



OPEN

SUBJECT AREAS:

SENSORS

IR SPECTROSCOPY

OPTICAL SENSORS

ENVIRONMENTAL MONITORING

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

Rui Lu¹, Boris Mizaikoff², Wen-Wei Li¹, Chen Qian¹, Abraham Katzir³, Yosef Raichlin⁴, Guo-Ping Sheng¹ & Han-Qing Yu¹Received
14 June 2013Accepted
7 August 2013Published
28 August 2013

Correspondence and requests for materials should be addressed to B.M. (boris.mizaikoff@uni-ulm.de) or H.-Q.Y. (hgyu@ustc.edu.cn)

¹Department of Chemistry, University of Science and Technology of China, Hefei 230026, China, ²Institute of Analytical and Bioanalytical Chemistry, University of Ulm, 89081 Ulm, Germany, ³School of Physics, Tel Aviv University, Tel Aviv 69978, Israel, ⁴Department of Applied Physics, Ariel University Center of Samaria, Ariel, Israel.

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 aqueous 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 spectrometry) 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_xBr_{1-x}) fibers are considered the most practical ATR



waveguide material¹¹, which provides access to the entire mid-infrared (MIR) spectral range of interests (3–18 μm)¹², and allows flexible tuning of its geometry¹³. $\text{AgCl}_x\text{Br}_{1-x}$ fibers have been demonstrated to offer direct and accurate detection of crude oil in a deionized water matrix¹⁴, and of water in hexane at ppm levels¹⁵. Hence, directly probing water contaminants may be achieved by immersing a ATR-based fiber into an aqueous solution serving as the active transducer¹⁶. 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})¹⁴ and other background molecules¹⁵. 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 a 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 $\text{AgCl}_x\text{Br}_{1-x}$ 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 geometry¹⁷. In this context, decreasing the fiber diameter or tapering a section of the fiber are both effective strategies to improve the analytical sensitivity¹⁸. 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 fibers¹³. 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 sensors¹⁹. On the one hand, particular chemical recognition membranes (e.g., polyisobutylene, ethylene-propylene copolymer, and Teflon AF) have been reported to selectively enrich the targeted species at the fiber surface and within the evanescent field facilitating their detection²⁰. 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 coating¹⁹. Thus, in our system a hydrophobic ethylene/propylene copolymer (E/P-co) coating, which is ideally suited for enrichment of hydrophobic hydrocarbons²¹ including CHCs^{2,22} 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 factors, e.g., flow velocity, flow channel height, and analyte diffusion properties within the aqueous phase²², 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 analyte 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 coefficient² 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

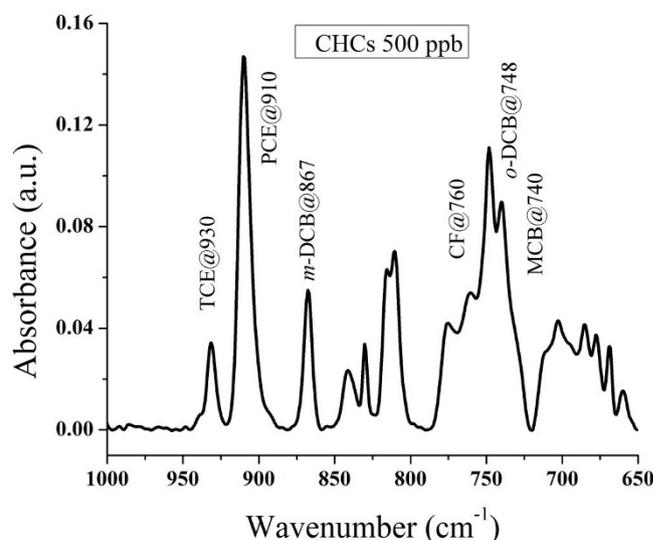


Figure 1 | IR absorption spectrum of the CHCs mixture at 500 ppb (v/v) after 30-min enrichment. All peaks are labeled for clarity.

