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Simultaneous Quantitative Determination of Benzene, Toluene, and Xylenes in Water Using Mid-Infrared Evanescent Field Spectroscopy

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Attenuated total reflection mid-infrared spectroscopy is applied for simultaneous detection and quantification of the environmentally relevant analytes benzene, toluene, and the three xylene isomers. The analytes are enriched into a thin polymer membrane coated onto the surface of an internal reflection waveguide, which is exposed to the aqueous sample. Direct detection of analytes permeating into the polymer coating is performed by utilizing evanescent field spectroscopy in the fingerprint range ($> 10\ \mu\text{m}$) of the mid-infrared (MIR) spectrum ($3\text{--}20\ \mu\text{m}$) without additional sample preparation. All investigated compounds are characterized by well-separated absorption features in the evaluated wavelength regime. Hence, data evaluation was performed by integration of the respective absorption peaks. Limits of detection lower than 20 ppb (v/v) for all xylene isomers, 45 ppb (v/v) for benzene, and 80 ppb (v/v) for toluene have been achieved. The straightforward experimental setup and the achieved detection limits for these environmentally relevant volatile organic compounds in the low-ppb concentration range reveal a substantial potential of MIR evanescent field sensing devices for on-line in situ environmental analysis.

Contamination of drinking water, groundwater, and seawater with volatile organic compounds (VOCs) poses a significant health risk to humans.^{1,2} In recent years, the awareness of the public toward the problem of groundwater, surface water, drinking water, and seawater contamination with VOCs increased considerably. Pollutants such as chlorinated hydrocarbons, aromatic hydrocarbons, and within the latter category especially benzene, toluene, and xylenes (BTX) are among the most commonly detected organic contaminants in water.^{3–9} As an example, benzene oc-

cupies a permanent place among the 10 most relevant priority pollutants in the listings of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).¹⁰ Hence, considerable interest in developing analytical tools for the determination of such contaminants is evident prioritizing continuously operating in situ devices capable of BTX detection and quantitative discrimination at trace concentration levels.

Standard methods for BTX analysis include purge-and-trap and static headspace gas chromatography (GC) combined with flame ionization detection, among other GC techniques with hyphenated more sophisticated detection systems.^{11,12} As an alternative to these methods, solid-phase extraction techniques have been introduced for preconcentration of environmental samples and chromatographic analysis after elution of enriched species with suitable organic solvents.^{13,14} However, these classical analytical approaches are usually confined to a laboratory environment and require costly, error-prone, and time-consuming sampling procedures or include increasingly restricted use of organic solvents.

During the last years, some attempts have been reported to detect hydrophobic organic pollutants via UV, Raman, and IR spectroscopic methods directly at solid sorbent phases after the extraction step.^{15–19} While these methods proved to be less sensitive than conventional chromatographic analysis, there is an undoubted potential for discontinuous on-site pollution measurements due to the availability of field-deployable instrumentation. Direct detection of aromatic hydrocarbons in water based on UV

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derivative spectroscopy was proposed by Vogt et al.^{20,21} However, field applicability of this transmission-based method may be restricted due to a potential influence of turbidity in real-world samples.

Consequently, increased efforts are focused on technologies enabling the molecule-specific determination of organic pollutants in aqueous environments such as attenuated total reflection infrared spectroscopy (ATR-IR).^{22–24}

Evanescent field spectroscopy utilizes internal reflection elements based on ATR crystals or mid-infrared (MIR)-transparent optical fibers serving as waveguide and optical transducer. Hence, absorption spectroscopy at or near the waveguide surface is enabled via the evanescent field.^{25,26} Chemical MIR sensors enrich analytes into a thin polymer membrane coated onto the waveguide surface providing interaction of the evanescent field with enriched analyte molecules. Such sensor systems enable measurements within a period of several minutes instead of comparatively long analysis time for methods based on sampling and discontinuous assessment. Detailed information derived from spectroscopic data allows identification and quantification of a wide range of VOCs at laboratory and field conditions.^{22,27–34} With regard to applicability in real-world environments, the accuracy of this method has been proven to be independent of aqueous sample properties including turbidity, salinity, or acidity at expected levels.³⁵ A similar approach utilizing a polymer-coated fiber-optic evanescent wave sensor system operating in the near-infrared regime for the detection of BTX and gasoline (sum parameters) compounds in water has been introduced by Buerck et al.³⁶

