



Non-targeted evaluation of selectivity of water-compatible class selective adsorbents for the analysis of steroids in wastewater



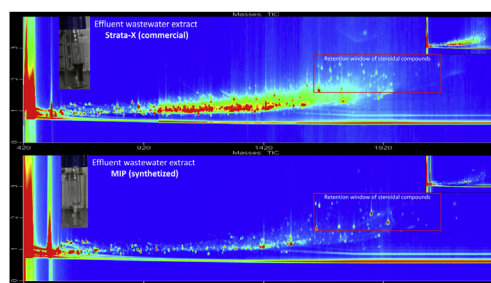
Matias Kopperi, Marja-Liisa Riekkola*

Laboratory of Analytical Chemistry, Department of Chemistry, P.O. Box 55, FI-00014 University of Helsinki, Finland

HIGHLIGHTS

- GC × GC–TOFMS and LC–MS were utilized to evaluate performance of adsorbents.
- Nontargeted approach was proposed to quantify adsorbent selectivity toward steroids.
- Affinity toward steroids and matrix removal potential of adsorbents was measured.
- Water-compatible MIPs were successfully used to extract steroids in wastewater.
- Commercial and synthetic adsorbents were compared for the extraction of steroids.

GRAPHICAL ABSTRACT



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ABSTRACT

Selective adsorbents for solid-phase extraction are needed to meet the low concentration requirements of new environmental quality standard directives, especially for the analysis of estrogens in wastewater. In this work, bulk polymerization procedures were first optimized for the synthesis of non-imprinted polymers (NIP) with low non-specific adsorption of nonpolar compounds in aqueous environments. Water-compatible molecularly imprinted polymers (MIP) were then synthesized by increasing the selectivity of the polymer towards steroids with a testosterone template (average imprinting factor > 10). In addition, the affinity of synthesized entrapped β -cyclodextrin–epichlorohydrin polymers (ECD) towards steroids was clarified. The polymers were applied to the extraction of spiked wastewater effluent samples and their performance compared to commercially available adsorbents. The selectivity of the studied adsorbents was evaluated utilizing liquid chromatography – mass spectrometry as well as comprehensive two-dimensional gas chromatography – time-of-flight mass spectrometry. Affinity between adsorbents and steroids as well as matrix removal potential were measured with targeted methodologies, and two novel non-targeted methodologies were proposed to quantitatively measure adsorbent selectivity by utilizing chemometrics. Semi-quantitative selectivity was measured from the ratio of peak areas between steroidal and other compounds. Semi-qualitative selectivity was calculated from the ratio between the number of tentatively identified steroidal and other compounds. The synthesized polymers provided good matrix removal potential (ion suppression 15–30%) and semi-qualitative selectivity (~4 units) compared to the commercial adsorbents (ion suppression 45–80%,

* Corresponding author.

E-mail address: marja-liisa.riekkola@helsinki.fi (M.-L. Riekkola).

selectivity < 3 units). Simple non-targeted approaches provided a novel method of quantifying the selectivity of extraction.

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1. Introduction

The European Commission upholds the Water Framework Directive, which sets environmental quality standards (EQS) for selected priority substances in surface waters [1]. The main source of emerging organic contaminants (EOC) in the environment is municipal wastewater treatment. Wastewater is such a complex matrix that analysis of these contaminants at trace levels requires very effective sample preparation methods and often new EQS-concentrations are under the detection levels of the monitoring laboratories. To overcome the sensitivity problem, laboratories often use either larger sample volumes for extraction or large-volume injection. The compounds can also be derivatized to increase detector response and thus decrease the required sample volume [2]. Sensitivity of the method can also be increased by using selective extraction methods. The most common sample preparation method for wastewater is solid-phase extraction (SPE) with a very generic hydrophilic-lipophilic-adsorbent [3]. The extracts also often require further clean-up to remove interfering compounds prior to analysis. To eliminate this additional step, more selective extraction techniques are required to achieve the sufficient sensitivity.