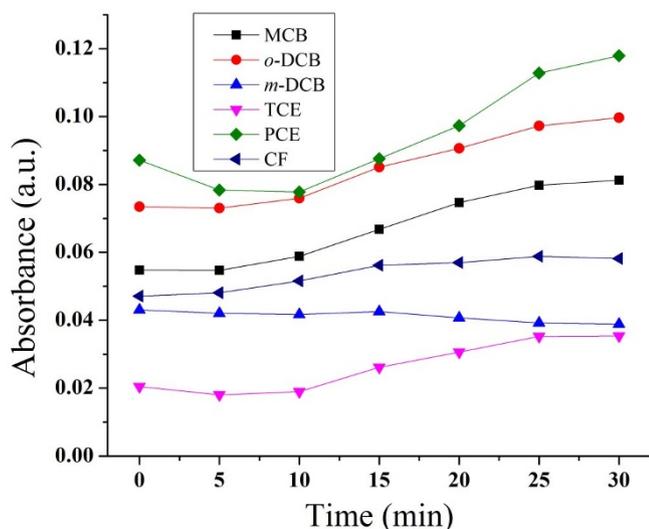


Figure 2 | Typical enrichment curves for the CHCs components in water at a concentration of 300 ppb (v/v). A diffusion equilibrium was reached after about 30-min enrichment.

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,

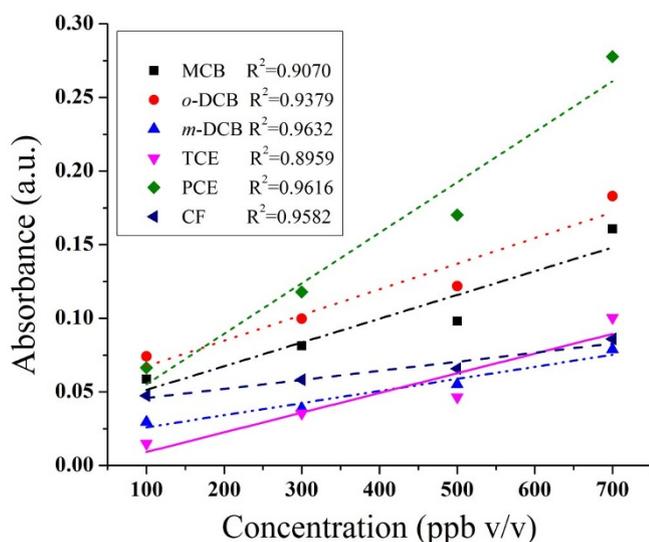


Figure 3 | Calibration curves for CHCs in the concentration range of 100–700 ppb (v/v). TCE at 930 cm^{-1} , PCE at 910 cm^{-1} , m -DCB at 867 cm^{-1} , CF at 760 cm^{-1} , o -DCB at 748 cm^{-1} , and MCB at 740 cm^{-1} .

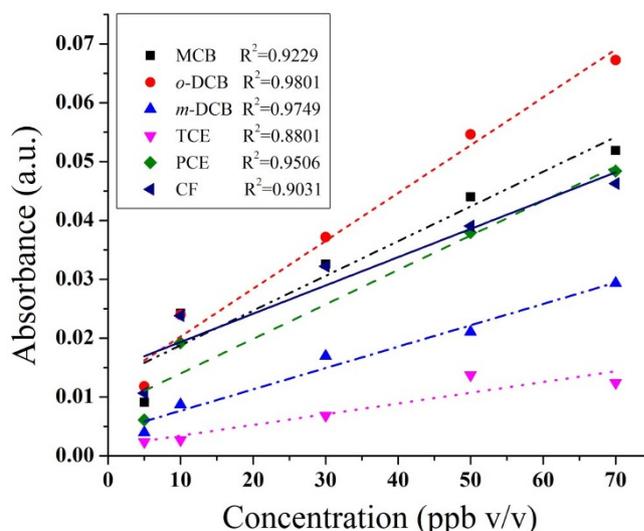


Figure 4 | Calibration curves for CHCs mixture in the concentration range of 5–70 ppb (v/v).

