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Optimization of a Polydimethylsiloxane Based Passive Sampler of Common Household Volatile Organic Compounds

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Optimization of a Polydimethylsiloxane Based Passive Sampler of Common Household Volatile Organic Compounds

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Jennifer Lynn Osborne

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Abstract

Dangerous volatile organic compounds, or VOCs, can accumulate as indoor air pollution within homes causing health problems in the habitants. In order to determine the concentration of VOCs in such areas a field-deployable sampler is necessary. The focus of this work has been to develop an inexpensive, reusable, sensitive field-deployable passive sampler for monitoring VOCs in indoor air. We have devised a sampler that uses polydimethylsiloxane (PDMS), which is a common inexpensive, non-polar adsorbent. The sampler is comprised of an aluminum bottle coated with the PDMS. In operation, the coated portion is exposed to the air to be sampled. The bottle is then screwed into the top portion which keeps the material sealed-in. The sample from the aluminum bottle is then transferred to the GC for analysis using a Gas Phase Sampling Device (GSPID). In this work, sample equilibration time (in the bottle), GSPID gas flow rate and the sample loop filling times were optimized. Solutions containing toluene, ethylbenzene, and *o*-xylene were used as representatives for common household VOCs. Butanone was used as an internal standard in order to control reproducibility.

I. Introduction

A. Background

Volatile organic compounds, or VOCs, are hydrocarbon compounds with low boiling points that generally fall between 50 and 250° C[1]. Exposure to VOCs can have detrimental health effects such as headaches, nausea and vomiting[1]. There are also more serious long term effects such as liver and kidney damage[1]. Many of these compounds are also carcinogenic[1].

Because of the volatile nature of these compounds the most common form of exposure is through inhalation. There are many sources of VOCs in the environment including the evaporation of solvents and fuels, incomplete fuel combustion, nail polish and cigarette smoke[1]. According the United States EPA the common forms of household VOCs are found in "paints, paint strippers, and other solvents; wood preservatives; aerosol sprays; cleansers and disinfectants; moth repellents and air fresheners; stored fuels and automotive products; hobby supplies; dry-cleaned clothing"[2].

Concentrations of indoor VOCs have been calculated to be as much as 1000 times more concentrated than in outdoor environments. There is no current standard for Permissible Exposure Limits, PELs, of VOCs in non-industrial settings with the exception of formaldehyde, which OSHA has set forth a PEL of 0.75 ppm, and an action level of 0.5 ppm[2]. OSHA regulates the PEL of many common VOCs in occupational settings including benzene, toluene, ethylbenzene and xylenes.

In order to quantify the VOCs in an environment a sampling device is necessary. There are two major categories of air sampling systems: passive samplers and active samplers[1]. Active samplers require the use of a pump to circulate large samples of air

through the sampler, while passive samplers are devices that are exposed to air environments without the use of a pump. There are benefits and drawbacks to each form of sampling. Active samplers can take large samples at once and are therefore thought to have better reproducibility; however they tend to be rather expensive and can be quite cumbersome[1]. Passive samplers are not capable of sampling such large volumes of air at once however; they are much less expensive and much more portable than the active samplers[1].

Passive Samplers are also commonly referred to as diffusive samplers[9]. "A diffusive sampler is a device which is capable of taking samples of gas of vapor pollutants at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the sampler" [9]. Diffusion is the mechanism of the transport of the analyte to the surface of an adsorbent.

Fick's first law of diffusion is an equation that describes the rate of diffusion of a passive sampler[10]:

$$F \approx -\frac{DA\Delta C}{L} \approx -\frac{ADC}{L}$$

In this equation F is equal to the flux or rate of diffusion in μg/s, D is equal to the diffusion coefficient of the analyte in cm^2/s, A is equal to the cross-section area of the sampler, and ΔC/L is equal to the concentration gradient, C_A is the concentration of the analyte in the environment and C_S is the concentration of the analyte at the surface of the adsorbent, and L is the distance between C_S and C_A. In order to optimize the rate of diffusion of the sampler we must optimize the surface area and proximity of the analyte

to the adsorbent. The diffusivity is not a variable that can be optimized as it a natural characteristic of the analyte.

Polydimethylsiloxane, (PDMS) is a commonly used adsorbent that is both effective and inexpensive. PDMS was chosen to be the polymer adsorbant for the sampler because in addition to being effective and inexpensive it is easy to prepare and easy to desorb. The chemical structure for PDMS is displayed in figure 1. PDMS is inert, non-toxic and non-flammable.

Solid phase microextraction is a method that is commonly used for the sampling of VOCs. The analyte is extracted from an environment onto a sorbent surface and then desorbed into the port of a separating instrument.

B. Statement of Problem

Although various standards have been established, measuring these compounds with reproducibility at low concentrations can become quite expensive and difficult to achieve. Because of the volatile nature of these compounds they are difficult to sample and quantify with accuracy and precision. In order to efficiently sample such compounds in indoor environments it is necessary to develop a sampler that is inexpensive, simple to prepare and operate, reusable, storage efficient and sensitive. It is also necessary to develop a means of efficiently transporting the sample from the sampler to the means of analysis.

C. Previous Methods

In previous studies Reiser and coworkers studied the quality of indoor air at a Swiss technical university where employees and students developed a sickness and headache after their building had been renovated. These researchers found that the concentrations of total volatile organic compounds in the indoor air were elevated in both laboratory halls and reference rooms. The source of the VOCs was identified to be the vinyl (PVC) flooring. These authors used thermal desorption / gas chromatography / mass spectrometry / FID (TD/GC/MS/FID) in their studies[3].

Hayashia and coworkers investigated the indoor air quality of common Japanese detached houses and found that: when the ventilation system was changed from the air-supply type to the air-exhaust type, the indoor concentrations of formaldehyde (a VOC) increased. They also found that VOCs emitted from wood treatment chemical could accumulate in the beam spaces. Furthermore, they found that VOC accumulation in ventilated crawl space (under first floor) and truss space under roof were lower compared to that found in beam space. On the basis of this findings, the authors recommended strict control of ventilation rates to keep indoor concentration of VOC low[4].

Dodsona and coworkers studied 55 residences in Boston and found that Concentrations of many volatile organic compounds (VOCs) are often higher inside residences than outdoors. Concentrations automobile-type VOCs (e.g. benzene, toluene, ethylbenzene, and xylenes) were up to 5–10 times higher in the garage than indoors. Basement/indoor concentration ratios were significantly greater than unity for methylene chloride, ethylbenzene, m,p-xylene, and o-xylene. Summer ratios (Basement/indoor) tended to be higher than winter ratios[5].

There are several other reports that bring attention to the significance of studying VOCs in indoor air[6-8].

