

Photonic crystal slot waveguide for high sensitivity on-chip near-infrared optical absorption spectroscopy of xylene in water

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ABSTRACT

We experimentally demonstrate a 300 μ m long silicon photonic crystal slot waveguide for on-chip near-infrared absorption spectroscopy. Based on the Beer-Lambert absorption law, our device combines slow light in photonic crystal waveguide with high electric field intensity in low-index 75nm wide slot, which effectively increases the optical absorption path length of the analyte. We demonstrate near-infrared absorption spectroscopy of xylene in water, independent of near-infrared absorption signatures of water, with a hydrophobic PDMS sensing phase that extracts xylene from water. Xylene concentrations up to 100ppb (parts per billion) (86 μ g/L) in water were measured.

Keywords: photonic crystal slot waveguide, on-chip absorption spectroscopy, near-infrared integrated spectrometer, xylene sensor in water.

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1. INTRODUCTION

Pollution of water resources in the United States and the world can have serious and wide-ranging effects on the environment and human health. A significant contamination activity relates to production, storage and transportation of petroleum derivatives, such as gasoline and diesel fuel and organic solvents, as spills and leaks of these liquids through pipeline ruptures can contaminate soils, superficial water and groundwater. Aromatic hydrocarbons in petroleum have attracted considerable attention due to their toxicity. Efforts have been focused on the determination of benzene (B), toluene (T), ethylbenzene (E), and the xylenes (X), a class of aromatic compounds known as BTEX [1, 2]. The threat posed by global terrorism should also be underlined. Due to enormous significance of keeping drinking water clean and free from intentional and unintentional contamination, an elaborate in-situ and highly sensitive sensing technology with remote monitoring capacity is an absolute necessity. Commercial infrared spectrometers are large, heavy and expensive. A lab-on-chip infrared absorption spectrometer is thus highly desirable for portable and distributed sensing applications.

In recent years, integration of integrated optics with microfluidics has opened a new area of optofluidics, which allows further scaling of lab-on-chip devices and improved functionality, such as freedom from electromagnetic interference, capacity for remote sensing and most significantly, on-chip spectroscopy. Many research directions have emerged to demonstrate optical sensing on a chip. Each of the techniques such as fluorescence [3], surface plasmon resonance [4] and interferometry [5] has interesting properties making them suitable for sensing purposes. However, with the vast number of unknown analytes (organic and inorganic solids, liquids and gases) in the Earth, precise identification of substances is necessary. Labeling of individual analytes can be considered as an option in the above techniques. However, individual labeling is a pain-staking task and furthermore, not all substances in our planet can be labeled for sensing purposes.

Infrared (IR) absorption measurements are the simplest label free techniques for detection and identification of substances based on their unique spectral signatures. It is widely used in applications in organic [6] and inorganic chemistry, studies of polymer degradation in forensic analysis [7], water content or moisture characterization in agricultural and food products [8], fuel quality control [9], hydrocarbon processing [10] and refining and petroleum characterization [11] to name a few. Infrared spectroscopy relies on the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete vibrational modes. Molecular absorption at bond-stretching and bond-bending resonant frequencies leads to signatures in the transmission spectra of the analyte, thereby enabling analyte detection and identification. Although various complex schemes have been demonstrated [12] to increase absorption path lengths, present state-of-the-art dimensions are still large to be accommodated on a chip.

2. PRINCIPLE OF OPERATION

The principle of infrared absorption spectroscopy is based on the Beer-Lambert law. According to this law, transmitted intensity I is given by:

$$I = I_0 \exp(-\gamma\alpha L) \dots\dots(1)$$

where I_0 is the incident intensity, α is the absorption coefficient of the medium, L is the interaction length and γ is the medium-specific absorption factor determined by dispersion enhanced light-matter interaction. In conventional free-space systems, $\gamma = 1$; thus L must be large to achieve a suitable sensitivity of measured I/I_0 .

For lab-on-chip systems, L must be small, hence γ must be large. Mortensen et al showed [13] using perturbation theory that

$$\gamma = f \times \frac{c/n}{v_g} \dots\dots\dots(2)$$

where c is the velocity of light in free space, v_g is the group velocity in medium of effective index n and f is the filling factor denoting relative fraction of optical field residing in the analyte medium. Equation 2 shows that slow light propagation (small v_g) significantly enhances absorption. Furthermore, greater the electric field overlap with analyte, greater the effective absorption by the medium. Both conditions of small v_g and high f are fulfilled in a photonic crystal slot waveguide.

