



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



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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.

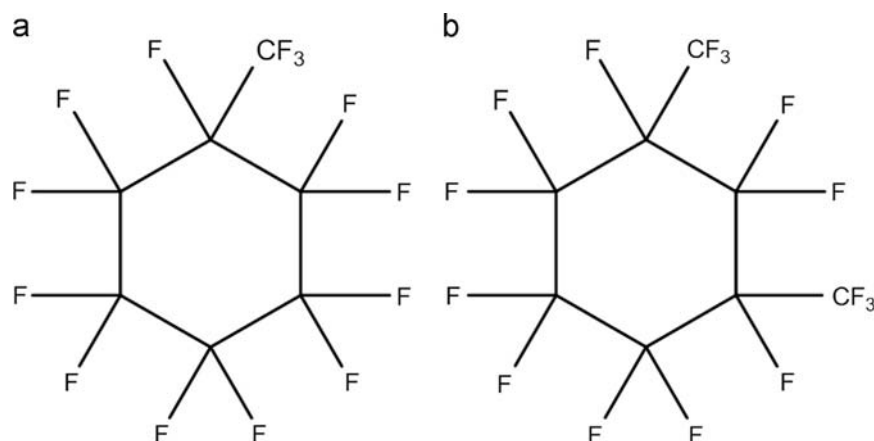


Fig. 1. Molecular structure of (a) perfluoromethylcyclohexane and (b) perfluoro-1,3-dimethylcyclohexane.

Table 1

Physical properties of perfluoromethylcyclohexane (PMCH) and perfluoro-1,3-dimethylcyclohexane (PDCH).

	Perfluoromethylcyclohexane	Perfluoro-1,3-dimethylcyclohexane
Molecular weight (g mol ⁻¹)	350	400
Density (g mL ⁻¹)	1.788	1.828
Boiling point (°C)	76	102
Melting point (°C)	-37	-70
Vapor pressure (kPa)	14	4.8

2.4. Spectral data analysis

The PFC-characteristic infrared absorption features were evaluated via peak area analysis using the software package OPUS (Bruker Optics, Ettlingen, Germany). For PMCH, the region between 985 and 963 cm⁻¹ was integrated, whereas the range from 916 to 900 cm⁻¹ was used for PDCH. For all spectra the polymer coated ZnSe in deionized water was used as a background.

2.5. Validation of stock solutions via gas chromatography

The concentration of the dissolved PFCs in aqueous and in isopropanol stock solutions was analyzed using a gas chromatograph (Varian CP3800) equipped with an electron capture detector (GC-ECD). An Agilent J&W CP-Sil 5 CB column was used in split mode (100:1 split ratio). The column conditions used are as follows: initial column temperature was 30 °C; final column temperature was 180 °C; and program column rate was 40 °C/min. A purge-and-trap strategy was followed (EST Encon preconcentrator) with the samples automatically supplied via an auto-sampler (EST model 8100). The PFCs were solvent extracted from the water phase using n-pentane followed by analysis with GC-ECD. Quantitative data was obtained by comparison with standards and calibration curves were generated over the 0–4000 µg/L concentration range. The limit of detection was determined to be 10 µg/L and 5 µg/L for the PMCH and PDCH, respectively.

3. Results and discussion

3.1. PFC solubility in water

At present, limited information exists in the literature on the solubility of PFCs in water. Since the current study is focussed on

quantifying trace amounts of PFC in aqueous solutions, it was deemed necessary to determine their solubility such that standards could be prepared containing known concentrations for sensor calibration purposes. Saturated aqueous solutions of PMCH and PDCH were allowed to equilibrate with time and the dissolved analyte concentration in water was determined using GC-ECD. Equilibrium between the analyte and water was achieved relatively fast (i.e., <2 days) at room temperature. Furthermore, the dissolved PMCH concentration in water was determined at 171 ± 57 ppb (one standard deviation, 10 replicate measurements), whereas the concentration of PDCH in water was determined to be 67 ± 39 ppb (one standard deviation, 10 replicate measurements). One of the issues with accurately determining the solubility of PFCs in water is their substantial volatility, which renders obtaining reproducible results a significant challenge. Consequently, all solutions prepared during this study were exclusively using glassware only (including stoppers and stir bars) and avoiding any headspace. Furthermore, the stirring rate was kept constant and low (500 rpm) to minimize the formation of air bubbles and subsequent outgassing of PFCs.

