ELSEVIER

Journal of Chromatography A, 902 (2000) 227–250

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Review

Analytical-scale microwave-assisted extraction

Cecilia Sparr Eskilsson*, Erland Björklund

Department of Analytical Chemistry, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

Abstract

Microwave-assisted extraction (MAE) is a process of using microwave energy to heat solvents in contact with a sample in order to partition analytes from the sample matrix into the solvent. The ability to rapidly heat the sample solvent mixture is inherent to MAE and the main advantage of this technique. By using closed vessels the extraction can be performed at elevated temperatures accelerating the mass transfer of target compounds from the sample matrix. A typical extraction procedure takes 15–30 min and uses small solvent volumes in the range of 10–30 ml. These volumes are about 10 times smaller than volumes used by conventional extraction techniques. In addition, sample throughput is increased as several samples can be extracted simultaneously. In most cases recoveries of analytes and reproducibility are improved compared to conventional techniques, as shown in several applications. This review gives a brief theoretical background of microwave heating and the basic principles of using microwave energy for extraction. It also attempts to summarize all studies performed on closed-vessel MAE until now. The influences of parameters such as solvent choice, solvent volume, temperature, time and matrix characteristics (including water content) are discussed.

Keywords: Reviews; Microwave-assisted extraction; Extraction methods; Pharmaceutical analysis; Pesticides; Phenols; Metals; Polymers; Polynuclear aromatic hydrocarbons; Polychlorinated biphenyls

Contents

*Corresponding author. Fax: +46-46-222-4544.
E-mail address: cecilia.sparr_eskilsson@analykem.lu.se (C. Sparr Eskilsson).

0021-9673/00/$ – see front matter
PII: S0021-9673(00)00921-3

1. Introduction

Qualitative and quantitative analysis concludes a procedure of sample preparation. The extraction step is the least evolved part of most analytical procedures, and still today Soxhlet extraction (developed by F. Soxhlet in 1879) is of use in many routine laboratories. In the last decade there has been an increasing demand for new extraction techniques, amenable to automation, with shortened extraction times and reduced organic solvent consumption — preventing pollution in analytical laboratories and reducing sample preparation costs [1,2]. Driven by these purposes advances in sample preparation have resulted in a number of techniques such as microwave-assisted extraction (MAE) [3–5], supercritical fluid extraction (SFE) [6–8] and pressurised liquid extraction (PLE, Dionex trade name ASE, for accelerated solvent extraction) [9]. The similarity between these techniques is the possibility of working at elevated temperatures and pressures, which drastically improves the speed of the extraction process. Table 1 summarizes the most common extraction techniques for solid matrices and presents their advantages and drawbacks.

One of the main advantages using MAE is the reduction of extraction time when applying microwaves. This can mainly be attributed to the difference in heating performance employed by the microwave technique and conventional heating. In conventional heating a finite period of time is needed to heat the vessel before the heat is transferred to the solution, while microwaves heat the solution directly. This keeps the temperature gradient to a minimum and accelerates the speed of heating. Additionally MAE allows for a significant reduction in organic solvent consumption as well as the possibility of running multiple samples. These are of course minimum criteria for modern sample preparation techniques and are all fulfilled to a great extent by MAE. Consequently MAE is an attractive alternative to conventional techniques, as seen by the increasing number of scientific papers published during the last years (Fig. 1).

This review gives a short theoretical background of microwave heating and the basic principles of using microwave energy for extraction. The influence of parameters such as solvent choice, solvent volume, temperature, time and matrix characteristics (including water content) are discussed. Two types of microwave heating systems are commercially available for the analytical laboratory: an open- and a closed-vessel system. This paper focuses on closed-vessel MAE, which is normally used in analytical scale laboratories, and attempts to summarize all studies performed until now. The reader interested in open-style systems, usually called focused Soxhlet extraction or focused microwave-assisted solvent extraction (FMASE), should read excellent papers by Letellier et al. [10,11] and Garcia-Ayuso and coworkers [12–14].

2. The history of analytical-scale microwave-assisted extraction

Although microwave energy has great potential for rapidly heating materials, microwave ovens have

Table 1
Comparison of traditional and recent extraction techniques

	Extraction technique					
	MAE	FMASE	PLE	SFE	Soxhlet	Sonication
Brief description	Sample is immersed in a microwave-absorbing solvent in a closed vessel and irradiated with microwave energy.	Sample is immersed in a microwave-absorbing solvent in an open vessel and irradiated with microwave energy.	Sample and solvent are heated and pressurized in an extraction vessel. When the extraction is finished, the extract is automatically transferred into a vial.	Sample is loaded in a high pressure vessel and extracted with supercritical fluid (most commonly carbon dioxide at pressures of 150–450 bar and temperatures of 40–150°C). The analytes are collected in a small volume of solvent or onto a solid-phase trap, which is rinsed with solvent in a subsequent step	Sample is placed in a glass fibre thimble and, by using a Soxhlet extractor, the sample is repeatedly percolated with condensed vapours of the solvent.	Sample is immersed in solvent in a vessel and placed in an ultrasonication bath.
Extraction time	3–30 min	10–60 min	5–30 min	10–60 min	3–48 hrs	10–60 min
Sample size	1–10 g	1–30 g	1–30 g	1–5 g	1–30 g	1–30 g
Solvent usage	10–40 ml	10–150 ml	10–100 ml	2–5 ml (solid trap) 5–20 ml (liquid trap)	100–500 ml	30–200 ml
Investment	Moderate	Moderate	High	High	Low	Low
Advantages	• Fast and multiple extractions • Low solvent volumes • Elevated temperatures	• Fast extractions • Low solvent volumes	• Fast extractions • Low solvent volumes • Elevated temperatures • No filtration required • Automated systems	• Fast extractions • Minimal solvent volumes • Elevated temperatures • Relatively selective towards matrix interferences • No clean-up or filtration required • Concentrated extracts • Automated systems	• No filtration required	• Multiple extractions
Drawbacks	• Extraction solvent must be able to absorb microwaves • Clean-up step needed • Waiting time for the vessels to cool down.	• Extraction solvent must be able to absorb microwaves • Clean-up step needed • Waiting time for the vessels to cool down.	• Clean-up step needed	• Many parameters to optimize, especially analyte collection.	• Long extraction times • Large solvent volumes • Clean-up step needed	• Large solvent volumes • Repeated extractions may be required • Clean-up step needed

only recently appeared in analytical laboratories. In 1975 Abu-Samra et al. were the first researchers ever to use a microwave domestic oven in the laboratory, performing trace analysis of metals from biological samples [15]. Since then microwave digestion methods have been developed for different sample types such as environmental, biological, geological, and metallic matrices, as well as for fly ashes and coal. Over the years procedures based on microwave ovens have replaced some of the conventional hot plate and other thermal digestion techniques that have been used for decades in chemical laboratories. Applications of microwave-assisted techniques in other fields of analytical chemistry, such as sample

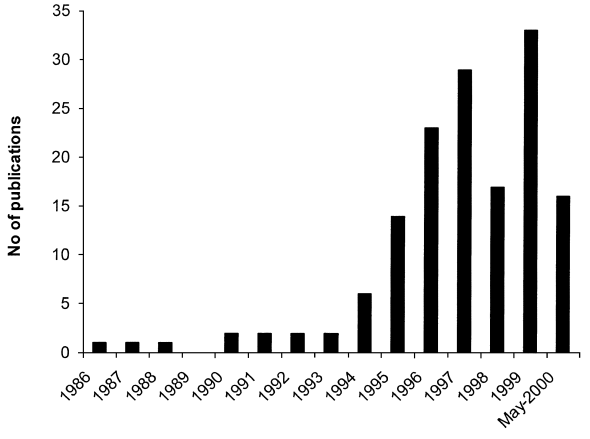

Fig. 1. Number of scientific publications on closed-vessel MAE from 1986 to May 2000, based on a search in Chemical Abstracts.

drying, moisture measurements, chromogenic reactions, speciation and nebulization of sample solutions can be found in a recent review by Jin et al. [16].

From digestion procedures, the step to extraction procedures is not far. Even so, it would take more than 10 years before the first publication on extractions appeared. In a paper from 1986, Ganzler et al. [17] presented the extraction of crude fat and antinutrients from food and pesticides from soil. They applied the same solvents as normally used in Soxhlet. Between 0.5 and 1 g of sample was extracted in 2–3 ml solvent for less than 5 min using a microwave oven commonly used in the kitchen. The reported recoveries were comparable with values obtained with conventional methods. Other early papers, by the same author, dealt with the extraction of pyrimidine-glucoside in seeds and fava beans [18], and the extraction of drugs from seeds and rat faeces [19]. A patented variant of MAE is the microwave-assisted process (MAP) developed by Environment Canada [20]. MAP applications mainly cover extractions of substances from biological materials and extend from analytical-scale methods to industrial processes. The first application of MAP was performed in 1991 and dealt with the extraction of essential oils from plant products [21].

In the beginning of the 1990s various research groups in Europe started to use microwave ovens (built for digestion) for the extraction of additives from polyalkenes [22,23] using solvents as trichloroethane and mixtures of acetone and heptane. In 1993, Onuska and Terry [24] evaluated the extractability of various pesticides in sediment samples. Extraction parameters such as solvent choice, moisture level and extraction time were investigated. In the same year Steinheimer [25] extracted atrazine from soils and water samples. In the food technology area, Greenway and Kometa [26] extracted vitamins from foodstuffs. These works were followed by an extensive paper by the group of Lopez-Avila [27], presenting extraction procedures of organic compounds such as polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and phenols among others from standard reference soils and sediments. This work was part of an evaluation of new sample preparation techniques initiated by the US Environmental Protection Agency (EPA). This was also the starting point for numerous laboratories to study the analytical possibilities of MAE in environmental applications. Since then, microwave heating has been applied to extract organic contaminants, such as PAHs [28–30], polychlorinated biphenyls (PCBs) [29,31,32], pesticides [33–36], phenols [37,38] and metals [39–41] from various matrices, e.g., soils, sediments and atmospheric particles. Today MAE has become relatively mature and some standard methods have been published, mainly for organic compounds in solid matrices [42–45].

3. Basic principles

3.1. Heating using microwave energy

The principle of heating using microwave energy is based on the direct effect of microwaves on molecules by ionic conduction and dipole rotation. In many applications these two mechanisms take place simultaneously. Ionic conduction is the electrophoretic migration of ions when an electromagnetic field is applied. The resistance of the solution to this flow of ions will result in friction and, thus, heat the solution. Dipole rotation means realignment of dipoles with the applied field. At 2450 MHz, which is the frequency used in commercial systems, the dipoles align and randomize 4.9×10^{9} times per

second and this forced molecular movement results in heating [46–48].

The ability of a solvent to absorb microwave energy and pass it on in the form of heat to other molecules will partly depend on the dissipation factor (tan δ). The dissipation factor is given by the following equation [46,48,49]:

$$\tan \delta = \varepsilon''/\varepsilon'$$

where ε'' is the dielectric loss (a measure of the efficiency of converting microwave energy into heat) and ε' is the dielectric constant (a measure of the polarizibility of a molecule in an electric field). Polar molecules and ionic solutions (usually acids) will absorb microwave energy strongly because they have a permanent dipole moment that will be affected by the microwaves. However non-polar solvents such as hexane will not heat up when exposed to microwaves. In Table 2, selected physical parameters, including dielectric constants and dissipation factors, are shown for solvents that are used in more than 90% of the applications.

