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Allylated cyclodextrins as effective affinity materials in chemical sensing of volatile aromatic hydrocarbons using an optical planar Bragg grating sensor

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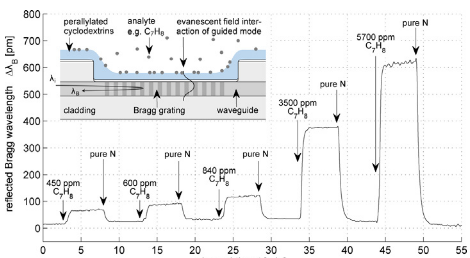
GRAPHICAL ABSTRACT



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ABSTRACT

We report on the application of perallyl-substituted α-, β- and γ-cyclodextrins to an optical planar Bragg grating refractive index sensor for the effective sensitization of the sensor for airborne volatile aromatic hydrocarbons. Thereby, the emphasis of this work lies on the comparison of the different cyclodextrin types regarding their suitability as affinity material assessed by the sensors sensitivity and response behavior. The opto-chemical sensor device showed an immediate and quick response to the application of the investigated analytes benzene, toluene and *m*-xylene as well as a linear dependence on the concentration of those analytes. Studies on the sensors sensitivity depending on the applied cyclodextrin types revealed a generally higher sensitivity for the sensor sensitized with perallyl-substituted β-cyclodextrins. Here, the sensor systems detection limit was found to 60 ± 4 ppm for benzene, 18 ± 3 ppm for toluene and 3.8 ± 0.5 ppm for *m*-xylene. The response time and recovery time were found to approximately 30 s and 40 s, respectively, depending on the applied cyclodextrin and the chosen analyte.

1. Introduction

The early detection of harmful substances could be decisive for the health and physical integrity of a human being. Especially in the gas phase some substances pose an enhanced risk since they may be potentially explosive, corrosive or hazardous and are not always noticeable by the human senses. Within the list of hazardous compounds volatile aromatic hydrocarbons (VAHs) are a frequently named group of chemicals with diversified effects to the human body. A short-term exposure to some VAHs could therefore lead to irritation of the respiratory system and the eyes, may cause headache, dizziness and at higher levels even death [1–3].

Therefore, the necessity of an early detection of those hazardous substances is of significant importance. Accordingly, the requirements to a respective VAH sensitive sensor system are huge. Beside a high sensitivity and reliability the system has to respond in real time and should provide a low detection limit. In this respect, optical sensor systems represent an adequate technology that meets

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these high standards while complementing the possibility of a low attenuated remote diagnosis as well as non-emission and non-sensitivity to electromagnetic fields. The optical sensor system used in this study is based on an optical planar Bragg grating (PBG) structure, wherein the guided mode interacts with the immediate vicinity above the grating structure resulting in a refractive index sensitive sensor. To enhance the sensitivity of the system, the sensitive region of the sensor is coated with cyclodextrins, a conical molecular formation of glucose units, which is well known to form inclusion complexes with aromatic hydrocarbons [4–6]. By this measure, the VAHs temporarily dwell on the surface leading to an enhanced interaction of these molecules with the sensor.

Accordingly, this study discusses the ability of different perallyl-substituted cyclodextrins as an affinity material in the opto-chemical sensing of volatile aromatic hydrocarbons at an optical planar Bragg grating refractive index sensor. Therefore, the study evaluates, compares and discusses the influence of the most common cyclodextrin types α, β and γ on the sensitivity and response behavior of the sensors sensitized by the respective affinity materials.

2. Experimental

2.1. Reagents

2.1.1. Affinity material

Many sensor platforms are not sensitive to small traces of VAHs. This also applies for the used PBG sensor system. However, those sensor systems can be sensitized by applying a suitable affinity material to their sensitive area. In this study, perallyl-substituted cyclodextrins were applied to the PBG sensor system by dip coating.

Cyclodextrins are cyclic architectures of glucose units which are obtained by the enzymatic degradation of starch. They are among the best known and best studied host components of the host–guest chemistry, whereat a host–guest complex is defined by a non-covalent binding of two or more molecules of unique structure, mainly caused by van der Waals forces [7]. In their construction, cyclodextrins are composed of several D-glucopyranoside units connected by a α-1,4-glucosidic linkage. The amount of the glucose units determines whether it is a α- (six units), β- (seven units) or γ-cyclodextrin (eight units), and thus has an effect on the cavity diameter of these cyclodextrins (Fig. 1) [8,9].

The specific arrangement of the glucopyranoside units leads to a hydrophilic exterior and hydrophobic interior of the torus like architecture and gives the cyclodextrins a water solubility and the ability to form inclusion complexes with non-polar and hydrophilic molecules. Therefore, cyclodextrins are well known to form inclusion complexes with aromatic hydrocarbons such as benzene, toluene and xylene [4–6].

