Determination of Chlorinated Hydrocarbons in Water Using Highly Sensitive Mid-Infrared Sensor Technology

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Chlorinated aliphatic hydrocarbons and chlorinated aromatic hydrocarbons (CHCs) are toxic and carcinogenic contaminants commonly found in environmental samples, and efficient online detection of these contaminants is still challenging at the present stage. Here, we report an advanced Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) sensor for in-situ and simultaneous detection of multiple CHCs, including monochlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, trichloroethylene, perchloroethylene, and chloroform. The polycrystalline silver halide sensor fiber had a unique integrated planar-cylindric geometry, and was coated with an ethylene/propylene copolymer membrane to act as a solid phase extractor, which greatly amplified the analytical signal and contributed to a higher detection sensitivity compared to the previously reported sensors. This system exhibited a high detection sensitivity towards the CHCs mixture at a wide concentration range of 5–700 ppb. The FTIR-ATR sensor described in this study has a high potential to be utilized as a trace-sensitive on-line device for water contamination monitoring.

Chlorinated aliphatic hydrocarbons and chlorinated aromatic hydrocarbons (CHCs) are a class of highly toxic and persistent contaminants commonly found in the environment1, which pose a substantial threat to the ecological system and human health2. Thus, effective monitoring and control of these contaminants are essential. For the detection of CHCs in acqueous environment, a variety of chromatographic (e.g., high-performance liquid chromatography (HPLC)3, gas chromatography (GC)4, gas chromatography and mass spectrometry (GC/MS)5) and spectroscopic (e.g., ultraviolet-visible (UV)6, Raman7, and fluorescence8 spectroscopy) methods have been proposed and used. These techniques generally show high a detection sensitivity, however, usually involve complex and time-consuming pre-concentration/extraction steps9, and are mostly confined to laboratory use. At present, sensitive online detection techniques for in-situ and continuous monitoring of CHCs in water are still lacking. This gap has inspired the present study to develop more suitable online detection techniques through taking advantage of the inherent molecular selectivity of infrared attenuated total reflectance (ATR) spectroscopy.

Fourier transform infrared spectroscopy (FTIR) spectroscopy is known as a rapid and non-destructive detection technology for organic constituents due to the generated fingerprint spectra. Especially, the combined use of ATR with FTIR enables a direct examination of liquid phase samples without further preparation, and has gained increasing popularity in recent years. ATR uses the principle of internal total reflection to generate an evanescent field, which emanates at the waveguide surface and penetrates a few micrometers into the adjacent sample volume10. However, a major challenge of FTIR-ATR is its relatively low detection sensitivity, which limits its practical implementation. The detection sensitivity of FTIR-ATR is largely governed by the properties of the ATR waveguide. Typically, crystalline ATR elements are used, which may be divided into three main categories according to the material properties: glass-like fibers (e.g., chalcogenides and heavy metal fluorides), polycrystalline (e.g., silver halides) or crystalline fibers (e.g., sapphire), and hollow waveguides (e.g., hollow silica or sapphire tubes)11. Among these, silver halide (AgCl,Br1-x) fibers are considered the most practical ATR
waveguide material\(^\text{14}\), which provides access to the entire mid-infrared (MIR) spectral range of interests (3–18 \(\mu\)m\(^\text{12}\), and allows flexible tuning of its geometry\(^\text{15}\)). AgCl\(_{x}\)Br\(_{1-x}\) fibers have been demonstrated to offer direct and accurate detection of crude oil in a deionized water matrix\(^\text{14}\), and of water in hexane at ppm levels\(^\text{15}\). Hence, directly probing water contaminants may be achieved by immersing a ATR-based fiber into an aqueous solution serving as the active transducer\(^\text{14}\). However, ppm-level detection sensitivity is still insufficient to meet the detection requirements for CHCs in real water samples, as most constituents are usually present at ppb levels. Moreover, the considerable background noise signals in real water samples presents an additional challenge. The detection sensitivity may be significantly lowered by reducing the spectral noise arising from the interfering absorbance of water (O-H stretching vibration at 3300 cm\(^{-1}\); O-H bending vibration at 1640 cm\(^{-1}\); combination vibration at 2100 cm\(^{-1}\); and libration vibration at 750 cm\(^{-1}\))\(^\text{14}\) and other background molecules\(^\text{15}\). Thus, to improve the detection sensitivity, efforts are needed to further increase the signal-to-noise ratio of such fiberoptic ATR transducers.

