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Application of molecularly-imprinted polymers in solid-phase microextraction techniques

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ABSTRACT

In spite of the huge developments in analytical instrumentation during the past two decades, sample preparation is still considered as the most critical step in the whole analytical process. It is required in order to remove interferences and preconcentrate target analytes. Efforts have been made to improve selectivity during extraction. Molecularly-imprinted polymers (MIPs) have affinity for the original template molecule and have been used in applications, such as chemical separation, selective extraction, catalysis, or molecular sensing. In the present review, we describe the application of MIPs in the various modes of solid-phase microextraction.

Contents

Abbreviations: ACF, Acesulfame; BPA, Bisphenol A; CE, Capillary electrophoresis; CMIP, Conducting molecularly-imprinted polymer; CNT, Carbon nanotube; CW-DVB, Carbowax and polydivinylbenzene; DMSO, Dimethylsulfoxide; DVB, Divinyl- benzene; EE-SPME, Electrochemical solid-phase microextraction; EGDMA, Ethylene glycol dimethacrylate; ES, Estrogen; FA, Folic acid; FQ, Fluoroquinolone antibiotic; GC-MS, Gas chromatography-mass spectrometry; HPLC-FD, High-performance liquid chromatography analysis with fluorescence detection; HPLC-PAD, High-performance liquid chromatography with photodiode-array detector; In-tube SPME, In-tube solid-phase microextraction; Lyz, Lysozyme; MAA, Methacrylic acid; MIMSPE, Molecularly-imprinted micro-solid-phase extraction; MIP, Molecularly-imprinted polymer; MIPPy/MWCNT, Molecularly-imprinted polypyrrole/multi-walled carbon nanotube; MMA, Methyl methacrylate; MMIP, Magnetic molecularly-imprinted polymer; Ni-Ti, Nickel-titanium; OFL, Ofloxacin; OPP, Organophosphorus pesticide; OPPy, Overoxidized polypyrrole; ORMOSIL, Organically-modified silicate; PA, Polyacrylate; PAA, Polyacrylic acid; PDMS, Polydimethylsiloxane; PDMS-DVB, Polydimethylsiloxane and polydivinylbenzene; PBDE, Polybrominated diphenyl ether; PET, Poly(ethylene terephthalate); PMME, Polymer monolith microextraction; QCM, Quartz-crystal microbalance; SA, Salicylate; SLM, Supported liquid membrane; SPME, Solid-phase microextraction; SSF, Stainless steel fiber; TAT, 2,4,6-trisacrylamido-1,3,5-triazine; TBZ, Thiabendazole.

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1. Introduction

In this review, we present a brief introduction to the concept of imprinting templates in polymers and how it is achieved in practice, followed by a discussion of how molecularly-imprinted polymers (MIPs) have been used in combination with solid-phase microextraction (SPME). There are some reviews in this field that consider SPME and/or MIP [1,2]. The major part of this review deals with applications of MIPs in different modes using SPME fibers.

2. Molecularly-imprinted polymers

Molecular imprinting involves making an artificial tiny lock for a specific molecule that serves as miniature key. MIPs are synthetic materials with artificially generated recognition sites able to rebind a target molecule specifically in preference to other closely-related compounds.

The synthesis of MIPs starts by positioning the functional monomers around the template molecules (which serve as an analogue of the eventual target analyte). The monomers interact with sites on the template via covalent or non-covalent interactions. They are then polymerized and cross-linked around the template, leading to a highly cross-linked, three-dimensional network polymer. After polymerization, the template is removed, making available cavities, complementary to the template molecule in size and shape, and ready for specific recombination with the template [3–5] {see Fig. 1 [6]}. Molecular imprinting introduces molecular memory into the solid matrix, which becomes capable of selectively recognizing the target molecule. MIPs possess many intriguing characteristics (e.g., mechanical, chemical and thermal stability, low cost, and ease of preparation), which further extend their application. MIPs have been successfully used to recognize molecules over a wide molecular-weight range, from volatile molecules to peptides and proteins, and even viruses and cells [7].

2.1. Synthesis of MIPs

There are three different approach to MIP preparation: non-covalent, covalent and semi-covalent imprinting [8,9].

