FIBRE-OPTIC CHEMICAL SENSORS: FROM MOLECULAR ENGINEERING TO ENVIRONMENTAL ANALYTICAL CHEMISTRY IN THE FIELD

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1. Abstract

Fibre-optic chemical sensors or optodes can be an attractive alternative to current electrochemical or electronic devices in terms of monitoring stability, electrical hazards, size, target analytes, versatility, simplicity, ruggedness and cost. In order to show up their full potential, dedicated optoelectronic instrumentation and tailor-made optical indicators must be developed. We have recently combined efforts between industry and university in order to carry out a R+D project that spans from molecular design of novel luminescent Ru(II) polypyridyl dyes, to the probe engineering, fabrication, characterisation, validation and in-situ monitoring with optical devices based on waveguides and active sensing heads, capable of continuously monitoring relevant parameters in waters. Two examples of how the fibre-optic analysis of dissolved oxygen and carbon dioxide have been tackled by a suitable design of the indicator molecules, are discussed. Results on oxygen monitoring with optodes in the biological treatment pool of a wastewater sanitation plant are presented as well.

2. Introduction

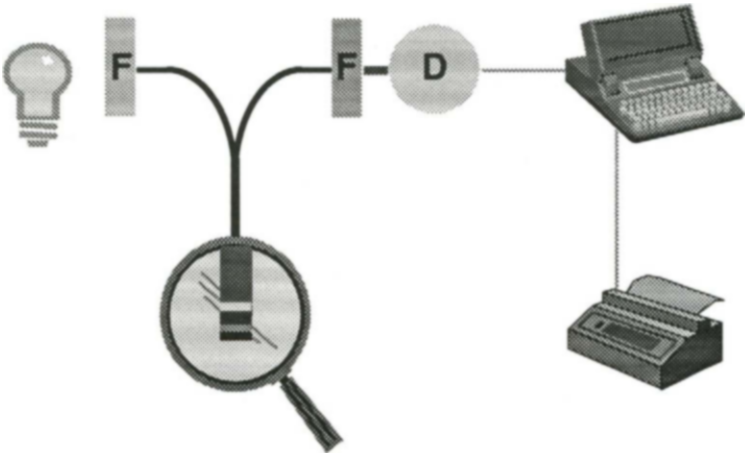
Continuous sensing of relevant chemical determinands is a matter of growing interest in environmental monitoring. This is due to the fact of natural variations of their concentration (daily, seasonal, locational,...), as well as human-induced changes such as those caused by industrial pollution, domestic waste, transportation media, etc. It is nowadays recognized that prevention activities, e.g. improvement of industrial procedures or advanced monitoring, are far more cost-effective than remediation procedures to be used once the damage has been inflicted. It is not surprising, therefore, the current striving of the industrialized nations to deploy all kind of environmental sensors in the atmosphere and the hydrosphere.

In connection to the new technologies for protection of the environment, the european parliament and the EU council underline in their Decision no. 1110/94/EC the necessity of focusing the efforts in RTD on the instrumental technologies required for environmental observation, surveillance, and research. "This implies, particularly, a contribution to the development of technologies for observation of the Earth, [...], including herein sensors, observation technologies and surveillance of different biosphere behaviours, as well as a main development of the required analytical technologies for the different matrices. [...]. It is also to be included here all those instruments related to prevention of natural catastrophes and to pollution control of industrial installations."

Many techniques have been developed so far in response to specific regulatory or public safety requirements. The sensitivity, specificity and the versatility of optical techniques of analysis well established in the laboratory environment, make spectroscopy a very popular method on which to base continuous monitoring systems. Unfortunately, the features that make spectroscopy so desirable have, to date, made it costly and complex compared to the largely unexpensive mecanical and electrical sensors; the situation, however, may change in the nearest future.