D. Instrumentation

The analysis of atmospheric VOCs requires methods of separation and detection. By injecting the compounds onto a gas chromatography column they can be separated and identified based on their differing volatilities. The most volatile organics will have the lowest boiling points; therefore, they will be the first ones to come off of the column, followed by the compounds of higher boiling points. Various forms of detectors can be used to quantify the analytes. In this study flame ionization detection (FID) will be used as the means of VOC detection.

E. Approach

We have addressed the issue of the need for an effective means of monitoring VOCs by developing a passive sampler. The first step was to design a solution to represent the VOCs commonly found in indoor air pollution. Three compounds were selected according to their volatilities, gas chromatography retention times, boiling points, densities and polarities. The compounds chosen for the solution were benzene, toluene, ethylbenzene, and *o*-xylene (BTEX). Some common properties for these compounds have been displayed in table 1.

There are 3 primary steps involved in the sampling process. The analyte must first be collected using a sampler. The analyte must be transferred from the sampler to the instrument where the sampled is then analyzed. Therefore the procedure can be broken

down to sampling, transfer and analysis. The GC-FID was chosen for analysis, leaving the necessity for development of the sampling and transfer methods.

In order to collect the analyte in a passive sampler, the surface must be coated with an absorbent. We coated the cap material with an adsorbant called polydimethylsiloxane (PDMS). The semi-polar nature of the structure is shown in figure one. The idea is that the material is non-polar enough to bind the VOCs from the environment, but polar enough to easily release them to be quantified.

Cap materials were also investigated. PDMS coated and un-coated caps were exposed to similar environments and the differences were recorded in order to ensure that minimal analyte was adsorbed by the cap material.

One approach to transferring our analyte to the GC-FID utilized a popular method known as solid-phase micro extraction (SPME). The SPME also utilizes a PDMS coated tip which would be used to first adsorb the analyte then inject it onto the GC-FID for analysis.

An aluminum bottle was developed in order to increase the reproducibility of the procedure. The bottle screws into the top of the aluminum cap. It has a septum at the top to allow injection of internal standard as to serve as an injection site for the SPME.

Another approach to the transfer of the analyte was a Gas Phase Sampling Injection Device (GPID). The GPID is a system which flows helium through gas lines to carry the analyte to a sampling loop where it is then purged into the GC. The schematics of the GPID are shown in figure 2.

In an attempt to increase the sensitivity of the system the cross sectional area of the sampler was increased by increasing the diameter of the bottle. The larger bottle was

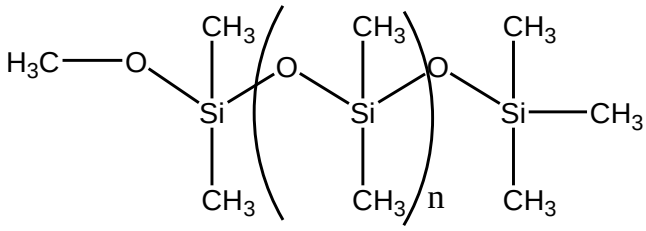
similar to the small bottle system except that instead of screwing into the sampling cap it consisted of a dual clamp system.

The final method of transferring our sample to the injection port of the GC was a combination of the large bottle sampler with an automated GPID. In this device valves A and B were automated in order to improve reproducibility. The only valve that remained manual was the injection valve.

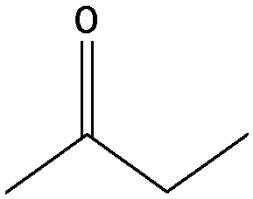
Table 1. This table shows the compounds that have been chosen to represent common indoor air pollution. They have been selected based on these qualities.

Compound	*Log K_{ow}	*Boiling Point (^oC)	*Vapor Pressure (mmHg @ 25^oC)	Retention Time (min.)
Benzene	2.15	80.1	100.84	2.51
Toluene	2.69	110.6	28.47	3.18
Ethylbenzene	3.15	136.3	9.51	4.21
o-Xylene	2.77	144	6.62	4.65

**Ref.: F.A. Esteve-Turillas; A. Pastor; M. de la Guardia; Anal. Chim. Acta 593 (2007) 108 -116*



polydimethylsiloxane



butanone

Figure 1 - Structures of the sampling adsorbant, internal standard and indoor VOC samples.

