HYDROGELS COUPLED WITH MONITORING ELECTROCHEMICAL TOOL FOR A CLEANING OF GRAPHIC ARTWORKS

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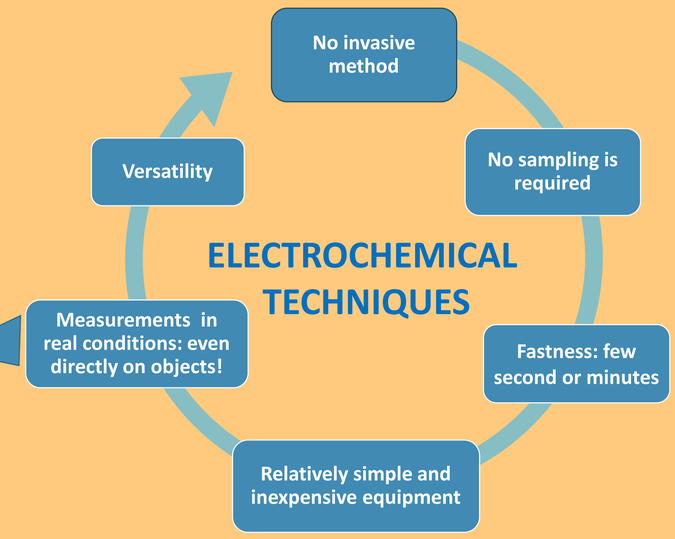
biosensors
MDPI

New methodologies for the characterization of chemical composition and the monitoring of cleaning processes of paper and wood artifacts are based on tuned electrochemical sensors with screen printed electrodes (SPE) coupled with a portable instrumentation. **Electrochemical biosensors** are well suitable to be used for the characterization of several important materials used in Cultural Heritage artifacts such as paper, paintings, textiles, metals or glass, with the aim of determining their composition, health state and/or the effectiveness of conservation or restoration interventions. Opportune biosensors could be indeed applied to determine both inorganic than organic compounds present as components, pollutants or degradation products of artworks. In this work, two different application of sensors coupled with hydrogel is presented to underline the potentiality of these tools in cultural heritage.

CONSIDERATION TO BE MADE ON CHOOSING AN ANALYTICAL METHOD FOR CULTURAL RELICS ANALYSIS:

- ✓ NO INVASIVENESS: the physical integrity of the object is safeguarded
- ✓ NO DESTRUCTIVENESS: the bulk of the sample is recoverable after analysis
- ✓ FASTNESS: large assemblages of samples are analyzable
- ✓ UNIVERSALITY: materials and objects of various shape, size and composition are analyzable
- ✓ VERSATILITY
- ✓ AVAILABILITY AND COST: instrumentation easily available worldwide

ELECTROCHEMISTRY[1)]



DESCRIPTION OF THE HYDROGEL/ELECTROCHEMICAL TOOL

The monitoring tool is composed by a flow sampling plate in contact with a hydrogel (Gellan gel) coupled with the electrochemical biosensor. The flow system is composed by two flow ways: one for the direct determination of the degradation product of paper and the other, equipped with an enzymatic bioreactor, for the determination of glue. The flow sampling system is constituted by a plate in Perspex on which a serpentine with 12 channels. In the serpentine, the buffer flows continuously (moved by a peristaltic pump), up through the gel to an electrochemical thin layer cell, containing a screen-printed biosensor. The thin layer cell is a LCEC (liquid chromatography–electrochemistry cell) from Bio-Analytical Systems (West Lafayette IN, USA), adapted for screen printed electrodes (SPEs).. The working and carrier buffer was 0.05 M phosphate buffer + 0.1 M KCl, pH 6.8. The buffer flow (0.1 mL/min) was regulated by a peristaltic pump, connected directly to the plate. Amperometric measurements were carried out using a portable potentiostat connected to a laptop computer

MONITORING THE CLEANING PROCESS OF PAPER ARTWORKS WITH NON-INVASIVE DIAGNOSTIC TOOL

HOW?

We chose to monitor during time the amount of glucose, a cellulose and starch paste degradation product.
The reaction is reported below:

$$Glu\cos e + O_2 \xrightarrow{Glu\cos e-oxidse} Gluconic \quad acid + H_2O_2$$

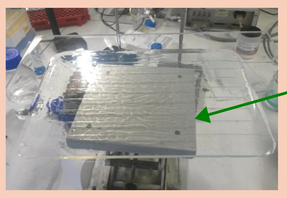
The produced H_2O_2 was detected amperometrically using a screen-printed electrode modified with Prussian Blue (*b*PB-SPE), and used at an applied potential of –50 mV *vs* pseudoreference Ag. By immobilizing the glucose oxidase (GOx) on the working electrode area, a glucose biosensor was assembled and used for the detection of glucose.

...using a innovative and non invasive material as cleaning agents, such as the GELLAN GEL, together with a SAMPLING FLOW SYSTEM coupled to a specific ELECTROCHEMICAL BIOSENSOR [2)].

