Trace Electroanalysis of Perfluorinated Alkyl Substances with Molecularly Imprinted Polymer Sensors †

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† Presented at the 5th International Symposium on Sensor Science (I3S 2017), Barcelona, Spain, 27–29 September 2017.
Published: 4 December 2017

Pollution of natural and drinkable waters by perfluorinated alkyl substances (PFAS) is a problem of global concern [1]. Molecularly imprinted polymers (MIPs) are promising materials being explored extensively as recognition elements for sensors since they offer improved stability, cost effectiveness and rapid fabrication [2]. In this study, the preparation and characterization of novel sensors for PFAS based on the electrosynthesis of MIPs is reported. In particular, we focus on the trace detection of perfluorooctane sulphonate (PFOS), for which recommended concentration limits in water are the lowest (60 pM). The PFOS-sensitive MIP was prepared by electropolymerization of o-phenylenediamine (o-PD) on a gold electrode in the presence of the analyte as the template. The template molecules were then removed from the modified electrode surface by using suitable solvents. Electrochemical methods and scanning electron microscopy were used to monitor the electropolymerization, template removal and binding of the analyte. A ferrocenyl derivative was used as the reporting electrochemical probe which generates the analytically useful voltammetric signal. The incubation of the MIP-modified electrode in PFOS containing samples resulted indeed in the progressive suppression of the electrochemical signal of the reporting probe, which scaled inversely with the PFOS content. Conditions for achieving a linear dependence between voltammetric signals and concentration of PFOS in the sample were optimized, obtaining a detection limit of 38 pM [3] and a dynamic range extended over 2 orders of magnitude. Real water samples were analysed, providing results in satisfactory agreement with those obtained by HPLC-MS-MS measurements. A similar approach was applied also to develop a sensor for perfluorooctanoic acid (PFOA). To the best of our knowledge, this is the first example of use of MIP-modified electrodes for the detection of perfluorinated alkyl pollutants at ultra-trace concentration levels.

Conflicts of Interest: The authors declare no conflict of interest.

References

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