Analytical Methods

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IR-ATR Chemical Sensors Based on Planar Silver Halide Waveguides Coated with an Ethylene/Propylene Copolymer for Detection of Multiple Organic Contaminants in Water[**]

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Infrared (IR) spectroscopy is among the most powerful analytical techniques available today.[1] IR spectra may be segmented into the near-, far-, and mid-infrared spectral regime, among which the mid-infrared region is the most widely used for molecular spectroscopy. Transmission–absorption spectroscopy is the most straightforward IR method for analyzing solid- and gas-phase samples.[2] However, direct measurement of liquid-phase samples by using conventional Fourier-transform infrared (FTIR) spectroscopy in the transmission mode is frequently limited by strong background absorptions of the matrix and usually requires thin-film transmission cells.[3]

In this context, attenuated total reflectance (ATR) spectroscopy, which is based on the principles of internal total reflection,[4] offers a useful alternative.[5] Conventional IR-ATR spectroscopy has been widely used for the analysis of liquid samples or solid/liquid interfaces.[3] Among other parameters, the detection performance and achievable sensitivity of IR-ATR measurements is largely determined by the properties of the ATR waveguide. Today, a wide variety of commercial ATR crystals is available made from for example, zinc selenide (ZnSe), germanium, thallium bromoiodide (KRS-5), or silicon.[6] However, they are limited in achievable sensitivity and/or spectral window. Alternatively, IR transparent optical fibers, especially silver halide fibers,[7] have emerged as a potential replacement of conventional IR-ATR waveguides. Their advantages include comparatively low material costs,[8] along with a flexible and tailorable waveguide geometry, which facilitates a significantly enhanced measurement sensitivity.

Silver halide fibers provide access to the entire mid-IR spectral range of interest (3–18 μm).[7] A variety of silver halide fibers with different geometries have been reported for sensing applications including cylindrical fibers,[9] planar fibers,[10] and planar fibers with cylindrical extensions at both ends.[11] Despite their inherent advantages, the achievable sensitivity of chemical sensors based on such fibers is usually limited to ppm levels in aqueous solution;[9g] this limitation has in turn limited their applicability. An approach to increase the sensitivity has been demonstrated by using quantum cascade lasers instead of conventional FTIR spectrometers.[10a] Alternatively, the surface of the waveguide may be coated with a polymer membrane for enhanced extraction, enrichment, or recognition of molecular constituents,[7] as shown for chemically modified ATR crystals[12] with significantly improved sensitivity.[13] However, to date advantage has not been taken of planar silver halide fibers serving as active transducer combined with molecular enrichment membranes for establishing highly miniaturized IR-ATR chemical sensors, which at the same time enable discrimination of several molecular constituents within a single measurement.

In this study, we explore the feasibility of using polymer-coated planar silver halide sensing elements for enhancing the sensitivity for the determination of aromatic hydrocarbons in aqueous solution. To this end, ethylene/propylene copolymer (E/P-co), a polymer capable of enriching multiple constituents, was coated onto the surface of planar fiberoptic sensing elements with cylindrical extensions facilitating optical coupling at both ends. This configuration has been demonstrated to enable up to 13-times larger absorbance compared to conventional cylindrical fiber sensing elements.[11] Several monocyclic aromatic hydrocarbons (MAHs), including benzene, toluene, *p*-xylene, *m*-xylene, and *o*-xylene, were simultaneously quantified at trace levels.

The silver halide ($AgCl_xBr_{1-x}$) fibers used in this study were flattened by using a press tapering procedure (Figure 1a). The general principle of mid-infrared fiber evanescent wave spectroscopy is illustrated in Figure 1b.

