Interface electronic system for measuring air acidity with optical sensors

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Abstract
Environmental acidity is a key parameter in Cultural Heritage conservation issues since it has a direct impact on degradation of both exposed and stored materials. Unfortunately, most of the acidity sensors now available are electrodes, which are not able to measure pH in gaseous phases and, therefore, are not suitable for measuring the environmental acidity of the air. This paper describes the development of an interface electronic system designed for the practical application and using of environmental acidity sensors prepared by the Sol-Gel procedure. These chemical sensors were investigated previously. They have optical response: their colour changes reversibly depending on the pH of the surrounding environment (air). A simple portable unit with a wireless ZigBee interface has been designed and developed to measure the environmental acidity in museums, showcases, store and exhibition rooms and several Cultural Heritage buildings. Main achievements of the interface electronic system have focused, on the one hand, on conversion of the optical signal of sensors into an electric current and, on the other hand, on the computer interfacing to obtain quantitative data of environmental pH. Quantitative data are obtained through the calibration curve of sensors and the software designed for managing the whole system.

Keywords
Electronic system; Optical sensors; Acidity; Wireless; Heritage conservation; pH.

1. Introduction
The pH is a chemical parameter used in a wide range of scientific, technical, industrial and domestic activities. It is commonly measured by means of electrodes of different characteristics depending on the application field. Most of them are based on an electrochemical response and are able to operate in liquid media, as well as in humid solids and/or soft solids [1,2,3]. Other pH sensors work by means of an optical response, such as Sol-Gel based sensors. As it is well-known, materials prepared by this procedure are suitable hosts for transductors and sensors. Their residual porosity and cross-linked polysiloxane network favour the physical entrapment of sensitive phases (chemicals, biochemicals, live microorganisms, etc.) and, at the
same time, preserve main features of such phases to remain them active and even reversible [4]. Some Sol-Gel pH sensors are based on the optical radiometric excitation [5], the refractive index of optical fibers [6], the concentration of some gaseous substances [7], and the luminescent emission of a given dye [8,9,10]. Another group of optical pH sensors prepared by the Sol-Gel procedure are based on the visible absorption/transmission response of the sensitive phase [11,12].

Since final application of the present research is evaluation of whole acidity of the air to which Cultural Heritage items are exposed, the sensors needed must be able to detect reversibly all the acid/basic species present in the air that could affect conservation of Heritage materials (e.g., metals, glasses, textiles, papers, leathers, woods, etc.). In this line, Sol-Gel optical pH sensors were designed, prepared and characterized to monitor the acidity/basicity of gaseous environments as is the air. According to former experience of some of the present authors [13], these sensors were designed to be applied for Cultural Heritage conservation under several requirements. Such requirements are concerned with accuracy, reliability, fast response, good chemical resistance, easy preparation and handling, small size, low cost and low energy consumption. However, the use of such acidity sensors was conditioned by the measurement of their optical response with a conventional visible spectrophotometer, which is normally available at the laboratory. This conventional equipment uses to be of big size, non-portable, high cost, and quite often needs to be operated by skilled personnel. Therefore, the application of environmental pH sensors for conservation issues was seriously limited due to these non portable laboratory equipments. Such constraints constitute in fact a practical drawback since Cultural Heritage items can not be usually moved to laboratory facilities.

The present work aims at solving such practical drawback providing an electronic interface system which can be used in situ with environmental acidity sensors (formerly designed and currently adapted), recording their optical response and supplying quantitative data of environmental pH by means of a wireless technology.

2. Experimental

2.1. Synthesis and properties of environmental acidity sensors
Environmental acidity sensors employed in the present work consist of a thin Sol-Gel layer (thickness ranging from 200 to 400 nm) obtained by dip-coating upon a common soda lime glass slide [14]. Following Carmona et al. [15], the colloidal suspension (Sol) is synthesized from silicon tetraethoxide (Si(OCH₂CH₃)₄), ethanol (CH₃CH₂OH), hydrochloric acid (commercial concentrated) and an organic dye (3′-3″-dichlorophenolsulfonephthalein) as the sensitive phase. Molar ratio of the Sol components was 1 alkoxide / 8 ethanol / 0.8 HCl / 10⁻⁴ organic dye. The organic dye was selected according to the pH range in which environmental pH changes could affect conservation of Cultural Heritage items. That is, around the theoretical neutral conditions at pH=7.