Recently, an alternative setup utilizing polymer-coated ATR-IR sensor systems for detecting VOCs in the gas phase was introduced by Yang et al.^{37,38} In this approach, VOCs are detected in the headspace of either a heated or a gas-stripped sample solution. Analytes are enriched into a thin PDMS layer, which is coated onto a suitable ATR waveguide, and spectroscopically

detected. Although this setup may find its applications, for instance, in detection of (semi)volatile organic compounds in aggressive environments, it seems preferable to directly measure in the liquid phase for the following reasons: (i) compounds with low volatility are addressable with a direct sensor, (ii) a direct measurement represents the least complicated sensor setup only consisting of a transducer head exposed to the sample solution, avoiding prior sample preparation or extraction, and (iii) less parameters have to be controlled compared to headspace sensing and no stripping system is required.

In this study, we will demonstrate the potential of mid-infrared ATR spectroscopy based on chemically modified optical transducers for speciated direct detection and quantification of multicomponent mixtures containing benzene, toluene, and xylene isomers in aqueous solution at low-ppb (v/v) concentration levels.

EXPERIMENTAL SECTION

Materials. Ethylene/propylene copolymer (60:40) was purchased from Aldrich (Milwaukee, WI). Methanol, *n*-hexane, benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene were purchased from Aldrich and were of analytical grade. Deionized water was used for preparation of all solutions and for sensor regeneration.

Preparation of Ethylene/Propylene Copolymer Thin Films. A 1% (w/v) coating solution of ethylene/propylene copolymer (E/P-co) was prepared by dissolving 0.5 g of granular polymer under reflux in 50 mL of *n*-hexane. Prior to coating, a new ATR crystal was thoroughly rinsed with methanol. About 300 μ L of clear, hot solution was applied to the surface of the ATR crystal using an Eppendorf pipet. The crystal was kept at room temperature for at least 2 h, ensuring evaporation of most of the solvent. Subsequently, the polymer coating was exposed to hot air treatment with a hot air gun at 150 °C for 5 min to remove remaining traces of solvent. The thickness of the layer was determined by differential weighing to be 4.2 μ m.

For sensing applications of trace components it is essential to coat the transducer surface with (chemo)selective membranes excluding interfering matrix components overlapping or masking absorption features of the investigated analyte. This is of particular importance when measuring in strongly IR-absorbing matrixes such as water. In the present study, a thin layer of hydrophobic ethylene/propylene copolymer is coated onto the waveguide surface. While hydrophobic analytes partition into the hydrophobic membrane, water and other polar components are widely excluded from the analytical volume probed by the evanescent field. Additionally, the polymer coating enhances the sensitivity of the sensor by enriching hydrophobic analytes in the polymer membrane following the principles of solid-phase extraction. One approach to roughly estimate the enrichment factor for a particular analyte is to relate obtained absorption peak heights from measurements with uncoated waveguides to results achieved with polymer-coated transducers. However, limited solubility of BTX in water and strong absorptions of the water matrix in the fingerprint region of the MIR spectral range prohibit direct ATR measurements with uncoated crystals. Hence, analyte solutions with a concentration of 1% in methanol have been prepared for an estimation of the achievable enrichment factors. ATR spectra of methanolic solutions have been recorded with uncoated ZnSe crystals. Peak heights for each analyte have been normalized and correlated to peak heights obtained for an enrichment measure-

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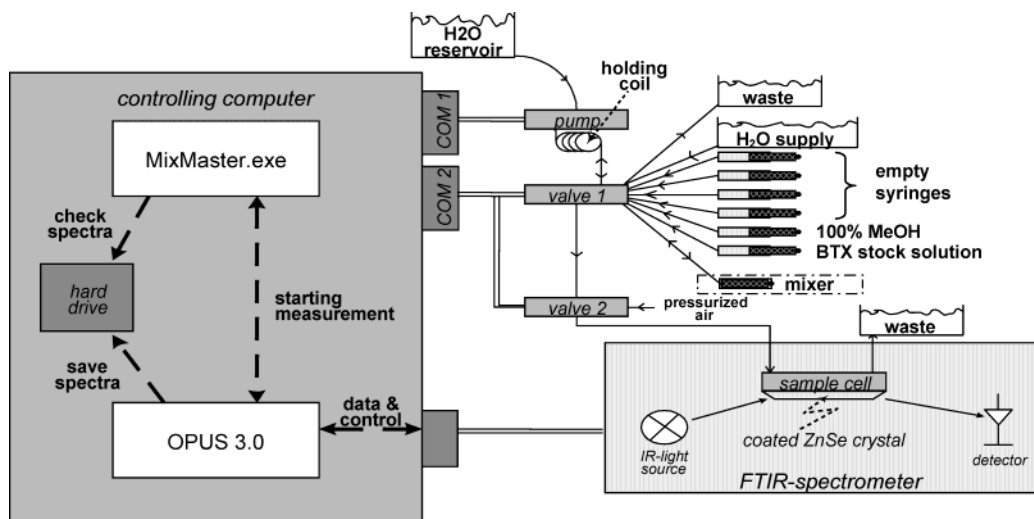