A simple comparison between methanol and water shows that methanol has a lower dielectric constant but a higher dielectric loss than water. This indicates that methanol, compared to water, has lower ability to obstruct the microwaves as they pass through, but a higher ability to dissipate the microwave energy into heat. In closed vessels, the solvent can be heated well above its normal boiling point, thus enhancing extraction efficiency and speed. Some elevated temperature values for commonly used solvents are also presented in Table 2.

The fact that different chemical substances absorb microwave energy to different extents implies that the heating imparted to the surrounding media will vary with the chemical substances used. Hence, for samples with non-homogeneous structural characteristics, or that contain various chemical species with different dielectric properties dispersed into a homogeneous environment, it is possible to produce a selective heating of some areas, or components of the sample. This phenomenon is sometimes called superheating. More theoretical considerations about superheating effects and superheating behaviour of different solvents can be found in a paper by Baghurst and Mingos [50].

3.2. Extracting solvent mechanisms

The extraction heating process may occur by a number of mechanisms: the sample could be immersed in a single solvent or mixture of solvents that absorb microwave energy strongly (Mechanism I); the sample could be extracted in a combined solvent containing solvents with both high and low dielectric losses mixed in various proportions (Mechanism II); samples that have a high dielectric loss can be extracted with a microwave transparent solvent (Mechanism III) [48]. Usually extractions and partitioning of solutes may occur by any one of these

Table 2
Physical constants and dissipation factors for some solvents commonly used in MAE. All data from Ref. [48]

Solvent	Dielectric constant[a], ε'	Dipole moment[b]	Dissipation factor, tan δ ($\times 10^{-4}$)	Boiling point[c] (°C)	Closed-vessel temperature[d] (°C)
Acetone	20.7			56	164
Acetonitrile	37.5			82	194
Ethanol	24.3	1.96	2500	78	164
Hexane	1.89			69	–[e]
Methanol	32.6	2.87	6400	65	151
2-Propanol	19.9	1.66	6700	82	145
Water	78.3	2.3	1570	100	
Hexane–acetone (1:1)				52	156

[a] Determined at 20°C.
[b] Determined at 25°C.
[c] Determined at 101.4 kPa.
[d] Determined at 1207 kPa.
[e] – indicates no microwave heating.

three heating mechanisms or as a combination. This topic is discussed in more detail in Section 5.2.1.

4. Instrumentation

The experimental set-ups as they appeared in the first publications and also in some later investigations, were mainly laboratory-built systems based on domestic ovens [19,51,52]. Today MAE equipment designed for laboratory purposes is safe to work with and offers the user various ways to control the extraction process. Commercial systems used for closed-vessel MAE consist of a magnetron tube, an oven where the extraction vessels are set upon a turntable, monitoring devices for controlling the temperature and pressure, and a number of electronic components.

The extraction process starts with loading of the sample into the extraction vessel, followed by solvent addition and closing of the vessel. Microwave radiation is applied and a pre-extraction step is initiated in order to heat the solvent to the set values. The time needed to reach the set values will depend on the effect applied as well as the number and type of samples. Normally the heating takes less than 2 min. The sample is further irradiated and extracted for a certain time (static extraction step), usually in the range of 10–30 min. When the extraction is concluded the samples are allowed to cool down to a temperature reasonable to handle (normally not exceeding 20 min). Prior to analysis the addition of an internal standard and/or a clean-up step might be of need.

4.1. Microwave-assisted systems

A commonly used commercial closed-vessel system (based on the number of published scientific papers) is the MES-1000 microwave solvent extraction system, supplied by CEM (Matthews, NC, USA) from which the authors also have experience. This system allows for up to 12 extraction vessels to be irradiated simultaneously, applying 950 W of microwave energy at 100% power. One of the vessels is a reference vessel controlling heat and pressure. The pressure is measured by means of a water manometer and the temperature probe is a fiber optic with a phosphorous sensor, which allows temperatures in the range of 20–200°C to be selected. Extraction conditions such as the percentage power input, the pressure and the temperature can be varied accordingly. The samples are placed into lined Teflon PFA (perfluoroalkoxy) vessels with a volume of 100 ml. The vessels are located in a carousel, which rotates through 360° during the operation. In the center of the carousel and connected to each vessel is a chamber, which acts as a collection vessel for escaping vapors in the event of solvent leakage.

A product review presenting various microwave systems has previously been published by Erickson [53]. In Table 3, an up-to-date presentation of closed-vessel instruments available on the market is shown. All systems included in the table have temperature and pressure control units, except the MWS-1, which has no temperature control. It should be pointed out that only two systems (CEM's MARS-5 and Milestone's Ethos SEL) are dedicated for extraction with organic solvents. All other sys-

Table 3
Summary of commercially available closed-vessel microwave-assisted extraction/digestion systems

	Manufacturer						
	Anton Paar	Berghof	CEM	Milestone	Ol Analytical	Plazmatronika	Questron Tech.
	www.anton-paar.com	www.berghof.com	www.cemx.com	www.milestonesci.com	www.oico.com	www.plazmatronika.pl	www.qtechcorp.com
Model	Multiwave	MWS-1	MARS 5	Ethos SEL	Model 7195	UniClever	QLAB 6000
Max. number of samples	12	6	14	50	12	1	12
Special features	Magnetic stirrer Vessel cooling system		Magnetic stirrer Carboflon® inserts	Magnetic stirrer Weflon™ inserts	Waterless pressure sensor		Vessel cooling system
Adaptation to solvent extraction	No	No	Yes, built-in solvent detector	Yes, built-in solvent sensor	No	No	No

tems presented in Table 3 are mainly built for digestion procedures. For security reasons it is not always recommended by the manufacturers of the digestion systems to use their systems for extraction purposes.

Many of the newer versions of equipment incorporate multiple extractions of more than 12 samples. The option to have magnetic stirring in each extraction vessel is also featured in some systems. Efficient stirring allows for a continuous contact of the sample surface with fresh solvent. Positive effects of mixing during the MAE procedure has been reported for food applications [54]. When crop suspensions were mixed with magnetic stirrers in the vessels the temperature reached the maximum value within a shorter time, and hence shortened the total extraction time.

CEM's Carboflon and Milestone's Weflon bars are chemically inert fluoropolymer, which absorb microwave energy and transfer heat to the surrounding medium. The polymer bars can therefore be used to heat non-polar solvents. Weflon has for example been used with hexane for the extraction of organochlorine compounds from fatty tissues [55,56].

4.2. Safety features

All commercial systems usually include specific safety features such as rupture membranes for the extraction vessels. These membranes are designed to burst at pressures exceeding 200 p.s.i. (ca. 14 bar). Other safety features are a solvent vapor detector (which interrupts the supply of microwaves when detecting traces of solvent), an exhaust fan to evacuate air from the instrument cavity, and finally an isolator that diverts reflected microwave energy into a dummy load to reduce the microwave energy within the cavity. The manufacturer Milestone offers equipment with resealable vessels that are secured with a calibrated torque wrench. If the pressure exceeds the vessel limits, a spring device allows the vessel to open and close quickly, thus releasing the excess pressure. Another safety feature is the movable wall, preventing the door from being blown away. The door moves in and out releasing pressure from the microwave cavity.

Most manufacturers offer more than one type of vessel which differ in terms of materials, volumes, and capability of withstanding pressures. The vessels are typically made of microwave transparent materials (e.g., glass, polyether imide or tetrafluoromethoxyl) and are lined with PFA or Teflon liners. Vessel volumes in the range of 100–270 ml are available. Typical pressures reached with closed-vessel systems are below 200 p.s.i., but today's technology can handle up to 1500 p.s.i. (CEM's MARS-5, Milestone's Ethos-1600 and Plazmatronika's UniClever system).

5. Method development

5.1. Pretreatment

In many applications the sample is pre-treated prior to loading into the extraction vessel. Since most applications are based on environmental samples such as soils, sediments and similar matrices, the first step involves either air-drying [57,58] or freeze-drying [28,39,59], sometimes followed by a grinding and/or sieving procedure. The particle sizes of the extracted materials are in the range of 100 μm–2 mm. In some cases the pre-treatment can be in the opposite order beginning with wet sieving followed by a drying step [32]. Pellets of polymers for the extraction of additives are usually freeze-ground prior to the extraction [23,60]. For other applications dealing with food and tissue matrices, once again freeze-drying [52,61,62], homogenization [33,63] and/or grinding [52] seem to be the most commonly used pre-treatments.

In resemblance to Soxhlet, SFE and PLE it has been suggested that anhydrous sodium sulfate can be added to soil samples to handle water during the MAE procedure [38]; and anhydrous sodium sulfate has been used as an absorbent for more liquid-like samples such as grape juice [64]. Likewise, for must samples, the absorbing agent Amberlite XAD-2 has been utilized [65]. Soil samples have in some cases been mixed with activated charcoal to decrease analyte–matrix interactions [37]. For soils and sediments the effect of soaking the sample in water prior to the extraction has been evaluated [58,66], since water in the matrix may increase the extraction efficiency. A combined sample preparation methodology was used for water samples containing

organic pollutants, which were extracted with solid-phase extraction (SPE) discs followed by a second extraction step of the SPE discs using MAE [67].

5.2. Parameter's influence on the extraction process

Optimization of MAE conditions has been reported in several applications. Many researchers have used factorial, central composite and orthogonal array designs to find optimal conditions [39,68,69]. The most commonly studied parameters are solvent composition, solvent volume, extraction temperature, extraction time and matrix characteristics including water content.

5.2.1. Choice of solvent

A correct choice of solvent is fundamental for obtaining an optimal extraction process. When selecting solvent, consideration should be given to the microwave-absorbing properties of the solvent, the interaction of the solvent with the matrix, and the analyte solubility in the solvent. Preferably the solvent should have a high selectivity towards the analyte of interest excluding unwanted matrix components. Another important aspect is the compatibility of the extraction solvent with the analytical method used for the final analysis step. Optimal extraction solvents cannot be deduced directly from those used in conventional procedures. If the solvent molecule is not able to absorb microwave energy there will be no heating and hence no effective extraction.

Recalling the mechanisms described in Section 3.2, Mechanism I (a single solvent that absorbs microwave energy strongly) can be exemplified by the extraction of atrazine with water [70]. Likewise, pure ethanol (95%) can be used as a cheap solvent for the extraction of taxanes [71]. Dichloromethane (DCM) was found to be the optimum solvent for the extraction of low-molecular mass oligomers [72], while pure tetrahydrofuran (THF) was proven the best extractant for OCPs [73]. In some cases aqueous buffers (pH 10) have been utilized as for the extraction of imidazolinone herbicides [36], while Pino et al. used an aqueous solution of polyoxyethylene 10 lauryl ether (POLE) to extract PAHs from marine sediments [74]. Mechanism I also includes mixtures of strongly absorbing solvents seen in the extraction of felodipine from tablets [75]. During the method development the tablets were extracted with pure acetonitrile (ACN), pure methanol (MeOH), or a mixture of the two solvents. It was observed that small changes in solvent composition had large effects on the recoveries. The optimized solvent composition was found to be ACN–MeOH (95:5). Another example of using a solvent mixture is the extraction of atrazine and its polar metabolites that can be recovered from soils using DCM–MeOH (90:10) [35]. The use of this organic solvent provided a significant increase in selectivity in comparison to a basic aqueous solvent. Additionally, arsenic species were extracted from fish tissue using MeOH–water in the proportions (80:20) [76].

