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The latest trends in the miniaturized treatment of solid samples

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ABSTRACT

Miniaturization is a recognized trend in many analytical application areas, including the analysis of trace organic compounds in food and environmental samples. The many impressive advances achieved in recent decades in the analytical instrumentation used in this study area allowed a progressive reduction in the initial amount of sample used for analytical determinations without affecting the accuracy of the final result. This evidence promoted the development of a plethora of novel, miniaturized, analytical techniques for the treatment of liquid matrices. However, progress in the treatment of (semi-)solid matrices was much more limited, probably due to the greater complexity of the matrices and the persistent lack of appropriate small-scale instrumentation. Despite these shortcomings, research in this field remains active. This review covers recent advances and the latest trends in this research area.

Contents

1. Introduction

Greening the analytical process is a current demand in many application fields, especially those involving the treatment of relatively large amounts of samples through preparation protocols encompassing several independent treatment steps. The determination of minor compounds in complex matrices, such as foodstuffs and environmental samples, is representative of this type of analysis. In these research areas, the very low levels at which specific compounds need to be accurately determined, combined with the complexity of the matrix in which they are entrapped, frequently makes it essential to use laborious multistep sample-preparation procedures. As a consequence, conventional treatment procedures in these types of analysis use relatively large amounts of reagents and solvents, have long analysis times and generate relatively large amounts of wastes per sample analyzed. In most cases, integration of the different treatment steps is very limited, resulting in continual exposure of the analyst to chemicals and making procedures prone to analyte loss and/or degradation due to the continuous sample manipulation. In this context, any modification that contributes to solving (or at least minimizing) any of these shortcomings of conventional sample-treatment methodologies or to greening them should be considered advantageous.

The many efforts in the past two or three decades in sample preparation have yielded a number of well-accepted, established extraction and preconcentration techniques that are able to fulfill (at least partially) some of these requirements for the miniaturized treatment of liquid and viscous samples. Representative examples, such as single-drop microextraction (SDME), solid-phase microextraction (SPME) and its in-tube version, or stir-bar sorptive extraction (SBSE), are highlighted in review papers in this Special Issue. The latest additions in hollow-fiber microextraction (HFME) [1] and related modern solvent-based microextraction techniques [2], dispersive liquid-liquid microextraction (DLLME) [3], or miniaturized solid-phase extraction (SPE) [4,5] and other SPE-based techniques [6], can be found in recent literature. However, developments in the treatment of semi-solid and solid samples have been much more limited [7].

The analysis of semi-solid and solid matrices typically starts with the exhaustive extraction of the target analytes from the complex

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matrix in which they are entrapped. The essentially non-selective nature of these treatments, particularly when dealing with the analysis of trace components, usually made essential the subsequent purification and/or preconcentration of the extracts obtained. For these subsequent treatment steps, previously mentioned analytical techniques for preparing liquid and viscous samples are applied. Selection among them depends primarily on the nature of the analytes, the solvent in which they are dissolved and the complexity of the extract, but also on the selectivity and the sensitivity of the analytical technique used for final instrumental determination of the target analytes. The latter, together with the selectivity of the technique used for extract purification, determines the need for one or several of these sample-treatment procedures.

In general, and probably due to the analytical demands to be fulfilled during the extraction step in the treatment of (semi-)solid matrices (viz extraction conditions should ensure matrix structure disruption, efficient solvent penetration and exhaustive recovery of target compounds), there have been no real fundamental additions in the field in recent years. However, the miniaturized versions of already existing extraction techniques [e.g., matrix solid-phase dispersion (MSPD), pressurized liquid extraction (PLE) or ultrasound-assisted extraction (UAE)] have taken advantage of progress made in other fields (e.g., the development of novel materials and nanotechnologies). Thereby, novel approaches with improved features were reported. In addition, several other analytical strategies were tried in attempts to increase the selectivity of the extraction process.

