## Unusual amperometric detection of ions using machine learning applied to hexacyanoferrate and graphene oxide modified electrodes

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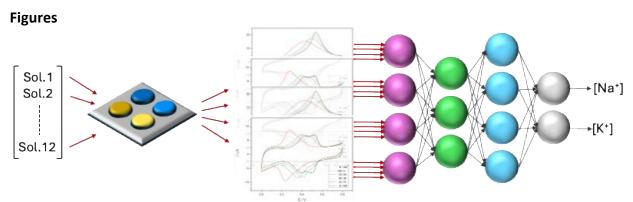
The quantification of electrolytes (e.g. Na<sup>+</sup> and K<sup>+</sup>) in biological fluids leads to important physiological information connected to the hydration state and to the occurrence of severe pathologies. For this reason, many devices have been developed so far for the monitoring of ions in serum, saliva and sweat. The approach normally used is the use of ion selective electrodes (ISE), one for each ion to be determined. Despite effective, they suffer from matrix effects which limit their accuracy and the sensitivity is limited, due thermodynamic reasons, to 59 mV/decade.

As an alternative approach for the quantification of Na<sup>+</sup> and K<sup>+</sup>, we have recently proposed the use of a multi-sensor platform consisting of four poorly selective amperometric sensors (Fig. 1)<sup>1</sup> based on iron and nickel hexacyanoferrates (Fe-HCF and Ni-HCF) and reduced graphene oxide (RGO) as sensing elements. The voltammetric signals obtained by the sensors of the platform were used to train an artificial neural network (ANN) capable of analyzing such complex inputs to finally determine the concentrations of Na<sup>+</sup> and K<sup>+</sup> ions in solutions at different ionic strengths and even containing NH<sub>4</sub><sup>+</sup> as an interferent. The sensing strategy is based on the differential intercalation of ions within both RGO<sup>2,3</sup> and HCF<sup>4,5</sup>, resulting in distinct voltammetric signals.

Aiming at quantifying ions possessing different ionic radius and permeability throughout the coatings, the number of electrodes in the platform was increased to also include copper and cobalt hexacyanoferrates as sensing elements, either coated or not with an external layer of RGO. The resulting multi-electrode platform was tested in more complex solutions containing variable concentration of Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> demonstrating the capability of the platform to discriminate among solutions at different ion composition.

## References

- [1] L. Malavolta, I. Bracaglia, G. Cazzador, A. Kovtun, L. Tomasi, C. Zanardi, V. Palermo, Sens. Act. B Chem. 427 (2025) 137194.
- [2] V. Quintano, A. Kovtun, F. Biscarini, F. Liscio, A. Liscio, V. Palermo, Nanoscale Adv. 3 (2021) 353.
- [3] L. Lancellotti, A. Bianchi, A. Kovtun, M. Gazzano, T. D. Marforio, Z. Y. Xia, M. Calvaresi, M. Melucci, C. Zanardi, V. Palermo, Nanoscale 16 (2024) 7123
- [4] J.Q. Ang, B.T.T. Nguyen, Y. Huang, C.S. Toh, Electrochim. Acta 55 (2010) 7903.
- [5] J. Joseph, H. Gomathi, G.P. Rao, Electrochim. Acta 36 (1991) 1537.



**Figure 1:** schematic representation of deep learning approach applied to the quantification of Na<sup>+</sup> and K<sup>+</sup> by a 4-electrode platform composed by Fe-HCF/RGO and Ni-HCF/RGO modified electrodes<sup>1</sup>.

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