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ANALYTICAL MICROEXTRACTION TECHNIQUES

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Analytical Microextraction Techniques

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FOREWORD

Sample preparation involving extraction is normally required prior to analysis by chromatography, electrophoresis, or mass spectrometry. The main purposes of the sample preparation are to clean-up the sample, to make it compatible with the analytical instrumentation, and to enrich the analytes of interest. Sample clean-up is intended to remove major matrix components from the sample, which can interfere with the analyte detection or which can reduce the performance of the analytical instrumentation. Enrichment of the analytes is intended to improve the trace level detectability.

Most sample preparation in routine laboratories today is performed with classical extraction techniques, like solid-phase extraction or liquid-liquid extraction. However, in the scientific literature, a large number of research papers have been published on the development of microextraction techniques. The difference between the classical extraction techniques and the microextraction techniques is the mass / volume of the extraction phase, which has been substantially down-scaled in the latter.

The field of microextraction was essentially initiated in 1990 by Professor Janusz Pawliszyn and his co-workers by the introduction of solid-phase microextraction (SPME). In the years after this, a large number of scientific papers related to SPME emerged, SPME became commercially available, and several other microextraction techniques different from SPME were introduced. In general, a main driving force for all the activities in the field of microextraction has been to reduce the consumption of hazardous organic solvents and other materials required for sample preparation (green chemistry). In addition, the development of different microextraction techniques has been motivated by reduced sample volumes, reduced extraction times, improved analyte enrichments, improved sample clean-up, and improved compatibility with analytical instrumentation.

Definitely microextraction techniques will replace traditional methods in the future, but this will take time. Meanwhile, a lot of progress takes place, and microextraction is currently a very active field of research within analytical chemistry. New techniques and methods based on these are continuously being developed. Some of them are based solid-phase extraction principles, and includes solid-phase microextraction, stir bar sorptive extraction, microextraction by packed sorbent, dispersive micro-solid phase extraction, magnetic solid phase extraction, and thin film extraction. Others are based on liquid-liquid extraction principles, like single-drop microextraction, membrane-based microextraction, hollow-fibre microextraction and dispersive liquid-phase microextraction. In addition to all this, new materials are also entering the field of microextraction, like nanoparticles, ionic liquids and novel solid gels. All this you can read about in this e-book, which is a very comprehensive

guide to the most important developments of analytical microextraction techniques. Enjoy the reading!

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PREFACE

The miniaturization of the preliminary steps of the chemical measurement process is one of the challenges of Analytical Chemistry as it clearly facilitates the reduction of dimensions of the whole analytical process, being also favorable for the design of portable analyzers and opens up a door for on-site analysis. Among the substeps included in sample treatment, extraction techniques are unavoidable for the majority of the samples, either for analyte preconcentration, interference removal or conditioning prior to instrumental analysis. Therefore, their miniaturization must be systematically considered.

The new microextraction techniques, including the solid and liquid formats have emerged in this context. The advances and innovations in this field affect not only on the units designed for analytes isolation but also on the new materials that are used. They are characterized to be more efficient than classical ones, thus yielding better enrichment factors. This results in an enhanced sensitivity/selectivity of the whole analytical process.

The Anaytical Microextraction Techniques ebook is fully devoted to this subject matter of increasing interest in the last decades. It is divided into three parts. The first one, composed of four chapters, deals with the general aspects of microextraction techniques in the green chemistry context. It also affords the use of new phases, which results in more efficient devices, fully compatible with the green chemistry principles.

The second part of this ebook is fully devoted to micro solid phase extraction. It starts with the reference technique in this context: solid phase microextraction. Next, fully consolidated formats such as stir bar sorptive extraction and microextraction by packed sorbents are afforded. Dispersive solid phase extraction is usually employed for interference removal. However, its applicability for analytes isolation and preconcentration has been recently evaluated. In this ebook, it is considered in two chapters, one of them dealing with the use of magnetic nanoparticles. Their role is crucial to simplify the extraction process avoiding the need for centrifugation and/or filtration. This section concludes with a chapter devoted to thin film microextraction.

The liquid phase microextraction is compiled in section 3 where single drop and membrane-based ones are presented. Single drop microextraction was the first miniaturized technique developed in the liquid-liquid format, reducing the volume of solvent needed to the low microliter level. Since its proposal, several alternatives have been reported aimed at increasing the versatility of the initial approach. The use of porous materials (flat membranes or hollow fiber) as support of the liquid phase, allows the use of large volumes of solvent, which results in higher enrichment factors.

This ebook would serve as a useful reference to readers to provide the current state of the art of this research area as well as to stimulate the developments of innovative approaches on the topic.

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CHAPTER 1

Green Microextraction

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Abstract: In the present chapter, the microextraction techniques have been considered from the perspective of the Green Analytical Chemistry and an attempt has been made in order to propose a modified eco-scale suitable to provide a green certification of the extraction steps in the frame of the consideration of reagents and energy consumption and waste generation. Especially important is the evaluation of the intrinsic toxicity and risks associated to the use of reagents and the need of an accurate evaluation of the amounts of reagents and wastes in order to avoid misclassifications. It has been proposed a new eco-scale, called "Green Certificate", based on the application of a color code associated to a letter; from A to G, being A the greenest one, that gives an idea of how much green an analytical methodology is. In short, it is evident that the microextraction enhances the method greenness providing class A steps in front of classical analytical preconcentration and matrix removal which changes the method category to class D.

Keywords: Eco-scale, Green analytical chemistry, Green certificate, Green evaluation, Hollow-fiber liquid phase microextraction, Liquid phase microextraction, Single drop microextraction, Solid phase microextraction, Solvent microextraction, Stir bar sorptive extraction, Stir cake sorptive extraction, Stir rod sorptive extraction.

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1.1. INTRODUCTION

In recent years, the interest and attention of the scientific chemistry community in the development of green practices has increased substantially. From the texts and books edited by Paul Anastas between 1994 and 1998 devoted to Green Chemistry [1 - 4] the activity in the frame of Green Chemistry has considerably been increased.

Analytical methods are used to solve problems. Using, as inputs, preliminary information and knowledge related to a particular problem, solvents, reagents, samples, energy and instruments, the analysts can solve a specific problem. On the other hand, the outputs of those processes are results, data and models, in other words, solutions to the defined problem.

However, on the other side, the outputs of analytical methodologies are harmful wastes that create risks for operators and damage the environment [2]. In 1999 [3], J. Namiesnik proposed the term Green Analytical Chemistry (GAC) to include important parameters such as wastes, amount and toxicity of employed reagents, as important criteria to select the most appropriate methodology to solve a specific problem, thus creating a new frame for the previously named environmentally friendly analytical chemistry [4].

The twelve principles of GAC, proposed by A. Gałuszka *et al.* [5] can be found elsewhere and include:

1. Direct analytical techniques.
2. Minimize sample size and number of samples.
3. *In situ* measurements.
4. Integration of analytical processes and operations to reduce energy and reagents usage.
5. Automation and miniaturization of methods.
6. Avoid derivatization.
7. Avoid waste generation and provide appropriate waste management.
8. Multi-analyte or multi-parameter methods.
9. Minimize the use of energy.

10. Preferable use of reagents obtained from renewable sources.
11. Elimination of toxic reagents.
12. Increase of the safety of the operator.

Taking into consideration the 12 mentioned principles, in-field direct analysis can be considered as the greenest alternative: i) there are no reagents implied, ii) the method do not generate analytical wastes, iii) the risks to operators and the environment are generally, minimal. However, those remote, non invasive and direct analytical techniques can not be used in all the situations and because of that greener analytical method, in many cases, implies the reduction of the energy and reagents consumption, take care about the side effects of sample treatments, mainly isolation/enrichment steps of analytes and minimize the wastes.

Although, in many cases, direct analysis of samples is not possible and a sample preparation step should be included in the analytical method. The evolution of these sample preparation tools from the classical extraction methods such as soxhlet and liquid–liquid extraction (LLE) to the new and innovative solutions in solid phase extraction (SPE) [6] pursues the following objectives: i) miniaturization of the device, ii) multiclass compound extraction and iii) automation and/or high-throughput determination (Fig. **1**).

Analytical microextraction can be defined as a sample preparation step using volumes in the microliter or nanoliter range of extracting phase (solid, semi-solid polymeric or liquid material). In summary, analytical microextraction includes the aforementioned guidelines of sample treatment evolution, especially in the frame of miniaturization, automation, on-site analysis and time efficiency, most of them directly related with the twelve principles of GAC.