Once the thin layer is deposited by dip-coating on the substrate (glass slide), the sensor is partially densified at about 60°C for several days (Gel). After this soft heat-treatment the sensors (coated glass slides) are cut to the appropriate size to be used with the measurement devices (4.0 x 2.5 x 0.1 cm). The sensors appearance is transparent and homogeneous (fig. 1). Their colour changes reversibly depending on the pH of the surrounding environment, either in liquid or in gaseous phases. Other experimental details can be found in [15].

In order to calibrate and to assess the sensors’ properties, their optical response was evaluated by visible spectrophotometry using an Ocean Optics equipment with the following characteristics: a CUV-UV Cuvette Holder with SMA 905 terminations for coupling to fiber optics, which is optimized for applications from 200 nm to 2 µm; a DH-2000-BAL Deuterium Tungsten Halogen light source with a stable output from 215 to 2000 nm; and an HR4000 0.02 nm optical resolution spectrometer with a response range from 200 to 1100 nm.

Fresh buffered solutions prepared from Hydrion Buffer Salt® (Aldrich) were employed to fix pH conditions of the sensors in liquid phase for all the measurements undertaken to calibrate and to assess the sensors’ properties. Before recording each spectrum, the sensors were immersed into the corresponding buffered solution for 10 min.
Response time of the sensors was evaluated by subjecting them to vapours of aqueous ammonia inside a controlled atmosphere vessel. The sensors were exposed for 30 min to a fixed concentration of ammonia. Once the sensors were sensitized, the corresponding optical absorption spectra were recorded. Successive spectra were recorded at different times, while the same sensor was maintained in the same position inside the spectrophotometer sample holder.

Reversibility of the sensors’ optical response was checked by dipping them into two extreme pH buffered solutions (pH=3 and pH=11) for 10 min in successive runs and recording the corresponding optical absorption spectra each time.

Thermal resistance of the sensors was assessed by introducing them into: 1) a climatic chamber Dycometal CCM-25/81 (for low and medium temperatures) and 2) a conventional laboratory stove with forced air ventilation (for high temperatures). The sensors were maintained 2 h at each test temperature from -10°C to 60°C, by steps of 10°C.

The chemical resistance of the sensors was checked against different liquid reagents (salts, acids, hydroxides, solvents, and buffered solutions), whose pH ranged from 1 to 14. The sensors were dipped into such liquids from 1 to 30 min. Spectra obtained from sensors before and after the tests were recorded.

Photostability to UV-Vis radiation was checked in previous works [15]. Results showed that neither UV nor Vis radiations cause serious damage in the sensitive layer of the sensors. After a continuous maximum exposure time of 16 h the optical response of the sensors diminished less than 15%.

2.2. The interface electronic system
The main goal of this work was to design a measurement module that could be used along with the optical sensors described above with the aim at providing quantitative data of environmental pH in field applications. An important requirement of that module was that it should be portable, since the user should remain near each sensor location for recording a pH measurement. Furthermore, after measuring the
response of all the sensors, the user has to download the data into a personal computer for later analysis and/or storage.