A novel type of device for monitorization or quantitation of chemical parameters (ions, gases, organic chemicals,...) via light guides, has evolved recently from the fruitful combination of (apparently) disparate fields such as organic and analytical chemistry, photochemistry, polymer technology, telecommunication engineering, optoelectronics, physical optics and spectroscopy. Those devices have been called fibre optic chemical sensors (FOCS®) or "optodes" (from the greek "optical way"; the term "optrode"® has been used as well, because of the similarity of application to the classical electrodes).
Basically, a typical device of this kind (Figure 1) consists of a light source, the radiation of which (usually wavelength-selected) is launched into the core of a wave guide. The optical fibre carries the light to the sensitive tip, - the true "heart" of the device -, that contains an appropriate indicator (reagent layer) immobilized onto a polymer matrix.

Figure 1. Basic constituents of a fibre-optic chemical sensor (F: wavelength selectors; D: photon detector).



Some optical property (absorbance, reflectance, luminescence, reflectivity, refraction index,...) of this layer undergoes a measurable change upon (selective) interaction with the analyte of interest; in this way, the modified optical radiation is guided back via the fiber optics to a photon detector, the electrical signal of which is amplified and recorded analogical or digitally. A proper calibration allows measurement of the determinand concentration.

Optodes and practical optical sensing schemes have been developed successfully for quantitating gases (oxygen, carbon dioxide, ammonia, sulfur dioxide,...), cations (pH, potassium, calcium, copper, surfactants...), anions (chloride, iodide, cyanide, sulfide,...), organic pollutants (oils, chlorinated hydrocarbons,...), and physical parameters (turbidity, temperature,...) Our group has contributed to this field with optodes for pH, H_2S, iron, CO_2, oxygen, alcohols, humidity, and detergents, among other analytes. The advantages of using fibre optic sensors for chemical analysis and, particularly, environmental monitoring are noticeable: (a) as opposed to classical electrodes, the optical sensors require neither a reference signal (subject to fouling or drift), nor are subjected to electrical interferences (e.g. damage caused by electromagnetic fields of thunder storms); (b) they are easily miniaturisable to allow access to narrow monitoring sites; (c) they do not consume analyte during the measuring process; (d) it is possible to design devices capable of detecting chemical species which can not be detected by any current electrical or electronic sensors; (e) optical wires are able to transport a higher information density than their electrical counterparts; (f) smart optical sensors may be competitive in terms of operation and maintenance versatility, simplicity, ruggedness, and cost. If additionally we incorporate to the sensing membrane some compound of biological origin such as an enzime, an antibody or a carrier, and a proper optochemical transducer (e.g. pH, oxygen, hydrogen,...), we will end up with a so-called biosensor, an optical detector the specificity and sensitivity of which allow detection and quantification of minute amounts of selected chemical species (e.g. pesticides, explosives, poisons, ...).

The design and construction of optical sensors and biosensors should overcome, of course, a number of potential drawbacks: interference of ambient light, long-term stability due to (photo)decomposition or leaching of the supported indicator, necessity of a mass transfer step in order to reach a stable response, the observance of a limited response interval in many cases (e.g. sensors of sigmoidal response), and the still limited number of commercial components specifically designed for this application. Actually, the last 15 years have wittnessed the birth, infancy, and the arrival to the adult age of fiber-optic chemical sensors in the basic research of academia and industry, yet the gap to marketing and practical applications of such devices has to be filled up. It is a challenge to researchers and technologists in this field to be able to minimise or suppress such limitations in order to reach maturity for optodes.