To validate the feasibility of using coated fiber segments for IR-ATR sensing of relevant environmental contaminants, benzene, toluene, *p*-xylene, *m*-xylene, and *o*-xylene were detected in mixture at different concentration ranges. First,

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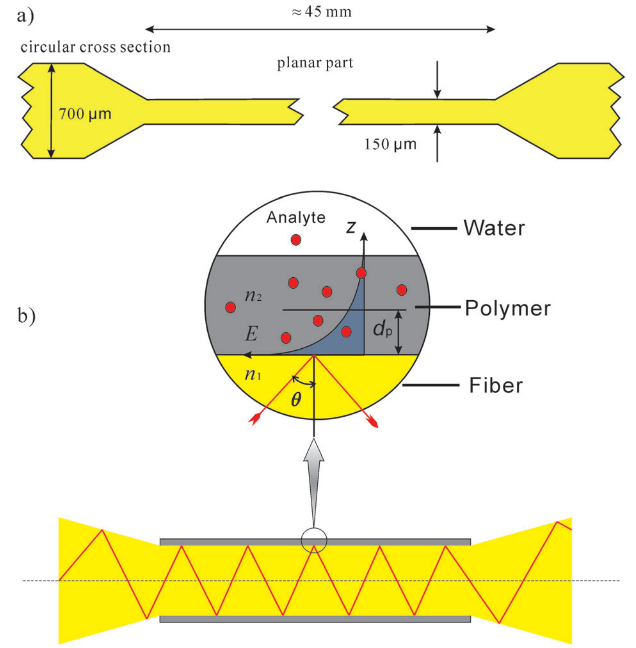

Figure 1. a) Schematic of fiber sensor cross-section. b) Principles of ATR sensing (n_1: refractive index of the fiber; n_2: refractive index of the polymer; E: evanescent field; d_p: penetration depth; θ: angle of incidence).

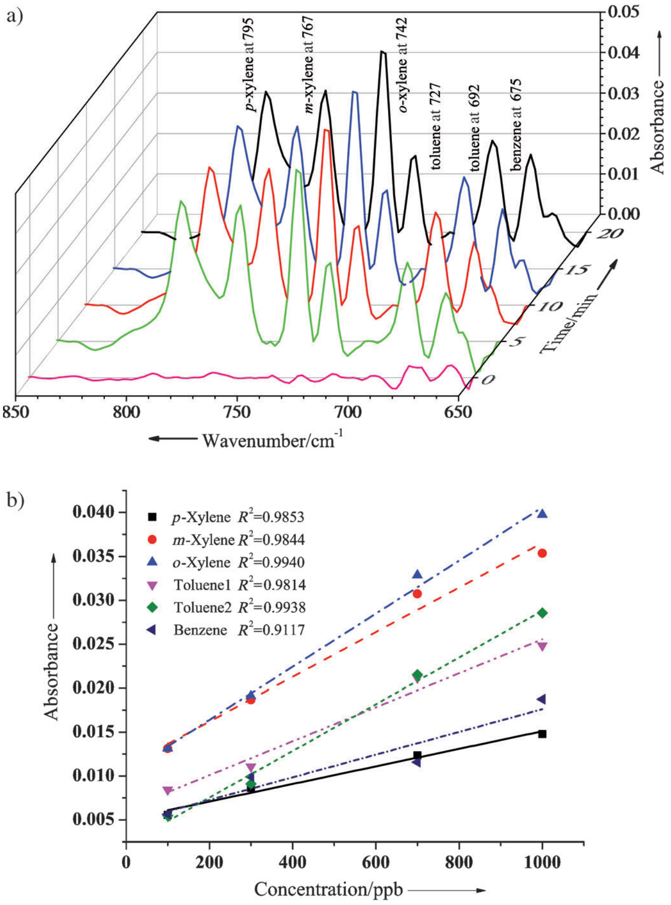

Figure 2. a) IR absorption spectra of 300 ppb MAHs in aqueous solution after enrichment for 0, 5, 10, 15, and 20 min, respectively. Only the relevant peaks are labeled for clarity. b) Calibration based on the IR absorbance of benzene, toluene, *p*-xylene, *m*-xylene, and *o*-xylene in the concentration range of 100 to 1000 ppb (v/v). (Toluene1: evaluation of the IR absorbance at 727 cm^{-1}; Toluene2: evaluation of the IR absorbance at 692 cm^{-1})