1.2. ANALYTICAL STRATEGIES OF MICROEXTRACTION

The extraction procedures can be classified according its exhaustive and non-exhaustive nature. The main objective of the exhaustive techniques is to extract analytes completely from the sample to the extraction phase. The main advantage of these techniques is that they do not require to extract the standards following the extraction procedure, because the analyte is transferred quantitatively to the extraction phase and thus, external standards dissolved in the extracting solvent

CHAPTER 2

Novel Sol-Gel Sorbents in Sorptive Microextraction

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Abstract: Despite remarkable advances in modern state-of-the-art analytical instruments featured with enhanced sensitivity and automated operation in recent years, the success of an analytical investigation still largely depends on the sampling and sample preparation techniques. The growing concerns about environmental pollution and public safety, solvent-free/solvent-minimized sorptive microextraction techniques have gained enormous popularity among practicing scientists over solvent intensive sample preparation techniques. A major share of the increasing popularity of sorptive microextraction techniques definitely goes to sol-gel coating technology. The enormous potential of sol-gel coating technology as a viable approach for creating hybrid organic-inorganic advanced material systems has been intuitively materialized, resulting in a large number of microextraction sorbents possessing unique selectivity, enhanced extraction efficiency, higher thermal, mechanical, chemical and solvent stability. The current chapter explains the basic principle of sol-gel coating technology as well as the step-by-step procedure to fabricate the coating, classifies and describes different sorptive microextraction sorbents, and presents the most recent developments in the field. Selected and representative applications of different sol-gel microextraction sorbents are also tabulated.

Keywords: Fabric phase sorptive extraction (FPSE), Green sample preparation, Inorganic-organic hybrid sorbents, Sample preconcentration, Sampling and sample preparation, Sol-gel coating, Sol-gel extraction media, Solvent-less extraction, Solvent-minimized extraction, Sorptive microextraction.

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2.1. INTRODUCTION

The introduction of solid-phase microextraction (SPME) by Pawliszyn and co-workers [1] in 1987 is considered to be a ground-breaking event in the field of analytical sample preparation that initiated a new era towards solvent-free/solvent-minimized extraction, miniaturization, reduction of multiple time consuming steps in sample preparation, and automation.

Following the inception of SPME, a number of other microextraction techniques including stir bar sorptive extraction (SBSE) [2], thin film microextraction [3], microextraction by packed syringe (MEPS) [4], micro solid-phase extraction (μ-SPE) [5], fabric phase sorptive extraction (FPSE) [6] have emerged over the period of two decades. All these techniques belong to a broader family named as ***sorbent-based sorptive microextraction*** and rely upon the partition equilibrium of the analyte(s) between the microextraction sorbent and the sample matrix. The microextraction sorbents used in sorbent-based sorptive microextraction may be a pseudo liquid absorbent (*e.g.*, polydimethylsiloxane, polyethylene glycol), or a solid adsorbent (*e.g.*, graphite, carbon nanotubes) or a mixture of both (*e.g.*, PDMS/Carboxen). As such, both absorption and adsorption processes may play role in analyte extraction and preconcentration process. Sorbent-based microextraction systems have significantly reduced the usage of toxic and hazardous organic solvents in sample preparation exercises and therefore are considered to be a significant step forward towards green analytical chemistry [7]. In addition to the significant reduction of organic solvent usage, sorbent-based microextraction systems also integrate sampling, extraction and preconcentration of target analyte into a single step, resulting in a simple, fast and convenient sample preparation process.

Considering the high volume of research in the field of sorbent-based sorptive microextraction, a large number of review articles and books have been published covering different aspects and applications of this modern sample preparation technique [8 - 12].

Over the period of last two decades, a number of new formats and modifications of sorbent-based sorptive microextraction systems have emerged, bringing new

attributes and unique applications in analytical sample preparation. A classification scheme of different sorptive-microextraction techniques that share the same principle of non-exhaustive equilibrium driven sample extraction and preconcentration is given in Fig. (**1**).

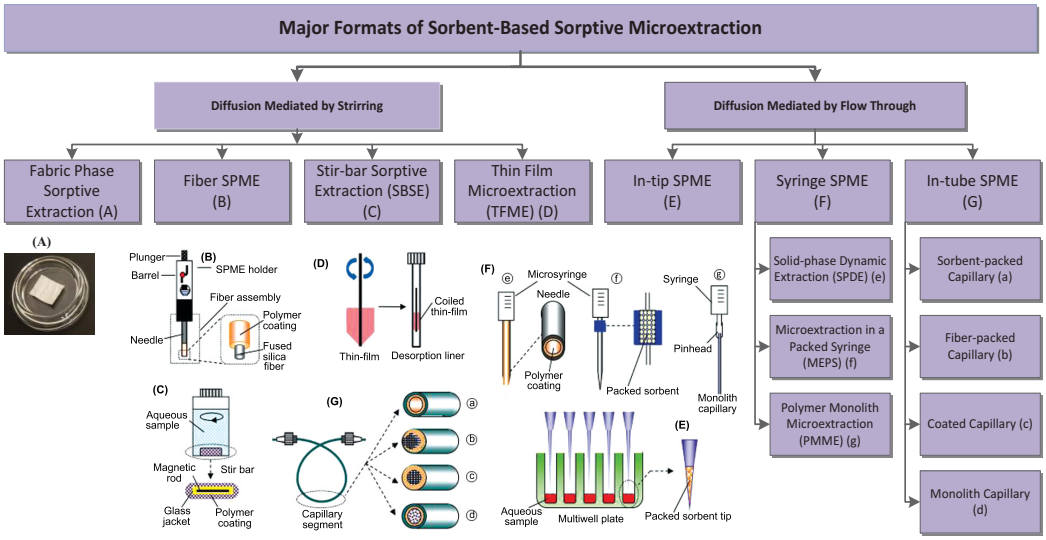

Fig. (1). Classification scheme of major sorption-based micrextraction techniques.

Among all the different formats and modifications of sorbent-based sorptive microextraction, fiber-SPME still dominates among all the developed formats and enjoys high popularity in a broad range of fields including environmental, pharmaceutical, food, toxicological, forensic applications.

2.2. WORKING PRINCIPLE OF SORBENT-BASED SORPTIVE MICROEXTRACTION

All sorbent-based microextraction techniques, regardless of their format, are based on the principle of equilibrium extraction. The extracting sorbents are immobilized either on the outer surface of a substrate (fiber-SPME, TFME, SBSE, FPSE, PSPME) or inside of a fused silica capillary (intube-SPME or CME) or inside of a hollow-fiber (HF-SPME). During the extraction, the microextraction device holding the sorbent may either be directly exposed to the sample matrix containing the target analyte(s) (direct immersion mode), or may be exposed to

CHAPTER 3

Ionic Liquids in the Microextraction Context

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Abstract: The structural versatility of ionic liquids (ILs), the wide range of interest properties that can present: low to negligible vapor pressure, from water-soluble to water-insoluble, from medium viscosity to high viscosity…, their synthetic tuneability, together with their impressive solvation abilities for analytes of quite different nature, make their use in microextraction techniques an obvious approach of great interest.

Thus, ILs and a group of interesting derivatives, such as polymeric ionic liquids (PILs) and IL-based surfactants, pure, mixed, or combined with other materials forming hybrid sorbents, have been used in all variants of liquid-phase and solid-based microextraction strategies.

This chapter will give an exhaustive overview of existing approaches that combine ILs and derivatives in liquid-phase microextraction (LPME) modes such as single-drop microextraction (SDME), hollow fiber liquid-phase microextraction (HF-LPME) and dispersive liquid-liquid microextraction (DLLME), including all their variants; and also in solid-based microextraction methods, such as micro-solid-phase extraction (μ-SPE), solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE), and stir-cake sorptive extraction (SCSE).

Keywords: Dispersive liquid-liquid microextraction, Environmental applications, Food applications, Hollow-fiber liquid phase-microextraction, Ionic liquids, Ionic liquid-based surfactants, Liquid-phase microextraction, Micro-solid-phase extraction, Polymeric ionic liquids, Single-drop microextraction, Solid-phase extr-

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action, Solid-phase microextraction, Stir-bar sorptive extraction, Stir-cake sorptive extraction.

3.1. INTRODUCTION

3.1.1. Ionic Liquids

Ionic liquids (ILs) constitute a group of non-molecular solvents characterized for presenting melting points below 100 ºC [1 - 3] and a number of outstanding properties [4], such as negligible vapor pressure at room temperature, high chemical and electrochemical stabilities, and capability to interact with a variety of analytes through different solvation mechanisms, among others. They are mainly formed by large and asymmetric organic cations, which contain a nitrogen or phosphorus atom, associated with an inorganic or organic anion. Fig. (**1**) shows a scheme of common structures of ILs and derivatives. Those IL which retain their liquid nature at room temperature are designated as room temperature ILs (RTILs).

