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Improvement of glassy sol-gel sensors for preventive conservation of historical materials against acidity

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Sensors based on sol-gel glassy coatings doped with 2[4-(dimethyl-amino) phenylazo] benzoic acid are able to change their optical absorption when they are submitted to different concentration of H_3O^+ and OH^-. The sensors behaviour in field tests was studied in Cracow (Poland), varying the normal procedure of operation to improve their response. Both the sensors optical parameters and the environmental conditions (temperature, humidity, pressure, SO_2 and NO_x concentrations) were measured. The sensors response was analysed in terms of their visible absorbance changes, which are due to local neutralisation reactions in the sensors surface by the join effect of acid pollutants and humidity. Correlations between the main acid pollutant (SO_2) concentration and the sensors response are established to provide a relation between the optical absorption and the environmental pH. The sensors are able to detect and monitorise environmental acidity, as well as to alert on the pollutant concentration that may damage most of the historical materials

Keywords: glassy coatings, sol-gel, sensors, environmental acidity, Heritage conservation.

Mejora de sensores vítreos sol-gel para la conservación preventiva de materiales históricos frente a la acidez.

Los sensores a base de recubrimientos vítreos sol-gel dopados con ácido 2[4-(dimetil-amino) fenilazo] benzoico son capaces de cambiar su absorción óptica cuando se someten a distintas concentraciones de iones H_3O^+ y OH^-. La respuesta de los sensores en ensayos de campo se estudió en Cracovia (Polonia) variando el procedimiento normal de uso, con el fin de mejorar su respuesta. Se midieron tanto los parámetros ópticos de los sensores como las condiciones ambientales (temperatura, humedad, presión y concentraciones de SO_2 y de NO_x). La respuesta de los sensores se analizó en términos de los cambios de su absorción visible. Dichos cambios se deben a reacciones locales de neutralización que tienen lugar en la superficie de los sensores, debido al efecto conjunto de los contaminantes de carácter ácido y a la humedad ambiental. Se establecieron correlaciones entre la concentración del contaminante principal (SO_2) y la respuesta de los sensores para elaborar una calibración directa entre la absorción óptica y el pH ambiental. Los sensores pueden detectar y evaluar la acidez ambiental, así como alertar sobre la concentración de contaminantes ácidos que pueden dañar a la mayoría de los materiales históricos.

Palabras clave: recubrimientos vítreos, sol-gel, sensores, acidez ambiental, conservación del Patrimonio

1. INTRODUCTION

Air pollutants contribute to damage historical objects whose materials are more or less sensitive depending on their provenance, time of production, storage and exhibition conditions, and previous cleaning and restoration works (1-6). Combination of air pollutants with environmental agents (relative humidity, temperature, atmospheric pressure, light, etc.) could enhance and/or start deterioration processes which often deal with deep corrosion and degradation mechanisms. One of the main chemical parameters affecting most of materials is acidity (7-10). Stones, mortars, ceramics, papers, textiles, leathers, glasses, metals, photographs, paintings, pigments, etc. are seriously deteriorated by acid environment. Acid rain formed by combination of pollutants (SO_2, NO_x, CO_2, etc.) and environmental humidity causes deep damage not only on people and living organisms, but also promotes chemical attack to the surface of works of art and other historical and cultural assets currently exhibited or outdoor maintained.

The monitoring of the air quality could be useful when a preventive conservation of historical works of art and other cultural heritage assets is intended. In comparison with other systems, chemical sensors provide a fast and accurate response against pollutants and give information about their concentration before degradation mechanisms advance or even start. Moreover, sensors with an optical response could be effective enough to give visual changes, which may be helpful to make an easy and fast evaluation (11-17). This kind of chemical sensors with optical response can be designed and synthesised by the sol-gel glassy coatings technology. Sensors based on the entrapment of a sensitive organic dye against acidity into a thin glassy sol-gel coating have been previously prepared (18-22). Apart from environmental simulations in the laboratory, some field tests have been carried out with the aim to check the sensors behaviour for a final calibration and real validation. Glassy sol-gel optical sensors include several

advantages: they can operate qualitatively without electrical devices or wires, they are reversible and re-usable, they have short response times, they are accurate enough for evaluation of the environmental acidity and they are inexpensive (23,24).

