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Quantifying sorption on membrane and surface binding interactions using mass spectrometry

H.T. Ngo*, L. Mackay, A. Cronshaw, M. Bradley, A.I. Schäfer

Univeristy of Edinburgh, UK

Contamination of freshwater supplies by micropollutants such as pharmaceuticals, personal care products & endocrine disrupting compounds raises considerable public concern [1, 2] . Water discharge from livestock, agriculture, waste water treatment plants, and landfills into the environment are main sources of micropollutants. Strong evidence for their effects on animals and humans, such as adverse reproductive outcomes, and changes in metabolism, neuroendocrine function and homeostasis and alike were reported by the Endocrine Society [2].

To remove micropollutants and natural organic matter from drinking water, membrane processes such as nanofiltration (NF) and ultrafiltration (UF) can be effective [3-5]. However, polymers have been reported to adsorb substantial amounts of organic contaminants. While membrane separation is predominantly a size or charge exclusion rather than adsorption process, high micropollutant sorption has been reported [3].

Adsorption and size exclusion, among several known separation mechanisms are essential in high initial retention of trace organics in NF membrane [3, 5, 6]. The retention then stabilizes and adsorption equilibrium is reached because of the limited adoptive capacity of the membrane. Hydrogen bonding and hydrophobic interactions were reported to play a central role in adsorption of steroid hormones on the membrane. High $\log K_{ow}$ compounds such as some pesticides are readily retained by both NF and UF membranes (>80%). Adsorption is also influenced by solution chemistry (e.g. pH, ionic strength, water matrix compounds such as organic matter or salt) and membrane properties (e.g. polymer type, charge, roughness and contact angle) at the condition of unsaturated adsorptive sites of membrane. Mechanisms underpinning such adsorptive interactions are to date not well understood as quantitative analysis of these interactions is a significant challenge [3]. Effective analytical surface techniques can facilitate this study and result in insightful understanding of organics adsorption on polymers.

In consequence, in this study a method based on mass spectrometry, which is used for quantifying adsorption and determination of surface binding interactions. Mass spectrometry (MS) such as Fourier Transform Ion Cyclotron Resonance (FTICR) and Matrix-assisted Laser Desorption/Ionization (MALDI) has played a crucial role in analytical research for decades [7-9]. They are effective tools for surface analysis due to the use of laser desorption and ionization techniques [10, 11] . Mass spectrometry has certain capabilities compared to other well-established tools, such as optical, spectroscopic, and especially, autoradiography and microscopic techniques [12] (from which an intensive amount of information about adsorption and interactions on membranes can be also obtained). However, rapid and sensitivity identification and increasingly quantification can be achieved from the mass spectrometric technique. FTICR-MS, for example, has a high resolution and sensitivity, large dynamic range and currently one of the tools giving the best quality data.

Using MS, different amounts of hormones deposited by pipettes or absorbed to the membrane by using a cross-flow nanofiltration system were analysed. Linear plots of the hormone quantity vs. averaged/normalized mass spectrometric signal intensity were established. In FTICR-MS, linear correlations can be obtained at lower concentrations as shown in **Error! Reference source not found.**. A linear relationship was obtained below 0.5 $\mu g/mm^2$ and the limit of detection was about 100 ng/cm^2 when the hormone is deposited on the membrane. In MALDI-MS, fitted linear relations with R^2=0.94 (see **Error! Reference source not found.**) could only be achieved between quantity and signal intensity by normalizing data using a suitable ion

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originated from the matrix as an internal standard [13]. The linearity range was from about 100 to 800 μg/mm^2 and the limit of detection (~100 μg/mm^2) is about 200 times that of FTICR-MS.

The quantification of surface binding interactions, as previously reported [11] was achieved by using MALDI-MS, based on determining positive x intercepts of linear graphs. These values correspond to the adsorption and retention affinity of the hormone to the surface, and depend on the properties of the hormone and the surface.

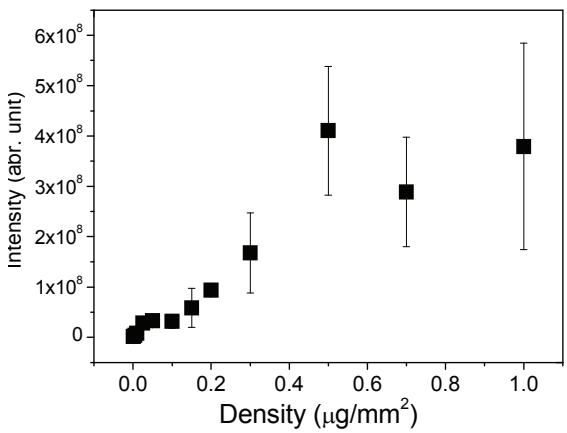

Figure 1 FTICR signal intensity vs concentration of testosterone solution deposited (0.5 μL for each sample) on polymer membrane (NF270)

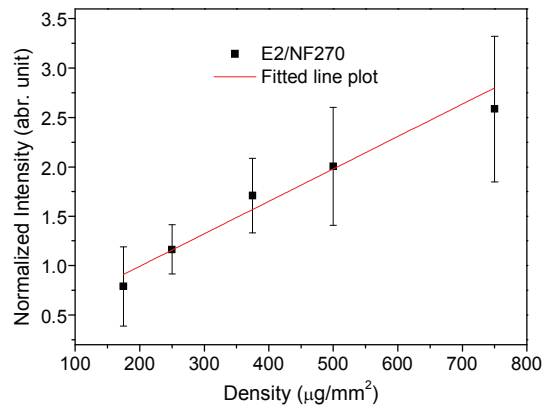

Figure 2 MALDI signal intensity vs concentration of estradiol (E2) solution deposited (0.5 μL for each sample) on polymer membrane (NF270) and the fitted line

Through adsorption analysis FTICR-MS exhibited significantly higher sensitivity, precision and high-throughput potential than MALDI-MS. Further research on various polymers – hormone interaction characterisation using MS is being carried out for a number of very exciting applications.

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