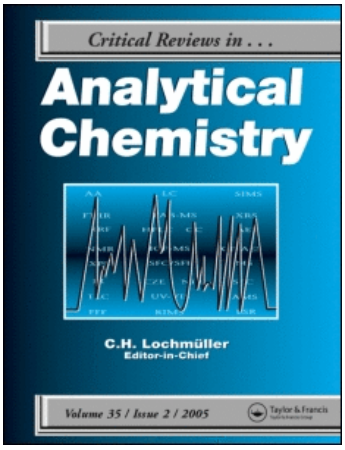

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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Online publication date: 03 June 2010

To cite this Article Lopez-Avila, Viorica(1999) 'Sample Preparation for Environmental Analysis', Critical Reviews in Analytical Chemistry, 29: 3, 195 — 230
To link to this Article: DOI: 10.1080/10408349891199392
URL: http://dx.doi.org/10.1080/10408349891199392

Critical Reviews in Analytical Chemistry, 29(3):195–230 (1999)

Sample Preparation for Environmental Analysis

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ABSTRACT: Sample preparation continues to be an important step in environmental analysis and a lot of progress has been made in the last decade toward the development of faster, safer, and more environmentally friendly techniques for sample extraction and extract clean up prior to instrumental analysis. This article focuses on the state of the art in sample preparation, particularly in the area of supercritical fluid extraction, microwave-assisted extraction, accelerated-solvent extraction for solid matrices, and both solid-phase extraction and solid phase microextraction for aqueous matrices. Driven by the need for faster, cheaper, and more sensitive analytical methods, advances in sample preparation have included not only automation but many developments in coupling sample preparation with instrumental analysis (e.g., supercritical fluid extraction coupled with immunoassays). Examples are presented for extraction of polynuclear aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls, phenolic compounds, triazine and chlorophenoxy acid herbicides, and organotin and organomercury compounds from solid matrices with supercritical carbon dioxide and modified supercritical carbon dioxide as well as organic solvents under microwave irradiation. Emerging trends in sample preparation such as *in situ* derivatization/extraction of analytes from solid matrices and solventless extraction techniques such as solid-phase microextraction are presented.

KEY WORDS: extraction techniques, supercritical fluid extraction, microwave-assisted extraction, accelerated-solvent extraction, solid-phase extraction, solid-phase microextraction, matrix solid-phase dispersion.

I. SAMPLE PREPARATION FOR SOLID MATRICES

Common extraction techniques for solid matrices include Soxhlet extraction, sonication extraction, supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), and accelerated-solvent extraction (ASE). Others, such as the shake method, are also in use, but they work well mainly for very porous matrices with fewer analytes to be extracted. Table 1 summarizes the most common techniques for solid matrices, and Table 2 presents their advantages and disadvantages.

The advantages of Soxhlet extraction include: (1) it allows use of large amount of sample (e.g., 10 to 30 g), (2) no filtration is required after the extraction, (3) the technique is not matrix dependent, and (4) many Soxhlet extractors can be set up to perform in unattended operation. Attempts made to automate the technique were somewhat successful, and a few commercial systems (e.g., Soxtec of Tecator/Perstorp Analytical and Soxtherm of O.I. Analytical) are available in which as many as six samples can be extracted in parallel with much shorter extraction times and less solvent use than the conventional Soxhlet. The most significant drawbacks of Soxhlet extraction are (1) long extraction times (e.g., up to 24 to 48 h), (2) large amount of solvent usage (300 to 500 mL per sample), and (4) the need for evaporation after sample extraction.

Sonication extraction is faster than the Soxhlet extraction (30 to 60 min per sample) and allows extraction of large amount of sample with a relatively low cost, but it still uses about as much solvent as the Soxhlet extraction, is labor intensive, and filtration is required after extraction.

The newer extraction techniques such as SFE, MAE, and ASE are very attractive because they are a lot faster, use much smaller amounts of solvents, and are environmentally friendly tech-

TABLE 1
Extraction Techniques For Solid Matrices

Extraction technique	Principles	Approved EPA Method
Conventional Soxhlet	Sample is placed in an extraction thimble and leached with hot solvent in a Soxhlet extractor for 8-12 hrs. Solvent evaporation/concentration is done separately.	3540
Automated Soxhlet	Sample is placed in an extraction thimble and immersed in boiling solvent for 30 to 60 min; thimble is then raised for Soxhlet extraction with solvent refluxing. Solvent evaporation/concentration is possible.	3541
Supercritical fluid extraction	Sample is placed in a high pressure cartridge or chamber and extracted with supercritical fluid (e.g., carbon dioxide at pressures of 150 to 450 atm and temperatures of 40 to 150°C). After depressurization, analytes are collected in a small volume of organic solvent or on a trap.	3560, 3561, 3562
Microwave-assisted extraction	Sample is placed in an open- or closed vessel, immersed in solvent, and heated with microwave energy	3546
Accelerated-solvent extraction	Sample is placed in extraction vessel and pressurized with solvent heated above its boiling point; the extract is automatically removed and transferred to a vial	3545

TABLE 2
Sample Preparation for Solid Matrices—Advantages and Disadvantages

Technique	Advantages	Disadvantages
Soxhlet Extraction	• Standard method • Large amount of sample (10-30 g) • Filtration not required • Not matrix dependent • Unattended operation • Low cost	• Long extraction time, up to 24-48 hrs • Large amount of solvent (300-500 mL) • Evaporation of extract is mandatory
Sonication	• Fast (30-60 min) • Large amount of sample (10-30 g) • Not matrix dependent • Low cost	• Large amount of solvent (300-500 mL) • Labor intensive • Filtration required • Exposure to solvent vapor
Supercritical Fluid Extraction (SFE)	• Fast (30-60 min) • Carbon dioxide is nontoxic, nonflammable, environmentally-friendly • Selectivity can be achieved by varying pressure, temperature, and modifier • Small amount of solvent (5-10 mL) • Filtration not required • No solvent exposure • Automated	• Limited sample size (<10g) • Matrix dependent • Modifier addition to improve efficiency • High cost
Microwave-Assisted Extraction (MAE)	• Fast (20-30 min) • Small amount of solvent compared to Soxhlet (30 mL vs. 300-500 mL) • Full control of extraction parameters (time, power, temperature) • Stirring possible • Higher temperatures • No drying agents are needed • As many as 12 samples can be processed simultaneously in one hour	• Extracts must be filtered • Polar solvent needed • Everything gets extracted (cleanup needed) • Moderate cost
Accelerated-Solvent Extraction (ASE)	• Fast (extraction time ~15 min) • Minimal solvent usage (15-40 mL) • No filtration needed • Automated (allows sequential extraction of up to 24 samples) • Easy to use	• High capital cost • Matrix dependent

