (only the first four data points were used to construct the calibration curves as most of our interest was in the ppt range; furthermore, higher concentrations tended to overload the detection system). The 1370 ppt data point was only used to specify a concentration higher than 1 ppb. Good linear relationships were obtained for all five compounds, with R^2 values ranging from 0.9967 to 0.9996. If the detection limit was defined at 3 times the noise level (to simplify the problem, the peak area from the blank sample was used as the noise level), the detection limits for the compounds could be calculated from the calibration curves. The results gave detection limits of 89 ppt for benzene, 6.8 ppt for toluene and below 2 ppt for the others.

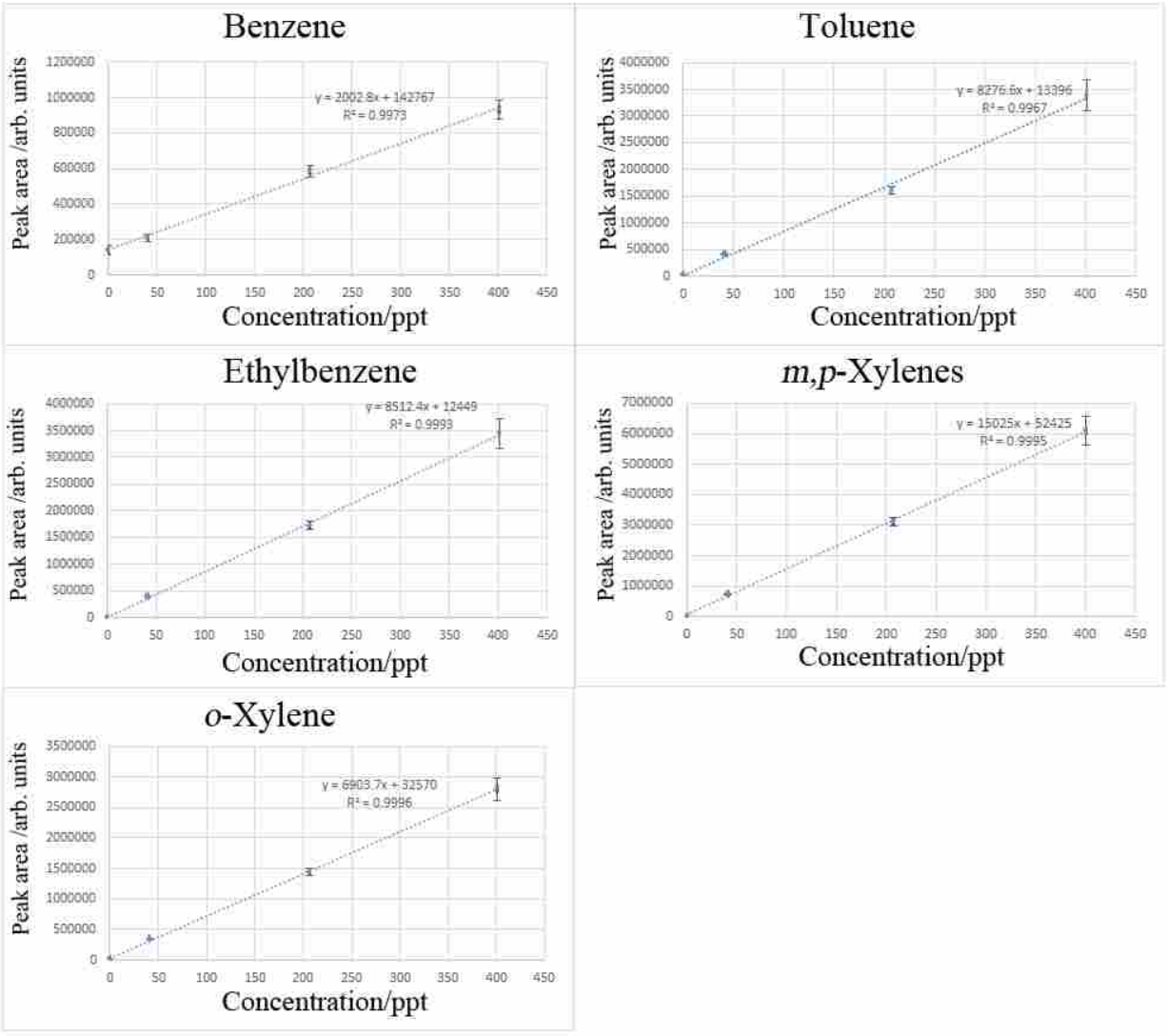

Figure 3.6 Calibration curves generated from high flow gas standards for BTEX compounds (error bars are included for at least duplicate measurements).

Experiments were conducted to survey the VOC concentrations in air at locations in and around the Brigham Young University campus using the high flow rate sampling system. The method used for sampling was 5.0 L/min sampling for 10 min followed by 20 mL/min desorption for 10 min at 300 °C to the needle trap, which was the same as for the calibration curve experiments. Inside the analytical laboratory, very high levels of benzaldehyde, acetophenone, toluene and xylene were found, with low levels of benzene and ethyl benzene as identified using the NIST mass spectral library. In a student office close to an LC-MS laboratory, high levels of limonene, toluene, xylene, nonanal and trichloromethane were found. At an outside location on campus, high levels of benzaldehyde, acetophenone, nonanal and decanal were found, as well as low levels of toluene and benzene. An interesting discovery was a relatively high level of trichloromethane in the student office. Trichloromethane is not a common solvent used in the laboratory. After further investigation, the origin of this compound was discovered to be from a biochemistry laboratory near the office.

Considering their effects on human health, quantitative analysis of BTEX levels and their variation in the analytical laboratory were studied. Experiments were performed during a 5-day period, and results from the measurements were quantitated using the calibration curves generated in Figure 3.6. As shown in Figure 3.7, among the five compounds monitored, toluene had the highest concentrations between 258 ppt and 2000 ppt, followed by benzene (107-987 ppt), *m,p*-xylenes (26-410 ppt), *o*-xylene (31-262 ppt) and ethyl benzene (29-188 ppt). Interestingly, instead of random concentration distributions, a clear pattern was observed for concentrations over time. For all five BTEX compounds, the highest levels occurred during the night (10-12 PM), which gradually decreased to the lowest level in the late

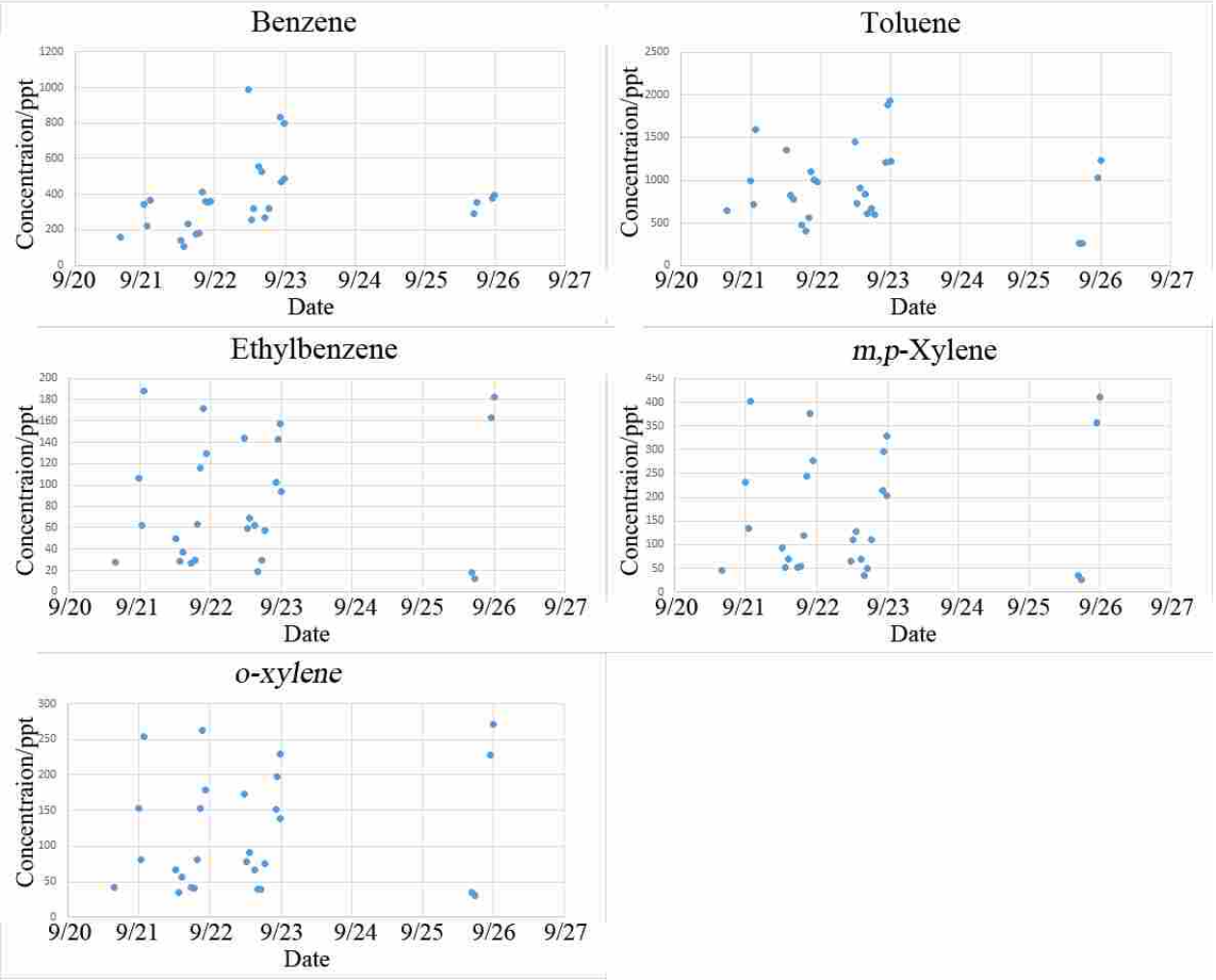

Figure 3.7 BTEX concentrations in the laboratory and their daily variations (2015).

