Fluorescent Optosensor for Humidity Measurements in Air

by **Maximino Bedoya**[a]), **Guillermo Orellana**[b]), and **María C. Moreno-Bondi***[a])

[a]) Laboratory of Optical Sensors, Department of Analytical Chemistry, Faculty of Chemistry, Universidad Complutense de Madrid, E-28040 Madrid

[b]) Laboratory of Applied Photochemistry, Department of Organic Chemistry, Faculty of Chemistry, Universidad Complutense de Madrid, E-28040 Madrid

Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

A fiber-optic sensor for relative-humidity (RH) monitoring in environmental samples is described based on the adiabatic photoreaction that produces an intramolecular charge-transfer excited state, which is the basis of the sensor response. The sensitive membranes are obtained immobilizing a highly fluorescent dye, 4-[2-(pyrazin-2-yl)-1,3-oxazol-5-yl]benzenamine (pzoxba; formerly called appzox), in hydroxypropylcellulose (HPC). The composition of the sensing films was optimized to a final ratio pzoxba/HPC of $1.8 \cdot 10^{-5}$ mol g^{-1} with a 100-μm membrane thickness. The optode response spans from 1.68 to 100% RH, with a detection limit of 0.56% (*Table 2*). Typical response times (t_{90}) to 0–100% relative humidity are 1–2 min, the relative standard deviation for repeated measurements being 0.77–1.8%. The optode is insensitive to typical organic vapor interferents of commercial capacitive sensors (see *Table 3*) as well as to molecular oxygen, an important quencher of other luminescence-based optical sensors. The proposed optode was successfully applied and validated for continuous monitoring of the relative humidity level in environmental samples.

1. Introduction. – Relative humidity (RH) has become a key parameter mainly for comfort reasons and for industrial processes [1–4]. Moreover, there is a growing need of developing automated control systems that allow the evaluation of this parameter in a wide range of industries such as the production of electronic devices, precision instruments, textiles, in cigar storage, production of dried foodstuffs, in agriculture, food processing and storage, or in the intelligent control of buildings to maintain a constant humidity level, among other areas [2–5]. Sometimes it is necessary to monitor the relative humidity, while in other occasions, the absolute humidity or the dew point have to be evaluated.

Different techniques have been developed for the determination of this parameter, with various complexity, precision, and accuracy. Conventional standard methods, such as the single hair hygrometer, the psycrometer, the chilled mirror dew point hygrometer, or the thermal conductivity technique, can be applied to that aim [6]. Nevertheless, in some situations, these methods are difficult or impossible to apply mainly because of their expensive maintenance and/or operational complexity. To overcome these limitations, different types of instruments and sensors have been described and/or commercialized for RH monitoring during the past years. Several devices exploiting different electrical properties such as resistance [7], capacitance [8], or potentiometry [9] have been reported. Other moisture sensors described in the literature are based on the oscillation frequency shift of a surface acoustic wave device [10][11].

Fiber-optic humidity sensors have also been described. Many of these devices are based on changes of the optical absorption properties of several inorganic salts, such as

$CoCl_2$ [12–16] or Co_3O_4 [17], or organic dyes [18–24], upon variations in relative humidity. Changes on the indicator luminescence intensity [25–30], the refractive index [31], or near-IR absorption spectroscopy [32][33] have also been applied for sensor development.

We demonstrated that the emission properties of the 4-[2-(pyrazin-2-yl)-1,3-oxazol-5-yl]benzenamine (pzoxba)[1]) were dramatically affected by the solvent polarity [34]. A bathochromic shift along with band broadening was observed in the emission spectra of the indicator dye as the polarity of the solvent increases. Such a result is attributed to its twisted intramolecular charge-transfer (TICT) excited state [34]. This fluorescent dye bears electron-donor (NH_2) and electron-acceptor (pyrazine) moieties in conjugated positions, linked through a heteroarene system. Such molecules display an equilibrium between the initially produced (planar) locally excited state, responsible for the strong emission of pzoxba in nonpolar solvents, and the TICT state, favored in polar solvents, provided that rotation around the C–N bond between the amino group and the benzene ring is not restricted. The TICT excited state gives rise to a significantly red-shifted emission band due to the solvent stabilization, the intensity of which is weaker as a consequence of fast decaying to the ground-state *via* nonradiative pathways. Moreover, in the presence of hydroxylic solvents, an intermolecular proton transfer to the TICT excited state might promote radiationless deactivation pathways. This principle was successfully applied to the monitoring of low-molecular-mass alcohols in gasolines by covalently binding the indicator to a cross-linked chloromethylated styrene-divinylbenzene copolymer [34]. Nevertheless, the selectivity of the device was largely influenced by the nature of the immobilizing support, so that suitable selection of this layer could render selective optosensing membranes for other species of environmental interest.

Therefore, we decided to use this fluorescent indicator for relative-humidity measurements upon immobilization in a hydrophilic support [35], where the selectivity and sensitivity towards the analyte are expected to be maximized. In this paper, we describe the behavior of pzoxba in different supports as well as the analytical performance, for relative humidity monitoring, of the fiber-optic chemical sensor fabricated with hydroxypropylcellulose membranes to immobilize the dye. The fluorescent optode was applied to relative humidity monitoring with CCD detection, and its response was validated by means of a commercial capacitative sensor placed in line during the measurements.

