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SCIENCE DIRECT
Talanta 64 (2004) 571–577
Talanta
www.elsevier.com/locate/talanta

Review

Focused microwave-assisted Soxhlet extraction: devices and applications

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Received 19 November 2003; received in revised form 16 February 2004; accepted 22 March 2004

Abstract

An overview of a new extraction technique called focused microwave-assisted Soxhlet extraction (FMASE) is here presented. This technique is based on the same principles as conventional Soxhlet extraction but using microwaves as auxiliary energy to accelerate the process. The different devices designed and constructed so far, their advantages and limitations as well as their main applications on environmental and food analysis are discussed in this article.

Keywords: FMASE; Environmental and food analysis; Soxwave; Microwave extraction

1. Introduction

Most of the times, analytical samples are not suitable for direct analysis because their complexity or incompatibility with the instrument. Hence, sample preparation methods have been and continue being in use for conditioning the samples before the detection–determination step. However, there is currently a need for the improvement of outdated solid sample preparation methods in different analytical areas such as environmental, food and agriculture sectors, industry, etc. [1].

Conventional sample preparation methods involve several steps, being the isolation of the target analytes from a solid matrix one of the most critical. The main problems arise from the possibility of loss or contamination during sample preparation, the long time required for completion of the leaching step, and large solvent consumption. Current tendencies are aimed at overcoming these problems either by the development of new methods, or the improvement of old solvent extraction methods.

Conventional Soxhlet extraction remains as one of the most relevant extraction techniques for isolating species from solid samples. This assertion is supported by the double use of convention Soxhlet: (a) as an extraction step in a given method and/or (b) as a well-established model for comparison of new extraction alternatives.

In conventional Soxhlet, the sample is placed in a thimble-holder and during operation gradually filled with condensed fresh solvent from a distillation flask. When the liquid reaches an overflow level, a siphon aspirates the whole content of the thimble holder and unloads it back into the distillation flask, carrying the extracted analytes in the bulk liquid. This operation is repeated until complete extraction is achieved. This performance makes Soxhlet a hybrid continuous–discontinuous technique. In as much as the solvent acts stepwise, the assembly can be considered as a batch system; however, since the solvent is recirculated through the sample, the system also bears a continuous character.

The most salient advantages of conventional Soxhlet are as follows: (1) the sample phase is repeatedly brought into contact with fresh portions of the solvent, thereby enhancing the displacement of the analyte from the matrix; (2) the temperature of the system is higher than the room temperature since the heat applied to the distillation flask reaches the extraction cavity to some extent; (3) no filtration is required. However, conventional Soxhlet extraction has also significant drawbacks as the long time required for the extraction

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doi:10.1016/j.talanta.2004.03.054

and the large amount of organic solvent wasted, which is not only expensive to dispose off but which can cause environmental pollution itself. Moreover, the conventional device is not easily automated.

There are two different ways to circumvent the drawbacks of conventional Soxhlet extraction, namely: (1) the use of one of the new alternatives (such as supercritical fluid extraction (SCF) [2], microwave-assisted extraction [3], pressurized liquid extraction [4], ultrasound-assisted extraction [5], etc.; (2) the improvement of conventional Soxhlet [6].

Different devices intending to obviate the main shortcomings of the conventional Soxhlet, but keeping its positive characteristics, have been developed [7,8]. High pressure in Soxhlet devices was achieved by placing the extractor in a cylindrical stainless steel autoclave or using supercritical fluid Soxhlet extractors. The main drawback of these approaches is the change from supercritical to liquid state of the extractant, which affects Soxhlet performance. Commercial automated Soxhlet devices (Soxtec HT and Büchi B811) have the possibility of developing three different steps (namely, boiling, rinsing, and recovery of the solvent) by switching a lever, thus obtaining a significant reduction of both time and extractant. Soxwave is a commercial device that operates similarly to Soxtec HT, but using microwaves instead of electric heating. The solvent and the sample are irradiated with microwave energy, making easier the rupture of the analyte–matrix bonds. The main drawback of Soxwave is its dependence on the extractant dielectric constant, since the interaction of the microwaves is only effective with solvents with high dielectric constant. Thus, efficient extractions are only obtained with polar solvents, and consequently, this device is not as universal as conventional Soxhlet is.

Focused microwave-assisted Soxhlet extraction (FMASE) is an approach developed by this research group in 1998 [9] using a prototype [10] based on the same principles as a conventional Soxhlet extractor but modified to facilitate accommodation of the sample cartridge compartment in the irradiation zone of a microwave oven. The main devices designed and constructed until now, as well as their main applications are presented in this article in order to show the potential of this new extraction technique in comparison with other conventional extraction approaches.

