

Manuscript Number:

Title: DETERMINATION OF O<sub>2</sub> USING COLOUR SENSING FROM IMAGE PROCESSING WITH MOBILE DEVICES

Article Type: Research Paper

Keywords: Oxygen; Optical gas sensor; Luminescence; Micro-camera; Portable instrumentation; Android; Camera phone.

Corresponding Author: Dr. antonio martinez,

Corresponding Author's Institution:

First Author: Nuria López

Order of Authors: Nuria López; antonio martinez; isabel perez de vargas; maria dolores fernandez; Miguel A Carvajal; Luis Capitan; Alberto Palma

Abstract: This paper presents a portable instrument designed and characterized for the determination of gaseous oxygen. It is based on quenching the luminescence intensity of the platinum octaethylporphyrin complex when it is excited, using a light-emitting diode (LED) with an emission peak at 380 nm. The luminescence emitted by the platinum complex is detected by taking an image with a colour CCD micro-camera integrated in the prototype which makes it possible to do a two-dimensional analysis of the luminescence. This image is processed by a microcontroller to obtain the red colour component of the RGB colour space, thus discarding any unnecessary colour information. The processing is carried out for the pixels over a large area of the sensing membrane, which allows for a statistical treatment of the obtained data. The measured R value for the membrane can be directly related to the concentration of the surrounding oxygen. The resulting instrument has been fully characterized and calibrated, including drifts due to temperature and time. In addition, an application for Android camera devices such as smartphones was developed in order to use them as detectors and image processors to provide a prediction of the gaseous oxygen concentration.

Suggested Reviewers: jongwon Park  
jp7r9@mst.edu

ANTONIO MOLINA DIAZ  
amolina@ujaen.es

Kevin Cantrell  
cantrell@up.edu

MANUEL MELGOSA  
mmelgosa@ugr.es

Otto Wolfbeis  
otto.wolfbeis@chemie.uni-r.de



## DETERMINATION OF O<sub>2</sub> USING COLOUR SENSING FROM IMAGE PROCESSING WITH MOBILE DEVICES

*N. López-Ruiz<sup>a</sup>, A. Martínez-Olmos<sup>a,\*</sup>, I.M. Pérez de Vargas-Sansalvador<sup>b</sup>, M.D. Fernández-Ramos<sup>b</sup>, M.A. Carvajal<sup>a</sup>, L.F. Capitan-Vallvey<sup>b</sup> and A.J. Palma<sup>a</sup>*

ECsens. <sup>a</sup>Department of Electronics and Computer Technology. <sup>b</sup>Department of Analytical Chemistry. Campus Fuentenueva, Faculty of Sciences, University of Granada, E-18071 Granada, Spain.

\* Corresponding author; email: [amartinez@ugr.es](mailto:amartinez@ugr.es)

### **Abstract**

This paper presents a portable instrument designed and characterized for the determination of gaseous oxygen. It is based on quenching the luminescence intensity of the platinum octaethylporphyrin complex when it is excited, using a light-emitting diode (LED) with an emission peak at 380 nm. The luminescence emitted by the platinum complex is detected by taking an image with a colour CCD micro-camera integrated in the prototype which makes it possible to do a two-dimensional analysis of the luminescence. This image is processed by a microcontroller to obtain the red colour component of the RGB colour space, thus discarding any unnecessary colour information. The processing is carried out for the pixels over a large area of the sensing membrane, which allows for a statistical treatment of the obtained data. The measured R value for the membrane can be directly related to the concentration of the surrounding oxygen. The resulting instrument has been fully characterized and calibrated, including drifts due to temperature and time. In addition, an application for Android camera devices such as smartphones was developed in order to use them as detectors and image processors to provide a prediction of the gaseous oxygen concentration.

**Keywords:** Oxygen; Optical gas sensor; Luminescence; Micro-camera; Portable instrumentation; Android; Camera phone.

## 1. Introduction

Oxygen sensing is highly demanded in many different areas where it plays an important role, ranging from environmental to life sciences and food packaging technology. Although electrochemical sensors for oxygen are broadly used for many applications, they suffer from some drawbacks [1], which justifies the growing interest in optical oxygen sensors. These sensors are based on materials that change their optical properties in the presence of either gaseous or dissolved oxygen. The most common optical properties monitored for oxygen sensing are absorption and luminescence.

Absorption-based sensors can use the change in colour, observed by eye, to offer qualitative or semiquantitative information or the change in absorbance or reflectance to obtain fully quantitative information by means of an external detection unit [2]. The chemistries used for absorption-based sensors [3] rely on: i) oxygen carriers such as oxyhemoglobin [4], myoglobin [5] or bis(histidinato) cobalt(II) [6] with different drawbacks like instability or irreversibility [7]; ii) redox systems, which typically are accompanied by problems of expense and stability and incorporate a dye, which can exist in both leuco and coloured form, along with a reducer such as a reducing sugar, some examples being methylene blue and glucose [7, 8] or 2,6-dichloroindophenol and fructose [9]; and iii) light-driven redox reactions in which a photoexcited dye, like riboflavin, is reduced by a sacrificial electron donor, like EDTA [3]. It has attractive advantages, even though it can be activated by visible radiation.

Luminescence-based sensors use the quenching by molecular oxygen of the emission from a luminophore immobilized in a permeable matrix, allowing for a more accurate measurement than the earlier absorption-based sensors and with tuneable oxygen sensitivity. However, they require instrumentation for measurement using either steady-state emission intensity or time-resolved emission lifetimes [3, 10].

A new strategy for oxygen that has received much attention in recent years is luminescence-based colorimetric sensing, in which the change in colour characteristics concomitant to luminescence quenching is used as the analytical property, thus combining the advantages of both luminescence and absorption-based devices [1].

Different examples of this type of sensor exist in the literature for diverse uses. The simplest is visual colour inspection, useful for applications like intelligent packaging. A

film containing the platinum octaethylporphyrin (PtOEP) complex and TiO<sub>2</sub> or ZnO as a scattering agent in ethyl cellulose shows a red–yellow–green change in colour when the O<sub>2</sub> concentration increases [11]. The inclusion of two luminophores (PtOEP and Pt 1,3,5-tri-(2-pyridyl)benzene complex) with different oxygen sensitivities and emission colours in the film makes detection possible across a broad range of concentrations [12]. In this respect, the paper by Evans and Douglas [2] that theoretically studies the colour space response (CIE x, y coordinates) of colorimetric luminescent films in order to model the change in colour is interesting.

