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Long Path-Length Axial Absorption Detection in Photonic Crystal Fiber

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In this paper, we present a long path-length axial absorption detection method in photonic crystal fibers (PCFs). A PCF, also called a holey fiber or microstructured fiber, is an optical fiber which consists of a periodic array of very tiny and closely spaced air holes on the scale of 1 μm running through the whole length of the fiber. Here, a PCF with porous microstructures was used as a sample container for absorption detection. Light was guided by total internal reflection and propagated axially in the air holes of PCFs that were filled with the solution of the absorbing species by vacuum pumping. Excellent linearity was obtained for different sample concentrations, and high sensitivity was achieved due to the long optical path length. In addition, as the dimension of the PCF is small, the sample volume is greatly reduced. Moreover, due to its robustness, the PCF can be coiled up to keep the footprint small, making it suitable for microchip absorption detection. It can be widely used for both off-chip and on-chip detection of absorbing species, such as ions, alkaloids, and biomolecules.

Absorption spectroscopy is one of the most widely used detection methods in chemical analysis. It employs the interaction of electromagnetic radiation with matter.[1] Different molecules absorb radiation of different wavelengths. Thus, from the absorption spectrum, one can determine the structure and concentration of the molecule. The spectra of substances are often obtained by a spectrophotometer. The sample, often liquid, is contained in an optical container called a cuvette. The cell is placed into the spectrophotometer and exposed to a light beam of varying wavelengths. The intensities of transmitted light are measured as a function of the wavelength of the radiation. As defined by the Beer−Lambert law, absorbance *A* of an absorbing species is given by

$$A = \varepsilon bc \qquad (1)$$

where ϵ is the molar absorption coefficient, *b* is the optical path length, and *c* is the concentration, implying that absorbance is directly proportional to the path length.

Normally, the path length of a rectangular cuvette style cell is short, ranging from 1 to 50 mm. If the concentration of an analyte is too low, the signal may be too small to be registered. Then one has to preconcentrate the analyte by extraction or reacting with ligands to form highly colored complexes with higher absorptivity, which is very troublesome. Alternatively, there exist different approaches to increase the path length so that lower concentrations may be detected. One example is two cells, where two separate cells were attached together to increase the path length,[2] but this method resulted in the increase of sample consumption and the path length is only doubled. Djordjevic et al. described a procedure for creating a bubble-shaped cell on a separation column.[3] The bubble cell provided an extended path length for absorption detection in capillary electrophoresis (CE), and 8-fold enhancement in sensitivity was realized. However, the distorted flow in the bubble cell due to the change in geometry gave rise to noticeable losses in efficiency and resolution. The application of a multireflection cell was also investigated.[4] Sensitivity enhancement of 10-fold was realized by using spherical mirrors to reflect the radiation within the cell several times. However, the optical setup of the multireflection cells was very complicated. In all of the above-mentioned methods, the light path was directed perpendicularly to the cells. The path length cannot be too large as it is difficult to transmit a collimated light beam without substantial light loss for extended distances in fluids.

Recently, a liquid core waveguide (LCW) cell for long-path absorption spectrophotometry has been reported.[5–8] The LCW cell usually consists of a narrow tube made of Teflon AF, and the sample solution is injected into the polymer tube. The material of the tube has a lower refractive index than that of the fluid. The source light is thus propagated axially through the LCW cell by total internal reflection. However, Teflon AF is one of the most expensive commercial polymers and the material is highly gas permeable, which can result in the evaporation of water from the sample solution inside the LCW cell.

Absorption detection is also one of the most promising detection methods on microchips for its flexibility and ease of

