Determination of Formaldehyde in Ambient Air

Using On-fiber Derivatization

With

Solid Phase Microextraction (SPME)

Visahini Kanthasamy

Department of Chemistry

McGill University

Montreal, Quebec, Canada

August 2010

A thesis submitted to McGill University and in partial fulfillment of the requirement of the degree of Master of Science

Abstract

Formaldehyde is an important intermediate in the gas-phase methane oxidation chain and plays an important role in the chemistry of the troposphere by influencing the odd hydrogen budget (HO_x = HO + HO_2), and thus the Earth's oxidative capacity. The evaluation of the importance of formaldehyde in atmospheric cycles requires accurate and precise measurements of its concentration in the atmosphere. In this work, the concentration of formaldehyde in unpolluted outdoor air will be determined using an on fibre derivatization-solid phase micro-extraction (SPME). This method consists of derivatizing formaldehyde to its pentafluorobenzyl oxime using 1,2,3,4,5-pentafluorobenzylhydroxylamine (PFBHA), extracting using SPME and then analyzing with gas chromatography with flame ionization detector. We herein present an improved methodology for detection of formaldehyde in ambient air using SPME and GC-FID, which gives a detection limit of 100-300 pptv, for our rapid, portable and environmentally benign technique. The developed methodology was used to measure the formaldehyde mixing ratios in chemistry labs (9.28 ± 0.26, 12.36 ± 0.11 ppbv), library (11.75 ± 0.57 ppbv), and basement of a building (6.79 ± 0.010 ppbv) and in a campus terrain (7.17 ± 0.040 ppbv). We observed a diurnal variation in the mixing ratios of formaldehyde measured in the city of Montreal. The implications of our results will be herein discussed.

Résumé

Le formaldéhyde joue un rôle important en tant qu'intermédiaire dans l'oxydation du méthane dans la phase gazeuse ainsi que dans les réactions chimiques de la troposphère en influençant le budget de radicaux hydroxyle et donc la capacité oxydative de l'atmosphère. Afin d'évaluer l'influence du formaldéhyde sur les cycles atmosphériques, la concentration atmosphérique exacte est requise et ce nécessite une méthodologie précise pour prendre des mesures. Dans ce travail la concentration du formaldéhyde dans l'atmosphère non polluée est mesurée à l'aide d'une fibre de micro extraction phase solide (SPME). Cette méthode consiste à dérivatiser le formaldéhyde en son oxime de pentafluorobenzyl avec du 1,2,3,4,5-pentafluorobenzylhydroxylamine (PFBHA), suivi par l'extraction et l'analyse par chromatographie phase gazeuse équipé d'un détecteur à ionisation de flamme (FID). Nous présentons une méthodologie améliorée pour détecter le formaldéhyde dans l'air ambiant à l'aide de la SPME et du GC-FID ; nous achevons une limite de détection de 100-300 pptv. La méthodologie a été utilisée pour déterminer les taux de formaldéhyde dans des laboratoires de chimie (9.28 ± 0.26, 12.36 ± 0.11 ppbv), dans une bibliothèque (11.75 ± 0.57 ppbv), dans le sous-sol d'un bâtiment (6.79 ± 0.010 ppbv), et sur un terrain au sein de l'université (7.17 ± 0.040 ppbv). Des mesures prises en 2009 au mois de juillet montrent que le taux atteint dans la journée et la soirée étaient de 8-12 ppbv et de 5-7 ppbv, respectivement; la méthodologie permet également de discerner les variations temporales.

Acknowledgements

I am heartily thankful to my supervisor, Dr. Parisa A. Ariya, whose guidance, encouragement and support from the beginning till now enabled me to develop an understanding of the subject and complete this thesis. I owe my deepest gratitude to Edward Hudson, who had offered invaluable support and had always been there for me whenever I needed any assistance. This project would have been difficult if it was not for his guidance. I would like to thank all the group members, especially Nermin Eltouny for all her help and Roya Mortazavi for keeping me motivated.

I would also like to thank the Chemistry Department at McGill, Environment Canada, and Quebec Ocean for financial assistance during my study. I also wish to thank Dr. Ross Hendry and his group for a giving me a great opportunity to participate in their Labrador Sea Mission 2009 and the crew members for their support during the cruise.

I also wish to express my deepest love to Suren Shanmugaratnam and my family for their love and support.

Table of Contents

List of figures

List of tables

Objectives:

There are several analytical methods that already exist for the determination of formaldehyde in ambient air. Just a few of them are able to give the low detection limits that are required for ultra trace analysis. These few methods that can achieve low detection are unfortunately either labor intensive, expensive, sensitive to environmental conditions, bulky or a combination of them. An optimal analytical technique would require an easily deployable method with few sample preparation steps and thus less contamination and waste, low cost, and practicality for field applications. In addition, a method that can be generalized for a simultaneous determination of a wide range of compounds and concentrations is also preferred. Therefore our objective was to combine an existing, simple, inexpensive sampling method namely solid phase microextraction (SPME) with derivatization to develop a portable methodology that is simple, practical, solventless, and environmentally benign and still gives comparable detection limits to the other available methods for determination of formaldehyde in unpolluted air. Our objective was to develop such a method which in the long run can be extended for analysis of a wide range of other carbonyl compounds that influence atmospheric chemistry.

In this work, we aimed to develop a methodology for the determination of formaldehyde in ambient air, that can detect mixing ratios in high parts per trillions to low parts per billion levels by combining solid phase microextraction and on-fibre derivatization with gas chromatography with a flame ionization

detector, that is comparable with the best existing technique with additional advantages of simplicity, low cost, environmental safe and portability.

Organization of the thesis:

This thesis consists of an introduction which gives an overview of the importance of formaldehyde in the atmosphere, concise description of other existing methods, their requirements and detection limits, and a detailed outline of the methodology developed, procedure of the experimental methods and presentation and discussion of the results obtained in this study. A conclusion and plans for future work are included at the end. References and other supplementary material, including tables of unit conversions are included in the appendix.

1.Introduction

Everyday large quantities of volatile organic compounds are released into the atmosphere by both anthropogenic and biogenic sources. These volatile organic compounds govern atmospheric photochemistry by influencing its oxidative capacity. Hydroxyl radicals drive the daytime chemistry in both polluted and unpolluted air by initiating chain reactions by attacking volatile organic compounds and CO. A major source of hydroxyl radicals in both clean and polluted air is the photodissociation of O_3 as follows [1-3].

$$O_3 + hv\ (\lambda < 340nm) \rightarrow O_2 + O\ (\ ^1D\ ,\ ^3P) \quad (1)$$

$$O\ (\ ^1D) + M \rightarrow O(\ ^3P) + M \quad (2)$$

$$O(\ ^1D) +\ H_2O \rightarrow 2OH \quad (3)$$

Any chemical species that influence the concentration of the hydroxyl radicals and other reactive radicals in the atmosphere plays an important role in atmospheric chemistry and thus needs to be identified and quantified accurately in order to gain a better understanding of our atmosphere. The concentration of these compounds are however difficult to measure since they are highly dependent on location and time. In particular, trace organic compounds are getting much attention due to their profound effects on the atmosphere despite the fact their concentrations are very low.

These volatile organic compounds can be directly emitted into the atmosphere through natural processes such as ocean spray, biogenic activity, and volcanic eruptions or from anthropogenic sources such as industrial processes and automobile exhausts. They can also result from chemical reactions of other compounds in the atmosphere or transported from place to place by moving air

masses. They can be removed from the atmosphere by phase transformation such as nucleation, condensation or dry/wet deposition [2].

Among volatile organic compounds, carbonyl compounds are of interest to many researchers since they are the intermediates in the photo-oxidation of other organic compounds and are a source of many important radicals [2, 3]. The concentration of carbonyl compounds in the atmosphere typically ranges from sub ppb (part per billion) in clean air to higher ppb in polluted air.

Aldehydes are an important class of carbonyl compounds that are of main interest due to their key participation in the photochemistry despite their trace concentrations, and due to their impact on health, since some of them are toxic and suspected carcinogens [2, 4-6].

1.1 The importance of formaldehyde

Formaldehyde is the highest concentration aldehyde present in the troposphere, with typical mixing ratio ranging from 0.3 to 2 ppbv in the remote atmosphere in Canada [1] (conversion table for concentrations and mixing ratio is found in the appendix). It is an important intermediate in the photochemical oxidation of atmospheric hydrocarbons. In unpolluted areas, the main source of formaldehyde is the oxidation of methane by hydroxyl radicals which can be described by the following equations.

$$CH_4 + OH \rightarrow CH_3 + H_2O \quad (4)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad (5)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (6)$$

$$CH_3O_2 + O_2 \rightarrow HCHO + HO_2 \quad (7)$$

In fact, in all the photo-oxidations of the compounds containing a methyl group as a substituent, formaldehyde results as a product (in the presence of NO_x). The reactions involving formaldehyde are also sources and sinks of reactive species such as carbon monoxide, hydroperoxyl radical, molecular hydrogen, formic acid and nitric acid. For instance the photolysis of formaldehyde yields H atoms and HCO radicals is as follows:

$$HCHO + h\upsilon\ (\lambda < 325\ nm) \rightarrow H + HCO \quad (8)$$

$$HCHO + h\upsilon\ (325\ nm < \lambda < 360\ nm) \rightarrow H_2 + CO \quad (9)$$

It may also be directly emitted by anthropogenic sources such as emissions from industries, automobile exhaust, stationary combustion and biomass burning.

The oceans can be a source or a sink for formaldehyde due to their high volatility through air-sea exchange. In the ocean, it can be produced from oxidation of dissolved organic matter by sunlight and other oxidizing agents [7]. Some marine microalgae have also been found to produce formaldehyde. For instance, the freshwater algae named *chlamydomona*s, release some low molecular weight aldehydes and ketones including formaldehyde [8]. Zhou et al.

[9] had found that the sea surface micro layer (SSML) was rich in low molecular weight carbonyls including formaldehyde. Higher photo production of the low molecular weight carbonyls was the reason for this enrichment and the enrichment factor ranged from 1.2 to 2.1 for formaldehyde. They had found that the formaldehyde concentration in the bulk water was about 3.88 nM and in the micro layer it was 34.4 nM (at open stations about 100 km east of Bahamas) and concluded the ocean was a sink of formaldehyde at that location [9]. Therefore, it is essential to know the concentration in the air above the ocean, in the micro layer and in the bulk water to determine the direction of flux and to fully understand the chemical cycles involved at a specific location.

Ozone depletion is catalyzed by bromine atoms and when these bromine atoms react with formaldehyde to form HBr the reaction is terminated [10, 11]. This reaction is of importance during the polar sunrise when the ozone is depleted significantly. High levels of formaldehyde were observed in Arctic surface air and failure of the atmospheric models to predict this had given rise to studies and experiments to identify the source. These experiments showed that the formaldehyde is photochemically produced in the snowpack and is transferred to the atmosphere through the air-snow interface [12]. It was thus clear that formaldehyde is a dominant source of oxidizing free radicals in the lower polar troposphere (78-372 ppt during the dark period and 52-690 ppt during the sun lit period) [10]. However there was also a study questioning how significant this source is [13]. Therefore, quantifying formaldehyde accurately would enable us to correct these models, understand the polar troposphere chemistry. This again

enforces the need for a method for identification and quantification of trace amounts of formaldehyde in unpolluted air.

Dry deposition has been measured and is one of the sinks of formaldehyde. Due to its high solubility, it may also be lost in rainwater as wet deposition. In addition, HCHO is thought to have a direct influence on hydrogen peroxide levels since the HCO radicals yield to HO_2 radicals which in turn recombine to form hydrogen peroxide as follows [2]. The H and HCO radicals are formed according to Equation 8.

$$H + O_2 \rightarrow HO_2 \quad (10)$$

$$HCO + O_2 \rightarrow HO_2 + CO \quad (11)$$

$$HO_2 + HO_2 \xrightarrow{M,H_2O} H_2O_2 + O_2 \quad (12)$$

Being a significant source and sink of hydroxyl radicals thus vastly influencing the HO_x (OH+ HO_2) budget and oxidative capacity of the troposphere, and being an important factor in air-sea exchange chemistry and chemistry of the polar troposphere, formaldehyde proves itself a significant compound to be studied. Therefore, accurate measurements of its concentration in the unpolluted atmosphere are crucial in understanding the chemistry of our atmosphere. We need sampling methods for formaldehyde that are not complex, and are inexpensive, with reduced experimental uncertainties and lower detection limits.

1.2 Existing methods for the determination of formaldehyde

Formaldehyde quantification in air is difficult owing to its polarity, high volatility and low concentration and high reactivity. Several methods had been employed in the past for the determination of formaldehyde in air.

In general, spectroscopic techniques have been successfully used to analyze lower molecular weight aldehydes since they have distinct absorption bands. Formaldehyde, for instance, had been measured by Fourier Transform Infrared (FTIR) and Tunable Diode Laser Spectroscopy (TDLS) and Differential Optical Absorption Spectroscopy (DOAS).

1.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

Long path Fourier transform infrared spectroscopy is an important technique in determination and quantification of trace pollutants. The problem in the application of FTIR to ambient air is the presence of H_2O, CO_2 and CH_4 which are present in significant concentrations and absorb strongly in certain regions of the spectrum masking the absorption of other compounds. Formaldehyde however, shows characteristic doublet at 2779 and 2781.5 cm^{-1}. A detection limit of 4 ppb was obtained by Tuazon et al. using long path FTIR. However, it required a path length of 2 km which was achieved by an eight-mirror multiple reflection cell with a 22.5 m base path. Similarly, a detection limit of 6 ppb was obtained using 1 km path length [14].

1.2.2 Tunabe Diode Laser Spectroscopy (TDLS)

Tunable diode laser spectroscopy (TDLS) is a very attractive method for determination of formaldehyde due to the very high spectral resolution of the lasers, allowing the measurement of a single rotational-vibrational lines in the spectrum [15]. TDLS typically measures absorbance in the IR region and the only difference from a typical IR spectroscopy is its source which, being a laser, enables one to scan very narrow line width. It also allows good time resolution, typically a few minutes, and is selective, and sensitive [16]. However, it also requires a long path cell to achieve the required sensitivity [15]. Absorbance down to 10^{-5} to 10^{-6} can be measured using multi pass cells corresponding to sub ppb of atmospheric pollutants. Using a wave number of 2781 cm^{-1}, a detection limit of 0.05 ppbv was achieved [1].

