



Recent molecularly imprinted polymer-based sample preparation techniques in environmental analysis



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ABSTRACT

In spite of the huge development in analytical instrumentation, the improvement of the selectivity during extraction and/or subsequent clean-up of sample extracts in environmental analysis is an area of intense research activity. At this regard, the incorporation of molecularly imprinted polymers (MIPs) in sample preparation appears as one of the most versatile and promising alternative. MIPs are tailor-made stable polymers with molecular recognition abilities, provided by the presence of a template during their synthesis and thus are excellent materials to provide selectivity to sample preparation. In the present review, the use of MIPs in sample preparation for environmental analysis, including its already well-established use in solid-phase extraction as well as its recent incorporation to other extraction techniques such as solid-phase microextraction, stir bar sorptive extraction and its combination with liquid membranes is described. The advantages and drawbacks of each methodology as well as the future expected trends are discussed.

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1. Introduction

The development of analytical instrumentation has been huge during last decades allowing eventually the determination of any compound in environmental samples. Typically, target analytes are determined by chromatographic techniques coupled to common detectors (UV, fluorescence) or, more recently, mass spectrometry (MS) or tandem MS. However, direct injections of crude sample

extracts are not recommended even when the selective detection provided by MS is used, since matrix components can inhibit or enhance the analyte ionisation, hampering accurate quantification. Thus, a clean sample is generally convenient to improve separation and detection, while a poorly treated sample may invalidate the whole analysis. Therefore, sample preparation is a key step of the whole analytical process, being critical for unequivocal identification, confirmation and quantification of analytes.

The main objectives of sample preparation are the removal of potential interferences, analyte preconcentration (especially in environmental water samples), converting (if needed) the analyte

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into a more suitable form for detection or separation, and providing a robust and reproducible method independent of variations in the sample matrix. More recently, new objectives have been set such as using smaller initial sample sizes, improvement of selectivity in extraction, to facilitate the automation, and to minimize the amount of glassware and organic solvents to be used [1]. Traditional liquid–liquid extraction does not fulfil current requirements in environmental analysis and it has been displaced from laboratories by new extraction techniques such as solid-phase extraction (SPE), solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE), and more recently by matrix solid-phase dispersion (MSPD), micro solid-phase extraction (MSPE) or liquid-phase microextraction (LPME), among others. All the mentioned techniques suffer from lack of selectivity making necessary an extensive optimisation of the typical steps involved. However, even after careful optimisation, some matrix components are co-eluted with target analytes making difficult to reach detection limits according to the nowadays stringent regulations.

Molecularly imprinted polymers (MIPs) are synthetic materials able to specifically rebind a target molecule in preference to other closely related compounds. These materials are obtained by polymerising functional and cross-linking monomers around a template molecule, leading to a highly cross-linked three-dimensional network polymer. The monomers are chosen considering their ability to interact with the functional groups of the template molecule. Once polymerisation has taken place, template molecule is extracted and binding sites with shape, size and functionalities complementary to the target analyte are established. The resulting imprinted polymers are stable, robust and resistant to a wide range of pH, solvents and temperature. Therefore, MIPs emulate natural receptors but without the associated stability limitations. In addition, MIPs synthesis is also relatively cheap and easy, making them a clear alternative to the use of natural receptors.

Three different approaches for the synthesis of MIPs have been reported: covalent, non-covalent and semi-covalent approaches. Wulff and Sarchan [2] introduced the covalent approach, which involves the formation of reversible covalent bonds between the template and monomers before polymerisation. Then, the template is removed from the polymer by cleavage of the corresponding covalent bonds, which are re-formed upon rebinding of the analyte. The high stability of template–monomer interaction leads to a rather homogenous population of binding sites, minimising the existence of non-specific sites. However, the difficulty of designing an appropriate template–monomer complex in which covalent bond formation and cleavage are readily reversible under mild conditions makes this approach rather restrictive.