niques. For example, SFE uses carbon dioxide for extraction or modified carbon dioxide and only small volumes of organic solvent are needed for collection of the extracted material. Carbon dioxide is a nontoxic, nonflammable, and environmentally friendly solvent. Furthermore, the extraction selectivity can be controlled by varying the pressure and temperature of the supercritical fluid and by addition of modifiers; SFE provides for easy removal and disposal of the extraction solvent; and SFE systems available commercially allow sample extraction in unattended operation (up to 44 samples can be extracted sequentially). The disadvantages of this technique include: (1) limited sample size; (2) the method recovery is dependent on the matrix; (3) carbon dioxide is a relatively nonpolar solvent and, thus, more polar solvents such as methanol are needed to improve the extraction efficiencies or polar pesticides; and (4) high cost of the equipment.

MAE is also very promising because (1) it is fast (e.g., 20 to 30 min per batch of as many as 12 samples); (2) uses small amounts of solvents when compared with the Soxhlet and sonication extraction (30 mL in MAE versus 300 to 500 mL in Soxhlet extraction); (3) allows full control of extraction parameters (time, power, temperature); (4) stirring of the sample is possible; (5) allows high temperature extraction; and (6) no drying agents are needed in MAE because water absorbs microwaves very fast and thus can be used to heat up the matrix. MAE has several drawbacks that contributed to its slow acceptance such as (1) extracts must be filtered after extraction, which slows down the operation; (2) polar solvents are needed; (3) clean up of extracts is needed because MAE is very efficient (e.g., "everything" gets extracted); and (4) the equipment is moderately expensive.

Accelerated-solvent extraction is a fairly new extraction method that was approved recently by the U.S. Environmental Protection Agency (EPA) as Method 3545. The extraction is done in a closed-vessel at elevated temperatures (50 to 200°C) and pressures (1500 to 2000 psi). This technique is attractive because (1) it is fast (e.g., extraction time is approximately 15 min per sample), (2) uses minimal solvent (15 to 40 mL), (3) no filtration is required after the extraction, and (4) the instrumentation allows extraction in unattended operation. At least 24 samples can be processed sequentially and different sample sizes can be accommodated (e.g., 11, 22, and 33-mL vessels are available).

A. Supercritical Fluid Extraction

1. Theoretical Considerations

Supercritical fluid extraction (SFE) is an extraction technique that uses a solvent in its supercritical state. Supercritical fluids have unique properties that place them between liquids and gases. Their viscosities are much lower than those of liquids and their surface tensions are very low. Thus, they can penetrate into the pores of solids much more easily than liquids. Their densities, however, are close to those of liquids, which means that their capacities for carrying dissolved materials are also similar to those of liquids.

Although many supercritical fluids have been investigated (N_2O, SF_6, NH_3), the most commonly used supercritical fluid is carbon dioxide (CO_2). It reaches the supercritical state at a relatively low pressure (i.e., 72.9 atm) and temperature (i.e., 31.3°C). It is nontoxic, nonflammable, noncorrosive, chemically very inert, and affordable. It is nonpolar, but its polarity can be adjusted with modifiers such as acetone, methanol, or hexane. Its rapid penetrating and solvating power provides high recoveries for many analytes.

Supercritical fluids can be used under a wide range of conditions. As long as they remain above the critical point, pressure and temperature can be varied, as can flow rates, extraction times, and modifiers. SFE efficiency is also affected by a multitude of other variables, including matrix type, analyte type, fluid type, moisture content of the matrix, vessel geometry, vessel orientation, restrictor type, and analyte collection system. More details on SFE principles can be found elsewhere.[1,2]

2. Instrumentation

The components of an SFE system include a carbon dioxide cylinder, a pump, an oven for the extraction vessel, a backpressure device (restrictor), and a collection system (Figure 1). Carbon dioxide required for analytical SFE should

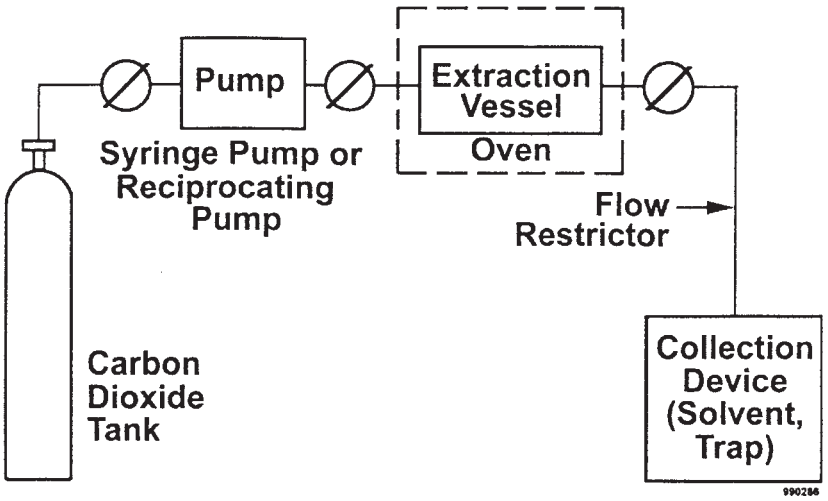

FIGURE 1. Basic components of the SFE system.

be of either SFE-grade or SFE-SFC-grade and is supplied as liquid carbon dioxide in a cylinder fitted with a dip tube. When working with modified carbon dioxide, a second pump is needed to add the modifier because it has been demonstrated that when using premixed carbon dioxide, the carbon dioxide to modifier ratio varies over the lifetime of operation of the cylinder.

