Monocyclic and Polycyclic Aromatic Hydrocarbon Quantification of Geochemical Fluids Using Mid-Infrared Attenuated Total Reflection Sensors

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Abstract

An improved analytical method for directly and rapidly quantifying various monocyclic and polycyclic aromatic molecules in geochemical fluids has been developed. This study reports on the application of a sensor based on attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) for determining the concentration of a number of volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). The sensor consists of a zinc selenide (ZnSe) waveguide with the surface modified by a thin poly(isobutylene) (PIB) coating. The sensitivity was investigated at different polymer film thicknesses and molecular weights. The analytical performance of the ATR-FTIR sensor was validated in the laboratory against a standard analytical technique for analyzing petroleum-based samples (i.e., GC-MS and GC-FID). It has been shown that the sensor may accurately quantify the benzene, toluene, ethylbenzene, xylenes and naphthalene (BTEXN) concentration in an oil-water mixture. The ATR-FTIR method overcomes the limitations associated with sampling/sample preparation and has the advantage that it may easily discriminate between meta and para-xylene, which is difficult with conventional analytical techniques. In addition, this technology may potentially be deployed in the field for geochemical mapping and to monitor in situ the concentration profile of a number of hydrocarbons in the geological formations (e.g. petroleum systems), as demonstrated for a first miniaturized prototype of an ATR-IR sensor system taking advantage of planar-tapered silver halide fibers.
Keywords: BTEX, PAH, polymer, mid-infrared sensor, attenuated total reflectance, mid-infrared spectroscopy, silver halide fibers.

1. Introduction

Considerable research effort has been directed towards developing analytical tools for identifying the type of organic molecules present and quantifying their concentration in a range of petroleum based systems (Rodgers & McKenna, 2011). Recent advances in gas chromatography (GC) and mass spectrometry (MS) have been able to provide invaluable compositional information and in most cases the concentration of many different hydrocarbon components in complex samples can be easily obtained (Ballesteros-Gomez & Rubio, 2011). The determination of hydrocarbons in crude oils typically involves several steps such as the collection of a representative sample followed by extraction/separation prior to molecular characterization and quantification using GC-MS (Audino et al., 2004). Consequently, there is a demand for improved analytical methods and measurement techniques for characterizing oil samples in their natural unperturbed state. Sampling/sample handling is one of the major contributors to uncertainty and over the past several decades there has been significant interest in using chemical sensors to address these issues (Lawrence, 2006; Lieberzeit & Dickert, 2007). Although many sensors are suitable for measuring hydrocarbon concentrations at very low levels (i.e., ppb to ppm or µg/L to mg/L), the majority of these devices struggle to separate the various signal contributions during the analysis of multi-component hydrocarbon mixtures (Pejcic et al., 2011b; Ueyama et al., 2002). Analyte selectivity remains a major challenge impeding the acceptance of most sensors for assaying complex geochemical and environmental samples.
One promising analytical tool that is capable of achieving reliable hydrocarbon identification and quantification in geochemical fluids is the mid-infrared (MIR) sensor based on attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Gonzalez et al., 2011; Mizaikoff, 2003; Pejic et al., 2009). Due to its inherent selectivity the ATR-FTIR has been successfully used to detect a wide variety of organic compounds such as phenols (Yang & Cheng, 2001), caffeine (Alcudia-Leon et al., 2008), organophosphonates (Bryant et al., 2007), adamantane (Luzinova et al., 2009), alkyl halides (Acha et al., 2000; Yang & Ramesh, 2005), aromatic hydrocarbons (Karlowatz et al., 2004; Young et al., 2011), and for the detection of oil-in-water as well as water-in-oil (Luzinova et al., 2012a; Luzinova et al., 2012b). The sensor consists of an IR light source, a MIR transparent waveguide to propagate the signal, and an optical transducer/detector. The waveguide is usually either a trapezoidal shaped zinc selenide crystal or an optical fiber based on a silver halide or chalcogenide material; the surface of the waveguide is in many cases coated with a thin polymer film. The analyte molecules in solution partition and enrich into the polymer membrane, and the generated evanescent field interacts with the analyte molecules. A hydrophobic coating allows non-polar hydrocarbon molecules to partition into the membrane, while water and other polar components are excluded from the analytical volume probed by the evanescent field extending a couple of micrometers into the adjacent medium. This method is based on the principles of solid-phase extraction, and it has been shown that detection limits of low ppb levels may be obtained under certain conditions (Karlowatz et al., 2004; Lin & Li, 2010; Roy & Mielczarski, 2002). Recent engineering advances in IR light sources, waveguides, and detectors/spectrometers have led to the development of miniaturized MIR sensing systems that are capable of being deployed directly in the field (Charlton et al., 2006; Kim et al., 2008; Wang et al., 2012). A portable MIR sensor has been remotely and successfully operated in marine systems during environmental monitoring of various chlorinated and aromatic
hydrocarbons (Kraft et al., 2003; Kraft & Mizaikoff, 2000; Mizaikoff, 1999). These studies revealed that the sensor is unaffected by salinity, turbidity and natural organic matter/organic pollutants.