This review covers recent developments and innovations regarding miniaturized treatment of semi-solid and solid samples, but, rather than presenting a comprehensive review of all additions to the field, we focus attention on those novel aspects and approaches that attracted interest from the scientific community in recent years. Focus is on literature published in the past five years to avoid as much as possible overlap with previous reviews on the same or closely-related topics {[6–8], among others}. We pay special attention to applications dealing with the analysis of minor (i.e., trace) organic components due to the greater difficulty typically associated with this type of determination, in which, in many instances, accuracy can be achieved only after exhaustive analyte extraction. Nonetheless, if relevant, application examples from closely-related areas are also discussed in so far as they involve chromatographic (or related separation) techniques for final instrumental determination. Interest is in techniques that are miniaturized *per se* rather than on conventional-sized techniques that are simply applied to analyze small-sized samples. In all instances, preference is for applications and techniques dealing with the analysis of real-life samples.

2. Matrix solid-phase dispersion (MSPD)

MSPD can be defined as a solid-solid extraction procedure, in which one phase is the investigated (semi-)solid matrix and the other an appropriate sorbent. In practice, the technique is applicable to liquid, viscous and solid samples. In a typical MSPD experiment with a (semi-)solid matrix, the tested sample structure is completely disrupted by abrasion with the selected extraction sorbent(s). During this mixing process, sample components are homogeneously dispersed on the sorbent surface. The resulting homogeneous, dried sample-sorbent(s) mixture is subsequently packed in an SPE cartridge-like column from which the investigated analytes are eluted with an appropriate extraction solvent. Depending on the nature of the MSPD sorbent selected, a (preliminary) clean-up step can be performed by irreversible retention on the column of specific matrix components. Alternatively, a previous washing step can be incorporated in the elution protocol before analyte elution from the column. In addition, a co-sorbent can be simultaneously packed in the SPE column below the MSPD mixture to perform extra in-column purification of the eluent from the MSPD column. When properly designed and optimized, MSPD (with or without co-sorbents) can yield ready-to-analyze extracts that are, in most cases, processed by gas chromatography (GC) or liquid chromatography (LC). A detailed discussion on the main experimental parameters controlling the efficiency of the MSPD process, the different MSPD configurations, mixtures and working protocols and the potential and the limitations of the different MSPD approaches can be found in a review included in this Special Issue and in other articles of a more specific nature [7,9].

Reversed-phase bonded materials have been widely used as MSPD sorbents for selective retention of medium-polar and non-polar matrix components. Normal-phase inorganic materials (e.g., bare silica, alumina or Florisil) are also used for MSPD. These materials provide less extensive retention than reversed-phase bonded materials, but stronger than that achieved with Celite, sand or diatomaceous earth. The use of C18 and other conventional dispersants continued in recent years, when these sorbents expanded their field by application to the determination of emerging pollutants, such as parabens [10,11], plasticizers [12] or fragrance allergens [13], just to mention a few examples (Table 1).

However, most recent trends in MSPD focus on the use of novel dispersant materials that provide improved retention and/or selectivity, further miniaturization of the process, and combined use with an additional source of energy to promote a more efficient matrix disruption, or special sorbents that improved selectivity and/or selectivity during MSPD, in particular molecularly-imprinted polymers (MIPs) [7,22]. Table 1 gives relevant analytical details of selected examples of representative miniaturized MSPD-based application.

The different benefits associated with the use of class-selective MIPs in the analysis of liquid analysis were amply illustrated in a number of studies [23]. The improved selectivity achieved in the retention process contributed to simplification of the subsequent clean-up and/or detection steps.