3.2. Infrared spectra of PFCs

To determine the most suitable absorption bands for the quantification of PFC compounds, IR spectra were collected using neat PFCs on an uncoated ZnSe ATR waveguide. Fig. 2 shows exemplary spectra of PMCH and PDCH in the spectral range of 1040–840 cm⁻¹, which provides the most characteristic peaks. According to the structures of the PFCs used (Fig. 1), both PMCH and PDCH comprise only C–F and C–C bonds. While a rather broad IR absorption band between 1400 and 1100 cm⁻¹ is characteristic of C–F stretching vibrations in polyfluoroalkanes [30,31], this spectral regime was not considered suitable for discriminating the different types of PFC molecules because of significant peak overlap. From 1040 to 840 cm⁻¹, the IR fingerprint spectra show a number of intense and distinct peaks, which may be attributed to various vibrations. Specifically, some of these peaks may be assigned to stretching vibrations of the C–C bonds of PMCH and PDCH. It is immediately evident from Fig. 2 that PMCH and PDCH provide some distinct IR absorption features, which not only enable their discrimination if present in a mixture, but also their quantification after enrichment into appropriate polymer coatings. For PMCH, the peak at 969 cm⁻¹ (i.e., corresponding to the C–C stretching vibration) was determined to be most suitable for quantitative studies, whereas PDCH was evaluated using the feature at 909 cm⁻¹ (corresponding to the C–C stretching vibration). The absorption peaks of PMCH were assigned by comparison of the acquired spectra to literature. Senyavin et al. [31] proposed

