Trends in Analytical Chemistry 89 (2017) 146–162

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Novel developments and trends of analytical methods for drug analysis in biological and environmental samples by molecularly imprinted polymers

Saeedeh Ansari [a, *], Majid Karimi [b]

[a] Department of Chemistry, Saveh Branch, Islamic Azad University, Saveh, Iran
[b] Department of Materials Science and Engineering, K.N. Toosi University of Technology, Tehran, Iran

ARTICLE INFO

Article history:
Available online 27 February 2017

Keywords:
Biological and environmental matrices
Biosensors
Drug analysis
Magnetic-MIP
MISPE
MISPME

ABSTRACT

Because of the low concentration levels in plasma, blood, urine, and other metabolites, adequate analytical methods should be used for quantification of drugs at the trace levels. Molecularly imprinted polymers (MIPs) are tailor made and stable polymers with special molecular recognition abilities that because of their high selectivity can be used for the extraction of selected target analytes and structurally related analogues in many bioanalytical approaches. Nowadays, MIPs are rapidly progressing for the analysis of drugs in biological, environmental, and pharmaceutical samples. In this review, we discuss the novel developments and uses of MIPs as new sorbents and fibers in solid phase extraction (SPE) and solid phase microextraction (SPME), ultrasonic-assisted SPE, sensitive sensors, magnetic separations or conjugating with carbon materials for trace and ultra-trace determination of drugs. We believe that our review will be of assistance to drug analysis and analytical methods with highly selective separations/detections.

1. Introduction

The analysis of biological and environmental samples for drugs quantification is a significant task in drug discovery. Till now, adequate analytical methods have been used to achieve high separation efficiency and low detection limits in the ppb or sub-ppb levels. However, the all of the advanced analytical processes can be impaired if an inappropriate sample preparation method has been used before the injection. So, selected analytical method and all of its instrumentations have an important role in the drugs analysis which is the theme of our discussion. The sample preparation has many different key roles such as the elimination of

Abbreviations: AIBN, 2,2azobisisobutyronitrile; ASA, Acetylsalicylic acid; CEL, Celecoxib; CF, Cephalosporin; CNT, Carbon nanotubes; COC, Cocaine; CV, Cyclic voltammetry; DFC, Diclofenac; DLLME, Dispersive liquid–liquid microextraction; DMSO, Dimethyl sulfoxide; DPV, Differential pulse voltammetry; DVB, Divinylbenzene; EC-in-tube SPME, Electrochemically controlled in-tube solid-phase microextraction; EGDMA, Ethylene glycol dimethacrylate; EIS, Electrochemical impedance spectroscopy; EME, Electromembrane extraction; EMMIP, Electromagnetic molecularly imprinted polymer; ENR, Enrofloxacin; FD, Fluorescence detection; FQ, Fluoroquinolone; GC/FID, Gas chromatography-flame ionization detector; GC–MS, Gas chromatography–mass spectrometry; GE, Gold electrode; HF-LPME, Hollow fiber liquid phase microextraction; HPLC/UV, High performance liquid chromatography with ultraviolet detection; HPTLC, High performance thin layer chromatography; ICPMS, Inductively coupled plasma mass spectrometry; IIP, Ion-imprinted polymers; IP-CPE, Ion-pair cloud-point extraction; LC–MS, Liquid chromatography–mass spectrometry; LOD, Limit of detection; LOQ, Limit of quantification; MAA, Methacrylic acid; MEPS, Microextraction by packed sorbent; MGCE, Magnetic glassy carbon electrode; MINP, Molecularly imprinted nanoparticle; MIP, Molecularly imprinted polymer; MISPE, molecularly imprinted solid phase extraction; MISPME, Molecularly imprinted polymer solid phase microextraction; MIT, Molecular imprinting technology; MMIP, Magnetic molecularly imprinted polymer; MNP, Magnetic nanoparticle; MNZ, Metronidazole; MOF, Metal organic framework; MWCNT, Multi-walled carbon nanotubes; NDV, N-desmethylvenlafaxine; NIP, Non-imprinted polymer; NSAID, Non-steroidal anti-inflammatory drug; ODV, O-desmethylvenlafaxine; SA, Salicylic acid; SBSE, Stir-bar sorptive extraction; SIT, Surface imprinting technique; SLM, Supported liquid membrane; SMIP, Surface molecular imprinted polymer; SPE, Solid-phase extraction; SPME, Solid-phase microextraction; TC, Tetracycline; TFA, Trifluoroacetic acid; TLTMC, Tulathromycin; UA-DSPME, Ultrasound-assisted dispersive solid phase microextraction; UCNP, Upconversion nanoparticles; UHPLC-MS/MS, Ultra-high performance liquid chromatography-tandem mass spectrometry; VEN, Venlafaxine; VPU, Vinylphenyl urea; WWTP, Wastewater treatment plant; μ-SPE, Micro-solid phase extraction.