The most common pump in SFE is the reciprocating pump or piston pump, which uses cooling of the pump heads to maintain the carbon dioxide in the liquefied state. Syringe pumps are also used, but they have a limited capacity. The ideal pump would deliver at a constant flow rate, and at pressures in the range of 3000 to 10,000 psi. The pressure is maintained inside the extraction vessel using either fixed or variable restrictors that are mechanically or electronically controlled. Most of the systems available commercially can be operated up to 150°C, but there are a few that can be heated up to 200°C (Table 3).

3. Specific Applications of SFE*

a. Petroleum Hydrocarbons

Petroleum hydrocarbons have been extracted from soil and sediment samples with supercritical carbon dioxide at 340 atm and 80°C and collected in tetrachloroethylene. To remove any polar compounds that get extracted under these conditions, the extracts are subjected to silica gel cleanup prior to infrared spectrometry.[3,4] Single-laboratory evaluation of this method (EPA Method 3560) indicates that that its performance is equivalent to the Soxhlet extraction method with Freon-113; method accuracy (percent recovery) is 80% or higher, and method precision (% relative standard deviation) is better than 20%. The method detection limit is 10 μg/g. An interlaboratory study of this method was reported by Lopez-Avila et al.[4] Fourteen laboratories participated in the extraction of four matrices, each in triplicate. The results indicated that the overall method accuracy for concentrations ranging from 614 to 32,600 mg/kg was 82.9%.[4] Method precision appeared to be matrix dependent and ranged from 17.3 to 45.4%. Extraction at higher temperatures (e.g., 150°C) works well for samples contaminated with heavy fuel oil but not for gasoline contaminated samples;[5] in this case, extraction at 65°C resulted in higher petroleum hydrocarbon recoveries when compared with Soxhlet extraction.

b. PAHs

There are numerous references in the literature dealing with the extraction of PAHs with supercritical fluids and in particular with

* Specific applications of SFE are given in tables.

TABLE 3
Features of Commercially Available SFE Systems

Product	SFX 3560	AutoPrep 44	SFX 2-10	SFX 220	7880 SFE	DGMS	Speed SFE-2	Speed SFE-4	TFE 2000
Manufacturer	Isco Lincoln, NE	Isco Lincoln , NE	Isco Lincoln, NE	Isco Lincoln, NE	Hewlett Packard Wilmington, DE	Marc Sims SFE Berkeley, CA	Applied Separations Allentown, PA	Applied Separation Allentown, PA	Leco St. Joseph, MI
Dimensions (w x d x h, in.)	22 x 18 x 30	36 x 26 x 29	13 x 10 x 10	13 x 10 x 10	18 x 21 x 33	36 x 20 x 28	16 x 20 x 36	16 x 20 x 36	17 x 22 x 24
Automated	yes	yes	no	yes	yes	no	no	yes	yes
Number of Samples	25	44	2	2	8	1	2	4	3
Max. system pressure (psi)	7500 or 10,000	7400 or 10,000	7500 or 10,000	7500 or 10,000	5560	6000	10,000	10,000	10,000
Max. pump flow rate (mL/min)	90 or 40	7	90 or 40	90 or 40	4.0	15	50 L/min (as gas)	50 L/min (as gas)	10 L/min (as gas)
Extractor vessel capacity (mL)	0.5-10	0.5-10	0.5-10	0.5-10	7.0	5-300	0.5-1,000	0.5-1,000	10
Max. oven temp. (°C)	150	150	150	150	150	100	250	250	150
Restrictor type	Fixed, variable	Variable	Fixed, variable	Fixed, variable	Variable	Variable	Variable	Variable	Variable, automated
Restrictor flow rate (mL/min)	0.5-10	1.0-7.0	0.5-10	0.5-10	0.5-4.0	0-15	0.5-10	0.5-10	0.5-3 L/min (as gas)
Static and dynamic flow	yes	yes	yes	yes	yes	yes	yes	yes	yes
Flow orientation	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical
Collection mode(s)	Solvent	Sorbent	Solvent	Solvent	Sorbent	Solvent, Sorbent	Solvent, Sorbent	Solvent, Sorbent	Sorbent (glass wool)

TABLE 4
Selected SFE Applications Reported in the Literature

Analyte	Matrix	Fluid	SFE Conditions	Reference
Petroleum hydrocarbons	Soils Sediments	CO_2	340 atm, 80°C, collection in tetrachloroethylene	3,4
Petroleum hydrocarbons	Soils	CO_2	40 MPa, 150°C	5
PAHs	Soils (cryogenic grinding)	CO_2	350 atm, 90°C Addition of dichloromethane as matrix modifier; collection in dichloromethane	6,7
PAHs	Soil	CO_2	See Table 5	8
PAHs	Marine sediment	CO_2 CO_2/10% methanol CO_2/10% toluene CO_2/10% diethylamine	400 atm 80°C, 200°C	10
PAHs	Fly ash	CO_2 CO_2/5% (1% TFA in toluene) CO_2/5% toluene	400 atm 90°C collection in a liquid/solid trap	11
PAHs	Soil	CO_2/20% methanol	70°C 250 atm	12
PAHs	Soil	CO_2 (Step 1) and CO_2/1% methanol/ 4% dichloromethane (Step 2) and CO_2 (Step 3)	80°C/121 bars (Step 1) 80°C/339 bars (Step 2) 100°C/334 bars (Step 3)	14
PCBs	Soil	CO_2/2% methanol	97°C 378 bar 10 min static/30 min dynamic Florisil trap	15
PCBs	Soil	CO_2	70°C 371 bar 16 min static/30 min dynamic C_{18}-bonded silica trap	15
PCBs	Soil	CO_2/1.7% methanol	70°C 371 bar 20 min static/20 min dynamic; sorbent:	15