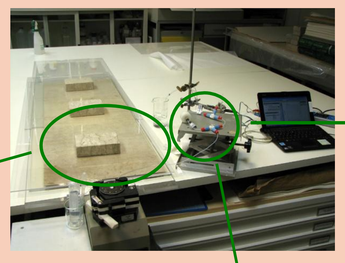
LE NOZZE DI PSICHE: BEFORE AND AFTER RESTORATION

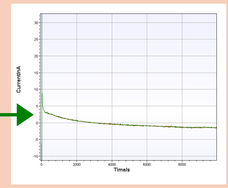
1° case of study [3)]

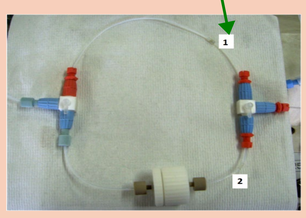
Monitoring in real time using electrochemical biosensor connected directly to the flow sampling plate ("*in continuous*" measurement)



Flow sampling system with a 12 channels serpentine

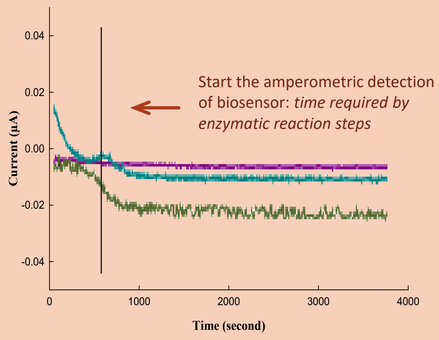






Flow system with two ways to monitor:
1. endogenous glucose
2. glucose produced by enzymatic gel + endogenous glucose

- **VIA 1**: Monitoring of endogenous glucosedue to cellulose degradation, removed by gellan gel during cleaning process
- **VIA 2**: Monitoring of glucose produced during the removal of starch paste by enzymatic gel
- **BUFFER**



Endogenous glucose (via 1)		Glucose produced by a-amylase gel	
Glucose (mM)	RSD% (n = 2)	Glucose (mM)	RSD% (n = 2)
5	0.3	15	1

DILUTION FACTOR

$$F = \frac{i_C}{i_F} * 100$$

(55 ± 3) %

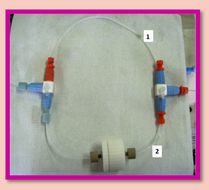
Working parameters:
Flow rate: 0,1 mL/min for via 1; 0.05 mL/min for via 2
Sampling time: 5000 s
Applied potential for amperometric measurements: - 50 mV vs

BREVIARIUM ROMANUM : BEFORE AND AFTER RESTORATION

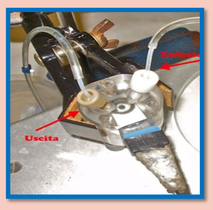
2° case of study

Bioreactor for cellulose analysis: the bioreactor was a hand-made cylindrical reactor in Plexiglas in which an ABC Immunodyne membrane (Pall Corporation, Ireland) was inserted into the flow system. The membrane has an immobilization surface of 300 cm^2, with a thickness of 150 µm. On the membrane 13 µl of mix enzyme solution of *Cellulase* (200 IU ml^{-1}) (from *Aspergillus Niger* ≥ 1.02 U/mg; from *Trichoderma reesei* ≥1 U/mg) in 0.1 M phosphate buffer at pH 8, were added on both membranes faces and incubated for 30 minutes at room temperature. The enzymatic membrane was freshly prepared before measurements

Plexiglass plate and gellan gel disk

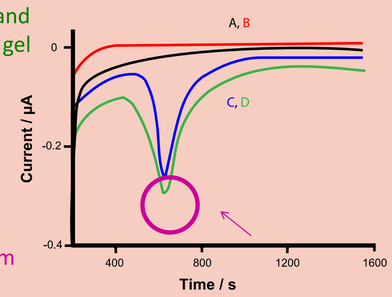


Two lines flow system



Biosensor for glucose in thin layer cell

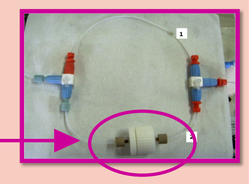
Application of a flow sampling plate + electrochemical biosensor to monitor the removal of cellulose from paper



Current vs time [s] measured by amperometry
- **A**: buffer
- **B:** untreated Breviarium paper
- **C:** Filter paper treatment with nanocellulose
- **D:** Breviarium paper treated with *Cellulase* enzymes.

*Applied potential: + 50 mV; measurements made in PBS pH 6.8

Cellulose fragments removed by gel $\xrightarrow[\text{by } \textit{T. resei} \text{ and } \textit{A. niger}]{\textit{Cellulase}}$ **glucose**



The removal of cellulose from *Breviarium* page is monitored by real-time monitoring tool following the amperometric signal [4)]

CONCLUSION

- ✓ In the field of restoration of paper artworks, more efforts have to be done in order to be able to know how to perform a restoration in the best way.
- ✓ Highly potential electrochemical sensors, which have been widely employed in other scientific areas, may be used to know the cleanup efficiency of the cleaning gels used.
- ✓ Biosensors, allows the monitoring of the removal of specific materials present on the artworks, giving the possibility to determine its health state. By choosing the appropriate enzymes to be immobilized there is the possibility to transform the electrochemical sensor in a probe selective to know the material present on artworks.
- ✓ In this way, it is possible to know when the cleanup process is complete, avoiding lengthy and sometimes unnecessary cleaning processes.
- ✓ Coupling the electrochemical system with suitable hydrogel (used as it is or with tuned agents) provides a very important and versatile tool for non-invasive analysis and monitoring of cleaning treatment of artworks.

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3) L. Micheli et al., Microchem. J. (2018) 138, 369-378.
4) Ricci, F., & Palleschi, G. (2005).. Biosensors and Bioelectronics, 21(3), 389–407.