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Talanta

journal homepage: www.elsevier.com/locate/talanta

A mid-infrared sensor for the determination of perfluorocarbon-based compounds in aquatic systems for geosequestration purposes



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ARTICLE INFO

Article history:

Received 15 May 2014

Received in revised form

8 July 2014

Accepted 9 July 2014

Available online 25 July 2014

Keywords:

Perfluorocarbon

Geosequestration

Groundwater monitoring

Mid-infrared spectroscopy

Attenuated total reflectance

Optical sensor

ABSTRACT

Perfluorocarbon (PFC) compounds have been used as chemical tracer molecules to understand the movement of supercritical carbon dioxide for geosequestration monitoring and verification purposes. A commonly used method for detecting PFCs involves the collection of a sample from either soil-gas or the atmosphere via carbon-based sorbents which are then analyzed in a laboratory. However, PFC analysis in aquatic environments is neglected and this is an issue that needs to be considered since the PFC is likely to undergo permeation through the overlying water formations. This paper presents for the first time an innovative analytical method for the trace level in situ detection of PFCs in water. It reports on the development of a sensor based on mid-infrared attenuated total reflection (MIR-ATR) spectroscopy for determining the concentration of perfluoromethylcyclohexane (PMCH) and perfluoro-1,3-dimethylcyclohexane (PDCH) in aquatic systems. The sensor comprises a zinc selenide waveguide with the surface modified by a thin polymer film. The sensitivity of this device was investigated as a function of polymer type, coating thickness, and solution flow rates. The limit of detection (LOD) was determined to be 23 ppb and 79 ppb for PMCH and PDCH, respectively when using a 5 μm thick polyisobutylene (PIB) coated waveguide. This study has shown that the MIR-ATR sensor can be used to directly quantify PFC-based chemical tracer compounds in water over the 20–400 ppb concentration range.

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1. Introduction

The need to reduce atmospheric carbon dioxide (CO₂) levels has led to considerable research in developing technologies and methods for mitigating problems associated with steadily increasing CO₂ concentrations. It has been demonstrated that the storage of captured CO₂ from large scale point emissions sources (power plants, gas processing, etc.) into deep subsurface geologic reservoirs is a potentially safe and effective approach for reducing CO₂ levels in the atmosphere [1]. Extensive research has been performed to identify and characterize suitable storage sites, which involves obtaining information on the storage capacity (how much CO₂ can be kept in a storage interval), containment security (ensuring that the CO₂ remains in the storage interval and not leak) and injectivity (ability to inject CO₂ with minimum numbers of injection wells while remaining below the rock fracture pressure). Site characterization is an essential step that is needed to

minimize the risk and uncertainty in relation to geosequestration. In particular, the environmental impact associated with the potential mobilization of toxic constituents (heavy metals, organic compounds, etc.) and their migration pathway into drinking and groundwater aquifers is recognized as an important area of monitoring and verification research [2–5].

One method for determining the effectiveness of long-term storage of CO₂ and its migration through the subsurface is the use of chemical tracer compounds, which are co-injected with the supercritical CO₂ [6]. Chemical tracers have been extensively used to understand how materials or substances are transported and dispersed within their immediate environment, as well as within entire ecosystems. Typically, a small amount (i.e., part per million (ppm) levels) of the tracer is (co)-injected into the formation containing the CO₂, and the presence of the tracer at the surface is indicative of a potential leakage process. According to Dugstad et al. [7] a tracer must be stable at the reservoir conditions, have a low background level and detection limit, have minimal environmental consequences, and should not absorb onto rocks. It is assumed that an ideal tracer behaves similar to CO₂ (i.e., they both migrate and leak at comparable rates), and that the tracer molecule does not interact with the surrounding sediment/geological formation.

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Perfluorocarbons (PFCs) have been used as chemical tracer compounds for understanding fluid movement underground, and for monitoring potential CO₂ leakage [8–12]. Although this group of compounds is generally inert, stable and have low background levels (i.e., femto levels), the monitoring of PFCs in geological environments is a major challenge considering that small concentrations are applied which can disperse over a potentially vast area/volume. In most cases, gas samples contain PFCs at levels typically lower than one part per billion which need to be collected over a period of time (e.g. days to months) from either soil-gas or the atmosphere using carbon-based sorbents and are then analyzed in a laboratory via thermal desorption gas chromatographic methods [9,13]. This process involves a series of steps which can be time consuming/hazardous, does not provide real-time information, and usually leads to large quantitative errors due to issues with sampling/sample handling of volatile compounds. More importantly, information concerning the partitioning behavior of PFC compounds into an overlying water formation (e.g. aquifer and groundwater) and possibly other bodies of water (e.g. lakes, rivers) is in many cases missing or does not exist. Although PFCs are generally immiscible with aqueous solutions [14], no data is available in the literature on the solubility of PFC compounds in water. In addition, the PFC solubility/partition coefficient in formation water as a function of temperature and pressure is not well known. Subsequently, there is a need for complementary and improved methods which will allow in situ monitoring of PFC tracers permeating through overlying bodies of water (e.g. aquifers and groundwater). To accurately determine the leak rate and location of PFCs, sensitive analytical methods (i.e., chemical sensors) that can be deployed in the field for monitoring PFCs in groundwater and wellbore water systems would be preferable. Although a wide range of sensors are available for monitoring aquatic environments [15], mid-infrared (MIR) sensors based on attenuated total reflectance (ATR) spectroscopy are among the most promising methods for directly detecting and quantifying organic compounds in complex environmental samples [16–18]. While this approach has been widely applied for the analysis of a range of hydrocarbon molecules [19–29], this is the first study demonstrating the potential of MIR-ATR sensors for the detection of PFC compounds in water.