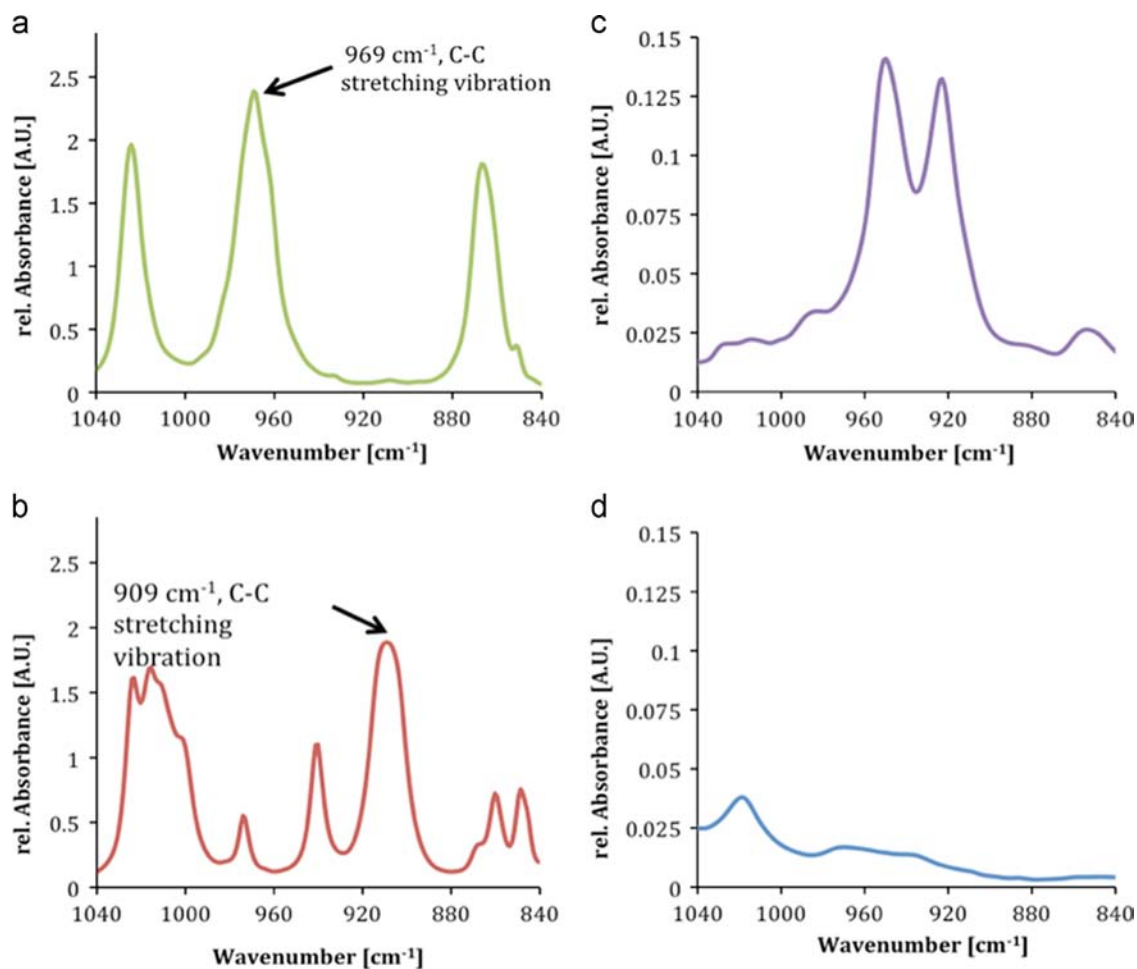


Fig. 2. IR spectra of the tracers (a) perfluoromethylcyclohexane and (b) perfluoro-1,3-dimethylcyclohexane contrasted by the IR spectra of the polymer coatings, (c) polyisobutylene, and (d) ethylene-propylene copolymer.

Table 2
C–C stretching bands of PMCH and PDCH and comparison to literature.

	PMCH		PCH	PDCH
Present study	867 cm ⁻¹ (s) 969 cm ⁻¹ (s) 1024 cm ⁻¹ (s)		– – – –	823 cm ⁻¹ (m) 909 cm ⁻¹ (s) 941 cm ⁻¹ (m) 1016 cm ⁻¹ (s) 1024 cm ⁻¹ (s)
Literature	870 cm ⁻¹ (s, vapor) ^a 975 cm ⁻¹ (s, vapor) ^a 1030 cm ⁻¹ (s, vapor) ^a	847–905 cm ⁻¹ (n. i., solid) ^b 946–969 cm ⁻¹ (n. i., solid) ^b 1020–1058 cm ⁻¹ (n. i., solid) ^b	870 cm ⁻¹ (vs, gas) ^c 978 cm ⁻¹ (vs, gas) ^c 1031 cm ⁻¹ (vs, gas) ^c	852 cm ⁻¹ (n. i., solid) ^b 986 cm ⁻¹ (vvs, gas) ^d 1048 cm ⁻¹ (n. i., solid) ^b

(m)—Middle, (s)—strong, (vs)—very strong, (vvs)—very very strong, and (n. i.)—no information.

^a [36,37].

^b [31].

^c [38].

^d [39].

that the bands between 1350 and 1200 cm⁻¹ arise from asymmetric and symmetric CF₂ vibrations while the region from 1220 to 1170 cm⁻¹ was assigned to the C–F stretch. The spectral range between 1100 and 670 cm⁻¹ was attributed to C–C stretching modes [31] and Table 2 compares the peak positions of the C–C stretching features in PMCH, PCH and PDCH. For comparison, Fig. 2 also shows the spectra of E/Pco and PIB in the spectral region of 1040–840 cm⁻¹. It is evident that both polymers provide spectral renders with very minor absorptions in this region, which renders them suitable for detecting the characteristic absorbances

of PMCH and PDCH after enrichment at 969 and 909 cm⁻¹, respectively.

3.3. Effect of polymer type and coating thickness

Two different polymers at various film thicknesses were investigated for the detection of PFCs. Generally, the polymer suitability is determined by the analyte–polymer partition and diffusion coefficients and these parameters play an important role in the analyte enrichment process [32]. A polymer membrane with

a large partition coefficient and diffusivity for the PFC molecule will typically have superior analytical performance in terms of sensitivity and response time. Fig. 3 displays the results of the related enrichment studies for PMCH, which shows that the absorbance signal arising from the extraction of PFC into the polymer strongly depends on the film thickness between 1 and 10 μm . It was anticipated that with increasing polymer thickness, more PFC is being extracted from the liquid phase and enriched at the ATR crystal surface, leading to a higher absorption signal. This effect is limited by the penetration depth of the infrared beam and its exponential decay in field intensity away from the waveguide surface. The electromagnetic field that extends from the surface of the waveguide into the optically rare medium (in our case the polymer) is referred to as the evanescent wave. The decay rate of the evanescent field depends directly on the wavelength of the radiation. The depth of penetration (d_p) of the evanescent wave was calculated at 972 cm^{-1} to be $2.11\text{ }\mu\text{m}$ into PIB by the following equation [33]:

$$d_p = \frac{\lambda}{2\pi n_1 [\sin^2 \theta - (n_2/n_1)^2]^{1/2}}$$

where n_1 is the refractive index of the optically denser medium (ZnSe crystal) and is 2.4 (from supplier), n_2 is the refractive index of the optically rarer medium (PIB) which is 1.51 (from supplier), λ is the wavelength of the incident IR radiation which at 972 cm^{-1} corresponds to $10.29\text{ }\mu\text{m}$, and θ is the angle of incidence which is 45° .