Analyte	Matrix	Fluid	SFE Conditions	Reference
PCBs	House dust	CO_2	40°C 200 bar	16
PCBs	Soil Marine sediment River sediment	CO_2	100°C 350 atm 20 min dynamic	17
PCBs	Fish tissue	CO_2	100°C 330 atm (cleanup after extraction on Florisil columns)	18
PCBs	Sediments	CO_2/15% dichloromethane	80°C 200 atm 60 min dynamic	19
PCBs	Human adipose tissue	CO_2	40°C 280 atm (in the presence of AlO_x as fat retainer)	20
Dioxins	Fly ash (pretreated with 1 M HCl)	CO_2	40°C, 80°C, 145°C 200 atm, 400 atm, 500 atm 60 min 250 μL of 10% TFA in toluene was added to matrix	22
Organochlorine pesticides	Soil	CO_2	50°C 20 MPa 10 min static/20 min dynamic Collection in isooctane	23
Organochlorine and organophosphorus pesticides	Soil	CO_2/3% methanol	40°C; 60°C; 80°C; 100°C; 120°C	24
Organochlorine pesticides	Soil	CO_2	50°C 250 atm 15 min static/40 min dynamic	25
Organophosphorus pesticides	Soil	CO_2/5% methanol	50°C 250 atm 15 min static/40 min dynamic	25
Triazines and urea herbicides	Soil	CO_2/10% methane	50°C 250 atm min/15 min static/40 min dynamic	25

TABLE 4 (continued)
Selected SFE Applications Reported in the Literature

Analyte	Matrix	Fluid	SFE Conditions	Reference
Imidacloprid Methiocarb Chlorothalonil Chlorpyrifos Endosulfan I/II Endosulfan sulfate	Vegetables (pepper, tomato)	CO_2	300 atm 50°C 200 μL methanol added to matrix	27
Atrazine	Soils	CO_2/7% acetone	42 MPa 80°C 10% methanol added to matrix 15 min static/30 min dynamic	30
Atrazine Simazine Ametrine Simetryne Prometryne	Soil	CO_2 CO_2/5% methanol CO_2/10% methanol	80°C 30 MPa Collection in ethanol 15 min extraction	31
Atrazine Deethyl atrazine Deisopropyl atrazine	Soil	CO_2 CO_2/20% acetone CO_2/5% triethylamine CO_2/20% triethylamine CO_2/20% methanol CO_2/20% methanol (0.65M TFA)	100°C/340 atm 150°C/340 atm 200°C/340 atm	32
Atrazine Deethyl atrazine Simazine Deethyl simazine	Sediment	CO_2 CO_2/acetone	80°C, 100°C, 120°C, 140°C density 0.71 g/mL 10 min static/30 min dynamic collection on trap at -20°C	33
Atrazine Diuron Benzsulfuron-methyl	Soils	CO_2 CO_2/5-30% modifier	40-150°C (atrazine) 40-100°C (diuron) 40-70°C (benzsulfuron methyl) 140-352 atm	34
Phenol o-cresol m-cresol p-cresol	Soils	CO_2 (in-situ derivatization)	115°C density 0.4 g/mL 5 min static/15 min dynamic 20 μL pyridine/115 μL acetic anhydride	35

Analyte	Matrix	Fluid	SFE Conditions	Reference
Pentachlorophenol	Wood Leather	CO_2	50°C 250 atm, 300 atm 10 min static/25 min dynamic 100 μL TEA 400 μL acetic anhydride	36
Chlorophenoxy acid herbicides	Soil	CO_2	100°C 400 atm 60 min static/ 30 min dynamic PFBBr/TEA collection in acetone	37
2,4-D Atrazine Simazine Alachlor	Soil	CO_2	66°C 20.3 MPa (3 min) and 34.4 MPa (17 min)	38
1,4-Phenylenediamine 2,4-Diaminotoluene Benzidine 4,4'-Methylenebis (2-chloroaniline) 3,3'-Dimethylbenzidine 3,3'-Dichlorobenzidine	Soil	N_2O	50°C 350 atm 10 min static/10 min dynamic 5% of 1,6-hexane-diamine in methanol was used as matrix modifier	39
2,4,6-Trinitrotoluene 1,3,5-Trinitrobenzene	Soil	CO_2/5% methanol	150°C 500 atm 5 min static/15 min dynamic	40
Dihardened tallow-dimethylammonium chloride (DHTDMAC)	Dried Sewage Sludge	CO_2/methanol	85°C 40.53 MPa	41
Organotin compounds	Soils Sediments	CO_2/5% methanol	450 atm 60°C 20 min static/30 min dynamic Complexing agent DEA-DDC	42
Methyl mercury	Reference materials	CO_2	40°C density 0.9 g/mL flowrate 1.5 mL/min amount of HCl: 100 μL static time: 10 min	44

TABLE 4 (continued)
Selected SFE Applications Reported in the Literature

Analyte	Matrix	Fluid	SFE Conditions	Reference
Vitamin A β-carotene	Vitamin supplements Calf liver tissue	CO_2	80°C 31 MPa 1 min static/40 min dynamic	45
Xanthene dyes (phloxine B, uranine)	Soil	CO_2	60°C 272 atm Na_4EDTA, n-butylamine, and methanol are added to soil prior to extraction. Additional reextraction at 60°C/476 atm after addition of methanol. Collection in methanol.	46
Fat	Foods	CO_2/10% ethanol CO_2	150°C 475 atm 30 min repetitive static/dynamic extraction	47
Cd^{2+}, Pb^{2+},Hg^{2+}	Sand filter paper	CO_2/5% methanol	45°C/250 atm (sand) 60°C/200 atm (filter paper) LiFDDC, NaDDC, DEA-DDC as complexing agent	49

supercritical carbon dioxide. The reader can find these references in the two books on SFE.[1,2] The discussion here focuses primarily on those SFE procedures that have been validated through interlaboratory studies. In the study by Dankers et al.,[6] which was evaluated by Lopez-Avila et al.[7] in a mini-round-robin study, a cryogenically milled sample (5 g) is extracted with supercritical carbon dioxide at 350 atm and 90°C for 20 min (dynamic mode). Dichloromethane (2 mL) is added as a static modifier to sample immediately prior to extraction and the extracted material is collected in dichloromethane. The extracts were subjected to silica chromatography prior to GC/MS analysis. The SFE method accuracy, which was determined relative to sonication extraction, indicates that method accuracy is greater than 80% when compounds are present at concentration above 1 mg/kg. The SFE method precision appear to be concentrations dependent; at concentrations above 1 mg/kg, the percent relative standard deviations were 27% or lower; at concentration below 1 mg/kg, the percent relative standard deviations were ranging from 19 to 80%.[7]

