Development and Application of Needle Trap Device

By

Ying Gong

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Declaration

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

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Abstract

Air is one of the most important resources in the world and is essential for life. With the development of industry, air pollution is becoming a severe problem. Air Pollution not only affects the quality of the air we breathe; it also impacts the land and the water. Volatile organic compounds (VOCs), which can cause short-term and long-term health problems, are found as contaminants in both indoor air and the environment. Therefore, it is necessary to develop accurate and convenient sampling methods to determine VOCs at trace levels in both community and occupational environment. The focus of this project is to develop the needle trap devices (NTDs) with appropriate sorbents and employ them to do air samplings by diffusive or active sampling mode. For diffusive sampling, the NTD with sorbent Carboxen1000 was developed to monitor benzene, toluene, ethylbenzene and o-xylene (BTEX) in the air, coupled with GC-MS. The factors such as sorbent strength, response time, face velocity, temperature and pressure, relative humidity and sampling duration were investigated. Method validations were done both in the laboratory and in field. The results demonstrate that the NTD with Carboxen1000 is a successful diffusive sampler for monitoring Time-weighted average (TWA) concentrations of BTEX. On the other hand, the NTD with divinylbenzene (DVB) coupled with GC-MS by thermal desorption was developed for sampling and analysis of volatile thiols. The factors such as sorbent strength, desorption efficiency were investigated. The applications, such as vegetable analysis and field sampling analysis, indicate that the NTD with sorbent DVB is a successful active sampler for determine volatile thiols in food and air samples.

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Dedication

I dedicate this thesis to my parents, my husband Yi and my son Kevin.

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List of Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
BET	Brunauer, Emmett, Teller
BTEX	Benzene, Toluene, Ethylbenzene, and o-Xylene
CMS	Carbon Molecular Sieves
DVB	Divinylbenzene
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
GC	Gas Chromatography
HS	Head Space
INCAT	Inside Needle Capillary Adsorption Trap
MS	Mass Spectrometry
NOISH	National Institute for Occupational Safety and Health,
NTD	Needle Trap Device
OEL	Occupational Exposure Limit
OSHA	Occupational Safety and Health Act
PAH	Polycyclic Aromatic Hydrocarbon
PDMS	Polydimethylsiloxane
SPME	Solid Phase Microextraction
TWA	Time-Weighed Average
VOC	Volatile Organic Compound

Chapter 1 – Introduction

1.1 Volatile organic compounds

Volatile organic compounds (VOCs) are those organic liquids or solids whose room temperature (20°C) vapour pressures are greater than about 0.52 mmHg and initial boiling points are less than or equal to 260°C.[1] VOCs can easily evaporate into air to contribute to air pollution. Common sources of VOCs include organic solvents, certain paint additives, fuels (gasoline and natural gas), adhesives, air fresheners, petroleum distillates, dry cleaning products, as well as many other industrial and consumer products ranging from office supplies to building materials. VOCs are also naturally emitted by a number of plants and trees.

Volatile organic compounds (VOCs) are found as contaminants in both indoor air and the environment. VOCs can cause short-term and long-term health problems. For example, the aromatic compound benzene is an established human carcinogen and may lead to leukemia with prolonged exposure.[2] VOCs are an important class of outdoor air pollutants because they are ubiquitous and associated with increased long-term health risks. VOCs are also an indoor air quality problem because humans spend, on average, nearly 90% of their time indoors.[3] Therefore, it is very important to monitor VOCs in the occupational and community environment, such as workplaces, chemical labs, offices and houses to ensure VOCs are under permissible exposure limits. This situation created the need to develop accurate and convenient sampling methods to determine VOCs at trace levels in the workplace or ambient air.

1.2. Sampling method for VOCs

Sampling is the most important step of any analytical procedure. If any mistake is made during this step, it could not be corrected later during analysis. It is significant to choose an appropriate sampling method before sampling, which depends on the physicochemical properties of target analytes and their expected concentration in the air from which they are being sampled. Other factors, such as sampling volume and expected behaviour of target analytes must be carefully taken into account. Sampling volume must be compatible with the sensitivity of the analytical method, and degradation and loss of target compounds must be eliminated.[4]

Conventional sampling methods for VOCs involve some approaches based on different sampling modes. Based on the length of sampling time, air sampling can be classified as grab sampling and time-weighted average (TWA) sampling. Grab sampling is designed to capture a pollutant sample at a specific point in time (often during “peak” exposure) for subsequent analysis, while TWA sampling approach is designed to collect the pollutants over a specified period of time.[5] Based on the extraction mode, air sampling involves collection of the whole air sample or preconcentration of air sample on sorbent.

1.2.1 Whole air sampling

Whole air samples can be collected in a container with a specified volume, which is transported to the laboratory for analysis. Containers for whole air sampling include stainless steel canisters, gas sampling bags and glass gas sampling bulbs.

1.2.1.1 Canisters

Canisters are designed according to U.S. EPA methods TO-14A and TO-15, which regulate the collection, storage and analysis of VOCs using treated air sampling canisters.[6-7] There are two primary approaches of sampling with canisters, either grab sampling or time-weighted average sampling. In the case of grab sampling, the canister valve is simply opened and the vacuum inside the canister draws an air sample in within several seconds. Grab sampling is most often used for discrete odour events, or for static concentration sample streams. For time-weighted average sampling, an additional flow controller or critical orifice is required to be placed in line with the canister and used to draw the air sample into the canister over a wide range of time, depending on the volume of the canister and the flow rate of the flow controller. In both cases, fine particulate filters are needed to set upstream of the canister before sampling to prevent particulates from entering.

There are some advantages of canister sampling. First of all, the actual air sample is collected without any breakthrough; no degradation problems occur from the trapping materials compared with sorbent sampling; it is possible to repeat the sample analysis due to a large volume of the sample collected. No source of power is required for canister samplings as the canister uses its own vacuum to draw an air sample in. In addition, unlike sorbent sampling the expected concentration of target analyte does not affect how canister sampling is to take place, making it easier to obtain accurate results.

However, there are also some drawbacks for canister samplings: [8] (1) VOCs in air samples are not stable in an untreated stainless steel canister,[6] therefore, it is necessary for canisters to pass through a passivation process to eliminate the internal surface reactivity inside before they are used for air sampling; (2) canisters must be cleaned completely between two samplings to limit background contamination and ensure cleaning effectiveness; (3) moisture should be removed from the sample before injection to the column; (4) trace level of VOCs must be preconcentrated prior to analysis, so sorbent or cryogenic trap should be used for preconcentration.

1.2.1.2 Gas sampling bulbs

Glass gas sampling bulbs are designed for the collection and storage of environmental air samples. There is a top cap with a Teflon/silicone septum in the middle of the sampling bulb, and a glass or Teflon stopcock at each end of the bulb. Before sampling, the bulb must have an evacuation and leak check. First, evacuate the sample bulb to 10 mmHg absolute pressure or less. Then leak check the sample bulb by isolating the bulb from the vacuum pump and allowing the bulb to sit for 10 minutes.[9] If there is no change in bulb vacuum, the bulb can be used for sampling. For sampling, the gas sample can be drawn into the evacuated bulb by opening the stopcock. Analytical samples can be withdrawn through the top cap and injected into GC for analysis.

The advantages of sampling bulbs compared with the air sampling bags include: the inside surface of the glass bulb is more stable than that of the air sampling bags, this can prevent the air sample from reacting with the inside surface; it can be reused by being purged with clean air at least twice; it can be evacuated first, and then sampled without a pump.

1.2.1.3 Air sampling bags

Air sampling bags provide a simple, economical method of collecting and transferring gas samples to the laboratory for analysis. Many gas samples with VOCs can be effectively collected by sample bags that are available in various sizes, normally from 500 mL to 100 L of volume. These flexible bags are usually made from polymer materials such as Teflon, Tedlar and aluminized polymer. Always leak check the bags prior to use by filling the bag and leaving it under pressure overnight. If the bag deflates, it should not be used for sample collection. For collecting samples, the bag is connected to Teflon tubing holding the bag into the area to be sampled. The pump draws a vacuum and results in a pressure difference that causes the sample to be drawn through the Teflon tubing into the bag. The collection method is simple; however, the selection of the bags, fittings and tubing are critical. Bags are not recommended for use with reactive compounds that might adhere to the bag's surface. Due to the chemical structure of the bag material, highly polar compounds will adhere to the inner surface of the bag. Additionally, low molecular weight compounds may permeate the bag.[10] It is possible to reuse air sampling bags for some applications, however, the bag could not be reused, if after sampling, compounds were found at ppb (parts per billion) concentrations, or compounds that are known to adhere to the surface of the bag. Prior to reuse, the bags must be evacuated, and then thoroughly cleaned and flushed after each use with purified air or nitrogen. It is recommended to perform an analysis of the final flush to ensure that the background levels presenting in the bag are acceptable for its intended use.

1.2.2 Sorbent Sampling

Sorbent sampling can collect larger volumes of gas samples than canister sampling. Furthermore, the sorbent sampling device, such as tubes, badges and needles, are easier to operate than canisters.[11] Generally sorbents are classified as porous organic polymers, polydimethylsiloxane and carbon sorbents including activated carbon, carbon molecular sieves and graphitized carbon blacks. Table 1.1 shows some physical properties of these sorbents.[12] It is important to choose suitable sorbents for VOCs sampling due to the properties of target compounds and sample matrix. Some points should be taken into account: (1) for very volatile organic compounds, breakthrough may occur such that the target analyte may pass through the sorbent without being trapped. Breakthrough of target analyte should be avoided by comparing the performance charts of different sorbents or combining more than one sorbent to construct a multi-bed tube;[13-16] (2) some sorbents have degradation problems due to high temperature desorption. It is important to choose suitable desorption temperature to ensure the desorption efficiency and avoid sorbent degradation;[17] (3) Humidity should be considered during the adsorption process. At high relative humidity, water adsorbed by the sorbent will reduce the sampling rate of target analytes and result in a breakthrough problem.[18] Water content may have an undesirable effect in the subsequent GC-MS analysis by causing degradation of chromatographic column.[19]

The collected compounds on the sorbent can be removed either by thermal desorption or solvent extraction. Thermal desorption is preferred due to its simple procedure; solvent extraction is more complicated, which can cause losses of volatiles and obscure the peaks of the target analytes in the chromatogram due to the large peak of solvent.[20]

Table 1.1 Characterization of various sorbents commonly used for adsorption and thermal desorption in air analysis

Adsorbent (Provider)	Type	Particle size[a] (mesh)	Sampling range[a]	T_{max}[a] (°C)	Density[a] (g mL^{-1})	Pore volume[a] (mL g^{-1})		Elemental composition (measured) (mass %)						Spec. surface area[a] (m^2 g^{-1})	Spec. surface area measured (m^2 g^{-1})	V_g^θ H_2O[b] 20 °C (mL g^{-1})
						Micro	Total	C	H	N	S	O	Cl			
Carbon molecular sieves																
Carboxen 563 (Supelco)	CMS	20/45	C2–C5	>400	0.53	0.20	0.59	81.4	2.6	–	10.6	4.7	0.1	510	495	778
Carboxen 564 (Supelco)	CMS	20/45	C2–C5	>400	0.60	0.19	0.50	88.7	0.8	–	5.8	2.4	0.6	400	460	276
Carboxen 569 (Supelco)	CMS	20/45	C2–C5	>400	0.58	0.07	0.39	93.7	0.3	–	4.0	1.1	0.4	485	387	257
Carboxen 1000 (Supelco)	CMS	60/80	C2–C5	>400	0.44	0.42	0.85	91.9	0.9	–	0.2	4.0	1.3	1200	915	418
Carboxen 1001 (Supelco)	CMS	60/80	C2–C5	>400	0.61	0.17	0.53	93.2	0.6	–	3.3	1.3	1.2	500	420	234
Carboxen 1003 (Supelco)	CMS	40/60	C2–C5	>400	0.46	0.47	0.8	95.8	0.28	–	2.41	0.92	0.61	1000	1045	79
Carbosieve SIII (Supelco)	CMS	60/80	C2–C5	>400	0.61	0.38	0.39	95.7	0.8	–	–	2.0	1.1	820	835	378
Carbosphere (Chrompack)	CMS	60/80	–	400	–	0.5	0.54	90.5	0.5	–	0.1	2.1	0.2	1000	1054	779
Graphitized carbon blacks																
Carbotrap F (Supelco)	GCB	20/40	>C20	>400	0.66	–	0.02	99.8	0.1	–	–	–	0.1	5	7	–
Carbotrap C (Supelco)	GCB	20/40	C12–C20	>400	0.72	–	0.02	99.7	0.1	–	–	–	0.2	10	9	–
Carbotrap (Supelco)	GCB	20/40	C5–C12	>400	0.36	–	0.58	99.9	0.1	–	–	–	–	100	95	–
Carbotrap Y (Supelco)	GCB	20/40	C12–C20	>400	0.42	0.003	0.12	99.6	0.2	–	–	–	0.3	25	34	–
Carbotrap X (Supelco)	GCB	20/40	C3–C5	>400	0.41	0.0	0.63	99.2	0.1	–	0.1	–	0.1	250	260	–
Carbograph 5 (LARA)	GCB	20/40	C3–C5	>400	–	–	–	100	–	–	–	–	–	560	230	–
Porous organic polymers																
Chromosorb106 (Supelco)	Styrene-divinyl-benzene-copolymer	60/80	Small molecule	250	–	0.09	1.33	92.1	7.8	–	0.2	0.7	0.3	750	926	173
Tenax TA (Supelco)	Poly-(2,6-diphenyl-)-p-phenylenoxide	60/80	C7–C26	350	0.25	0.002	0.05	84.5	4.4	–	0.1	6.4	0.4	35	24	39
Miscellaneous																
Tenax GR (Supelco)	30% Graphit; 70% Tenax	35/60	–	350	–	0.002	0.05	86.9	3.6	–	0.7	5.1	0.3	–	21	92
Activated carbon (Supelco)	Coconut Charcoal	20/40	C2–C5	220	0.44	0.5	0.54	93.7	0.9	–	0.1	3	0.2	1070	1015	1454

[a] Manufacturer's data. [b] Specific retention volume of water at 20 °C measured using the elution technique (see text). CMS: carbon molecular sieves, GCB: graphitized carbon blacks.

Sorbent sampling can be categorized as active sampling and passive sampling based on air transport mode.

1.2.2.1 Active sampling

Active sampling is performed by drawing air through a type of adsorbent media using a pump, such as a sorbent tubes, badges and packed needles. The compounds of interest are trapped on the sorbent inside the sampling device and then returned to the laboratory for analysis.

For active sampling the volume of air sample passed through the sorbent or collection device should be accurately measured. Before sampling, the flow rate of the pump should be calibrated by an air flow calibrator or a simple bubble meter in order to get accurate volume of air sample. It is important to choose an appropriate sampling rate and sampling volume due to breakthrough and diffusion problems. Different sorbents have specific breakthrough volumes depending on the properties of target compounds. NIOSH method 1500 and 1501 specify specific range of flow rates, minimum and maximum sampling volumes for hydrocarbons and aromatic hydrocarbons.[21] Under low flow rate less than 10 mL/min, analyte diffusion may occur and introduce significant error for sampling volume, while under high flow rate more than 200 mL/min, target compounds may pass through the sorbent without being adsorbed.

For sampling high volume air sample, it is feasible for active sampling device to use more than one sorbent. Different sorbents can be placed in the sampling device separated by glass wool to increase adsorbent strength. [22]

1.2.2.2 Passive sampling (Diffusive sampling)

The passive sampling process is controlled by a physical process such as diffusion through a static air layer or permeation through a membrane without the active movement of the air medium. The rate of diffusion depends on the properties of the compounds and the geometry of the sampler.

Passive sampling has become more attractive and acceptable since it was developed. There is no need for expensive pumps; samplers are simple and easy to operate for the less technically experienced person; costs are low; it can be put in high risk areas; and several samples can be collected at the same time. Passive sampling can provide results that are as accurate as active sampling.[23] Passive sampling is more suitable for long-term sampling in ambient, indoor and personal exposure applications.

However, there are some drawbacks for passive sampling: more than one sorbent can not be layered in one diffusive sampler, thus limiting the range of analytes that can be monitored;[24] the sampling volume can be calculated according to the sampling time, diffusion coefficient of the analyte and the geometry of the sampler, but sometimes it can be affected by temperature, humidity and air velocity which are usually small and not a problem by correction and special sampler design.[25]

1.2.3 TWA sampling

The time-weighted average (TWA) concentration is the average concentration of an analyte over a long period of time. There are two approaches to obtain a TWA concentration.[26] One method is to determine the concentrations of a large number of samples obtained at different time intervals of interest, and then average the concentrations for the total sampling time.

$$\overline{C} = \frac{C_1 t_1 + C_2 t_2 + C_3 t_3 + ... + C_{n-1} t_{n-1} + C_n t_n}{t_1 + t_2 + t_3 + ... + t_{n-1} + t_n} \qquad (1.1)$$

where $\overline{C}$ is the TWA concentration, C_1 is the analyte concentration obtained for time t_1, and the rest can be deducted by analog, until time t_n. The alternative approach is to collect one sample for a certain sampling period with one sampler, a variation of the first approach, when $t_1=t_n$. Determining the TWA concentration by the second approach is much easier due to the reduced number of samples and analyses.

TWA sampling with one sampler can involve both active or diffusive sampling methods.[27] An active approach involves the use of a pump to draw the sample air at a constant flow rate through a solid or liquid sorbent to extract the target analytes. This approach suffers from a number of difficulties, including relatively high unit cost, necessity of periodic replacement of pumps, limitation of sampling time by the batteries' life time and frequent calibrations. A diffusive sampling based on molecular diffusion, which can obviate the need for air sampling pumps, was first introduced in 1973. Since then, much research has been conducted to extend the application of diffusive TWA sampler. However, it also has some disadvantages, including the use of highly toxic solvents, it is not reusable，nor amenable to automation, and there is extensive background noise. In recent years, a number of types of samplers have been developed for diffusive TWA sampling, including the diffusive dosimeter, the Fan-Lioy diffusive PAH sampler, and the radial diffusive sampler. However, special equipment for thermal desorption and cryogenic concentration are needed.[28-30]

The needle trap device (NTD) is being continuously developed as a diffusive TWA sampler. It combines sampling and sample preparation in a single step without organic solvent, eliminating the aforementioned disadvantages of other diffusive TWA samplers, and has been employed extensively in environmental monitoring.[31-34]

1.3 Evolution of Needle Trap Device

The needle trap device (NTD) is an extraction trap that contains a sorbent inside the needle, from which the air can be drawn into and out of by a gas-tight syringe or can pass through the trap by diffusion.[35] VOCs in the air can be adsorbed inside the needle trap and thermally desorbed in the heated injector of a gas chromatograph, directly swept by the carrier gas into the capillary column for analysis. The needle trap device, which is a solventless sampling technique, can be used for both active and passive sampling. As a passive sampler compared to conventional methods, it has some advantages: neither a pump nor a solvent is required; it is reusable; it can be directly introduced into the GC injector and requires a relatively short time for sampling and analysis.

The needle trap device was first introduced in late 1970s as a Tenax-filled needle.[36] In earlier applications, a dedicated carrier gas purge line or an additional volume of clean air was needed to aid the introduction of desorbed analytes. It was only used as a fast screening tool for qualitative purposes.[37-38]

In 1997, the inside needle capillary adsorption trap (INCAT) with either a sort length of GC capillary column or an internal coating of carbon inside the needle was first introduced by M. E. McComb et al. The INCAT, however, was only used for qualitative purposes.[39] In 1999, the INCAT device was improved by Shojania et al.[40] This device was used for active and passive sampling for some VOCs. Although the analytes of interest were analyzed quantitatively, the proportional amount of each compound adsorbed relative to the amount sampled from the chamber ranged from 16.3 to 70.7% for BTEX (benzene, toluene, ethylbenzene and xylene). Thus, breakthrough and greater variation in the sampling efficiency occurred during sampling. In 2004, the INCAT was further improved by Robert Kubinec et al. In contrast with the INCAT device published previously, the Kubinec study modified the INCAT device to a closed sorption-desorption system, in which thermally desorbed analytes were repelled to the injector port of GC by the assistance of water vapor without additive make-up gas. The drawbacks involved the co-elution of benzene and toluene with water as a solvent peak, causing slightly worse detection and quantification limits in comparison with the purge and trap device method .[41]

In 2001 Dr. Pawliszyn's group developed a needle trap device that consisted of a 40 mm long 23 gauge stainless steel needle with a 5 mm of quartz wool packing section pointed 4 mm from the needle tip.[37] The analytes in an air sample were collected by drawing air across the NTD with a Luer-lock gas-tight syringe. The mass loading of particulate matter was performed by adjusting the volume of air pulled through the NTD and the particulates were then trapped by the sorbent inside the needle. The device was introduced to a gas chromatograph with FID or mass spectrometer detector by delivering 10 μl of clean air through a gas tight syringe to aid the introduction of the desorbed analytes. The results showed that the NTD can be used for airborne particulate sampling and analysis.