Relatively simple modifications of the IL structure (change in the nature of the IL anion, incorporation of a certain functional group in the IL cation…) are accompanied by dramatic modifications of their properties: from water soluble to water insoluble, from medium viscosity to high viscosity, and so on [4]. This can clearly be observed from Table **1** [5 - 7], in which the modifications of IL properties with a simple change of the anion nature are shown. As a result, ILs can be tailored for specific applications in a quite simple manner. The incorporation of a polar functional group can promote dipolar interactions between the IL and polar analytes. In the same manner, the incorporation of long aliphatic alkyl chains to an IL can enhance its extraction ability with nonpolar analytes [8].

Table 1. Physicochemical properties of a group of ILs containing the 1-butyl-3-methylimidazolium (C_4MIm^+) cation at 25 ºC (or at the specified temperature) [5 - 7].

IL anion	Abbreviation	Melting point (ºC)	Density ($g \cdot mL^{-1}$)	Viscosity (cP)
hexafluorophosphate	$C_4MIm\text{-}PF_6$	10	1.373	450

(Table 1) contd.....

IL anion	Abbreviation	Melting point (ºC)	Density (g·mL^{-1})	Viscosity (cP)
tetrafluoroborate	C_4MIm-BF_4	-81	1.208	219
chloride	C_4MIm-Cl	53	-	1.7 (30 ºC)
bromide	C_4MIm-Br	79	-	0.8 (30 ºC)

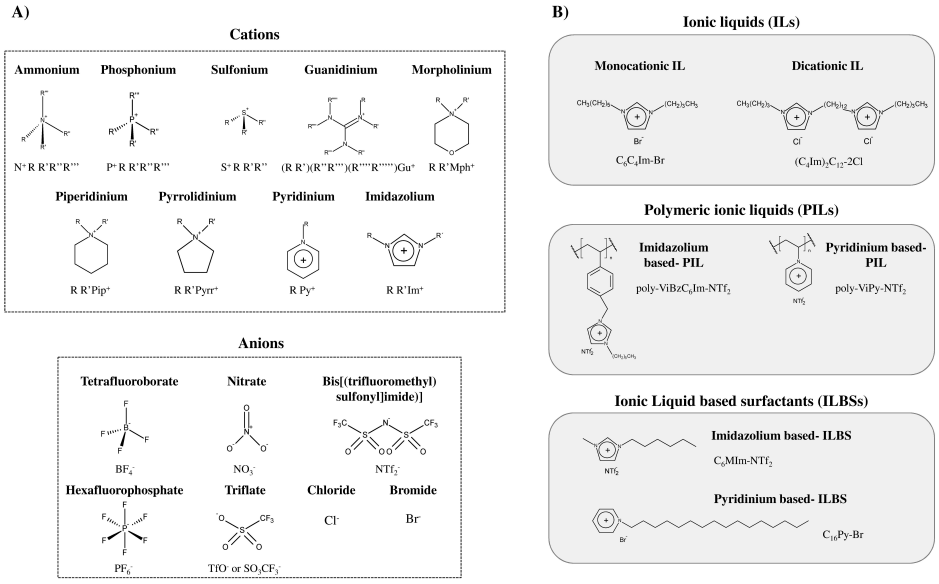

Fig. (1). A) Main cations and anions constituting the structures of ionic liquids and derivatives, and **B**) Examples of structures for ionic liquids, polymeric ionic liquids, and ionic liquids based surfactants.

It is also important to mention the impressive solvation ability of ILs, useful for polar to non-polar compounds. This is due to the electrostatic interactions associated with the cation and anion moieties comprised within the ILs, as well as their ability to undergo unique intermolecular interactions [8]. Their solvation ability has been explored with different models, being particularly successful the Abraham solvation parameter model [9].

ILs have also been subject of topic in Green Analytical Chemistry, given that they do not generate volatile organic compounds (VOCs), therefore being excellent candidates for substituting toxic chlorinated organic solvents [10]. Nevertheless,

CHAPTER 4

Application of Nanomaterials in Solid and Liquid Microextraction

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Abstract: Nanomaterials (NMs) have attracted great attention in sample preparation. In particular, because of their high surface-to-volume ratios, NMs facilitate the implementation of microextraction techniques. Additional advantages derived from NMs are the possibility of increasing the selectivity through the functionalization of their surfaces, and the improvement of mechanical and thermal stability of the extraction devices. This chapter summarizes the main uses of NMs in solid and liquid microextraction techniques, and representative examples of applications are presented.

The fabrication of coatings for fiber solid-phase microextraction (SPME) is the main objective in many of the scientific research developed in the area. For this purpose, a variety of NMs have been used such as carbon-based NMs, especially carbon nanotubes (CNTs) and graphene, metallic and silica-based NMs, and more recently, metal-organic frameworks (MOFs). NMs have also been used to prepare new sorbents for other microextraction techniques such as in-tube solid-phase microextraction(IT-SPME) and stir bar sorptive extraction (SBSE). The employment of magnetic nanoparticles (MNPs) has recently been introduced in microextraction, which leads to a new technique termed magnetic IT-SPME. Although the number of applications is still low, NMs are also receiving increasing attention in the main techniques of liquid phase microextraction namely, singe drop microextraction (SDME), hollow-fiber liquid-phase microextraction (HF-LPME) and dispersive liquid-liquid microextraction (DLLME).

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Keywords: Carbon nanotubes (CNTs), Dispersive liquid-liquid microextraction (DLLME), Fiber coatings, Fiber solid phase microextraction (fiber SPME), Graphene, Head space solid-phase microextraction (HS-SPME), Hollow-fiber liquid-liquid microextraction (HF-LPME), In-tube solid phase microextraction (IT-SPME), Liquid-phase microextraction (LPME), Magnetic in-tube solid phase microextraction, Magnetic nanoparticles (MNPs), Metal organic frameworks (MOFs), Metallic nanoparticles, Multi-walled carbon nanotubes (MWCNTs), Nanomaterials (NMs), Nanoparticles (NPs), Silica nanoparticles, Single-drop microextraction (SDME), Single-walled carbon nanotubes (SWCNTs), Solid phase microextraction (SPME), Stir-bar sorptive extraction (SBSE).

4.1. INTRODUCTION

The reduction of the efforts and materials used for sample preparation is an important demand of analytical laboratories. Consequently, methodologies traditionally used to isolate and pre-concentrate the analytes such as LLE,SPE, Soxhlet extraction and others, are being gradually replaced by more simple and environmental friendly techniques. Some of those techniques are miniature versions of regular methods such as micro SPE, while others are based on the employment of a small amount of extractive phase compared to the amount of sample. The later approach is the basis of microextraction techniques. Nowadays, the most popular microextraction techniques are SPME and SBSE, both based on the employment of a sorbent as extractive medium, as well as LPME in which the extractive phase is a solvent or mixture of solvents. There are numerous variations of each of these microextraction techniques which differ in the nature of the sorbent/solvent, the extent of the extraction process, and the geometry of the extraction device.

In the last years, many of the research contributions in the area of microextraction have been focused on the development of new extractive phases that provide better selectivity and extraction efficiency. Examples of such extractive phases are new polymers including MIPs, ILs and NMs [1 - 4].

Nanosized materials have become a hot issue of research in many areas of science and technology because of their attractive physical and chemical properties, wide variety of morphologies and relative low cost. In analytical chemistry NMs have been extensively used for different purposes such as the development of sensors,

the improvement of the separation performance in chromatographic and electrophoretic methods, and in sample preparation [5 - 7]. The most interesting feature of NMs for sample preparation is related to their high surface-to-volume ratios. This is particularly useful in the context of the reduction of the extractive phase dimensions. Consequently, an increasing effort is being focused on the application of NMs in microextraction. Additional advantages of NMs based sorbents are the enhancement of the selectivity through the functionalization of the NMs surfaces, and their better stability compared to other extractive media.

The term NMs is used for nanosized structures in which at least one dimension is in the nanometer size range, typically between 1 and 100 nm. Nanosized structures may be in the form of particles, tubes or pores [6]. There are several criteria to classify NMs based on their origin, chemical nature and homogeneity. In the context of their use as sorbents, NMs are typically classified as carbonaceous materials, metal/metal oxide nanoparticles (NPs) including magnetic NPs, silica NPs and MOFs [7]. Composites are also widely used in extraction because they combine the advantages of different phases in the same sorbent. So far carbon-based NMs and metallic NPs are the most explored phases in microextraction techniques. More recently, other NMs such MOFs have been tested for sample preparation but most applications still deal with SPE and μ-SPE procedures [8].

In the present chapter the main applications of NMs in microextraction will be discussed. Most attention will be focused on SPME because, as stated above, NMs are generally used as sorbents. In the last years, however, different studies have demonstrated the potential of NMs to improve the performance of LPME procedures by adding them to the sample or to the extractive phase. Consequently, the role of NMs in the main modalities of LPME will be also discussed. In Fig. (**1**) the main formats of solid and liquid microextraction techniques are depicted that have benefited from NMs.