Figure 1. Experimental setup.

ment of a 500 ppb (v/v) aqueous analyte solution with an E/P-co-coated ZnSe crystal after the partition equilibrium has been established. Following this approach, enrichment factors of >15,000 are estimated for benzene, toluene, and the xylene isomers, respectively.

Based on previous experience, ethylene/propylene copolymer proved to be a suitable material for enrichment of a wide range of hydrophobic compounds from aqueous solutions.^{39,40}

Instrumentation. Setup. Data were recorded in a spectral range of 600–1400 cm^{-1} using a Bruker Vector 22 Fourier transform infrared (FT-IR) spectrometer (Bruker Optik GmbH, Ettlingen, Germany) equipped with a liquid N_2 cooled mercury–cadmium–telluride detector (Infrared Associates, Stuart, FL). A total of 100 scans were averaged for each spectrum with a spectral resolution of 4 cm^{-1} . For ATR measurements, a vertical ATR accessory (Specac, Smyrna, GA) in combination with trapezoidal ZnSe ATR elements ($50 \times 20 \times 2$ mm, 45° ; Macrooptica Ltd., Moscow, Russia) and a stainless steel flow cell (custom-made, volume 280 μL , free contact area to ATR crystal 5.5 cm^2) were used. A custom-made mixing system (MixMaster)⁴¹ designed for handling volatile organic compounds assured accurate concentrations of sample mixtures and continuous flow of the analyte solutions through the ATR cell. A schematic of the experimental setup is shown in Figure 1.

Sample Preparation with MixMaster. To ensure a precise set of diluted standard solutions, a software-controlled automated mixing system (MixMaster) designed by our research group was applied.⁴¹ The main components comprise a high-precision piston pump (syringe volume 25 000 μL), which is attached to a selection valve with 10 ports and a two-way injection valve connected to the ATR flow cell. A C++ software interface allows controlling all parameters of the system including piston position, pump speed, and positions of the valves. Furthermore, measurements of the FT-IR spectrometer are triggered and synchronized by the

MixMaster control software. Stainless steel tubings connected via bulkhead unions are exclusively used, minimizing wall adsorption effects. By avoiding the use of polymer components within the MixMaster system and by providing headspace-free storage and mixing of solutions, MixMaster is especially suitable for high-throughput investigations of volatile organic compounds, e.g., during extensive sensor optimization and calibration. A detailed description of the mixing system is given elsewhere.⁴¹

A typical measurement cycle for sensor calibration comprises the following steps: (i) rinsing of the cell with water; (ii) collecting a background spectrum; (iii) preparing the analyte solution; (iv) up to 20-min rinsing of the flow cell with analyte solution while collecting absorption spectra every 2 min; (v) 25-min rinsing of the cell with deionized water to extract the analyte and regenerate the polymer layer.

The sample solution flow rate was held constant at 3 mL/min throughout all experiments. Methanol was used as a solution mediator, ensuring that the BTX mixture remains dissolved in aqueous solution. Previous works have shown that this procedure has no effect on the final sensor readings.³⁵ Dilutions were prepared from one primary stock solution with a concentration of 200 ppm (v/v) containing all compounds of the BTX group in pure methanol. Thorough mixing resulted in a total methanol concentration of 0.5% (v/v) in the investigated sample solutions. No significant interferences due to the measurement of analyte mixtures are expected within the investigated concentration range, as shown by previous studies of our research group.³¹