Mechanism II involves extraction with solvent mixtures containing solvents with both high and low dielectric losses. One of the most commonly used mixtures is hexane–acetone (1:1). Hexane will not heat in a microwave field but by mixing it with acetone heating will take place in a few seconds. Lopez-Avila et al. extracted 95 EPA listed semivolatile organics and found hexane–acetone (1:1) to be a promising extractant [77]. This solvent mixture has also been found advantageous for environmental contaminants such as PAHs [28,30,78], linear aliphatic hydrocarbons [79], phenols [38], OCPs [80] and phthalate esters [81]. Barnabas et al. [82] studied the effect of hexane–acetone ratio on PAHs recovery and found that the recoveries increased with an increased amount of acetone. For the extraction of PCBs from soil and sewage sludge, Enders and Schwedt found the highest recoveries using hexane–acetone in the proportions (3:1) [59]. Other mixtures of two organic solvents working according to mechanism II are ethyl acetate–cyclohexane (1:1), for the extraction of organochlorine compounds [63] and isooctane–acetone (1:1), for the extraction of PAHs [78]. Instead of using two organic solvents some approaches have incorporated water in a non-microwave absorbing solvent in order to improve the heating rate and polarity. Most commonly a small amount of water (10%) is added to hexane, xylene, or toluene [66].

When having a sample with a high dielectric loss (e.g., high water content), efficient extractions can be performed using pure, microwave transparent sol-

vents (Mechanism III). This is possible since the water inside the sample matrix will be locally heated. One example of this is the extraction of essential oils from plant materials applying MAP which is based on the fact that microwaves interact with the free water molecules present in the glands and vascular systems. Thus, such systems undergo a dramatic expansion, with subsequent rupture of the tissue, allowing the essential oil to flow towards the organic solvent [20].

5.2.2. Solvent volume

The amount of solvent needed for a single sample is often in the range of 10–30 ml. In some cases solvent volume may be an important parameter for efficient extractions. The solvent volume must be sufficient to ensure that the entire sample is immersed, especially when having a matrix that will swell during the extraction process. Hydrocarbons have been extracted from sediment samples in the range of 1–15 g with solvent volumes between 10 and 30 ml [79]. This investigation led to the conclusion that the proportion of sample in the extraction solution should not exceed 30–34% (w/v). Generally in conventional extraction techniques a higher volume of solvent will increase the recovery, but in MAE a higher solvent volume may give lower recoveries. This phenomenon has been shown by several groups. PCBs and PAHs were extracted from sewage sludge with decreased recoveries when the solvent volume was increased from 30 to 56 ml [83]. Chee et al. also reported this effect when extracting PAHs from 5 g sediment [28], where 30 ml solvent gave higher recoveries than 45 ml. Extraction of pharmaceutical tablets showed that when using larger volumes than 30 ml the tablets did not crack, resulting in lowered recoveries of the target compound. This was probably due to inadequate stirring of the solvent by the microwaves [75]. In the food technology area, free amino acids have been extracted from various foodstuffs [54], and samples containing relatively high amounts of proteins and fats showed higher yields when the extraction was performed with lower solvent volumes. However, the solvent volume did not influence the relative composition of the amino acids.

In some cases very small volumes are sufficient as demonstrated for phenol and methylphenol extracted from soils with 10 ml as the optimum volume for sample size up to 5 g [84]. For liquid samples, 10 ml solvent were enough to extract monoterpenols from 5 ml of must [85]. Daghbouche et al. found that at least 7 ml of solvent were needed to ensure a quantitative extraction of 0.2 mg oil from 25 ml water [86].

5.2.3. Temperature

The most investigated parameter in MAE is the extraction temperature, which is not surprising since the temperature is an important factor contributing to increased recoveries, not only for MAE but for all extraction techniques. When MAE is conducted in closed vessels, the temperature may reach well above the boiling point of the solvent. These elevated temperatures result in improved extraction efficiencies, since desorption of analytes from active sites in the matrix will increase. Additionally, solvents have higher capacity to solubilize analytes at higher temperatures, while surface tension and solvent viscosity decrease with temperature, which will improve sample wetting and matrix penetration, respectively. However as seen from the discussion below the effects of temperature are not always intuitive.

In several papers, above all in environmental applications, the usage of higher temperatures (100°C or more) often resulted in increased recoveries. These compounds are very insensitive to breakdown as demonstrated by Lopez-Avila et al. in a stability study for a number of organic pollutants during MAE [87]. When increasing the temperature from 50 to 145°C the recoveries of basic compounds decreased by about 10%, while for PAHs no significant decrease was observed. Consequently rather high temperatures can be applied during the extraction step. The optimum temperature for extraction of organic pollutants such as PAHs and petroleum hydrocarbons from soils and sediments was 115°C [28,88]. PAHs have also been extracted from spiked wood applying 120°C as the optimum temperature [89]. When extracting pesticides as triazines from soil, the optimal temperature depended on the polarity of the analyte as well as the type of soil, but temperatures between 80 and 100°C gave acceptable recoveries [34]. In other cases the extraction temperature influenced the extraction efficiencies to a

very small extent as demonstrated for several organic pollutants from standard reference soils and sediments [27]. Similar results were reported for the extraction of phthalate esters [81]. Two independent papers reported that there was no improvement in the recoveries of OCPs from sediments by raising the temperature from 100 to 120°C [73,80]. Several pesticides were extracted from crops at temperatures in the range of 80–120°C. The effect of temperature was significant only for one of the substances (chlorothalonil in lettuce) with 80°C giving the best recovery [33].

In applications dealing with thermolabile compounds, high temperatures may cause degradation of analytes. This has been reported for the extraction of sulfonylurea herbicides [35], applying settings normally used for triazines (ca. 100°C). The recoveries obtained were low, most probably due to decomposition of the analytes. Hence milder conditions were studied and the temperature had to be below 70°C to get full recoveries. Similar temperature effects have been observed when extracting spiked aromatic amines from leather at 40–80°C (C. Sparr Eskilsson and L. Mathiasson, Department of Analytical Chemistry, Lund University, Sweden, unpublished results). The lower temperature was preferable for this type of compounds.

For the extraction of amino acids from food, extraction temperatures between 40 and 80°C were investigated for two matrices [54]. For cauliflower the temperature had no effect on the extraction yields at values exceeding 40°C, but in the case of cheese a slight increase in recovery was obtained between 40 and 50°C.

In the polymer area, temperature often has a great effect on the recoveries. Because of the heating, the polymer undergoes swelling that makes it more permeable to the solvent. Marcato and Vianello extracted additives in polyalkenes and they demonstrated that a temperature of 125°C is optimal for a good extraction of additives from highly crystalline matrices [90]. Temperatures above 125°C may cause polymer collapse or fusion, while temperatures below 125°C may give insufficient swelling effects on these matrices with an accompanying incomplete recovery. Polymer matrices with a high content of amorphous fractions must be extracted at temperatures below 125°C, because at this temperature they collapse or they become excessively soluble in the extraction solvent used. This will give overall lower recovery of additives via encapsulation in the polymer when it coagulates at room temperature [90]. Costley et al. extracted oligomers from poly(ethylene terephthalate) (PET) film [72]. The optimal extraction temperature was set to 120°C and it was found that temperatures in excess of 125°C led to polymer fusion, which obstructed the extraction efficiency.

5.2.4. Extraction time

Extraction times in MAE are very short compared to conventional techniques. Often 10 min are sufficient, which is exemplified by the extraction of organic pollutants [27,81], but even 3 min have been demonstrated to give full recovery for pesticides from soils and sediments [24,70]. In the extraction of sulfonylurea herbicides from soils it was demonstrated that increasing the extraction time from 5 to 30 min did not adversely affect the recovery [35]. This was also found by Stout et al. when extracting the fungicide dimethomorph from soil [91]. No difference in recovery was found using 3 or 45 min extraction time. When extracting amino acids from food, no improvement in the extraction efficiency was observed applying longer irradiation times [54]. Additionally there was no evidence of breakdown or alteration of the amino acids caused by longer extraction times.

With thermolabile compounds, long extraction times may result in degradation, which was reported for the extraction of pesticides [33]. The extraction time was significant for one of the substances yielding the best recovery at the shortest time investigated (10 min). This was also observed in the extraction of aromatic amines from leather, where the recovery of some amines decreases with increasing extraction time, while others were unaffected (C. Sparr Eskilsson and L. Mathiasson, Department of Analytical Chemistry, Lund University, Sweden, unpublished results). For the extractions of pharmaceutical tablets a decrease in recovery could be seen when using an extraction time of 60 min or more [75]. This was explained by increased dissolution of the polymer matrix at longer extraction times, causing an increase in viscosity, which makes the matrix encapsulate the target analyte. Another polymer application (oligomers from PET film) showed that

by increasing the temperature to 125°C, comparable results to those obtained at 120°C and 120 min, could be reached already after 30 min [72].

5.2.5. Matrix characteristics and water content

The nature of the matrix in which the analytes of interest are bound can have a profound effect on the recoveries of the compounds. This has been illustrated by spiking experiments, where solid samples were spiked with the analytes of interest, and compared with extractions of native soils. In almost all cases higher recoveries were obtained from the spiked samples, demonstrating the effect of the stronger binding to the matrix in native samples [82]. In a study by Lopez-Avila et al. [77], recoveries for freshly spiked compounds in soil were reasonable, while the effects of aging showed a clear decrease for many of the contaminants. About 80% of the freshly added compounds had recoveries of between 80 and 120% for both OCPs and semivolatiles, while organophosphorus pesticides (OPPs) showed a slightly lower value (about 70% of the compounds were in this recovery range). However, the number of compounds with recoveries in the range of 80–120% decreased to 60 and 50% for OCPs and semivolatiles, respectively, after 24 h of aging, while the recoveries for OPPs were relatively unchanged even after 3 weeks of aging. Decreasing recoveries resulting from aging of matrices is a well-known phenomenon from studies performed with other sample preparation techniques such as SFE, and can be explained by native analytes being more strongly bound to the matrix than spiked due to longer contact times [92–96]. It is of course important to be aware of these aging effects when performing method development in order to achieve appropriate methods capable of exhaustive extractions.

According to a work by Lopez-Avila et al. [27] method performance was a function of the matrix for the extraction of organic pollutants. Four standard reference marine sediments and two certified soils were subjected to the same MAE method, and the recoveries of PAHs ranged from 60 to 100%. It was difficult to establish though, whether the recovery also was a function of analyte concentration since the different reference materials had different concentration levels. In another paper, PCBs were spiked and extracted from clay soil, topsoil and sand [97], where the highest recoveries were obtained for the sand matrix. Frost et al. investigated the extractability of a fungicide from weathered soil samples including a sandy loam soil and a sandy clay soil. The lowest recoveries were achieved for the sandy loam soil, which has the highest content of organic matter [98]. When several pesticides were extracted from crops (lettuces and tomatoes) the recoveries obtained for some of the compounds in the study were three times higher when extracting from tomatoes as compared to lettuce. This indicated that the extraction efficiency depended on the type of crop matrix [33].

