Interrogating Water Content in Organic Solvents by Planar Bragg Grating Sensor

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Abstract

We report on a planar Bragg grating evanescent field refractive index sensor capable of monitoring online the water content in organic solvents in the range from 0-100%. The sensor structure consists of a Bragg Grating buried in a planar multilayer silica on silicon structure in which both the waveguide and Bragg grating are introduced by UV radiation. Using this sensor, we have investigated the influence of varying water content on the reflected Bragg wavelength, i.e. effective refractive index, in different solvents. The measurements are accompanied by determining the refractive index and the density of the analyte. Karl Fischer Titration serves as a reference to calibrate our samples. Our results prove the capability of the sensor to measure online the water content up to 100% in the entire range of solvents, with a sensitivity on the order of 138nm/riu, corresponding to a minimum detectable index resolution of $7.3 \cdot 10^{-6}$ (e.g. in the case of ethanol). For higher refractive index samples the sensitivity increases as the effective index approaches the index of the waveguide of 1.46. Measurements of 2-butanol confirm this dependence. The observed nonlinear dependence of the Bragg wavelength on composition of aqueous solutions is attributed to the physicochemical properties of the solvents due to the presence of hydration shells around the solvent molecules.

Introduction

Organic materials such as ethanol and methanol are commonly used in the pharmaceutical industry as general solvents or as extraction agents. The water content as an impurity plays an important role in both their production process and usage. For example, a continuous monitoring of the water content is highly desirable during the purification process of absolute ethanol. From a user perspective, e.g., studies on the impact of the water content in ethanol on the gatifloxacin crystal form produced by recrystallisation revealed a significant influence on the solvate hydrate incorporation stoichiometry.[1]
Karl Fischer titration (KFT) is generally used for determining the water content in liquids. However, this method relies on sampling of the medium to be monitored and is very slow, inhibiting a real continuous and online monitoring. In addition, coulometric and volumetric KFT have to be distinguished to cover the entire range of water content from very low moisture to 100% water.
Optical techniques have gained considerable interest in sensing the composition of chemical liquids. Among others, near infrared spectroscopy has been applied to measure the water content with product commercially available.
Recently, fibre Bragg Grating sensors have been applied as refractive index sensors for chemical and biochemical sensing.[2,3,4,5] Etching of D-shaped fibres or planar side-polishing techniques has been applied to expose the Fibre Bragg Grating via evanescent field interaction to an analyte.[6,7,8] Various aqueous solutions of different organic materials, such as alcohols or glucose have been investigated, demonstrating the concept.[9] Using specific transducer layers with specific absorption properties deposited on the fibres, further potentials have been demonstrated, as, e.g., a hydrogen sensor or a pH sensor.[10]

In this paper, we report on a planar Bragg grating (PBG) sensor capable of monitoring online the water content in organic solvents in the range from 0-100%. The basic sensor structure was recently demonstrated by the present authors and others and consists of a Bragg grating buried in a planar multilayer silica on silicon structure in which both the waveguide and Bragg grating are introduced by UV radiation.[11] By a subsequent hydrofluoric acid etching step the cladding layer of the structure is partly removed, opening a sensing window in such a way that the evanescent field of the guided mode penetrates out into the sensing window. In this respect, the sensor is a refractive index (RI) sensor monitoring any physical or chemical changes on the surface that is associated with a change of RI of the medium in the sensing window. Contrary to previously reported fibre Bragg grating based RI sensors, the sensor under study is a planar structure allowing on chip integration of fluidic structures.[12] In addition, a temperature reference grating separated from the sensing window can be integrated onto the sensor chip, thus being isolated from the environment allowing us to factor any temperature effect in our results.

