Introduction

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Abstract One of the most important lines of action in the area of Green Analytical Chemistry has been the development of miniaturised techniques that involves reducing the use of toxic solvents and hazardous substances and decreasing the complexity, cost and time of the procedures. Numerous advances have been reached in this fields and currently, there exists a great number of microextraction techniques thanks, in part, to the development of novel materials, such as nanomaterials and green solvents. In this sense, two big groups of microextraction techniques can be considered: sorbent-based microextractions and solvent-based microextractions. This book pretends to compile, from a general point of view (not focus on just one area of application), the fundamentals, main applications, and novel developments of all these techniques. The main audience will be graduates, postgraduates and researchers. It would be a very interesting option as academic book, especially for those that are working in the development of sustainable extraction techniques.

Keywords Green chemistry · Sorbent-based microextraction · Solvent-based microextraction · New materials

Abbreviations

DLLME	Dispersive liquid–liquid microextraction
GAC	Green Analytical Chemistry
GSP	Green sample preparation
HF-LPME	Hollow-fibre liquid-phase microextraction
HLLME	Homogeneous liquid–liquid microextraction

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LLE	Liquid–liquid extraction
LSE	Liquid–solid extraction
μ-dSPE	Micro-dispersive solid-phase extraction
MSPD	Matrix solid-phase dispersion
μ-SPE	Micro-solid-phase extraction
SBSE	Stir bar sorptive extraction
SDME	Single drop microextraction
SLE	Solid–liquid extraction
SPME	Solid-phase microextraction

1 Introduction

Green Chemistry has gained significant impetus in recent years due to growing concerns about environmental degradation and the adverse impact of traditional chemical practices [1]. Green chemistry is founded on a set of 12 principles [2] aimed at minimizing the generation of hazardous waste, reducing the use of toxic substances, and promoting sustainability in chemical processes. It proposes innovative scientific solutions throughout the entire life cycle (design, manufacture, use, and disposal) of a chemical product. Although this new way of conceiving chemical processes has skyrocketed from its appearance in the texts from Paul Anastas (1994–1998) [2–5], it has its roots in the US Federal Pollution Prevention Act of 1990.

Initially directed to industrial-scale processes, the 12 principles were also adapted to different chemical fields, including analytical chemistry. However, some of them are not directly applicable to the analytical field and certain fundamental aspects of analytical chemistry were not included in the general version of the requirements. In this regard, accuracy, sensitivity, and reproducibility should be cautiously considered. Thus, Green analytical chemistry (GAC) is defined as the discipline dedicated to develop cleaner and eco-friendly methodologies to analyse low concentrations of different molecules in complex sample matrices, without compromising the analytical parameters [6, 7]. In 2013, Gałuzska et al. [8] tailored and adapted the 12 principles in order to suit analytical chemistry requirements: (i) use direct analytical techniques, (ii) utilise minimal sample size and reducing the number of samples, (iii) conduct in situ measurements is advocated for in the analytical process, (iv) integrate analytical operation to reduce energy and reagent consumption, (v) opt for automated and miniaturised methods, (vi) avoid derivatisation steps, (vii) prevent the generation of a large volume of waste and proper management of it, (viii) choose multi-analyte or multi-parameter methods, (ix) minimise energy usage, (x) prioritise reagents derived from renewable sources, (xi) eliminate or replace toxic reagents, (xii) ensure the safety of the operator.

A chemical analysis consists of several sequential steps: sampling, sample preparation, analytical measurement, and data evaluation. Undoubtedly, with the progress in instrumentation, the sample preparation is one of the critical aspects that determines whether an analytical procedure can be labelled as "green". This preparation step encompasses not only the dissolution of target analytes in an appropriate solvent but also involves homogenisation, extraction, cleanup, and concentration processes. Recently, López-Lorente et al. [9] proposed the 10 principles of green sample preparation (GSP) based on the fact that the first principle of GAC is often misunderstood, leading to a mistaken notion that avoiding the sample preparation step is the ideal green approach. This interpretation overlooks the potential advancements in the analytical field and not consider these situations, in which direct analysis is not feasible. Analytical Sciences encounter intricate and interconnected challenges, both in on-site and laboratory situations, and sample preparation is frequently required to address these complexities. Therefore, 10 principles of GSP are [9]: (i) prioritise in situ sample preparation, (ii) opt for safer solvents and reagents, (iii) focus on sustainable, reusable, and renewable materials, (iv) minimise waste generation, (v) reduce sample, chemical, and material quantities, (vi) maximise sample throughput, (vii) encourage integration of steps and automation, (viii) minimise energy usage, (ix) select the greenest post-sample preparation configuration, (x) ensure operator safety. By incorporating the principles of Green Chemistry, GAC and GSP into extraction protocols, analysts can achieve remarkable reductions in solvent usage, hazardous substances, waste generation, and energy consumption.