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 θ_c . Here, θ_c is defined as²³

$$\theta_c = \arcsin \frac{n_2}{n_1} \quad (1)$$

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

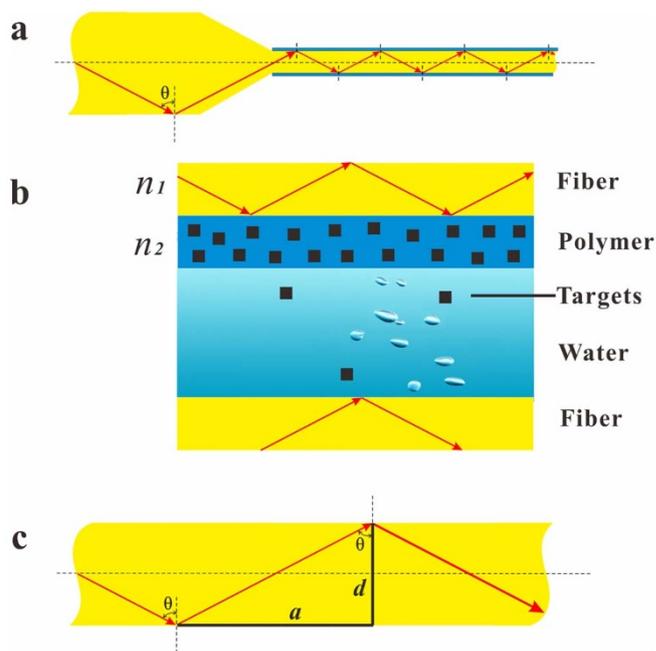


Figure 5 | Schematic diagrams of the detection principle. (a) an E/P-co coated planar-cylinder fiber, (b) the principle schematic, (c) an uncoated cylindrical fiber.



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 medium²⁴. Theoretically, the number of internal reflections (n) in a waveguide can be calculated as

$$n = \frac{L}{a} = \frac{L}{d \tan \theta} \quad (2)$$

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 θ , 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 fiberoptic waveguide, and approximately 50 times more compared to a commercial trapezoidal ZnSe waveguide element with only one usable detection surface²

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 following²⁴

$$E(x) = E_0 \exp\left(-\frac{x}{d_p}\right) \quad (3)$$

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

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

$$E_{total}(x) = \sum_{i=1}^n E_i(x_i) \approx nE(x) = nE_0 \exp\left(-\frac{x}{d_p}\right) \quad (4)$$

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 analytes²⁴, but also decreases the interference signals of water due to its hydrophobic nature. Hence, CHCs are preferentially partitioning into the polymer via Van der Waals forces or dipole-dipole interactions. The degree of enrichment, i.e, the amount of a target analyte absorbed by the membrane, is highly dependent on its equilibrium-state distribution between the polymer and water phase, which is expressed by the partition coefficient (K)²⁵. A higher value of K indicates that the analyte more efficiently enriches into the polymer. In our case, the K values of E/P-co for MCB, PCE, and CF were 258, 846, and 23 respectively²¹, thereby indicating the excellent enrichment capability for most CHCs. The relatively low value of CF is mainly due to its high water solubility²⁶.

However, it should be noted that for efficient detection via the evanescent field it is essential that the absorbed constituents rapidly diffuse into the polymer matrix toward the waveguide surface. Thus,

the diffusion of CHCs within the E/P-co coating as well as the coating thickness are also critical factors to determine the detection performance¹⁹.

The diffusion rate of hydrocarbons within polymers may be affected by a variety of factors including the degree of crystallinity, the glass transition temperature T_g of the polymer, and the size and structure of the hydrocarbon molecules. In the present system, amorphous E/P-co (i.e., 0% crystallinity)²¹ was adopted. The comparatively long distances between the disordered chains of amorphous E/P-co provide sufficient void volume, which facilitates rapid diffusion of CHCs. Additionally, the small molecular dimensions of CHCs in the range of 100–200 Å³ (calculated via ChemWindow by Roy and Mielczarski²) also favor rapid diffusion.

