

# OPTIMIZATION STUDY OF A FLUORIMETRIC SENSOR FOR DETERMINATION OF DISSOLVED OXYGEN IN SALINE AND NO-SALINE WATER, BASED ON THE TiO<sub>2</sub>-PHOTOCATALYTIC OXIDATION OF 2-ACETYL-PYRIDINE PICOLINOYL-HYDRAZONE

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**Abstract** – A fluorimetric sensor has been developed for determination of dissolved oxygen in natural waters. The sensor is based on the photooxidation of 2-acetylpyridine picolinoylhydrazone (APPH) using oxygen and TiO<sub>2</sub> as the catalyst. Firstly, the reaction mechanism has been studied. Secondly, an instrumental system for the determination of oxygen dissolved in water has been developed. Finally, the results obtained were validated by comparison with the Clark method.

**Keywords** – Oxygen, seawater, photocatalyst, fluorimetric, sensor

## INTRODUCTION

Oxygen concentration is closely related to many important chemical and biochemical reactions. Optical sensors have been developed as an alternative approach for O<sub>2</sub> sensing. Several complexes with O<sub>2</sub>-sensitive fluorescence characteristics have been used for the development of oxygen sensors measuring their fluorescence intensity or lifetime. Usually these optical oxygen sensors are based on collisional quenching by molecular oxygen of a fluorophore embedded in a support matrix [1].

The photocatalytic oxidation of organic compounds in water has received much attention and TiO<sub>2</sub> is used as a heterogeneous photocatalyst for this purpose. TiO<sub>2</sub> is photoactive in the UV region (<400 nm) and is currently considered the most promising catalyst for air and water photocatalytic decontamination. Water and oxygen molecules are considered necessary for the photooxidation process. For aqueous TiO<sub>2</sub> suspension system, it is believed that the <sup>•</sup>OH radicals from hole-trapping by surface hydroxyl groups are the primary oxidizing agents, and oxygen is a scavenger for photogenerated electrons [2].

## TiO<sub>2</sub>-APPH SENSOR AND DISSOLVED OXYGEN DETERMINATION

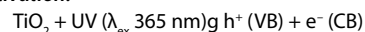
### A. Nature of the reaction

In the present study, an analytical methodology is developed to quantitatively determine the dissolved oxygen (DO) involved in the process of photooxidation of 2-acetylpyridine picolinoylhydrazone (APPH), using TiO<sub>2</sub> as the catalyst. The reaction yields a fluorescent product which is read at 445 nm with excitation at 365 nm. APPH was prepared by condensation of equimolar amounts of acetylpyridine and picolinoylhydrazide in absolute ethanol. The white product was filtered and recrystallized from ethanol [3]. APPH forms coloured systems with V(V), Ni(II), Co(II), Fe(II, III). Only the reaction with Ti(IV) gives rise to a fluorimetric system.

All attempts to find a stoichiometric relationship between Ti(IV) and APPH failed, because the fluorescence is not due to the formation of a chelate. Further experiments have shown that aerial oxidation of the APPH occurs being catalysed by Ti(IV); in the photooxidation, oxygen acts as an acceptor of photogen-

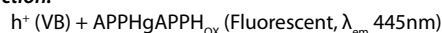
erated electrons. The proposed mechanism of the catalytic reaction is:

### Photocatalytic activation:

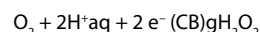


where h<sup>+</sup>(VB) and e<sup>-</sup>(CB) are a hole in the valence band and a photogenerated electron in the conduction band, respectively.

### Oxidation reaction:



### Reduction reaction:



### B. Preparation of the sensor and oxygen analysis

Before starting the calibration to determine the concentration of oxygen dissolved in water samples, the fluorimetric sensor is activated. Figure 1 shows the automatic system designed to activate the sensor and to carry out the analytical determinations. In first place, a small volume (100-300 µl) of a 40% aqueous-ethanolic solution of APPH 0.017% (w/v) and Ti(IV) 50 ppbv is injected through the solid phase of the sensor (C-18 and cationic resin). Subsequently, it is applied Milli-Q water deaerated with nitrogen, and Milli-Q water saturated with oxygen, in order to obtain the instrumental zero (fluorescence 0.0) and the fluorescent intensity equivalent to 100% oxygen saturation, respectively. Once it is obtained the corresponding regression line (fluorescence versus % dissolved oxygen), fluorescence of samples is measured using the instrumental system described. Samples and standards are pumped at a constant flow (1-3 ml/min). Preliminary results show that the proposed method exhibits good correlation with the reference method of Clark with low relative errors. Thus, at 20 °C and 1 atm of pressure, the relative errors for 10, 30, 50, 70 and 90% oxygen saturation were: -4, -0.33, -1.6, -0.71 and 0.8%, respectively (regression line: I<sub>f</sub> = 0,0923 [DO] - 0,136; R<sup>2</sup> = 0,9992).

Further experiments will be carried out using other solid phases in order to optimize the stability of the fluorimetric system and to improve the immobilization of the APPH-TiO<sub>2</sub> system with the aim of analysing a greater number of samples after the sensor activation.

## REFERENCES

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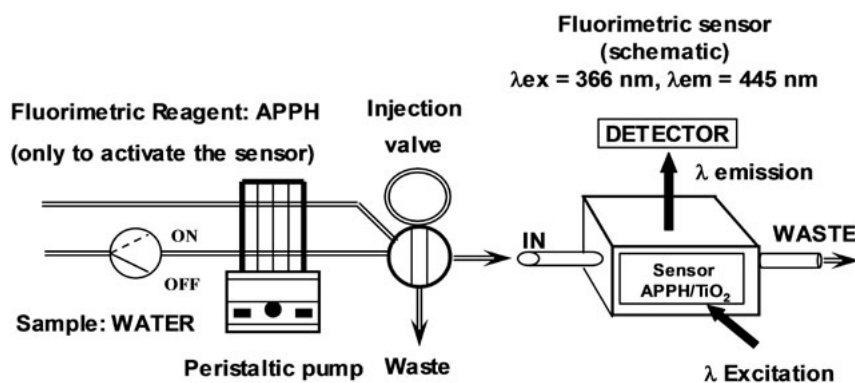


Figure 1. Manifold for continuous determination of dissolved oxygen in natural water using the proposed fluorimetric sensor.