Crude oil is a complex substance containing hundreds of mainly hydrocarbon compounds with a wide range of molecular weights. The hydrocarbon distribution of a crude oil varies considerably and the factors influencing the oil composition are discussed in greater detail elsewhere (Tissot & Welte, 1984). Understanding how oil is altered by chemical and/or physical processes is of significant research interest, and a number of papers have investigated the effect of oil-water interactions on the hydrocarbon distribution within a crude oil (Barman Skaare et al., 2007; Lafargue & LeThiez, 1996). Others have characterized the formation and/or produced water from the North Sea and showed that it contains dispersed oil along with a variety of organic compounds (Faksness et al., 2004). Detecting petroleum contaminants in water arising from oil spills and natural oil seeps are important issues in environmental science (Readman et al., 1992) and petroleum exploration (Kvenvolden, 2003).

A robust and portable analytical technique that may directly measure the concentration of volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) in geochemical samples would therefore be extremely valuable for understanding oil-water interactions (i.e., water washing, biodegradation) and issues relating to environmental geochemistry (i.e., petroleum contaminants, hydrocarbon distribution in a geological formation). An ATR-FTIR sensor based on a polyisobutylene coated zinc selenide (ZnSe) waveguide was investigated for the detection of benzene (B), toluene (T), ethylbenzene (E), xylenes (X) and naphthalene (N) in water containing dissolved crude oil. The objective of this paper is to evaluate the suitability of ATR-FTIR spectroscopy for the identification and quantification of BTEXN compounds in complex multi-component hydrocarbon solutions.
The potential of the mid-infrared spectroscopic sensor for determining hydrocarbons in petroleum-based systems (e.g. formation water) will be demonstrated by comparing its analytical performance to a standard method. Furthermore, first tests using a miniaturized mid-infrared sensor prototype providing similar sensitivity will be shown.

2. Experimental

2.1. Materials & reagents

Benzene (99%), toluene (99.8%), p-xylene (99%), m-xylene (99%), o-xylene (97%), ethylbenzene (99.8%), naphthalene (99%), and n-hexane were all obtained from Sigma-Aldrich and were used as purchased. All organic solvents were AR grade and used without further purification. Poly(isobutylene) (PIB) was supplied by Scientific Polymer Products, Inc. (Ontario, NY, USA). The molecular weight ($M_w$) of PIB was determined using gel permeation chromatography (polystyrene standards, chloroform solvent) and is 400,000. The glass transition temperature ($T_g$) was measured using a Mettler Toledo DSC and is -64 °C. Ethylene/propylene copolymer (60:40) was purchased from Sigma-Aldrich and used as provided.