Photonic crystal (PC) waveguides have demonstrated group velocity slow-down factors ~ 100 [14]. Slot waveguides have also demonstrated significant increase in the electric field intensity in a narrow low index slot in a high index ridge waveguide, by at least a factor of 10 [15]. Slow light in PC waveguides coupled with electric field intensity enhancement in a slot in the PC waveguide, can therefore reduce v_g and enhance f , thereby theoretically shrinking the required absorption path length by a factor of 1000, an order of magnitude greater than ring resonator devices [16].

During the past two decades, PC devices have attracted significant interest due to their unique dispersive properties that allow control and manipulation of light-matter interactions on length scales of the wavelength of light [17]. Various miniature applications have been demonstrated with PC microcavities and PC slot waveguides for light emission [18], cavity quantum electrodynamics [19] and electro-optical modulation [20]. PC devices have shown significant promise in sensing applications due to high sensitivity to refractive index changes of the ambient [21]. Change in refractive index of a medium caused by an analyte is however not sufficiently analyte-specific and is therefore not a unique signature of the analyte. In contrast, absorption spectrum of an analyte is based on analyte-specific molecular vibrations, and thus identifies the analyte uniquely. In this paper, we demonstrate a PC slot waveguide that enables near-infrared spectroscopy of xylene in water, xylene being chosen as a representative volatile organic compound (VOC) contaminant in water with environmental and human health significance.

3. DEVICE DESIGN FOR ON-CHIP SPECTROSCOPY

Schematic of our silicon PC slot waveguide device with geometry parameters is shown in Fig. 1(a). The PC waveguide is a W0.8 line defect with uniform lattice constant a , and width $0.8 \times \sqrt{3}a$. The device is coated with a thin $\sim 8\mu\text{m}$ film of poly-dimethyl siloxane (PDMS). Since PDMS is hydrophobic, use of PDMS ensures that absorption signatures of xylene are obtained without interference from strong near-infrared absorption of water. The PDMS cladding thickness chosen appropriately to avoid interaction between the guided optical mode in the slot and the water ambient. The band diagram of the defect-guided mode is calculated using three-dimensional plane-wave expansion method as shown in Fig. 1.

The geometry parameters are as follows: Radius of air-holes $r = 0.25a$, width of slot $w = 0.15a$. The design parameters are chosen to support a single PC waveguide slot guided mode within the photonic band gap. The mode profile of the guided slot mode is shown in the inset which shows the slow light mode strongly confined in the slot at the center of the PC waveguide. The device is $300\mu\text{m}$ long. Light is coupled into the PC slot waveguide via ridge waveguides with optical fiber input and output. Mode converters are designed to couple the light efficiently from the ridge waveguide into the slot. However, coupling losses can occur when light is guided from a low group index ridge waveguide to the high group index frequencies of the slow light region. An impedance taper within the photonic crystal waveguide is also designed where holes adjacent to PC slot waveguide are shifted in steps by $0.0025 \times \sqrt{3}a$ over 16 periods to enable gradual change in the group index and thus allow higher coupling efficiency into the slow light guided mode [22].

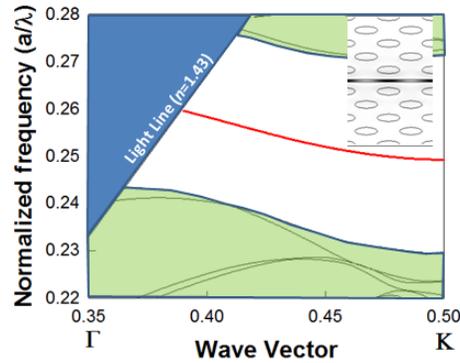


Figure 1: Dispersion diagram of PC slot waveguide device coated with PDMS sensing phase. Single mode guided below light line is shown by the red curve and mode profile is shown in the inset.