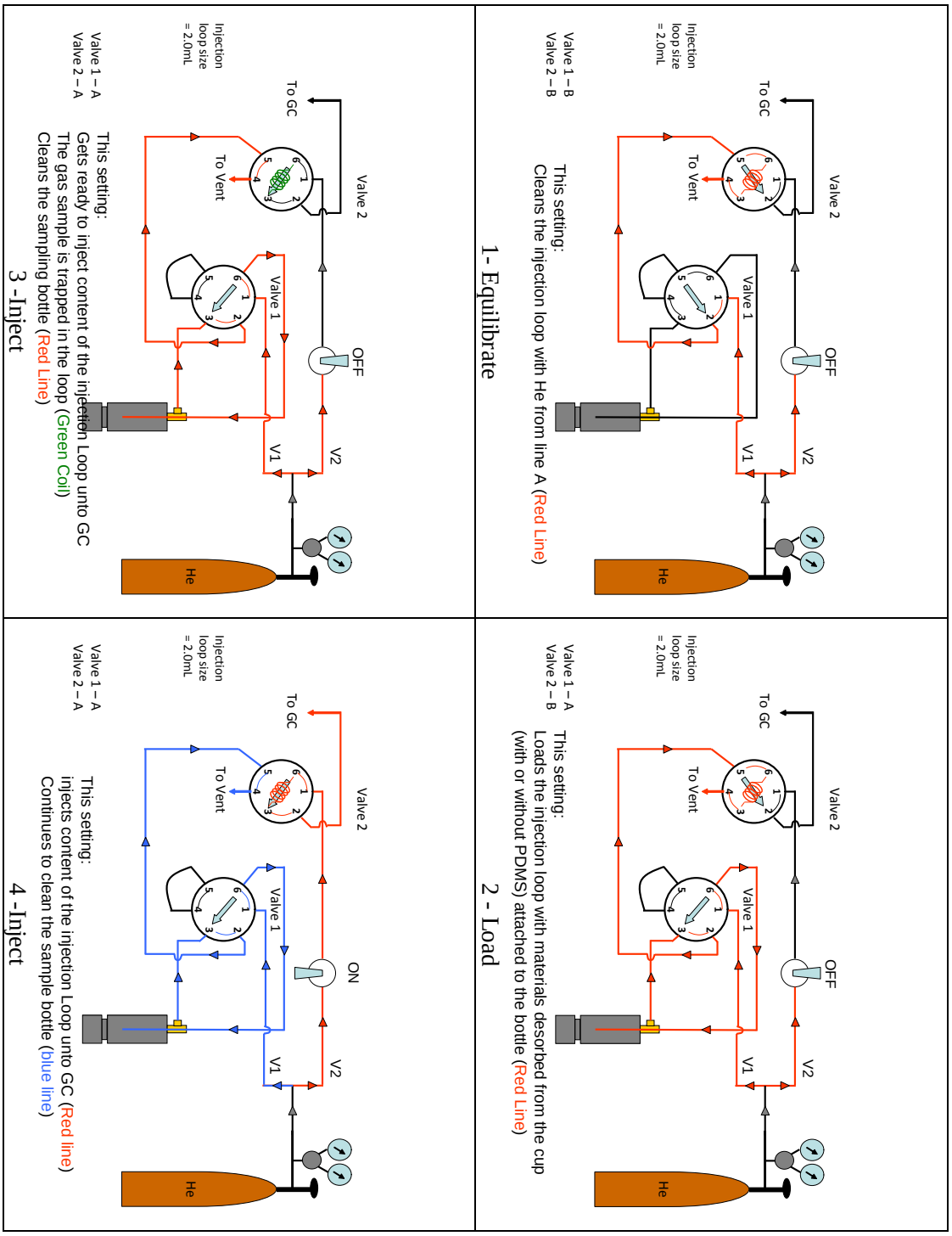


Figure 2 - Schematic of GPID. The GPID is a method of transferring the analyte of a passive sampler to the GC for analysis.

II. Experimental

A. Adsorbent preparation

The adsorbent used, polydimethylsiloxane was formed from a 10 to 1 mixture of Slyguard© 184 Silicone Elastomer Base and Slyguard© 184 Silicone Elastomer Curing Agent. After mixing the solution vigorously for 5 minutes, the liquid polymer was poured into the sampling cap. All gas was allowed to escape the solution before placing in the oven at 65°C. The PDMS hardened to a solid adsorbant material after baking overnight.

B. Cap material selection

The first study that was conducted was to find an appropriate material to use to contain the adsorbant material. Three materials were considered: a glass bottle cap, a Teflon cap and an aluminum cap. For each type of material analyses were conducted to compare the retention of the analyte in PDMS coated caps versus un-coated caps.

The procedure is displayed in Figure 3. The uncoated cap was placed in a 200 mL beaker and covered with parafilm. The parafilm was then punctured with a 10 µL syringe and 1.0 µL of the BTEX solution was injected. The BTEX was allowed to evaporate and equilibrate with the surface of the cap for 5 minutes. The cap was then placed in a 50 mL beaker and covered with parafilm The BTEX was allowed to diffuse from the surface of the cap for 5 minutes. An SPME tip was used to puncture the parafilm and the fiber with PDMS coating was exposed in the beaker for 1 minute. The collected material was then transferred and injected onto the GC-FID.

The same procedure was followed for the PDMS coated caps. In this procedure the BTEX diffused to and from the PDMS as well as the cap material. The results are displayed in Figure 5.

C. Internal standard

In order to improve the reproducibility of the method an internal standard was also selected. Butanone was selected because of its low boiling point (80°C), its high vapor pressure (71 mmHg at 20°C) and its semi-polar nature. Along with exposing the cap to an atmospheric of sample VOCs, the cap was also exposed to a standard quantity of Butanone. The resulting signals of the analyte were then divided by the signal from the butanone.

D. SPME with small aluminum bottle

A calibration curve was generated for the small bottle using the SPME using the procedure displayed in figure 4. An aluminum cap was placed in 200 mL glass sampling container with a 1 cm by 1 cm square piece of filter paper. The desired volume of BTEX was injected onto the paper and allowed to desorb from the filter paper and equilibrate with sampler for 5 minutes. The cap was then removed and screwed onto the top portion of the aluminum bottle. The SPME tip was then used to puncture through the septum at the top of the bottle. The tip was exposed to the interior environment of the bottle for three minutes then removed and the analyte was injected onto the GC-FID for analysis. The results of a calibration curve are shown in figure 6.

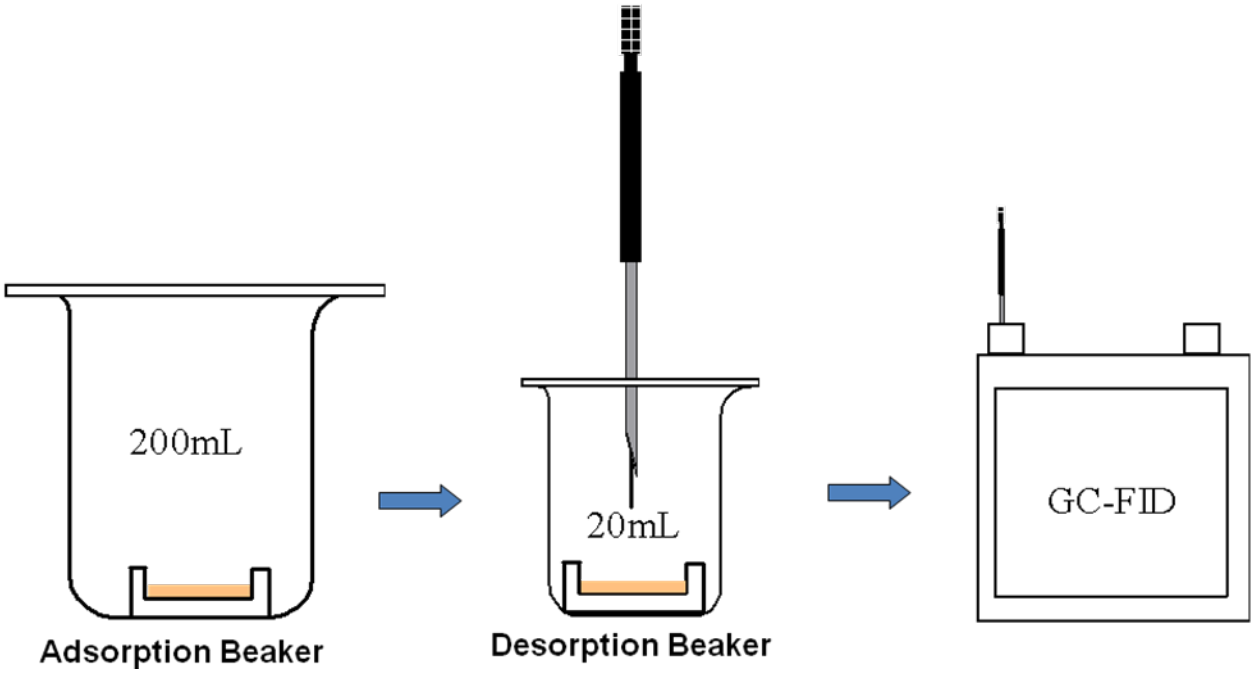


Figure 3. The procedure using an SPME transfer device. This procedure was used to determine which cap material would be most appropriate for these studies: glass, teflon or aluminum.