We have investigated the influence of varying water content on the reflected Bragg wavelength, i.e. effective RI, in different solvents such as methanol, ethanol or isopropanol. The measurements are accompanied by determining the RI and density. KFT serves as a reference to calibrate our samples. Our results prove the capability of the sensor to measure online the water content up to 100% in the entire range of solvents, with a high sensitivity, the latter depending on the RI of the analyte. In addition, we observe a pronounced nonlinear dependence of the Bragg wavelength on the composition. For smaller monoalcohols the RI shows a maximum with increasing water content that is discussed in terms of the physicochemical properties of the solvents due to the presence of hydration shells around the molecules of monoalcohols.

Experimental and Sensor structure

The planar Bragg grating sensor used in these studies consists of a multilayer layer silica on silicon structure in which both the waveguide and the grating are written by UV-laser radiation. The layers were deposited using flame hydrolysis deposition in such a way that the central layer was co-doped with germanium to provide photosensitivity to UV radiation at 244nm. For a further enhancement of the photosensitivity, the structure was exposed to hydrogen at 120bar for over 3 days to allow in-diffusion of hydrogen into the silica core. Using direct writing technique both the waveguide and grating are written simultaneously using an argon ion laser.[13] By a subsequent hydrofluoric etching step the cladding layer of the structure is partly removed, opening a sensing window in such a way that the evanescent field of the guided mode penetrates out into the sensing window. In addition, a temperature reference grating separated from the sensing window and thereby isolated from the environment can be integrated onto the sensor chip. For light coupling in and out the waveguide structure the sensor chip is pigtailed to a single-mode fibre. Figure 1 illustrates the sensor design.

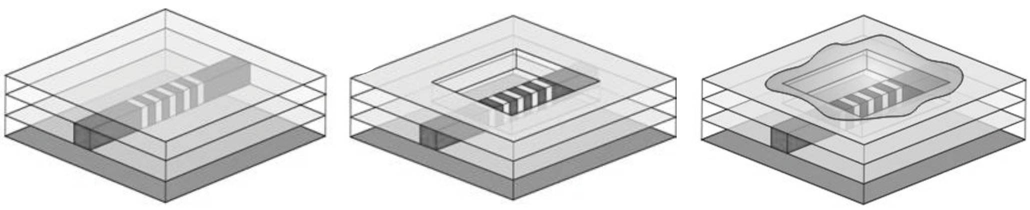

Figure 1: Illustration of the planar Bragg grating sensor showing i) the multilayer structure, ii) the waveguide with the Bragg grating being hatched (left) and iii) the opened sensing window (centre) with applied analyte (right).

The sensor structure works around 1550nm with a grating period on the order of 500nm (please refer to figure 2). This allows usage of conventional telecommunications components. Different sensors have been investigated with varying grating period and corresponding sensitivities. The measurement setup consists of a commercial Braggmeter (FiberSensing FS5200) launching a tunable laser into the connected PBG sensor. As due to the asymmetry of the waveguide, the characteristics of the Bragg grating sensor depends on the polarisation of the laser launched into it. Therefore, a computer controlled in-line polarizer allows selection and control of the polarisation throughout the measurements. Application of aqueous solutions of different solvents is obtained by an external fluidic pump system allowing real time changes of the composition.

To complete our experimental results, the water content of our samples has been determined according to standards by Karl-Fischer Titration (Metrohm KF-Coulometer 831), their RI was measured using either a refractometer (Mettler Toledo RA-510M) or a multi-wavelength refractometer (Atago DR-M 2/1550) and, finally, their density was determined with a density meter (Mettler Toledo DE 51).

Figure 2 shows a 3D-image of the central section of the sensing window, clearly resolving both, the waveguide and Bragg grating. The image was taken by a confocal laser-scanning microscope (Olympus

LEXT). The trench observed in this image has a size of 5 x 0.6µm² (width x depth) and results from an increased etching rate in the area of the waveguide, where the silica is damaged by the intense UV radiation during the writing process. This differential etching rate also reveals the fine grating structure, allowing determination of the grating period of this particular sensor to be 530nm.