We are currently engaged in an ambitious RTD project that spans from molecular design of novel optical indicators, to engineering, manufacturing, characterization, validation and in situ monitoring with optical devices based on fibre optics and "active" sensing heads (i.e., those containing a chemical indicator immobilised onto a polymer support and placed at the end of a light guide), capable of monitoring continuously the concentration of species that determine the quality of natural, industrial, irrigation, and drinking waters.
In order to perform in situ environmental monitoring, it is advisable to design small, battery-operated instrumentation based on solid-state technology (e.g. excitation with LED or laser

diodes, silicon photodiode detection, etc.). Typically, the detection system must be able to measure optical signals of a very low power (50 pW to 1 nW), with a signal-to-noise ratio better than 60 dB. Therefore, it is necessary to optimise the optoelectronic system in connection to the sensitive membranes of the device, in order to manufacture a low-cost portable instrument based on luminescence measurements (photoluminescent sensors have demonstrated usually to be more sensitive than absorbance-based devices, and more durable if based on emission decay determination or phase-sensitive detection rather than absolute luminescence intensity).

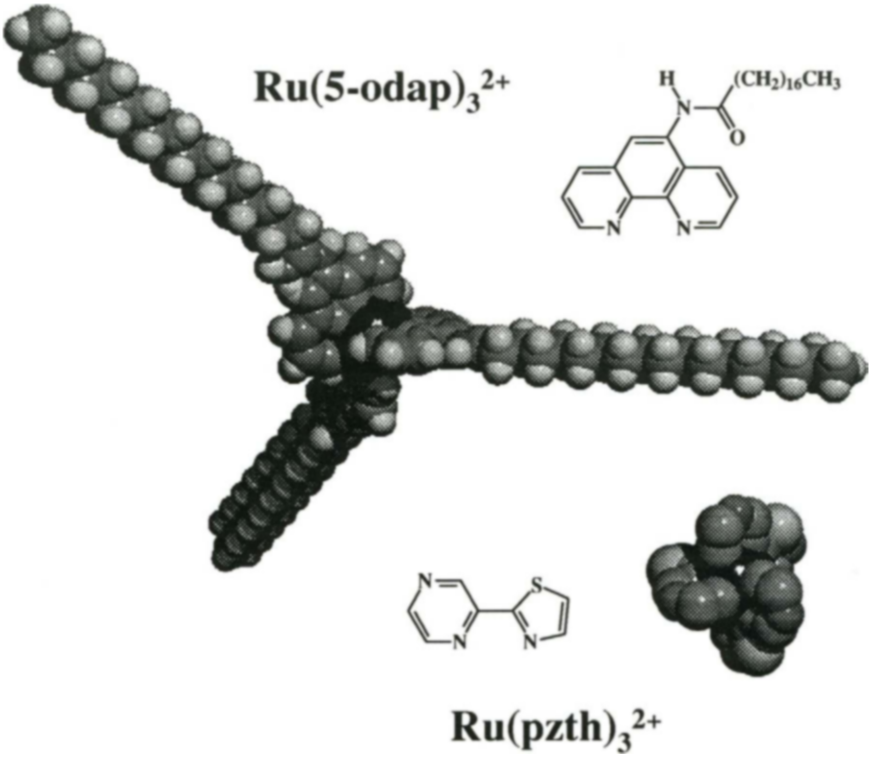
Moreover, it would be desirable that a single hardware might be used regardless the analyte being monitored, with the only change required being the sensitive tip of the optical fibre. To this end, it is our goal to design and prepare a single family of luminescent indicators capable of responding to the largest possible number of determinands relevant to water analysis (O_2, temperature, pH, CO_2, detergents, BOD and salinity).

Coordination compounds of ruthenium(II) and other transition metal ions with polyazaheterocyclic ligands are luminescent dyes with a high potential for chemical analysis. The spectroscopical and redox characteristics of such species can be finely "tuned" by a careful selection of the chelating ligands. They absorb strongly in the blue-green part of the electromagnetic spectrum and display significant luminescence in the red (600-750 nm; $10^{-3} < \Phi_{em} < 0.2$); these features fit nicely the performance of current emission and detection diodes. Their emission has a Stokes' shift larger than 150 nm, which facilitates separation of the scattered light that accompanies the measured luminescence, with simple coloured glasses. Moreover, the slight triplet character of the excited state of such complexes determines a rather long emission lifetime (0.03–6 μs); this feature enhances their sensitivity towards the analyte and makes possible to develop optical sensors using both fluorescence intensity and kinetics. In this way, based upon our experience in the synthesis, spectroscopy, photophysics and photochemical characterisation of luminescent complexes of ruthenium(II) with polyazaheterocyclic ligands, we have engineered such dyes to become the sought family of optical indicators to fabricate fibre-optic chemical sensors. Two cases in point from our research and development in this field will be presented in the following sections.