1.2.3 Differential Optical Absorption Spectroscopy (DOAS)

DOAS has high sensitivity for species that have a narrow absorption band. Formaldehyde has strongly banded absorption in 300-400 nm regions and thus has high sensitivity in DOAS. The advantage of DOAS is that it does not require a calibration to be done on-site. Using, different path lengths and different detectors, various ranges of detection limits were obtained. For instance, using photodiode array detector (PDA) and 5 km path length a detection limit of 200-500 ppt was achieved whereas with a 15 km path length it was lowered to 66-166 ppt [1].

1.2.4 Chromatography

Derivatization techniques combined with chromatography are often used, in which the carbonyl compound of interest is derivatized, separated and then quantitatively analyzed. They have proven to be useful techniques to stabilize the analytes, enhance chromatographic behavior and to improve the selectivity and sensitivity of the detection [17].

1.2.4.1 Liquid chromatography with derivatization

Formaldehyde is collected on solid sorbents such as silica gel, Florisil or C-18 cartridges that are coated with the derivatizing agent. The most common derivatizing agent that had been used in the past is 2, 4 –dinitrophenylhydrazine (DNPH) which reacts with the carbonyl to form a hydrazone [18-20]. The hydrazone is generally separated using HPLC [21, 22]. Tub et al. had cryogenically sampled formaldehyde and derivatized with DNPH (reaction time 30 min) and extracted the hydrazone with carbon tetrachloride. The extraction efficiency was 92 ± 6 % and the detection limit they were able to obtain was 0.03 ppv when 300 L of air was sampled. One drawback was that the hydrazones formed in DNPH solution deteriorated with time and thus had to be analyzed as fast as possible [23]. In addition, a negative interference due to ozone in the DNPH coated silica gel cartridges was observed. However, the 2, 4 – DNPH acetonitrile solutions in the impingers did not show this interferences. To prevent this, an ozone scrubber was recommended and usually copper tubing coated with potassium iodide was used in front of the cartridge to remove ozone interferences [24].

1.2.4.2 Gas chromatography with derivatization

Thomas et al. used a denuder tube coated with 2-hydroxymethylpiperdine (2-HMP) connected to a Tenax TA adsorbent trap. The formaldehyde was then passed through the tube where it was derivatized to hexahydrooxalo [3, 4-a] pyridine. The derivative was then analyzed by GC. They obtained a limit of detection of 0.51, 0.03 and 0.05 μg/sample [17].

Marcella et al. obtained a detection limit of 74ng/sample by using derivatisation with 3,5-bis(trifluoromethyl)phenylhydrazine (TFMPH) which was coated onto a silica solid phase extraction cartridges. Reaction of formaldehyde with TFMPH formed a hydrazone derivative and that was analysed with GC-ECD. The disadvantage of this method includes residual HCHO-TFMPH in blank cartridges which required multiple recrystallizations of TFMPH from hot ethanol[25].

1.2.5 Fluorescence

The above mentioned methods are common to most of the carbonyls. However, there exist some techniques that are specific to formaldehyde. For instance *in-situ* wet chemical methods, such as the Hantzch reaction in which the formaldehyde reacted is collected/reacted using a diffusion scrubber with ammonium acetate, acetic acid, and acetyl acetone to form diacetyldihydrolutidine and its fluorescence measured at 470 nm [1].

Sakai et al. used a flow injection system for analysis of formaldehyde in air. In their work, formaldehyde was reacted with 5, 5-dimethylcyclohexane-1, 3-dimedone to form a fluorescing derivative (excitation $\lambda = 395\, nm$ and emission

λ= 463nm) in the presence of ammonium acetate. The fluorescence intensity was strong and was pH dependent due to the deprotonation of the nitrogen which inhibited the intensity very much (Highest intensity was at pH = 5.5). They were able to obtain linearity between 25-100 ppb and 5-10 ppb [26].

Pinheiro et al. either passed air samples through glassimpingers that contained Fluoral P solution or through two SEP PAK silica cartridges that were coated with Fluoral P. Formaldehyde was then reacted with Fluoral P to form 3,5-diacetyl-1,4-dihydrolutidine which was excited at 410 nm that resulted in fluorescence at 510 nm. They were able to obtain a detection limit of 2.0 ng/mL with sampling time of 120 mins. This technique had low blank levels, high sensitivity, low detection limits and little sample preparation [27].

1.2.6 Absorbance

Reaction with chromotropic acid is commonly used for determination of formaldehyde as well. In this case, formaldehyde is scrubbed into aqueous solution with impingers that are filled with water and bisulfite solution. The formaldehyde was then reacted with chromotropic acid (4, 5-dihydroxynaphthalene-2, 7-disulfonic acid) in the presence of sulfuric acid which resulted in a violet colored compound. This method lacked in sensitivity and required long sampling times (hours) and use of hot sulfuric acid. In addition there were some positive interference from phenols and other organic compounds [28].

1.2.7 Biosensors

Biosensors based on formaldehyde dehydrogenase (FDH) or alcohol oxidase are also reported for determination of formaldehyde in air. Vianello et al. [29] had reported a conductometric long-life biosensor for continuous real time monitoring based on the following reaction.

$$CH_2O + NAD^+ + H_2O \rightarrow HCOO^- + NADH + 2H^+ \quad (10)$$

In this case, the formaldehyde was trapped into NAD^+ flowing solution. The change in conductivity of the stripping solution was then monitored by a flow conductivity cell. They were able to obtain a detection limit of 50 ppb [29].

1.2.8 Mass Spectrometry

Yu et al. [30] developed a method using gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS). In this method, atmospheric formaldehyde was collected using $NaHSO_3$ coated Sep-Pak silica cartridges and then derivatized by cysteamine of known $\delta^{13}C$ value. The $\delta^{13}C$ of the derivative which is a thiazolidine was determined by GC/C/IRMS. Then the $\delta^{13}C$ of formaldehyde was calculated by using the relationship between those three compounds. This method was proved to be accurate and highly reproducible. They had compared this method with the DNPH method and were able to attain a detection limit of 4.52 to 10.16 μg/m^3 with sampling time of six hours (DNPH method: detection limit 14.07 to 66.97 μg/m^3 , sampling time of 20-24 hours) [30].

Pararosaniline and sulfite were added to aqueous formaldehyde solution and this produced a derivative which has a purple color and absorbance maximum at 570 nm. The absorbance was temperature dependent. A detection limit of 25ppb was obtained using this reaction with a sampling rate of 1L/min for one hour. This method however showed some positive interference from other compounds such as acetaldehyde, acrolein and propionaldehyde [31] .

PTR-MS (Proton Transfer Reaction Mass Spectrometry) allows on-line measurements of volatile organic compounds in air and detects formaldehyde from ion signals at m/z 31 with high sensitivity (10-100 pptv) and high time resolution (0.1-10 s). However the measurements can be affected by humidity as follows.

$$H_3O^+ + HCHO \rightarrow HCHO.H^+ + H_2O \qquad (13)$$

Formaldehyde has proton affinity only slightly higher than that of water and therefore the reverse reaction is not negligible.

$$HCHO.H^+ + H_2O \rightarrow H_3O^+ + HCHO \qquad (14)$$

The rate of the reverse reaction is several orders of magnitudes smaller, but the concentration of water in the atmosphere is very high compared to that of formaldehyde and therefore overall rates of these reactions are comparable. Drying the air sample to a dew point of -30°C using a cold trap to condense and freeze the water vapor increased the formaldehyde sensitivity by a factor of seven [32]. There is also the possibility of interference from other compounds that produce same m/z 31 ions such as methylhydroperoxide, methanol and ethanol and thus require corrections [33].

1.2.9 Intercomparison of several methods

Intercomparison studies of these methods of measurements allows one to compare how accurate and precise these methods are. The comparison studies showed that the spectroscopic methods are reliable and specific to HCHO and the derivatization methods are in reasonable overall agreement with the spectroscopic methods. The above mentioned methods and their detection limits are tabulated below in Table 1 for comparison. Time resolution and portability are two factors that favor some methods over the others. For instance, DOAS, TDLS and Hantzsch reaction coupled with fluorescence all have time resolutions in minutes whereas for DNPH/HPLC it is in the order of few hours [34, 35]. Time resolution is an important factor since for instance the chromatographic methods with sample collection steps last few hours and this is comparable to formaldehyde removal life time [36]. FTIR, DOAS, and TDLS were generally in agreement within 15% of their mean value but diacetlydihydrolutidine and DNPH derivative method were lower by 15-25% than spectroscopic methods and enzymatic method was higher by 25% [37]. Sirju and Shepson showed that if ozone interference was removed, DNPH cartridge and TDLS agreed well with each other [38]. In addition, Benning and Wahner had showed that when ozone was removed, DNPH method and DOAS also agreed well [39].

1.2.10 Summary of the existing methods and their detection limits

Table 1: The detection limit of formaldehyde measurements using different techniques

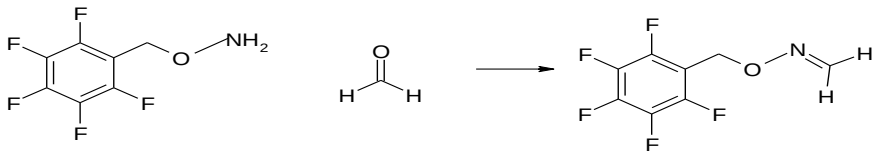
Technique	**Detection Limit**
Fourier Transform Infrared Spectroscopy (FTIR)	6 ppb (Path length = 1 km) [1] 4 ppb (Path length = 2km)[14]
Tunable Diode Laser Spectroscopy (TDLS)	0.05 ppb (Path length =150m) [1] 55 pptv[16] , 250 pptv[15]
Matrix Isolation IR	0.03 ppb[1]
DOAS with slotted disk detector	0.5 ppb (Path length = 5km) [1]
DOAS with photo diode array detector	0.2-0.5 ppb (Path length =5 km) , 0.066 to 0.166 ppb (Path length= 15 km) [1]
Hantzsch reaction with fluorescence	0.040 ppb [1]
DNPH/ HPLC	0.5 ppb [1], 160 pptv [34]. 0.03 ppbv(300L air sample)[23]
GC with pHID	42 pptv[36]
Fluorimetry (Hantsch reaction-1,3-cyclohexanedione/ NH4+)	50 pptv [10]
Fluorimetry (enzyme)	50pptv[40]
Derivatization with TFMPH	74 ng/sample [25]
Spectroflurometry with Fluoral P	2.0 ng/ml[27]
Derivatisation with pararosaniline	25 ppb [31]
Reaction with chromotropic acid	4 ppb (1 hr sampling at 1L/min)[28]
Proton transfer reaction mass spectrometry	10 -100 ppt [33]

1.3 Quantification of formaldehyde using SPME with on-fibre derivatization with PFBHA

Derivatization chromatographic methods have commonly been used since they are selective, inexpensive and widely available. Although, the DNPH derivatization provides a sufficiently low detection limit, its use in formaldehyde is limited due to the decomposition of the hydrazone at higher temperatures and sensitivity to light. Moreover, the DNPH derivative must be solvent-extracted and/or pre concentrated which might lead to sample contamination and is not environment friendly due to solvent usage. For gas chromatography, O-(2, 3, 4, 5, 6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) has been used to derivatize carbonyl compounds. It is an ideal derivatizing agent since it can be reversibly loaded onto the SPME fibre, is water soluble, and the oximes formed are thermally stable, and insensitive to light and oxygen. The oximes formed are easily analyzable by gas chromatography since they give a clear chromatogram with no other unknown peaks as the case in DNPH derivatization. Moreover, other aldehydes did not show any interference with the formation of formaldehyde oxime even at 100- fold higher concentrations [6].

Solid phase microextraction, a method developed by Pawlisyn and co-workers is a versatile tool that allows on-fibre derivatization. It combines sampling and pre-concentration into one step and does not require any solvent and is thus environmentally benign. Moreover, it is accurate, reproducible, portable, easy to use, sensitive and selective to large range of analytes, and reusable for more than 200 uses [41, 42]. Moreover it can be amenable to automation [6].

Solid phase microextraction combined with on-fibre derivatization with PFBHA (equation 13) requires minimal sample preparation and allows direct transfer of the analytes into the gas chromatograph. It therefore facilitates gas-phase analysis and allows on-site remote field applications with reasonable time resolution.



(13)

PFBHA HCHO PFBHA-HCHO oxime

In the current work, we employed on-fibre derivatization with PFBHA for determination of formaldehyde concentration in ambient air. Solid phase microextraction method coupled with derivatization with PFBHA had already been used to measure the formaldehyde in the atmosphere. However, our goal was to further develop that method to lower the detection limits so that it can be applied to ambient air analysis. Long term goal was to extend the developed method to the determination of other higher molecular weight carbonyl compounds in the atmosphere.

1.4 Solid phase microextraction (SPME) theory

A solid phase microextraction [43-46] device (Figure 1) is a simple, syringe-like device consisting of a silica rod (1 cm typically) coated with a polymeric phase which is covered with a metal sheath that allows the fibre to be retracted inside when not in use.

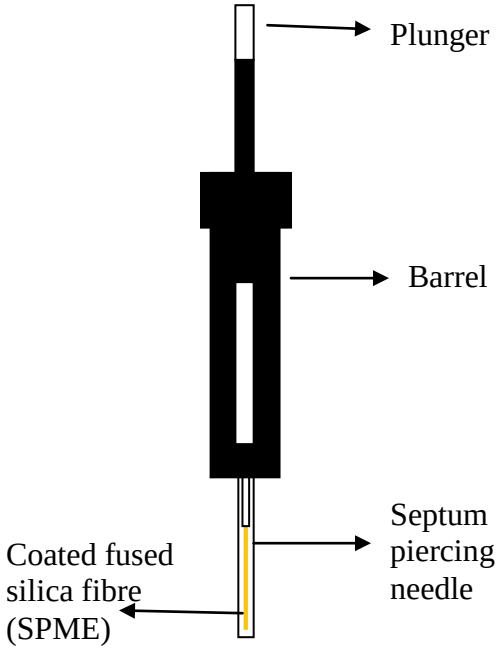


Figure 1: Solid phase microextraction fibre (SPME)

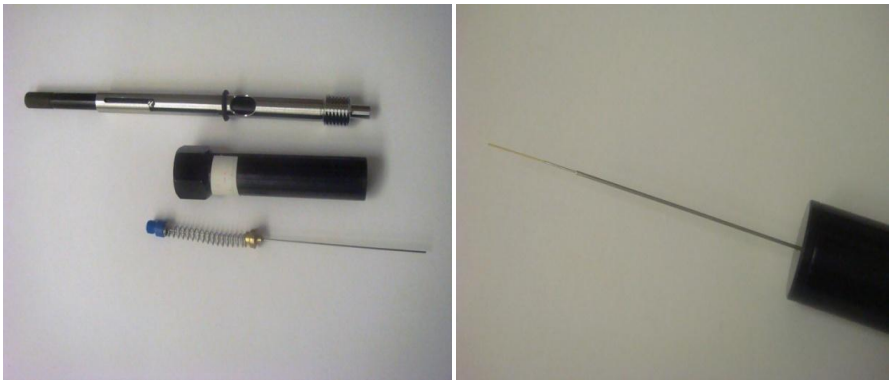


Figure 2 SPME fibre assemblies

When the fibre is exposed to the sample matrix, the analyte is either adsorbed or absorbed into the coating and this is then desorbed into the GC or HPLC depending on the requirement. SPME extraction is completed when the analyte

concentration reaches equilibrium between the sample matrix and the fibre coating. This implies that once the equilibrium is reached, the extracted amount of the analyte is constant within experimental error and therefore no change will be observed even if the extraction time is increased.