RESULTS

Water Equilibration. Despite the hydrophobic properties of the membrane, a considerable amount of water diffuses into the polymer coating over a period of several hours causing IR background absorptions as shown in Figure 2. A broad absorption band, caused by swelling of the polymer during the water diffusion process, occurring between 1000 cm^{-1} and the cutoff frequency of the detector around 600 cm^{-1} , significantly influences spectroscopic measurement due to the resulting baseline drift. In a simple sample matrix, this effect can be compensated by selecting suitable peak integration methods and integration limits. However, a stable baseline increases the reliability of the measurements and enables

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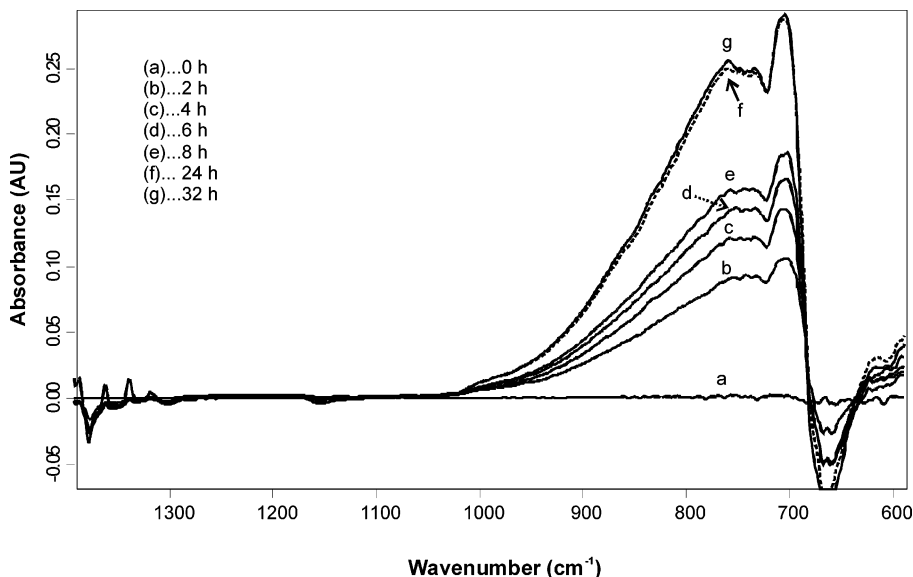


Figure 2. IR absorptions resulting from water diffusion into an E/P-co membrane with a thickness of $4.2\ \mu\text{m}$ coated onto the surface of a ZnSe ATR crystal over a period of 32 h. After 24 h (f), equilibrium conditions are reached and no further increase of water absorption features is observed.

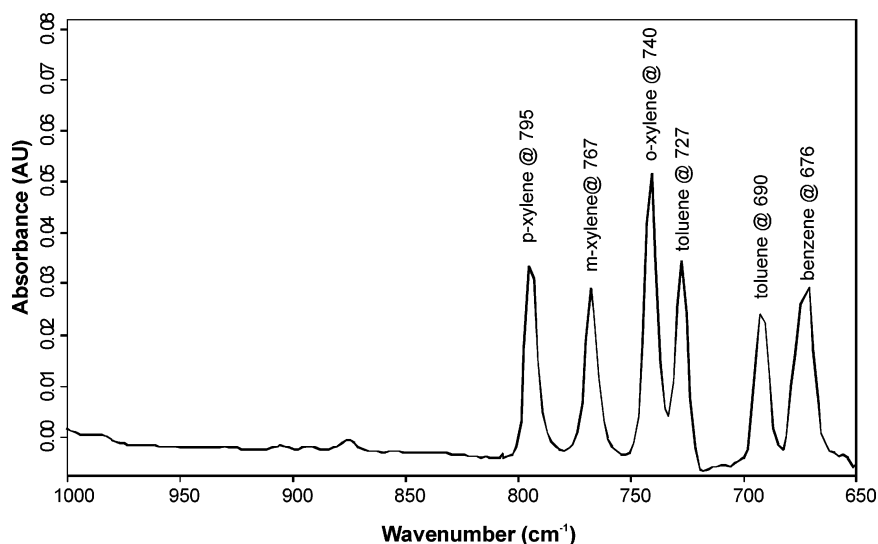


Figure 3. IR absorption spectrum of a BTX sample mixture in aqueous solution after enrichment into an E/P-co layer. Enrichment time, 20 min; concentration, 500 ppb (v/v) each.

automated data evaluation, as shown in a recent study by our research group.⁴² Figure 2 illustrates that water diffusion reaches equilibrium conditions before 24 h of exposure to the aqueous phase. Hence, prior to analysis, the coated waveguide has been equilibrated with deionized water for a period of at least 24 h.

