

2021
February 17-18**SC**
SmallChem**Small Chem**
International Online
Conference

February 17-18, 2021



Selective Discrimination of Toxic Polycyclic Aromatic Hydrocarbons in Water by Targeting π -Stacking Interactions

Ángel Campos-Lendinez, Jose Muñoz, Núria Crivillers, Marta Mas-Torrent

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are organic pollutants present in water environments which possess carcinogenic, mutagenic and teratogenic properties. The US Environmental Protection Agency (EPA) has promulgated a maximum contaminant level at **0.2 ppb in water**.

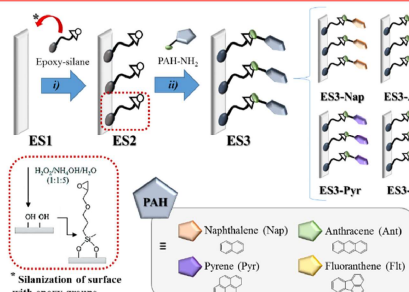
Common standard methods are based on spectroscopic bench-top laboratory instruments. Usually, this kind of techniques are not suitable for in-field analysis and require lengthy preconcentration, extraction and clean-up steps, which makes them tedious techniques.

The motivation of this project is to develop a novel sensitive electrochemical system for PAHs using carbon-based self assembled monolayers (SAMs) platforms. Different PAHs molecules are used as recognition agent since their planar aromatic structure allows excellent π - π interactions with PAHs with same structure.

METHODOLOGY

The PAH-based recognition agent was attached on ITO film coated glass following a two-step process:

- Surface activation and anchoring of silane-based molecules bearing an epoxy group on the ITO surface (from ES1 to ES2).
- The selected PAH recognition agent is attached to the silane-based groups via N-bond, resulting in ES3.



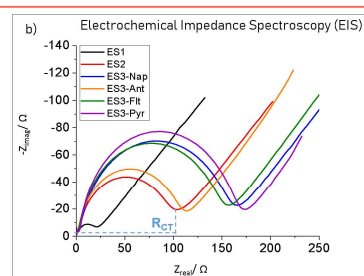
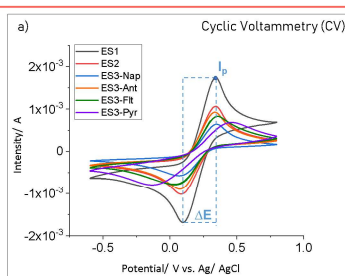
CHARACTERIZATION

Several characterization techniques were used to confirm the successful fabrication of the PAH-based recognition platforms.

By using electrochemical characterization techniques (cyclic voltammetry and impedance electrochemical spectroscopy), the silane SAM formation and the correct attaching of the PAH-based recognition unit to the surface is demonstrated.

Electrodes	ΔE (V)	I_p (μA)	R_{CT} (Ω)
ES1	0.24	1.73	22
ES2	0.25	1.05	105
ES3-Nap	0.27	0.64	208
ES3-Ant	0.27	0.93	112
ES3-Fit	0.32	0.83	156
ES3-Pyr	0.59	0.68	175

CV and EIS characterization of: bare ITO (black, ES1), ITO-silane (red, ES2) and the four different ITO-silane-PAH (blue, ES3-Nap; orange, ES3-Ant; green, ES3-Fit and purple, ES3-Pyr) electrodes using the Redox marker: 0.01 M $[Fe(CN)_6]^{3-/4-}$.

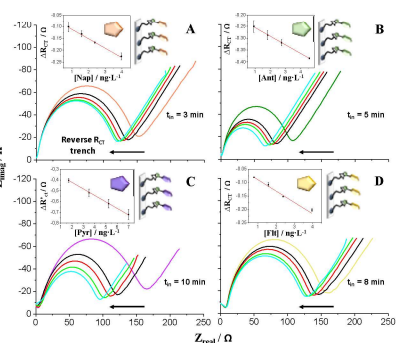


Electroanalytical Sensing Method

The electroanalytical sensing response is determined by monitoring impedimetrically (R_{CT} value) the π - π supramolecular interactions between the recognition agent and the PAH analyte, forming a sandwich complex, where ΔR_{CT} corresponds to the electron transfer resistance of the electrodes before (R_e) and after (R_i) incubation with the different PAH concentrations.

$$\Delta R_{CT} = R_i - R_o$$

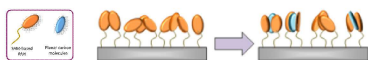
Each ES3 system exhibited excellent regression curves ($r^2 > 0.99$) with good sensitivities (i.e., slope) as well as extremely low limits of detection (LOD) for their corresponding PAH target in the order of ppt levels.