2.2. Film preparation

Prior to film deposition the surface of the ZnSe was cleaned with acetone soaked Whatman (Whatman International Ltd., Maidstone, England) lens-cleaning tissue followed by rinsing with acetone and drying by flowing high purity nitrogen gas for several minutes. A thin polymer film was deposited onto the ZnSe waveguide by placing 500 µL of a chloroform solution that contained PIB. The PIB solution concentration was varied between 0.5 to 1% w/v in order to study the effect of film thickness on the hydrocarbon sensitivity. The thickness of the layer was determined by differential weighing using the method reported elsewhere.
(Murphy & McLoughlin, 2003). In all cases, the PIB coated waveguide was allowed to dry overnight and IR spectra were collected to ensure that the solvent evaporated completely. All of the films were reproducible in thickness (<10% variation) and uniform in terms of quality and integrity.

For coating silver halide waveguides with a thin layer of ethylene/propylene copolymer (E/P-co), a 1% (w/v) coating solution was prepared by dissolving 0.5 g of granular polymer under reflux in 50 mL of n-hexane. Approximately 100 µL of clear hot solution was then applied to each side of the planar segment of a flat-tapered silver halide waveguide using an Eppendorf pipette. Thus obtained coated silver halide sensing elements were kept at room temperature for at least 2 h, thereby ensuring evaporation of the solvent and reconstitution of a homogenous polymer film with a thickness of approx. 5 µm.

Polycrystalline silver halide waveguides were prepared by the research team at Tel-Aviv University for transmitting IR radiation in the spectral range of 0.4-25 µm. The waveguides used herein are of the composition AgCl<sub>0.4</sub>Br<sub>0.6</sub> and are characterized by typical attenuation losses in the range of 0.5 dB/m at 10.6 µm (Saar et al., 1986). Silver halide waveguides with a planarized active sensing region (PWGs) were created via mechanical press-tapering of unclad cylindrical fiber segments with an initial diameter of 700 µm, yet providing attached cylindrical coupling segments facilitating coupling of IR radiation emanating from an FT-IR spectrometer into the waveguide. The flat-tapered segment has a thickness of approx. 150 µm, a width of 4 mm, and a length of 40 mm in the middle (see Figure 1).
2.3. Instrumentation

Sensor measurements were made using a Bruker Vertex 70 Fourier transform infrared spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector coupled to both waveguides, conventional ATR crystals and flat-tapered silver halide sensing elements. A trapezoidal (4 mm thick, 80 mm long, angle of incidence 45º) ZnSe was used as a multi-reflection waveguide. The ZnSe was mounted into a trough plate ATR unit and stainless steel flow cell, which was obtained from Pike Technologies (Madison, WI, USA). Analyte solutions were prepared in deionized water and pumped over the PIB-coated ZnSe surface using an Ismatec peristaltic pump (IDEX Corporation) at a constant flow rate of 1.5 ml min\(^{-1}\). Data were recorded in the 4000–650 cm\(^{-1}\) range using a spectral resolution of 2 cm\(^{-1}\) and a total of 32 scans were averaged for each spectrum. All experiments were performed at room temperature (21 ± 1 °C). Analytical calibration curves were established by dissolving the hydrocarbon compounds in deionized water in the concentration range between 0–100 ppm. Naphthalene standards were made by serial dilution of a saturated solution, which was prepared by weighing naphthalene (0.2 g, AR grade) into a glass Schott bottle that comprised deionized water (1000 ml) followed by constant stirring (~500 rpm) at room temperature (~21 °C) for 3 days. The solution was filtered through a 0.45 µm filter paper and the naphthalene concentration was verified by GC-MS (20.5 ± 0.5 ppm, experiment repeated on 3 separate occasions). To limit losses by volatility and degradation, all standards were prepared freshly and studies were performed within 5 hours.