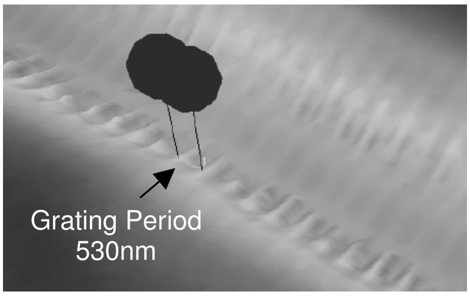

Figure 2: Topology of the sensing window in the area of the waveguide as measured by confocal laser scanning microscopy. Both the waveguide and the Bragg grating can be resolved. The grating period is determined to be 530nm for this sensor (marking points).

Experimental results

As the RI of the analyte approaches that of the core, the evanescent field of the guided mode penetrates stronger into the analyte and losses its guidance. Figure 3 shows exemplarily the dependence of the Bragg wavelength on the composition (effective refractive index) of both, aqueous ethanol solutions and a binary ethanol/toluol system. In the RI range of 1.32-1.36 the Bragg wavelength increases with increasing ethanol content with a sensitivity of averaged 138nm/riu and, taking into account the spectral resolution of the Braggmeter, with a minimum detectable index resolution of $7.25 \cdot 10^{-6}$. Within the ethanol/toluol system higher refractive indices can be accomplished. As the evanescent field of the guided mode in the waveguides penetrates stronger into the analyte with increasing RI, the index resolution rises up to $4.33 \cdot 10^{-6}$ for this binary system.

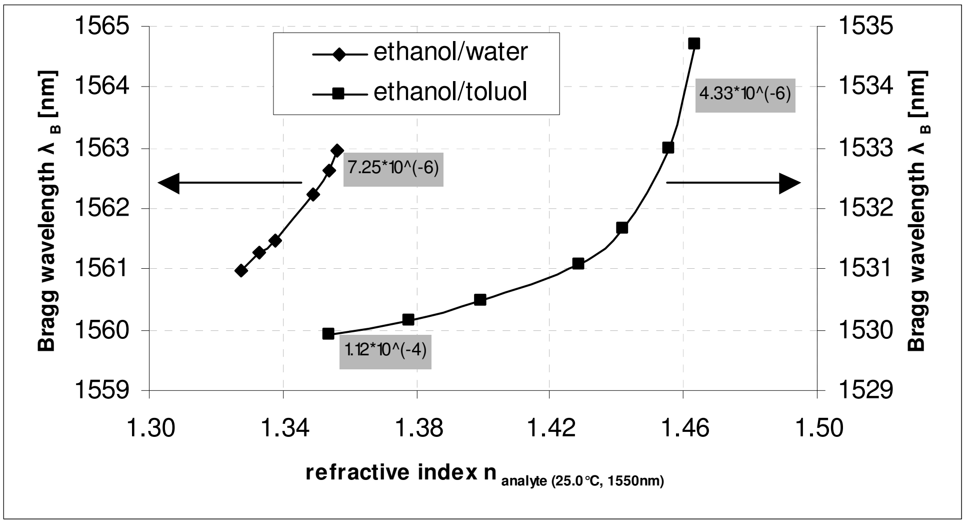

Figure 3: Bragg wavelength versus refractive index of the analyte.

The nearly instantaneous response of the sensor system on changes of the composition of the analyte in a closed fluidic system is demonstrated in figure 4, where the methanol content in an aqueous methanol solution has been increased step-wise by 10% every 100 seconds. This increase of the methanol content is associated with a sharp increase of the reflected Bragg wavelength. When the composition of the solution is balanced, the signal remains stable with a high signal-to-noise ratio (the wavelength varies by ≤ 4pm), revealing no significant cross sensitivity (for data analysis the temperature cross sensitivity can be referenced by the second Bragg grating). The inset of figure 4 depicts the change of the water content from 50% → 60% → 70% in methanol. As it is shown in figure 5, the Bragg wavelength (effective RI) has a maximum in this range with a change in the Bragg wavelength of less than 30pm. However, as the inset of figure 4 clearly reveals, the sensing system is capable to resolve this variation.