Imaging devices, such as digital CCD and CMOS cameras, along with luminescent films can be used for the two-dimensional analysis of oxygen distribution which is of great interest in fields like biological and medical research.

In this respect, a colour CCD camera (RGB coordinates) has been used for luminescence intensity imaging to obtain 2-D mapping of oxygen in biological applications using both commercial O<sub>2</sub> sensor patches and lab-made photopatterned hydrogel sensor arrays based on ruthenium complexes [13,14]. A similar proposal based on PDMS films containing the platinum(II)-5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)porphyrin (Pt-TPFPP) complex affords 2-D mapping using only the R coordinate [15].

A further simplification comes from the use of conventional digital cameras to acquire the image of the sensing film. Here, the 2-D distribution of analytes such as O<sub>2</sub> in aquatic systems and sediments is performed using films containing Pt-TPFPP [16] or PtOEP combined with an antenna dye that acts as an energy donor, increasing the brightness of the day [17]. The ratio of some RGB coordinates is used for calibration purposes. The simultaneous imaging of two parameters, pH (fluorescein isothiocyanate) and O<sub>2</sub> (Pt-TPTPP), can be achieved by means of a hydrogel film containing, all as microparticles, also containing a third fluorophore (diphenylanthracene), used as a reference. The three luminophores were selected to match each of the three colour channels of the camera, thus simplifying the procedure, using the RGB coordinate ratio as a selective analytical parameter [18].

Recently, digital cameras integrated in portable devices such as tablets and smartphones have been applied as image detectors because the built-in microprocessors can be programmed to carry out the image processing necessary to determine the analyte

concentration [19, 20]. Moreover, applications for open systems such as Android can be easily programmed and implemented in many smart devices.

In previous works, the authors presented portable instrumentation for the determination of gaseous oxygen based on the quenching of luminophore PtOEP [21-23]. In this work we use CCD micro-cameras, both external and included in a smartphone, to evaluate the possibilities for oxygen sensing, and in general for chemical sensing, with highly distributed and available imaging devices.

The sensing module of the prototype consists of a LED that emits in the UV with an emission peak at 380 nm and a colour CCD micro-camera to obtain an image of the sensing film. This image is processed by the integrated microcontroller to obtain the R coordinate of the RGB colour space that matches the PtOEP emission related to O<sub>2</sub> concentration. Following the same procedure for oxygen determination, an application for Android devices was developed and implemented in a smartphone camera. It allows the user to get a photograph of the sensing luminophore under excitation conditions and process the image in order to predict the gaseous oxygen concentration.

## **2. Experimental**

### *2.1. Reagents and materials*

The chemicals used were platinum octaethylporphyrin complex (PtOEP, Porphyrin Products Inc., Logan, UT, USA), 1,4-diazabicyclo[2.2.2] octane (DABCO; 98%), tetrahydrofuran (THF) and polystyrene (PS, average MW 280,000, T<sub>g</sub>: 100 °C, GPC grade), all three supplied by Sigma–Aldrich Química S.A. (Madrid, Spain). The O<sub>2</sub> and N<sub>2</sub> (>99%) gases were supplied in gas cylinders by Air Liquid S.A. (Madrid, Spain).

### *2.2. Instruments and software*

For the electrical characterization of the prototype, the following instrumentation was used: a mixed signal oscilloscope (MSO4101, Tektronix, USA), a 6½ digit multimeter (34410A,

Agilent Technologies, USA), a 15 MHz waveform generator (33120A, Agilent Technologies, USA) and a DC power supply (E3630A, Agilent Technologies, USA). A user interface made in Visual Basic© was used in a computer for calibration purposes. All chemicals were weighed using a DV215CD scale (Ohaus Co., Pine Brook, NJ, USA) with a precision of  $\pm 0.01$  mg.

The standard mixtures for instrument calibration and characterization were prepared using  $N_2$  as the inert gas by controlling the flow rates of the different high purity gases  $O_2$  and  $N_2$ , which entered a mixing chamber using a computer-controlled mass flow controller (Air Liquid España S.A., Madrid, Spain) operating at a total pressure of 760 Torr and a flow rate of  $500 \text{ cm}^3 \cdot \text{min}^{-1}$ .

### *2.3. Membrane preparation*

The sensing channel was prepared by casting the oxygen sensitive membrane on a quartz crystal ( $44 \text{ mm} \times 12.5 \text{ mm} \times 1.25 \text{ mm}$ ) using a spin-coating technique under ambient atmospheric conditions. The cocktail for preparing the oxygen-sensitive membrane was made by dissolving 0.5 mg of PtOEP and 12 mg of DABCO in 1 mL of a solution of 5% (w/v) PS in freshly distilled THF. The sensitive membrane was cast by placing a volume of  $15 \mu\text{L}$  of the cocktail on a quartz crystal. After depositing the sensing membranes, the quartz crystals containing them were left to dry in darkness in a THF atmosphere for 1 h. The obtained membranes were homogeneous, transparent and pink. The sensing membranes containing PtOEP in PS need to be cured in darkness for 9 days before their use [24]. When they are not in use they must be kept in the dark to extend their lifetime.

### *2.4. Description of the instrument*

The portable instrument presented here determines the concentration of gaseous  $O_2$  by measuring the intensity of the emission generated in the membrane which is quenched by the  $O_2$ . This intensity is quantified using the R coordinate of the RGB colour space obtained from image-processing the previously described sensing membrane.

The image processing is carried out using a PIC18F2550 microcontroller (Microchip Technology Inc., USA). This low-cost model was selected because it includes a USB module to allow communication with a computer, which is useful for calibration purposes.

The sensing module of the prototype consists of a light source, in this case a Light Emitting Diode (LED), to excite the luminophore and a colour camera that receives the generated luminescence. The arrangement of the elements in the sensing module, that is, the LED, the luminophore and the camera, is depicted in Figure 1. The sensing membrane is cast on one side of a 44×12.5×1.25 mm quartz crystal and the LED is placed at the short edge of the crystal. The camera is placed below the quartz crystal directly facing the membrane. Using this configuration, when the LED is activated, the generated radiation reaches the luminophore through the crystal; in this way, this element acts not only as a support for the membrane but also as a waveguide. The evanescent field generated inside the quartz crystal is enough to produce a steady-state excitation of the membrane that emits phosphorescence in the red region with a maximum at 645 nm. The luminescence intensity depends on the environmental oxygen concentration as a consequence of the quenching of excited luminophore.