Two possible solutions were proposed to fulfill these requirements: 1) a wireless sensor module that could be placed together with every sensor to form a wireless sensor network, or 2) a single measurement unit that could be used for gathering data manually. Taking into account that requirements and specific conditions for application in Cultural Heritage preservation, e.g. museums, showcases, cathedrals, etc. where large size indoor spaces should be covered, the second option was the most suitable for a first development under the standpoint of a low cost device. To develop an adequate platform, one last decision was necessary: the communication interface to be used between the measurement unit and the personal computer. To provide compatibility with the wireless sensor architecture and to foster reusability for its future design, a wireless interface was chosen. The low cost and ultra low power consumption characteristics of the ZigBee technology were definitive to make the final choice [16]. ZigBee is a wireless protocol based on the 802.15.4 standard designed to the Wireless Personal Area Networks (WPAN) for low data rates, which operates in the industrial, scientific and medical (ISM) radio bands at frequencies of 2.4 GHz (worldwide), 868 MHz (Europe) and 915 MHz (USA). For long battery life operation, a data rate of around 250 kbits per second is recommended for periodic or intermittent transmissions. Finally, the interface electronic system should be able to transform the optical response of the sensors into an electric current that, after the convenient calculation through the sensors’ calibration curve, give rise to a particular pH quantitative value. Thus, the concept applied is similar to that used for a conventional spectrophotometer. Consequently, electronic components such as LEDs, photodiodes and displays were employed. Particular characteristics of LEDs and photodiodes will be mentioned below. These components were installed in the corresponding device without any transformation or handling in the laboratory. Figure 2 shows a picture of the prototype built as the interface electronic system.

3. Results and discussion
3.1. Calibration, response time and other properties of the sensors

When environmental acidity changes, the sensitive phase entrapped into the thin layer of the sensors is able to change its optical absorption (colour) [17]. Visible spectra of the same sensor (recorded in the 350-700 nm range) at neutral conditions and in two extreme acid and basic pHs (3 and 11, respectively) are shown in figure 3.

The calibration curve of the sensors (figure 4) was built from the main absorption intensities (band at 575 nm from the corresponding spectra recorded by the spectrophotometer) of a set of sensors sensitized in buffered liquid phases at different pH values. For that purpose, at least three sensors were dipped into the first buffered solution for 10 min and then the corresponding spectra were recorded. After that, the sensors were immersed into distilled water for 10 min, prior to be immersed into the second buffered solution for 10 min, and so on. This procedure is repeated at least five times for each pH point of the calibration curve, which are the average result of the measurements obtained for each pH buffered solution. Experimental points in figure 4 were fitted to the equation:

\[ y = -0.0007x^3 + 0.0114x^2 - 0.0235x + 0.0467 \quad R = 0.9876 \]  

(1)

Monitoring of conservation conditions for Cultural Heritage items are usually undertaken in the range around pH=7 [18,19,20]. For a pH between 6 and 8 the calibration curve of figure 4 can be fitted to the linear function:

\[ y = 0.063x - 0.286 \quad R = 0.9993 \]  

(2)

Accuracy of the sensors' optical response is estimated at about 0.1 units of the pH scale.

Figure 5 shows the response time of the sensors in terms of intensity variation of the main absorption band at 575 nm as a function of the spectrum recording time. The spontaneous recovering of one sensor from basic pH (when exposed to ammonia vapours) to neutral conditions (after the recording of all the spectra inside the
spectrophotometer in air) indicates the sensor ability to change its absorption while the external pH is changing, due to the corresponding neutralization reaction.

As far as reversibility of the sensors is concerned, absorption intensity data recorded after alternative immersions into buffered solutions at pH=3 and pH=11, indicate a complete reversibility and absence of optical fatigue, at least after 12 cycles. This means that the sensors can be used many times.

The experiments accomplished to assess the thermal resistance of the sensors demonstrated that, for a given environmental pH, the optical response of the sensors after each run of thermal stabilization was constant throughout all the temperature range checked. Therefore, the sensors can be used for environmental acidity testing, both indoor and outdoor, of Heritage buildings during all seasons.

The intensity of the characteristic absorption band of the sensors before and after the experiments of chemical resistance was practically constant (maximum differences ±0.005 units of absorbance). This indicates a chemical resistance enough to be exposed to all possible indoor and outdoor environments, whatever the air pollutants are. The results of these experiments point out also the excellent resistance of the sensors against high humid environments and even under direct contact with liquid phases (water, condensation, fog, rain, snow, etc.).

3.2. Structure of the interface electronic system
The architecture of the interface electronic system follows that of a conventional spectrophotometer, as can be seen in the block diagram of figure 6. A LED is used to produce a visible radiation (λ=590 nm) in the range of the main absorbance band of the sensors. Likewise, a photodiode is used to detect the intensity of radiation that passes through it, which depends on the optical response of the sensors and, therefore, on the environmental pH detected.