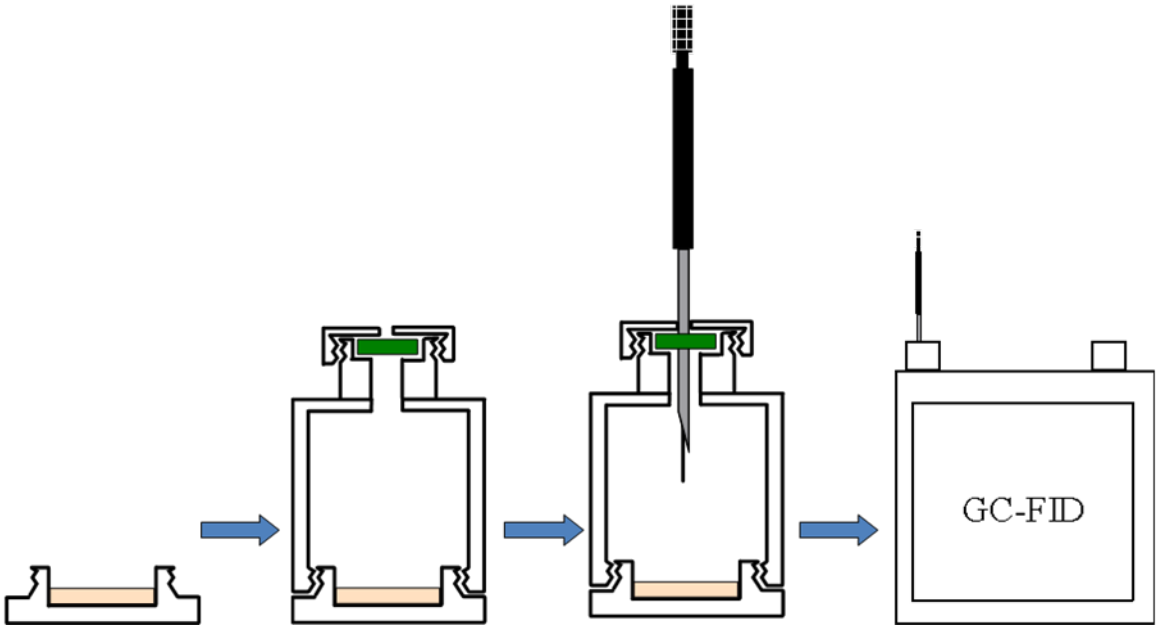


Figure 4. This procedure was used to generate a calibration curve for the SPME transfer method with the small bottle sampler.

E. Manual GPID optimization

(i) Operation

Once the sampler has been exposed to an environment of various concentrations of the BTEX solution a Gas Phase Sampling Injection Device (GPID) will be used to transfer the analyte from the sampler to the GC-FID. The GPID consists of a flow system of helium which will carry the analyte to the GC. The schematic for the GPID is displayed in figure 2. The system consists of two values, valve A and valve B, and an injection switch. During the equilibrium time both valves are in the Load position and the injection switch is off. This position is called Load-Load. During this time helium is flowing through the sample loop to vent while analyte is allowed to desorb from the PDMS and into a closed off atmosphere that include the inside of the bottle and a section of GC tubing. The next step, loop filling time, occurs when the system is in the Inject-Load position. This means that valve A is switched to the Inject position while valve B remains in Load and the injection switch remains in the off position. During this time the helium carries the desorbed analyte from the sampling bottle into the sample loop. Next valve B is switched to the Inject position and the injection valve is switch to the on position. At this point the helium carries the sample from the sample loop to the injection port of the GC. At the same time helium is used to purge the PDMS coated cap and any sample remaining on the adosrbant is sent to vent.

(ii) Flow rate

The optimum flow rate was found by exploring flow rates between 30 and 310 mL/minute. A PDMS coated cap was exposed to an environment of 5 ppm gaseous BTEX and 5 ppm of the internal standard, butanone. The cap was then removed and

attached to the bottle on the GPID. The analyte was allowed to desorb for 10 seconds while the GPID was in the load-load position. Valve A was switched to the inject position. The GPID was in this inject-load position for five seconds. The contents of the loop were then flushed onto the GC by turning valve B to the inject position and immediately flipping the ON/OFF switch to the ON position. The results are displayed in figure 7.

(iii) Desorption time

The desorption time of the system was determined by varying the load-load time of the GPID method. A PDMS coated cap was exposed to an environment of 5 ppm gaseous BTEX and 5 ppm of the internal standard, butanone. The cap was then removed and attached to the bottle on the GPID. The analyte was allowed to desorb for times varying between 10 seconds while the GPID was in the load-load position. Valve A was switched to the inject position. The GPID was in this inject-load position for five seconds. The contents of the loop were then flushed onto the GC by turning valve B to the inject position and immediately flipping the ON/OFF switch to the ON position. The results are displayed in figure 8.

(iv) Loop filling time

A PDMS coated cap was exposed to an environment of 5 ppm gaseous BTEX and 5 ppm of the internal standard, butanone. The cap was then removed and attached to the bottle on the GPID. The analyte was allowed to desorb for 10 seconds while the GPID was in the load-load position. Valve A was switched to the inject position. The amount of time that this GPID was in this position, inject-load, was referred to as the loop filling time. The results are displayed in figure 9.

(v) Analyte calibrations

Calibration curves were generated for uncoated caps and PDMS coated caps. The uncoated cap studies were conducted first in order to observe the performance of the GPID without adding the variable of the sampler. Next the PDMS coated sampler was used in conjunction with the GPID as the transport device to generate a preliminary calibration curve.

For the uncoated caps, first a volume of BTEX, ranging from one to five µL, was injected into the bottom of the uncoated sampling cap using a 10µL syringe. Also 1.0µL of butanone was injected for each analysis. The sample was allowed a ten second desorption time, followed by a five second loop filling time. Each point was run in triplicate.

The coated cap was placed in a 200 mL jar. A volume of BTEX, ranging from one to five µL was injected onto a 1.5cm by 1.5cm piece of filter paper using a 10µL syringe. The lid of the jar was secured and the jar was placed in the small oven at 25ºC. The BTEX and internal standard were allowed to evaporate and diffuse to the surface of the PDMS for ten minutes. The cap was removed from the glass jar and screwed onto the end of the small bottle attached to the GPID. The sample was allowed a ten second desorption time, followed by a five second loop filling time. The flow rate through valve A was 300 mL/sec and the flowrate through valve B was approximately 10psi. Each point was run in triplicate.

F. Automated GPID optimization

(i) Operation

In order to increase reproducibility of the procedure, the valves of the GPID were automated. The schematic for this device is shown in figure 3 with the automated values now denoted as 1 and 2. A computer system called Vcom was used to control the values. During the first setting, Equilibrate, valves 1 and 2 are both in the B position. During this time, the sample loop is being purged while the analyte is reaching equilibrium between the PDMS and the atmosphere within the bottle and the section of GC tubing. In the next setting denoted Load, valve 2 remains in the B position while valve 1 is switched into the A position. The helium then flows through the sample bottle to carry the sample to the 1.0 μL injection loop. Valve 2 is then switched to the A position and the injection switch is flipped to the on position, thus injecting the sample from the sample loop onto the GC.