Results and Discussion. – *Spectroscopic Features of pzoxba in Organic Solvents and Immobilized onto Different Solid Supports.* The emission properties of pzoxba are strongly affected by the solvent polarity. As it was previously pointed out, its emission maxima is red-shifted from 414 nm in hexane to 530 nm in EtOH [34]. This effect is a consequence of the strong interaction of polar H-bonding alcohols with the probe molecules *via* the unshared electron pairs of the latter. Pzoxba, with both an electron-donating and an electron-releasing group in conjugated positions, shows an extremely fast equilibrium between the initially produced planar locally excited state and the

[1]) Formerly abbreviated as appzox (from 5-(4-aminophenyl)-2-(2-pyrazinyl)-1,3-oxazole) [34].

twisted intramolecular charge transfer (TICT) excited state, responsible for the red-shifted emission band observed in polar solvents.

Different materials (glass fiber, PTFE (poly(tetrafluoroethylene), filter paper, *Nylon*, silicone and hydroxypropylcellulose (HPC)) were tested as supports of the moisture-sensitive fluorescent dye, to select the one providing the largest sensitivity, selectivity, and fastest response to the analyte. *Table 1* shows the spectroscopic characteristics of pzoxba immobilized onto the different solid supports and the normalized emission intensity from the dyed films measured when exposed to wet and dry air streams.

Table 1. *Fluorescence Excitation and Emission Maxima for pzoxba Immobilized on Different Supports.* Normalized variation of the emission intensity from the different optode membranes exposed to 0% (I_0) and 100% (I_{100}) relative humidity at 20° and barometric pressure of 705 Torr.

Solid Support	λ_{ex}/nm	λ_{em}/nm	$(I_0-I_{100})/I_0$
Nylon	345	459	0
Glass fiber	385	540	0.063
PTFE	396	471	0.139
Silicone	360	460	0.181
Filter paper	396	500	0.318
Hydroxypropylcellulose	390	496	0.866

The absorption and fluorescence maxima change as a function of the polarity of the indicator support. The latter exert two different actions: firstly they stabilize to a different degree the TICT excited state of adsorbed pzoxba and secondly, they control the interaction of H_2O vapor with the immobilized dye.

The most red-shifted emission maxima were obtained for glass-fiber membranes, indicating a strong stabilization of the TICT state, almost similar to that observed (λ_{em}^{max} 540 nm) for pzoxba dissolved in EtOH [34]. On the contrary, *Nylon* and silicone provide similar stabilization to photoexcited pzoxba in toluene, as deduced from the emission maxima observed in those environments. The highest sensitivity to humidity was obtained for the dye entrapped in HPC films. At the same time, this support provided the shortest response and recovery time (88 s and 150 s, resp.) for 0–100% relative-humidity changes. The high hydrophilicity of HPC and its ability to absorb H_2O [35], compared to that of the other supports tested, are likely to be responsible for the high sensitivity observed with this material.

The behavior of the sensing membranes upon exposure to different RH values was investigated by means of the HPC fluorescent layers. As shown in *Fig. 1*, the emission band of the dye in the sensing membrane shifts to the red, and its intensity drops with increasing humidity values. This effect is a consequence of the formation of the TICT excited state of the dye with increasing H_2O vapor concentrations in the measuring gas samples.

Optimization of the Sensitive Layers. To evaluate the effect of some characteristics of the film on the fluorescence intensity of the dye in the absence of analyte, the thickness of the sensing layers as well as the indicator/polymer ratio were optimized. With this purpose, different sensitive membranes with a defined thickness were prepared by immobilizing increasing amounts of pzoxba in a constant amount of HPC.

