Microwave-enhanced Solvent Extraction of Organics in Environmental Analysis

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Microwave-enhanced solvent extraction is often used as an approach for the extraction of organic pollutants from environmental matrices. The approach uses microwave technology to heat organic solvent in contact with the sample in either a sealed (pressurized) or an open (atmospheric) vessel. The major advantage of the use of microwave technology over traditional extraction approaches (e.g. Soxhlet extraction) is the speed of the process. Apart from the principles of microwave heating, the article also describes the instrumentation required to affect the extraction process. Finally, selected environmental applications are considered with respect to class of compound, i.e. polycyclic aromatic hydrocarbons (PAHs), hydrocarbons, polychlorinated biphenyls (PCBs), pesticides, and emerging (polar) pollutants from solid matrices, as well as applications in the use of microwave technology for recovery of organic pollutants from aqueous matrices.

1 INTRODUCTION TO ENVIRONMENTAL ORGANIC SAMPLE PREPARATION

Analysis of organic pollutants in the environment is necessary because of past or present industrial activity, accidental spillage, and deliberate (unlicensed) disposal, all of which can have ecotoxicological effects on living organisms. In order to assess the potential damage, remediate known sites, or simply have an early warning of potential problems requires environmental measurement of the levels of organic pollutants. Organic pollutants are located in all compartments of the environment. So, typically, we refer to pollution in terms of natural waters (e.g. lakes, rivers, groundwater, and potable water), solid or semisolid matrices (e.g. soil, sludge, and vegetation), and the atmosphere (e.g. air). In this article, we are concerned principally with solid-type matrices, although some attention is given to aqueous sample preparation. A recently published book discusses the different types of sample preparation approaches for both liquid and solid samples of environmental origin.(1)

Preparation of solid samples for organic analysis can traditionally be subdivided into two classes, with heating and without heating. In the latter case, we refer to the use of shake flask, while in the former Soxhlet extraction. Shake flask extraction involves placing a solid sample into a container together with an organic solvent and agitating, either manually or by the use of a laboratory shaker, for a given period of time. Subsequently, the organic solvent containing the extract is removed via filtration, a separating funnel, or decanting. Soxhlet extraction involves refluxing warm organic solvent through the sample repeatedly for several hours. This is achieved by heating organic solvent, contained in a round-bottomed flask, on an isomantle. The vaporized solvent is then condensed, via a water-cooled condenser, which falls into a thimble-containing sample. This, in turn, returns to the round-bottomed flask. The whole process is repeated frequently until the pre-set extraction time is reached. As the extracted organic pollutant normally has a higher boiling point than the solvent, it is preferentially retained in the flask and fresh solvent recirculates. This ensures that only fresh solvent is used to extract the organic pollutant from the sample in the thimble. A disadvantage of this approach is that the organic solvent is below its boiling point when it passes through the sample contained in the thimble. In practice, this is not necessarily a problem as Soxhlet extraction is normally done over long time periods, i.e. 6, 12, 18, or 24 h.

More recently, alternative approaches have become available. In addition to the shake flask approach, it is possible to agitate the sample using a sonic bath or sonic probe. Modifications of Soxhlet extraction have appeared, which offer some degree of solvent reduction

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and automation, e.g. Soxtec. Perhaps the biggest changes have occurred in terms of the instrumentation available for extraction of pollutants from solids. The 1980s saw the arrival of commercial apparatus for supercritical fluid extraction (SFE), while the early 1990s the commercial availability of microwave-assisted extraction (MAE) closely followed in 1995 by accelerated solvent extraction (ASE).

This article is concerned with the use of microwave technology for the extraction of organic pollutants from environmental (solid and liquid) matrices. The first papers on the subject were published in 1986(2) using a domestic microwave oven; it was not until the 1990s that commercial microwave systems became available. This article only considers the research published since 2006 to illustrate the applications of microwave technology.

2 PRINCIPLES OF MICROWAVE HEATING FOR ORGANIC SOLVENTS

Microwaves are high-frequency electromagnetic radiation. The most commonly used frequency of operation of microwaves is 2.45 GHz. The choice of solvent for MAE is essential. The solvent must be able to absorb microwave radiation and pass it on in the form of heat to other molecules in the system. The ability to pass on this energy is measured in terms of the dissipation factor (tan δ), see Equation (1):

$$\tan\,\delta = \frac{\varepsilon''}{\varepsilon'} \qquad (1)$$

where ε'' is the dielectric loss (a measure of the efficiency of conversion of microwave energy into heat energy) and ε' is the dielectric constant (a measure of the polarizability of a molecule in an electric field).

This polarizability is achieved by the reorientation of permanent dipoles by the applied electric field. This means that under microwave conditions, a polarized molecule will rotate to align itself with the electric field at a rate of approximately 10^9 times per second. This results in a very rapid heating. An estimate of the ability of the microwave oven to couple to any molecule can be obtained by considering its ε' values (Table 1). It is not surprising to find, therefore, that polar solvents, such as water, acetone, and methanol (MeOH), all readily absorb microwaves and hence are heated up when subjected to microwave radiation, while nonpolar solvents, such as hexane and toluene, do not heat up when they are subjected to microwave irradiation. In addition, as the extraction process typically takes place in a closed vessel, the solvent chosen can be heated well above its normal boiling point (Table 1). This will reduce the time required for the extraction process.

Table 1 Solvent properties for microwave-assisted extraction

Solvent	Dielectric constant[a]	Boiling point (°C)[b]	Closed-vessel temperature (°C) at 175 psig[b]
Hexane	1.89	68.7	NH
Dichloromethane	—	39.8	140
Acetone	20.7	56.2	164
Methanol	32.63	64.7	151
Acetonitrile	37.5	81.6	194
Acetone : hexane (1 : 1, v/v)	—	52	156

NH, no heating in microwave; psig, pounds per square in gauge.
[a] See *CRC Handbook of Physics and Chemistry*.(3)
[b] Adapted from Renoe.(4) (1 psi = 6894.76 Pa.)

3 APPARATUS FOR MICROWAVE-ENHANCED SOLVENT EXTRACTION

All microwave systems consist of a microwave generator (magnetron), a wave guide (for transmission of microwaves from the generator to the cavity), a resonance or microwave cavity (where the extraction vessels are located), extraction vessels, and a temperature sensor (all of which are under computer control). Two types of microwave-heating systems are potentially available: an open-vessel (atmospheric) system and a closed-vessel (pressurized) system. In the open-vessel (atmospheric) system, individual sample vessels are heated sequentially. A typical commercial system is the STAR system (CEM, Matthews, NC, USA) [Note: It is noted that open-vessel (atmospheric) microwave systems are often available for acid digestion of samples rather than extraction of organic compounds.] A typical generic example of an atmospheric MAE system is shown in Figure 1. This system is operated by introducing the sample and solvent into a glass container, fitted with a water condenser to prevent loss of volatile compounds and solvent. The sample container is located within a protective glass sheath. The organic solvent is then heated, by means of microwave energy, and refluxed through the sample.

A range of commercial closed-vessel pressurized MAE systems are available (e.g. Ethos EX and MARS, from Milestone and CEM, respectively). A schematic diagram of a pressurized MAE system is shown in Figure 2. The Ethos EX (Milestone Inc., Sorisole, Italy) can operate with up to 42 extraction vessels (vessel volume, 65 mL) or as few as six extractions vessels (vessel volume, 270 mL). The system allows direct temperature monitoring and control in a single reference vessel. In addition, a contact-less solvent sensor allows simultaneous determination in the event of a vapor release inside the cavity. The microwave energy output of

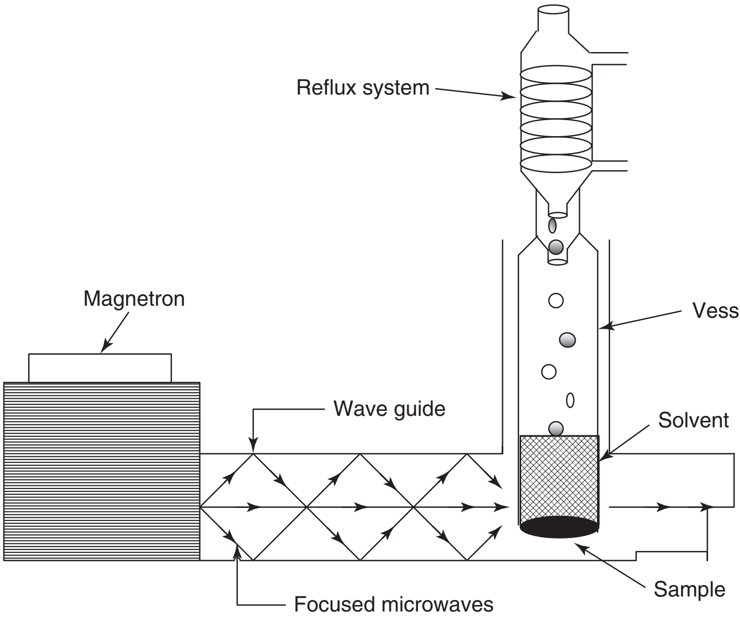

Figure 1 Schematic diagram of an atmospheric microwave-assisted extraction system.