One significant change in the procedure was the removal of the compound benzene. In order to make the research environment safer, benzene was removed from the analysis. Therefore the solution for these trials will be referred to as TEX instead of BTEX.

(ii) Loop filling time

In order to obtain the optimal loop filling time, analyses with varying times for loop filling were conducted. These times ranged from one second to 35 seconds. For each analysis the system was saturated in TEX solution in an uncoated large bottle cap. The system was saturated because there was a build up of analyte within the system. By saturating the system we were able to produce a significant signal over the background and continue studies. Each analysis was performed in triplicate and the signal of the area

counts for each peak were plotted and compared. The results of the optimization are displayed in figure 13.

(iii) Flow rate optimization

In order to determine the optimal flow rate, flow rates were varied until a signal was achieved. Again, for this study the system was saturated with TEX solution on a large uncoated cap. Each analysis was performed in triplicate and the signal of the area counts for each peak were plotted and compared. A fifteen second injection time was allowed for each analysis. The results are shown in figure 14.

(iv) Desorption time and callibrations

The optimization of desorption time is unable to achieve due to build up with analyte within the system. This also prevented us from developing preliminary calibration curves.

H. Instrumentation

The sample was then injected to the GC-FID. An HP-5 column was used to separate the VOC based on their differing boiling points. The initial temperature of the oven was 65°C with ramps at 10 and 15 minutes of 120°C and 200°C respectively.

III. Results and Discussion

A. Regular sampling caps with SPME transfer

The results from the cap studies are displayed in figure 5. Aluminum was selected to be used as the material for the sampling caps because, as seen in figure 4, the aluminum absorbs significantly less analyte than the PDMS material. Also aluminum is a malleable metal that is easy to machine.

Next we were able to calibrate the system using the machined bottle with SPME transfer. The results are show in figure 6. We were able to achieve reasonable linearity for all four compounds with R^2 values ranging from 0.91 to 0.98. The low R^2 values were thought to have come from the small surface of the SPME that was used to transfer the analyte form the sampler to the GC-FID.

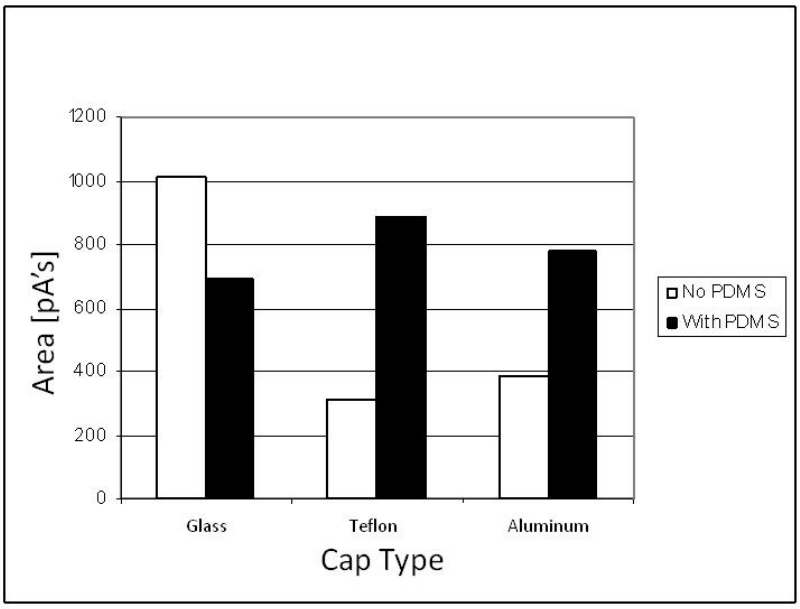


Figure 5. This figure shows the comparison of three different cap materials. Both uncoated and PDMS coated caps were exposed to an environment of gaseous o-xylene. A PDMS fiber SPME was used to transfer the analyte from the caps to the GC-FID. The response areas of the coated and uncoated caps were compared.

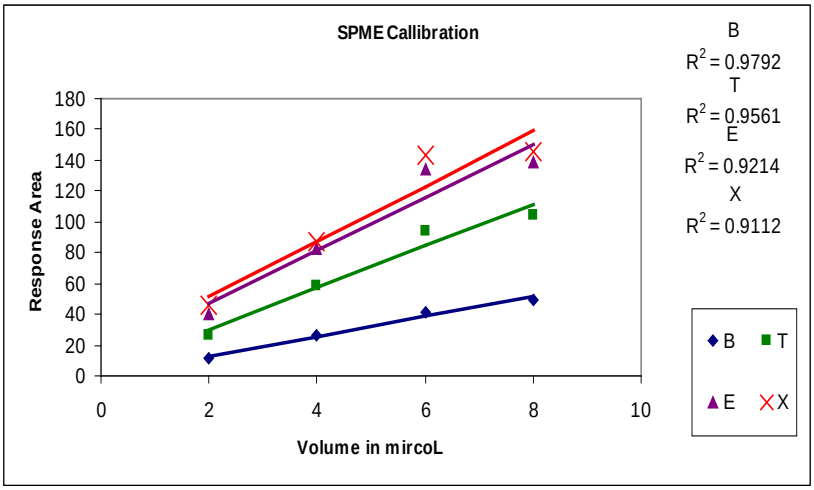


Figure 6. This figure shows the calibration of the PDMS caps using the PDMS SPME fiber to transfer the sample from the sampler to the GC-FID.

B. Small bottle samplers with manual GPID

The results for the optimization for flow rate, desorption time and loop filling time are displayed in figures 7-9.

The optimization of the flow rate is displayed in figure 7. From 50 to 200 mL/min the signal for ethylbenzene and xylene continued to increase. This is because there was not sufficient air flow at 50 mL/min to carry optimal amounts of ethylbenzene and xylene to the sample loop. From 150 to 300 mL/min there is a significant decrease in the amount of signal from all 4 compounds. This was because the sample was actually being flushed through the sample loop and passed on to vent. The GPID was found to have peak sensitivity at approximately 100 mL/minute.

The optimization of the desorption time is shown in figure 8. From zero to 20 seconds the signal gradually increases because with more time more analyte is allowed to desorb from the surface of the PDMS and this be carried to the sample loop. After twenty seconds the signal begins to decrease. This was likely due to a leak within the system. The desorption time had peak response area at approximately 20 seconds

The optimization of loop filling time is displayed in figure 9. From one to three seconds there is a steady increase in the signal area count. This is due to allowing more time to ensure that more analyte is carried to the sample loop prior to injection. Also the signal begins to decrease after 5 seconds. This was because at this point the helium was pushing the sample through the sample loop and on to vent. The loop filling time had peak response area at approximately 3.5 seconds.