Figure 1

The objective of this configuration for the sensing module in the prototype is to reduce the interference of the visible radiation of the LED in the image captured by the camera, which could cause over-exposure of this device. The LED is biased by means of a stable configurable current source that generates an output in the range of 6 to 120 mA.

The micro-camera is model TTL- $\mu$ CAM (4DSystems, Australia). This device uses an OmniVision CMOS VGA colour sensor and an on-board serial interface to allow communication with the microcontroller via a UART port using predetermined embedded commands. The micro-camera offers different resolutions (80×60, 160×120, 320×240 or 640×480) and output formats to capture the image (RAW or JPEG). Despite the slower communication using RAW images, this format is easier to process since there is no need for decompression to obtain the colour information. The RAW image uses 16 bits in 565-RGB format (5 bits for the red, 6 bits for the green and 5 bits for the blue component), which means that the range for the R component is from 0 to 31. Also, 332-RGB and 444-



RGB are available, but due to the lower resolution for the R coordinate, they were discarded. A spatial resolution for the 320×240 picture was selected according to the dimension of the  $\mu$ -LCD included in the design. Once the membrane is excited with the LED, the transmitted radiation is captured in a photograph. This image is shown on a  $\mu$ -LCD touch screen, model 32PT-SGC (4DSystems, Australia), which also allows the user to interact with the instrument. The dimensions of the screen are 56×77.6×3.7 mm and 3.2' diagonal and the resolution is 240×320 QVGA with 65K colours, sufficient for the purposes described here. The RAW image provided by the micro-camera is sent directly to the  $\mu$ -LCD since the two elements admit the 240×320 resolution, simplifying communication between them. The microcontroller sends embedded commands to control the response of the  $\mu$ -LCD and the micro-camera through the serial port. The main advantage of using a screen is that it avoids the use of external storage elements since all the information of the pixels is saved directly in the  $\mu$ -LCD. If necessary, it is possible to save the image in the micro-SD memory card built into the display. A DS1624 temperature sensor (Maxim, USA) is included in the design, providing a temperature measurement with a resolution of 0.03125 °C. This data is sent to the microcontroller in digital format via two-wire serial communication. The instrument needs a 5 V power supply which can be obtained from a PP3 9 V battery using a voltage regulator, from an AC/DC external adaptor or via a USB port.

### *Measurement procedure*

The measurement of the gaseous oxygen concentration is based on the intensity of the luminescence emitted by the sensor when it is excited by a UV light source. The intensity of this light is quenched by the surrounding oxygen. Therefore, the information concerning the O<sub>2</sub> concentration can be extracted by measuring the red component of a photograph of the sensing membrane taken under stable excitation conditions [13], as shown in Figure 2, where the R coordinate of the image of the membrane is presented for different oxygen concentrations. As can be seen, the intensity of the image decreases as the surrounding O<sub>2</sub> increases.

Figure 2

As previously described, the image is loaded in the  $\mu$ -LCD in 565-RAW format which means that the red component of every pixel is stored in the first 5 bits of the data. To obtain a measurement of the R value from the whole membrane, the instrument proceeds as follows: the LED is polarized through a fixed 19 mA current generated by the current source. This value is selected to provide an intensity of the luminescence in the absence of oxygen that corresponds to the red scale maximum in the image, i.e., 31 units. The phosphorescence emission intensity of the PtOEP membrane undergoes a transient characterized by a rise in the time from 10 to 30 seconds [25, 26]. In this work it is assumed that after 30 seconds of illumination, the membrane is in a stable excitation state and the picture is taken and sent to the  $\mu$ -LCD where it is stored. The elapsed time between the activation of the LED and the photograph of the membrane must be kept constant for every measurement since the excitation with the UV radiation produces an increase in the temperature over time that affects the intensity of the emitted luminescence, as it will be described below. From the image stored in the  $\mu$ -LCD, the microcontroller successively takes the R information from every pixel inside a defined region of the image that corresponds to the active area of the sensing membrane. From these data, the mode of the R values is selected as the R value for the whole membrane [27].

### *2.5. Android application*

Since there is an increasing interest in the use of mobile smartphones and similar devices such as tablets, the development of an Android application was carried out for the same purpose described above for the portable instrument, i.e., the determination of the gaseous oxygen concentration from an optical sensor image. To implement the application, Eclipse was chosen as the integrated development environment (IDE) since the plugin needed to integrate Android is more developed than for other IDEs and, also, a phone emulator can be used for debugging purposes.

The structure used to take the images using this kind of devices is similar to that shown in Figure 1, replacing the  $\mu$ CAM with the other camera device where the application is running. As can be seen, with this design, an external light source is needed in order to produce the excitation of the luminophore. Once the sensing membrane is placed facing the

membrane, the Android application is started and a photograph of the membrane is captured, as shown in Figure 3 (a), where light source used to produce the excitation can be seen as well as the excited luminophore. Figure 3 (b) shows how the photograph can be cropped to obtain the membrane's area of interest which is processed to calculate the value of the R component. In this way, non-uniform regions such as the edges of the membrane are discarded. The acquisition of images using camera devices such as smartphones to obtain an estimation of luminescence intensity has been previously described although the image processing was not carried out using the smartphone [13]. In our study, the application developed makes use of the device's internal resources to perform the required image processing, making it unnecessary to export the image to an external computer. The application dismisses the green and blue information, using only the red pixels from the cropped image to obtain the histogram of the R coordinates present in the area. The mode of the red coordinate distribution provides the final value which is used to obtain the oxygen concentration.

