## How artificial intelligence can help in an unusual detection of ions in sweat by graphene oxide and hexacyanoferrate modified electrodes

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The analysis of biological fluids, like sweat and saliva, is attracting the interest of many research activities since they may allow rapid and easy diagnosis of important diseases, as an alternative route to the more invasive analysis of blood and serum. In particular, the quantification of electrolytes (e.g. Na<sup>+</sup> and K<sup>+</sup>) leads to important physiological information connected to the hydration state and to the occurrence of severe pathologies. For this reason, many wearable devices have been developed so far for the continuous monitoring of ions in the body. The approach normally used is the inclusion of highly selective sensors, one for each target species, consisting of ion selective electrodes (ISE). Despite effective, they suffer from heavy matrix and interference effects which limit their accuracy, and from a limited sensitivity due to the physico-chemical principle at the basis of the detection of these ions.

As an alternative analytical approach for the quantification of Na<sup>+</sup> and K<sup>+</sup>, we have recently proposed the use of a multi-sensor platform containing four diverse amperometric sensors (Fig.  $1)^1$ . The sensing elements were obtained for deposition of redox active iron and nickel hexacyanoferrates (Fe-HCF and Ni-HCF) and reduced graphene oxide nanosheets (RGO).

The signals obtained by the various sensors of the same 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  $NH_4^+$  as an interferent.

The sensing strategy is based on the differential intercalation and diffusion behaviours of Na<sup>+</sup> and K<sup>+</sup> ions within both RGO<sup>2,3</sup> and HCF<sup>4,5</sup>, resulting in distinct voltammetric signals. The neural network was trained using massive datasets comprising 327 variables as columns and over 4 million samples as rows.

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 8-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>.

## References

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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.