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Preliminary steps of the analytical process. From sampling to detection*

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Abstract: An overview of current ways of automating or accelerating the preliminary steps of the analytical process is presented as a way of emphasizing the role of these steps in the final results. Sampling and weighing, dissolution, leaching or physical removal, in addition to clean-up and preconcentration are the steps discussed along with this overview.

INTRODUCTION

The preliminary steps of the analytical process are the pending goals of today's analytical chemistry. Meanwhile, detection and data treatment have experienced enormous development in the last 20 years, whereas preliminary steps have improved in only some of their different aspects, the others being at present based on old-fashioned procedures. The delay is partially due to the variety of samples (e.g., matrix, physical state, origin), which in turn require different treatment in each case. An intended critical overview of the preliminary steps, starting from sampling and finishing at introduction of the detector is presented with special emphasis on automation as the only way for eliminating overload in analytical laboratories.

When starting from a solid problem [1], the steps involved in the overall analytical process are: (1) sampling and weighing; (2) dissolution, leaching, or physical removal; (3) clean-up; (4) preconcentration; (5) individual separation; and (6) detection and data treatment.

ACCELERATING OR AUTOMATING THE PRELIMINARY STEPS OF THE ANALYTICAL PROCESS

The automation of a step is not always the best option; on the contrary, acceleration of the step by applying an appropriate source of energy can constitute the cheapest and most advantageous solution. In each case, both the acquisition and maintenance costs, number of samples to be treated, the pressing for the results, etc., must be counterbalanced before making decisions. The ways for either accelerating or automating these steps are as follows:

Sampling and weighing

The automation of sampling and the development of the subsequent weighing step in a manner similar to a human analyst is only possible by either a robotic station or (in a more dedicated, limited, and inexpensive version) a workstation (the latter can be devoted only to weighing). Obviously, robotic equipment is more complex and costly than other automated alternatives. This aspect, together with the fact

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that the robotic development of a given step is slower than when it is performed by other automated alternatives, makes it advisable to use robotic stations for steps that are possible to be developed only by robots.

Dissolution, leaching, or physical removal

After weighing, dissolution, leaching, or physical removal (in the case of volatile analytes or their volatile products) are necessary when direct solid analysis (e.g., glow-discharge emission spectrometry, laser-induced breakdown spectrometry, graphite furnace atomic spectrometry, etc. [1]) is not performed.

Dissolution

Complete dissolution of a solid is preferred when (i) the sample is easy to solubilize, (ii) the analytes of very different chemical characteristics must be determined, or (iii) the analytes are difficult to separate from the matrix. Dissolution of solid samples requires a digestion step most times, which can be accelerated using high temperature and pressure [2], microwaves [3], or ultrasound assistance [4]. Between these auxiliary energies, microwaves are the most widely used, both in closed-multimode and open-focused devices.

Commercial, multimode microwave digestors are provided with a variable number (from 8 to 24) of closed vessels, as shown in Fig. 1A, where high pressure is created before microwave irradiation. The arrangement of the vessels in the module is shown in Fig. 1B. Very drastic conditions can be reached in this way, which, in turn, yield short digestion times; nevertheless, the procedures are nonautomatable, as the sample must be manually weighed and introduced into the vessel. The different chemicals to be used for facilitating this step depend on the type of sample and auxiliary energy applied, as well as on the other working conditions.

Open-focused microwave-assisted digestors involve both no overpressure in the sample vessel—which is not necessarily open to the atmosphere—and the presence of a wave guide, which directs and focuses the radiation to the sample (see Fig. 1C). The absence of overpressure also makes the safety