In many cases the matrix moisture improves the extraction recoveries. With respect to soil and sediment samples, there are discussions whether the sample should be in a wet or a dry state for the extraction to be as efficient as possible. The effect of this parameter, of course, also depends on the extraction solvent used in the method. Except for increasing the polarity of the extracting solvent, the water added (or naturally occurring in the sample) will always have an effect on the microwave-absorbing ability and hence facilitate the heating process. It may also have a swelling effect on the matrix and/or influence the analyte–matrix interactions, making the analytes more available to the extracting solvent. In an early work on extraction of pesticides from sediments, the moisture of the sediment was a significant parameter for good recoveries. The best recoveries were obtained at a water level of 15% (which was also the saturation level of the sediment) using isooctane as extraction solvent [24]. Similar investigations were performed where the objectives were to study the general effect of water in MAE and how it can effect the extraction of OCPs from soil with hexane as the extraction solvent. These experiments were done with peat, due to its high organic matter content. Different percentages of water (0–45%) added to the soil were assayed and it was found that an addition of water between 15 and 25% gave an efficient extraction. It was concluded that it is not possible to perform a good MAE for completely dry as well as very wet samples when hexane is used as the extraction solvent [99]. Examples where the moisture of the matrix seemed not to affect the recoveries were in the extraction of PAHs from wet (20% water) and dry soil [27,87] and extraction of

hydrocarbons from marine sediment [79]. Extractions performed with different combinations of solvents have demonstrated that recoveries of neutral compounds (mainly benzene and phthalate substances) are higher for dry soils than for wet soils [87]. The recoveries of basic compounds, benzoic acid, and to some extent phenolic compounds were higher from wet soil than those from dry soil. The saturation of peat soil with water had a positive effect on the extraction efficiency when applying MAP for the extraction of contaminants using hexane–acetone (1:1) as solvent [78]. This increase could be attributed to the fact that the water added to peat might be trapped within the organic matter structure. When the water was heated, the structure of the organic matter was disrupted, releasing bound contaminants that could not be extracted from the relatively dry peat sample. Herbicide extractions from humic rich sandy soil samples using DCM–MeOH (90:10) showed full recoveries when the samples were mixed with water (10%), but decreased recoveries were observed when the amount of water exceeded 10% [58].

Other applications where the moisture effect has been examined are extractions of biomass and tissue. If the biomass was freeze-dried to a moisture level of less than 10% and additionally soaked in water prior to extraction, full recovery of a taxane compound was achieved [71], but the extraction of a drug from swine tissue showed that higher recoveries were obtained from freeze-dried samples compared to wet samples [62].

5.2.6. Other parameters

Elevated pressures are used mainly to keep the solvent at temperatures higher than their boiling point (at atmospheric pressure). An improved extraction might also be achieved for analytes trapped in matrix pores, by the organic solvent being forced into the pores at higher pressures. Due to the correlation between the temperature and the pressure, temperature is often the investigated parameter. When using ovens without temperature control, the pressure in the vessel may instead be optimized [38,40,70].

The choice of power setting is governed by the number of vessels processed simultaneously (e.g., the total volume of solvent that will be heated). The power should be chosen to minimize the time needed to reach the set temperature and to avoid a ''bumping'' phenomenon in temperature during the extraction. Young investigated the influence of applied power on the extraction of a fungal metabolite from spores [52]. The highest recovery was obtained at a power of 375 W. At higher power (750 W), problem with tubes leaking materials occurred. The influence of irradiation power on the time required for the microwave extraction has been investigated for the extraction of hydrocarbons in soil [79]. At 300 W the time required to obtain good recoveries was 9 min and at 500 and 700 W the best results were achieved within 6 min. Extractions of mineral oils showed that recoveries increased with increasing time and power. At 520 W only 1 min was required, whereas at 130 W about 7 min was needed for a quantitative extraction [100].

The extraction process might also be influenced by pH. Stout et al. demonstrated that with increasing pH the recoveries of herbicides in soil increased, but the extracts became darker due to co-extracted humic acids [36].

In some applications the effect of sample weight (analyte concentration) has been investigated. In the case of the extraction of atrazine from soil, the sample weight did not play an important role [70]. When varying the ratio (grams of biomass and milliliters of extraction solvent) from 0.12 to 0.24 for the extraction of taxanes, a slight decrease in recovery was found [71]. This parameter though, is dependent on the concentration (unknown) of the target compounds and the sensitivity of the detection in the final analysis step.

5.3. Additional clean-up

In a majority of the MAE applications, a more or less laborious clean-up step is required before the final analysis. A minor step could be a simple filtration of the extract using glass wool [24,27], glass microbore filters [57] or membrane syringe filters [75]. Instead of filtration, a centrifugation step, with or without cooling, can be performed to separate the extract from particles [29,51,70]. In the case of sediments rich in organic matter a centrifugation step was found necessary prior to analysis [101].

More extensive clean-up procedures have been

performed using solid-phase microextraction (SPME) [102] and disposable SPE cartridges packed with C_{18} [98,103], silica [104] or ion-exchange material [105] for removal of interfering compounds. Extracts from fatty tissue and highly contaminated samples have been cleaned by gel permeation chromatography [55,106,107]. When extracting PCBs from environmental matrices, alumina columns [59,108] or silica columns [32] have been used to remove very polar compounds. MAE procedures of pesticides from crops, soils and sediments are often completed with a liquid–liquid extraction (LLE) clean-up step [33,73,91]. When extracting methylmercury from sediments clean-up of the extract was carried out by complexation followed by a LLE step [39,41].

Since elemental sulphur is present in most soils and sediments, and is sufficiently soluble in most common organic solvent, extracts must be treated to remove sulphur prior to GC analysis. This can be done by addition of tetra-butyl ammonium hydroxide [32] or copper [66,108].

6. Applications

6.1. Persistent organic pollutants

Persistent organic pollutants (POPs) are ubiquitous contaminants that have a negative impact on wildlife and human health [109–113]. Good examples of POPs are PCBs, with unique chemical characteristics such as heat resistance and chemical inertness [114]. MAE is an attractive technique for the extraction of these types of compounds from a number of environmental matrices, applying elevated temperatures for a fast extraction performance. POPs are stable at relatively harsh extraction conditions, as demonstrated for PAHs extracted at 145°C for 20 min with a variety of different solvent mixtures [87]. Consequently several applications are present in the literature. A summary of scientific publications related to MAE of POPs is seen in Table 4.

Lopez-Avila et al. presented one of the first publications on this subject in 1994 [27]. A large number of native and spiked contaminants (PAHs, base/neutral compounds, phenols and OCPs) were extracted from various soils and sediments. They mainly used acetone–hexane (1:1) as solvent and studied the recoveries at different temperatures and extraction times. It was demonstrated that PAH recoveries (17 PAHs) increased from 70 to 75% when increasing temperature from 80 to 115°C. However a further increase of the temperature to 145°C did not improve the recoveries. Additionally it was shown that a 5- or 10-min extraction procedure was sufficient for most of the compounds investigated. In a subsequent publication by Lopez-Avila et al. [77] the developed extraction methodology (acetone–hexane, 1:1, 115°C, 10 min) was applied to 187 compounds and four Arochlors (listed in EPA methods 8250, 8081 and 8141A) with a broad spectrum of recoveries ranging from 50 to 80%.

Even though the recoveries are not impressive for all compounds in the multi-residue method, later investigations have verified that the MAE methodology using acetone–hexane (1:1) at 115°C for 10 min has an extraction performance similar to or better than other extraction techniques for a variety of organic contaminants [115]. The advantages in terms of improved recoveries using hexane–acetone have been further demonstrated in a later publication where several solvents were tested including hexane–acetone (1:1), DCM–acetone (1:1), toluene–MeOH (10:1), and methyl *tert*.-butyl ether [87]. Identical extraction conditions as those used by Lopez-Avila et al. (acetone–hexane, 1:1, 115°C, 10 min) [27,77] have also been found optimal in orthogonal array design procedures for the extraction of PAHs in marine sediment where a number of solvents were tested including DCM, acetone–hexane (1:1), acetone–light petroleum (1:1) and MeOH–toluene (9:1) [28]. Likewise the same solvent mixture was applied with success for PAHs in certified marine sediments [29]. Similar optimization procedures have also been performed on spiked petroleum hydrocarbons in sediments and soils [116], where acetone (115°C, 5–15 min) was found more efficient than DCM. Other researchers that have performed optimization with orthogonal array designs are Hsu and Chen [68], but their final method was slightly different with a solvent mixture of acetone–hexane (9:1) at 70°C for 20 min. The combination of acetone–hexane (1:1) at 115°C for 10 min was used for spiked PCBs on clay soil, topsoil and sand, with recoveries close to 80% [97].

Table 4
Selected closed-vessel MAE applications of POPs reported in the literature

Analytes	Matrix	Equipment	Solvent	Temperature (°C)	Extraction time (min)	Recovery (%)	Reference method	Refs.
PAHs	Standard reference soils and sediments	CEM's MDS-2000	Hexane–acetone (1:1)	115	10	65–115	Certified values. MAE method compared to Soxhlet, Sonication and SFE	[27,115]
PAHs	Spiked fly ash	CEM's MES-1000	Hexane–acetone (1:9)	70	20	90	–	[68]
PAHs	Standard reference and native sediments	CEM's MES-1000	Hexane–acetone (1:1)	115	5	75–135	Certified values. MAE method compared to Soxhlet	[28]
PAHs	Standard reference sediment and air particles samples	CEM's MES-1000	Hexane–acetone (1:1)	115	10	75–100	Certified values	[29]
PAHs	Native, contaminated soil	CEM's MES-1000	Acetone	120	20	75–105	Soxhlet. MAE method compared to FMASE, PLE and SFE	[57]
PCBs	Standard reference soil and sediments	CEM's MES-1000	Hexane–acetone (1:1)	115	10	70–110	Certified values. MAE method compared to Soxhlet	[77,97]
PCBs	Standard reference sediment	CEM's MES-1000	Hexane–acetone (1:1)	100	10	55–120	Certified values. MAE method compared to Soxhlet and sonication	[117]
PCBs	Standard reference soil	?	Hexane–acetone (26:74)	No control	40	94–110	Certified values. MAE method compared to Soxhlet and PLE.	[123]
PCBs	Standard reference sediment	Milestones's Mega 1200	Hexane–acetone (1:1)	No control	15	73–93	Certified values. MAE method compared to Sonication.	[32]
PCBs	Standard reference soil	CEM's MES-1000	Hexane–acetone (1:1)	155	5	87–107	Certified values. MAE method compared to Soxhlet	[108]
PAHs, PCBs	Standard reference soil and sediment	CEM's MES-1000	Hexane–acetone (1:1)	115	10	70–125	Certified values	[124]
Polychlorinated dibenzodioxins (PCDDs)/polychlorinated dibenzofurans (PCDFs) and PCBs	Standard reference sediment	CEM's MES-1000	Hexane–acetone (1:1)	100	20	80–105	Certified values. MAE method compared to Soxhlet	[31]
PCDD/PCDFs	Sewage sludge, fly ash, sediment	CEM's MES-1000	Toluene	125	20	80–400	Soxhlet	[106]
PAHs, PCBs and aliphatic hydrocarbons,	Native, contaminated sediment	Domestic oven, Moulinex	Toluene–water (9:1)	No control	6	97–107	Soxhlet. MAE method compared to sonication	[66]
Petroleum hydrocarbons	Spiked soil and sediment	CEM's MES-1000	Acetone	115	15	80–100	–	[88]

In other cases rather similar conditions (acetone–cyclohexane, 1:1, 100°C, 10 min) has given good recoveries for PCBs in certified harbour sediments [117]. Likewise Chiu et al. [31] reported excellent recoveries when applying MAE (acetone–cyclohexane, 1:1, 100°C) for the extraction of PCBs and dioxins in marine and lake sediments, as compared to Soxhlet data (toluene, 20 h) and certified values. However, the solvent, was in this case heated for a somewhat longer time period of 20 min. Carro et al. instead increased the temperature to 155°C in order to generated exhaustive PCB extractions at similar conditions [108]. Apart from the commonly used combination of acetone–hexane, there has been reports of other types of solvents. Schlabach et al. suggested toluene for the extraction of dioxins in various environmental samples [106]. However, they experienced recovery problems for the added ^{13}C-labeled internal standards. Pastor et al. [66] proposed a mixture of toluene–water (10:1) for the extraction of multi-residues including linear hydrocarbons, PAHs, DDTs and PCBs, but according to their own data the differences in recoveries when applying this solvent mixture was very small compared to hexane/acetone (1:1).