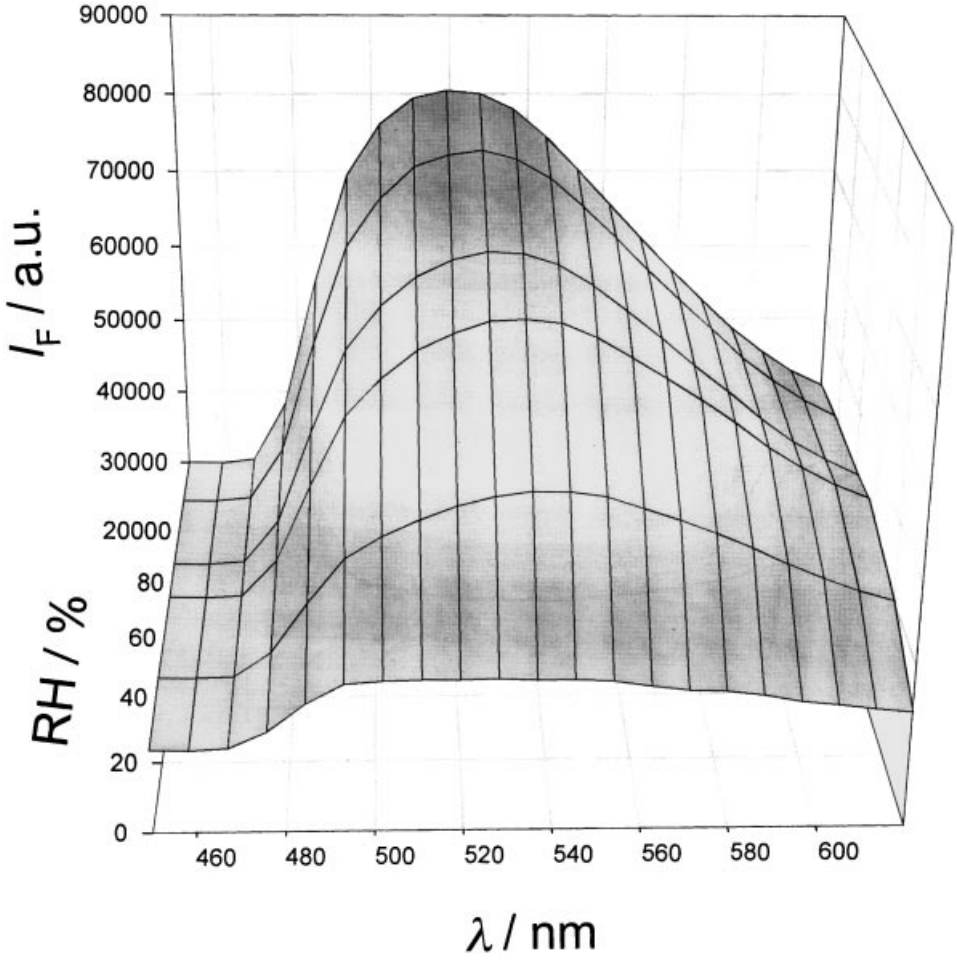

Fig. 1. *Emission spectra* (uncorrected for instrumental response) *of immobilized pzoxba in HPC layers when exposed to different relative humidity* (RH/%) *samples.* λ_{exc} 360 nm; 20°.

The response of the resulting fluorescent membranes is shown in *Fig. 2, a*. The emission intensity of the films increases linearly with increasing dye loading, up to a certain dye/polymer ratio ($1.8 \cdot 10^{-5}$ mol g^{-1}) where the signal levels off, probably due to an inner-filter effect. The fluorescence intensity increases also with membrane thickness up to a constant value (*Fig. 2, b*). Thicker layers were more robust and easier to prepare that the thin ones, although the response times obviously increased with film thickness. Therefore, a compromise value of 100 μm was finally selected for the development of the sensing membranes.

Temperature is a factor that affects the current value of H_2O vapor pressure and may influence the emission signal of the membranes. In fact, some authors have pointed out the substantial effect that temperature may exert on the response of the optical

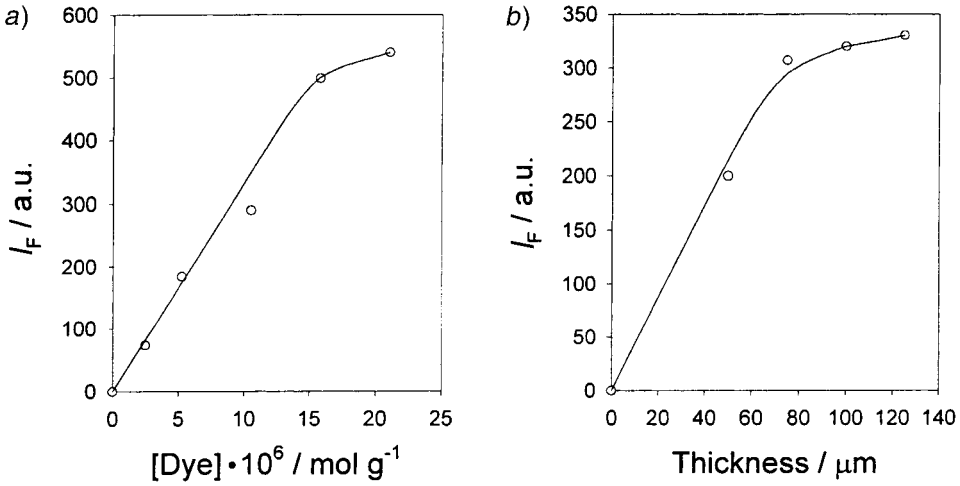

Fig. 2. *Fluorescence emission intensity of pzoxba-doped hydroxypropylcellulose* (HPC), *at 0% relative humidity:* a) *as a function of the dye concentration in 0.038 g of HPC,* b) *as a function of the layer thickness at a dye concentration of* $18 \cdot 10^{-6}$ *mol* g^{-1}. λ_{exc} 390 nm, λ_{em} 496 nm; 20°.

sensors to RH [15]. To evaluate the temperature dependency on the pzoxba optode response, the sensing layers were placed in a thermostatized flow-through cell and a H_2O-saturated air stream was generated in a chamber at the measuring temperature. The normalized fluorescence signal obtained with the optode, as it is shown in *Fig. 3*, raises with increasing temperatures up to 25° and then decreases substantially. This behavior could be explained considering the combined effect of several opposite factors. Elevation of temperature increases the H_2O vapor pressure and, consequently, the amount of H_2O molecules in the sampling gas to produce a more effective fluorescence quenching. However, as temperature increases, the fluorescence of the dye in the absence of the analyte decreases, as shown in *Fig. 4*.

Another experiment was performed by keeping constant the amount of H_2O in the sampling gas at different temperatures. In that case, a termostatized gas-bubbling bottle was used to saturate the N_2 stream with H_2O at 5°. This H_2O-saturated gas was then passed through a second gas-bubbling bottle at a temperature set in the 5–20° range. The response function obtained with the optode under these conditions is shown in *Fig. 4*. The RH values at the different temperatures tested (*Fig. 4*, inset) were calculated by assuming an ideal behavior for the sample moist gas stream, and by using the tabulated H_2O-vapor pressures as a function of temperature [36]. As shown in *Fig. 4*, for a constant analyte level, the sensor response decreases as the temperature increases. This observation would indicate that the association equilibrium between the indicator and the H_2O molecules is more effective at low temperatures and/or the absorption of H_2O on the HPC polymer is higher at lower temperatures.