In general, selective recognition by MIPs is not favored in aqueous samples [23], so direct use of MIPs as dispersants in MSPD of water-containing samples is relatively difficult and, consequently, rare in the literature. The problem can be solved by developing improved water-compatible MIPs {e.g., in the simultaneous isolation of fluoroquinolones in serum samples by selective molecularly-imprinted MSPD [24] or of Sudan dyes in egg yolk [16]}. This latter application study, although involving a viscous sample, can be considered an illustrative example of current trends in this research field. In this study [16], 0.1 g of yolk were dispersed on 0.2 g of a newly synthesized kind of aniline-naphthol MIP microspheres selective for Sudan dyes from egg yolk. The resulting mixture was transferred to an empty cartridge (5 cm × 8 mm i.d.) in which 5 mg of MIP were prepacked to act as co-sorbent. After washing the column with 4 mL of methanol:water (1:1, v/v), the target analytes were selectively eluted with 3 mL of acetone:acetic acid (95:5, v/v). The collected extract was concentrated to 1 mL and then used as dispersive solvent during DLLME of the four investigated Sudan dyes. The method showed satisfactory linear response in the evaluated range 0.02–2.0 μg/g, with recoveries better than 87% and RSDs below 6%.

Graphene and carbon nanosorbents exhibit selectivity for planar compounds similar to that of conventional carbon-based sorbents. However, their improved loading capabilities can contribute to significant reduction in the amount of sorbent required for many applications, making possible the scaling down of the MSPD process. In a typical example, chemically-converted graphene was used by Liu et al. [19] to develop a straightforward MSPE-based methodology allowing simultaneous extraction and purification of PBDEs and their methoxylated and hydroxylated analogs (MeO-PBDEs and

Table 1
Selected representative application studies involving miniaturized matrix solid-phase dispersion (MSPD). Reported studies are organized on the basis of the material used as dispersant

Matrix (mg)	Analyte	Dispersant (mg)	Extraction solvent	Recovery (RSD)[a]	Extra treatment	Ref.
Human placental (250)	Parabens and benzophenone-ultraviolet filters	C18 (1000)	EtOAc[b] (20 mL)	95–106 (5–14)	Cc [c] + LLE + Centrif.[d] + Cc	[10]
Bivalves (100)	Di(2-ethylhexyl) phthalate	C18 (100)	ACN[e] (1.2 mL)	91 (15)	Dilution with H_2O + in-tube SPME	[11]
Cosmetics (100)	Plasticizers and synthetic musks	Anhydrous Na_2SO_4 (200) + Florisil (400)	EtOAc (1 mL)	84–104 (3–15)	NR[f]	[12]
Personal care products (200)	Fragrance allergens and preservatives	Anhydrous Na_2SO_4 (200) + Florisil (400)	EtOAc (2 mL)	78–115 (1–15)	Derivatization	[13]
Soil (200)	Triazines	Atrazine-MIP (200)	H_2O (5 mL) + MeOH (5 mL)	61–97 (1–5)	Cc	[14]
Strawberry and tomato (200)	Triazines	Atrazine-MIP (600)	Acetic ester (5 mL) + DCM[g] (10 mL)	54–98 (1–4)	Cc	[14]
Orange (100)	Auxins	l-tryptophan-MIP (100)	DCM: acetic acid (95:5, v/v; 3.0 mL)	88–104 (3–4)	Cc	[15]
Egg yolk (100)	Sudan I-IV	MIP microspheres (200)	Acetone:acetic acid (95:5, v/v; 3 mL)	87–104 (3–7)	Cc + DLLME	[16]
Butter (500)	Hormones	Graphitized MWCNTs[h] (300) + MWCNTs (100)	EtAcO (10 mL)	85–112 (2–9)	LLE[i] + Centrif. + Filtration	[17]
Cortex Magnoliae (50)	Honokiol and magnolol	Carboxyl-modified MWCNTs (60)	MeOH (1.5 mL)	90–101 (4–5)	Dilution + filtration	[18]
Soils, tree bark, fish (100)	PBDEs[j], MeO-BDEs[k], OH-BDEs[l]	Chemically converted graphene (10)	*n*-C_6[m]:DCM (1:1, v/v; 0.5 mL) + acetone (1 mL)	29–116 (3–20)	Cc	[19]
Fruits (200)	OPPs[n] and triazines	C8 (200) + UAE[h] (1 min)	EtOAc (0.7 mL)	68–139 (2–17)	Cc	[20]
Fish (100)	OCPs[o]	Anhydrous Na_2SO_4 (100) + C18 (400) + UAE (10 min)	ACN (1.5 mL)	39–82 (3–8)	DLLME	[21]