The extraction volume is of importance as discussed previously, and in one of the more recent papers 30 ml was suggested as appropriate [108]. This solvent volume has been used frequently also by other research groups [27,29,77,97,106,115]. The same solvent volume (30 ml) has also been found optimal in two mixed level orthogonal array designs performed by Chee et al. [28,116]. There have been reports though were 20 ml [31,117] as well as 40 ml [57,68] of solvent have been used. However, not only the total volume should be considered, but rather the ratio between the solvent and the sample as demonstrated by Pastor et al. [66].

The water content of the sample can also influence the extraction process. Chee et al., [116] reported significantly lower recoveries for petroleum hydrocarbons when 10% water was added to the sample. It was suggested that analytes might be trapped inside the pores of the solid matrices by physically bounded water, making them inaccessible to the extraction solvent. However there have been contradicting results presented by Pastor et al. [66] showing that the effects of water are small. A more detailed discussion regarding effects of water contents is found in Section 5.2.5.

In most POP publications presented so far, Soxhlet has been used as a reference method, and in nearly all cases MAE has proven to be an equal or better choice. There have been recent reports though that Soxhlet still is the best choice in terms of obtaining an exhaustive extraction of PAHs [57] compared to pressurized and atmospheric MAE, SFE and PLE. This conclusion is however in doubt, and in fact regarding the comparison to pressurized MAE, only one out of 16 investigated PAHs was significantly higher for Soxhlet. The conditions applied for SFE might not be appropriate (70°C, 20% methanol) since it is well known that somewhat higher temperatures are favourable for these types of compounds [118]. Likewise modifiers capable of dipole–induced dipole interactions and $\pi-\pi$ interactions such as toluene, diethylamine and DCM are normally the better choice for PAHs in SFE [119]. Regarding the time applied in PLE, a 5-min static step might be to short as demonstrated in several later publications [120–122]. Zuloaga et al. [123] compared MAE with PLE and Soxhlet for the extraction of PCBs in soil. By extracting with 15 ml of acetone–hexane (74:26) for 40 min (no temperature stated), they obtained values close to certified values, as well as values obtained with PLE at 100°C, using acetone–hexane (75:25) for 10 min. Although not significant, Soxhlet values (acetone–hexane, 75:25, for 24 h) were somewhat lower than the other applied techniques. MAE performance using acetone–hexane (1:1) at 115°C for 10 min has also been proven to generated data similar to or better than Soxhlet (acetone–hexane, 1:1, 18 h), sonication (DCM–acetone, 1:1, 3 times 3 min) and SFE (carbon dioxide modified with 10% methanol, 450 bar, 120°C, 60 min dynamic) for a large number of organic contaminants [115]. In the same study the RSDs obtained with MAE were lower than for any of the other investigated techniques, but it should be mentioned that MAE also generated the dirtiest extracts in terms of sulphur extraction (verified by GC–MS), which in some cases decreased MAE recoveries for native analytes in certified material. SFE on the other hand generated relatively sulphur-free extracts, as demonstrated also by others [96]. To overcome the sulphur problem, some researchers have reported the possibility

of removing the sulphur prior to extraction by shaking the raw extracts with activated copper [108].

6.2. Pesticides

A large number of pesticides have been extracted with MAE as seen in Table 5.

The most studied groups of pesticides are OCPs and OPPs. Already in 1993, OCPs were extracted from spiked sediments using isooctane–ACN (1:1) applying an extraction time of 5 min or less [24] with recoveries higher than those obtained after 6 h of Soxhlet extraction. The year after, 20 OCPs were extracted from six certified reference marine sediments and soils (5 g of each) with 30 ml hexane–acetone (1:1) at 80–145°C for 5–20 min [27]. No degradation of OCPs was observed using pure solvents. When soil was present in the extraction vessels the recoveries were quantitative (82–169%, RSDs 8–23%, $n=3$) for all the compounds, even though γ-chlordane had a recovery of 74%. In a subsequent study, the list of compounds was expanded and the MAE method evaluated with spiked soil samples (freshly spiked or aged for 24 h or 14 days) [77]. Nearly a hundred OPCs and OPPs were extracted from 5-g samples using 30 ml of hexane–acetone (1:1) at 115°C for 10 min. A decrease in recovery with increased aging time is evident in the case of OCPs, and especially pronounced for captafol, captan and dichlone with recoveries dropping from about 100 down to 20%. Even so, the recoveries were at least 7% higher for MAE than for both sonication and Soxhlet, while the RSD values were comparable for the three techniques. For OPPs, 35 out of 47 compounds were fully extracted from freshly spiked soil. Significant improvement in recoveries was found when extracting aged soil samples which was attributed to the presence of water in the matrix (e.g., the recovery of phosphamidon increased from 17 to 98%). Another research group used similar extracting conditions and OCPs were quantitatively extracted (recoveries from 71 to 91%) from spiked marine sediment [80]. For 2 g of aged marine sediment, an MAE method with an extraction time of 6 min, 10 ml toluene and 1 ml of water provided a complete extraction of DDTs as compared to Soxhlet [66]. Molins et al. extracted different soil types, with freshly spiked and aged residues of OCPs, using 30 ml hexane with 20% water at 115°C for 20 min [99]. The obtained results showed that the same conditions could be used for both spiked and aged compounds.

Other investigations on OCPs have been performed, extracting pesticides from spiked sand, soil and air filters with MAP using 30 ml acetone–hexane (1:1) at 115°C for 10 min [124]. The obtained recoveries were all above 80%. Silgoner et al. extracted 17 OCPs from spiked sediments for 30 min at 100°C using THF as extraction solvent [73] with recoveries ranging from 74 to 99%. The optimal method was applied on contaminated sediment (SETOC 70), and the results were comparable to results obtained from an optimized SFE method and a sonication method. Extractions of OCPs in tissues have been reported by Hummert et al. [56,107] and Weichbrodt et al. [63], using ethyl acetate–cyclohexane (1:1) for MAE and PLE. The results were quantitative for both techniques. Because of the water contents in fish tissue, the MAE procedure required two extraction steps. During the first step water was removed, while the second step quantitatively extracted OCPs with pure solvent. This made MAE less convenient and more time consuming for samples with high water content. For extractions from fatty tissues (seal blubber and pork fat), ethyl acetate–cyclohexane (1:1) and hexane with Weflon has been used successfully [56,107]. OCPs, OPPs and five other pesticides were extracted from spiked water samples (Millipore, tap and sea) using SPE discs with a subsequent MAE elution [67]. The SPE discs were carefully rolled up and transferred into the MAE vessel and positioned well below the surface of the eluting solvent. The optimal conditions were 10 ml acetone at 100°C for 5 min. Recoveries above 80% were obtained for all compounds, except for fenchlorphos when extracting pure spiked water. When extracting spiked sea water more than half of the OCPs and OPPs had mean recoveries below 80% and recoveries for pure water spiked with humic acid followed the same trend.

MAE of triazines from agricultural soils and associated surface and ground water was first reported in 1993 [25]. Atrazine, desethylatrazine, desisopropylatrazine and simazine were determined (10 g sample, 40 ml DCM–MeOH, 90:10, at 115°C for 20 min) in spiked (freshly and aged 300 days) sea

Table 5
Selected closed-vessel MAE applications of pesticides reported in the literature

Analytes	Matrix	Equipment	Solvent	Temperature (°C)	Extraction time	Recovery (%)	Reference method	Ref.
OCPs	Spiked sediment	Domestic oven, Kenmore	Isooctane	No control	5×30	74–95	– MAE method compared to Soxhlet	[24]
OCPs	Standard reference soils and sediments	CEM's MDS-2000	Hexane–acetone (1:1)	115	10 min	75–170	Certified values. MAE method compared to Soxhlet and sonication	[27]
OCPs	Spiked sediment	CEM's MES-1000	Hexane–acetone (1:1)	100	10 min	71–93	– MAE method compared to Soxhlet	[80]
OCPs	Freshly spiked and aged soil samples	CEM's MES-1000	Hexane–acetone (1:1)	115	20 min	70–105	–	[99]
OCPs	Standard reference sediment	Milestones's Mega 1200	Tetrahydrofuran	100	30 min	83–120	Sonication. MAE method compared to SFE	[73]
OCPs, OPPs	Freshly spiked and aged soil samples	CEM's MES-1000	Hexane–acetone (1:1)	115	10 min	80–120	– MAE method compared to Soxhlet and sonication	[77]
OCPs, OPPs and other pesticides	Spiked sea and tap water (e.g., MAE elution of SPE discs)	CEM's MES-1000	Acetone	100	5 min	63–98	Conventional liquid–liquid extraction	[67]
p′,*p*-DDE	Naturally contaminated fatty tissue of seal	Milestones's Mega 1200	Ethyl acetate–cyclohexane (1:1)	No control	7×30	96	Conventional liquid extraction method	[107]
DDT	Fatty tissue of mammals	Milestones's Mega 1200	*n*-Hexane with Weflon	No control	7×30	95–100	Soxhlet	[56]
DDT	Native, contaminated sediment	Domestic oven, Moulinex	Toluene–water (90:10)	No control	6 min	100–103	Soxhlet	[66]
DDT	Fatty fish tissue	Milestones's Mega 1200	Ethyl acetate–cyclohexane (1:1)	No control	7×30	80	Conventional extraction method. MAE method compared to PLE and FMASE	[63]
OCPs, triazines, etc.	Spiked soil sample	CEM's MES-1000	Hexane–acetone (1:1)	115	10 min	85–125	–	[124]
Triazines	Freshly spiked and aged soils	CEM's MES-1000	DCM–MeOH (90:10)	115	20 min	89–103	Conventional liquid extraction method	[125]
Triazines	Spiked soil	MK-1	Water	No control	4 min	90–97	–	[70,126]
Imidazolinones	Spiked plant tissue	CEM's MES-1000	Water	125	3 min	97–103	–	[105]

Table 5. Continued

Analytes	Matrix	Equipment	Solvent	Temperature (°C)	Extraction time	Recovery (%)	Reference method	Ref.
Imidazolinones	Freshly spiked and aged field-treated soils	CEM's MES-1000	0.1 *M* NH_4OAc–NH_4OH (pH 10)	125	3 min	82–102	–	[36,103]
Phenylureas	Freshly spiked and aged soils	CEM's MES-1000	DCM–MeOH (9:1)	70	10 min	93–109	–	[58]
Sulfonylureas	Freshly spiked and aged soil samples	CEM's MES-1000	DCM–MeOH (9:1)	60	10 min	80–100	–	[35]
Hexaconazole	Native, contaminated soil	Milestones's Mega 1200	Acetone	115	15 min	53–102	Soxhlet. MAE method compared to PLE and SFE	[98]
Dimethomorph	Aged field-treated soil	CEM's MES-1000	ACN–water (9:1)	125	3 min	54	– MAE method compared to sonication	[91]
Dacthal, chlorpyrifos, chlorothalonil, diazinon, permethrin, methoxychlor and azinphos-methyl	Field-incurred crops	CEM's MSP-1000	IPA–light petroleum (1:2)	100	10 min	30–120	Conventional liquid extraction	[33]

clay soil [125]. In comparison to the conventional method (including steps of shaking, filtration and LLE) the MAE method offered increased sample throughput, a 4-fold reduction of solvent consumption and improvement of recoveries. The conventional method had recoveries of about 70%, while MAE reached 100% for both freshly and aged matrices. Hoogerbrugge et al. also reported the extraction of triazines from spiked soil samples (nine different types) [34]. They studied the effect of solvent, temperature, soil type and the amount of soil with respect to the volume extract. By using water as the extraction solvent, the analytes could be directly quantified in an enzyme-linked immunosorbent assay (ELISA) system [70]. In another work it was found that MeOH and acetone–hexane (1:1) are the best organic solvents for extracting atrazine, simazine and prometryne from soils; however, water was just as efficient as the organic solvents [126].