The prototype of the interface electronic system was based on the Texas Instrument’s EZ430-RF2480 demonstration kit [21]. Despite other development platforms that include ZigBee functionalities were previously evaluated, this
demonstration kit was finally chosen due to its low cost and low power consumption [16]. The demonstration kit includes a target board, model CCZACC06, and an EZ430 USB emulator board. The CCZACC06 is formed by a CC2480 2.4GHz Z-Accel ZigBee network processor connected to a MSP430F2274 microcontroller [22]. The Z-Accel processor runs a proprietary ZigBee stack code, which handles all the critical timing and intensive processing of the ZigBee protocol tasks, leaving free the resources of the microcontroller to handle application requirements. The MSP430F2274 microcontroller is a 16-bit ultra-low-power microcontroller, which includes a universal serial communication interface with two modules (UART and SPI), a 10-bit Analog to Digital converter (ADC), four digital Input/Output ports (I/O PORTS) and embedded emulation logic accessed via Spy-Bi Wire interface (SBW). These resources were used as follows: the UART module is connected to a LCD of two lines with 16 characters per line; two digital I/O lines from port P3 to connect two pushbuttons to implement a simple keypad for controlling the system; a digital I/O line from port P3 to control the LED emission; the 10-bits integrated ADC to measure the output of the signal conditioning block; and the Spy-Bi-Wire interface for emulation and debugging.

In order to reduce power consumption, the LED current is controlled by the microcontroller through a digital I/O line from port P3, used to turn on the LED through a transistor into a low colector-emiter configuration (actuator block in fig. 6), produced by Zetex Semiconductors, model ZXTN23015CFH. The LED is directly powered from the 5 volts output of the power supply module.

The signal conditioning circuit of the photodiode follows the typical approach for this type of sensors, as is shown in figure 7. It includes a current to voltage converter module with a T-network feedback resistor, an offset compensation module, which includes compensation of the dark current of the photodiode, and a module with a low-pass gain filter. All the modules mentioned are based in a single supply rail-to-rail operational amplifier of Microchip, model MCP6281, especially designed for photodiode signal conditioning, due to its low noise characteristics.
As mentioned above, the output of the signal conditioning module is then measured by the 10-bit ADC of the microcontroller MSP430. For this purpose, an external 1.8 volts, 0.1% accuracy voltage reference, from National Semiconductors model LM4128, is connected to the pin of the MSP430 microcontroller. This is explained by the low accuracy of the internal voltage reference of the microcontroller (only 6%), which may introduce an additional error to the measurements.

Since the system is powered by two AA batteries in series, and some of the modules need to be powered by different voltages, a power supply module provides the required voltage levels for each of the modules already mentioned. A step-up high efficiency DC-DC converter from MAXIM, model MAX1674, is employed to carry out this task. This converter is configured to operate with a 5 volts output by connecting the FB input to GND, in addition to a 22 µH inductor and some capacitors of values 0.1 µF and 47.0 µF, respectively.

A simple user interface has been included, which employs minimum hardware resources. It consists of three light touch snap action switches, model EVQ11, from Panasonic, and a LCD of 2 lines with 16 characters per line. The LCD module includes a NHD-0216K3Z-NSW-BBW-ND from New Heaven Displays, formed by a conventional parallel LCD, with a S6A0069 driver, and a Microchip microcontroller, model PIC16F690. This latter adds serial communication to the LCD by conversion of the parallel data of the LCD to a serial data interface, and vice versa. Figure 6 shows the LCD module connected to the MSP430 UART. This MSP430 is a low power microcontroller, which works with a maximum of 3.3 volts digital levels, while the microcontroller PIC16F690 works with a maximum of 5.0 volts digital levels. Thus, a SN74LVC1T45, single-bit, dual-supply bus transceiver, from Texas Instruments, is introduced between them to perform the correct voltage translations.