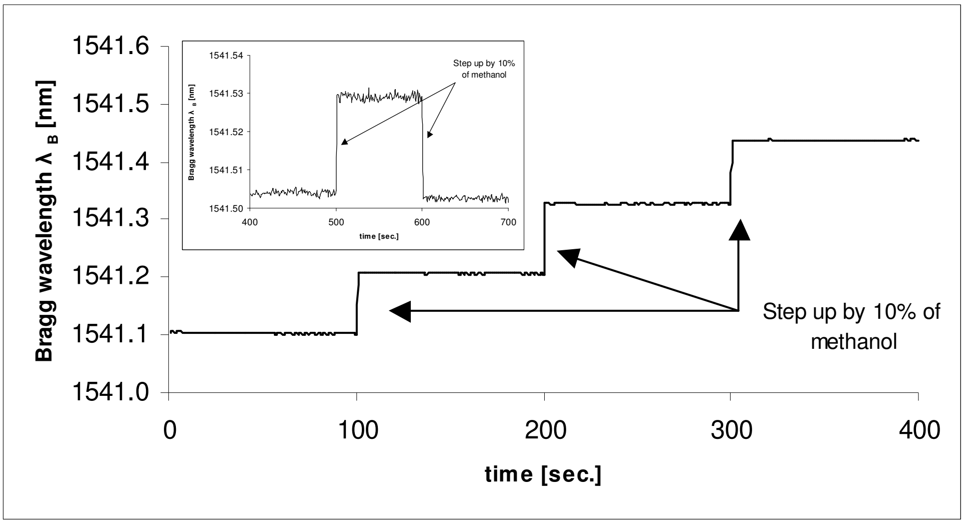

Figure 4: Change of the Bragg wavelength upon step-wise increase of methanol content in aqueous solution. The inset depicts the small variation of λ_B around the maximum of the refractive index.

The variation of the Bragg wavelength upon changes in the composition of the aqueous solution is shown in figure 5 over the entire range between pure water (0% methanol) and pure methanol (percentage given in % w/w). The Bragg wavelength initially increases with increasing methanol content, having a maximum at about 60% methanol content and decreases with further increase of methanol. This nonlinear dependence of the RI and water content is a result of the volume contraction occurring in aqueous solutions of smaller monoalcohol molecules. This behaviour has recently been reported in a theoretical and comparative study by Herráez et *al.*, who showed that the excess molar volumes in monoalcohols and water mixtures is negative.[14] Calculating the refractive index of the mixtures according to the Gladstone-Dale formula revealed that the RI of binary monoalcohol-water solutions is strongly nonlinear, showing a maximum for methanol at a mole fraction around 0.63.