From 2002 to 2005, the same group developed two other types of needle trap devices. One type of NTD, shown in Figure 1.1, was designed with a sealed tip in which PDMS particles, DVB particles and Carboxen particles were packed layer by layer. The lengths of the layers were 3, 2, and 2 mm, respectively, and quartz wool was packed between the tip of the needle and the side port.[42]

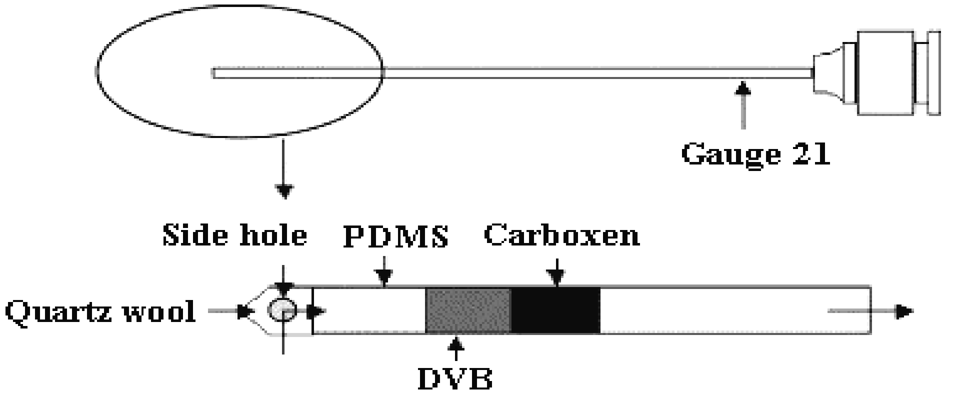


Figure 1.1 Schematic of the NTD packed with PDMS, DVB and Carboxen particles

The second type of NTD in which Carboxen1000 was packed near the blunt tip of the needle was designed with a side hole (i.d. 0.016in.) positioned 3 cm from the tip of the needle, as illustrated in Figure 1.2.[42] The carrier gas enters the needle through side hole, passed through the sorbent, and aided the delivery of desorbed analytes into the GC column. This desorption method was convenient and no carry over was observed. This type of NTD used to quantitatively detect BTEX was simpler and more convenient than the design associated with the modification of the carrier gas line or an additional volume of clean air injection.

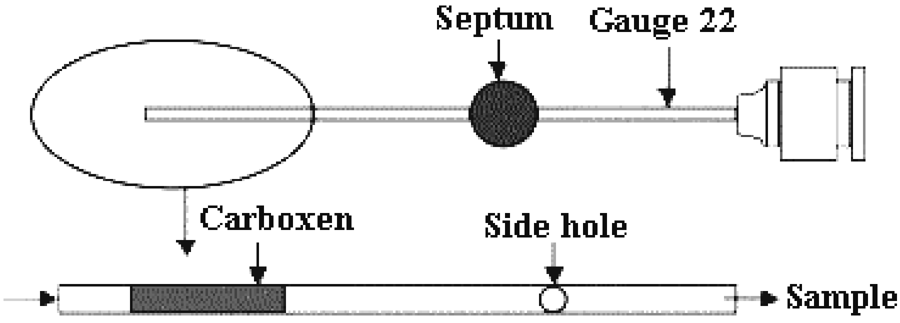


Figure 1.2 Schematic of the needle trap with a side hole

1.4 Objectives

The objectives of this project were to develop a suitable and simple method to prepare NTD; verify this kind of NTD can do successful diffusive sampling; investigate the environmental effect on sampling performance of NTD; validate this method against other methods; develop simple, easy carrying, safety personal diffusive samplers to monitor both personal exposure in the occupational environment and ambient air quality; validate this method in field sampling against NIOSH method 1501.

In addition, thiol compounds such as propanethiol and butanethiol, were sampled and analysed using NTD with divinylbenzene sorbent for active sampling and GC-MS analysis. Sampling and analysis methods were developed, and some flavour vegetables and field samplings were investigated in this project.

1.5 References

1. N. Peterson**,** *Evaluation of VOC Definition Based on Vapor Pressure,* Joint Services

Environmental Management Conference & Exposition ***2005***

2. J.Q. Xiao, S.M. Levin, *American Journal of Industrial Medicine* 37 (1), **2000**, 44-61

3. N.E. Klepeis, W.C. Nelson, W.R. Ott, J.P. Robinson, A.M. Tsang, P. Switzer, J.V. Behar, S.C. Hern, W.H. Engelmann, *J. Expo Anal Environ Epidemiol* 11, **(2001)**, 231-252.

4. Central Pollution Control Board, Ministry of Environment & Forests, Govt of India, *Sampling Considerations*, *Manual on Sampling, Analysis and Characterisation of Hazardous Waste* **2000,** 3-25

5. U.S. Environmental Protection Agency, *Identification of Time-weighted average sampling and Measurement Techniques to Support Human Exposure Studies,* EPA 600/R-04/043, **2004**

6. U.S. Environmental Protection Agency, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,* Compendium Method TO-14 A, 2nd Edition. **1999**

7. U.S. Environmental Protection Agency**,** *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,* Compendium Method TO-15, 2nd Edition. **1999**

8. J.P. Hsu, G. Miller, V. Moran, *J Chromatogr Sci* 29 **(1991)** 83-88

9. K. Ballschmiter, P. Mayer, Th. Class, *Fresenius' Journal of Analytical Chemistry*, 323(4) **(1986)** 334-339

10. U.S. Environmental Protection Agency, *General Air Sampling Guidelines,* Version 2.0. **2003**

11. S. Batterman, G.Z. Zhang, M. Baumann, *Atmospheric Environment*, 32(10), **1998**, 1647-1655

12. K. Dettmer, W. Engewald, *Anal Bioanal Chem,* 373 **(2002)** 490-500

13. J. Brown, B. Shirey, *Technical Report*, Supelco,

14. J.M. Sanchez, R.D. Sacks, *Anal. Chem*., 75 **(2003)** 978-985

15. C.H. Feng, S. Mitra, *J. Microcolumn Separations,* 12 (4), **2000**, 267-275

16. C.J. Lu, E.T. Zellers, *Anal. Chem*., 73 **(2001)** 3449-3457

17. D. Helmig, *J. Chromatogr. A*，732（**2005**）414-417

18. J.M. Sanchez, R.D. Sacks, *Anal Chem*, 75 **(2003)** 2231-2236

19. J.M. Guillot, B. Fernandez, P.L. Cloirec, *Analysis*, 28 **(2000)** 180-187

20. M. Haper, *J. Chromatogr. A*，885（**2000**）129-151

21. National Institute for Occupational Safety and Health, *Manual of Analytical Methods*, Fourth Edition, US Department of Health and Human Service, **1994**

22. U.S. Environmental Protection Agency**,** *Determination of Volatile Organic Compounds in Ambient Ai using active sampling onto sorbent tuber,* EPA/625/R-96/010b, **1999**

23**.** B. Zabiega, T. Górecki, E. Pyzyk, J. Namiesnik, *Atmospheric Environment* 36 **(2002)** 2907–2916

24. S. Battermam, T. Metts, P. Kalliokoski, *J. Environ. Monit.*, 6 **(2002)** 870-878

25. R.H. Brown, *Pure Appl. Chem.*, 65 **(1993)** 1859-1874

26. P.A. Martos and J. Pawliszyn, *Anal. Chem*., 71 **(1999)** 1513-1520

27. K. Elke, E. Jermann, J. Begerow, L. Dunemann, *J. Chromatography A,* 826 (**1998**) 191-200

28. P. Bruno, M. Caputi, M. Caselli, G. de Gennaro, M. de Rienzo, *Atmospheric Environment,* 39 **(2005)** 1347-1355

29. J.H. Cross. *Environ. Sci. Technol.,* 37 **(2003)** 1633-1638

30. Z. Fan, K.H. Jung, P.J. Lioy. *Environ. Sci. Technol.,* Published on Web 09/02/**2006**

31. A. Wang, F. Fang, J. Pawliszyn, *J. Chromatogr. A*, 1072 **(2005)** 127-135

32. Y. Chen, J. Pawliszyn, *Anal. Chem.,* 75 **(2003)** 2004-2010

33. G. Ouyang, Y. Chen, J. Pawliszyn, *Anal. Chem.,* 77 **(2005)** 7319-7325

34. J. Pawliszyn, *Anal. Chem.,* 75 **(2003)** 2543-2558

35. J. Pawliszyn, *U. S. Pat. Appl. Publ.,* US 20010032521 **(2001)**

36. F. Raschdorf, *Chimia,* 32 **(1978)** 478-483

37. J.A. Koziel, M. Odziemkowski, and J. Pawliszyn, *Anal. Chem.* 73 **(2001)** 47-54

38. S. Shojania, M.E. McComb, R.D. Oleschuk, H. Perreault, H.D. Gesser, A. Chow, *Can. J. Chem.* 77 **(1999)** 1716-1727

39. M.E. McComb, R.D. Oleschuk, E. Giller, H.D. Gesser, *Talanta* 44 **(1997)** 2137-2143

40. S. Shojania, R.D. Oleschuk, M.E. McComb, H.D. Gesser, A. Chow, *Talanta* 50 **(1999)** 193-205

41. R. Kubinec, V.G. Berezkin, R. Gorova, G. Addova, *J. Chromatography B* 800 **(2004)** 295-301

42. A. Wang, F. Fang, J. Pawliszyn*, J. Chromatogr. A* 1072 **(2005)** 127-135

Chapter 2 –Development of needle trap device and BTEX analysis

2.1 Introduction

BTEX, the acronym for benzene, toluene, ethylbenzene and o-xylene, are volatile monoaromatic hydrocarbons that are commonly found together in crude petroleum and petroleum products. They are also produced as solvents and materials for the manufacture of pesticides, plastics, and synthetic fibers.[1] The main source of BTEX contamination is the leakage of gasoline from poorly maintained underground storage tanks. Other sources of BTEX contamination are automobile exhaust， industrial emissions, furnishing and painting materials, burning processes and other consumer products.[2-4] Acute exposures to high levels of BTEX components can cause skin and sensory irritation, central nervous system depression, and effects on the respiratory system. Prolonged exposure to these compounds has similar effects, as well as other effects on the kidney, liver and blood systems. According to the U.S. Environmental Protection Agency (U.S. EPA), there is sufficient evidence from both human and animal studies to believe that benzene is a human carcinogen.[5] Workers exposed to high levels of benzene in occupational settings were found to have an increased incidence in leukemia.[6]

In this project, sampling and analysis methods were developed to monitor BTEX as the target compounds. Table 2.1 lists the properties of these compounds.[7]

Table2.1 The physical properties of BTEX

Compounds	**Molecular formulas**	**Molecular weight**	**Boiling point(℃)**	**V_p(mmHg) (25℃)**	**D_g(cm^2/sec) (25℃)**
Benzene	C_6H_6	78	80.1	95.3	0.093
Toluene	C_7H_8	92	110.6	28.4	0.084
Ethylbenzene	C_8H_{10}	106	136.2	6.5	0.075
o-Xylene	C_8H_{10}	106	144	6.6	0.072

2.2 Experimental section

2.2.1 Chemicals and materials

BTEX (benzene, toluene, ethylbenzene, o-xylene) were purchased from Sigma-Aldrich (ON, Canada). Permeation tubes were purchased from Kin-Tech Laboratories (Texas, USA). All 22-gauge needles were purchased from Dyna Medical Corporation (Ontario, Canada). All side holes were made in-house by the machine shop at the University of Waterloo. Hydrogen, nitrogen, helium, compressed air and carbon dioxide were obtained from Praxair Canada Incorporated (Ontario, Canada). Carboxen1000, Carboxen1012, Carboxen1016 and gold wire were purchased from Sigma-Aldrich (Ontario, Canada). The 5-min epoxy glue was purchased from Henkel Canada (Ontario, Canada). The narrow-neck liner was purchased from SGE Analytical Science (Texas, USA).

2.2.2 Preparation of needle trap device

NTD consists of a 22-gauge needle and a sorbent positioned a distance 3 cm from the tip of the needle (Figure 2.1). The procedure to prepare a NTD is as follows: a metal wire was used to indicate the position inside the needle where the sorbent would be packed; about 1 cm of gold wire was tightly coiled into a 22-gauge needle and fixed in the required position; then an aspirator was used to aspirate the sorbent into the needle until it came to the required position; small quantity of 5-minute epoxy glue was used to immobilize the sorbent. To prevent the glue from blocking the needle, an aspirator was connected to the needle to draw the air through the NTD before the glue solidified. The NTD was then conditioned in a GC injector at 300°C for 2 h to remove impurities. Finally, the two ends and side hole were sealed with Teflon caps and tubing.

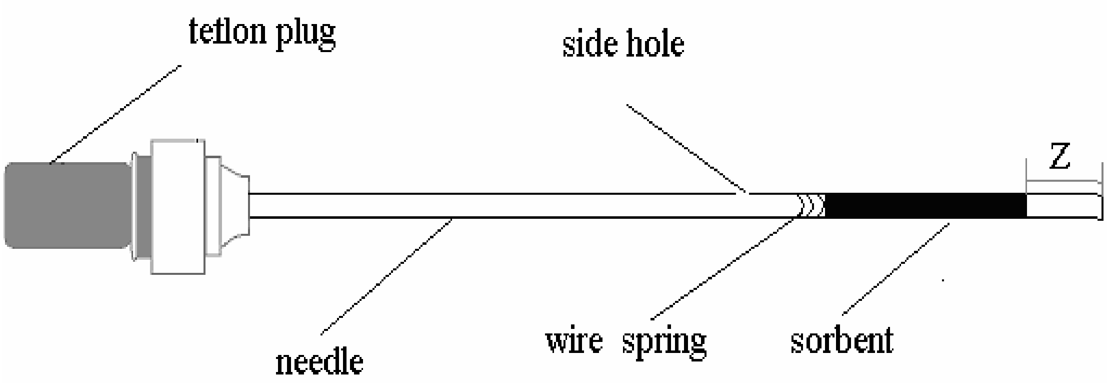


Figure 2.1 Schematic of diffusive needle trap device for diffusive sampling

2.2.3 Standard gas system

The standard gas generating system, illustrated in Figure 2.2, was used for the development of the analysis methods and subsequent evaluation of TWA diffusive sampling performance of NTD in this project.

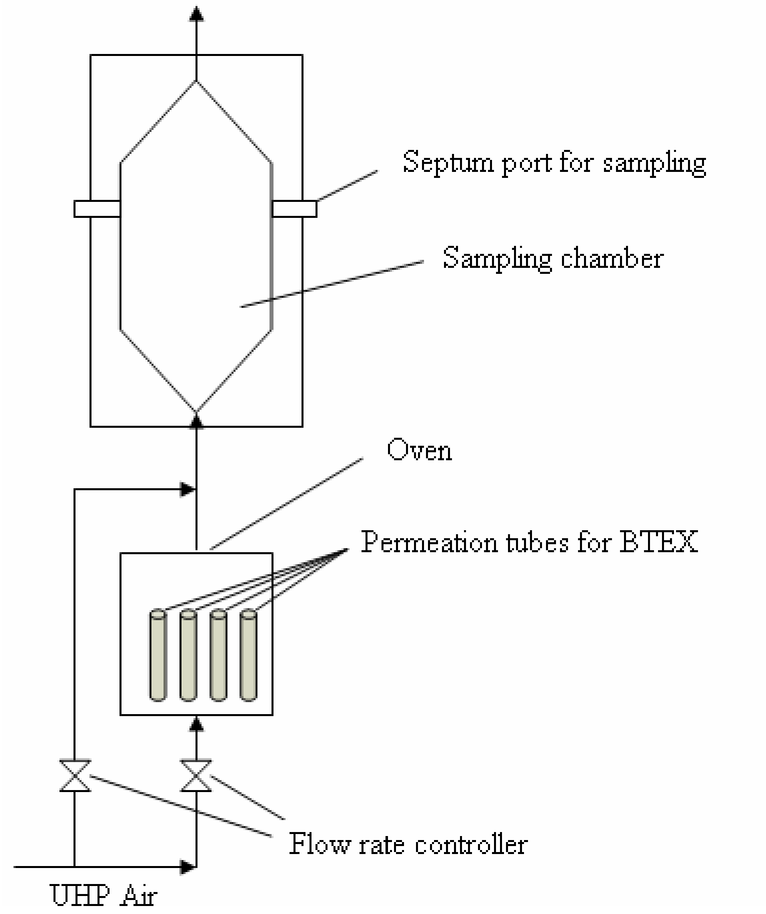


Figure 2.2 Schematic of the standard gas system

This system, which has proven to be continuous, available and convenient, can generate a wide range of VOC concentrations and mixture of various gases.[8] It consists of a continuous standard gas generator and air sampling chamber (Figure 2.3). The standard gas generator consists of permeation tubes and a permeation oven. All permeation tubes are placed inside a glass cylinder, which is held inside a permeation oven and swept by constant flow of dilution air. The theoretical analyte concentrations for the target compounds are achieved in the chamber and can be calculated using equation 2.1

$$C = \frac{R_p}{R_{air}} \tag{2.1}$$

Where C is the theoretical concentration of target compound, ng / mL; R_p is the permeation rate of this compound, ng/min; and R_{air} is the flow rate of air, mL/min. Different concentrations of BTEX can be obtained by adjusting the temperature of the permeation oven and the flow rate of air.

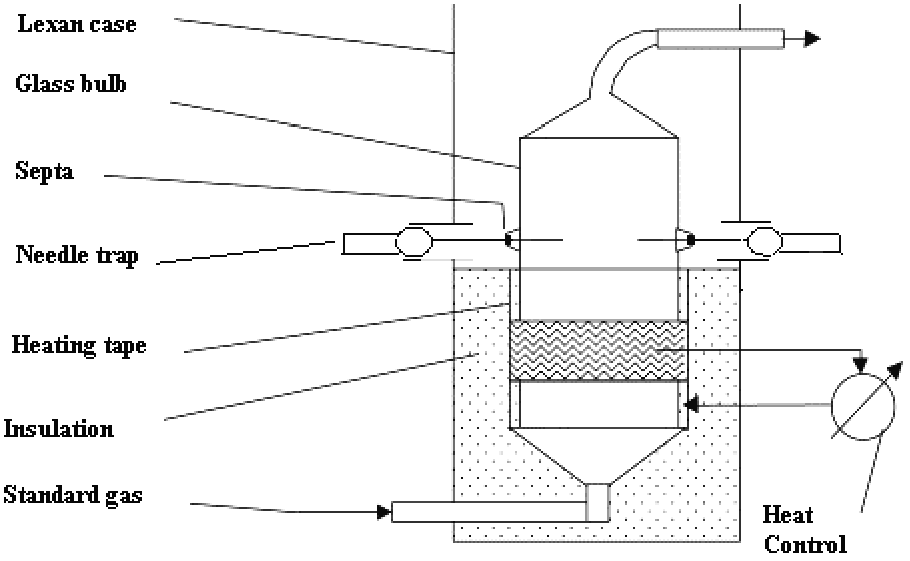


Figure 2.3 Schematic of sampling chamber for NTD extraction

2.2.4 Instrumentation

A Varian CP-3800 Gas Chromatograph (GC) equipped with a Varian 2000 Mass Spectrometer (Varian Inc., Ontario, Canada) was used to separate and analyze the target compounds extracted by the needle trap device. A narrow-neck glass liner (i.d. 0.8 mm) was connected to a VF-5ms GC capillary column (30 m× 0.25 mm, DF=0.25 μm). Figure 2.4 shows a schematic diagram of the system.

The injector temperature was maintained at 300°C. After sampling, the NTD was put into the GC injector in which the helium carrier gas entered the side hole of the NTD, flowed through the sorbent, and carried the desorbed compounds into the GC column. The column temperature program was maintained at 35°C for 1.5 min and then ramped at 20°C/min to

120°C and held for 1 min. The flow rate of carrier gas was set at 2.5 mL/min. The compounds were then separated by the GC column and detected by mass spectrometry.