CHAPTER 5

Principles and Developments of Solid-Phase Microextraction

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Abstract: Sample preparation has been commonly considered a critical step of the analytical process. In this sense, remarkable efforts have been made to develop efficient sample preparation techniques which could overcome the limitations of conventional approaches. Since its inception in the early 1990's, solid-phase microextraction (SPME) has become a widespread miniaturized sample preparation technique for extraction and preconcentration of target analytes from a large variety of matrices. Interestingly, sampling, extraction, enrichment and sample introduction can be integrated into a single step in SPME. This book chapter focuses on the basic principles and current state of the art of SPME. Specifically, both thermodynamic and kinetic aspects of the SPME technique are discussed in detail. In addition, those experimental variables that show a paramount role in the extraction process, and should therefore be optimized and controlled for optimal performance, are considered. Valuable contributions that enabled the development of this solventless technique and current challenges are identified. Other related SPME devices, such as internally cooled SPME, in-tube SPME and membrane SPME, are also described.

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Keywords: Automation, Direct immersion, Divinylbenzene, Fiber coatings, Gas chromatography, Headspace, High-performance liquid chromatography, In-tube SPME, Internally cooled SPME, Kinetics, Membrane-SPME, Molecularly imprinted polymers, Poly(dimethylsiloxane), Polymeric ionic liquids, Preconcentration, Sample preparation, Sample preparation, Sol-gel sorbents, Solid-phase microextraction, Thermodynamics.

5.1. INTRODUCTION

Sample preparation has been recognized as a critical step of the analytical process, being even considered as the bottleneck of the overall process. Enrichment of target compounds, transfer of the analytes into a solvent compatible with the analytical instrumentation, minimization of potential interferences, and efficient sample clean-up, are among the main aims of sample preparation techniques. In this regard, liquid-liquid extraction and solid-phase extraction have been conventionally employed prior to the determination of relevant compounds in a variety of samples. In spite of their suitable performance, these classical techniques do not fulfill several of the challenges in analytical chemistry, including miniaturization, portability, and environmental sustainability. Furthermore, the necessity to determine relevant compounds at very low concentrations in matrices of different complexity, especially when dealing with reduced sample volumes, made the improvement of sample preparation techniques being of paramount importance. The inception of solid-phase microextraction (SPME) involved a huge advance in this sense. SPME was firstly introduced by Arthur and Pawliszyn in 1990 as an alternative to conventional sample preparation methods [1]. SPME is a non-exhaustive sample preparation technique based on the exposure of a small amount of extracting phase to the sample (or to the headspace above the sample) for extraction and preconcentration of target compounds. SPME enables the integration of sampling and sample preparation. Furthermore, its small size makes SPME being highly convenient for on-site analysis and monitoring, as well as *in vivo* analysis [2]. A variety of coating fibers for extracting analytes of different polarity and volatility are nowadays commercially available. Nevertheless, the development of novel SPME fibers with improved mechanical, chemical and thermal stability is a current trend in analytical chemistry, as discussed in sections below. Selected milestones in the development of the SPME technique are shown

in Fig. (**1**).

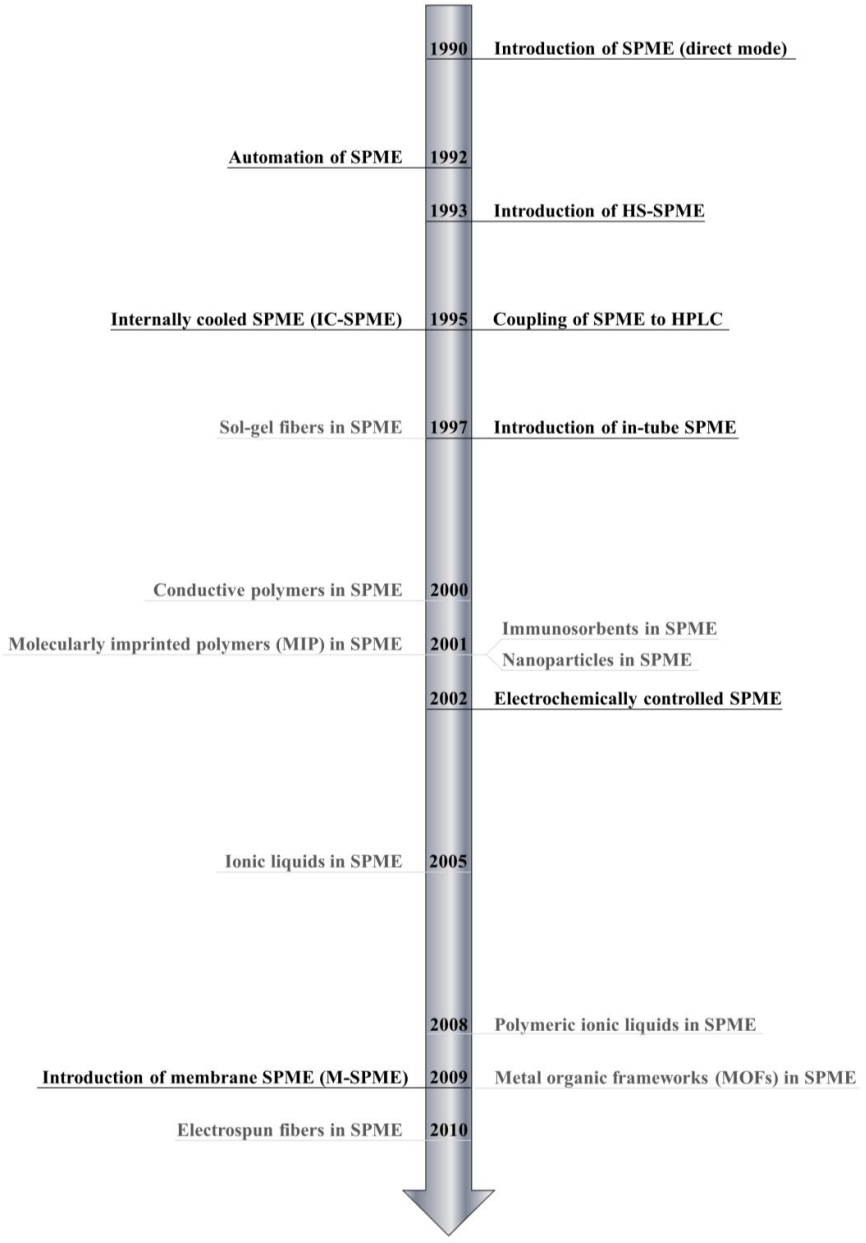

Fig. (1). Selected milestones in the development of the SPME technique.

CHAPTER 6

Stir Bar Sorptive Extraction and Related Techniques

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Abstract: From the sorption-based methods available nowadays, stir bar sorptive extraction (SBSE) became a well-established analytical technique for sample preparation, in which hundreds of applications in almost all scientific areas have already been proposed in the literature. This remarkable analytical tool shows great capacity for static microextraction and outstanding performance to operate at the ultra-trace level, in particular for the analysis of complex systems. Furthermore, is very effective, present easy manipulation in comparison to other alternative techniques and great reproducibility for the analysis of priority and emerging organic compounds. Recently, related static microextraction techniques were introduced, with particular emphasis to bar adsorptive microextraction (BAμE) that operates under the floating sampling technology, in which has demonstrated high analytical capacity and remarkable performance. This novel concept has also proved great effectiveness for ultra-trace analysis of organic compounds with polar characteristics, in particular from complex systems. The present contribution describes the fundamental principles, the experimental methodology, the main applications, as well as, the analytical potential of these novel microextraction techniques.

Keywords: Activated carbons, BAμE, Enrichment methods, Floating sampling, GC-MS, HS, LC-MS, LD, Microextraction techniques, Nanostructured materials, PDMS, Polymeric coatings, Real matrices, Sample preparation, SBSE, Sorbent phases, Sorption-based methods, Static microextraction TD, Trace analysis.