4. DEVICE FABRICATION

Devices were fabricated on silicon-on-insulator (SOI) wafer with 230nm top silicon layer and 3 μ m buried oxide. 45nm thermal oxide was grown on top of silicon as etch mask for pattern transfer. PC slot waveguides, tapers, and strip waveguides are patterned in one step with e-beam lithography followed by reactive ion etching. Scanning electron micrograph (SEM) of fabricated structure is shown in Fig 2. PDMS top cladding was prepared by spinning a 10:1 mixture of Sylgard Elastomer 184 from Dow Corning, NY (refractive index $n=1.43$) and curing agent, followed by oven-baking for 3 hrs at 90°C. The device processing prior to PDMS deposition is exactly the same as in a previous demonstration of methane detection with the photonic crystal slot waveguide [15]. We thus have a robust platform for various kinds of on-chip optical spectroscopy that can be tailored for each individual sensing environment.

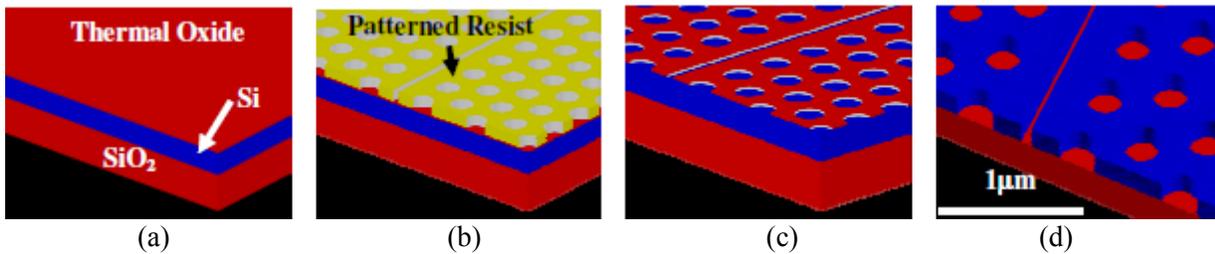


Figure 2: Fabrication steps of a PC slot waveguide (a) Growth of thermal oxide (b) E-beam Resist (ZEP-520A) patterning (c) Transfer of resist pattern to thermal oxide by RIE using CHF_3 followed by resist strip (d) Transfer of pattern from thermal oxide to Si by RIE in HBr and Cl_2 . [Legend: Silicon (blue), Silicon Dioxide, SiO_2 (red)]

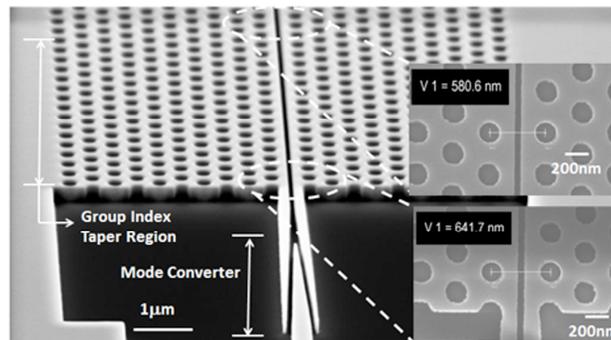


Figure 3: Scanning electron micrograph (SEM) images of photonic crystal slot waveguide devices with the mode converter and photonic impedance taper fabricated for efficient coupling of light from a ridge waveguide into the photonic crystal waveguide.

Scanning electron micrograph (SEM) images are shown in Fig. 3 for fabricated devices. Absorption signature of xylene in near-infrared extends from 1665nm to 1745nm with absorption peaks at 1674nm, 1697nm and 1720nm respectively

[23]. Three lattice constants $a=455\text{nm}$, 458nm and 460nm are selected for three devices so that slow light propagation occurs at individual absorbance maxima.

5. EXPERIMENTAL SETUP

The devices were tested on a Newport six-axis auto-aligning station. Input light from a broadband source (SuperK Versa from NKT Photonics, Denmark) was TE-polarized and butt-coupled to / from the device with polarization maintaining single mode tapered lensed fiber with mode field diameter $\sim 3\mu\text{m}$. Experimental transmission spectrum through PDMS filled slot in absence of analyte in Fig. 3 shows that the band edge is red-shifted $\sim 3\text{nm}$ from design (dotted black line). Sample solutions were prepared by transferring $200\mu\text{l}$ of xylene into a sealed beaker with 200ml of deionized (DI) water, followed by continuous stirring for 12 hrs at room temperature, as described in ref. [24]. The entire device is wetted with sample solution, similar to a real environment. Transmitted light was analyzed with an optical spectrum analyzer, in the presence and the absence of xylene in water.