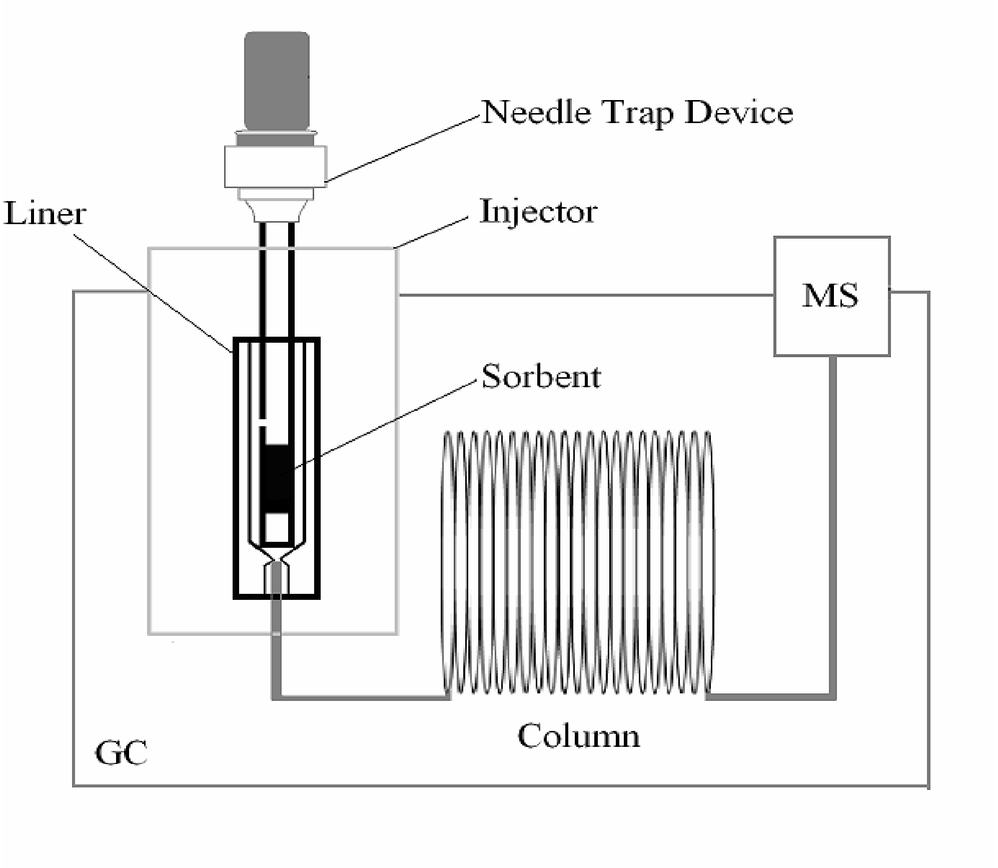


Figure 2.4 Schematic diagram of GC gas chromatograph, a needle trap device, narrow-neck glass liner，capillary column and mass spectrometer

2.3 Results and discussion

2.3.1 Selection of sorbent

Adsorption is a surface phenomenon and parameters that influence the ability of analytes to access and interact with the surface must be considered and controlled, such as particle size and sharp, surface area, pore size and pore shape. In addition, the sorbents used for a NTD must have some special physical properties due to the special shape of the needle. They should be mechanically and thermally stable, spherical, have the proper hardness, and be sized around 60-100 mesh.

Carbon molecular sieve (CMS) prepared by pyrolysis of a polymeric particle precursor are porous and have an amorphous carbon framework.[9] The pores, which include micro-, meso- and macropores, make the CMS material suitable for adsorption of small molecules, such as VOCs. Carbon molecule sieves differ in micro/meso/macro pore ratio. The adsorption occurs predominately in the micropores. The macro- and mesopores act as funnels, directing the analyte into and out of the micropores.

Carboxen ™ are carbon molecular sieve products, which differ in their pore structure, and are manufactured by Supelco. The carboxen materials are produced from sulfonated polymers.[10] The choice of CMS adsorbents depends entirely on the analytes that will be separated and quantified. The goal of this study was to choose the suitable sorbent that can adsorb target compounds as an ideal sorbent, and are also able to release the analytes during the desorption process. Table 2.2 lists some carbon molecular sieves such as Carboxen1000, Carboxen1012 and Carboxen1016 that meet the requirements for making the NTDs mentioned above.

Table2.2 The physical characteristics of chosen sorbents [9]

Adsorbent	**BET surface area[1] (m^2/g)**	**Density (g/mL)**	**Porosity (mL/g)**			**Micropore Diameter (Å)**
			micro-	**meso-**	**macro-**	
Carboxen-1000	1200	0.48	0.44	0.16	0.25	10-12
Carboxen-1012	1500	0.50	-	0.66	-	19-21
Carboxen-1016	75	0.40	-	0.34	-	-

1. Brunauer, Emmett, Teller (BET) surface area calculation

Three NTDs with Carboxen1000, Carboxen1012 and Carboxen1016 were used to do active sampling for BTEX from the standard gas system. The sampling volumes were 1.0 mL. Then the needle trap device were put into the GC injector which held temperature at 300°C, desorption time were 1.5 min.

The masses loaded on the sorbent were shown in Figure 2.5. The results showed that Carboxen1000 adsorbed more BTEX than carboxen1012 and carboxen1016. The possible reason is that they have different micro/meso/macro pore ratios and carboxen1000 has more micropores where adsorption predominately occurred.[9]

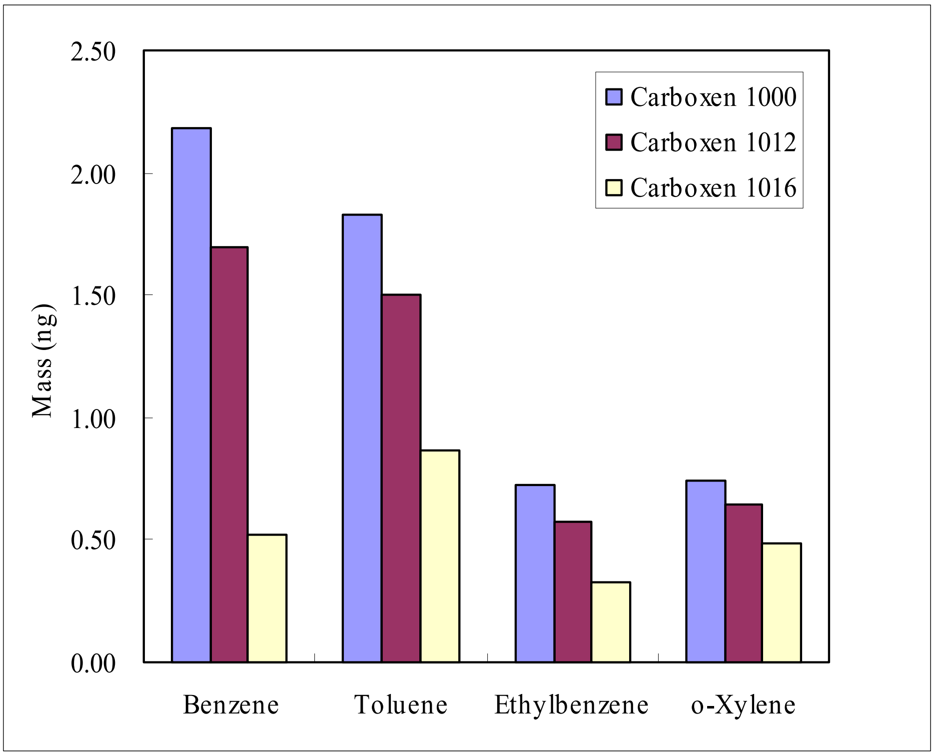


Figure 2.5 Mass of BTEX loaded on Carboxen1000, Carboxen1012, and Carboxen1016

2.3.2 Desorption efficiency

Thermal desorption is a process that the organic compounds adsorbed on the sorbent can be separated from the sorbent without thermally destroying them. Thermal desorption efficiency is the ratio of the mass of the compound which can be recovered from the sorbent to the mass of the compound originally adsorbed. Since it is a thermal process, temperature is the only significant parameter to govern it. It is true that better desorption efficiencies are usually obtained at higher temperatures. However, other factors must be considered, since the process depends on mass transfer, heating time and the amount of compounds.

In this project, two main factors that can affect the desorption efficiency of the needle trap device were investigated. First, at lower temperatures the adsorbed compound does not have enough energy to overcome the force between the sorbent and the target compound, resulting in carryover problem. With increasing temperature, more molecules of the compound get enough energy to escape from the sorbent resulting in decreased carryover. However, higher temperatures may cause the degradation of the sorbent and decomposition of the compounds. Therefore, the selection of suitable temperature is very important to ensure desorption completely and avoid changes of the sorbent and analytes. A series of experiments was conducted to choose the appropriate temperature for BTEX desorption. The results were presented in Figure 2.6. It was observed from the figure that 300°C was the proper temperature for BTEX to be desorbed completely from Carboxen1000. The desorbed masses of BTEX did not increase with increasing temperature.

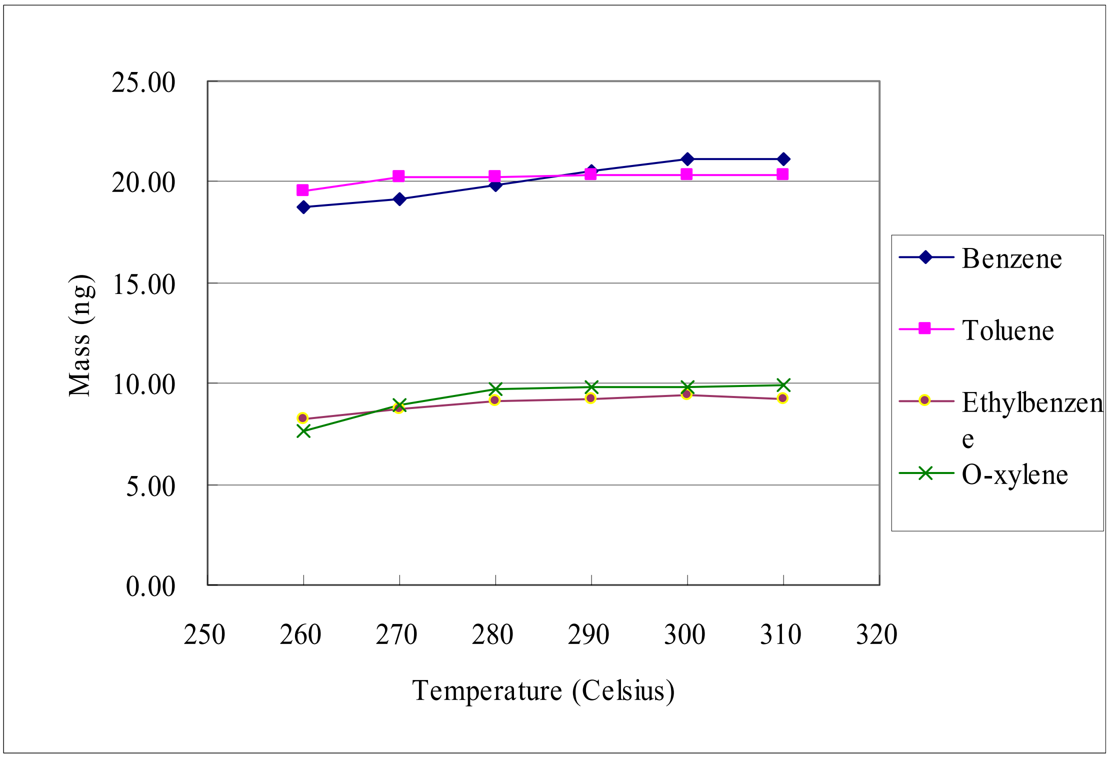


Figure 2.6 Mass desorbed at different desorption temperature

Thermal desorption efficiency also depends on desorption time. If the desorption time is too short, the adsorbed compounds will not have enough time to transfer from the inside of the sorbent to the surface of the sorbent, resulting in carryover. On the other hand, keeping the NTD at a high temperature might cause some negative effects and decrease the lifetime of the NTD. Therefore, it is necessary to select proper desorption time to ensure the target analytes desorbed completely and not to keep the NTD at high temperature for longer time. Experiments were performed at 300°C for different desorption time from 0.2 to 1.2 min. It was observed from Figure 2.7 that 1.0 min was the suitable desorption time for BTEX.

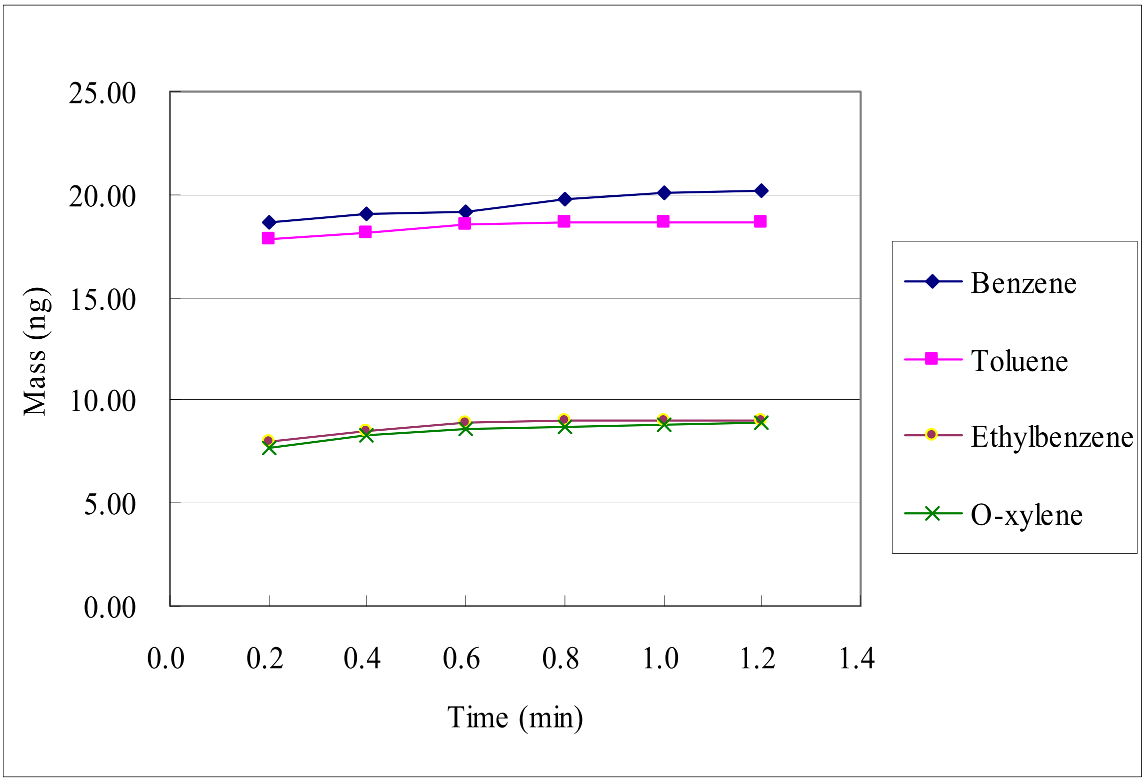


Figure 2.7 Mass desorbed for different desorption times

2.4 Conclusion

A simple and feasible method was developed to make NTDs with suitable sorbent such as Carboxen1000, Carboxen1012 and Carboxen1016. The standard gas system which can generate constant BTEX concentrations with a certain range was set up to be used to investigate operational parameters for NTDs. Carboxen1000 was chosen as an appropriate sorbent for sampling BTEX by comparing the amount of loaded mass on Carboxen1000, Carboxen1012 and Carboxen1016. A series of experiments was performed to investigate thermal desorption efficiency, and 300°C and 1.0 min were found to be optimal thermal desorption temperature and time for BTEX with Carboxen1000.

2.5 References

1. O. Misiaczek, J. Paca, M. Halecky, A.M. Gerrand, M. Sobotka, C.R. Soccol, *Braz. Arch. Biol. Technol.*, 50 (5) **(2007)**, 871-877.
2. S.C. Lee, M.Y. Chiu, K.F. Ho, S.C. Zou, X.M. Wang**,** *Chemosphere*, 48(3) **(2002)** 375-382
3. P. Roose, G.V. Thuyne, C. Belpaire, M. Raemaekers, U.A.Th. Brinkman, *J. Environ. Monit.,* 5 (**2003)** 876 - 884
4. L.H. Jing, S.M. Steinberg, B.J. Johnson, *Journal of the Air & Waste Management Association,* 51**(2001)** 1359-1366
5. K. Elke, E. Jermann, J. Begerow, L. Dunemann, *J. Chromatogr. A,* 826 **(1998)** 191-200
6. R.A. Rinsky, *Environmental Health Perspectives*, 82 **(1989)** 189-191
7. Ministry for the Environment New Zealand, *Guidelines for the Assessment and Management of Petroleum Hydrocarbon Contaminated Sites in New Zealand*, Appendix 4K, **1999**
8. J.A. Koziel, P.A. Martos, J. Pawliszyn, *J. Chromatography A,* 1025 **(2004)** 3-9
9. M. Buchanan, B. Betz and K. Buckendahl, *the Reporter*, Supelco, 22 **(2006)** 15-16
10. K. Dettmer, W. Engewald, *Anal. Bioanal. Chem.* 373 **(2002)** 490-500

Chapter 3 – Three prerequisite for successful diffusive sampling

3.1 Introduction

The phenomenon of mass transfer through a layer of gas can be described by Fick's first law.[1-3] In order to achieve successful diffusive TWA sampling, three prerequisites should be satisfied. Firstly, the concentration of the analyte in the bulk of the gas system, C_{bulk}, must equal the concentration of the analyte at the face of the needle tip. Secondly, the sorbent of the NTD must be a zero sink for the target analytes, where the concentration of the analyte at the gas/sorbent interface for the sampling period is essentially zero, $C_{sorbent}=0$. Thirdly, a diffusive sampler should respond proportionally to the change in sample concentration at the face of the sampler.

Figure 3.1 presents a diagram of the needle trap diffusive sampler. The sampler consists of a sorbent positioned a distance Z from the needle tip of the fixed area A. The rate at which

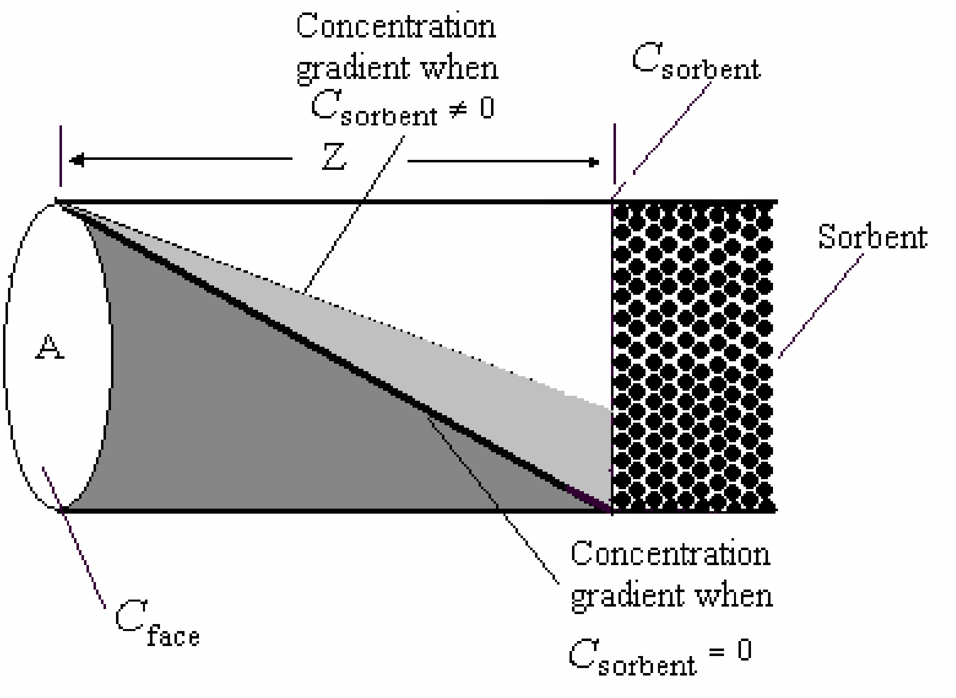


Figure 3.1 Schematic of diffusive needle trap sampler

gas is transferred through the needle by diffusion can be stated by Fick's first law

$$J = \frac{dn}{A\,dt} = -D\,\frac{dC}{dZ} \tag{3.1}$$

where J is the flux of analyte, mol/s cm^2; dn is the mole of analyte passing through a cross-sectional area A for a time dt, mol; dt is the time of instant sampling period, s; A is the diffusion path cross-section area, cm^2; D is the analyte diffusion coefficient, cm^2/s; C is the analyte concentration at distance Z, mol/cm^3; and Z is the distance along the diffusion path, cm.

