Dual Wavelength Integrated Optical System for Chemical Ion-Selective Sensing

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Abstract: A novel compact dual-wavelength analyser for Integrated Waveguide Absorbance Optodes (IWAOs) is reported. The main innovation is the introduction of a reference wavelength to correct possible unspecific optical changes of the system.
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1. Introduction

In this work we report a novel compact opto-chemical dual wavelength analyser. It includes two different light sources, one of them used as the working wavelength and the other used as a reference signal to correct any deviation due to unspecific optical interferences or non-chemical processes. Light Emitting Diodes (LEDs) are used as light sources, and are modulated and controlled by a Digital Signal Processor (DSP), which also executes two lock-in amplification processes to separate the two wavelengths at detection.

Trends in the optical sensing field are the combination of fibre optics with bulk optodes, to exploit their attained technological improvements. An even more promising technology is planar waveguide chemical sensing as it allows the implementation of automated mass fabrication methodologies. IWAOs are sensing platforms, which confer versatility, robustness and mass production capabilities besides high sensitivity on conventional bulk optodes. However, for the feasible application of such sensors in field more compact, portable and automated system and mass production exchangeable transducers are needed. We present a microfabricated circuit of curved ARROW planar waveguides constructed with silicon micromachining for an easy exchangeability. Over the ARROW circuit constructed by IC technology an ion-selective membrane is deposited, the whole forming an Integrated Waveguide Absorbance Optode (IWAO). Some of them have been previously proposed for ion determination in water and studied by our research group [1-3]. The optical membrane works as a selective recognition region while acting as part of the light guiding planar structure. For the novel analyser testing, our research group has formulised two ion-selective optodes, one for calcium determination and the other for mercury.

2. System

The complete analyser consists of the opto-chemical sensor and the novel compact optical system. The sensor is based on Antiresonant Reflecting Optical Waveguide (ARROW) structures and on chemically active membrane. The measurement system includes a PC and a DSP which controls two optical sources (LEDs) which are detected and separated using lock-in amplification.

2.1. Sensor

Three main parts of the IWAO can be distinguished (Figure 1.a): (1) the transducer based on a curved planar waveguide, where the optical sensing membrane is deposited on, (2) the V-grooved auxiliary support, where the optical fibres from and to the analyser are fixed, and (3) the steel mounting platform, which permits the alignment of the transducer waveguides to the optical fibres by simply manually inserting a new transducer.

There are three differentiated regions in the transducer (Figure 1.b): a narrow curved input ARROW waveguide (20μm width), a free propagation region, and a wider output ARROW waveguide (50μm width). The free propagation region is where the ion-selective membrane is placed; this cavity is 500μm long and 250μm width (Figure 1.c). The waveguides are defined using complementary metal oxide semiconductor (CMOS) [4,5] compatible processes over a silicon wafer. The transducer was finally cut to a 14x15 mm chip.

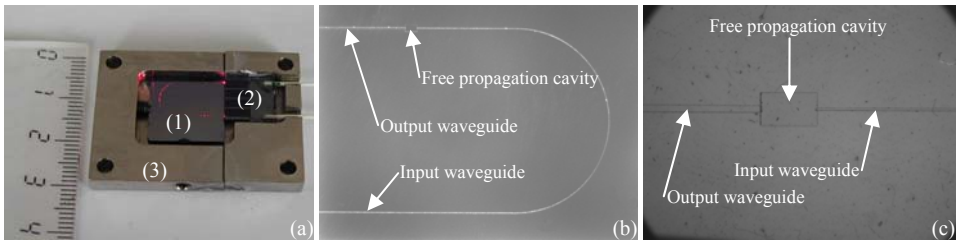

Fig. 1. (a) Photograph of an IWAO: (1) Transducer; (2) V-grooved platform; (3) connexion platform. (b) Individual transducer. (c) Detail of the free propagation cavity..

2.2. Optode

The membranes contain an ion-selective ionophore, a lipophilic ionic salt to maintain the electroneutrality, and a pH indicator, whose spectral properties depend on the activity of the competing ions in the sample solution, the proton and the analyte. Such optodes rely on concentration changes within the bulk of the sensing membrane and follow the ion-exchange mechanism between the membrane and the aqueous solution (as shown in Figure 2.a). More detailed mechanistic descriptions can be found in the literature [6].

