A Detailed Justification for the Selection of a Novel Mine Tracer Gas and Development of Protocols for GC-ECD Analysis of SPME Sampling in Static and Turbulent Conditions for Assessment of Underground Mine Ventilation Systems

Susanne Whitney Underwood

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Kray Luxbacher
Nino Ripepi
Emily Sarver

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Abstract

Tracer gas surveys are a powerful means of assessing air quantity in underground mine ventilation circuits. The execution of a tracer gas style ventilation survey allows for the direct measurement of air quantity in locations where this information is otherwise unattainable. Such instances include inaccessible regions of the mine or locations of irregular flow. However, this method of completing a mine ventilation survey is an underused tool in the industry. This is largely due to the amount of training required to analyze survey results. As well, the survey is relatively slow because of the time required to perform analysis of results and the time required to allow for the total elution of tracer compounds from the ventilation circuit before subsequent tracer releases can be made. These limitations can be mitigated with the development of a protocol for a novel tracer gas which can be readily implemented with existing technology. Enhanced tracer gas techniques will significantly improve the flexibility of ventilation surveys. The most powerful means to improve tracer gas techniques applied to mine ventilation surveys is to alter existing protocols into a method that can be readily applied where tracer surveys already take place.

One effective method of enhancing existing tracer gas survey protocols is to simply add a second tracer gas that can be detected on a gas chromatograph – electron capture detector (GC-ECD) using the same method as with the existing industry standard tracer, sulfur hexafluoride (SF_6). Novel tracer gases that have been successfully implemented in the past called for complex analysis methods requiring special equipment, or were designed for inactive workings.

Experimentation with perfluoromethylcyclohexane (PMCH) and SF_6 allowed for ideal

chromatographic results. PMCH is a favorable selection for a novel tracer to work in tandem

with SF_6 due to its chemical stability, similar physical properties and detection limits to SF_6, and

its ability to be applied and integrated into an existing system. Additionally, PMCH has been

successfully utilized in other large-scale tracer gas studies.

      Introduction of a novel tracer gas will make great strides in improving the versatility of

underground tracer gas ventilation surveys, but further improvement to the tracer gas technique

can be made in simplifying individual steps. One such step which would benefit from

improvement is in sampling. Solid phase microextraction (SPME) is a sampling method that is

designed for rapid sampling at low concentrations which provides precise results with minimal

training. A SPME extracting phase ideal for trace analysis of mine gases was selected and a GC-

ECD protocol was established. The protocol for fiber selection and method optimization when

performing trace analysis with SPME is described in detail in this thesis. Furthermore, the

impact of sampling with SPME under varying turbulent conditions is explored, and the ability of

SPME to sample multiple trace analytes simultaneously is observed.

Acknowledgements

Table of Contents

List of Figures

List of Tables

1 Introduction

1.1 Preface

This thesis contains three primary documents which have been submitted for scholarly review or are prepared for submittal. Chapter 3, *Selection of a novel mine tracer gas for assessment of ventilation systems in underground mines*, was submitted to the 2012 SME peer review conference proceedings and was presented at said conference in Seattle, WA. Chapter 4, *Gas chromatograph- electron capture detector method for solid phase microextraction sampling of mine gases*, has been submitted to the Journal of Chromatography A and is currently under review. Chapter 5, *Evaluation of solid phase microextraction as a sampling method in turbulent conditions and for the simultaneous sampling of multiple trace analytes*, is ready for submission to the Journal of Occupational and Environmental Hygiene. Additionally, a literature review introducing tracer gas analysis and its application to mine ventilation surveys, perfluorocarbon tracers, and solid phase microextraction is included.

1.2 Background

Mine ventilation surveys executed via tracer gas surveys are a direct means of determining air quantity in an underground ventilation circuit. The application of a tracer gas survey allows for the measurement of air quantity in locations of a mine with irregular flow or where the cross-sectional area cannot be measured to accommodate a more traditional mine ventilation survey, as well as locations which are inaccessible to personnel [1]. Unfortunately, tracer gas surveys are an underused tool in the mining industry, however, due to the large amount of training required to analyze the results as well as the process being relatively slow. While a tracer gas survey is a powerful tool, the time necessary to gather all pertinent information can be daunting due to the time required to transport the gas samples from the collection site to the location where they can be analyzed, as well as the time necessary for the applied tracer to completely elute from the ventilation circuit before another tracer release can take place.

1.3 Objectives

While the scope of this research project is large, two primary objectives are addressed in this thesis. The objectives addressed in this thesis are designed to meet the objectives of the research project, but also to enhance existing tracer gas survey protocols as applied in the mining industry. The research objectives listed below are discussed in the following sections.

- Objective 1: Improve existing methodologies for tracer gas surveys by making them more flexible and to reduce the time required to execute a comprehensive survey

- Objective 2: Investigate sampling methods which will simplify tracer gas surveys on-site that can be easily integrated into existing protocols

1.3.1 Objective 1

The major factor hindering tracer gas surveys in underground mines is the existence of only one industry standard tracer gas: sulfur hexafluoride (SF_6) [2]. SF_6 is used as the industry standard because it is a non-toxic compound which is chemically and thermally stable. It exists as a gas with a minute atmospheric presence of 3 molar parts per trillion (ppt) in the ambient atmosphere [3]. This tracer gas is easily detected down to a few parts per trillion when performing analysis with a gas chromatograph with an electron capture detector (GC-ECD) [2]. Limitations arise with the use of only one tracer gas because only parameters under investigation can be observed, eliminating the ability to monitor baseline conditions. Additionally, the application of only one tracer reduces the number of data points which can be collected. Most significantly, the execution of a comprehensive ventilation survey requires that the circuit be observed in segments with sufficient time allowed for the total elution of the tracer gas from the mine before subsequent segments can be observed. These limitations can be mitigated with the development of a protocol for a novel tracer gas which can be used in tandem with SF_6.

This thesis will discuss the selection of a tracer gas novel to the mining industry. The protocol for adjusting existing analysis methods employing SF_6 will be discussed. This thesis will also emphasize the non-toxic nature of the selected tracer compound such that it may be released in active workings of underground mines. Additionally, the response of the selected tracer will be discussed in relation to the response of SF_6 to analysis systems.

1.3.2 Objective 2

When tracer gas surveys are executed at underground mines, samples are often shipped to off-site laboratories for analysis, eliminating the need for miner training in gas chromatography analytical methods. This practice leaves the major need for miner training in the realm of sampling. Traditional sampling mechanisms in underground mines include glass syringe bottles with tight fitting rubber stoppers [4], disposable plastic syringes and Tedlar bags [2], and evacuated containers [5]. The performance of these sampling mechanisms was previously evaluated for the broader research project [6], but the application of solid phase microextraction (SPME) was reevaluated in this thesis.

SPME sampling was reevaluated due to the limited training required to apply the sampling mechanism on-site and the robust, precise results consistently obtained with its application. This thesis will detail the selection process of the appropriate SPME fiber for mine ventilation surveys, as well as a protocol for developing an optimized method for sample analysis with a GC-ECD. Furthermore, the impact of sampling with SPME under turbulent conditions and sampling multiple mine tracer gases simultaneously will be studied.

2 Literature Review

2.1 Introduction to Trace Analysis

Gas chromatography (GC) is the premiere technique employed to achieve separation and analysis of volatile compounds. GC is used to analyze both organic and inorganic compounds of any phase including gases, liquids, and solids. GC allows for rapid analysis which is simultaneously efficient and sensitive. Methods used in GC analysis allow for quantitative analysis of small samples while achieving high accuracy at a relatively low cost. The primary limitation of GC analysis is limited to the characteristics of the sample. Analytes must be volatile and must not be thermally labile. Large samples of pure compounds and samples that require intense preparation are also a limiting factor. Finally, GC analysis alone cannot be used to identify or confirm the identity of a peak. A secondary method such as GC with mass spectrometer is necessary for confirmation of peak identity [7].

The instrumentation of a GC unit includes five primary components: sample inlet, column, oven, detector, and data system. When a sample is injected into a GC unit, it is injected at the sample inlet. A carrier gas constantly flows through the sample inlet through the column, and finally to the detector. The carrier gas serves as a vehicle for transporting the sample through the system. The flow rate of the carrier gas is controlled to ensure reproducible retention times. Upon departure from the sample inlet, the sample flows with the carrier gas into the column, which is enclosed in the oven. The oven maintains the temperature of the column allowing for isothermal analysis (constant temperature) or analysis using temperature programming. Columns in a GC system can either be packed or capillary. If a capillary column is used, it may be either a wall coated open tubular (WCOT), porous layer open tubular (PLOT), or a support-coated open tubular (SCOT) column. Each type of column contains a mobile and

stationary phase. While the sample is inside the column, the individual components within the sample partition between the gas and liquid phases creating separation based upon the relative solubility of the components in the liquid phase and the sample relative vapor pressures. Separation allows for the components of the sample to pass through the detector individually for quantification. [7].

The selection of the detector for a GC unit defines the types of analytes which may be observed in the unit. While many specialized detectors exist for GC units, the most popular detectors include the flame ionization detector (FID), the thermal conductivity detector (TCD), and the electron capture detector (ECD) [7]. The FID is the most widely used GC detector. The FID employs an oxy-hydrogen flame to burn the sample to produce ions. The ions are collected and an ion current is produced. The FID allows for sensitive analysis for organic compounds only and is a stable analysis method with excellent linearity [8]. The TCD is a differential detector that employs filaments incorporated into a Wheatstone Bridge circuit that measures the thermal conductivity of the analyte in the carrier gas in comparison with the thermal conductivity of the carrier gas alone. The TCD is universal with moderate sensitivity and linearity [9]. The ECD is a highly sensitive, highly selective detector with only fair linearity that is employed for compounds that capture electrons [10]. The ECD uses a ^{63}Ni source that releases radioactive β^- particles. The β^- particles then collide with the make-up gas, nitrogen. The results of collision include the production of free electrons with a high standing current. When an electronegative analyte elutes from the column and enters the detector, it captures free electrons. The ECD measures the difference in the standing current and the reduced current when the analyte captures free electrons [7].

2.2 Overview of Trace Analysis Applied to Mine Ventilation Surveys

Ventilation controls exist in underground mines to provide a sufficient quantity and quality of air to locations of the mine where personnel travel and work. The air supplied to personnel should be safe to breath and provide reasonable comfort [1]. The ability to measure air quantity is important to be able to determine the adequacy of existing ventilation systems in underground mining operations. Additionally, the knowledge of air quantity will aid in rescue and recovery efforts in a post mine-disaster situation. As such, the measurement of air quantity through mine ventilation surveys occurs in all underground coal mines. Air quantity is typically determined using Equation 2.1. Q is the quantity of air measured in ft^3/min, A is the cross-sectional area at the point of measurement recorded in ft^2, and V is the air velocity in units of ft/min. When air quantity is calculated, the cross-sectional area and the air velocity must be measured. Common methods of determining air velocity include the use of smoke tubes, vane anemometers, velometers, and pitot tubes [11]. The cross-sectional area is typically measured directly.

$$Q = AV \hspace{5cm} \text{Equation 2.1}$$

Determination of air quantity using direct measurement (i.e., via Equation 2.1) is common because it is a rapid method with a low cost. However, in situations where direct measurements of air velocity and/or cross-sectional area may not be observed, other methods of determining air quantity must be applied. One such method of quantifying airflow is the tracer gas technique. In addition to being applicable to locations inaccessible to personnel, due to either location or safety in the case of an emergency, and locations of irregular cross-sectional area, the tracer gas technique for ventilation surveys may be used in areas of the mine where flow is irregular [11]. Tracer gas surveys may also be employed in locations of excessively

turbulent flow, such as a main shaft [1]. Furthermore, tracer gas surveys are favorable in situations where there is any of the following conditions exist: there is recirculation of return air into intake air, there is leakage from adjacent mines, there is lost air, or there are unknown transit flow times through stoped areas [12].

The tracer gas technique allows for the direct measurement of the air quantity by controlling the injection rate of tracers into the observed ventilation circuit, which provides a means of measuring air flow [1]. Following the release of the tracer gas into the mine atmosphere, the gas is recaptured and analyzed in a gas chromatograph (GC) to determine the air quantity. Tracer gases that have been used to varying degrees of success in mine surveys include hydrogen, nitrous oxide, carbon dioxide, ozone, radioactive krypton 85, and sulfur hexafluoride (SF_6) [1].

2.2.1 Performance of a Mine Ventilation Tracer Gas Survey

Tracer gas surveys can be accomplished through two different methods. The first method is a continuous release of tracer which allows for a steady state to develop downstream of the release point and is best applied to high velocity airways. Once the tracer gas has been sufficiently mixed into the mine air downstream, samples are collected so that the concentration of tracer present can be observed [1]. Analysis of concentration of the tracer is achieved through GC analysis. The air quantity is then determined using Equation 2.2. Again, Q is the quantity of air measured in ft^3/min, Q_g is the feed rate of the tracer measured in ft^3/min, and C is the concentration of the tracer gas in the sample measured in ft^3/ft^3 [11].

$$Q = \frac{Q_g}{C}$$ Equation 2.2

The other method of conducting a tracer gas survey is better applied to portions of a ventilation circuit where airflow is slow. This method requires the release of a known mass of

the tracer gas into the system. Following the release, the presence of the tracer gas is observed

downstream forming a peak with the passage of time [1]. The resultant air quantity is a function

of the various concentrations of tracer in samples over time, and can be calculated by Equation

2.3. The variables Q and Q_g have been previously defined; C_{av} is the average of the measured

concentrations in units of ft^3/ft^3, and τ_T is the total time for which tracer(s) were measured in

minutes [11].

$$Q = \frac{Q_g}{C_{av}\tau_T}$$
Equation 2.3

2.2.2 Disadvantages of Tracer Gas Mine Ventilation Surveys

The tracer gas technique of performing ventilation surveys is an advantageous tool, but

the technology is lacking due to the large amount of time required to complete a survey. The

time limitation is largely due to the fact that SF_6 is the only tracer compound applicable in the

mining industry as a standard [2]. SF_6 is a favorable tracer gas because it is non-toxic, odorless,

colorless, and both chemically and thermally stable. Additionally, SF_6 is a manmade product

which is already present at approximately 3 ppt in the ambient atmosphere [3]. SF_6 is the mining

industry standard tracer gas for ventilation surveys for the aforementioned reasons, as well as the

fact that only small volumes of the gas are required to trace large ventilation systems. Also, SF_6

may be measured accurately down to a few parts per trillion when utilizing a GC-ECD system

[2].

In addition to the time requirements of tracer gas surveys, another significant limitation is

the fact that, at present, these surveys are only performed with a single tracer. This means that

only the parameter under investigation can be monitored, and precludes monitoring of baseline

ventilation conditions. Additionally, the use of one tracer reduces the amount of data points

which could be collected to allow for a more comprehensive ventilation survey. The most

detrimental impact of having only one trace compound is the time that must be allowed for a full ventilation survey to take place. When a ventilation survey calls for multiple injects of SF_6, the survey must be divided into different portions for each injection to allow sufficient time for the previously injected tracer to elute completely from the ventilation survey. The application of additional tracers is expected to help resolve the problems associated with single-gas surveys [2].

2.2.3 Previously Studied Tracer Gases for Mining Applications

In one particular study, a selection of Freon gases, or chlorofluorocarbon gases, were tested to be used in tandem with SF_6 with the successful implementation of one as a tracer compound to be used in tandem with SF_6 [2]. Freon gases were tested as tracers because they satisfy the general tracer requirements: non-toxic, non-corrosive, non-radioactive, chemically stable, thermally stable, odorless, colorless, readily obtainable, inexpensive, easily stored and transported, of gaseous form at mine temperatures and pressures, and not naturally occurring in the environment. Additionally, Freon gases are compatible with the existing sampling systems for SF_6, and they are able to be measured in a method similar to that of SF_6. Freon gases known to have been previously tested include Freon-12, Freon-13, Freon-13B1, Freon-22, Freon-23, and Freon-116 [2]. Of the Freon gases tested, only two could be measured with sensitivity similar to that of SF_6: Freon-12 and Freon-13B1. The method used to analyze the Freon gases in tandem with SF_6 used a Perkin-Elmer Sigma model 2000 gas chromatograph paired with an electron capture detector. The method requires the application of two separate columns to be used in tandem in a parallel system incorporating a switching valve located in the oven of the gas chromatograph which allows each column to be placed in turn on stream with the detector. The system requires a molecular sieve 5A column for SF_6 and Freon-13B1 and a Porapak Type P column for Freon-12. The Freon gases were sampled using plastic syringes and tedlar bags.

Samples were collected and stored for 24 hours before analysis took place to simulate real world delays during analysis. Tedlar bags proved to be a reliable means of sample collection, but plastic syringe proved to be susceptible to sample loss, particularly during their initial use. When the plastic syringes were used for a second time, sample loss was reduced, which indicates that initial loss was probably due to adsorption of the trace compounds onto the internal part of the plastic syringe. While sample loss was reduced for plastic syringes, the amount of loss was still at an unacceptable level for Freon-13B1, reducing sampling options to only sampling via tedlar bags. The results of the experimentation with Freon gases as mine tracers was successful; however, background levels of Freon gases must be measured before analysis due to their widespread application as a refrigerant and propellant in aerosol cans [2].

Another tracer compound for which a methodology has been produced is ^{133}Xe [13]. The radioactive isotope may serve as a trace compound because it is detectable at a concentration of 4.5×10^{-10} µg/g. ^{133}Xe has a sufficiently short half-life to encourage a specific activity characteristic amenable to detection at low concentrations, but, at 5.25 days, the half-life is not so short that it will decay within the timeframe of the testing period. The decay of the tracer during testing would result in a difficult testing method that would not allow for reproducibility. ^{133}Xe is a noble gas. As such, ^{133}Xe is both chemically and physiologically inert. As a radioactive element, ^{133}Xe decays by beta emission, but it also releases gamma-rays and X-rays. The use of ^{133}Xe as a trace compound requires the use of the pulse-dilution tracer method utilizing total-count measuring for trace analysis [13].