BTX Enrichment Characteristics. Figure 3 shows an exemplary spectrum of a mixture of benzene, toluene, and the three xylene isomers with a concentration of 500 ppb (v/v) each after an enrichment time of 20 min into an E/P-co layer. Corresponding absorption peaks have been labeled for clarity. Typical absorption bands of benzene, toluene, and the three xylene isomers can be identified resulting from molecule-specific aromatic C–H out of plane vibrations in the fingerprint region of the mid-infrared spectrum. Band assignment has been performed via single-component enrichment experiments leading to the following

allocation of the absorption features: benzene at $676\ \text{cm}^{-1}$, toluene at 690 and $727\ \text{cm}^{-1}$, *o*-xylene at $740\ \text{cm}^{-1}$, *m*-xylene at $767\ \text{cm}^{-1}$, and *p*-xylene at $795\ \text{cm}^{-1}$. Each analyte shows distinctive absorption features, which are not or only slightly overlapping. Hence, during this first study, conventional peak integration of the IR absorption bands was applied. More complex samples will be evaluated using chemometric data evaluation techniques particularly suitable for optical sensors.⁴³

As has been recently shown by Phillips et al.,⁴⁴ achieving steady-state conditions for polymer-coated sensor systems is not only dependent on the partitioning behavior of analytes into the polymer layer. Factors such as analyte diffusion properties within the aqueous phase, flow channel height, and flow velocity

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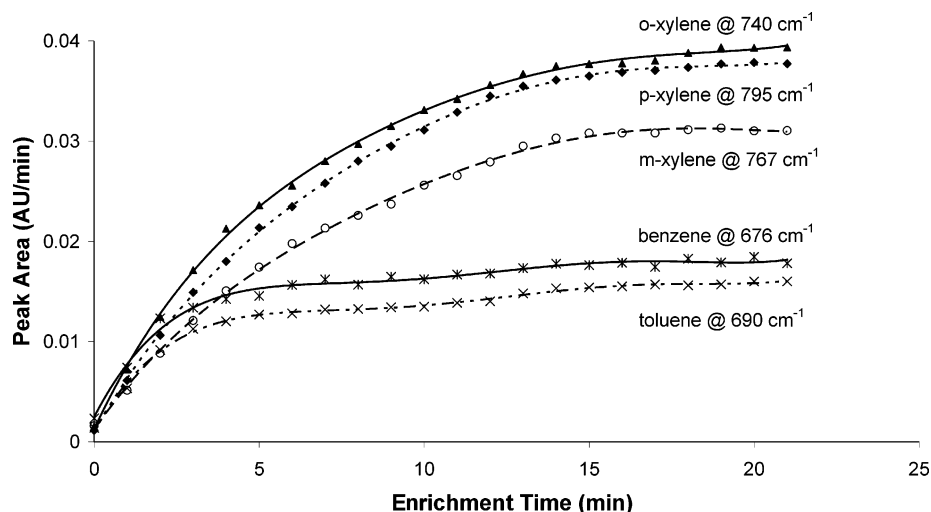


Figure 4. Typical enrichment curves for the BTX components in water at a concentration level of 1 ppm (v/v) each into an E/P-co coating. Equilibrium of the diffusion process is reached after ~18 min of enrichment time.

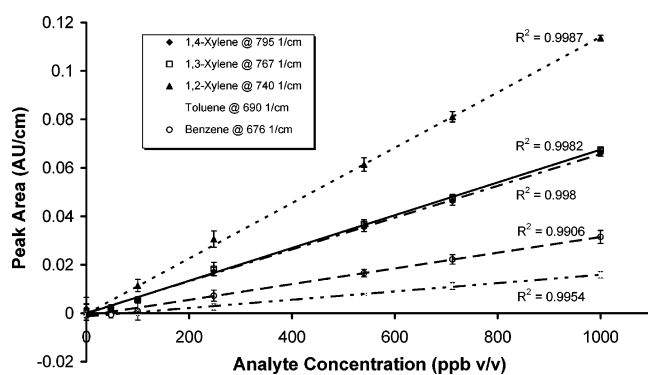


Figure 5. Calibration graphs for benzene, toluene, and the xylene isomers in the concentration range of 0–1000 ppb (v/v) based on peak area integration. The error bars represent the standard deviation of five consecutive measurements.

substantially affect the response of the chemical sensor. The only tunable parameter of the ATR flow cell used throughout the present study was the flow velocity. Evaluating preliminary experiments, the flow velocity of the analyte solution was set to 3 mL/min, which enabled measurements in the time regime of several minutes without using excessive amounts of analyte solution.