An intermediate option is the semi-covalent approach [3,4]. In this case, the template is also covalently bound to a functional monomer before polymerisation, but the template rebinding is based only on non-covalent interactions. Finally, the non-covalent approach was introduced by Arshady and Mosbach [5], and nowadays it is by far the most used for the preparation of MIPs. The non-covalent approach is based on the formation of relatively weak non-covalent interactions (i.e. hydrogen bonding, ionic interactions) between template molecule and selected monomers before polymerisation. The experimental procedure is rather simple and a wide variety of monomers able to interact with almost any kind of template are commercially available. However, it is not free of some drawbacks since template–monomer interactions are governed by an equilibrium process during the pre-polymerisation step. Thus, in order to displace the equilibrium towards the formation of the template–monomer complex, a high amount of monomer is used. Consequently, the excess of free monomers is randomly incorporated to the polymeric matrix leading to the formation of non-selective binding sites.

The use of MIPs as selective sorbent materials allows performing a customized sample treatment step prior to the final determination. Thus, their use in solid-phase extraction, so-called molecularly imprinted solid-phase extraction (MISPE), is by far the most advanced technical application of MIPs [6–13]. Besides, last recent years have seen a growing interest in the combination of MIPs with other sample preparation techniques such SPME and SBSE, among others. Accordingly, the present paper pretends to describe the most recent molecularly imprinted polymer-based sample preparation techniques in environmental analysis, describing the different approaches most employed as well as highlighting selected applications.

2. Molecularly imprinted solid-phase extraction (MISPE)

As mentioned above, MISPE is the more advanced technical application of MIPs and in fact some companies already commercialise cartridges packed with proper MIPs for the determination of target analytes in different samples. In parallel, several research groups over the world are active in this field and the papers published describing the synthesis and use of MIPs for SPE is huge. Different modes of MISPE have been assayed, including batch SPE, where the MIP is incubated with the sample, conventional off-line SPE, where the MIP is packed into cartridges, and several modes of on-line SPE.

2.1. Off-line protocols

In off-line MISPE, a small amount (15–500 mg) of imprinted polymer is packed into polyethylene cartridges. Then, after the conditioning, loading and washing steps, analytes are eluted, ideally free of co-extractives, and the elution extract is further analysed by chromatographic techniques.

Last years have seen a huge development of off-line MISPE methods for the determination of a great variety of analytes in environmental samples such as river water, groundwater, wastewater, sea water and soil extracts. In general, sample is loaded onto the MIP cartridge in a low-polarity solvent, since in such media specific interactions are maximized, and after a washing step for the removal of compounds non-specifically bound to the polymeric matrix, analytes are eluted with a solvent able to disrupt the typical non-covalent interactions between the analyte and the imprinted polymer.

Aqueous samples can also be directly loaded onto MIP cartridges. In this case, MIPs behave like a reverse-phase sorbent and thus both target analytes and matrix components are retained through non-specific interactions. Then, a washing solvent able to remove matrix components and to re-distribute non-specifically bound analytes to the selective imprints is introduced. However, the success of such procedure is not always achieved and thus efforts have been directed towards the synthesis of water-compatible MIPs by incorporating hydrophilic surface properties to the polymer in order to reduce non-specific hydrophobic interactions. This goal can be mainly achieved by using polar porogens [14–16], hydrophilic comonomers (e.g. 2-hydroxyethyl methacrylate, acrylamide) or cross-linkers (e.g. pentaerythritoltriacylate, methylenebis(acrylamide)) [17–19] and/or designed monomers capable of stoichiometrically interacting with the template functionalities [20,21]. Such approaches have provided recognition of target analytes by MIPs in aqueous media to a certain extent and thus, further research in this field is expected in the coming years.

2.2. On-line protocols

In spite of the clear advantages of on-line protocols, few papers has been published since the first work by Masqué et al. [22]. This

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