3. Experimental Section

The oxygen indicator tris(5-octadecamide-1,10-phenanthroline)ruthenium(II), abbreviated Ru(5-odap) (Figure 2), has been prepared from 5-odap (0.65 mmol) and ruthenium trichloride trihydrate (0.19 mmol, Janssen), by heating the solution at reflux in ethyleneglycol (20 mL, Panreac p.a.) under argon for 4 h. The orange complex ion is then precipitated upon addition of 10 mL of water and three drops of concentrated hydrochloric acid. The excess of ligand was separated by column chromatography through Sephadex® LH-20 (Pharmacia) by elution with methanol; after solvent removal, the fraction containing the tris-chelate complex was purified further using preparative TLC on silicagel (Merck) and a n-butanol-water-acetic acid mixture (8:2:1 v/v/v) as eluent.

Figure 2. Chemical structures of the luminescent Ru(5-odap)$_3^{2+}$ and Ru(pzth)$_3^{2+}$ oxygen and carbon dioxide indicators, respectively.



The acetate salt of Ru(5-odap)$_3^{2+}$ was finally obtained by precipitation of an alcohol solution of the cation with concentrated acetic acid. The purified indicator gave a microanalysis (C, H, N) within 0.4 %. UV-VIS [CH_3OH; λ/nm (ε/L mol^{-1} cm^{-1})]: 449 (17750), 270 (92300), 252 (67700), 220 (76800). The ligand 5-odap was prepared from 5-aminophenanthroline (obtained by chemical reduction of the commercial 5-nitro derivative, Sigma) and stearic acid (Aldrich), using a typical procedure for the synthesis of amides from hindered or unreactive amines via the intermediate carbonate with ethylchloroformate. The synthesis of tris[2-(2-pyrazinyl)-1,3-thiazole]ruthenium(II), Ru(pzth), has been reported already One-component RTV silicone 732 was from Dow Corning. Oxygen, nitrogen and carbon dioxide from cilinders (Air Liquide or Praxair) were mixed within 0.5% of the nominal values using a three-channel mass flow controler electronic unit (ICP, Madrid). The gas mixtures are saturated with water for all the CO_2 measurements and for determinations of dissolved O_2.

For laboratory optimisation of the response, the optical sensing membranes were placed into a flow-through cell previously described, to which the common end of a glass or silica fibre-optic bifurcated bundle was connected. Gas or aqueous samples can be easily measured with such a device.

Two types of portable instruments have been used for the chemical analysis with optodes. The first one is a commercial Guided Wave model 260 spectrometer (El Dorado Hills, CA, USA); this system employs a 5-volt, 20-watt tungsten-halogen lamp as excitation source, and a red-sensitive Hamamatsu photomultiplier tube to detect the emitted light from the remote sensor head, after grating monocromation. A portable Toshiba TX-3200 computer holds the necessary interface card and serves to process and analyse the data. The LAP-1000 is a custom-made laptop fibre-optic spectrometer we have assembled to measure with optodes, both in the laboratory and in the field. Into a 46x33x16 cm aluminum-plastic case, it holds a 12-volt 10-Hz Ocean Optics (Eerbeek, NL) PX-1 xenon flashlamp fitted with an SMA connector for waveguides, and a Oriel (Strattford, Connecticut, USA) Instaspect IV CCD detector (1024 x 256 pixel) attached to a Oriel MS-256 1/8-m spectrograph. The full-length ISA interface card which powers the CCD, fires the strobe, collects the signal and synchronises the excitation and recording events is placed into the mini-docking unit of a Olivetti Echos P-100 laptop computer loaded with the original Oriel software for instrument control and data processing. Both portable spectrometers use the same pair of wide band-pass (400 nm) and cut-on (530 nm) coloured glass filters in the excitation and emission channels, respectively, unless otherwise stated.