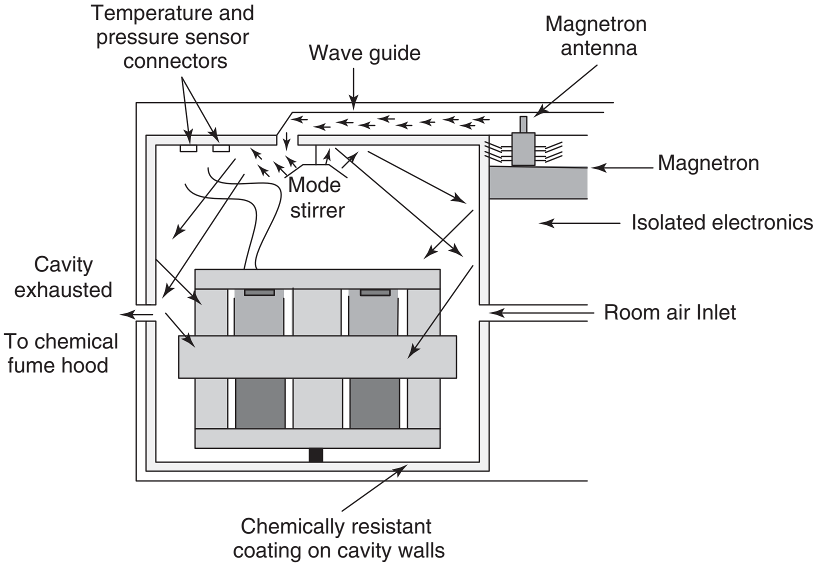

Figure 2 Schematic diagram of a pressurized microwave-assisted extraction system.

this system is 1600 W at a frequency of 2450 MHz at 100% power. Maximum pressures (between 10 and 35 bar) and maximum temperatures (between 180 and 260 °C) are all possible depending on the chosen number of vessels and their construction. All the sample vessels are held in a carousel that is located within the microwave cavity. Each vessel has a vessel body and an inner liner; the sample is placed inside the inner liner. The liner is made of tetrafloromethoxyl polymer (TFM) fluoropolymer, except for the 42-extraction-vessel system in which case the liner is made of perfluoroalkoxy polymer (PFA). If solvent leaking from the extraction vessel(s) does occur, the solvent monitoring system will automatically shut off the magnetron but allow the exhaust fan to continue working, venting the fumes into external ducting.

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The MARS 6 (CEM Corp., USA) can operate with up to 40 extraction vessels (vessel volume, 75 mL) or as few as 14 extractions vessels (vessel volume, 100 mL). An integral floor-mounted IR sensor allows temperature measurement in every vessel in the carousel. The microwave energy output of this system is 1800 W at a frequency of 2450 MHz at 100% power. Maximum pressures (between 200 and 1500 psi) and maximum temperatures (between 200 and 300 °C) are all possible depending on the chosen number of vessels and their construction. All the sample vessels are held in a carousel that is located within the microwave cavity. Each vessel has a vessel body and an inner liner; the sample is placed inside the inner liner. The liner is made of TFM Teflon®, PFA Teflon, or glass. If solvent leakage from the extraction vessel(s) does occur, the solvent monitoring system will automatically shut off the magnetron but allow the exhaust fan to continue working, venting the fumes into external ducting.

[Note: Both manufacturers have developed polar stir bars, which will be heated by microwave radiation, thereby allowing nonpolar solvents to be used. Milestone uses Weflon™, while CEM uses Carboflow®.]

4 APPLICATIONS OF MICROWAVE-ENHANCED SOLVENT EXTRACTION IN ENVIRONMENTAL ANALYSIS

4.1 Extraction from Solid Matrices

4.1.1 *Atmospheric Microwave-enhanced Solvent Extraction*

Most of the MAE applications found in the literature deal with pressurized MAE. There are fewer works that report the use of atmospheric MAE; this is probably due to the prevalence of commercial pressurized systems. A focused-Microwave™ Synthesis System (CEM) with stirring and cooling options was applied to the extraction of PAHs in marine sediments by Pino et al.(5) The authors proposed the use of aqueous solutions containing aggregates of the ionic liquid (IL) 1-hexadecyl-3-methylimidazolium bromide (HDMIm-Br) as an alternative extraction medium (instead of the traditional organic solvents). The IL is considered a green solvent as it possesses high thermal stability and negligible vapor pressure. It is also able to form aggregates, such as surfactants, resulting in a high partition coefficient. In this work, atmospheric MAE was done under optimized operating conditions by irradiating the sediment sample (0.1 g) with 9 mL of 45 mM IL in a 40 mL Pyrex® tube under the microwave power of 180 W to reach a maximum temperature of 90 °C for 6 min. After irradiation and cooling, the supernatant was removed, filtered, and then 20 μL of the IL extract containing PAHs was injected into the high-performance liquid chromatography (HPLC) system using a fluorescence detector (FL). The Community Bureau of Reference (BCR)-535 river harbor sediment was used to determine the accuracy and precision of the extraction method. The results for the majority of the PAHs investigated (including pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, and indeno(1,2,3-cd)pyrene) were in good agreement with certified values. The average recoveries of the PAHs, excluding indeno(1,2,3-cd)pyrene, were 91.1% with a relative standard deviation (RSD) ranging between 3.4% and 10%; detection limits ranged between 0.8 and 53.0 ng g^{-1}. The method was then applied to the extraction of marine sediments having known low amounts of organic matter and low contamination levels for PAHs compared to the BCR-535-certified sediment. The results showed that pyrene and benzo(b)fluoranthene were quantified in one sample at concentrations of 0.5 and 0.35 mg kg^{-1}, respectively, whereas benzo(b)fluoranthene was also detected in another sample at a concentration of 0.42 mg kg^{-1}. The rest of the sediment samples contained some of the PAHs at levels close to or lower than the quantification limits of the method.

This work was extended to use another IL 1-hexadecyl-3-butylimidazolium bromide (HDBIm-Br) for the extraction of 15 + 1 European Union (EU)-priority PAHs in toasted cereals ('gofios') including wheat, barley, rye, and maize corn.(6) The extracts obtained from the atmospheric MAE were then analyzed by HPLC with ultraviolet (UV) detection and a single-channel FL detector. The MAE-operating parameters were optimized using a 2^3 factorial design with two central points. In this study, the following procedure was employed as the optimum: an amount of 'gofio' (0.1 g) was irradiated with 4.5 mL of 40 mM HDBIm-Br aqueous solution in a 25 mL Pyrex® tube under the microwave power of 50 W to reach a maximum temperature of 80 °C in 4 min with a hold time of 10 min. The extract was centrifuged and the supernatant transferred for the HPLC analysis without any further cleanup or preconcentration step. The spiked wheat 'gofio' samples at two different levels were used to validate the method. It was found that average extraction recoveries were 86.3% at the highest spiked level, and 87.2% at the lowest spiked level, whereas the RSD values lower than 12.6% were obtained in all cases. The detection limits ranged between 0.003 and 1.037 mg kg^{-1}. The method was then applied to the extraction of five samples for each 'gofio'. The results showed good extraction performance for all PAHs with the average recoveries of 90.6%, 89.1%, and 88.4% for

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barley, rye, and maize corn, respectively, and the RSD values lower than 13%.