The method reported by Gere et al.,[8] which was implemented by the U.S. EPA as Method 3561 (Table 5), uses three steps. In Step 1, extraction is performed with supercritical carbon dioxide at 119 atm and 80°C (10 min static and 10 min dynamic) at a flow rate of 2 mL/min; the extracted material is collected on a trap held at –5°C and subsequently removed from the trap with an organic solvent (the composition of the solvent depends on the instrumental analysis). The extraction is then continued at 333 atm and 120°C with modified supercritical carbon dioxide (the modifier is either methanol-water or methanol-dichloromethane depending on the analysis) at a flow rate of 4 mL/min. During Step 2, the trap temperature is raised to 80°C to prevent modifier from condensing onto the trap and the nozzle temperature is kept at 45°C. In Step 3, the extraction temperature and pressure remain the same as in Step 2, but the fluid is carbon dioxide. This procedure is quite tedious, and it is difficult to implement on any other commercial SFE systems. However, it appears that the "matrix effect" can be minimized by using this approach.[14]

Low- and high-temperature SFE of PAHs were investigated by Hawthorne and Miller;[9] these authors reported a significant change in recovery by increasing the temperature from 50 to 350°C (e.g., the average recovery of 17 PAHs was 56% at 50°C, 81% at 200°C, and 90% at 350°C). The use of high temperatures is, however, not practical when using commercial systems, because the O-rings on the extraction vessels can easily leak when subjected to temperatures in excess of 200°C.

Yang et al.[10] reported on the combined temperature/modifier effects on the recovery of PAHs from marine sediment, diesel soot, and air particulate matter. In the Yang study the pressure was maintained at 400 atm and the temperature was varied from 80 to 200°C; from the three modifiers investigated (e.g., methanol, toluene, and diethylamine), diethylamine was found to give the best recoveries for all matrices investigated. Friedrich et al.[11] reported that carbon dioxide modified with toluene containing small amounts of reactive substances such as triethylamine (TEA) or trifluoroacetic acid (TFA) gives significantly higher recoveries of PAHs from fly ash than unmodified carbon dioxide or carbon dioxide/toluene.

For a comparison study of SFE with Soxhlet, open-vessel MAE, closed-vessel MAE, and ASE, the reader should refer to Reference 12. Based on the data presented in that study (e.g., extraction recoveries, cost of instrumentation, solvent volume, extraction time, and sample weight), the method of choice still appears to be Soxhlet extraction.

Increased recoveries of PAHs extracted with carbon dioxide or modified carbon dioxide in a solid-liquid trap was reported;[13] the recoveries were found to be about 20% higher that those achieved with the collection in a solvent and there was no dependence on the flow rate of the extraction fluid.

Based on the literature data and work done in this laboratory, it can be concluded that (1) low-molecular-weight PAHs can be extracted efficiently with carbon dioxide, but they can be easily lost if the collection device is not a sorbent trap or some sort of solid-liquid device; (2) higher-molecular-weight PAHs can only be extracted efficiently with modified carbon dioxide (e.g., toluene containing triethylamine or trifluoroacetic acid was found to work well for fly ash); (3) higher temperatures seem to give increased

TABLE 5
SFE Operating Conditions for the SFE Methods Approved by U.S. EPA.

Analyte Class	SFE Conditions
Petroleum hydrocarbons (Method 3560)	Extraction
	Pressure: 5100 psi (340 atm) Density: 0.785 g/mL Temperature: 80°C Extraction Fluid: CO_2 Static equilibration time: 0 Dynamic extraction time: 30 min Flow rate: 1.1-1.5 mL/min (as liquid CO_2)
	Extract Collection
	Solvent: tetrachloroethylene (spectrophotometric grade) Volume: 3 mL
Volatile PAHs (Method 3561)	Extraction - Step 1
	Pressure: 1750 psi (119 atm) Density: 0.30 g/mL Temperature: 80°C Extraction fluid: CO_2 Static equilibration time: 10 min Dynamic extraction time: 10 min Flow rate: 2.0 mL/min (as liquid CO_2)
	Extract Collection - Step 1
	Trap packing: C_{18}-bonded silica
	Trap temperature: -5°C
	Nozzle temperature: 80°C (variable restrictor)
	Reconstruction of Collected Extracts - Step 1
	Rinse solvent for HPLC extract: 50:50 (v/v) THF-acetonitrile Rinse solvent for GC extract: 75:25 (v/v) dichloromethane-isooctane Collected fraction volume: 0.8 mL Trap temperature: 60°C Nozzle temperature: 45°C (variable restrictor) Rinse solvent flow rate: 1.0 mL/min
Less Volatile PAHs (Method 3561)	Extraction - Step 2
	Pressure: 4900 psi (333 atm) Density: 0.63 g/mL Temperature: 120°C Extraction fluid (for HPLC extract): 95:1:4 (v/v/v), CO_2-methanol-water Extraction fluid (for GC extract): 95:1:4 (v/v/v), CO_2-methanol-dichloromethane Static equilibration time: 10 min Dynamic extraction time: 30 min Flow rate: 4.0 mL/min
	Extract - Step 2
	Trap packing: C_{18}-bonded silica Trap temperature: 80°C Nozzle temperature: 80°C (variable restrictor) Reconstitution of collected extracts: none

TABLE 5 (continued)
SFE Operating Conditions for the SFE Methods Approved by U.S. EPA.