[a] Recovery (RSD), as %.
[b] EtAcO, Ethyl acetate.
[c] Cc, Concentration.
[d] Centrif., Centrifugation.
[e] ACN, Acetonitrile.
[f] NR, Not required.
[g] DCM, Dichloromethane.
[h] MWCNTs, Multi-walled carbon nanotubes.
[i] LLE, Liquid-liquid extraction.
[j] PBDEs, Polybrominated diphenyl ethers.
[k] MeO-BDEs, Methoxy-brominated diphenyl ethers.
[l] OH-BDEs, Hydroxy-brominated diphenyl ethers.
[m] *n*-C_6, *n*-Hexane.
[n] OPPs, Organophosphorus pesticides.
[o] OCPs, Organochlorine pesticides.

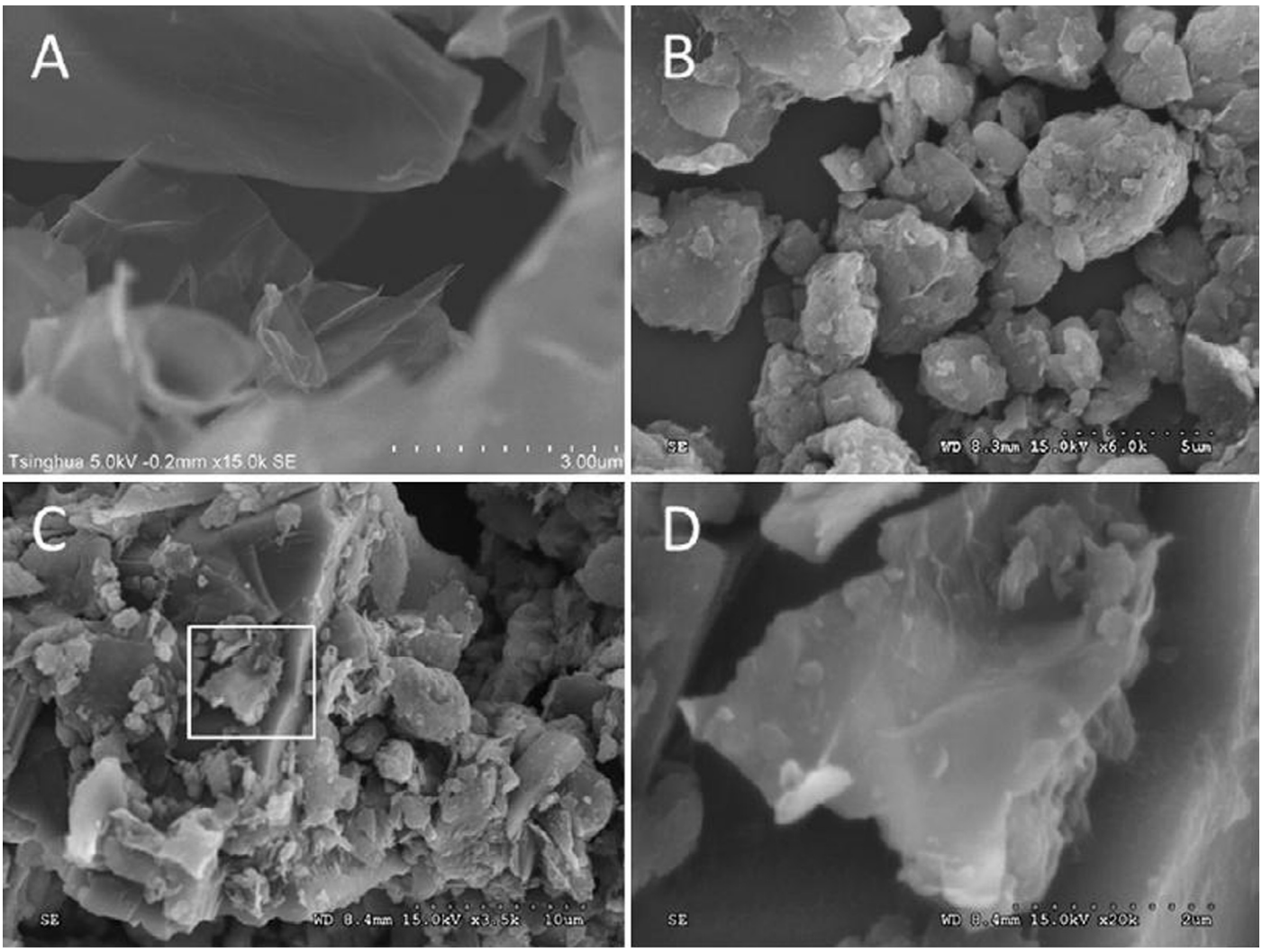

Fig. 1. SEM images of (A) chemically-converted graphene (CCG), (B) soil sample after grinding, (C) ground mixture of CCG and soil, and (D) magnification of (C) showing a semi-transparent CCG sheet attached on the surface of a soil particle. {Adapted from [19]}.

OH-PBDEs, respectively) from matrices of very different natures, including soil, tree bark and fish. In a typical experiment, 100 mg of the freeze-dried, homogenized and sieved sample were dispersed on 10 mg of graphene. A homogenous mixture of sample and disperser was achieved in only 5 min, as demonstrated by SEM and TEM analysis of the resulting mixed material (Fig. 1). The resulting mixture was packed in a 1 mL SPE cartridge on top of 50 mg of anhydrous sodium sulfate and 50 mg of Florisil that acted as co-sorbents. Then, the target analytes were extracted following a two-step elution procedure involving 0.5 mL of n-C_6:DCM (1:1, v/v; 0.5 mL) for the quantitative elution of non-polar PBDEs and MeO-PBDEs, and 1 mL of acetone for subsequent separate extraction of the OH-PBDE analogues. The optimized methodology provided quantitative recoveries of the target compounds for soil and tree bark (recoveries in the 