As exposed previously, the user interface consisted in three switches, two of them connected to a dual channel switch de-bouncer of MAXIM, model MAX6917, thereby ensuring a clean interface with the microcontroller. Since the CCZACC06 has an inadequate switch for the system requirements, it is replaced by another EVQ11.
The EZ430-RF2480 demonstration kit also includes the EZ430 USB Emulator Board, which provides a real-time debugging and programming interface that simplifies the development. It allows the user to program and debug using the serialized JTAG protocol developed by Texas Instruments, known as Spy-Bi-Wire. The former Emulator Board is also useful for serial communication between a PC and the MSP430, since it replies all the data sent by the UART of the microcontroller to a virtual serial COM port at the PC.

A key aspect in the design of a spectrophotometer-like device is to find the best-matched LED-photodiode combination for the particular application. Taking into account the visible absorbance response of the pH sensors, several combinations of LEDs and photodiodes, with wavelengths peaked near the sensors maximum absorbance, were tested. A label was assigned to each LED according to the following code: L1 for Lumex Opto Components’ SSL-LX100133XGC, L2 for Avago Technologies’ HLMP-EL08-X1000 [23], L3 for Chicago Miniature Lighting’s CMD264-UBD, and L4 for Kingbright’s WP7113LGD. Table 1 shows the main characteristics of each LED.

As explained earlier, the main absorption band of the sensors is at 575 nm, while a secondary band appears at 430 nm. Thus, the behavior of both bands was tested. For that purpose a LED with wavelength peaked at 430 nm is also evaluated.

**Table 1. Main characteristics of each LED tested.**

<table>
<thead>
<tr>
<th>LED</th>
<th>Wavelength peak (nm)</th>
<th>Forward voltage (V)</th>
<th>Nominal current (mA)</th>
<th>Axial intensity (mcd)</th>
<th>Viewing angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>570</td>
<td>2.10</td>
<td>30</td>
<td>1600</td>
<td>8</td>
</tr>
<tr>
<td>L2</td>
<td>592</td>
<td>2.02</td>
<td>20</td>
<td>7200</td>
<td>8</td>
</tr>
<tr>
<td>L3</td>
<td>430</td>
<td>4.90</td>
<td>20</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>L4</td>
<td>568</td>
<td>2.50</td>
<td>2</td>
<td>3</td>
<td>30</td>
</tr>
</tbody>
</table>

The same concept was applied for the following photodiodes: P1 and P2 for Osram Opto Semiconductors SFH3710 and SFH2430 [24], respectively, and P3 for Vishay
Semiconductor TEMD6010FX01. Table 2 displays the main characteristics of each photodiode including the sensitivity at the two absorption bands of the sensors.

Table 2. Main characteristics of each photodiode tested.

<table>
<thead>
<tr>
<th>Photodiode</th>
<th>Wavelength peak (nm)</th>
<th>Sensitivity at 575 nm (% of peak sensitivity)</th>
<th>Sensitivity at 430 nm (% of peak sensitivity)</th>
<th>Sensitive area (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>570</td>
<td>99</td>
<td>50</td>
<td>0.29</td>
</tr>
<tr>
<td>P2</td>
<td>570</td>
<td>99</td>
<td>18</td>
<td>7.00</td>
</tr>
<tr>
<td>P3</td>
<td>540</td>
<td>92</td>
<td>53</td>
<td>0.27</td>
</tr>
</tbody>
</table>

First, the DC and the AC voltage at the output of a simple signal conditioning circuit was measured with a 6½ digits multimeter from Hewlett Packard, model 34401A. This was accomplished to determine the sensitivity and noise level for each LED/photodiode combination. Second, the stabilization time of the best candidates was measured. As a result, combinations L2P1 and L2P2 showed the best overall features. Third, the stability of both combinations was analyzed by taking real pH measurements according to the following procedure: three buffered solutions with pHs 2.0, 7.4 and 11.0 were used as standards; each sensor was kept into distilled water at least for 10 min before starting the measurement process to ensure proper hydration; to analyze repeatability and possible hysteresis, each measurement cycle consisted in taking one measurement of the sensors for each buffered solution and repeating the process three times; to analyze stability, each measurement cycle was also repeated three times at different time intervals; for each measurement the sensor was kept into the buffered solution for 5 min, then cleaned and introduced in a mechanical fixture to ensure constant distance and alignment between all the elements, and, once the measurement was taken, it was cleaned with distilled water to avoid cross-contamination of the buffered solutions; the minimum, maximum, and mean output voltage of a simple signal conditioning circuit was measured with the already mentioned 6½ digits multimeter; a reading of the multimeter was also recorded before each measurement for a direct coupling between the LED and the photodiode.
Measurement results were analyzed to determine sensitivity, non linearity, repeatability, and possible hysteresis for each combination, as is shown in table 3. Then, the measurements were repeated for the best candidate combinations at different excitation current levels to determine the minimum excitation current needed to achieve a resolution of 0.1 in pH units. Combination L2P2 showed the best overall results and, therefore, was chosen for the final design.

