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FULL PAPER

Stir bar sorptive extraction as a sample preparation technique for chromatographic analysis: An overview

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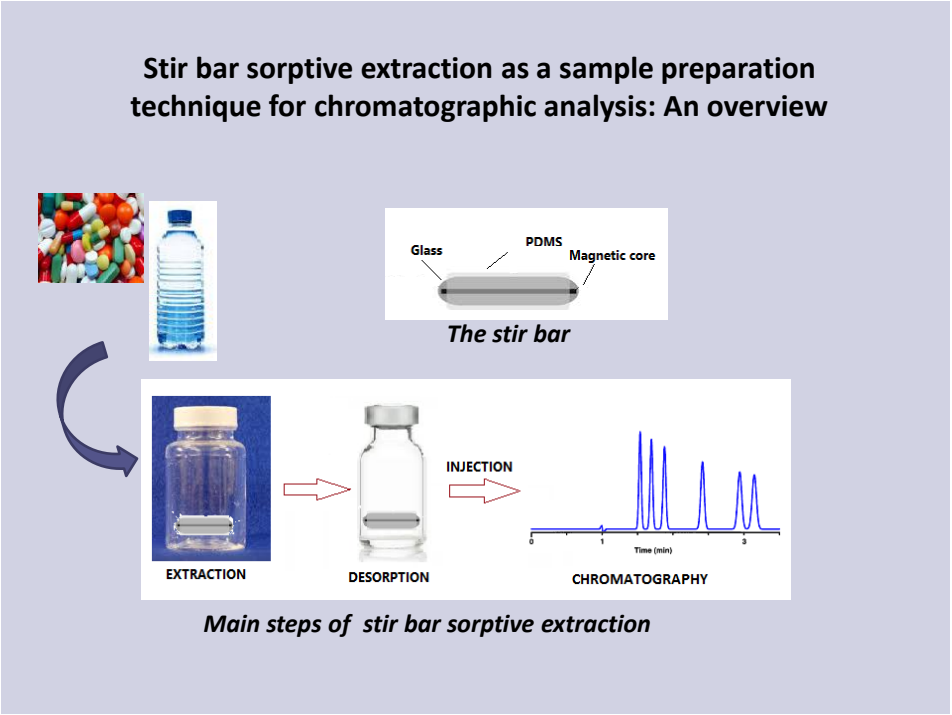
ABSTRACT: Sample preparation is an important step in chemical analysis. The present article gives an overview about the Stir bar sorptive extraction (SBSE) as a technique for sample preparation for chromatographic analysis. Stir bar extraction, desorption steps and optimization of the extraction conditions like ph, extraction time, addition of an inert salt, addition of an organic modifier and stirring speed have been discussed. Extraction mechanism, advantages, disadvantages and some applications in water, environmental, pharmaceutical and food analysis have been also discussed. The application of SBSE can be considered as an attractive alternative to classical extraction methods by reducing the consumption of and exposure to the solvent, disposal cost, and extraction time.

KEYWORDS: Stir bar sorptive extraction, Sample preparation, Separation, Pre-concentration.

GRAPHICAL ABSTRACT



Introduction

There are four main steps in chemical analysis process, sampling, sample preparation, measurement, and data analysis. Sample preparation was probably the single and the most neglected area in analytical

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chemistry related to the great interest in instruments. The principal objectives of sample preparation for residue analysis are; isolation of the analytes of interest from as many interfering compounds as possible, dissolution of the analytes in a suitable solvent and pre-concentration. In an analytical method, sample preparation is followed by a separation and detection procedure. The selection of a preparation method is dependent upon: (1) the analyte(s), (2) the analyte concentration level(s), (3) the sample matrix, (4) the instrumental measurement technique, and (5) the required sample size [1-4]. Only few kinds of samples can be introduced to chromatographic analysis without any preparation. In these cases, the lack of reliable calibration is the major problem. Moreover, sample preparation allows the separation and/or pre-concentration of analytes and makes the determination methods more selective and sensitive. Sample preparation step requires ca. 61% of the total time to perform the complete analysis, and is responsible for about 30% of the total analysis error [5]. There are many sample preparation techniques for gas chromatography, but some of these methods suffer from inconveniences such as, lengthy separation, limitation of the volume of sample solution investigated, time consuming, multi steps, lower enrichment factor and consumption of organic harmful solvents [6]. Extraction with large quantities of toxic solvents is difficult to justify the multi-residue determinations and solventless sample preparation technique which should be favored [7]. There is a trend in modern analytical chemistry to combine extraction and pre-concentration of the analyte in a single step to keep the sample preparation time and the related errors at the minimum using solventless techniques as alternatives to liquid extraction. These methods include solid phase extraction (SPE), solid phase micro extraction (SPME), In-tube solid phase micro extraction, and stir bar sorptive extraction (SBSE), which can combine sampling and pre-concentration in one step. Stir bar sorptive extraction (SBSE) is being developed to deliver more sorptive-phase mass and surface area. In this technique, the phase, similar to gas chromatography (GC) stationary phases, is coated and bonded onto a magnetic stir bar. The stir bar is then immersed into the liquid sample for extraction [8]. The availability of different materials is one of the advantages that sorptive techniques have over other extraction techniques. [9] This technique was used for the first time by Baltussen et al. in 1999 [10]. There is a wide range of compounds which can be extracted successfully to trace analysis by SBSE such as pesticides, steroids, fatty acids, and drugs [11-15]. Stir bar overcomes the major disadvantage of SPME which is the amount of available phase. The large amount of polydimethylsiloxane (PDMS) on the surface of stir bar relatively to SPME fiber enhances its sensitvity and the recovery of the analytes.

