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Europium(III) ion detection in water by a new luminescent optical fibre sensor

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Abstract:
A new europium(III) luminescent optical fibre sensor based on a tridentate bis(phosphinic amide)-phosphine oxide $PhPO(C_6H_4POPhN(CH(CH_3)_2)_2)_2$ is described. The ligand was successfully immobilized on PVC membrane on optical fibre by dip coating technique. The reaction between europium(III) ion and ligand produced a strong luminescent complex of stoichiometry [1:2], which possessed a maximum emission peak at 612 nm. The sensor luminescence response showed an exponential behavior versus logarithmic concentration of europium(III) ions (10^{-8} - 10^{-3} M) in aqueous solution with a correlation factor of R^2 = 0.9918, and an acceptable response time (t_{90}-t_{10}) of 92 seconds. This optode is the first luminescent optical fibre sensor for detecting europium(III) ions in water.

Key words: Optode, Europium (III) ions, Luminescence, Dip Coating, Plastic Coating.

Introduction

It has been demonstrated that rare earth elements (REEs) provoke alterations and damages in animals [1]. Furthermore, REEs can accumulate in humans producing liver damage and lung embolisms when they are inhaled during long-term exposure in working environment. Europium is an important member of REEs, which is used as component in fluorescent lamps, lasers, ceramics and catalysts for oil and nuclear industries. Lastly, the growing increase in dumping, toxic properties and adverse effects of europium has encouraged the need of its determination [2].

The combination of the advantages of optical sensors and the excellent properties of optical fibres together with the sensitized luminescence of lanthanides and the great characteristics of polymer inclusion membranes has been successfully employed for the development of the sensor.

Experimental

The sensitized 4f-luminiscence of lanthanides [40] technique is widely used for the trace determination of europium(III) ions [3]. Europium(III) ion presents a photophysical and coordination chemistry for the formation of luminescent complexes, showing high Stokes shift, long luminescence lifetimes and narrow band emission spectra. The sensing element used in this work (Fig 1) reacts with Europium (III) ions forming a complex that absorbs energy from UV-visible radiation at the characteristic wavelengths of the sensing material, emitting in the visible region to the characteristic emission wavelengths of europium(III).

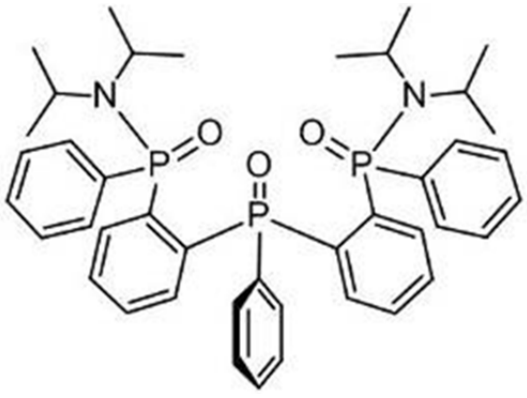

Fig. 1. Chemical structure of the sensing material.

The deposition solution was prepared by stirring of a mixture of 89 mg of PVC, 174 mg of bis(2-ethylhexyl) sebacate, 4 mg of ligand and 4.0 mL of THF [4]. Once this membrane cocktail was prepared, it was always kept in refrigerator until its immediate use.

The optical fibre was cut perpendicularly at one end using a precision fibre cleaver; thereafter, a 2 cm long part of the cladding was removed. Finally, this segment was cleaned with absolute ethanol for eliminating dirtiness and impurities.

Once the (200/230 μm) multimode plastic-clad silica optical fibre was prepared, it was dipped into the deposition solution for 1 second and pulled out at a fixed speed of 11 mm/s using a dip coater. The pull out speed was fixed at 11 mm/s in all the depositions. Then, the coated optical fibre was treated at 80 ºC during 15 minutes, followed by a cooling stage of 5 minutes at room temperature [5]. This process was repeated as many times as number of layers were to be deposited.

The sensor response was registered immersing firstly it in 25 mM hydrogen phthalate buffer solution at pH 5.0 during 10 minutes for recording the baseline. Subsequently, it was gradually immersed in different europium(III) standard solutions (10^{-8} – 10^{-3} M of Eu^{3+} in the mentioned buffer solution) during 10 minutes. After each immersion, the luminescence intensity of the sensor was measured at $\lambda_{exc/em}$ = 254/612 nm.

