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Review

Recent developments and future trends in solid phase microextraction techniques towards green analytical chemistry

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ABSTRACT

Solid phase microextraction find increasing applications in the sample preparation step before chromatographic determination of analytes in samples with a complex composition. These techniques allow for integrating several operations, such as sample collection, extraction, analyte enrichment above the detection limit of a given measuring instrument and the isolation of analytes from sample matrix. In this work the information about novel methodological and instrumental solutions in relation to different variants of solid phase extraction techniques, solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE) and magnetic solid phase extraction (MSPE) is presented, including practical applications of these techniques and a critical discussion about their advantages and disadvantages. The proposed solutions fulfill the requirements resulting from the concept of sustainable development, and specifically from the implementation of green chemistry principles in analytical laboratories. Therefore, particular attention was paid to the description of possible uses of novel, selective stationary phases in extraction techniques, inter alia, polymeric ionic liquids, carbon nanotubes, and silica- and carbon-based sorbents. The methodological solutions, together with properly matched sampling devices for collecting analytes from samples with varying matrix composition, enable us to reduce the number of errors during the sample preparation prior to chromatographic analysis as well as to limit the negative impact of this analytical step on the natural environment and the health of laboratory employees

Contents

1. Introduction

The basic tools used for implementing pro-ecological policy at the international level are, among others, economical tools (subventions and fees), environmental control and monitoring systems, scientific research, ecological education as well as legal and

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administrative tools which regulate the protection, management and proper use of natural resources and benefits by popularizing the principles of sustainable development. The idea of sustainable eco-development was presented for the first time in 1987 in report of the World Commission on Environment and Development [1]. In the report, it was stated that the further development of human civilization and the fulfillment of socio-economic needs of the present generation will be only possible if the natural resources are properly managed and the relationship between economic growth and caring for the environment and the health of the present and future generations is consciously maintained, while the long-term effects of industrial activities are also considered. The particular significance is associated with the implementation of sustainable development in the professional life of chemists on both, laboratory and industrial scale, as manifested by the application of the green chemistry rules [2]. These rules are a direct response to the legal act on preventing pollution at the source that was passed by the US Congress in 1990, and mark the end of environmental protection based on court orders and strict control [3]. The term green chemistry was coined by P. Anastas in 1991 within the framework of the US Environmental Protection Agency (EPA) program [4]. As a result, the comprehensive US Green Chemistry Program was established in 1993 which involved the cooperation among many governmental agencies and research institutions, international scientific cooperation as well as worldwide activities in the field of education and information dissemination [5]. While Anastas and co-workers were elaborating the ideas of green chemistry, the first paradigms of green analytical chemistry were presented [6]. In 1997 it was stated that an integrated approach to analytical chemistry should include the impact of this branch of chemistry on the environment [7]. The term Green Analytical Chemistry (GAC), introduced in 1999 [8], became an integral part of chemical nomenclature, and numerous reviews [9–15] and original studies have been published under this label. The principles of green analytical chemistry are implemented at each stage of analytical procedure (Table 1)[16–45].

Table 1
Application of the green chemistry rules to specific operations at different stages of analytical procedure.

Step of analytical procedure	Description	Ref.
Sample collection	Miniaturized in-line and on-line systems	
	In situ and *in vivo* sampling of analytes	[16]
	Passive dosimeters	[16,17]
Sample preparation prior to analysis	Application of green solvents:	[19]
	superheated water	[20]
	supercritical water	[21]
	supercritical carbon dioxide	[22]
	ionic liquids	[23]
	supramolecular solvents	[24]
	Safe, nontoxic and easy to utilize solvents	
	Solvent-free techniques for sample preparation prior to analysis	[25–27]
	Automation of analytical techniques	
	Extraction techniques aided by external factors:	
	microwaves	[28–30]
	ultrasound	[31,32]
	ultraviolet radiation	[33]
Measurement	Analytical instrumentation using “green” mobile phases:	
	ethanol	[34]
	superheated water	[35]
	supercritical carbon dioxide	[29]
	Miniaturization of analytical instrumentation (lab-on-value)	
	Recirculation of mobile phase in HPLC[a] (isocratic elution), application of higher pressure, shorter columns with smaller diameter, and a column bed with smaller particle size; reduced use of mobile phase	[36]
	Techniques for direct determination of analytes in samples	[37]
	Microsystems for complete chemical analysis	[38–41]
	Sensor techniques	[42,43]
	Direct coupling of measurement instruments with the sampling equipment	
	Real-time measurements	
	Remote sensing	[44,45]

[a] HPLC—high performance liquid chromatography.

Proper monitoring of compounds present in samples at trace or ultra-trace levels usually requires a preliminary step of isolation/enrichment of analytes because the majority of analytical techniques are not sensitive enough for direct determination of trace compounds. To minimize the amount of waste at the sample preparation step, safe non-toxic extraction media are used [46] and novel microextraction techniques are introduced that are less time and labor consuming compared to multi-step procedures. These microextraction techniques allows the integration of activities such as, sampling, extraction and analyte enrichment to the level above the method detection limit, as well as the analyte isolation from sample matrix which cannot be directly introduced into a measuring instrument [47]. This new green approach of analytical chemists to their work is often described in literature as the three Rs, which stands for replace, reduce and recycle (replacement of toxic solvents with green solvents, reduction of solvent consumption and waste production, and solvent recycling) [48].

By definition microextraction means, all modes of these techniques require handling small volumes of extraction medium under strictly defined extraction conditions. The large number of variable parameters (extraction time, temperature, pH, salt concentration, stirring rate, sample volume, *etc.*) and relationships between them often require the moving away from the classical approach to optimization, which does not take into account the interactions between the variables. Moreover, chemometric tools can assess the statistical significance of the independent variable effects being investigated as well as to evaluate their interaction effects. Nowadays, chemometrics offer several experimental design plans that could be easily use to find the optimal conditions and also to validate the experimental procedure [49]. Some of them are well known and have been utilized in microextraction techniques *e.g.*: Plackett–Burman design [50], Doehlert design [51], Box-Behnken design [52], Central composition design [53].

This deep review summarizes the current state-of-the-art and the future prospects of green analytical chemistry with special emphasis on environmentally friendly sample preparation techniques. In this paper, microextraction solventless techniques are discuss in detail, based on the most relevant, representative and the most recent scientific references. This review provides very detailed information, which could be very helpful in making a decision concerning the choice of a particular solution in order to use it in practice analytical and to make sample-pretreatment greener.

2. Novel solutions in the field of solid-phase microextraction technique

Solid-phase microextraction (SPME) is one of the most popular green techniques used for sample preparation prior to analysis. The technique was proposed for the first time and applied in practice by Pawliszyn and Arthur [54]; it became commercially available in 1993. SPME is widely used in chemical analysis for sampling a wide spectrum of analytes present in media in different physical state that are characterized by complex matrix composition, *e.g.* environmental, biological and food samples [55–59]. Among many