* Corresponding author.
E-mail addresses: ansarisaeedeh@gmail.com (S. Ansari), majidkarimi007@gmail.com (M. Karimi).

http://dx.doi.org/10.1016/j.trac.2017.02.002
0165-9936/

interferences, preconcentration, converting the analytes to appropriate form for separation and/or detection. Because of the low concentration levels of drugs in plasma and the variety of the metabolites, the selected extraction technique should be virtually exhaustive [1].

In most cases, the complex matrix and their low concentration of analyte strongly limit and lower the characteristic efficiency of most analytical methods and persuade the researchers to introduce novel preconcentration and/or separation techniques. Till now, several analytical methods such as solid-phase extraction (SPE) [2], solid-phase microextraction (SPME) [3], dispersive liquid-liquid microextraction (DLLME) [4], electrochemical [5] and ion-pair cloud-point extraction (IP-CPE) [6] have been applied for drugs quantification in biological and environmental samples [7] and pharmaceutical preparations [8] using high performance liquid chromatography with ultraviolet detection (HPLC/UV) [9], fluorescence detection (FD) [10], gas chromatography–mass spectrometry (GC–MS) [11], liquid chromatography–mass spectrometry (LC–MS) [12], high performance thin layer chromatography (HPTLC) [13] and spectrofluorometric [10] to overcome such limitations.

The molecular imprinting was first investigated in 1949 by Dickey using the concept of instructional theory [14]. In the years around 1985 to 2000, the enantiomer separations in liquid chromatography (LC) evaluation, which were reported by Mosbach, Sellegren and co-workers [15,16], provided deep impression for the practical possibility of molecular imprinting technology (MIT) as new bio-mimic materials. Notably, molecularly imprinted polymers (MIPs) had been widely studied in drug analysis during a few decades from 1990, since the separation of drugs and structurally related compounds is pretty complicated [17]. Fig. 1 presents the milestones for the molecular imprinting technology and application of MIPs in the bioanalytical extraction techniques.

MIPs are the synthesized and stable polymers with special molecular recognition abilities that can be used for the selective extraction of selected molecules. In these tailor-made polymers, the recognition sites are imprinted in the polymer matrix by the presence of a template during their synthesis which is formed according to the shape, size, and the functional groups of the template molecule [18]. The interaction between the self-assembled complex of the functional monomers and target molecules achieve with the templates via hydrogen bonding, electrostatic interaction, and hydrophobic interaction. This complex prepared with an excess of crosslinking agent, large amount of porogenic solvents, and an accurate polymerization initiator. Because of its characteristics such as easy preparation, good performance, high selectivity and reusability, potential applications to an extensive range of target molecules and chemical stability, MIPs are widely utilized in various fields of analytical chemistry such as food, drugs, biological and environmental samples [18]. According to the recent rapid developments, novel MIP-based procedures such as MIPs as SPE sorbents (MISPE), MIPs as SPME sorbents (MISPME), MIPs in sensor technology, MIPs in magnetic separation, and MIPs conjugated with carbon materials have been introduced regarding the biological and/or environmental samples and pharmaceutical compounds analysis. These matrices are very complex and highly selective adsorbents are necessary to ensure a robust and selective analysis. Due to the selectivity and elimination of interferences are the most important features of MIPs, combination of such materials with liquid chromatography [19], capillary electrophoresis [20], capillary electrochromatography [21], SPE [22], SPME [23], sensors [24], enantiomeric separations [25], catalysis [26] and etc. lead to simplifying, avoiding matrices effect, and also significant improvement. The schematic image of the MIP preparation is summarized in Fig. 2.