The analyte first diffuses from solution into the polymeric coating and then further diffuses inside the polymer towards the ZnSe–polymer interface. Once the analyte has reached the evanescent field, it can be detected by its specific IR absorption pattern. When the coating is saturated with the perfluorinated compound, the maximum signal can be detected. Since diffusion inside the polymer is considerably slower than in an aqueous solution, only a few molecules reach the evanescent field at a certain coating thickness. As expected, the PMCH absorbance at

equilibrium conditions increased with increasing coating thickness up to $5\text{ }\mu\text{m}$. At $10\text{ }\mu\text{m}$, the signal was roughly the same or even slightly lower than on a $5\text{ }\mu\text{m}$ coating, since only few analyte molecules diffuse deep enough into the coating to be able to interact with the IR radiation in the evanescent field. This is true for both polymers, PIB and E/Pco.

With increasing coating thickness it is evident that achieving equilibrium conditions requires extended partitioning periods ($> 1\text{ h}$). It is apparent in Fig. 3 that there are differences in sensitivity for detecting PMCH with the investigated polymers. E/Pco appeared to be slightly more sensitive; however, the diffusion of PMCH was more rapid into PIB. The period taken to achieve 90% of the maximum absorbance value (i.e., the T_{90} time) for a $5\text{ }\mu\text{m}$ PIB coating was approximately 100 mins compared to approximately 115 mins for E/Pco. Subsequently, a $5\text{ }\mu\text{m}$ coating thickness was determined as the optimum, and was used for all further studies reported herein. In terms of the most suitable polymer for detecting PFCs, it appears that both E/Pco and PIB performed equally well; however, PIB was selected for the subsequent studies based on the faster response time.

3.4. Effect of solution flow rate

As demonstrated in the previous section, the diffusion of PFCs into a polymer coating proceeds rather slowly. To determine if the sensitivity is also influenced by the PFC mass transport, studies were performed at varying flow rates of 1, 2 and 5 mL min^{-1} . Fig. 4 reveals that with increasing solution flow rate the sensitivity slightly increases. Also, it was revealed that at higher flow rates the absorbance signal reached equilibrium more rapidly. For the 1 and 2 mL min^{-1} flow rates the absorption signal does not reach equilibrium within 180 mins on a PIB coating. It is assumed that not enough analyte is being transported to the polymer film by the solution flow to reach equilibrium conditions. At a flow rate of 5 mL min^{-1} , the T_{90} -time is 100 mins. On an EPco coating, no