2. Focused microwave-assisted Soxhlet extractors

The focused microwave-assisted Soxhlet extraction can be performed with different devices and different instrumental configurations depending on the method to be developed. Since 1998, three different prototypes have been designed and constructed. Each prototype has its own advantages and disadvantages with respect to the others. The main aspect of each prototype are commented.

The first prototype was constructed by Prolabo (Paris, France). The extractor design is based on the same principles as a conventional Soxhlet extractor modified to facilitate accommodation of the sample cartridge compartment in the irradiation zone of a microwave oven. The latter was also modified by making an orifice at the bottom of the irradiation zone, thus enabling connection of the cartridge compartment to the distillation flask through a siphon as illustrated in Fig. 1. The device, which enables focused microwave-assisted Soxhlet extraction, retains the advantages of conventional Soxhlet extraction while overcoming restrictions such as the long extraction time and non-quantitative extraction of strongly retained analytes due to the easier cleavage of analyte–matrix bonds by interactions with focused microwave energy (200 W maximum power), unavailability for automation (substituting the glassware for pumps) and the large volumes of organic solvent wasted. Unlike a conventional Soxhlet extractor, the microwave-assisted system allows recycling of up to 75–85% of the total extractant volume. In addition, solvent distillation in the FMAS extractor is achieved by electrical heating, which is independent of the extractant polarity, thus avoiding the principal problem of commercial focused microwave devices such as those of the Soxwave series from Prolabo. This device is suitable when organic solvent of low boiling point is used as the length of the glassware does not allow working with water or high boiling point solvents.

The main advantage of this first prototype is its versatility. In addition to the standard configuration commented above, different instrumental configurations can be accomplished.

This first FMAS extractor is equipped with a glassware of a design similar to that of the Soxhlet extractor, which can be substituted by a pump serving the functions of the glassware with additional advantages such as the ability to

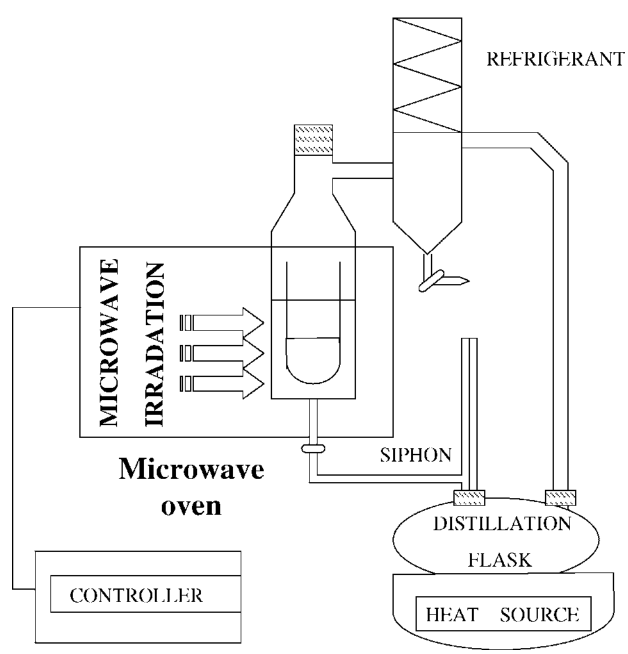

Fig. 1. Scheme of the first FMAS extractor (standard configuration).

couple the FMAS extractor with other dynamic devices. In this case, the glass siphon is substituted by a two channel piston pump used to deliver the extractant and to aspirate the extract after microwave irradiation. The FMAS is connected to either other apparatuses and instruments using a flow injection (FI) interface [11].

The last possible configuration of this first prototype is an automatic approach. Two piston pumps equipped with flexible tubes are used for solvent aspiration and siphoning substituting the glassware (Fig. 2). The aim of these pumps is to achieve a more strict control of both the contact time between the sample and the fresh solvent (by aspirating the latter at preset intervals) and the introduction of fresh solvent into the cartridge at a preset flow-rate [9].