Figure 4 shows typical diffusion curves of the investigated analytes plotting the integrated peak area versus the enrichment

time. After 18 min of enrichment, the diffusion process reaches equilibrium conditions for the given analyte mixture and data evaluated at this interval or thereafter delivers reliable results.

Figure 5 shows the obtained calibration graphs for the investigated analytes in aqueous solution. Calibration of the sensor was performed by five repetitive measurements of a concentration series ranging from 50 ppb (v/v) to 1 ppm (v/v) for each analyte in the mixture. Error bars for each data point represent the calculated standard deviation derived from five repetitive measurements each. Prior to each measurement, the polymer coating was regenerated by rinsing the flow cell with water at a flow velocity of 3 mL/min for 25 min, which efficiently removed all analytes from the sensing membrane.

Data evaluation has been performed by peak area integration due to clear separation of the investigated absorption peaks. The integrated areas are plotted versus the concentration resulting in linear fit functions with R^2 values generally >0.99 included in Figure 5. Detection limits for each analyte in the mixture have been calculated according to IUPAC by the 3σ criteria (3 times standard deviation of the peak-to-peak noise related to the slope of the linear regression function) and resulted in LODs in the low-ppb range in the mixture for all examined analytes. These values represent a significant improvement compared to previously

Table 1. Overview on the Most Common Spectroscopic Measurement Approaches for BTX Determination in Water

method	FT-IR-ATR	FT-IR-ATR ³⁸	FT-IR-transmn ¹⁶	UV-transmn ¹⁹	UV derivative spectroscopy ²¹	photo-acoustic ⁴⁸	SPME-NIR ³⁶
SPME matrix	EP/Co	PIB	Parafilm	PDMS	none	none	PDMS
simultaneous detection	yes	no ^a	no ^a	no ^a	yes	no ^a	no ^a
time/ measurement ^b (min)	20	20	> 30	90	1	40	20
benzene LOD; ppb (v/v)	45		160	18	±50	308	
toluene LOD; ppb (v/v)	80	292	652	5	±50	954	173
o-xylene LOD; ppb (v/v)	10		72	4	±50		
m-xylene LOD; ppb (v/v)	20		886		±50		
p-xylene LOD; ppb (v/v)	20		57	3	±50		129

^a The authors wish to emphasize that this statement does not imply that simultaneous detection of analytes is generally impossible with the methods listed in Table 1. However, in the cited reference data utilized for the determination of LODs is derived from single-analyte experiments only. ^b This period only refers to the actual measurement and does not account for other steps such as sensor equilibration, calibration, data evaluation, etc.

reported results using headspace ATR-IR measurements for similar analytes with significantly higher limits of detection.^{37,38} The LODs from this work and other relevant spectroscopic approaches to BTX determination in aqueous solution are summarized in Table 1.

With respect to the achieved LODs and the time needed per measurement, the sensor system presented in this study shows competitive or superior performance to all other relevant spectroscopic approaches reported for BTX analysis. Furthermore, 20 min/measurement cycle for quantitative simultaneous determination of five components is a reasonable time frame for a wide variety of analytical applications including wastewater or effluent monitoring, remediation process surveillance, or drinking water monitoring contingent upon improved sensitivity of the proposed sensing technology. With the introduction of appropriate chemometric data evaluation techniques, remote analysis will be further facilitated.^{45–47} As proof of feasibility for on-line wastewater monitoring, a sensor system similar to the device discussed in this study has successfully been applied to the measurement of *o*-xylene in urban pond water (see Supporting Information, Figure S-1).