Nyquist plots corresponding to the impedance sensing at the (A) ES3-Nap, (B) ES3-Ant, (C) ES3-Pyr, and (D) ES3-Fit recognition platforms before and after interacting with their corresponding PAH target at different concentrations (t_{inc} : incubation time). Inset: calibration plot with their corresponding error bars ($n=9$). EIS measurements obtained utilizing a 0.1 M KCl solution containing 10 mM $[Fe(CN)_6]^{3-/4-}$ as the redox marker

Proposed Mechanism

The diminishment of R_{CT} after PAH-PAH interaction can be accounted by the SAM reorganization. This fact induces the formation of empty channels that expose the electrode surface, favoring the penetration of the $[Fe(CN)_6]^{3-/4-}$ redox marker toward the electrode.

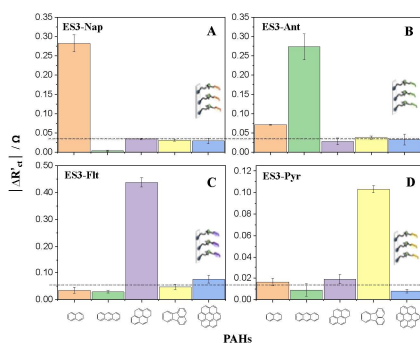


Interferences

Anti-interference experiment was performed adding separately five different PAH species, such as Nap, Ant, Pyr, Flt, and coronene (Cor), with two, three, four, four, and seven aromatic rings, respectively ($[PAH]_x = 2$ ppt) and analysing the relative charge transfer resistance (R_{CT}).

$$\Delta R'_{CT} = \Delta R_{CT} / R_o$$

Each ES3 system is much more sensitive and, therefore, selective to the PAH target equal to its recognition agent, with interfering signals mostly lower than 10% in the same concentration range. This effect reflects the formation of preferential supramolecular π -stacking interactions between molecules exhibiting the same aromatic skeleton over other PAH components.



Electrochemical anti-interfering assay at the (A) ES3-Nap, (B) ES3-Ant, (C) ES3-Pyr, and (D) ES3-Fit using five different PAH analytes (Nap, Ant, Pyr, Flt, and Cor) with a 2 ppt concentration (dashed line: 10% of the signal derived from its corresponding PAH target, $\pm 10\%$). Bar charts are represented with their corresponding error bars ($n=9$). Redox marker: 10 mM $[Fe(CN)_6]^{3-/4-}$.

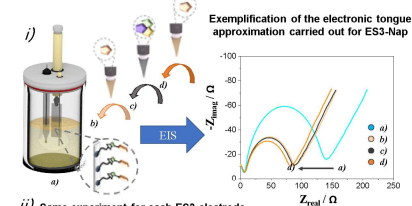
ANALYTICAL RESULTS

Approximation to Electrochemical Tongue

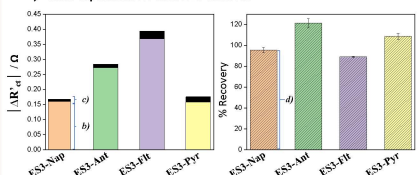
An electronic tongue approximation was also carried out in order to evaluate the applicability of the developed method in a complex mixture solution. The specific followed protocol for ES3-Nap was:

- ES3-Nap measurement in a three-electrode configuration cell.
- Addition of 2 ppt of Nap (its intrinsic PAH target).
- Three interferences (Ant, Flt, and Pyr) at 2 ppt each were dropped into electrochemical cell.
- Finally, an additional 2 ppt of a Nap aliquot ($[Nap] = 4$ ppt) was spiked for exploring the sensing discrimination in a complex matrix media.

The same methodology was carried out for the other three ES3 recognition platforms (ES3-Ant, ES3-Pyr, and ES3-Fit). A significant increase in the electrochemical signal owing to the interferences was not found in all the cases, demonstrating that the PAH-based platforms are selective for PAH analytes of the same nature.



Same experiment for each ES3 electrode



CONCLUSIONS

- The development of ultrasensitive carbon-based SAM platforms for the simple, rapid and selective electrochemical discrimination of small organic pollutants (i.e., PAHs) in water was achieved.
- Electrochemical impedance spectroscopy (EIS) technique has been successfully used for sensing several PAHs, yielding to detection limits at ppt levels.
- Interestingly, this method is general and can be customized towards the determination of specific PAH targets taking advantage of excellent π - π interactions occurring between molecules exhibiting the same aromatic skeleton.
- The synergistic combination of surface engineering employing nanostructured carbon materials with impedimetric readout is an appealing strategy for the fabrication of novel environmental sensors.

For further
information

CONTACT PERSON

REFERENCES

2021
February 17-18**SC**
SmallChem

acampos@icmab.es

- Muñoz, J.; Crivillers, N.; Mas-Torrent, Chemistry—A European Journal (2017) 23, 15289-15293.
- Muñoz, J.; Campos-Lendinez A.; Crivillers N.; Mas-Torrent M., ACS Appl. Mater. Interfaces (2020) 12, 26688-26693