Here, we describe an advanced FTIR-ATR sensor with ppb-level sensitivity towards detection of water contaminants like CHCs. This high sensitivity was enabled by the adoption of an unique fiber geometry, as well as an efficient enrichment coating at the fiber surface, which greatly enhanced the analytical signal for CHCs while reducing the background noise levels. First of all, a planar AgCl\(_{x}\)Br\(_{1-x}\) fiber segment serving as active transducer with cylindrical extensions at both ends was used. It has been reported that the intensity of the evanescent field in ATR spectroscopy may be substantially enhanced by tuning the waveguide geometry\(^\text{17}\). In this context, decreasing the fiber diameter or tapering a section of the fiber are both effective strategies to improve the analytical sensitivity\(^\text{18}\). Especially, the geometry of a planar sensing region with fiberoptic couplers at both ends has been reported to substantially increase the number of internal reflections, thereby leading to enhanced signals - up to one order of magnitude - compared to conventional cylindrical fibers\(^\text{17}\). In addition, to further amplify the detection signal and reduce the noise, a polymer membrane was coated onto the sensor surface. Polymeric enrichment coatings have been proven as an effective strategy to enhance the detection sensitivity and robustness of IR fiberoptic sensors\(^\text{18}\). On the one hand, particular chemical recognition membranes (e.g., polysiloxane, ethylene-propylene copolymer, and Telfon AF) have been reported to selectively enrich the targeted species at the fiber surface and within the evanescent field facilitating their detection\(^\text{19}\). On the other hand, the interference of water and other species can be dramatically reduced using a hydrophobic membrane; furthermore, to a certain degree the sensor may also be protected from harsh environments by such a coating\(^\text{19}\). Thus, in our system a hydrophobic ethylene/propylene copolymer (E/P-co) coating, which is ideally suited for enrichment of hydrophobic hydrocarbons\(^\text{20}\) including CHCs\(^\text{22}\) was used.

In this study, the combined use of the integrated planar-cylinder fiber geometry and of a highly-sensitive E/P-co coating substantially enhanced the detection sensitivity of the FTIR-ATR sensor for CHC monitoring, thereby far exceeding the state-of-art performance of such sensors. Furthermore, simultaneous and in-situ detection of six common CHCs pollutants including monochlorobenzene (MCB), 1,2-dichlorobenzene (o-DCB), 1,3-dichlorobenzene (m-DCB), trichloroethylene (TCE), perchloroethylene (PCE), and chloroform (CF) at ppb levels was successfully achieved. Consequently, the present study may guide the design and implementation of highly sensitive FTIR-ATR sensors for online monitoring of CHCs in complex aqueous environments and pollution scenarios.

Results

A mixture of PCE, TCE, CF, o-DCB, MCB, m-DCB (each with a concentration of 500 ppb (v/v) was prepared and used for testing the sensor. The ATR spectrum of the mixture after 30-min enrichment is shown in Figure 1. The characteristic absorption bands of each CHC could be readily identified according to molecule-specific C-H vibrations in the fingerprint region of the IR spectrum. To reduce the measurement interference caused by peak overlapping at between 740 and 770 cm\(^{-1}\), several strategies were adopted, e.g., using the peak height as the indicator for analyte concentration calibration; processing the spectrum data using baseline correction and curve-fitting. The peak at 776 cm\(^{-1}\) is ascribed to PCE, which has two feature peaks. Therefore, to avoid interference, the other peak of PCE at 910 cm\(^{-1}\) was chosen for its concentration calibration. Thus, all CHCs could be simultaneously detected, discriminated, and quantified within a single measurement. The characteristic bands for quantitative determination of these CHCs are: TCE at 930 cm\(^{-1}\), PCE at 910 cm\(^{-1}\), m-DCB at 867 cm\(^{-1}\), CF at 760 cm\(^{-1}\), o-DCB at 748 cm\(^{-1}\), and MCB at 740 cm\(^{-1}\).

Although the sensor performance might be affected by many factor, e.g., flow velocity, flow channel height, and analyze diffusion properties within the aqueous phase\(^\text{22}\), in our system only the flow velocity was tunable. This parameter was set to 0.2 mL/min to enable measurements in the time regime of several minutes without using excessive amounts of anlyte solution.

For maximizing the analytical signal, a certain period of time is needed to allow sufficient enrichment of the analytes. The infrared absorbance of selected CHCs vs. the enrichment time in a typical measurement scenario is illustrated in Figure 2. It is clearly evident that for all analytes a diffusion equilibrium is reached after approximately 30 min, which was adopted during the subsequent experiments.