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6.1. INTRODUCTION

Due to the very high complexity presented by many matrices, the modern sample enrichment techniques run towards the great simplification, miniaturization, easy manipulation of the analytical devices, strong reduction or absence of organic toxic solvents, as well as, low sample volume requirements in agreement with the green analytical chemistry principles [1]. For trace analysis in particular, the sorption-based methods have demonstrated to be the best choice enabling the direct microextraction, mainly of volatile and semi-volatile compounds, from almost all types of aqueous matrices. Moreover, these solvent-free approaches have demonstrating high-throughput to enhance selectivity and sensitivity prior to the application of chromatographic or hyphenated techniques. Although, some of the currently well-established methodologies use active or dynamic sampling mode, such as solid phase extraction (SPE), the passive or static sampling mode has gained more acceptances in almost all the scientific areas, due to the cost-effectiveness, much easier manipulation with emphasis to solid-phase microextraction (SPME) [2] and stir bar sorptive extraction (SBSE) [3]. These enrichment techniques combine the extraction and concentration of the analytes simultaneously, having the possibility to use immersion or headspace (HS) sampling modes in only a single step. On the other hand, they reduce the manipulation, the overall time required for sample preparation, and are indicated to be combined with the great sensitivity of the modern analytical instrumentation. SBSE in particular, was introduced as a novel sample preparation method based on the same principles of SPME, which has been successfully applied to monitor traces of priority organic compounds in many complex matrices, due to the very high sensitivity exhibited. A good indicator of the greatest advantages over other sorbent-based techniques is the number of publications related with SBSE that strongly increased in the last years, reaching up to several hundreds of scientific articles. Furthermore, many review articles had already been reported covering a wide range of features concerning SBSE principles, method development and applications [4 - 9]. Nevertheless, once commercial stirbars still had presented some analytical limitations, in particular for the enrichment of the polar organic compounds, several analytical solutions and related techniques have been proposed. For this reason, bar adsorptive microextraction (BAμE) was introduced

as an alternative and complementary static microextraction technique for ultra-trace analysis [9 - 11].

6.2. STIR BAR SORPTIVE EXTRACTION (SBSE)

6.2.1. Fundamentals

The SBSE technique belongs to the silicone-type sorbents since uses just the polydimethylsiloxane (PDMS) polymeric phase and is commercially known with the trademark Twister®. Fig. (**1.a**) depicts the SBSE analytical device, which is constituted by magnetic stir bars incorporated into a glass jacket (10 to 20 mm in length) typically coated with 24-126 μL (0.3 to 1.0 in thickness) of PDMS, a nonpolar polymeric phase characterized to promote hydrophobic interactions with target molecules, where the retention mechanism occurs mainly through Van-der-Waals forces but also hydrogen bonds can be formed with oxygen atoms of the sorbent network, depending on the molecular structure of the analytes. Furthermore, this polymer has interesting diffusion and thermo-stable properties allowing to operate in a wide range of temperatures and, because of that, this solventless approach was firstly proposed to be associated with thermal desorption (TD) following gas chromatography (GC) analysis. The substantial volume of PDMS involved, in relation to the SPME fibbers (up to 0.5 μL for100 μm film thickness), promotes a lower phase ratio between the sorbent phase and the sample media, which provides an increasing capacity, and quantitative recoveries can be reached by SBSE, especially for nonpolar solutes. This approach enables to increase the sensitivity by a factor within 50 and 250, in comparison to SPME, decreasing the detection limits to the ultra-trace level (parts-per-trillion) many times. In the SBSE theory [3, 9], the efficiency of the analyte partitioning between the PDMS phase of the stir bar and the water sample (W), presents a similar behaviour as the distribution described by the octanol-water partition coefficients ($K_{PDMS/W} \approx K_{O/W}$) during the static equilibrium. In general, nonpolar analytes are characterized to have values of log $K_{O/W}$ higher or equal to 3, whereas for the polar are lower. Thus, the $K_{O/W}$ and the phase ratio (β=V_W/V_{PDMS}, in which V_W is the water sample volume and V_{PDMS} is the PDMS volume), are important parameters to predict the theoretical recovery by using the following expression:

CHAPTER 7

Microextraction by Packed Sorbent (MEPS): Theory, Developments and Applications

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Abstract: Sample preparation is a critical issue in bioanalysis since the matrix is often complex. A good sample preparation technique will remove the possible interferences from the sample matrix pre-concentrate the analyte and to be reproducible independent of the sample matrix. Recent developments of sample preparation techniques are directed toward automation, the smaller sample volumes and online coupling of sample preparation units and detection systems. Microextraction in packed syringe (MEPS) is a new type of solid-phase extraction (SPE) technique that is miniaturized and can be fully automated. In MEPS the solid bed is integrated in the injection syringe. The MEPS syringe can be used online for both extraction and injection of samples. The present chapter gives an overview of MEPS technique, including the MEPS description, formats, sorbents, experimental and protocols and factors that affect the MEPS performance. We also summarize MEPS recent applications in bioanalysis, environmental and food analysis.

Keywords: Applications, Experimental protocols, Microextraction by packed sorbent (MEPS), Sorbents.

7.1. INTRODUCTION

Owing to the need of daily rotation of results from huge numbers of biological samples in big pharmaceutical companies, it is essential to apply sample preparation methods with high throughput properties. Sample preparation as the first step in the analysis procedure has an important role in many different fields

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such as bioanalysis and environmental analysis. Additionally sample preparation methods utilizing small sample volumes (10-50 μL) should be useful for clinical and preclinical studies. This can give new possibilities for handling of samples from children. As well, it allows serial collection of more than one time point from the same animal, such as mice or rat. Such sample preparation methods will save money and time in drug discovery and development. To obtain this purpose the integration of the sample preparation with the analysis apparatus and miniaturization were significantly required.

Microextraction by packed sorbent (MEPS) is a new technique for miniaturized solid phase extraction (SPE) that can be connected online to GC or LC without any modifications and can handle small sample volumes. MEPS technique is easy to use, fully automated, of low cost and rapid. In comparison with previously used methods, MEPS significantly decreases the sample handling time, decreases the sample volumes and the solvent required.

This chapter provides an overview on the emerging technique microextraction by packed sorbent (MEPS). The recent developments in MEPS device and finding ways for automated application are presented. MEPS provides differentiation from the conventional SPE and in some applications it could replace the need of the analytical column in LC/MS/MS (*i.e.*, directly used online with the MS detector). In addition, factors affecting the MEPS performance and extraction procedures will be discussed.

7.2. MEPS DESCRIPTION AND THEORY

MEPS is a self-acting kind of solid phase extraction (SPE) technique. MEPS was emerged in 2004 by Dr. Abdel-Rehim [1]. The MEPS technique was developed to meet the request of automated and high-throughput sample preparation methods. The MEPS technique is fully automated, reduces the handle time and handles small sample volumes, it is simple and inexpensive. The fast process and the ease of the sample preparation process are advantages of MEPS. The main attributes of MEPS is the decrease of the sample and solvent used (10-50 μL) and the elution solution can be injected directly into GC or LC instruments.

In MEPS 1–4 mg of sorbent is packed in the barrel of a gas-tight syringe

(100–250 µL), or in a special container positioned between the needle and the barrel as a cartridge (Fig. **1**).

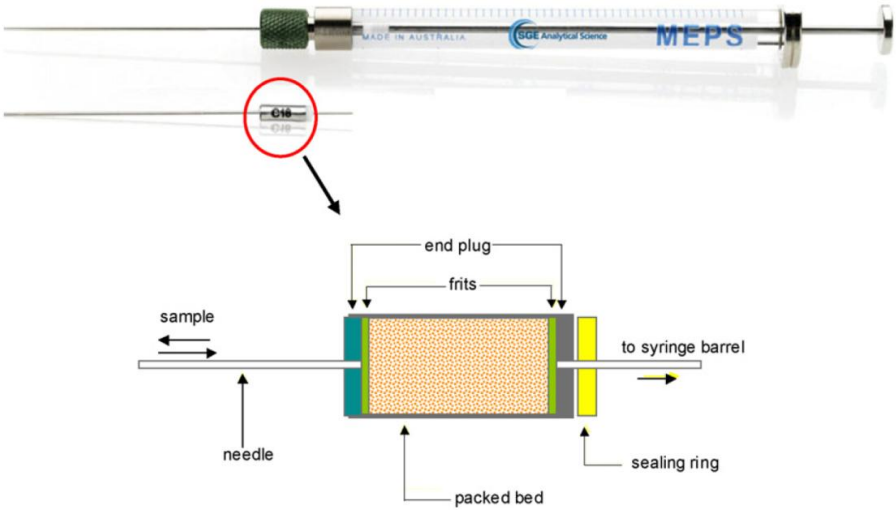

Fig. (1). MEPS syringe [2].

In MEPS the sample solution is withdrawn through the syringe by an autosampler and when the sample solution has passed through the solid phase, the analytes are adsorbed to the solid sorbent. Then the solid phase is washed once or more with water to remove the proteins and other interfering materials. Finally, for desorption of analyte organic solvent, such as methanol or the LC mobile phase (20–50 µL) can used and directly through the analytical instrument's injector.

The MEPS processing, extraction and injection steps are performed online using the same syringe. The main concept of MEPS and SPE techniques is approximately similar and, both techniques build on the same principles and therefore the transferring of a method from traditional SPE to MEPS would be quite straight forward. Typical MEPS is designed in the syringe format and a gas-tight glass syringe is used (the syringe volume is 100, 250 or 500 µL). The solid sorbent may be embedded in a small container situated between the barrel and the needle, as mentioned above. Miniaturization is critical point in MEPS technique, thereby only approximately low volume of solvents is required for elution of the analytes from the adsorbent, a quantity that is suitable for direct introduction into the analysis instrument.