As commented before, the main drawback of this first FMAS extractor is the difficulty of using water or high boiling point solvents as extractants with the standard configuration. In this case, modifications based on substituting the glassware by piston pumps and Teflon tube is required. To enable the use of water as extractant using a single extraction module, a new prototype was designed. This second prototype was constructed by SEV (Puebla, Mexico) and called MIC II. It is based on the same principles of the previous FMAS extractor. It consists of a single unit where the shortening of the distillation glassware allows reception of the water vapor on a refrigerant connected to the top of the sample cartridge vessel with minimal losses in the way, its condensation, and dropping on the solid sample. In this prototype, the siphon is substituted by a valve (see Fig. 3) that allows the filling of the vessel or its draining to the distillation flask. This second prototype has as main advantage the availability to work with water or other high boiling point extractant. Since the unloading of the extract from the sample vessel can be controlled by switching a valve, in addition to the variables susceptible of being optimized in FMASE (namely, power of irradiation, irradiation time and number of cycles), a new variable named delay time (interval during which the sample is in contact with the solvent after microwave irradiation and before draining from the irradiation vessel) can be controlled in order to improve the extraction process [12].

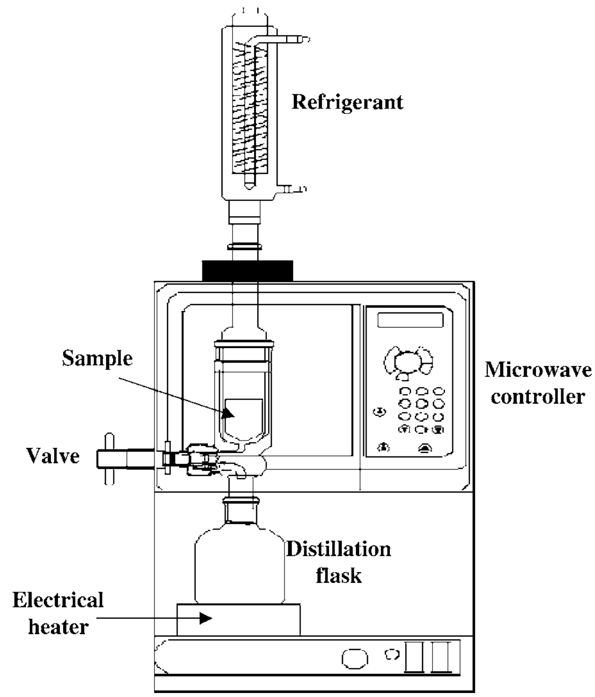

Fig. 3. Scheme of the MIC II.

Finally, a fully automated focused microwave-assisted Soxhlet extractor was designed and constructed (SEV, Puebla, Mexico). This last extractor (Fig. 4), called MIC V, operates with two extraction units, which allow the simultaneous processing of two samples. It also includes an optical sensor that is positioned at a given siphon height to have the magnetron start irradiation of the sample when the solvent reaches the preset level. A solenoid valve is included in the bottom of the siphon, which is switched on at the end of the irradiation step to empty the sample vessel. The optical sensor can be placed along the siphon, which has a length of 18 cm, but only the first 5 cm are irradiated with

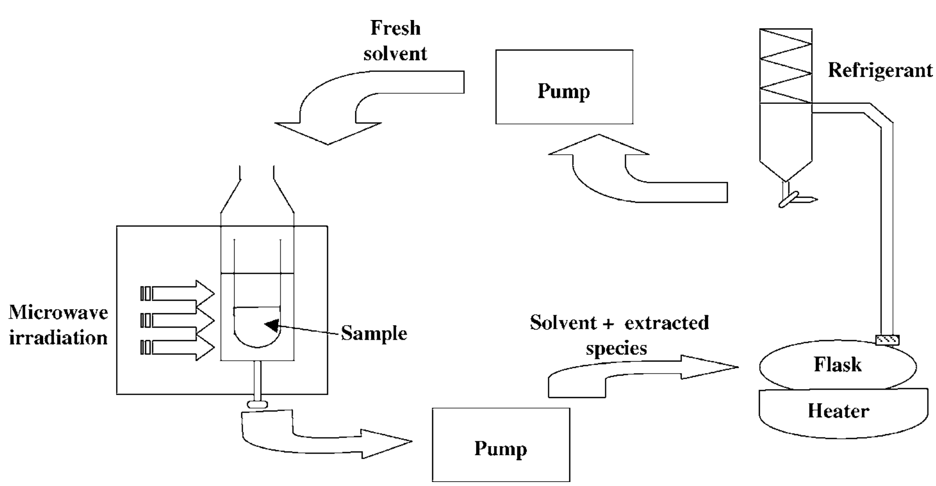

Fig. 2. Automatic approach of the first FMAS extractor.