The calibration plot for the GPID is show in figure 10. Here we see an inversion of the order of analytes. This is to be expected because instead of exposing a PDMS coated surface to a gaseous BTEX environment, we injected straight BTEX solution. This was to reduce the number of variables within the procedure so that we were primarily looking at the performance of the GPID, the transfer device, and not the PDMS sampler. The compounds of higher vapor pressure evaporated more readily and therefore were more prevalent with the liquid injection. The slopes and R^2 values are displayed in table 2.

The calibration plot for the PDMS coated caps with the GPID is displayed in figure 11. The slopes and R^2 values are displayed in table 2. The low R^2 value of 0.81 is likely due to the low sensitivity of the system to benzene because of it high volatility. This warranted the use of an internal standard.

In figure 12 the calibration of BTEX using butanone as an internal standard is displayed. The y-axis represents the area count of the analyte divided by the area count of butanone. The slopes and R^2 values are displayed in table 2. Using this method we were able to increase all of the R^2 values above 0.98.

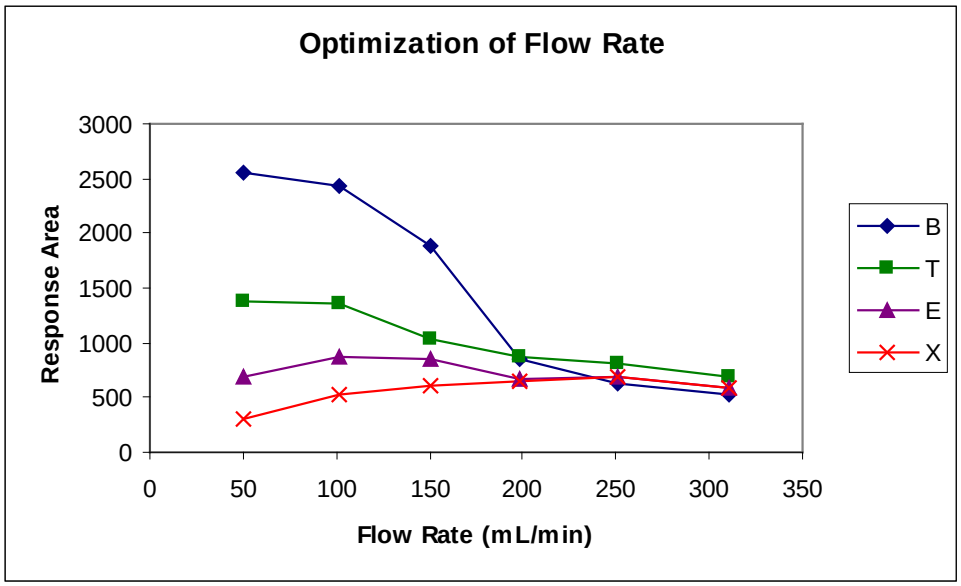


Figure 7. This figure show the optimization of the flow rate for the manual GPID system with the small bottles. Small uncoated sample caps were used with liquid injections of the BTEX solution.

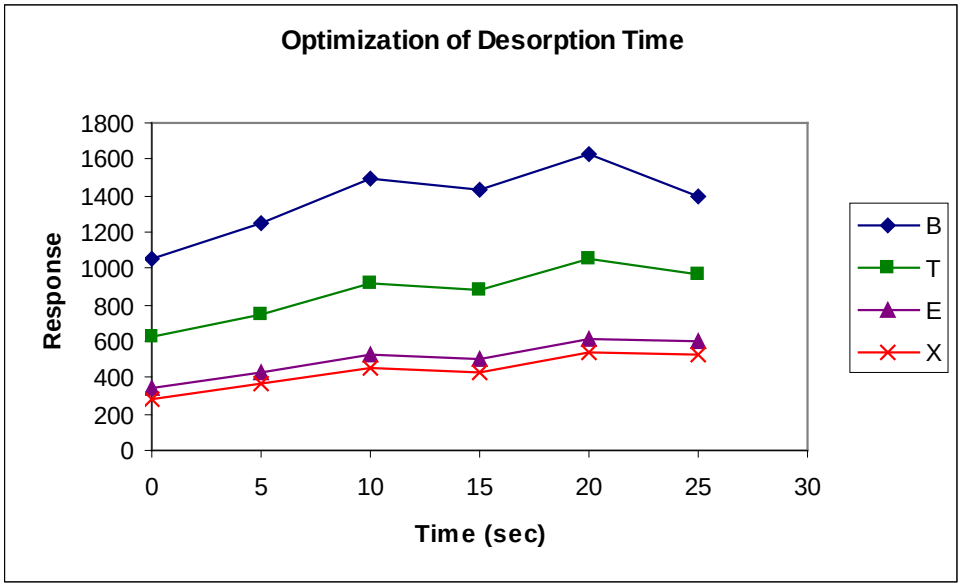


Figure 8. This figure displays the results of the optimization of desorption time. The optimal time was determined to be approximately 20 seconds. Small uncoated sample caps were used with liquid injections of the BTEX solution.

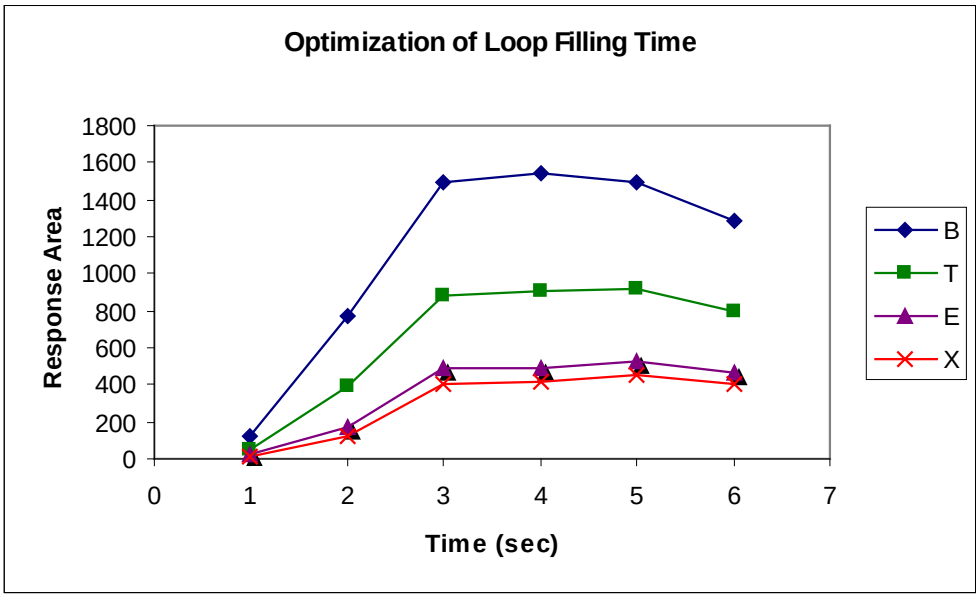


Figure 9. This figure shows the optimization of the time allowed for helium to carry the sample from the bottle to the sample loop. Small uncoated sample caps were used with liquid injections of the BTEX solution.