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(1) Hollas, J. M. *Modern Spectroscopy*; John Wiley & Sons: Chichester, England, 2004.
(2) Sakai, T.; Maeda, Y.; Ura, N. *Talanta* **1999**, *49*, 989.
(3) Djordjevic, N. M.; Widder, M.; Kuhn, K. *Electrophoresis* **2005**, *20*, 189–192.
(4) Moosavi, H. S.; Jiang, J. T.; Lester, L.; McKinnon, G.; Harrison, D. J. *Electrophoresis* **2000**, *21*, 1291–1299.
(5) Tao, S. Q.; Winstead, C. B.; Xian, H.; Soni, K. *J. Environ. Monit.* **2002**, *4*, 815–818.
(6) Li, Q. Y.; Morris, K. J.; Dasgupta, P. K.; Raimundo, I. M.; Temkin, H. *Anal. Chim. Acta* **2003**, *479*, 151–165.
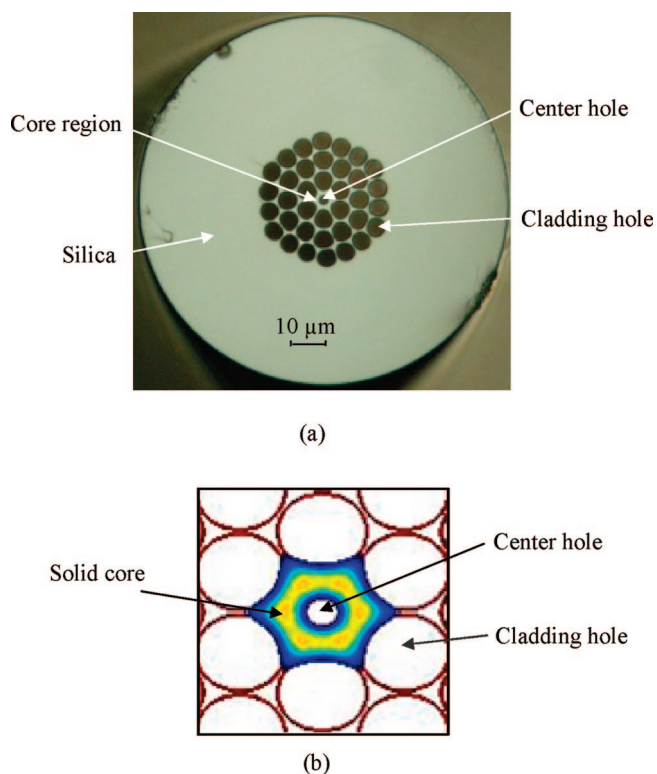(7) Dallas, T.; Dasgupta, P. K. *Trends Anal. Chem.* **2004**, *23*, 385–392.
(8) Tao, S. Q.; Gong, S. F.; Xu, L.; Fanguy, J. C. *Analyst* **2004**, *129*, 342–346.

setup. However, the optical path length represented by the microchannel depth or width is generally shorter than 30 μm, which poses a severe problem for sensitive and reliable absorption detection.[9] Despite a wide range of possible applications of microchips, few examples of absorption detection on microchip platforms are found.[10–12]

In this paper, we propose an approach of using a photonic crystal fiber (PCF) as a miniaturized waveguide cuvette for long path-length axial absorption detection. PCFs, originally made of silica glass, are characterized by having a cladding pattern of micrometer-sized air holes along the entire length of the fiber.[13] PCFs exhibit unique properties such as low power loss, single-mode transmission, and high nonlinearity, which are attractive for applications in fiber-optic communications, highly sensitive sensors,[14,15] and other areas that cannot be realized in a standard optical fiber.[16] Recently, the PCF has also attracted attention in electrophoretic separation. As the micrometer-sized air holes allow microvolume infiltration of liquid, they can be used as a bundle of capillaries for electrophoretic separation.[17] The PCF could sustain a high electric field up to 1000 V/cm due to efficient heat dissipation, and faster and efficient separation was achieved. In an index-guided PCF, although the majority of light is confined inside the fiber core by the mechanism of total internal reflection similar to a step index single-mode fiber (SMF), a portion of light could escape from the core and travel in the air holes.[18] As the air holes may be filled with solutions of absorbing species, the interaction of light with absorbing species allows PCFs to be used as miniaturized waveguide cuvettes for axial absorption detection. The PCF could also be inserted into a microchannel. Coupling of light from an external light source to a PCF in a microchip could be achieved using planar waveguides.[19] Since absorbance is proportional to the optical path length, sensitivity by axial absorption detection is expected to be higher than that of the conventional on-chip perpendicular detection method. In this work, a PCF was filled with cobalt(II) chloride ($CoCl_2$) solution. A calibration plot by axial absorption was constructed and compared with absorbance obtained by a standard spectrometer as well as the on-chip perpendicular detection method. Integration of the PCF with a microchip for on-chip axial absorption detection was also proposed.