In the non-covalent imprinting – the most widely used method of synthesis, due to its relative simplicity – a template is mixed with an appropriate functional monomer, a suitable porogenic solvent, cross-linking agents and catalysts or polymerization initiators. Specific binding sites are formed by self-assembling the template and the functional monomer, which should be capable of forming a fairly stable complex with the template (e.g., by dipole interaction, hydrogen bonding, or ion pairing). After synthesis, the template is removed from the polymer simply by exhaustively washing it with solvents – usually using a Soxhlet-type apparatus. The resulting materials are dried, sieved and finally used.

In the covalent approach, the template and the functional monomer are covalently bound prior to polymerization; the template is removed from the polymer matrix after synthesis by cleaving the covalent bonds before the washing step. Sorbents prepared using covalent imprinting tend to have well-defined, more homogeneous binding sites than those resulting from the non-covalent approach, as the interactions between template and functional monomers are much more stable during the polymerization.

For the semi-covalent approach, the interaction between template and monomer during polymerization is covalent; however, the target molecule rebinds with the monomer via a non-covalent interaction.

One of the popular applications of MIPs is sample preparation, which accompanies SPME.

3. Solid-phase microextraction

SPME was pioneered in the early 1990s by Pawliszyn and Lord [10]. This technique uses a thin polymer film coating on a fiber to extract analytes from aqueous or gaseous samples. SPME can integrate sampling, extraction, preconcentration and sample introduction into a single step. The technique is very simple, fast, solvent-free, inexpensive, easily automated, and reliable, and it has been applied to both headspace and direct aqueous sample analysis with excellent sensitivity and good selectivity.

The introduction of new polymeric fibers, the development of new experimental configurations and the improvement of automatic devices will undoubtedly lead to the application of SPME to different fields of chemical analysis [11]. The efficiency of the preconcentration depends principally on the type of stationary phase and its thickness. But other parameters of the process are also important (i.e., sample volume and temperature, fiber exposure time, extraction vial volume and sample stirring). The materials used for coating fibers include: polydimethylsiloxane (PDMS), polyacrylate (PA), also mixtures of: polydimethylsiloxane and poly(divinylbenzene) (PDMS-DVB), and Carbowax and polydivinylbenzene (CW-DVB), Carbowax and molecularly-imprinted resin (CW-TPR). The non-polar PDMS fiber was the first polymer to be used for SPME and, to date, this coating is most used, extracting only non-polar analytes very well. However, according to the principle of “like dissolving like”, polar compounds are more likely to be extracted by polar coatings (e.g., PA and CW-DVB). The CW-DVB fiber is strongly polar, but its maximum temperature is only 265°C, which limits its application range. Moreover, silica fibers are fragile and must be handled with great care, so more robust SPME fibers with long life and relatively low cost are highly desirable.

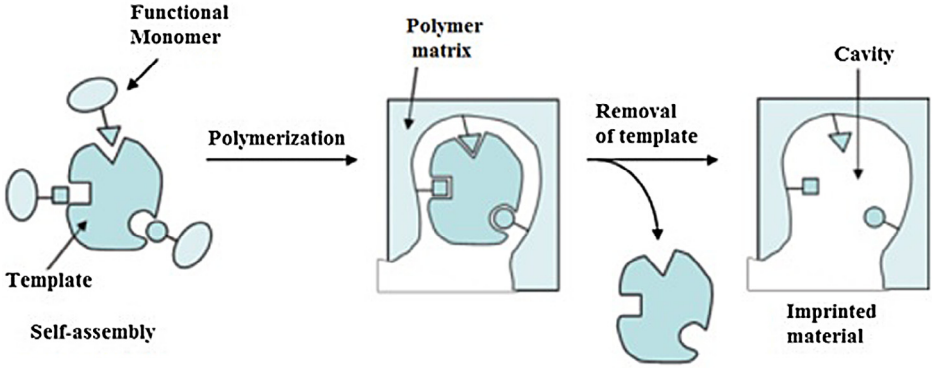

Fig. 1. Molecularly-imprinted polymer [6].