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Host-Tailored Sensors for Carnitine Potentiometric Measurements based on Surface Molecular Imprinting

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A novel surface molecularly imprinted polymer (MIP) is presented for Carnitine (CRT), a potential biomarker of ovary cancer. It consists in a 3D polymeric network created on top of graphene layers and around the target template. The polymeric structure was obtained after radical polymerization of (vinylbenzyl)trimethylammonium chloride, 4-styrenesulfonic acid and vinyl pivalate, including in the reaction mixture ethylene glycol dimethacrylate as cross-linker and ammonium persulfate as initiator. Non-imprinted polymer (NIP) material was also produced, by excluding the template from the procedure.

The imprinted material was further used for the selective determination of CRT by potentiometric transduction. A selective membrane was prepared for this purpose by using the MIP material as ionophore, and dispersing it in a plasticized poly(vinylchloride) matrix with a suitable charged lipophilic additive. All membranes were casted over a solid conductive support made of graphite and applied over the smaller end of an insulin syringe. The best membranes were also applied over conductive glass/plastic. Control membranes were also produced by replacing MIP by NIP material.

The potentiometric performance of the above electrodes was evaluated against CRT solutions of increasing concentrations. Overall, the best devices displayed linear response with average slope and detection limit of 47.28 mV.decade⁻¹ and 3.55x10⁻⁶ mol.L⁻¹, respectively. The effect of pH upon the potentiometric response was evaluated for different buffer solutions (within 2-9) and the best performance for this sensor was obtained with HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer of pH 5.2. Good selectivity was observed against albumin, ascorbic acid, glucose, creatinine and urea, tested for concentrations up to their normal physiologic levels in urine. The application of the devices to the analysis of spiked samples showed recoveries ranging from 91% (± 6.8%) to 118% (± 11.2%), with relative errors below -20%.

Overall, the combination of the MIP sensory material with a suitable selective membrane and electrode design has lead to a promising tool for point-of-care applications, when applied to field monitoring of CRT in biological samples.

Keywords: Carnitine; Surface Molecularly imprinted sensors; Graphene; Solid conductive supports; Potentiometry; Urine.