87–116% range for soil, and in the 60–112% range for tree bark; at the lowest investigated spiking levels of 0.25 ng/g and 1.0 ng/g, respectively). For fish, satisfactory recoveries were also obtained for PBDEs and MeO-PBDEs spiked at the 1.0 ng/g level (74–114%), while different results were found for OH-PBDEs (in the 29–87% range). In all instances, RSDs below 20% were obtained. Compared to conventional sorbents, the relatively soft structure of graphene required little disruption of the matrix structure by mechanical grinding of the sample-disperser mixture. Therefore, in contrast to the basic MSPD approach, in this type of MSPD process, we postulate that extraction is probably accomplished by inter-particle shearing. The lipophilic polyaromatic plane of the chemically-converted graphene has also been suggested as playing a relevant role during the extraction of planar compounds in this type of process.

The feasibility of improving the efficiency of MSPD by applying auxiliary energy has also been evaluated, in this case almost exclusively using miniaturized formats. Due to their flexibility, simplicity and accessibility, the application of ultrasound was typically preferred in these studies. With this aim, both baths [21] and sonoreactors [20] were evaluated, the latter being more efficient due to the more focused application of the energy, but also demanding more careful optimization of the experimental parameters when dealing with the analysis of relatively labile analytes, such as pesticides [20]. Despite its many positive features and potential for the fast treatment of complex (particularly highly sorptive) samples, use of ultrasound-assisted MSPD (US-MSPD) is apparently still rather limited.