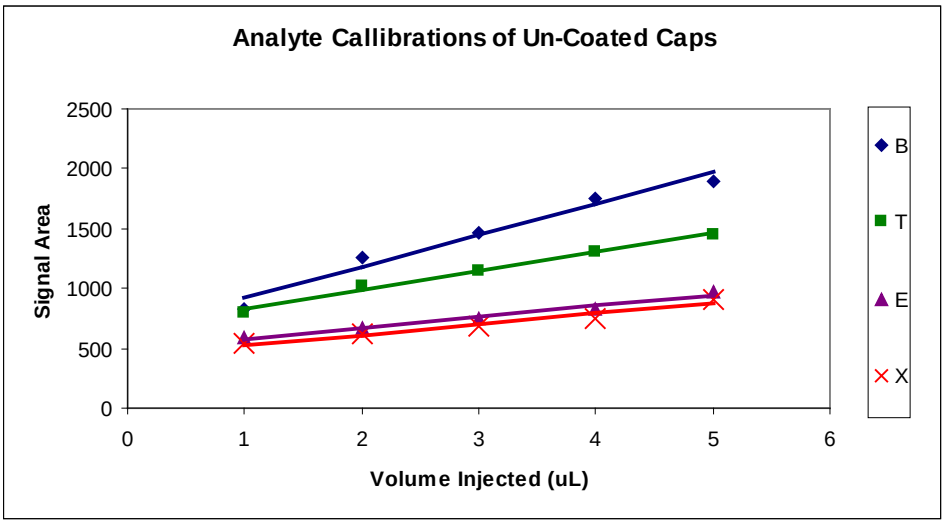


Figure 10. This figure shows the calibration of the initial GPID system using liquid injections of the BTEX solution on an uncoated small cap.

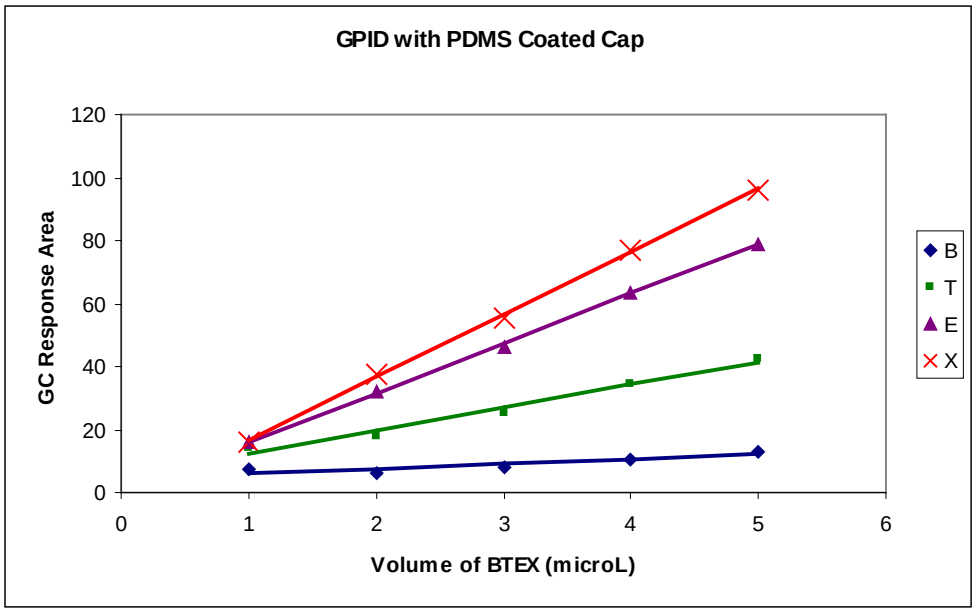


Figure 11. This figure displays the calibration of PDMS coated caps with the GPID. The caps were exposed to volumes ranging from one to five µL in a 200mL closed environment for five minutes.

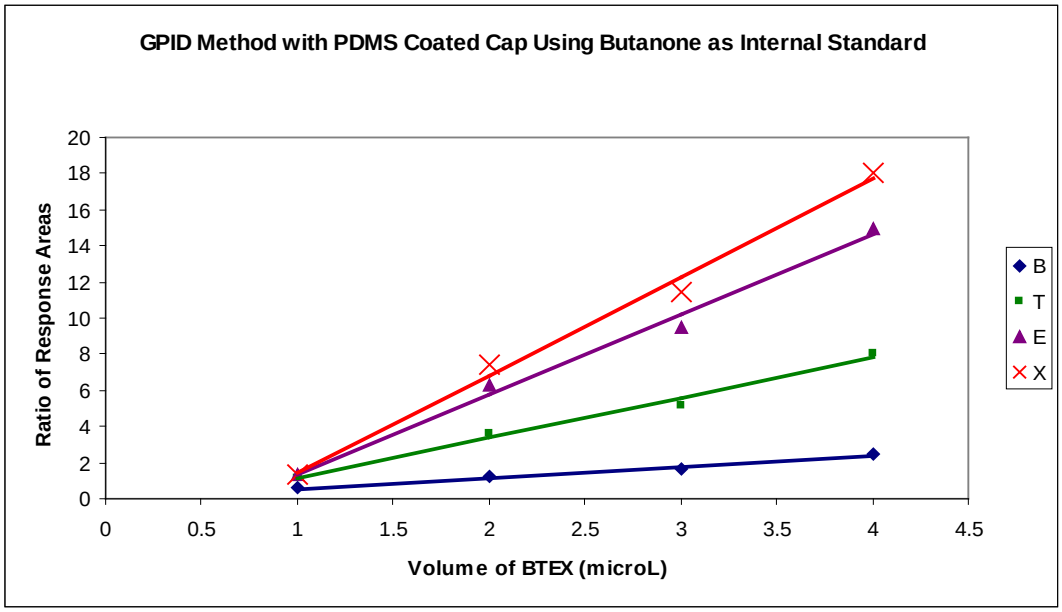


Figure 12. This figure shows the calibration of the BTEX using PDMS coated caps and the GPID as the method of transferring the analyte to the GC-FID.

Table 2. This table displayed the slopes (sensitivity) and R^2 values from figures 9-11

	Un-Coated Caps		PDMS Coated Caps External		PDMS Coated Caps Internal	
	Sensitivity	R^2	Sensitivity	R^2	Sensitivity	R^2
Benzene	263.000	0.9716	1.584	0.8125	0.609	0.9892
Toluene	161.010	0.9886	7.287	0.9837	2.235	0.9899
Ethylbenzene	92.883	0.9808	15.739	0.9993	4.412	0.9914
Xylene	89.015	0.9653	18.892	0.9992	5.421	0.9916

C. Large bottle samplers with automated GPID

The optimization for the loop filing time for the large bottle sampler with the automated GPID is displayed in figure 13. The loop filling time increased to 15 seconds. With a higher loop filling time, we would expect to be able to achieve greater reproducibility,

The optimization for the flow rate is displayed in figure 14. The flow rate is displayed in terms of PSI of helium through valve A. The preliminary optimization for the flow rate was approximately 10 PSI.