Table 3. Sensitivity (S), repeatability (R), and non linearity (NL) of the LED/photodiode pairs tested.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>L1P2</th>
<th>L2P2</th>
<th>L3P2</th>
<th>L1P1</th>
<th>L2P1</th>
<th>L3P1</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (mV/pH units)</td>
<td>-11.6</td>
<td>-63.7</td>
<td>12.2</td>
<td>-7.0</td>
<td>-40.0</td>
<td>4.2</td>
</tr>
<tr>
<td>R (pH units)</td>
<td>0.4</td>
<td>0.8</td>
<td>0.6</td>
<td>0.0</td>
<td>0.2</td>
<td>3.8</td>
</tr>
<tr>
<td>NL (pH units)</td>
<td>0.4</td>
<td>0.5</td>
<td>1.6</td>
<td>0.1</td>
<td>0.6</td>
<td>5.2</td>
</tr>
</tbody>
</table>

With the aim to improve the interface electronic system and minimize the errors introduced by the influence of temperature and humidity in the electronic components, two probes were added: one for temperature and another one for relative humidity. An analog temperature sensor from Maxim, model DS600 (±0.5°C accuracy) [25], and a relative humidity probe from Measurement Specialties, model HM1500LF (±3% RH accuracy, maximum time constant 10s) [26], were selected. On the basis of these improvements, the measurements do not need to be taken at a constant room temperature and humidity. These environmental parameters do not control directly the electronic device but, since they could affect the response of the electronic components, the system performs a self-calibration process prior to any set of measurements, thereby adjusting the system to the current temperature and humidity detected by the device. In this way, a minimization of measurement errors is achieved.

Additionally, the electronic interface system is complemented with a simple user-friendly application running on a PC. This application, developed in LabVIEW [27], obtains all the data measured and allows the user to export such data to a spreadsheet. As is specified earlier, ZigBee is the protocol selected to communicate with the PC. Therefore, it requires a wireless compatible interface. To perform that
task a combination of a CCZACC06 connected to an EZ430 was employed. Such combination provides two bidirectional interfaces connected in series, the first one from Zigbee to UART, and the second one from UART to USB. At the PC side, the USB driver of the EZ430 provides a virtual serial COM port, which allows the LabVIEW application to communicate properly with the device.

3.3. Behaviour of the interface electronic system

Calibration with the interface electronic system, that is, the calibration curve of the sensor built from data provided by the device, was carried out by means of different set of sensors sensitized in several buffered solutions ranging the whole pH scale. The experimental procedure was as follows: for each particular pH, at least three sensors were immersed into the corresponding buffered solution for 10 min. Then, their optical response (visible absorption wavelength in nm), measured by the interface electronic system, was recorded. Average of visible absorption values measured by the device was calculated and assigned to the pH of the particular buffered solution used. This procedure is repeated at least five times for each pH point of the calibration curve (fig. 8).

The same conventional spectrophotometer described in the experimental section for calibration and evaluation of the sensors’ optical properties, was used to test the new interface electronic system. The measurements taken with the spectrophotometer and those taken with the interface electronic system were compared for the same set of sensors, sensitized with different buffered solutions corresponding to several pH values. The spectrophotometer was warmed-up for at least 20 min in order to ensure a stable light source. Then, it was calibrated using the software provided by the manufacturer before taking the measurements. The interface electronic system was likewise warmed-up for 5 min before recording pH data.