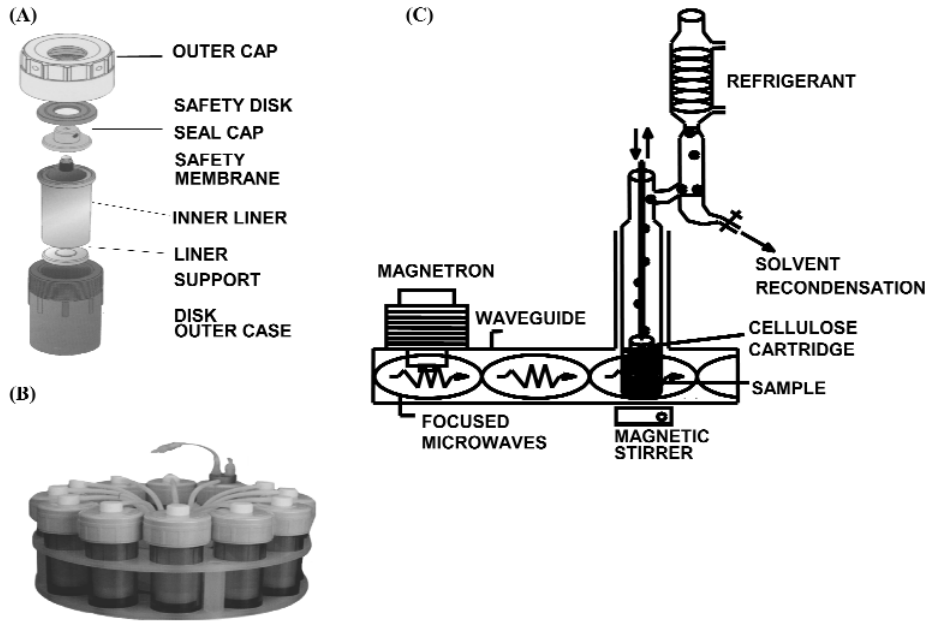

Fig. 1 (A) Elements of a high-pressure, microwave-assisted vessel. (B) Arrangement of the vessels in the module. (C) Scheme of an open-focused, microwave-assisted system.

units, mandatory in closed vessels, unnecesssary. The main advantages of these devices are the high-power density, which increases efficiency by a factor of 10 relative to the use of a multimode device, and the facility for adding reagents or fresh solvent during the process; but only one flask is irradiated at a time.

Leaching

Lixiviation (or leaching) is the term for defining a process that allows removal of some components from a solid. Instead of this specific name, scientists prefer the most generic term "extraction" (e.g., supercritical fluid extraction or SFE [5], microwave-assisted extraction or MAE [6], etc.), which is much less self-explanatory. This process, whatever its name, is more desirable than digestion or total dissolution, in general, as the leachate or "extract" contains less-potential interferents and so, the subsequent clean-up and separation steps can be either avoided or minimized. In general, this process can also be assisted by the same type of energy as dissolution. The types of energy used for accelerating this step are the same as for digestion (i.e., ultrasound, high pressure and temperature, and microwaves, mainly).

Ultrasound can be used either in discontinuous and continuous leaching approaches, the latter being the most appropriate for being automated. In addition, it can be coupled on-line with the subsequent steps of the analytical process [7] for overall, full automation.

After the boom of SFE, more than 20 years ago, it appeared as the panacea. Subsequent research showed its limitations, especially related to the different behavior of spiked and natural samples [8], thus establishing its real field of application [9]. At the same time, a new perspective is open presently with the use of extractants under subcritical conditions—that is, below their critical point but at temperatures above their boiling point and pressures high enough for keeping them in liquid state. Water is one of the most promising of these leachants (both without and with additives for enhancing its function) as it takes advantage of the characteristic of lowering its dielectric constant by raising the temperature under moderate pressure. The most significant shortcoming of water leaching, particularly when used in a continuous fashion, is dilution of the target analytes, which calls for subsequent preconcentration (and usually also clean-up) steps. Subcritical liquid extraction—also known as pressurized fluid extraction, pressurized solvent extraction, high-pressure solvent extraction, etc., none of which reflects the high working temperature—can be implemented both in discontinuous and continuous approaches. The most representative examples of the former are the devices commercialized by Dionex, which also coined the name of accelerated solvent extraction or ASE. The most outstanding feature of ASE devices is the sequential treatment of the samples, which can be located in the extractor in vessels of different size (from 1 to 100 ml), the number of which ranges between 12 and 24. Each unit—vessel and additional equipment—is as shown in Fig. 2A, in which one or several extraction cycles can be developed by filling the extraction cell (where the sample is located) with extractant and subjecting the content to high pressure and temperature under static conditions, then collecting the extract. After finishing the preset cycles, the residual extract is purged from the extraction cell to the collection vial using a suitable gas. The main features of ASE are that a partition equilibrium of the analytes between the extractant and the matrix is established in each cycle; the system must be purged with gas after extraction, but the extracts are more concentrated than in continuous approaches.