2.4. Spectral data analysis

The infrared absorption features were evaluated by peak area analysis using the software package OPUS (Bruker Optics). Replicated measurements were performed and the peak areas from each spectral region were averaged.
2.5. Total petroleum hydrocarbon solution preparation

Total petroleum hydrocarbons (TPH) dissolved in water were prepared according to a procedure outlined elsewhere (Tsvetnenko & Evans, 2002). Briefly, this involved placing North West Shelf (Australia) crude oil (70 ml) into a glass flask that contained deionized water (900 ml) and allowing the mixture to equilibrate for a period of 3 days at room temperature (~21 °C). The flask was sealed and the solution constantly stirred using a magnetic stirrer bar at a rotation speed of ~500 rpm.

2.5. Gas chromatography-mass spectrometry (GC-MS)

The concentration of the various solutions used during the ATR-FTIR study was analyzed using GC-MS. The BTEX compounds were determined on a HP 6890 GC / Agilent 5973 MSD with an EST Encon purge-and-trap concentrator. Helium was bubbled through the water sample and the vapour was swept through a sorbent trap (Vocarb 3000). Naphthalene was liquid/liquid extracted with dichloromethane and analyzed on a HP 6890 GC / Agilent 5973N MSD. Concentrations were determined by comparison with standards using electronic integration.

3. Results and Discussion

3.1. Calibration and sensitivity determination

Analyzing low levels of VOCs in water matrices is a significant challenge and there is a great deal of research in understanding the influence of sampling/sample preparation on the analytical precision and accuracy during quantification (Demeestere et al., 2007). Since the VOC concentration in water may vary considerably during solution preparation/storage, it is recommended that the calibration standards are prepared in sealed glass containers with very
little headspace and the aqueous solutions analyzed almost immediately. Although organic solvents (i.e., methanol) have been used to disperse and stabilize the VOC during the preparation of stock standard solutions (Kraft & Miziaikoff, 2000; Lima et al., 2011), we avoided their use in this study in order to minimize potential issues that may arise from solvent/matrix effects during the measurement of complex samples. Despite extreme care to minimize volatilization, it was found by GC-MS that the loss during the preparation of the BTEX standards directly in deionized water may vary between 20 to 60%, and this depended on the type of hydrocarbon, the concentration and the method of preparation (i.e., vigorous shaking versus ultrasonication, storage time prior to analysis). To obtain accurate and reproducible calibrations, the solutions were analyzed almost immediately using the ATR-FTIR (<4 hrs) and the concentrations were determined using GC-MS. Subsequently, all of the standards used in the construction of the calibration curves have been verified using GC-MS.

A number of polymeric-based materials have been previously used for extracting different types of hydrocarbon compounds (Flavin et al., 2006; Regan et al., 2003; Yang & Ramesh, 2005). However, very few polymers are appropriate in terms of having no or very little interfering absorption bands in the mid-infrared region of interest. PIB was found to be suitable for the detection of benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, and naphthalene since it has no significant spectral interferences in the region between 800 to 650 cm$^{-1}$. Although it has been revealed that poly(ethylene-co-propylene) (EPCO) may be more sensitive (Karlowatz et al., 2004), some studies suggest that films prepared from EPCO are more susceptible to delamination compared to PIB (Beardslee et al., 2010). We have shown previously that the hydrocarbon sensitivity of the PIB film does not change considerably with water exposure time (Pejcic et al., 2011a), and this is an important issue to consider with respect to continuous long-term monitoring of hydrocarbons in geochemical
fluids. Nevertheless, the present study is focused on developing a robust analytical tool for directly quantifying various aromatic hydrocarbons via ATR-FTIR spectroscopy and using this technique to determine their concentration in a multi-component mixture. ATR-FTIR measurements were made in aqueous solutions comprising different levels of hydrocarbons and Figure 2 shows the infrared spectra of the PIB coated waveguide when exposed to the BTEX compounds. The spectra were collected after an enrichment time of 60 min and the IR absorption peaks for the various hydrocarbons have distinct molecular signatures, which correspond to C–H bending vibrations (out-of-plane bending). The out-of-plane bending vibrations of the aromatic compounds are strong and characteristic of the number of hydrogens in the ring. The following band assignments were obtained from the single component experiments: benzene at 674 cm\(^{-1}\), toluene at 727 cm\(^{-1}\), ethylbenzene at 696 cm\(^{-1}\), \(o\)-xylene at 741 cm\(^{-1}\), \(m\)-xylene at 767 cm\(^{-1}\), and \(p\)-xylene at 794 cm\(^{-1}\), which are consistent with values published elsewhere (Karlowatz et al., 2004). There is a slight overlap of the ethylbenzene peak at 696 cm\(^{-1}\) with toluene (peak at 693 cm\(^{-1}\)) and \(m\)-xylene (peak at 690 cm\(^{-1}\)) suggesting that the presence of these compounds may interfere with the determination of ethylbenzene. In addition, ethylbenzene has absorption bands present at 745, 771 and 788 cm\(^{-1}\), which may interfere with the peaks due to \(o\)-xylene, \(m\)-xylene and \(p\)-xylene. Although these ethylbenzene absorption bands are of much lower intensity, they are likely to cause interference problems during the quantification of the xylene isomers. The purpose of this study is to evaluate the suitability of the ATR-FTIR method for quantifying a number of monocyclic and polycyclic aromatic hydrocarbons in a complex oil-water mixture.