	Extraction - Step 3
	Pressure: 4900 psi (333 atm) Density: 0.63 g/mL Temperature: 120°C Extraction fluid: CO_2 Static equilibration time: 5 min Dynamic extraction time: 10 min Flow rate: 4.0 mL/min
	Extract Collection - Step 3
	Trap packing: C_{18}-bonded silica Trap temperature: 80°C Nozzle temperature: 80°C (variable restrictor)
	Reconstitution of Collected Extracts - Step 3
	Rinse solvent for HPLC: 50:50 (v/v) THF-acetonitrile Rinse solvent for GC: 75:25 (v/v) dichloromethane-isooctane Collected fraction volume: 0.8 mL Trap temperature for HPLC extract: 80°C Trap temperature for GC extract: 60°C Nozzle temperature: 45°C (variable restrictor) Rinse solvent flow rate: 1.0mL/min
Organochlorine pesticides (Method 3562)	Extraction
	Pressure: 4330 psi (300 atm) Temperature: 50°C Density: 0.87 g/mL Extraction fluid: CO_2 Static equilibration time: 20 min Dynamic extraction time: 30 min Flow rate: 1.0 mL/min
	Extract Collection
	Trap packing: C_{18}-bonded silica Trap temperature: 20°C Nozzle temperature: 50°C (variable restrictor)
	Reconstitution of Collected Extracts
	Rinse solvent: n-hexane Collected fraction volume: 1.3 mL Trap temperature: 50°C Nozzle temperature: 30°C (variable restrictor) Rinse solvent flow rate: 2 mL/min
PCBs (Method 3562)	Extraction
	Pressure: 4417 psi (305 atm) Temperature: 80°C Density: 0.75 g/mL Extraction fluid: CO_2 Static equilibration time: 10 min Dynamic extraction time: 40 min Flow rate: 2.5 mL/min
	Extract Collection
	Trap packing: Florisil Trap temperature: 15-20°C Nozzle temperature: 45-55°C (variable restrictor)

TABLE 5 (continued)
SFE Operating Conditions for the SFE Methods Approved by U.S. EPA.

	Reconstitution of Collected Extracts The reconstitution process consists of four rinse steps. The first rinse is used to elute the analytes of interest from the trapping material. All four rinse steps are performed with a recommended trap temperature of 38°C, a nozzle temperature of 30°C, and a flow rate of 1.0.
	Rinse Substep 1 - Analyze
	Rinse solvent: n-heptane Collected rinse volume: 1.6 mL
	Rinse Substep 2 (discard)
	Rinse solvent: n-heptane Collected rinse volume: 1.6 mL
	Rinse Substep 3 (contains interfering compounds, such as lipids, hydrocarbons, and PAHs) - discard
	Rinse solvent: dichloromethane-acetone (1:1) Collected rinse volume: 4.0 mL (to waste)
	Rinse Substep 4: (reactivate Florisil) - discard
	Rinse solvent: n-heptane Collected rinse volume: 3.0 mL (to waste)

extraction efficiencies; and (4) sample pretreatment prior to extraction (e.g., drying and grinding) is needed.

c. PCBs

PCBs can be extracted with carbon dioxide (see Table 5 for Method 3562) at 305 atm and 80°C; the extracted material is collected on a Florisil trap and subsequently eluted with heptane followed by dichloromethane-acetone (1:1). A slightly higher temperature (100°C) and pressure (350 atm) was employed by Lopez-Avila and co-workers[17] to extract PCBs from five reference materials and 29 soil samples collected from a site previously contaminated with PCBs; there was an excellent agreement between the SFE data and the Soxhlet extraction data. Unmodifed carbon dioxide seems to work well even for the fish tissue[18] and human adipose tissue.[20] In these two applications, activated basic alumina was incorporated in the extraction process as a fat retainer.

Modified carbon dioxide was reported by Bowadt et al. in an interlaboratory study,[15] and Tong and Imagawa.[19] The modifier was 1.7 to 2% methanol in the Bowadt study and 15% dichloromethane in the Tong and Imagawa study. Use of a higher percentage of modifier allows use of lower pressure (e.g., 200 atm); however, there is always the possibility that the modifier would facilitate extraction of undesirable background material that can interfere with the chromatographic analysis. A critical evaluation of the various SFE procedures reported for PCBs is found in Reference 21.

d. Organochlorine and Organophosphorus Pesticides

The organochlorine pesticides (e.g., DDT, DDE, DDD, aldrin, heptachlor) are usually extracted with supercritical carbon dioxide under the same conditions as PCBs (Table 5). However, a decrease in recovery was reported for soils with high content of organic matter (e.g., 35%) and use of modified carbon dioxide provides a suitable solvent in such case especially when other classes of pesticides need to be recovered as well.[25] Van der Velde et al.[23] investigated the effects of pressure, extraction time, static and dynamic extraction, restrictor type, and collection solvent on the SFE of the organochlorine pseticides and reported that the optimum conditions for the extraction of organochlorine pesticides are 50°C and 20 MPa, 10 min static followed by 20 min dynamic with collection of the extracted material in isooctane.[23]

The effects of soil matrix on the SFE of organochlorine pesticides and organophosphorus pes-

ticides were investigated by Snyder et al.[24] by comparing recoveries obtained by SFE with carbon dioxide alone and those with carbon dioxide modified with 3% methanol (at 350 atm, 50°C, 10 min static and 10 min dynamic). A detailed review of the SFE of compounds of agricultural significance can be found elsewhere.[26]

e. Triazine Herbicides

A summary of SFE conditions reported in the literature can be found in a review article prepared by Dean et al.[28] Supercritical carbon dioxide has been investigated for the extraction of triazine herbicides,[29] but a more polar fluid is needed to improve the extractability of these type of compounds. Schneider[30] and Robertson and Lester[33] used carbon dioxide modified with 7% acetone. Schneider even added methanol directly to the soil sample to improve the extraction yields. Yarita et al.[31] compared extraction efficiencies using carbon dioxide alone and carbon dioxide modified with 5 and 10% methanol. The recovery of triazine herbicides is poor even with 10% methanol but addition of water to the soil-enhanced SFE recovery.[31] Methanol containing trifluoroacetic acid (TFA) as modifier and higher temperatures (e.g., 200°C) were found to be the most effective in recovering atrazine and its degradation products.[32]

f. Organotin and Organomercury Compounds

Organotin compounds can be extracted by SFE after complexation with diethylammonium diethyldithiocarbamate (DEA-DDC); carbon dioxide modified with 5% methanol at 450 atm and 60°C works better than carbon dioxide alone but the monoalkyltin species could not be recovered quantitatively even at 600 atm.[42] Methylmercury was extracted from marine samples with carbon dioxide at 40°C and a density of 0.90 g/mL using HCl as matrix modifier (100 μL) and using a 10-min static extraction.[44] Work done in this laboratory showed that organomercury compounds can be separated from inorganic mercury salts by SFE with carbon dioxide modified with 5% methanol and then analyzed by gas chromatography with atomic emission detection (after derivatization with pentyl magnesium bromide).