CONCLUSION

A chemical sensor technology for simultaneous and direct detection of BTX in aqueous solution based on polymer-coated mid-infrared evanescent wave sensing is presented. The investigated sensor characteristics include the enrichment time, sensitivity, and reproducibility. Linear relationships between characteristic absorption peak areas versus input concentrations with R^2 values

of >0.99 could be obtained for each analyte along with high reproducibility demonstrated for five consecutive measurements. With the presented measurement setup, equilibrium conditions for this diffusion-based sensor were achieved within ~ 18 min, which is comparable to other membrane-based chemical sensor systems. Sensitivity in the low-ppb (v/v) concentration range for all BTX compounds and simultaneous quantitative detection in mixtures represent a significant improvement compared to any ATR-IR sensor reported to date for this class of analytes. At the present stage of development, the sensor system is already suitable serving as an analytical method for on-line, in situ process monitoring of multiple organic components at low-ppb concentration levels. Further optimization of the presented method includes aspects such as flow cell design for minimized response time and advanced chemometric data evaluation enabling remote unattended operation. Hence, multicomponent measurements with FTIR-ATR techniques in the low-ppb and even sub-ppb concentration range are foreseeable soon.

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SUPPORTING INFORMATION AVAILABLE

Additional Information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information for Manuscript:

Simultaneous Quantitative Determination of Benzene, Toluene and Xylenes in Water Using Mid-Infrared Evanescent Field Spectroscopy

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Abstract

This supplementary information section contains continuous measurement series of various concentrations of o-xylene added to urban pond water utilizing a sensor system based on attenuated total reflection mid-infrared (ATR-IR) spectroscopy. The analyte is enriched into a thin polymer membrane coated onto the surface of an internal total reflection waveguide, which is exposed to the aqueous sample. Direct detection of analytes permeating into the polymer coating is performed utilizing evanescent field spectroscopy in the fingerprint region ($> 10\ \mu\text{m}$) of the mid-infrared (MIR) spectrum ($3\text{--}20\ \mu\text{m}$) without additional sample preparation. Data evaluation was performed by integration of the characteristic absorption peak of o-xylene at $740\ \text{cm}^{-1}$. The presented data clearly demonstrates the potential of polymer coated evanescent field sensors for real-world applications in water quality monitoring.

Continuous Detection of o-Xylene in a Natural Matrix (Pondwater)

Materials

Ethylene/propylene co-polymer (60:40) was purchased from Aldrich (Milwaukee, WI). Methanol, o-xylene, were purchased from Aldrich (Milwaukee, WI) and were of analytical grade.

Pond water was used for preparation of all solutions and for sensor regeneration. The pond water was sampled from a domestic goldfish-pond in Atlanta, GA, USA.

Preparation of Ethylene/Propylene Co-polymer Thin Film

The coating procedure adheres to the description in the main manuscript with following modification: 210 μL of the hot coating solution were applied resulting in a film thickness of approx. 3.3 μm determined via differential weighing.

Preparation of the o-Xylene Samples

A 1 % (v/v) solution of o-xylene in methanol was prepared and diluted with pond water to 20, 50, and 80 ppm (v/v) of analyte concentration. Additional methanol was added to keep the amount of methanol constant at 1 % (v/v). The sample solutions have been freshly prepared prior to each measurement ensuring minimal losses due to evaporation.

Instrumentation

Data was recorded in the spectral range of 400 cm^{-1} to 1600 cm^{-1} using a Bruker Equinox 55 Fourier transform infrared (FT-IR) spectrometer (Bruker Optics, Billerica, MA) equipped with a liquid N_2 cooled mercury-cadmium-telluride (MCT) detector (Infrared Associates, Stuart, FL). A total of 100 scans were averaged for each spectrum with a spectral resolution of 4 cm^{-1} . For this continuous study spectra were recorded every minute for a period of approx. 8 hours. For ATR measurements a horizontal ATR accessory (Specac, Smyrna, GA) utilizing trapezoidal ZnSe ATR elements ($72 \times 10 \times 6\text{ mm}$, 45° ; Macrooptica Ltd., Moscow, Russia) and a stainless steel flow-cell (custom made, Volume: 2 ml, free contact area to ATR crystal: 7.2 cm^2) were used. Solutions were pulled through the flow-cell via an Alitea C8-Midi peristaltic pump (Watson-Marlow Alitea, Wilmington, MA) at a constant flow rate of 4.5 mL/min.

Results

After equilibration with water as described in the main manuscript the sensor was exposed to neat pond water samples for several hours. No significant further changes of the absorption spectra could be observed. Following, the sensor was exposed to pond water samples spiked with o-xylene and an increasing absorption feature at 740 cm^{-1} (aromatic C–H out of plane vibration of o-xylene) could be observed after a measurement time of one minute already.