afternoon (4-6 PM). While the reason for this pattern is unknown, it may be caused by custodial cleaning in the night (around 7-10 PM) using solvent that contains BTEX, or because the ventilation system after working hours may not be as efficient as during the day-time.

3.4 Conclusions

A high flow air sampling system was developed that is capable of detecting ppt levels of VOCs in less than 30 min using GC-MS for analysis. It can be used to profile VOC levels as well as spatial and temporal distributions. The advantages of this system include: (1) it provides a relatively high concentration factor, on the order of 10^4 to 10^5 (from 50-100 L to 1-2 mL); (2) it demonstrates a low detection limit; (3) it has potential for detecting very low levels during on-site analysis and (4) it can be customized for specific applications.

However, there are still problems to resolve and intrinsic disadvantages with this high flow rate sampling system. First, instead of manual operation, an automated system is needed to improve repeatability and stability. Additional sorbent materials should be evaluated in order to improve the relatively large loss of volatile compounds for comprehensive VOC analysis. Also, the sample transfer process should be optimized to improve the recovery ratio. Overall, this high flow VOC air sampling system demonstrates a significant advance in for low level VOC analysis in the field.

3.5 References

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Chapter 4 Equilibrium Distribution System*

4.1 Introduction

Gas chromatography-mass spectrometry (GC-MS) is a mature technique that has become the most widely used tool for characterization of volatile organic mixtures.[1,2] In order to obtain reliable results when using GC-MS, appropriate calibration of both the GC and the MS must be performed before measurements are made. Compared with the development of GC-MS instrumentation, calibration methods have changed little over the decades. An interesting observation is that conventional calibration procedures for GC-MS still address GC and MS separately. MS is typically calibrated using perfluorotributylamine (PFTBA) or other perfluoro compounds to fix the MS mass-to-charge (m/z) scale as well as the relative intensities of detected ions from low to high m/z. The reason these compounds are used is because they can provide diagnostic peaks across the relevant mass range; for example, electron ionization (EI) of PFTBA yields characteristic m/z fragments of 69, 100, 119, 131, 219, 262, 414, and 464.[3] Most commercial GC-MS instruments are supplied with a PFTBA vial for introducing vapor into the MS ion source for calibration purposes.

In comparison, GC is typically calibrated (or its performance is evaluated) using a mixture of gaseous standards or standards dissolved in a solvent. A number of methods for preparing and using gas reference materials have been developed, among which the most accurate and widely

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Xie, X.; Truong, T. V.; Murray, J. A.; Contreras, J. A.; Tolley, H. D.; Lee, M. L., Equilibrium distribution sampling device for preparation of calibration mixtures for gas chromatography-mass spectrometry. *Anal. Methods* **2013,** *5* (22), 6312-6318.

used is micrograviметric preparation, which involves carefully weighing the gases.[4,5] Other methods include dilution vial,[6] permeation tube,[7] dynamic dilution,[8] and thermal desorption.[9,10] Most of the aforementioned techniques either involve time-consuming preparation, are only possible for large scale production (e.g., the micrograviметric method), need long equilibrium time, require equipment that is difficult to set up, or do not yield long-lasting standards. As mentioned earlier, standard mixtures of volatile and semi-volatile organic compounds are oftentimes prepared by carefully weighing the exact amounts of selected standards and dissolving them together in a volatile solvent to give the desired concentrations. Normal alkanes are convenient to add to a calibration mixture for GC to calculate retention indices as well as validate the chromatographic efficiency. Various other compounds, such as in the Grob test mixture, have been used to evaluate column inertness and selectivity.[11-13] Typically, liquid or gaseous standards are injected with a syringe to perform the calibration.

Conventional GC-MS calibration methods result in several shortcomings. First, separate calibration processes increase the time needed for calibration, and this is critical for time-limited applications that are often important during on-site analysis.[14] Furthermore, liquid injection of standard solutions can be undesirable (i.e., sample split and elimination of the solvent peak before turning on the ion source are often needed). Also, analyte adsorption on the walls of the container, reaction between analytes themselves or with the solvent, evaporation, and sample degradation create problems for quantitative calibration.

To address shortcomings in sampling and injection of samples in liquid matrices, the technique of solid phase micro extraction (SPME) was reported by Arthur and Pawliszyn in 1990,[15] which

has become a popular and widely used equilibrium-based solvent-less sampling method for GC and GC-MS. For SPME, an adsorbent such as poly(dimethylsiloxane) (PDMS) is coated on a fiber for use in sampling. Due to its inertness and predictability, PDMS has served as an extracting polymer for numerous other techniques. Thin PDMS films have been coated inside fused silica capillaries for GC columns, thick PDMS films have been coated on stir bars for sorptive extraction[15,16] and in capillary tubes for open tubular trapping,[17,18] and PDMS particles have been used in extraction cartridges for a variety of applications.[19,20]

On-site sample analysis continues to rise in popularity because of the desire to provide rapid results as well as to eliminate the possibility of sample compromise during transport and storage.[21] Many field-portable instruments are becoming available to meet these demands, including portable GC-MS.[14] One issue associated with portable instrumentation and on-site analysis is the lack of convenient test mixture forms for instrument calibration. A simple, robust and easy-to-use standard mixture form is greatly needed.

In the work described in this chapter, inspired by a report by Wang et al. concerning the generation of standards for SPME by dissolving them in vacuum pump oil and sampling the headspace,[22] a new method to prepare vapor standards was explored. Instead of dilution with a gas or liquid, standard vapor mixtures were prepared using a measured mass of PDMS particles as a standard reservoir. Constant headspace concentration was achieved by rapid partition of analytes between granular heat-conditioned PDMS and its associated headspace. This equilibrium distribution sampling (EDS) method is simple, quantitative, reproducible, environmentally-friendly, and robust. For this work, an attempt was made to develop a method to

simplify standard preparation for simultaneous validation and calibration of both the GC and MS components of a portable GC-MS system. This method would ultimately improve the performance of our high flow air sampling system for analysis using a portable GC-MS system by providing better instrument calibration and a stable internal standard.

4.2 Experimental

4.2.1 Chemicals and materials

Methylene chloride (HPLC grade, 99.9%) was obtained from Mallinckrodt (St. Louis, MO, USA); toluene (HPLC, 99.8%) and methyl salicylate (99%) were from Fisher Scientific (Pittsburgh, PA, USA); and all other chemicals were from Sigma Aldrich (St. Louis, MO, USA), including benzene (HPLC, 99.8%), heptanes (99%), bromoform (99%), *n*-undecane (99%), toluene-d8 (99.6%), acetone (HPLC), methyl-tert-butyl ether (99.8%), methylcyclohexane (99%), bromopentafluorobenzene (99%), 1,2-dibromotetrafluorobenzene (99%), tetrabromoethane (98%) and *n*-tetradecane (99%). Sylgard® 184 silicone elastomer kit was obtained from Dow Chemical (Midland, MI, USA). Glass vials (7.4 mL) were obtained from Fisher Scientific. The gas standard EPA TO-14 Calibration Mix 1 (39 components including 1.05 ppm toluene in nitrogen) was purchased from Scott Specialty Gases (Plumsteadville, PA, USA).

4.2.2 Instrumentation

Most of the GC and GC-MS analyses (except those conducted using a portable GC-MS system as indicated) were performed using two instruments: an Agilent 7820A GC-FID system (Santa Clara, CA, USA) and an Agilent 5890 GC system coupled to an Agilent 5972 MSD. A 0.75 mm

i.d. liner for SPME, and a 4 mm i.d liner for liquid injection (Restek, Bellefonte, PA, USA) were used with a split/splitless injector, and an Agilent HP 7673 auto sampler was used for liquid injection. Helium was used as carrier gas. Fused silica capillary columns (30 m × 250 μm i.d. × 0.25 μm film of DB-5) were obtained from Agilent.