The application of ATR-FTIR for determining PAH concentration has received much less attention in the literature and the analytical performance of PIB was investigated. Figures 3a and 3b show the respective infrared spectra and diffusion curves of the PIB coating when
exposed to naphthalene at different concentrations. The characteristic absorption peak for naphthalene occurs at 781 cm⁻¹ and this does not overlap with any of the BTEX compounds. However, the diffusion of naphthalene was relatively slow and after ~50 mins the enrichment process reached equilibrium. Unsurprisingly, the response time varied with concentration and the time taken to achieve a steady state was typically longer at higher concentrations. This is probably related to a polymer swelling process at high analyte levels which increases the free volume and has been documented elsewhere (Pejcic et al., 2011a). In addition, it took more than 60 mins for the IR signal to return to baseline after it had been exposed to 21 pm naphthalene. By contrast, the diffusion process of the PIB film in benzene and toluene solutions were much more rapid and the time taken to reach equilibrium was < 20 mins (not shown). Generally, higher response times were observed for naphthalene, xylenes and ethylbenzene compared to toluene and benzene, and this is consistent with the diffusion coefficient being smaller for the larger molecules (Flavin et al., 2006).

It is evident that the intensity of the peaks in Figures 2 and 3a increase with increasing concentration and this is consistent with the hydrocarbon molecules partitioning into the polymer film. The calibration curves were made by integrating the absorbance peaks and Figure 4 shows a plot of the peak area versus concentration of the PIB coating exposed to the individual BTEXN compounds dissolved in deionized water. The absorbance increases linearly with increasing concentration for all hydrocarbons and this is in agreement with the Beer-Lambert law. In general, the PIB responded linearly over the 0–80 ppm range with a correlation coefficient (r²) of greater than 0.97 for the BTEX analytes. However, the r² was much larger (r² > 0.998) in the range between 0 to 40 ppm, and the calibration curves were used in this region for the quantification of BTEX compounds in the multi-component hydrocarbon mixtures. Table 1 summarizes the calibration data obtained on the change in
peak area as a function of concentration. Interestingly, the slope of the curve increases with hydrocarbon molecular weight/hydrophobicity and this may be purely coincidental.