EXPERIMENTAL SECTION

Materials. The PCF used for this study was fabricated in our laboratory. It was made from pure silica with a refractive index

(9) Gotz, S.; Karst, U. *Anal. Bioannal. Chem.* **2007**, *387*, 183–192.
(10) Collins, G. E.; Lu, Q.; Pereira, N.; Wu, P. *Talanta* **2007**, *72*, 301–304.
(11) Salimi-Moosavi, H.; Jiang, Y.; Lester, L.; Mckinnon, G.; Harrison, D. J. *Electrophoresis* **2000**, *21*, 1291.
(12) Malcik, N.; Ferrance, J. P.; Landers, J. P.; Caglar, P. *Sens. Actuators, B* **2005**, *107*, 24–31.
(13) Russell, P. S. J. *Science* **2003**, *299*, 358–362.
(14) Hoo, Y. L.; Jin, W.; Shi, C. Z.; Ho, H. L.; Wang, D. N.; Ruan, S. C. *Appl. Opt.* **2003**, *42*, 3509–3515.
(15) Monro, T. M.; Belardi, W.; Furusawa, K.; Baggett, J. C.; Broderick, N. G. R.; Richardson, D. J. *Meas. Sci. Technol.* **2001**, *12*, 854–858.
(16) Russell, P. S. J. *J. Lightwave Technol.* **2006**, *24*, 4729–4749.
(17) Sun, Y.; Kwok, Y. C.; Nguyen, N. T. *Electrophoresis* **2007**, *28*, 4765–4768.
(18) Chillcce, E. F.; Cordeiro, C. M. B.; Barbosa, L. C.; Cruz, C. H. B. *J. Non-Cryst. Solids* **2006**, *352*, 3423–3428.
(19) Mogensen, K. B.; Ali, J. E.; Wolff, A.; Kutter, J. P. *Appl. Opt.* **2003**, *42*, 4072–4079.

Figure 1. (a) Scanning electron micrograph (SEM) of the cross section of a PCF. A solid core was surrounded by three layers of big air holes which serve as cladding. A small hole was introduced to the solid region at the centre of the lattice. The diameters of the big and small air holes are 6.2 and 3.1 μm, respectively. (b) Simulated power distribution. Most of the guided light power is confined within the solid region of the core with 0.37% of total power extending into the holey region.
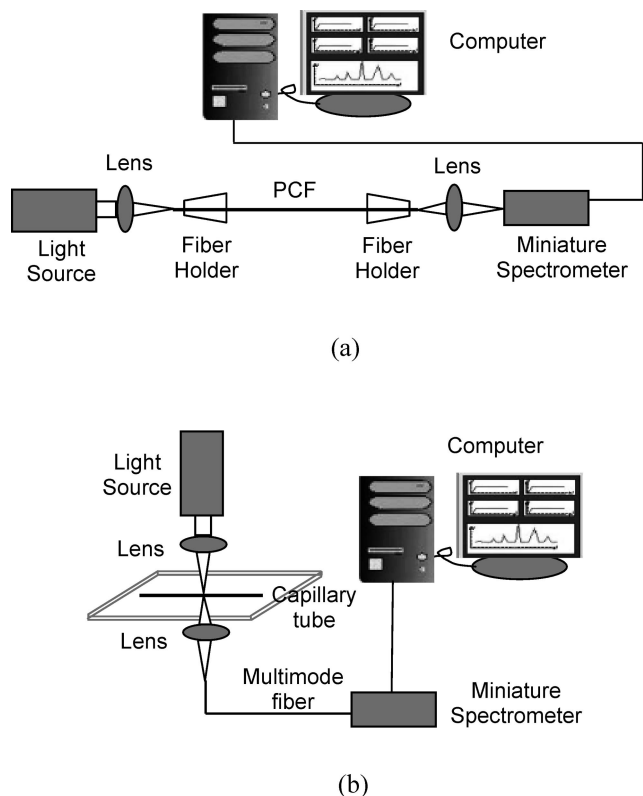
1.45 using a stack-and-drawing technique.[20] Figure 1a shows a scanning electron micrograph (SEM) of the PCF. A small hole (labeled "center hole") was introduced in the core region. The core region was surrounded by three layers of bigger air holes (labeled "cladding hole") for cladding purpose. The PCF fiber had an o.d. of 125 μm, and the diameters of the cladding and center air holes were 6.2 and 3.1 μm, respectively. Here, the cladding and center air holes were filled with solutions of absorbing species to show possible applications in liquid sensing through absorbance measurement. The corresponding simulated power distribution is shown in Figure 1b.