The same group has recently expanded the applicability of IL-based surfactants toward extraction of other complex solid samples.(7) A group of organic pollutants from marine sediments including three PAHs, five alkylphenols (i.e. bisphenol-A (BPA) or nonylphenol), and one paraben were analyzed by HPLC using a diode array detector (DAD). Two IL-based surfactants, i.e. 1-hexadecyl-3-methyl imidazolium bromide (C_{16}MIm–Br) and 1-hexadecyl-3-butyl imidazolium bromide ($C_{16}C_4$Im–Br), were used as the extraction media in an MAE procedure. An in situ preconcentration step was applied to the microwave extract before the HPLC analysis. The following proven conditions were selected: sediment sample (0.1 g), extraction temperature of 90 °C, 40 mM of both IL-based surfactants, and extraction volumes of 5 and 3 mL for C_{16}MIm–Br and $C_{16}C_4$Im–Br, respectively. The extraction efficiency and reproducibility of the optimized MAE procedure were assessed by undertaking extraction of spiked blank sediments. The results (Figure 3), for the nine organic contaminants, showed that average extraction recoveries ranged between 98.7%, at the intermediate spiked level, and 104.2% at the lowest spiked level for the $C_{16}C_4$Im–Br. For C_{16}MIm–Br, the average extraction recoveries ranged between 87.9% at the lowest level and 95.9% at the intermediate level. The RSDs were in the range 4.4–21% and 7.1–14% for the lowest and intermediate spiked levels, respectively. The reference material BCR-535 certified for three of the nine PAHs included in this study was also analyzed to evaluate the performance of the method with satisfactory accuracy obtained.

A method using MAE followed by dispersive liquid–liquid microextraction (DLLME) was developed for the extraction of 16 PAHs from smoked fish.(8) A microwave oven (Delonghi type molecular weight (MW) 602) was used to accelerate alkaline saponification and primary extraction. Final separation and quantification of the extracts were carried out by gas chromatography (GC) with mass spectrometry (MS) detection. Microwave parameters were optimized using the 'single-factor-at-a-time' method. The optimized operating parameters varied were as follows: extraction time (0.5, 2, and 3.5 min), microwave energy (500 MHz), ethanol ratio in the hydrolyzing solvent (30%, 40%, 50%, 60%, and 70%), and the volume of 2 M KOH hydrolyzing solution (6, 8, 10, 12, 14, and 15 mL). It was found that the optimum conditions were as follows: fish sample (1 g) was extracted in 12 mL of 2 M KOH and 50% ethanol ratio for 2 min using microwave energy of 500 MHz. After MAE, the sample solution was centrifuged, and then the aqueous phase was transferred for DLLME procedure. It was concluded that MAE–DLLME method coupled with GC/MS provided an excellent enrichment factor and good repeatability with RSDs ranging between 2.8% and 8.9%. The recoveries of 16 PAHs in smoked fish ranged between 82% and 105%. The limit of detection (LOD) and limit of quantitation (LOQ) of the method were 0.11–0.48 and 0.36–1.6 ng g^{-1}, respectively.

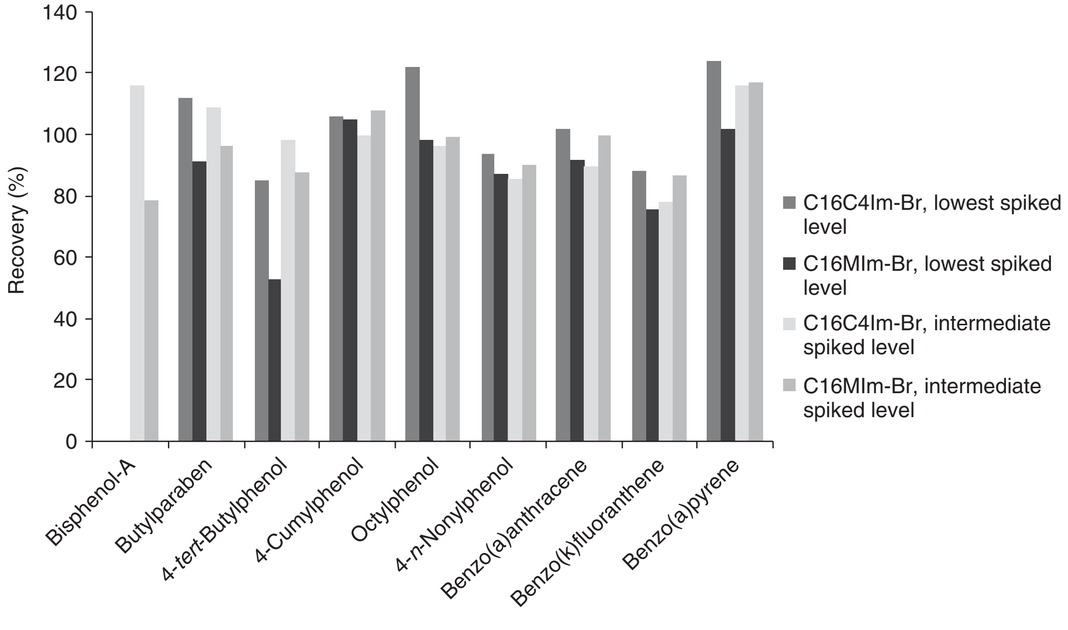

Figure 3 Extraction of organic contaminants spiked at two different levels.(7). (Adapted from Ref. 7. Copyright 2012, Elsevier.)

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4.1.2 Pressurized Microwave-Enhanced Solvent Extraction

Pressurized MAE is by far the most common approach that has been utilized for the extraction of organic pollutants from solid environmental matrices. Accordingly, this section has been subdivided with respect to the organic pollutant of interest.

4.1.2.1 Polycyclic Aromatic Hydrocarbons PAHs are the most commonly studied organic pollutant by MAE. MAE has been a method of choice to extract PAHs from solid matrices because of its efficiency, low volume of organic solvent used, and time-saving feature. Itoh et al.(9) evaluated the differences among three extraction methods, i.e. Soxhlet, PLE, and MAE applied for the extraction of PAHs from lake sediment. MAE was carried out using a MarsX system (CEM). Three solvent systems were tested: 30 mL DCM, ethyl acetate (EtAc), or DCM : EtAc (1 : 1 v/v). A 5-g sediment sample and 400 μL of the surrogate solution were placed into a glass vessel and kept overnight in the dark. The mixture was then extracted at 1200 W under temperature ramp to 100 °C within 10 min. It was found that DCM : EtAc was the best extraction solvent. After that, the extraction time was optimized by investigation of the extraction efficiency at 10, 20, or 30 min at a fixed temperature of 150 °C. After cooling, the extract was filtered through a glass-fiber filter and transferred to a glass vial and a small amount of activated copper powder added to remove elemental sulfur. After that, the extract was filtered through a 0.1 μm polytetrafluoroethylene (PTFE) membrane filter and concentrated using a rotary evaporator in a stream of N_2 gas, and the solvent was replaced with toluene. The concentrated extract was cleaned up using a silica gel solid-phase extraction (SPE) cartridge with a Zymark RapidTrace automation system (Hopkinton, MA, USA). For the recovery test, the ^{13}C-PAHs were spiked at comparable levels to those in the sediment extracts during the cleanup and concentration steps. The extracts were analyzed for the five PAHs using GC/MS and quantified using isotope-dilution mass spectrometry (IDMS). It was found that the optimum conditions for MAE was extraction with DCM : EtAc at 150 °C for 30 min. The comparison of different extraction techniques under optimized conditions was made, and the results showed that all techniques provided good repeatability for the PAHs studied with RSDs $<$ 5.2%. Differences in the extraction efficiencies of the techniques were observed for the native PAHs with the results decreased in the order PLE $>$ MAE $>$ Soxhlet, as shown in Figure 4. In the same year, this research group(10) developed an alkaline MAE followed by SPE for extraction of PAHs in a sediment sample and compared this technique with those obtained by without alkaline, conventional alkaline extraction, and other techniques reported in the earlier study,(9) i.e. Soxhlet, usual MAE with DCM : EtAc, and PLE. Before MAE, a 5 g sediment sample was placed in a PTFE vessel, a surrogate solution was added, and kept in the dark overnight. The optimum alkaline MAE conditions were extraction using 30 mL of 1 M KOH/MeOH at 150 °C for 30 min. The extracts were then filtered and diluted with Milli-Q water followed by the SPE treatment. It was concluded that 16 of 18 PAHs provided acceptable recoveries (60–120%) and high precision ($<$16%), indicating that the alkaline MAE is an effective technique for determination of the PAHs. PAH concentration obtained by the alkaline MAE were 1.3–37% higher than those obtained by without alkaline and the method requires less solvent and takes less time than conventional alkaline extraction. In addition, observed concentrations using the developed technique were comparable to those using usual MAE (96–103%) and lower than those using PLE (81–92%) except for benzo[*ghi*]perylene. The same group applied the MAE approach to the extraction of PAHs in dust samples.(11) Five solvent systems were evaluated: 30 mL DCM, MeOH, or MeOH : toluene (1 : 3, 1 : 1, or 3 : 1 v/v). Before performing the MAE, the sample (200 mg of the tunnel dust or 40 mg SRM1650b Diesel particulate matter) and 400 μL of the surrogate solution were placed into a glass vessel and kept overnight in the dark. The mixture was then extracted for 20 min with the solvent at 1200 W under temperature ramp to 160 °C within 10 min. It was found that extraction using MeOH : toluene, 1 : 3, v/v at 160 C for 40 min is optimum. After cooling, the extract was filtered through a glass-fiber filter and transferred to a glass vial and a small amount of activated copper powder added to remove the elemental sulfur. After that, the extract was filtered through a 0.2-μm PTFE membrane filter and concentrated using a rotary evaporator at 60 C in a stream of N_2 gas, and the solvent was replaced with toluene. The concentrated extract was cleaned up using SPE. The results (Figure 5) for the PAHs showed that the extraction efficiencies relative to those obtained with the MeOH : toluene, 1 : 1 v/v mixture were relatively different among solvents and PAHs. It was clearly indicated that for lighter PAHs (MW $\leq$ 202 amu), MeOH : toluene was slightly more effective than DCM and MeOH. However, for heavier PAHs (MW $\geq$ 252 amu) except dibenzo[*ah*]anthracene, it was significantly more effective. Therefore, it was suggested that DCM and MeOH were not suitable for extraction of increasing PAH MWs.