Molecularly imprinted polymers (MIP) are one of the most selective adsorbents for sample extraction. MIPs are formed when a template molecule interacts with a suitable monomer while a cross-linker binds them together through polymerization. After the synthesis, the template is removed and a selective binding site for the template molecule is imprinted onto the polymer. Based on a selection of a suitable template molecule compounds with similar structures can also be extracted. MIPs are usually polymerized in the presence of nonpolar organic porogens in order to stabilize the interactions between template and functional monomer. However, the use of organic porogens makes the polymer very hydrophobic. Previous studies have often overlooked the fact that the selectivity of the MIP may be hindered by the hydrophobic nonspecific binding of non-polar compounds in aqueous samples [4,5]. Therefore, efficient utilization of MIPs in wastewater analysis requires further efforts in the synthesis of water-compatible polymers in combination with the development of new template molecules [6].

MIPs have previously been used for the analysis of pharmaceutical compounds [7–11], estrogens and other steroidal compounds [12–15] in surface and wastewater. MIPs have also been used to analyze steroids in urine [16–19] and milk samples [20,21]. Most of these studies utilize one or two template molecules to extract the corresponding compounds, and occasionally the adsorption of additional compounds with similar structures has been studied. However, it is often difficult to carry out extensive study on compound class selectivity with conventional approaches that focus only on a few selected compounds. Therefore, a method is proposed here that allows the quantification of class selectivity with non-targeted analysis by comparing the number of tentatively identified analytes of interest, or their detector response, to that of matrix constituents. Definitions of semi-qualitative and semi-quantitative selectivity are introduced to differentiate non-targeted results from those achieved by targeted methods with reference materials.

MIP materials can be applied to different sample preparation techniques. The most popular application is the packing of the synthesized MIP into SPE-cartridges [7,8,10,11]. Some novel applications exploit MIPs in solid-phase microextraction (SPME) [18,20] and as a coating in stir-bar sorptive extraction (SBSE) [13]. However, in order to reliably compare different laboratory-made adsorbents, the extraction itself should be kept as simple and repeatable as possible. One such methodology is the use of bulk adsorbent with magnetic stirring, also known as dispersive solid-phase extraction (dSPE).

An interesting future approach is the utilization of MIPs for the direct removal and destruction of EOCs during wastewater treatment [6,22]. Another promising application is solid-phase extraction with entrapped β -cyclodextrin–epichlorohydrin polymers (ECD) [23–25]. Steroidal compounds form inclusion complexes with hydrophobic cavities inside cyclodextrin polymers, which increases the selectivity of extraction compared to the commercial hydrophilic-lipophilic adsorbents most commonly employed in wastewater analysis.

The first goal of this study was to synthesize class selective molecularly imprinted polymers (MIP) with particular interest in their water-compatibility. In the first step, synthesis of non-imprinted polymers (NIP) was optimized reducing their non-specific binding in water samples. Then the selectivity towards steroids was increased by molecular imprinting with a suitable template molecule. In addition, ECD-polymer synthesis adapted from literature was also optimized. The affinities between the synthesized polymers and steroids before and after molecular imprinting were measured with liquid chromatography – mass spectrometry (LC–MS). The second goal of the study was to utilize non-targeted statistical approaches for the evaluation and comparison of the adsorbent properties by comprehensive gas chromatography – time-of-flight mass spectrometry (GC \times GC–TOFMS). Although several attempts are found in the literature [26] for the quantification of analytical selectivity, a straightforward methodology is still lacking. In this study a novel non-targeted approach is proposed to measure both qualitative- and quantitative selectivity of adsorbent materials via statistical analysis of mass spectral data.

2. Materials and methods

2.1. Reagents and solutions

Methanol, dichloromethane, chloroform, toluene and acetone were purchased from VWR International (Radnor, PA, USA), acetic acid was from Merck Millipore (Billerica, MA, USA) and pyridine from J.T.Baker (Deventer, The Netherlands). All solvents were HPLC grade, and pyridine was purified by distillation in the laboratory every two months. Distilled water was purified using a Millipore Direct-Q 3 UV system (0.05 μ S cm^{-1} conductivity; Billerica, MA, USA) and sodium hydroxide pellets were from FF-Chemicals (Haukipudas, Finland). Epichlorohydrin (EPI; purity \geq 99%) was purchased from Fluka Chemie GmbH (Buchs, Switzerland). Methacrylic acid (MAA; purity \geq 99%), 2-hydroxyethyl methacrylate (HEMA; purity \geq 99%), acrylamide (purity \geq 99%), ethylene glycol dimethacrylate (EGDMA; purity \geq 98%), trimethylolpropane trimethacrylate (TMPTMA; purity \geq 90%), divinylbenzene (DVB;

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