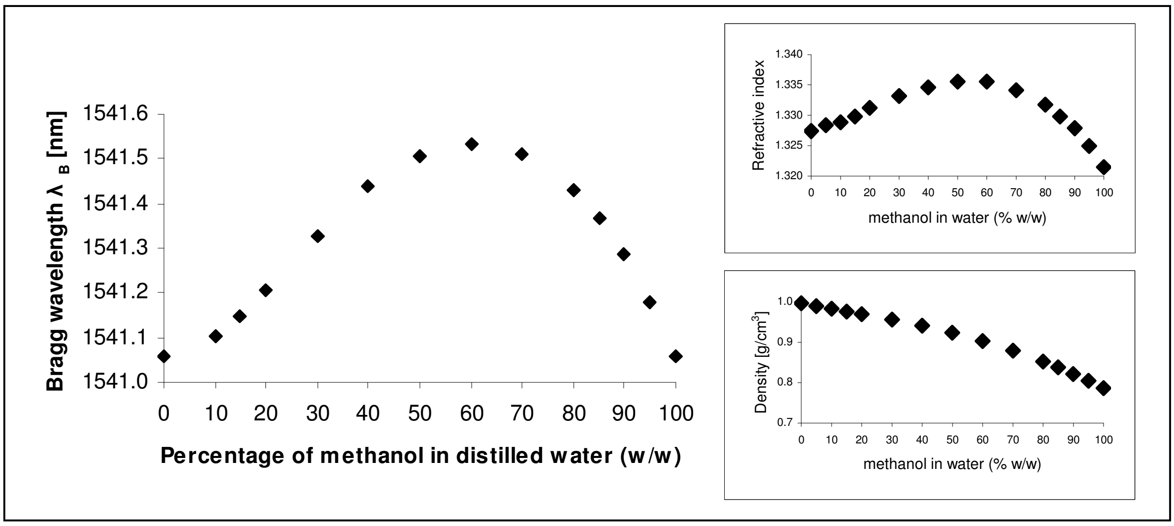

Figure 5: Bragg wavelength (effective RI) versus composition of distilled water and methanol (% w/w). The insets show both the refractive index and density.

The insets of figures 5 show both the variation of the RI and the density of the solvents. The refractive index reveals qualitatively the same behaviour as the Bragg wavelength (effective refractive index), showing a nonlinear dependence and a pronounced maximum around 60% w/w. Differences in the relative values between pure water and pure methanol can attributed to the fact that, firstly the planar Bragg grating refractive index sensor under study interrogates changes in the effective refractive index while the refractometer determines the refractive index. Secondly, both systems access (slightly) different wavelengths. However, the entire set of data (refractive index and density) is in full agreement with the theoretical work of Herráez et *al.*
Studying aqueous solutions of methanol, ethanol, isopropanol and 2-butanol reveals that the maximum of the effective refractive index shifts in case of ethanol towards higher content of the solvent and disappears in monoalcohols with more carbon atoms in the chain (e.g. isopropanol and butanol), as predicted by Ref. 14.

As for industrial applications, e.g., drying of ethanol, the water content has to be monitored, in general, over a smaller range of water content, figure 6 details the variation of the Bragg wavelength in the range of 95.5 - 100% w/w ethanol/water. The total shift of the Bragg wavelength in this range is on the order of 50pm, which can be clearly resolved. Measuring the entire range of water content from 0 - 100% w/w we have estimated a sensitivity of up to 138nm/riu, corresponding to a minimum detectable index resolution of up to $7.3 \cdot 10^{-6}$ for water contents up to 60% w/w, whereas for a water content above 85% w/w, which corresponds to an area where the Bragg wavelength decreases with increasing water content, the sensitivity is on the order of $3.8 \cdot 10^{-5}$.