An analyte can be extracted either from the headspace or directly from the sample.

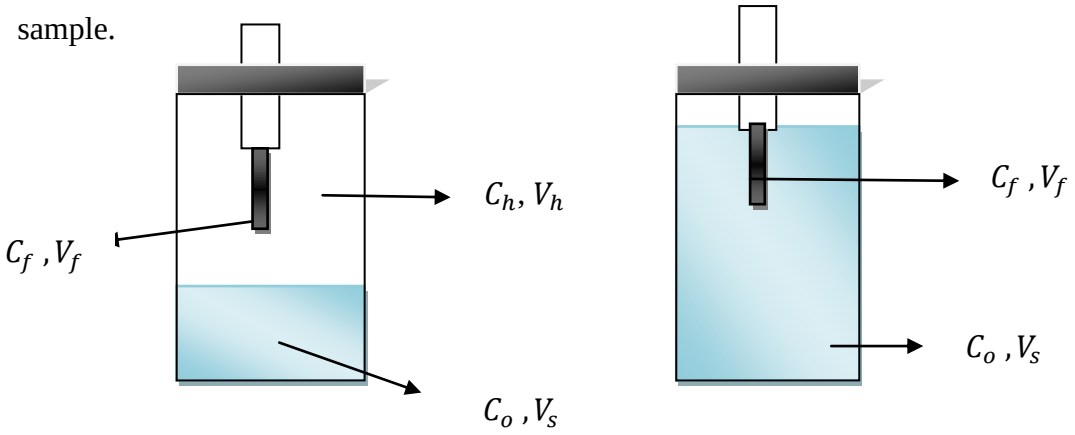


Figure 3: Modes of extraction using SPME (headspace and direct)

In the headspace extraction mode, the analyte is partitioned between the solution, the headspace and the fibre coating. In the direct extraction mode, however, the partitioning is only between the sample and the fibre coating.

In the first case, the amount of analyte extracted is given by the following equation:

$$n_f = \frac{K_{fs}K_{fh}K_{hs}V_fV_s\,C_o}{K_{fh}K_{fs}K_{hs}V_f + K_{hs}V_h + V_s} \tag{14}$$

Where

$K_{fh} = \frac{C_f}{C_h}$: The partition coefficient of an analyte between coating and the headspace

$K_{hs} = \frac{C_h}{C_s}$: The partition coefficient between headspace and the solution

$K_{fs} = \frac{C_f}{C_s}$: The partition coefficient between fibre coating and the solution

$V_{s,} V_f \; and \; V_h$: Volume of the sample, fibre coating, and the headspace respectively

$C_o \, , C_f , C_h$: The concentration of the analyte in the sample, fibre coating and the headspace respectively.

This equation implies that it is not important where the fibre is placed as long as the $V_f , V_h , and \; V_s$ are kept constant. Therefore, the choice of extraction mode is dependent on the type of matrix. If the sample matrix is contaminated for instance, then headspace sampling is preferred as to avoid damages to the fibre coating [41, 42].

In direct sampling, the factors for headspace can be eliminated and the equation then becomes,

$$n_f = \frac{K_{fs} V_f V_s \, C_o}{K_{fs} V_f + V_s} \tag{15}$$

In this study, the derivatizing agent (PFBHA) was headspace extracted and the fibre was then exposed to the formaldehyde gas standard or air sample for simultaneous adsorption of formaldehyde and formation of formaldehyde-PFBHA oxime. The adsorption of PFBHA can be expressed by equation 14. The formaldehyde adsorption and oxime formation, however, is no longer an equilibrium process.

In the case of derivatization on the fibre, the fibre is loaded with the derivatizing agent and is exposed to the analyte where it is extracted and

derivatized simultaneously. This process is no longer an equilibrium process and can be expressed as follows:

$$PFBHA + S \overset{k_1, k_{-1}}{\longleftrightarrow} PFBHA * S \quad (16)$$

$$Carbonyl + S \overset{k_2, k_{-2}}{\longleftrightarrow} Carbonyl * S \quad (17)$$

$$Carbonyl + PFBHA * S \overset{K*}{\rightarrow} Oxime * S \quad (18)$$

$$Oxime * S \overset{k_3}{\rightarrow} Oxime + S \quad (19)$$

Where Carbonyl is the analyte, PFBHA is the derivatizing agent, and Oxime is the product. Equation 16 describes the absorption/desorption of the PFBHA onto the fibre and it was experimentally found that $k_1 \gg k_{-1}$ at room temperature and therefore one can safely assume that the desorption of loaded PFBHA only occurs in the GC-inlet. Equation 17 expresses the possibility of a carbonyl to directly adsorb onto the fibre coating. However, since PFBHA is loaded excessively to the fibre prior to exposure to formaldehyde, the adsorbent sites are saturated with PFBHA and therefore $k_2 \approx 0$. It was experimentally found that equation 18 is the rate limiting step of this process and to ensure that it is completed, longer exposure times at low concentrations and short exposure times at high concentrations must be employed. It was also shown from other studies that $k_3 \approx 0$ at room temperature [6, 48].

Therefore as long as the derivatizing agent is present on the coating, the analyte will be extracted and derivatized and this results in an exhaustive extraction if the sample volume is small. When the sample volume, sampling rate, length of exposure time are kept constant, and PFBHA is in excess, a linear

relationship between the oximes formed and the concentration of formaldehyde is obtainable and that was used for constructing a calibration curve in this study.

1.4.1 Adsorbent Coatings

The extraction efficiency is dependent on the distribution constant K_{fs} which is dependent on the type of coating and its selectivity towards the analyte. To date, there are several types of coatings that are available for different analytes based on their volatility and polarity. These coatings are either made of pure polymer or are mixture of two different polymers. Polydimethylsiloxane, the most common coating used in environmental analysis, is a liquid polymer used for non-polar to semi-polar compounds where the analyte is absorbed into the coating. In case of PDMS/DVB (polydimethylsiloxane/divinylbenzene), divinylbenzene microspheres are suspended in PDMS [41, 42]. Their pores have the ability to adsorb analytes and retain them and thus this coating is more suitable for trace analysis [41]. It is generally used in the analysis of moderately polar compounds and amines. The other type of coatings that are available include polyacrylate (polar compounds), carbowax/divinylbenzene (for polar compounds), carboxen/PDMS (for highly volatile compounds) etc [41, 42].

Thickness of the fibre coating, i.e., the volume of the fibre, also determines the sensitivity of the method. As the equation 15 suggests, increasing the volume of the coating will increase the amount of the analyte adsorbed/absorbed. However, it would result in an increase in the equilibration time. One could also increase the fibre length if it is practical to do so [41, 42].

1.4.2 Extraction and desorption conditions

1.4.2.1 Factors affecting extraction efficiency

The extraction step is the more crucial step compared to the desorption step since it affects parameters such as the speed, sensitivity, accuracy and precision of the experiment.

The extraction efficiency can be improved by changing the sample pH, salt concentration or temperature as required. An increase in temperature would increase the diffusion coefficient of the analyte and decreases the coating/sample distribution coefficient. The coating can be cooled and the solution can be heated simultaneously to improve the sensitivity of the method.

The speed of extraction depends on how fast the analytes are transferred to the coating. Agitation transfers the analyte from the solution to the headspace and to the coating efficiently. Typically a magnetic stirrer is used since it is inexpensive and readily available. However, its rotational speed must be kept constant and the base plate of the stirrer must be thermally isolated from the vial. If not, the change in equilibration time would result in poor measurement precision.

1.4.2.2 Derivatization

Polar compounds generally are difficult to extract and thus need derivatization. An analyte can be either derivatized prior to, during or after the extraction. Derivatizing before or during the extraction enhances the selectivity and sensitivity of the extraction and detection. Post extraction on the other hand improves the chromatographic behavior [41].

1.4.3 Desorption conditions

Desorption, on the other hand is related to efficiency of the chromatographic separation and precision of quantification. It affects the quality of the data obtained. When the fibre is injected into the inlet the increase in temperature decreases the coating/gas partition coefficient and the analyte is desorbed. The constant flow of the carrier gas then helps transport and focus the analyte into the column. For SPME analysis, a narrow bore GC-injector inlet is required because the standard ones have a large volume, and thus produce very low linear flow rates resulting in slow transfer of analytes and poor resolution. Typically, two minutes of desorption time is sufficient to release all the compounds from the fibre coating. However, longer desorption times could be employed to eliminate any carryover effects [41].

1.4.4 Challenges with the coating

Phase stripping results either by swelling of the coating due to solvent absorption (in case of direct extraction) or from damage that results from the injector port septum. When the septum nut is too tight and when the needle pierces it, some septum pieces end up in the needle opening and this strips the coating off. Septum coring can be reduced by using pre-drilled septa and by not over tightening the septum unit [41].

2.Methodology

2.1 Analytical techniques: Qualitative and quantitative analysis of formaldehyde.

2.1.1 Gas Chromatography with flame ionization detector

We developed a method for detecting formaldehyde in the atmosphere using gas chromatography with a flame ionization detector (GC-FID, HP 6890). A flame ionization detector, the commonly used detector for carbon containing compounds, detects the analyte by measuring the current generated by the electrons that result from burning the carbon compounds in the introduced sample. The current measured at the electrode is proportional to the number of carbon ions hitting the detector per unit time. The specifications of the GC we use and the conditions at which it was used are given below.

2.1.1.1 Operating conditions:

GC-FID (HP 6890 GC, Agilent, Palo Alto, CA) analysis was performed on an HP5 column (30 m x 0.32 mm I.D.; 1.0 µm film) using splitless injection, He carrier gas with 2.5 ml min^{-1} with constant flow, injector at temperature of 275°C and oven was kept at 50°C for 2 min, then increased by 15°C/min to 200°C with no final hold. The detector was kept at 300° C.

2.1.1.2 Identification of formaldehyde oxime and PFBHA

The PFBHA and formaldehyde PFBHA oxime were identified by comparison with previously reported retention times for these compounds (E. D. Hudson, pers. 36comm.). Peaks were automatically integrated using HP Chemstation software.

2.1.2 Solid phase microextraction (SPME)

Extraction and pre-concentration of the formaldehyde derivative was done using solid phase micro-extraction. Solid phase microextraction, combines extraction and pre-concentration of the analyte from the matrix. When the fiber is exposed to the sample, the analyte is either adsorbed onto or absorbed into the coating depending on the type of coating. The absorbed/adsorbed analyte is then desorbed, separated and quantified using the GC-FID.

SPME is an attractive method due to its selectivity, versatility, low cost, and simplicity. In addition, it does not require any solvent or any other materials for pre-concentration or extraction and thus is environmentally benign and does not produce waste. In this case, we have compared three different coatings : Polydimethylsiloxane (PDMS) , Polydimethylsiloxane/ Divinylbenzene (PDMS/DVB), and polymethylsiloxane/Carboxen (PDMS/CAR) and found PDMS/DVB to be more suitable for our needs. Thus, all the experiments here were done using PDMS/DVB fibers (Figure 4).

2.1.2.1 SPME extraction conditions:

Prior to using the fiber for analysis, every single one was conditioned for 0.5 hours at 250 °C (PDMS and PDMS/DVB), and 1 hour at 300 °C (PDMS/CAR) as per the suppliers instructions. This step was necessary to prevent any carry over effects from manufacturing processes. Although conditioning was not necessary prior to each analysis, a GC column blank and a fiber blank was done every day to make sure there is no contamination of the fibre.

Our analysis required three steps: a) exposure of the fibre to the derivatizing agent, b) exposure of the loaded fibre to either the formaldehyde gas standard or air matrix c) subsequent desorption into the GC-FID. First the extraction time of the derivatizing agent (PFBHA) and the desorption time of the oxime were optimized. The extraction conditions such as temperature of the solution, stirring rate were all kept constant. All extraction conditions were reproduced as much as possible and kept constant throughout the analysis to ensure good reproducibility.

In a typical run, fibre was exposed to the headspace of PFBHA solution for five minutes (constant temperature and stirring rate), retracted, exposed to formaldehyde standard/ sample (no stirring, room temperature) for 30 minutes and desorbed into GC for 10 minutes, and then removed and cooled before using for subsequent analysis. Whenever the fibre was needed to be stored for a few minutes with the PFBHA loaded or sampled, the tip was capped with a septum to avoid contamination and/or loss of the analyte/derivatizing agent.

2.1.2.2 *Challenges*

There were a several challenges with the use of SPME. First of all, the fibres from the same lot had different extraction efficiencies and thus had to be calibrated independently. Secondly, although fibres are generally robust, PDMS/DVB fibre coatings seemed a bit less robust. After about 50 uses, the coating starts to lose its integrity. Cracks, discoloration of the coating, falling off the coating material were observed with exhaustive use of the fibre. The physical

damage however, can be reduced by ensuring that there are no obstacles in the liner for instance septum pieces.