Portet-Koltalo et al.(12) optimized the pressurized MAE conditions to simultaneously extract PAHs, nitroPAHs, and aliphatic hydrocarbon from a particularly refractory carbonaceous matrix, namely spiked diesel particulate

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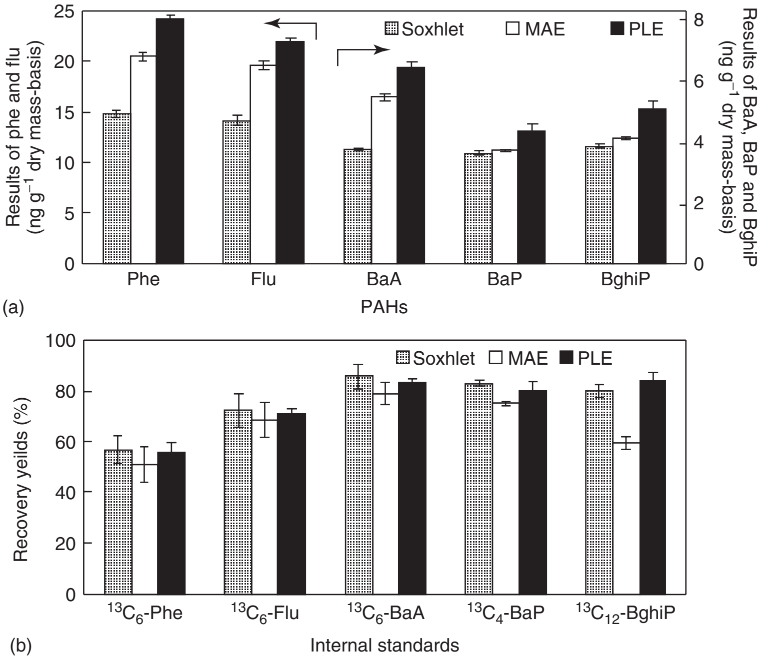

Figure 4 Extraction of PAHs (a) and recovery yields of ^{13}C-PAHs (b) by Soxhlet (with hexane/acetone for 16 h), MAE (with DCM/EtAc at 150 °C for 30 min), and PLE (with toluene at 150 °C under 15 MPa). Error bars indicate the standard deviation ($n = 3$).(9). (Reproduced from Ref. 9. Copyright 2008, Elsevier.)

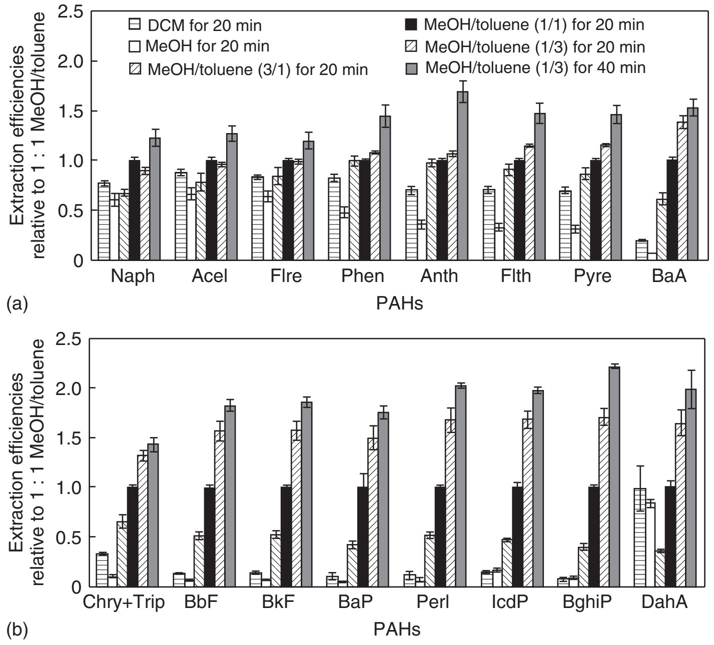

Figure 5 (a, b) Extraction of PAHs obtained by MAE under different conditions.(11). (Reproduced from Ref. 11. Copyright 2011, Elsevier.)

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matter. The extracts were analyzed by GC/MS. The MAE was carried out using the MarsX microwave accelerated extraction system (CEM). Spiked samples were left for 30 min in contact with 100 μL of a standard mixture of 28 PAHs, nitroPAHs, and *n*-alkanes. The sample mixtures were then irradiated with the solvent under MAE optimum conditions. A second-order central composite design was used to investigate the dependence of operating variables including temperature, extraction time, and solvent volume. The amount of sample (100 mg) and microwave power (1200 W) were kept constant. These variables were considered between strict operating limits, i.e. temperature, 80–140 C, extraction time, 5–37 min, and solvent volume, 6–30 mL. In addition, the influence of the nature of solvent (dichoromethane, tetrahydrofuran, and chloroform) on extractability by MAE was observed and it was found that it was not an influential factor. It was concluded that solvent volume was the most influential factor and kept at a medium level; temperature and time were not influential as main factors but interacted with the other factors. The optimum conditions were temperature, 140 °C, extraction time, 37 min, and 18 mL dichloromethane (DCM). After this optimization, the authors managed to improve the difficult extraction of a complex mixture of PAHs, nitroPAHs, and *n*-alkanes from the spiked sample by testing other solvents. The results showed that among heterocyclic aromatic solvents, pyridine was the most effective and an increase in the basic character of the extracting mixture (by adding of 17% of diethylamine to pyridine) provided the quantitative results for all of the PAHs examined.

The same group(13) compared the hot Soxhlet, ASE, and SFE with the MAE previously developed(12) to extract PAHs, their nitrated derivatives, and heavy *n*-alkanes from a highly adsorptive particulate matter resulting from the combustion of diesel fuel in a diesel engine.

Similar to their previous results,(12) the solvent used to provide quantitative extraction of PAHs was the mixture of pyridine and diethylamine, whereas the extraction of the nitrated PAHs was significantly improved by the use of pyridine with the addition of a small amount of acetic acid. The results of comparing MAE, SFE, and ASE to hot Soxhlet showed that the techniques yielded quantitative extraction efficiencies for all PAHs ($\geq$85%, $\geq$79%, and $\geq$72%, respectively). It was concluded that SFE seemed to be the best technique in terms of solvent and time consumption, and selectivity. The advantages of MAE and ASE over the other techniques were being easy to implement and the ability to simultaneously extract multiple samples in an automated system.

MAE combined with μ-SPE was proposed as a single extraction–cleanup procedure for the analysis of five PAHs from soil samples prepared as slurries with water.(14) Graphite fiber was used as the sorbent in μ-SPE. The following optimum conditions were used: solvent, 10 mL water; temperature, 50 C (with 2 min ramp time); extraction time, 20 min; and elution time, 5 min using acetonitrile with sonication. GC/flame ionization detector (FID) and GC/MS were employed to analyze the PAHs in the sample extracts, providing LOD ranging between 2.2 and 3.6 ng g^{-1} and between 0.0017 and 0.0057 ng g^{-1}, respectively. Good reproducibility (RSD $<$ 10.2%) was obtained. The linear range were between 0.1 and 50 or 100 μg g^{-1} for GC/FID analysis and 1 and 500 or 1000 ng g^{-1} for GC/MS analysis. The MAE was compared with sonication-assisted extraction (SAE) and agitation-assisted extraction (AAE), and it showed higher chromatographic signals among the three methods with the same graphite fiber as sorbent to extract the PAHs. The MAE-μ-SPE method was then applied to extract PAHs in different soil samples (river and marine sediments) with satisfactory results.