System Setups. The setup for axial absorption measurement was adopted from that designed for evanescent field sensing[21] and is shown in Figure 2a. The PCF was supported and aligned by two three-axis translation stages with fiber holders (Thorlabs, New Jersey). Light from a 7 W broad-band halogen light source (Ocean Optics, Florida) was coupled into the core of the PCF by means of a 20× objective lens (Ocean Optics, Florida). Transmitted light exiting from the end face of the PCF was focused by another 20× lens to a standard multimode fiber (FL-400, Ocean Optics, Florida), which directed the light to a USB2000 miniature

(20) Knight, J. C.; Birks, T. A.; Russell, P. J.; Atkin, D. M. *Opt. Lett.* **1996**, *21*, 1547–1549.
(21) Cordeiro, C. M. B.; Franco, M. A. R.; Chesini, G.; Barretto, E. C. S.; Lwin, R.; Cruz, C. H. B.; Large, M. C. J. *Opt. Express* **2006**, *14*, 13056–13066.

(a)

(b)

Figure 2. (a) Setup for axial absorption measurement. (b) Setup for perpendicular absorption measurement.

spectrometer (Ocean Optics, Florida). The spectrometer measures transmitted light as a function of wavelength with a resolution of 0.2 nm.

For comparison of sensitivity, perpendicular absorption detection was performed using a conventional fused-silica capillary tube with an i.d. of 40 μm and an o.d. of 120 μm (Postnova Analytics Inc., Utah). A capillary was used instead of the PCF because light reflection at the multiple solid-hole interfaces in the PCF may affect the accuracy of perpendicular detection. The polyimide coating of the silica capillary was removed to create a detection window. The setup is adapted from the microchip-based absorption detection technique[12] and is shown in Figure 2b. The incident light from the same halogen light source was focused by a 20× lens and directed perpendicularly to the capillary. The transmitted light was focused by a 20× lens into a multimode fiber, which directed the light to the same miniature spectrometer. The optical path length was equivalent to the i.d. of the capillary, i.e., 40 μm, which was the same as the diameter of holey region of the PCF.

Chemicals and Procedures. Hydrated cobalt(II) chloride ($CoCl_2 \cdot 6H_2O$) was purchased from Sigma-Aldrich (Missouri), and it was dissolved in deionized water (Barnstead E-pure system, Iowa) to prepare solutions of $CoCl_2$ of concentrations between 5 and 200 mM. The absorption property of $CoCl_2$ was characterized by a standard spectrometer (Cary 50 Conc, Varian Inc., CA). It has a maximum absorption at 510 nm. The PCF was filled with $CoCl_2$ solution or deionized water by a vacuum pump. Absorbance at each wavelength was calculated according to eq 2:

$$A = \log \frac{I_{H_2O}}{I_{CoCl_2}} \qquad (2)$$
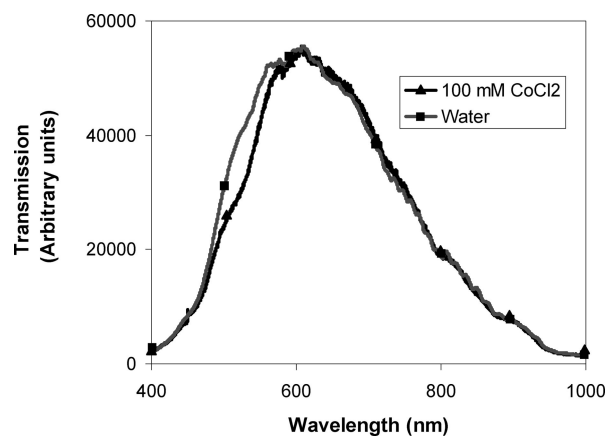
Figure 3. Upper curve: transmission spectrum of water contained in a 50 cm PCF by axial absorption detection. Lower curve: transmission spectrum of 100 mM $CoCl_2$ solution contained in a 50 cm PCF. Triplicates were done, and the relative standard derivation was less than 3%.

where I_{H_2O} is the transmitted light intensity of deionized water and I_{CoCl_2} is the transmitted light intensity of the $CoCl_2$ solution.