In this study, the hydroxyl groups of the cyclodextrins have been substituted by *O*-allyl fragments in order to obtain a highly viscous and more coating-suitable material named (2,3,6-tri-*O*-allyl)-cyclodextrin. The required synthesis was performed at room temperature by the method of Leydet et al. where the cyclodextrins are treated by an excess of sodium hydroxide and allylchloride in dimethyl sulfoxide. The structure and purity were confirmed by ^{1}H NMR spectroscopy [10].

2.1.2. Analytes

To investigate the sensitivity of the PBG sensor system toward volatile aromatic hydrocarbons, benzene, toluene, and *m*-xylene were used as representative analytes. The analytes were used as analytically pure materials and employed as purchased by Carl Roth GmbH +Co. KG.

2.2. Apparatus

2.2.1. Sensor chip

The sensor chip used in this study is composed of three silica (SiO_2) layers, which are grown on a silicon wafer (Fig. 2), where the middle layer is germanium doped and therefore photosensitized. In this layer a waveguide as well as several refractive index perturbations are inscribed resulting in so called Bragg grating structures, which serve as dielectric mirrors for a specific wavelength according to Eq. (1).

$$\lambda_B = 2 \cdot n_{\text{eff}} \cdot \Lambda \tag{1}$$

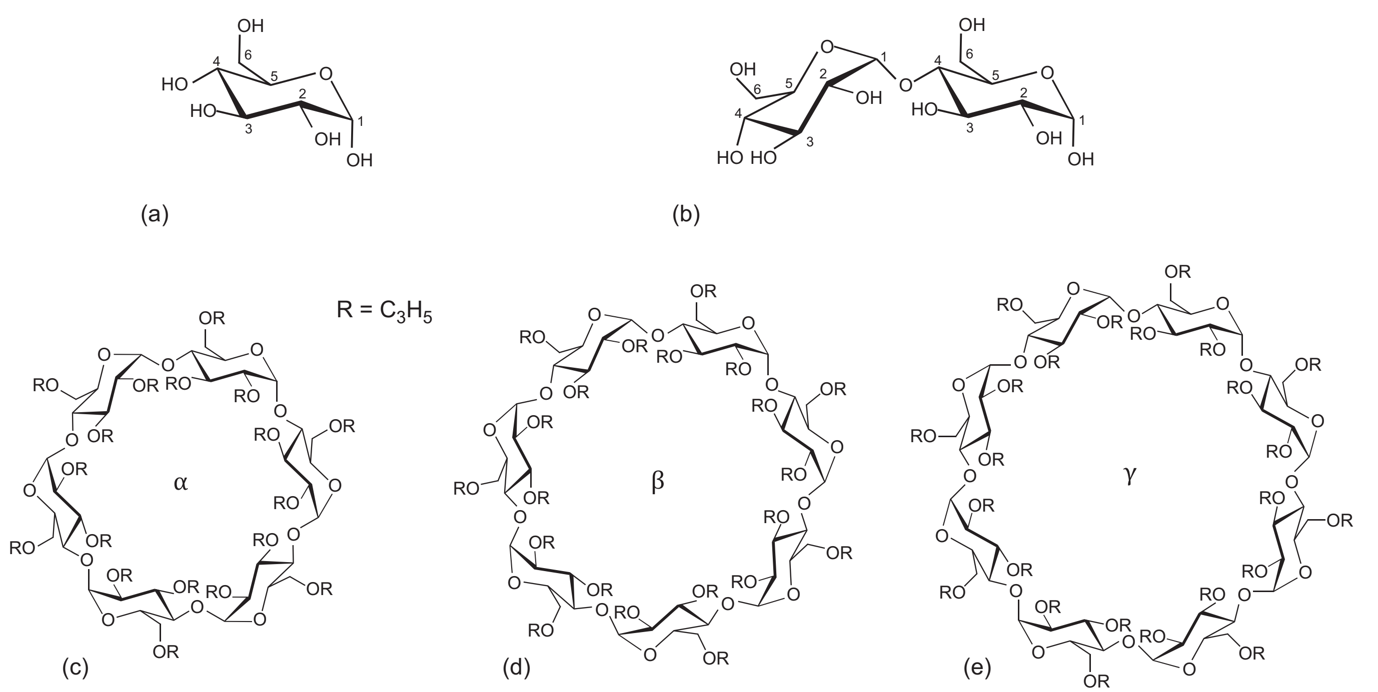

Fig. 1. Representation of a monosaccharide (a), its glycosidic linkage (b) and the perallylated α-cyclodextrin (c), β-cyclodextrin (d) and γ-cyclodextrin (e).