The MAE followed by HPLC with DAD and FL detection was optimized and validated for analysis of 16 PAHs (United States Environmental Protection Agency (USEPA) priority pollutants), dibenzo[*a*,*l*]pyrene and benzo[j]fluoranthene in fish.(15) Response surface methodology was applied in this study for optimization. The optimization results indicated that maximum recoveries of the PAHs obtained using the following MAE conditions: extraction time (20 min), temperature (110 °C), solvent volume (acetonitrile or hexane : acetone 1 : 1 v/v, 10 mL), and stirring speed (medium). Validation of the method using spiking assays at four levels and using SRM 2977 revealed that recoveries of all PAHs with the exception of naphthalene and chrysene (not identified due to peak overlapping) were in the range 58.5% and 99.7% and RSD values were lower than 7%. Quantitation limits ranged between 0.15 and 27.16 ng g^{-1} wet weight. The results obtained by this approach when applied to the analysis of the PAHs in sardine, chub mackerel, and horse mackerel were as follows: naphthalene (1.03–2.95 ng g^{-1} wet weight), fluorene (0.34–1.09 ng g^{-1} wet weight), and phenanthrene (0.34–3.54 ng g^{-1} wet weight).

4.1.2.2 Hydrocarbons The MAE approach followed by GC/MS for the analysis of hydrocarbons in chert rock samples was reported.(16) Microwave-operating parameters were evaluated using D-optimal designs. The operating parameters varied were as follows: solvent (DCM, 40–60% : hexane, 20–40% : acetone, 10–20%), temperature (90–130 °C), and extraction time (5–20 min). The MAE was performed by placing 2 g sample in a PTFE vessel by adding 15 mL of solvent mixture. When the irradiation was completed, the sample was centrifuged

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and the supernatant was concentrated to dryness using nitrogen blowdown evaporation and redissolved in 200 μL *n*-hexane. It was found that the proven conditions were solvent (60% DCM : 30% hexane : 10% acetone), temperature (110 °C), and extraction time (15 min). The approach was then compared with focused ultrasound extraction (FUSE) using the same real sample. The results indicated that concentrations obtained for geological chert by both MAE and FUSE were highly comparable for the $C_{27}H_{56}$–$C_{35}H_{72}$ *n*-alkanes ($p > 0.1$). However, MAE provided slightly better reproducibility (RSD < 11% for MAE and RSD < 18% for FUSE) and allows the simultaneous extraction of up to eight samples. The LODs of the MAE-GC/MS were in the range 30–80 ng g^{-1}.

The MAE conditions using nonionic surfactant solutions for extraction of aliphatic hydrocarbons in petroleum source rocks were investigated.(17) The following MAE-operating variables were optimized: 10 mL of solvent solution (0.02 M Brij 35, 0.02 M C12E10, and 0.025 M triton X-100), temperature (60–120 °C), extraction time (10–50 min), and irradiation power (300–1200 W). The amount of the sample was fixed at 1.2 g. Brij 35 was selected as the most efficient solvent. The optimum temperature, extraction time, and irradiation power were 105 °C, 50 min, and 600 W, respectively. After irradiation, the sample was centrifuged and filtered through a 0.45-μm cellulose acetate membrane followed by GC/MS analysis. As no standard reference material (SRM) for petroleum source rock was available for the analysis, extraction efficiencies of *n*-alkanes and acyclic isoprenoid hydrocarbons between MAE and Soxhlet extraction were compared. The results showed that MAE is more efficient than Soxhlet extraction as the extracted amounts of almost all alkanes and acyclic hydrocarbons from the sample are much higher using MAE compared to those using Soxhlet.

4.1.2.3 Polychlorinated Biphenyls Similar to other kinds of organic pollutants, the conventional method of PCB analysis consists of a number of complicated steps, requires large amounts of solvent, and is time-consuming. Hence, MAE has been developed for the extraction of PCBs from environmental samples as it significantly reduced the extraction time and solvent consumption. A fully automated MAE followed by GC/electron capture detector (ECD) or high-resolution gas chromatography (HRGC)/resolution mass spectrometry (HRMS) for the determination of PCBs in whale blubber was validated.(18) A total of 2–5 g of the sample was placed into the PFA-lined vessel, 10 mL of the saponifying solution (ethanoic 1 M KOH : water, 1 : 1 v/v) and a 20 mL extractant (*n*-hexane) were added. Extraction with microwave energy was done by irradiating the sample mixture at 20 psi (with increments of 5 psi at 5–40% of 950 W magnetron power) for 25–30 min. The hexane layer (5–10 mL) was pipetted for cleanup by multilayer silica gel column chromatography or automated sample preparation device (SPD-600GC, Miura Co. Ltd., Japan). The surrogate standard solution was added to the extract before the GC/ECD or HRGC/HRMS analysis. The approach was validated by the analysis of a certified reference material (CRM) (SRM 1588b: cod liver oil). The results were in good agreement with the certified values for almost all PCB congeners with an RSD of 1–7%, except for 2,2′,5-trichlorobiphenyl, 2,2′,3,4,4′,5′,6-heptachlorobiphenyl and 2,2′,3,3′,4,4′,5,5′,6-nonachlorobiphenyl. The quantification limit of total PCBs in whale blubbers was 41 ng g^{-1}.

Comparison of Soxhlet extraction, ASE, and MAE for the determination of PCBs and PBDEs in soil and fish samples has been made.(19) The soils, which had been collected from electronic-waste-dismantling areas, were freeze-dried and sieved through a 16-mesh sieve. Fish samples were obtained from a lake polluted by discharge of effluent wastewater from a municipal sewage treatment plant. The fish muscles were stripped, freeze-dried, and homogenized. Both soil and fish samples were stored at −20 °C until extraction. About 3 g of soil or 2 g of fish sample was mixed with 3–4 g of anhydrous sodium sulfate and placed into the extraction cylinders. Then, 30 mL *n*-hexane : acetone (1 : 1 v/v) was added and the extraction was carried out under the following conditions: temperature (115 °C, with 10 min ramp time), extraction time (15 min), and microwave power (1200 W). The extracts were centrifuged and the supernatant was transferred into a flat bottom flask. The extracts were spiked with 10 μL of the surrogate standard of PCBs and PBDEs, the sample cleanup procedure was performed, and analyzed using HRGC/HRMS. The results (Figure 6) indicated that ASE and MAE provided higher yield than Soxhlet extraction for the determination of PCBs in the soil samples, whereas those for fish samples were comparable among the three extraction methods for PCBs. For PBDEs, it was noted that the specified conditions could lead to nonconformity of the extraction performance. Therefore, it was suggested for PBDEs that the extraction conditions with high temperature require careful optimization of different matrices to avoid degradation of higher brominated congeners.

4.1.2.4 Pesticides Sample aging, either artificially or by natural weathering, is an important factor to consider when evaluating any new extraction technique. However, it is unfortunate to note that most published methods for MAE are based on freshly spiked samples. Smalling and Kuivila(20) evaluated the MAE conditions on the

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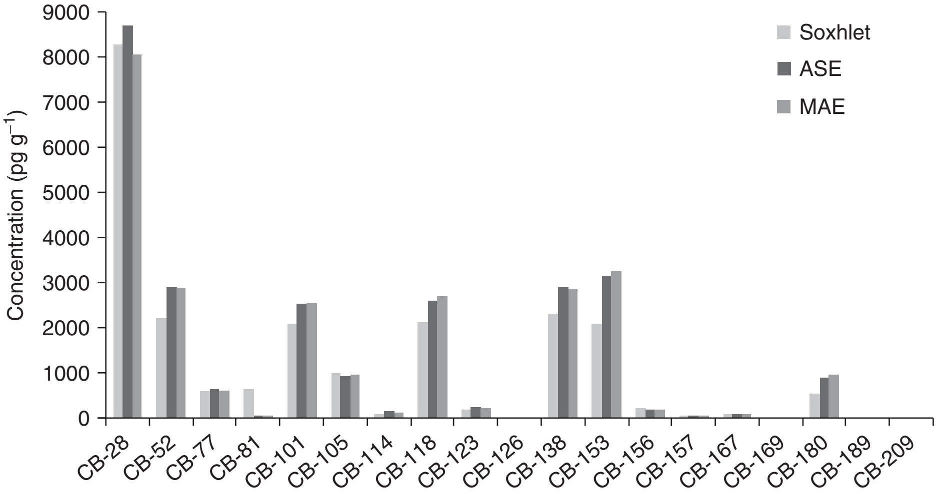