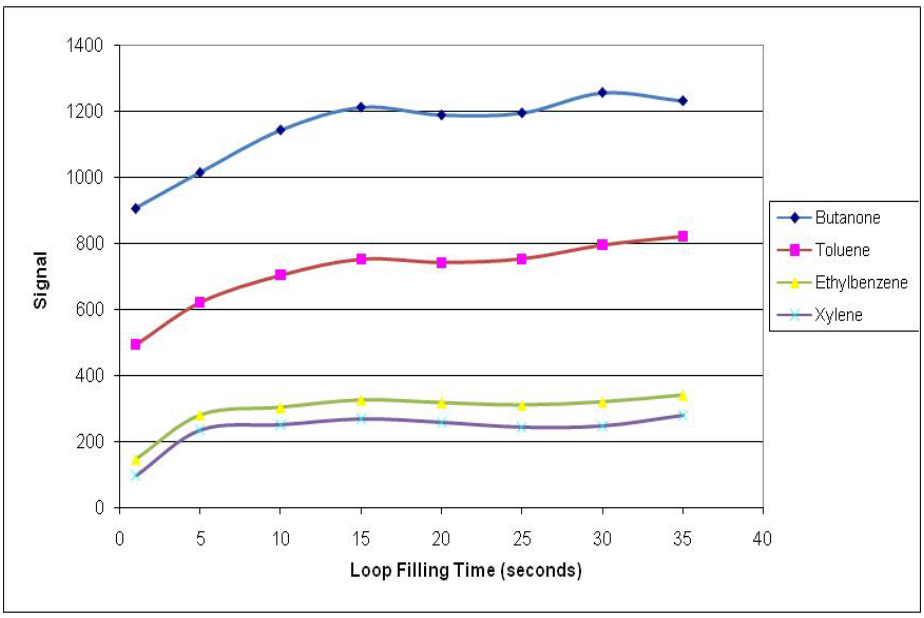


Figure 13. This figure show the optimization of the flow rate for the automated GPID system with the large bottles. The optimal loop filling time was 15 seconds.

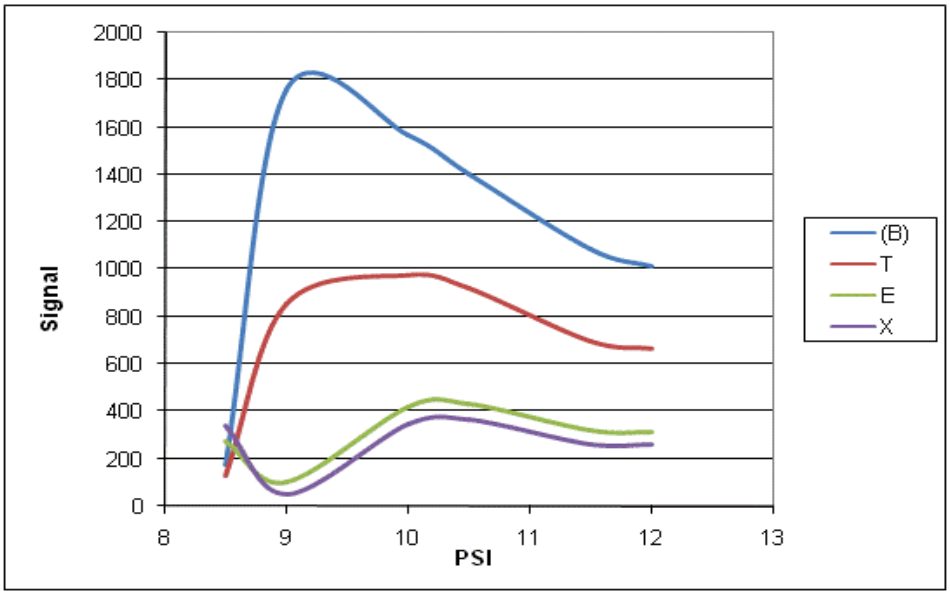


Figure 14. This figure shows the optimization of the flow rate through valve A with the automated GPID with the large bottle. The optimal signal for the analytes was achieved at approximately 10 PSI.

IV. Conclusions

We have been successful in capturing environmental VOCs, including butanone, benzene, toluene, ethylbenzene, and o-xylene, on the polydimethlysiloxane adsorbant. The sampler consists of a two piece metal bottle system.

We have also been successful in finding methods of transferring our analyte from the sampler to the GC-FID. Both the SPME and GPID procedures were successful in transferring the sampled material from the PDMS to the GC.

We have shown that the GPID in conjunction with the small bottle sampler is sensitive and reproducible by forming calibration plots with reasonable R^2 values.

Although we were unable to generate a calibration for the large bottle on account of analyte build up within the automated valve system, we were able to achieve success in optimizing some of the parameters of the GPID.

In our studies we have shown that our passive sampling device has the potential to reproducibly quantify atmospheric VOCs. However, our findings are only the results of preliminary studies. The data that we have collected is only a preliminary study of the system. There is still a great deal of research that remains to be investigated. Upon further devolpment and improvement of the system, the conditions will need to be re-optimized.

V. Future Direction

A. Analyte build-up studies

One study includes the investigation of the build up of the analyte that occurs within the system. By heating the sample loop t o 100°C the build up material was able to be reduced, however it was not eliminated. It is possible that a significant amount of the analyte builds up in the tubing. One possible option could be to change the tubing system to stainless steel. This could eliminate the pores form the system, which are a possible culprit for the analyte retention.

B. Automated injection valve

Another way to increase the reproducibility could be to automate the injection valve of the injection device. The injection time has a direct influence on the area counts of the peaks because the longer that the gas is allowed to carry the analyte from the sample loop to the injection port of the GC, the more analyte will be injected per analysis. If there is variability in the injection times of the analytes, reproducibility is decreased. A third valve could be place on the automated system and could be controlled using the same Vcon software.

C. Comparing bottle surface areas

With the larger surface area of the cap, the reproducibility of the system should be increased. This could be studied by conducting studies using the GPID injection system with both the large and the small bottles and comparing the %RSD values of the analyte concentrations in environments of varying VOC concentrations.

D. Increasing concentration gradient

We also hope that in the future in our field studies we will be able to increase the rate of diffusion to the surface of the PDMS, the flux, by controlling the concentration gradient. By creating a wind block we hope to increase the concentration of the analyte in the area directly surrounding the sampler thus decreasing L in Fick's law and thus increasing the flux.

VI. Works Cited

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