This paper reports on the development and analytical performance of an infrared-based sensor for the detection of various PFC compounds in water. A MIR sensor incorporating a polymer-coated zinc selenide (ZnSe) waveguide serving as the ATR transducer was investigated for the identification and quantification of PFCs. The purpose of the polymer film is to facilitate the extraction of PFC molecules into the analytical volume that is probed. The overall aim of this study is to evaluate the suitability of MIR-ATR for sensing chemical tracer compounds for applications relating to geosequestration/geochemistry (e.g. monitoring and verification) and environmental analysis (e.g. identification and quantification of organic contaminants in natural waters).

2. Experimental

2.1. Materials and reagents

Perfluoromethylcyclohexane (PMCH, 94%) and perfluoro-1,3-dimethylcyclohexane (PDCH, 90%) were purchased from Alfa Aesar (Ward Hill, MA, USA) and used without further purification. Some experiments were also undertaken using PDCH (80%) which was obtained from Sigma Aldrich (St. Louis, MO, USA). The molecular structures of PMCH and PDCH are shown in Fig. 1, and Table 1 summarizes their most relevant physical properties. Ethylene-propylene copolymer (E/Pco) and Poly(isobutylene) (PIB) were

supplied by Scientific Polymer Products, Inc. (Ontario, NY, USA) and used as provided.

2.2. Waveguide surface preparation and coating deposition

Trapezoidal (4 mm thick, 80 mm long, 10 mm wide; angle of incidence: 45°) zinc selenide (ZnSe) ATR waveguides were used as a multi-reflection transducer (provides 10 reflections). Prior to coating deposition, the surface of the waveguide was cleaned by wiping with acetone-wet lens-cleaning tissue (Whatman International Ltd., Maidstone, England) followed by rinsing with acetone and drying by flowing high purity nitrogen gas for several minutes. E/Pco films of different thickness were prepared by dissolving the polymer in tetrahydrofuran within the concentration range between 0.10 and 0.98 wt%. PIB coatings were prepared by polymer dissolution in n-hexane and the film thickness was adjusted by varying the concentration between 0.14 and 1.41 wt%. The polymer-coated waveguides were allowed to dry overnight and IR spectra were collected to confirm that the solvent had completely evaporated. The variability in polymer coating thickness was evaluated by independently repeating the coating deposition about 10 times. All of the obtained coatings were reasonably reproducible in thickness (< 14% variation), and uniform in terms of homogeneity and integrity.

2.3. Instrumentation and sensor system

All measurements were performed using a Bruker Vertex 70 Fourier transform infrared spectrometer equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector. The ZnSe waveguide was mounted into an ATR unit providing a trough plate equipped with a stainless steel flow cell (Pike Technologies, Madison, WI, USA). Prior to PFC studies, all polymer coatings were allowed to equilibrate in deionized water for a period of 24 h. All PFC solutions were pumped across the polymer-coated ZnSe surface using a peristaltic pump (Ismatec, IDEX Corporation) and experiments were performed at room temperature. Data were recorded in the spectral range between 4000 and 650 cm⁻¹ at a spectral resolution of 2 cm⁻¹ by averaging 100 scans for each spectrum. In the following paper, only the spectral range comprising the relevant PFC absorption features (1040–840 cm⁻¹) is shown.

The polymer coatings were evaluated at different coating thicknesses and solution flow rates by exposing them to deionized water containing a known quantity of PMCH. A saturated PMCH solution was established by adding PMCH (100 µL) into a sealed glass flask containing deionized water (250 mL), and allowing the solution to equilibrate at room temperature (20 ± 1 °C) for at least 24 h. To minimize the problem of slow PFC diffusion into water, the saturated PMCH solution was continuously stirred at approximately 500 rpm using a glass stir bar. In some experiments that involved the calibration of the MIR-ATR sensor, isopropanol (5% v/v) was added to help improve the stability/solubility of the PFC in water. Analytical calibration solutions were prepared by dissolving the respective PFC (stock solutions of 981 ppm (w/v) for PMCH and 872 ppm (w/v) for PDCH in isopropanol) in deionized water containing 5% v/v isopropanol as a solubility mediator. Each sensor calibration was independently repeated 3 times; the concentrations of the PFC stock solutions were verified via gas chromatography. To limit evaporation losses due to the volatile nature of the PFCs, all standards were freshly prepared and all subsequent studies were performed within less than 6 h. Glass stoppers and glass stir bars were used throughout these studies to further minimize PFC losses.

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