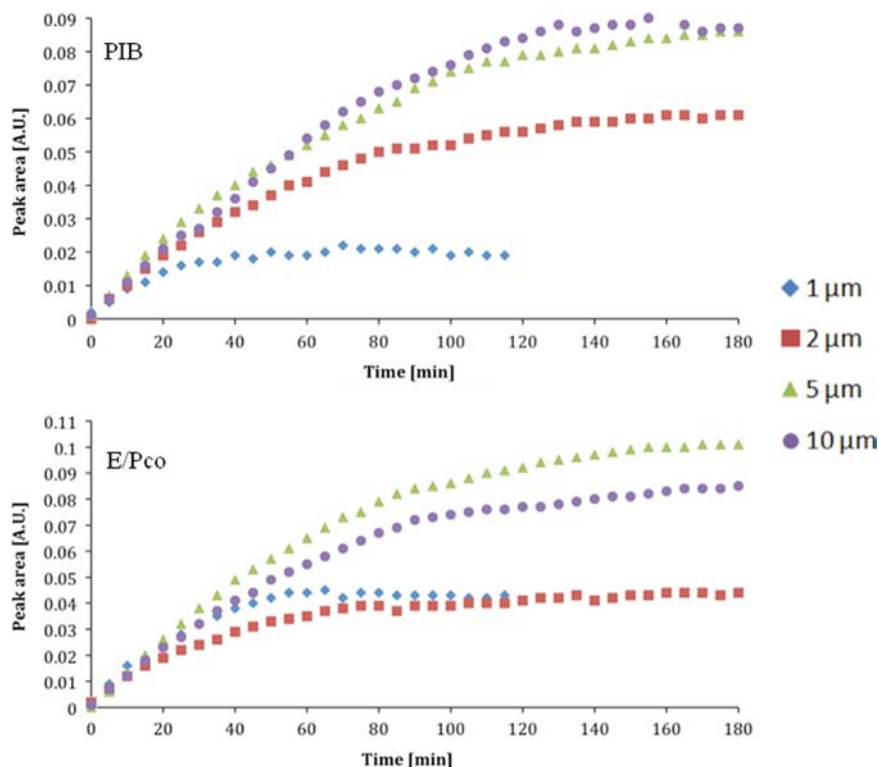


Fig. 3. Influence of polymer type and polymer coating thickness on the extraction of PMCH. All experiments were performed at a flow rate of 5 mL min^{-1} with a saturated aqueous solution of PMCH ($171 \pm 57\text{ ppb w/v}$).

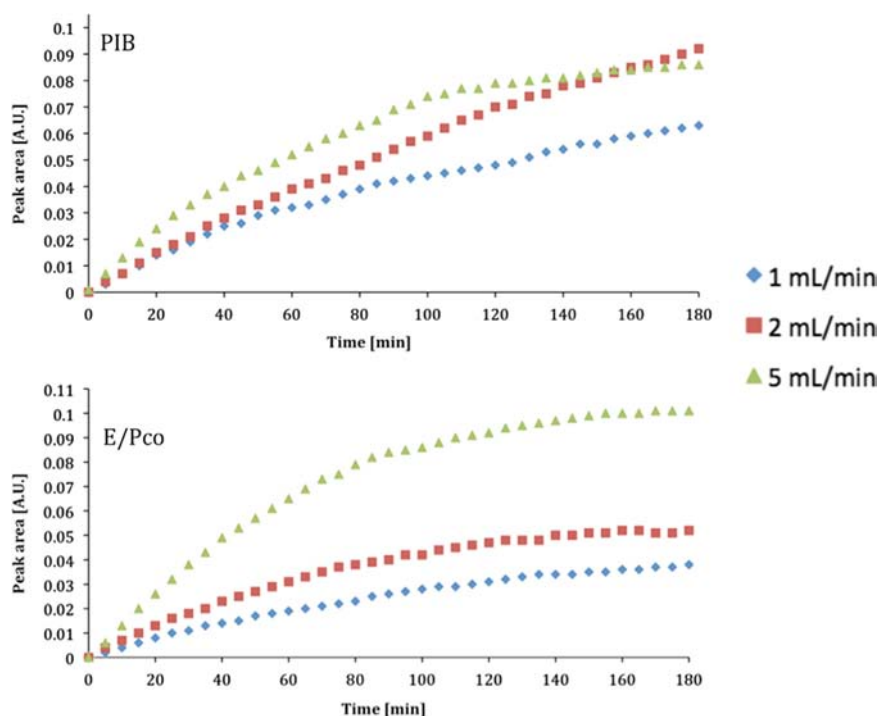


Fig. 4. Study on the effects of solution flow rate. All experiments were performed at a coating thickness of 5 μm with a saturated aqueous solution of PMCH (171 ± 57 ppb w/v).

Table 3

Mass and amount of PMCH transported across the coating during 195 min at different flow rates.

Flow rate [mL min^{-1}]	Total volume [mL]	Total mass of analyte [μg]	n (Analyte) [μmol]
1	195	33	0.094
2	390	67	0.191
5	975	167	0.477

equilibrium could be achieved at a solution flow rate of 1 mL min^{-1} , again due to the very low amount of analyte in the solution. At 2 and 5 mL min^{-1} , 90% of the equilibrium value was reached after 125 and 115 mins, respectively. Assuming a mean concentration of 171 ppb of PMCH in the saturated solutions, the following amounts of analyte that was pumped over the polymer during 195 mins was calculated (see Table 3). This study has shown that equilibrium is achieved faster and that more PFC analyte is being enriched in the evanescent field at high solution flow rates. Also, the sensor design and geometry has a considerable influence on the sensing performance and this has been previously reported [34]. Since a commercial ATR trough plate was used, the sensor geometry could not be changed and optimized in this study.