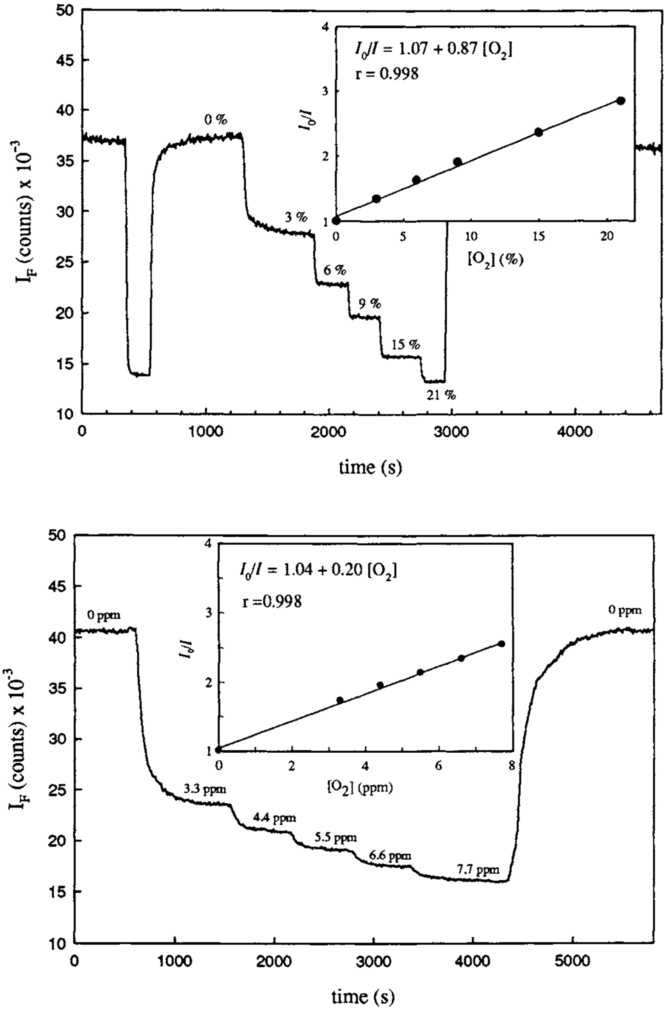
4. Results and discussion

Tris(1,10-phenanthroline)ruthenium(II), or Ru(phen)$_3^{2+}$, has been so far one of the most popular luminescent indicators to measure molecular oxygen.[Erreur! Signet non défini.] This analyte is able to quench the fluorescence of the dye with a rate constant of 4 x 10^9 L mol^{-1} s^{-1} in aqueous solution. However, being a water-soluble salt, it is impossible to dissolve it either directly into the hydrophobic silicone membranes (or the like) required to sense oxygen in water, or in a solvent compatible with the organic polymer (halogenated or aromatic hydrocarbons).

Therefore, the luminescent cation needs to be immobilized onto a solid support compatible with the silicone prepolymer, - typically silica gel or glass powder -, previously to fabrication of the membrane. Adsorption of the indicator on the support leads always to inhomogeneous excited-state quenching and strongly non-linear dose–response curves.