Extraction Procedure

Stir bars have three essential parts: (a) a magnetic stirring rod which is necessary for transferring the rotating movement of a stirring plate to the liquid sample, (b) a thin glass jacket that covers the magnetic stirring rod and (c) a layer of polydimethylsiloxane (PDMS) sorbent into which the analytes are extracted. The glass envelope which is essential to prevent the decomposition of the PDMS layer would otherwise be catalysed

by the metals in the magnetic stirring rod [14,16].

Extraction step

In this step, the stir bar is added to the liquid sample and stirred. After extraction, the stir-bar is removed, rinsed with distilled water in order to remove other sample components, and then dried on a paper tissue to remove water. The partition coefficient of the solutes between the PDMS and the aqueous phase is controlling the extraction of solutes from the aqueous phase. The capacity of PDMS for the analyte is not influenced by the presence of large amount of water or other analytes, since all analytes have their own partitioning equilibrium into the PDMS phase [17,18].

Desorption step

The extraction step is followed by a thermal or liquid desorption before chromatographic separation and detection. Thermal desorption (TD) inserts the stir-bar in the heated GC injection and moves the desorbed analytes to the column for the next step.

Thermal desorption is used in case of thermally stable volatile and semi-volatile solutes and gas chromatography (GC), while Liquid desorption (LD) is the alternative when thermally labile solutes are analysed. Besides, the separation is carried out using liquid chromatography (LC). In liquid desorption, the stir bar is placed in a small amount of a proper solvent (GC) or the mobile phase (LC). LD methodologies has high sensitivity and reproducibility. The main drawback of the SBSE technique is the desorption step, especially to LC, because of the complexity in the automation [17].

Optimizing extraction conditions

There are many factors affecting the extraction process, the most studied are pH, extraction time, addition of an inert salt, addition of an organic modifier and stirring speed, followed by extraction temperature, sample volume and the volume of the acceptor phase [12]. Sample pH is the most important factor in order to control the form of the analyte to be extracted. Highly acidic or highly basic conditions are not recommended to extend the stir bar life time. Organic modifiers like methanol are used to reduce the adsorption of the analyte on the glass walls, but this amount must be optimized since addition of methanol may increase the solubility of the analyte in the aqueous phase. All these factors are well reviewed and discussed in details by Prieto et al. [12]. Addition of salts reduces the water solubility of polar organic analytes, and, therefore, increases their extraction efficiency, although high salt concentrations may decrease the extraction efficiency by increasing solution viscosity hindering analytes diffusion. Lancas et al. have reviewed the developments of SBSE with a focus on the development of new instrumental approaches and sorbent phases. They discussed many theoretical and technical details related to SBSE [18].

Optimization is normally accomplished by measuring analyte recovery as a function of the extraction time. The optimum conditions are obtained when no additional recovery is observed even when the extraction time is increased further [14].

Coated stir bar

In sorptive extraction, the properties of the extraction phase determine the extraction efficiency and selectivity. An ideal material for coating a stir bar should be capable of enriching the target molecules with high concentration factors, whilst leaving other interfering substances in the sample matrix. It is also worth mentioning that molecularly imprinted polymers (MIPs) are tailor-made

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materials with high selectivity for a target molecule. Since only the PDMS is available as extraction phase on commercial stir bars, the large majority of applications use this coating. Attempts have been made to apply other coatings in recent years. For years, the only commercially available coating for SBSE was the non-polar polymer, polydimethylsiloxane (PDMS), meaning that SBSE was largely unsuitable for the direct extraction and analysis of polar compounds [19]. To overcome this limitation, polar coatings based on different materials prepared by sol–gel technology, monolithic approach, polyurethane foam or activated carbons have been tested as SBSE coating [11,20,21]. The crucial issues are associated with development of coating method to obtain stable and reproducible coating on the substrate with a magnetic core. Up to now, several coating methods have been reported for preparation of stir bars apart from the commercial PDMS tube jacketed on the glass [22-24]. Recently, SBSE stir bars with the polar coating materials polyacrylate (PA) and ethylene glycol-PDMS copolymer (EG-Silicone) have been marketed [25].

Applications of stir bar sorptive extraction

Water and Environmental analysis

The main advantage of SBSE is that it can be applied to recover trace levels of volatile organic compounds (VOCs) and semi-volatile compounds.