Continuous approaches (Fig. 2B) have, as main differences with the static ones, the existence of (1) a preheater for leaving the extractant to the preset temperature before entering into contact with the solid sample and (2) a restrictor, placed at the end of the system to maintain constant pressure inside the extraction cell during extraction. When a hybrid discontinuous–continuous method is implemented, the only change required in the continuous extractor is an inlet valve before the preheater. The advantages of this latter approach with respect to the continuous one are that the static extraction step favors analyte desorption in a small volume of extractant; the dynamic extraction step displaces the partition equilibrium to total removal of the analytes, and no purging of the system with a gas after extraction is

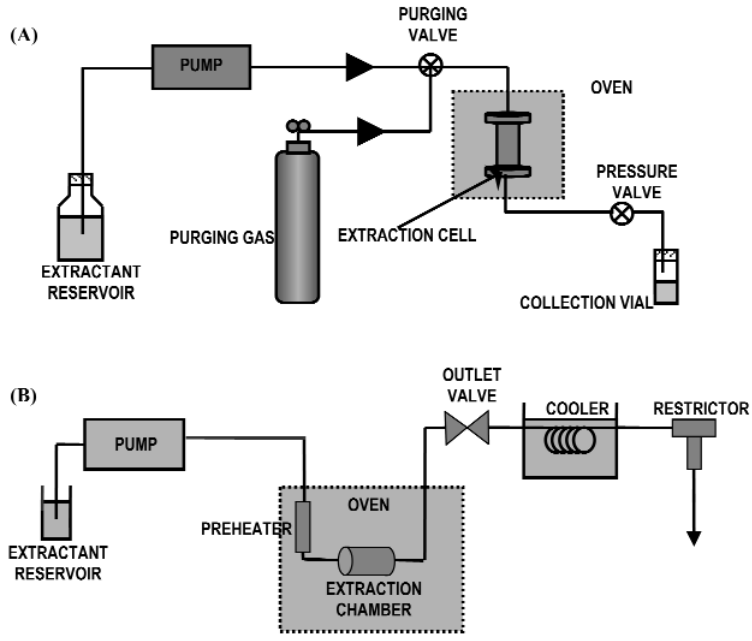

Fig. 2 (A) Schematic diagram of an ASE system. (B) A continuous high-temperature and -pressure approach (for details, see text).

required. When concentration of the extract is required, retention on a solid support, liquid–liquid extraction, evaporation, etc., are implemented after leaching.

Microwave-assisted leaching can be carried out using the same approaches as for microwave-assisted digestion. In addition to the use of closed, discontinuous approaches, open approaches can be partially automated by assisting the device in Fig. 1C with a piston pump for both delivery of the extractant into the sample vessel and removal of the extract from it, as shown in Fig. 3A. Other very effective approaches, such as focused microwave-assisted Soxhlet extraction [10,11], have recently been reported.

Physical removal of the analytes

The removal of volatile analytes (or volatile derivatives) from solid (or liquid) samples is a simpler and more selective goal than those previously discussed. In addition to well-known techniques such as headspace (both static and dynamic purge-and-trap-modes) and gas-diffusion, a more recent technique (namely, analytical pervaporation [12,13]) must be taken into account as more versatile and easy to automate.