3.2. Effect of PIB film thickness and molecular weight

Some of the factors that affect the partitioning behaviour and the diffusion properties were studied and Figure 5a shows the enrichment curves for toluene as a function of polymer film thickness. The coating thickness on the ZnSe waveguide was controlled by varying the concentration of PIB in the solvent. It is evident that the peak intensity arising from toluene increases with PIB thickness and this is indicative of an increase in the amount of toluene that partitions into the film. However, the time taken for toluene to reach equilibrium was much longer for the 8.4 µm (10-20 mins) film compared to the 4.5 µm (5-10 mins). The increased response time with film thickness is consistent with toluene taking longer to diffuse through the polymer membrane into the region of the evanescent wave. Similar absorption and diffusion profiles were observed for the other aromatic hydrocarbons.

Figure 5b shows the variation in toluene sensitivity as a function of PIB molecular weight. It is evident that the amount of toluene that partitions into the PIB film does not vary significantly with polymer molecular weight. However, it was found that the time for the IR signal to reach equilibrium was slightly longer for the higher molecular weight. In addition, the amount of water in the film was a factor of ~3 lower for the higher molecular weight PIB film (i.e., 1,912,000 g/mol) compared to the others after it had been soaked in deionized water for one hour (not shown). This may be either due to PIB adhesion onto the ZnSe substrate being greater for the high molecular weight film and/or the water diffusion processes being slower. Despite some differences in the rate of molecular diffusion, this study confirms that the amount of hydrocarbon absorbed is independent of the polymer molecular weight and that
this cannot be used to control the sensor sensitivity. However, previous studies have shown using a polyethylene coating that the ATR-FTIR sensitivity depends significantly on the density of the polymer (Heinrich et al., 1990).

3.3. Analysis of total petroleum hydrocarbon solution

To test the applicability of the established method for an unknown sample, a crude oil-water mixture was prepared and analyzed using the PIB-coated ATR-FTIR sensor. Characterization of the oil-water mixture was also performed using gas chromatography and the TPH was determined to be 19.0 ± 0.6 ppm, noting that the hydrocarbons present in the water soluble fraction was of interest in this study. Figure 6 shows a typical chromatogram of the water dissolved fraction and more than 65% of the components in the TPH solution comprise C₆ to C₉ compounds (i.e., benzene, toluene, ethylbenzene, xylenes, alkylated benzenes, methyl phenols). This may not be surprising considering that these compounds are generally more soluble/miscible in water compared to some of the other hydrocarbon molecules (i.e., >C₁₀) that are present in the oil and is consistent with reports which found that the light aromatics and light end hydrocarbons are preferentially solubilized in water (Faksness et al., 2004; Lafargue & LeThiez, 1996). Table 2 displays the GC determined concentrations and it is evident that the BTEXN compounds are present at low ppm levels. ATR-FTIR measurements were made on the TPH solution and the IR spectra collected over a period of time are shown in Figure 7. It is apparent that a number of hydrocarbons are extracted into the PIB film and the peak intensities gradually increase with time. After ~40 mins the extraction process reached equilibrium for most of the hydrocarbon compounds. Quantification studies have also been performed using a lower film thickness (i.e., 4.5 µm) and the time taken to achieve equilibrium was much more rapid (<20 min) as expected (not shown). The evolution of additional IR peaks was also observed in the region between 800 to 900 cm⁻¹ and this is
consistent with other hydrocarbons partitioning from the TPH solution. It is not the purpose of the present study to identify all hydrocarbon components by infrared spectroscopy; however, Figure 7 illustrates the potential of using the ATR-FTIR sensor to quantify many different compounds other than just BTEXN. Compared to the standard GC technique (see Figure 6b), the sensor can easily distinguish between the meta and para-xylene compounds.