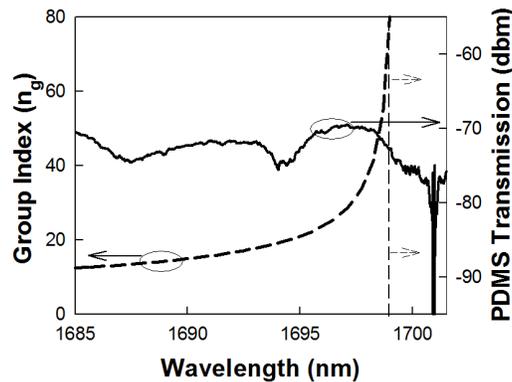


Figure 4: (left scale) Group index vs. wavelength (dashed curve) as designed with the band edge at 1698nm (dotted black line). (right scale) Experimental transmission spectrum (solid curve) in PDMS infiltrated slotted PC waveguide (without analyte), showing that the band edge is shifted in the fabricated device to 1701nm .

Since PDMS is very thin, the response time is a few seconds only. Measurements are performed immediately after the analyte is introduced. Using eq. 1, the difference in the transmitted intensity through PDMS clad PC slot waveguide is calculated in the presence and the absence of xylene and the absorbance of xylene determined [15].

6. EXPERIMENTAL RESULTS

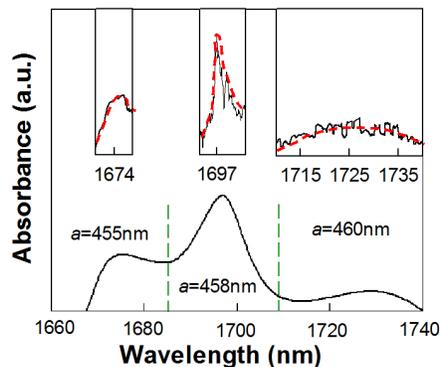


Figure 5: Theoretical spectrum of xylene obtained from ref. [23] divided into 3 regions as shown by dotted lines. Experimental transmission spectrum centered on absorbance maxima in each section is plotted in respective insets for 100ppm (v/v) concentration.

Measurements are performed for all three lattice constants. The theoretical spectrum of xylene [23] shown in Fig. 5, divided into 3 sections shown by dotted green lines. Experimentally obtained xylene spectrum is shown for each section, corresponding to individual lattice constants, in insets of Fig. 5. Good correspondence is observed between experimentally observed absorption peaks and theoretical spectrum.

7. DISCUSSION

To determine the detection limit, xylene concentration in DI water was varied from $10^{-5}\%$ or 100ppb (v/v) to 1% by volume. The intensity of the strongest absorbance peak at 1697nm is plotted in Fig. 6 as a function of xylene concentration in water.

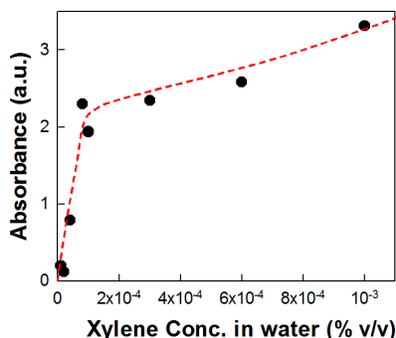


Figure 6: Absorbance magnitude vs. xylene concentration in water (%v/v).