2.2 Materials and supplies

Table 2: Information about chemicals and apparatus used

Materials and supplies	Supplier	Other specifications
Ultra high purity He	MEGS	
Extra dry air	MEGS	
Hydrogen	MEGS	
Formaldehyde	Sigma-Aldrich	37 wt. % in H_2O Contains methanol as stabilizer
Methanol (HPLC)	Sigma-Aldrich	HPLC grade
HPLC water	Sigma-Aldrich	HPLC grade
MilliQ water	Simpak ®	From Simplicity 185 machine
Potassium permanganate	Sigma-Aldrich	
PFBHA	Fluka	Purity ≥ 99.0%
Toluene		Fisher Scietific
DMDCS in Toluene	Sigma-Aldrich	
C-18 (Carbon 17%)	Silicycle chemical divison	Ultra pure, reversed phase silica gel, particle size 40-63µm (230-400 Mesh)
Gas tight syringes		Hamilton Co.
Teflon bags	Chromatographic Specialties	25L ,18"x24"
SPME fibres	Supelco	PDMS /DVB :65µm,T_{max} =270 C PDMS/CAB : 75µm,T_{max} =320 C PDMS : 100µm,T_{max} =280 C
SPME holders	Supelco	
Green septa	Supelco	11 mm pre-drilled, pre-conditioned , ready to use septa

2.3 Experimental steps

2.3.1 Preparation of glassware

All glassware was washed thoroughly with soap, ethanol and MilliQ water (18.2 $M\Omega\,\mathrm{cm}^{-2}$). The glassware except volumetric glassware and the glass pipettes were baked in a muffle furnace (~450°C) for about 24 hours. The volumetric glassware and the magnetic stir bars were dried in an oven at 125°C. The flasks and flow tubes used were silylated prior to use in order to prevent formaldehyde from being adsorbed on to the glass wall.

2.3.2 The process of silylation

Glass surfaces are highly adsorptive due to the presence of SiOH groups. To minimize adsorption of polar compounds and therefore prevent any loss of sensitivity, it was important to protect those OH groups and that was done by using by the silylation process (Figure 4).

The glassware to be silylated was washed thoroughly with soap and water and then rinsed with MilliQ water. The washed glassware was then dried in the oven overnight and was cooled. Then it was rinsed with about 10 ml of 5% dimethyldichloridesilane (DMDCS). The glassware was slowly coated with this solution and this was repeated two more times. After that, it was rinsed off with enough toluene three times. Finally, the toluene was rinsed off with methanol and the glassware was left again in the oven overnight.

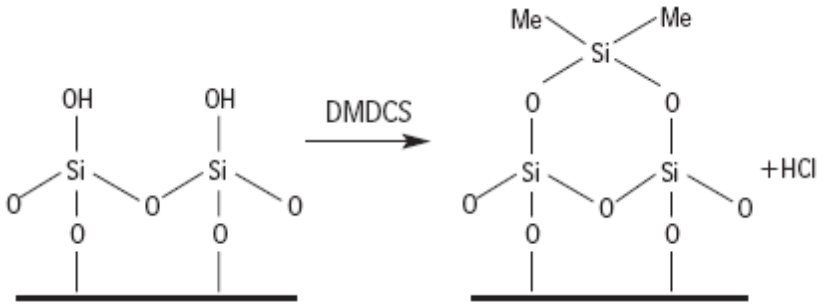


Figure 4 Protecting OH groups from the glass surface by the use of DMDCS [49]

2.3.3 Preparation of PFBHA solution

A PFBHA solution was prepared by dissolving 60 mg of PFBHA in 5 ml of MilliQ water giving a concentration of 12mg/ml. A clean, baked pipette was used to transfer the PFBHA powder to the vial in order to prevent any contamination. This solution was then purged with Argon for a few minutes to displace the air from the headspace and the solution. One ml of the above solution was taken into a customized 2.5 ml glass vial and was again purged with argon for few minutes. The rest of the solution was kept in that vial, wrapped with aluminum and parafilmed in the fridge till needed. Typically, it was kept for up to a month and no contamination or changes were observed.

The 2.5ml vial was placed in an aluminum block on a stirrer to prevent any heat produced from continuous stirring affecting the solution temperature. It was stirred for about 30 minutes prior to extraction, giving enough time for the PFBHA in the headspace and the solution to reach equilibrium. A series of extractions (n=5) done after 30 minutes, showed that the peak areas of PFBHA extracted agreed with each other with in 0.86% (Figure 1A, in appendix).

2.3.4 Formaldehyde standard preparation

Formaldehyde (37% in water) was diluted with HPLC grade methanol to make liquid standards as required. The volumetric flasks with the solution were wrapped with aluminum foil, capped, parafilmed at the top, placed in a zip-loc bag and were placed in the fridge till needed. Typically, the stock solution was kept for about a month. The stock solution was diluted to make the working solutions as required.

Formaldehyde gas standards were prepared in a 25 L FEP bag (Chromatographic Specialties). The FEP bag was always flushed with N_2 (g) three times between each use. The bag was then filled with N_2(g) and was spiked with the formaldehyde in MeOH solution using a gas tight syringe (250µL, Hamilton Co.) and was left for 30 minutes before extraction. No stirring was used since natural convection is sufficient to achieve good mixing.

2.3.5 Air sampling

Air sampling was generally done be exposing the fibre into the air directly for 30 minutes and then retracting in, capping the tip with a gas tight septum, transporting back into the lab and desorbing into the GC. When a comparison between other types of sampling was done, two Teflon-membrane pumps were used to fill and evacuate the all-Teflon bag or to flow the air through the flow tube. A flow rate of 3.0L/min was used to fill in the Teflon bag and a flow rate of 0.7L/min was used for flowing air through the flow tube for 30 minutes.

2.3.6 Purification experiments

2.3.6.1 Solid phase extraction

A clean, baked pipette was blocked at the tip with glass wool and then packed with about 0.5g of C-18 silica (Silicycle chemical divison) and was washed with few milliliters of MilliQ water. PFBHA solution was then passed through and the first few drops were discarded and the rest was collected in a clean vial. The resulting PFBHA solution was then compared with the ordinary PFBHA solution for the effectiveness of formaldehyde removal (Figure 10).

2.3.6.2 $KmnO_4$ distillation

A round bottom flask was filled with 1L MilliQ water with 96mg of $KmnO_4$ crystals and few drops of concentrated H_2SO_4. The mixture was then heated and the distilled water was collected at the end and the PFBHA solution prepared using this water was compared with that made from normal MilliQ as well for the contamination level in the blanks (Figure 12)

2.3.6.3 Photolysis

A glass flask with a quartz window was filled with 1L of MilliQ water. 200µl of 30% H_2O_2 was added to facilitate the photolysis. This water was irradiated with UV light (~254nm, for 2 ½ days, Oriel 6281 W Hg Lamp). The pH of the MilliQ was 7.51 and that of resulting photolyzed MilliQ was 7.69 which are comparable. The PFBHA solutions prepared from photolysed water was then compared with that prepared from normal MilliQ water for any differences in formaldehyde concentration (Figure 8).

2.3.6.4 Different types of water

PFBHA solution prepared from normal MilliQ water was also compared with the ones prepared from HPLC water, boiled MilliQ water to see if there is any improvement in lowering formaldehyde background concentrations (Figure 12)

2.3.7 Preservation/ storage experiments

Preservation/storage of a loaded fiber was done by extracting the PFBHA onto the fiber and then capping the tip with clean green septa that are usually used for GC-inlets. The loaded fiber was then placed on an aluminum foil on top of a pack of dry ice in a Styrofoam box. The box was then closed and was taped shut and was kept in a cool place.

2.4 Field campaign

Field analysis was done on a cruise to Labrador Sea that lasted two weeks (May 17 to June 01 2009).

The 2009 Labrador Sea Mission HUD2009015 on CCGS Hudson (Figure 5) departed St.John's Newfoundland on Sunday, 17 May 2009 and returned to Halifax, Nova Scotia on Monday 01 June, 2009.

Figure 5 The CCGS Hudson at St-John's Harbor on July 17, 2009

Physical, chemical and biological measurements were done in both AR7W line and Halifax line by the principal investigators on the ship (Figure 6).

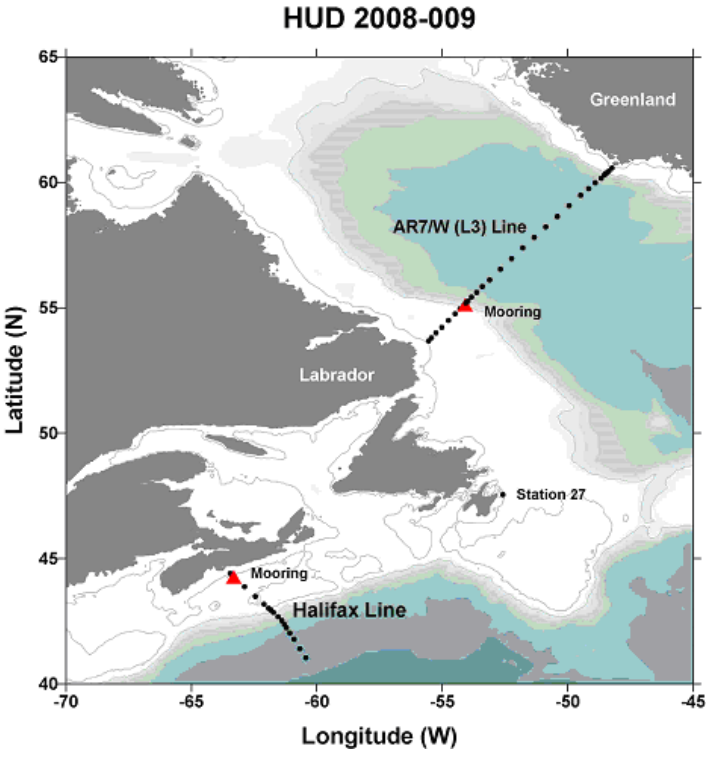


Figure 6 The trajectory of CCGS Hudson on Labrador Mission 2009

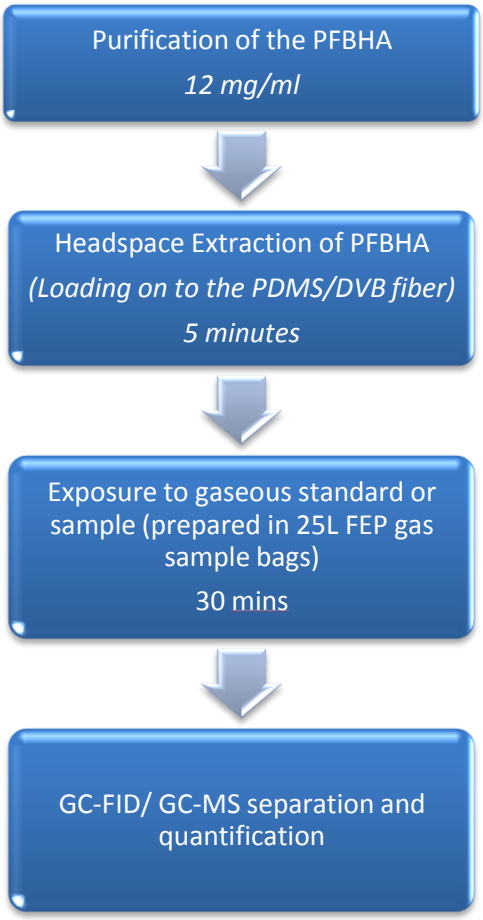
About eight days was spent on stations along the AR7W line and four days along Halifax line.

For analysis of the concentration of formaldehyde in marine air using our developed methodology, five stations along the Labrador line and three stations along the Halifax line were sampled. Air samples were collected, away from ship exhaust by flushing the Teflon bag three times and then filling it with the air with a flow rate of 4.0L/min for 5 minutes (Figure 7a and 7b). Two membrane pumps were used and the pump that was used to fill in the air was fitted with a Teflon filter to avoid any water droplets or particles from getting into the bag. The filled bag was then brought into lab that was set-up inside the ship (Figures in the appendix), and was analyzed as usual.

Figure 7a Collection of marine air in Teflon bag on Hudson during the Labrador mission 2009

Figure 7b Collection of marine air in Teflon bag on Hudson during the Labrador mission 2009

2.5 Schematic of the procedure of the methodology developed



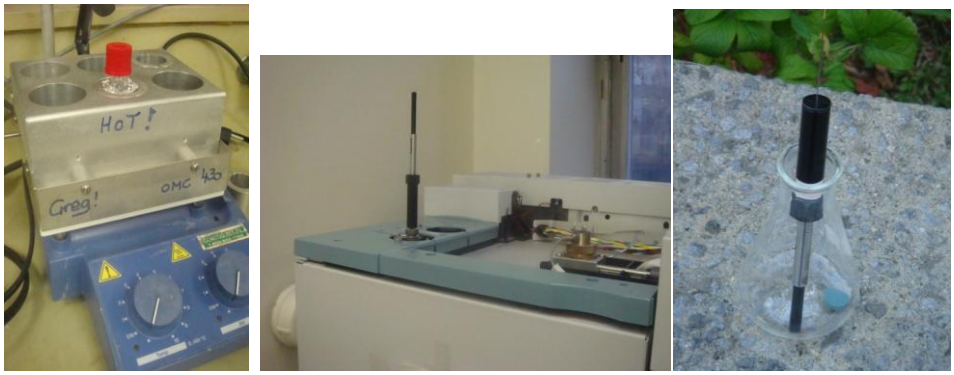


Figure 8: The schematic of the procedure that was developed in this work

2.6 Error Analysis

Typically, the peak areas of formaldehyde-PFBHA oxime peak areas had relative standard deviations varying from 1% to 16%. This associated error mainly resulted from a) errors introduced in sample preparation b) Error in synchronization of timing and GC-start-up c) Error from FID response.

In a series of runs, reproducibility of peak areas for the same concentration gives a measure of reproducibility of the detector response and of sample introduction. For PFBHA (number of runs = 5), the peak areas agreed with each other with a relative standard deviation of 0.86% (Figure 1A, Appendix). In addition, the variation in retention times for the formaldehyde oxime and PFBHA gives a measure of the error introduced by the coordination between or the lack thereof between injection of the SPME fibre into the GC injector port and starting the run. This reproducibility is represented in figure 9 and the corresponding relative standard deviations are given in table 3.

