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Review

New coatings for stir-bar sorptive extraction of polar emerging organic contaminants

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ABSTRACT

Stir-bar sorptive extraction (SBSE) is a sample-preparation technique that allows the sorptive extraction and preconcentration of emerging organic contaminants (EOCs) from complex matrices. Since its introduction, this technique has been widely applied in environmental, food and biological research, followed by gas chromatography (GC) or liquid chromatography (LC). However, the single commercially-available coating for SBSE, based on polydimethylsiloxane (PDMS), has become its principal limitation, so use of SBSE has been reduced to the extraction of apolar or moderately polar compounds. In recent years, there has been growing interest in developing more polar in-house coatings for SBSE and, therefore, extend the applicability of this sorptive extraction technique. Different approaches to synthesis of polar coatings for SBSE have been developed, with sol–gel technology and monolithic materials being notable examples. This review focuses on the commonest and novel strategies for synthesizing new coatings for SBSE to enhance the extraction of polar EOCs and their applications.

Contents

1. Introduction

Over the past few decades, scientific concern about environmental pollution has increased and environment-friendly methodologies have gained popularity, including modified and less hazardous sample pre-treatments [1]. In addition, environmental analysis has focused on the extraction and the determination of a wide range of emerging organic contaminants (EOCs) with an apolar or moderately polar character because sample-preparation techniques were incapable of extracting many compounds with such different chemical properties simultaneously. Thus, the aim of sample pre-treatments has been to extract more polar contaminants, simplify the manipulation of the sample, reduce the volumes of sample and organic solvent used, miniaturize the analytical devices, and remove the maximum of interferences from complex matrices [2].

For the analysis of liquid samples, conventional liquid-liquid extraction (LLE) was further replaced by less time-consuming solid-phase extraction (SPE), these being the most well-established techniques for preconcentration and clean-up from aqueous sample in many different research fields [3]. However, great efforts

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have been concentrated on the development of extraction techniques with lower solvent consumption and low sample handling, so novel sorption-based extraction techniques, such as solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE) or microextraction by packed sorbent (MEPS), and new miniaturized solvent-based extraction techniques, such as single-drop microextraction (SDME), dispersive liquid–liquid microextraction (DLLME) or hollow-fiber liquid-phase microextraction (HF-LPME), have been introduced and discussed in the past few decades [3–6].

While the main advantage of SPE is the high availability of commercial sorbents, other sorptive techniques, such as SPME and SBSE, are still restricted in this respect, so limiting the range of analyte classes that can be extracted. In particular, SBSE is an enrichment technique based on SPME principles [7], first introduced by Baltussen et al. [8]. The SBSE device comprises a magnetic stir bar covered with a polymeric coating that enables the distribution of the analytes between the sample and the small amount of extracting phase [9,10]. In contrast to SPME, the volumes of extraction phase found in SBSE stir bars (24–126 μL) are larger than in SPME fibers (maximum 0.5 μL), which leads to higher amounts of analytes being extracted from the samples [11]. Many publications have demonstrated the applicability of SBSE in different research areas due to its versatility in both sampling [immersion and headspace (HS)] and desorption modes [liquid (LD) or thermal desorption (TD)] [4,10,12].

In SBSE, to promote the transfer of the analytes onto the extracting phase, several variables affecting the extraction step should be evaluated, including extraction time and temperature, sample pH, addition of an inert salt, stirring rate and sample volume. As for TD, desorption time and temperature are the most important variables to be tested, while organic solvent nature, desorption time and volume are the most common variables studied in LD [4,7]. All factors affecting the development of SBSE have been extensively reviewed in several publications [4,7,13]. Moreover, another parameter to take into account in SBSE is the coating, it being an essential factor in enhancing the retention of the analytes. However, the only commercially-available coating for SBSE, until recently, was polydimethylsiloxane (PDMS). This main disadvantage limits SBSE to apolar compounds [4,11].

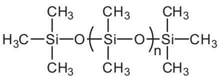
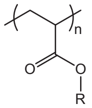
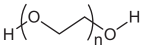
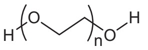
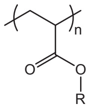
So far, several SBSE-related reviews have been reported, mainly focusing on SBSE applications in environmental, food and biological analysis [4,11,12,14,15], on SBSE-method optimization [4,15], novel sorptive extraction techniques related to SBSE [2,10], and, more recently, on development of new in-house coatings for SBSE [4,9,10]. This review extensively covers the state of novel commercial and in-house coatings for SBSE since 2004, and, in particular, their application in the analytical field for the extraction of polar pollutants from complex matrices.

2. Commercially-available coatings for SBSE

For years, PDMS has been the only commercially-available extracting phase for SBSE, commercialized under the name Twister by Gerstel. Current reviews [4,12,15,16] highlight a great number of publications in which the PDMS coating has been applied to the extraction of many EOCs from environmental, food and biological matrices. Nevertheless, this limitation has become the principal disadvantage of SBSE, focusing on the extraction of apolar or moderately polar analytes (generally for those with $\log K_{o/w} > 3$) [16]. As a consequence, the present trend in analytical chemistry and environmental analysis is control and determination of EOCs, mainly with polar behavior, in the environment.

In this respect, very recently, SBSE stir bars with polar coatings were marketed by Gerstel. These new stir bars are coated with poly(ethyleneglycol) (PEG)-modified silicone (EG Silicone Twister) and polyacrylate (PA) with a proportion of PEG (Acrylate Twister). We should note that the EG Silicone Twister is commercially available, while Acrylate Twister was still undergoing pilot tests at the time of writing. The structures of these new coatings are presented in Table 1, which shows the enhancement of polarity through hydroxyl and ester groups from PEG and PA structures, respectively. Although they have been synthesized to improve PDMS stir-bar performance, both Acrylate and EG Silicone Twisters are

Table 1
Structures and application of novel commercially available coatings for stir-bar sorptive extraction (SBSE)

Coating Phase*	Structure	Analyte	Matrix	Sampling Mode	Desorption	Analysis	Ref.
PDMS (Twister®) PA (Acrylate Twister®) PEG (EG Silicone Twister®)	 $H_3C-Si(CH_3)_2-O-[Si(CH_3)_2-O]_n-Si(CH_3)_2-CH_3$ PDMS (Twister®)	VOCs	Food and cosmetic	Immersion/ HS	TD	GC-MS	[18]
PDMS (Twister®) PA (Acrylate Twister®) PEG (EG Silicone Twister®)	 PA and PDMS-based (Acrylate Twister®)  PEG and PDMS-based (EG Silicone Twister®)	PPCPs	Wastewater	Immersion	LD	LC-MS/MS	[19]
PEG (EG Silicone Twister®)	 PEG and PDMS-based (EG Silicone Twister®)	Bisphenols	PCPs	Immersion	TD	GC-MS	[20]
PA (Acrylate Twister®)	 PA and PDMS-based (Acrylate Twister®)	Benzothiazole	Untreated wastewater	Immersion	TD	GC-MS	[17]

GC–MS, Gas chromatography-mass spectrometry; HS, Headspace; LD, Liquid desorption; LC-MS/MS, Liquid chromatography-tandem mass spectrometry; PA, Polyacrylate; PCP, Personal-care product; PEG, Poly(ethylene)glycol; PPCP, Pharmaceuticals and personal-care product; TD, Thermal desorption; VOC, Volatile organic compound
*Commercial name in brackets