Abstract. Here we report in detail on the design and application of novel evanescent wave fiber-optic sensors based on multimode PMMA optical fiber coated with ion-selective optode membrane and in analogy with ion-selective electrodes called ion-selective fiber (ISF) optodes. Unlike for conventional silica multimode optical fibers, the absorbance of the cladding of ISF follows Beer-Lambert law. ISF absorbance spectra are very similar to that of conventional planar membranes and, therefore, could be treated in the same well-established manner. The greatest advantages of proposed ISF optodes include a good optode membrane adhesion to inert support/waveguide, possibility of optode use in nontransparent and colored solutions, as well as easy assembly and handling. We present a complete theoretical description of absorbance/transmittance of ISF based optodes, discuss parameters useful for ISF optode design, and demonstrate and discuss the experimental proof of the concept.

Introduction

The advantages of fiber optic for preparation of chemical sensors have been recognized as early as in 1970-80s and the major advantages named were its great potential for sensor miniaturization (as low as 125 um), chemical inertness and low cost of the fiber material, insensitivity to electric (field) perturbations, and possibility of remote sensing. Optical fibers (OF) used for fabrication of chemical sensors were so far based on conventional multimode silica optical fibers. Most fiber optodes configurations had the sensing element either placed at the distal end of the fiber or replaced partially removed cladding. The fiber was then used to interrogate a variation of absorbance, fluorescence, or refractive index of the sensing element using OF as an inert light transmitter.

Moreno et al. reported on a multimode silica FO sensor with a partially removed cladding replaced with Bromocresol Purple (BCP) containing Tecoflex® membrane. The sensor is provided with a mirror at a distal end of the fiber and is interrogated in transmission mode using white light source and CCD spectrometer. Interestingly, the shape of the spectra recorded for BCP in acidic form is very similar to that reported for this dye in solution, whereas the basic band recorded in the presence of ammonia is heavily deformed. Moreover, it appears that the rise of basic band (600 nm) is not accompanied by decrease of the corresponding acidic band. The obtained calibration curve is similar to that reported in [MacCraith] and indicates deviation of optode absorbance from Beer-Lambert law. Spichiger et al. introduced optodes with transducing elements based on multiple internal reflections (MIR) in a waveguide covered with sensing membrane of lower refractive index. The sensing membranes were conventional plasticized PVC bulk optode membranes that demonstrated their usual well-know behavior. The sensors realized in this fashion employ waveguides prepared from sapphire [], LaF_3 [], glass [], and even plastic foil (PEN or PET) []; in [Hisamoto] the sensing coating itself served simultaneously as a sensing element and a waveguide. Most of these sensors were interrogated using monochromatic light sources. They were merely characterized by signal variation dependence on target analyte concentration, reversibility and response time. The absorbance spectra of these optodes, when reported [], yielded spectra series with characteristically non overlapping isosbestic point ascribed to a variable evanescent wave penetration depth and variable effective path length of the guided light wave []. Puyol et al. developed optodes similar to that described in [Hisamoto]: the sensing membrane acts not only as a sensor element but also as a waveguide []. In proposed optode design, light passes through the membrane connecting two spatially separated waveguides. The construction enables light to avoid interaction with the sample in contact with the sensing membrane and permits optode measurements in colored and turbid samples.

Bulk optodes constructed without use of optical fiber most often look like a thin (2-10 um) colored thin films deposited on transparent glass support mounted in a flow-through cell and interrogated in transmission mode []. Major disadvantages of such construction are poor adhesion of optode films to glass and limitation of the application to transparent and colorless solutions. Although the latter could be compensated using an appropriate reference solution & membrane, it is quite tedious and complicated for practical applications. Recently introduced micro-spheres optodes [], based on essentially the same membranes as bulk optodes make use of fluorescent properties of the chromoionophores doped in the membrane, therefore overcoming both abovementioned limitations of bulk optodes.

Here we present in detail a new concept of optode construction based on multimode PMMA optical fiber that eliminates most disadvantages of earlier proposed optodes with MIR transducing elements. The proposed optode construction has a simple assembly and is extremely robust: it is highly insensitive to light injection angle, precision of the optode membrane thickness, variation of the changes in the refractive index of the sample with concentration, and the color and turbidity of the measured sample.