As with conventional tracer gas technique ventilation surveys, the measurement of cross-sectional area is not required to determine air flow; however, the utilization of the total-count method for measurement of the tracer means that radioactivity is measured to indicate tracer

10

concentration. Trace analysis is completed using a radioactive detector system which contains a large-area proportional counter, amplifier, high voltage generator, and datalogger.   The radioactive detector system is sufficiently sensitive to detect ^{133}Xe because it detects both low-energy gamma-ray emitters and β emission. Radioactive trace analysis is employed in the field, and has successfully been used in model and abandoned mines. Application of the method requires baseline measurements both before and after the release and capture of the radioactive tracer, which is released in a pulse-dilution method. The duplication of baseline measurements ensures that the radioactive material has eluted from the mine [13].

Tracer gas surveys have also been applied to the evaluation of auxiliary ventilation systems, which can be heavily influenced by leakage in tubing. Formerly these airflows and pressure losses were measured using pitot tubes and pressure gauges, a method which is time consuming and can be imprecise when compared with the tracer gas method. The application of SF_6 as a tracer gas allows for the survey to be completed rapidly with only two to three persons required to complete the survey [14].

Tracer gas surveys can be used to determine the cause of anomalies within a ventilation circuit. For instance, SF_6 has been successfully used in a tracer gas survey to determine not only the presence of air movement within the sealed regions of a mine, but also the direction in which the air was moving [15]. This study ascertained the knowledge that air was leaking from old workings of another seam, and that atmospheric pressure changes have a significant impact of not only seal leakage, but also on the concentration of gas samples gathered at seal sample pipes. Additionally, SF_6 was the tracer gas employed to determine air velocity in the gob of a coal mine to determine if the caved in regions of the mine were properly ventilated. Furthermore, SF_6 was

used to determine that reverse leakage from an intake airway was cause by the pressure pulses instigated by a traveling train in the adjacent airway [15].

2.3 Introduction to Perfluorocarbon Tracers

The term perfluorocarbon tracer, or PFT, defines a group of volatile organic compounds [16] which can be individually quantified during trace analysis. The compounds are fully fluorinated hydrocarbons. The overwhelming presence of fluorine in PFTs qualifies this group of compounds as ideal tracers because they have properties such as: low atmospheric background levels, an atmospheric lifetime on the order of 3,000 years, inert qualities, and the ability to be detected at trace levels in the parts per trillion range with a GC-ECD [17]. PFTs are sensitive to detection due to their reaction with free electrons; they have great stability where their counterparts would degrade due to thermal or environmental conditions,; and they tend to be non-toxic [18]. PFTs are particularly sensitive to detection via a GC-ECD because the high number of fluorine atoms present paired with the structure of the molecules causes PFTs to have high electron affinities on the order of three eV [19]. The stability of PFTs is a direct result of the strong fluorine-carbon bond which forms the basis of their chemical structure [19].

The discussed characteristics of PFTs make them ideal tracers for a variety of applications including underground leak detection, atmospheric transport and diffusion studies, and oil and gas reservoir studies [19]. PFCs containing 1 to 4 carbon atoms are gases, 5 to 19 carbon atoms are liquids, and 20 to 24 atoms are solids [20]. The boiling points for PFCs existing as liquids range between 44.5 and 125.2^{0}C [21]. PFCs are also particularly non-polar [22]. Their non-polar state reduces their vulnerability to loss by adsorption. The susceptibility of PFTs to sample loss due to high volatility is a problem when using PFTs as liquid tracers.

2.3.1 Non-toxicity of PFTs

Due to their non-toxic nature, perfluorocarbon compounds (PFCs) have been used in a variety of medical applications. One well documented application of PFCs in the medical field is the application of a perfluorochemical liquid as a surfactant in subjects with respiratory ailments. For instance, with PFCs existing as high density compounds with low surface tension, liquid PFCs are used in partial liquid ventilation in premature infants with severe respiratory distress syndrome because they act as a surfactant, physically opening the alveoli [23]. The research stemmed from the successful application of the partial liquid ventilation treatment with perfluorochemical liquid in premature lambs ailed by respiratory distress syndrome [24]. The perfluorochemical liquid has also been used to treat congenital diaphragmatic hernia in lambs [25]. Piglets were used to model the impact of treating adults affected with respiratory distress syndrome with perfluorocarbon associated gas exchange [26]. Canine lung injuries were also successfully treated with partial liquid breathing via perfluorochemical liquid [27]. The injected PFCs leave the respiratory system via exhaled air, but trace amounts were found to remain in the subjects of the various studies. The residual PFCs present in all subjects had no adverse effects due to the non-toxic nature of PFCs.

The application of perfluorocarbon liquids in vitreoretinal surgeries, or any surgical process treating the eye, macula, or vitreous fluid, has been extensively evaluated with the discovery of no adverse effects associated with the use of these compounds [28]. Due to their non-toxic nature and their ability to carry oxygen, the ability of PFCs to serve as red blood cell substitutes has been investigated [29]. PFCs have also served as synthetic oxygen-carrying solutions in anesthetized patients during surgery without impacting the body in any manner outside of increasing the mixed venous oxygen tension in the patient [30]. PFCs have also been

used as a medium for contrast enhancement in animals and people [31]. Beyond their medical applications, perfluorocarbon resins are used in the lubricating and softening of human and animal skin due to their inert nature [32]. Due to their non-toxic nature, PFCs are the preferred tracers used to tag illicit drugs and money which come into direct contact with people [33].

2.3.2 Methods of Analysis

The analysis of PFCs is a subject which has acquired a great deal of attention due to the application of the compounds to long term atmospheric tracing experiments. The chromatographic methods of analysis have focused on the column type, the polymeric extracting phase, and detector selections. While PFCs have low polarity in common, they also have multiple degrees of polarity and varying physical properties presents a conundrum when attempting to apply one general methods to the gamut of compounds [20]. Early efforts to separate PFCs were limited to success with only the lighter of the compounds due to the existence of only packed columns. Middle weight PFCs with four to nine carbon atoms were successfully separated in a packed column with graphitized carbon black serving as the solid support coated with a moderately polar stationary phase [34]. It is likely that the greatest success when using packed columns was found with the use of graphitized carbon black as the solid support because it is completely nonpolar, is able to be heated to high temperatures accommodating a wider variety of boiling points, and it has small, nonporous particles allowing for stable suspensions and compact layers [35]. Later capillary columns were successfully used to achieve ultrasensitive and selective separation of various PFCs [36]. Further success was found with the commercial production of PLOT columns due to their affinity for fixed gases, light hydrocarbons and volatile solvents [37]. PLOT columns allow for the separation of PFCs whose boiling points are very close to one another because their application increases resolution

14

by removing liquid phase as a factor influencing the chromatographic results, and in turn eliminating column bleed [38]. Alumina chloride (Al_2O_3/Na_2SO_4) has proved to be the best stationary phase used in PLOT columns to optimize sensitivity when performing analysis of PFTs [39].

Several detectors have been used during analysis of PFCs with varying degrees of success. The TCD has been used to successfully quantify PFCs containing between four and nine carbon atoms [34]. Some PFCs, perfluoroalkanes specifically, have been successfully detected with the FID [40] with relatively low sensitivity. This low response was attributed to the dilution instigated by the carrier gas as the analytes pass over the detector [41]. Sensitivity when performing analysis of PFCs with an FID can be increased with the application of a hydrogen rich flame [42]. The most documented success achieved during the separation of PFCs has used the ECD. Early studies showed that the sensitivity of the ECD to varying PFCs ranged from low to high [43]. Since then ECD sensitivity has improved to the low parts per trillion range [44]. Femtogram levels of detection are achievable with electron-capture negative ion chemical ionization mass spectrometry [36], but it is not necessary with the achievable sensitivity of the ECD.

2.4 Applications of Perfluoromethylcyclohexane in Trace Analysis

Perfluoromethylcyclohexane (PMCH) has a molecular weight of 350 g/mol and the following chemical formula: C_7F_{14}. The chemical structure of PMCH is displayed in Figure 2-1 [45]. Having seven carbon atoms, PMCH exists as a liquid at room temperature. PMCH has a boiling point of 76^0C [46], but, like all PFCs, it is highly volatile. The density of PMCH is 1.8 g/cm^3 [47]. PMCH is non-toxic, but can be irritating to the eyes or skin when direct contact

occurs and can be irritating to the respiratory system when inhaled [48]. Symptoms are alleviated with a thorough rinsing with water.
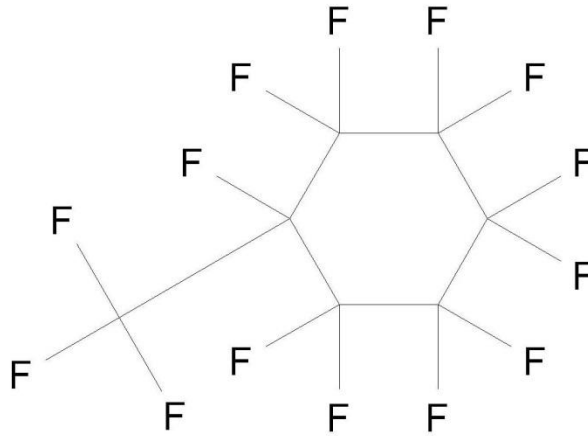
Figure 2-1: Chemical Structure of PMCH

2.4.1 Use as a Gaseous Tracer

PMCH in its standard liquid form is often used as a tracer liquid in oil and gas reservoirs, but is most commonly applied as an atmospheric tracer where it is vaporized and dispersed in its gaseous. The movement to understand the impact of humans on climate and the environment on regional and global scales has allowed for the method of releasing PFCs including PMCH to develop. PMCH was the tracer gas released in a neighborhood to understand the processes dictating flow and pollutant dispersion on this scale [49]. On a larger scale, PMCH was mixed with a stream of nitrogen gas which was then heated and enabled the release of PMCH gas from designated points in Dayton, Ohio and Sudbury, Ontario. This allowed for the simulation of the transport and diffusion of pollutants sampling 1000 km from the release points in the Cross-Appalachian Tracer Experiment [50]. The Across North America Experiment was comprised of 66 tracer releases from two locations that were sampled up to 3000 km away However, due to the frequency of releases, individual tracer plumes were not able to be separated [51]. PMCH was selected as one of the tracer gases to be used in the European Tracer Experiment to

16

determine atmospheric long-range transport models to assess the threat of point source releases across Europe. Tracer gases released from France were tracked at 168 ground stations across 20 countries [52].

Beyond long range transport and diffusion modeling PMCH is used as a tracer gas to measure air infiltration and ventilation in homes and commercial buildings and to pinpoint leak sources in a variety of systems. Methodologies employing PMCH as a tracer gas to measure the magnitude and point sources of air infiltration in home ventilation systems have been extensively developed [44]. Methodologies have also been developed for more complex ventilation circuits employing two HVAC systems. With regard to leak detection, PMCH gas can be used in tandem with other PFTs to locate and size leaks at depth within a variety of soils with resolutions of fractions of an inch [53]. PMCH has been successfully applied to leak detection applications in subsurface barriers [54] and buried natural gas pipelines [53]. PMCH can also be used as a tracer gas to improve leak testing in components of operating systems of the electric utility industry, as well as rapid screening of the seal of packaged foods [55].

2.4.2 Use in Tandem with SF_6

PMCH and SF_6 are known to be good tracer gases with a great deal of existing literature to allow for methodologies for new applications to be readily developed. Like PMCH, SF_6 has been discovered to be a powerful atmospheric tracer [3] and has been successfully employed as an atmospheric tracer gas in Perth to develop an urban dispersion model [56]. Also like PMCH, SF_6 has been used as a tracer gas to measure air infiltration rates in homes [57]. However, the analytical cost of using the two tracer gases in tandem presents significant challenges. Initial success for the simultaneous analysis of both gases was met with a two column GC system as applied in oil and gas reservoirs [58]. More recently, an alumina chloride PLOT column has

been considered, which allows for the simultaneous analysis of both PMCH and SF6 in one simple GC-ECD system [6].

2.5 Solid Phase Microextraction

Solid Phase Microextraction (SPME) is a solvent-free sampling mechanism capable of integrating sample extraction, concentration and introduction of the sample into a GC in a simple method which can be applied on-site [59]. Designed to be a sampling device for complex liquid and gaseous matrices, many of the original applications of SPME were in water analysis. SPME was developed to alleviate the disadvantages of the existing solid phase extraction (SPE) technologies. SPE is a means of liquid-liquid extraction in which analyte is absorbed onto a solid support and then desorbed by means of thermal desorption or applications of a solvent. The disadvantages of SPE include necessary modifications to the GC injector port when desorbing analytes via thermal desorption, significant increases in analysis time, high variation, and loss of analyte to the plastic SPE cartridges [60]. The resultant SPME product is an inexpensive, easy to use sampling device that has all of the advantages of SPE technologies, but few of the pitfalls.

2.5.1 Theory of SPME

SPME is a process based on equilibration; when collecting a sample with SPME, a small amount of extracting phase coats a fiber. The extracting phase collects sample for a predetermined amount of time, beginning as soon as the fiber contacts the matrix. When sufficient time is allowed, the extracting phase will reach concentration equilibrium with the matrix being sampled; once concentration equilibrium occurs, the extracting phase will no longer collect sample. This process can be described as a multiphase equilibration process where the phases considered include the extracting phase and a homogeneous matrix. The mass of analyte collected in field situations where the matrix being sampled has a very large volume is expressed

18

in Equation 2.4. The mass of analyte collected is defined as n, K_{fs} is the fiber coating-sample

matrix distribution constant, V_f is the fiber coating volume, and C_0 is the initial concentration of

a given analyte in the sample. The volume of sample collected by the SPME fiber is directly

proportional to the concentration of analyte in the matrix without any dependence on sample

volume [61].

$$n = K_{fs}V_f C_0 \hspace{5cm} \text{Equation 2.4}$$

2.5.2 Function of SPME

SPME works in two primary phases. Solute absorption from matrix onto the fiber occurs

during the first phase. A SPME fiber traditionally consists of a small amount of solid extracting

phase coated onto a small fused silica rod. Essentially, the SPME fiber functions much like an

inverted segment of a capillary column. SPME fibers can be exposed directly to headspace or

solution [62].

Transfer of analytes from the SPME fiber into the GC system occurs during the second

phase. SPME may be applied to GC or liquid chromatography (LC). Additionally, SPME is a

capable sampling method to achieve robust results when using a portable GC on-site [63] in

addition to its ability to be analyzed on a traditional GC system with either manual or automated

injections. Analytes that have adsorbed onto the fiber are thermally desorbed into the GC unit at

the sample inlet. The use of SPME requires that the sample inlet be fitted with a septa designed

for high heat applications, and a glass liner with an inner diameter of a specified inner diameter

[64].

2.5.3 Fiber Type

SPME fibers are contained within an apparatus for use, but the fiber itself consists of a

needle, plunger and fiber core. Three types of cores exist for SPME fibers. The first and

original core is the fused silica core. The fused silica core is made of standard optical quartz, and is favorable for its endurance of high heat and general durability. Fused silica, however, is fragile. Due to the fragility of fused silica, Stableflex fibers were created. Stableflex fibers are fused silica with a plastic coating. The advantage of Stableflex fibers is their flexibility. The third core available is a metal core. Metal fibers are inert because they do not contain iron. They are favorable because better bonding with the fiber coating is achieved compared to the bonding of coating with fused silica and Stableflex fibers. Additionally, metal fibers do not require glue to attach the fiber into the assembly, and there are no extraneous peaks with metal fibers. Metal fibers, however, are more expensive than the traditional fused silica and Stableflex fibers [64].

2.5.4 Fiber Coating

Common extracting phases applied to the fibers include carboxen (CAR), polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate, polyethylene glycol (PEG), and combinations of the aforementioned phases. When selecting an extracting phase for a SPME fiber, the adsorptive qualities, polarity, porosity, and coating thickness should be considered. The adsorptive qualities are largely dependent on whether the selected extracting phase is a liquid coating such as PDMS or polyacrylate or a solid coating like CAR [65]. Liquid coatings extract analyte via absorption such that the analyte partitions through the extracting phase while solid coatings extract via adsorption where the analyte collects on the surface of the extracting phase [66]. Adsorbent fibers physically trap or chemically bond analytes to the fiber. Adsorbent fibers are porous materials with high surface areas. The porous qualities of adsorbent fibers make them better for trace analysis. Additionally, increasing porosity causes the analytes to be retained more tightly. Varying pore size increase analyte selectivity. Fibers can be micro-, meso-, and macro-porous [64]. The limited capacity of adsorbent fibers causes analytes to

20

compete for sites. Absorbent fibers, on the other hand, achieve extraction by partitioning. Analytes partition into the liquid phase such that the thickness of the coating is of high importance. A coat of higher thickness increases sample capacity, but it also increases extraction time and desorption time. The elimination of competition amongst analytes for sites on the fiber allows for fibers capable of high capacity. Finally, polarity of the coating impacts the analyte selectivity. More polar phases allow for better recovery, but have a shorter life.

2.5.5 Sample Extraction and Recovery

Sample extraction with SPME is achieved by exposing the fiber to the sample. Care should be used when the fiber is exposed to ensure that it does not come into direct contact with anything but the sample due to its fragile nature. If the sample is contained, the first step in sample extraction is to pierce the sample septum with the fiber secured within the apparatus. Then the fiber should be exposed for the appropriate amount of time. Once the sampling time has elapsed, the fiber should be withdrawn back inside the apparatus. Only once the fiber is retracted should the needle be withdrawn from the sample container.

When employing SPME for sample analysis, sample extraction is affected directly by time. In order to achieve reproducibility, the fiber should be exposed to the sample for the same amount of time during each use. Every fiber reaches a point of equilibrium in which the fiber is fully saturated. This time can be measured by creating an uptake or equilibrium curve which plots the resultant peak areas as processed through a GC against the time during which the fiber was exposed to the sample matrix [67]. The time of equilibrium is influenced by kinetic effects [68].