CHAPTER 8

Miniaturized Dispersive Solid-phase Extraction

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Abstract: The usefulness of dispersive extraction techniques leans on their ability to maximize the interaction between the sample and the extractant phase, thus increasing the extraction efficiency. As far as dispersive solid phase extraction is concerned, it was initially developed to increase the selectivity of the analytical process because the solid was added to retain the potential interferents from the sample matrix. In spite of its efficient sample clean-up, the sensitivity is its Achilles' heel as no preconcentration is usually achieved. Recently, the use of few milligrams of sorbent which is dispersed in a liquid sample for analytes isolation has raised a new miniaturized extraction technique, the so-called dispersive micro solid-phase extraction. This alternative is mainly focused on sensitivity enhancement. The chapter begins with a short contextualization of this extraction technique, followed by a brief description of the first approach in this context, *viz*, dispersive solid phase extraction. Next, the main contributions in the field of dispersive micro solid-phase extraction in this context will be described on the basis of the nature of the solid used. Also, the combination with dispersive liquid phase microextraction and the expected evolution of this miniaturized extraction technique are included.

Keywords: Auxiliary energies, Carbonaceous solids, Conventional sorbents, Dispersive extraction, Dispersive liquid-liquid microextraction, Dispersive solid phase microextraction, Dispersive sorbent, Enrichment factors, Green chemistry, Miniaturization, Molecularly imprinted polymers, Nanostructured sorbents, Polymeric sorbents, Silica-based sorbents, Solid phase microextraction.

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8.1. INTRODUCTION

The evolution of Analytical Chemistry has been lead by three trends: automation, simplification and miniaturization. While the former is clearly consolidated in any analytical laboratory, the other two are still being developed. The improvement of the sample pre-treatment operations is the target of these tendencies taking into consideration the influence they have in the basic (sensitivity, selectivity and precision) and productivity-related (cost, time, personal and environmental risks) analytical properties. Therefore, many research efforts are focused on the simplification and miniaturization of the sample pretreatment, as it is practically an unavoidable step of the analytical process.

The determination of a family of compounds in a given sample usually involves its isolation from the matrix (to increase the selectivity) and preconcentration (for sensitivity enhancement) prior to the instrumental measurement. According to the above commented tendency, the introduction of novel microextraction techniques is highly recommended in order to reduce the amount of sample and organic solvents as well as the time, cost and manipulation needed. This tendency is in good agreement with the principles of Green Chemistry often described in the literature as the three Rs: replace, reduce and recycle [1]. Solid phase microextraction and liquid phase microextraction can be considered as consolidated miniaturized sample treatment techniques, given their full acceptance in routine laboratories, particularly when automated or even fully integrated analytical instrumentation is used.

The main requirement of any microextraction technique is that the extractant media used should be highly efficient in analyte extraction taking into account the reduced amount used. In this context, dispersive-based procedures have gained relevance in the last years as they enhance the contact surface area between the sample and the extractant and thus the kinetics of the overall extraction procedure while reducing the amount/volume of the solid/liquid extractant phase needed [2].

8.2. DISPERSIVE SOLID PHASE EXTRACTION

Dispersive solid-phase extraction (DSPE) was first proposed by Anastassiades *et al.* in 2003 as a powerful tool to enhance the selectivity of the measurement. It

is commonly known as QuEChERS, acronym of quick, easy, cheap, effective, rugged and safe, its main analytical features [3]. DSPE requires the presence of an organic solvent, for analyte partitioning; salts, to favour analyte transference from the sample to the organic media and a dispersive sorbent to retain the coextracts while maintaining the analytes dissolved in the organic phase. Each of the three elements plays a different role in the extraction and they must be carefully chosen to improve the efficiency of the process. They are briefly commented on. The organic solvent must be selected taking into account the analyte polarity, as it is responsible for the extraction of the target compounds. In this regards, acetonitrile is by far the most used as it permits the extraction of both polar and non-polar compounds. Its compatibility with liquid chromatography is also advantageous in this context. Magnesium sulphate and sodium chloride are used during the extraction process (i) as salting out agents and (ii) to favour phases' separation. The amounts added are determined by the analyte hydrophobicity, as a rule. The dispersive sorbent added depends on the type of interferences to be retained. Primary secondary amine, graphitized carbon black, RP-C_{18} and alumina are commonly used. In addition to the sorbent nature, the amount used is also critical, as it has to retain the interferents (selectivity improvement) while minimizing analyte adsorption (sensitivity of the measurement). The amount added is usually in the low milligram level, *viz*. 10 mg. After a centrifugation step, the organic phase can be directly used or concentrated, usually by an evaporation/redissolution step, prior to the instrumental measurement step, commonly by a chromatographic technique.

This general procedure was mainly designed to analyze horticultural samples on account of the complexity of the matrices and the low concentration of the target compounds (mainly pesticides). The presence of co-extracted compounds in the chromatogram makes difficult the unequivocal identification of the pesticides, even when detectors with high discrimination capabilities, such as mass spectrometry, are employed.

The former procedure was modified by Lehotay *et al.* in 2005 to improve the recovery of certain pesticides [4]. Recently, Anastassiades *et al.* have reported a second evolution of their initial proposal to expand the application range of the DSPE to samples with different water and acid contents [5]. DSPE has also been

CHAPTER 9

Solid Phase Extraction Based on Magnetic Nanoparticles

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Abstract: Magnetic nanoparticles (MNPs) are attracting great interest for developing solid phase extraction (SPE). Nanoparticles involved in SPE processes present clear advantages with respect conventional SPE materials because of their high stability, simple preparation, and the short time involved in the sample preparation; avoiding time-consuming column passing and filtration, as it is in conventional SPE methods. In this e-book chapter, the progress involving MNPs used for SPE is presented and discussed. Taken into account the different types of MNPs used in this field, the different MNPs obtained by attaching inorganic components (*e.g.*, metal oxides, carbon, noble and semiconductor metals), or organic molecules (*e.g.*, surfactants and magnetic molecularly imprinted polymers, MMIP), are described through recent reported analytical applications of MNPs in SPE. The potential transfer of these analytical tools for daily work in routine laboratories is also pointed out.

Keywords: Analytical applications, Bioanalytical analysis, Clean-up, Environmental analysis, Food analysis, Functionalization, Magnetic nanoparticles, Magnetic solid phase extraction, Metal oxides, Modified surfactants, Molecular imprinted polymers, Preconcentration, Sample preparation, Silica, Synthesis schemes, Titanium oxide, Zirconium-coated.

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9.1. INTRODUCTION

Currently, analytical chemistry tends to exploit and improve the chemical properties of nanoparticles (NPs), especially the capacity of adsorption, for their use as a reversible sorbent in extraction and preconcentration processes, which were considered among the most attractive analytical applications. NPs with magnetic properties (magnetic nanoparticles, MNPs) can be easily handled by using external magnetic devices. Recently, SPE procedures involving MNPs (magnetic solid phase extraction, MSPE) have intensely been increased for the preconcentration of many analytes, as well as for elimination of interferences (clean-up), solving interesting analytical problems. Thus: (i) high extraction efficiency; (ii) increase of the extraction rates; (iii) easy recovery of the sorbent after the extraction by using a magnetic device, involving clear advantages with respect to centrifugation and filtration procedures.

The use of MNPs in analytical field has recently been reported in different applications. Thus, for the preconcentration of pollutants in water [1, 2], soil [3] and biological samples [4]; and the selective sorption of biological compounds as proteins [5] and DNA [6]. Aspects related to the magnetization are also discussed [7] from a practical point of view. From an applied side, two main issues can be considered: (i) the sample analyses involving reduced sizes of samples; and (ii) the use of very small amount of samples.

9.2. PRACTICAL ASPECTS

MSPE is a physical process in which they magnetic material (solid) and a liquid (sample or analytes) are involved. The magnetic solid phase presents a more attraction to the analytes or interferences than the solvents in which they are dissolved. The use of MNPs for performing MSPE has introduced the advantages that the nanoscale and nanomaterials present. In fact, sorptive microextraction processes can be easily carried out involving MNPs. The general batch procedures based on the use of MNPs and used in SPE are shown in Fig. (**1**). In the first step, and after conditioning, the MNPs are introduced in the sample solution containing the sample (analytes and interferences). Sorption of the analytes and/or the interferences takes place. According to the main purpose of the sample

preparation, two procedures can be distinguished in the second step. Thus, if the analytes must be preconcentrated to increase the sensibility, MNPs are associated with the analytes and this combination is concentrated by using and external magnetic device. After separation of the remaining solution, analytes are eluted from the MNPs using an appropriate solvent. Then, the determination step takes place. On the other hand, if the interferences must be removed for sample clean-up purposes, they are retained in the MNPs and, thus, concentrated in the magnetic field. The remaining solution is easily separated and analytes determined in it.