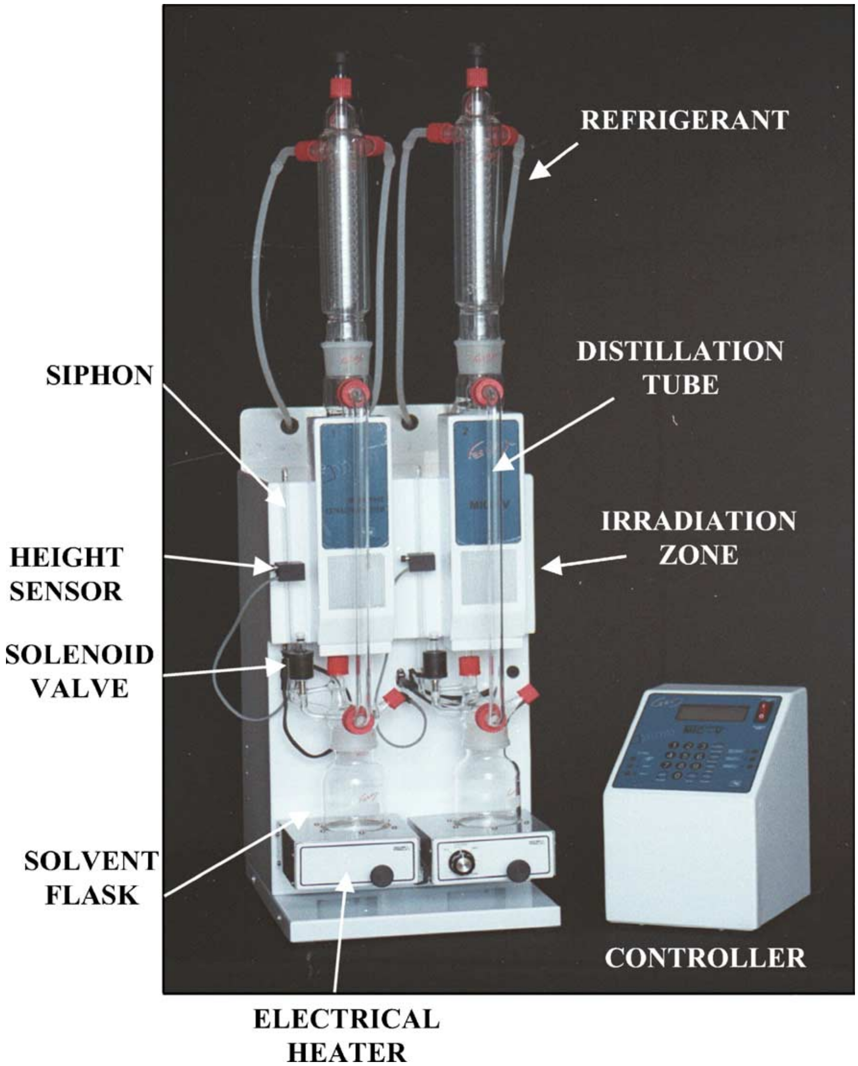

Fig. 4. Picture of the MIC V.

microwaves. The higher the position of the optical sensor along the siphon, the higher the extractant volume put into contact with the target sample in each cycle. Another parameter related with the extractant volume, and thus with the position of the optical sensor, is the unloading time, which is the time during which the solenoid valve remains in its unload position. It is also possible to couple this last prototype to other steps of the analytical process through an FI interface, by introducing a Teflon tube in the distillation flask This prototype overcomes the disadvantages of the previous devices based on the same principles and enables fully automated extraction of two samples simultaneously [13].

3. Applications of FMASE

Focused microwave-assisted Soxhlet extraction has been mainly applied to the environmental and food analysis fields. Tables 1 and 2 show the application of FMASE to both fields, respectively, presenting the types of sample and analyte/s extracted in each case as well as some features of the methods. The different applications of each device are commented below.