In any case, the simplicity of operating MSPD, its flexibility in incorporating new sorbents and its combination with other analytical techniques guarantee further development in this field in coming years.

3. Enhanced solvent-extraction techniques

Extraction efficiency can be enhanced by heating or shaking a sample, or by using a fluid or solvent with a high diffusion rate. The former is the basis of microwave-assisted extraction (MAE) and UAE, while the latter is the principle of other techniques, such as supercritical fluid extraction (SFE), PLE or subcritical water extraction (SWE). The many advantageous features of these modern, well-established techniques for the treatment of semi-solid and solid samples were widely documented in review papers [7,25] and application studies. However, the development of their corresponding miniaturized (i.e., scaled down) counterparts is still rare and essentially limited to home-made devices that, despite their positive features and analytical potential, do not seem to attract enough attention from companies for them to proceed to large-scale production and commercialization. Advantageous features frequently associated with these miniaturized systems compared to large-scale instruments include the extra saving of energy, reagents and, in many instances, sample consumption, reduced waste generation, and its potential portability and/or coupling to the rest of the analytical procedure.

In general, progress concerning these types of miniaturized technique has been rather limited over the years and this general trend remained recently. The difficulty of setting up some of these home-made miniaturized systems may be one of the main limitations when trying to develop such analytical approaches for the treatment of (semi-)solid samples. This could have been particularly true for SFE or MAE. No miniaturized SFE system has been described in the literature.

Regarding MAE, since the introduction of the rather complex but coupled set-up proposed by Colmsjö's group [26,27] some 10 years ago, research on this technique focused mainly on the development of novel applications {also for coupled systems [28]}, rather than the development of new concepts. In this context, Gao et al. [29] evaluated the feasibility of on-line ionic liquid (IL)-based dynamic MAE-LC-DAD for the determination of lipophilic constituents in *Salvia miltiorrhiza* Bunge. In this study, a suspension containing the sample (180 mg of root) and the extraction solvent was continuously passed through the MAE system for extraction and on-line filtration of the target analytes before transfer to the LC-DAD instrument. Once optimized, the method provide limits of detection (LODs) for tanshinone I, cryptotanshinone, and tanshinone IIA of 0.014 mg/g, 0.009 mg/g, and 0.009 mg/g, respectively, recoveries of 91–102%, and inter-day and intra-day RSDs lower than 2%, so the coupled procedure showed an analytical performance similar to off-line IL-based, ethanol-based MAE, and IL-based LLE. However, in contrast with these procedures, complete sample preparation was done in a shorter time and in a closed system, which prevented analyte loss and/or contamination.

Finally, the recent proposal of a portable (although not miniaturized) novel instrument for *in-situ* MAE could indeed be considered an interesting addition to the field [30]. However, further miniaturization of these types of device would still be desirable.

Application of ultrasound to analytical studies started only some 20 years ago. Since then, the technique has been used for the fast, simple, quantitative and reproducible extraction of analytes of very different nature from widely divergent matrices [31]. Ultrasonication involves the application of sound waves with frequencies above 20 kHz, which travel through a matter/liquid producing negative pressure and bubbles or cavities. When a bubble can no longer absorb the energy from the ultrasound, it implodes. The whole process is named cavitation and creates microenvironments with high temperatures and high pressures that speed the removal of analytes from the sample matrix [32]. The technique is recognized as a relatively inexpensive, green, flexible analytical approach that, as indicated in previous sections, can easily be combined with other sample-preparation techniques to yield improved and/or faster extraction and purification processes.

The devices most frequently used for USE are baths, sonoreactors or probe systems, each having its own advantages and shortcomings. Baths are more widely used and have typically been preferred for the development of miniaturized and coupled analytical approaches [33,34]. However, they have a number of disadvantages that negatively affect experimental precision, the lack of uniformity of the distribution of the ultrasound energy and power decline over time being among the most relevant.