To validate the performance of the as-prepared sensor for CHC detection, the absorbance vs. concentration calibration functions for each analyte in the mixture in different concentration ranges were experimentally determined (Figs. 3 and 4) confirming the excellent analytical accuracy of the developed sensor system for simultaneous detection of multiple CHCs both at moderate (100–700 ppb) and low (5 to 70 ppb) concentration ranges (\(R^2\) values above 0.9 for all analytes except for TCE). The slightly poorer detection performance for TCE is likely attributed to the reduced enrichment of this compound and a lower absorbance coefficient\(^\text{21}\) compared to other CHCs. The difference in the calibration slope/sensitivity between different concentration ranges was originated from the different rates of CHCs diffusing into the polymer, which is governed by both thermodynamics and dynamics. At a higher concentration, more time is needed...
to achieve diffusion equilibrium. Therefore, the insufficient enrichment of CHC at a higher analyte concentration might have led to a lower sensitivity compared with that at a lower concentration. In addition, the higher range of concentration variation (i.e., 600 ppb) under the high concentration conditions might have also contributed to the lower $R^2$ compared with that under the low concentration conditions when a linear correlation is not strictly followed. The obtained results confirm that the IR-ATR fiberoptic sensor could serve as an efficient device to probe trace amounts of multiple CHCs in aqueous environments with high sensitivity, wide detection ranges, and reduced background interferences.

**Discussion**

The utility of ATR techniques has greatly advanced IR spectroscopy as a flexible and tunable in-situ detection technology. IR-ATR spectroscopy has proven to be an effective method for directly probing water contaminants, yet, to date its detection resolution remains insufficient to meet practical implementation requirements. Here, we demonstrate that the detection capability of such sensor systems could be remarkably enhanced toward practically relevant detection levels by combining a unique transducer geometry with an appropriate enrichment coating.

The combined planar-cylinder geometry of the transducer facilitated an increased number of internal reflections, and led to an amplified absorbance signal (Fig. 5a and c). According to Snell’s law, total internal reflection occurs at the interface of two dielectric media, if light is incident from the optically denser medium at the interface at an angle large than the critical angle $\theta_c$. Here, $\theta_c$ is defined as:

$$\theta_c = \arcsin \frac{n_2}{n_1}$$

where $n_1$ and $n_2$ are the refractive indices of the waveguide and the surrounding medium, respectively.

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**Figure 2** | Typical enrichment curves for the CHCs components in water at a concentration of 300 ppb (v/v). A diffusion equilibrium was reached after about 30-min enrichment.

**Figure 3** | Calibration curves for CHCs in the concentration range of 100–700 ppb (v/v). TCE at 930 cm$^{-1}$, PCE at 910 cm$^{-1}$, $m$-DCB at 867 cm$^{-1}$, CF at 760 cm$^{-1}$, $o$-DCB at 748 cm$^{-1}$, and MCB at 740 cm$^{-1}$.

**Figure 4** | Calibration curves for CHCs mixture in the concentration range of 5–70 ppb (v/v).

**Figure 5** | Schematic diagrams of the detection principle. (a) an E/P-coated planar-cylinder fiber, (b) the principle schematic, (c) an uncoated cylindrical fiber.
By interaction of the incident and reflected light wave, an exponentially decaying evanescent field is established, which penetrates exponentially decaying a certain distance into the surrounding medium. Theoretically, the number of internal reflections (n) in a waveguide can be calculated as

\[ n = \frac{L}{a} = \frac{L}{d \tan \theta} \]  

(2)

where \( L \) is the length of the total sensing length, \( d \) is the waveguide thickness, \( a \) is the distance between each reflection.

Thus, with the same \( L \) level and given the same incident light angle \( \theta \), the waveguide with a planar-cylinder integrated geometry allows more internal reflections compared to a purely cylindrical waveguide without flattened segment. It is estimated that there are hundreds of internal reflections present within this configuration, i.e., approximately 5 times more compared to a conventional fiber optic waveguide, and approximately 50 times more compared to a commercial trapezoidal ZnSe waveguide element with only one usable detection surface.

In an IR-ATR system, the amplitude of the evanescent field \( E(x) \) within a medium decreases exponentially with the distance \( x \) to the fiber-medium interface following

\[ E(x) = E_0 \exp \left( -\frac{x}{d_p} \right) \]  

(3)

where \( E_0 \) represent the intensity and \( d_p \) is the light penetration depth.