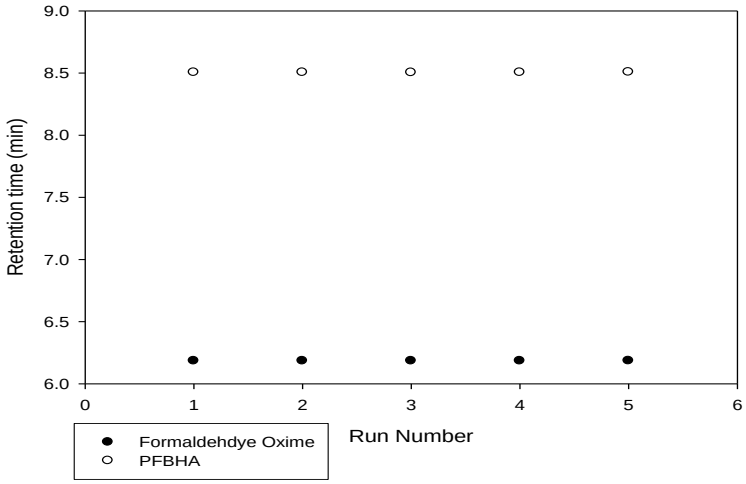


Figure 9 Reproducibility of the retention times of PFBHA and formaldehyde-PFBHA oxime peaks

Table 3: Study of retention times and their reproducibility

	Retention time (min)	**Relative standard deviation (%)**
PFBHA	8.5054 ± 0.0015	0.017
HCHO-PFBHA oxime	6.1842 ± 0.0004	0.007

Sample preparation in this work includes preparation of PFBHA solution, formaldehyde liquid standards and gas standards. In this case, the errors can be introduced by the syringe used which is said to be 1% from the supplier, Teflon bag, the flow meters, the vacuum line, balance, pipettes, and balance to name a few. In addition, the error associated with the timer is important since it influences the extraction time of PFBHA, extraction time of formaldehyde and desorption time in the GC-injector port. However, these errors are of less appreciable compared to the error associated with the formaldehyde contamination in the blank and the error associated with the simultaneous adsorption of formaldehyde and formation of oxime which is sensitive to the temperature of the atmosphere, and fluctuations in the stirring which results in fluctuations in the transport of analytes.

3.Results and discussion

Typically a method development using SPME would consist of selection of the fibre coating, selection of the extraction mode, optimization of extraction conditions, optimization of desorption conditions, and construction of a calibration curve using the relationship between the instrument response and the concentration. The method developed will then be applied in the real world measurements.

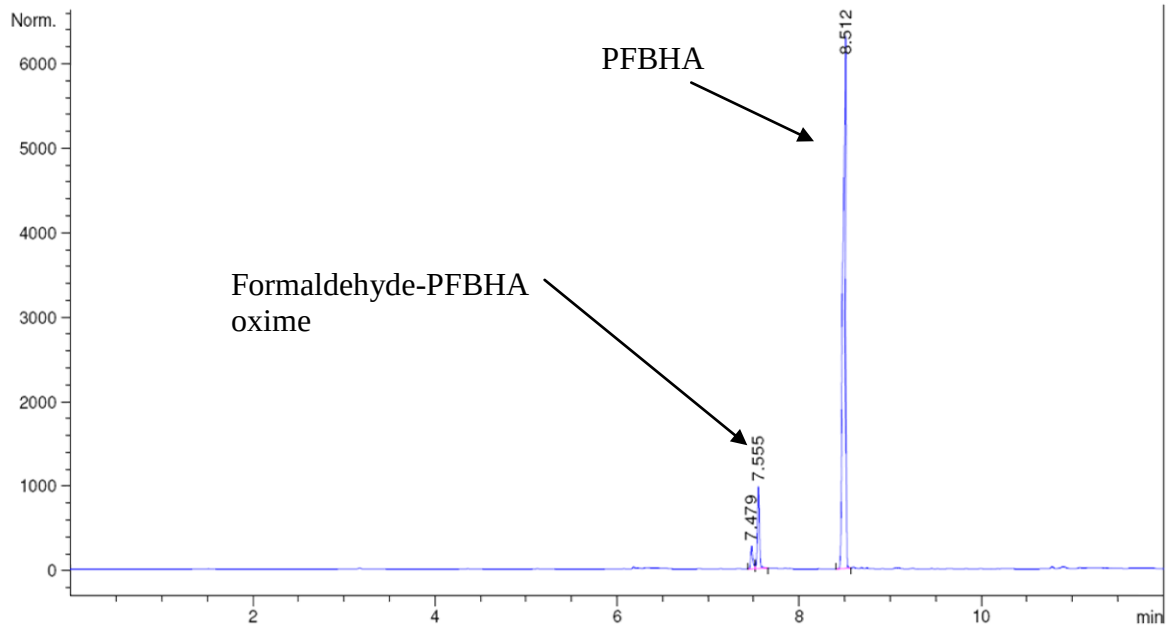


Figure 10: Sample chromatogram of a typical run

3.1 Selection of the fibre

Different coatings have different sensitivity to different types of analytes depending on their polarity and volatility. It is essential to find a coating that has high affinity for the analyte we are interested in since it would increase the sensitivity of the method.

Our first task was then to find a suitable coating of the SPME fibre for analysis of formaldehyde. Three different coatings (PDMS, PDMS/DVB, and PDMS/CAR) were compared for their efficiency of loading the derivatizing agent (PFBHA). These three coatings are the commonly used coatings to analyze semi-volatile to volatile compounds in liquid and gaseous matrices in environmental analysis [41]. Since the amount of formaldehyde that would be derivatized on the fibre is proportional to the amount of derivatizing agent available on the fibre, it is important to choose a coating that has higher affinity to PFBHA with good reproducibility. It also should adsorb formaldehyde and form the oxime efficiently on the coating.

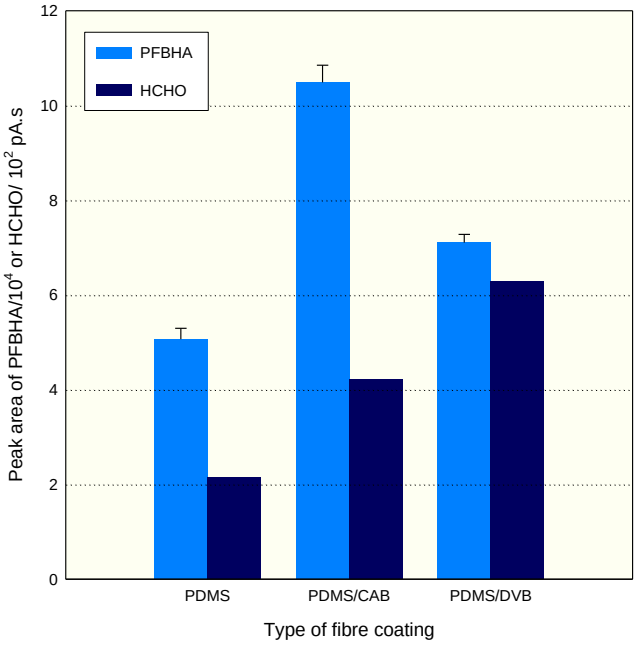


Figure 11: Comparison of three different coatings for efficiency and selectivity of PFBHA and formaldehyde oximes (n = 3, and error bars are standard deviations)

From the results, PDMS/DVB gave good compromise between efficient PFBHA extraction and reproducibility. In addition, it adsorbed and formed formaldehyde

oxime efficiently compared the other two fibers and therefore was selected as a suitable fibre coating for our method development.

3.2 Adsorption time profile of PFBHA

PFBHA extraction would be completed when equilibrium between the PFBHA in the solution, headspace and the fibre coating is reached. After reaching equilibrium, increase in extraction time will not increase the amount of PFBHA extracted on the fibre. To visualize this, an adsorption time profile was obtained by extracting PFBHA for different lengths of time and the result is given in Figure 12.

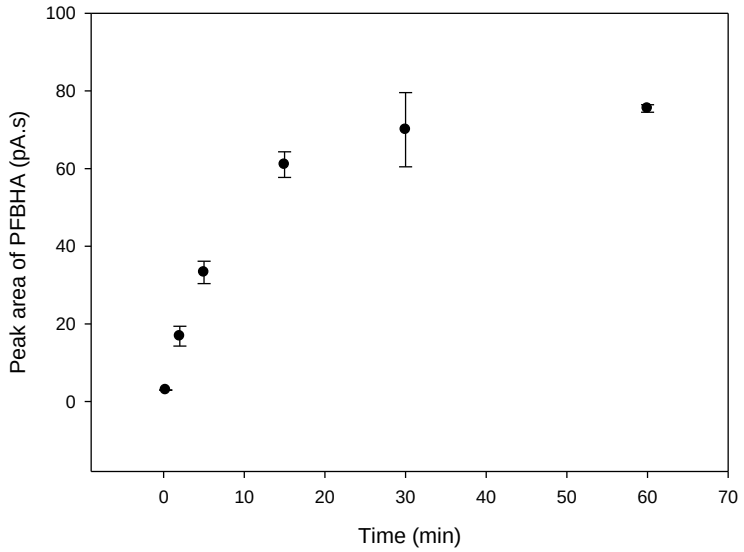


Figure 12: Adsorption time profile for the extraction of PFBHA (n = 2, error bars are standard deviations)

One can see a rapid increase in the PFBHA extracted in the first 15 minutes and then a slower increase. Finally, a plateau is reached after an hour of extraction. However, it is not necessary for the equilibrium to be reached between the

PFBHA in the solution, headspace and on the fibre coating to be able to do the analysis as long as the extraction conditions are kept constant.

The amount of PFBHA extracted at pre-equilibrium can be given by the following equation using a dynamic model for transportation of analyte [50].

$$n = [1 - \exp(-at)]\frac{K_{fs}V_fV_s}{K_{fs}V_f + V_s}C_0 \qquad (20)$$

Where, n is the amount of PFBHA extracted and a is a constant depending on extraction phase, headspace and sample volume, mass transfer coefficients, distribution coefficients, surface area of extraction phase. K_{fs} is the partition coefficient between fibre coating and the solution, V_f, V_s are the volume of the fibre and sample respectively, and C_o is the concentration of PFBHA in the solution. This equation suggests that there is a linear relationship between n and C_o implying that the SPME analysis is feasible before equilibrium if agitation conditions, sampling time and temperature are constant. Generally, extraction at equilibrium however would increase the sensitivity since the amount of the analyte extracted on the coating is at maximum. However, if the sensitivity is not the major issue, reducing the extraction time gives better time resolution of the analysis. In our case, PFBHA, being the derivatizing agent, is only expected to be in excess on the fibre coating. It is also important to note that as t → ∞, this equation reduces to equation 15. Therefore an hour of extraction is not required. Already at five minutes, the PFBHA extracted in sufficient for the formaldehyde concentrations that is required in this study. Therefore five minutes was chosen as a suitable PFBHA extraction time. To obtain reproducible results, all the other extraction conditions such as stirring rate, temperature were kept constant as

much as possible . The reproducibility of PFBHA extraction is given in figure 1A and for five runs, the relative standard deviation was only 0.86%.

3.3 Effect of temperature

The amount of PFBHA on the coating at particular time is dependent on the amount of PFBHA available in the headspace at that time. Increasing the temperature of the solution would increase the rate of transfer of PFBHA molecules into the headspace and therefore the equilibrium or any given concentration will be reached faster. This implies that more PFBHA can be extracted in less time. To investigate the impact of temperature on extraction efficiency, PFBHA solution was heated to different temperatures, extracted and the results are plotted in Figure 13.

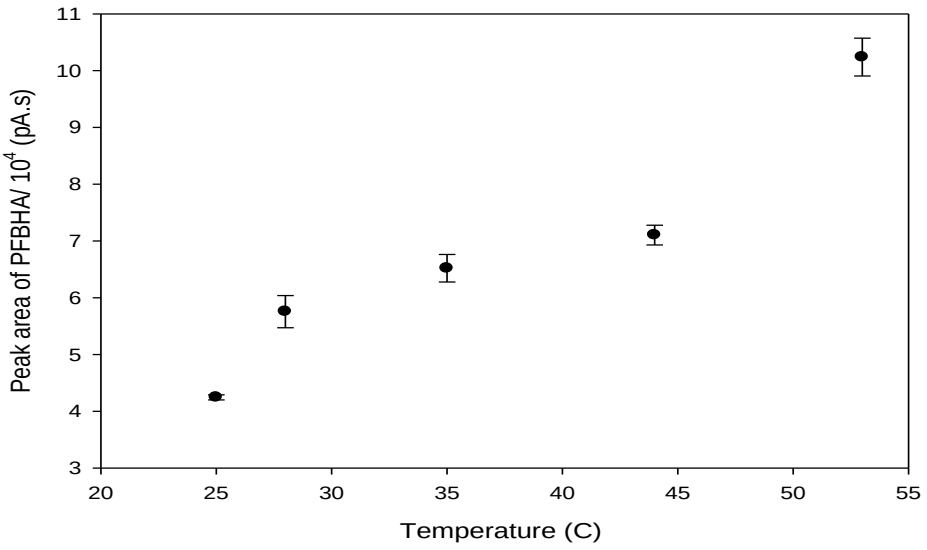


Figure 13: Effect of temperature of the solution on the amount of PFBHA extracted (n=2, error bars are standard deviations)

As expected, increasing the solution temperature was a way to increase efficiency of PFBHA extraction in shorter time. However, it is important to remember that increasing the temperature will decrease distribution of a volatile analyte on to the fibre. For instance, if both the sample and the fibre temperature change from T_o to T, the distribution constant (K_{fs}) changes according to the following equation [41].

$$K_{fs} = K_0 \exp\left(\frac{-\Delta H}{R}\right)\left(\frac{1}{T} - \frac{1}{T_o}\right) \quad (21)$$

Where K_o is the distribution constant when both fibre and sample are at T_o (in K), ΔH is the molar change in enthalpy of analyte when it moves from the sample to coating and R is the gas constant. The sample here is the headspace and increasing T decreasesK_{fs}.

A hot headspace is then not preferred. If a simultaneous heating of the solution and cooling of the fibre can be achieved, it would simultaneously increase the coating/headspace distribution constants of the analyte and increase the solution/headspace partition coefficient. Zhang and Pawliszyn have shown that the sensitivity can be enhanced significantly by heating the sample and simultaneously cooling the fibre with CO_2 [51]. In this work however, PFBHA was extracted at room temperature sufficient PFBHA was extracted with good reproducibility at room temperature (RSD < 5%).

3.4 Derivatization time

On fibre derivatization is not an equilibrium process but an exhaustive extraction process. The analyte is derivatized on the fibre as long as the derivatizing agent is

present. This can be seen in the figure 14. The non linearity at low concentration end is due to the inclusion of blank concentration. The blank formaldehyde concentration is highly variable and this makes it difficult to determine the linearity.