Results

The optimum number of deposited layers was five and its estimated deposition thickness was 284 ± 40 nm. Fig. 1 demonstrates that the buffer solution did not have influence on the sensor response and the appearance of the three emission peaks tallied with the characteristic line-type bands of europium(III) ion in the formed luminescent complex [1:2]. The maximum emission peak was observed at 612 nm.

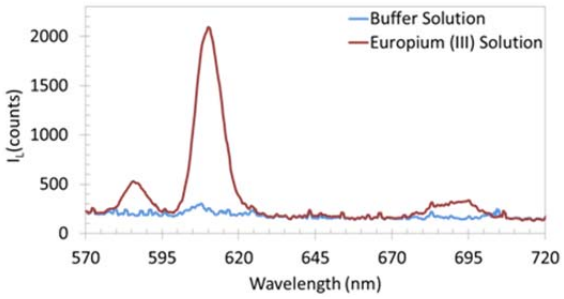

Fig. 2. Luminescence spectra from the optimized optical fibre sensor at two different cases: after immersion in the buffer solution (blue line) and after immersion in 10^{-4} M of Eu^{3+} in the buffer solution (red line). Integration time of 1500 ms and average of 4.

The sensor response was considered as the difference between the luminescence intensity of the sensor before and after exposure to europium(III) ion. It followed an exponential behaviour versus the logarithmic concentration of europium(III) ions from 10^{-8} to 10^{-3} M of Eu^{3+} (five orders of magnitude) with very high correlation coefficients in both configurations. Fig. 3 depicts the sensor response for different europium(III) ion concentrations in aqueous solution.

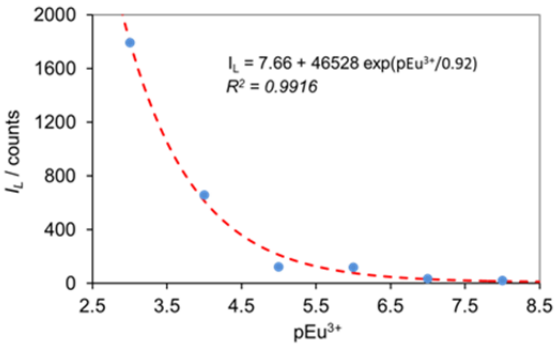

Fig. 3. Calibration graph of the europium(III) optical fibre sensor. The europium(III) solutions ranged from pEu^{3+} 3 to 8 (10^{-3} M to 10^{-8} M concentrations, respectively) in the buffer solution. λ_{em} = 612 nm, integration time of 5000 ms and average of 3.

The approximation correlation coefficient R^2 = 0.9918, which opens the possibility of having an alarm sensor for the detection of europium(III) ions in environmental samples. The response time was also studied: Fig. 4 shows the dynamic response of the sensor when it was immersed in 100 μM europium(III) solution. The response time obtained was 92 seconds.

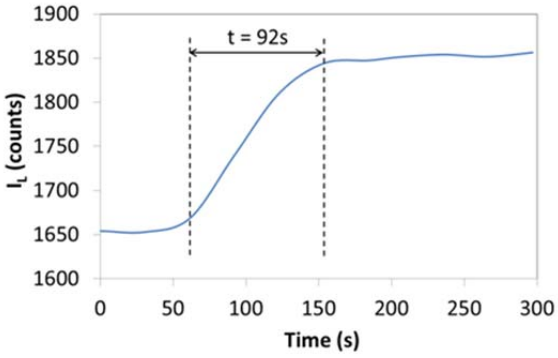

Fig. 4. Temporal response of the sensor with [Eu^{3+}]= 1.0 x 10^{-4} M. The measurements were performed integrating the luminescence intensity between 605 and 615 nm.

Conclusions

An optical fibre probe based on the sensing material immobilized on a PVC membrane has been used for detecting europium(III) ions in water. Dip coating technique was followed to deposit the sensing material on the optical fibre. The number of fixed layers was optimized to five: its thickness was 284.4 ± 39.8 nm. The luminescence measurements were made at $\lambda_{exc/em}$= 254/612 nm. The luminescence probe showed an exponential behaviour versus

concentration of europium(III) ions from 10 nM to 1 mM: response time shorter than 2 minutes.

The development of this type of probe is a potential alternative for environmental monitoring. The sensor is small, easily prepared, and stable. It could be used as an alarm type sensor for detecting the presence of europium(III) ions in water.

Acknowledgements

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