Typical chromatographic operating parameters included 260 °C inlet temperature, 1:20 split, 310 °C transfer line temperature between the GC and MSD, and temperature program with initial temperature of 35 °C for 0.5 min, and then ramp to 250 °C at 35 °C/min, with a final hold time of 0.25 min. The FID operating conditions were: 250 °C, 450 mL/min air, 40 mL/min hydrogen, 15 psi make-up helium flow, and 5 Hz data rate. The MSD operating parameters for all experiments were: 164 °C EI source temperature, 35–350 m/z mass range, 35 μA emission current and full scan mode. All data were collected using Agilent Chemstation and then the processed data were exported as peak areas to Microsoft Excel (Redmond, WA, USA) or Microcal Origin (Northampton, MA, USA) for final processing; quantitation was based on integrated peak areas.

Actual calibration runs were demonstrated using a hand-portable GC-MS (TRIDION™-9, Torion Technologies, American Fork, UT, USA). The TRIDION-9 was equipped with a low thermal mass GC column assembly containing a 5 m x 100 μm i.d. x 0.4 μm film of MTX-5 from Restek. The TRIDION-9 contains a miniaturized toroidal ion trap mass spectrometer with a mass range from 50 to 500 Daltons. Operating conditions for the portable GC-MS include: 1.1 A filament current, – 1,950 V electron multiplier voltage, 270 °C transfer line, 270 °C injector, and temperature program with initial temperature of 50 °C for 10 s, then ramped to 270 °C at 2 °C/s (1 °C/s for the Grob test mixture), with a final hold time of 20 s. Sampling was accomplished at

room temperature (~20 °C) for 30 s, using an SPME fiber coated with a 65-µm film of DVB/PDMS (Supelco, Bellefonte, PA, USA).

4.2.3 Preparation of granular PDMS particles

Sylgard® 184 silicone elastomer and initiator were mixed together in a 250 mL beaker according to the instructions that came with the Sylgard kit at a ratio of 10:1, and then vacuum was applied at 27 in. Hg for 2 h to degas. The mixture was polymerized at 100 °C for 35 min in an oven, followed by cutting the PDMS into small blocks (approximately 3 mm square) with a razor blade. The chopped PDMS was then baked at 250 °C for 8 h to remove the last traces of solvent, and finally ground into granular form with a glass rod and sieved between 250 and 180 µm sieves. Some large particle PDMS material was evaluated without the grinding and sieving steps.

4.2.4 Preparation of calibration vials and sampling procedures

A measured amount of granular PDMS (1-2 g) was introduced into a glass vial (7.4 mL), and pure liquid analytes were introduced onto the PDMS using a syringe. A Mininert® valve (VICI, Houston, TX, USA) was used as a cap as shown in Figure 4.1. The initial time required for distribution equilibrium was from 2 h to 3 days, depending on the volatilities of the analytes and the temperature. After initial equilibrium was reached, an SPME fiber containing a 100-µm film of PDMS was used to manually sample the analytes in the vial and deliver them to the GC injection port where desorption for 30 s was accomplished; alternatively, a 500-µL gas-tight syringe from Hamilton (Reno, NV, USA) with detachable needle tip was used. The amount and form of the PDMS was different for different experiments. Different standard mixtures were prepared for evaluation of the EDS system as described in Table 4.1.

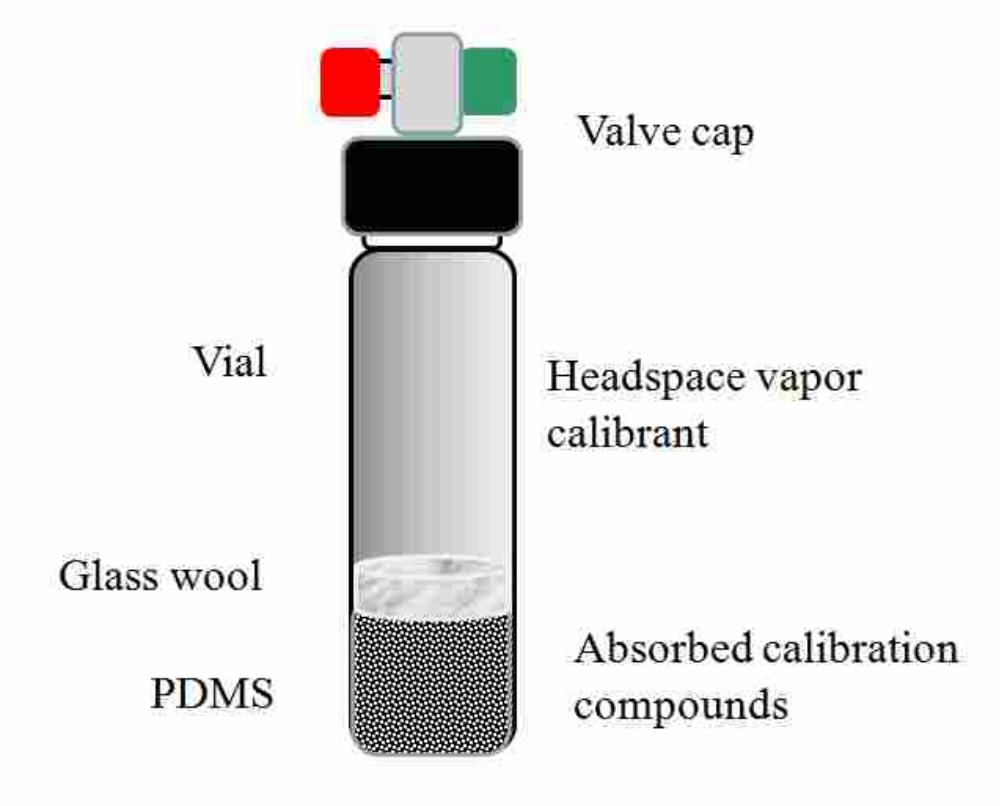

Figure 4.1 Configuration of the EDS device, containing a glass vial with adsorbent material and valve cap.

Table 4.1 Preparation of different EDS

Experiment	PDMS amount and format	Amount of compound added/μL[a]					
		1	2	3	4	5	6
Effect of PDMS size	2.0 g, 3 mm blocks	1.0	2.0	2.8	5.5	19.5	21.1
	2.0 g, 10 mm blocks						
	2.0 g, solid block, 14.53 mm o.d.						
Comparison of EDS system with conventional liquid standard mixture	No PDMS	4 μL of stock solution, prepared by mixing 0.4 mL methylene chloride (14.3%, v/v), 0.1 mL toluene (3.6%, v/v), 0.1 mL bromoform (3.6%, v/v), 0.2 mL *n*-undecane (7.1%, v/v), 1.0 mL methyl salicylate (35.7%, v/v) and 1 mL *n*-tetradecane (35.7%, v/v).					
	2.0 g, 200 μm particles	4.0	20.2	28.0	55.0	195.0	211.0
Relationship between analytes added and amount extracted	2.0 g, 200 μm particles	0.4	2.0	2.8	5.5	19.5	21.1
		0.8	4.0	5.6	11.0	40.0	42.2
		0.1	0.5	0.7	1.4	5.0	5.0
Stability	2.0 g, 200 μm particles	0.4	2.0	2.8	5.5	19.5	21.1

[a]Compounds 1-6 represent: (1) methylene chloride, (2) toluene, (3) bromoform, (4) *n*-undecane, (5) methyl salicylate, (6) *n*-tetradecane

Six analytes were selected to perform most tests by considering compound volatility, polarity and m/z values: methylene chloride, toluene, tribromomethane, *n*-undecane, methyl salicylate and *n*-tetradecane. Two temperature control devices were used to perform thermostated experiments: a Neslab RTE-110 refrigerated bath/circulator from Thermo Scientific (Newington, NH, USA) and a home-made aluminum heating block controlled using an OMEGA CSC32 Mini Benchtop Controller (Stamford, CT, USA). The RTE-110 system generated temperatures from 10 °C to 80 °C, while the home-made heating block provided temperatures from room temperature to 200 °C.