Relative Humidity Measurements: Analytical Characterization. The normalized signal from the fluorescent sensor exposed to different RH values, together with its response function, is depicted in *Fig. 5*. The optode response can be fitted in the

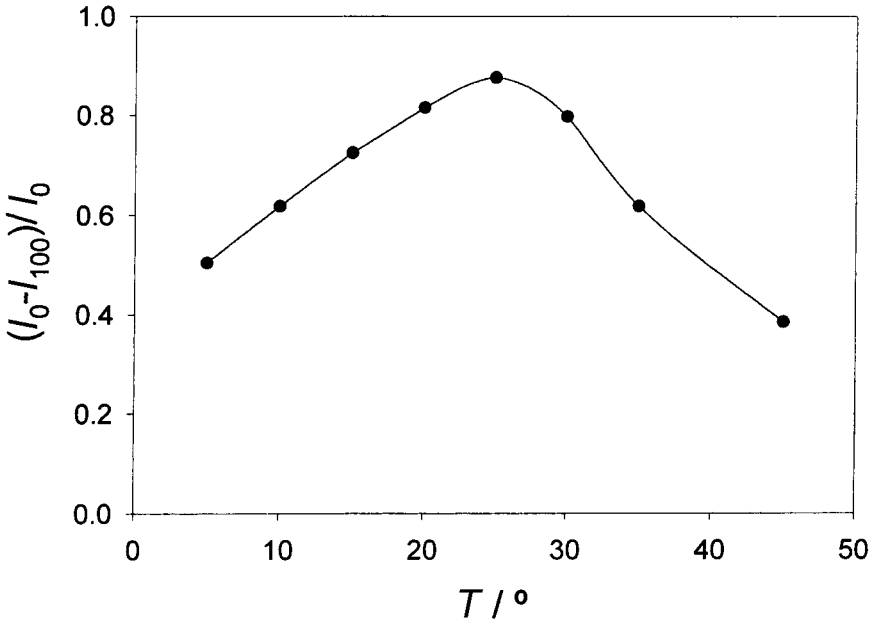

Fig. 3. *Influence of temperature on the normalized fluorescence intensity obtained with the optode for the determination of a 100% relative humidity gas sample.* λ_{exc} 390 nm, λ_{em} 496 nm.

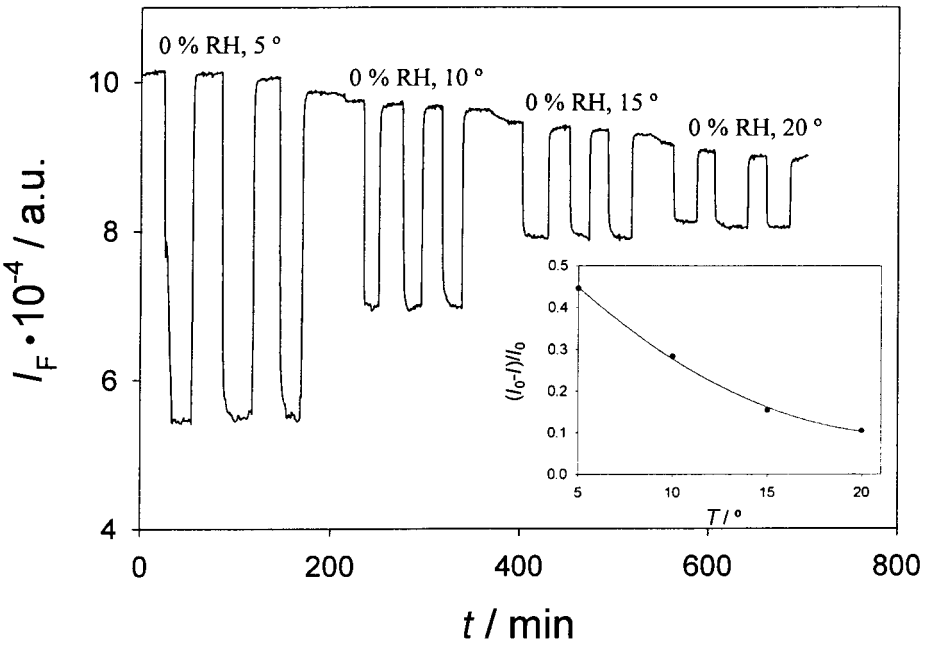

Fig. 4. *Response function obtained with the optode for 6.543 Torr constant water pressure in the air stream sample at different temperatures* (5–20°). Inset: *Normalized emission intensity as a function of temperature.* λ_{exc} 390 nm, λ_{em} 496 nm.

0–100% RH range to a second order polynomial function (uncertainty values are calculated at a 95% confidence limit) according to *Eqn. 1*.

$$(I_0 - I)/I_0 = (28 \pm 8) \cdot 10^{-6}\ \mathrm{RH}^2 + (50 \pm 8) \cdot 10^{-4}\ \mathrm{RH} + (1 \pm 2) \cdot 10^{-2}\ (r = 0.9988) \quad (1)$$

The detection limit, calculated as the RH that produces a normalized signal equal to that of the blank plus three times the standard deviation of 50 measurements of a dry gas stream (blank), was 0.56% RH, lower or comparable to those reported in the literature for optical sensors (0.5% RH, 10.2% RH) [22][29]. The quantification limit, calculated according to the IUPAC definition [37] as the RH that produces a normalized signal equal to the blank plus ten times the standard deviation of the blank, was 1.86% RH. The precision of the sensor was evaluated in terms of the relative standard deviation (r.s.d.) for at least five replicates of wet gas streams of various RH values, obtained by using standard saturated salt solutions [38]. The results, as shown in *Table 2*, were in the 0.77–1.8% range, significantly better then reported values (5.8%, 4%, 3%) [20][30][27]. The analytical characteristics of the optode membranes are summarized in *Table 2*.