Figure 3

### 3. Results and Discussion

The luminophore selected was the PtOEP complex which has a very long lifetime ( $\tau_0 \sim 100\text{-}200 \mu\text{s}$  depending on the chemical nature of the polymer matrix), visible absorption (B(0), the Soret band, at 380 nm and Q(0) at 533 nm), Stokes displacement (emission at 650 nm), phosphorescence quantum yield ( $\sim 0.2$  under ambient conditions) [28] and a reasonable photostability in the conditions studied. In a polystyrene host its phosphorescence lifetime is 91  $\mu\text{s}$  [29] and the absorption spectrum shows the B(0) (Soret band) peak located at 383 nm and the Q(0) at 537 nm. The weak long-wavelength absorption around 580 nm is probably due to some aggregate absorption [28] (PtOEP concentration 0.8%) and the phosphorescence emission is centred at 645 nm (Figure 4).

Figure 4

Emission from PtOEP film appears at 645 nm irrespective of the excitation used according to Kasha's rule. In this case, the possible excitation wavelengths are 383 and 537 nm, which correspond to UV and green light respectively. Digital cameras are usually much more sensitive to green light than UV; therefore in the following section, the shortest

excitation wavelength is used to produce less optical interference in the imaging system, which is designed to measure only the red emission from the sensor. The UV light source used is a LED with an emission peak covering the absorbance wavelength of the PtOEP complex, as shown in Figure 4. The Q(0) band of PtOEP is the currently used for phosphorescence excitation purposes; nevertheless in some cases excitation at the Soret band has been reported [30, 31].

### *3.1. Instrument calibration*

The aim of this study is to measure the concentration of environmental gaseous oxygen by means of custom-developed portable equipment that processes images of a sensitive membrane of PtOEP complex. The phosphorescence intensity of the membrane determines the O<sub>2</sub> concentration using the R coordinate of the RGB colour space.

As discussed above, the sensing luminophore containing the PtOEP complex can be excited at two different wavelengths in order to obtain an emission of light whose intensity depends on the surrounding oxygen concentration. In a previous work, a green LED with peak emission at 525 nm was used [21-23]. However in this case, a LED with emission in the UV band was selected since it causes only negligible direct and stray optical interference in the image acquired to predict the O<sub>2</sub> concentration. The response of the sensing membrane was evaluated in the full 0-100 % O<sub>2</sub> range using six replicas at room temperature (21 °C). The measurements were performed after equilibrating the instrument atmosphere for 2 min with the gas mixtures obtained with the gas blender indicated above.

The obtained results are presented in Figure 5. As was expected, the intensity of the luminescence, or the R value, is higher for low values of oxygen concentration and decreases when the O<sub>2</sub> rises.

Figure 5

The response curve in Figure 5 can be fitted to a Freundlich isotherm for luminescence which models a non-linear Stern-Volmer behaviour and can be represented in the simplest form as [32]:

$$\left(\frac{R_0}{R}\right) - 1 = \alpha [O_2]^\beta \quad (1)$$

where  $R_0$  represents the intensity of the emitted luminescence in the absence of oxygen, and  $\alpha$  and  $\beta$  are fitting parameters. These constants are considered to provide some physical information about the sensors:  $\beta$  is a measure of the heterogeneity of the system and the curvature of the Stern-Volmer plot, and  $\alpha$  is the  $K_{SV}$  of the oxygen [33]. The fitting curve for the response of the sensor is presented in Figure 6, for which  $\alpha = 0.11$  and  $\beta = 0.647$  (correlation factor  $r^2 = 0.996$ ).

Figure 6

The resolution achieved when the image corresponding to the whole membrane surface is processed is 0.2 % at 21 % oxygen. Nevertheless, processing such an extensive area takes a long time for the microcontroller, since the communication with the  $\mu$ -LCD is based on a slow serial bus. To reduce the instrument's computation time, a smaller area of 40×40 pixels covering the central region of the sensing membrane was selected and processed. Although the position of the selected area in the image of the membrane is not relevant, it is important that this area not be close to the edge of the membrane, since lower luminescence is generated in these regions due to an increase in thickness and thus in autoquenching, as can be seen in Figure 2. With this configuration, the resolution achieved is 0.2 % oxygen and the processing time is 2 minutes. Therefore, the resolution does not undergo any degradation when a small area is selected instead of the whole membrane.

The limit of detection (LOD) was obtained using the standard criteria:  $LOD = y_b + 3s_b$ , where  $y_b$  is the average blank signal and  $s_b$  is the standard deviation of the blank, which is determined using ten replicas. As happens with the resolution, the value of the LOD depends on the area of the membrane considered to obtain the R coordinate. In the best case, when the whole image is selected, the LOD is 0.28 %  $O_2$ . In the case described above, where only an area of 40×40 pixels is treated, the resulting LOD is 1.5 %.

Finally, a study of the instrument's time stability was carried out, taking measurements for 8 days at 3-hour intervals at 21 %  $O_2$ . The data show a time drift in the value of the measured R of 0.038 % per day of the full scale range which implies a time drift in the predicted oxygen concentration of 0.035 % of the reading per day. Although the excitation

source is a high energy emission in the UV band derived from the LED, the sensing membrane showed good photostability and its response was not significantly affected, as can be seen from the low value of the time drift [34].

### *3.2. Camera phone calibration*

The Android application described above was installed in a model HTC Desire HD smartphone with the Android 2.2 operative system. This device was selected because of the built-in high resolution digital camera with an 8 megapixel resolution. Moreover, this camera uses 8 bits to code each colour coordinate R, G, B, in contrast to the  $\mu$ CAM used in the instrument described which uses only 5 bits to code the R coordinate. This difference was expected to provide better results in terms of resolution. As explained above, it is necessary to use an external light source to excite the sensing membrane. In this case, the UV LED with peak emission at 380 nm was selected. The measurement procedure is the same described in section 2.4, i.e., the LED is switched on and after a delay time of 30 seconds six replicas are taken with the mobile phone which is placed at a fixed distance of 15 cm from the membrane. The entire system is in the dark to prevent any external light interference. The calibration curve obtained is similar to that shown in Figure 6, with fitting parameters  $\alpha = 0.123$  and  $\beta = 0.511$ , and a correlation factor of 0.998. With this configuration, the resulting resolution is 0.004 % at 21 % O<sub>2</sub>, whereas the LOD is 0.7 %. Therefore, the use of a camera phone as an image detector provides great advantages in terms of resolution thanks to its high-quality camera. Moreover, the processing time to predict the oxygen concentration from the image is much lower using this smartphone, meaning that the response time of the system is also improved.