4.2.5 Calibration curves

In order to quantify the amount extracted by the SPME fiber, two calibration curves were constructed via conventional syringe injection; one was constructed using the GC-MSD system and the other using the GC-FID system. The procedures were similar for generating both calibration curves. A six-component standard solution (1 µg/µL each) was prepared by adding 187.5 µL of methylene chloride, 288.4 µL of toluene, 86.5 µL of bromoform, 337.8 µL of *n*-undecane, 212.9 µL of methyl salicylate and 327.7 µL of *n*-tetradecane to a 250 mL volumetric flask and then adding benzene (or henxane) to a volume of 250 mL. Other concentrations were obtained by diluting the standard solution with benzene (or henxane) solvent to give 30 ng/µL, 50 ng/µL, 70 ng/µL, 100 ng/µL, 300 ng/µL, 500 ng/µL, and 700 ng/µL. Calibration curves were constructed by injecting 1.0 µL of each of these solutions into the GC-MSD system five times (i.e., 5 replicates) with an auto sampler. For the GC-FID calibration curves, 3.0 µL each of 5.0 ng/µL, 10 ng/µL, 30 ng/µL, 50 ng/µL, 100 ng/µL, 300 ng/µL, and 500 ng/µL solutions were injected three times manually. For each dilution, the replicate %RSD values were below 10% for

GC-MSD and 5% for GC-FID measurements. Averages of the measurements were used for constructing the calibration curves as shown in Figure. 4.2.

4.3 Results and discussion

In order to validate this new EDS method for preparing standard mixtures of volatile and semi-volatile organic compounds, the effect of PDMS form, relationship between analytes dispersed and amount extracted, reproducibility, long term stability, quantitation, effect of temperature on distribution, and re-equilibrium time after temperature change were studied.

4.3.1 Effect of PDMS form and particle size

Different PDMS forms were tested to determine the most appropriate form and particle size, including solid PDMS synthesized in the bottom of a 7.4 mL vial (14.53 mm diameter), 10 mm blocks, and 3 mm blocks. Similar amounts of the three PDMS forms were introduced into 7.4 mL vials at room temperature. Using the same methods for introducing test analytes into the vials, letting them come to equilibration, and SPME sampling, we determined how fast the vials achieved equilibrium and how stable the headspace concentrations were after equilibrium. We found that the smaller PDMS particles reached equilibrium faster. After an initial equilibration period of 120 h, headspace above each of the 3 PDMS forms was sampled five times sequentially (approximately 10 min between each consecutive sample). Changes in measured amounts for repeated samples are summarized in Table 4.2. The results indicate that the smaller particle forms provided more rapid distribution equilibration and, thus, more consistent signal intensity (i.e., smaller or insignificant decreasing slope over repeated measurements) in a short

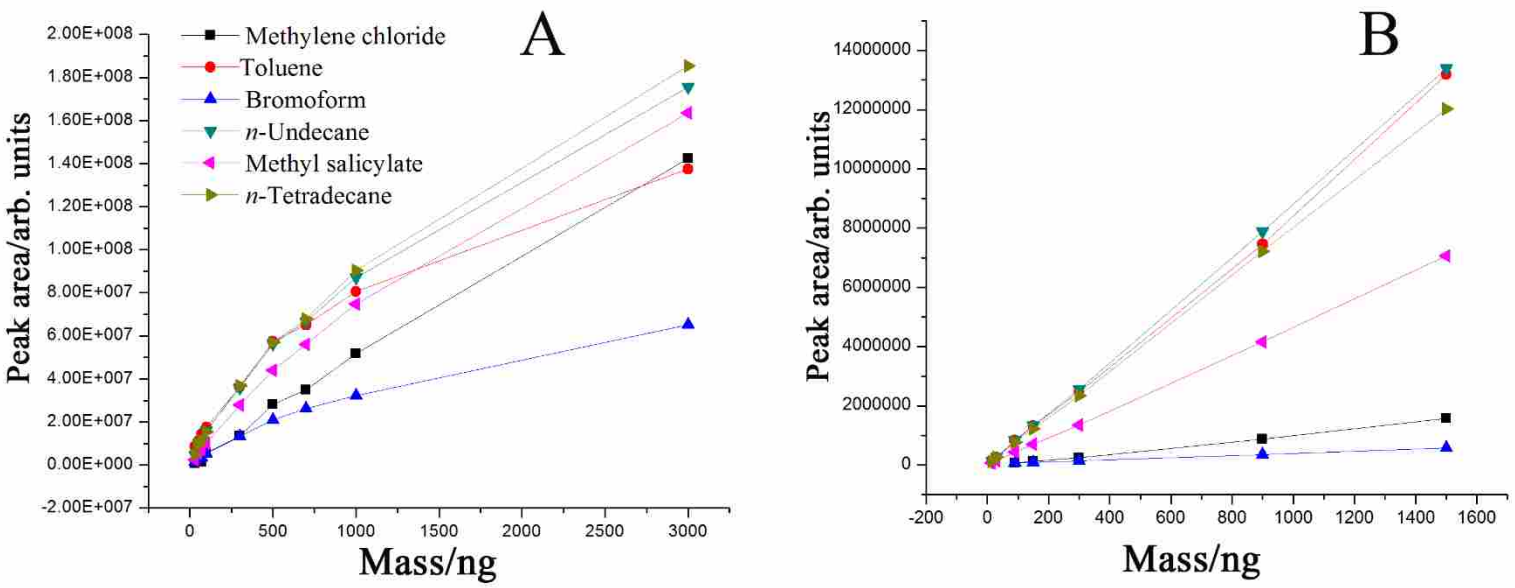

Figure 4.2 Calibration curves obtained using conventional syringe liquid injection of a standard solution and analysis using (A) GC-MSD and (B) GC-FID.

Table 4.2 Repetitive sampling of EDS vial headspace containing different forms of PDMS.

Form	Methylene chloride		Toluene		Bromoform		*n*-Undecane		Methyl salicylate		*n*-Tetradecane	
	%RSD	Slope[a]	%RSD	Slope[a]	%RSD	Slope[a]	%RSD	Slope[a]	%RSD	Slope[a]	%RSD	Slope[a]
Solid	2.17	ns	0.58	ns	1.01	-8.09	2.31	-3.46	2.24	-2.36	3.16	ns
10 mm blocks	4.92	ns	0.34	ns	0.35	ns	0.66	ns	0.89	ns	3.73	ns
3 mm blocks	0.43	ns	0.14	ns	5.40[b]	ns	0.77	0.16	1.77	ns	3.35	ns

[a]Slope refers to the change in measured amount of compound per repeated measurement (5 measurements total). Units are in ng/run, negative sign indicates a decrease, and "ns" means not statistically significant at $\alpha = 0.05$.
[b]This data point is suspected to be inaccurate, causing an apparent increase; omitting this data point gave an %RSD of 0.77% and a slope of -0.07 ng/run.

period of time. In later experiments, particles of approximately 200 μm in size performed even better; therefore, we used these smallest PDMS particles for subsequent experiments.

4.3.2 Comparison of the EDS system with sampling above a liquid standard

A comparison experiment was conducted to compare vapor sampling using the EDS system (i.e., containing polymer sorbent) with sampling the headspace above a standard mixture prepared without the polymer. The amounts of analytes initially added to the two vials were chosen to provide similar peak areas in the chromatograms (within 7%) for 30-s SPME fiber extraction at room temperature. Approximately 3 per day were taken (consecutively, with approximately 15-min delay between each sample) from each of the two vials over a 30-day period using SPME. GC-MS analyses were conducted for each of the approximately 100 samples per vial. Comparisons were made by assigning the peak areas in the first run of the day after equilibrium was reached (usually, this occurred at day 3) as 100%. Peak areas of runs on subsequent days were reported as percentages of these amounts.

The difference between the EDS vial and the vial containing no PDMS was most significant for the most volatile compounds. For example, the signal decreased for toluene to approximately 20% of the original value after 30 days when no substrate was present. In contrast, with 2.0 g of PDMS, the signal remained above 90%. On the other hand, the least volatile compound (*n*-tetradecane) showed no signal decrease (with PDMS or without PDMS) which was due to the large amounts added and their low vapor pressures (i.e., greater than 10 times more added than the volatile compounds in order to produce comparable peak areas). As the sampling processes were conducted during multiple days, the first few runs of each day gave higher signal response.

Possible reasons for this phenomenon include adsorption on the active vial walls, which would lead to higher concentration in the vapor phase, or relatively slow equilibrium of the system, i.e., initial 95% equilibrium is fast (i.e., approximately 10 min), while complete equilibrium requires much longer time.

4.3.3 Stability

In order to use this device for generating standards, stability and reproducibility are very important properties. As mentioned in the previous section, a daily cyclic trend in signal intensity was observed at room temperature during repetitive sampling. To eliminate instability contributions from the vial and MS detector, we evaluated the EDS system under more controlled conditions, i.e., using a deactivated glass vial and GC-FID system. A 7.4 mL glass vial was deactivated by silanization[23] before the desired amounts of analytes were added. The vial was then placed in a 45 $^{\circ}$C heating block. The vial headspace was analyzed using an SPME fiber at various times during a 43-day period. Under these conditions, all %RSD values were below 4.5% and no significant signal fluctuations were observed (Table 4.3). After more than 114 runs, less than 5% signal decrease for all compounds was observed except for methylene chloride, which decreased approximately 15% due to possible leaking at the cap. The reasonableness of these results can be appreciated with a simple calculation. Assume that 2.0 μL of toluene (or 1.73×10^5 ng) are added to the EDS device. Each extraction consumes approximately 84 ng (determined from a calibration curve), which is less than 0.005% of the total. Therefore, 100 runs would consume only 0.4% of the total. For long intervals between samplings, i.e., 3 days and 20 days, no observable initial signal increase was observed.