g. Other Applications

There are numerous other applications of SFE for compounds of environmental significance reported in the literature. They include, for example, SFE of: polychlorinated dibenzodioxins and dibenzofurans,[22] phenolic compounds,[35,36] chlorophenoxy acid herbicides,[37] aromatic amines,[39] nitroaromatic compounds,[40] cationic surfactants,[41] vitamin A and β-carotene,[45] xanthene dyes,[46] fatty materials,[47] and metal ions.[43,48,49]

B. MAE

1. Theoretical Considerations

Microwaves are high-frequency electromagnetic waves placed between radio frequency and the infrared regions of the electromagnetic spectrum (their frequencies range from 0.3 to 300 GHz). In contrast to conventional heating where the heat penetrates slowly from the outside to the inside of an object, microwave energy is "cold" producing heat (heating takes place by dielectric loss). Therefore, the heating appears right in the core of the body that is being heated, and the heat spreads from the inside to the outside of that body. The microwave energy affects molecules by ionic conduction and dipole rotation. In ionic conduction, the ions in solution will migrate when an electromagnetic field is applied. The resistance of solution to this flow of ions will result in friction and, thus, heating of the solution. Dipole rotation means realignment of the dipoles with the applied field. At 2450 MHz, the dipoles align and randomize 4.9×10^9 times per second; this forced molecular movement results in molecular "friction" and, thus, heating of the solution.[50]

Selection of proper solvent is the key to a successful extraction. In selecting solvents, consideration should be given to the microwave-absorbing properties of the solvent, the inter-

action of the solvent with the matrix, and the analyte solubility in the solvent (the principle of "like dissolves like" is still applicable in MAE). The larger the dipole moment of the solvent the faster the solvent will heat under microwave irradiation. For example, hexane (dipole moment is <0.1 Debye) will not heat, whereas acetone with a dipole moment of 2.69 Debye will heat in a matter of seconds. Thus, a mixture of hexane-acetone is an ideal solvent for compounds of environmental significance, and many applications described here use hexane-acetone (1:1).

Other important factors under consideration include: (1) the compatibility between the extraction solvent and the analytical method used in the analysis of the extract (the less polar solvents seem to be preferred for gas chromatographic analysis, whereas the more polar ones for liquid chromatographic analysis and immunoasay techniques) and (2) the selectivity of the solvent. Little has been reported in the literature on the selectivity of MAE because the technique is so efficient that it cannot be regarded as a selective extraction technique. "Everything gets extracted" so a cleanup step after the extraction is needed in almost all cases.

When MAE is conducted in closed vessels, the temperature achieved during the extraction will be greater than the boiling points of the solvents. For most of the solvents (e.g., acetone, acetone-hexane, dichloromethane-acetone), the temperature inside the vessel is two to three times the boiling point of the solvent. These elevated temperatures result in improved extraction efficiencies of the analyte from the sample matrix.

2. Instrumentation

The equipment (Figure 2) used for closed-vessel MAE consists of a magnetron tube, an oven where the individual extraction vessels (closed vessels) are set up on a turntable or rotor, monitoring devices for temperature and pressure, and electronic components. It usually includes specific safety features such as rupture membranes for the extraction vessels, an exhaust fan to evacuate air from the instrument cavity, a solvent vapor detector (monitors the presence of solvent vapor in the microwave cavity and shuts off the microwave energy whenever solvent vapor is detected in the instrument cavity), an expansion container (the extraction vessels are connected to this ex-

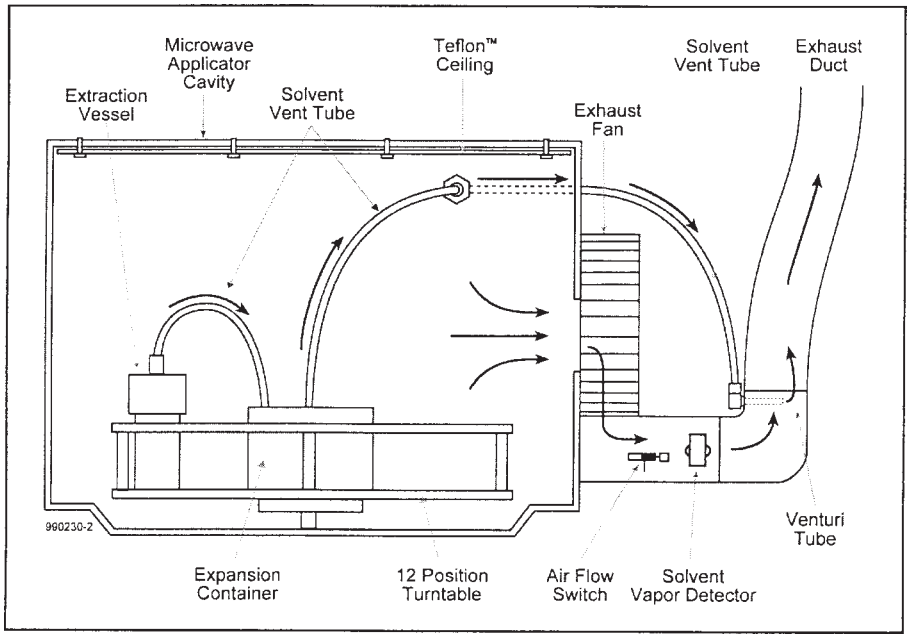

FIGURE 2. Schematic diagram of closed-vessel MAE system from CEM Corporation, USA.