For a given diffusive sampler, such as the one shown in Figure 6, both the area A of the needle tip and the path length Z are constant, therefore dZ=Z, and Equation 3.1 can be rearranged as

$$dn = -AD\,\frac{dC}{dZ}\,dt = -AD\,\frac{dC}{Z}\,dt \tag{3.2}$$

the negative sign indicates that the concentration of the analyte must decrease in the direction of diffusion. dC is the gradient of analyte concentration between the face of the needle tip and the sorbent.

For an ideal sorbent, $C_{sorbent} = 0$, $dC = \Delta C = C_{sorbent} - C_{face} = -C_{face}$, therefore,

$$n = D\,\frac{A}{Z}\int C_{(t)}\,dt \tag{3.3}$$

the expression DA/Z is referred to as the sampling rate R and has dimensions of cm^3/min.[4] Hence, it is recognized that R is dependent on both the diffusion coefficient of the given analyte and the geometry of the diffusive sampler used. So $R = DA/Z$ and equation 3.3 reduced to

$$n = R\int C(t)dt \tag{3.4}$$

When the analyte concentration of bulk is constant, then

$$n = RCt$$

$$R = \frac{n}{Ct} = \frac{DA}{Z} \tag{3.5}$$

If the amount of analyte that is loaded at time *t* can be tested, then the concentration of the bulk can be obtained.

$$C = \frac{nZ}{DAt} \tag{3.6}$$

3.2 Experimental Section

3.2.1 Zero sink

Zero sink was validated by a simple test that the needle trap sampler was exposed both continuously and intermittently to the standard gas chamber of BTEX.[5] For continuous exposure, the NTD was exposed to the standard gas chamber for 60 min; for intermittent exposure, the NTD was exposed to the standard gas chamber for 20 min and then to clean air for 20 min. This process was repeated three times. The total exposure time to BTEX for intermittent was also 60 min and total exposure time for clean air was 40 min. These experiments were conducted at room temperature and the same relative humidity. After sampling, the adsorbed BTEX were thermally desorbed in the GC injector at 300°C and then separated by the column and detected by the mass spectrometer. Figure 3.2 is the schematic of the procedure of continuous and intermittent exposure.

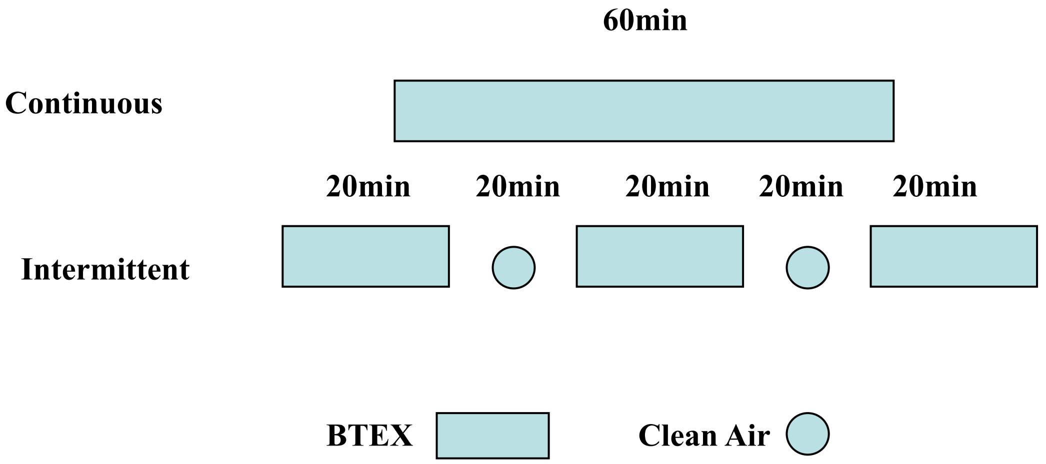


Figure 3.2 Schematic of the procedure of experiment for zero sink

3.2.2 Effect of face velocity on diffusive sampling performance

A graduated flow-through chamber with three different diameters 1.0 , 2.75, and 4.75 cm, was connected downstream of the sampling chamber in the standard gas system shown in Figure 3.3. There are three septum ports on each position of different diameters. The needle trap diffusive sampler with Carboxen1000 (Z=0.98 cm) was inserted into the sampling chamber perpendicularly to the gas flow direction, sampling at the standard gas system that flow rate was 102 mL/min for 1 hour at 25°C. The adsorbed BTEX were thermal desorbed in the GC injector at 300°C and then separated by the column and detected by the mass spectrometer. The sampling rates for BTEX were calculated at 1.44, 4.29, and 32.48 cm/min respectively.

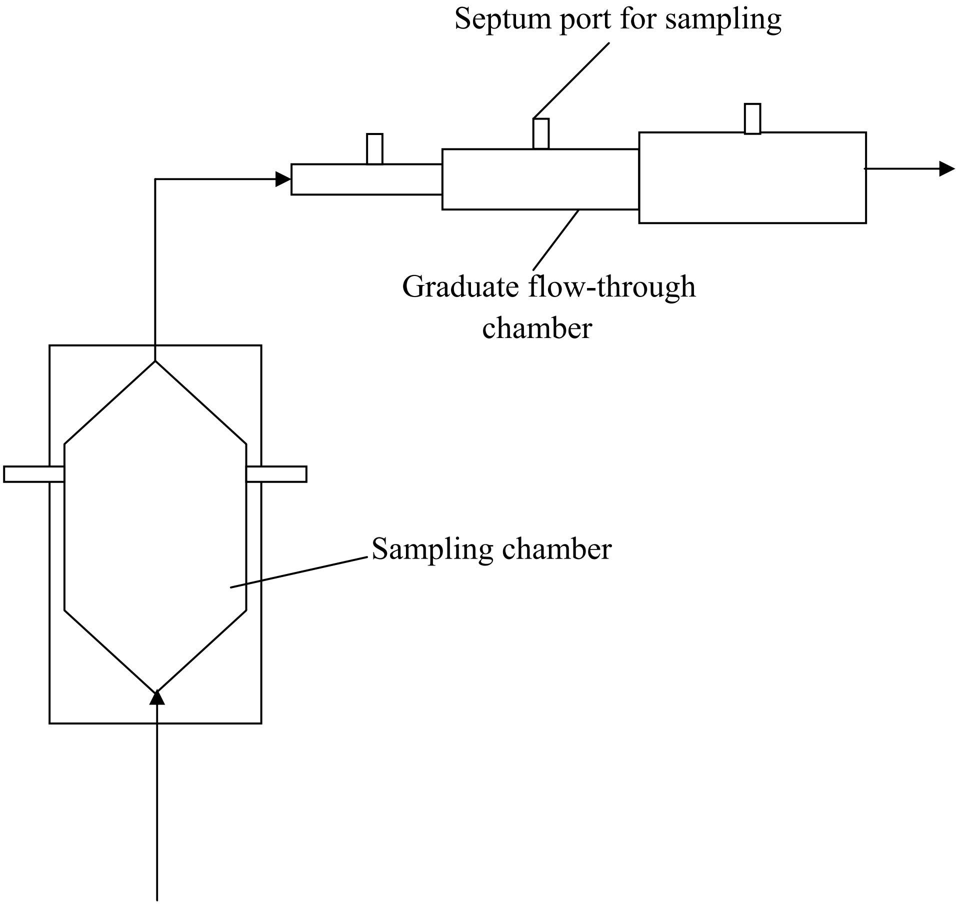


Figure 3.3 Schematic of the graduated flow-through chamber with three different diameters

3.3 Results and discussion

As above mentioned, in order to achieve successful diffusive TWA sampling, the first prerequisite that needs to be satisfied to employ Fick's first law is that the sorbent inside the NTD should be zero sink for the target analytes. The sampling rate of a diffusive needle trap sampler depends on the sorption efficiency of the sorbent. For a sorbent with high sorption efficiency, the concentration of the analyte adsorbed at the sorbent surface, $C_{sorbent}$, will be very small compared to the concentration at the needle tip, C_{face}. In this situation, it is assumed that the sorbent is a zero sink for the adsorbed analyte.

Zero sink ensures that once the analyte is adsorbed, it does not change the mass loading rate of additional analyte. Zero sink was validated by exposing the needle trap sampler both continuously and intermittently to the standard gas chamber. If the sorbent were to exhibit adequate sorption efficiency, the mass of each analyte on the sorbent should be the same for both continuous and intermittent exposures. Three NTDs with different diffusion length 0.37, 0.48, 0.65cm respectively were used to do the zero sink tests. The average adsorbed mass percentages of intermittent to continuous exposure for BTEX, shown in Figure 4, were 99%, 101%, 103% and 98% individually. The results indicate that Carboxen1000 behaves like zero sink for BTEX, presumably because of its strong affinity and the capability.

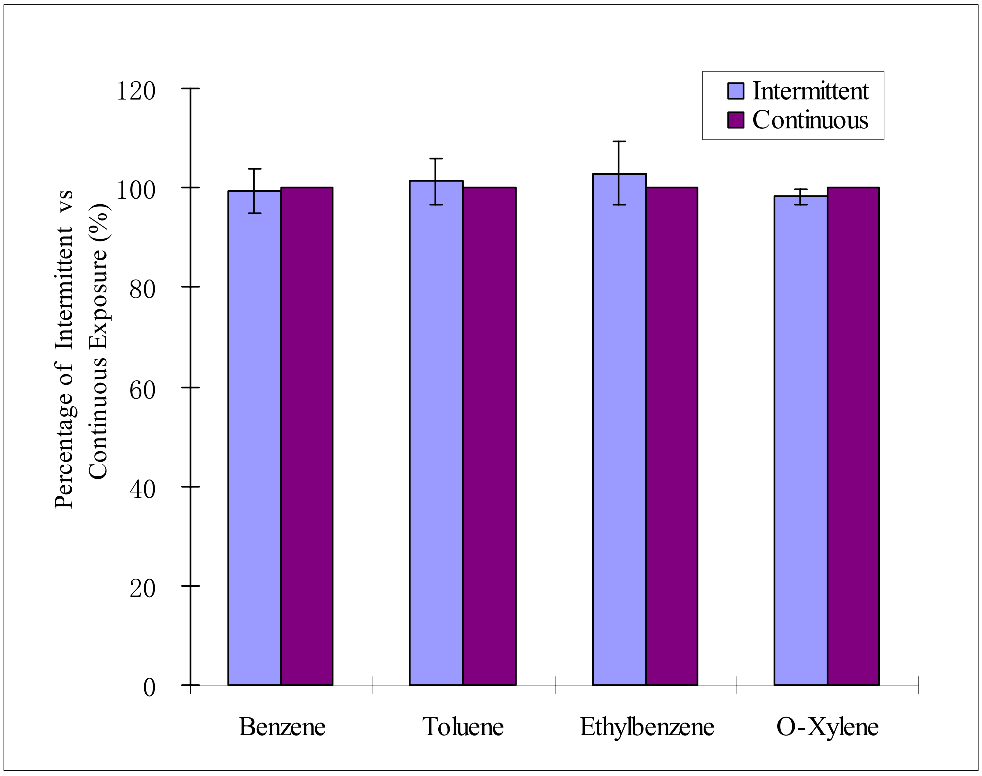


Figure 3.4 Comparison between intermittent and continuous diffusive TWA sampling

The second prerequisite is that the NTDs should have short response time to the change in sample concentration at the face of the sampler. Fick’s first law assumes steady state conditions. In practice, the ambient level of analytes is likely to change considerably over time. That the diffusive needle trap sampler produces a truly integrated response and does not miss short-lived transients before the analytes are trapped by the sorbent has been previously demonstrated.[6-8] The response time, a molecule takes to diffuse into the sorbent from the needle tip, is calculated by the following equation[9]

$$t = \frac{Z^2}{2D} \tag{3.7}$$

where t is the response time (s), Z is the length of the diffusion path (cm), and D is the analyte diffusion coefficient (cm^2/s). Using the NTD in this study, where the diffusion length is less than 1.0 cm, and the smallest analyte diffusion coefficient among BTEX is 0.073 cm^2/s，the response time should be less than 7.0 s.[10] Obviously, the sampling time of a diffusive needle trap sampler is much longer than the response time, which ensures that the sample collected represents a real TWA concentration.

The NTD must meet the third prerequisite that the bulk analyte concentration, $C_{bulk,}$ must equal the analyte concentration at the tip of the needle, C_{face}. The sampling rate of the diffusive needle trap sampler relies on diffusion length, Z, the cross-sectional area, A, and the diffusion coefficients of the target analytes, D. Theoretically, the diffusion length is the distance between the sorbent surface and the external face of the needle tip. But in practice, the effective diffusion length is not identical to the theoretical length, and may be greater or less depending on circumstances.[11-12]

When face velocity is low, there may be insufficient air to carry analyte molecules to the sampler surface from where they are being removed by diffusion. In this case, the effective diffusion length may be higher than the theoretical length because of a boundary layer between the static air within the needle and moving air outside, which contributes to the effective diffusion length and decreases with increased face velocity. [13] Thus, a diffusion sampling with a minimum face velocity is required and once this minimum face velocity is satisfied, the sampling rate will not be sensitive to the velocity over a wide range.[5]

When face velocity is high, the static air layer within the needle may be disturbed. It resulted in a decrease in effective diffusion length. Thus, a sampler with a small cross-section and long nominal diffusion length will be relatively unaffected by air velocity, provided that the diffusion length to diameter ratio of the sampler is greater than 2.5 to 3.[13] Since the diameter of the needle used in this study was 0.04 cm and the nominal diffusion length was greater than 0.4 cm, the ratio (0.4/0.04 = 10) was larger than 2.5 to 3.0, so high face velocity was not a factor.

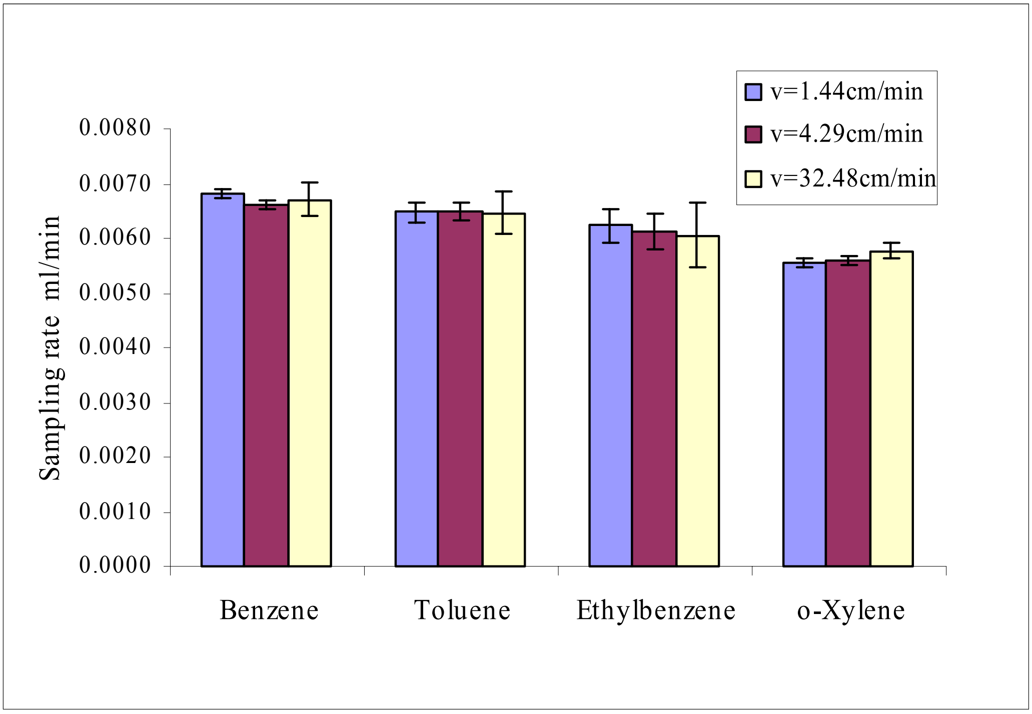


Figure 3.5 Sampling rate vs. face velocity for BTEX with Carboxen1000 at different face velocity (Z=0.98 cm)

The results, presented in Figure 3.5, show the relationship between the sampling rates and face velocity for BTEX with Carboxen1000. The NTD was inserted into the sampling chamber perpendicularly to the gas flow direction, sampling for a period of time at 25°C prior to thermal desorption and GC/MS analysis. The sampling rates for BTEX were tested at 1.44, 4.29, and 32.48 cm/min respectively. The average sampling rates and relative standard deviations obtained at three different face velocities were 0.0067 cm^3/min and 1.5% for benzene, 0.0065 cm^3/min and 0.3% for toluene, 0.0061 cm^3/min and 1.5% for ethylbenzene, 0.0058 cm^3/min and 2.0% for o-xylene. These results indicate that there was no significant impact of face velocity within this range on sampling rates. In reality, the face velocities of both indoor and outdoor are larger than 1.44 cm/min.[14-16] Therefore, the results of this work demonstrated that NTD can be used for TWA diffusive sampling without having to take into account the face velocity.

3.4 Conclusion

The needle trap device packed with Carboxen1000 was used to do diffusive sampling for BTEX at standard gas system. Three prerequisites for successful TWA diffusive sampling were investigated. The results showed that Carboxen1000 is zero sink for BTEX; the response time for these NTDs used in this project was less than 7 seconds, and the sampling time of the diffusive needle trap samplers was much longer than the response time; the face velocity did not have significant effect on sampling rate and the needle trap diffusive sampler can be used to do TWA diffusive sampling without considering face velocity. Therefore, the needle trap diffusive sampler with Carboxen1000 met all three prerequisites of Fick's first law. It can be used to do TWA diffusive sampling for BTEX.

3.5 References

1. F.J. Hearl, M.P. Manning *Am. Ind. Hyg. Assoc. J.* 41(11) **(1980)** 778-783

2. M.S. Young and J.P. Monat, *Am. Ind. Hyg. Assoc. J.* 43(12) **(1982)** 890-896

3. V.E. Rose, J.L. Perkins, *Am. Ind. Hyg. Assoc. J.* 43(8) **(1982)** 605-621

4. R.H. Brown, R.P. Harvey, C.J. Purnell, K.J. Saunders, *Am .Ind. Hyg. Assoc. J.,* 45 **(1984)** 67-75

5. R.H. Brown, *J. Environ. Monit.,* 2 **(2000)** 1-9.

6. F.J. Hearl, M.P. Manning, *Am. Ind. Hyg. Assoc. J***.,** 41(11) **(1980)**778-783.

7. R.H. Brown, J. Charlton and K.J. Saunders, *Am. Ind. Hyg. Assoc. J.,* 42 **(1981)** 865-869.

8. H. Hori and I. Tanaka, *Am Ind. Hyg. Assoc. J.,* 54 **(1993)** 95-101.

9. W.J. Lautenberger, E.V. Kring and J.A. Morello, *Am. Ind. Hyg. Assoc. J,.* 41 (10) **(1980)** 737-747.

10. Ministry for the Environment New Zealand, *Guidelines for the Assessment and Management of Petroleum Hydrocarbon Contaminated Sites in New Zealand*, Appendix 4K, **1999**

11. D. W. Underhill and C.E. Feighley, *Anal. Chem***.,** 63 **(1991)**1011-1013.

12. Z.H. Fan, K.H. Jung, and P.J. Lioy, *Environ. Sci. & Techno,l* 40 (19) **(2006)** 6051-6057.

13. S.R. Coleman, *Am. Ind. Hyg, Assoc. J.*, 44 **(1983)** 929-936.

14. M. Teitel and J. Tanny, Flow, *Turbulence and Combustion,* 74 **(2005)** 21-47.

15. P.E.J. Baldwin and A.D. Maynard, *Annals of Occupational Hygiene* 42(5) **(1998)**

303-313.

16. Z.H. Fan, K.H. Jung, and P.J. Lioy, *Environ. Sci. & Technol* **2006,** 40 (19), 6051-6057.

Chapter 4 –Environmental effect on sampling performance and field sampling

4.1 Introduction

Active samplers have been used to sample VOCs in air for analysis for many years.[1] Diffusive samplers are widely used to monitor the personal exposure of VOCs both in community and workplace environment recently.[2-5] Comparing to active samplers, diffusive samplers offer a number of advantages: there is no need for pump, avoiding cost, maintenance and calibration; it is easy to carry due to its lightweight and small size; and it is also user-friendly to operate without technically trained personnel. Recent years active and diffusive sampling coupled with thermal desorption techniques were well developed.[3, 6-9] This technique overcomes some disadvantages from solvent desorption, such as decreased sensitivity due to dilution of target compounds, introducing impurities of the solvent, not reusable without renewal of sorbent.