Figure S-1 shows the continuous measurement of o-xylene in pond water over a period of 8 hours for a repetitive concentration trace of 3 different levels (50, 80, and 20 ppm v/v). Concentrations have been changed every 30 to 35 minutes. The trace at 740 cm^{-1} clearly shows that o-xylene partitioning never reaches equilibrium conditions for the selected observation window. However, it is evident that the response time of the sensor to changing concentrations of the sample solution is $< 1\text{ min}$, which is an essential aspect for rapid on-line data evaluation and e.g. threshold monitoring. Appropriate multivariate data evaluation techniques, which should enable prediction of the equilibration concentration of analytes for a calibrated system after very short enrichment times are currently developed in our research group.

Slightly increasing peak area values from one repetition to the next along with a minute positive off-set after regenerating the sensor with neat pond water (see minute 300 to 420) indicate that the broad water absorption band in the spectral region between 1000 cm^{-1} and the cut-off frequency of the detector (around 600 cm^{-1}) was still slightly increasing throughout the measurement. Recently, our research group has developed a multivariate method for automated recognition and correction of baseline drifts (Ref. 42 and 47 in the main manuscript). As most chemical sensing systems are affected by baseline drifts due to ageing, degradation, and swelling of the molecular recognition interface, this generic solution enables the application of membrane based sensing devices in real-world environments.

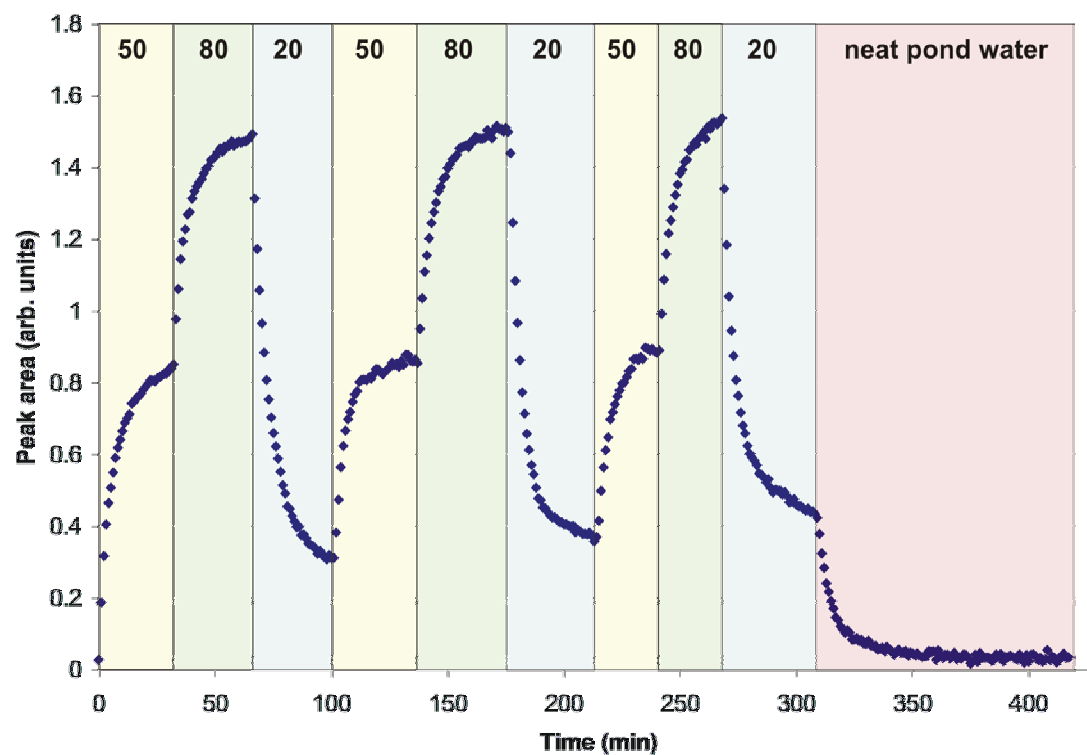


Figure S-1: Trace of the peak area of the absorption band of o-xylene at 740 cm^{-1} with time during enrichment-based IR-ATR sensing. Concentration trace: 50 ppm; 80 ppm; 20 ppm (in pond water; the sensor was exposed to each concentration for approx. 30 to 35 min) followed by neat pond water for sensor regeneration.