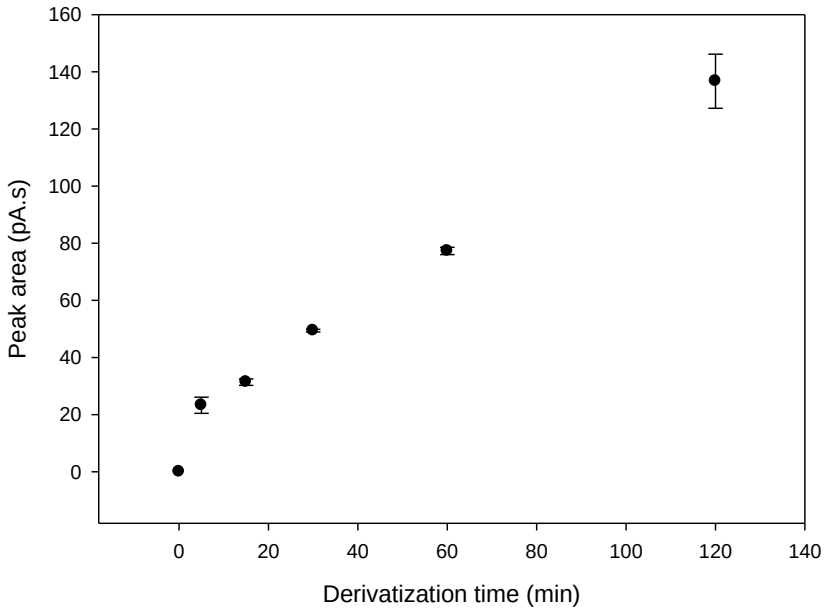


Figure 14: The amount of formaldehyde derivatized for different lengths of exposure time (n=2, error bars are standard deviations, sample volume 20L)

However, it is essential to find a suitable formaldehyde exposure time that would allow on-site environmental analysis at a remote location in a timely manner. Although, an increased formaldehyde exposure time would result in an increased oxime formation on the fibre thus an increased sensitivity, 30 minutes was chosen for this work since it gave a good compromise between sensitivity and time resolution.

3.5 Lowering the blank formaldehyde concentration

A major challenge in this work was to reduce the contamination of formaldehyde in the PFBHA solutions. Formaldehyde is an ubiquitous aldehyde that is found in

tens of ppb in indoor air [1]. We, however, were interested in ambient air concentrations which are three orders of magnitude lower than that present in typical indoor air. Therefore, it was difficult to prepare solutions that are totally free of formaldehyde since it was difficult to identify various sources and factors contributing to the background formaldehyde levels. Typically, formaldehyde contamination can result from contamination in the PFBHA solutions, methanol that was used to prepare formaldehyde standards, carryover effects such as from the FEP sampling bags. The formaldehyde contamination in the PFBHA solutions can result from contamination in the MilliQ water, PFBHA and/or headspace air. Therefore we tried to purify either the water or the solution or the headspace and the results are shown in figures 8-12.

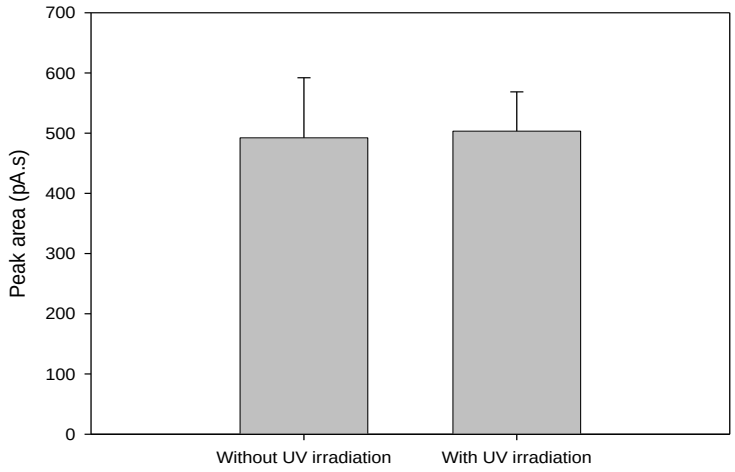


Figure 15: Comparison between PFBHA solutions prepared from UV-irradiated and non-irradiated MilliQ water (n=3, error bars are standard deviations)

First we tried to photolyze the formaldehyde from the regular MilliQ into H and HCO radicals (equation 8). However there was no significant difference observed with both solutions (t-test, 95% confidence level, $p > 0.05$). This may have been

result of simultaneous photolysis of higher molecular weight organic compounds into formaldehyde.

An attempt was made to boil off the volatile compounds from the MilliQ water (Figure 16). The formaldehyde oxime from the PFBHA solution made from boiled water was 21% less than that found in unpurified PFBHA solution. Although, it showed slight improvement on the blank contamination levels, statistical analysis showed that the difference is insignificant (t-test, 95% confidence level, $p = 0.18 > 0.05$). Moreover, the set-up involved an open Erlenmeyer flask covered with aluminum foil and was prone to exposure to lab air.

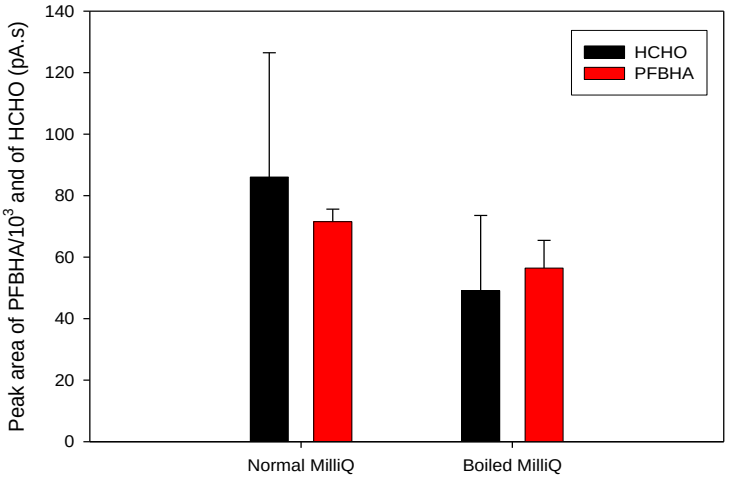


Figure 16: Comparison between PFBHA solutions prepared from boiled and normal MilliQ water (n=3, error bars are standard deviations)

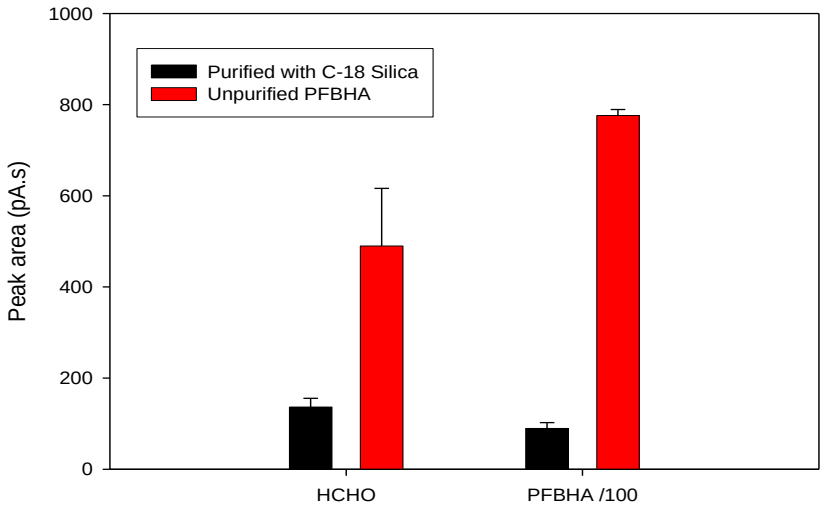


Figure 17: Comparison between solid phase extracted PFBHA solutions and non purified PFBHA solutions (n=3, error bars are standard deviations)

Solid phase extraction using a column packed with C-18 silica was used to purify the PFBHA solution itself. It was in fact effective in removing the formaldehyde oxime from the PFBHA solutions. Student's t-test showed that the mean values for formaldehyde-oxime peak areas for both treated and untreated PFBHA solutions were in fact different (t-test, 95% confidence level, $p = 0.04 < 0.05$) . The drawback was that the PFBHA concentration was reduced significantly in the solution. Among the methods used for the lowering formaldehyde contamination, this one proved to be somewhat effective. However, this solid-phase extraction must be done freshly since the solution can draw formaldehyde from the surrounding air.

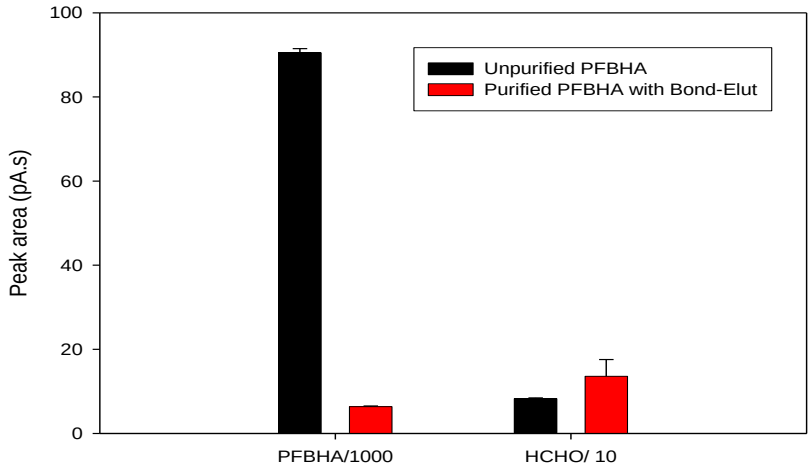


Figure 18: Comparison between solid phase extracted PFBHA solutions and non purified PFBHA solutions (n=3, error bars are standard deviations)

Bond-Elut was a commercially made solid phase extraction cartridge of C-18 silica. This however, in contrast to our expectation, did not reduce the blank level contamination and it actually introduced more contamination in the PFBHA solution. This might have been result of lab-air exposure.

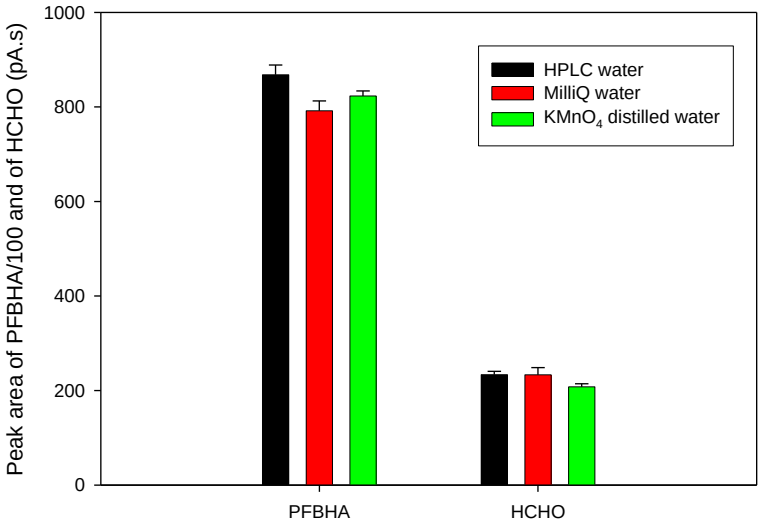


Figure 19: Comparison between PFBHA solutions prepared from three different types of water (n=3, error bars are standard deviations)

PFBHA solutions prepared from HPLC water, KMnO4 distilled water did not show any significant difference from the solution prepared from regular MilliQ water (F_{stat} = 8.91< $F_{critical}$=9.55). Overall, none of the above purification steps resulted in effective removal of background formaldehyde in PFBHA blanks.

3.6 Comparison of FEP bags

Formaldehyde standards were prepared in 25L FEP bags (Chromatographic Specialties Ltd). It was essential to verify if different bags had different blank levels and any history effects from the previous uses. Therefore, blanks of three different FEP bags with different history were analyzed (Figure 13). The statistical results showed that there is no statistical difference between the bags ($F_{statistical}$ = 0.055 < $F_{critical}$= 9.55). However, it is wise to verify this before using different bags for the same analysis.

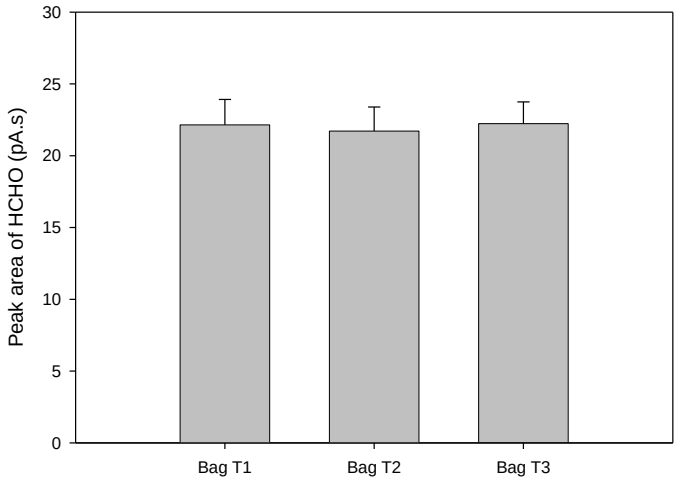


Figure 13: Comparison between three different FEP sampling bag blanks (n=3, error bars are standard deviations)

3.7 Application of this method in a field campaign

An opportunity to go on a cruise to Labrador Sea had given a chance to apply this method to analyze clean marine air. Unfortunately, the detection limit of the method obtained in the ship was higher than required (Appendix) and thus we were not able to report the results. However, the results gave some feedback on the potential of the methodology developed, its application in a field, the challenges involved and the improvements needed. The values from the table below (Table 4) show that the methodology at this stage was able to probe the differences in concentration of formaldehyde in clean marine air and polluted coastal area air and this was indeed useful information.