a higher concentration range of 100–1000 ppb (v/v) for the mixture was investigated. The absorbance changes during 20 min are shown in Figure 2 a. It is apparent that the MAH mixture was efficiently extracted into the E/P-co film, and that the absorbance values have substantially increased within the first 5 min of measurement time. Thereafter, no further variation of the absorbance values was observed, thus suggesting that the partition equilibrium was already achieved. Nevertheless, an enrichment time of 20 min was selected herein consistent with previous studies.[13] Based on the fingerprint of the mid-infrared spectra, the typical absorption bands of these MAHs were readily identified. The corresponding absorption features are for *p*-xylene at 795 cm^{-1}, *m*-xylene at 767 cm^{-1}, *o*-xylene at 742 cm^{-1}, toluene at 727 and 692 cm^{-1}, and benzene at 675 cm^{-1}. Despite some spectral overlap, these distinctive absorption features enabled direct quantification without using multivariate statistics.

Accordingly calibration functions of the investigated analytes in solution were established (Figure 2 b). The concentration range was from 100 ppb (v/v) to 1000 ppb (v/v) for each analyte. Two peaks of toluene were evaluated at 727 and 692 cm^{-1}. The R^2 value of the calibration function for benzene was slightly lower than those of other analytes, possibly because the 675 cm^{-1} peak was near the cut-off wavelength (650 cm^{-1}) of the used mercury–cadmium–telluride (MCT) detector. Baseline variations resulting from minute background absorbances (as evident at 0 min in Figure 2 a) explain why the obtained calibration functions do not necessarily cross the zero coordinate point (Figure 2 b).

The IR spectra of MAH mixtures at lower concentrations (10–100 ppb (v/v)) were also studied. An exemplary spectrum and the corresponding calibration functions are shown in Figure 3. The spectrum of the analytes at 10 ppb was obtained after baseline correction. Two new peaks were observed at 779 and 690 cm^{-1} (Figure 3 a), which were ascribed to *m*-xylene. These two peaks were not observed at high concentrations owing to spectral overlap with the broad absorption band of *p*-xylene (at 795 cm^{-1}) and of toluene (at 692 cm^{-1}). Compared to the spectra at high concentrations, the peak of *o*-xylene shifted from 742 to 740 cm^{-1}, of toluene from 692 to 690 cm^{-1}, and of benzene from 675 to 676 cm^{-1}.

To quantify the analytes, the peaks at 795, 767, 740, and 727 cm^{-1} were selected for *p*-xylene, *m*-xylene, *o*-xylene, and toluene, respectively. The calibration functions are shown in Figure 3 b). The high values of R^2 for the obtained calibrations indicate that such miniaturized coated fiber segments could be used for the detection of trace contaminants with high reliability. The calibration function of benzene is not shown here owing to a significantly lower R^2 value resulting from the indicative absorption feature close to the cut-off of the used MCT detector.

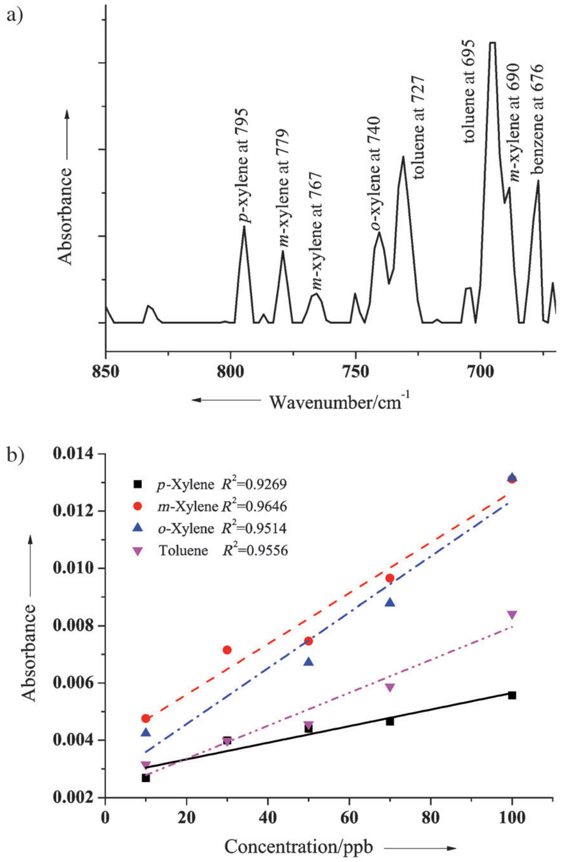

Figure 3. a) IR absorption spectrum (after baseline correction) of a 10 ppb (v/v) MAH aqueous solution after 20 min of enrichment. The relevant peaks are labeled for clarity. b) Calibration of toluene, *p*-xylene, *m*-xylene, and *o*-xylene in the concentration range of 10 to 100 ppb (v/v).

