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α-Cyclodextrin Functionalized Planar Bragg Grating Sensor for the Detection of Small Arene Traces in Solvent Vapour

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Abstract:
We report on an optical sensor system, which is highly sensitive to small traces of arenes in solvent vapour. The sensor system is based on a planar Bragg grating refractive index sensor which is sensitised towards arenes by applying a thin layer of substituted α-cyclodextrins to the sensor surface by dip coating. In our studies using benzene as a representative of arenes, the dependence of the spectral shift of the reflected Bragg wavelength on variation of the benzene concentration was found to 8 pm/100 ppm. Considering the spectral resolution of the interrogation system with reliable signal identification, this leads to a minimum detectable benzene concentration of 75 ppm.

Key words: Bragg grating, refractive index sensor, aromatic hydrocarbons, host-guest interaction

Introduction

Arenes are commonly used as a solvent and a component of pesticides and insecticides, whose use can cause an increased pollution to agricultural and urban areas [1, 2]. Analysis systems for gas detection are commonly based on electronic components, which usually allow their application in potentially explosive atmospheres only under an appropriate added expense. In this respect, optical sensor systems represent a perfect alternative, as they are characterised by low signal attenuation, high sensitivity with simultaneous non-emission and non-sensitivity to electro-magnetic fields which recommends their usage in potentially explosive atmospheres.

In this study, we therefore used an optical planar Bragg grating (PBG) refractive index sensor, which is sensitive to its immediate vicinity. Accordingly, it is possible to significantly increase the sensitivity against a certain analyte by a respective modification of the sensor surface. The special design and its associated properties offer a highly sensitive sensor system which has been used in previous studies i.a. for the analysis of liquid media [3, 4] and DNA hybridization [5].

Experimental

The sensor used in these studies is based on a silica on silicon multilayer structure, in which a periodic perturbation of the refractive index was written into the cladding sheathed core using direct UV writing method. Through partly removal of the cladding above the Bragg grating structure, the evanescent field of the guided mode is initiated to penetrate into the immediate surrounding medium leading the sensor to act as a refractive index sensor (figure 1). Further details of the PBG sensor structure and its fabrication have been published by the authors and others in [3-6].

The inscribed Bragg grating causes a wavelength selective reflection (referred to as the Bragg wavelength λ_B), which is depending on the lattice spacing and the effective refractive index, combining the material and environmental refractive indices. In order to account any temperature caused cross-sensitivity, a second and unaffected reference grating is inscribed.

To sensitise the sensor against arene, ethyl substituted α-cyclodextrines are immobilised to the sensor surface by dip coating. Cyclodextrin are cyclic oligosaccharides with a hydrophilic exterior and a hydrophobic cavity and are therefore a suitable candidate to form inclusion complexes with non-polar lipophilic solvents such as aromatic hydrocarbons [7, 8]. To confirm the coating, the spectral shift of λ_B is monitored during the process.

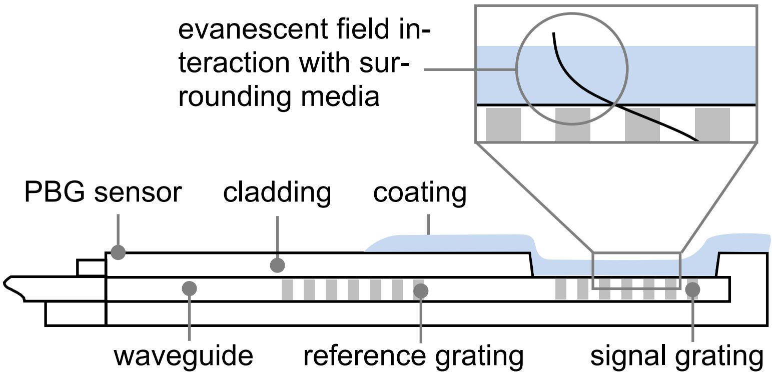

Fig. 1: Principle of the used planar Bragg grating refractive index sensor interacting with its surrounding media.

Benzene, a volatile organic compound, composed of six carbon atoms in a ring is the parent compound of most aromatic hydrocarbons and used in this experiment as a representative for arenes. It is applied as analytically pure material and employed as purchased. In the experiments, the analyte is exposed to the sensor surface by the use of a fumigation system based on the principle of dynamic saturation method, whereby a complementary gas (in this experiment nitrogen) is brought into contact with the condensed phase of the analyte at a certain temperature to ensure saturation condition. By diluting the saturated nitrogen with pure nitrogen, a defined final concentration is reached and applied to the sensor [9].