The coating thickness is a critical parameter that affects the diffusion time²⁷. An appropriate coating thickness may be estimated according to the penetration depth (d_p) of the evanescent field, which can be expressed by

$$d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2 \theta - n_2^2}} \quad (5)$$

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

Hence, an approximated value of d_p was calculated as:

$$d_p = \frac{10}{2\pi\sqrt{2.2^2 \times \sin^2(75^\circ) - 1.48^2}} = 1.04 \mu\text{m} \quad (6)$$

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 time²¹. 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 enables 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 been 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) techniques³² and coupling of membrane inlets GC/MS³³, 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 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 recovered³⁴,

Table 1 | Comparisons of Current Methods for Determination of CHCs and other VOCs

	GC/FID	GC/MS	MI-PTRMS	Membrane GC/MS	HPLC	UV	Raman	Fluorescence	QCM	ELISA	FTIR-ATR
direct measurement	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
simultaneous for multiple analytes	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
in-situ	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
continuous	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
real-time	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
sensitivity	ppb ^a	ppt ^b	sub-ppb	ppt	sub-ppt	ppb	ppm ^c	ppt	ppm	sub-ppb	ppb

^apart per billion.

^bpart per trillion.

^cpart per million.

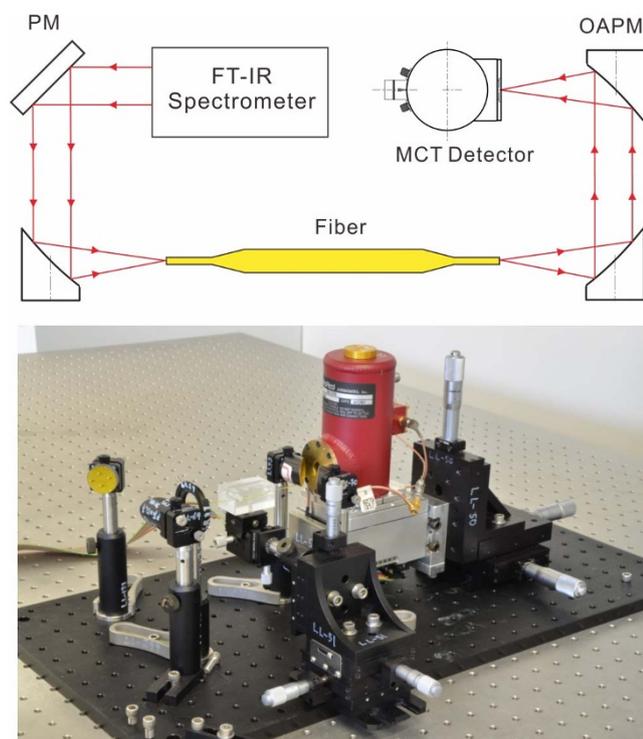


Figure 6 | Schematic (upper) and optical image (bottom) of experimental setup. PM = planar mirror, OAPM = off-axis parabolic mirror.

while ELISA may only detect one specific target at a time, and is fairly costly³⁵. In comparison, spectroscopic methods are relatively simple and allow rapid detection. However, UV spectroscopy may not discriminate individual compounds in a mixture of VOCs⁶, while Raman spectroscopy⁷ may only reach detectivities at the ppm level for VOCs even when combined with a solid-phase microextraction preconcentration step. Fluorescence spectroscopy⁸ 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 turbidity³⁶, thus implying a substantial potential for the detection of other organic pollutants in environmental matrices³⁷. 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-co

enrichment 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*-DCB, MCB, *m*-DCB, *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 inference to the sensor readings according to previous studies³⁶.

An integrated planar-cylinder fiber was used as active transducer, which consisted of a flattened silver halide fiber segment (refractive index of the waveguide $n_1 = 2.237$, length 45 mm, thickness 150 μm) with fiberoptic extensions (length 15 mm, thickness 700 μm) 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 film³⁸. The film thickness was controlled at 2.9 μm , which approximately matched the information depth of the evanescent field.

Evanescence field measurements were performed by focusing the external collimate 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: 25.4 mm; Janos Optics, Townshend, USA). Light from the distal end of the transducer was focused onto a liquid nitrogen-cooled photoconductive mercury-cadmium-telluride detector (detector element 1×1 mm, Infrared Associates, USA). Spectra were recorded in a frequency window of 4000–400 cm^{-1} averaging 128 scans at a spectral resolution of 2 cm^{-1} . A schematic along with an image of the experimental setup is shown in Figure 6.