The objectives of the present work are focussed on the design and preparation of sol-gel optical sensors in which a sensitive pH organic dye is entrapped into a polysiloxane network. In such a way the organic dye maintains its chemical properties. The study of the sensors optical response includes their characterisation under both liquid media in the laboratory and real environmental conditions in field tests measurements. In this latter task, parameters such as SO_2 and NO_x concentration, relative humidity and temperature were also monitored. Finally, this research is aimed at improving the sensors response, varying their standard starting conditions, in order to elaborate better calibration relationships.

2. EXPERIMENTAL

Sensitive coatings were prepared from a sol obtained by hydrolysis of silicon tetraethoxide (TEOS, $Si(OEt)_4$) in aqueous-acetone medium, catalysed by HCl (0.1 M). Molar ratio TEOS/Acetone/HCl was 1/8/4. 2[4-(dimethyl-amino) phenyl-azo] benzoic acid (methyl red) was used as pH sensitive organic dye. Dye concentration, in respect of the SiO_2 weight to be obtained after hydrolysis and complete polycondensation of TEOS, was 3 wt %.

The coatings application upon the substrates (common glass slides) was performed by dip-coating technology using a home-made coater. Drawing rate was in the 5-35 cm min^{-1} range. Coatings thickness varied from 250-450 nm. Once the coatings were obtained on the glass substrates, the samples were thermally treated at 60^0C for 3 days in a forced air stove. After such partial densification treatment, the sensors are ready to be used under both liquid and gaseous media.

Optical response of the sensors was recorded with a Shimadzu model 3100 spectrophotometer in the 300-800 nm wavelength range. The current methodology consisted of recording the sensors optical absorbance or transmission, before and after the exposure to the corresponding liquid media or real gaseous environment. To evaluate the sensors behaviour under liquid conditions, buffered solutions ranging over the whole pH scale were used from Hydrion (Sigma-Aldrich).

Environmental parameters (relative humidity, temperature and atmospheric pressure) were monitored by conventional automatic meteorological stations. Such stations were placed as close as possible to the selected sites for field tests measurements with the sensors. Likewise, concentration of the main gaseous acid pollutants (SO_2 and NO_x) was determined by the monitoring stations. SO_2 content was measured by recording the characteristic SO_2 level in the air with a Thermo Model 43C, once activated by ultraviolet radiation. The detection range and the precision of the equipment were 1-500 and 1 ppb, respectively. NO_x concentrations were analysed by means of a conventional device based on chemiluminescence.

Two places downtown Cracow (Poland) were selected for the sensors exposure. The first was the Wawel Royal Castle site, with a high and symbolic cultural and historical value. The second was Krasinskiego Avenue, with heavy and intense traffic. Both places are located near the Vistula River and very close to the automatic meteorological stations, which were able to provide data on atmospheric parameters day by day. Since relative humidity, temperature and atmospheric pressure did not change out of the range in which the sensors response is independent of them; average data of these parameters were estimated and taken into account for further calculations (section 3.2 of results and discussion). Before exposure, the sensors were maintained up to 3 days in distilled water to ensure appropriate surface hydration. Then, they were submitted to a pH=9 buffered solution for 4 h.

The environmental monitoring by means of both the sensors and the conventional meteorological stations was carried out during two consecutive weeks, between March and April 2004. The sensors were always exposed during 24 h. The same sensor was used for each set of measurements.

3. RESULTS AND DISCUSSION

3.1. Optical behaviour under liquid conditions. Laboratory tests.

The sensors optical response under liquid conditions is summarised in fig. 1. The sensors appearance under acid conditions is deep pink, while under basic conditions is yellowish orange. These colours are obviously connected with the methyl red tautomeric forms (fig. 1a). The characteristic absorption band when the sensor is submitted to an acid buffered solution is centred at 493 nm, and the corresponding band when submitted to a basic buffered solution is peaked at 457 nm (fig. 1b). Intermediate pH solutions give rise to intermediate sensors response with optical absorption bands between the two former extremes.