In addition, the limits of detection (LODs, calculated according to IUPAC using the 3σ criteria)[13] of the analytes were calculated as: *p*-xylene, 5 ppb; *m*-xylene, 2 ppb; *o*-xylene, 6 ppb; toluene, 3 ppb; and benzene, 4 ppb (Figure 3 b). Compared to a previous study,[8] the LODs of these MAHs obtained with the IR-ATR sensing system herein were substantially decreased by at least one order of magnitude. Most importantly, the obtained LODs are all below the allowed concentrations in drinking water, as regulated by the US Environmental Protection Agency.[14] Therefore, the developed chemical IR-ATR sensor reveals the required detection sensitivity for environmentally relevant drinking water quality monitoring implementations.

The improvement in detection sensitivity was mainly attributed to the use of planarized fiber segments combined with E/P-co thin-film coatings serving as in situ extraction membrane. Firstly, the geometry of the planar fiber facilitated 424 internal reflections; thus, the analytical signal could be significantly enhanced.[11] In comparison, a cylindrical fiber sensing element without planar segment provides for 91 internal reflections, while commercial trapezoidal ZnSe ATR elements provide a maximum of 16 internal reflections.[12] Secondly, the thickness of the E/P-co film deposited on the planar segment of the fiber surface was tailored to a thickness of approximately 7.6 μm, which ideally matches the information depth of the evanescent field. While hydrophobic MAHs are readily enriched into the polymer, water is effectively excluded from the evanescent field. As a result, the background (matrix) absorbance of water could be drastically decreased. In addition, the waveguide is protected from corrosive components contained in the sample matrix, thereby ensuring an extended lifetime of the sensor during continuous application.

In summary, a planar IR-ATR fiberoptic sensor coated with E/P-co was developed for simultaneous in situ detection of multiple relevant MAHs in aqueous solution. This sensing system exhibited an exceptionally high sensitivity and selectivity, excellent reliability, and a large dynamic detection range compared to conventional IR sensing systems. Particularly, the LODs of environmentally and health-relevant MAHs were decreased by at least one order of magnitude compared to currently available ATR systems. Therefore, at the present stage of development the sensing system herein may readily be used for in situ and parallel monitoring of multiple relevant (drinking) water contaminants at low ppb levels, thus holding substantial promise for practical detection applications.

Experimental Section

Methanol, *n*-hexane, benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene were of analytical grade. Deionized water and a small amount of methanol (1%, v/v) as solubility mediator were used for preparation of various solutions to entirely dissolve the aromatic constituents at higher concentrations. According to a previous study, methanol at such low levels does not affect the spectral characteristics.[15]

Planar silver halide fiber segments were fabricated to produce waveguides with a possibly high number of internal reflections. The dimensions of the planar segment of the fiber were: length: 45 mm, thickness: 150 μm, width: 4 mm. This geometry was established by press-tapering a 700 μm diameter cylindrical fiber at the central segment, thereby providing remaining cylindrical coupling waveguides of approx. 15 mm length at both ends of the planarized segment.

E/P-co (60:40) was purchased from Aldrich (Milwaukee, USA). A sample of 1% (w/v) E/P-co was prepared by dissolving granular polymer (0.5 g) under reflux in *n*-hexane (50 mL) and was used as the coating solution. About 80 μL of clear, hot solution was dip-coated onto both surfaces of the planar silver halide fiber segment by using an Eppendorf pipette. The waveguide was kept at room temperature for at least 2 h to ensure full evaporation of the solvent. After optimization, the thickness of the coating layer was reproducibly 7.6 μm, which was determined by differential weighing.