Some such kinetic effects include stirring and agitation, which reduces the equilibrium time, and may increase the sample temperature. When stirring/agitation of the sample is

consistent, the precision for all analyses increases. While unnecessary for volatile compounds, compounds with high distribution constants require agitation. Sample extraction may also be improved with alterations to the salt and pH of the sample. Salt increases analyte uptake, but is not helpful when collecting large, nonpolar analytes. Reducing the pH for acidic compounds and increasing the pH for basic compounds will improve sample extraction. Finally, direct versus headspace sampling impacts extraction [64].

Sample recovery is performed in the same fashion as sample extraction. The SPME apparatus pierces the GC inlet septum. Following the penetration of the septum, the fiber is exposed. The analyte desorbs from the phase coating the fiber while it is exposed in the sample inlet of the GC. Following the completion of analysis, the fiber is retracted back into the SPME apparatus, at which time the apparatus may be removed from the GC unit. Sample recovery is directly impacted by fiber selection, sample modifications, extraction time, desorption conditions, inlet design, and column selection [69]. The application of SPME to sampling during the course of underground mine ventilation surveys may introduce a robust on-site sampling mechanism which could simplify survey procedures, encouraging an increase in the use of the technique.

3 Selection of a Novel Mine Tracer Gas for Assessment of Ventilation Systems in Underground Mines

3.1 Abstract

The tracer gas method of conducting ventilation surveys is a means of determining air quantity in underground mines with knowledge of the concentration of the tracer in the atmosphere and the flow rate at which the tracer is being released. The technique is useful in inaccessible areas of underground mines and areas where traditional point measurement of velocity is not practical. Sulfur hexafluoride (SF_6) is the industry standard tracer [2] used in underground mines because it is safe, stable, and not naturally occurring in the mine environment. The implementation of a second tracer will increase the versatility of the tracer gas technique allowing for simultaneous releases for the study of interrelated ventilation circuits, and for conducting multiple experiments in less time. This paper will detail the selection of perfluoromethylcyclohexane (PMCH) as a novel tracer with sensitivity, physical properties, and analysis characteristics similar to SF_6. Methods for the release of liquid PMCH into underground mines will be recommended, and the vulnerabilities of sample loss due to condensation of vapor PMCH will be explored. Finally, the benefits and implications of using PMCH as a second tracer will be discussed.

3.2 Introduction

The measurement of air quantity through mine ventilation surveys is a common occurrence in underground mining operations. The knowledge of air quantity in the mine is significant in the determination of the adequacy of existing ventilation systems, and in providing information after a mine disaster [11].

While the calculation of air quantity from the direct measurement of air velocity and cross-sectional area is most commonly used due to the ease with which these surveys may be conducted, the low cost of the equipment, and the small amount of time it demands, it is not always a feasible means to determine air quantity. Places where traditional point measurement of velocity is not practical include locations in the mine which are inaccessible to personnel, locations where the cross-sectional area cannot be measured through simple measurement or photographic methods, and locations that are not deemed safe in the case of an emergency. Also, equipment used for point measurement is not always appropriate for very low velocities, such as leakage through stoppings. The tracer gas technique of determining the air quantity is a viable method of conducting ventilation surveys where other methods are not applicable. Additionally, the tracer gas technique is advantageous in areas where air flow is irregular [11].

The tracer gas technique allows for the direct measurement of the air quantity. The tracer gas technique requires the release of a tracer element into the mine atmosphere, which can later be analyzed. There are two general methods of conducting the tracer survey. One method calls for the continuous release of the tracer into the airway allowing equilibrium to be reached. Samples are collected and processed by means of a gas chromatograph (GC) which, combined with the knowledge of the method, produces a peak area that indicates the concentration of the tracer in the collected sample. The air quantity is then determined using Equation 3.1. The quantity of air, Q, measured in cubic feet per minute (ft^3/min), Q_g is the feed rate of the tracer measured in ft^3/min, and C is the concentration of the tracer gas. This concentration is typically unit less, but measurements may be classified on a volumetric basis so that samples may be measured in units of cubic feet per cubic feet (ft^3/ft^3). The tracer gas technique may also be implemented by releasing a known mass of tracer into the airway and collecting samples until

the tracer has passed through the point of collection. The resultant air quantity is a function of the various concentrations of tracer in samples over time, and the final relationship defined in Equation 3.2. The variables Q and Q_g are measured in ft^3/min, C_{av} is the average of the measured concentrations, a unitless number that may be classified volumetrically in units of ft^3/ft^3, and τ_T is the total time for which trace elements were measured in minutes.

$$Q = \frac{Q_g}{C}$$
<div style="text-align:right">Equation 3.1</div>

$$Q = \frac{Q_g}{C_{av}\tau_T}$$
<div style="text-align:right">Equation 3.2</div>

While the tracer gas technique adds variability to the available means of determining air quantity, ventilation surveys are still limited in inaccessible regions because the tracer gas technique is a slow method. Not only is the speed of the survey limited by the amount of time required by the gas chromatograph to process samples, but also by the need to allow background levels of the tracer element to be removed from the ventilation system. The industry standard for mine tracer gas applications is sulfur hexafluoride (SF_6). The addition of a second, novel tracer element will increase the versatility of tracer surveys in that multiple airways/leakages could be traced simultaneously, eliminating the problem of the long wait time between runs with the use of only one tracer element. Use in a mine setting requires that the tracer element be easily detected and analyzed, absent from the mine air, not absorbed by chemical or physical means in the air way, and non-reactive, toxic, corrosive, nor explosive [11]. Additional desirable properties of tracer elements include that they are readily attainable, easily transported, and inexpensive. To be used in tandem with SF_6 the tracer must exhibit high sensitivity (similar to that of SF_6) to obtain desirable chromatographic results. Perfluorocarbon tracers (PFTs), specifically perfluoromethylcyclohexane (PMCH), meet the demands required of a novel tracer.

3.3 Background

The knowledge that PMCH is a suitable mine tracer warrants further investigation of the chemical. While PMCH is a liquid at room temperature, it is highly volatile with a boiling point of 76^0C [70]. As such, PMCH vaporizes at a relatively low temperature, and will remain in the vapor state through cooler temperatures. PMCH has a molecular weight of 350 g/mol, which is favorable because it is much heavier than SF_6 (molecular weight of 146 g/mol). The difference in molecular weights will allow for the easy separation of peaks during GC analysis. The chemical formula of PMCH is C_7F_{14}, and it contains no unsaturated bonds as seen in Figure 3-1. The fully saturated bonds cause PMCH to be extremely stable both chemically and physically. As such, PMCH is also biologically inert so that, even if ingested or inhaled, it is not harmful to humans [71]. In addition to being safe for people at trace levels, PMCH is safe to use in the environment. The fully saturated fluorine atoms do not react with the ozone ensuring that PFTs do not affect the ozone layer [71]. Also, the ambient background of all PFTs is approximately 0.03 parts per trillion making any single PFT an ideal trace element [71].
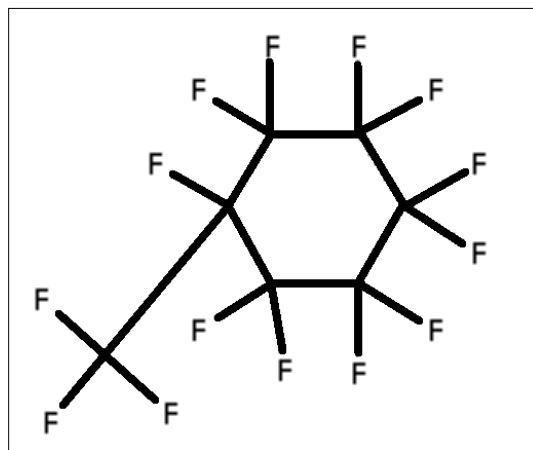
Figure 3-1: Fully Fluorinated PMCH Structure [5]

PMCH has been used extensively as a tracer element in industries outside of mining. One such study used PMCH to study the dispersion mechanisms in the atmosphere of an urban

environment. On three separate occasions PMCH was released into a neighborhood setting in a vapor state, and samples were collected anywhere from one to nine kilometers from the site of release, with measured concentrations ranging from 0.003-2.16 $\mu g/m^3$ [49]. In this case PMCH was successfully incorporated as a tracer gas in an open environment/neighborhood setting, and was traced at very low concentrations a great distance from the source. PMCH was also used as a tracer in much the same fashion in the European Tracer Experiment, in tandem with perfluoromethylcyclobutane (PMCB) [72].

Further application of PMCH as a tracer element includes its use in oil and gas reservoirs. As within the ambient atmosphere, the background of PFTs is also very low in underground settings so as not to interfere with tracer experimentation. In one case, PMCH is used in tandem with SF_6 to study flow patterns between injection and production wells. PFTs are favorable for these purposes due to their high detectability at low concentrations and chemical inertness, as well as their successful use in atmospheric transport studies and marine studies. Results from this reservoir study measured PMCH tracers in the parts per billion range [58].

Another instance in which PMCH was used as a tracer gas element was in home ventilation systems. In order to determine where in the ventilation system heated or cooled air is lost, PMCH was introduced to directly measure air infiltration in homes under actual living conditions. The study was designed to be long term to best determine where air infiltration occurred, and the study neither suffered sample loss of the volatile PMCH vapor to condensation, nor were there any side effects on residents in the home. Additionally, adsorption losses of the PMCH tracer gas were negligible. [44].

Based on the three discussed uses of PMCH as a tracer gas, it is evident that a human population can safely be exposed to vapor PMCH without fear of harmful side effects.

Additionally, PMCH has been used as a successful tracer in both open environments, as well as enclosed ventilation systems, indicating negligible sample loss to absorption of the tracer to exterior elements, as well as limited condensation of the tracer. Furthermore, PMCH is proven to be readily detectable at very low concentrations and great distances from its source. In one case the minimum detection limits of various PFTs were evaluated. An Al_2O_3/Na_2SO_4 column was successfully implemented in experimentation. The limit of detection of PMCH was determined to be 50 pg [39]. When considering the volume of air that flows through underground mines, it is apparent that the determined detection limits fall far below the ppm range routinely used in mine ventilation survey evaluations.

The use of multiple tracers in mine ventilation applications is, by no means, a novel concept. Gases such as nitrous oxide and helium have been used as mine tracers with little success due to their low detectability [2]. A gas with low detectability would be difficult to manage in an underground mine due to the vast volume that would be required to be released in order to be detectable in tandem with SF_6. Freon gases including Freon-13B1 and Freon-12 were also selected as acceptable tracers to be used with SF_6 due to their properties making them suitable tracers for underground applications, their compatibility with existing sampling systems, and due to the fact that they are able to be measured in the same or a similar method as SF_6 [2]. The resultant method used a two column system GC with an electron capture detector (ECD). The results of the experimentation with Freon gases as mine tracers was successful; however, background levels of Freon gases must be measured before analysis due to their application as a refrigerant and propellant in aerosol cans [2].

Further experimentation with mine tracers applied the use of ^{133}Xe, a radioactive isotope of xenon gas. This isotope of xenon gas is a suitable radioactive tracer because it is chemically

and physiologically inert, and its half-life of 5.25 days is sufficiently long that it will not decay before the completion of the testing and that it will be sufficiently detectable. The radioactive tracer was released in abandoned mines. Background measurements were observed before and after the release/capture of the radioactive tracer to ensure that pooling and absorption of the tracer did not occur. The radioactive tracer was released using a pulse-dilution method, and was detected using a radioactive detector designed for the study [13].

3.4 Application

A primary consideration in the selection of a novel tracer to use in underground mining applications is the sensitivity of the new element relative to that of SF_6. PMCH is known to be an exceedingly sensitive tracer. As discussed, it has been successfully used as a tracer element in both gaseous and liquid states to high levels of success. SF_6 and PMCH have been successfully used in tandem in oil and gas reservoirs. In one case SF_6 and PFTs including PMCH as well as PMCB, perfluoromethylcyclopentane (PMCP), perfluorodimethylcyclohexane (PDMCH), and perfluorotoluene were successfully used simultaneously in analysis. Each of the aforementioned PFTs is a fully saturated compound. A GC with an ECD was used to detect the tracer elements, utilizing two columns in tandem [58]. The successful use of PMCH and SF_6 in tandem in oil reservoirs indicates that PMCH is a promising option for a novel tracer in mine survey applications.

In order to successfully use a two tracer system in mining applications, it is important to have a simple analysis protocol to minimize analysis time, maintenance, and training. As such, a two column system is not suitable.

An ECD is used to detect the concentration of tracer in the air samples. The ECD uses a ^{63}Ni source that releases radioactive β^- particles. The β^- particles then collide with the make-up

gas consisting of nitrogen and helium. The results of collision include the production of free electrons and a high standing current. When an electronegative analyte elutes from the column and enters the detector, it captures free electrons. The ECD measures the difference in the standing current and the reduced current when the analyte captures free electrons. The mechanics of the ECD makes it a highly selective detector. [7].

As demonstrated with other tested tracers, including carbon tetrafluoride (CF_4) and carbon octafluoropropane (C_3F_8), difficulties were encountered in selecting a tracer with sufficient sensitivity to be able to be used simultaneously with SF_6, as well as separated from oxygen in air. Both Freon gases CF_4 and C_3F_8 were experimented with using SBP-1 Sulfur, ZB-624, TG Bond Q+, and TG Bond Q columns. These two Freon gases were selected due to the previous success of Freon gas application as mine ventilation tracers [2], as well the fact that they do not pose known health risks to people, have molecular weights sufficiently different from SF_6 to indicate that separation is possible, and they are both readily available in compressed gas cylinders. Additionally, the presence of fluorine compounds in their chemical makeup indicate that they should be easily detectable using an ECD. In order to be selected as the novel tracer, it was important that one or both of the Freon gases be successfully applied in tandem with SF_6. To satisfy this requirement, the selected novel tracer must be as sensitive as SF_6 on the same method. A method of detection using one column on a GC-ECD is desirable, and the Freon gas must present itself as a Gaussian shaped peak that is clearly separated from both air and SF_6 on chromatograms.

While testing the selected Freon gases on the SBP-1 Sulfur column, sufficient separation between peaks could not be achieved, nor were the peak areas of the Freon gases comparable to

those of SF_6. The resultant average retention times and peak areas of the pertinent gases for the

two experimental methods are listed in Tables 3-1 and 3-2, respectively.

Table 3-1: Average Retention Time of Gases on SBP-1 Sulfur Column

Column Temperature	Average Retention Time (min)			
	O_2	SF_6	CF_4	C_3F_8
40^0C	1.10	1.22	1.10	1.20
20^0C	1.08	1.19	1.10	1.24

Table 3-2: Average Peak Area of Gases on SBP-1 Sulfur Column

Column Temperature	Average Peak Area		
	SF_6	CF_4	C_3F_8
40^0C	$8.91x10^7$	$1.43x10^4$	$1.44x10^4$
20^0C	$7.69x10^7$	$1.56x10^4$	$1.30x10^4$

While testing on the ZB-624 column, similar problems were encountered as with the

SBP-1 Sulfur column. Additionally, CF_4 was not detected using the ZB-624 column. The

resultant retention times and peak areas of the pertinent gases for the three experimental methods

are listed in Tables 3-3 and 3-4, respectively.

Table 3-3: Average Retention Time of Gases on ZB-624 Column

Column Temperature	Average Retention Time (min)			
	O_2	SF_6	CF_4	C_3F_8
40^0C	2.14	2.22	---	2.23
20^0C	2.14	2.22	---	2.27
0^0C	2.14	2.24	---	2.17

Table 3-4: Average Peak Area of Gases on ZB-624 Column

Column Temperature	Average Peak Area		
	SF_6	CF_4	C_3F_8
40^0C	$5.93x10^7$	$2.07x10^3$	$1.02x10^4$
20^0C	$6.12x10^7$	---	$8.63x10^3$
0^0C	$6.57x10^7$	---	$2.20x10^5$

Testing on the TG Bond Q+ column produced similar results as with the ZB-624 column. Difficulties were encountered with the production of peaks from CF_4. The resultant retention times and peak areas of the pertinent gases for the three experimental methods are listed in Tables 3-5 and 3-6, respectively.

Table 3-5: Average Retention Time of Gases on TG Bond Q+ Column

Column Temperature	Average Retention Time (min)			
	O_2	SF_6	CF_4	C_3F_8
40^0C	1.94	2.22	2.12	3.49
20^0C	1.96	5.22	---	5.22
0^0C	1.96	9.65	---	9.84

Table 3-6: Average Peak Area of Gases on TG Bond Q+ Column

Column Temperature	Average Peak Area		
	SF_6	CF_4	C_3F_8
40^0C	5.93×10^7	2.79×10^3	1.15×10^5
20^0C	1.091×10^8	---	6.15×10^4
0^0C	1.100×10^6	---	4.13×10^4

Testing using the TG Bond Q column resulted in adequate separation of C_3F_8 from oxygen, but not from SF_6. CF_4 was not able to be analyzed on the selected column as it produced no peaks, compared to the limited peaks produced using the ZB-624 and TG Bond Q+ columns. The resultant retention times and peak areas of the pertinent gases for the five experimental methods are listed in Tables 3-7 and 3-8, respectively.

Table 3-7: Average Retention Time of Gases on TG Bond Q Column

Column Temperature	Average Retention Time (min)		
	O_2	SF_6	C_3F_8
60^0C	2.30	3.10	3,09
50^0C	2.33	3.42	3.41
40^0C	2.24	3.88	3.88
20^0C	2.27	5.74	5.70
0^0C	2.27	10.6	---

Table 3-8: Average Peak Area of Gases on TG Bond Q Column

Column Temperature	Average Peak Area	
	SF_6	C_3F_8
60^0C	2.56×10^7	3.34×10^5
50^0C	2.60×10^7	4.18×10^5
40^0C	7.26×10^6	3.88×10^3
20^0C	4.50×10^6	1.960×10^3
0^0C	3.70×10^6	---

In each case, the CF_4 and C_3F_8 peaks could not be separated from either oxygen or SF_6.