Table 4: Qualitative data from the analysis of marine air during the Labrador Mission 2009 on CCGS Hudson (L3: station along the Labrador line, HL: Station along Halifax line, BDL: Below detection limit)

Station no	**Peak area (average)**	**STD**	**RSD**	**HCHO(ppb)**	
L3_22	73.90	3.82	5%	-0.44	BDL
L3-27	74.66	5.05	7%	-0.38	BDL
L3_19	65.81	7.73	12%	-1.08	BDL
L3_16	60.18	3.11	5%	-1.53	BDL
L3_11	73.63	8.84	12%	-0.46	BDL
HL_6	84.33	1.84	2%	0.39	BDL
HL_8	83.90	5.59	7%	0.35	BDL
HL_3	85.15	12.09	14%	0.45	BDL

To improve the method, PFBHA solutions were purged with Argon for 3 minutes and this had indeed helped to lower the formaldehyde levels in blanks. With this minor modification, calibration curves were obtained with two different fibers (Figure 21) and the results are given in the table 5.

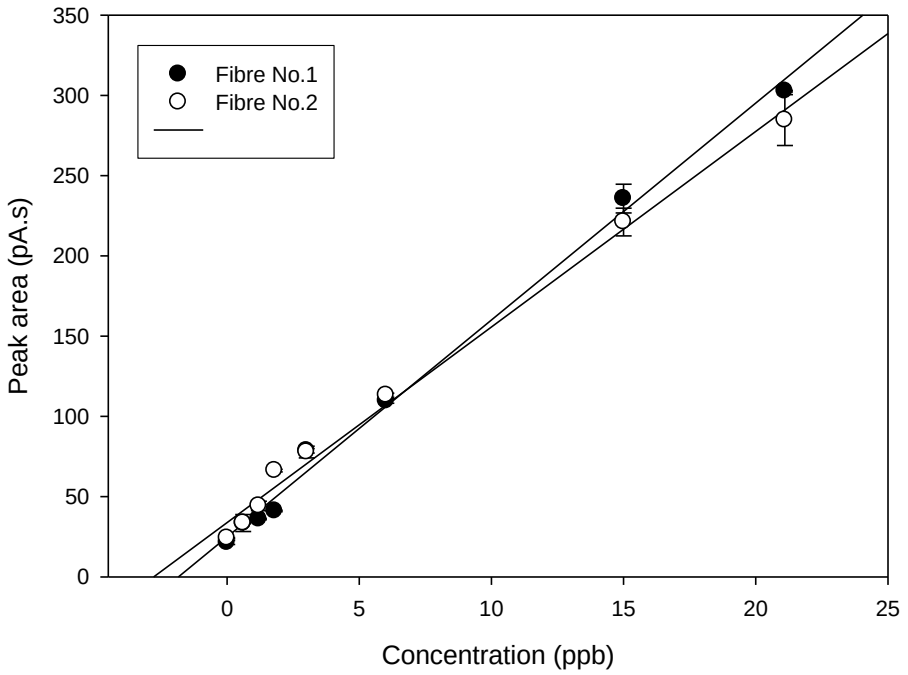


Figure 21: Formaldehyde oxime peak area as a function of concentration with two different PDMS/DVB fibres (n=2, error bars are standard deviations)

Table 5: The limit of detection from the calibration curve for determination of formaldehyde using two different fibers (Limit of detection = three times the standard deviation of the blank divided by the slope)

Fibre Number	**LOD (ppb)**
16.3	0.0914 ± 0.0031
16.1	0.278 ± 0.018

The method developed using on-fibre derivatization of formaldehyde using PFBHA gave a detection limit of 100-300 ppt. The two fibers had different sensitivity resulting in two different detection limits, emphasizing that each fibre should be calibrated separately. This is a drawback of this methodology since, in field application for instance, every fibre must be calibrated before use and doing so consumes time and therefore multiple fibers and consistent sampling are required. In addition, if the fibre is damaged during an analysis, it must be repeated with another fibre which should again be calibrated.

3.8 Comparison of modes of sampling

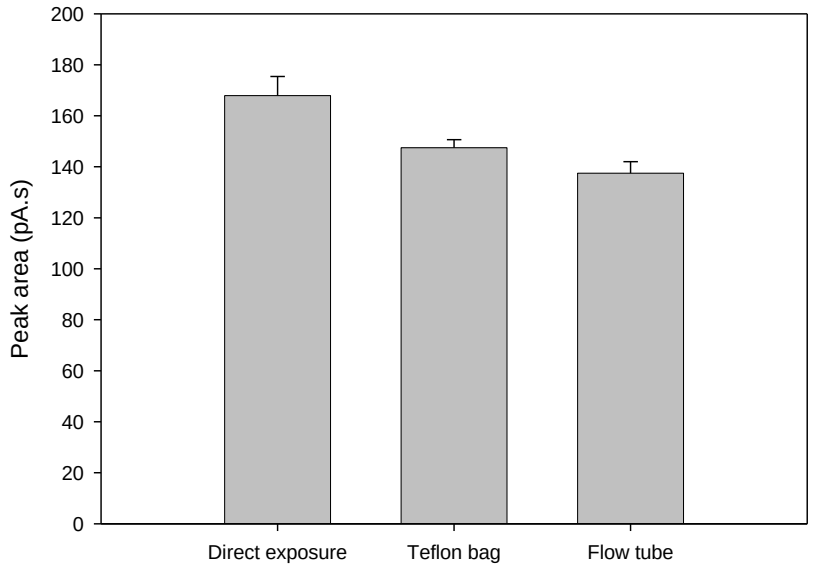


Figure 22: Comparison between three different modes of sampling (n =2, error bars are standard deviations)

Air sampling can be done in several ways. The first and easy way is to expose the fibre directly into the air, retract back inside after sampling, bring it to the lab and analyze. This second way is to flush the FEP sampling bag (same volume as the one used for standard preparation), flush it three times with the air using peristaltic pump, fill it with the air, extract, and then analyze. Another way is to use a flow tube where the air is pumped at a certain flow rate (0.7L/min) for 30 minutes and extract, and then analyze. The results obtained were statistically different ($F_{Statistical} = 16.61 > F_{critical} = 9.55$). However, the last two methods required usage of Teflon tubes, metal connections and peristaltic pumps. This introduces more sources of error and possible ways to lose formaldehyde and thus lose sensitivity due to its adsorption on to other materials and therefore directly

exposing the fibre is preferred. Further investigation regarding this will be done in the future.

Using direct exposure of the fibre mode of sampling, several sites in McGill University were sampled. The results obtained are given below.

Table 6: Results from several sampling sites at McGill University

Sampling site	**Concentration (ppb)**
Chemistry lab 1	9.28 ± 0.26
Chemistry lab 2	12.36 ± 0.11
Outside library	11.75 ± 0.57
Basement	6.79 ± 0.01
Campus terrain	7.17 ± 0.04

The results showed typical concentrations that are expected for indoor and polluted outdoor air. The spread in the relative standard deviations from 0.1% to 5% can be attributed to the variability of light intensity of different light sources in indoors and cloud coverage in outdoor and thus the fluctuations in the photolysis and hydroxyl radical concentrations which influences the formaldehyde concentrations.

A method developed for determination of formaldehyde would be more useful if it can probe the difference in concentration of formaldehyde in air and such method was developed in this study. In order to examine this, the air from campus terrain was sampled at different times in a day for several days and the result is given in figure 23.

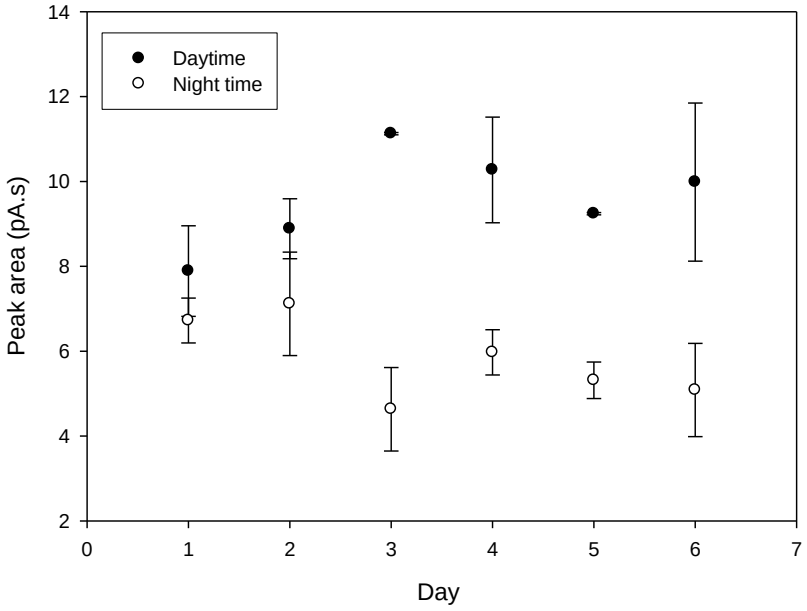


Figure 23: Formaldehyde concentration at two different times in a day. (Day time = around 1.30pm -3.00 pm; evening time = 7.30pm-9.00 pm; n=2; Fibre number 16.1)

As can be seen from the figure above, formaldehyde concentrations at day time was higher than that at night time in most of the cases and comparable in few cases. In both day time and night time, reaction with hydroxyl radicals, photolysis and other reactions take place in the air. During the day time, photolysis of other compounds and of ozone is very effective. Hydroxyl radicals are formed efficiently in the day time by photolysis of ozone (Equation 1 and 3). Therefore, all higher weight hydrocarbons react with OH more efficiently and a higher amount of formaldehyde concentration is observed.

In some cases, however, sources and sinks of formaldehyde during the daytime and night time may be comparable and such is observed. Further sampling over a month or so might give further insight and simultaneous measurements of other

carbonyls would also increase our knowledge of the processes and the differences that take place in the day and night time.

In any sampling method, it would be convenient if the samples can be stored without losing their integrity, brought back and analyzed at the lab. This would eliminate the need of bringing the instruments to the location and would facilitate the analysis, reduce the cost and labor involved in transportation of the instruments. It has been suggested that capping the tip of the sampled fibre with Thermogreen septa, Teflon faced silicon septa or stainless steel tubing with dead end tight glass tubing and storing in a refrigerator in a box filled with dry ice may be an efficient way for storing fibers [52]. Keeping the loaded fibers at low temperature would decrease fibre/air partition coefficient and thus would enable one to store the fibre for a period of time. In order to check this, the loaded fibers were capped with the Thermogreen septa, laid on aluminum foil and were placed in a dry-ice packed Styrofoam box and were compared to the one that was capped with the septa and kept at room temperature. The results were inconclusive as to how effective they are and it will be further investigated in the future.

4. Conclusion and future work

4.1 Conclusion

We developed a methodology for the determination of formaldehyde in unpolluted air where it's mixing ratio range from 0.3 to 2 ppbv. Formaldehyde was derivatized on the solid-phase microextraction fibre (SPME) which combines sampling and pre-concentration to one single step with no other additional chemicals. The fibre was first doped with the derivatizing agent (PFBHA), then exposed to formaldehyde and was the oxime that formed was desorbed into the GC column and was analyzed with FID detector. A detection limit of 100-300 ppt was obtained. Few samples, both from outside air and indoor air were sampled to show the versatility of the method and application for real time measurements. SPME sampling and GC-portable would allow fast on-site analysis and therefore reduce the potential transport effect.

4.2 Future work

Any new developed method requires validation with an existing, approved method. For determination of formaldehyde in unpolluted air, EPA approved method consists of extracting formaldehyde with DNPH coated silica cartridges where it is derivatized to a hydrazones which would then be analyzed using UV-detector. As our labs moved twice during last few months, we were not able to do the comparison. Therefore the validation is yet to be done in the coming in the future. In addition, SPME sampling would be generalized for determination of other larger molecular weight carbonyl compounds as well. This generalization can be simpler since they are not abundant in the lab air and thus the background

contamination would be very much lower and thus resulting in lower detection limits.

The analysis done on the marine air from the Labrador Sea was unfortunately not successful at our initial detection limit. However, after improving the detection limit, it is now possible to analyze the clean marine air. This will be done in the St-.Laurent River in the future. Storage of the PFBHA loaded fibre, and then the formaldehyde sampled fibre will be further investigated. Further improvements in manufacturing these fibre coatings must be also done to take at least the fibers from the same lot to have the same sensitivity within experimental errors. In addition, it is preferable to make these coatings more robust so that fibre damages can be reduced.

Appendix

Table 1A Conversion between units of concentration in ppm, ppb, ppt and molecules cm^{-3} (assumption: 1 atm, 25 °C)

Parts per	**Unit**	**Molecules, atoms or radicals /cm^3**
$\mathbf{10^6}$	1 ppm	2.46×10^{13}
$\mathbf{10^8}$	1 pphm	2.46×10^{11}
$\mathbf{10^9}$	1 ppb	2.46×10^{10}
$\mathbf{10^{12}}$	1 ppt	2.46×10^{7}

$$1\frac{\mu g}{m^3} = ppm \times 40.9\ (MW) = pphw\ \times 0.409\ (MW) = ppb\ \times 0.0409\ (MW)$$
$$= ppt\ \times (4.09 \times 10^{-5})(MW)$$

