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Solid phase microextraction (SPME) sampling under turbulent conditions and for the simultaneous collecting of tracer gases

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ABSTRACT

Solid phase microextraction (SPME) is a solvent-free method of sample collection. 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 a sample to a gas chromatograph (GC) for analysis by means of thermal desorption. In this paper, the performance of SPME under dynamic conditions was investigated. Additionally, the competence of SPME sampling for the simultaneous analysis of multiple trace analytes was also evaluated. 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. The results of this paper showed that the performance of the 100 μm PDMS SPME fiber was both precise and rapid under dynamic conditions. This SPME fiber was also able to simultaneously collect sulfur hexafluoride (SF_6) and perfluoromethylcyclohexane (PMCH) with adequate sensitivity.

1. Introduction

Ventilation systems are designed to provide a comfortable working atmosphere while exhausting airborne contaminants. In order to maintain these systems, ventilation surveys are conducted to assess performance, identify flow paths, and troubleshoot ventilations circuits. One method of conducting ventilation surveys, especially in areas that are inaccessible, is with the aid of tracer gases. Modern tracer gases are anthropogenically generated and designed to be inert, non-toxic, and easily detectable. Tracers are exceptionally versatile and can be deployed across a wide range of scales from large open terrain to a laboratory HVAC system [1,2]. One of the more popular tracer gases is sulfur hexafluoride (SF_6).

SF_6 is a fully fluorinated symmetric molecule with a molecular weight of 146.055 g/mol. The fully fluorinated structure affords SF_6 a high detection sensitivity when using electron capture based detection methods. SF_6 has been widely used in both building ventilation and atmospheric tracing studies. Such studies include the identification of ventilation system failure in a garment manufacturing facility, the evaluation of engineering controls intended to reduce worker exposure to metalworking fluids, and the determination of ventilation circuit flow rate and capture efficiency [3,4]. These examples show how tracer gases are used to maintain and enhance occupational health and safety. The maintenance of a safe and healthy working environment is at the core of underground mine ventilation.

Underground mine ventilation surveys are conducted to maintain existing controls, plan for expansions, and improve existing systems [5]. A mine ventilation survey typically produces information about air quantity, air velocity, and flow resistance. From the standpoint of health and safety, air quantity is of the utmost importance because of its direct dilution of harmful gases. In certain situations, a survey may need to be conducted in an area that is either inaccessible or hazardous. In these cases, tracer gases are utilized. SF_6 is the standard tracer gas used across the mining industry. Although this tracer has been used for over three decades by the mining industry, consistent, representative sampling remains a major challenge. Solid phase microextraction (SPME), a relatively new sampling medium that is both durable and highly precise, shows great potential for use in mine tracer gas studies.

2. Solid phase microextraction (SPME)

SPME is a solvent-free sampling method based on the sorption of analytes onto a fiber coated with a polymer based extracting

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phase [6]. The extracting phase can be customized to achieve exceptional selectivity in both liquid and air sampling applications. SPME has been extensively applied in physicochemical, environmental, food, flavor, fragrance, pheromone, pharmaceutical, clinical, and forensic applications [7]. SPME has also been used to fulfill new requirements for both sample detection limits and sampling times in the area of occupational health and safety and applied in on-site exposure assessment situations to achieve precise analysis when employing unexperienced workers [8,9].

The high precision of SPME can be achieved because the fiber functions as a passive diffusion monitor. Traditional sampling techniques require an active component, such as the manipulation of a syringe plunger, in which an operator must act on a mechanism. Air sampling in this manner potentially allows the propagation of manual sampling errors. This issue is especially prevalent in air sampling mediums such as syringes and Tedlar bags. In contrast, SPME is an equilibrium sampling technique.

Equilibrium sampling in terms of SPME represents the manner in which analytes independently diffuse into the fiber. This diffusion occurs at a rate that is representative of their molar concentrations in the medium from which they are collected. The concentrations of the analytes within the fiber are proportional to their concentrations in the sampling medium at any given fiber exposure time interval. As such, SPME is expected to perform well in steady-state release studies in which the tracer is evenly distributed in the flow stream. The passive nature of the SPME sample collection mechanism will potentially eliminate much of the operator error present in traditional tracer gas evaluations. These characteristics in conjunction with SPME's ability to perform trace-level volatile analysis gives this tool great potential for application in tracer based mine ventilation studies.