Table 4.3 EDS reproducibility test results at 45 °C for a total of 114 EDS analyses.[a,b]

	Methylene chloride	Toluene	Bromoform	*n*-Undecane	Methyl salicylate	*n*-Tetradecane
Average[c] /ng	264.4	84.3	848.5	124.8	343.3	41.1
Standard deviation /ng	11.5	1.2	16.8	1.5	5.2	1.6
Relative standard deviation/%	4.43	1.39	1.98	1.22	1.52	3.98
Mass decrease[d] /ng/run	-0.33	-0.02	-0.45	-0.02	-0.08	-0.03
Percent decrease /%/run	-0.12	-0.03	-0.05	-0.02	-0.02	-0.07
Standard error of percent decrease/%	-0.0041	0.0028	0.0026	-0.0031	0.0036	0.0094

[a]Sampling and analysis conditions were as described in Section 4.2.
[b]GC-FID system with deactivated vial.
[c]Average amount (114 analyses) introduced before a 20:1 split.
[d]Percent change determined as decreasing slope over time for the 114 analyses.

Furthermore, with 10 runs a day, no observable gradual signal decrease was observed as well (the average number of runs each day was 5). It was found that under controlled conditions, signal fluctuations and significant downward drift were nearly eliminated.

4.3.4 Relationship between analytes added and amount extracted

To investigate the relationship between analytes dispersed in the EDS vial and amounts extracted by the SPME fiber, experiments were conducted using vials containing the same amount of PDMS (2.0 g) but different amounts of analytes. As shown in Table 4.4, the amounts extracted at room temperature with an SPME fiber for 30 s gave positively correlated relationships, although not linear. This non-linearity suggests that the distribution of analytes between the gas and solid phases was not simply equilibrium-based, and some adsorption on the surface most likely occurred. As long as these relationships are known, the EDS system can be used for quantitation, since the amounts extracted can be determined based on the amounts introduced into the vials.

4.3.5 Quantitation

The distribution of analytes between the PDMS particles and headspace depends primarily on the individual analyte distribution coefficients between these two phases, and the temperature dependences of the distribution coefficients. Therefore, in order to perform quantitative calibration, either an active temperature control device or a previously generated look-up table is required to provide the extracted amount as a function of temperature. A look-up table for a temperature range of 10 $^{\circ}$C to 45 $^{\circ}$C for the six test compounds was generated from multiple measurements of 3 replicate vials equilibrated at each temperature (Table 4.5). Using

Table 4.4 Relationship between analyte amount added to and extracted from the EDS system based on measurements.[a,b,c,d]

	Volume added/μL	Mass extracted /ng / RSD/%	Volume added/μL	Mass extracted/ng / RSD/%	Volume added/μL	Mass extracted /ng / RSD/%
Methylene chloride	0.1	72.2 / 7.4	0.4	175.6 / 3.9	0.8	397.0 / 6.5
Toluene	0.5	25.1 / 13	2.0	324.5 / 2.7	4.0	756.2 / 4.7
Bromoform	0.7	237.6 / 7.3	2.8	1131.6 / 2.0	5.6	1817.6 / 2.6
n-Undecane	1.4	29.0 / 10.3	5.5	92.1 / 3.2	22.0	237.9 / 4.5
Methyl salicylate	5.0	9.2 / 9.6	19.5	286.2 / 2.2	40.0	583.4 / 4.1
n-Tetradecane	5.0	ND[d]	21.1	12.7 / 5.6	42.2	58.4 / 5.9

[a]Sampling and analysis conditions were as described in Section 4.2; data are average of 3 measurements
[b]GC-MSD system.
[c]Amount introduced before a 10:1 split
[d]Below detection limit

Table 4.5 Look-up table for six calibration compounds at various temperatures.[a,b]

Temp /°C	Methylene chloride[c]	Toluene[c]	Bromoform[c]	*n*-Undecane[c]	Methyl salicylate[c]	*n*-Tetradecane[c]
10	146.5 / 0.12	46.6 / 0.1	258.4 / 0.13	4.8 / 6.76	18.8 / 1.85	NA
15	155.3 / 0.96	54.7 / 1.29	350.5 / 0.84	11.1 / 2.70	31.8 / 1.51	0.6 / 7.35
20	167.8 / 0.31	66.2 / 1.05	466.5 / 0.23	21.8 / 2.57	54.9 / 0.93	3.0 / 12.19
25	181.2 / 0.35	75.7 / 0.24	567.8 / 0.53	38.0 / 0.49	88.2 / 0.46	6.4 / 0.63
30	189.2 / 0.91	85.5 / 1.55	692.2 / 0.69	58.0 / 1.61	130.5 / 1.09	12.1 / 0.06
35	188.5 / 0.97	91.3 / 0.40	776.0 / 0.02	81.7 / 0.68	183.2 / 0.80	20.6 / 1.40
40	195.8 / 0.84	102.8 / 0.84	903.8 / 0.73	121.2 / 0.45	273.5 / 0.82	37.6 / 0.61
45	199.8 / 2.78	111.5 / 0.93	1021.0 / 0.57	168.1 / 3.47	385.1 / 3.26	62.4 / 4.33

[a]Sampling and analysis conditions were as described in Section 4.2.
[b]GC-FID system with deactivated vial.
[c]Amount extracted/ng / RSD/%

this table, the amounts extracted at any specific temperature can be determined by interpolation. A table with smaller temperature intervals can be generated if desired. From this table, we observe that the extracted amount of a compound increases as the temperature increases, and the amounts of less-volatile compounds increase more rapidly as the temperature increases compared to more volatile compounds.

4.3.6 Re-equilibrium after changing the temperature

Another important property of the EDS device is the time required for establishment of distribution equilibrium when changing between different temperatures, i.e., the time it takes for the device to be ready to use after a temperature change. We measured the equilibrium times from changing the temperature of a calibration vial from room temperature (approximately 22-23 $^{\circ}$C) to 45 $^{\circ}$C, from 10 $^{\circ}$C to 45 $^{\circ}$C and from 45 $^{\circ}$C to 10 $^{\circ}$C by physically moving the calibration vial between two heating blocks, each of which was previously set at the desired temperature, and measuring the amount extracted over time using SPME. In all three cases, as shown in Figure 4.3, approximately one hour was required to reach steady state. However, we found that 90% equilibrium could be reached in approximately 10 min for rapid semi-quantitative measurements.

4.3.7 Reproducibility between EDS devices

More than 50 EDS devices were prepared during this research period. All of the PDMS fabrication and sampling steps were manually conducted, and PDMS particles were fabricated in more than 20 different batches. Within the same batch of PDMS particles, the signal intensity