3.5. Determination of the diffusion coefficient

The diffusion coefficient was determined via curve fitting according to Fieldson and Barbari [35]. A one-dimensional diffusion of the PFCs through the polymer with a constant diffusion coefficient is assumed and it is expected that Fickian diffusion behavior is followed. The following equation was used to fit the curve to the experimental data and determine the diffusion coefficient:

$$A_t = A_\infty \left[1 - \exp\left(0.242 - \frac{D\pi^2}{4L^2}t\right) \right]$$

where A_t —absorption at a time t , A_∞ —absorption at equilibrium, D —diffusion coefficient, L —coating thickness, and t —time.

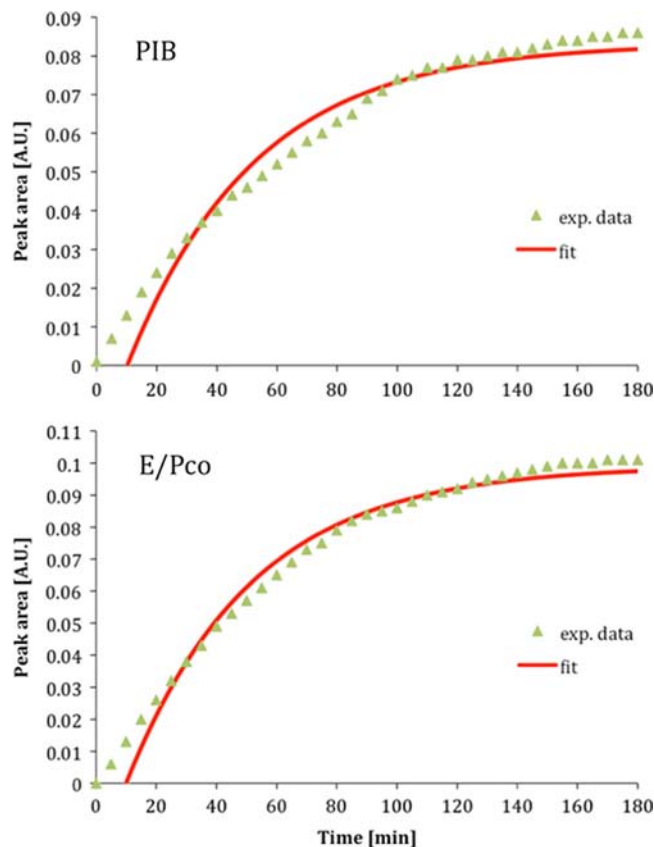


Fig. 5. Fickian diffusion fit of experimental data for both polymers (i.e., PIB and E/Pco) at a coating thickness of 5 μm and at a flow rate of 5 mL min^{-1} .

Fig. 5 shows the experimental data along with the fitted curves for both polymers, PIB and E/Pco at a coating thickness of 5 μm and a flow rate of 5 mL min^{-1} . For PIB, the coefficient of

determination R^2 is 0.93 and for E/Pco R^2 is 0.95. Hence, the obtained fit is in reasonable agreement with the experimental data, especially at the crucial region of the diffusion curve when equilibrium conditions are achieved. The absorption at the equilibrium state is only minutely underestimated by the fitted curve. The diffusion coefficients for PMCH were calculated for both polymers at a coating thickness of $L=5\ \mu\text{m}$ resulting in $3.99 \times 10^{-15}\ \text{m}^2/\text{s}$ for PIB, and $4.06 \times 10^{-15}\ \text{m}^2/\text{s}$ for E/Pco. From a sensing viewpoint, thin polymer films are preferable ($< 10\ \mu\text{m}$) since it has been shown elsewhere that the rate of diffusion depends on the film thickness [32].