However, there is a problem for NTD diffusive sampler that the effective sampling rate should be determined under the same conditions before it is used to do diffusive sampling .[10] The sampling rate normally depends on the geometry of the sampler and diffusion coefficient of target compound and equals to the effective sampling rate in ideal condition. In practice, some factors may affect the sampling rate, such as face velocity, sorbent strength, response time, atmospheric temperature and pressure, relative humidity, and sampling duration , to name a few.

In Chapter 3 it was demonstrated that sorbent strength, response time and face velocity are not significant factors that affect diffusive sampling performance of the NTD with Carboxen1000. In this chapter, a series of experiments was performed to investigate the effect of other factors on diffusive sampling performance, such as temperature, pressure, relative humidity, and sampling duration. In addition, storage stability and method accuracy should be taken into account to assure accurate result. Storage stability of BTEX with carboxen1000 was investigated. Method validations were done not only in the lab, but also in field sampling.

4.2 Experiment section

4.2.1 Chemicals and materials

BTEX (benzene, toluene, ethylbenzene, o-xylene) were purchased from Sigma-Aldrich (Ontario, Canada). The timer and digital humidity meter were purchased from VWR International (Ontario, Canada). The in-line impinger trap was purchased from Supelco (Ontario, Canada). The 75 µm Carboxen/PDMS fibers and holders, ORBO-32 tubes, gas purifiers, syringes, Thermgreen septa, and vials were purchased from Supelco (Ontario, Canada). Personal air pumps and Mini-buck calibrator were purchased from A. P. Buck (Florida, USA). The personal diffusive sampler holders were made by the machine shop at the University of Waterloo.

4.2.2 Standard gas system

To investigate the effect of temperature on mass loading rate, three different temperatures, including 25, 30 and 35°C, were obtained by adjusting the controller of the heater. In order to generate different levels of relative humidity, an in-line impinger trap was installed between two sampling chambers. The schematic of the gas sampling system with different relative humidity is shown in Figure 4.1. Different levels of relative humidity were obtained by adjusting the water level in the in-line impinger trap at different heights.[11-12] The digital humidity meter was used to measure the relative humidity.

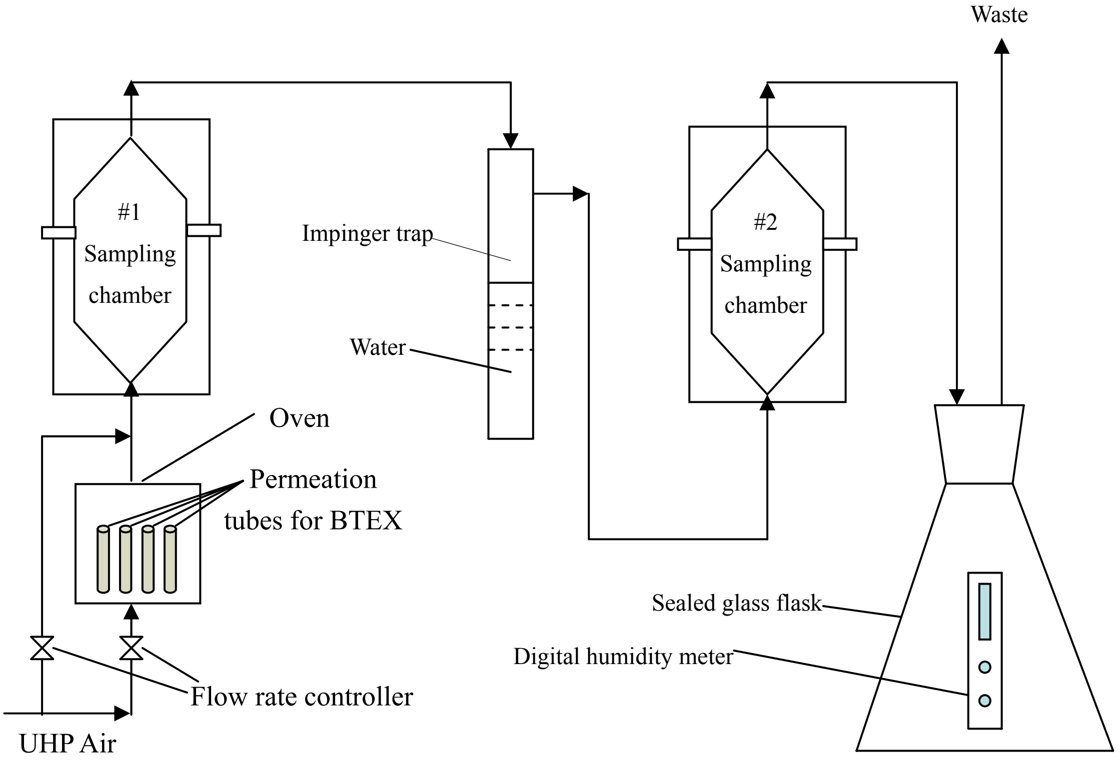


Figure 4.1 Schematic of gas sampling system with different relative humidity

4.2.3 Charcoal tubes sampling

Method validations were done against NIOSH method 1501 and other method not only in the lab, but also in field. A personal sampling pump was connected to the small ORBO-32 tube with flexible connecting tubing to collect the air sample. Before sampling, the flow rate of the personal sampling pump was calibrated by using Mini-buck calibrator. The sampling volume was 5.2L for the standard gas system sampling and 8.0L for the field sampling. The flow rate of the personal sampling pump was controlled at 115ml/min in field sampling. The compounds adsorbed on the charcoal were desorbed with 1mL of carbon disulfide in 2mL of vials with PTFE-lined caps.

4.2.4 Instrumentation

A Varian CP-3800 Gas Chromatograph (GC) equipped with a Varian 2000 Mass Spectrometer with a VF-5ms GC capillary column (30m× 0.25mm, 0.25μm film thickness) was used to separate and analyze the target compounds extracted by different samplers, such as NTDs, SPME fibers and charcoal tubes.

The injector was maintained at 300°C for NTDs and 250°C for SPME fibers. For liquid injections, the injector was initially kept at 40°C for 0.5 min and ramped to 250°C at 100°C /min. For all injections, the column temperature program was maintained at 35°C for 1.5 min and then ramped at 25 °C/min to 120°C and held for 1.1 min; total running time was 6.0 min. The carrier gas flow rate was set at 2.5 mL/min. The compounds were then separated by the GC column and detected by mass spectrometry.

4.2.5 Personal diffusive sampler

In this project, two types of simple and easily portable TWA diffusive samplers were developed to monitor the toxic gases and vapours in both occupational and community environment.

The first type of the NTD diffusive sampler consists of two components: a sampler holder and a NTD. On the back of the sampler holder there is clip which can fix the sampler to the front pocket or under the collar. The sampler holder consists of one metal plate and four Teflon chips that have a hole in the center of the chip to let the needle passing through and seal the side hole and the tip of the needle. Figure 4.2 is the schematic diagram of the back of the holder, sealing position and sampling position of the needle trap diffusive sampler.

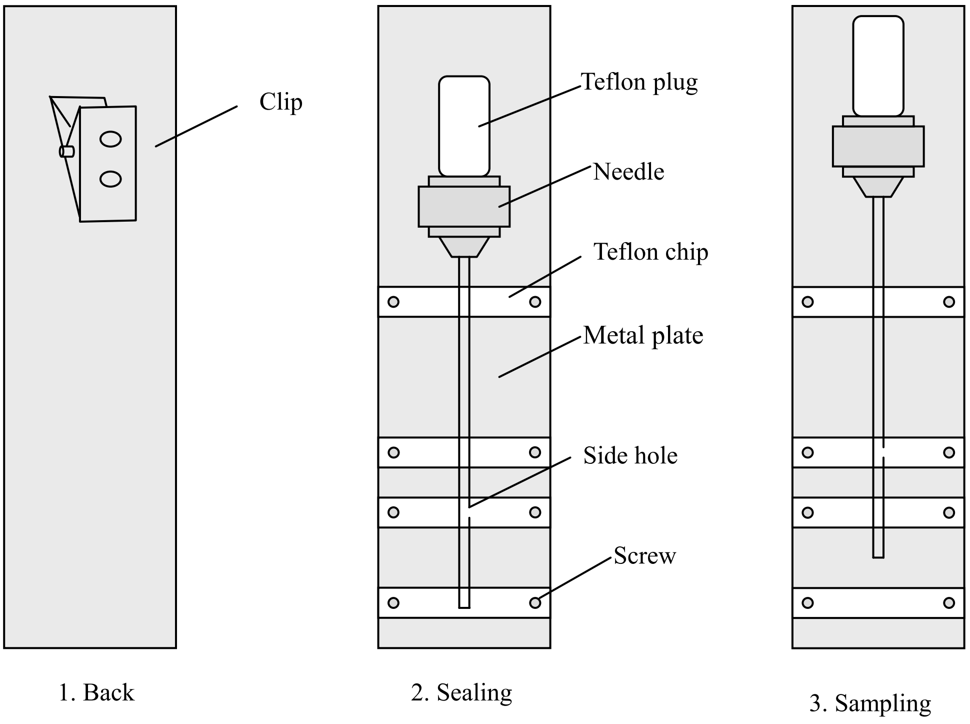
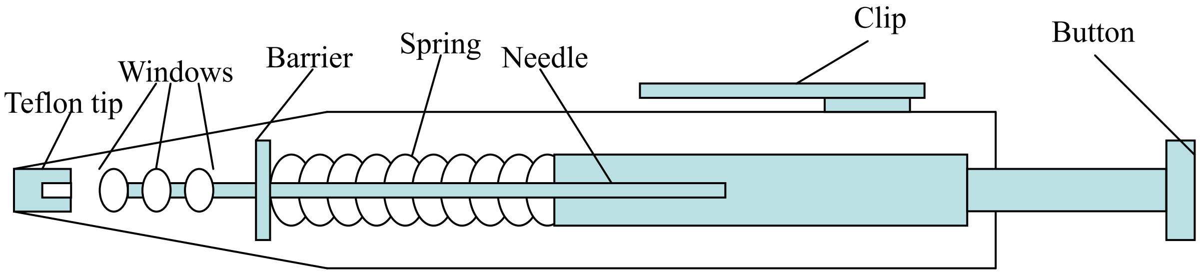
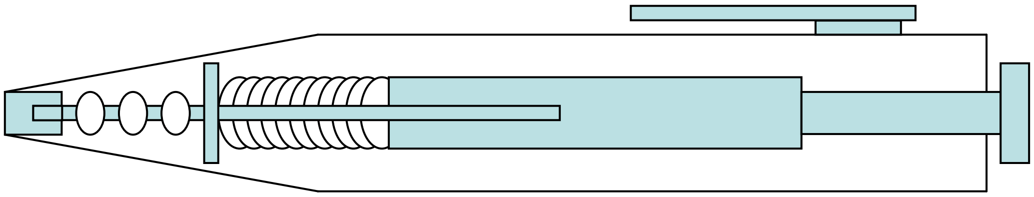


Figure 4.2 Schematic of needle trap device diffusive sampler

Another type of diffusive sampler is a pen-like sampler that can also be used in automation sampler. Figure 4.3 shows two status of the sampler. When the button at the end of the pen is pressed, the needle is at forward position and the tip of the needle is sealed by the Teflon tip fixed in the tip of the pen; this position is sealing status of the sampler. Before sampling, the needle is retracted by pressing the button. The tip of the needle is exposed to the space of the pen where air can move in and out through three windows on each side of the pen; this position is sampling status of the sampler. This type of sampler is lighter and more user-friendly than the first type. But it is more complicated to load the NTD in the holder than the first one.



Sampling position



Sealing position

Figure 4.3 Schematic of needle trap device pen-like diffusive sampler

4.3 Results and discussion

4.3.1 Effect of environmental factors on sampling performance

Environmental conditions such as temperature, pressure, relative humidity and sampling duration have been investigated the effects on NTD diffusive sampler performance before it was used to do field sampling.

For a diffusive sampler, the mass loading rate U can be derived from equation 3.5

$$U = \frac{n}{t} = \frac{DAC}{Z} \tag{4.1}$$

The diffusion coefficient of a given compound depends substantially on temperature and pressure, equation 4.2 shows the relationship among them[13-14]

$$D = \frac{KT^{\frac{3}{2}}}{P} \tag{4.2}$$

where K is a constant related to molecular weight and volume, T is ambient temperature (K), P is absolute pressure (Pa). The concentration of this compound can be derived from ideal gas law $C = \frac{P}{RT}$, then $U \propto T^{\frac{1}{2}}$. Therefore, the mass loading rate is proportional to the square root of the temperature and independent of pressure. This mathematical relationship between mass loading rate and temperature was proved by determining the mass loading rate at 25, 30, and 35°C. The experimental results, presented in Figure 4.4, show that with temperature increasing, the mass loading rates of BTEX slightly increased. This trend is consistent with theoretical prediction.

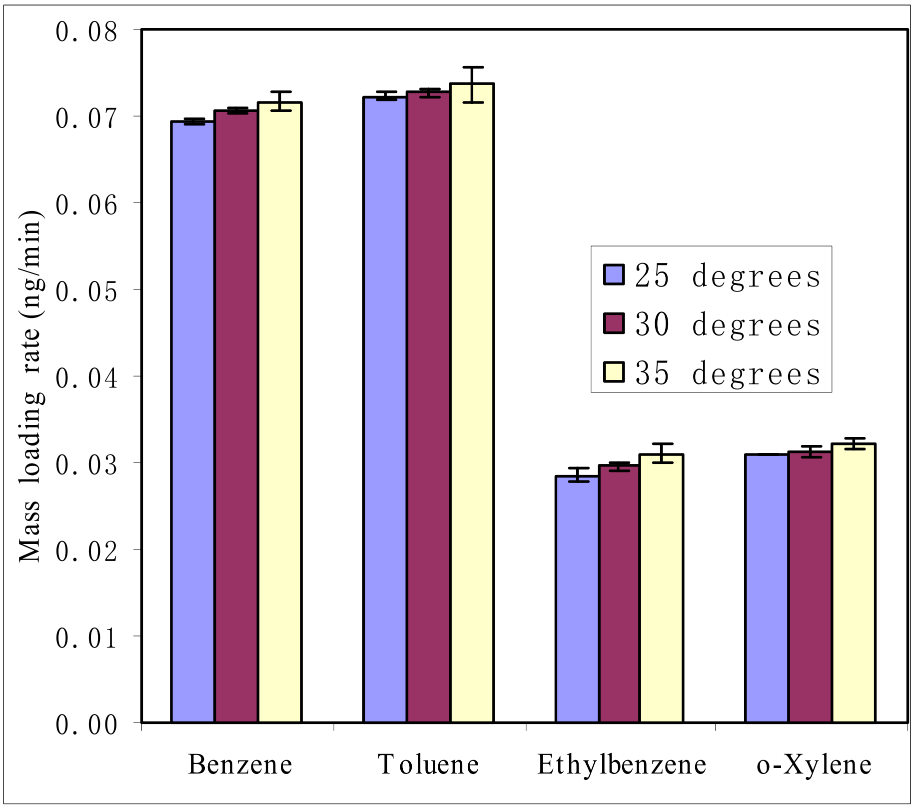


Figure 4.4 Effect of temperature on mass loading rate for BTEX (Z=0.45 cm)

In practice, the effect of temperature can be eliminated by calibrating diffusion coefficient at sampling temperature. The diffusion coefficients of many VOCs in air at 25 °C are known. If sampling is performed at a different temperature, T (K), the coefficient of the target compound at this temperature can be adjusted using the following equation[15]

$$D_T = D_g(\frac{T}{298}) \qquad (4.3)$$

where D_T is the diffusion coefficient (cm^2/s) of the compound at temperature T, D_g is the diffusion coefficient (cm^2/s) of the compound at 298 K, and T is the sampling temperature (K). Figure 4.5, 4.6 and 4.7, show the comparison between experimental mass loading rates for BTEX and theoretical mass loading rates that were calculated using calibrated diffusion coefficients at specific sampling temperature 25, 30 and 35°C. No significant difference was observed from the experiment results at different temperature. It demonstrated that the temperature effects on mass loading rates for BTEX can be eliminated by calibrating the diffusion coefficients of BTEX at sampling temperature.

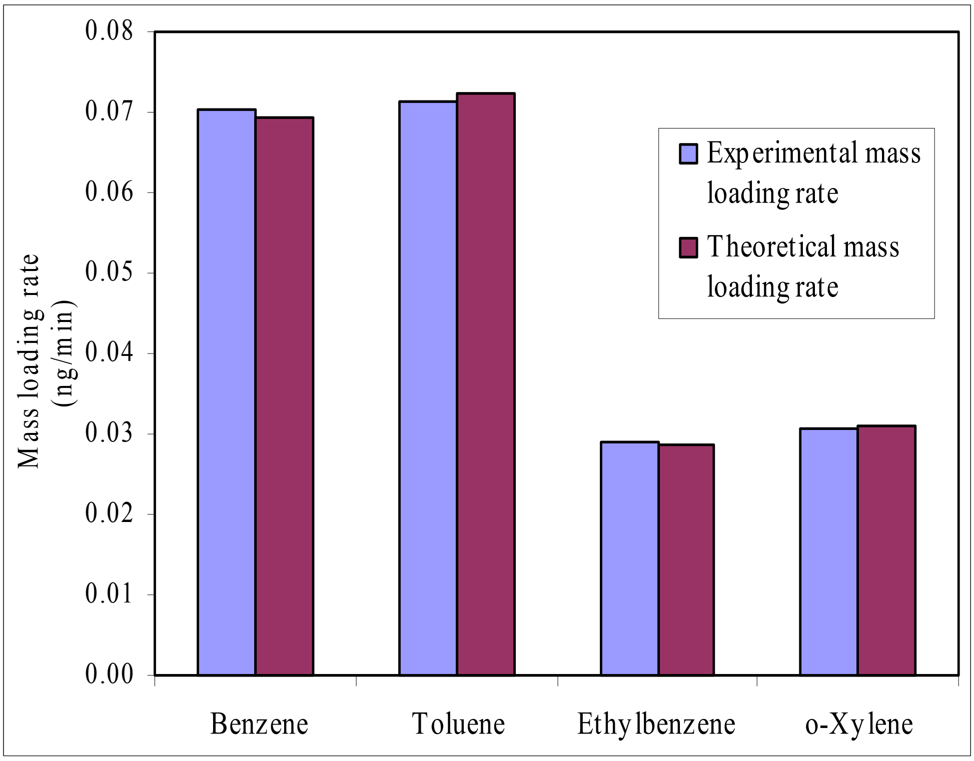


Figure 4.5 Comparison between experimental mass loading rates and theoretical mass loading rates for BTEX at 25 °C (Z=0.45 cm)

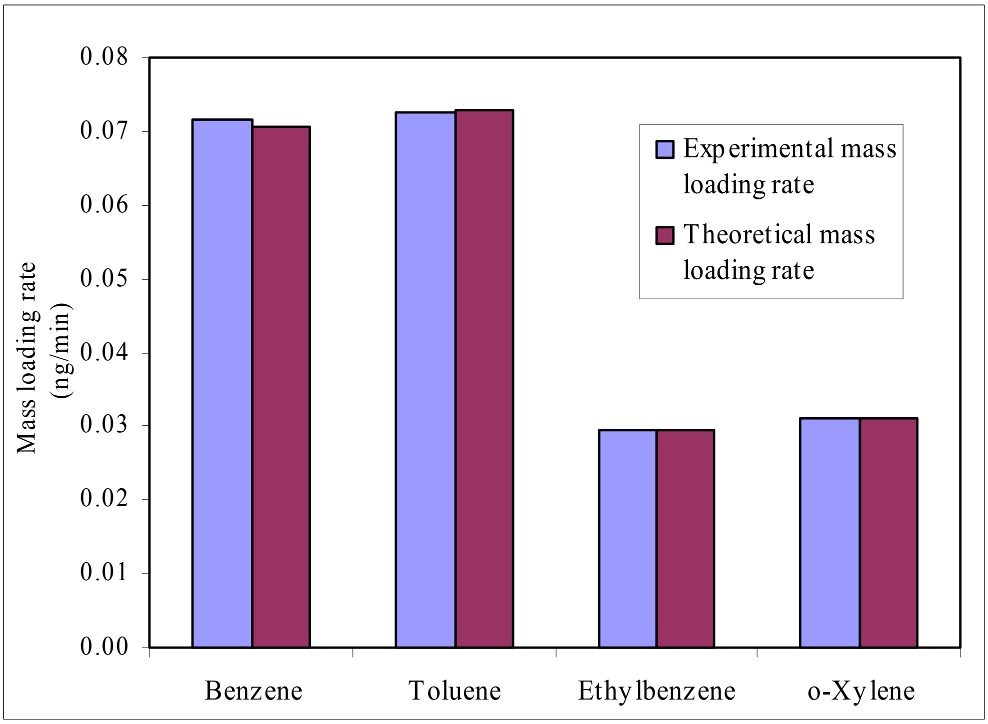


Figure 4.6 Comparison between experimental mass loading rates and theoretical mass loading rates for BTEX at 30°C (Z=0.45 cm)