### *3.2. Temperature Dependence*

As discussed above, the temperature has a notable influence on the quenching produced by the oxygen in the light emission of a luminophore [34]. This effect has to be evaluated and compensated for if the mobile devices are to work well. With this aim, a study of the instrument response for different temperatures was carried out. A thermostatic chamber, with a lateral hole for the connexion to a computer and gas tubing entrance, made it

possible to maintain a controlled temperature between  $-50\text{ }^{\circ}\text{C}$  and  $+50\text{ }^{\circ}\text{C}$  with an accuracy of  $\pm 0.5\text{ }^{\circ}\text{C}$  for thermal characterization of the instrument.

Figure 7 represents the response of the instrument at different temperatures. The curves were obtained using six replicas for each oxygen concentration at a given temperature. As can be seen, the increase in the temperature reduces the phosphorescence of the membrane causing a lower red signal. This effect was modelled introducing the thermal dependence in the fitting parameter  $\beta$  which can be expressed as a polynomial function of the temperature in the form  $\beta = 3 \cdot 10^{-5} \cdot T^3 - 0.0023 \cdot T^2 + 0.048 \cdot T + 0.3978$  ( $r^2 = 0.980$ ) with T in Celsius degrees, while parameter  $\alpha$  is independent of the temperature. This model was included in the instruments so that the drifts in the measurement due to temperature are compensated for.

Figure 7

#### 4. Conclusions

In this work, two mobile devices were designed to measure gaseous oxygen based on the luminescence intensity quenching of the PtOEP complex. Both of them measure the intensity of the light generated by the luminophore when it is excited at certain wavelengths from the digital image processing of a photograph of the membrane, thus relating this intensity to the oxygen concentration. The first system is a custom-designed prototype which uses an integrated  $\mu$ -camera to acquire the picture of the oxygen sensor. The image is processed by the microcontroller which is the core of the developed instrument. The prototype has an internal LED that emits in the UV band and acts as a light source to excite the luminophore. In addition, a temperature sensor is included to correct sensor temperature drifts. A complete study of the characteristics of this instrument was carried out, showing that the response curve of the sensor can be fitted to a non-linear Stern-Volmer function and including an evaluation of the time and temperature drifts. The second system consists of a commercially available smartphone with a high-resolution digital camera in which an application for Android developed by the authors runs. This application takes a photograph of the excited membrane and allows the user to manually select the region of interest of the image to be processed to extract the intensity of the generated luminescence.

The maximum resolution and limit of detection that can be achieved with this prototype are 0.2 % and 0.28 % at 21 % O<sub>2</sub>, respectively. Using the smartphone, the resolution in the prediction of the oxygen concentration can reach a value as low as 0.004 % at environmental O<sub>2</sub> concentration and an LOD of 0.7%. As can be seen, the resolution achieved with the phone is improved due to the high-quality camera in the device. Nevertheless, the smartphone does not constitute an autonomous system since it requires an external light source to excite the sensor, as well as a temperature sensor to correct for temperature drifts.

### **Acknowledgements**

We acknowledge financial support from the *Ministerio de Ciencia e Innovación, Dirección General de Investigación y Gestión del Plan Nacional de I+D+i* (Spain) (Projects CTQ2009-14428-C02-01 and CTQ2009-14428-C02-02) and the *Junta de Andalucía (Proyectos de Excelencia P08-FQM-3535 and P10-TIC-5997)*. These projects were partially supported by European Regional Development Funds (ERDF).

### **References**

1. X.D. Wang, H.X. Chen, Y. Zhao, X. Chen, X.R. Wang, X. Chen, Optical oxygen sensors move towards colorimetric determination, *TrAC, Trends Anal.Chem.* 29 (2010) 319.
2. R.C. Evans, P. Douglas, Controlling the Color Space Response of Colorimetric Luminescent Oxygen Sensors, *Anal.Chem.* 78 (2006) 5645.
3. A. Mills, Oxygen indicators and intelligent inks for packaging food, *Chem.Soc.Rev.* 34 (2005) 1003.
4. Z. Zhujun, W.R. Seitz, Optical sensor for oxygen based on immobilized hemoglobin, *Anal.Chem.* 58 (1986) 220.
5. K.E. Chung, E.H. Lan, M.S. Davidson, B.S. Dunn, J.S. Valentine, J.I. Zink, Measurement of Dissolved Oxygen in Water Using Glass-Encapsulated Myoglobin, *Anal.Chem.* 67 (1995) 1505.



6. A. Del Bianco, F. Baldini, M. Bacci, I. Klimant, O.S. Wolfbeis, A new kind of oxygen-sensitive transducer based on an immobilized metallo-organic compound, *Sens.Actuators B* 11 (1993) 347.
7. S.K. Lee, M. Sheridan, A. Mills, Novel UV-Activated Colorimetric Oxygen Indicator, *Chem.Mater.* 17 (2005) 2744.
8. Mitsubishi Gas Chemical Co.Inc. Ageless Eye. <http://www.mgc.co.jp/eng/company/materials/products/ageless/related/index.html> (accessed Feb. 2012).
9. K. Eaton, A novel colorimetric oxygen sensor: dye redox chemistry in a thin polymer film, *Sens.Actuators B* 85 (2002) 42.
10. S.M. Borisov, C. Krause, S. Arain, O.S. Wolfbeis, Composite material for simultaneous and contactless luminescent sensing and imaging of oxygen and carbon dioxide, *Adv.Mater.* 18 (2006) 1511.
11. S.R. Ricketts, P. Douglas, A simple colorimetric luminescent oxygen sensor using a green LED with Pt octaethylporphyrin in ethyl cellulose as the oxygen-responsive element, *Sens.Actuators B* 135 (2008) 46.
12. R.C. Evans, P. Douglas, J.A.G. Williams, D.L. Rochester, A novel luminescence-based colorimetric oxygen sensor with a "traffic light" response, *J.Fluoresc.* 16 (2006) 201.
13. J. Park, W. Hong, C.S. Kim, Color intensity method for hydrogel oxygen sensor array, *IEEE Sens.J.* 10 (2010) 1855.
14. J. Park, C.S. Kim, A simple oxygen sensor imaging method with white light-emitting diode and color charge-coupled device camera, *Sens.Lett.* 9 (2011) 118.
15. P. Bhagwat, G.S. Achanta, D. Henthorn, C.S. Kim, Colorimetric phosphorescence measurements with a color camera for oxygen determination, *Proc.SPIE* 8025 (2011) 80250B.
16. X.D. Wang, R.J. Meier, M. Link, O.S. Wolfbeis, Photographing Oxygen Distribution, *Angew.Chem., Int.Ed.* 49 (2010) 4907.
17. M. Larsen, S.M. Borisov, B. Grunwald, I. Klimant, R.N. Glud, A simple and inexpensive high resolution color ratiometric planar optode imaging approach: application to oxygen and pH sensing, *Limnol.Oceanogr.: Methods* 9 (2011) 348.
18. R.J. Meier, S. Schreml, X.D. Wang, M. Landthaler, P. Babilas, O.S. Wolfbeis, Simultaneous Photographing of Oxygen and pH In Vivo Using Sensor Films, *Angew.Chem., Int.Ed.* 50 (2011) 10893.