3.6. MIR-ATR sensor calibration

To validate the feasibility of using a polymer coated ZnSe waveguide for MIR-ATR sensing of PFC tracer compounds in water, PMCH and PDCH were analyzed at a variety of different concentrations using a PIB coating. The IR spectra were collected after an enrichment period of 1.5 h and Fig. 6 shows the spectra as a function of PFC concentration. As expected, the peak intensity for both PMCH and PDCH increased in a linear fashion with increasing concentrations. Some differences were observed in the baseline below $900\ \text{cm}^{-1}$ and this is mainly attributed to the amount of water in the polymer film diminishing with

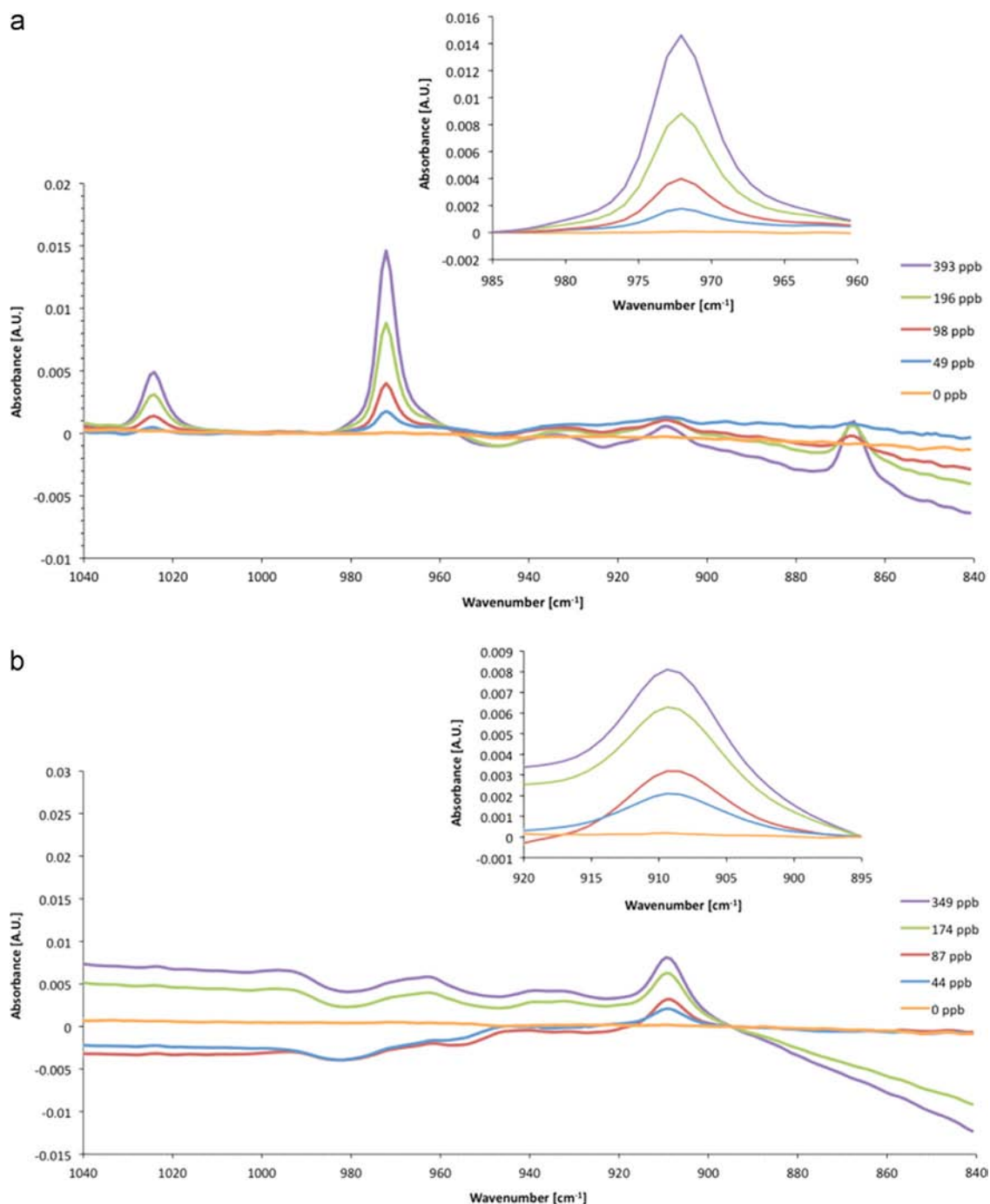


Fig. 6. IR absorption spectra of (a) perfluoromethylcyclohexane and (b) perfluoro-1,3-dimethylcyclohexane as a function concentration. A PIB coating of thickness of $5\ \mu\text{m}$ and solution flow rate of $5 \pm 0.5\ \text{mL min}^{-1}$ was used.