Figure 3-2 displays the unsatisfactory overlay of C_3F_8 and oxygen on a SBP-1 Sulfur column.

Figure 3-3, meanwhile, displays the unacceptable difference in detectability between SF_6 and

C_3F_8 while using a TG Bond Q column.
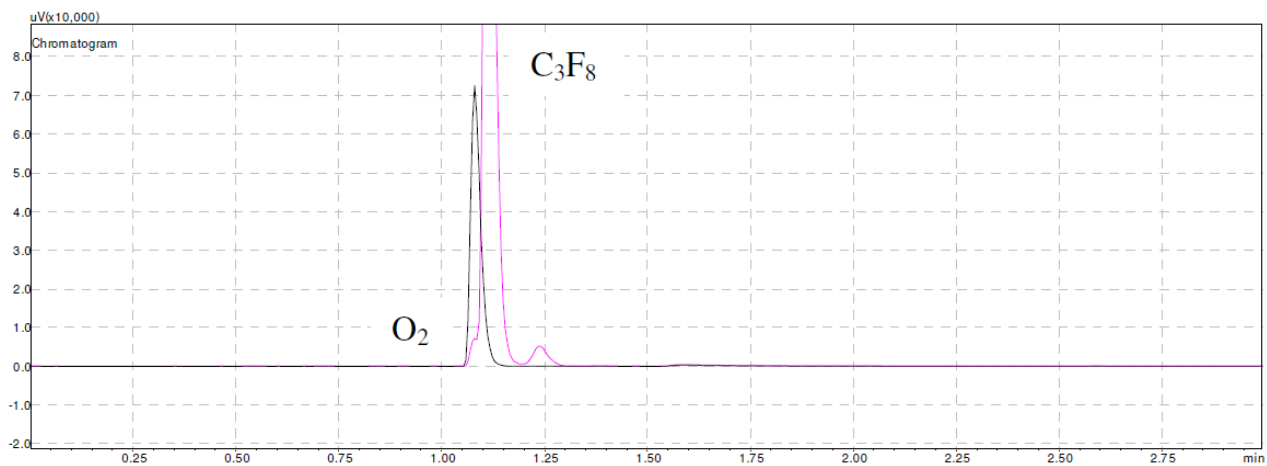
Figure 3-2: Comparison of Syringe Blank (Black) and 10 µL Injection of Pure C_3F_8 at 20^0C

(Pink)
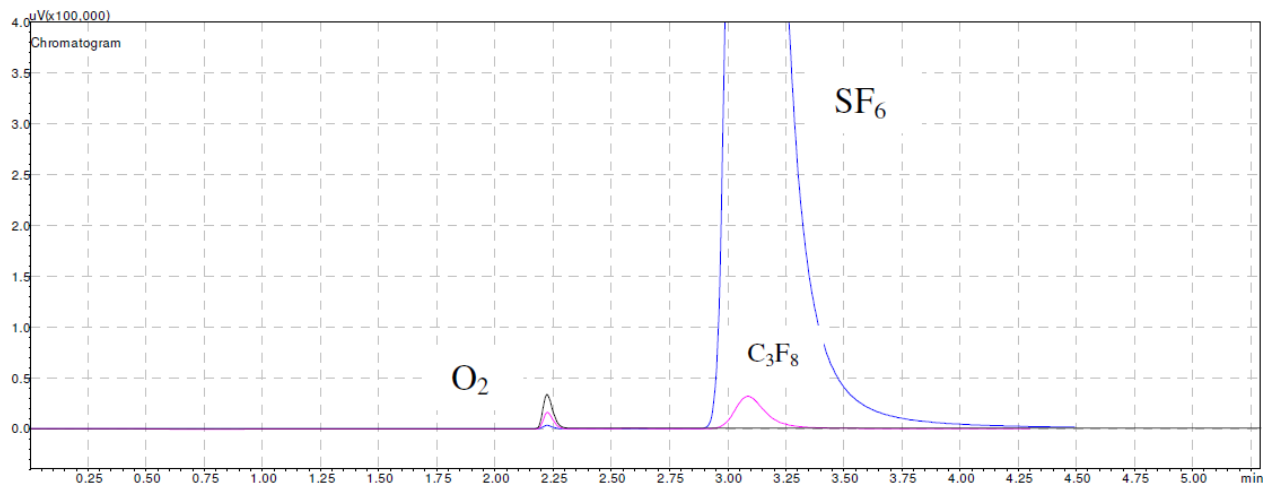
Figure 3-3: Overlay of Syringe Blank (Black), 1 μL SF$_6$ Injection (Blue) and 10 μL C$_3$F$_8$

Injection (Pink)

PMCH was tested on a HP-AL/S column. The HP-AL/S column was selected due to its previous successful application using PMCH as a tracer [39]. Experimentation on the HP-AL/S column resulted in successful peak separation of oxygen, SF$_6$, and PMCH, as well as Gaussian shaped peaks. Additionally, the detectability of PMCH is sufficiently similar to that of SF$_6$ so that a method may be developed on the HP-AL/S column to apply PMCH as a novel tracer. The resultant retention times and peak areas of the pertinent gases for three experimental methods are displayed in Tables 3-9 and 3-10, respectively. The characteristics of the selected column are detailed in Table 3-11.

Table 3-9: Average Retention Time of Gases on HP-AL/S Column

Column Temperature	Average Retention Time (min)		
	O$_2$	SF$_6$	PMCH
70^{0}C	2.09	2.43	9.61
67^{0}C	2.07	2.44	9.69
65^{0}C	2.08	2.48	9.74

Table 3-10: Average Peak Area of Gases on HP-AL/S Column

Column Temperature	Average Peak Area	
	SF$_6$	PMCH
70^{0}C	3.44x10^7	4.95x10^7
67^{0}C	4.24x10^7	6.34x10^7
65^{0}C	6.18x10^7	7.97x10^7

Table 3-11: HP-AL/S Column Characteristics

Column Name	HP-AL/S
Column Type	Capillary
Column Length	30 m
Inner Diameter	0.250 mm
Film Thickness	5 μm

The protocol established for the separation of PMCH in the selected column is detailed in Table 3-12. PMCH contains a significant amount of impurities requiring the use of temperature programming to remove the impurities from the column. The initial temperature of the column is relatively low at 67^{0}C and held for sufficient time to allow SF$_6$ to elute. PMCH requires a higher temperature for both elution, as well as separation from contaminants. The selected split ratio of 50:1 allows for the development of Gaussian shaped peaks for both PMCH and SF$_6$ during analysis. In application, the split ratio may be adjusted and then corrected for quantitative analysis to the split ratio determined in protocol. The resultant analysis of PMCH in tandem with SF$_6$ had desirable peak shapes and separation as seen in Figure 3-4. The developed protocol is a balance of satisfactory separation and efficient analysis time.

Table 3-12: Standard GC Protocol for HP-AL/S

Split Injector Temperature	150^{0}C
Split Ratio	50:1
Pressure	16.2 psi
Carrier Gas	He
Total Flow	60.8 mL/min
Make Up Gas	N$_2$
Column Flow	1.15 mL/min
Linear Velocity	30 cm/s
Septum Purge Flow	2.0 mL/min
Detector Temperature	200^{0}C
Initial Column Temperature	67^{0}C hold 2.75 min
Ramp	120^{0}C/min
Final Temperature	180^{0}C hold 12.30 min
Total Program Time	15.99 min
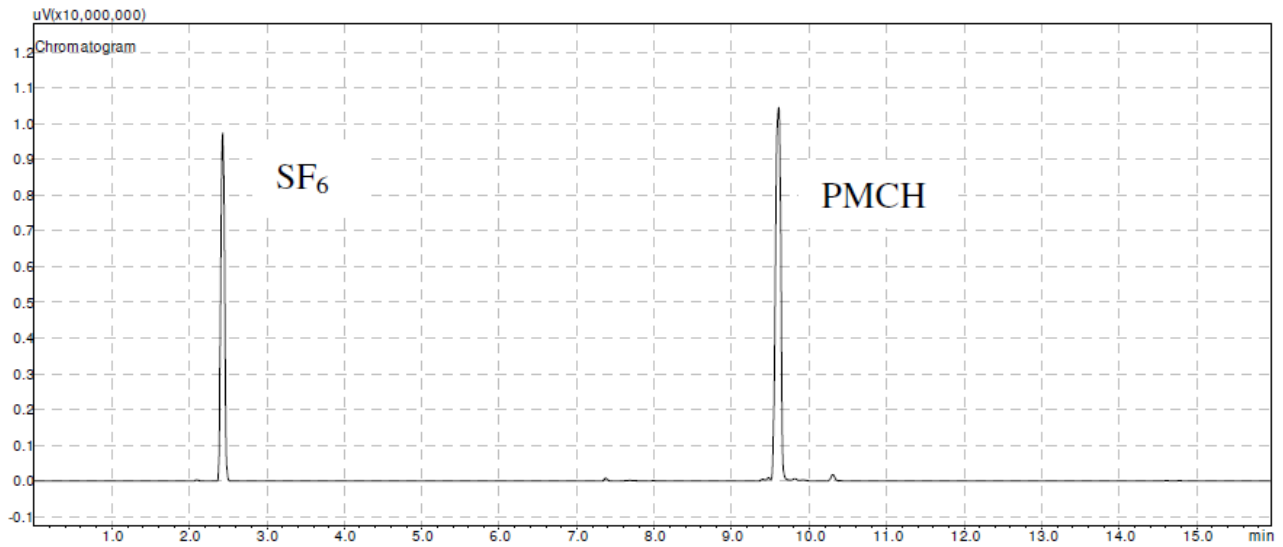
Figure 3-4: 1 mL Injection of a Sample of 100 ppm SF$_6$ & PMCH in N$_2$

The success of the developed protocol and the inherent sensitivity of PMCH make it a favorable choice for a novel tracer gas in underground mining applications. The total analysis time is approximately 16 minutes, which could be shortened with the use of other PFTs whose molecular weights are smaller. Two such PFTs include PMCB and PMCP. Both compounds have a molecular weight of 300, substantially smaller than the molecular weight of PMCH which

is 350. PMCP and PMCB also have lower boiling points than that of PMCH: 47-53^{0}C and 45^{0}C, respectively. PMCP, however, is incompatible with strong oxidizing agents and metals, and may evolve into CO, CO2, or hydrogen fluoride if it encounters incompatible materials [73]. PMCB must avoid products of combustion, heat, strong oxidizing agents, and must be kept cold when stored [74]. PMCH is the most suitable PFT for underground mining applications based on the conditions which must be avoided with the selection of either PMCP or PMCB.

3.5 Future Work

PMCH has been successfully established as a tracer element meeting the demands for use in mine ventilation surveys. However, there is still much that is unknown about the fluorocarbon. For instance, while studies have not suffered from sample loss, there is minimal information available on PMCH vulnerabilities to condensation. Additionally, an efficient method of release suitable for underground mining applications must be developed.

3.5.1 Sample Loss Considerations

Other tracer gas studies have not shown significant sample loss when using PMCH such that further investigation into the matter is not warranted. This conclusion may be drawn based on the results of other studies that sample loss will be negligible in underground mining applications because PMCH has been used as a tracer in its vapor state in a variety of environments.

The European Tracer Experiment implemented the use of PFTs in a study to model the atmospheric transport across Europe. Tracer elements were released and traced for three days during experimentation. While a great deal of information on the condensation habits of PMCH is not readily available, the European Tracer Experiment used Equation 3.3 to model the relationship between vapor pressure and temperature such that dew point may be determined.

P_{PMCH} is the vapor pressure in units of mbar and T is the temperature in units of K. [72]. This relationship may serve as an indication of the possibility of sample loss to condensation should the pressure of the surveyed region be available. However, the relationship does not serve to indicate the amount of loss which may be endured should the dew point be reached. Based on various studies, including the home air infiltration study [44], it may be concluded that the threat of sample loss to condensation is minimal.

$$\log P_{PMCH} = 8.439 - \frac{1872}{T}$$
<div align="right">Equation 3.3</div>

3.5.2 Methods of Release

One possible obstacle to bypass with the selection of PMCH as a novel tracer is the method of release into a mining atmosphere. The European Tracer Experiment used a chimney system to release vapor PMCH directly into the atmosphere continuously for a set amount of time [72]. While a chimney method is not applicable in an underground mine, there are three likely means of release to be considered. The first is with the use of a permeation tube which will, when placed in an environment whose temperature is strictly controlled, release vapor PMCH at a steady, known/calibrated rate [75]. The emission rate of PMCH from a permeation tube would be limited by the temperature in which it is contained. A second means uses a fluoroelastomer plug impregnated with a known mass of PMCH, and employed in the home ventilation system analysis of air infiltration [44]. The plug naturally emitted PMCH vapor at a slow rate over a period of more than five years. The third means of release is purchasing cylinders containing vapor PMCH in nitrogen. Such containers are capable of releasing PFT vapors up to 100 mg/min as controlled by a mass flow controller, but must be contained below their dew point [70]. Each method of release has been successfully implemented in various applications and could well be practical in a mine ventilation survey.

3.6 Conclusions

　　Improvement of the versatility of ventilation surveys is important in underground mining applications. Improved tracer gas techniques can significantly improve the flexibility of ventilation surveys. Radioactive gas and Freon gas tracers have been successfully used in the past, but a novel tracer that may be used in active workings with a simple analysis method is desirable. Two Freon gases, CF_4 and C_3F_8 were tested in tandem with SF_6 on various columns with various methods with little or no success. Peak separations between the Freon gases and oxygen or SF6 were not readily achievable, nor were Gaussian shaped peaks captured. Experimentation with PMCH and SF_6 allowed for peak separation and the development of Gaussian shaped peaks. PMCH is a favorable selection for a novel tracer to work in tandem with SF_6 due to its chemical stability, similar physical properties and detection limits to SF_6, and its ability to be applied and integrated into an existing system. Additionally, PMCH has been successfully utilized in other large-scale tracer gas studies. A method using a Shimadzu GC-2014 with ECD and HP-AL/S column was developed to simultaneously detect SF_6 and PMCH. While there is yet much to be learned about the compound, future work will focus on the development of an efficient method of release into an underground mine.

4 Gas Chromatograph – Electron Capture Detector Method for Solid Phase Microextraction Sampling of Mine Gases

4.1 Abstract

Precise methods for the quantification of tracer gases in underground mine ventilation studies are vital to the maintenance and design of mine ventilation systems, which in turn, play a critical role in mine safety and productivity. This study was undertaken to determine if solid phase microextraction (SPME) is a feasible sampling method for quantitative tracer gas analysis as applied to underground mine ventilation. This paper details an optimized method for SPME sampling techniques, as well as a simple GC-ECD method. Both methodologies are rapid and reproducible. An equilibrium curve relating fiber exposure time under static conditions and a methodology for creating a calibration curve using a SPME sampling method is also described.

4.2 Introduction

A tracer gas ventilation survey is performed by releasing a tracer which is easily detected and analyzed, absent in normal mine air, chemically stable and inert, non-toxic and non-explosive [11]. Tracer gas ventilation surveys are especially applicable in areas of a mine where point measurement of velocity and quantity are difficult, such as inaccessible areas and areas with highly irregular cross sections. The standard tracer gas employed by the mining industry is sulfur hexafluoride (SF_6) [2]. A tracer gas ventilation survey may be executed by a continuous release of tracer or a pulse release of tracer [4]. When using the continuous release method, sufficient time must be allowed for thorough mixing and air samples are taken downstream.

An integral step in the performance of a tracer gas survey is sampling. Sampling must be completed in a standardized manner which allows for reproducible results, but is also convenient with regard to application, storage and transportation, as well as cost effectiveness. The manner

of sampling must also be sensitive as the concentrations of tracer achieved in samples are often quite small due to the relatively large quantities of air being sampled. Traditional sampling methods applied in underground mines include glass syringe bottles with tight fitting rubber stoppers [4], disposable plastic syringes and Tedlar bags [2], and evacuated containers [5]. A comprehensive study of these common sampling methods was performed comparing the precision, sensitivity, robustness, convenience, and cost of these sampling devices [6]. This study concisely summarized the advantages and disadvantages of various sampling methods, but a sampling method novel to the mining industry was also investigated: solid phase microextraction (SPME). The results of the investigation showed that, while SPME fibers were the least sensitive of the sampling methods, they allowed for the lowest amount of error.

SPME is a highly sensitive, simple and inexpensive sampling technique originally designed for liquid and gaseous matrices. SPME works in two phases. Solute absorption from the matrix into the fiber occurs during the first phase. A SPME fiber consists of a small amount of solid extracting polymeric phase coated onto a small fused silica rod. SPME fibers can be exposed directly to headspace of liquids and solids or solutions requiring minimal sample preparation efforts [76]. Transfer of analytes from the SPME fiber into the GC system occurs during the second phase. Analytes that have adsorbed onto the fiber are thermally desorbed into the GC sample inlet [77].

The application of SPME as a sampling device in underground mines is encouraging because it is a solvent free extraction method designed for rapid sampling at low concentrations. The use of SPME is proven to be precise, but has not yet been proven to be sufficiently sensitive for underground mine ventilation surveys [6]. However, SPME has been proven to be a rapid sampling method for trace elements with a high molecular mass [78]. The sensitivity of SPME

fibers is limited to the capacity and selectivity of the extracting phase. In order to use SPME as a sampling method in the field, the tip must be sealed, but storage time may be extended by keeping the fiber cool [79]. The application of SPME as a sampling mechanism in underground mines warrants further investigation to prove that a method can be developed using a GC-ECD to achieve accurate and reproducible quantification of tracer gases considering the precision inherent to the sampling method and the ease with which samples may be collected and stored.