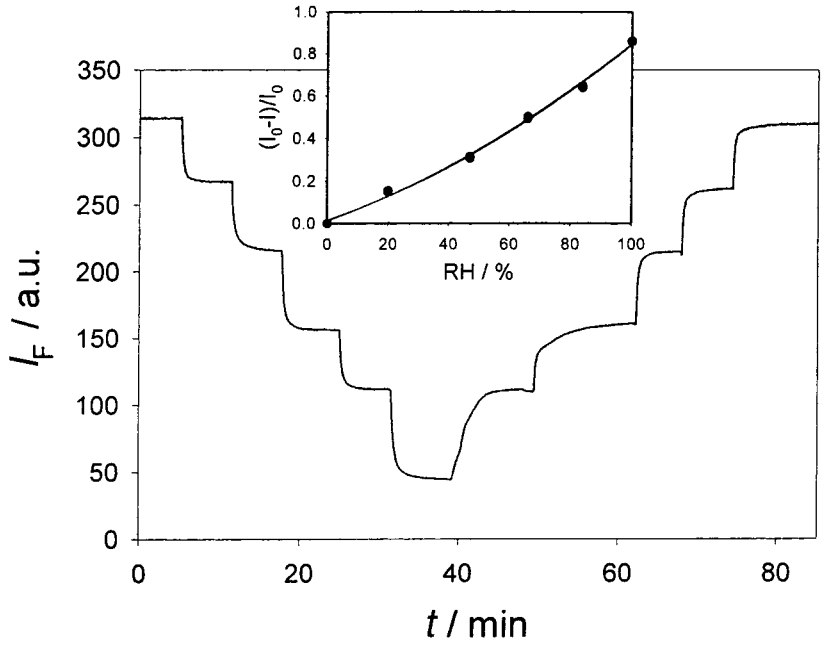

Fig. 5. *Response function and calibration curve of the optode for RH monitoring.* Inset: *Direct* (0–100% RH) *and reverse* (100–0% RH) *calibration plots.* λ_{exc} 390 nm, λ_{em} 496 nm; 20°.

Table 2. *Analytical Features of the Fluorescent pzoxba/HPC Optode Interrogated with the Two Instruments Used for the Measurements.* See text for instrumental configuration.

Fluorometer	Detection limit (% RH)	Quantification limit (% RH)	% RH	Repeatability % r.s.d [a] [b]	Reproducibility % r.s.d [a] [b] [c]
LS-50	0.56	1.86	100	0.81 ($n=6$)	6.7 ($N=6$)
			84	0.77 ($n=5$)	3.0 ($N=6$)
			66	1.8 ($n=7$)	4.5 ($N=4$)
			20	1.3 ($n=6$)	3.0 ($N=6$)
LFA-1000	7.7	16.4	47	2.2 ($n=10$)	–[d])

[a]) r.s.d. = relative standard deviation. [b]) *n:* number of measurements in one day. [c]) *N:* number of testing days (five measurements per day). [d]) Not determined

The response time (t_{90}) of the fluorescent membrane is in the order of 1–2 min, when going from low- to high-RH gas samples, faster than that obtained for other luminophores or chromophores immobilized in different supports [15][17][27]. Nevertheless, the response time increases up to 3.5 min when going from high- to low-RH values. This effect has also been observed by other authors [15] and attributed, in part, to the time necessary for the replacement of the atmosphere in the test cell and the desorption of the analyte from the sensing layers.

As shown in *Fig. 5*, the calibration curves obtained in going from high to low RH values are not statistically different (at a 95% confidence limit) from those obtained in the opposite way. Therefore, it can be concluded that the sensitive membranes show no hysteresis. This characteristic represents a clear advantage for environmental monitoring over other sensors described in the literature [15][20].

When the optode was exposed to consecutive RH step changes between 0 and 100%, the repeatability of the measurements was remarkably high (*Table 2*) yielding a standard deviation of 0.81% for a RH of 100% ($n=6$). The same fluorescent layer was tested for longer measuring times. The mean of the normalized fluorescence signal, from 0 to 100% RH, is shown in *Fig. 6*. After a 16 days period, the membranes are degraded and should be replaced. The observed degradation is mainly due to the degradation of the HPC originated by the calibration standard saturated solutions. The reproducibility in the preparation of the optode membranes (five units) was 10.3% (r.s.d.) for a moist gas stream of 20% RH.

Response to Interferent Compounds. Only those chemical species that may affect the locally excited/TICT excited state equilibrium and are able to penetrate the HPC membrane are expected to interfere in the response of the RH sensor based on pzoxba. *Table 3* shows the concentration of the different solvent vapors tested that produce a change in the analytical signal equivalent to that originated by a 2.5% RH air stream, as stated for the commercially available devices [39]. A comparison of these data with those reported for some capacitive sensors for relative humidity monitoring [39] is also presented in *Table 3*, as well as the limits for human exposure proposed by the American Conference of Governmental Industrial Hygienists [40]. The fluorescent optode showed no response to ethylene glycol (= ethane-1,2-diol) and is more selective than the capacitive sensor, except when acetic acid or propan-2-ol are used. Moreover, all the assayed vapor concentrations are above the tabulated limits for human exposure,