The FTIR measurements were performed by focusing the external collimated IR beam from a Bruker Vertex 70 spectrometer (Bruker Optics Inc, Germany) onto the end facet of a fiber by using a gold-coated off-axis parabolic mirror (OAPM, focal length: 25.4 mm; Janos Optics Co, USA). Light from the distal end of the fiber was focused onto a liquid-N_2-cooled mercury–cadmium–telluride detector (Infrared Associates, USA) using a set of two OAPMs. The IR data were recorded within a spectral range of 1000 to 650 cm^{-1}. For each spectrum, a total of 100 scans were averaged at a spectral resolution of 4 cm^{-1}.

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[1] B. H. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, Wiley, Hoboken, **2005**, pp. 1–13.
[2] B. H. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, Wiley, Hoboken, **2005**, pp. 15–44.
[3] J.-M. Andanson, A. Baiker, *Chem. Soc. Rev.* **2010**, *39*, 4571–4584.
[4] N. J. Harrick, *Phys. Rev. Lett.* **1960**, *4*, 224–226.
[5] J. Fahrenfort, *Spectrochim. Acta* **1961**, *17*, 698–709.
[6] B. Mizaikoff, *Meas. Sci. Technol.* **1999**, *10*, 1185–1194.
[7] B. Mizaikoff, *Anal. Chem.* **2003**, *75*, 258A–267A.
[8] E. M. K. S. Simhony, A. Katzir, *Appl. Phys. Lett.* **1986**, *49*, 253–254.
[9] a) B. Mizaikoff, R. Gobel, R. Krska, K. Taga, R. Kellner, M. Tacke, A. Katzir, *Sens. Actuators B* **1995**, *29*, 58–63; b) B. Mizaikoff, K. Taga, R. Kellner, *Vib. Spectrosc.* **1995**, *8*, 103–108; c) J. E. Walsh, B. D. MacCraith, M. Meaney, J. G. Vos, F. Regan, A. Lancia, S. Artjushenko, *Analyst* **1996**, *121*, 789–792; d) M. Jakusch, B. Mizaikoff, R. Kellner, *Sens. Actuators B* **1997**, *38*, 83–87; e) H. Steiner, M. Jakusch, M. Kraft, M. Karlowatz, T. Baumann, R. Niessner, W. Konz, A. Brandenburg, K. Michel, C. Boussard-Pledel, B. Bureau, J. Lucas, Y. Reichlin, A. Katzir, N. Fleischmann, K. Staubmann, R. Allabashi, J. M. Bayona, B. Mizaikoff, *Appl. Spectrosc.* **2003**, *57*, 607–613; f) Y. Luzinova, B. Zdyrko, I. Luzinov, B. Mizaikoff, *Anal. Chem.* **2012**, *84*, 1274–1280; g) Y. Luzinova, B. Zdyrko, I. Luzinov, B. Mizaikoff, *Analyst* **2012**, *137*, 333–341.
[10] a) C. Charlton, A. Katzir, B. Mizaikoff, *Anal. Chem.* **2005**, *77*, 4398–4403; b) J. Chen, Z. Liu, C. Gmachl, D. Sivco, *Opt. Express* **2005**, *13*, 5953–5960.
[11] E. M. Kosower, G. Markovich, Y. Raichlin, G. Borz, A. Katzir, *J. Phys. Chem. B* **2004**, *108*, 12633–12636.
[12] G. Roy, J. A. Mielczarski, *Water Res.* **2002**, *36*, 1902–1908.
[13] M. Karlowatz, M. Kraft, B. Mizaikoff, *Anal. Chem.* **2004**, *76*, 2643–2648.
[14] N. M. García, L. M. L. Nollet in *Chromatographic analysis of the environment*, *Vol. 14* (Eds.: L. M. L. Nollet), CRC, Boca Raton, **2005**, pp. 513–544.
[15] M. Kraft, B. Mizaikoff, *Int. J. Environ. Anal. Chem.* **2000**, *78*, 367–383.