Comparison between measurements of both devices was undertaken following a similar procedure to that previously described: three buffered solutions covering the typical pH range for applications to Cultural Heritage conservation were used (table 4). Firstly, the sensors were properly hydrated for 10 min in distilled water and then one measurement for each buffered solution (immersion time 10 min) was taken
through both devices. This process was repeated at least three times. Resulting data are shown in Table 4. The pH was quantitatively determined using calibration curves constructed before (Fig. 4 and Fig. 8). Resulting data displayed in Table 4 indicate that maximum error and standard deviation associated to pH measurements taken with the spectrophotometer were generally higher than those taken with the interface electronic system. This fact is explained by the calibration curves and their respective fits. The obtaining of the equivalent pH from absorbance data provided by the conventional spectrophotometer is carried out by means of a linearly fitted calibration curve using the Least Squares Fitting Method. However, the interface electronic system here developed employs a piecewise function with linear functions in all the intervals.

Table 4. Results of pH measurements obtained with the interface electronic system and a conventional spectrophotometer at a constant temperature.

<table>
<thead>
<tr>
<th></th>
<th>Interface electronic system</th>
<th>Spectrophotometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Measured pH</td>
<td>Average</td>
</tr>
<tr>
<td>6.00</td>
<td>5.97  6.00  6.03 6.00 0.03 0.03</td>
<td>5.89  5.81  5.86 5.85 0.19 0.04</td>
</tr>
<tr>
<td>6.86</td>
<td>6.83  6.86  6.91 6.87 0.05 0.04</td>
<td>6.70  6.70  6.78 6.73 0.16 0.05</td>
</tr>
<tr>
<td>7.40</td>
<td>7.33  7.44  7.42 7.40 0.07 0.06</td>
<td>7.39  7.40  7.40 7.40 0.01 0.01</td>
</tr>
</tbody>
</table>

4. Conclusions

Chemical and physical properties of the pH environmental sensors used in this work have resulted suitable for the application proposed and provide an accurate and short time response. In addition, they also present some outstanding advantages, such as thermal and chemical resistance, reversibility, small size, easy handling and low cost.

The interface electronic system designed and applied jointly with the pH sensors has demonstrated to be useful for in situ field measurements. The system may replace a conventional spectrophotometer and provide accurate data (0.1 units of the pH scale). It is able also to manage and store both optical absorption and pH data,
correlated by the corresponding calibration curve of the sensors' response. The
system uses conventional and inexpensive electronic components, which results in a
small, robust, and easy handling apparatus. Other additional advantages of the
interface electronic system here developed that can be highlighted are a shorter
warming-up period and a lower error in the pH measurements, in comparison with a
conventional spectrophotometer.

The use of this interface electronic system valorizes the pH optical sensors and
makes possible their real application in both indoor and outdoor Cultural Heritage
sites, since they are able to work properly under a very wide variety of environmental
conditions, even strongly polluted ones.

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HAR2012-30769 from the Spanish MINECO. A. Llorente-Alonso and J. Pena-Poza
acknowledge contracts to the Consolider Ingenio 2010 program.

References
[1] Glass resistant and accurate pH electrode for general purpose, e.g. Orion pH
electrode model 8104BNUWP ROSS Ultra.

[2] Glass pH electrode for special conditions (soils, dirty, colloids, viscous and
organic materials), e.g. Orion pH electrode model 9272BN PerpHecT Sure-Flow.

[3] pH meter for general purpose (simultaneous measurements of pH, conductivity,
temperature and relative humidity), e.g. Orion portable meter model Star A221.


**Figure captions**

Fig. 1. An environmental pH sensor prepared by the Sol-Gel procedure.

Fig. 2. Prototype of the interface electronic system. A. AA Batteries. B. CCZACC06 Target Board. C. LED/photodiode combination. D. User Interface.

Fig. 3. Optical absorption spectra derived from a sensor sensitized under pH 3, 7 and 11, respectively.

Fig. 4. Calibration curve of the sensors built from the spectrophotometer data.

Fig. 5. Response time of the sensors.

Fig. 6. Block diagram of the interface electronic system.

Fig. 7. Signal conditioning block diagram.