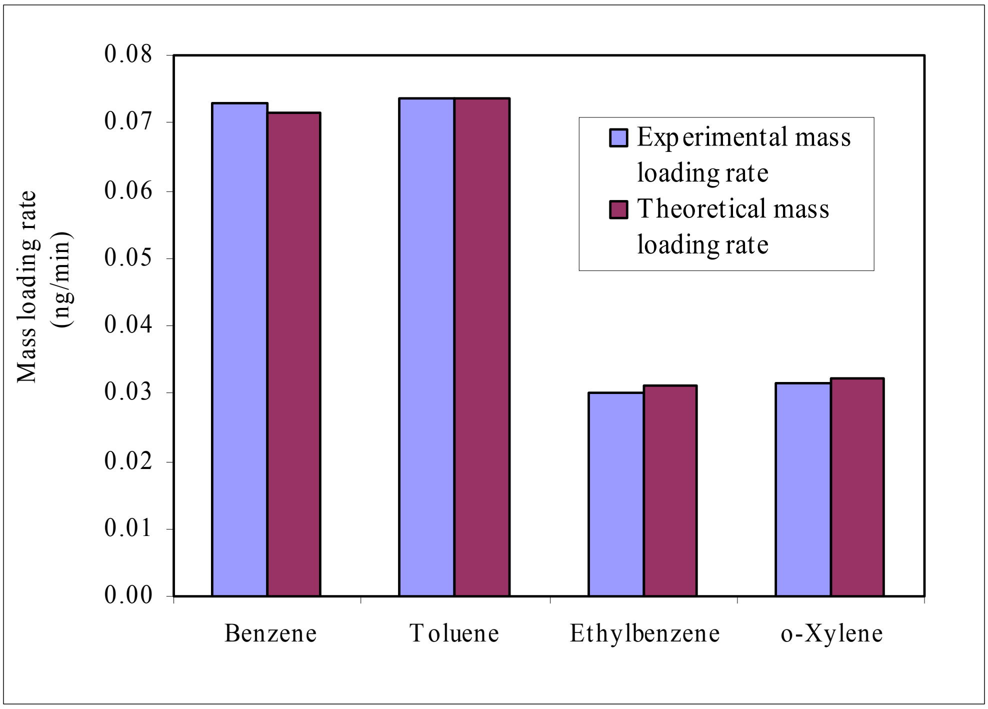


Figure 4.7 Comparison between experimental mass loading rates and theoretical mass loading rates for BTEX at 35°C (Z=0.45 cm)

In this study, the effect of relative humidity was also investigated. A series of experiments was performed to determine sampling rates at different relative humidity, including 17%, 42%, and 52%. The relative humidity was generated by passing the air sample through the headspace of an in-line impinger trap with water inside. Although BTEX are insoluble in water relatively, there are still trace amount of BTEX dissolved in water. Therefore, there were tiny differences of the concentrations for BTEX between #1 and #2 sampling chamber in Figure 4.1. Before diffusive sampling, the concentrations of BTEX were calibrated first by using NTD active sampling; after sampling they were double checked and no change was observed. The results, shown in Figure 4.8, indicated that at relative humidity less than 42%, the sampling rates of BTEX were very close; while higher than 42%, the sampling rates of BTEX were slightly affected by relative humidity. Compared with theoretical sampling rates of BTEX, the biggest difference was found between experimental and theoretical sampling rate of ethylbenzene; and this difference resulted in 14% of relative error of the result, which is within the acceptable range of ±20% suggested by U.S. EPA compendium Method TO-17.[16] Therefore, there is no significant impact of relative humidity on the sampling rate within this range. The possible reason is that Carboxen1000, which behaves as a hydrophobic sorbent, was far from saturation during TWA diffusive sampling; so the competition between the target analytes and water molecules for occupying the micropores was not strong enough to affect the adsorption of target analytes.[11]

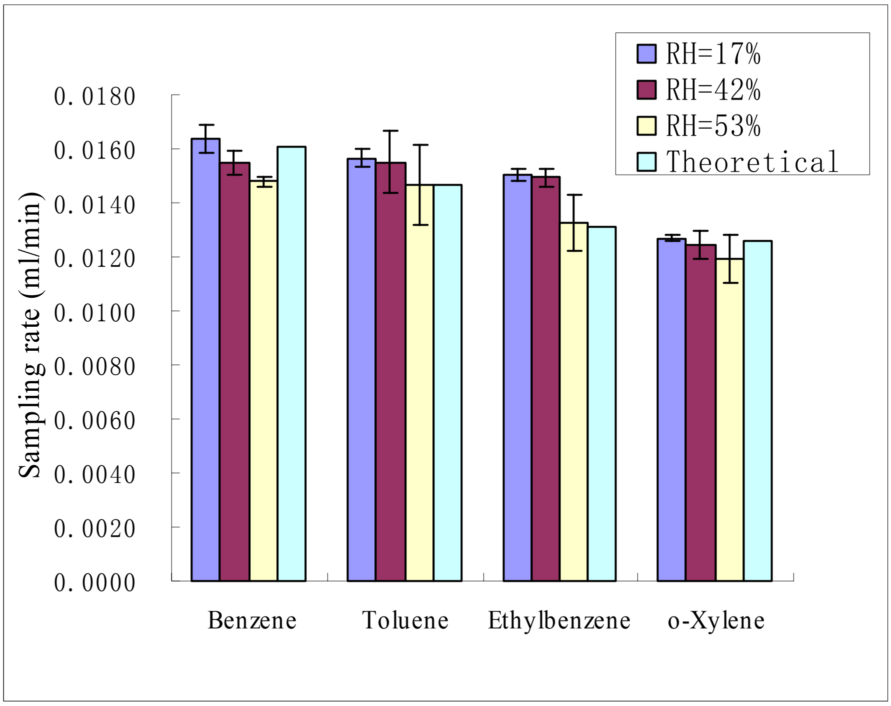


Figure 4.8 Effect of relative humidity on TWA sampling rates for BTEX with Carboxen1000 (Z=0.45 cm)

4.3.2 Sampling duration

The mass loading rate of a diffusive sampler may be constant for a period of exposure time. It depends on exposure time, the concentrations of sample, the strength of sorbent and the amount of sorbent.[2,17] Constant mass loading rate means that the adsorbed compounds do not effect the mass loading rate of additional analyte. In other words, the sorbent is zero sink for the target compound. With increased amount of adsorbed analyte, a small amount of the analyte may exist on the surface of the sorbent, and the mass loading rate will decrease and breakthrough will occur. A NTD, packed with Carboxen1000 and a 0.52 cm of diffusion length, was exposed to BTEX in the sampling chamber with a diffusive sampling time ranged from 1 to 95 h to examine the effect of sampling duration on mass loading rates of BTEX. The concentrations of BTEX in the sampling chamber were 4.94, 5.52, 2.21, 2.31 ng/mL respectively. The results, shown in Figure 4.9, illustrate that the adsorbed mass of BTEX on the NTD increased linearly (R^2 ranged from 0.990 to 0.992) within the sampling duration of 1-95 h. These results indicate that Carboxen1000 act as zero sink for BTEX during this sampling duration within this concentration range.

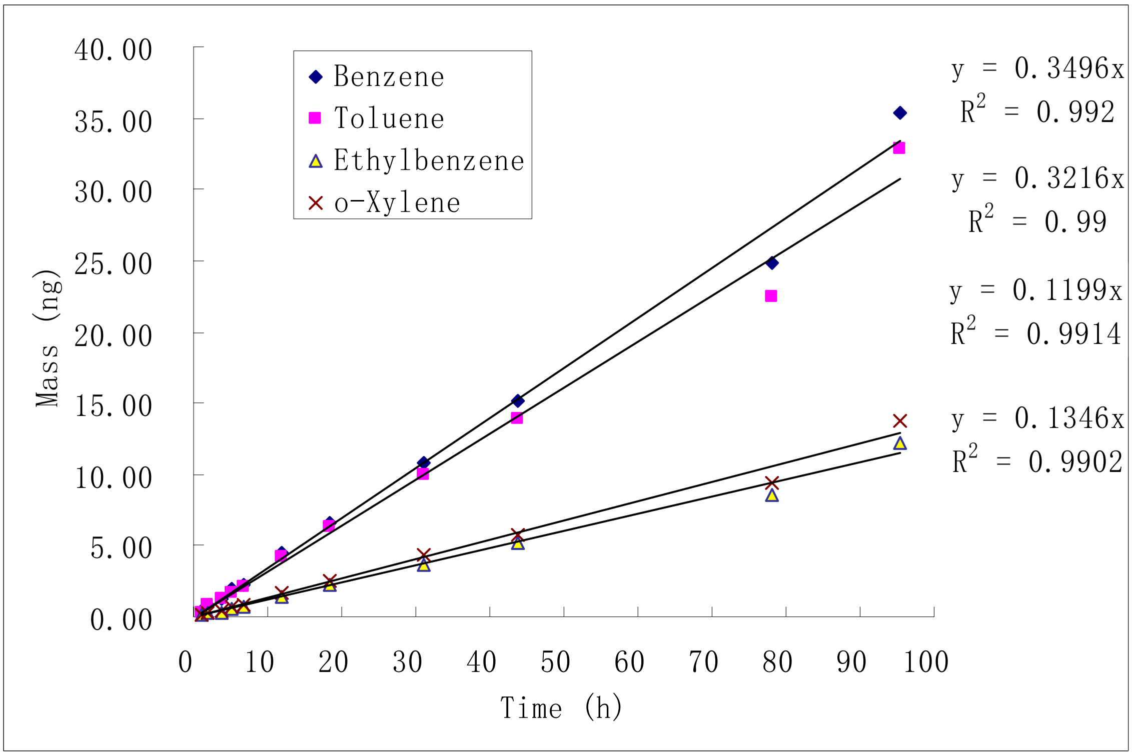


Figure 4.9 The mass of BTEX collected on NTD with Carboxen1000 during sampling duration of 1-95 h

4.3.3 Storage stability

Storage stability is very important for field TWA sampling. If storage is unstable, analytes adsorbed inside the sampler may be lost, introducing experimental error. The storage stability of NTD with Carboxen1000 for target BTEX compounds was tested by active sampling. The NTD was used to sample a 4.0 ml sample of BTEX from the standard gas system and injected into the GC/MS. Breakthrough was then tested for this NTD and none was found to have occurred. Next, the same 4.0 ml volume of BTEX was sampled and sealed in NTD with Teflon tip and tubing for 24 h at 24.5°C; then it was injected into the GC injector and analyzed by the GC/MS. The results from the analysis, presented in figure 4.10, show that there were not significant differences of collected mass for BTEX between the two cases described above. The recoveries of BTEX were 97.9%, 98.6%, 98.4% and 99.8%, respectively. Therefore, the needle trap sampler with Carboxen1000 has good storage stabilities for BTEX.

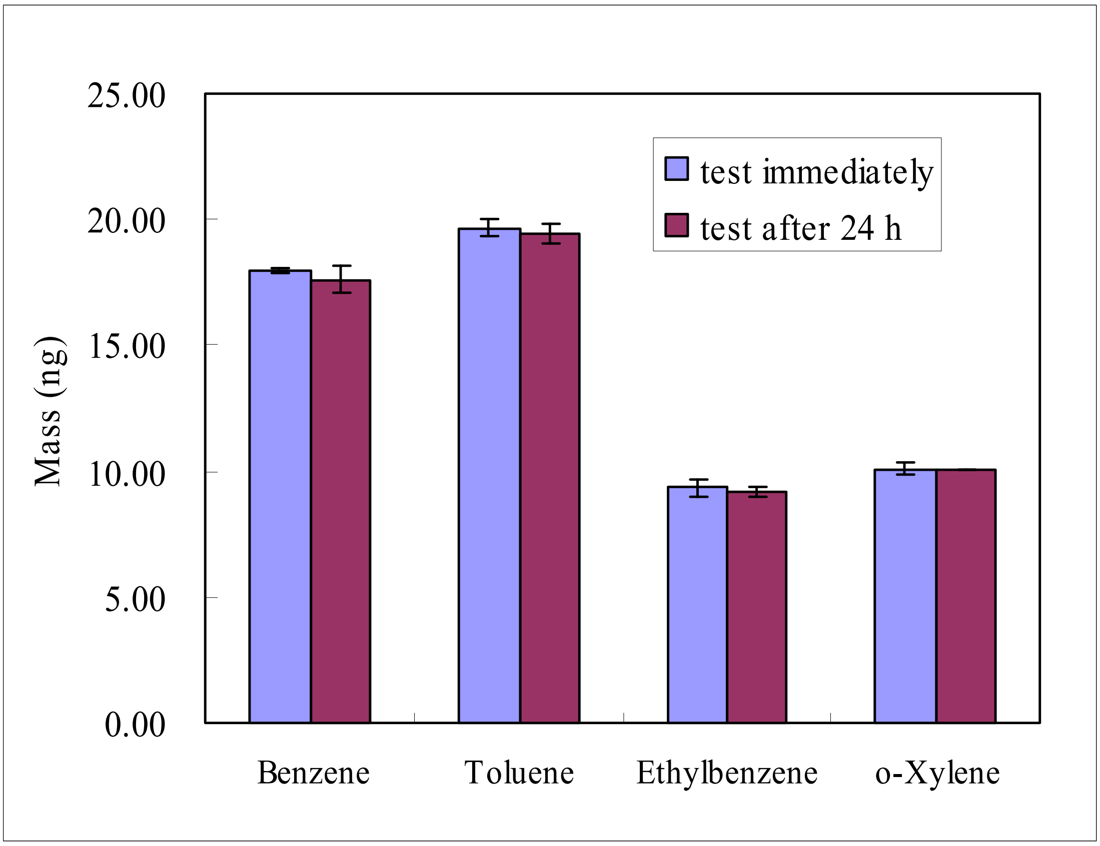


Figure 4.10 Storage stability tests for BTEX with Carboxen1000 at 24.5°C for 24 h

4.3.4 Verification of theoretical mode

According to Fick's first law, ideally the theoretical sampling rate of a diffusive sampler, which depends on the geometry of the sampler and individual analyte that has a particular diffusion coefficient in air, is equal to the experimental sampling rate. In practice, some factors may affect the sampling rate, such as face velocity, sorbent strength, response time, atmospheric temperature and pressure, relative humidity and sampling duration. If the theoretical sampling rate is equal to the experimental sampling rate under experimental condition, the concentration of target analyte can be calculated directly using the theoretical sampling rate, the adsorbed mass and sampling time without determining the experimental sampling rate.

In order to use equation 3.6 to determine the concentration of target analyte, the ratio of theoretical sampling rate obtained by calculation to experimental sampling rate obtained by analysis should be close to one.

The theoretical sampling rate R_T (cm^3/min) of a needle trap sampler, where the diffusion length, Z (cm), and cross-section area of the surface, A (cm^2), are known, was calculated according to $R_T = \frac{DA}{Z}$, where D is the analyte diffusion coefficient (cm^2/s).

This diffusive sampler was then used to do TWA sampling with a standard gas mixture of BTEX for an expected time. The experimental sampling rate was calculated according to $R_E = \frac{n}{Ct}$, where the concentration C (ng/mL) of each analyte was calculated from the permeation rate of the analyte and the flow rate of the carrier air, n is the loading mass (ng) of this analyte that can be determined by GC-MS, and t is the sampling time (s).

Verification of theoretical model was done by using six different NTDs with different diffusion length. The results, presented in Table 4.1, show good agreements between the theoretical and experimental sampling rates. The reason why the experimental and theoretical sampling rates differed slightly may be because of insignificant factors such as non-ideal sorbent, error of diffusion length measurement and humidity.

Table 4.1 Theoretical and experimental sampling rates of six needle trap devices with different diffusion lengths

Needle	Diffusion length (cm)	Benzene		Toluene		Ethylbenzene		O-xylene	
		R_T (mL/min)	R_E (mL/min)	R_T (mL/min)	R_E (mL/min)	R_T (mL/min)	R_E (mL/min)	R_T (mL/min)	R_E (mL/min)
1	0.44	0.016	0.016	0.015	0.015	0.013	0.015	0.013	0.013
2	0.63	0.012	0.011	0.011	0.010	0.009	0.011	0.009	0.009
3	0.78	0.009	0.010	0.009	0.010	0.008	0.009	0.007	0.008
4	0.73	0..010	0.010	0.009	0.010	0.008	0.010	0.008	0.006
5	0.58	0.013	0.011	0.011	0.010	0.010	0.010	0.010	0.009
6	0.49	0.015	0.014	0.014	0.013	0.012	0.011	0.012	0.010

R_T: Theoretical sampling rate

R_E: Experimental sampling rate

4.3.5 Method validation and field sampling

4.3.5.1 Validation in the lab

TWA diffusive sampling with NTD is a new method, for which it is essential to compare with other established methods. Validations were done in standard gas system against charcoal tube sampling from NIOSH method 1501, SPME, and NTD active sampling.[18] In the standard gas system, temperature was 25°C, relative humidity was 21%, air velocity was 3.05cm/min and the concentrations of BTEX were 1.57, 1.74, 0.79, 0.88 ng/mL respectively. The results are presented in Figure 4.11, from which no significant differences were found between NTD TWA diffusive sampling and other methods including Charcoal tube sampling, SPME, and NTD active sampling. The concentrations of BTEX determined by TWA diffusive sampling with NTD were 1.52, 1.69, 0.81, 0.89 ng/mL, which are close to the concentrations of BTEX calculated using the permeation rates of BTEX and flow rate of air in the standard gas system. Good agreements between TWA diffusive sampling and other methods were achieved.

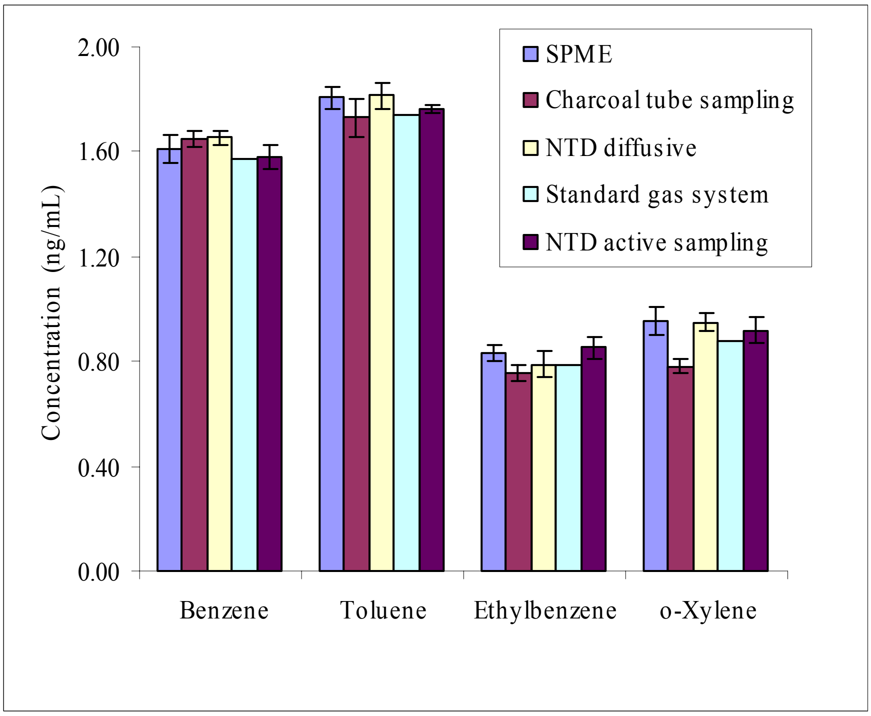


Figure 4.11 Comparison of concentrations of BTEX determined by needle trap TWA diffusive sampling and other methods, as well as standard gas system

4.3.5.2 Validation in field and field sampling

Although laboratory validation may consider some parameters that might influence the diffusive sampling performance of the NTD, it is not often possible or feasible to simulate practical field sampling conditions. Therefore, it is necessary to compare the NTD diffusive sampling performance with NIOSH method 1501 in field sampling.