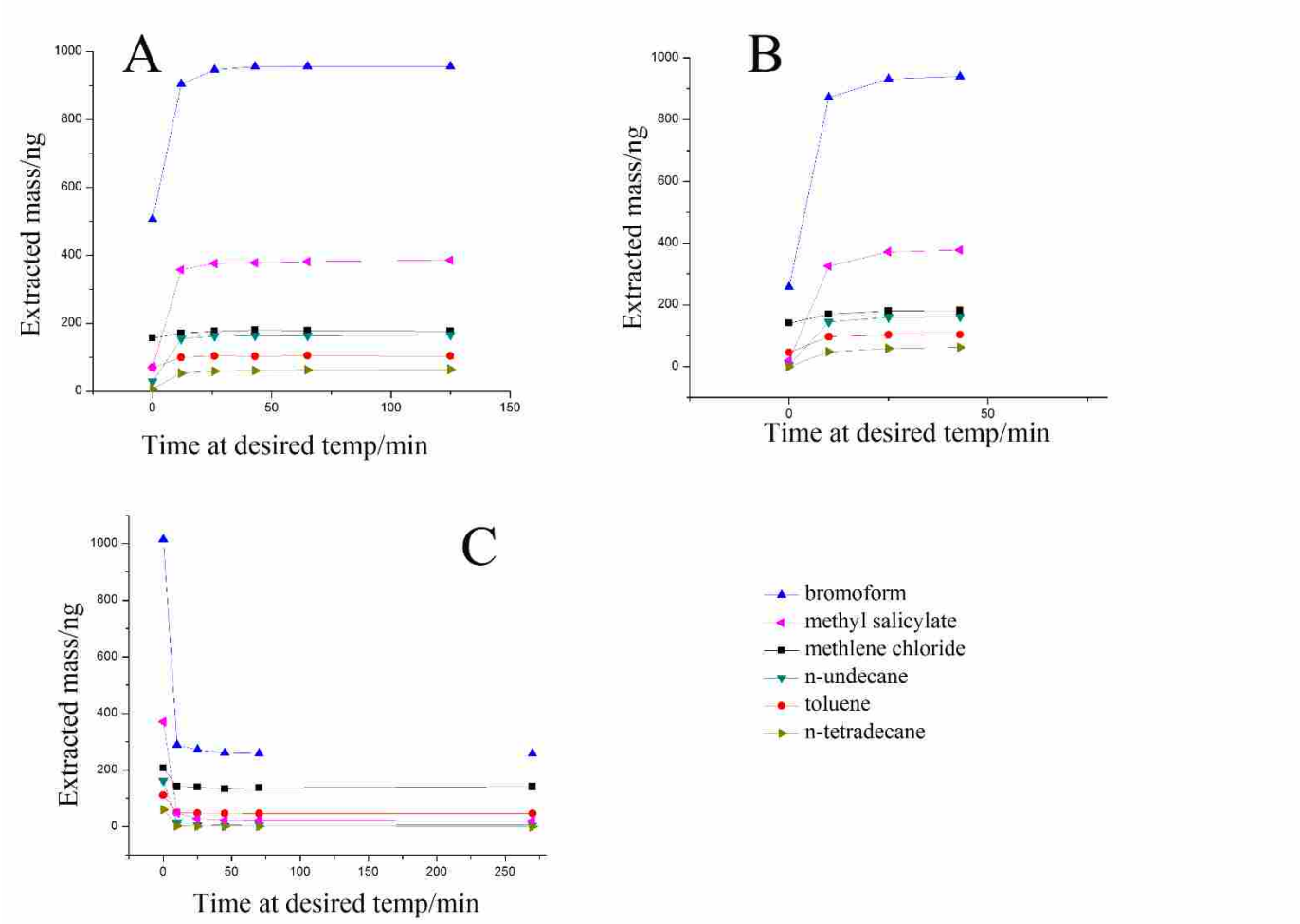

Figure 4.3 Time required for re-equilibrium of test analytes in an EDS vial (A) from room temperature (22-23 ˚C) to 45 ˚C, (B) from 10 ˚C to 45 ˚C, and (C) from 45 ˚C to 10 ˚C.

%RSD values between devices were approximately 5-7% for the different analytes. The variation from batch to batch varied as much as 20%. Unless better control of the conditions (e.g., temperature, time, and particle distribution) for preparation of PDMS particles can be obtained, batch-specific calibration will be required.

4.3.8 Distribution coefficient and mechanism

The EDS devices work very well for generating stable analyte vapor; however, the mechanism behind solute distribution in these devices is still unclear. In principle, the equilibrium distribution sampling device can be considered to be a closed two-phase system (vapor phase and polymer phase). In order to simplify the problem, a simple system was set up with a 7.4 mL vial (total volume 8.5 mL) containing 2.0 g PDMS and 2 μL toluene. Experiments were conducted to measure actual headspace concentrations and calculate distribution coefficients, which were then compared with reference values.

Measurements (3 duplicate sets, i.e., 6 devices prepared in duplicate at 3 different times, with 7 or more measurements for each of the 6 devices, for a total of 50 measurements in over 30 days at room temperature) gave an average peak area of 1.36×10^5, with a maximum relative standard derivation of 22.6 %. A 1.0-ppm toluene gas standard was used to determine the concentration, with a result of 20.3 ppm. In comparison, liquid solution standard calibration gave 16.0 ppm. The distribution coefficient (i.e., concentration in the solid phase divided by concentration in the gas phase) can be calculated using the measured headspace concentration. With a headspace concentration of 16.0 to 20.3 ppm, the distribution coefficient was calculated to be 1.10×10^4 to 1.38×10^4.

4.3.9 Measurement of the headspace concentration of toluene in an EDS vial

Three identical sets of model EDS devices were prepared at different times, each containing duplicate devices. All PDMS particles used were fabricated in one batch to reduce variation. Each device was sampled with a gas-tight syringe and analyzed using GC-FID. The peak areas were then quantified using two approaches: comparison to an injection of 1.0 ppm commercial standard toluene sample, and a liquid injection calibration curve.

Measurements were first conducted using a 500 μL gas-tight syringe. The tip of the syringe was heated to 200 $^{\circ}$C before each sampling to reduce sample carry-over. An Agilent 7820A GC-FID system was used for detection. Three duplicate sets of devices (6 devices total) were prepared by adding 2 μL toluene into 2-dram vials with 2 g PDMS at different times. After approximately 3 days equilibrium at room temperature, each device was sampled and analyzed using a 500 μL gas-tight syringe multiple times during a 30-day test period. Two 1.0 ppm standard toluene air bags were sampled and analyzed at the same time to provide a quantitative reference. Using a 1.0 ppm toluene gas standard, the concentration in the headspace was found to be 20.3 ppm (see Table 4.6).

Two liquid calibration curves were also constructed by injecting 1.0 μL standard solutions of toluene in methanol. The first included six data points (1.6 ng, 4.0 ng, 10 ng, 20 ng, 40 ng and 100 ng, each with at least duplicate measurements) and gave a calibration curve of $y = 4369.2\ x + 4793.5$, with $R^2 = 0.9935$. Another calibration with nine data points (0.25 ng, 0.5 ng, 1.0 ng, 3.0 ng, 5.0 ng, 7.0 ng, 10 ng, 30 ng, and 50 ng) gave a calibration curve of $y = 2997 + 4733.6\ x$,

Table 4.6 Headspace concentration determined using a standard gas sample and gas-tight syringe.

Vial designation (set / number)	Average peak area	RDS/%[a]
1 / 1	1.46×10^5	16.2
1 / 2	1.76×10^5	22.9
2 / 1	1.46×10^5	16.4
2 / 2	1.34×10^5	17.9
3 / 1	1.18×10^5	23.9
3 / 2	1.21×10^5	23.7
1.0 ppm standard	6.72×10^3	15.7
Average of all vials	1.36×10^5 (20.3 ppm[b])	22.6

[a] Percentage RSD was calculated for each set and device using repeat observations.
[b] Calibrated concentration using the 1.0 ppm standard.

with $R^2 = 0.9987$. With an average peak area of 1.36 x10^5, the liquid calibration curve 1 gave a result of 16.6 ppm, while curve 2 gave 15.5 ppm. The average is 16.0 ppm (see Table 4.7).

4.3.10 Calculation of the partition coefficient using headspace concentration

According to simple partition theory, as an analyte enters a closed system, it is distributed between the vapor phase and solid/polymer phase. The ratio of concentration of analyte in the sorbent/polymer to concentration of analyte in the vapor phase is defined as the partition coefficient, K (or distribution coefficient if more than just simple partition is involved):

$$K = \frac{C_2}{C_1} \tag{4.1}$$

where C_2 is the concentration in the polymer phase, and C_1 is the concentration in the gas phase.

In our EDS system, as the total volume, PDMS amount and analyte amount are known, and the headspace concentration can be measured, we can easily calculate the distribution coefficient.

$$m = C_1V_1 + C_2V_2 \tag{4.2}$$

$$K = \frac{C_2}{C_1} = \frac{(m - C_1V_1)/V_2}{C_1} \tag{4.3}$$

where m is the total amount of analyte added (m = 2.0 µL x 0.8669 mg/µL = 1.73 mg), V_2 is the volume of the polymer (PDMS density is 0.965 g/mL, V_2 = 2.0 g /(0.869 g/mL) = 2.07 mL), V_1 is the headspace volume (vial volume is 8.5 mL, V_1 = 8.5 - V_2 = 8.5-2.07 = 6.43 mL), and C_2 is the headspace concentration (C_1 is 16.0 to 20.3 ppm). At 25 ˚C and 1 atm, the toluene concentration can be converted from ppm to mg/m^3 using the following equation:

$$\text{X ppm} = (\text{Y mg/m}^3)(24.45)/(\text{mw}) \tag{4.4}$$

For $C_1 = 16.0$ ppm, converted into $16.0 \times \frac{92.14}{24.45}\frac{\text{mg}}{\text{m}^3} = 60.3\ \frac{mg}{\text{m}^3}$, mw = 92.14 g/mol

Table 4.7 Data measured by liquid injection for construction of calibration curves.