Preparation of Ru(5-odap)$_3^{2+}$ has overcome such problems while maintaining the same interesting indicator features of its phen parent. Figure 3a shows the response function to oxygen in the gas phase of a 150-µm RTV silicone membrane prepared by uptake of Ru(5-odap)$_3^{2+}$ from a 0.2 mmol L^{-1} solution of the dye in dichloromethane. The inset depicts the associated (linear) calibration curve. Fabrication of a similar membrane with Ru(phen)$_3^{2+}$ using the same procedure is prevented by the almost negligible solubility of this indicator in the required organic solvent. The obtention of a linear dose-response plot allows a two-point calibration procedure to be developed, a highly desirable feature for the commercial aplication of any sensing device. At a total gas flow of 200 cm^3 min^{-1}, the response time for a 90% signal change (t_{90}) is 6 s for a 0–21% O_2 concentration increase and 48 s for a 21–0% reverse variation step. Unlike the oxygen electrode, the optical sensor is able to measure continuously for a long time in the gas phase without damage or drift, since it uses a "dry" sensing membrane and no reference electrode is required.

Figure 3. Response of the Ru(5-odap)$_3^{2+}$-containing luminescence optode to the oxygen concentration in (a) nitrogen and (b) water, at 25 ºC and 711 Torr atmospheric pressure, using the portable CCD spectrometer LAP-1000 (see Experimental Section). Insets: Corresponding dose/response plots (background corrected) in gas.



The optode performs equally well in water measurements. Figure 3b shows the sensor response to dissolved oxygen and the corresponding calibration curve. Compared to gas-phase measurements, the longer response time, both to direct and reverse analyte concentration changes (t_{90} of 3.1 and 9.8 min, respectively), is a consecuence of the (slower) diffusion kinetics of molecular oxygen in the aqueous phase and the neccesity of water-saturating thoroughly the gas mixtures before entering the flow-through measuring cell. Moreover, the observed smaller oxygen sensitivity of the optical sensor in water compared to that in gas phase may be a consequence of penetration of water vapour into the indicator layer. The commercial formulation of the silicone prepolymer contains already silica powder as filler, the hydration of which probably reduces the membrane uptake of oxygen, a hydrophobic species.

We have tested one of our oxygen optodes in the in-situ continuous monitorisation of this chemical species into the secondary treatment pool (microorganism-catalysed oxydation) of a municipal water-treatment plant. Figure 4 shows a typical three-day response obtained with the fibre-optic sensor directly introduced into the sewage (Figure 5). For the sake of comparison, hourly measurements were taken by the station employees using a commercial oxygen electrode (Danfoss) permanently installed in the same monitoring site; therefore, no readings have been taking off-hours.

The measurements have been performed with our GW-260 spectrometer (see Experimental Section). In order to correct the readings for variations in the lamp output, mostly due to over 15 ºC temperature difference between day and night, the sensor luminescence signal at 648 nm was always ratioed to the scattered light from the lamp at 520 nm by employing a proper combination of band-pass and cut-on coloured-glass filters (445 and 530 nm, respectively). The data depicted in Figure 4 demonstrates that real time in situ monitoring of dissolved oxygen with optodes is possible indeed; obviously, longer tests and extensive validation have to be performed before a commercial device can be launched, with the essential pressure and temperature corrections incorporated too.

This issues, as well as fabrication of a dedicated portable luminescence spectrometer, are being addressed in our industrial-university R+D project (1997-1999).

Figure 4. Comparison between in-situ measurements of dissolved oxygen in the biological treatment pool of a water sanitation plant taken with the luminescence optode (every 5 min) and a commercial electrode (every 60 min during working hours). The oxygen electrode trace has been offset by –1 ppm for the sake of clarity. The emission intensity in the absence (I_0) and in the presence of the analyte (I) has been corrected for the lamp output (I_r, see text).