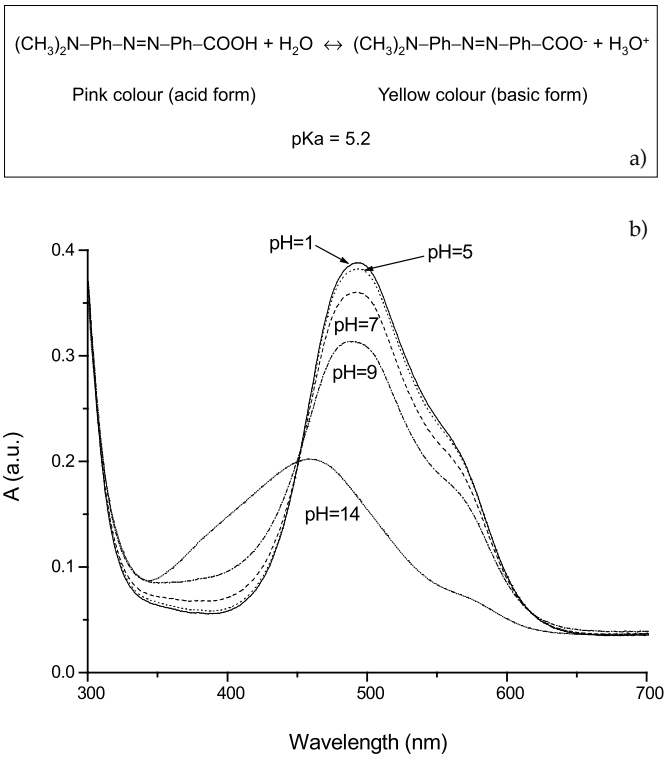

Fig. 1.- a) Tautomeric forms of the organic dye employed as a pH sensitive dopant entrapped in the sensors sol-gel coatings, b) optical absorption spectra of the sensors submitted to different buffered solutions.

Calibration of the sensors under liquid conditions was carried out by measuring the variation of the sensors optical transmission (colour), as a function of the solution pH. The experiment was performed as follows: the sensor was successively dipped into several buffered solutions at different pH for 5 min each run. During the experiment a fast response time was observed (~1 min), as well as a reversible behaviour, i.e. the sensors were able to change from pink to orange and vice-versa when submitted to appropriate buffered solution. Fig. 2 shows the plot of the optical transmission intensity at λ=480 nm, versus the pH of the liquid phase. As can be observed, the lower the pH, the lower the sensor transmission percentage, which corresponds to a deeper pink colour.

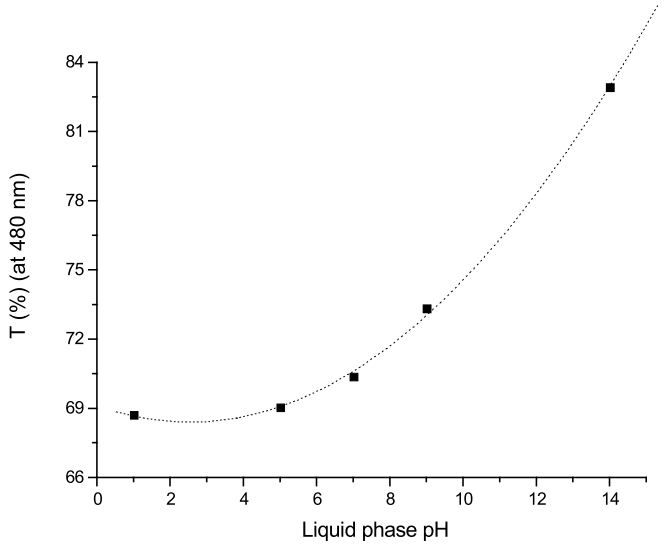

Fig. 2.- Optical transmission intensity of the sensors measured at λ= 480 nm versus the pH of the liquid phase to which the sensors were dipped.