Figure 6 Extraction of PCBs from soil sample.$^{(19)}$. (Adapted from Ref. 19. Copyright 2010, Elsevier.)

simultaneous determination of 85 current-use pesticides including herbicides, insecticides, fungicides, as well as several degradates and the legacy organochlorine insecticides in bed and suspended sediments. Wet sediments were spiked and allowed to equilibrate for 1 h. The spiked samples (~10 g) were extracted two times for 10 min each using a MSP 1000 MAE system (CEM). The MAE variables considered were temperature (70, 100, and 120 °C), solvents (DCM : MeOH 9 : 1 v/v; DCM : acetone 1 : 1, v/v; hexane : acetone 1 : 1, v/v). The cleanup procedures including Florisil, silica gel, or prepacked SPE cartridges were applied to the sample extracts before GC/MS analysis. It was found that extraction of the spiked sample at 120 °C resulted in poor recoveries for the fungicide, while the results tested at 70 and 100 °C showed minimal degradation with slightly better recoveries at 100 °C. Elevated temperatures of extraction, typically above the boiling point of the solvent used, are important, leading to a complete extraction of all pesticides from the sample matrix. Therefore, the authors carried out further experiment using both the real sediment samples and a CRM (SRM 1941b, Organics in marine sediments) for extraction at 100 and 120 °C. The results indicated that the concentrations or recoveries of all pesticides measured were higher when extracted at 120 °C compared to 100 °C. Therefore, the compromised MAE procedure to extract all pesticides was extracting the same sample twice, first at 100 °C (to minimize lose of fungicides) and again at 120 °C (to ensure a complete extraction of aged pesticides). For the investigation of the solvent used, water was added to each sample to make approximately 50% of moisture content to decrease the variation in sample moisture and to increase the efficiency of the microwave digestion. The results for the same chemical class yielded similarly for the different solvent systems, one or two compounds per chemical class obtained from each solvent system is shown in Figure 7. The mean recoveries for all compounds measured by the method ranged from 71% to 118% depending on compounds and compound class with the method detection limits ranging from 0.6 to 8.9 μg kg^{-1} dry weight.

The nature of the MAE process is such that heating can only occur if the solvent has a permanent dipole moment. As an alternative to the conventional approach for the determination of organochlorine pesticides (OCPs) in animal feed, Iglesias-García et al.$^{(21)}$ utilized a microwave oven (Anton Paar Multiwave, Graz, Austria) for the sample extraction. Pig feed samples (1 g) were extracted with 15 mL of hexane–acetone (1 : 1, v/v). The microwave program applied was as follows: 1 min ramp from 100 to 800 W, 4 min hold at 800 W, 0 W for 2 min, 1 min ramp from 100 to 800 W, and 4 min hold at 800 W. The extracts were filtered and concentrated using a rotary evaporator. After MAE extraction, the extracts were cleaned up using SPE procedure and analyzed by GC/ECD followed by GC/MS. The method was validated by analysis of spiked samples and a CRM (CRM-115 BCR, animal feed). The results, for the CRM, showed that recoveries for the OCPs obtained from the method ranged from 83.0% to 122.9% and the RSDs were between 10.2% and 23.9%, whereas the recoveries of the spiked samples ranged from 78% to 127% with the RSD less than 10%, except for endrin (very low recoveries due to the analyte was strongly retained by the SPE sorbent) and methoxychlor (recoveries over 150% due to poor separation and matrix effect). In addition, the MAE results were similar to those obtained by the Soxhlet extraction (Figure 8).

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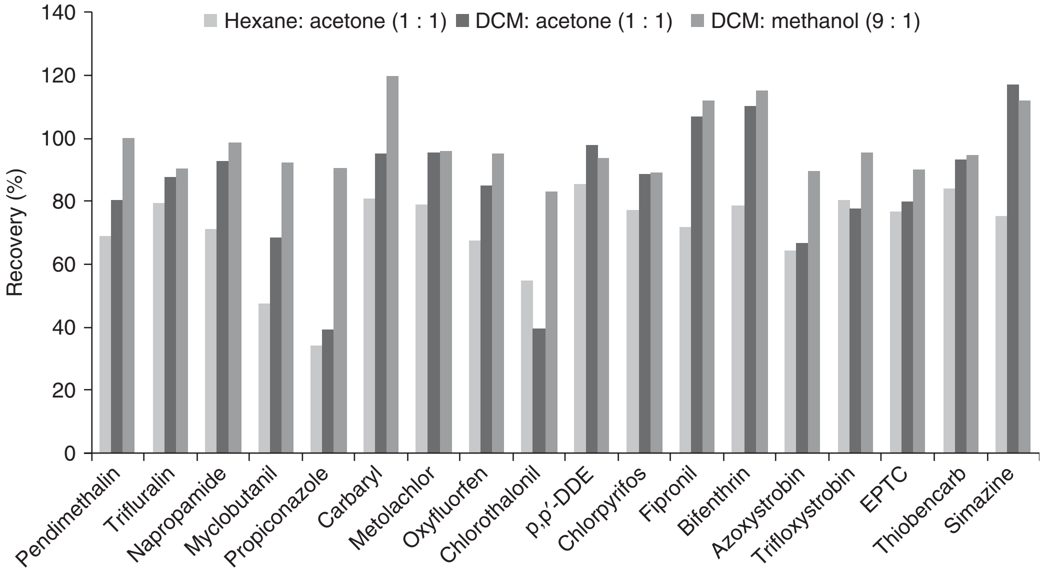

Figure 7 Extraction of pesticides in sediment.(20). (Adapted from Ref. 20. Copyright 2008, Elsevier.)

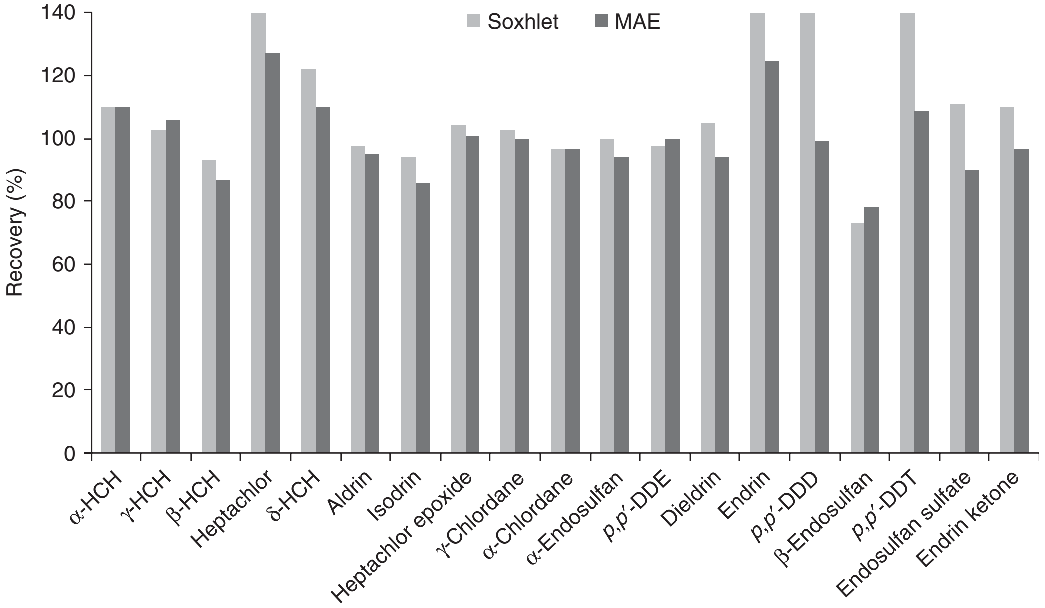

Figure 8 Extraction of organochlorine pesticides in spiked animal feed.(21). (Reproduced with permission from Ref. 21. Copyright 2008, Springer.)