Thus, after \( n \) internal reflections within the waveguide, a total \( E_{\text{total}}(x) \) may be obtained (usually: \( x_1 = x_2 = \ldots = x_n \)):

\[ E_{\text{total}}(x) = \sum_{i=1}^{n} E_i(x_1) = nE_0 \exp \left( -\frac{x}{d_p} \right) \]  

(4)

Therefore, the absorbance increases with \( n \), i.e., more internal reflections led to higher absorbance signals.

In addition to the geometric effect, the use of an E/P-co coating in the present system also considerably amplified the detection signal via the selective enrichment of CHCs. It has been reported that E/P-co not only facilitates the selective enrichment of non-polar analytes, but also decreases the interference signals of water due to its hydrophobic nature. Hence, CHCs are preferentially partitioning via the selective enrichment of CHCs. It has been reported that E/P-co coating not only facilitates the enrichment of CHCs in the range of 100–200 Å calculated via ChemWindow by Roy and Mielczarski also favor rapid diffusion.

The coating thickness is a critical parameter that affects the diffusion rate. An appropriate coating thickness may be estimated according to the penetration depth \( d_p \) of the evanescent field, which can be expressed by

\[ d_p = \frac{\lambda}{2\pi n_1^2 \sin^2 \theta - n_2^2} \]  

(5)

where \( \lambda \) is the wavelength of the incident light. For our system, the typical values of these variables are: \( n_1 = 2.2 (\text{AgClO}_3 Br_1) \); \( n_2 = 1.48 \) (E/P-co); \( \theta = 75^\circ \); \( \lambda = 10 \mu m \) (i.e., 1000 cm\(^{-1}\)).

Hence, an approximated value of \( d_p \) was calculated as:

\[ d_p = \frac{10}{2\pi \times 2.2^2 \times \sin^2(75^\circ) - 1.48^2} = 1.04 \mu m \]  

(6)

It is recommended that the coating thickness should be roughly three times of the penetration depth to ensure sufficient detection sensitivity via enrichment enhancement, yet an acceptable short response time. Thus, in the present studies a coating thickness of 2.91 μm was selected as optimal. In addition, the E/P-co coating not only allows an augmentation of the analytical signal, but also offers protection to the waveguide via isolation from corrosive or fouling substances, therefore extending the long-term stability of the sensor.

Nowadays, a number of detection techniques are being used for the analysis of CHCs and other volatile organic compounds (VOCs). Table 1 shows a comparative evaluation of their performance. For conventional chromatography (including GC/FID, GC/MS and HPLC)\(^{28,31}\), off-line sample pretreatment and preconcentration steps are required. Although latest attempts circumventing this step via e.g., membrane inlet proton transfer reaction mass spectrometry (MI-PTRMS) techniques\(^{32}\) and coupling of membrane inlets GC/MS\(^{33}\), the rather complex operating procedures and high instrumental costs still limit their widespread application. Other techniques such as quartz-crystal microbalance (QCM) sensors, and enzyme-linked immunosorbent assay (ELISA) also allow for direct and in-situ measurements. However, the operation of QCMs in liquid is complicated and time-consuming, as the film coated on the gold electrode of an QCM needs to be exposed to hot air after analyte absorption, and detection may not start/continue until the initial resonance frequency of the quartz crystal has been recovered\(^{34}\).

| Table 1 | Comparisons of Current Methods for Determination of CHCs and other VOCs |
|-----------------------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| direct measurement | GC/FID | GC/MS | MI-PTRMS | Membrane GC/MS | HPLC | UV | Raman | Fluorescence | QCM | ELISA | FTIR-ATR |
| simultaneous for | X | X | X | X | X | X | X | X | X | X | |
| multiple analytes | X | X | X | X | X | X | X | X | X | X | |
| in-situ | X | X | X | X | X | X | X | X | X | X | |
| continuous | X | X | X | X | X | X | X | X | X | X | |
| real-time | X | X | X | X | X | X | X | X | X | X | |
| sensitivity | ppb\(^a\) | ppt\(^a\) | sub-ppb | ppt | sub-ppt | ppb | ppm\(^c\) | ppt | ppm | sub-ppb | ppb |

\(^a\)part per billion.

\(^b\)part per trillion.