- Acha, V. *et al.* ATR-FTIR sensor development for continuous on-line monitoring of chlorinated aliphatic hydrocarbons in a fixed-bed bioreactor. *Biotechnol. Bioeng.* **68**, 473 (2000).
- Roy, G. & Mielczarski, J. A. Infrared detection of chlorinated hydrocarbons in water at ppb levels of concentrations. *Water Res.* **36**, 1902 (2002).
- Liska, I. Fifty years of solid-phase extraction in water analysis - historical development and overview. *J. Chromatogr. A* **885**, 3 (2000).
- Wilkins, A. L., Singh-Thandi, M. & Langdon, A. G. Pulp mill sourced organic compounds and sodium levels in water and sediments from the Tarawera River, New Zealand. *Bull. Environ. Contam. Toxicol.* **57**, 434 (1996).
- Martinez, E. *et al.* Multicomponent analysis of volatile organic compounds in water by automated purge and trap coupled to gas chromatography-mass spectrometry. *J. Chromatogr. A* **959**, 181 (2002).
- Wittkamp, B. L., Hawthorne, S. B. & Tilotta, D. C. Determination of aromatic compounds in water by solid phase microextraction and ultraviolet absorption spectroscopy. 1. Methodology. *Anal. Chem.* **69**, 1197 (1997).
- Wittkamp, B. L. & Tilotta, D. C. Determination of BTEX compounds in water by solid-phase microextraction and raman spectroscopy. *Anal. Chem.* **67**, 600 (1995).
- Carr, J. W. & Harris, J. M. In situ fluorescence detection of polycyclic aromatic hydrocarbons following preconcentration on alkylated silica adsorbents. *Anal. Chem.* **60**, 698 (1998).
- Lin, W. & Li, Z. Detection and quantification of trace organic contaminants in water using the FT-IR-attenuated total reflectance technique. *Anal. Chem.* **82**, 505 (2010).
- Hanick, N. J. *Internal Reflection Spectrometry*. Interscience Publishers: New York, 1967.
- Mizaikoff, B. Mid-IR fiber-optic sensors. *Anal. Chem.* **75**, 258A (2003).
- Griffiths, P. R. & Christopher, C. C. *Handbook of Vibrational Spectroscopy*. John Wiley & Sons: New York, 2002.
- Kosower, E. M. *et al.* Surface-enhanced infrared absorption and amplified spectra on planar silver halide fiber. *J. Phys. Chem. B* **108**, 12633 (2004).
- Luzinova, Y. I. *et al.* In-situ trace analysis of oil in water with mid-infrared fiberoptic chemical sensors. *Anal. Chem.* **84**, 1274 (2012).
- Luzinova, Y. I. *et al.* Detecting trace amounts of water in hydrocarbon matrices with infrared fiberoptic evanescent field sensors. *Analyst* **137**, 333 (2012).
- Küpper, L. *et al.* Novel developments in mid-IR fiber-optic spectroscopy for analytical applications. *J. Mol. Struct.* **563–564**, 173 (2001).
- Simhony, S. *et al.* Evanescent wave infrared spectroscopy of liquids using silver halide optical fibers. *J. Appl. Phys.* **64**, 3732 (1988).
- Vongsvitvut, J. *et al.* Characterization of supported cylinder-planar germanium waveguide sensors with synchrotron infrared radiation. *Appl. Spectrosc.* **58**, 143 (2004).