Preliminary studies have already shown that SPME can be used to individually collect SF_6 as well as perfluoromethylcyclohexane (PMCH), a newly selected tracer for underground mines, using a fiber coated with 100 μm of polydimethylsiloxane (PDMS). Sample collection in these past studies was conducted in isolated nitrogen purged environments in order to compare the affinity of different SPME phases for each tracer. However, these experimental parameters are not representative of conditions in an underground mine.

Although exact environmental circumstances cannot be replicated in a laboratory environment, the ability of SPME to sample in a turbulent environment with the presence of air can be evaluated. In addition to determining the feasibility of applying SPME under dynamic conditions, the ability of SPME to simultaneously collect multiple tracers must also be observed. This is largely due to the fact that if SPME is used in the field, multi-analyte sampling is critical for multi-tracer studies. The application of SPME to the simultaneous measurement of the two tracers has not yet been investigated.

3. Methods and materials

In this study, SPME was evaluated based on its ability to sample SF_6 and PMCH from a turbulent air stream. Experiments were conducted in order to elucidate the impact of a dynamic environment on SPME sample recovery and analysis. Although commonly present mine gases, such as acetylene, were not added to the flow stream, these analytes are not expected to impact the analysis because the PDMS fiber does not have an affinity for the missing gases. Additional SPME experiments were conducted to determine the efficacy of using SPME to simultaneously sample SF_6 and PMCH in a nitrogen purged environment under static conditions.

Particular interest was paid to the sample capacity of the fiber when sampling these two high molecular weight tracers and its impact on detection sensitivity. The effect of sample uptake kinetics, partition coefficients, and boundary layer-analyte interactions were not evaluated because of the low concentration, non-rapid sampling nature of steady-state mine scale tracer studies. In such studies, the tracer would be given sufficient time for even mixing in the flow stream thus producing a constant tracer concentration across the cross section of the airway. Once thoroughly mixed, the tracer release would continue until all of the desired air samples had been collected. As a result, a steady-state study would allow for an unconstrained sampling period. The issues associated with rapid sampling and the achievement of temporal resolution is therefore not significant and is beyond the scope of this study. All SPME samples were analyzed using a gas chromatograph (GC) equipped with an electron capture detector (ECD).

3.1. SPME sampling under turbulent conditions

The first portion of the experiment was designed to determine how a dynamic environment affected SPME sample recovery by comparing samples collected under varying turbulent conditions. The controlled, turbulent environment was created using the apparatus depicted in Figs. 1 and 2.

A fully developed turbulent flow stream is necessary to allow for the uniform mixing of the tracer in the apparatus [10]. An air pump capable of producing up to 200 L/min (LPM) was used to force air into the apparatus in a blowing-type system. In order to control the flow quantity of the air stream, a variable area flow meter equipped with an adjustable valve was installed in-series with the pump. The airflow in the apparatus entered from the inlet located at the bottom of the apparatus. The airstream would then move through the main body of the vessel and exit through the outlet located at the top of the apparatus.

The tracer gas used during testing was SF_6. The SF_6 was released from a compressed gas cylinder. A mass flow controller was connected to the gas cylinder to control the exact amount of SF_6 released. SF_6 was mixed with the airflow at the inlet of the apparatus. The SPME sampling port perpendicularly intersected the flow stream at the outlet of the apparatus. The port was capped with a septum, which isolated the flow stream from the laboratory environment. The sampling port was designed to allow the SPME fiber to pierce the septum and intersect the airstream at the center of the outlet. This configuration allowed for the sample to be collected by the direct immersion of the 100 μm PDMS SPME fiber in the flow stream.

The Reynolds number was calculated first to indicate whether the flow induction potential of the air pump was sufficient to produce turbulent flow. Turbulent flow is essential for the uniform mixing of a tracer gas in an airway. The achievement of turbulent flow in underground mines is not an issue because typical Reynolds numbers exceed 10,000. However under laboratory conditions, the apparatus' ability to meet this constraint needed to be verified.

Using the psychometric conditions in the laboratory, the dry air density was found to be 1.21 kg/m^3. The Reynolds number was determined using Eq. (1) where ρ is density of air in units of kg/m^3, u is the air velocity 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).

$$\mathrm{Re} = \frac{\rho u h_d}{\mu} \quad (1)$$