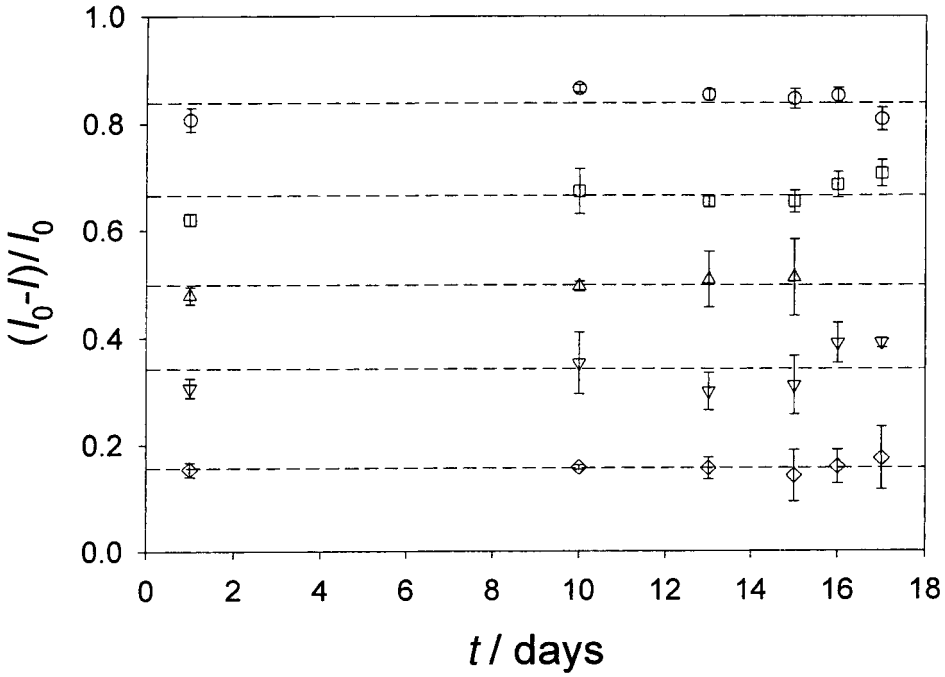

Fig. 6. *Normalized fluorescence intensity signal obtained with the optode, as a function of the operational time and relative humidity of the sample* (◇ 20%, ▽ 47%, △ 66%, □ 84% and ○ 100%). λ_{exc} 390 nm, λ_{em} 496 nm; 20°.

except that of acetic acid. No interference from O_2 and CO_2 was observed at the concentrations present in air, and the calibration curves obtained for the optical sensor were identical when dry Ar or air were used for the preparation of the synthetic gas calibration samples. This behavior represents an important advantage of the pzoxba/HPC optode over those using phosphorescent indicators that are readily quenched by oxygen [26][28].

Table 3. *Gas-Phase Concentration of Different Interferent Species that Produce a Signal Variation Equivalent to That Measured for 2.5% RH with the pzoxba/HPC Optosensor and a Capacitive Sensor, as well as the Limits for Human Exposure Proposed by the American Conference of Government Industrial Hygienists.*

Interferent	Optical sensor/g m^{-3}	Capacitative sensor/g m^{-3}[a])	Limits for human exposure/g m^{-3}[b])
Acetone	19	8	2.400
Ethanol	7	6	1.900
Ethyl acetate	120	15	1.400
Ethylene glycol	no response[c])	3	no data
Propan-2-ol	6	12	0.980
Acetic acid	$1 \cdot 10^{-3}$	2	0.020
Propan-1-ol	5	no data	0.500
Methanol	2	no data	0.260

[a]) From [39]. [b]) From [40]. [c]) 3.40 g m^{-3} Maximum concentration exposed.

Application to Environmental Monitoring. To evaluate the performance of the developed optode for ambient relative humidity monitoring, it was necessary to use a portable instrument. To that aim, the response of the sensing membranes was evaluated with our custom-made *LFA-1000* fiber-optic spectrometer, based on CCD detection (see *Exper. Part*). The analytical characteristics of the fluorescent pzoxba/HPC optode for this instrument are summarized in *Table 2*. The optode sensitivity with the portable instrument turned out to be lower than that observed with the bench-top fluorometer (*i.e.* higher detection and quantification limits were obtained with the former). The reason for such a difference may lay in the wavelength-selection system (broad-band filters) of the *LFA-1000* instrument compared to the double-monochromator of the commercial apparatus, that leads to a lower signal background in the latter.

The relative humidity of the air samples was evaluated with both the optical and capacitive sensors every 20 s. The RH mean value ($n = 10$) was found to be 40.2% ($s_{n-1} = 0.3\%$) and 41% ($s_{n-1} = 2\%$) for the optical and electrical sensors, respectively. The *F*-test was used to compare the standard deviations of both set of data, and significative differences were found at a 95% probability level. Therefore, an appropriate *t*-test method was applied, taking into consideration that the population standard deviations are not equal, to compare the mean humidity values obtained with both techniques. No significative differences were found in this case at a 95% probability level.

Conclusions. – A simple, inexpensive, and sensitive optode for the determination of relative humidity in environmental samples is described. The sensor is based on a highly fluorescent indicator (pzoxba) immobilized on hydroxypropylcellulose, for the development of the membranes sensitive to H_2O vapor. The working principle is based on the formation of a weakly emitting twisted intramolecular charge transfer excited state in the presence of low amounts of atmospheric H_2O vapor. The optode shows excitation and emission wavelengths in the VIS region and a large *Stokes* shift (> 100 nm) that allow the use of simple filters for separation of the excitation and emission wavelengths. The optode was evaluated in combination with a conventional fluorometer and a custom-made portable instrument containing a CCD detector. In both cases, an excellent sensitivity and reproducibility was obtained. The RH-sensitive membranes are easy to fabricate, simple to use, and stable for at least 15 days. Their sensitivity to organic-solvent vapors is, in general, lower than that shown by a capacitance-type sensor. The device was successfully applied and validated for continuous monitoring of atmospheric RH by means of a portable CCD-based fiber-optic instrumentation. Therefore, the optode could become an excellent alternative to other types of sensors commercially available.