Extractions of imidazolinone herbicides have been reported in three papers by Stout et al. [36,103,105]. Imazethapyr is the most widely used member of the class and served as a representative. Extraction from spiked soils (four types) and crops have been performed with pure water as well as buffer solution (pH 10) at 125°C for 3 min. The obtained recoveries were satisfactory, reaching recoveries in the range of 80–100% [36,105]. In the latest of these publications LC–MS–MS was used for the final analysis, where recoveries of imazethapyr at 1–50 ppb averaged 92% [103]. Other herbicides investigated are sulfonyl- and phenylurea herbicides. With selected MAE conditions [10 g sample, 20 ml DCM–MeOH, 90:10, 60°C, 10 min] recoveries of sulfonylurea herbicides ranged from 70 to 100% with RSDs between 1 and 10% [35]. Determination of phenylurea herbicides from soil samples involved a single-residue method for linuron and a multi-residue method for linuron and five related compounds. Using optimized MAE conditions [5 g soil, 0.5 ml water, 20 ml DCM–MeOH, 90:10, 70°C, 10 min] recoveries from spiked soil ranged from 80 to 100% with RSDs below 12% ($n=9$) and recoveries from real samples ranged from 41 to 113% with RSDs ranging from 1 to 35% [58].

The fungicide hexaconazole has been extracted from weathered soils (sandy loam soil and sandy clay soil) collected 0–52 weeks after hexaconazole application [98]. The levels of hexaconazole in each soil were initially quantified by Soxhlet extraction. By using MAE (5 g in 30 ml acetone at 115°C for 15 min), SFE (carbon dioxide modified with 20% methanol, 245 bar, 55°C, 20 min dynamic) and PLE

(5 g in acetone at 140 bar, 100°C, 10 min) with a following SPE step, it was found that PLE produced the cleanest extracts with no interfering peaks in the chromatograms. In contrast both MAE and SFE required another pre-chromatographic clean-up step, especially for the high organic content soil. SFE gave results similar to MAE, whereas PLE gave good recoveries for all sample types used in the study and was the only method to give comparable results to those obtained using Soxhlet. Another investigated fungicide is dimethomorph, which has been extracted from fortified soil samples [91]. Out of the three extraction techniques evaluated (shaking, sonication and MAE), the MAE method [20 g in 20 ml ACN–water, 90:10, 125°C, 3 min] gave the best extractability of the analyte at trace levels. Field-incurred pesticide residues (of dacthal, chlorpyriphos, chlorothalonil, diazinon, permethrin, methoxychlor and azinphos-methyl) from several crops (10 g samples) were extracted with 30 ml 2-propanol (IPA)–light petroleum (1:2) [33]. Using the optimized MAE settings (100°C, 10 min) pesticide recoveries were comparable to those obtained with the conventional method (shaking and LLE).

6.3. Phenols

In 1994 Lopez-Avila et al. studied the extraction behaviour for 14 phenolic compounds from reference soils and sediments using acetone–hexane (1:1) as solvent [27]. For the phenols tested no degradation was found when using solvent only (recoveries ranged from 80 to 111%). When soil matrix was present in the extraction cell, recoveries of about 70% were obtained for 10 of the studied compounds, and for the remaining four compounds recoveries ranged between 10 and 60%. This was probably due to degradation in the presence of soil matrix. In three publications from 1997, Llompart et al. reported measurements of both phenol and methylphenol isomers in spiked and real soil samples [37,69,84]. MAE–derivatisation experiments were performed by blending the soil with small volumes of pyridine and acetic anhydride (in situ catalytic acetylation) and the extracting solvent hexane, prior to GC analysis. At optimal conditions (0.5–5 g soil, 10 ml hexane, 800 μl acetic anhydride, 200 μl pyridine, at 130°C for 5 min) the recovery for phenol was 110%, and the recoveries for *o*-, *m*-, and *p*-cresols were around 50, 90 and 80%, respectively [84]. When comparing the data to results obtained by EPA's standard sonication method, as well as to data obtained by optimized SFE and MAE methods, the MAE recoveries were twice as high for all investigated soils. For soils containing more than 5% charcoal SFE recoveries improved a lot when a derivatisation step was included, while for MAE the difference in recovery was not significant [37]. Another approach, using acetone–hexane (80:20) at 130°C for 10 min, extracting 1–5 g of spiked soil in 10 ml solvent gave recoveries in the range of 89–104% for phenol, *o*-, *m*-, and *p*-cresols [69]. Using MAP conditions of 30 ml acetone–hexane (1:1) at 115°C for 10 min, for extractions from sand, soil and air filters, recoveries above 80% were obtained [124]. MAE of phenol, 2-chloro-, methyl- and nitrophenols as well as 2,4-dichlorophenol from spiked soil was studied by Egizabal et al. [38]. Overall better recoveries were obtained with optimized MAE (15 ml acetone–hexane, 1:1, at 26 p.s.i. for 16.5 min) compared to Soxhlet (200 ml acetone–hexane, 70:30, for 8 h). In both methods, recoveries obtained for 2-methylphenol were low (50 and 15%, respectively). This was attributed to interactions between the alkyl groups and the soil matrix.

6.4. Metals

Methylmercury (MeHg) has successfully been extracted from both spiked sediments and reference material [39,41]. Compared to a conventional extraction procedure (acid leaching–manual extraction), the MAE method using 10 ml toluene with 400 μl 6 *M* HCl at 120°C for 10 min, produced equivalent recoveries [39]. Another study on MeHg was performed recently by Lorenzo et al., comparing the extraction efficiency of three different techniques (shaking, SFE and MAE) [41]. The MAE method (same as above) produced almost identical extracts, as compared to the conventional method (demonstrated by GC chromatograms). In general, the conventional shaking method and the SFE procedure (pure carbon dioxide, 200 bar, 40°C, 0.5 ml/min, 5 min static, 45 min dynamic) generated similar recoveries, whereas MAE outperformed both methods, especially for sandy sediments. The lower recoveries

obtained for the conventional method and the SFE procedure could, in some cases, be attributed to losses in the clean-up steps after the extractions. MAE appears to be much less dependent on the sediment matrix, thus providing a more reliable and advantageous extraction procedure. It should be mentioned though, that SFE was performed at only 40°C. Earlier studies performed on MeHg extractions from sediments applying SFE, utilised higher temperatures in the range of 40–125°C [127].

Determination of Pb, Zn and Cu in soils using a sequential microwave extraction procedure has been reported by Campos et al. [128]. The procedure distinguished the metals in their various chemical forms (e.g., bound to carbonate, oxides and organic matter). A similar approach has been investigated for heavy metals in sewage sludge by changing the shaking procedures in the conventional method (developed by Tessier et al. [129]) with MAE procedures [40]. No significant differences in recoveries were obtained for Ni, Pb and Zn, which were all about 100%. For the organic matter–bound metals, the extraction behaviour differed for the various metals when using microwave heating. In this case Pb was excessively leached, whereas Cr was not recovered. It should be emphasized though that when replacing the traditional shaking by microwave heating the treatment time was reduced in some steps from 5 h to 30 s. Promising results were shown for Ni and Zn, reducing the time from 17.5 h to merely 2 min.

Semi-metals as arsenic species have been extracted from fish tissue (reference material DORM-2) using MAE for 0.10 g sample with 10 ml MeOH–water (80:20) at 65°C for 4 min [76]. All of the arsenic species investigated remained intact and could be fully extracted from the samples.

6.5. Polymers

In the field of polymers, early works by Freitag and John [23] and Nielson [22] dealt with extractions of additives as antioxidants from polypropylene (PP) and polyethylene (PE) using domestic ovens. Above 90% of the substances were recovered from powdered polymer within 6 min using acetone–heptane (1:1) [23]. The solvent mixture cyclohexane–IPA (1:1), 20 min extraction time with stirring every 5 min, also worked well [22]. In some cases the resins were extracted as pellets (not ground) and full recoveries were achieved using MAE, except for the additive Irganox 1010 which could be extracted at no better than 50% recovery without grinding.

Extraction of low-molecular mass oligomers and cyclic trimers from PET film has been investigated by Costley et al. [72]. Traditionally, PET has been extracted with xylene for 24 h using Soxhlet, but at optimized MAE conditions (8 g, 40 ml DCM, 120°C) good recoveries could be obtained after 120 min. At temperatures over 120°C the polymer fused using DCM.

In 1997 Vandenburg et al. reviewed analytical extraction of additives from polymers using different extraction techniques [130]. A couple of years later they compared extraction efficiency of MAE, PLE and techniques at atmospheric pressure for the extraction of additives from PP [60]. Pellets, freeze-ground particles as well as freeze-ground polymer sieved in fractions were extracted at optimized MAE conditions (0.3 g in 30 ml IPA at 150°C or acetone at 140°C). The stability of Irganox 1010 was studied and it was found that when using acetone at 140°C, the recovery dropped to 57% after just 7 min, indicating rapid degradation of the compound. However, using IPA a recovery of 98% was obtained after heating at 140°C for 30 min. Complete extractions of all studied compounds were achieved using IPA for 5 min at 150°C or for 10 min at 140°C. IPA also swells the polymer without causing extensive dissolution. PLE and MAE can result in significantly faster extractions with the same recoveries as refluxing at atmospheric pressures.

Recently Marcato and Vianello presented a large study on MAE of additives in polyalkenes [90]. Two MAE processes were reported: a one-step MAE [2.5 g polymer, 25 ml ethyl acetate–hexane, 75:25, 125°C, 15 min] useful for additives with low-medium dipolarity (like stabilizers, flame retardant, antistatics, etc), and a two-step MAE (a micronizing step with MAE conditions depending on the polymer matrix extracted, followed by a manually shaking step using the MAE vessels), useful for additives with either high dipolarity (like organic salts, nucleating agents, etc.) or high molecular mass. Both proposed processes have been tested on commercially common polymeric matrices as for example PP

and ethylene–propylene copolymer (Supersoft), demonstrating excellent recoveries.

6.6. Pharmaceuticals and natural products

A major field in analytical chemistry dealing with sample preparation on a routine basis is the pharmaceutical industry, but so far relatively few papers have been published in this area using MAE. An early work from 1990, using a domestic oven, dealt with extraction of a blood flow enhancer, and its metabolite from rat faeces [19]. By using a solvent mixture consisting of MeOH–water–acetic acid (HAc) (50:47.5:2.5) a recovery of 80% was achieved. In a couple of works by Akhtar et al., incurred antibiotics as chloramphenicol in eggs [131] and sulphamethazine in swine tissue [62] have been determined using a household microwave oven. The conditions used were 15 ml ACN and 2 ml IPA for 10 s and 20 ml MeOH for 25 s, respectively. A similar application is the extraction of 3-nitro-4-hydroxyphenylarsonic acid, a general growth promoter, from swine tissue [51] using 25 ml ethanol with 0.5 ml HAc for 9 s in a domestic oven. Outside the field of biological matrices, the authors extracted felodipine and one of its degradation products from tablets [75]. By optimizing the extracting solvent (5% MeOH in ACN) the whole tablets could be extracted with full recovery without grinding the tablet prior to extraction.