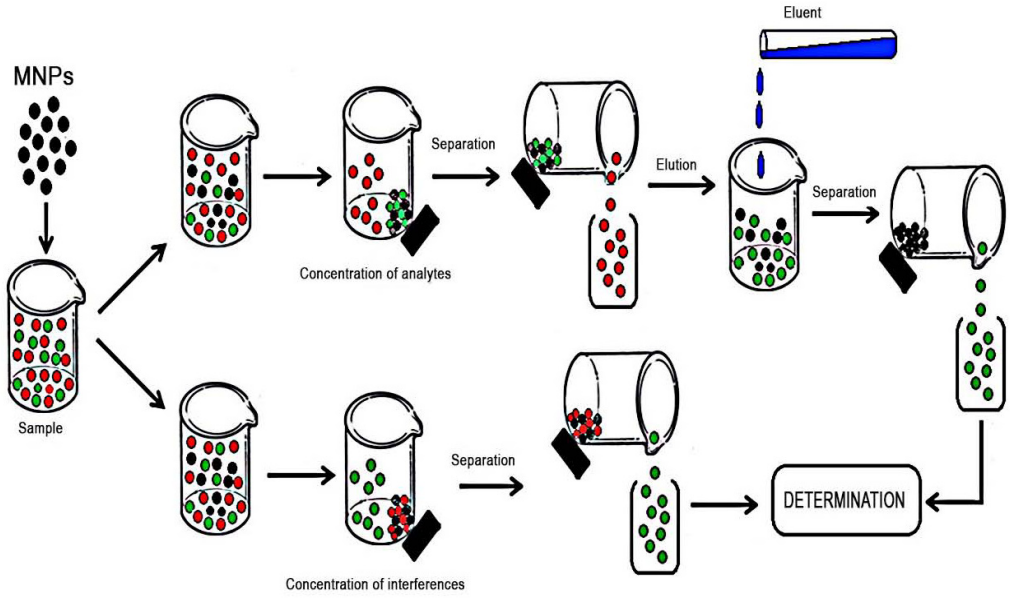

Fig. (1). Extraction experimental alternatives to carry out SPE with MNPs.

9.3. MAIN TYPES OF HYBRID MAGNETIC NANOPARTICLES USED IN SPE

The procedures employed for the synthesis of a hybrid MNPs used in SPE includes the synthesis of the magnetic particle and their surface modification for producing the final coating hybrid nanoparticles. The main type of hybrid nanomaterials used for this purpose is shown in Fig. (**2**), the following sections briefly describe the involved procedures.

CHAPTER 10

Solid-Phase Microextraction Under the Thin Film Format

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Abstract: Thin film microextraction (TFME) is considered as a type of solid-phase microextraction (SPME). There has been a growing interest in TFME as a novel sample preparation technique, which was originally introduced to address the limiting uptake rate and capacity sometimes observed with fiber microextraction. The inherent properties of TFME technique such as the excellent sample clean-up and the larger surface to volume ratio, enhance the sensitivity and the extraction rates. This e-book article is mainly focused on the fundamental principles behind and in the diverse existing TFME configurations, paying particular attention to cotter pin supported format, copper mesh holder and 96-blade format.

Keywords: : Autosampler, Field sampling, *In-vivo* sampling, Membrane-based TFME, Microextraction, On-site extraction, Sample preparation, Solid phase microextraction (SPME), Sorptive tape extraction, Stirring integrated TFME, Thin film microextraction (TFME), 96-blade (thin film) SPME.

10.1. INTRODUCTION

Solid-phase microextraction (SPME) is a sample preparation technique developed by Pawliszyn in the early 1990s which integrates sample clean-up, analyte isolation, and pre-concentration in a single step [1]. This technique appeared

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to address the need for a rapid and solvent-free extraction technique. SPME is based on the partitioning of the analytes between the sample and the extraction phase, which is typically immobilized on a fiber support. For direct immersion, the amount of analyte extracted when equilibrium conditions are reached (n_e) by SPME can be described as [2]:

$$n_e = \frac{K_{es} V_e V_s C_0}{K_{es} V_e + V_s} \quad \textbf{(1)}$$

Where K_{es} is the distribution constant between the extraction phase and the sample matrix, V_e represents the sorbent phase volume, V_s is the sample volume and C_0 is the initial concentration of a analyte in the sample matrix. Since in the majority of the extractions the sample volume is higher than the extraction phase, this equation can be simplified to:

$$n_e = K_{es} V_e C_0 \quad \textbf{(2)}$$

According to **Equation 2**, the mass of analyte extracted depends on the sorbent phase volume (V_e). There are two possible strategies to increase the extraction phase volume:(i) make greater in size the thickness of the coating or (ii) expand the surface area. However, when thicker coatings are employed larger times are needed to reach the equilibrium (t_e), which gives rise low sample throughput because the overall rate of extraction is controlled by the diffusion from the bulk solution through the boundary layer to the extraction coating (**Equation 3**):

$$t_e = t_{95\%} = 3\frac{\delta K_{es}(b-a)}{D} \quad \textbf{(3)}$$

where *(b-a)* is the thickness of the coating, *D* represents the diffusion coefficient and δ is the thickness of the boundary layer. Based on **Equation 3** [3],the thinner the thickness of the sorbent phase is, the shorter the time required to reach the extraction equilibrium it would be.

On the other hand, large surface area accelerates the initial rate of extraction as it

is shown in **Equation 4** [3]. As a consequence, a thin film with a large surface area-to-volume ratio ensue in an improvement of the extraction efficiency without sacrifice the extraction time assuming the same conditions.

$$\frac{dn}{dt} = \left(\frac{DA}{\delta} \right) C_o \qquad \textbf{(4)}$$

Where (n) is the amount of analyte extracted over the sampling time (t) and (A) is the surface area of the extraction phase. On the basis of the previous discussion, the superficial area of a SPME phase directly affects to the extraction kinetics and this theoretical fact has led to the development of thin film microextraction (TFME) by Prof. Pawliszyn group in 2003 [3]. According to the inventors group, TFME can be divided in two different modes depending on the use of the membranes or brushes as extracting phase [4].

10.2. THIN FILM MICROEXTRACTION UNDER THE MEMBRANE CONFIGURATION

Membrane-based TFME makes use of a thin membrane of polydimethylsiloxane (PDMS), the classical SPME coating, as extraction phase. In the classical configuration the membrane is attached to a deactivated stainless steel rod and it is deployed, in a flag shape, to exploit all its potential area during extraction (see Fig. **1**). After the extraction, which can be accomplished both in the direct immersion and headspace mode, the membrane is coiled around the rod which is finally introduced in a glass liner for gas chromatography/mass spectrometry (GC/MS) analysis. The first approach of TFME, which was directly towards the analysis of several polycyclic aromatic hydrocarbons (PAHs) from water samples, demonstrated the superior features of TFME over classical SPME [3]. In summary, TFME presents a higher extraction rate and capacity owing to the larger area and higher volume of extractant phase (at least 4 times) in the membrane format over the fiber shape. In fact, while a typical 100 μm PDMS fiber presents an area of 10 mm^2, a 1 cm x 1 cm membrane sheet presents a surface area of 200 mm^2 (two faces of 100 mm^2 each one) due to its planar structure.

CHAPTER 11

Single-drop Microextraction and Related Techniques

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Abstract: The number of applications of liquid phase microextraction (LPME) techniques has undergone a dramatic increase during the last years. Miniaturisation of sample preparation encompasses several advantages, *i.e.*, low consumption of extractants, integrated operation, ease of clean-up, large preconcentration factors, apart from an increased greenness, as compared to classical solvent extraction. Among LPME, single-drop microextration (SDME) approaches have deserved much interest. Versatile and adaptable procedures to every each analyte and matrix have been reported. Extractants are not only limited to organic solvents, but ionic liquids (ILs) and even aqueous solvents can be also employed. Whereas, analytical techniques based on chromatographic/electrophoretic separations and some modes of atomic spectrometry were applied in early applications, SDME has also been exploited in combination with other detection approaches such as UV-*vis* spectrophotometry, fluorospectrometry, chemiluminescence, *etc*. This has spread the use of SDME to almost every application area. In this chapter, the state of art of SDME and its main modes is reviewed.

Keywords: Anions, Atomic-spectrometry, Continuous-flow, Direct-immersion, Directly-suspended, Electrophoresis, Elements, Gas-chromatography, Headspace, Ionic-liquids, Liquid-chromatography, Mass-spectrometry, Microextraction, Organic-compounds, Organometals, Single-drop, Speciation, Three-phases, Trace-analysis, Two-phases.