The classical least squares and linear regression analysis in conjunction with a single analyte calibration in standard solutions was used here for the quantitative analysis of BTEXN in the TPH solution. Multivariate analytical methods such as principal component analysis (PCA) or artificial neural networks (ANN) are normally employed to determine the hydrocarbon concentration in a multi-component complex mixture (Silva et al., 2009). However, we found that interferences and interaction effects arising from the presence of many hydrocarbon components in the TPH solution do not drastically affect the quantification of BTEXN under our experimental conditions. Table 2 compares the actual concentrations determined using GC to those measured with the ATR-FTIR sensor, and it is evident that the sensor and GC results are almost identical. The relative error was generally less than 30% and the difference between the actual GC and ATR-FTIR measured concentration appears to be mainly due to losses during solution storage/handling. By contrast, Regan et al. (Regan et al., 2003) observed that the infrared diffusion and enrichment profiles of certain hydrocarbon compounds are effected by the presence of more than one component in the BTEX mixture. It was shown that the xylene isomers inhibit ethylbenzene from entering a PVC based film and the authors concluded that the infrared sensor response depends on the presence of other hydrocarbon components (Regan et al., 2003). However, they performed studies on a plasticized PVC film in solutions that contained BTEX compounds at a concentration of 100 ppm. Notwithstanding, analytical errors are likely to occur for the ATR-FTIR sensor
particularly when analyzing solutions that comprise some of these hydrocarbons at much higher concentrations.

In future, such sensing systems may be significantly reduced in size yet maintaining their analytical performance and molecular selectivity. This is shown for the example of a miniaturized IR sensor concept taking advantage of planar-tapered silver halide sensing elements serving as the active transducer coated with an E/P-co membrane. Figure 8 shows spectra of a mixture of benzene, toluene, and the xylene isomers at a sample concentration of 300 ppb (v/v) obtained after an enrichment time of 60 min into the E/P-co membrane. The corresponding absorption peaks have been labelled for clarity (benzene at 676 cm\(^{-1}\), toluene at 690 and 727 cm\(^{-1}\), o-xylene at 740 cm\(^{-1}\), m-xylene at 767 cm\(^{-1}\), p-xylene at 795 cm\(^{-1}\)) (Karlowatz et al., 2004). Similar to the measurements using the conventional ATR crystal, each analyte remains clearly discernible via distinctive absorption features using this prototype miniaturized IR sensing setup. Further reduction of the system dimensions will be achieved in future by replacing the FTIR spectrometer with broadly tuneable quantum cascade lasers covering the spectral range of interest (Young et al., 2009).

4. Conclusions

This study has shown that the ATR-FTIR sensor may be used to distinguish and accurately quantify benzene, toluene, ethylbenzene, xylene isomers and naphthalene in a complex oil-water mixture. The amount of hydrocarbon extracted into the PIB film was proportional to the concentration in solution and linear relationships \(r^2 > 0.998\) between absorption peak areas and concentration were obtained in the range 0 to 40 ppm for BTEX and 0 to 20 ppm for naphthalene. A simple calibration method using the classical least squares and linear regression analysis was used to perform quantitative analysis of BTEXN in the multi-
component mixture. It was found that the hydrocarbon-polymer partition process for the single analytes was independent of the amount and type of hydrocarbons present in the aqueous solution. The sensitivity of the ATR-FTIR sensor was shown to depend significantly on the polymer film thickness. Reversibility studies revealed that the time needed to completely remove the analyte from the PIB film during water washing was much longer (typically >30 mins) and this depended on the type of analyte and its concentration. Further studies are being planned to determine if the sensor can distinguish between different sources and types of crude oil in water. In addition, experiments are being planned to optimize the response (i.e., time and sensitivity) and used to directly assay real samples from the field. It is expected that this work will lead to the development of a miniaturized field deployable device for monitoring hydrocarbons in the geological formation (i.e., oil reservoirs and produced water). Potential miniaturization of such sensing concepts is demonstrated with a prototype sensing system replacing the ATR crystal with a planar-tapered silver halide waveguide revealing comparable sensitivity.