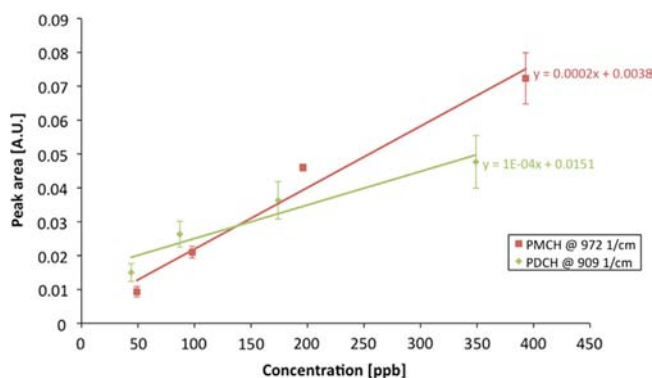


Fig. 7. Calibration of the MIR-ATR sensor with a PIB coating (5 μm) for perfluoromethylcyclohexane (evaluating the peak area at 972 cm^{-1}) in the concentration range of 49–393 ppb (w/v) and for perfluoro-1,3-dimethylcyclohexane (evaluating the peak area at 909 cm^{-1}) in the concentration range of 44–349 ppb (w/v). The error bars represent the standard deviation of three measurements.

increasing PFC concentration. More importantly, the baseline shift did not significantly influence the analysis of the PMCH and PDCH peaks which occur above 900 cm^{-1} . It is noteworthy that for PMCH the peak at 972 cm^{-1} occurred at a slightly higher wavenumber when enriched into the polymer coating compared to the IR spectra of the neat compound (see Fig. 2). However, the peak for PDCH (i.e., 909 cm^{-1}) did not appear shifted, which suggests that either weak molecular interactions between PMCH and PIB are occurring or that immobilization of the molecule within the polymer matrix affects the vibrational motion. These interactions are considerably weak (i.e., electrostatic or van der Waals interactions) since the coating may be entirely regenerated by flushing the sensor with pure water. It is important to note that the diffusion process was relatively slow since it took just over one hour to completely remove the PFC analyte from the surface and generate a fresh polymer film for sensing (not shown). To minimize problems that may arise from memory effects all calibrations were generated by first measuring the PFC analyte at low concentrations followed by successive measurements at higher concentrations. Accordingly, calibration functions of the studied PFC analytes were established in a concentration range of 49–393 ppb (w/v) for PMCH and 44–349 ppb (w/v) for PDCH providing a goodness-of-the-fit (R^2) for PMCH of 0.97, and for PDCH of 0.92, respectively, as shown in Fig. 7. The R^2 value for PDCH ($R^2=0.92$) was slightly lower compared to PMCH ($R^2=0.97$). Furthermore, the slope of the calibration function for PMCH is twice the value of PDCH, which indicates that the sensitivity for PMCH is twice as high as for PDCH. The signal, which was still three times higher than the standard deviation of the response of the lowest concentration was determined as the limit of detection (LOD) and the signal which was still ten times higher as the limit of quantification (LOQ). In relation to the slope of the established calibration function this resulted in a LOD of 23 ppb and a LOQ of 76 ppb for PMCH and a LOD of 79 ppb and a LOQ of 265 ppb for PDCH. This study demonstrates that the MIR-ATR sensor is able to directly quantify PFCs in water down to ppb concentrations and the detection limit varied significantly with the type of PFC molecule. Despite the promising analytical results, further research is still needed to improve the sensor response time and sensitivity particularly in the context of real-time environmental monitoring of PFCs in groundwater.

4. Conclusions

In summary, we have shown that perfluorocarbon tracer compounds may readily be analyzed at low concentration levels in water using a mid-infrared sensor based on attenuated total reflection spectroscopy. This sensing system exhibited good

sensitivity, and a large dynamic concentration range rendering the quantification of PFCs suitable for water monitoring applications relating to carbon dioxide storage. We believe that the MIR-ATR sensor is complementary to traditional methods of PFC based analysis that employ carbon-based sorbents. Further studies are being planned which will focus on improving the sensor response time and the use of a more sensitive waveguide geometry (i.e., planar fiber optic waveguides) potentially in combination with broadly tunable quantum cascade lasers as advanced IR light source for field deployment.

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