19. J.L. Delaney, C.F. Hogan, J. Tian, W. Shen, Electrogenerated Chemiluminescence Detection in Paper-Based Microfluidic Sensors, *Anal.Chem.* 83 (2011) 1300.
20. A. Garcia, M.M. Erenas, E.D. Marinetto, C.A. Abad, I. de Orbe-Paya, A.J. Palma, L.F. Capitan-Vallvey, Mobile phone platform as portable chemical analyzer, *Sens.Actuators B* 156 (2011) 350.
21. A. Martinez-Olmos, I.M.P. de Vargas-Sansalvador, A.J. Palma, J. Banqueri, M.D. Fernandez-Ramos, L.F. Capitan-Vallvey, Multisensor probe for soil monitoring, *Sens.Actuators B* 160 (2011) 52.
22. A.J. Palma, J. López-González, L.J. Asensio, M.D. Fernandez-Ramos, L.F. Capitan-Vallvey, Microcontroller-Based Portable Instrument For Stabilised Optical Oxygen Sensor, *Sens.Actuators B* 121 (2007) 629.
23. I.M. Perez de Vargas-Sansalvador, C. Fay, T. Phelan, M.D. Fernandez-Ramos, L.F. Capitan-Vallvey, D. Diamond, F. Benito-Lopez, A new light emitting diode-light emitting diode portable carbon dioxide gas sensor based on an interchangeable membrane system for industrial applications, *Anal.Chim.Acta* 699 (2011) 216.
24. I.M. Perez de Vargas-Sansalvador, M.A. Carvajal, O.M. Roldan-Munoz, J. Banqueri, M.D. Fernandez-Ramos, L.F. Capitan-Vallvey, Phosphorescent sensing of carbon dioxide based on secondary inner-filter quenching, *Anal.Chim.Acta* 655 (2009) 66.
25. D.B. Papkovsky, Luminescent porphyrins as probes for optical (bio)sensors, *Sens.Actuators B* 11 (1993) 293.
26. I.M. Perez de Vargas-Sansalvador, A. Martinez-Olmos, A.J. Palma, M.D. Fernandez-Ramos, L.F. Capitan-Vallvey, Compact optical instrument for simultaneous determination of oxygen and carbon dioxide, *Mikrochim.Acta* 172 (2011) 455.
27. K. Cantrell, M.M. Erenas, I. Orbe-Paya, L.F. Capitan-Vallvey, Use of the Hue Parameter of the Hue, Saturation, Value Color Space As a Quantitative Analytical Parameter for Bitonal Optical Sensors, *Anal.Chem.* 82 (2010) 531.
28. A.K. Bansal, W. Holzer, A. Penzkofer, T. Tsuboi, Absorption and emission spectroscopic characterization of platinum-octaethyl-porphyrin (PtOEP), *Chem.Phys.* 330 (2006) 118.
29. M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, Highly efficient phosphorescent emission from organic electroluminescent devices, *Nature* 395 (1998) 151.
30. K. Oguri, H. Kitazato, R.N. Glud, Platinum octaethylporphyrin based planar optodes combined with an UV-LED excitation light source: An ideal tool for high-resolution O<sub>2</sub> imaging in O<sub>2</sub> depleted environments, *Marine Chemistry* 100 (2006) 95.

31. H. Lu, Y. Jin, Y. Tian, W. Zhang, M.R. Holl, D.R. Meldrum, New ratiometric optical oxygen and pH dual sensors with three emission colors for measuring photosynthetic activity in cyanobacteria, *J.Mater.Chem.* 21 (2011) 19293.
32. E.R. Carraway, J.N. Demas, B.A. De Graff, J.R. Bacon, Photophysics and photochemistry of oxygen sensors based on luminescent transition-metal complexes, *Anal.Chem.* 63 (1991) 337.
33. P. Douglas, K. Eaton, Response characteristics of thin film oxygen sensors, Pt and Pd octaethylporphyrins in polymer films, *Sens.Actuators B* 82 (2002) 200.
34. D.B. Papkovsky, New oxygen sensors and their application to biosensing, *Sens.Actuators B* 29 (1995) 213.

## Figure captions

Figure 1: Sensing scheme of the instrument.

Figure 2. Photographs of the membrane for different O<sub>2</sub> concentrations.

Figure 3. Photograph of the membrane taken with the camera phone (a) and manual selection of the region of interest (b).

Figure 4. Absorption and emission spectra of the PtOEP and excitation spectrum of the LED.

Figure 5. Response of the sensing membrane.

Figure 6. Calibration curve of the instrument.

Figure 7: Thermal dependence of the instrument.