Fig. 8. Calibration curve of the sensor built from the interface electronic system data.
Biographies

**Alvaro Llorente-Alonso** finished in 2010 his studies in Telecommunication Engineering at the Technical University of Madrid (UPM), specialty of electronic systems. His degree project was entitled “Electronic system for environmental data acquisition”. Since February 2011 his research activities have taken place at the Institute of History (IH-CCHS), Spanish National Research Council (CSIC). His main professional interests are: electronics and technology applied to solving scientific and research challenges; sensors and actuators; and environmental monitoring, mainly for Cultural Heritage preservation.

**Javier Pena-Poza** obtained in 2008 his degree in Chemistry at Autónoma University of Madrid (Spain). His MSc dissertation was entitled “Application of chemical sensors for environmental evaluation and Heritage conservation”, 2010. Since 2009 he is assistant scientist at the Institute of History (IH-CCHS), Spanish National Research Council (CSIC). His main research interests are: synthesis of environmental sol-gel based sensors; environmental monitoring for Cultural Heritage conservation; and archaeometry of glasses and pottery.

**Dr. Guillermo de Arcas** BSc in Telecommunications Engineering by the Technical University of Madrid in 1996, MSc in Electronic Engineering by the University of Alcala in 1998, and PhD by the Technical University of Madrid in 2004. Since 1998 he is full time associate lecturer in the Electronic and Control Systems Department of the Technical University of Madrid, where he teaches courses on analog and instrumentation electronics. Dr. de Arcas is engaged at the Instrumentation and Applied Acoustics Research Group of this university, where he conducts his research in the field of instrumentation electronics, with special emphasis in the application of virtual instrumentation technologies to very diverse scientific fields such as acoustics, fusion devices and environmental monitoring.

**Dr. Manuel García-Heras** is PhD in History with Special Doctorate Award (1997) from the Complutunese University of Madrid. He was postdoctoral Fulbright research fellow (1999-2011) at the Museum Conservation Institute (Smithsonian Institution,
Washington D.C., USA), and postdoctoral research assistant (2002-2005) at the National Center for Metallurgical Research (CENIM-CSIC, Madrid, Spain). From 2005 he is tenured senior scientist at the Institute of History (IH-CCHS-CSIC, Madrid, Spain). His main interest of research is focused on the interaction between experimental sciences and history, combining scientific and historic views to approach technological and conservation issues of ancient materials. This interest is carried out mainly in the fields of archaeometry and conservation/prevention science.

**Dr. Juan-Manuel Lopez** BSc in Telecommunications Engineering by the Technical University of Madrid in 1990, MSc in Telecommunications Engineering by the Technical University of Valencia in 1997, and PhD by the Technical University of Madrid in 2004. His professional beginning was as R&D engineer of meteorological remote monitoring systems in the Spanish company SEAC Inc. Since 1990 he is full time lecturer at the Technical University of Madrid, where he teaches courses on analog and instrumentation electronics.

He is engaged at the Instrumentation and Applied Acoustics Research Group of this university, where he works in the fields of metrology in acoustics, electroacoustical instrumentation and virtual instrumentation, with special emphasis in the research on data acquisition and real time data processing architectures for fusion devices.

**Dr. Maria-Angeles Villegas** received her PhD in 1987 by the Autónoma University of Madrid (Spain), on "Preparation and study of glasses obtained by the sol-gel procedure". She was a postdoctoral fellow at the Glass Department (Institute of Ceramic and Glass, CSIC, Madrid, 1988-1989). She is senior scientist in a permanent position at CSIC, firstly at the Institute of Ceramic and Glass (1990-2000), then at the National Center for Metallurgical Research (2001-2007) and up to now at the Institute of History (IH-CCHS). Her main research interests are: conservation science; environmental sol-gel based sensors; protective systems for historical materials; optically active glassy coatings and sol-gel nanocomposites; archaeometry of glasses, ceramics and metals.
Figure 1
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Interface electronic system for measuring air acidity with optical sensors

Highlights
- First experimental method for measuring pH in the air.
- A portable ZigBee prototype for measuring environmental acidity.
- Electronic system for preventive conservation of Cultural Heritage.
- Combination of a photodiode and a LED for quantitative measurement of optical pH sensors.