Other parameters concerning the sensors behaviour were already investigated (21). When sensors sensitisation proceeded under liquid conditions, response time recorded was about 1 min. As far as reversibility concerns, good reversible response without optical fatigue was observed, at least up to 50 cycles. During all the experiments carried out under liquid media, no memory effect of sensors was recorded. In other words, the sensors optical behaviour when exposed from acid to basic pH and from basic to acid pH is practically the same. Nevertheless, due to the higher stability of the basic tautomeric form of the organic dye in the polysiloxane matrix, some reversibility minor deviation occurs (25).

3.2. Optical behaviour under gaseous conditions. Field tests.

Since the objective of the present work was the sensors response improvement during field tests measurements, they were firstly sensitised at pH=9 under liquid medium. Thus, the sensors starting colour was yellowish orange, which corresponds to the basic tautomeric form of the entrapped organic dye. In this way the presence of even small amount of acid pollutants could neutralise such basic tautomeric forms, dealing with the sensors change of colour towards a pinkie hue.

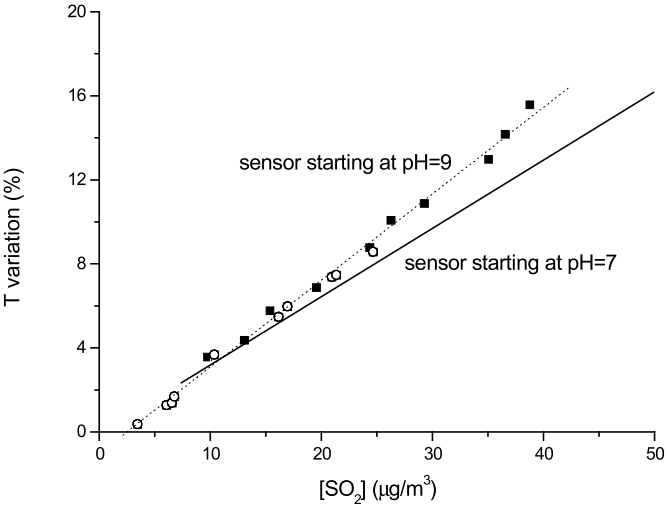

Fig. 3.- Variation of the sensors optical transmission at the maximum spectral intensity before and after their exposure in field tests, versus the SO_2 concentration detected by automatic meteorological stations. Black squares: data from Krasinskiego Avenue; white circles: data from Wawel Royal castle; continuous line: former data from both places (according to ref. 20).

The variation of the sensors optical transmission at the maximum spectral intensity, before and after their exposure downtown Cracow, versus the SO_2 concentration detected by the meteorological stations, is shown in fig. 3. Data obtained from both the Wawel Royal castle and Krasinskiego Avenue can be fitted to a linear equation. The continuous line in fig. 3 indicates the corresponding fit found for data formerly recorded in the same Cracow places, by using the same sensors under standard starting conditions (i.e. previously sensitised with a buffered solution at pH=7). The different slopes of the lines in fig. 3 indicate that the higher the starting pH of the sensors, the higher the transmission percentage changes recorded. This means that modulation of the sensors optical response is possible by adjusting the starting conditions, i.e. controlling the relative proportion of basic/acid tautomeric forms of the sensitive organic dye entrapped in the sol-gel coating.

The present optical sensors can be used for monitoring environmental acidity as far as a simple correlation between the SO_2 concentration detected by the meteorological stations and the environmental pH is accomplished. As Garcia-Heras et al. proposed (22), simple calculations based on the reactions:

$$SO_2 + ½\ O_2 \rightarrow SO_3 \qquad [1]$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad [2]$$

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \qquad [3]$$

give rise to the formula:

$$pH = -\log 10.8 \times 10^{-10} \times [SO_2] \times RH \times t/P \qquad [4]$$

where $[SO_2]$ is the SO_2 concentration in $\mu g/m^3$ detected by the meteorological stations, RH is the relative humidity (average from measurements, 79.5 %), t is the temperature (average from measurements, 277.14^0 K) and P is the atmospheric pressure

(average from measurements, 712.5 mm Hg). Equation [4] allows the representation of the environmental pH changes as a function of the SO_2 concentration detected (fig. 4).