Calibration curve 1		Calibration curve 2	
Amount injected /ng	Peak area/arb. units (RSD/%)[a]	Amount injected /ng	Peak area/arb. units (RSD/%)[a]
1.6	0.60×10^4 (3.2)	0.25	0.268×10^4 (17)
4	0.10×10^4 (8.0)	0.5	0.401×10^4 (1.4)
10	4.43×10^4 (13)	1.0	0.606×10^4 (15)
20	1.02×10^5 (8.7)	3.0	1.91×10^4 (5.0)
40	2.01×10^5 (10)	5.0	2.44×10^4 (3.5)
100	4.32×10^5 (23)	7.0	3.07×10^4 (2.8)
		10	5.46×10^4 (5.6)
		30	1.50×10^5 (7.4)
		50	2.36×10^5 (3.8)
EDS average	1.36×10^5		
Calc. Conc./ppm	16.6[b]		15.5[c]
Ave./ppm	16.0		

[a] RSD values were calculated for 2-3 repeated measurements for each dilution.
[b] Concentration based on calibration curve 1.
[c] Concentration based on calibration curve 2.

$$K = \frac{(m - C_1 V_1)/V_2}{C_1} = (1.73 \text{ mg} - (60.3 \frac{\text{mg}}{\text{m}^3})(6.43 \text{ mL x } 10^{-6} \frac{\text{m}^3}{\text{mL}})/(2.07 \text{ mL x } 10^{-6} \frac{\text{m}^3}{\text{mL}})/$$

$$(60.3 \frac{\text{mg}}{\text{m}^3}) = 1.38 \times 10^4 \quad (4.5)$$

For $C_1 = 20.3$ ppm, converted into $20.3 \text{ x } \frac{92.14}{24.45} \frac{\text{mg}}{\text{m}^3} = 76.5 \frac{\text{mg}}{\text{m}^3}$

$$K = \frac{(m - C_1 V_1)/V_2}{C_1} = (1.73\, mg - (76.5 \frac{\text{mg}}{\text{m}^3})(6.43\, m\text{L x } 10^{-6} \frac{\text{m}^3}{\text{mL}})/ (2.07 \text{ mL x } 10^{-6} \frac{\text{m}^3}{\text{mL}})/$$

$$(76.5 \frac{\text{mg}}{\text{m}^3}) = 1.09 \times 10^4 \quad (4.6)$$

4.3.11 Construction of a calibration curve

For construction of a calibration curve, three duplicate sets, each set containing eight 2-dram devices with 2.0 g PDMS, were prepared. In each set, the eight devices were divided evenly into 4 groups, and then 0.1 µL, 0.5 µL, 1.0 µL, and 2.0 µL of toluene were added into vials of each group, respectively. Each device was sampled and analyzed using the gas-tight syringe and GC-FID for more than 6 times after equilibrium. The results are summarized in Table 4.8 and used to construct the calibration curve (Figure 4.4).

4.4 Applications

4.4.1 GC-MS system calibration

The most popular calibration compound for MS, perfluorotributylamine, is not useful for evaluating the performance of GC (i.e., almost no retention). Typical test compounds for GC, such as normal alkanes and polarity mixtures (e.g., the Grob test mixture), are not particularly useful for MS calibration. In order to calibrate the GC and MS with one test sample, a calibration

Table 4.8 EDS headspace concentrations for different amounts of toluene.

Device #	Toluene amount/μL	Peak area/arb. units[a]	Conc./ppm[b]	RSD/%
1	0.5	2.85×10^4	4.25	40.0
2	0.5	3.51×10^4	5.22	70.2
3	1.0	6.10×10^4	9.08	16.3
4	1.0	5.94×10^4	8.84	18.6
5	2.0	1.41×10^5	20.99	18.5
6	2.0	1.37×10^5	20.37	27.0
11	0.1	0.479×10^4	0.71	26.5
12	0.1	0.482×10^4	0.72	21.7

[a] Average of three sets.
[b] Determined using a 1.0 ppm toluene standard gas sample.

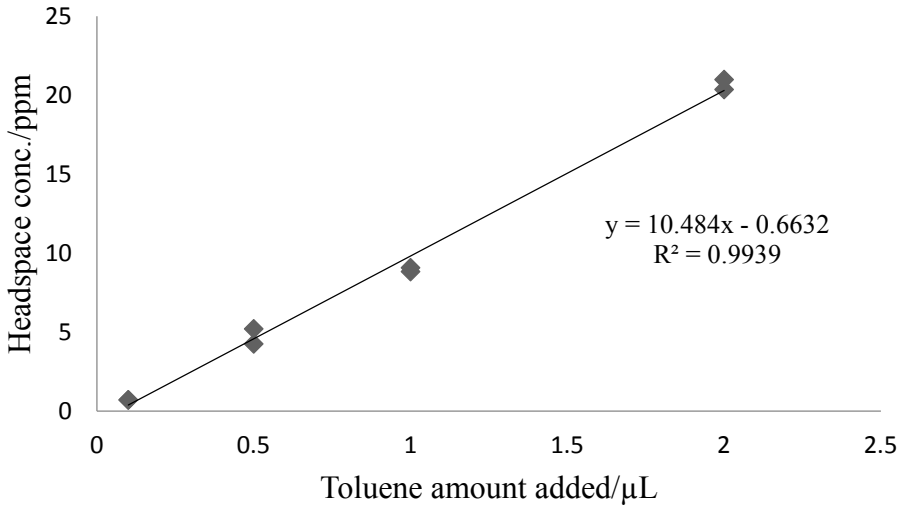

Figure 4.4 Calibration curve constructed using eight EDS devices and different amounts of toluene.

mixture is needed that contains: (1) normal alkanes to index compound retention with the Kovats retention indices, RI; (2) compounds with a variety of polarities to test for GC column inertness and selectivity; and (3) compounds that produce mass fragments that cover the mass range of interest in MS. Perfluorotributylamine has characteristic mass fragments (m/z) from electron ionization (EI) of 69, 100, 119, 131, 219, 262, 414, and 464.[3] To fulfill the requirements for both GC and MS, we selected the following compounds, which provide corresponding m/z values given in parenthesis: methyl-tert-butyl ether (73), methylcyclohexane (55, 83), toluene-d8 (98, 100), tetrachloroethene (94, 129, 166), bromopentafluorobenzene (117, 167, 246, 248), bromoform (171, 173, 175), 1,2-dibromotetrafluorobenzene (148, 306, 308, 310), methyl salicylate (92, 120, 152), and tetrabromoethane (184, 186, 188, 263, 265, 267, 269, 346). These compounds not only provide peaks that cover m/z values from 55 to 346, but also give many characteristic isotopic peaks which help in calibrating the mass spectrometer. For GC, acetone (RI = 470), *n*-heptane (RI = 700), and *n*-tetradecane (RI = 1,400) cover the GE retention range from 470 to 1400. Not all of these test analytes are necessary for all applications; any of these or other compounds can be added to the vial for specific purposes. These selected compounds behave well in the EDS system; stable signals can be obtained for compounds spanning a wide volatility range. Figure 4.5A shows a total-ion chromatogram of this calibration mixture obtained using a hand-portable GC-MS system. Obviously, this EDS device can be easily used in the field for GC-MS calibration.

4.4.2 GC column validation

Much effort has been spent in developing GC column validation methods to test separation efficiency, adsorptive activity, acid-base behavior, selectivity, and stationary phase film