4.3 Experimental Apparatus

A Shimadzu 2014 GC with an electron capture detector (ECD) was used to quantify analytes during this study. Helium serves as the carrier gas with nitrogen as the make-up gas. GC Solutions© serves as the software to display and analyze the chromatographic results. A porous layer open tubular (PLOT) alumina chloride column is used for separation of tracer gases. The column is a capillary column allowing for rapid analysis times. The column name is HP-AL/S as supplied by Agilent; column specifications include length of 30 meters (m), inner diameter of 0.250 millimeters (mm), and film thickness of 5 micrometers (µm). Glass liners with 0.75 mm inner diameter are placed in the injection port to enhance sample recovery from the SPME fiber and to ensure a high linear flow rate [80].

4.4 Fiber Selection

All SPME fibers contain one of three types of solid core: fused silica, Stableflex, and metal. Fused silica cores are favored due to their ability to endure high heat and general durability. Stableflex fibers are more flexible than the traditional fused silica fiber due to their plastic coating. Metal fibers reduce extraneous peaks due to the lack of adhesive required to attach the extracting phase to the fiber. The polymeric extracting phase is the element which

absorbs the sample. Each type of core is coated with an extracting phase based on the analytes of interest. The extracting phase is selected based on adsorptive qualities, polarity, and capacity.

Polydimethylsiloxane (PDMS) was selected as the extracting phase for the analysis of tracer gases employed in mine surveys. PDMS is a high viscosity, rubbery liquid which extracts sample via absorption rather than adsorption [65]. PDMS was selected because it has a universal nature with regard to the analytes it can collect. This universal nature is largely due to the non-polar quality of PDMS, which also supplies this extracting phase with a longer life relative to more polar phases. As a non-polar extracting phase, PDMS is sensitive to non-polar analytes [81] such as SF_6. As an absorbent extracting phase, PDMS achieves sample extraction by the partitioning of the analytes into the phase, rather than adsorption onto the surface area of the fiber [82]. This absorbent quality of the fiber increases the capacity of the fiber to collect a larger volume of sample, but it also increases the amount of time required for sample extraction and desorption.

The thickness of the PDMS phase was optimized via experimentation of three commercially available coating thicknesses; 7, 30, and 100 µm. Each thickness was used for the analysis of a 4 parts per million (ppm) by volume standard of sulfur hexafluoride (SF_6) in nitrogen. This standard was created by first filling a Tedlar bag with ultrapure SF_6. Then a gas-tight glass syringe was employed to inject 1.2 microliters (µL) of pure SF_6 taken from the Tedlar bag into a 275 milliliter (mL) glass sampling bulb with a dual stopcock. The resultant concentration is 4 ppm by volume. The effect of the coating thickness was observed at the onset of experimentation to select the most encouraging fiber with a method similar to the method employed for syringe injections of SF_6 standards on the same system. The GC method used to observe the impact of extracting phase thicknesses when using SPME as a sampling technique is

described in Table 2. Methods were then adjusted slightly as necessary for each coating

thickness.

Table 4-1: GC Parameters for SF_6 Syringe Injections

Split Injector Temperature	230 degrees Celsius (^{0}C)
Split Ratio	20:1
Total Flow	26.1 milliliters per minutes (mL/min)
Column Flow	1.15 mL/min
Linear Velocity	30 centimeters per second (cm/s)
Septum Purge Flow	2 mL/min
Detector Temperature	200^0C
Initial Column Temperature	67^0C hold for 2.75 min
Column Ramp Temperature	40^0C/min
Finial Column Temperature	180^0C hold for 0.5 min
Total Program Time	6.07 min

The first coating thickness observed was the 7 μm PDMS fiber. All results were

unsatisfactory with the thinnest coating. Separation of oxygen and SF_6 was not achieved,

eliminating the ability to quantify peak area.

The second coating thickness observed was the 30 μm PDMS fiber. The results observed

with the 30 μm fiber were very similar to the results observed with the 7 μm fiber. Separation

between oxygen and SF_6 was never achieved.

Successful chromatography results were achieved employing the 100 μm PDMS SPME

fiber. Increasing the thickness of the extracting phase increases the capacity of the fiber to

collect sample, making fiber more sensitive [83]. SF_6 was separated from oxygen for all applied

methods, to varying degrees of success. An image of the successful separation of SF_6 and

oxygen is displayed in Figure 4-1. The method used was isothermal at 67^0C with a linear

velocity of 24 cm/s and a split ratio of 20:1. The 100 μm coating was selected as the final fiber;

further optimization is discussed in the following section.
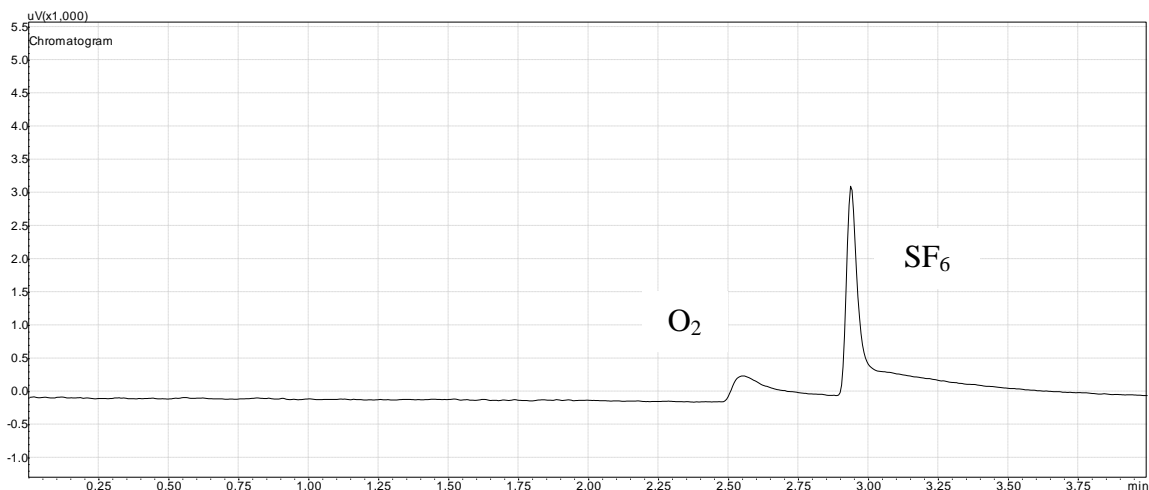
Figure 4-1: Successful Separation of Oxygen and SF6 Using a 100 μm PDMS Fiber

4.5 Method Optimization

The degree of success of this GC method is determined by the degree of separation of SF_6 from oxygen and the peak symmetry for the successful integration of peak areas. SPME sampling methods will typically display peak tailing as a result of the relatively slow desorption of analyte(s) from thick fibers [84].

The GC method was optimized to achieve a reliable chromatographic result when using SPME. The parameters which were adjusted include: depth of the fiber within the injector port during desorption; split versus splitless injections; linear velocity of the carrier gas; and the column temperature. A 5 ppm by volume standard of SF_6 in nitrogen was created in the same manner as previously discussed, altering the injection volume of SF_6 to 1.25 μL, to be used during method optimization.

The first parameter optimized was the depth of exposure of the SPME fiber within the injector port during sample extraction. Sample release from a SPME fiber is achieved through thermal desorption. In order to achieve successful desorption, a glass liner with an inner diameter of 0.75 mm without glass wool was used. The fiber should be exposed in the middle of

45

the glass liner to optimize sample recover [80]. The depth of exposure of the fiber within the

glass liner at the injector port was first optimized by utilizing the measurement tool on the side of

the Supelco SPME fiber holder. Chromatograms were obtained at depths of 3, 4, and 4.4 units,

with 4.4 being the maximum depth of exposure. The sensitivity increased with depth of

exposure, and, after observing the resultant chromatograms overlaid in Figure 4-2, the optimum

depth of exposure was 4.4 units as indicated by the Supelco SPME fiber holder.

The SPME fiber was then used to make injections of the SF_6 standard at various injector

port temperatures ranging from 260-270^{0}C. The impact of varying the injector port temperature

in this range is minimal. Increasing the injector port temperature results in a slight increase in

sensitivity of the GC-ECD to the analytes. As such, an injector port temperature of 270^{0}C was

selected based upon the slight increase in sensitivity.
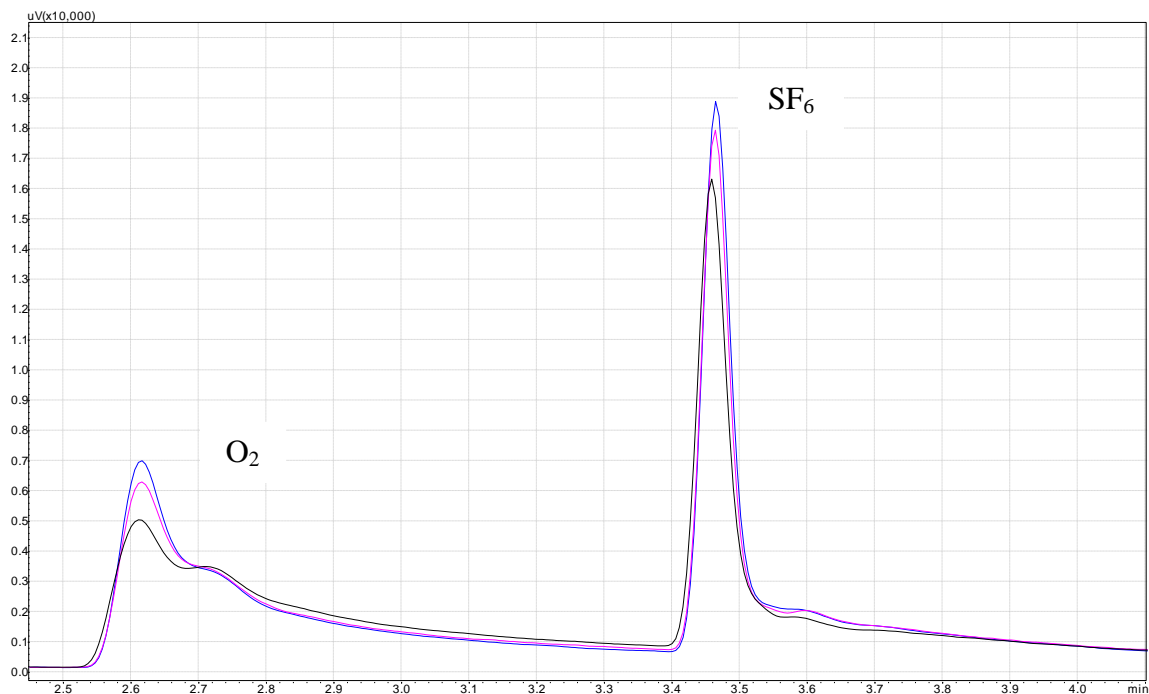
Figure 4-2: Overlay of Injections at Unit Depths of 3 (black), 4 (pink), and 4.4 (blue) units

The second set of parameters to be optimized was the benefit of split versus splitless injections, as well as the optimization of a sampling time in the case of splitless injections. When using a capillary column, smaller split ratios increase chromatographic sensitivity. With the small volume of sample injected from a SPME fiber, it is imperative to enhance sensitivity wherever possible. Initial testing detailed in the Fiber Selection portion of this paper displays chromatographic results when employing a method with split injection. Previously referenced chromatograms had a common problem of a high degree of tailing; for these reasons, development of a splitless method was emphasized. Splitless injection means for a fixed period of time, the split valve is closed, thus all sample vapors pass directly into the column, optimizing sensitivity. Two parameters must be optimized for a splitless injection: 1) the sampling time, which is the time delay prior to opening the split valve and: 2) the split ratio after the valve is opened. The impact of opening the split valve 1.00, 0.75, 0.50, 0.25, and 0.10 minutes following the injection was observed. Reducing this sampling time dramatically reduces the presence of peak tailing. For these tests a split ratio of 30:1 was employed. 30:1 was selected for the fact that proper chromatographic practices encourage the use of split ratios between 20:1 and 100:1 [7], as well as to encourage the flow to sweep efficiently through the injector port once the splitter is engaged. Figure 4-3 displays the isolated view of the selected sampling time of 0.1 minutes where separation of oxygen and SF_6 has been achieved, and tailing of SF_6 has been eliminated.
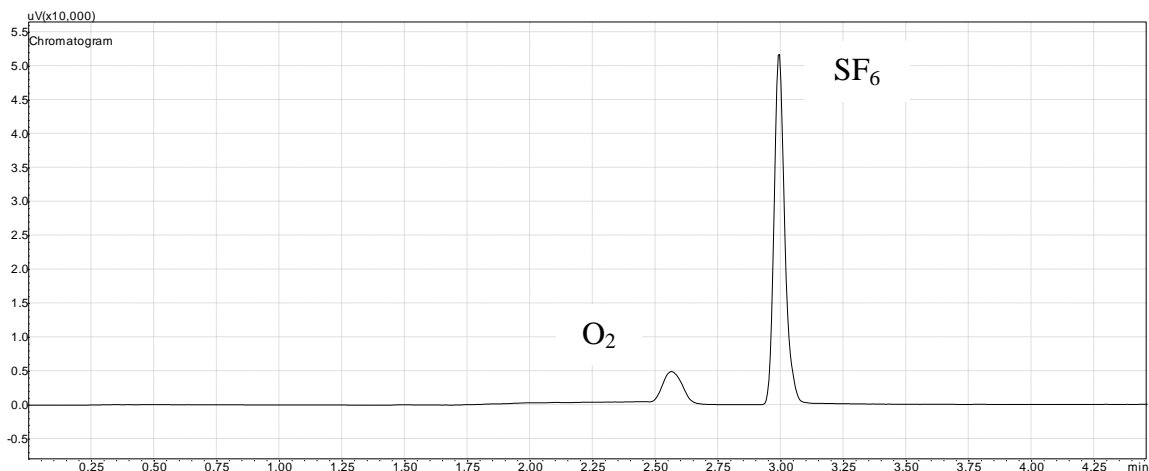
Figure 4-3: Chromatogram when Employing a Sampling Time of 0.1 min

The linear velocity of the carrier gas was the next parameter to be optimized. When using helium as a carrier gas, the optimum flow rate is 24 cm/s as derived from the Van Deemter plot [7]. When using traditional syringe injections to introduce sample to a GC, the linear velocity may be increased to decrease analysis time without largely impacting efficiency. Increasing linear velocity from the optimum point when using SPME, however, degrades analysis, making a linear velocity of 24 cm/s the best option. Figure 4-4 displays the overlay of a chromatogram with a linear velocity of 24 cm/s and a linear velocity of 40 cm/s, with all other parameters the same. The analytes clearly elute sooner when using a faster linear velocity; however, separation of oxygen and SF_6 is degraded to a degree that results are not reproducible.
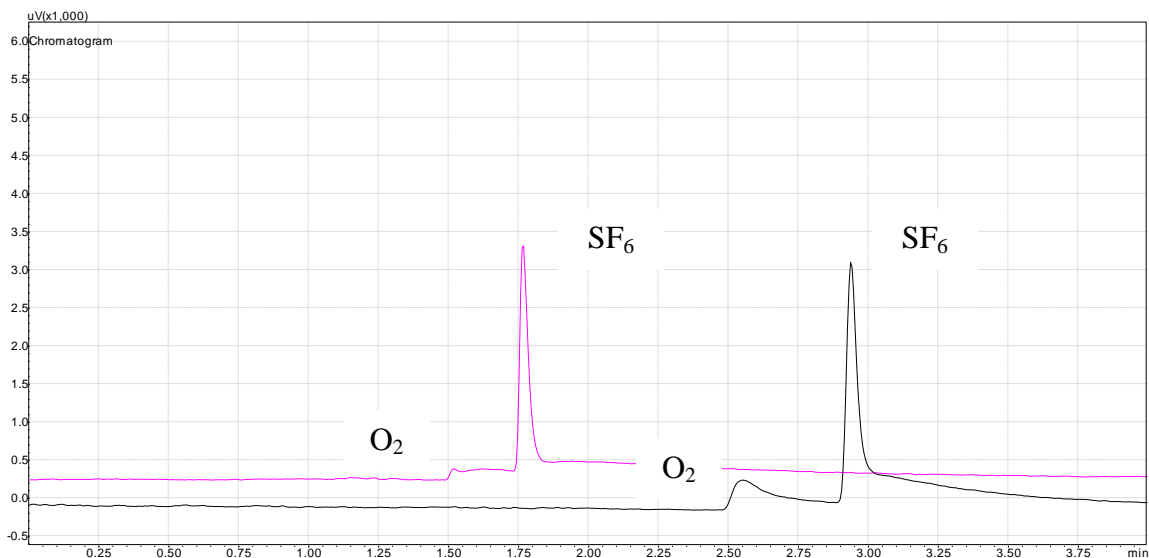
Figure 4-4: Overlay of Chromatograms at 24 cm/s (Black) and 40 cm/s (Pink)

       The next parameter optimized was the column temperature. An isothermal approach was initially used to decrease the time required to cool the oven between runs. The column was tested at 50^0C, 67^0C, and 100^0C under isothermal conditions. Figure 4-5 displays the resultant chromatograms at the various column temperatures. The isothermal method was optimized at 67^0C. This was the selected temperature because it resulted in the greatest sensitivity. Employing an isothermal method, however, does not allow for the chromatogram to return to baseline conditions following the elution of peaks, limiting the ability of the software to accurately integrate the peak areas.
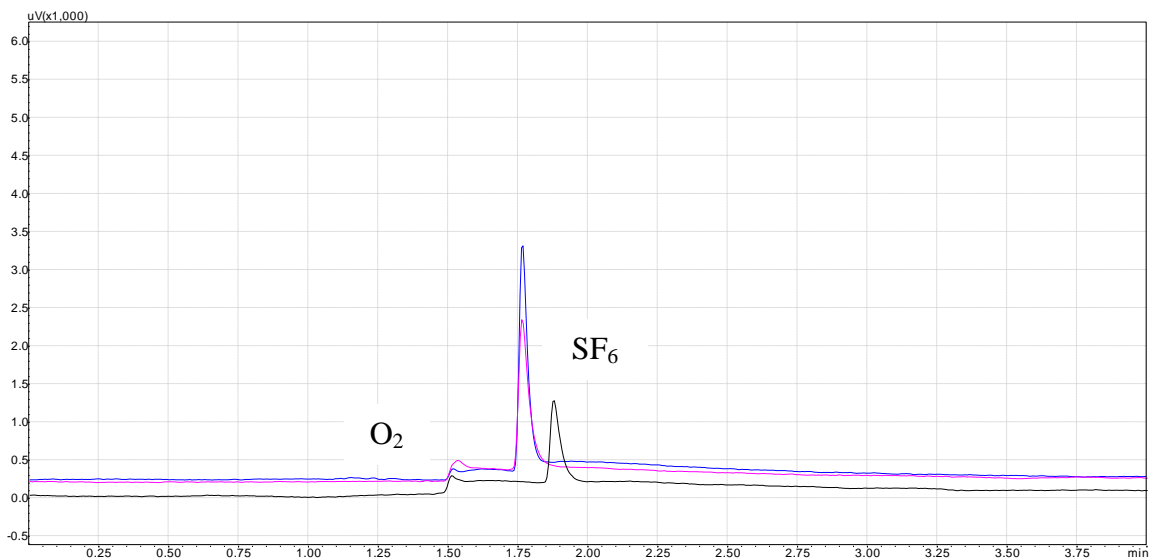
Figure 4-5: Overlay of Chromatograms from 50^0C (Black), 67^0C (Blue), and 100^0 (Pink)

Temperature programming methods were then tested following the unsatisfactory results with isothermal methods. Previous work with SPME indicates that temperature programming with a colder column initially usually improves chromatographic results [85]. An initial column temperature of 35^0C was employed. The final column temperatures observed were 67^0C, 80^0C, 90^0C, and 100^0C. Increasing the final temperature decreases the time of elution of SF_6, but sacrifices the degree of separation between oxygen and SF_6 peaks. The optimal final temperature was 80^0C.