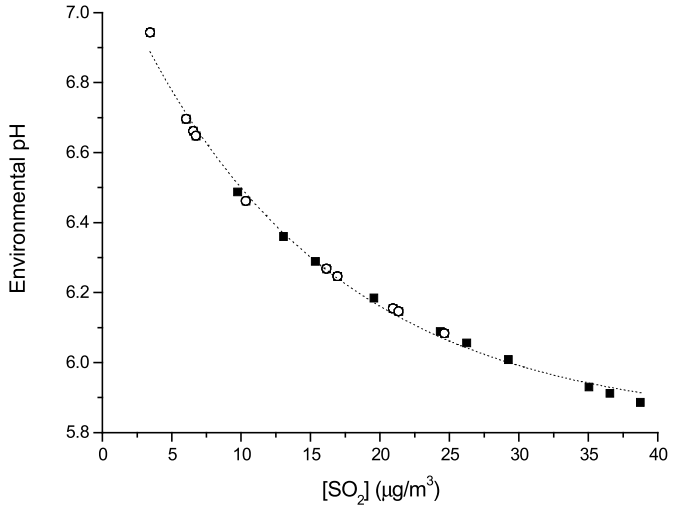

Fig. 4.- Calculated environmental pH as a function of the SO_2 concentration detected by automatic meteorological stations.

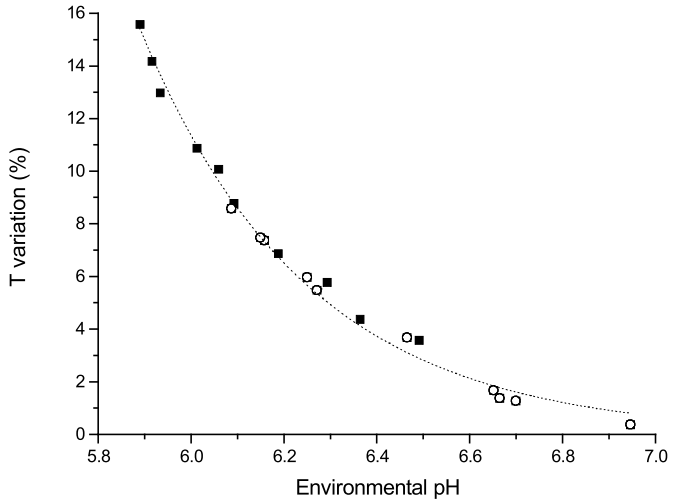

Fig. 5.- Variation of the sensors optical transmission at the maximum spectral intensity before and after their exposure in field tests, versus the calculated environmental pH, for each SO_2 concentration detected by automatic meteorological stations. Black squares: data from Krasinskiego Avenue, white circles: data from Wawel Royal castle.

Combination of data from figs. 3 and 4 yields a direct relationship between the environmental pH and the variation of the sensors optical transmission, i.e. their change of colour (fig. 5). As expected, the higher the variation of the optical transmission of sensors, the lower the environmental pH detected. The curve of fig. 5 also indicates that pH detection accuracy is about 0.1. Relative standard deviation of experimental data in fig. 5 is around 2 %. The corresponding fitting curve could be used as a calibration curve for semi quantitative acidity evaluations.