RESULTS AND DISCUSSION

For a normal index-guided solid-core PCF fiber, light is confined in the core region by total internal reflection as the effective index of the core is usually higher than that of the cladding. However, to be used as a flow cell for absorbance detection, the fiber should allow light to penetrate into the hole region and travel through the filled solution. By introducing the defect hole, the effective index difference between the core and the cladding was getting smaller; thus the fiber became more "weakly guiding" and more light was expected to interact with the absorbent species. The light distribution inside the fiber was simulated using a full-vector beam propagation method,[22] and the result is shown in Figure 1b. At every point of internal reflection at the silica−hole interface, a small portion of the field penetrates the wall and decays exponentially. It was calculated that at 510 nm, the maximum absorption wavelength of $CoCl_2$, although most of the guided light power was confined within the solid region of the core, 0.37% fraction of optical power managed to leak into the holey region. The evanescent field allowed interaction of light with the absorbing species infiltrated in the hollow channels. In eq 1, absorbance is expressed by $A = \varepsilon bc$. This equation implicitly states that the power fraction of the light that propagates through the sample f is 100%, and the assumption is only valid for standard cuvette measurements. While as in a PCF, f is smaller than 100%, expression for the absorbance in the experiments should include a term for the power fraction of the light that propagates through the sample solution, and eq 1 could be modified as
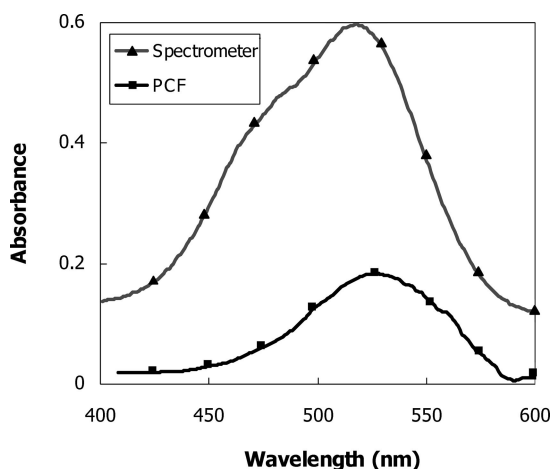
$$A = \varepsilon bcf \qquad (3)$$

where f is the power fraction. In sensors based on microstructured fibers, f typically depends on both the wavelength and the structural parameters of the fiber.

Figure 3 shows the spectra transmitted through the water-filled PCF and through the fiber filled with 100 mM $CoCl_2$ by

(22) Feit, M. D.; Fleck, J. A. *Appl. Opt.* **1980**, *19*, 1154–1164.

Figure 4. Upper curve: absorption spectrum of 100 mM CoCl₂ solution contained in a 1 cm cuvette by a standard spectrometer. Lower curve: absorption spectrum of 100 mM CoCl₂ solution contained in a 50 cm PCF by axial absorption detection. Triplicates were done, and the relative standard derivation was less than 3.5%.
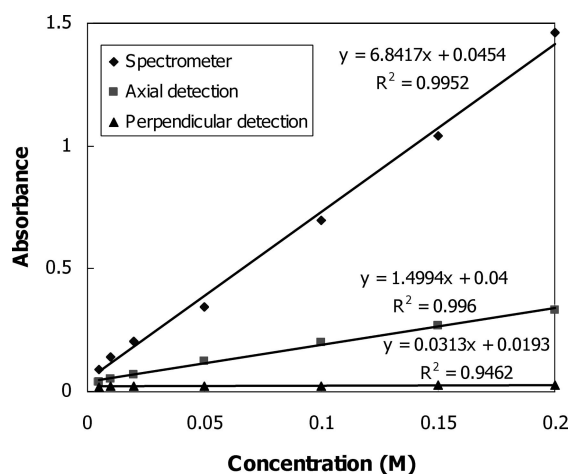
Figure 5. Upper curve: calibration plot for a standard spectrometer. Middle curve: calibration curve for axial absorption detection using a 50 cm PCF. Lower curve: calibration plot for perpendicular absorption detection using a capillary with an i.d. of 40 μm. Absorbance at 510 nm was measured. Triplicates were done, and the relative standard derivation was less than 3%.

axial absorption detection. For the water-filled PCF, the transmission band was from 400 to 1000 nm, whereas when the fiber was infiltrated with CoCl₂, the expected decay of the intensity in the absorption region of 480 to ~560 nm was observed. The corresponding absorbance in the PCF was calculated by eq 2 and compared to the absorbance measured by a standard spectrometer as shown in Figure 4. It can be seen that the two spectra resembled each other well except the maximum absorbance in the PCF occurred at 520 nm, which was 10 nm away from the adsorption maximum of 510 nm measured by the spectrophotometer.