The used interrogation system by Stratophase Ltd. (SIS:Lab2) integrates a tuneable laser and an unified photo detector. The system is characterised by a spectral resolution of 2pm at a refresh rate of 2 Hz. Through multiple peak detection and tracking, the system permits monitoring the shift of the reflected wavelength λ_B and therefore the time-based response of the sensor system.

To verify the response of the interrogation system, the analyte concentration was increased stepwise with intermediate washing of pure nitrogen. The respective change of the reflected wavelength is then recorded by the measurement system SIS:Lab2.

Results and discussion

The response of the sensors is expressed in a shift of the intensity maxima of the reflected wavelength λ_B.

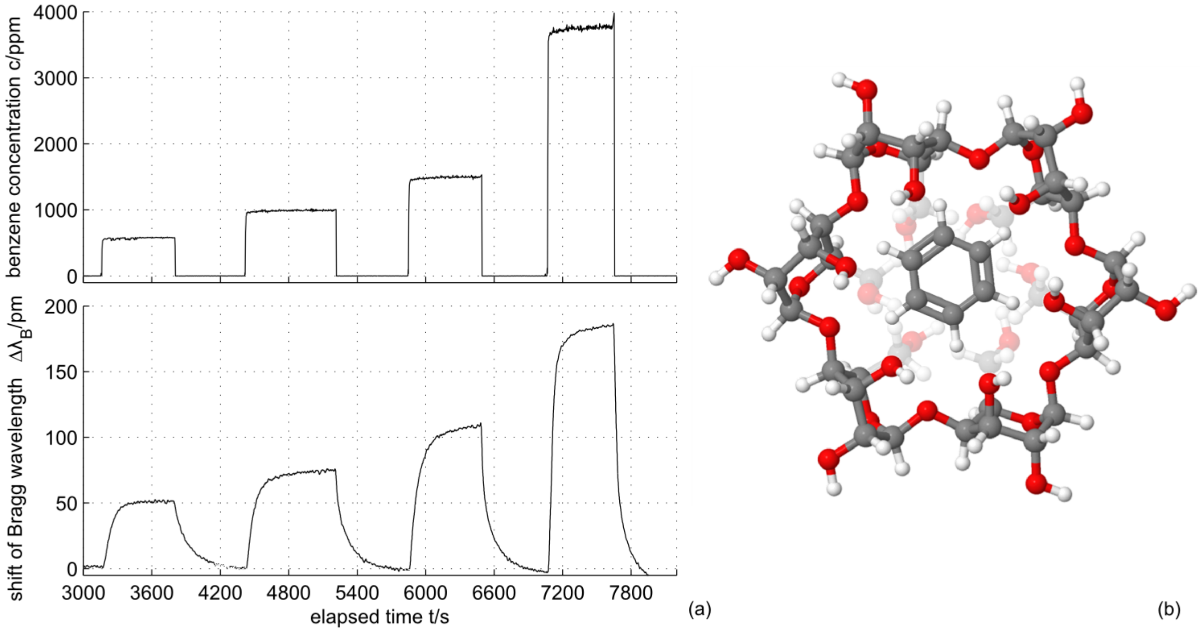

Fig. 2: (a) Variation of the benzene concentration (upper graph) in comparison to the Bragg wavelength shift (lower graph) of the α-cyclodextrin coated sensor. (b) Molecular representation of an inclusion complex formation of benzene in alpha cyclodextrin.

Figure 2 shows the response of the sensor coated with hexakis(2,3,6-tri-O-ethyl)-α-cyclodextrin to varying concentrations of benzene in solvent vapour.

The overall shift of λ_B was found to increase with increasing concentration of the analyte and decreases with decreasing its concentration, respectively. For each analyte concentration, the temporal response is characterized by an initial sharp rise of the Bragg wavelength followed by a slower multi-exponential shift towards an equilibrium state. The decrease to the initial unexposed value indicates the reversibility of the sensor system.

In our studies a linear relationship between the analyte concentration and the sensor response could be identified, where the sensitivity was found to 8 pm/100 ppm. Based on these findings and under consideration of the spectral resolution of the interrogating system of 1 pm, acquisition steps of 12.5 ppm are predicted. However, a reliable evaluation of the analyte concentration is assumed when the condition $\Delta\lambda_B \geq 3 \cdot \sigma$ is fulfilled. The standard deviation of the interrogation systems background noise σ was found to 2 pm. In this respect, we find a minimum detectable benzene concentration of 75 ppm.

These findings testify the ability of the system to be highly sensitivity against arenes such as benzene at the sensor surface sensitized with allylated cyclodextrin. The high sensitivity, the quasi-instantaneous response and the reversibility of the system show the suitability of this sensor structure as a sensor for arenes.

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