Table 2A Conversion of other relevant units

Temperature	1K = 273 .15+ 1°C
Pressure	1 atm = 760 torr = 101.3kPa

Gas constant (R) = 8.314472 J/K.mol = 0.082057 L atm/ K mol

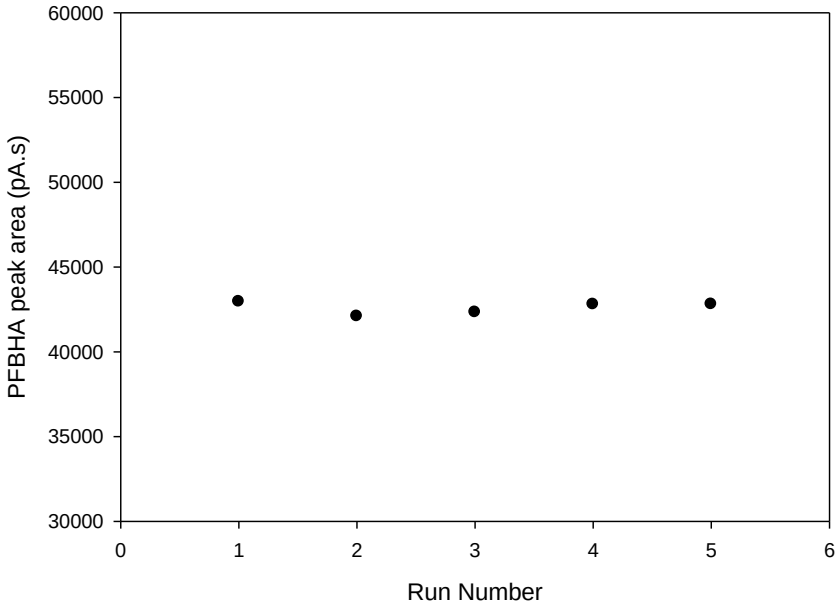


Figure 1A Examination of PFBHA extraction reproducibility

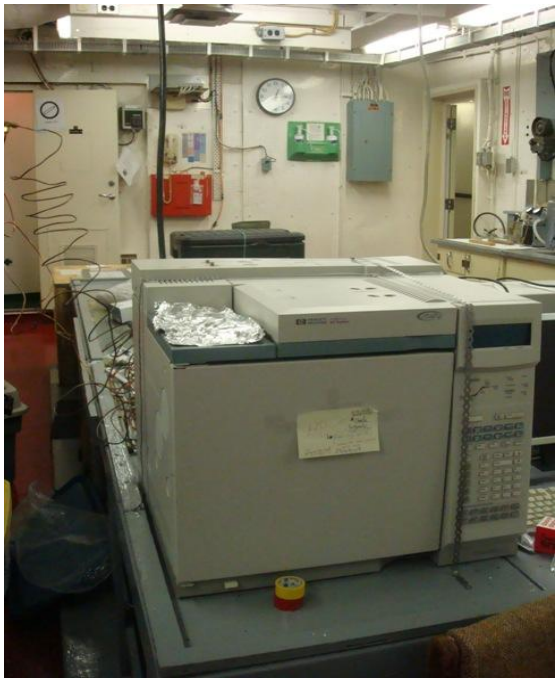


Figure 2A: The GC at the lab in CCGS Hudson during Labrador Mission 2009

Figure 3A. Ozone and Nox analyzers in CCGS Hudson during Labrador Mission 2009

Figure 4A: Gas cylinders for the GC in CCGS Hudson during Labrador Mission 2009

Table 3A: Ozone and NO_x data obtained for the marine air collection sites during the Labrador Mission 2009

Station No	Event No	Type	Date	O_3 (ppb)	NO (ppb)	NO_2(ppb)	NO_x (ppb)
L3_22	28	FEP bag	20-May-09	47.9	N/A	N/A	N/A
L3_27	49	FEP bag	21-May-09	45.3	0.6	2.5	3.1
L3_27	50	Canister	21-May-09	44.4	0.6	2.5	3.1
L3_19	85	FEP bag	22-May-09	34	0.3	1	1.2
L3_19	87	Canister	22-May-09	34	0.3	1	1.2
L3_16	113	FEP bag	23-May-09	27.5	-0.2	0.3	0.1
L3_16	116	Canister	23-May-09	27.5	-0.2	0.3	0.1
L3_11	165	FEP bag	25-May-09	29.5	0.2	1	1.1
L3_11	166	Canister	25-May-09	29.5	0.2	1	1.1
HA_6	190	FEP bag	29-May-09	37.5	0.3	0.9	1.1
HA_6	191	Canister	29-May-09	37.5	0.3	0.9	1.1
HA_8	198	FEP bag	30-May-09	27.7	0.6	0.9	1.6
HA_8	199	Canister	30-May-09	27.7	0.6	0.9	1.6

References

1. J.Finlayson-Pitts, B. and J. James N.Pitts, *Chemsitry of Upper and Lower Atmosphere*, New York: Academic Press, Inc.
2. Carlier, P., H. Hannachi, and G. Mouvier, *THE CHEMISTRY OF CARBONYL-COMPOUNDS IN THE ATMOSPHERE - A REVIEW.* Atmospheric Environment, 1986. **20**(11): p. 2079-2099.
3. Koppmann, R., *Volatile Organic Compounds in the Atmosphere*. 2007, Germany: Blackwell Publishing.
4. Wang, Q., J. O'Reilly, and J. Pawliszyn, *Determination of low-molecular mass aldehydes by automated headspace solid-phase microextraction with in-fibre derivatisation.* Journal of Chromatography A, 2005. **1071**(1-2): p. 147-154.
5. Matsumoto, K., S. Kawai, and M. Igawa, *Dominant factors controlling concentrations of aldehydes in rain, fog, dew water, and in the gas phase.* Atmospheric Environment, 2005. **39**(38): p. 7321-7329.
6. A.Martos, P. and J. Pawliszyn, *Sampling and determination of formaldehyde using solid-phase microextraction with on-fibre derivatization.* Anal. Chem, 1998. **70**: p. 2311-2320.
7. Kieber, R.J., X. Zhou, and K. Mopper, *Formation of Carbonyl Compounds from UV-Induced Photodegradation of Humic Substances in Natural Waters: Fate of Riverine Carbon in the Sea.* Limnology and Oceanography, 1990. **35**(7): p. 1503-1515.
8. Nuccio, J., P.J. Seaton, and R.J. Kieber, *Biological Production of Formaldehyde in the Marine Environment.* Limnology and Oceanography, 1995. **40**(3): p. 521-527.
9. Zhou, X. and K. Mopper, *Photochemical production of low-molecular-weight carbonyl compounds in seawater and surface microlayer and their air-sea exchange.* Marine Chemistry, 1997. **56**(3-4): p. 201-213.
10. Sumner, A.L., et al., *Atmospheric chemistry of formaldehyde in the Arctic troposphere at Polar Sunrise, and the influence of the snowpack.* Atmospheric Environment. **36**(15-16): p. 2553-2562.
11. P.A.Ariya, et al., *Measurements of C2-C8 hydrocarbons during the Polar Sunrise Experiment 1994: Further evidence for halogen chemistry in the Arctic troposphere.* Journal of Geophysical Research, 1998. **103**(D11): p. 13169-13180.
12. Sumner, A.L. and P.B.Shepson, *Snowpack production of formaldehyde and its effect on the Arctic troposphere.* Nature, 1999. **398**(6724): p. 230-233.
13. Dassau, T.M., et al., *Investigation of the role of the snowpack on atmospheric formaldehyde chemistry at Summit, Greenland.* J. Geophys. Res., 2002. **107**(D19): p. 4394.
14. Tuazon, E.C., et al., *A kilometer pathlength fourier-transform infrared system for the study of trace pollutants in ambient and synthetic atmospheres.* Atmospheric Environment (1967), 1978. **12**(4): p. 865-875.

15. Fried, A., et al., *Airborne tunable diode laser measurements of formaldehyde.* Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy, 1999. **55**(10): p. 2097-2110.
16. Harris, G.W., et al., *Measurements of formaldehyde in the troposphere by tunable diode laser absorption spectroscopy.* Journal of Atmospheric Chemistry, 1989. **8**(2): p. 119-137.
17. Thomas, C.P., C.D. McGill, and R. Towill, *Determination of formaldehyde by conversion to hexahydrooxazolo[3,4-a]pyridine in a denuder tube with recovery by thermal desorption, and analysis by gas chromatography mass spectrometry.* Analyst, 1997. **122**(12): p. 1471-1476.
18. Nishikawa, H. and T. Sakai, *DERIVATIZATION AND CHROMATOGRAPHIC DETERMINATION OF ALDEHYDES IN GASEOUS AND AIR SAMPLES.* Journal of Chromatography A, 1995. **710**(1): p. 159-165.
19. Grosjean, D. and K. Fung, *Collection efficiencies of cartridges and microimpingers for sampling of aldehydes in air as 2,4-dinitrophenylhydrazones.* Analytical Chemistry, 1982. **54**(7): p. 1221-1224.
20. Kuwata, K., et al., *DETERMINATION OF ALIPHATIC-ALDEHYDES IN AIR BY LIQUID-CHROMATOGRAPHY.* Analytical Chemistry, 1983. **55**(12): p. 2013-2016.
21. Kuntz, R., et al., *RAPID-DETERMINATION OF ALDEHYDES IN AIR ANALYSES.* Analytical Letters Part a-Chemical Analysis, 1980. **13**(16): p. 1409-1415.
22. Lipari, F. and S.J. Swarin, *Determination of formaldehyde and other aldehydes in automobile exhaust with an improved 2,4-dinitrophenylhydrazine method.* Journal of Chromatography A, 1982. **247**(2): p. 297-306.
23. Tuß, H., et al., *Method for determination of formaldehyde in air in the pptv-range by HPLC after extraction as 2,4-dinitrophenyl-hydrazone.* Fresenius' Journal of Analytical Chemistry, 1982. **312**(7): p. 613-617.
24. Arnts, R.R. and S.B. Tejada, *2,4-Dinitrophenylhydrazine-coated silica gel cartridge method for determination of formaldehyde in air: identification of an ozone interference.* Environmental Science & Technology, 1989. **23**(11): p. 1428-1430.
25. Marsella, A.M., J.T. Purdham, and S.A. Mabury, *A New Method for the Measurement of Airborne Formaldehyde Using Derivatization with 3,5-Bis(Trifluoromethyl) Phenylhydrazine and Analysis by GC-ECD and GC-MS/SIM.* International Journal of Environmental Analytical Chemistry, 2000. **76**(3): p. 241 - 256.
26. Sakai, T., et al., *Fluorimetric flow injection analysis of trace amount of formaldehyde in environmental atmosphere with 5,5-dimethylcyclohexane-1,3-dione.* Talanta, 2002. **58**(6): p. 1271-1278.
27. Pinheiro, H.L.C., et al., *Spectrofluorimetric determination of formaldehyde in air after collection onto silica cartridges coated with Fluoral P.* Microchemical Journal, 2004. **78**(1): p. 15-20.

28. Altshuller, A.P., D.L. Miller, and S.F. Sleva, *Determination of Formaldehyde in Gas Mixtures by the Chromotropic Acid Method.* Analytical Chemistry, 1961. **33**(4): p. 621-625.
29. Vianello, F., et al., *On-line detection of atmospheric formaldehyde by a conductometric biosensor.* Biosensors & Bioelectronics, 2007. **22**(6): p. 920-925.
30. Yu, Y.K., et al., *Development of a compound-specific carbon isotope analysis method for atmospheric formaldehyde via NaHSO3 and cysteamine derivatization.* Analytical Chemistry, 2006. **78**(4): p. 1206-1211.
31. Miksch, R.R., et al., *Modified pararosaniline method for the determination of formaldehyde in air.* Analytical Chemistry, 1981. **53**(13): p. 2118-2123.
32. Jobson, B.T. and J.K. McCoskey, *Sample drying to improve HCHO measurements by PTR-MS instruments: laboratory and field measurements.* Atmospheric Chemistry and Physics. **10**(4): p. 1821-1835.
33. S.Inomata, et al., *Technical note: Determination of formaldehyde mixing ratios in air with PTR-MS: Laboratory experiments and field measurements.* Atmos. Chem.Phys, 2008. **8**: p. 273-284.
34. Gilpin, T., et al., *Intercomparison of six ambient [CH2O] measurement techniques.* J. Geophys. Res., 1997. **102**(D17): p. 21161-21188.
35. Vairavamurthy, A., J.M. Roberts, and L. Newman, *Methods for determination of low molecular weight carbonyl compounds in the atmosphere: A review.* Atmospheric Environment. Part A. General Topics, 1992. **26**(11): p. 1965-1993.
36. Hopkins, J.R., et al., *A simplified apparatus for ambient formaldehyde detection via GC-pHID.* Atmospheric Environment, 2003. **37**(18): p. 2557-2565.
37. Lawson, D.R., et al., *Formaldehyde Measurement Methods Evaluation and Ambient Concentrations During the Carbonaceous Species Methods Comparison Study.* Aerosol Science and Technology, 1990. **12**(1): p. 64-76.
38. Sirju, A.P. and P.B. Shepson, *LABORATORY AND FIELD INVESTIGATION OF THE DNPH CARTRIDGE TECHNIQUE FOR THE MEASUREMENT OF ATMOSPHERIC CARBONYL-COMPOUNDS.* Environmental Science & Technology, 1995. **29**(2): p. 384-392.
39. Benning, L. and A. Wahner, *Measurements of Atmospheric Formaldehyde (HCHO) and Acetaldehyde (CH3CHO) during POPCORN 1994 Using 2.4-DNPH Coated Silica Cartridges.* Journal of Atmospheric Chemistry, 1998. **31**(1): p. 105-117.
40. Heikes, B., et al., *Formaldehyde over the central Pacific during PEM-Tropics B.* J. Geophys. Res., 2001. **106**(D23): p. 32717-32731.
41. Pawliszyn, J., *Solid Phase Microextraction: Theory and Practice*. 1997, New York: Wiley-VCH.
42. Wercinski, S.A.S., *Solid Phase Microextraction: A Practical Guide*. 1999, California: Marcel Dekker, Inc.

43. Gorecki, T., X. Yu, and J. Pawliszyn, *Theory of analyte extraction by selected porous polymer SPME fibres.* The Analyst, 1999. **124**: p. 643-649.
44. Ouyang, G. and J. Pawliszyn, *SPME in environmental analysis.* Anal Bioanal Chem, 2006. **386**: p. 1059-1073.
45. Alpendurada, M.d.F., *Solid-phase microextraction: a promising technique for sample preparation in environmetnal analysis.* Journal of Chromatography A, 2000. **889**: p. 3-14.
46. Prosen, H. and L. Zupancic-Kralj, *Solid-phase microextraction.* Trends in analytical chemistry, 1999. **18**(4): p. 272-282.
47. J.S.Aulakh, et al., *A Review on Solid Phase Micro Extraction—High Performance Liquid Chromatography (SPME-HPLC) Analysis of Pesticides* Critical Reviews in Analytical Chemistry, 2005
35(1): p. 71-85.
48. A.Koziel, J., J. Noah, and J. Pawliszyn, *Field sampling and determination of formaldehdye in indoor air with solid-phase microextraction and on-fiber derivatization.* Environmental Science & Technology, 2001. **35**: p. 1481-1486.
49. Crissman, J., *Deactivating glass surface with dimethyldichlorosilane (DMDCS).*
50. Ai, J., *Solid phase microextraction for quantitative analysis in nonequilibrium situations.* Anal. Chem, 1997. **69**: p. 1230-1236.
51. Z.Zhang and J. Pawliszyn, *Quantitative extraction using an internally cooled solid phase microextraction device* Analytical Chemistry, 1995. **67**(34-43).
52. Chai, M. and J. Pawliszyn, *Analysis of Environmental Air Samples by Solid-Phase Microextraction and Gas Chromatography/Ion Trap Mass Spectrometry.* Environmental Science & Technology, 1995. **29**(3): p. 693-701.