Under actual condition, field validation was done by monitoring BTEX in a newly painted apartment, using the NTD diffusive samplers shown in Figure 4.2 and charcoal tubes from NIOSH method 1501. Four TWA diffusive samplers and seven charcoal tubes were used to sample the air, sampling time was 8 h and sampling volume was 8 L per charcoal tube. The results were presented in Figure 4.12. The concentrations of BTEX determined by NTD diffusive sampling were 0.21, 0.13, 0.07, 0.02 ng/mL; and by charcoal tube sampling were 0.22, 0.14, 0.08, 0.02 ng/mL. No significant difference was observed between these two methods. It demonstrates that NTD with Carboxen1000 can do successful diffusive sampling for BTEX not only under controlled conditions, but also under practice conditions.

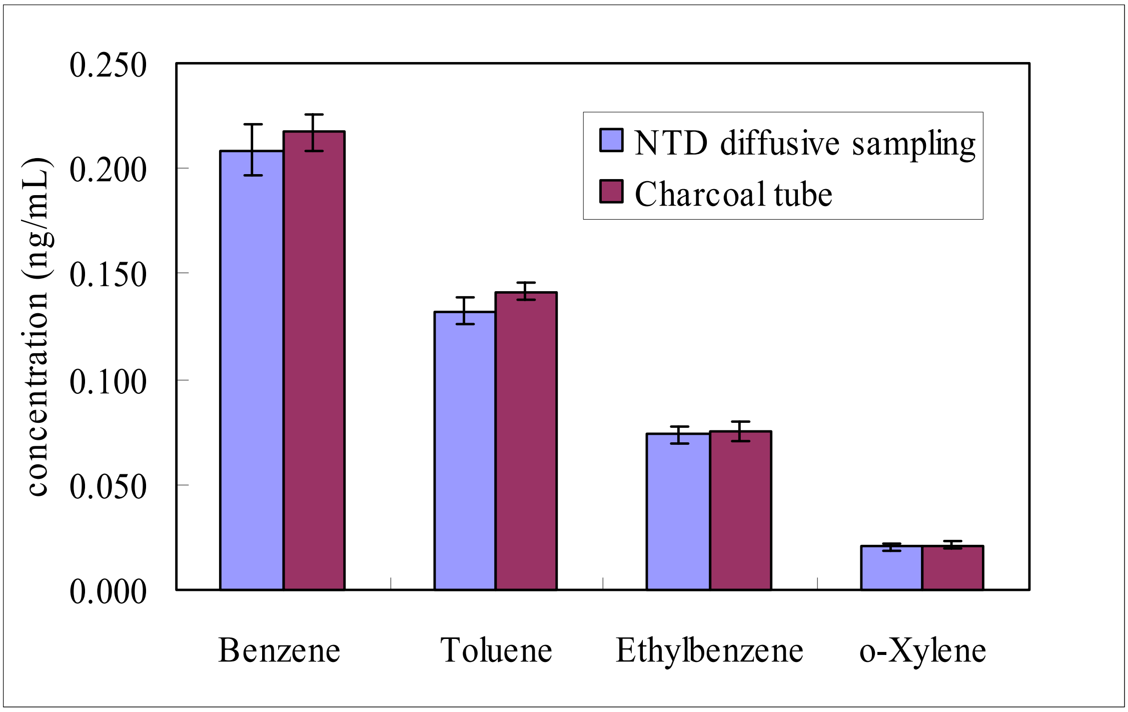


Figure 4.12 Comparison of results for needle trap diffusive sampling against NIOSH method 1501

Field diffusive samplings using the NTDs were also performed in the garage, living room, bedroom and shed. The sampling durations were 24 h and 40 h respectively. The results, shown in Table 4.2, indicate that benzene was only detected in the shed and the concentrations of toluene, ethylbenzene, and o-xylene were much higher than that of monitored air in other places; the concentrations of toluene, ethylbenzene, and o-xylene in the living room and bedroom were lower than that in the garage.

Table 4.2 Determined concentrations of BTEX in the garage, living room, bedroom, and shed

Sampling place	C, ng/mL (B)	C, ng/mL (T)	C, ng/mL (E)	C, ng/mL (X)
Garage	n.d.	0.40	0.55	0.43
Living room	n.d.	0.02	0.04	0.03
Bedroom	n.d.	0.29	0.03	0.06
Shed	4.75	55.20	8.49	8.90

4.4 Conclusion

The results of this study show that the NTD with carboxen1000 met all three prerequisites of applying Fick's first law for successful diffusive sampling, viz. zero sink, short response time and insensitivity to face velocity. The NTD can be used for TWA diffusive sampling without considering face velocity due to the very small diameter of the needle. It is affected slightly by temperature which can be calibrated by calculating the diffusion coefficient at sampling temperature. There is no significant impact of relative humidity on the sampling rate within the range from 17% to 53%. There was good agreement between theoretical and experimental sampling rate for BTEX TWA diffusive sampling with the NTD. In addition, method validations were done both in the laboratory and in field. It was demonstrated that the accuracy of TWA diffusive sampling with NTD is similar to that of charcoal tube, SPME and NTD active sampling methods.

The NTD with Carboxen1000 has been demonstrated to be a successful diffusive sampler for monitoring TWA concentrations of BTEX under low relative humidity. Further efforts have to be made to conduct a series of experiments on new sorbents and under different environmental conditions to monitor a greater range of VOCs. These NTD diffusive samplers will be useful and convenient for monitoring both personal exposure in the occupational environment and ambient air quality.

4.5 References

1. S. Batterman, T. Metts, P. Kalliokoski, *J. Environ. Monit.*, 4 **(2002)** 870-878
2. B. Strandberg et al., *Atmospheric Environment*, 39 **(2005)** 4101-4110
3. Y. Fung and Z. Wu, *Analyst*, 121 **(1996)** 1955-1961
4. R.H. Brown and M.D. Wright, *Analyst,* 119（**1994**）75－77
5. Z.H. Fan, K.H. Jung, and P.J. Lioy, *Environ. Sci. & Technol* **2006,** 40 (19), 6051-6057
6. A.P. Wang, F. Fang, J. Pawliszyn, *J. Chromatogr. A*, 1072 **(2005)** 127-135
7. P.A. Martos and J. Pawliszyn, *Anal. Chem.*, 71 **(1999)** 1513-1520
8. S. Shojania, R.D. Oleschuk, M.E. McComb, H.D. Gesser, A. Chow, *Talanta,* 50 **(1999)** 193-205
9. M.E. McComb, R.D. Oleschuk, E. Giller, H.D. Gesser, *Talanta,* 44 **(1997)** 2137-2143
10. R.H. Brown, *J. Environ. Monit.*, 2 **(2000)** 1-9
11. Y. Chen and J. Pawliszyn, *Anal. Chem.,* 75 **(2003)** 2004-2010

12. J. Koziel, M. Jia, and J. Pawliszyn, *Anal. Chem.,* 72 **(2000)** 5178-5186

13. J. Piiper and H. Worth, *Respiration Physiology*, 41 **(1980)** 233-240.

14. C.V. Paganelli, A. AR, H. Rahn and O.D. Wangensteen, *Respiration Physiology* **1975,** 25, 247-258.

15. S. Batterman, T. Metts, P. Kalliokoski, *J. Environ. Monit.* 4 **(2002)** 870-878.

16. E.A. Woolfenden, W.A. McClenny, Method To-17, *Determination of Volatile Organic Compounds in Ambient Air using Active Sampling onto Sorbent Tubes,* EPA/625/R-96/010b, U.S. Environmental Protection Agency, Research Triangle Park, NC, **1997**

17. R.H. Brown, R.P. Harvey, C.J. Purnell, K.J. Saunders, *Am .Ind. Hyg. Assoc. J.* 45 (2) **(1984)** 67-75

18. National Institute for Occupational Safety and Health, *Manual of Analytiacl Methods* 1501, **1994**.

Chapter 5– Active sampling and analysis for thiol compounds

5.1 Introduction

Thiol compounds, which are often referred to as mercaptans, contain the functional group -SH bonded to a carbon atom. Many thiols are colourless liquids that often have strong and repulsive odours, particularly for those of low molecular weight. Thiol compounds are found in crude petroleum; and they are also produced by certain plants and animals, for instance allylthiol and propanethiol are released when onions are cut; and butanethiol derivatives are present in skunk secretions.[1] In our daily life, thiols are present in variety of foods such as cheese, poultry and other meat products, some vegetables, wine and beer.[2-6] Thiol compounds can take part in a wide variety of chemical reactions. Their principal uses are in jet fuels, pharmaceuticals, industrial solvents and livestock-feed additives. In addition, thiols are often added to the odourless natural gas to warn of gas leaks because of their very low odour thresholds e.g. the odour threshold of propanethiol is 0.00074 PPM.[7]

Thiol compounds are commonly emitted into the air from industrial processing such as handling or degradation of organic materials, oceans, marshes, soils and vegetation.[8-10] Thiols are strong irritants and can be toxic at high concentration. Exposure to a high concentration of thiols can cause headache, nausea, vomiting, lung irritation and inflammation of the eye, nose and throat; prolonged exposure can lead to breathing problems, unconsciousness and muscle spasms.[11] These irritant effects, however, normally disappear quickly after exposure to fresh air.

Health and safety requirements for some thiols are established by some organizations such as OSHA (Occupational Safety and Health Administration), NIOSH (National Institute for Occupational Safety and Health) and ACGIH (American Conference Governmental Industrial Hygienists). The exposure limits of methanethiol, 1-ethanethiol and 1-butanethiol are prescribed by these organizations.[12] Workers must not be exposed to airborne concentrations of a toxic chemical that exceed the occupational exposure limit (OEL) for this chemical. Therefore, it is necessary to monitor workplace air quality to ensure that the airborne levels of thiols do not exceed their OELs.

Previous sampling methods of thiols were conducted by different methods, such as glass tube with sorbent inside active sampling followed by solvent desorption, direct headspace syringe sampling, headspace solid-phase microextraction (HS-SPME) and head space solid-phase microextraction with in-fibre derivatization.[4,5,12,13] However, there are some drawbacks from previous methods. Glass tubes with sorbent active sampling require the use of organic solvents to extract the adsorbed thiols; a cryogenic trap has to be used to concentrate the headspace analytes for direct headspace syringe sampling; HS-SPME and HS-SPME with in-fibre derivatization need special operating conditions, e.g. extraction temperature, extraction time and extraction matrix, moreover, in-fibre derivatization requires an appropriate derivatization reagent.

NTD active sampling coupled with GC-MS appears to be a fast and convenient method for analyzing thiols in air or other matrices. It also reduces sampling time and increases sensitivity.

5.2 Experiment section

5.2.1 Chemicals and materials

1-propanethiol (99%) and 1-butanethiol (99%) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). All 22-gauge needles were purchased from Dyna Medical Corporation (Ontario, Canada). All side holes were made in-house by the machine shop at the University of Waterloo. Hydrogen, nitrogen, helium, compressed air and carbon dioxide were obtained from Praxair Canada Incorporated (Ontario, Canada). Carboxen1000, Carboxen1003 and Carbosieve S-III were purchased from Supelco (Ontario, Canada); HayeSep Q (Divinylbenzene) was purchased from Krackeler (N.Y., USA); XAD-2 (Polystyrene divinylbenzene) was purchased from Restek (PA, USA). The 5-min epoxy glue was purchased from Henkel Canada (Ontario, Canada). The narrow-neck liner was purchased from SGE Analytical Science (Texas, USA). Permeation tubes were made in the laboratory. The AP-20 air sampling pumps were purchased from Komyo (Kinagawa, Japan). The timer was purchased from VWR International (Ontario, Canada). A food chopper was purchased from Hamilton Beach (Ontario, Canada). Plastic sampling bags were purchased from SKC (PA, USA). Gas tight syringes were purchased from Hamilton (NV, USA).

5.2.2 Preparation of needle trap device

NTD consists of a 22-gauge needle with a side hole, 3 cm from the tip of the needle and selected sorbent (Figure 5.1). The procedure to prepare a NTD is as follows: a metal wire was used to indicate the position inside the needle where the sorbent would be packed; about 1 cm of gold wire was tightly coiled into a 22-gauge needle and fixed in the required position; then an aspirator was used to aspirate the sorbent into the needle until it came to the tip of the needle; small quantity of 5-minute epoxy glue was used to immobilize the sorbent. To prevent the glue from blocking the needle, an aspirator was connected to the needle to draw the air through the NTD before the glue solidified. The NTDs were conditioned in a GC injector at specific temperature for 2 h to remove impurities, e.g. it was 300°C for Carboxen1000, Carboxen1003 and Carbosieve S-III; 275°C for HayeSep Q and 240°C for XAD-2[14]. Finally, the two ends and side hole were sealed with Teflon caps and tubing.

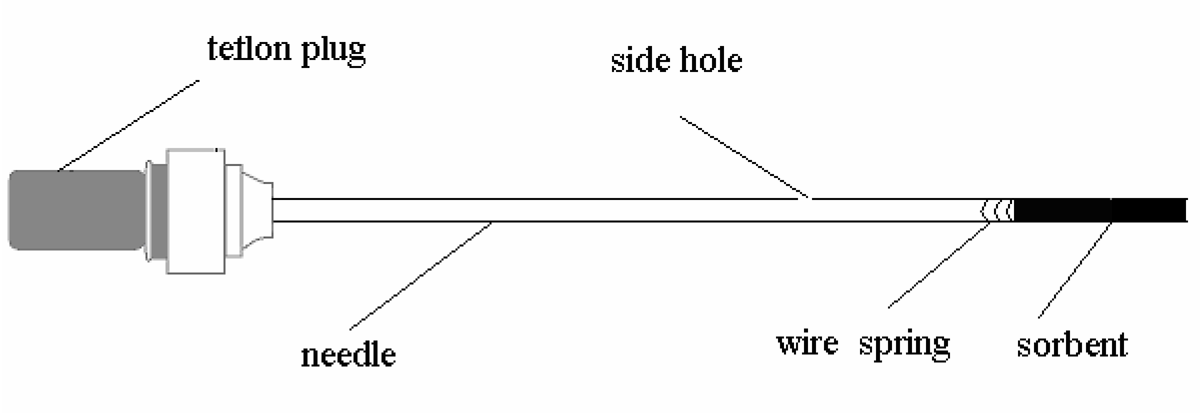


Figure 5.1 Schematic of the needle trap device for active sampling

5.2.3 Standard gas system

A standard gas generating system, illustrated in Figure 5.2, was used for the development of the analysis methods for 1-propanethiol and 1-butanethiol.

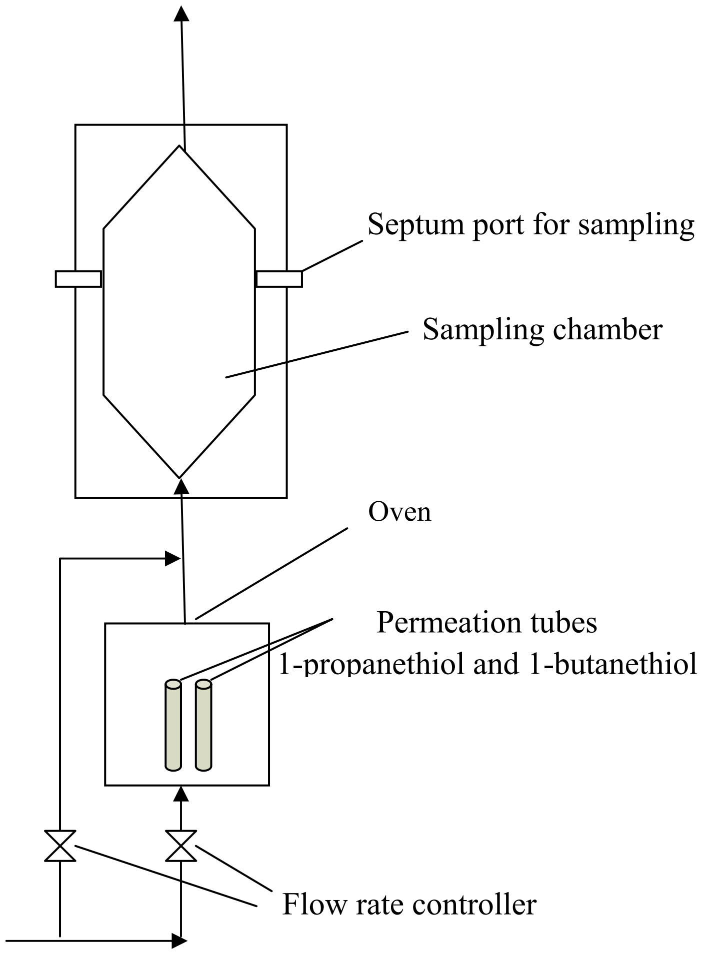


Figure 5.2 Schematic of the standard gas system

This system, which has proven to be continuous, available and convenient, can generate a wide range of VOC concentrations and mixture of various gases.[15] It consists of a continuous standard gas generator and air sampling chamber (Figure 2.3). The standard gas generator consists of permeation tubes and a permeation oven. All permeation tubes are placed inside a glass cylinder, which is held inside a permeation oven and swept with constant flow of dilution air. The theoretical analyte concentrations for the target compounds are achieved in the chamber and can be calculated using equation 5.1.

$$C = \frac{R_p}{R_{air}} \tag{5.1}$$

Where C is the theoretical concentration of target compound, ng /mL; R_p is the permeation rate of this compound, ng/min; and R_{air} is the flow rate of air, mL/min. Different concentrations of the thiols can be obtained by adjusting the temperature of the permeation oven and the flow rate of air.

5.2.4 Instrumentation

A Varian CP-3800 Gas Chromatograph (GC) equipped with a Varian 2000 Mass Spectrometer (MS) (Varian Inc., Ontario, Canada) was used to separate and analyze the thiol compounds extracted by the needle trap device. A narrow-neck glass liner was connected to a SPB-5 GC capillary column (30m× 0.25mm, DF=0.25μm). Figure 2.4 shows a schematic diagram of the system.

The injector temperature was maintained at 270°C. After sampling, the NTD was put through the septum and entered the GC injector, where the helium carrier gas entered the side hole of the NTD, flowed through the sorbent, and carried the desorbed compounds into the GC column. The column temperature program was maintained at 40°C for 1.5 min and then ramped at 20°C/min to 100°C and held for 1 min. The carrier gas flow rate was set at 2.0 mL/min. The compounds were then separated by the GC column and detected by mass spectrometry.

5.2.5 Sample preparation and field sampling

Some vegetables including garlic, yellow onion and red onion were finely chopped using a food chopper and put into 1 L plastic sampling bag into which 1 L of helium was pumped through the septum injection port. A specific volume of gas in the sampling bags was sampled using NTD with sorbent DVB coupled with a gas tight syringe and analyzed by the GC-MS. The same volume of gas samples were sampled and analyzed until the concentrations of target thiols did not change.

Field samplings were also performed in a kitchen and over toilet in the washroom. 100 mL of air was sampled in these area using NTDs with sorbent DVB coupled with an AP-20 air sampling pump. The adsorbed compounds were then thermal desorbed in the GC injector and analyzed by the GC-MS.

5.3 Results and discussion

5.3.1 Selection of sorbent

There are a number of different sorbents commercially available. In order to choose appropriate sorbents, some factors should be considered. First, the sorbent must be sufficiently strong to retain target analytes during sampling and weak enough to release them during thermal desorption. The sorbent must be inert to active species and hydrophobic to avoid adsorption competition from water molecules. Temperature stability is also significant factor for a sorbent to ensure that desorption at relative high temperatures does not cause any decomposition of the sorbent. Due to the special shape of the needle, mechanical strength should be taken into account. If the sorbent was friable, the particles would be easier to be broken to block the needle during packing.[16]

Five sorbents, including Carboxen1000, Carboxen1003, Carbosieve S-III, XAD-2 and HayeSep Q (DVB), were chosen to perform the sorbent screening test due to the factors mentioned above. 5 mL of standard gas mixture with 1-propanethiol and 1-butanethiol was sampled by the needle trap devices with different sorbents, and then put into the GC injector and thermally desorbed at 275°C, followed by separation and detection. The results of screening, shown in Figure 5.3, indicated that HayeSep Q (DVB) had the best adsorption performance over the other four sorbents.