Acknowledgements

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References


Table 1  ATR-FTIR calibration data for various hydrocarbons studied over the 0 to 40 ppm concentration range (with the exception of naphthalene which was between 0 to 20 ppm). A PIB film was prepared by depositing onto the ZnSe waveguide a chloroform solution (500 µl) containing 1.0% w/v PIB. Note that the film thickness was determined gravimetrically to be 8.4 ± 0.5 µm.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Response (AU/ppm)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>674</td>
<td>y = 0.0062x + 0.0021</td>
<td>0.9991</td>
</tr>
<tr>
<td>Toluene</td>
<td>727</td>
<td>y = 0.0164x + 0.0047</td>
<td>0.9984</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>696</td>
<td>y = 0.018x + 0.0001</td>
<td>0.9994</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>741</td>
<td>y = 0.034x + 0.0095</td>
<td>0.9995</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>767</td>
<td>y = 0.0278x + 0.0012</td>
<td>0.9995</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>794</td>
<td>y = 0.0218x – 0.0065</td>
<td>0.9989</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>781</td>
<td>y = 0.0954x + 0.0055</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

Table 2  Comparison between the actual hydrocarbon concentrations in the TPH solution determined by GC and that measured using the ATR-FTIR. The results are the average of 3 separate measurements on different days and using freshly prepared TPH solutions.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>ATR-FTIR</th>
<th>GC-FID/GC-MS</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.5 ± 0.6 ppm</td>
<td>2.7 ± 0.3 ppm</td>
<td>7.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.7 ± 0.5 ppm</td>
<td>4.8 ± 0.9 ppm</td>
<td>18.7</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.5 ± 0.1 ppm</td>
<td>0.4 ± 0.1 ppm</td>
<td>25.0</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.8 ± 0.2 ppm</td>
<td>0.8 ± 0.1 ppm</td>
<td>0.1</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>2.2 ± 0.2 ppm</td>
<td>2.0 ± 0.1 ppm</td>
<td>30.0</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.4 ± 0.1 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.25 ± 0.05 ppm</td>
<td>0.25 ± 0.05 ppm</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Figure 1. Experimental set-up of fiber optically coupled planar-tapered silver halide waveguide sensor (PM = planar mirror, OAPM = off-axis parabolic mirror, WG = waveguide, MCT = mercury-cadmium-telluride).
Figure 2. Infrared spectra of a PIB-coated ZnSe waveguide exposed to (a) benzene, (b) toluene, (c) ethylbenzene, (d) ortho-xylene, (e) meta-xylene, and (f) para-xylene at different concentrations dissolved in deionized water. Note that the polymer film thickness was 8.4 ± 0.5 μm.
Figure 3a. Infrared spectra of a PIB-coated ZnSe waveguide exposed to naphthalene at different concentrations dissolved in deionized water. Note that the polymer film thickness was $8.4 \pm 0.5 \mu m$.

Figure 3b. Transient response of the PIB-coated ZnSe waveguide when exposed to different concentrations of naphthalene dissolved in deionized water. Note that the polymer film thickness was $8.4 \pm 0.5 \mu m$. 
Figure 4. ATR-FTIR calibration graphs of a PIB-coated ZnSe waveguide exposed to various hydrocarbons dissolved in deionized water. Note that the polymer film thickness was 8.4 ± 0.5 µm.
Figure 5a. The effect of film thickness on the enrichment curve for toluene into a PIB coated ZnSe waveguide. Note that the toluene solution concentration was 5 ppm.

Figure 5b. The effect of PIB molecular weight on the ATR-FTIR sensitivity for toluene.
Figure 6a. Chromatogram of the dissolved North West Shelf crude oil in deionized water.

Figure 6b. Chromatogram of the dissolved North West Shelf crude oil in deionized water (expanded region).
Figure 7. Infrared spectra of a PIB-coated ZnSe waveguide exposed to the TPH solution as a function of time. Note that the polymer film thickness was 8.4 ± 0.5 µm.
Figure 8. IR absorption signal obtained at planar silver halide waveguide sensor of a BTX sample mixture in aqueous solution after enrichment into an E/P-co layer (enrichment time: 60 min; concentration: 300 ppb (v/v) for each constituent).