Fig. 6 shows that the Beer-Lambert law is followed linearly for small concentrations between 100ppb (v/v) to ~1ppm (parts per million) (v/v); at higher concentrations, absorbance curve deviates from linearity, potentially due to reduced uptake of xylene by the $8\mu\text{m}$ thin PDMS film as it reaches saturation. The detection limit of 100ppb (v/v) [$\sim 86\mu\text{g/L}$] demonstrated in our $300\mu\text{m}$ long device is lower than near infrared detection limits observed with PDMS disks in water (3mg/L) [24]. The device is more sensitive than some other methods which require pre-processing for salinity to enhance sensitivity [25]. Our device is more than an order of magnitude smaller in length than PDMS disks above. The detection limit of our device is better than $400\mu\text{g/L}$ demonstrated with 11 meter long optical fibers [26]. Also, response time in our device is a few seconds compared to ~60 minutes [24] due to small PDMS thickness for xylene to diffuse. We believe that at the lower end, sensitivity is limited by the offset of the absorbance peak from design to $\sim n_g=20$ due to fabrication errors, as shown in Fig. 5. The detection limit can be enhanced by at least a factor of 3 in current devices in the near-infrared by better control of fabrication that positions the band edge closer to the peak absorbance as designed. It must be noted that in the mid- infrared, $20\mu\text{g/L}$ (v/v) detection limit was demonstrated with 50mm long sample cells [27]. The PC slot waveguide device, with dispersive properties determined by Maxwell's equations, is readily scalable to mid-infrared. Since xylene has approximately 2 orders of magnitude larger absorption cross-section in the mid infrared, few hundred parts per trillion (ppt) detection limits are possible in PC slot waveguide devices on $300\mu\text{m}$ length scales at longer wavelengths. In analyte solutions with mixtures of various volatile organic compounds, multiple PC waveguides can be fabricated simultaneously, each with a different lattice constant, as in the present work to measure absorption spectrum in the corresponding wavelength range, and identifying the analytes uniquely by comparing with known infrared absorbance databases.

8. SUMMARY

In summary, we have demonstrated a $300\mu\text{m}$ long silicon PC slot waveguide device that combines slow light with electric field enhancement to increase the effective absorbance path length and thus achieve on-chip near infrared spectroscopy of xylene in water with detection limit 100ppb ($86\mu\text{g/L}$). Our device is five times more sensitive for xylene in water than existing devices in the near-infrared on more than an order of magnitude smaller length scale. Remote sensing is enabled by optical fibers. Lasers and detectors can be integrated on-chip to create a complete integrated broadband miniature absorption spectrometer.