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11.1. INTRODUCTION

In an attempt to overcome some of the drawbacks inherent to classical solvent extraction techniques (*i.e.*, liquid-liquid extraction), a plethora of miniaturised techniques have been proposed during last years.

Since first works by Dasgupta' group, using drops as collectors of gaseous substances such as ammonia and sulphur dioxide from air [1], several techniques have been developed that have in common the disposal of a microvolume of extractant phase (*i.e.*, acceptor phase) using mostly a chromatographic syringe as support. The implementation of a syringe has provided a smart and wise way to accomplish solvent drop microextraction.

Initial prototypes addressing solvent drop microextraction were developed by Liu and Dasgupta in 1996 [2], using a chloroform microdrop suspended in a larger sample drop to extract sodium dodecyl sulphate (SDS). First report making use of a microsyringe for performing drop microextraction was published by Jeannot and Cantwell [3], who also suggested for the first time the name of 'single-drop microextration' (SDME).

The SDME technique encompasses a variety of approaches depending on how the solvent microvolume is configured (*i.e.*, at the tip of a microsyringe or directly suspended), the number of phases involved in the transfer of the analyte from the donor to the acceptor phase (*i.e.*, two- of three-phase systems) or the confinement of the sample solution in a vial (static approach) or its displacement over the acceptor phase (dynamic approaches). Mass transport is generally limited by diffusion, so agitation of the sample solution is needed to improve the convective transport in order to shorten the diffusion distance.

Classification of SDME techniques usually relies on the number of phases involved in the process. Among two-phases SDME, the following modes have been reported: direct immersion single-drop microextraction (DI-SDME), headspace single-drop microextraction (HS-SDME), continuous flow microextraction (CFME), directly suspended drop microextraction (DSDME), solidification floating organic drop microextraction (SFODME) [4 - 7]. Some variants of any of the above modes, such as drop-to-drop microextraction

(DDME) can be considered as miniaturised versions of DI-SDME.

The liquid-liquid-liquid microextraction (LLLME) mode involves a three-phase mass transfer and can be considered a solvent microextraction with simultaneous back-extraction. This mode is well suited for hydrophilic compounds in combination with those techniques requiring an aqueous acceptor solution such as reverse-phase high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). All these approaches will be discussed in detail in next section.

11.2. SDME: MICROEXTRACTION MODES

As has been previously mentioned, a variety of SDME modes and related techniques has been reported in the literature with the aim of achieving efficient extraction and preconcentration of target compounds, while solving the limitations identified in preliminary SDME modes. The evolution of the number of publications per year concerning SDME modes and related techniques, as well as the frequency of use of these miniaturised sample preparation approaches, is shown in Fig. (**1**).

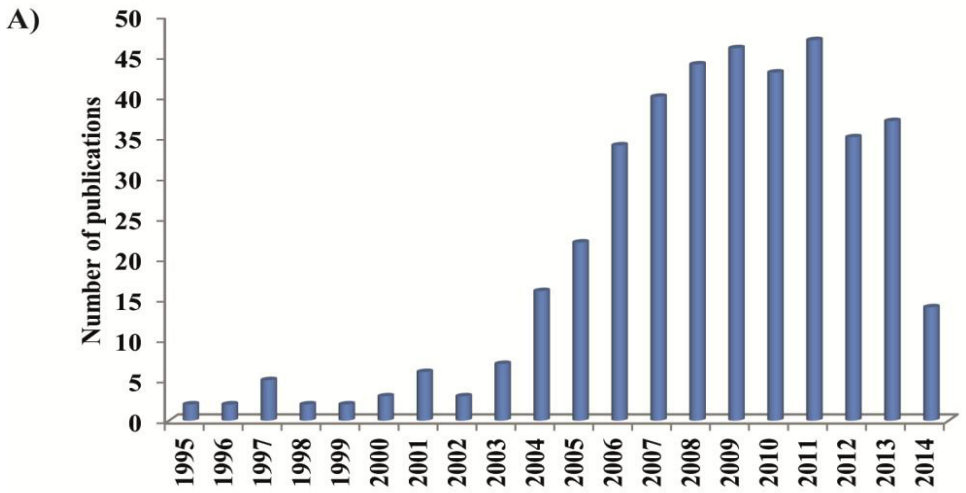

Fig. 1 contd.....

CHAPTER 12

Membrane-Based Microextraction Techniques with Emphasis on Hollow-fiber Microextraction

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Abstract: Various membrane-based extraction techniques are used in analytical chemistry mainly for pretreatment before analyte determination using chromatographic or other techniques. Membrane extraction can also be applied for the extraction of various metal ions and is then followed by atomic absorption or similar detection techniques. They allow high selectively for a number of analytes from chemically more or less complex samples and high concentration enrichment, easily thousands of times. Currently, the most common format for membrane extraction utilizes hollow-fiber membranes, which permit easy and versatile operation with a minimum of cost. A number of applications have been presented involving determination of polar and medium-polar compounds as acids and bases in samples of environmental and biological origin, usually in combination with liquid chromatography and mass spectrometry. For other analytes in which membrane extractions are various metal ions, the membrane extraction is followed by techniques like atomic absorption and similar. Also applications to non-polar compounds in mainly environmental samples, followed by gas chromatography, are described in the literature.

In this chapter, the basic theoretical principles for the common variants of membrane extraction are described. Guidelines for the selection of operational parameters as well as concrete advice for the practical implementation are provided.

Keywords: Biomedical samples, Chromatography, Determination of acids, Determination of bases, Enrichment, Environmental samples, Extraction, Food samples, Hollow fibers, Mass spectrometry, Membrane extraction, Sample prepa-

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ration, Selectivity, Supported liquid membrane (SLM).

12.1. INTRODUCTION

An important area of current research in analytical chemistry aims to the development of alternative extraction techniques meeting some of the disadvantages of classical techniques, such as solvent extraction or solid phase extraction. These activities are somewhat moderated by the fact that the area of chemical analysis (especially regarding environmental and pharmaceutical applications, but also in other areas) is heavily regulated by various international and local rules, leading to the acceptance of new technology being slow and costly.

The use of membranes for extraction in analytical chemistry has been increasing during recent years. Such techniques have a number of clear advantages over other extraction techniques, especially concerning selectivity, enrichment power and automation potential, but also economy and occupational health aspects. They can selectively extract and enrich analytes from chemically more or less complex samples in very efficient ways [1 - 8].

In membrane extraction, the membrane separates the sample phase (often called donor solution) from the acceptor phase and the analyte molecules pass through the membrane from the donor to the acceptor. This principle gives a clear advantage over other sample preparation techniques, as all compounds that reach the analytical instrument must travel through the membrane, acting like a barrier between the sample and the analytical instrument. There is no direct connection and no possibility for transferring compounds into the analytical instrument in other ways. This leads to a high selectivity, *i.e.* efficient discrimination between analytes and various unwanted matrix compounds.

There are in principle two variants of liquid membrane extraction, three-phase systems and two-phase systems [1, 2].

The three-phase system (aq/org/aq), where analytes are extracted from the aqueous sample into an organic liquid, immobilized in a porous hydrophobic membrane support, and further to a second aqueous phase, is suitable for the

extraction of polar compounds (acidic or basic, charged, metals, *etc.*) and it is compatible with reversed phase HPLC.

The two-phase system (aq/org), where analytes are extracted into an organic solvent separated from the aqueous sample by a hydrophobic porous membrane is suitable for more hydrophobic analytes and compatible with gas chromatography.

Both these techniques utilize a supported liquid membrane (SLM) *i.e.* an organic liquid supported in the pores of a hydrophobic porous material. In this paper, the focus is on basic and practical considerations for two- or three-phase supported liquid membrane extraction systems in hollow fibers, techniques which are nowadays usually called as hollow fiber liquid phase microextraction (HF-LPME).

Earlier, similar extractions were mainly performed in flat-sheet format, which is described in detail in the literature [1 - 3] and also in a practical tutorial [4]. The hollow-fiber techniques were developed especially in pharmaceutical applications by Rasmussen and Pedersen-Bjergaard [5, 6] and Lee with coworkers [7].

One main advantage with HF-LPME is that it is not sensitive to the presence of particles in the sample. Clogging (as for instance when using solid phase extraction (SPE)) is no problem, which means that filtration is not required prior to extraction of turbid samples.

It is possible to successfully apply HF-LPME to slurries, as was recently described with sewage sludge [9] and in biological samples [10]. Furthermore, compared to LLE, there is no problem with the formation of emulsions in the water-organic interface, which otherwise can be a significant practical problem.

Using hollow fibers, it is possible to perform extractions for sample clean-up and enrichment with very cheap and simple equipment, leading to efficient enrichment and high enrichment factors (easily thousands of times) for ultra-trace analysis. The current “record” [11] seems to be 28 000 times.

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