The standard configuration of the first prototype developed has been used mainly in food analysis for the extraction of the fat content from different matrices such as olive [14] and oleaginous seeds [15] (sunflower, rape and soybean), cheese [16], milk [17], fried and prefried foods [18] and sausage products [19]. In all cases, the FMASE was faster than the reference method obtaining drastic reduction in the extraction time. For example, for the extraction of the fat content from fried and prefried foods, 55 min are needed by FMASE versus the 8 h required by the reference method [18]. For the extraction of the fat content from seeds, the time was reduced from 8 h to 20–25 min and moreover, the proposed method was less-labor intensive as the official method entails halting the extraction twice to grind the sample [14]. When using cheese [16] and milk samples [17], the extraction time was reduced from 6 and 10 h to 40 and

Table 1
Applications of FMASE to environmental samples

FMASE extractor	Sample	Analyte/s	Extractant	Extraction time	Features	Ref
Prolabo	Fly ash	Dioxins	Toluene	120 min	Standard configuration. Comparison with SFE obtaining better results for difficult matrices	[20]
Prolabo	Soil	*N*-Methylcarbamates	Acetonitrile	2.5 h	Standard configuration. Suitability for the extraction of thermolabile compounds	[21]
Prolabo	Soil	PAHs	Acetonitrile	30–60 min	Coupling of the FMAS extractor to a fluorescence detector through an FI interface	[11]
Prolabo	Soil	Alkanes, PAHs and herbicides	Dichloromethane	50–60 min	Automatic approach using two piston pumps instead of the glassware	[9]
MIC II	Soil	Acid herbicides	Water	48 min	Use of water as extractant. Coupling of several steps, filtration–preconcentration–chromatographic analysis	[12]
MIC II	Sediments	Linear alquilbenzene sulfonates	Water	<2 h	Screening approach based on the coupling of the FMAS extractor to a fluorescence detector through an FI interface	[22]
MIC V	Soil	PCBs	*n*-Hexane–acetone (25:75)	70 min	Fully automated extraction of two samples simultaneously.	[23]
MIC V	Soil	NPAHs	Dichloromethane	1 h	Drastic reduction of the extraction time (1 h vs. 24 h required by the EPA reference method)	[24]

50 min, respectively. Better quality of the extracts was also obtained possibly due to the shorter time required by the FMASE method. Milk fat obtained by FMASE undergone lesser chemical transformation of triglycerides during the extraction process [17].

Environmental applications of the standard configuration of the first prototype have been the extraction of dioxins from fly-ash [20] and that of *N*-methylcarbamates from soil [21]. For the extraction of dioxins from fly-ash, FMASE was compared with supercritical fluid extraction (SFE) and

Table 2
Applications of FMASE to food analysis

FMASE extractor	Sample	Analyte/s	Extractant	Extraction time	Features	Ref
Prolabo	Olive seeds	Fat content	*n*-Hexane	20–25 min	Standard configuration. Substantial shortening of the extraction time (8 h by ISO method)	[14]
Prolabo	Cheese	Fat content	*n*-Hexane	40 min	Standard configuration. Performance of the hydrolysis and extraction steps with the same device	[16]
Prolabo	Oleaginous seeds	Oil content	*n*-Hexane	3 h	Standard configuration. Use of a special sample cartridge constructed with low porosity paper	[15]
Prolabo	Milk	Lipids	*n*-Hexane	50 min	Standard configuration. Shorter time of the overall process (50 min vs. 10 h by the conventional method	[17]
Prolabo	Prefried and fried foods	Fat content	*n*-Hexane	55 min	Standard configuration. Fat quality monitoring approach	[18]
Prolabo	Sausage productos	Lipids	*n*-Hexane	45 min	Standard configuration. Use of samples as received without water adjustment usually required by Soxhlet	[19]
MIC V	Sunflower seeds	Pesticide residues	Dichloromethane	45 min	Avoidance the sample manipulation during the extraction step required by the ISO reference method	[25]
MIC V	Bakery products	Fat content	*n*-Hexane	30–55 min	Drastic reduction of the extraction time (30–55 min vs. 16–8 h by the AOAC reference extraction method	[26]

