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A new and simple optical sensor for the detection of formic acid unleashed by wooden storage or display materials used in museums and responsible for accelerating glass deterioration

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Introduction

Organic pollutants such as formic acid, acetic acid and formaldehyde released by some materials (mainly wood) used for storage and display can play an important role on the alteration of the glass structure due to the alkali leaching process. It as been determined that formic acid when present inside storage or display cabinets is the one that affects most glass integrity, accelerating and deepening the alkali leaching from the silica matrix. As this situation can affect many museums on their glass collections, monitoring this compound would be of great importance for indoor preservation purposes. An optical sensor based on the layer-by-layer (LbL) electrostatic self-assembly process is under development to identify indoor formic acid based on the immobilization of chemo-responsive dyes in polymeric structures. The sensors are based on an optical response resulting from the reaction between immobilized dyes and the referred organic pollutant.

Materials and Methods

The used polyelectrolytes were Polyethylenimine (PEI), Poly(acrylic acid) (PAA) and Polyvinylpyrrolidone (PVP).

Several pH indicator dyes – Erythrosine B, Methyl red and Congo red - were incorporated in between the polymeric layers of LBL assembled films as well as the solvatochromic Reichardt's dye. The acid-base indicators were chosen according to their pKa values. In order to be able to identify the presence of formic acid by changing their colours, *pKa* values of these indicators must me as close as possible as the *pKa* value of formic acid.

The polymeric matrix were deposited on common float glass.

Table 1: pKa value of formic acid

	pKa from literature
Formic acid	3.74

Table 2: pKa values determined for the different acid-base indicators.

Acid-base indicators	*pKa* in literature (aqueous solution) [1]	Experimental *pKa* (aqueous solution)	Experimental *pKa* (LBL matrix)
Congo Red	4.10	4.05	1.95
Methyl Red	4.95 – 5.06	5.53	0.90
Erythrosine B	4.10	4.04	2.50

Results and Discussion

After perform a series of tests, it was possible to exclude all the dyes except Methyl red, that showed specificity to detect formic acid when incorporated in LbL matrix.

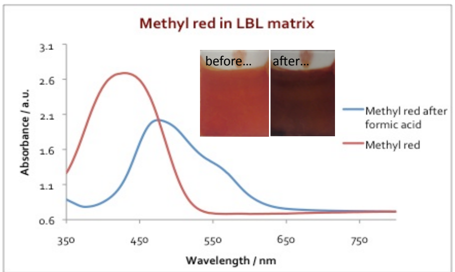

Fig.1: Absorbance spectra of the produced sensor with Methyl red.

The sensor's reaction to pure formic acid vapours was tested and the result is presented in the absorbance spectra above and respective pictures.

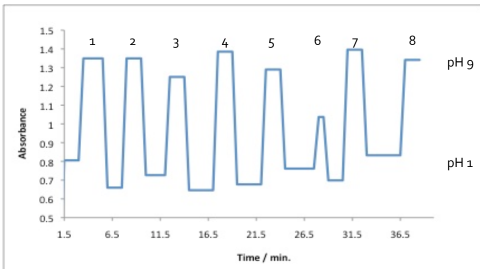

Fig.2: Methyl red reversibility chart

To test reversibility of the sensors produced with acid-base indicators, these were submitted to several cycles of vapour exposure to acid followed by a base. As an example the obtained reversibility spectrum of Erythrosine B is presented. This sensor is reversible at least for 10 cycles.

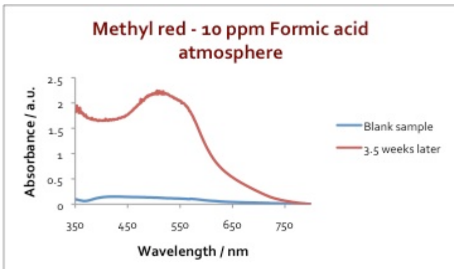

Fig.3: Methyl red in LBL matrix before and after an exposure to an atmosphere of 10ppm concentration of formic acid

Tests were performed in order to determine the sensors detection limits. The sensors have showed response to an atmosphere of 10ppm of formic acid after 25 days exposure.

Conclusions and future work

So far, these simple and low cost sensors have shown a good response in terms of identifying very low quantities of indoor formic acid. Photosensitivity tests were performed to this sensor and it showed good resistance to light exposure.

In order to determine this sensor's detection limits some tests are under development. Also *in situ* tests are being performed in order to evaluate the response of this sensor in museum cabinets.

Bibliography:
[1] Sabnis, Ram Wasudeo (Ed. 2008). Handbook of Acid-Base Indicators. CRC Press, Library of the Congress Cataloging Publication Data.

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