First sample preparation protocols were laborious, time-consuming, and require large amounts of resources, generating hazardous waste. The appearance of analytical microextraction protocols exemplifies a harmonious alliance between environmental responsibility and analytical efficiency. As a result of the intensive research, analytical microextraction protocols frequently offer similar or enhanced selectivity and sensitivity. By minimising interferences and matrix effects, these protocols contribute to accurate and reliable results, reducing the need for reanalysis and further resource consumption. Although the first publications with the word "microextraction" appeared in the 1940s [10, 11], it was not until the 1990s when a real revolution occurred in this field with the development of solid-phase microextraction (SPME) by Arthur and Pawliszyn [12].

One of the primary concerns in traditional analytical methods is the excessive use of organic solvents, which can be harmful to both human health and the environment. Analytical microextraction protocols significantly reduce solvent consumption by employing miniaturised extraction techniques, such as sorbent-based microextraction and solvent-based microextraction. These approaches use reduced amounts of solvents or are solvent-free, thereby reducing the environmental impact and minimising waste generation. In this sense, the use of alternative, non-hazardous extraction phases disminishes toxicity and increases sustainability. These green alternatives offer comparable or improved extraction efficiencies while, the overall environmental footprint of the analytical process is substantially reduced.

It should be mentioned that analytical microextraction protocols, owing to their miniaturised nature, often require lower energy consumption compared to traditional sample preparation techniques, which not only contribute to sustainability but also lead to cost savings and faster analysis, thus promoting economic and environmental benefits. Also, while traditional sample preparation methods can generate substantial amounts of waste (including disposable extraction columns, cartridges, and excess solvents), miniaturised protocols can substantially minimise waste production by utilising reusable or disposable miniaturised extraction devices.

Based on their nature, extraction procedures can be categorised as exhaustive and non-exhaustive protocols. Exhaustive techniques fully extract analytes from the sample, while non-exhaustive methods do not transfer all compounds to the extraction phase. Exhaustive protocols often involve labor-intensive and costly procedures, and thus it is advisable to replace batch equilibrium techniques with flow-through techniques. On the contrary, non-exhaustive approaches can be employed under equilibrium or non-equilibrium conditions. In equilibrium non-exhaustive methods, the underlying principle is similar to equilibrium exhaustive techniques, but the main difference lies in the reduced capacity of the extraction phase, which is insufficient to completely extract analytes from the sample. The miniaturisation of the preparation steps of the analytical process faces its own challenges but, on contrast, it reduces dimensions of the whole analytical process, and advances to the design of portable analysers and on-site analysis. The progress in this field is not only oriented to the development of innovative solutions for isolating analytes, but also on the development of novel and alternative materials. These materials are distinguished by their heightened efficiency compared to traditional ones, leading to enhanced sensitivity and selectivity of the analytical process.