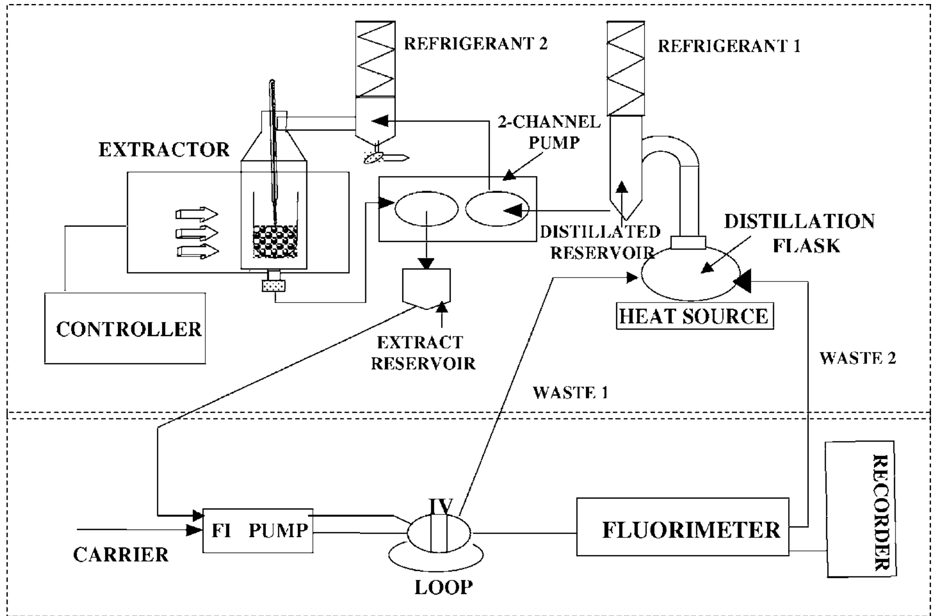

Fig. 5. Coupling of the first FMAS extractor to a fluorimeter through an FI interface.

conventional Soxhlet extraction. The extraction of dioxins using SFE was quantitative for some samples, but no more than 10% (relative to the Soxhlet extraction) could be extracted from samples containing more than 15% of activated charcoal. However, FMASE provided quantitative recoveries from all kind of sample (even the most difficult ones) in less than 2 h compared with the 48 h required by the EPA reference method [20]. FMASE was proved as a suitable extraction tool for the extraction of *N*-methylcarbamates from soil. Due to the thermolability of these compounds, conventional Soxhlet can not be used. The EPA reference method is based on a series of tedious solid-liquid and liquid-liquid extraction steps that take around 6 h. FMASE provides similar results to those of the EPA method but in a shorter time (2.5 h versus 6 h) and avoiding sample manipulation during the whole extraction step [21].

The coupling of the FMAS extractor to a fluorimeter through an FI interface (Fig. 5) has allowed real-time on-line monitoring of the PAHs extracted from solid samples in each Soxhlet cycle providing qualitative and semiquantitative information from natural and spiked samples [11]. Hence, the extraction kinetics can be monitored and the end of the leaching step determined with independence of the sample matrix, thus avoiding the use of extraction times in excess. The precision provided by this method expressed as relative standard deviation ranged between 2.59 and 4.77%.

For the extraction of pollutants of different polarity (namely, alkanes, PAHs and herbicides) from the same soil matrix, the automatic approach of the first FMAS extractor (Fig. 2) was selected [9]. The proposed approach provided efficiencies similar or even higher than those obtained by conventional Soxhlet with extraction times at least eight times shorter (50–60 min versus 8 h). Recoveries higher than those provided by conventional Soxhlet could be due to the higher temperature reached in the cartridge, which makes possible the release of strongly adsorbed or bound fractions of the target analytes, difficult to remove at the temperatures reached in the conventional device.

The second FMAS extractor, MIC II (Fig. 3) has been exclusively used in the environmental field for the extraction of acid herbicides from soil [12] and for that of linear alkylbenzene sulfonates (LAS) from sediment [22]. In both cases, the main advantage was the use of water as extractant, thus providing clean methods. Moreover, in both cases, the extractor was coupled to subsequent steps of the analytical process. For the extraction of acid herbicides from soil, the FMAS extractor was coupled to a filtration, preconcentration and chromatographic steps, thus providing a fully automated method. For the extraction of LAS, the extractor was coupled to a fluorimeter that allowed the on-line monitoring of the extract providing a fast screening system.

The first application of the last prototype constructed so far (Fig. 4) was the extraction of PCBs from differently aged soil [23]. This prototype allowed the extraction of two samples simultaneously with a drastic reduction of the extraction time (70 min versus 24 h for the conventional Soxhlet extraction). Extraction of nitro-PAHs has also been accomplished using this prototype [24]. In this case, the reduction in the extraction time was also important, from 24 h by the EPA reference method to 60 min by the proposed approach.

This last prototype has also been applied to food analysis. Pesticides residues from sunflower seeds [25] and the fat content from bakery products [26] have been extracted using this fully automated FMAS extractor. The extraction of pesticide residues from seeds was performed in a single extraction step (45 min versus at least 7 h needed by the conventional method) avoiding sample manipulation during the extraction step [25]. For the extraction of the fat content from bakery products such as snacks and cookies, the reduction in the extraction time was also significant (from 16 and 8 h to 55 and 35 min, respectively). Moreover, moisture adjustment, required by the conventional Soxhlet method before extraction, was not required when using FMASE.

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