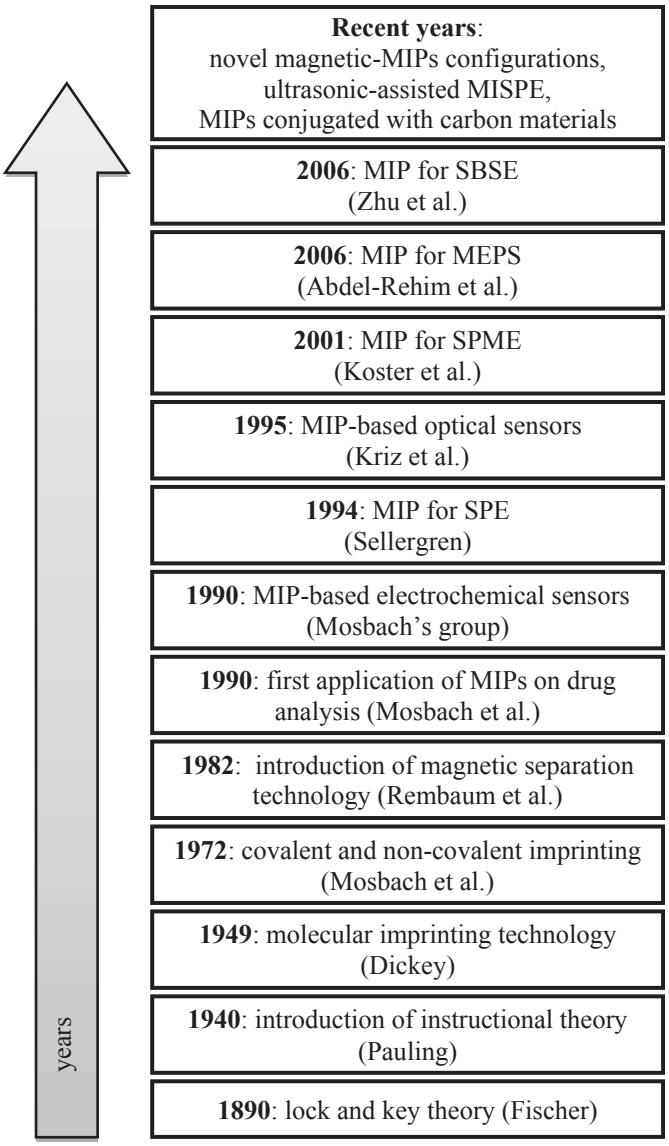

Fig. 1. Milestones in molecular imprinting technology and application of MIPs in the bioanalytical extraction techniques.

Today, SPE is the standard and most commonly sample preparation technique in bioanalysis field which has many potential advantages such as high extraction recovery, broad selectivity and cleaner extract using different sorbents. SPE is widely used for the extraction of trace amounts of various organic compounds and metal ions from the biological and environmental samples. A cleaner extract that is free of matrix interferences is the main goal of the SPE. However, the retention of the analyte is based on the non-specific interaction with the traditional SPE sorbents such as C18 silica and activated carbon. Thus, the lack of selectivity arises, that causes co-extraction of matrix interference components with target analyte [27]. So, a sorbent with high selectivity and specificity for the target analyte is required to overcome this problem.

Recent developments and trends in SPE method focus on the high-throughput, miniaturization of the process, and the utilization from selective sorbents. Therefore, to increase the bioanalytical method sensitivity and selectivity, the synthesis and design of more selective sorbents such as MIPs are required. In this regard, due to their individual features, the MIPs have attracted much attention in the recent decades. However, the small particle size of the MIPs was