Figure1

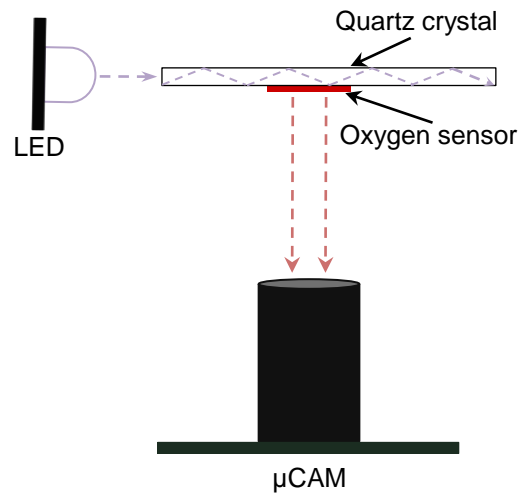


Figure 1

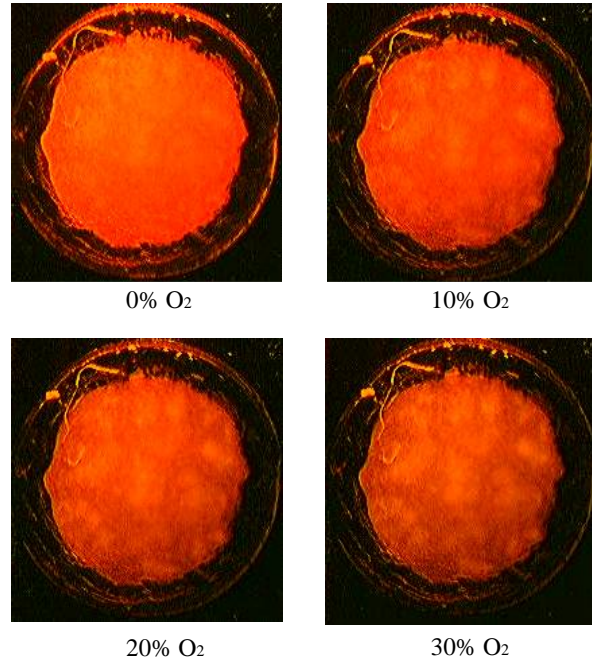


Figure 2

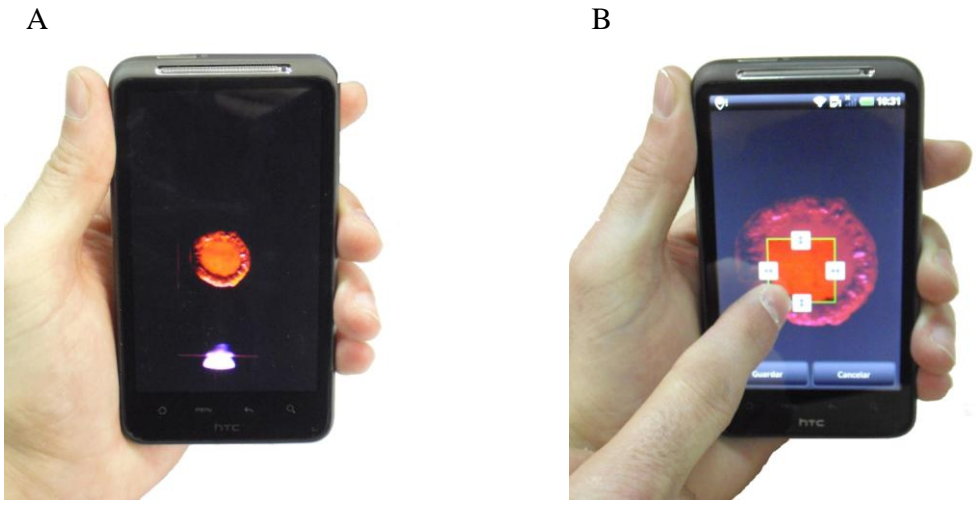


Figure 3

Figure4

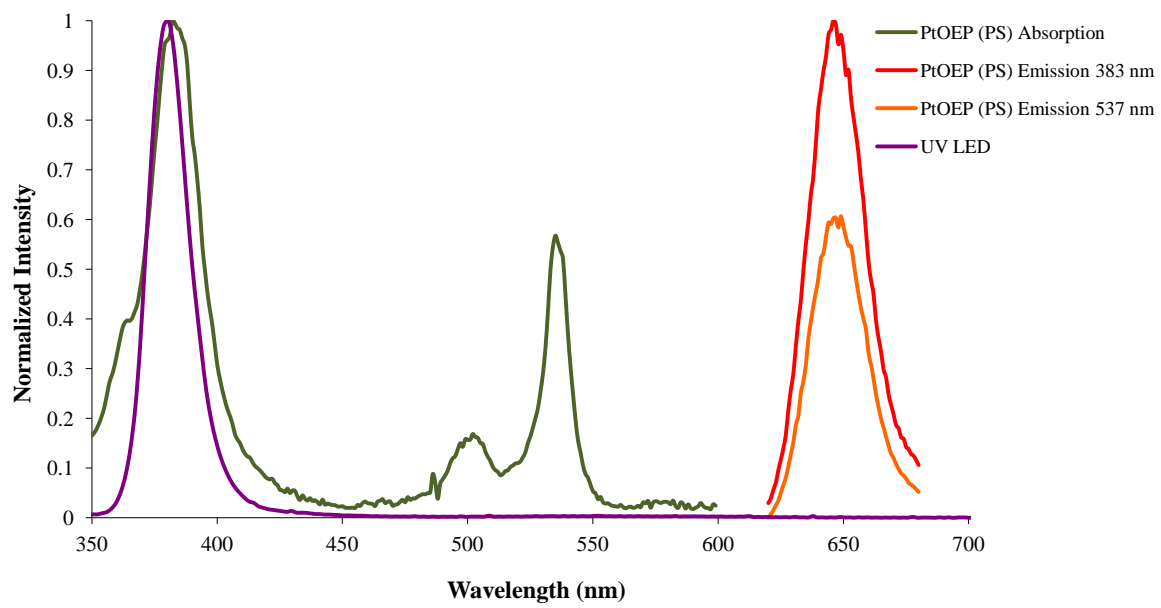