\(^c\)part per million.
while ELISA may only detect one specific target at a time, and is fairly costly\(^6\). In comparison, spectroscopic methods are relatively simple and allow rapid detection. However, UV spectroscopy may not discriminate individual compounds in a mixture of VOCs\(^5\), while Raman spectroscopy\(^7\) may only reach detectivities at the ppm level for VOCs even when combined with a solid-phase microextraction preconcentration step. Fluorescence spectroscopy\(^8\) allows simultaneous detection of multiple species, but it may only detect luminescent contaminants and suffers from severe interference by the chlorine atom within the CHCs and other fluorescence quenching substances in water.

Hence, IR-ATR sensors appear to be among the most promising methods to directly detect multiple CHCs and other VOCs with high sensitivity and accuracy. Using appropriate polymer matrices for in-situ enrichment at the fiber surface along with advanced sensor geometries, limits of detection at mid- to low-ppb levels may be achieved, thus suggesting a high potential for practical implementation in water contamination monitoring.

More importantly, our previous studies have demonstrated that such detection processes are not interfered by salinity, humic acids, and turbidity\(^8\), thus implying a substantial potential of other organic pollutants in environmental matrices\(^9\). However, despite these prospects, currently there are still some challenges remaining toward real-world implementations. For example, the detection accuracy and sensitivity for selected contaminants - such as TCE in the present study - are yet to be improved to meet the practical demands; the long-term performance may be affected by long-term diffusion of water and other substances into the polymer coating. Therefore, future efforts are needed to further improve the detection sensitivity and stability of such sensing systems. This can be achieved by a further optimization of the fiber design, material, and operations (e.g., solvent flow rate and enrichment time) as well as a combined use of this method with other high-precision techniques (e.g., tunable quantum cascade lasers in lieu of FTIR).

In summary, CHC detection by using an advanced IR-ATR sensor system with a dedicated transducer geometry and an E/P-coating was evaluated. This sensor enables sensitive, rapid, and simultaneous detection of several CHCs at ppb concentration levels in one-step measurement procedure without any sample pretreatment. Furthermore, a substantial improvement in both the detection range (5–700 ppb) and sensitivity over previously reported IR-ATR sensors has been obtained. Thus, this IR-ATR sensor may be used as a powerful tool for on-line, in-situ, and sensitive probing of multiple water pollutants, and has a substantial potential for practical water contamination monitoring.

**Methods**

Methanol, PCE, TCE, CF, o-DCA, MCB, m-DCA, n-hexane (all of analytical grade) and E/P-co (60:40) were purchased from Aldrich (Milwaukee, USA). All solutions were prepared using deionized water. A minute amount of methanol was added serving as solubility mediator to ensure full dissolution the CHCs in water, which causes no interference to the sensor readings according to previous studies\(^10\).

An integrated planar-cylinder fiber was used as active transducer, which consisted of a flattened silver halide fiber segment (refractive index of the waveguide \(n_i = 2.28\), length 45 mm, thickness 150 \(\mu\)m) with fiberoptic extensions (length 15 mm, thickness 700 \(\mu\)m) at both ends (Fig. 6).

E/P-co solution (1%, v/v) was prepared by dissolving E/P-co into \(n\)-hexane. Then, the solution was dip coated onto the fiber surface to form a thin film\(^11\). The film thickness was controlled at 2.9 \(\mu\)m, which approximately matched the information depth of the evanescent field.

Evanescent field measurements were performed by focusing the external collimated IR beam from a Bruker Vertex 70 spectrometer (Bruker Optics, Billerica, USA) onto the facet of the cylindrical extension connected to the flattened silver halide fiber segment using a gold-coated, off-axis, parabolic mirror (OAPM, focal length 28.4 mm, Janos Optics, Towson, USA). Light from the distal end of the transducer was focused onto a liquid nitrogen-cooled photodiode detector (e.g., tunable quantum cascade lasers in lieu of FTIR).

In conclusion, this sensor may be used as a powerful tool for on-line, in-situ, and sensitive probing of multiple water pollutants, and has a substantial potential for practical water contamination monitoring.

**Figure 6** Schematic (upper) and optical image (bottom) of experimental setup. PM = planar mirror, OAPM = off-axis parabolic mirror.

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**Author contributions**

R.L., B.M. and H.Q.Y. designed the experiments; R.L., C.Q. and Y.R. conducted the experiments; R.L., B.M., A.K. and H.Q.Y. contributed to the planning and coordination of the project; R.L., B.M., W.W.L., G.P.S. and H.Q.Y. wrote and edited the manuscript. All authors contributed to discussion about the results and the manuscript.

**Additional information**

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