In this book, the fundamentals of each microextraction technique are exhaustively described and the main applications, the trends and the last developments are discussed in a general and didactic way. It is divided in two different big groups: solvent-based microextractions and sorbent-based microextractions (Fig. 1). The first one, composed of five chapters, comprise those sections devoted to micro-solid-phase extraction (μ-SPE), micro-dispersive solid-phase extraction (μ-dSPE) (also known as dispersive-micro-solid-phase extraction (d-μSPE)), solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE), and matrix solid-phase dispersion (MSPD). The second part include those chapters dealing with single drop microextraction (SDME), hollow-fibre liquid-phase microextraction (HF-LPME), homogeneous liquid–liquid microextraction (HLLME), and dispersive liquid–liquid microextraction (DLLME). All of them include the fundamentals and general aspects of microextraction techniques, and novel developments (incorporating new materials and automation, if applicable). Moreover, certain particular aspects, such as the use of magnetic sorbents for μ-dSPE or the assistance by microwaves, ultrasounds or vortex in solvent-based microextractions, were also incorporated. The evolution of these techniques from the classical liquid–liquid extraction (LLE), solid–liquid extraction (SLE), and liquid–solid extraction (LSE) tries to achieve miniaturisation of the devices, enable multiclass analytes extraction, and implement automation.

This book could constitute a reference for novel researchers (including master, Ph.D. students and researchers working in this area) to learn the fundamentals of each technique, their advantages, and disadvantages. Also, it could serve as a guide to select the most suitable technique to solve each specific problem posed at the laboratory.

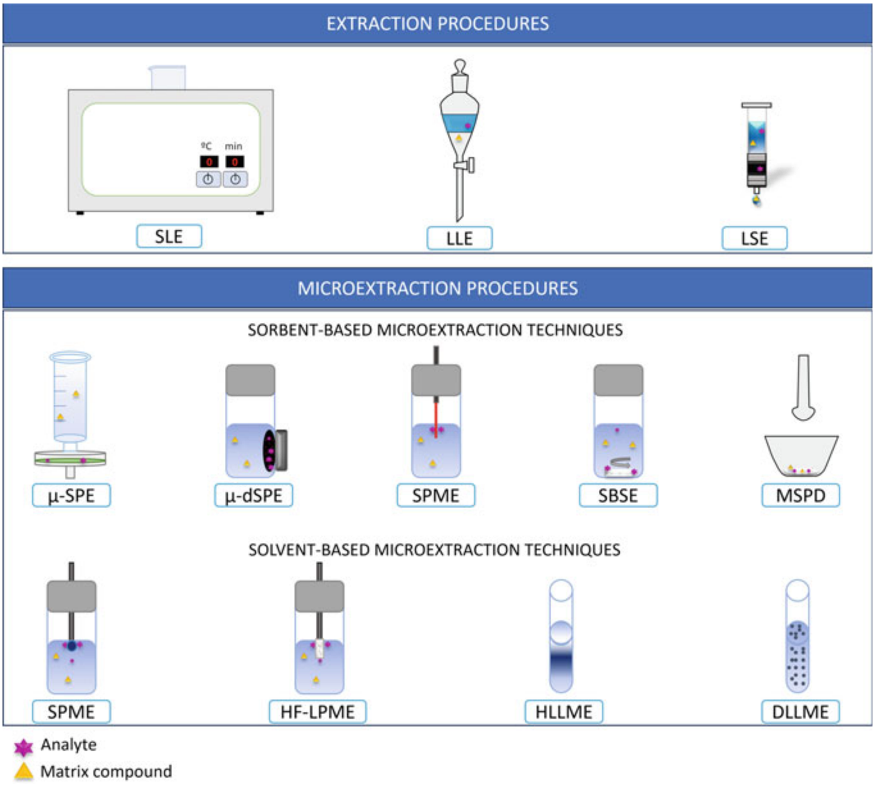

Fig. 1 Extraction and microextraction methods. Representative examples of each category are illustrated

2 Conclusions

Analytical chemists play a significant role in ensuring a sustainable future by incorporating green analytical protocols into their routines and research practices. The mutually beneficial collaboration between green chemistry and Analytical field not only contributes to a cleaner environment but also advances towards more sustainable and economically viable activities. Embracing this synergy offers a promising pathway for future advancements in analytical methodologies while safeguarding our planet’s ecological balance.

This book explores the dynamic relationship between analytical microextraction protocols, highlighting how they complement each other and how they can help to achieve environmentally friendly and efficient analytical processes.

In the future, a growing utilisation of microextraction methods is anticipated. Due to their intrinsic advantages, we strongly advocate for the miniaturisation of standard techniques. It should be noted that similar or superior performance should be provided by these microextraction protocols to ensure an effective replacement.

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