Figure 4



Figure5

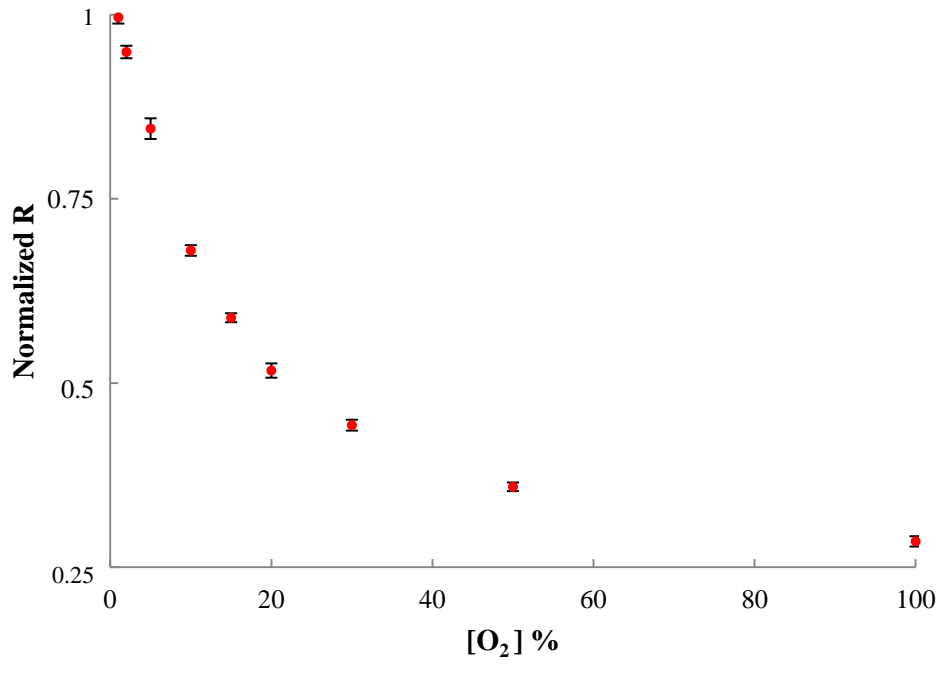


Figure 5

Figure6

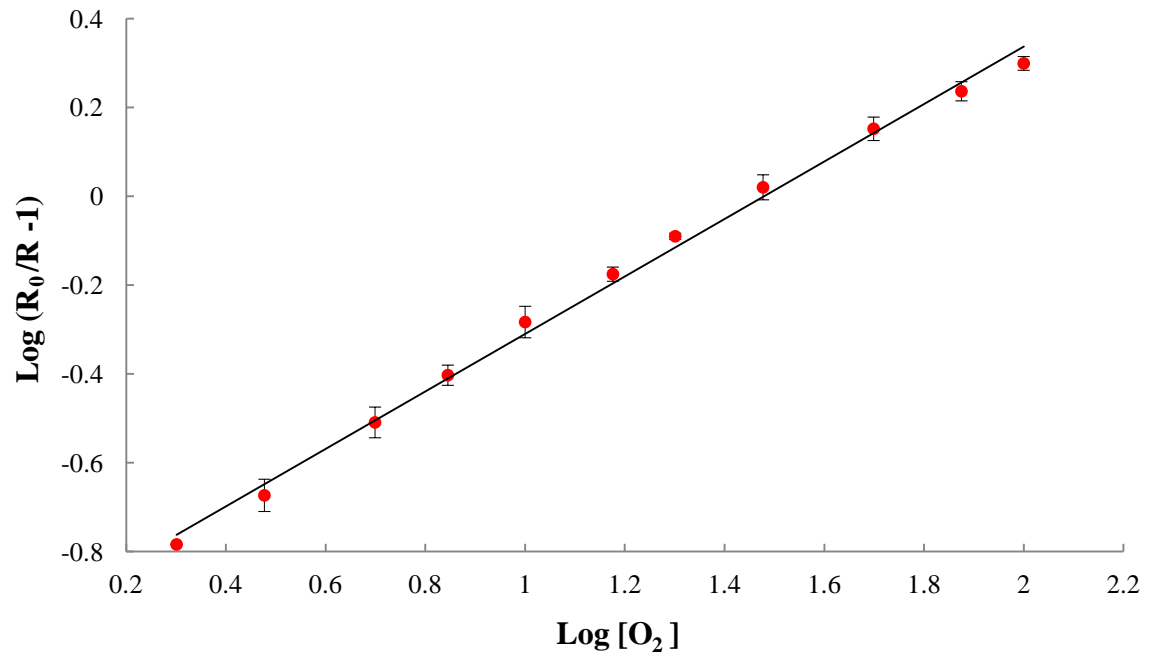


Figure 6

Figure7

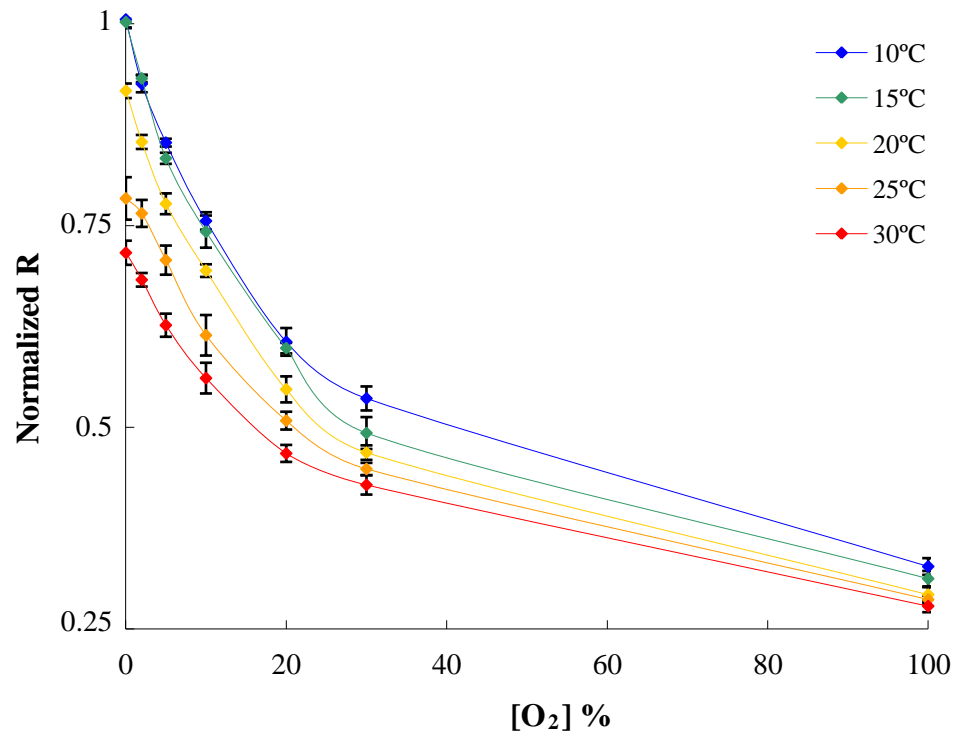


Figure 7