The final method parameter optimized was the time to initiate the heating of the column during the temperature program. The column was heated as rapidly as possible, so the ramp rate is set to 100^0C/min. This ramp was initiated at 0.05, 0.15, and 0.5 minutes. The temperature ramp initiation time has a slight, consistent impact on the time of elution of SF_6. The longer temperature ramp initiation times directly result in a later time of elution of analytes as compared to shorter time intervals before the column temperature is increased. A time of 0.05 minutes was selected for this parameter. A resultant chromatogram of a 5 ppm volumetric standard of SF_6 in

50

nitrogen under the optimized method is displayed in Figure 4-6. The parameters of the

optimized method for a 100 μm PDMS SPME fiber is detailed in Table 3.
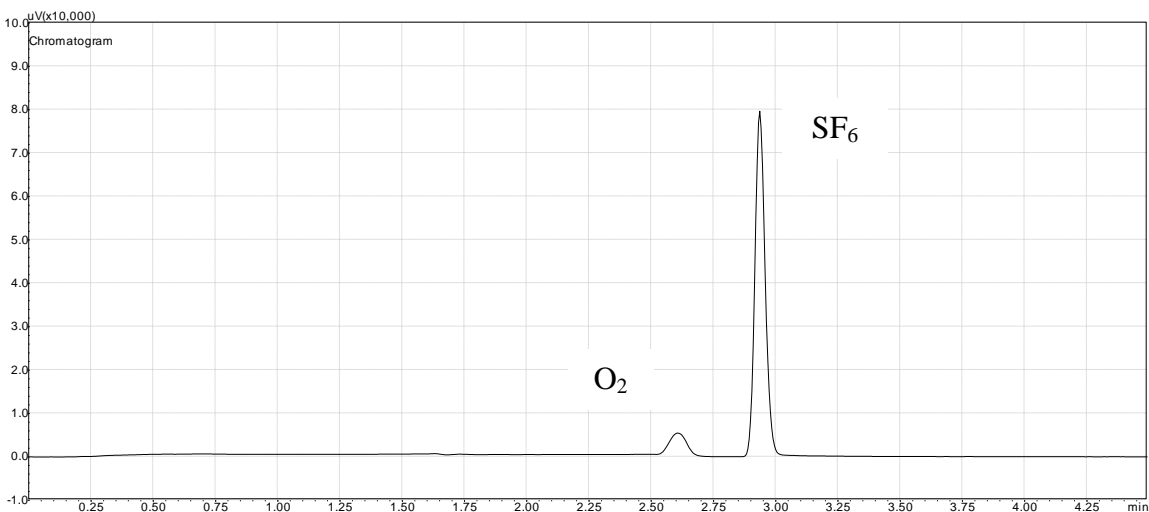
Figure 4-6: Chromatogram of 5 ppm SF_6 in Nitrogen Using Optimized Method

Table 4-2: Method Specifications for 100 μm PDMS Fiber

Split Injector Temperature	270^0C
Sampling Time	0.1 min
Split Ratio	30:1
Total Flow	29.2 mL/min
Column Flow	0.91 mL/min
Linear Velocity	24 cm/s
Septum Purge Flow	1 mL/min
Detector Temperature	200^0C
Initial Column Temperature	35^0C for 0.05 min
Temperature Ramp Rate	100^0/min
Final Column Temperature	80^0 for 4 min
Total Program Time	4.54 min

4.6 Equilibrium Curve

The use of SPME as a quantitative sampling method requires an equilibrium curve. An

equilibrium curve plots peak area versus time of fiber exposure to the sample. When SPME

sampling is utilized sampling time must be consistent if samples are to be quantified. Also,

caution must be exercised due to the risk of overloading the fiber. The equilibrium curve developed will provide the safe range of exposure times to ensure reproducible results when sampling with SPME. Equilibrium is achieved when additional sampling time does not permit the collection of more sample [86], reaching a plateau in the detector response to the observed concentration. The time of equilibrium can be reduced by kinetic reactions [87], so this paper details the development of an equilibrium curve under static conditions, resulting in the longest equilibrium time.

A 100 μm PDMS SPME fiber was used in the development of the equilibrium curve. A standard of 5 ppm by volume SF_6 in nitrogen was created in the same fashion as previously discussed. The fiber was exposed to the standard at various increments of time, as timed by a stopwatch. The fiber was moved directly from the standard to the injector port at the start of each run and remained inside the injector port for the duration of each run. SPME fiber assemblies designed for field work are gas tight; however, the assemblies used to execute the detailed experiments were designed for laboratories. As such, the exposure time of the SPME fiber assemblies used to air was limited. The test was repeated three times for each exposure, allowing for the calculation of percent relative standard deviation (%RSD). Resultant %RSD values below 10% indicate high precision. Table 4 displays the numerical results of the equilibrium curve, while Figure 4-7 depicts the developed equilibrium curve.   A third order polynomial trend line fits the data with a satisfactory R^2 value of 0.98 as displayed in Figure 4-7.

Table 4-3: Chromatographic Results at Various Sampling Times

Sample Name	Exposure Time (s)	Retention Time (min)	Peak Area	Average Peak Area	Std. Dev	% RSD
090412_16	10	2.921	8.50E+04	8.87E+04	3.29E+03	3.71
090412_17		2.918	8.99E+04			
090412_18		2.917	9.13E+04			
090412_1	20	2.922	1.67E+05	1.64E+05	7.28E+03	4.45
090412_2		2.927	1.69E+05			
090412_3		2.934	1.55E+05			
090412_4	30	2.927	2.24E+05	2.16E+05	9.11E+03	4.22
090412_5		2.921	2.06E+05			
090412_6		2.923	2.18E+05			
090412_7	40	2.92	2.24E+05	2.26E+05	2.03E+03	0.90
090412_8		2.931	2.28E+05			
090412_9		2.921	2.27E+05			
090412_10	50	2.926	2.42E+05	2.49E+05	7.57E+03	3.04
090412_11		2.921	2.57E+05			
090412_12		2.922	2.49E+05			
090412_13	60	2.913	2.26E+05	2.41E+05	1.69E+04	7.02
090412_14		2.918	2.59E+05			
090412_15		2.913	2.37E+05			
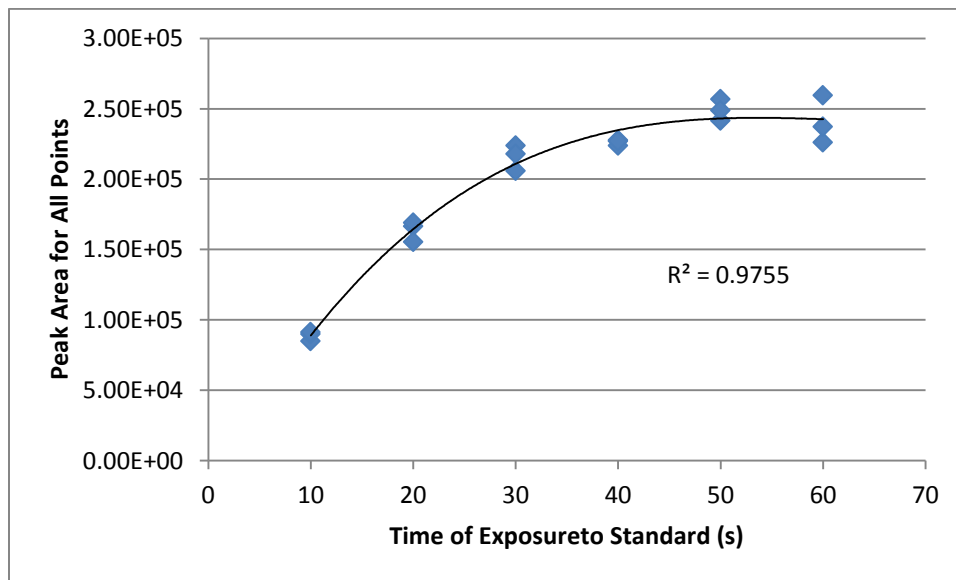
Figure 4-7: Equilibrium Curve for 100 μm PDMS SPME Fiber

4.7 Calibration Curve

A calibration curve is essential for the quantification of results when using a GC. The calibration curve described contains four standard concentrations of SF_6 in nitrogen. The similar transfer efficiencies of SPME injections and syringe injections allow for the development of a calibration curve with standard syringe injection [88], but a calibration curve derived from SPME injections was developed to eliminate the need to correct for the slight difference in transfer efficiencies. The four concentrations studied are 0.36, 0.73, 5.5, and 10.0 ppm by volume. These concentrations were selected due to the readily measurable volume of SF_6 required to create the standard. These standards were developed in the same manner as previously discussed. A sample calculation is provided to detail how the volumetric concentration is derived from a known injection volume in Equation 4.1.

$$\frac{V_{SF_6}}{V_{SF_6} + V_{N_2}} = Volumetric\ Conc \qquad\qquad \text{Equation 4.1}$$

$$\rightarrow \frac{\dfrac{0.1\mu L}{10^6 \frac{\mu L}{L}}}{\dfrac{0.1\mu L}{10^6 \frac{\mu L}{L}} + 0.275L} \times 10^6$$

$$= 0.36\ PPM\ by\ Volume$$

Each standard was analyzed three times. All injections are executed manually. A %RSD value of less than 10% indicates satisfactory results. Four standards of SF_6 in nitrogen were created by injecting 0.1, 0.2, 1.50, and 2.75 µL SF_6 into the glass bulb to develop standards at concentrations of 0.36, 0.73, 5.5, and 10.0 ppm, respectively. Following the third injection of each standard, the % RSD was calculated. The resultant % RSD values were 7.49% for 0.36 ppm, 3.83 % for 0.73 ppm, 1.557 % for 5.5 ppm, and 1.111% for 10.0 ppm. Higher %RSD

values are encountered for lower concentrations; for this reason, standards containing $0.1\,\mu L$ and $0.2\,\mu L$ of SF_6 were used to increase confidence in the lower portion of the calibration curve. A linear trend line fits the data defined by the following equation: $concentration\ (PPM) = 2 \times 10^{-5}\ peak\ area\ + 0.34\ PPM$. An R^2 value of 0.9994 indicates a high degree of confidence in the precision of the curve.

4.8 Conclusions

SPME has inherent characteristics making it a desirable option for sampling in the mining industry. Primarily, SPME is a precise method in the hands of a variety of users for rapid sampling of analytes present in low concentrations, and is highly portable in a rugged environment. When applying SPME to sampling during underground mine ventilation surveys, sensitivity will be increased by using a SPME fiber with a PDMS bonding phase. The thickest coating of 100 µm of extracting phase is the optimum thickness to allow for sufficient recovery of the non-polar analytes without being overloaded with oxygen from air. Recovery of sample during analysis with a GC-ECD system can be optimized with the use of a splitless method with a short sampling time, an initially cool column with a rapid ramp of temperature, and a moderate linear velocity of the carrier gas.

When using SPME for quantification of analytes, two items are necessary to properly analyze samples: an equilibrium curve and a calibration curve. The equilibrium curve indicates the time period where sampling can be optimized via time of exposure of the fiber to the sample and provide the most reproducible results. A proper equilibrium curve will be fit with a third order polynomial equation to allow for the initial linear relationship between time of exposure of the fiber to the sample and peak area, and then to indicate the time where the fiber is saturated. In practice, the SPME fiber should be exposed to the sample for the same amount of time to

allow for the most reproducible results. The calibration curve is necessary to allow for quantification of analytes when using a GC system for analysis. A calibration curve may be developed with high confidence when using SPME due to the precision SPME allows for, as indicated by the high R^2 value achieved.

The developments discussed in this paper indicate that SPME is sufficiently sensitive to sample tracers used in underground mine ventilation surveys. This work details a methodology for the use of SPME in mine ventilation surveys. Future work will test for the ability of SPME to sample SF_6 under turbulent conditions and to indicate to what degree varying flowrates will impact sample recovery. Additionally, the ability of SPME to simultaneously sample multiple tracers including SF_6 and perfluorocarbon tracers will be observed.

5 Solid Phase Microextraction Sampling Under Turbulent Conditions and for the Simultaneous Sampling of Multiple Trace Analytes

5.1 Abstract

Solid phase microextraction (SPME) is a solvent free method of sample extraction. SPME is an appealing method for sample collection because it is designed for the sampling of trace level analytes with short sampling times in a variety of environments. Additionally, SPME can be used to directly deliver sample to a gas chromatograph (GC) for analysis by means of thermal desorption with minimal training. An optimized method for SPME sampling of SF_6 under static conditions was developed in previous work. In this paper, that work is expanded to investigate turbulent conditions under varying flow rates. Additionally, the competence of SPME sampling for simultaneous analysis of multiple trace analytes is evaluated under static conditions. This work is discussed in the context of underground mine ventilation surveys, but is applicable to any industry in which ventilation circuits must be evaluated.

5.2 Introduction

The typical aims of occupational ventilation systems are to provide a comfortable working atmosphere, and to exhaust airborne contaminants when necessary. Ventilation surveys are applied to a wide variety of industries to assess exposure and design of ventilation circuits, to assess pathways for toxins, and to characterize existing ventilations circuits to design improvements. One common method of conducting ventilation surveys is with the aid of tracer gases which can be applied to a variety of ventilation circuits, in terms of complexity and scale. The circuit observed may be as large and unrestricted as open land with irregular terrain to determine the expected impact of an accidental release of harmful gases [89], or limited to a circuit as small as a university teaching lab where air movement is minimal [90]. A popular

tracer gas is sulfur hexafluoride (SF_6), which is used because it is inert, non-toxic, non-corrosive, and detectable at low concentrations.

SF_6 has been used in many applications for ventilation surveys. For example, it was employed to determine failures in a ventilation system in a garment manufacturing facility which allowed for one individual infected with tuberculosis to be detected [91]. Additionally, it was used to evaluate engineering controls intended to reduce worker exposure to metalworking fluids. Finally, SF_6 was used to determine the flow rate and capture efficiency of the ventilation circuit[92]. These examples give only a cursory review of the many applications of tracer gases in consideration of occupational health and safety; they are also considerably useful when evaluating underground mine ventilation systems.

Mine ventilation surveys are conducted in underground mines to gain knowledge about the existing ventilation system and to provide information in the case of emergencies [11]. The aim of a survey may be to measure air quantity, velocity, pressure, and/or temperature. The measurement of air quantity is typically obtained through air velocity surveys and cross-sectional area measurements. Then, Equation 5.1 can be applied to compute volumetric airflow rates, Q, typically expressed in units of m^3/s (or ft^3/min). V is velocity in m/s (or ft/min), and A is the cross-sectional area in m^2 (or ft^2). However, in situations where the cross-sectional area or velocity cannot be directly measured (e.g., inaccessible regions), air quantity must be measured using tracer gases – and SF_6 is indeed the industry standard [2]. However, a major challenge of SF_6 surveys, in both mining and other applications, is sampling. A durable, low cost air sampling method that requires minimal training is needed.

$$Q = VA$$ 　　　　　　　　　　　　　　　　Equation 5.1

5.2.1 SPME as Viable Sampling Method

Solid phase microextraction (SPME) is a sampling method designed to facilitate rapid, on-site sample gas extraction by sorbing analytes onto a polymeric extracting phase [79]. A SPME fiber assembly consists of a silica fiber core coated in a polymeric extracting phase encased in a septum piercing needle. A plunger allows for the fiber to be easily expelled from and withdrawn back into the needle, which serves as a means to access samples and to protect the fiber. SPME has been extensively applied in physicochemical, environmental, food, flavor, fragrance, pheromone, pharmaceutical, clinical, and forensic applications [93]. SPME technologies have also been developed as an alternative technique to evaluate worker exposure to benzene, toluene, ethylbenzene, and xylene (BTEX). In a recent BTEX study, SPME was able to fulfill new requirements for both sample detection limits and sampling times better than traditional methods [94]. As a passive sampling method that requires little to no sample preparation, SPME has also been applied in on-site exposure assessment situations to achieve precise analysis where skilled GC operators were not always available [95].