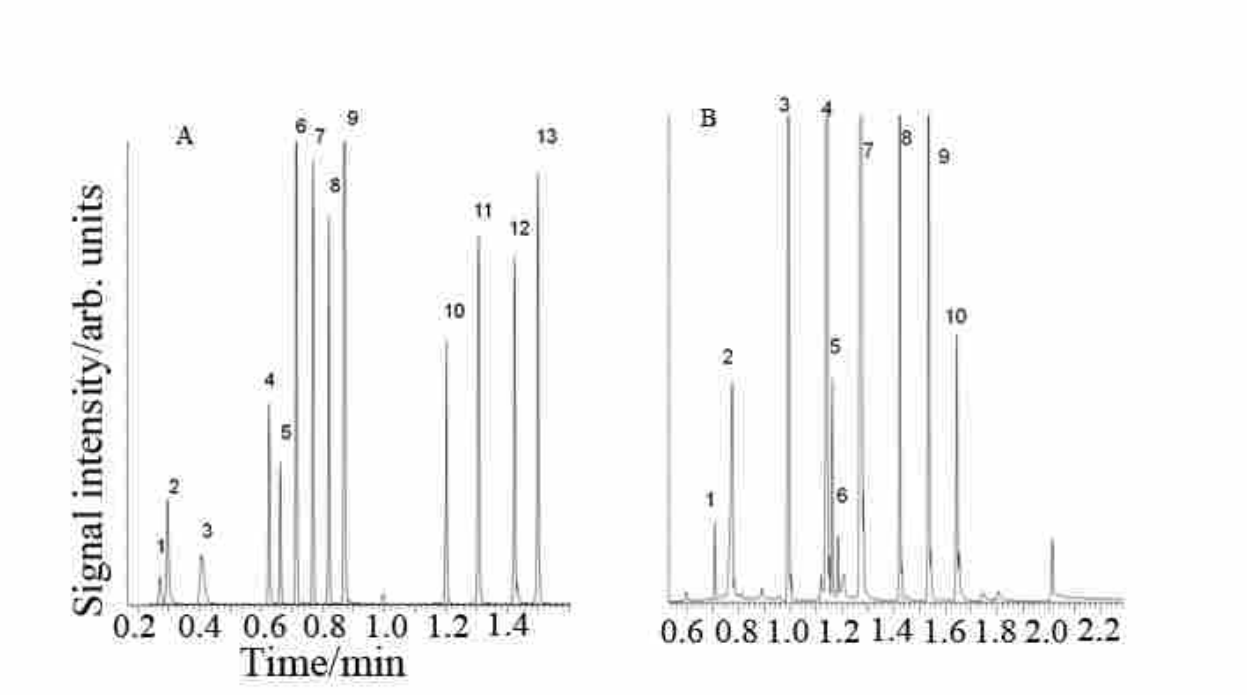

Figure 4.5 Chromatograms of (A) GC-MS calibration mixture and (B) Grob test mixture using the EDS device. Conditions: see Section 4.2.2. (A) Compound identifications: (1) acetone, (2) methylene chloride, (3) methyl-*tert*-butyl ether, (4) *n*-heptane, (5) methylcyclohexane, (6) toluene-d8, (7) perchloroethylene, (8) bromopentafluorobenzene, (9) bromoform, (10) 1,2-dibromotetrafluorobenzene, (11) methylsalicylate, (12) tetrabromoethane, (13) *n*-tetradecane. (B) Compound identifications: (1) *n*-decane, (2) *n*-undecane, (3) 1-nonanal, (4) 2,3-butanediol, (5) 1-octanol, (6) 2,3-butanediol isomer, (7) methyl decanoate, (8) methyl undecanoate, (9) methyl dodecanoate, (10) 2,6-dimethylphenol.

thickness, the most popular involving various Grob test mixtures.[12,13] After initial publication in the 1980s, different compositions of Grob mixtures have been reported for different purposes.[25,26] However, the general composition has remained almost the same. For the same reasons as outlined for a GC-MS calibration mixture, our EDS system is attractive for generation of column test mixtures. Different column validation mixtures have been tested in our laboratory including, but not limited to Grob (Figure 4.5B), alkane, amine, alcohol, and monochloro alkane mixtures.

4.4.3 Internal standard generator

Another interesting application for this EDS system is use as an internal vapor standard generator. By displacing a certain volume (e.g., 100 μL) of headspace from the vial, a constant concentration of analyte vapor can be obtained to be used as an internal standard.

4.4.4 On-site generation of a calibration curve

One unique aspect of the EDS system is that the extracted amounts increase with temperature, and there is no solvent to affect the extraction. As demonstrated earlier in this paper, a calibration curve can be easily generated by changing the temperature within a specific range. Also, researchers can use different EDS devices to generate different concentrations at a given temperature. This is especially useful in the field where preparation of solutions in liquid solvents is not convenient.

A set of experimental calibration vials was prepared by adding different amounts of toluene (0.1, 0.5 1.0 and 2.0 µL) into 2-dram vials, each containing 2.0 g of PDMS. A linear calibration from 0.7 to 20 ppm was constructed using these four EDS vials, with an R^2 of 0.9939.

4.5 Future improvements in the EDS device

The EDS devices described in this chapter were constructed of readily available materials for use in demonstrating the principles of operation. Design improvements are currently being studied to provide more robustness, better gas-tight seal, ease in changing test mixtures, and practical temperature control in the field. These improvements should facilitate the use of EDS for practical field applications.

4.6 Conclusions

A novel approach to prepare standard mixtures by diluting calibration analytes in granular PDMS was developed. Compared to conventional standard preparation methods, this equilibrium-based method provides multiple advantages: it is solventless, long-lasting, stable, simple and robust. Traditional liquid solvents are not required, and the calibration mixtures are stable for long periods and for many injections.

The technique can be adjusted for ambient temperature variations, and the method is quantifiable. The extracted amounts of analytes can be adjusted by controlling the composition or the temperature. Within a test period of 43 days, an EDS device was sampled and analyzed by GC and GC-MS more than 114 times, and the amounts of analytes measured were all within 4.5% RSD and above 87% of the initial runs. This approach is important for meeting the needs

of on-site GC-MS analysis and on-site high flow sampling, since on-site calibration and internal standard addition are relatively simple using the device reported in this work.

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Chapter 5 Conclusions and Recommendations for Future Work

5.1 Conclusions

The results of my research clearly indicate that high flow rate air sampling is a reasonable approach to detect ppt (part per trillion) levels of VOCs. Both approaches investigated, i.e., multi-capillary trap and concentric packed trap, can be used to sample air at high flow rate (>5.0 L/min) and achieve detection limits as low as single digit ppt for some compounds.

Both approaches have their advantages and disadvantages, and can be selected based on the requirements of the applications of interest as listed in Table 5.1. In general, the multi-capillary trap provides a simple solution for performing exhaustive high flow rate VOC sampling. The multi-capillary trap can be constructed relatively easily and is compatible with conventional TD (thermal desorption) systems. On the other hand, selection of sorbents is relatively limited, and detection limits may not be as low as desired. In contrast, the concentric packed trap employs a more complicated design, utilizes more sorbent and provides greater potential. It can provide high breakthrough volume and low detection limits because of a larger sorbent volume. It is limited mainly by its bulk structure, large thermal mass and large breakthrough volume.

Therefore, the multi-capillary high flow trap is suitable for exhaustive sampling of compounds with boiling points higher than approximately 80 ˚C, and it can be easily used with conventional

Table 5.1 Comparison of multi-capillary and concentric packed high flow rate traps.

	Multi-capillary trap	Concentric packed trap
Maximum flow rate	5-6 L/min	>10 L/min
Detection limits	ppt	<ppt
Sorbent selection	Those that can be coated onto the capillary wall	Any sorbent material
Sorbent amount	< 1 g	>1 g
Breakthrough volume	10-500 L	>500 L
Thermal mass	Small	Large
Desorption volume	Relatively small	Relatively large
Analyte range	Boiling point >80 ◦C	Wide range
Fabrication	Relatively simple	More complicated
Compatibility	Compatible with conventional TD systems	Special desorption system needed

TD systems. The concentric packed trap is more complicated and can be used to trap a wider range of compounds with better detection limits.

5.2 Future work for the multi-capillary high flow trap

Future work needed for the multi-capillary high flow trap lies in three areas. First, exploration of the amounts and types of sorbents that could be used as coatings in the multi-capillary trap would be very helpful to expand its applications. Stronger sorbents, e.g., Carboxen 1000 and Carboxen 569, thick sorbent layers and multiple sorbents would allow trapping of more volatile compounds. Second, comprehensive evaluation of the multi-capillary high flow trap should be performed, including trapping of very volatile and semi-volatile compounds, effect of humidity and matrix interference. Third, the desorption process for the multi-capillary trap should be further optimized to improve the recoveries of different analytes. Different desorption methods could be required for different compounds. Finally, the performance of the multi-capillary trap using conventional TD systems should be evaluated to provide users with an easy adapter for high flow rate air sampling.

Applications of the multi-capillary high flow rate trap system for both laboratory and on-site analysis should be explored. The easiest way to perform on-site high flow rate sampling is by using a conventional TD on-site analysis system, i.e., simply replacing the conventional TD tube with a multi-capillary trap and sampling at high flow rate. The conditions for use of the multi-capillary high flow trap should be fully optimized in the laboratory before using it for on-site analysis.

5.3 Future work for the concentric packed high flow trap

The concentric packed high flow trap is more complex and much more optimization is required. First, the desorption process must be optimized to increase the recovery ratios for analytes of interest. Also, a better thermal desorber must to be designed and constructed to improve the transfer of analytes from the high flow trap to the second-stage trap. Ideally, this thermal desorber should be battery powered so that it is field portable. A comprehensive survey of various sorbents for various analytes (from very volatile to semi-volatile) should be performed to design the right traps for the right applications. Also, the effect of humidity, high background matrices and other factors should be evaluated to fully understand the performance of the trap.

Applications of the concentrically packed high flow trap should be explored, including on-site surveys of various low level VOCs. By using this trap to map the spatial and temporal distributions of various VOCs, it should be possible to identify the sources and trends of a wide range of pollutants.

5.4 Future work for the equilibrium distribution system

Understanding more fully the principles of equilibrium distribution and exploring other potential applications are two areas that should be further explored. Various sorbent materials and analytes should be evaluated to generate data needed for other applications. A more fundamental understanding of how analytes distribute among different phases and what factors affect this distribution is greatly needed. Various applications based on this technology should be explored, including sample preparation, standard generation, and on-site instrument calibration.