Sonoreactors and sound probes are *per se* miniaturized systems, which provide more focused ultrasound energy and, consequently, more efficient cavitation, which can shorten the analytical time. However, the sample often needs to be cooled due to the large amount of heat dissipation (especially with probes), volatile and labile analytes can be lost, and tip erosion occurs over time.

In general, UAE with sonoreactors and probes is usually faster than with baths, but, in many instances, more demanding during optimization. In recent years, probe systems were usually preferred over sonoreactors for the development of analytical applications. This is particularly true when dealing with the analysis of size-limited samples, for which minimum sample manipulation is highly advisable to prevent analyte losses and contamination. In a recent representative study, a UAE probe-based method was proposed for the quantitative extraction of endogenous PCBs from biological tissues using a small sample of 50 mg [35]. The extraction step was completed in an 1.5-mL Eppendorf in 40 s with 150 µL of *n*-hexane. After centrifugation for 2 min, the supernatant was directly aspirated into a 5-mL polypropylene tip for disposable pipette extraction (DPX) with acidic silica. The purified extracts were then eluted into a GC microvial for final instrumental separation plus detection. Complete sample preparation was done in only 15 min. Recoveries were in the 85–123% range for a large majority of the studied PCB congeners, and the RSDs were generally less than 14%. When combined with GC ion-trap mass spectrometry [GC-ITD(MS/MS)] for final determination, LODs in the low-ng/g range were obtained. The method was proposed for fast screening of PCBs in non-contaminated biological matrices (including foodstuffs). However, it was subsequently used, with minimum modifications, for the accurate determination of other classes of micropollutants in size-limited solid biological samples {i.e., 2 mg of contaminated zebrafish embryos [36,37]}. The procedure has potential for automation and at-line coupling of the different analytical operations. However, the development of on-line sample-preparation procedures requires a different type of set-up. Examples involving dynamic UAE (DUAE) with on-line purification of the extracts are still scarce in the literature. In open systems, the sample is placed in a refillable column, which is immersed in an ultrasonic bath, and the extraction solvent is flowed continuously through the sample and transferred on-line to instrumental analysis [38]. In closed systems, the column containing the sample is filled with the extraction solvent, placed in a water bath and sonicated with an ultrasonic probe while the solvent is moved back and forward within the extraction column to prevent sample compaction [39]. The purified eluent from this type of system can be collected in a microvial or on-line, and subjected to the next step of the analytical procedure.

Since its introduction some 20 years ago, under the commercial name of accelerated solvent extraction (ASE), PLE has experienced fast development and is a widely-accepted exhaustive, relatively green extraction technique for preparing (semi-)solid and viscous matrices. In PLE, a sample, typically dispersed on a drying or inert sorbent, is packed in a stainless-steel cell, inserted in a valve-based flow-through system, and extracted with a preselected solvent for a defined time at a specific temperature. In most applications, extraction temperatures above the solvent boiling point are used to ensure quantitative analyte recovery within a short extraction time. In

general, static extraction approaches have been preferred to dynamic ones, most probably to reduce solvent consumption and prevent analyte dilution. In all instances, the extraction pressure should be selected to keep the solvent as a liquid during the extraction process. PLE-extract purification can be done off-line or in-cell by packing an appropriate sorbent at the bottom of the extraction cell. The latter approach provides extracts ready for analysis. However, somewhat surprisingly, it is still less frequently used than could be anticipated on the basis of its simplicity and obviously advantageous features. The simplicity of optimizing PLE conditions, partly due to the nature of the process being essentially independent of analyte and matrix, is considered an extra advantage of this non-selective, efficient and fast extraction technique.

PLE is widely used for the treatment of environmental, food and plant samples, employing (large-scale) commercial instruments and sample sizes in the gram range and above. Treatment of small samples (i.e., below 1 g) is typically done with extraction cells of ~5 mL, which results in consumption of reagents and solvents (typically of a few grams and 50–100 mL) essentially identical irrespective of the initial amount of sample. Apart from undesirable analyte dilution, the large eluate volume makes it (virtually) impossible to couple these PLE systems with subsequent steps of the analytical process.

