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Miniaturized solid-phase extraction techniques

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ABSTRACT

More than 80% of analysis time is spent on sample collection and sample preparation, so sample preparation is a critical part of the analytical process. Traditionally, liquid-liquid extraction was developed and employed to screen for general unknowns. However, solid-phase extraction (SPE) is becoming highly popular as an alternative, due to its simplicity and economy in terms of time and solvent. This review summarizes the current state of the art and the future prospects for green analytical chemistry with special emphasis on environment-friendly sample-preparation techniques based on the solid phase. We discuss in detail miniaturized SPE techniques, based on the most relevant, most representative and most recent scientific references.

Contents

1. Introduction

Analytical laboratories have an essential role in environmental protection because, without their work, it would not be possible to monitor pollutants in air, water or soil. However, analytical activities involve the use of many reagents and solvents, thus generating toxic residues. For these reasons, green analytical

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chemistry (GAC) was introduced in 2000 to reduce or to remove the side-effects of analytical practices on operators and the environment [1]. Although it is relatively new area of activity within green chemistry, GAC has attracted a great deal of interest among chemists. It concerns the role of analytical chemists in making laboratory practices more environmentally friendly [2,3].

GAC is focused on developments in instrumentation and methodologies, reduction of the negative impact of chemical analyses on the environment, and also enabling analytical laboratories to be sustainable in terms of costs and energy. Despite the concept of GAC providing a wonderful ideology, it also poses a number of challenges associated with reaching a compromise between the increasing quality of the results and the improving environmental friendliness of analytical methods. As a result, the guidelines and the principles of green chemistry have been introduced to provide a framework for GAC [3]. Also, components of green analysis are well known and are presented in many critical reviews.

It is well known that more than 80% of analysis time is spent on sample collection and sample preparation, so sample preparation is a critical part of the analytical process and should be part of any curriculum for teaching analytical chemistry [4].

There are different ways to make sample preparation “green” [5]. First, it is necessary to eliminate, or at least to reduce, the amounts of solvents and reagents used in the analysis. Otherwise, solvent recovery and reuse are recommended. Furthermore, green media, such as agro-solvents, ionic liquids (ILs), supercritical fluids or superheated water, are preferable, rather than petrol-based solvents. The scale of analytical operations should be reduced and instruments should be miniaturized. Integration of operations and automation (or robotization) of sample preparation are also important. Moreover, application of factors enhancing the effectiveness of sample preparation (e.g., high temperature and/or pressure, microwave and UV radiation, and ultrasound energy) also impact on the “green” character of the whole procedure. These recommendations are largely met by using miniaturized SPE. There is a large number of review papers focused on different aspects of “green” sample preparation for chromatographic analysis [2,4–6].

Traditionally, liquid-liquid extraction (LLE) was developed and employed to screen for general unknowns. However, solid-phase extraction (SPE) is becoming more popular than LLE for analyte preconcentration and matrix removal, due to its simplicity and economy in terms of time and solvent [4,7]. SPE has gained wide acceptance because of the inherent disadvantages of LLE, whose drawbacks include [7]:

(1) inability to extract polar compounds;
(2) being laborious and time-consuming;
(3) expense;
(4) tendency to form emulsions;
(5) need for evaporation of large volumes of solvents; and,
(6) disposal of toxic or flammable chemicals.

Moreover, recent regulations concerning to the use of organic solvents have made LLE techniques unacceptable. LLE procedures that require several successive extractions to recover more than 99% of the analyte can often be replaced by SPE methods [8]. Due to the fact that SPE is a more efficient separation process than LLE, it is easier to obtain a higher recovery of the analyte by using a reduced volume of solvents I the elution step [8]. Furthermore, SPE does not require the phase separation required for LLE, and that eliminates errors associated with variable or inaccurately-measured extract volumes [8].

Due to these advantages, it is no wonder that SPE technique has become the object of improving and creating even better, more modern and greener solutions for sample preparation, so a number of green techniques characterized have been introduced.

Fig. 1 shows the milestones of SPE. However, there are some disadvantages of SPE techniques:

(1) perceived difficulty in mastering its usage (method development);
(2) wide range of chemistries, many choices for manipulating solvent and pH conditions make it difficult to grasp;
(3) often several steps are required (and additional time necessary); and,
(4) greater cost per sample than simple LLE.

To overcome these drawbacks, novel microextraction techniques introduced require less time and labor than multi-step procedures of SPE. These microextraction techniques allow the integration of activities (e.g., sampling, extraction and analyte enrichment to the level above the method limit of detection (LOD), and analyte isolation from the sample matrix that cannot be directly introduced into a measuring instrument) [9]. We can consider as green the following SPE techniques: magnetic SPE (MSPE), solid-phase microextraction (SPME) and stir-bar sorptive extraction (SBSE).

This review summarizes the current state of the art and the future trends of GAC with special emphasis on environment-friendly sample-preparation techniques based on the solid phase. We discuss in detail miniaturized SPE techniques, based on the most relevant, most representative and most recent scientific references.

2. Solid-phase microextraction (SPME)

SPME is one of the most popular green techniques used for sample preparation in analytical chemistry. SPME was introduced into analytical practice by Pawliszyn and Arthur in 1990 as an attempt to redress limitations inherent in SPE and LLE. Since then, there has been an intensification of research in order to elaborate new methodical solutions in many research facilities around the world, which could increase use of this technique [10]. SPME is a kind of SPE, whereby SPME eliminated its two most substantial faults SPE (i.e., the length of time for extraction and, more importantly, the need to use organic solvents) [10].

Sample preparation using SPME gained appreciation among a large group of analytical scientists, above all thanks to [9,11]:

(1) the possibility of simultaneous download, concentration and analyte determination, which significantly shortened the time to make an analysis;
(2) high sensitivity (possibility to determine the substance at the ppt level);
(3) small sample size;
(4) simplicity and speed of analysis, where use of complicated equipment, tools and devices or precise operations was not required;
(5) cost minimization, by eliminating expensive and toxic organic solvents and multiuse of SPME fibers;
(6) small fibers, which allow the device to download samples in *in situ* conditions;
(7) possibility of automation;
(8) possibility of joining with other instrumental techniques – most often with gas chromatography (GC), liquid chromatography (LC), high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) in the off-line or on-line modes.

The numerous advantages of SPME mean that it is almost universal, because it allows analysis of many kinds of sample in different physical states, liquid, gas and solid, often with very complex matrixes, and it provides determination of analytes at trace and ultra-trace levels [12]. All those features make SPME a hot topic in the development of analytical chemistry and one of most chosen techniques for sample preparation and analyte enrichment. Because