Extraction of four common booster biocides (Diuron, TCMTB, Irgarol 1051, and Dichlofluanid) in harbor sediments was reported.(22) The sediment, which had been collected from marinas and fishing harbors of Gran Canaria Island, was freeze-dried, ground, homogenized, and stored in the dark at −18 °C until the analysis. The sediment sample (1 g) was spiked with the target compounds and left at room temperature for 12 h. The MAE optimization procedure employed a 2^3 factorial design in the screening stage and a response surface design in the second stage. A volume of 10 mL of MeOH was fixed as it was found that the solvent volume had less influence on the extraction. The MAE optimum conditions were microwave power of 200 W and extraction time of 6 min. Then, the extracts were filtered and combined with an optimized volume of Milli-Q water before the SPE procedure. The HPLC-MS/MS was used to determine the biocidal concentrations in the sample. The approach provided recoveries ranged between 76.1% and 99.7% with the RSD less than 7%. The detection limits ranged between 0.1 and 0.3 ng g^{-1}.

Nonpolar solvents cannot absorb microwave energy and unable to heat sample for extraction. Recently, a new microwave absorption tube was designed to be used to heat the sample directly, enabling the application of nonpolar solvent in microwave extraction for determination of organophosphorus pesticides (OPPs) from fresh vegetables.(23) The microwave apparatus consisted of a portable microwave oven, PTFE vessels, and microwave absorption tube. Graphite powder filled in a glass tube was used as a microwave absorption tube. Fresh samples were chopped and homogenized with food processor. The sample was spiked with standard solutions and stored for 24 h in the dark at room temperature. Then, 3 g of sample, 25 mL of hexane, and microwave absorption tube were placed in microwave extraction vessel and irradiated under 425 W at 70 °C for 8 min. The extract was concentrated and dissolved in 1 mL of hexane, filtered, and then directly analyzed by GC/MS. The recovery results indicated that for all seven OPPs, the recoveries ranged from 76.5% to 109.4%, and the RSDs were less than 13%. The LODs and LOQs were in the range 0.15–0.54 and 0.5–1.8 µg kg^{-1}, respectively.

4.1.2.5 Emerging (Polar) Pollutants Apart from the extraction of nonpolar organic pollutants (e.g. PAHs and hydrocarbons) from environmental samples, considerable attention has also been given for the scientific literature on the use of MAE for the extraction of a range of organic compounds that are sometimes referred to as emerging (polar) pollutants. These emerging pollutants include such classes of compounds as drugs of abuse, flame retardants, industrial additives and agents, perfluorinated compounds, personal care products, pharmaceuticals, steroids and hormones, and surfactants (as well as their transformation products).(24)

The approach for determination of various estradiol-mimicking compounds in sewage sludge has been reported.(25) The 10 compounds investigated in this study include BPA, 17β-estradiol, estradiol, 17α-ethynylestradiol, 4-octylphenol, octylphenol monoethoxylate, octylphenol polyethoxylate, 4-nonylphenol, nonylphenol monoethoxylate, and nonylphenol polyethoxylate. Raw sludge samples (blanks) were spiked with the standard mixtures in MeOH, stirred to homogenize, and air-dried for 12 h in the dark at room temperature. The spiked sludge samples were extracted with 5 mL of MeOH under a microwave power of 300 W for 10 min. The extracts were filtered and diluted with an optimized volume of Milli-Q water before the SPE cleanup step. The samples were then analyzed by HPLC-MS/MS. The recoveries of the analytes, spiked at 10 and 100 ng g^{-1} level, were determined. It was found that the sample analyzed gave recoveries ranging from 71.7% to 103.1%, with RSD lower than 11.1% and LODs ranging from 0.6 to 3.5 ng g^{-1}. The method was then applied to the extraction of the phenols from three wastewater treatment plants; the results showed that all of the analytes in this study were found in almost all samples with the concentrations ranging from 0.9 to 710 ng g^{-1}. Navarro et al.(26) have developed the MAE and cleanup procedure for the analysis of alkylphenols and17β-estradiol in zebrafish homogenate. The spiked fish homogenate was prepared and kept at −20 °C for a month before the extraction. The optimized conditions for the MAE were 5 mL of acetone, microwave power 504 W (80% of the maximum irradiation power), and extraction time 15 min. After completion of the MAE, the supernatant of the sample was filtered and concentrated. The extract was then subjected to the SPE or gel permeation chromatography (GPC) cleanup step followed by GC/MS analysis. When compared to focused ultrasound solid–liquid extraction (FUSLE), the MAE provided comparable results for 4-*n*-octylphenol and octylphenol, while higher recoveries were obtained for 4-*tert*-octylphenol and 17β-estradiol. The RSDs ranged from 7% to 25%.

The merits of ultrasound-assisted extraction (USE), MAE, and pressurized liquid extraction (PLE) for the extraction of BPA and its chlorinated derivatives in sewage sludge samples were compared.(27) The blank spiked samples were used for method validation. The samples (1 g) were extracted under the following optimum MAE conditions: solvent (10 mL of EtAc with 400 µL of Milli-Q water added to facilitate the heating process), extraction temperature (90 °C), microwave power (1000 W), and extraction time (10 min). The extracts were centrifuged and the supernatant was decanted into a glass vial, concentrated, and redissolved with the mobile phase. The samples were then analyzed using HPLC-MS/MS. The results (Figure 9) showed that average recoveries of the BPA and its chlorinated derivatives were closed to 100% (97.0–103.1%) for the three analytical methods with the variability below 6%.

Recent reviews have highlighted the application of MAE for the extraction of a range of emerging (polar) pollutants including BPA, surfactants (i.e. alcohol ethoxylates, alcohol phenyl ethoxylates, and linear alkylbenzene sulfonates), flame retardants (i.e. polybrominated diphenylethers), pharmaceutical compounds (e.g. nonsteroidal anti-inflammatory drugs), estrogens (e.g. testosterone), and personal care products (i.e. synthetic musks)

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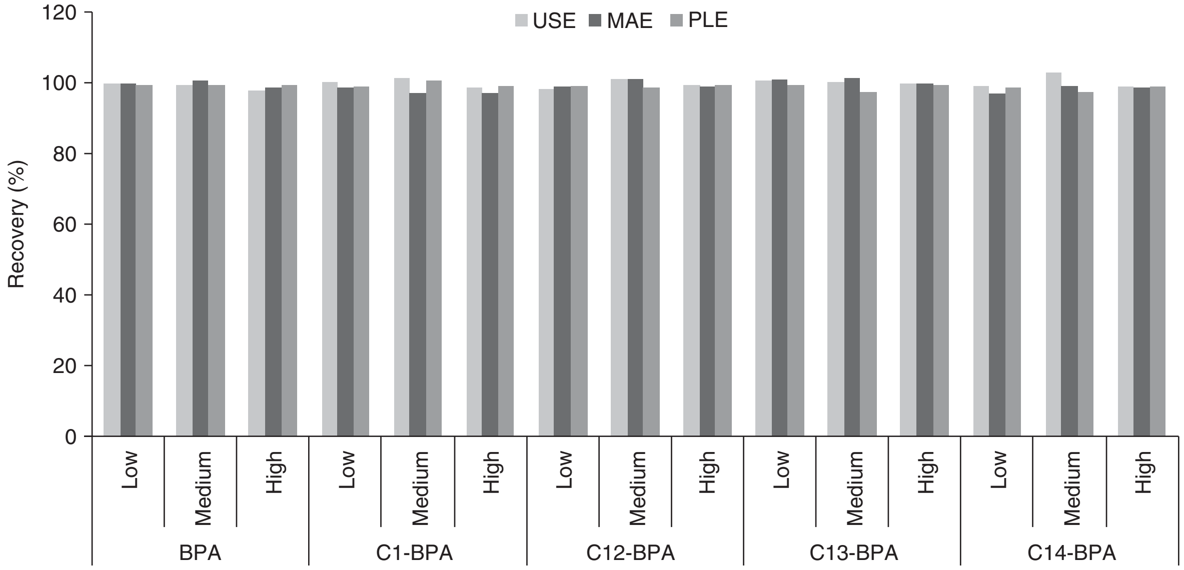

Figure 9 Extraction of bisphenol-A and its chlorinated derivatives in sewage sludge.(27). (Adapted from Ref. 27. Copyright 2012, Elsevier.)

from biological tissues, house dust, sediments, sewage sludge, and soil.(24,28)

4.2 Extraction from Aqueous Matrices

4.2.1 *Semipermeable Membrane Device-Microwave-Assisted Extraction*

Semipermeable membrane devices (SPMDs) have been used to bioaccumulate the lipophilic contaminants in water, sediment, and air for research or monitoring studies. The analytes in field-deployed SPMDs are recovered by the following steps: cleaning of the SPMD surface, extraction of the analytes, cleanup of the extracts, and chemical analysis of extracts. In the extraction step, the researchers(29) employed MAE as an alternative to dialysis, which is the routine procedure to extract polybrominated diphenyl ethers (PBDEs) and polychlorinated naphthalenes (PCNs) in spiked water, spiked SPMDs, and field SPMDs deployed at the sewage treatment plant. A two-level full factorial design 2^3 plus a center point was used for optimization of microwave extraction conditions. An Ethos SEL Labstation (Milestone Inc., Italy) was used for MAE. After the accumulation of analytes on SPMDs, the SPMDs were inserted into 100-mL extraction vessels and 60 mL of the solvent (hexane : acetone, 1 : 1 v/v) was added. The extraction time was maintained at 1 min at the temperature of 85 °C, setting at a maximum power of 1000 W. The extracts were then diluted to 5 mL with DCM and submitted to the GPC cleanup before the GC/MS/MS analysis. The recovery of MAE was comparable to the dialysis method; the recovery of MAE was between 72% and 91% for PBDEs and between 96% and 103% for PCNs with the RSDs lower than 15% for all analytes.