Moreover, qualitative use of the sensors is possible by visual comparison with a colour scale built from the two main colours at extreme pH (e.g. yellowish orange from pH=9 starting conditions, and the corresponding pink colour from an acid pH for final conditions). Obviously, intermediate pHs correspond to intermediate mixed colours from the two extreme pure colours. This kind of qualitative environmental pH evaluation is very useful when indoor atmosphere of museums, exhibition halls, showcases and other limited spaces would be monitorised. Some tests were carried out indoor Wawel Royal castle: sensors were placed close to ancient leather pieces, historical tapestries and stained glass windows. Fast qualitative evaluations were reached with the added value of the sensors small size and the absence of other devices and wires.

The role of NO_x as an air acid pollutant has been already investigated. It is possible that NO_x gaseous emissions in the presence of air humidity will form nitric acid. In fact, such an acid is one of the main components of acid rain. However, some authors have also pointed out the catalytic function of nitrogen oxides in the SO_2 oxidation reaction (equation [1]) (26,27). Moreover, intense light, high temperature and intense traffic (which increase gaseous emissions of volatile hydrocarbons) enhance the formation of NO and atomic oxygen from NO_2. Then, due to the combination of atomic oxygen with environmental oxygen O_2, ozone O_3 can be generated. Keeping in mind these reactions, as well as the low reactivity of NO_2 in comparison with SO_2 and O_3 (27), it seems possible that, under the conditions described, NO_x emissions will not contribute directly to decrease the environmental pH.

The plot of the sensors optical transmission variation versus the NO_x concentration, detected by the meteorological stations (fig. 6), shows disperse data. This indicates that both parameters are working independently. Another possible explanation involves an insensitive behaviour of the sensors when exposed to the HNO_3 generated from NO_x and environmental humidity. However, such behaviour could be discarded, since the sensors were currently sensitised in the laboratory when dipped into HNO_3 aqueous solutions of different concentration. Therefore, since no correlation has been found between the sensors response and the NO_x concentration detected, we assume, according to several authors (26,27), the role of NO_x as a catalyst for reaction [1].

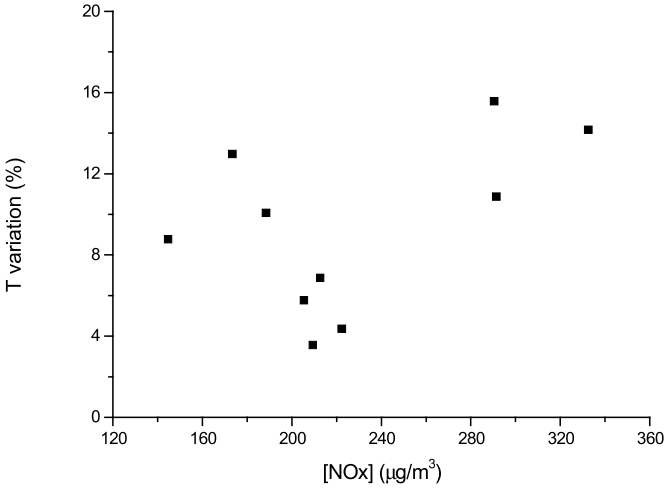

Fig. 6.- Variation of the sensors optical transmission at the maximum spectral intensity before and after their exposure in field tests, versus the NO_x concentration detected by the automatic meteorological station located at Krasinskiego Avenue.

Nevertheless, possible interaction and interferences between SO_2 and NO_x in the sensors surface under humidity can not be discarded and need to be further investigated. The environmental pHs estimated by the present sensors are within the range previously determined by Turzanski and Wertz (28) in Cracow during 2002.

4. CONCLUSIONS

Chemical sensors with optical response based on sol-gel coatings technology have been prepared and characterised. Such sensors are able to fast monitor environmental acidity generated by SO_2 under humid atmosphere.

The sensors optical response was improved by using them previously treated under pH=9. In this case, small changes in the environmental acidity give rise to a fast change in the sensor optical transmission (colour). This fact allows their use as visual sensors for qualitative evaluation of the air acidity in museums and outdoors for preventive conservation of historical materials.

Since no correlation between the sensors optical response and the detected NO_x concentration has been recorded, the effect of NO_x as a catalyst of the SO_2 oxidation reaction is assumed.

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