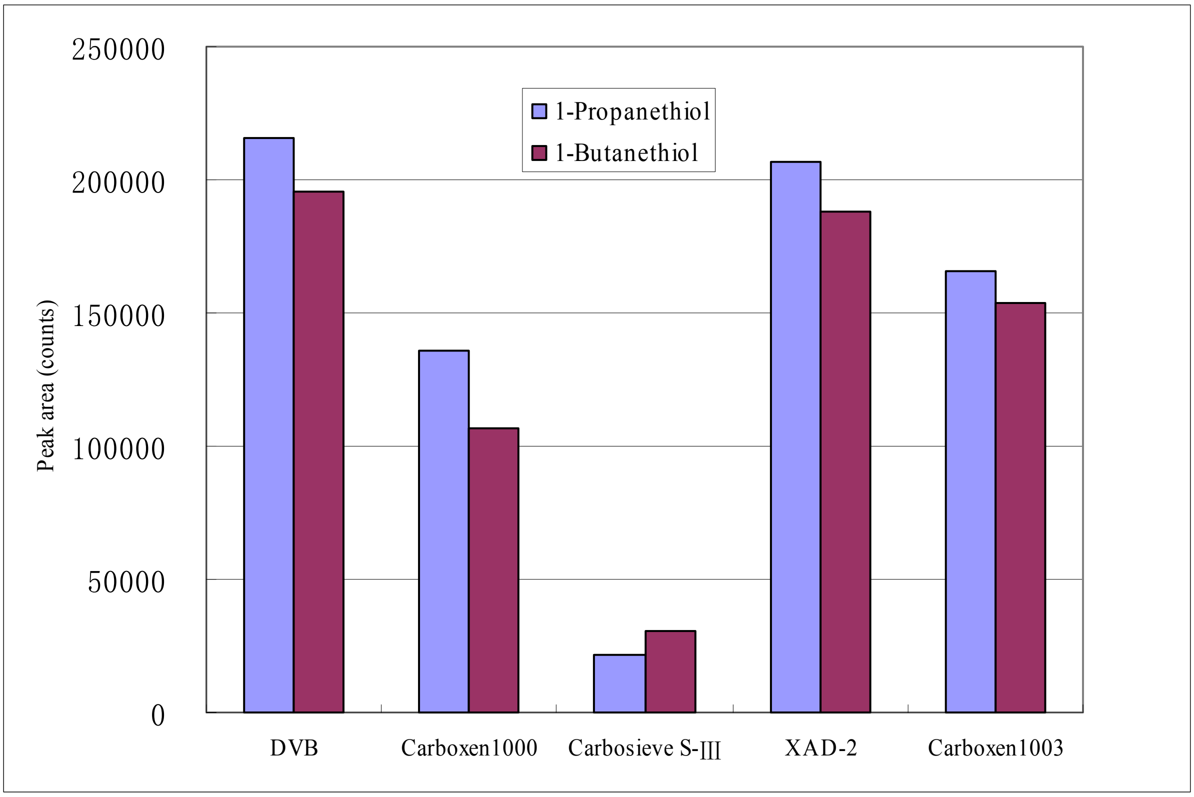


Figure 5.3 Comparison of the adsorption performance of different sorbents for 1-propanethiol and 1-butanethiol

5.3.2 Desorption temperature

As discussed in Chapter 2, the temperature is a significant parameter that governs thermal desorption efficiency. Higher temperatures can provide more energy to help the adsorbed compounds escape from the sorbent, while it is possible for the sorbent to become unstable or decompose at higher temperature. If the temperature was too low, part of the adsorbed compounds would not have enough energy to overcome the force between these compounds and sorbent, resulting carryover problem. Therefore, selection of suitable temperature is very important to ensure desorption completely and no any decompositation of sorbent and analytes. Experiments were performed to select the appropriate temperature for thiol compounds desorption. 5 mL of gas sample in the standard gas system was sampled by active sampling using NTD with sorbent DVB, and then desorbed at different temperature 235, 245, 255, 265, 275°C for 1.5 minutes individually, followed by GC-MS analysis. The results shown in Figure 5.4 indicate that 265-275°C was a proper temperature range for 1-propanethiol and 1-butanethiol to be desorbed from DVB. The maximum limit temperature for DVB is 275°C, therefore 270°C was selected as appropriate desorption temperature in this project.

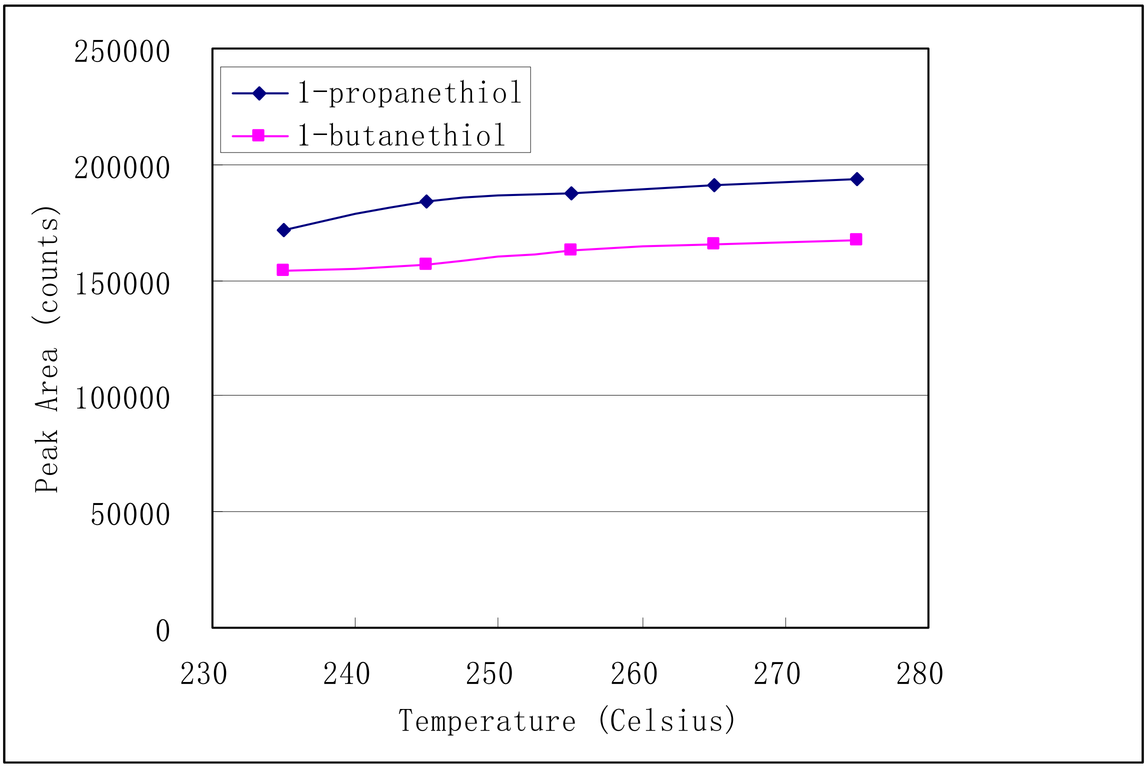


Figure 5.4 Comparison of adsorbed mass of 1-propanethiol and 1-butanethiol at different desorption temperature

5.3.3 Desorption time

Thermal desorption efficiency also depends on desorption time. If the desorption time was too short, the adsorbed compounds did not have enough time to transfer from the inside to the surface of the sorbent, resulting carryover. On the other hand, keeping the NTD at a high temperature might cause some negative effects and decrease the lifetime of the NTD. Therefore, it is necessary to select appropriate desorption time to ensure the target analytes desorbed completely and not to keep the NTD at high temperature for longer time. Experiments were performed at 270°C for different desorption time from 0.2 to 1.0 min. 5 mL of gas sample in the standard gas system was sampled by active sampling using NTD with sorbent DVB, and then desorbed at 270°C individually, followed by GC-MS analysis. It was observed from figure 5.5 that 1.0 min was the suitable desorption time for 1-propanethiol and 1-butanethiol.

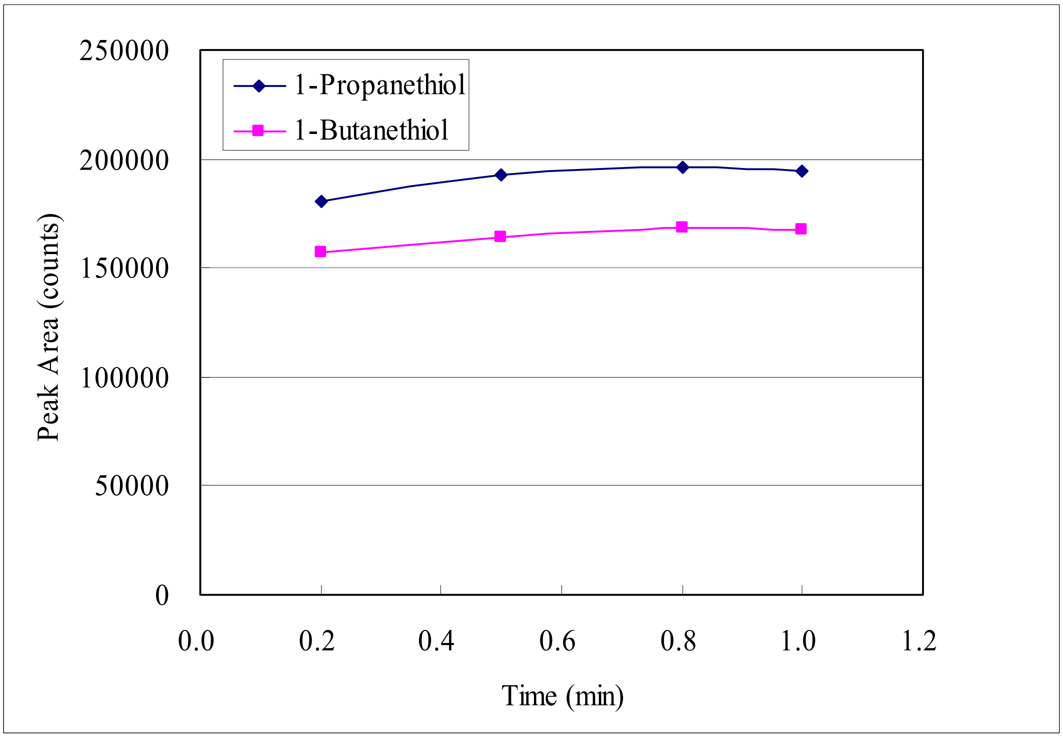


Figure 5.5 Comparison of desorbed mass of 1-propanethiol and 1-butanethiol for different desorption time

5.3.4 Calibration curve

In order to determine the target thiols in real samples, the calibration curves of target thiols were obtained using the optimal parameters investigated above. The permeation rates of target thiols were determined by putting the permeation tubes of 1-propanethiol and 1-butanethiol into glass cylinder at 45°C oven for 14332 min. The concentrations of target thiols were calculated using equation 5.1 in which the permeation rates of target thiols were shown in Table 5.1 and the flow rate of air was 402 mL/min.

Table 5.1 The permeation rates of 1-propanethiol and 1-butanethiol

Name of compound	Time duration	Mass of permeation tube(g)		Permeation rate
	(min)	Before	After	(ng /min)
1-Propanethiol	14332	16.7236	16.7119	816.4
1-Butanethiol	14332	16.744	16.7368	502.4

Different volumes of standard gas mixtures of 1-propanethiol and 1-butanethiol, 5.0, 10.0, 15.0, 20.0 and 25.0 mL, were sampled using NTD with sorbent DVB at the sampling chamber in standard gas system. The mass of target analytes sampled were calculated by using the volume times the concentration of the analytes. The calibration curve for 1-propanethiol and 1-butanethiol were obtained and shown in Figure 5.6. The correlation coefficients of target thiols were 0.9985 and 0.9987, respectively. It showed good linearity within the ranges, from 10 to 50 ng for 1-propanethiol and from 6 to 30 ng for 1-butanethiol.

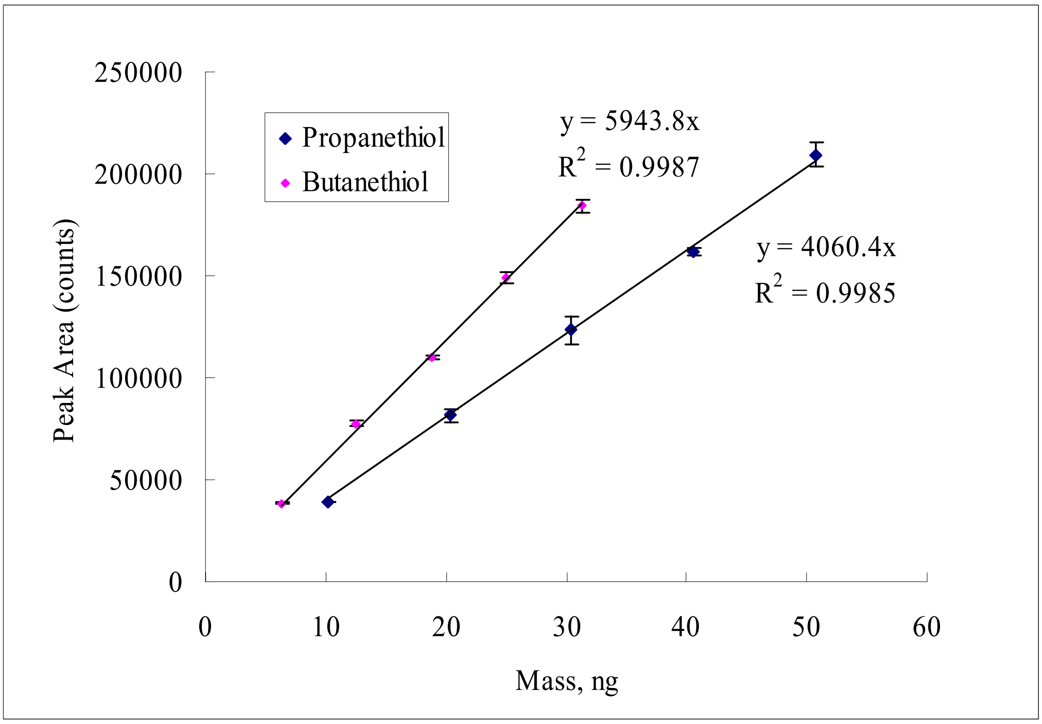


Figure 5.6 Calibration curves of 1-propanethiol and 1-butanethiol for NTD with sorbent DVB

5.3.5 Applications

Vegetables including garlic, yellow onion and red onion were analyzed for 1-propanethiol and 1-butanethiol. Samples were prepared according to the method described in the experimental section. The NTD with sorbent DVB coupled with a gas tight syringe was used to conduct active sampling and the GC-MS was used to separate and detect the compounds adsorbed on the NTD. Each sample was determined several times for different intervals after sampling preparation until the concentrations of target analytes were not change. Table 5.2 lists the concentrations of target analytes detected in garlic, yellow onion and red onion and the reproducibility of 6 duplicate samples. It was observed from the results that the concentration of 1-propanethiol in yellow onion was much higher than that in garlic and red onion, while 1-butanethiol was only detected in red onion.

Table 5.2 Determined concentrations of 1-propanethiol and 1-butanethiol in garlic, yellow onion and red onion.

	Garlic		Yellow onion		Red onion	
	Concentration (μg/g)	Reproducibility (% RSD) n=6	Concentration (μg/g)	Reproducibility (% RSD) n=6	Concentration (μg/g)	Reproducibility (% RSD) n=6
1-propanethiol	2.4	4	45.7	5	1.1	1
1-butanethiol	n.d.	n/a	n.d.	n.a.	0.1	4

n.d. = not detected n/a = not available

Field sampling was also conducted by NTD active sampling with sorbent DVB coupled with an AP-20 air sampling pump in a kitchen and over the toilets in washrooms. 100 mL of air sample was aspirated through the NTD by the sampling pump, and then thermally desorbed in the injector, followed by seperation and detection in GC-MS. The results presented in Table 5.3 show that there was 1-propanethiol existing in the kitchen and no target analytes were detected in the air over the toilet.

Table 5.3 Determined concentrations of 1-propanethiol and 1-butanethiol in kitchen and over toilets

	Kitchen		Tiolet1		Toilet2	
	Concentration (μg/mL)	Reproducibility (% RSD) n=3	Concentration (μg/mL)	Reproducibility (% RSD) n=3	Concentration (μg/mL)	Reproducibility (% RSD) n=3
1-propanethiol	2.6	3	n.d.	n/a	n.d.	n/a
1-butanethiol	n.d.	n/a	n.d.	n.a.	n.d.	n/a

5.4 Conclusion

A simple and feasible method was developed to make the NTDs with the suitable sorbent for active sampling. The standard gas system, which can generate constant concentrations of 1-propanethiol and 1-butanethiol with the permeation tubes, was set up to be used to investigate operational parameter for NTDs. HayeSep Q (DVB) was selected as an appropriate sorbent for sampling thiols by comparing the amount of loaded mass on different sorbents. A series of experiments was performed to investigate thermal desorption efficiency, and 270°C and 1.0 min were found to be optimal thermal desorption temperature and time for target analytes with DVB.

The needle trap device with DVB coupled with GC-MS by thermal desorption was developed for sampling and analyses of volatile thiols. The calibration curve obtained by sampling in the standard gas system of thiols showed good linearity within the ranges, from 10 to 50 ng for 1-propanethiol and from 6 to 30 ng for 1-butanethiol. The applications, such as vegetable analysis and field sampling analysis, demonstrated that NTD with sorbent DVB can be a successful active sampler for determine volatile thiols in food and air samples.

5.5 References

1. Columbia University Press, *The Columbia Electronic Encyclopedia,* 6th ed. **2007**

2. M.I. Farbood, J.H. MacNeil, *Journal of Food Science,* 43 (1) **(1978)** 139-140

3. G. Mosciano, *Perfumer & Flavorist,* 26 **(2001)** 68-69

4. Q. Wang, J.M. Chong, J. Pawliszyn, *Flavour Fragr. J.,* 21 (3) **(2006)** 385-394

5. M. Mestres, O. Busto, J. Guasch, *J. Chromatogr., A* 773 **(1997)** 261-269

6. P. G. Hill, R.M. Smith, *J. Chromatogr. A,* 872 **(2000)** 203-2137.

7. L. Jacobson, J. Lorimor, J. Bicudo, D.Schmidt, *Livestock and Poultry Environmental Stewardship (LPES) Curriculum,* **2001**

8. C.S. Petinal, R. Alzaga, C.G. Jares, M. Liompart, J.M. Bayona, *Anal. Chem.* 77 **(2005)** 6012-6018

9. P. Warneck, *Chemistry of the Natural Atmosphere*., 2nd ed. **2000**

10. K.C. Li, D. Shooter, *Intern. J. Environ. Anal. Chem.,* 84 (10) **(2004)** 749-760

11. K.H. Kilburn, R.H. Warshaw, *Toxicol. Ind. Heath* 11 **(1995)** 185-197

12. National Institute for Occupational Safety and Health, *Manual of Analytiacl Methods* 2542, **1994**.

13. M. Mestres, M.P. Marti, O. Busto, J. Guasch, *J. Chromatogr. A,* 849 **(1999)** 293-297

14. T. R. Crompton, *Preconcentration Techniques for Natural and Treated Waters* **2003**

15. J.A. Koziel, P.A. Martos, J. Pawliszyn, *J. Chromatogr. A,* 1025 **(2004)** 3-9

16. E. Woolfenden*, Indoor Built Environ* 10 **(2001)** 222-231

Chapter 6 – Summary

The needle trap device in conjunction with GC-MS by thermal desorption was developed for sampling and analysis of VOCs. It offers some advantages over other sampling devices: it is inexpensive, reusable, solventless and easy to operate. It also integrates sample preparation and separation into one step, reduces the analysis time and obviates target compounds lost in transportation from the sampler to the GC.

It was demonstrated in this thesis that the NTD with Carboxen1000 met all three prerequisites of applying Fick's first law for successful diffusive sampling. The NTD with sorbent Carboxen1000 can be used for TWA diffusive sampling of BTEX without experimental sampling rate calibration. The factors such as sorbent strength, response time and face velocity can be ignored. It is affected slightly by temperature which can be calibrated by calculating the diffusion coefficient at sampling temperature. There is no significant impact of relative humidity on the sampling rates of BTEX within the range from 17% to 53%. There was good agreement between theoretical and experimental sampling rate. Method validations were done both in laboratory and in field. It was demonstrated that there was not significant difference between NTD diffusive TWA sampling and other conventional sampling methods. The NTD with Carboxen1000 has been demonstrated to be a successful diffusive sampler for monitoring TWA concentration of BTEX. Further efforts should be made to investigate more appropriate sorbents under different environmental conditions to monitor a greater range of VOCs.

Needle trap device with DVB coupled with GC-MS by thermal desorption was developed for sampling and analyses of volatile thiols. HayeSep Q (DVB) was selected as an appropriate sorbent for sampling thiols by comparing the amount of loaded mass on different sorbents. Experiments were performed to investigate thermal desorption efficiency, and optimal thermal desorption temperature and time were found for target analytes with DVB. The applications, such as vegetable analysis and field sampling analysis, demonstrated that NTD with sorbent DVB can be a successful active sampler to determine volatile thiols in food and air samples.

This research indicates that needle trap device with different types of sorbents coupled with GC can monitor a greater range of VOCs in air.