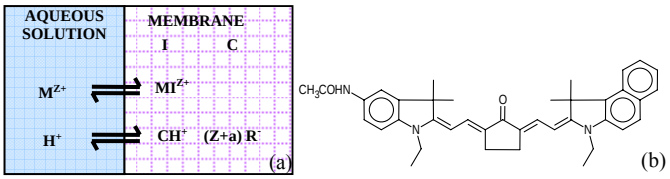

Fig. 2. (a) Cationic exchange, where M: analyte, I: Ionophore, C: chromoionophore (pH indicator/ dye), R⁻: anionic additive. (b)Chemical structure of the employed ketocyanine dye.

The fabricated optodes use the same dye as a chromophore, a previously synthesized and characterized ketocyanine dye [2]: cyanine 5ee (Figure 2.b). It presents an absorption maximum that matches the wavelength of the working LED.

2.3. Measurement system

The main innovation of the measurement system is the introduction of a reference wavelength (λ_2) into the optical sensor, along with the sensing wavelength (λ_1). This reference wavelength is located out of the main absorption peak of the dye, thus providing a signal, which depends only on physical changes of the system (such as fibre bending, membrane hydration or refractive index changes) and not on the presence or absence of the analyte. In the case of the ketocyanine dye used, cyanine 5ee, the absorbance spectrum presents a maximum around 750nm, so we have chosen the sensing wavelength to be 780nm and the reference wavelength at 850nm (Figure 3), which is located out of the absorption bands of the dye and as closer to the working wavelength as possible in order to assure that physical changes on guided light affect equally to both wavelengths.

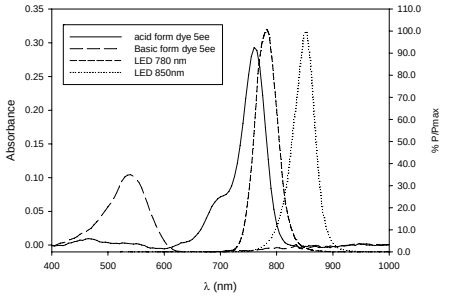

Fig 3. Localisation of the absorption bands of the dye and the emission LEDs.

Figure 4.a schematically shows all the components that are enclosed in the measurement system and the fibre connections with the sensor. This system is shown open in Figure 4.b, where all the inside elements are indicated.

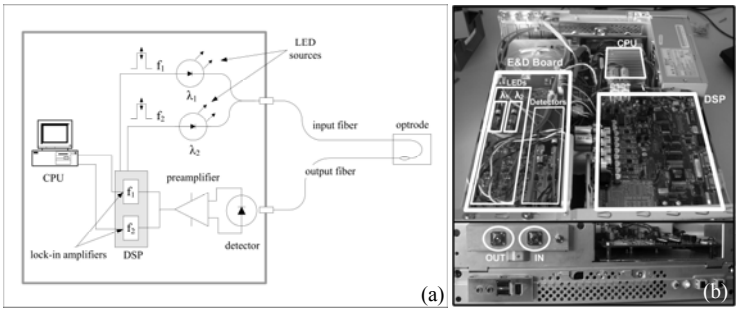

Fig. 4. (a) Scheme of the compact optochemical analyser. (b) Photograph of the compact optical measurement system.

Lock-in amplification performed by the DSP improves the signal to noise ratio and, as a consequence, the dynamic range of the instrument. Moreover, if the working wavelength λ_1 is modulated at f_1 (480Hz) and the reference λ_2 at another frequency f_2 (1200Hz), the use of two lock-in amplifiers allows the detection of both signals using just one optical detector, without the need of optical filters or any other complex optical system. The LEDs electronic control and the detection system are integrated in the same Printed Circuit Board (PCB), labelled as "E&D Board" in Figure 4.b.

The lock-in amplifiers and the control of the two LEDs are implemented in the same DSP, thus reducing costs and space. In fact, the whole electronic system (E&D Board and DSP) has been included in a small PC case along with a mini-ITX main board, which controls it via RS232; resulting in a portable measurement system containing the optical sources, the detector, the lock-in amplifiers and a computer which performs the data processing and also provides a handy interface to save and export data.

3. Results and discussion

The system response has been evaluated using two optodes, a calcium-selective and a mercury-selective one. The analyte content in different standard solutions has been evaluated by means of a Flow Injection Analysis (FIA) system and with the aid of a newly designed and fabricated flow cell.