Recently, SBSE has been applied to a range of compounds including volatile aromatics, halogenated solvents, PAHs, PCBs, pesticides, preservatives, odour compounds and organotin compounds in many different kinds of water samples. This method has the potential to considerably reduce extraction and analyze time when compared with SPE or LLE [26,15]. Garcia-Falcon et al. optimized the conditions of stir bar sorptive extraction (SBSE), followed by high-performance liquid chromatography with a fluorescence detector, for determining eight polycyclic aromatic hydrocarbons (PAHs) in water samples. Detection (0.5–7.3 ng/L) and quantitation (1.0–22 ng/L) limits were estimated and the method presented good linearity, good precision and sensitivity [27]. A stir bar coated with β-cyclodextrin-bonded-silica (CDS) as a novel sorbent has been developed and used by Faraji et. al. to analyze seven phenolic compounds in aqueous samples followed by thermal desorption and gas chromatography-mass spectrometric detection. The porous structure of CDS coating provides high surface area and allows high extraction efficiency. Under the studied conditions, linearity range of 0.1–400 µg/L, limit of quantifications of 0.08–3.3 µg/L and method detection limits of 0.02–1.00 µg/L have been obtained. The recovery of different natural water samples was higher than 81.5% [28]. Silva et al. studied stir bar sorptive extraction with polyurethane (PU) and polydimethylsiloxane (PDMS) polymeric phases followed by high-performance liquid chromatography with diode array detection [SBSE(PU or PDMS)/HPLC-DAD] for the determination of six acidic pharmaceuticals [o-acetylsalicylic acid (ACA), ibuprofen (IBU), diclofenac sodium (DIC), naproxen (NAP), mefenamic acid (MEF) and gemfibrozil (GEM)], selected as non-steroidal acidic anti-inflammatory drugs and lipid regulators model compounds in environmental water matrices. The limits of detection and quantification were between 0.40–1.7µg/Land and 1.5–5.8µg/L, respectively [29]. SBSE procedures for

pesticide residues in food and environment have been reviewed by Rojas et al. [15].

Pharmaceuticals

In recent years, Solid phase extraction (SPE) has increasingly been used to extract and estimate drugs, excipients, or degradation products in pharmaceutical formulations especially when a method needs to be stable indicating that the extraction involves a complex formulation matrix such as a cream. Despite obvious advantages of SPE, one of the major factors associated with this technique is its cost along with other problems such as clogging/plugging of cartridges, or channeling [30-33]. In contrast to conventional SPE with packed-bed cartridges, the SPME syringe assembly design allows the combination of all the steps of sample preparation into one step and thus reduces sample preparation time, the use of organic solvents and disposal costs. The foremost advantage of the technique is improved detection limits [34].

A new stir bar sorptive extraction (SBSE) technique coupled with HPLC-UV method for quantification of diclofenac in pharmaceutical formulations has been developed and validated by Kole et al. They used commercially available polydimethylsiloxane stir bars (TwisterTM) for the method development. The SBSE extraction recovery of the diclofenac was found to be 70% and the LOD and LOQ of the validated method were found to be 16.06 and 48.68 ng/ml, respectively. Furthermore, a forced degradation study of a diclofenac formulation leading to the formation of structurally similar cyclic impurity (indolinone) was carried out [35].

Kassem reviewed a significant number of applications for analysis of some important central nervous system drugs in biological fluids utilizing stir bar sorptive extraction (SBSE) technique covering the years from 2000 to 2008 and showing the advantages of this technique over the classical extraction techniques [36].

Food Analysis

Ridgway et al. made a comparison between static headspace analysis and stir bar sorptive extraction (SBSE) for the quantitative determination of furan. The SBSE technique was optimized and evaluated using two example of food matrices (coffee and jarred baby food). The use of the SBSE technique in most cases gave comparable results to other methods like static headspace method, using the method of standard additions with d4-labelled furan as an internal standard. In using the SBSE method, limits of detection down to 2 ng/g were achieved with only a 1 h extraction [37]. Possible advantages of SBSE include the use of larger sample sizes compared to automated headspace methods and the increased robustness of stir bars as compared to SPME fibers. There is also the potential for ‘remote’ sampling using the stir bars, as extraction is performed off-line, also enabling the possibility of sampling at lower than ambient temperature.Compared to direct SBSE sampling, headspace sorptive extraction (HSSE) may also offer some advantages, such as more selective extraction and hence a reduction in potential matrix affects [29]. The ongoing acceptance of sorptive extraction techniques into official methods clearly indicates that they offer satisfactory reliability and robustness for routine sample processing purposes [15, 38]. The most important limitations of SBSE are related to the manual performing of stir-bar removing from the sample, rinsing, drying

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and in some cases additional back extraction step in a proper solvent is needed.

Conclusion

Stir-bar solvent extraction (SBSE) is a simple analytical technique used for sample preparation to improve trace analysis. It is a valid alternative for many separation and pre-concentration procedures due to its high recoveries and concentration factors. The application of SBSE offers an attractive alternative to classical extraction methods by reducing the consumption of and exposure to the solvent, disposal cost, and extraction time. The performance of SBSE can be enhanced by stir bar surface coating to increase the extraction selectivity and sensitivity.

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