In the area of natural products an early work on vitamins from foodstuffs have been reported [26]. The fungal metabolite ergosterol was extracted from hyphae and spores [52] and in this study the results using SFE were substantially lower than those for MAE. Extractions of a taxane compound, paclitaxel (which has an antimitotic effect in mammalian systems) from *Taxus* biomass, showed slightly lower recoveries (90%) using 95% ethanol at 85°C for 10 min, compared to those obtained with a conventional shaking method (methanol, overnight) [71]. Terpenic compounds, responsible for a variety of aromas in musts and wines can be extracted with good recoveries using MAE [85].

6.7. Miscellaneous

Phthalate esters have successfully been extracted from marine sediment and soil [81]. MAE [5 g sample, 30 ml acetone–hexane, 1:1, 115°C, 10 min] allowed comparable or higher recoveries of the six phthalate esters studied (70–91%) compared to Soxhlet (66–90%) and sonication (65–89%). The precision for the MAE results were far better than using the conventional methods. Recently, Youngman and Green [132] extracted long-chain hydrocarbons (C_{60} and C_{70}) from fullerene-containing carbon soot using a mixture of toluene–ACN (95:5). In the food technology area, MAE has been used for the extraction of synthetically flavour ingredients in products as potato chips [102] and amino acids from foodstuffs [54]. In a couple of publications, Daghbouche et al. have reported extractions of oils and greases from water samples into an organic solvent phase under pressurized microwave heating [86,100]. An approach for the determination of sunscreen agents in cosmetic products using small volumes of methanol has recently been published [133]. Solvent residues (toluene, xylene and acetone among others) have successfully been extracted from indicator pads used for protective clothing [134].

Some specialized technical approaches using microwave include determination of airborne substances (lindane, fenpropimorph, metazachlor) which were trapped on solid adsorbents and then desorbed by microwave heating [135]. Gas-phase MAE has been reported for the determination of aromatic contaminants (volatile organic compounds, VOCs, for example toluene and chlorobenzene) in soil and water [136,137]. In this process, the sample is heated and VOCs are vaporized into the headspace of the sample. It was noted that the microwave approach gave higher detector responses, better precision and higher sample throughput.

On-line methodology of MAE has been reported for PAH determinations in standard reference sediments [138]. Samples were slurried in acetone and pumped through tubings in the microwave cavity. The effluent collected was then manually extracted in a LLE step with hexane prior to GC–MS analysis. A comparison of an EPA microwave-assisted method and the on-line extraction procedure indicated that whilst recoveries were comparable, the continuous flow extraction system was the more reproducible.

Recently, Ericsson and Colmsjö presented a dynamic microwave-assisted extraction process exem-

plified by the determination of PAHs from a standard reference sediment [139]. During the extraction, fresh methanol was continuously pumped through the extraction vessel containing the sample, which was maintained at a slight overpressure in order to keep the solvent in a liquid state. Parameters as temperature and extraction time were found to be important and with the final conditions (140°C, 40 min at a flow-rate of 2 ml/min) recoveries of PAHs were comparable to those obtained with Soxhlet. An additional clean-up step was in this case needed before GC analysis, but this novel approach offers the possibility to perform on-line clean-up and quantitative analysis.

7. Final remarks

MAE has risen rapidly in the latest decade, and for most applications it has proven to be effective compared to traditional extraction techniques. The major benefits are decreased extraction times, reduced solvent consumption and increased sample throughput. The technique is easy to use and the systems are cheaper compared to other modern techniques such as SFE and PLE. Although careful method development may generate some extraction selectivity, there is a need for additional clean-up after completed extraction. For some applications only a filtration step is needed, whereas for others solid-phase extraction or additional liquid–liquid extraction steps have to be performed to be able to use the final analytical technique. Compared to SFE this is a disadvantage, since clean-up is usually not needed for this relatively selective technique. However, method development is often more complex in SFE and additionally sample throughput is not as high as in MAE. In PLE the filtration step is ''included'' in the technique, but in resemblance to MAE a clean-up step is often of need. By considering economical and practical aspects, MAE is a strong competitor to other recent sample preparation techniques.

References

[1] H.B. Wan, M.K. Wong, J. Chromatogr. A 754 (1996) 43.
[2] C.F. Poole, S.K. Poole, Anal. Comm. 33 (1996) 11H.
[3] V. Lopez-Avila, Crit. Rev. Anal. Chem. 29 (1999) 195.
[4] M. Letellier, H. Budzinski, Analusis 27 (1999) 259.
[5] V. Camel, Trends Anal. Chem. 19 (2000) 229.
[6] S.B. Hawthorne, Anal. Chem. 62 (1990) 633A.
[7] S. Bøwadt, S.B. Hawthorne, J. Chromatogr. A 703 (1995) 549.
[8] R.M. Smith, J. Chromatogr. A 856 (1999) 83.
[9] E. Björklund, S. Bøwadt, T. Nilsson, Trends Anal. Chem. 19 (2000) 434.
[10] M. Letellier, H. Budzinski, P. Garrigues, S. Wise, Spectroscopy 13 (1997) 71.
[11] M. Letellier, H. Budzinski, L. Charrier, S. Capes, A.M. Dorthe, Fresenius J. Anal. Chem. 364 (1999) 228.
[12] L.E. García-Ayuso, M. Sánchez, A. Fernández de Alba, M.D. Luque de Castro, Anal. Chem. 70 (1998) 2426.
[13] L.E. García-Ayuso, J. Velasco, M.C. Dobarganes, M.D. Luque de Castro, J. Agric. Food Chem. 47 (1999) 2308.
[14] L.E. García-Ayuso, M.D. Luque de Castro, Anal. Chim. Acta 382 (1999) 309.
[15] A. Abu-Samra, J.S. Morris, S.R. Koirtyohann, Anal. Chem. 47 (1975) 1475.
[16] Q. Jin, F. Liang, H. Zhang, L. Zhao, Y. Huan, D. Song, Trends Anal. Chem. 18 (1999) 479.
[17] K. Ganzler, A. Salgó, K. Valkó, J. Chromatogr. 371 (1986) 299.
[18] K. Ganzler, A. Salgó, Z. Lebensm. Unters. Forsch. 184 (1987) 274.
[19] K. Ganzler, I. Szinai, A. Salgó, J. Chromatogr. 520 (1990) 257.
[20] J.R.J. Paré, J.M.R. Bélanger, S.S. Stafford, Trends Anal. Chem. 13 (1994) 176.
[21] J.R.J. Paré, US Pat., 5 002 784 (1991).
[22] R.C. Nielson, J. Liq. Chromatogr. 14 (1991) 503.
[23] W. Freitag, O. John, Angew. Makromol. Chem. 175 (1990) 181.
[24] F.I. Onuska, K.A. Terry, Chromatographia 36 (1993) 191.
[25] T.R. Steinheimer, J. Agric. Food Chem. 41 (1993) 588.
[26] G.M. Greenway, N. Kometa, Analyst 119 (1994) 929.
[27] V. Lopez-Avila, R. Young, W.F. Beckert, Anal. Chem. 66 (1994) 1097.
[28] K.K. Chee, M.K. Wong, H.K. Lee, J. Chromatogr. A 723 (1996) 259.
[29] K.K. Chee, M.K. Wong, H.K. Lee, Environ. Monit. Assess. 44 (1997) 391.
[30] M. Pineiro-Iglesias, P. López-Mahía, E. Vázquez-Blanco, S. Muniategui-Lorenzo, D. Prada-Rodríguez, E. Fernández-Fernández, Fresenius J. Anal. Chem. 367 (2000) 29.
[31] C. Chiu, G. Poole, M. Tardif, W. Miles, R. Turle, Organohalogen Comp. 31 (1997) 175.
[32] Z.C. Kodba, J. Marsel, Chromatographia 49 (1999) 21.
[33] H.M.J. Pylypiw, T.L. Arsenault, C.M. Thetford, M.M.J. Incorvia, J. Agric. Food Chem. 45 (1997) 3522.
[34] R. Hoogerbrugge, C. Molins, R.A. Baumann, Anal. Chim. Acta 348 (1997) 247.
[35] N. Font, F. Hernández, E.A. Hogendoorn, R.A. Baumann, P. van Zoonen, J. Chromatogr. A 798 (1998) 179.