19. Flavin, K. *et al.* A comparison of polymeric materials as pre-concentrating media for use with ATR/FTIR sensing. *Int. J. Environ. Anal. Chem.* **86**, 401 (2006).
20. Walsh, J. E. *et al.* Sensing of chlorinated hydrocarbons and pesticides in water using polymer coated mid-infrared optical fibres. *Analyst* **121**, 789 (1996).
21. Göbel, R. *et al.* Investigation of different polymers as coating materials for IR/ATR Spectroscopic trace analysis of chlorinated hydrocarbons in water. *Appl. Spectrosc.* **48**, 678 (1994).
22. Fedorov, A. G. *et al.* Model-based optimal design of polymer-coated chemical sensors. *Anal. Chem.* **75**, 1106 (2003).
23. Walsh, J. E. *et al.* Midinfrared fiber sensor for the in-situ detection of chlorinated hydrocarbons. *SPIE Proceeding* **233** (1995).
24. Mizaikoff, B. Mid-infrared evanescent wave sensors - a novel approach for subsea monitoring. *Meas. Sci. Technol.* **10**, 1185 (1999).
25. Jakusch, M. & Mizaikoff, B. Selective polymer materials: Absolute determination of their sorption properties. *SPIE Proceedings* **4205**, 93 (2001).
26. Haynes, W. M. *CRC Handbook of chemistry and physics*. CRC Press/Taylor and Francis: Boca Raton, FL. 2012.
27. Langenfeld, J. J., Hawthorne, S. B. & Miller, D. J. Quantitative analysis of fuel-related hydrocarbons in surface water and wastewater samples by solid-phase microextraction. *Anal. Chem.* **68**, 144 (1996).
28. Hennion, M. C. Solid-phase extraction: method development, sorbents, and coupling with liquid chromatography. *J. Chromatogr. A* **856**, 3 (1999).
29. Zhang, Z. & Pawliszyn, J. Quantitative extraction using an internally cooled solid phase microextraction device. *Anal. Chem.* **67**, 34 (1995).
30. Silva, F. C., de Carvalho, C. R. & de Cardeal, Z. L. Solid-phase microextraction method for the quantitative analysis of styrene in water. *J. Chromatogr. Sci.* **38**, 315 (2000).
31. Chen, M. *et al.* Analyses of nitrobenzene, benzene and aniline in environmental water samples by headspace solid phase microextraction coupled with gas chromatography-mass spectrometry. *Chin. Sci. Bull.* **51**, 1648 (2006).
32. Boscaini, E. *et al.* Membrane inlet proton transfer reaction mass spectrometry (MI-PTMMS) for direct measurements of VOCs in water. *Int. J. Mass Spectrom.* **239**, 171 (2004).
33. Chang, C. C. & Her, G. R. On-line monitoring trihalomethanes in chlorinated water by membrane introduction-fast gas chromatography mass-spectrometry. *J. Chromatogr. A* **893**, 169 (2000).
34. Ayad, M. M., El-Hefnawey, G. & Torad, N. L. Quartz crystal microbalance sensor coated with polyaniline emeraldine base for determination of chlorinated aliphatic hydrocarbons. *Sens. Actuator B-Chem.* **134**, 887 (2008).
35. Sanvicens, N. *et al.* Determination of haloanisols in white wine by immunosorbent solid-phase extraction followed by enzyme-linked immunosorbent Assay. *J. Agric. Food Chem.* **54**, 9176 (2006).
36. Kraft, M. & Mizaikoff, B. A mid-infrared sensor for monitoring of chlorinated hydrocarbons in the marine environment. *Int. J. Environ. Anal. Chem.* **78**, 367 (2000).
37. Karlowatz, M., Kraft, M. & Mizaikoff, B. Simultaneous quantitative determination of benzene, toluene, and xylenes in water using mid-infrared evanescent field spectroscopy. *Anal. Chem.* **76**, 2643 (2004).
38. Mizaikoff, B. *et al.* Water monitoring using infrared fiber optic sensors. *Proceedings of OCEANS' 98 Conference* 1401 (1998).

Acknowledgements

The authors wish to thank the National Basic Research Program of China (2011CB933700), the Natural Science Foundation of China (51129803 and 21261160489) and the Program for Changjiang Scholars and Innovative Research Team in University, China for the partial support of this work.

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

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Lu, R. *et al.* Determination of Chlorinated Hydrocarbons in Water Using Highly Sensitive Mid-Infrared Sensor Technology. *Sci. Rep.* **3**, 2525; DOI:10.1038/srep02525 (2013).



This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported license. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-nd/3.0>