Use of extraction cells with a size adapted to that of the minimum sample amount required to ensure sample representativeness and analyte detectability would contribute to solving these shortcomings. However, none of the commercially-available systems fulfills these requirements, so miniaturized PLE is possible with only small-scale, home-made instruments. Setting up such an instrument is relatively simple and, as a proof of concept, micro-PLEs have been used for the determination of, e.g., endogenous PAHs [40] and chloroanilines [41] in soils and sediments, or PAHs in atmospheric particulate matter [42]. In these studies, only a few mg of sample were used for the analysis, which was done in a single step with minimum solvent consumption (i.e., less than 100 μL).

However, in most cases, large-volume injection became essential to ensure proper analyte detection. Miniaturized PLEs have also been used for the simultaneous extraction and purification of different classes of POPs from fat-containing biotic tissues [43] and feedstuffs [44]. In the former study, silica modified with sulfuric acid was used for MSPD of the investigated foodstuff and as co-sorbent for the in-cell removal of the remaining lipids. Using *n*-hexane as extraction solvent and relatively soft extraction conditions (40°C and 12 MPa), PCB extracts were ready for analysis in only 15 min with minimal consumption of reagents (3.5 mL of solvent and 3.5 g of sorbent).

In the latter study, essentially similar soft extraction conditions were used for the simultaneous extraction of PCBs and PBDEs from feedstuffs (50°C and 10.5 MPa). However, the highly sorptive nature of this matrix required an increase in selectivity of the extraction solvent to ensure quantitative recovery of PBDEs with reduced solvent consumption. After optimization, the PLE procedure consisted of two 10-min static extraction cycles using *n*-hexane and *n*-hexane:DCM (1:1, v/v) as extraction solvents. Complete sample preparation was done in a single step with only 8 mL of solvent and 3.5 g of sorbent. 250 mg of sample sufficed for accurate determination of endogenous PCBs and PBDEs in non-contaminated feedstuffs at the ng/g level.

The dynamic extraction mode has generally been adopted in on-line coupling of SWE with subsequent analyte separation plus detection, typically been done by LC [45]. In most of these applications, a GC oven was used as heating chamber due to the high temperatures at which water is heated in this technique (typically, 100–300°C). Since the extraction temperature is high, cell eluent requires cooling down and depressurization before analyte concentration. These extra elements complicate setting up such home-made devices, and could explain the limited progress in this field despite its remarkable analytical potential.

4. Conclusions

The analysis of trace components in complex (semi-)solid foodstuff and environmental samples is frequently recognized as a complex procedure that, in most cases, involves demanding, multistep, sample-preparation protocols requiring relatively large amounts of sample and reagents, long analytical times and generating much waste. The improved selectivity and sensitivity provided by most of the analytical instruments in use in modern laboratories would allow a significant reduction in the initial amount of sample used for these determinations without compromising the accuracy of determination, especially when combined with large-volume-injection techniques. However, compared to advances for liquid and viscous matrices, advances in miniaturizing the sample treatment of (semi-)solid matrices are still rather limited, for reasons that range from the greater complexity of the solid matrices to the lack of appropriate commercial miniaturized instrumentation required to implement some of these methodologies.

Despite these difficulties, research in this particular area has been increasing over the years. New concepts and different approaches have promoted further miniaturization of the processes and integration of several treatment steps has been reported. Interestingly, and in agreement with other application fields, available extraction techniques have benefited from advances achieved in other study areas, particularly new materials and nanotechnologies. Improved features associated with some of these novel nano-sized and biomimetic materials have been used to enhance the efficiency and/or the selectivity of analytical protocols, stimulating new advances and application studies, but also modifying our conventional approach to method development and demanding deeper understanding of the processes involved in sample treatment.

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