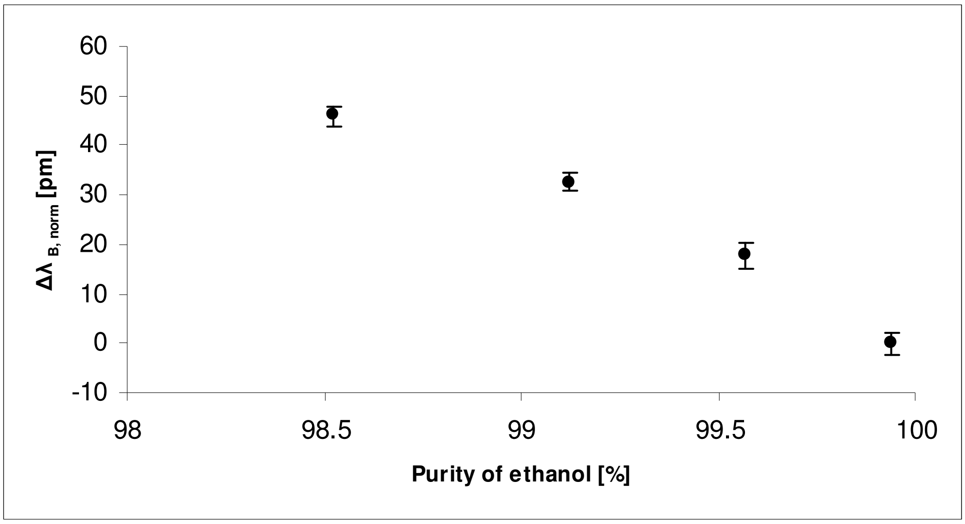

Figure 6: Change of the Bragg wavelength upon water content in aqueous ethanol solution.

Measurements on other solvents confirm the high selectivity and sensitivity of the sensor. For isopropanol the minimum detectable index resolution is $1.6 \cdot 10^{-5}$ (up 60% w/w isopropanol/water) and $6.5 \cdot 10^{-6}$ (60-100% w/w), respectively. In case of aqueous 2-butanol solutions the minimum detectable index resolution varies between $1.6 \cdot 10^{-5}$ for lower refractive indices and $1.5 \cdot 10^{-6}$ for higher refractive indices (please note that 2-butanol is not soluble in the entire range between 0 and 100% water).

Beside monoalcohols, Tetrahydrofuran has been studied which is an important solvent, e.g., in the production of polyvinyl chloride, polystyrene, varnish and adhesives. Figure 7 shows the dependence of the Bragg wavelength on the composition of an aqueous Tetrahydrofuran solution. Similar to the behaviour in aqueous monoalcohol solutions, λ_B increases with increasing water content, following the trend of the refractive index. The minimum detectable index resolution reaches a value of $4.4 \cdot 10^{-6}$ in the range of higher water contents (>60%) and has a value of $1.0 \cdot 10^{-5}$ at lower water contents.

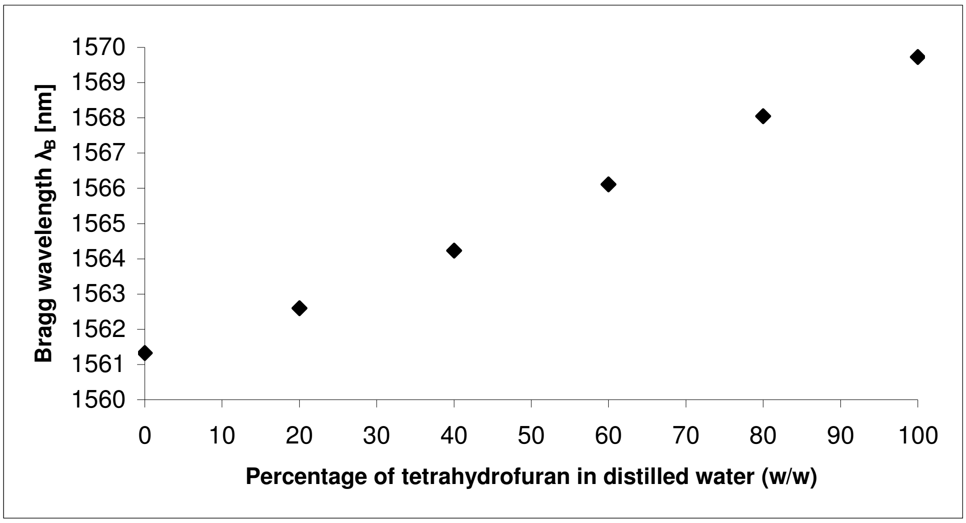

Figure 7: Change of the Bragg wavelength upon water content in aqueous tetrahydrofuran solution.

Summary

In summary, we have evaluated a planar Bragg grating refractive index sensor for online process control of the water content in organic solvent. Our results clearly show the potential of the transducer system as a highly sensitive and selective sensor. The application potential of the sensor has been demonstrated by measuring selected examples from the chemical and pharmaceutical industry.

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