Previous works with SPME have identified it is a robust sampling method. A method has been developed to optimize sensitivity of the SPME fiber during sampling extraction and GC-ECD analysis [96]. The direct application of SPME to many types of ventilation systems, particularly mine ventilation systems, is largely dependent on whether the method can be used to precisely quantify tracer gas in turbulent flow.

Sample extraction by SPME is achieved by employing the septum piercing needle to access the sample, placing the needle and fiber directly inside of the sample matrix. SPME can be applied to the sampling of liquid, gas, and headspace matrices. The plunger is then used to expel the fiber from the needle to expose the fiber directly to the sample. The fiber is exposed to

the sample for a predetermined amount of time to allow for equilibrium of analyte to be achieved within the fiber, the sample matrix, and the headspace of the container in which the sample is held [79]. Sample extraction with SPME is influenced by agitation of the sample matrix, temperature, pH, and salt. While sampling in typical mine atmospheres, pH and salt are not significant factors. While temperature can certainly vary in mines, the temperatures for the discussed laboratory experiments were controlled to reduce factors impacting SPME sample sorption. Air sampling in turbulent conditions has a parallel impact on sample extraction with SPME as stirring or agitation in a liquid sample. Stirring encourages shorter equilibration times because diffusion of analytes toward the fiber is enhanced [97].

In addition to determining the feasibility of applying SPME to sampling in turbulent conditions, the ability of SPME to extract multiple analytes simultaneously must be observed. This is largely due to the fact that while tracer gas analysis is a useful method for assessment of ventilation circuits at many scales, the method can be a relatively slow means of assessment. The speed of the survey is hindered by analysis times and tracer gas background reduction time in the case of multiple surveys. The use of multiple tracer gases, however, might allow for a more flexible ventilation survey. Perfluorocarbon tracers, specifically perfluoromethylcyclohexane (PMCH), may be analyzed with SF_6 with minimal alterations to the GC-ECD protocol [96]. The ability to apply SPME to the simultaneous measurement of the two tracers has not been investigated to date, and is expected to be heavily dependent on the sensitivity of the PDMS polymeric extracting phase to PMCH.

5.3 Testing Objectives

In this study, the practicality of using SPME to sample directly from a ventilation system was considered based on the ability of SPME to extract sample from a turbulent air stream.

Experiments were conducted in order to elucidate the impact of turbulence on SPME sample recovery and required sampling time. Additionally, SPME experiments were conducted to determine the efficacy of using SPME to simultaneously sample SF_6 and PMCH under static conditions.

5.4 Experimental Methods

5.4.1 SPME Sampling Under Turbulent Conditions

The first portion of testing was performed to determine how turbulence affects SPME sample recovery by comparing samples collected under turbulent conditions to those collected under static conditions. A turbulence vessel was constructed as depicted in Figure 5-1. A fully developed turbulent atmosphere will allow for flow to be mixed uniformly in the inlet and the outlet of the apparatus [98], thus preventing inconclusive sampling as a result of poor mixing or layering at the outlet. An air pump was connected to push air through the turbulence vessel in a blowing-type system. A variable area flow meter controlled the amount of air pushed into the system. A separate fan was placed inside the turbulence vessel to encourage the thorough mixing of gases within the chamber. The tracer gas used during testing was sulfur hexafluoride (SF_6), which was ultrapure and contained inside a compressed gas cylinder. A mass flow controller was connected in series with the gas cylinder to control the exact amount of SF_6 released. While copper tubing was used to connect the cylinder to the mass flow controller, all other connections were made with flexible plastic tubing. SF_6 joined the flow of air into the vessel at the inlet, and a sampling port was located at the outlet of the vessel. The sampling port was capped with a septum, which allowed for sample extraction from the turbulent flow stream with either SPME fibers or via evacuated containers.
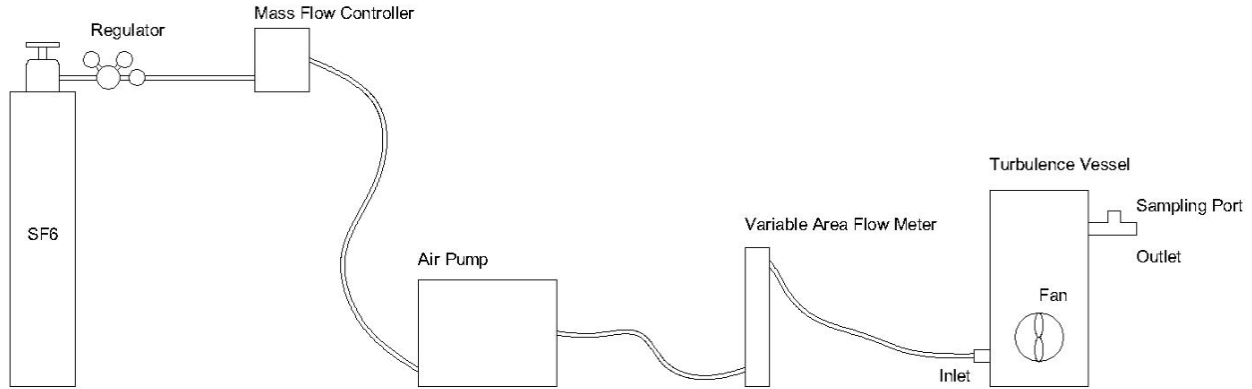
Figure 5-1: Turbulence Vessel Configuration

The Reynolds number was calculated first to indicate if turbulent conditions existed in the inlet and the outlet of the vessel. Before this calculation, however, the actual air density was first computed [1]. This was achieved by using a sling psychrometer to measure the wet and dry bulb temperatures, t_w and t_d, respectively, in the room, along with the barometric pressure, P. Unless otherwise specified, all calculations employ temperature units of degrees Celsius and pressure units of Pascals (Pa). The wet saturation vapor pressure, e_{sw}, and the latent heat of evaporation, L_w, were calculated using the wet and dry bulb temperatures and barometric pressure. The equations for wet saturation vapor pressure and the latent heat of evaporation are given in Equations 5.2 and 5.3, respectively.

$$e_{sw} = 610.6 exp^{\frac{17.27 t_w}{237.3 + t_w}} \qquad \text{(Pa)} \qquad \text{Equation 5.2}$$

$$L_w = 1000\ 2502.5 - 2.386 t_w \qquad \text{(J/kg)} \qquad \text{Equation 5.3}$$

Determination of the wet saturation vapor pressure and the latent heat of evaporation allow for calculation of the specific humidity, X_s, which can in turn be used to evaluate moisture content, X. Equation 5.4 is used to calculate specific humidity, and Equation 5.5 is used to calculate moisture content.

$$X_s = 0.622 \frac{e_{sw}}{P - e_{sw}} \qquad \text{(kg/kg dry air)} \qquad \text{Equation 5.4}$$

$$X = \frac{L_w X_s - 1005 \ t_w - t_d}{L_w + 1884 \ t_w - t_d} \qquad \text{(kg/kg dry air)} \qquad \text{Equation 5.5}$$

Knowing the barometric pressure and the moisture content, the actual vapor pressure, e, was then calculated (Equation 5.6) – and ultimately, the actual air density, ρ, could be calculated (Equation 5.7) The actual air density allows for a more accurate evaluation of the Reynolds number.

$$e = \frac{PX}{0.622 + x} \qquad \text{(Pa)} \qquad \text{Equation 5.6}$$

$$\rho = \frac{P - 0.378e}{287.04 \ t_d + 273.15} \qquad \text{(kg air/m}^3) \qquad \text{Equation 5.7}$$

A Reynolds number greater than 4,000 indicates turbulent flow, and, in turn, the thorough mixing of gases [99]. The calculation to determine Reynolds number is given in Equation 5.8 where ρ is density of air in units of kg/m^3, u is the velocity based on the cross-sectional area of the airway in units of m/s, h_d is the hydraulic diameter (in the case of circular pipes h_d is the actual diameter) in m, and μ is the dynamic viscosity in kg/m/s. The velocity of air is calculated using the cross-sectional area of the outlet and the volumetric flow rate indicated by the flow meter (i.e., via manipulation of Equation 5.1). With a calculated air density of 1.21 kg/m^3, the minimum flow of air necessary to achieve a turbulent atmosphere within the outlet is 44 L/min.

$$Re = \frac{\rho u h_d}{\mu} \qquad \text{Equation 5.8}$$

The mass flow controller releases SF$_6$ in units of standard cubic centimeters per minute. In order to determine the expected concentration of SF$_6$ at the outlet of the turbulence vessel, a series of calculations were performed. The mass flow controller is designed to release gas at a standardized temperature and pressure, and is calibrated as such; therefore, the actual flow rate of

63

SF_6 being released must be determined using the ideal gas law [100]. The ideal gas law is applied as shown in Equation 5.9 to find the volume of SF_6 in the laboratory (V_2) from the known volume of SF_6 in the mass flow controller (V_1). As indicated in the user manual of the mass flow controller, the temperature and pressure values of SF_6 within the controller are known to be 14.696 psia and 25^0C, respectively [101]; the temperature and pressure of air were measured in the laboratory. Once the calculation for the volume of SF_6 is complete, the actual flow of SF_6 from the mass flow controller may be determined. P values in Equation 5.9 are representative of pressures in units of standard atmosphere (atm), V is volume in liters (L), and T is temperature in Kelvin (K); when observing the difference in volume of gas between two states, the ideal gas law can be reduced to eliminate the number of moles of gas, n, and the gas constant, R, since these quantities will remain constant. Once determining the value V_2 and subsequently the volumetric air flow rate, the concentration of SF_6 in the outlet could be calculated using Equation 5.10.

$$\frac{P_1 V_1}{nRT_1} = \frac{P_2 V_2}{nRT_2} \rightarrow \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \rightarrow V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$
<div align="right">Equation 5.9</div>

$$\frac{Q_{SF_6}}{Q_{Air} + Q_{SF_6}} \times 10^6 = Volumetric\ Concentration\ (PPM)$$
<div align="right">Equation 5.10</div>

The above series of calculations provides a means to determine the concentration of SF_6 present within the sampling port of the turbulence vessel. The results of these equations were continually reevaluated with changes in air density. The amount of SF_6 released into the vessel was varied to alter the concentration in the outlet. The flow of air pumped into the vessel could also be varied to this end, as well as to control the Reynolds number. Thus, multiple scenarios could be developed in the sampling port, which had the same concentration of SF_6 with varying Reynolds numbers.

5.4.2 Simultaneous Measurement of Multiple Tracer Gases under Static Conditions Using SPME

The second portion of testing required a much different apparatus set up due to the nature of the experiments. The sampling of multiple tracer gases was performed under static conditions. A standard of SF_6 and PMCH was mixed in a 275 mL glass bulb with dual stopcocks. The glass bulb was flushed and then filled with ultrapure nitrogen. An injection of pure SF_6 gas was then made into the glass bulb. An injection of pure PMCH in vapor state was subsequently injected into the same glass bulb. The PMCH was taken from a vial which had previously been evacuated of atmosphere and then injected with a mass of liquid PMCH. The liquid PMCH was allowed to vaporize, filling the headspace of the formerly evacuated container with pure PMCH vapor. In order to determine the ability of SPME to sample multiple tracer gases simultaneously, 15 µL each of SF_6 and PMCH were injected into the glass bulb. This protocol ensured the presence of the same volumetric concentration of SF_6 and PMCH in the standard, which allowed for an evaluation of the sensitivity of the PDMS extracting phase of the SPME fiber to both tracer gases, simultaneously.

5.5 Results

5.5.1 Turbulent Conditions

The impact of using a 100 µm PDMS SPME fiber to extract sample in a turbulent atmosphere was observed first by comparing equilibrium curves derived under various flow rates. An equilibrium curve was developed to determine the optimum sample time, or the minimum time for which the fiber has extracted the largest sample volume it is capable of collecting [102]. The equilibrium curve was created by exposing a SPME fiber to a scenario of SF_6 in air for various, predetermined amounts of time, and then processing the samples through a Shimadzu 2014 GC-ECD. The exposure times of the SPME fiber to the standard were then

compared to the resultant peak areas to create the equilibrium curve [67]. The impact of turbulence on sample extraction when using a SPME fiber as the sampling mechanism was observed by comparing equilibrium curves developed under varying conditions.

Three scenarios were created to derive three equilibrium curves for comparison: Scenario 1 had a Reynolds number of 4,596, Scenario 2 had a Reynolds number of 6,434 and Scenario 3 had a Reynolds number of 6,894. The scenarios were developed in the turbulence vessel with steady flow rates of SF_6 and air. The chromatographic results for scenarios 1, 2, and 3 are displayed in Tables 5-1, 5-2, and 5-3, respectively. The flow rates of SF_6 and air entering the vessel were altered to induce varying Reynolds numbers while maintaining the same volumetric concentration of SF_6. Table 5-4 displays the flow rates of SF_6 and air entering the system, along with resultant Reynolds numbers to achieve a volumetric concentration range of 5 through19 ppm of SF_6 in air. Table 5-4 also includes a static scenario developed in earlier works [96]. Each equilibrium curve contains fifteen points because the employed scenario was sampled three times for each sampling time. The average value was plotted. The scenario was sampled three times to allow for the calculation of a standard deviation, and, in turn, a percent relative standard deviation (%RSD) to indicate the precision of the results. The %RSD can be calculated as shown Equation 5.11, and %RSD values less than 10% indicated precise results. The resultant chromatograms were interpreted using GC Solutions software (Shimadzu). All samples were taken from the turbulent air stream via the sampling port by the SPME fiber. A function of best fit was generated for each equilibrium curve, and the function which best fit the data was determined to be a third-order polynomial. An overlay of the calibration curves at the aforementioned flow rates is displayed in Figure 5-2.

Table 5-1: Chromatographic Results for Scenario 1

Sample Name	Exposure Time (s)	Retention Time (min)	Peak Area	Average Peak Area	Standard Deviation	%RSD
20121117_4	10	2.661	3.00E+06	3.13E+06	1.54E+05	4.91
20121117_2		2.660	3.09E+06			
20121117_5		2.659	3.30E+06			
20121117_6	20	2.659	4.11E+06	4.07E+06	9.00E+04	2.21
20121117_7		2.654	3.97E+06			
20121117_8		2.654	4.13E+06			
20121117_9	30	2.661	4.53E+06	4.56E+06	6.05E+04	1.33
20121117_11		2.651	4.63E+06			
20121117_12		2.656	4.52E+06			
20121117_13	40	2.655	4.68E+06	4.24E+06	3.87E+05	9.12
20121117_14		2.677	4.01E+06			
20121117_15		2.674	4.02E+06			
20121117_17	50	2.669	4.44E+06	4.35E+06	2.25E+05	5.18
20121117_21		2.670	4.09E+06			
20121117_20		2.659	4.51E+06			

Table 5-2: Chromatographic Results for Scenario 2

Sample Name	Exposure Time (s)	Retention Time (min)	Peak Area	Average Peak Area	Standard Deviation	%RSD
20121120_01		2.674	2.16E+06			
20121120_02	10	2.675	2.35E+06	2.27E+06	9.55E+04	4.21
20121120_03		2.675	2.29E+06			
20121120_04		2.673	2.61E+06			
20121120_05	15	2.669	2.91E+06	2.81E+06	1.69E+05	6.02
20121120_07		2.659	2.89E+06			
20121120_08		2.671	2.95E+06			
20121120_09	20	2.674	2.80E+06	2.84E+06	9.85E+04	3.47
20121120_11		2.677	2.76E+06			
20121120_13		2.676	2.82E+06			
20121120_15	25	2.670	3.15E+06	2.90E+06	2.24E+05	7.74
20121120_16		2.676	2.72E+06			
20121120_17		2.676	2.72E+06			
20121120_18	30	2.678	2.99E+06	2.91E+06	1.63E+05	5.58
20121120_19		2.676	3.02E+06			

Table 5-3: Chromatographic Results for Scenario 3

Sample Name	Exposure Time (s)	Retention Time (min)	Peak Area	Average Peak Area	Standard Deviation	%RSD
20121121_12	1	2.673	8.74E+05	8.50E+05	7.42E+04	8.72
20121121_13		2.687	7.67E+05			
20121121_14		2.676	9.10E+05			
20121121_09	3	2.672	1.14E+06	1.12E+06	1.82E+04	1.63
20121121_10		2.675	1.10E+06			
20121121_11		2.677	1.11E+06			
20121121_03	5	2.659	1.45E+06	1.43E+06	1.04E+05	7.30
20121121_04		2.664	1.32E+06			
20121121_05		2.662	1.52E+06			
20121121_6	10	2.679	1.41E+06	1.44E+06	9.61E+04	6.66
20121121_7		2.678	1.37E+06			
20121121_8		2.675	1.55E+06			
20121121_15	15	2.676	1.61E+06	1.66E+06	8.55E+04	5.17
20121121_16		2.675	1.61E+06			
20121121_17		2.669	1.75E+06			

Table 5-4: Summary of Scenarios with Resultant Equilibrium Times

Scenario	Air Flow Rate (Lpm)	SF_6 Mass Flow Rate (SCCM)	Reynolds Number	Expected Concentration (ppm)	Equilibrium Time (s)
Static	---	---	0	5	45
Scenario 1	50	1.0	4596	19	30
Scenario 2	70	1.4	6434	19	15
Scenario 3	75	1.4	6894	18	5

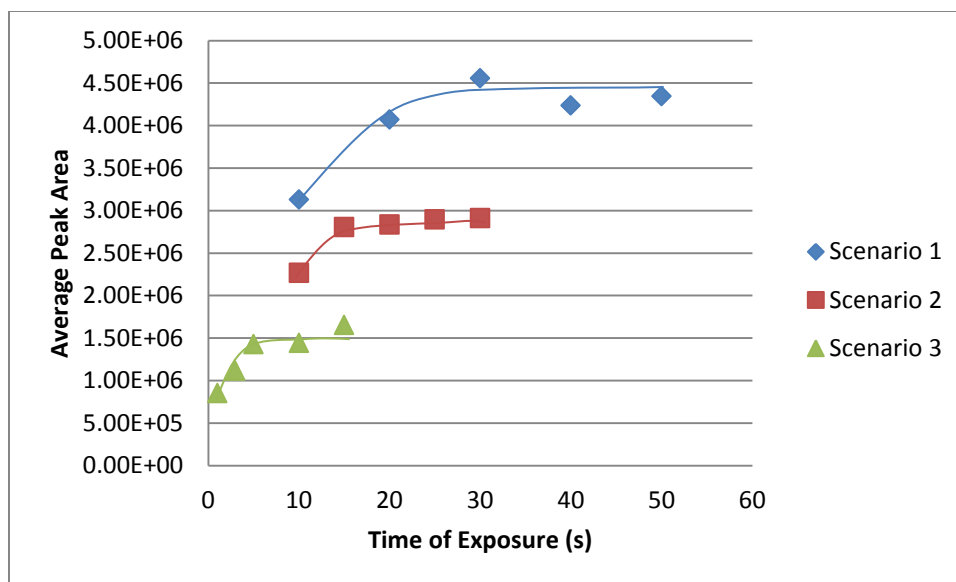$$\%RSD = \frac{Std.Dev.}{Average} \times 100\%$$ Equation 5.11

Figure 5-2: Overlay of Equilibrium Curves from Varying Scenarios

5.5.2 Simultaneous Measurement of Multiple Analytes

The ability of the SPME fiber to simultaneously sample multiple analytes was observed following the evaluation of the feasible application of SPME fibers to sample extraction in turbulent conditions. A 100 μm PDMS SPME fiber was used to sample the standard directly from the glass sampling bulb under static conditions. The SPME fiber delivered the extracted sample directly to the GC-ECD for analysis. The standard was analyzed three times to allow for the calculation of %RSD, as previously discussed. The parameters of the GC method employed are discussed in Table 5-5. The GC-ECD method was altered from that employed during turbulence testing to allow for PMCH to elute from the GC system. PMCH is a heavier tracer gas with a molecular weight of 350 g/mol [45], as opposed 146 g/mol for SF_6 [21]. As such, PMCH requires more time to elute from the system than does SF_6 [7]. Pure PMCH contains contaminants, including other perfluorocarbon tracers, which must be cleaned from the system, requiring a higher column temperature.