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REFERENCES

- [1] Bedient, P.B., "Groundwater Contamination, Transport and Remediation," Prentice Hall PTR, (1994).
- [2] Cheremisinoff, P.N., "Benzene: Basic and hazardous properties," Marcel Dekker Inc., (1979).
- [3] Chabinye, M.L., Chiu, D.T., McDonald, J.C., Stroock, A.D., Christian, J.F., Karger, A.M., and Whitesides, G.M., "An integrated fluorescence detection systems in PDMS for microfluidic applications," *Anal. Chem.* **73**, 4491 (2001).
- [4] Dostalek, J., Ctyroky, J., Homola, J., Brynda, E., Skalsky, M., Nekvindova, P., Spirkova, J., Skvor, J., and Schrofel, J., "Surface plasmon resonance biosensor based on integrated optical waveguide," *Sensors & Actuators B* **76**, 8 (2001).
- [5] Schmitt, K., Scirmer, B., Hoffmann, C., Brandenburg, A., and Meyrueis, P., "Interferometric biosensor based on planar optical waveguide sensor chips for label-free detections of surface bound bioreactions," *Biosensors Bioelectronics* **22**, 2591 (2007).
- [6] Peter, K., Vollhardt, C., and Schore, N.E., "Organic Chemistry: structure and function", Macmillan, (2003).
- [7] Botonjic-Sehic, E., Brown, C.W., Lamontagne, M., and Tsaparikos, M., "Forensic Application of Near-Infrared Spectroscopy: Aging of Bloodstains," *Spectroscopy* **24**(2), 42 (2009).
- [8] Woodcock, T., Downey, G., O'Donnell, C.P., "Better quality food and beverages: the role of near infrared spectroscopy," *Journal of Near Infrared Spectroscopy* **16**(1), 1(2008).
- [9] Felizardo, P., Baptista, P., Uva, M.S., Menezes, J.C., and Correia, M.J.N., "Monitoring biodiesel fuel quality by near infrared spectroscopy," *Journal of Near Infrared Spectroscopy* **15**(2), 97 (2007).
- [10] Mattioda, A.L., Rutter, L., Parkhill, J., Head-Gordon, M., Lee, T.J., and Allamandola, L.J., "Near infrared spectroscopy of nitrogenated polycyclic aromatic hydrocarbon cations from 0.7 to 2.5 μ m," *Astrophys. J.* **680**(2), 1243 (2008).
- [11] Pasquini, C., and Bueno, A.F., "Characterization of petroleum using near-infrared spectroscopy: quantitative modeling for the true boiling point curve and specific gravity", *Fuel* **86**(12-13), 1927 (2007).
- [12] Thorpe, M.J., Moll, K.D., Jones, R.J., Safdi, B. and Ye, J., "Broadband Cavity ringdown spectroscopy for sensitive and rapid molecular detection," *Science* **311**, 1595 (2006).
- [13] Mortensen, N.A., and Xiao, S.S., "Slow-light enhancement of Beer-Lambert-Bouguer absorption," *Appl. Phys. Lett* **90**(14), 141108 (2007).
- [14] Notomi, M. "Extremely large group-velocity dispersion of line-defect waveguides in photonic crystal slabs," *Physical Review Letters* **87**, 253902 (2001).
- [15] Lai, W-C., Chakravarty, S., Wang, X., Lin, C-Y., and Chen, R.T., "On-Chip methane sensing by near-IR absorption signatures in a photonic crystal slot waveguide," *Optics Letters* **36**, 984 (2011).
- [16] Robinson, J.T., Chen, L., and Lipson, M., "On-chip gas detection in silicon optical microcavities," *Optics Express* **16** (6), 4296 (2008).
- [17] Yablonovitch, E., "Inhibited Spontaneous Emission in Solid-State Physics and Electronics," *Phys. Rev. Lett.* **58**, 1059 (1987); John, S., "Strong localization of photons in certain disordered dielectric superlattices," *Phys. Rev. Lett.* **58**, 2486 (1987).
- [18] Chakravarty, S., Bhattacharya, P., and Mi, Z., "Electrically injected quantum-dot photonic crystal microcavity light emitting arrays with air-bridge contacts," *IEEE Photon. Tech. Lett.* **18**, 2665 (2006).
- [19] Vuckovic, J., and Yamamoto, Y., "Photonic crystal microcavities for cavity quantum electrodynamics with a single dot", *Appl. Phys. Lett.* **82** (15), 2374 (2003).
- [20] Lin, C-Y., Wang, X., Chakravarty, S., Lee, B-S., Lai, W-C., Luo, J., Jen, A-K-Y., and Chen, R.T., "Electro-optic polymer infiltrated silicon photonic crystal slot waveguide modulator with 23dB slow light enhancement," *Appl. Phys. Lett.* **97**, 093304 (2010).
- [21] Chakravarty, S., Topol'ančik, J., Bhattacharya, P., Chakrabarti, S., Kang, Y., and Meyerhoff, M.E., "Ion detection with photonic crystal microcavities," *Opt. Lett.* **30**, 2578 (2005).
- [22] Wang, X., Chakravarty, S., Lee, B-S., Lin, C-Y., and Chen, R.T., "Ultra-efficient control of light transmission through photonic potential barrier modulation," *Opt. Lett.* **34**(20), 3202 (2009).
- [23] Burns, D.A., *Handbook of near-infrared analysis*, (3rd Edition, Hoboken: Taylor and Francis Ltd, 2007).
- [24] Albuquerque, J.S., Pimentel, M.F., Silva, V.L., Raimundo, M., Rohwedder, J.J.R., and Pasquini, C., "Silicone Sensing Phase for Detection of Aromatic Hydrocarbons in Water Employing Near-Infrared Spectroscopy," *Anal. Chem.* **77** (1), 72 (2005).

- [25] Lima, K.M.G., Raimundo, I.M., and Pimentel, M.F., "Improving the detection limits of near-infrared spectroscopy in the determination of aromatic hydrocarbons in water employing a silicone sensing phase" *Sens. & Act. B-Chem.* **125**(1), 229 (2007).
- [26] Buerck, J., Roth, S., Kraemer, K., Scholz, M., and Klaas, N., "Application of a fiber-optic NIR-EFA sensor system for in situ monitoring of aromatic hydrocarbons in contaminated groundwater," *J. Hazard. Mater.* **83**, 11 (2001)
- [27] Silva, A.M.F., Pimentel, M.F., Raimundo, M.F., and Almeida, Y.M.B., "A PVC sensing phase for determination of aromatic hydrocarbons in water employing mid-infrared spectroscopy," *Vibration. Spectros.* **46** (1), 39 (2008).