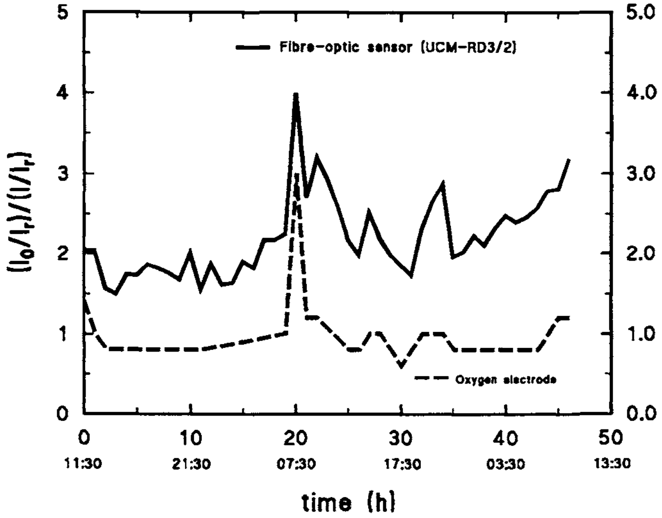
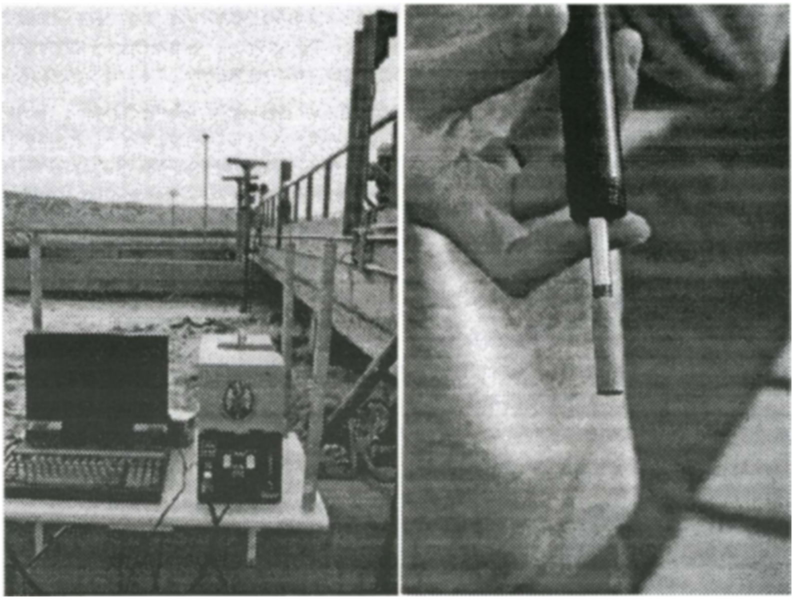
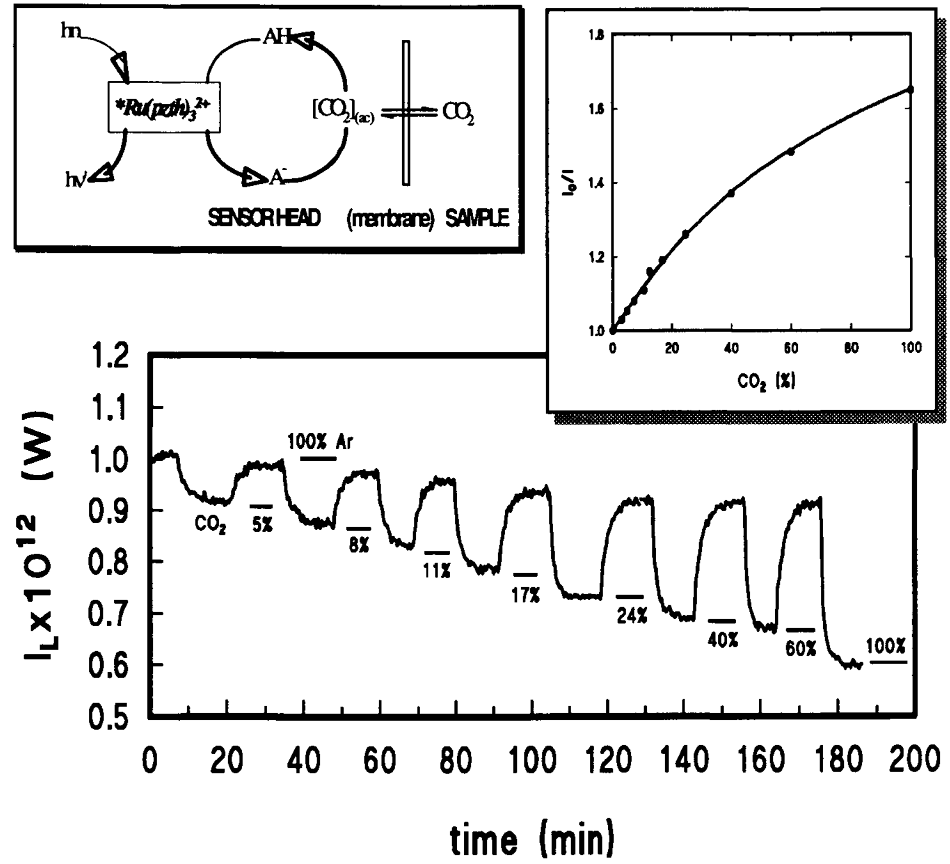