70

Table 5-5: GC Operating Parameters for Simultaneous Analysis of SF_6 and PMCH with SPME

Split Injector Temperature	270^0C
Sampling Time	0.1 min
Split Ratio	30:1
Total Flow	29.2 mL/min
Column Flow	0.91 mL/min
Linear Velocity	24 cm/s
Septum Purge Flow	1 mL/min
Detector Temperature	200^0C
Initial Column Temperature	35^0C for 0.05 min
Temperature Ramp Rate I	$100^0C/min$
Hold Column Temperature	80^0 for 4 min
Temperature Ramp Rate II	$100^0C/min$
Final Column Temperature	180^0C for 10.5 min
Total Program Time	16 min

Resultant chromatograms indicate that the 100 μm PDMS SPME fiber is indeed able to simultaneously sample multiple tracers under static conditions. The GC Solutions software integrated the peak areas of both SF_6 and PMCH such that the resultant %RSD values were below 10%, indicative of high precision. The overlay of the resultant chromatograms when sampling multiple tracer gases simultaneously is displayed in Figure 5-4. Tables 5-6 and 5-7 display the numerical results for SF_6 and PMCH, respectively.
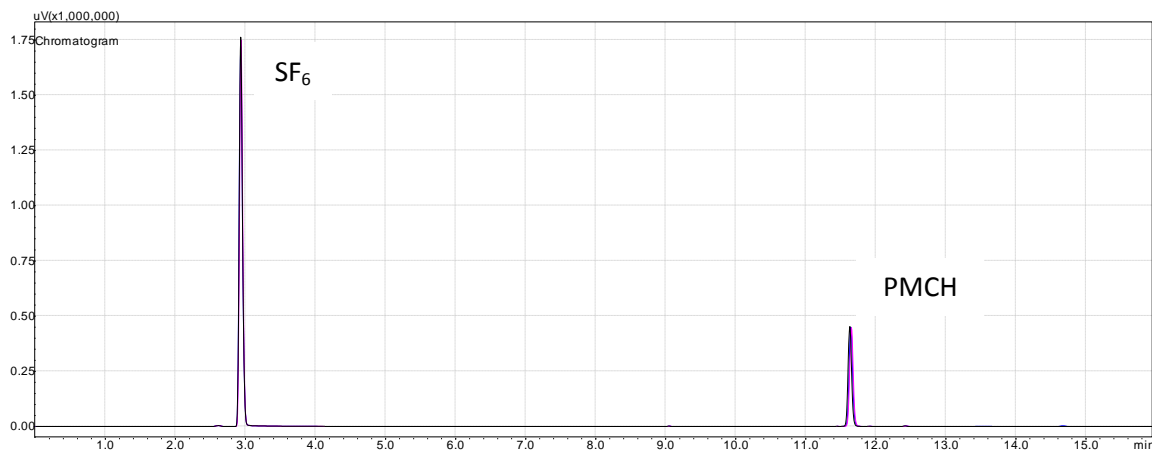

Figure 5-3: Overlay of Resultant Chromatograms when Sampling Multiple Tracer Gases

Table 5-6: Numerical Results for SF_6 when Sampling Multiple Tracer Gases Simultaneously

Sample Name	Expected Concentration (ppm)	Retention Time (min)	Peak Area	Average Peak Area	Std Dev	%RSD
090912_18		2.935	5.86E+06			
090912_19	55	2.931	5.85E+06	5.93E+06	1.28E+05	2.17
090912_20		2.931	6.08E+06			

Table 5-7: Numerical Results for PMCH when Sampling Multiple Tracer Gases Simultaneously

Sample Name	Expected Concentration (ppm)	Retention Time (min)	Peak Area	Average Peak Area	Std Dev	%RSD
090912_18		11.651	1.60E+06			
090912_19	55	11.643	1.58E+06	1.60E+06	1.76E+04	1.097
090912_20		11.628	1.62E+06			

5.6 Discussion

Concerning the ability of the SPME fiber to be applied to sample extraction in turbulent conditions, the chromatographic results displayed in Table 5-1 indicate high confidence in the precision of the results obtained based on consistently low %RSD values. Figure 5-2 illustrates the differences in equilibrium times between the three scenarios; as expected, the most turbulent condition (i.e., Scenario 3) reaches equilibrium the fastest. This result is even more obvious from Figure 5-4, which directly shows the relationship between Reynolds numbers and the resultant equilibrium time. In addition to the three scenarios discussed, Figure 5-3 contains a point representing the equilibrium time under static conditions where the Reynolds number is zero as obtained in previous work [96]. A linear trend line fits the data well with an R^2 value of 0.9 and clearly enforces the theory that kinetic interactions of the matrix with the SPME fiber reduces the necessary time for concentration equilibrium to occur between the extracting phase of the SPME fiber and the sample matrix.
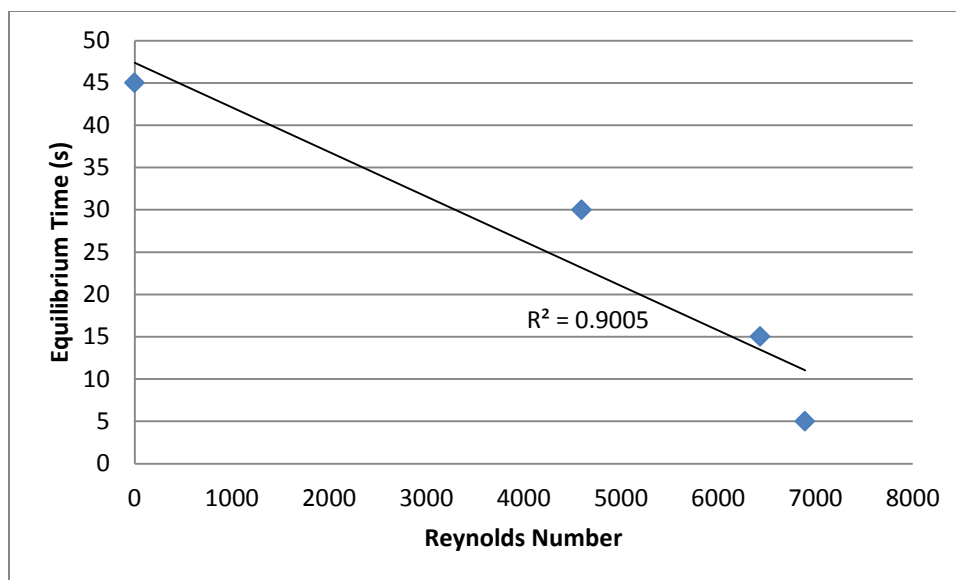
Figure 5-4: Reynolds Number versus Equilibrium Time

The displayed results in Figure 5-3 indicate a high confidence in the ability of a 100 μm PDMS SPME fiber to simultaneously sample multiple tracer gases under static conditions. This confidence is derived from the presence of reproducible results as indicated by the low %RSD values. The test also indicates, however, that PMCH has a weaker response to the selected SPME fiber than does SF_6. This conclusion can be drawn because the SPME fiber was exposed to the same concentration of SF_6 as PMCH, but the resultant peaks are significantly larger for SF_6 than for PMCH. The peak shape, however, is sharp and ideal for both tracer gases with minimal tailing present. Additionally, the peaks of the individual tracer gases are well resolved from one another as a result of the altered GC-ECD method. All factors considered, the selected SPME fiber is capable of simultaneously sampling multiple tracer gases under static conditions. Further work will include the simultaneous sampling of multiple tracer gases under turbulent conditions as well as sampling of tracer gases in an underground mine.

5.7 Conclusions/Future Work

In this study a range of volumetric concentrations were observed for the impact of kinetic interactions on equilibrium time via scenarios with altering Reynolds numbers. The results of this paper conclusively prove that increasing turbulence within a sampling matrix reduces the necessary time to achieve equilibrium between the sample matrix and the SPME fiber. These results are encouraging for applications of SPME fibers as a rapid sampling mechanism in a variety of industries because sampling procedures with SPME are not only easily employed and robust for the most unskilled user, but they are also very fast. Future work necessary to further understand the impact of kinetic interactions on sampling with SPME is to observe for changes in the capacity of the fiber for varying Reynolds numbers.

The second portion of this research studied the impact of sampling multiple trace analytes with SPME. The trace analytes observed were SF_6 and PMCH in the vapor state. When prepared in a static standard with equal parts SF_6 and PMCH the SPME fiber was able to collect both analytes. Having a standard of the same volumetric concentration of SF_6 and PMCH in nitrogen, the response of the SPME fiber to both trace analytes was expected to be equal. However, the SPME fiber showed a greater affinity for absorbing SF_6 as compared to PMCH. While the response of SPME to PMCH was only a portion of the response of SPME to SF_6, the peaks produced for both analytes were ideal for chromatography indicating a sufficient ability of SPME to simultaneously sample multiple tracers. Future work should be done to observe the ability of SPME to simultaneously sample multiple tracers in turbulent conditions, as was done with SF_6 in the first portion of this paper.

To gain a more comprehensive understanding of the ability of SPME to be applied in on-site situations, the impact of kinetic interactions on fiber capacity must be observed.

Additionally, the ability of SPME to collect multiple tracer analytes in turbulent conditions must be observed. Then, the ability of SPME to perform in the field must be observed. Finally, the ability of SPME fibers to retain sample should be observed. While analytes only desorb from SPME fibers via thermal desorption, due diligence calls from this final observation.

6 Conclusions

Tracer gas surveys are a powerful means of assessing air quantity in underground mine ventilation circuits. In many instances, tracer gas surveys are the only means of acquiring information about a ventilation circuit, but their limitations due to time and training requirements are daunting. Enhanced tracer gas techniques will significantly improve the flexibility of ventilation surveys. The most powerful means to improve tracer gas techniques applied to mine ventilation surveys is to alter existing protocols into a method that can be readily applied where tracer surveys already take place. The research objectives defined for this thesis were designed to facilitate improvements to existing tracer gas ventilation survey techniques.

One effective method of enhancing existing tracer gas survey protocols is to simply add a second tracer gas that can be detected on a gas chromatograph – electron capture detector (GC-ECD) using the same method as with the existing industry standard tracer, sulfur hexafluoride (SF_6). Radioactive gas and Freon gas tracers have been successfully used in the past, but a novel tracer that may be used in active workings with a simple analysis method is desirable. Novel tracer gases that have been successfully implemented in the past called for complex analysis methods requiring special equipment, or were designed for inactive workings. Compounds from two groups were considered to develop a methodology for a novel tracer gas to be implemented in tandem with SF_6 for the purposes of this study: Freon gases and perfluorocarbon compounds. Compounds from these groups were selected due to their known sensitive responses to GC-ECD systems and their non-toxic nature.

Experimentation with Freon gases lead to unsatisfactory chromatographic results due to differences in sensitivity between the tested gases and SF_6, and poor separation between peaks. On the contrary, experimentation with perfluoromethylcyclohexane (PMCH) and SF_6 allowed for peak separation and the development of Gaussian shaped peaks. PMCH is a favorable

76

selection for a novel tracer to work in tandem with SF_6 due to its chemical stability, similar physical properties and detection limits to SF_6, and its ability to be applied and integrated into an existing system. Additionally, PMCH has been successfully utilized in other large-scale tracer gas studies. A method using a Shimadzu GC-2014 with ECD and HP-AL/S column was developed to simultaneously detect SF_6 and PMCH. Future work with PMCH will require the development of a release method for the tracer compound due to its existence as a liquid at normal temperatures and pressures. The most promising means of releasing PMCH as a tracer gas is via a source containing liquid PMCH capped with a fluoroelastomer plug which will steadily release the tracer gas over time. The selection of PMCH as a novel tracer gas to be used in tandem with SF_6 satisfies research objective one of this thesis which was designated to improve existing methodologies for tracer gas surveys by making them more flexible and to reduce the time required to execute a comprehensive survey.

Introduction of a novel tracer gas will make great strides in improving the versatility of underground tracer gas ventilation surveys, but further improvement to the tracer gas technique can be made in simplifying individual steps. One such step which would benefit from improvement is in sampling. SPME has inherent characteristics making it a desirable option for sampling in the mining industry. Primarily, SPME is a precise method in the hands of a variety of users for rapid sampling of analytes present in low concentrations, and is highly portable in a rugged environment. The greatest impact that will result from implementing SPME as a sampling device is the ease of use of the mechanism and the requirement of minimal training to obtain precise results.

When applying SPME to sampling during underground mine ventilation surveys, sensitivity will be increased by using a SPME fiber with a PDMS bonding phase. The thickest

coating of 100 μm of extracting phase is the optimum thickness to allow for sufficient recovery

of the non-polar analytes without being overloaded with oxygen from air. Recovery of sample

during analysis with a GC-ECD system can be optimized with the use of a splitless method with

a short sampling time, an initially cool column with a rapid ramp of temperature, and a moderate

linear velocity of the carrier gas. The identification of SPME as a robust sampling mechanism

for tracer gas surveys satisfies research objective two for this thesis, which was designated to

investigate sampling methods which will simplify tracer gas surveys on-site that can be easily

integrated into existing protocols.

When using SPME for quantification of analytes, two items are necessary to properly

analyze samples: an equilibrium curve and a calibration curve. The equilibrium curve indicates

the time period where sampling can be optimized via time of exposure of the fiber to the sample

and provide the most reproducible results. Once the fiber has been exposed for the determined

equilibrium time, the capacity of the fiber will be filled so that overexposure will not impact

analytical results. The calibration curve is necessary to allow for quantification of analytes when

using a GC system for analysis. A calibration curve may be developed with high confidence

when using SPME due to the precision SPME allows for, as indicated by the high R^2 value

achieved during experimentation.

To further understand sampling with SPME, a range of volumetric concentrations were

created in three scenarios to observe the impact of kinetic interactions on equilibrium time via

scenarios with altering Reynolds numbers. The results of this study conclusively proved that

increasing turbulence within a sample matrix reduces the necessary time to achieve equilibrium

between the sample matrix and the extracting phase of the SPME fiber.   These results are

encouraging for applications of SPME fibers as a sampling mechanism in a variety of industries

because sampling procedures with SPME are not only easily employed and robust for the most unskilled user, but they are also very fast.

The impact of sampling multiple trace analytes with SPME was also observed. The trace analytes observed are SF_6 and PMCH in vapor state. When prepared in a static standard with equal parts SF_6 and PMCH the SPME fiber was able to collect both analytes. Having a standard of the same volumetric concentration of SF_6 and PMCH in nitrogen, the response of the SPME fiber to both trace analytes was expected to be equal. However, the SPME fiber showed a greater affinity for SF_6 as compared to PMCH. While the response of SPME to PMCH was only a portion of the response of SPME to SF_6, the peaks produced for both analytes were ideal for chromatography indicating a sufficient ability of SPME to simultaneously sample multiple tracers.

Future work to further improve the tracer gas technique of conducting mine ventilation surveys includes developing a reproducible means of releasing PMCH at a sufficient rate to achieve similar concentrations as SF_6 during surveys. Additionally, the GC-ECD method could be altered to accommodate other compounds from the perfluorocarbon group in addition to SF_6 and PMCH in one simple method. Additional tracer compounds can only increase the flexibility of ventilation surveys. Future work with SPME calls for determining the impact on fiber capacity due to kinetic interactions between the extracting phase of the fiber and the sample matrix. Furthermore, the impact of sampling multiple compounds under turbulent conditions with SPME should be observed. Future work should contribute to the simplification of tracer gas surveys and practicality of executing ventilation surveys in this manner in underground mines.

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