3.1. Calcium Measurements

Figure 5.a shows the obtained signals for calcium determination using the proposed analyser and a conventional configuration (transmission mode) for comparison purposes. The absorbance change is multiplied using the compact analyser for every analyte concentration. As well as the sample throughput as the sensitivity are improved. For instance, the obtained detection limit is 1.41×10^{-4}M meanwhile using the conventional system it is 5.99×10^{-4}M. This demonstrates the advantages of using IWAOs as optical platforms for absorbance measurements. On the other hand, in order to prove the appropriateness of the use of the two wavelengths, the obtained signals with and without the correction are plotted in Figure 5.b. Sometimes, one of the problems of optodes is that the refractive index of the membrane changes while it is hydrating at the beginning of the experiments. This effect can be directly corrected using the reference wavelength information, because the guiding properties of both wavelengths vary in the same manner due to changes of this refractive index.

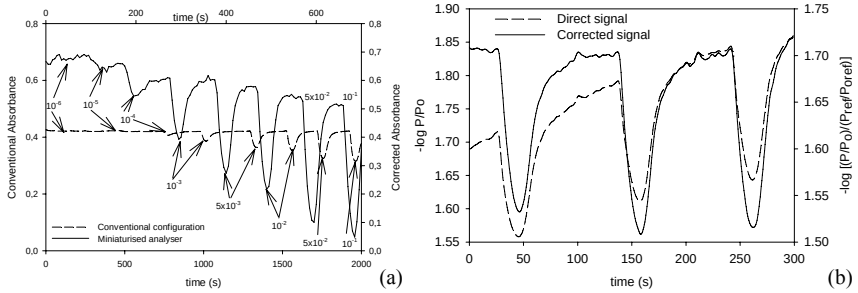

Fig. 5. (a) Output using a conventional spectrophotometer and the miniaturised analyser. (b) Recorded signals at the beginning of the membrane hydration.

3.2. Mercury Measurements

A mercury-selective optode has been also developed for water samples measurements and it has also been used to test the features of the system. Figure 6.a shows the calibration curve of the mercury-selective optode. As it can be noticed, the detection limit is still too high for environmental applications (1.45ppm), however the optimisation as well as of the FIA system as of the membrane formulation is currently being performed. Concerning the usefulness of the reference wavelength, the plasticised PVC membrane shows the same problem of hydration as the previous one, which can be corrected with the new dual wavelength analyser. Figure 6.b shows the direct signal and the corrected one, while different mercury standard solutions are injected in a FIA system. It can be noticed in the Figure 6.b a slight negative drift in the base line signal during a calibration, this effect can not be corrected with the dual wavelength because it is ascribed to the loss of components due to chemical or photochemical processes by the continue irradiation of the light sources. We are currently studding to improve the dye stability by modifying their structure or adding stabilizing agents to the membrane. Moreover, a final application of the analyser in field could be performed with a non-continuous irradiation.

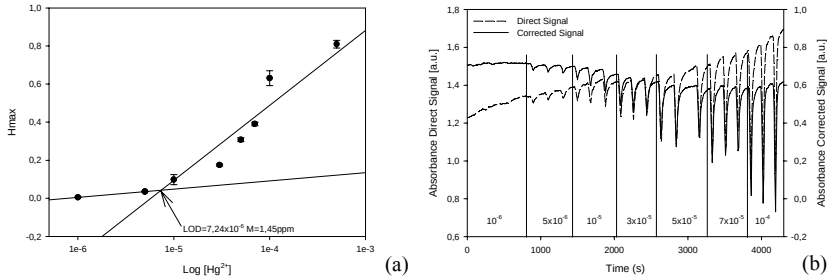

Fig. 6. (a) Calibration curve of the mercury-selective optode. (b) Recorded signals during a calibration, where each mercury solution is injected in triplicate.

4. Conclusions

A rugged, compact, portable and easily automated optochemical measurement system has been developed for the feasible application of integrated waveguide absorbance optodes (IWAOS) in field. The main innovation is the new developed compact optical system which works with two different wavelengths, one as the working wavelength and the other as a reference. The reference provides a signal that depends only on physical changes of the system correcting the output signal of the sensor.

To demonstrate the feasibility of the new analyser, an IWAO has been activated with two ion-selective optodes and applied for the determination of calcium and mercury ions in water samples.

5. Acknowledgement

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6. References

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