Figure 5. Experimental setup for continuous dissolved oxygen monitoring with optical fibre sensors in the biological treatment pool of a wastewater sanitation plant.



Ru(II) complexes with polyazaheterocyclic ligands can be also engineered to respond to a very different analyte such as carbon dioxide If pyridine-type moieties such as those contained in the 1,10-phenanthroline chelating ligands are replaced by pyrazine rings (Figure 2), the electronically excited state of the corresponding coordination compound turns out sensitive to the solution acidity. Irreversible protonation of the luminescent state competes with radiative deactivation to the ground state, so that both the emission intensity and lifetime are quenched as the pH of the medium is lowered. Permeation of CO_2 through a hydrophobic membrane into an aqueous gel layer containing immobilized $Ru(pzth)_3^{2+}$, placed at the distal end of a fibre-optic bundle, leads to an acidity change thanks to the (reversible) hydration of the analyte gas to hydrogencarbonate ion (Figure 6).

Figure 6. Response of the $Ru(pzth)_3^{2+}$-containing luminescence optode to the carbon dioxide concentration in water-saturated argon, at 25 ºC and 711 Torr atmospheric pressure, using the portable GW-260 spectrometer (see Experimental Section). Insets: Working principle of the optical sensor and corresponding dose/response curve.



The pH variation is sensed immediately by the luminescent indicator the signal of which, after appropriate calibration, yields the concentration of CO_2 in a gas or liquid phase, or HCO_3^- /CO_3^{2-} dissolved in water upon conversion into CO_2 in a similar (but optical) way to the conventional carbon dioxide (pH) electrode.

Figure 6 depicts the response of the CO_2 optode to the concentration of this determinand in gas mixtures. The response is fully reversible provided the sensor head is kept properly hydrated. This is not a problem for CO_2 monitoring in aqueous samples, but may be a drawback for vapor-phase determinations. The non-linearity of the calibration curve, compared to the response of the oxygen optode, is intrinsic to the acid-base photochemistry involved and not to inhomogeneous environment around the immobilised Ru(II) indicator.
In conclusion, success of fibre-optic sensors for environmental and industrial monitoring depends heavily in the photochemistry involved. Tailor-made optical indicators are required in order to exploit fully the performance of dedicated optoelectronic devices and to jump the gap between academic research and comercial exploitation.

Acknowledgements. Part of this research has been funded by the Spanish Government Agency CICYT (project no. AMB95-0689-C02). D.G.-F. and M.D.M. gratefully thank Universidad Complutense de Madrid for doctoral grants. J.D. acknowledges CICYT for a doctoral grant at INTERLAB Group R+D unit. The authors thank V. Llorente and A. Parrilla of Canal de Isabel II water company for their help and assistance to perform in situ measurements.

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