[36] S.J. Stout, A.R. daCunha, D.G. Allardice, Anal. Chem. 68 (1996) 653.
[37] M.P. Llompart, R.A. Lorenzo, R. Cela, K. Li, B.J.M.R. Paré, J.R.J. Paré, J. Chromatogr. A 774 (1997) 243.
[38] A. Egizabal, O. Zuloaga, N. Etxebarria, L.A. Fernández, J.M. Madariaga, Analyst 123 (1998) 1679.
[39] M.J. Vazquez, A.M. Carro, R.A. Lorenzo, R. Cela, Anal. Chem. 69 (1997) 221.
[40] B. Pérez-Cid, I. Lavilla, C. Bendicho, Anal. Chim. Acta 378 (1999) 201.
[41] R.A. Lorenzo, M.J. Vázquez, A.M. Carro, R. Cela, Trends Anal. Chem. 18 (1999) 410.
[42] ASTM D5258, Standard Test Method For Acid Extraction of Elements from Sediments using Closed Vessel Microwave Heating, American Society for Testing and Materials, Philadelphia, PA, 1996.
[43] ASTM D5765, Standard Practice for Solvent Extraction of Total Petroleum Hydrocarbons from Soils and Sediments using Closed Vessel Microwave Heating, American Society for Testing and Materials, Philadelphia, PA, 1996.
[44] ASTM D6010, Standard Practice for Closed Vessel Microwave Solvent Extraction of Organic Compounds from Solid Matrices, American Society for Testing and Materials, Philadelphia, PA, 1996.
[45] EPA Method 3546, Microwave Extraction of VOC's and SVOC's (Organophosphorus pesticides, Organochlorine pesticides, Chlorinated herbicides, Phenoxy Acid Herbicides, PCBs, etc.), EPA SW-846 update III, US Environmental Protection Agency, 1999.
[46] H.M. Kingston, L.B. Jassie (Eds.), Introduction to Microwave Sample Preparation, American Chemical Society, Washington, DC, 1988.
[47] J. Thuéry, in: E.H. Grant (Ed.), Microwaves: Industrial, Scientific and Medical Applications, Artech House, Boston, MA, 1992.
[48] L. Jassie, R. Revesz, T. Kierstead, E. Hasty, S. Metz, in: H.M. Kingston, S.J. Haswell (Eds.), Microwave-Enhanced Chemistry, American Chemical Society, Washington, DC, 1997, p. 569.
[49] J.R. Dean, L. Fitzpatrick, C. Heslop, in: A.J. Handley (Ed.), Extraction Methods in Organic Analysis, Sheffield Academic Press, Sheffield, 1999, p. 166.
[50] D.R. Baghurst, D.M.P. Mingos, J. Chem. Soc., Chem. Commun. (1992) 674.
[51] L.G. Croteau, M.H. Akhtar, J.M.R. Belanger, J.R.J. Pare, J. Liq. Chromatogr. 17 (1994) 2971.
[52] C.J. Young, J. Agric. Food Chem. 43 (1995) 2904.
[53] B. Erickson, Anal. Chem. 70 (1998) 467A.
[54] Á. Kovács, K. Ganzler, L. Simon-Sarkadi, Z. Lebensm.-Unters. Forsch. A 207 (1998) 26.
[55] W. Vetter, M. Weichbrodt, A. Batista, B. Luckas, Organohalogen Comp. 40 (1999) 305.
[56] K. Hummert, W. Vetter, B. Luckas, Chromatographia 42 (1996) 300.
[57] N. Saim, J.R. Dean, M.P. Abdullah, Z. Zakaria, J. Chromatogr. A 791 (1997) 361.
[58] C. Molins, E.A. Hogendoorn, E. Dijkman, H.A.G. Heusinkveld, R.A. Baumann, J. Chromatogr. A 869 (2000) 487.
[59] B. Enders, G. Schwedt, J. Prakt. Chem./Chem.-Ztg. 339 (1997) 250.
[60] H.J. Vandenburg, A.A. Clifford, K.D. Bartle, J. Carroll, I.D. Newton, Analyst 124 (1999) 397.
[61] I.R. Pereiro, A. Wasik, R. Lobinski, J. Anal. Atom. Spectrom. 13 (1998) 743.
[62] M.H. Akhtar, M. Wong, S.R.H. Crooks, A. Sauve, Food Addit. Contam. 15 (1998) 542.
[63] M. Weichbrodt, W. Vetter, B. Luckas, Organohalogen Comp. 40 (1999) 309.
[64] S. Bureau, A. Razungles, R. Baumes, C. Bayonove, J. Food Sci. 61 (1996) 557.
[65] N. Carro, C.M. García, R. Cela, Spectroscopy 13 (1997) 61.
[66] A. Pastor, E. Vázquez, R. Ciscar, M. de la Guardia, Anal. Chim. Acta 344 (1997) 241.
[67] K.K. Chee, M.K. Wong, H.K. Lee, Anal. Chim. Acta 330 (1996) 217.
[68] T.-B. Hsu, Y.-S. Chen, Organohalogen Comp. 27 (1996) 450.
[69] M.P. Llompart, R.A. Lorenzo, R. Cela, J.R.J. Pare, Analyst 122 (1997) 133.
[70] G. Xiong, J. Liang, S. Zou, Z. Zhang, Anal. Chim. Acta 371 (1998) 97.
[71] M.J.I. Mattina, W.A.I. Berger, C.L. Denson, J. Agric. Food Chem. 45 (1997) 4691.
[72] C.T. Costley, J.R. Dean, I. Newton, J. Carroll, Anal. Commun. 34 (1997) 89.
[73] I. Silgoner, R. Krska, E. Lombas, O. Gans, E. Rosenberg, M. Grasserbauer, Fresenius J. Anal. Chem. 362 (1998) 120.
[74] V. Pino, J.H. Ayala, A.M. Afonso, V. González, J. Chromatogr. A 869 (2000) 515.
[75] C. Sparr Eskilsson, E. Björklund, L. Mathiasson, L. Karlsson, A. Torstensson, J. Chromatogr. A 840 (1999) 59.
[76] K.L. Ackley, C. B'Hymer, K.L. Sutton, J.A. Caruso, J. Anal. Atom. Spectrom. 14 (1999) 845.
[77] V. Lopez-Avila, R. Young, J. Benedicto, P. Ho, R. Kim, W.F. Beckert, Anal. Chem. 67 (1995) 2096.
[78] M.M. Punt, G.S.V. Raghavan, J.M.R. Bélanger, J.R.J. Paré, J. Soil Contam. 8 (1999) 577.
[79] E. Vázquez Blanco, P. López Mahía, S. Muniategui Lorenzo, D. Prada Rodríguez, E. Fernández Fernández, Fresenius J. Anal. Chem. 366 (2000) 283.
[80] K.K. Chee, M.K. Wong, H.K. Lee, J. Chromatogr. A 736 (1996) 211.
[81] K.K. Chee, M.K. Wong, H.K. Lee, Chromatographia 42 (1996) 378.
[82] I.J. Barnabas, J.R. Dean, I.A. Fowlis, S.P. Owen, Analyst 120 (1995) 1897.
[83] B. Enders, G. Schwedt, GIT Fachz. Lab. 40 (1996) 172.
[84] M.P. Llompart, R.A. Lorenzo, R. Cela, J.R. Jocelyn Pare, J.M.R. Belanger, K. Li, J. Chromatogr. A 757 (1997) 153.
[85] N. Carro, C.M. García, R. Cela, Analyst 122 (1997) 325.
[86] Y. Daghbouche, S. Garrigues, M. de la Guardia, Analyst 121 (1996) 1031.
[87] V. Lopez-Avila, R. Young, W.F. Beckert, J. AOAC Int. 81 (1998) 462.
[88] K.K. Chee, M.K. Wong, H.K. Lee, Environ. Monit. Assess. 44 (1997) 587.

[89] L. Pensado, C. Casais, C. Mejuto, R. Cela, J. Chromatogr. A 869 (2000) 505.
[90] B. Marcato, M. Vianello, J. Chromatogr. A 869 (2000) 285.
[91] S.J. Stout, B.W. Babbitt, A.R. DaCunha, M.M. Safarpour, J. AOAC Int. 81 (1998) 1054.
[92] N. Alexandrou, J. Pawliszyn, Anal. Chem. 61 (1989) 2770.
[93] M.D. Burford, S.B. Hawthorne, D.J. Miller, Anal. Chem. 65 (1993) 1497.
[94] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, J. Pawliszyn, Anal. Chem. 67 (1995) 1727.
[95] E. Björklund, S. Bøwadt, L. Mathiasson, S.B. Hawthorne, Environ. Sci. Technol. 33 (1999) 2193.
[96] S.B. Hawthorne, E. Björklund, S. Bøwadt, L. Mathiasson, Environ. Sci. Technol. 33 (1999) 3251.
[97] V. Lopez-Avila, J. Benedicto, C. Charan, R. Young, Environ. Sci. Technol. 29 (1995) 2709.
[98] S.P. Frost, J.R. Dean, K.P. Evans, K. Harradine, C. Cary, M.H.I. Comber, Analyst 122 (1997) 895.
[99] C. Molins, E.A. Hogendoorn, H.A.G. Heusinkveld, P. Van Zoonen, R.A. Baumann, Int.J. Environ. Anal. Chem. 68 (1997) 155.
[100] Y. Daghbouche, S. Garrigues, A. Morales-Rubio, M. de la Guardia, Anal. Chim. Acta 345 (1997) 161.
[101] I.R. Pereiro, A. Wasik, R. Lobínski, Fresenius J. Anal. Chem. 363 (1999) 460.
[102] Y. Wang, M. Bonilla, H.M. McNair, J. High Resolut. Chromatogr. 20 (1997) 213.
[103] S.J. Stout, A.R. DaCunha, M.M. Safarpour, J. AOAC Int. 80 (1997) 426.
[104] J.R.J. Paré, G. Matni, J.M.R. Bélanger, K. Li, C. Rule, B. Thibert, V. Yaylayan, Z. Liu, D. Mathé, P. Jacquault, J. AOAC Int. 80 (1997) 928.
[105] S.J. Stout, A.R. da Cunha, G.L. Picard, M.M. Safarpour, J. Agric. Food Chem. 44 (1996) 3548.
[106] M. Schlabach, A. Biseth, H. Gundersen, M. Oehme, Organohalogen Comp. 23 (1995) 105.
[107] K. Hummert, W. Vetter, B. Luckas, Organohalogen Comp. 27 (1996) 360.
[108] N. Carro, Y. Saavedra, I. García, M. Llompart, J. Microcol. Sep. 11 (1999) 544.
[109] S. Report, Ambio 19 (1990) 13.
[110] F. Wania, D. Mackay, Ambio 22 (1993) 10.
[111] F. Wania, D. Mackay, Environ. Sci. Technol. 30 (1996) 390A.
[112] J.E. Kihlström, M. Olsson, S. Jensen, Å. Johansson, J. Ahlbohm, Å. Bergman, Ambio 21 (1992) 563.
[113] V.M. Zakharov, A.V. Yablokov, Ambio 19 (1990) 266.
[114] M.D. Erickson (Ed.), Analytical Chemistry of PCBs, 2nd Edition, CRC Press, Boca Raton, FL, 1997.
[115] V. Lopez-Avila, R. Young, N. Teplitsky, J. AOAC Int. 79 (1996) 142.
[116] K.K. Chee, M.K. Wong, H.K. Lee, Environ. Monit. Assess. 44 (1997) 587.
[117] Y.Y. Shu, C. Chiu, R. Turle, T.C. Yang, R.C. Lao, Oraganohalogen Comp. 31 (1997) 9.
[118] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, J. Pawliszyn, Anal. Chem. 65 (1993) 338.
[119] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, J. Pawliszyn, Anal. Chem. 66 (1994) 909.
[120] P. Popp, P. Keil, M. Moeder, A. Paschke, U. Thuss, J. Chromatogr. A 774 (1997) 203.
[121] D.W. Kenny, S.V. Olesik, J. Chromatogr. Sci. 36 (1998) 66.
[122] E. Björklund, S. Bøwadt, T. Nilsson, L. Mathiasson, J. Chromatogr. A 836 (1999) 285.
[123] O. Zuloaga, N. Etxebarria, L.A. Fernández, J.M. Madariaga, Trends Anal. Chem. 17 (1998) 642.
[124] K. Li, J.M.R. Bélanger, M.P. Llompart, R.D. Turpin, R. Singhvi, J.R.J. Paré, Spectroscopy 13 (1997) 1.
[125] C. Molins, E.A. Hogendoorn, H.A.G. Van Harten, D.C. Van Zoonen, R.A. Baumann, Chromatographia 43 (1996) 527.
[126] G. Xiong, B. Tang, X. He, M. Zhao, Z. Zhang, Z. Zhang, Talanta 48 (1999) 333.
[127] H. Emteborg, E. Björklund, F. Ödman, L. Karlsson, L. Mathiasson, W. Frech, D.C. Baxter, Analyst 121 (1996) 19.
[128] E. Campos, E. Barahona, M. Lachica, M.D. Mingorance, Anal. Chim. Acta 369 (2000) 235.
[129] A. Tessier, P.G.C. Campell, M. Bisson, Anal. Chem. 51 (1979) 844.
[130] H.J. Vandenburg, A.A. Clifford, K.D. Bartle, J. Carroll, I. Newton, L.M. Garden, J.R. Dean, C.T. Costly, Analyst 122 (1997) 101R.
[131] M.H. Akhtar, L.G. Croteau, C. Dani, K.A. ElSooud, Spectroscopy 13 (1997) 33.
[132] M.J. Youngman, D.B. Green, Talanta 48 (1999) 1203.
[133] Y. Shih, F.-C. Cheng, J. Chromatogr. A 876 (2000) 243.
[134] E. Vo, S.P. Berardinelli, R.C. Hall, Analyst 124 (2000) 941.
[135] J. Scharf, R. Sarafin, J. High Resolut. Chromatogr. 18 (1995) 253.
[136] J.R.J. Paré, J.M.R. Bélanger, K. Li, M.P. Llompart, R. Singhvi, R.D. Turpin, Spectroscopy 13 (1997) 89.
[137] J.R.J. Paré, J.M.R. Bélanger, D.E. Thornton, K. Li, M.P. Llompart, M. Fingas, S.A. Blenkinsopp, Spectroscopy 13 (1997) 23.
[138] S.L. Cresswell, S. Haswell, J., Analyst 124 (1999) 1361.
[139] M. Ericsson, A. Colmsjö, J. Chromatogr. A 877 (2000) 141.