The middle curve in Figure 5 is the calibration plot when axial absorption detection was performed using a 50 cm PCF. Excellent linearity, i.e., $R^2 = 0.996$, was observed. This shows that a PCF is suitable as a miniaturized waveguide cuvette for absorption spectrometry. The upper and lower curves in Figure 5 are the calibration plots obtained by the spectrometer and perpendicular absorption detection, respectively. By comparing the slopes of
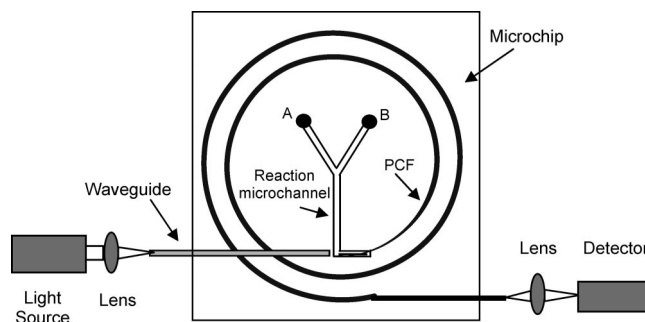
Figure 6. Proposed concept of integration of a PCF with a microchip for on-chip long path-length axial absorption detection.

absorbance over concentration in Figure 5, it was found that the sensitivity of axial absorption detection using a 50 cm PCF was 4.56 times smaller than that of the spectrometer and 46.25 times greater than that of perpendicular absorption detection, while the length of the fiber was 50 times and 12 500 times longer than a standard cuvette and microchannel, respectively. This makes sense if the power fraction of the light that propagates through the sample f is considered. In this case $f = 0.37\%$, and according to eq 3, the sensitivity of axial absorption detection using a 50 cm PCF is expected to be 5.4 times smaller than that of a spectrometer and 47.9 times greater than that of perpendicular absorption detection, which matched the experimental results well. Although the 50 cm PCF could not obtain the same absorption as in a 1 cm cuvette, much less sample was consumed by using the fiber. The total sample volume for the 50 cm PCF was 94 nL, whereas the total volume for the cuvette was 3 mL, which means that only 5.4 times less sensitivity was achieved in the PCF with 30 000 times less sample.

For on-chip integration, there will be a volume mismatch if one were to collect the fluid from the microchip with a cuvette and then measure with a spectrometer. Hence, with the use of a PCF, even though it could be 50 cm, the volume will be more similar. Moreover, due to its robustness, a PCF can be coiled up to keep a small footprint, making it suitable for microchip absorption detection. One possible way to integrate a PCF with a microchip is shown in Figure 6. Suppose the microchip has a Y-shaped microfluidic channel with an L-shaped turn at the end. One side of the PCF can be inserted to the microchannel perpendicular to the reaction channel. After reactants A and B totally mix and react in the reaction channel, the final product will be injected into the PCF. To measure the transmission through such a structure, light from a halogen lamp can be directed into the waveguides using an optical fiber and coupled into the PCF. Light will travel through the spiral fiber and interact with the reaction product in the air holes of the PCF. At the other end of the PCF, light will be collected and measured by a photodetector. In comparison to current perpendicular detection on a microchip, much higher sensitivity can be achieved by the long path-length axial absorption detection in the PCF.

CONCLUSIONS
In conclusion, we demonstrated that a PCF can be used as a miniaturized waveguide cuvette for long path-length axial absorption detection. As light is propagated axially along the PCF, theoretically any desired path length can be selected, thus allowing

much lower concentrations to be determined. Solutions could be easily filled by vacuum pumping. The small cross-sectional area of the air holes keeps the reagent and sample consumption at a minimum. In comparison to a conventional cuvette, only 5.4 times less sensitivity was achieved in the PCF with 30 000 times less sample. Moreover, the silica material is chemically and biologically inert and well prevents the evaporation of water. The PCF could be employed either as a miniaturized cuvette for a miniature spectrometer or as an integrated part of a microchip for on-chip absorption detection. Future work will include the modification of the PCF structure to further increase the sensitivity.