Experimental Part

Chemicals. The synthesis and structural characterization of the fluorophore 4-[2-(pyrazin-2-yl)-1,3-oxazol-5-yl]benzenamine (pzoxba) has been reported elsewhere [41]. All the solvents used were of spectroscopic grade from *Aldrich*, *Merck*, or *Scharlab*. Air and Ar, both of a purity higher that 99.995%, were purchased from *Liquid Carbonic*. Pure cellulose sheets, grade *2* (filter papers), from *Whatman*, were acetylated following the procedure described by *Boltinghouse* and *Abel* [15]; *Nylon ASTM 325-44* from the *Swiss Silk Bolting Cloth Mfg. Co.*, poly(tetrafluoroethylene) membranes *FSLW02500*, fiber-glass membranes *AP40* from *Millipore*, and hy-

droxypropylcellulose from *Aldrich* were tested as supports for the indicator dye. Alternatively, silicone membranes were prepared with poly(dimethylsiloxane), ethyltriacethoxysilane, dibutyltin dilaurate from *ABCR*, and pyrogenic silica gel from *Sigma*. All other chemicals used were of anal. reagent grade.

Instrumentation. Emission spectra: *Perkin-Elmer LS-50B*, interfaced to a *486DX4* computer for instrument control and data processing (λ_{exc} 390 nm; λ_{em} 496 nm; emission cut-off filter at 430 nm). Alternatively, the *LFA-1000* custom-made portable fiber-optic spectrometer was used to interrogate the fluorescent optodes. This spectrometer holds a 12-V, 10-Hz *Ocean-Optics-PX-1* Xe flashlamp fitted with an *SMA* connector and an *Oriel-Instaspect-IV* CCD detector (1024 × 256 pixel), attached to an *Oriel-MS-256-1/8 m* spectrograph into a 46 × 33 × 16 cm aluminium-plastic case. The *Oriel* interface card, which powers the CCD, fires the strobe, collects the signal, and synchronizes the excitation and emission events, is placed into the mini-docking accessory of an *Olivetti-Echos-P-100* laptop computer loaded with the original *Oriel* software for instrument control and data acquisition. Wide band-pass (360 nm) and cut-off (470 nm) colored glass filters were used in the excitation and emission channels, respectively.

A capacitative sensor for relative humidity monitoring, *Testo 625*, was used to validate the optode response.

Fiber-optic measurements were carried out in a homemade stainless-steel flow-through cell previously described [34]. A randomly distributed bifurcated bundle (25 + 25 glass fibers, 6.5-mm diameter at the common end) from *Dolan-Jenner*, connected to the *Perkin-Elmer* fluorometer *via* the *Perkin-Elmer* fiber adapter, or alternatively, a bifurcated quartz bundle (14 optical fibers, 500-μm each) from *Fiberguide Industries*, connected to a CCD spectrometer, carried the light to and from the flow-through cell. The sensitive layer was placed at the measuring cell, on top of a 2-mm thick optical glass adjacent to the common end of the fiber bundle.

Argon or air streams of variable moisture content, with a total flow rate of 5 l min^{-1} controlled with a rotameter *Aalborg*, were prepared by bubbling dry gases through thermostatized (20.0 ± 0.5°) salt-saturated aqueous solutions of defined humidity [38]. Alternatively, H_2O-sat. air, obtained by bubbling dry air through several gas wash bottles, was mixed with dry air in a defined proportion by means of two calibrated rotameters and fine control valves to vary the volumetric ratios of both streams. In both cases, the sample gas flow was passed through the optical sensing cell, and the reference capacitive sensor was placed immediately after the optode. The airflow passing through both devices was thermostatized at 20.0 ± 0.5° with a *Haake-D8-GH* circulator.

Membrane Preparation. Different aliquots (1.4 – 12 ml) of a 33 μM dye soln. in $CHCl_3$ were placed in brown glass vials and evaporated in an oven at 40°. After solvent removal, 0.038 g of hydroxypropylcellulose were weighted in each container and dissolved in 0.5 ml of abs. EtOH. With this viscous soln., layers of different thickness were extended over a transparent polyester film (125 μm thickness), after allowing them to dry in a dessicator for 24 h. Circles of 2-cm diameter were cut from there and placed in the measuring flow-through cell. The sensitive layers were always stored in a dessicator between measurements.

Selectivity Measurements. The optical-fiber sensor was fitted to a three-necked round-bottom flask (576 ml), and the remaining openings were closed by two rubber septums. Samples were introduced into the vessel with a *Hamilton* gas-tight syringe (Bonaduz, Switzerland) through one of the septums, while the other was used to introduce an Ar stream to vent the vessel at controlled temp. (20°).

Application to Environmental Monitoring. The sensing membrane was placed at the tip of the optical fiber bundle, in a flow-through cell thermostatized at 20°. The cell inlet was connected to a peristaltic pump, and the output was connected on line with a capacitive sensor for system validation.

This project has been funded by the Spanish Government Agency *CICYT* under contracts no. AMB95-0689-C02 and AMB98-1043-C01/C02.