4.2.2 *Cloud Point Extraction-Microwave-Assisted Back-Extraction*

Cloud point extraction coupled with microwave-assisted back-extraction was developed for the analysis of organophosphorous pesticides (OPPs) including phorate, diazinon, parathion-methyl, fenthion, and quinalphos in human urine.(30) The procedure is as follows: 200 µL of isooctane was added into the preconcentrated analytes obtained from cloud point extraction of 10 mL sample, and the back-extraction was performed under the microwave power of 700 W for 2 min in a domestic microwave oven (LG, Tianjin, China). After microwave extraction, two distinct layers were formed: surfactant-rich phase (less than 200 µL, lower layer) and the isooctane phase (200 µL, upper layer). The isooctane phase was transferred and centrifuged for 1 min at 3000 rpm. The supernatant extract was then analyzed by GC/flame photometric detector (FPD). The spiked recoveries at 1.00 and 5 ng mL^{-1} were used to evaluate the accuracy of the method. The results showed that the recoveries ranged between 85% and 107% with the RSDs less than 9%. The LODs and LOQs of the method were in the range 0.04–0.08 and 0.12–0.24 ng mL^{-1}, respectively, for the five OPPs. The approach is considerably cheaper

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and easier than SPE and solid-phase microextraction (SPME).

4.2.3 *Gas-Phase Microwave-Assisted Extraction*

The vaporization of the PAHs from water sample using microwave energy has been described by Wei and Jen.(31) The aqueous sample (20 mL) is heated via a microwave oven, vaporizing the PAHs into the headspace (HS) of the sample. The microwave irradiation was carried out at 145 W for 30 min. The evaporated PAHs were absorbed directly on an SPME fiber (a 65-μm PDMS/DVB) in the HS and introduced into GC with FID. The approach was validated using the PAH-spiked water, and the results obtained were favorable. Compared to other SPME methods, the microwave-assisted-HS-SPME (MA-HS-SPME) gave a shorter time to complete the sample pretreatment for PAHs. The same group(32) also applied the microwave energy to accelerate the vaporization of chlorophenols (CPs) from aqueous sample. The optimum procedure was as follows: 10 mL aqueous sample was irradiated with 3.0 μL of 1-octanol under the microwave power of 167 W at a temperature of 45 °C for 10 min. In this work, they used the hollow fiber liquid-phase microextraction (LPME), mounted on the needle tip of the microsyringe, for absorption of the analytes in the HS and introduced into GC with ECD. The approach was applied to analyze the CPs in an actual complex aqueous sample, a leachate sample collected from the landfill. The analysis results of the spiked sample were satisfactory with recovery between 83% and 102% and RSD below 10.4%. The approach was compared to water-bath HS-LPME method; the MA-HS-LPME gave higher extraction efficiencies for CPs. The same group(33) has continued to develop the one-step microwave-assisted HS controlled-temperature liquid-phase micro-extraction (MA-HS-CT-LPME) for sampling of DDT and its main metabolites in complicated aqueous samples followed by GC/ECD analysis. This method employed an external cooling system that controls the temperature of the dense cloud of analyte–water vapor formed in the HS LPME sampling zone. Heating of the sample was performed using microwave power of 249 W for 6.5 min. The method efficiently yielded accurate and precise results with the spiked recoveries between 95.5% and 101.3% for agricultural field water, between 94% and 99.7% for seawater, and between 93.5% and 98% for river water. The RSDs were less than 11.6% for all cases. In addition, the method was validated by analysis of an aqueous CRM and compared with the results obtained by liquid–liquid extraction (LLE). The MA-HS-CT-LPME results were generally agreed with those obtained by LLE.

Table 2 Recommendations for pressurized-microwave-assisted extraction

Variable	Operating condition
Temperature	>115 °C but <145 °C
Pressure	<200 psi (Note: Extraction vessels should have a safety feature, e.g. rupture membrane that prevents this pressure being exceeded.)
Microwave power	100%
Extraction time (time at parameter)	>5 min but < 20 min. (Note: Longer time is recommended if more than 12 vessels are to be extracted simultaneously.)
Extraction solvent volume	30–45 mL per 2–5 g of sample
Extraction solvent	Hexane–acetone (1 : 1, v/v) has been the most commonly used Other solvents also appear to be satisfactory, e.g. acetone

5 CONCLUSIONS

The use and application of MAE continue to expand. However, as you will be aware after reading this article, the diversity of operating conditions and solvent choice suggested by others, merely adds to the difficulty in accepting MAE in the laboratory. To assist the reader in this choice, Table 2 contains guidelines for MAE method development. As pressurized MAE is the most common approach, details for this mode of operation only are provided. The parameters shown in Table 2 are based on the use of a microwave system capable of delivering a minimum power of 900 W. Ideally, the microwave system should be equipped with the following safety features: a fan and appropriate ducting to allow ventilation of the cavity in the event of an organic vapor release, a solvent sensor that automatically shuts off the microwave source in the event of an organic solvent leakage (minimizing the risk of fire), and extraction vessels that automatically vent into a solvent collection system at a pre-set pressure (to minimize the risk of explosion).

ABBREVIATIONS AND ACRONYMS

AAE	Agitation-assisted Extraction
ASE	Accelerated Solvent Extraction
BCR	Community Bureau of Reference
BPA	Bisphenol-A
CP	Chlorophenol
CRM	Certified Reference Material
DAD	Diode Array Detector
DCM	Dichloromethane

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DLLME	Dispersive Liquid–liquid Microextraction
ECD	Electron Capture Detector
EtAc	Ethyl Acetate
EU	European Union
FID	Flame Ionization Detector
FL	Fluorescence Detector
FPD	Flame Photometric Detector
FUSE	Focused Ultrasound Extraction
FUSLE	Focused Ultrasound Solid–liquid Extraction
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
HDBIm-Br	1-hexadecyl-3-butylimidazolium Bromide
HDMIm-Br	1-hexadecyl-3-methylimidazolium Bromide
HPLC	High-performance Liquid Chromatography
HRGC	High-resolution Gas Chromatography
HRMS	Resolution Mass Spectrometry
HS	Headspace
IDMS	Isotope-dilution Mass Spectrometry
IL	Ionic Liquid
LLE	Liquid–liquid Extraction
LOD	Limit of Detection
LOQ	Limit of Quantitation
LPME	Liquid-phase Microextraction
MA-HS-CT-LPME	Microwave-assisted HS Controlled-temperature Liquid-phase Micro-extraction
MA-HS-SPME	Microwave-assisted-HS-SPME
MAE	Microwave-assisted Extraction
MeOH	Methanol
MS	Mass Spectrometry
MW	Molecular Weight
OCP	Organochlorine Pesticide
OPP	Organophosphorous Pesticide
PAH	Polycyclic Aromatic Hydrocarbon
PBDE	Polybrominated Diphenyl Ether
PCB	Polychlorinated Biphenyl
PCN	Polychlorinated Naphthalene
PFA	Perfluoroalkoxy Polymer
PLE	Pressurized Liquid Extraction
PTFE	Polytetrafluoroethylene
RSD	Relative Standard Deviation
SAE	Sonication-assisted Extraction
SFE	Supercritical Fluid Extraction
SPD	Sample Preparation Device
SPE	Solid-phase Extraction
SPMD	Semipermeable Membrane Device
SPME	Solid-phase Microextraction
SRM	Standard Reference Material
TFM	Tetrafloromethoxyl Polymer
USE	Ultrasound-assisted Extraction
USEPA	United States Environmental Protection Agency
UV	Ultraviolet

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