Review

Stir bar sorptive extraction: Recent applications, limitations and future trends

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ABSTRACT

Stir bar sorptive extraction (SBSE) has generated growing interest due to its high effectiveness for the extraction of non-polar and medium-polarity compounds from liquid samples or liquid extracts. In particular, in recent years, a large amount of new analytical applications of SBSE has been proposed for the extraction of natural compounds, pollutants and other organic compounds in foods, biological samples, environmental matrices and pharmaceutical products. The present review summarizes and discusses the theory behind SBSE and the most recent developments concerning its effectiveness. In addition, the main results of recent analytical approaches and their applications, published in the last three years, are described. The advantages, limitations and disadvantages of SBSE are described and an overview of future trends and novel extraction sorbents and supports is given.

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1. Introduction

Sample preparation is perhaps one of the most important stages of the analytical process. This step becomes more important as the complexity of the samples increases and when the concentration levels to be detected are minimal. In fact, selecting the detection technique for an analysis is currently considered easier than choosing the sample treatment technique.

Sample preparation involves clean-up and pre-concentration procedures aimed to improve the sensitivity, specificity and selectivity of the analytical methods. Current trends in analytical chemistry focus on miniaturization of these steps and of the amount of toxic reagents in order to reduce wastes [1,2]. Solid phase microextraction (SPME), micro-liquid–liquid extraction (MLLE), dispersive liquid–liquid extraction (DLLE) or stir bar sorptive extraction (SBSE) are the most popular among all the techniques proposed in recent years for reducing wastes. In the last 10 years, these techniques have been widely applied in hundreds of families of compounds, in all analytical fields. During the last few years, research has focused on miniaturization of the entire sample preparation workflow, including the collection of smaller sample sizes that leads to complete automation of almost all these procedures that are tailored to this small sample size.

SPME was developed in the early 90 s by Arthur et al. [3] and was the first modern solventless extraction technique for organic compounds. The technique soon became very popular due to its broad application field, simplicity, and low cost, among other reasons. However, at the beginning, the extraction procedure was completely manual with the consequent loss in reproducibility and sample throughput capacity. This limitation was overcome with the advent of commercial solutions that coupled the extraction fibers to generic autosamplers, allowing a completely automated and unattended analysis in both immersed and head space fiber extraction modes. This new extraction technique was successfully applied by modifying previously well-defined methods [4] and it was also used in novel applications [5]. Different fibers that would allow the extraction of compounds with very different polarities and molecular weights were developed to broaden the applications of SPME. However, because of its limitations, SPME is not the preferred technique for the analysis of organic compounds. Due to the low fiber volume, the mass of analyte extracted was limited by the kinetics of the extraction process, and it was mainly affected by sample volume [6,7]. Certainly, SPME can be applied to very small to extremely large volumes (i.e., an entire lake), but if quantitative recoveries are needed, only small sample volumes could be analyzed, affecting consequently to the sensitivity of the methods. Other limitations include that the precise control of the extraction time, since the extraction is developed out of the equilibrium state; the premature contamination and degradation of the fiber; the displacement effects due to the matrix compounds; and its relatively low specificity that requires the use of several fibers for multiresidue analysis. SBSE has overcome some of these limitations by allowing larger solid phase volumes.

SBSE was introduced in 1999 by Baltussen et al. [8] who proposed a novel application involving polydimethylsiloxane (PDMS) polymer as sorbent for solid phase extraction. PDMS is coated onto a glass-coated magnetic bar. Sampling is done by directly introducing the SBSE device into the aqueous sample. While stirring, the bar adsorbs the organic compounds to be extracted. The bar is removed from the sample, rinsed with deionized water and dried. After sorption, the compounds are chemically desorbed in a liquid or gas chromatography inlet, but capillary electrophoresis (CE) [9] or even inductively coupled plasma (ICP) [10,11] can also be used. SBSE was developed by Gerstel GmbH & Co. KG (Mülheim an der Ruhr, Germany) and is commercialized under the trade name Twister®. Although the first applications of SBSE were published in 2001 [12] and it cannot be considered a novel technique, nowadays a large amount of new applications are being continuously developed. This technique has been successfully applied to all analytical fields, including environmental, clinical and food analysis, and to a large variety of matrices including soils, environmental water and wastewater, solid and liquid foods, gaseous samples, and biological fluids. Due to the high pre-concentration capacity, broad spectrum of applications and simplicity, SBSE is becoming one of the most studied sample extraction techniques for the analysis of organic compounds. However, it has some disadvantages such as the limited spectrum of analyte polarities for the available stationary phases, the presence of strong matrix effects and the need of high control of extraction conditions.

There are few reviews on SBSE in the literature, and they mainly focus on the general theoretical principles of this technique [13] or the recently developed applications [14–16]. In contrast, the present review offers a different point of view. The text is divided into three sections: (1) a review of current procedures and approaches used in SBSE and the correlation between the results obtained and the theoretical data; (2) a review of the most recent trends in SBSE applications published in the last four years; and (3) discussion of the main disadvantages and limitations of SBSE that must be overcome in the future in order to improve this technique. The information presented is intended to be useful for the development of future applications and solutions to overcome the limitations of the technique.

2. Theoretical data and actual data obtained

The theory behind SBSE is the same as that of SPME. Baltussen et al. made an extensive study of the theory and thermodynamic principles of SBSE in 1999 [8]. Previously, they had published other approaches related to this technique that finally led to the development of SBSE [17]. Although, the objective of the present work is not to discuss these principles, some concepts must be explained.

It is well known that the extraction efficiency of SBSE and SPME —in PDMS stationary phases—is correlated to the octanol-water partitioning coefficient ($K_{o/w}$) and to the phase ratio (β). The equations that guide the partition between the liquid and the stationary phases are

$$\frac{m_{SBSE}}{m_0} = \frac{K_{o/w}/\beta}{1+(K_{o/w}/\beta)} \tag{1}$$

$$\beta = \frac{\text{Volume of sample}}{\text{Volume of stationary phase}} \tag{2}$$

where m_{SBSE} is the mass of analyte in the sorbent and m_0 is the mass of the analyte in solution. Both equations are equally valid regardless of the stationary phase or the nature of the sample, but if the stationary phase is not PDMS, the $K_{o/w}$ constants cannot be applied and other appropriated partitioning constants must be used.

The phase ratio is responsible for the better extraction efficiency of SBSE over SPME because the volume of stationary phase used in SBSE is about hundreds to thousands times higher than the one used in SPME. According to this theory, for a sample volume of 10 mL, a quantitative extraction using SPME is only possible for compounds with a log $K_{o/w}$>5, while for SBSE, a quantitative extraction can be obtained for compounds with log $K_{o/w}$>2.7 using a common PDMS stir bar.

However, it is possible to obtain quantitative extraction (100%) using the SBSE technique? Certainly, there is a huge number of substances with log $K_{o/w}$ values higher than 2.7. Quantitative