REFERENCES

[1] A. Wexler, 'Humidity and Moisture', Reinhold, New York, 1965, Vol. 1.
[2] E. Traversa, *Sens. Actuators, A* **1995**, *23*, 135.
[3] H. Arai, T. Seiyama, in 'Sensors: A Comprehensive Survey', Eds. W. Gopel, J. Hesse, and J. N. Zemel, VCH, Weinheim, 1992, Vol. 3, p. 981.
[4] M. J. Lipsett, D. J. Shusterman, F. F. Beard, in 'Patty's Industrial Hygiene and Toxicology', Eds. G. D. Clayton and F. E. Clayton, 4th edn., Wiley, New York, 1994, Vol. II, p. F4552.
[5] T. Toyota in 'Intelligent Sensor Technology', Ed. R. Ohba, Wiley, Chichester, 1992, p. 140.
[6] R. H. Perry, D. W. Green, J. O. Maloney, 'Manual del Ingeniero Químico', McGraw-Hill Inc., 1998, Vol. I, p. 12.

[7] Y. Sakai, M. Matsuguchi, T. Hurukawa, *Sens. Actuators, B* **2000**, *66*, 135.
[8] Ch. B. Park, Y. H. Lee, S. B. Yi, *Sens. Actuators, B* **1993**, *13–14*, 86.
[9] Y. Sakai, *Sens. Actuators, B* **1995**, *23*, 63.
[10] A. E. Hoyt, A. J. Ricco, J. W. Bartholomew, G. C. Osbourn, *Anal. Chem.* **1998**, *70* 2137.
[11] K. Korsah, C. L. Ma, B. Dress, *Sens. Actuators, B* **1998**, *50*, 110.
[12] A. P. Russell, K. S. Flecher, *Anal. Chim. Acta* **1985**, *170*, 209.
[13] D. S. Ballantine, H. Wohltjen, *Anal. Chem.* **1986**, *58*, 2883.
[14] Q. Zhou, M. R. Shahriari, D. Kritz, G. H. Sigel, *Anal. Chem.* **1988**, *60*, 2317.
[15] F. Boltinghouse, K. Abel, *Anal. Chem.* **1989**, *61*, 1863.
[16] A. Kharaz, B. E. Jones, *Sens. Actuators, A* **1995**, *46–47*, 491.
[17] M. Ando, T. Kobayashi, M. Haruta, *Sens. Actuators, B* **1996**, *32*, 157.
[18] K. Wang, K. Seiler, J. P. Haug, B. Lehmann, S. West, K. Hartman, W. Simon, *Anal. Chem*. **1991**, *63*, 970.
[19] S. Otsuki, K. Adachi, *Polymer J.* **1995**, *25*, 697.
[20] R. Narayanaswamy, I. M. Raimundo Jr., *Analyst* **1999**, *144*, 1623.
[21] T. E. Brook, M. N. Taib, R. Narayanaswamy, *Sens. Actuators, B* **1997**, *38–39*, 272.
[22] G. J. Mohr, U. E. Spichiger-Keller, *Mikrochim. Acta* **1998**, *130*, 29.
[23] S. Otsuki, K. Adachi, T. Taguchi, *Sens. Actuators, B* **1998**, *53*, 91.
[24] P. J. Skrdla, S. S. Saavedra, N. R. Armstrong, S. B. Mendes, N. Peyghambarian, *Anal. Chem.* **1999**, *71*, 1332.
[25] S. Otsuki, K. Adachi, *J. Photochem. Photobiol., A: Chem*. **1993**, *71*, 169.
[26] J. M. Costa-Fernández, M. E. Díaz-García, A. Sanz-Medel, *Sens. Actuators, B* **1997** *38–39*, 103.
[27] J. M. Costa-Fernández, A. Sanz-Medel, *Anal. Chim. Acta* **2000**, *407*, 61.
[28] D. B. Papowsky, G. V. Ponomarev, S. F. Chernov, A. N. Ovchinnikov, I. N. Kurochkin, *Sens. Actuators, B* **1994**, *22*, 57.
[29] M. M. F. Choi, O. L. Tse, *Anal. Chim. Acta* **1999**, *378*, 127.
[30] M. M. F. Choi, S. Shuang, *Analyst* **2000**, *125*, 301.
[31] A. D. Stuart, P. E. Grazer, *Int. J. Photoelectron.* **1988**, *3*, 177.
[32] A. Fong, G. M. Hieftje, *Anal. Chem.* **1995**, *67*, 1139.
[33] X. Zhou, P. A. Hines, K. C. White, M. W. Borer, *Anal. Chem.* **1998**, *70*, 390.
[34] G. Orellana, A. M. Gómez-Carneros, C. De Dios, A. A. García-Martínez, M. C. Moreno-Bondi, *Anal. Chem*. **1995**, *67*, 2231.
[35] S. Otsuki, K. Adachi, *Anal. Sci.* **1993**, *9*, 299.
[36] R. C. Weast, in 'CRC Handbook of Chemistry and Physics', 1st student ed., CRC Press Inc., Boca Ratón, Florida, 1988, p. D113.
[37] Eurachem/Citac Guide 'The Fitness for Purpose of Analytical Methods', D. Holcombe, LGC, Teddington (U.K.), 1998, p. 43.
[38] S. Budavari, in 'The Merck Index, 10th edn.,' Ed. Merck and Co., Whitehause Station, New Jersey, 1983, p. MISC98.
[39] *Rotronic AG* (Switzerland), Catalogue 2000/01.
[40] R. C. Weast, in 'CRC Critical Handbook of Chemistry and Physics', 60th edn., CRC Press Inc., Boca Ratón, Florida, 1974, p. D123.
[41] G. Orellana, A. M. Gómez-Carneros, C. De Dios, A. A. García-Martínez, M. C. Moreno-Bondi, Span. Pat. 2,065,268, 1993.

Received June 1, 2001