Clean-up

A subsequent step to digestion or leaching—or a first step when working with liquid samples—is clean-up, devoted to total or partial removal of the interferents, mainly by using techniques such as liquid–solid extraction, dialysis, or filtration. This last technique is mostly implemented after leaching, as in suspension particles appear when cooling the extract. Filtration can be in-line arranged as shown in Fig. 3B by locating the filter in the loop of an auxiliary injection valve. In this arrangement, cleaning of the filter is performed after extract filtration by circulating a rinsing solution in the opposite direction to filtration.

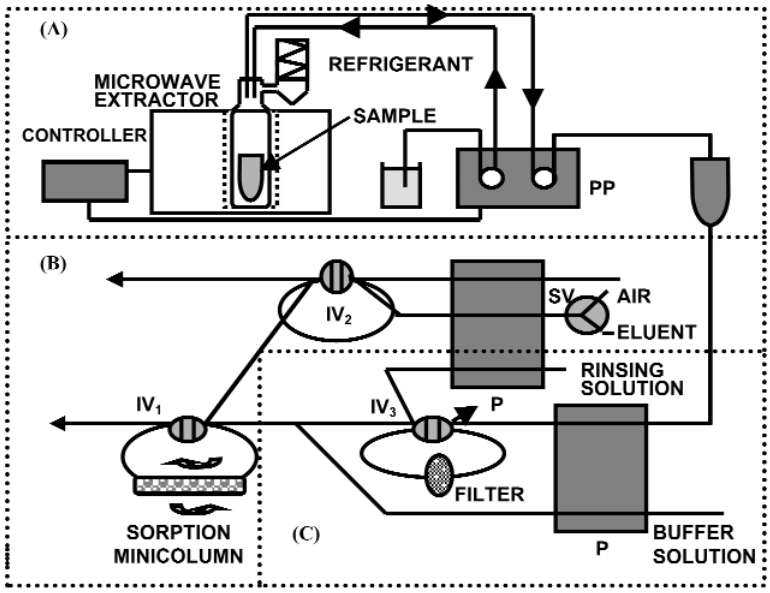

Fig. 3 (A) Focused microwave extractor assisted by a piston pump for delivering of the extractant and removal of the extract. In-line filtration (B) and preconcentration (C) approaches. SV, selecting valve; IV1, IV2, and IV3 are auxiliary valves for preconcentration, elution, and filtration, respectively; PP, piston pump; P, peristaltic pump.

Preconcentration

Preconcentration of the analytes is mandatory when their level is below the limit of the method used for quantitation or detection. The technique more commonly used for preconcentration is liquid–solid extraction, followed by liquid–liquid extraction, both susceptible of being implemented in a discontinuous or continuous manner. When in discontinuous functioning, the former uses commercial, disposable cartridges. In-line inclusion of a solid-phase preconcentration step can be developed with optimum results if the reusable minicolumn is located in the loop of an auxiliary injection valve, as shown in Fig. 3C, for avoiding increased compactness of the packed material by performing retention and elution in opposite directions. In addition, a second auxiliary valve can be used for inserting the eluant into an air carrier, thus minimizing the volume of the former and increasing the preconcentration effect as a result. Research on the material packed in the minicolumn is a field of great interest aimed at obtaining more selective supports that provide higher preconcentration factors. Solid-phase microextraction [14], the miniaturized version of solid-phase extraction, is also a technique with a growing application. Liquid–liquid extraction, which can also be implemented in discontinuous and continuous approaches, allows automation only by the latter approach which, in addition, can involve separation or not of the two immiscible phases [15].

Individual separation

After appropriate clean-up and concentration, if required, the last step prior to introduction at the detector is individual or in-group separation. This step is usually accomplished by a high-resolution separation technique such as chromatography in any of its versions (gas, liquid, or supercritical fluid) depending on the mobile phase, diameter of the column, packing, etc., or by capillary electrophoresis. The features of the treated sample to be introduced and the type of detector to be used after the separation step establish the type and specific characteristic of the equipment to be used in this step.

Detection and data treatment

These last two steps are fully automated most times. Nevertheless, new and increasingly more sophisticated instruments and chemometric packages appear in the market almost everyday.

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