pansion container through vent tubing; in case the membrane ruptures, due to increased pressure in the vessel, then vapor is removed through the rupture vent tube), and an isolator located in the wave guide that diverts reflected microwave energy into a dummy load to reduce the microwave energy within the cavity. One manufacturer of microwave equipment uses resealable vessels. In this case, vessels are placed on a sample rotor and secured with a calibrated torque wrench for uniform pressure. If the pressure exceeds the vessel limits, a spring device (Milestone's patented technology) allows the vessel to open and close quickly, thus releasing the excess pressure. These sample rotors are available with PFA and TFM liners with pressure ratings of 435 to 1450 psi. Another safety feature that was added to the microwave system is the "movable wall". To prevent the door from being blown away, a door frame on spring-loaded, high-impact steel bars was added such that the door moves out and in to release pressure from the microwave cavity. Figure 3 shows a schematic diagram of the open-vessel MAE system (Prolabo, France) and Table 6 summarizes the features of commercially available MAE systems.

Typical pressures reached with most closed-vessel systems (first generation) were 105 psi, but today's technology can handle pressures as high as 1500 to 1600 psi. A special rotor, which houses six thick-walled vessels capable of working at 1600 psi, is available commercially on several systems, including the CEM's MARS-5, Milestone's Ethos-1600, and Plazmatronika's Uni-Clever system. In the Milestone system, for example, if the operating pressure inside the vessel exceeds the vessel limits, a special spring device will allow the vessel to open and close, thus reducing the pressure.

The vessels are typically made of microwave transparent materials (e.g., polyether imide, or TFM [tetrafluoromethoxyl] polymer) and are lined with perfluoroalkoxy or Teflon liners. A new microwave system introduced recently by one manufacturer uses magnetic stir bars that allows extraction with polar and nonpolar solvents while

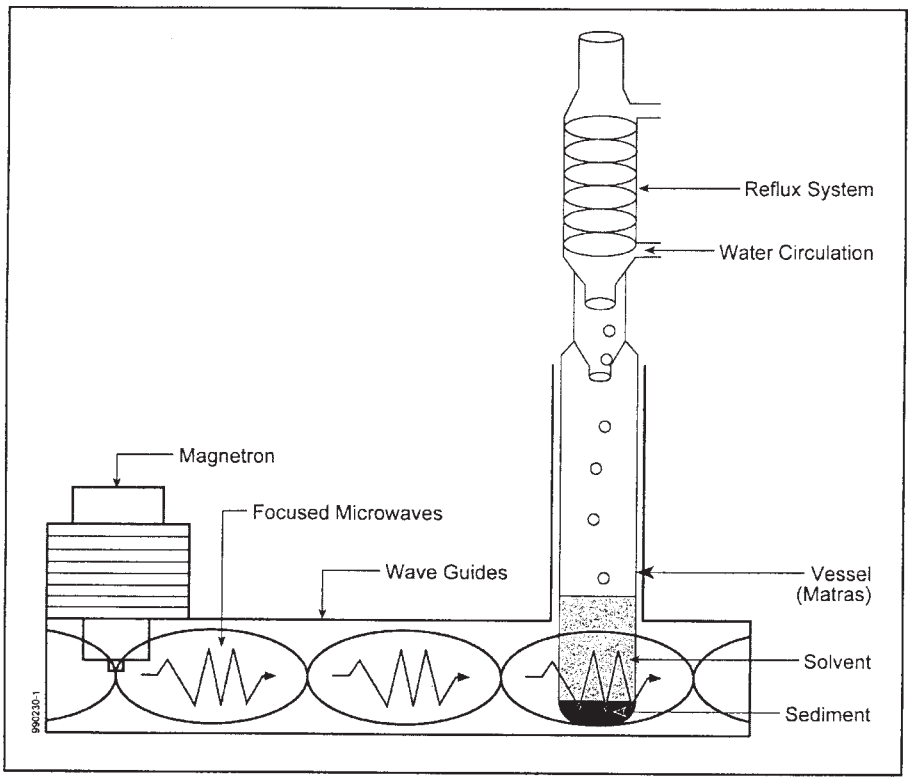

FIGURE 3. Schematic diagram of open-vessel MAE system from Prolabo, France.

agitating the sample and solvent to achieve efficient mixing and improve analyte recoveries.

Figure 4 shows a schematic of CEM's lined digestion vessel with and without temperature and pressure control. Vessel body and cap are made of Ultem, a polyetherimide. The cap and cover of the control vessel are modified to allow a pressure-sensing tube and a fiber-optic temperature probe. The fiber-optic probe is microwave transparent and is positioned in the control vessel using a glass thermal well. Infrared temperature sensors are also used to monitor the temperature inside the vessel. As the turntable revolves, the infrared sensor measures the temperature of each vessel. More detail on the pressure and temperature feedback control can be found elsewhere.[52]

Additional features such as magnetic stirring of the extraction solvent inside multiple sample vessels is possible, at least on one commercial system (Ethos 1600 Labstation from Milestone, Inc.). Moreover, nonpolar solvent, such as hexane, can now be heated at elevated temperatures by use of magnetic stir bars made of Milestone's proprietary fluoropolymer Weflon (this polymer absorbs the microwave energy and subsequently transfers heat to the surrounding medium).

All closed vessel systems that are available commercially are multivessel systems that evenly space the vessels on a carousel or rotor and rotate them through a pattern on a 360° oscillating turntable. A product review on commercially available microwave systems was published recently in *Analytical Chemistry*.[51]

3. Specific Applications of MAE*

a. PAHs

Work done by Lopez-Avila et al.[52] indicated that PAHs, with the exception of more volatile compounds such as naphthalene can be extracted quantitatively (recovery > 80%) from soil and sediment matrices with hexane-acetone (1:1) at temperatures of 115°C. Typical extraction times for batches of up to 12 samples (5 g each) are 10 min at 100% power (1000 W). The lower recoveries of naphthalene, acenaphthene, and acenaphthylene were attributed to the presence of

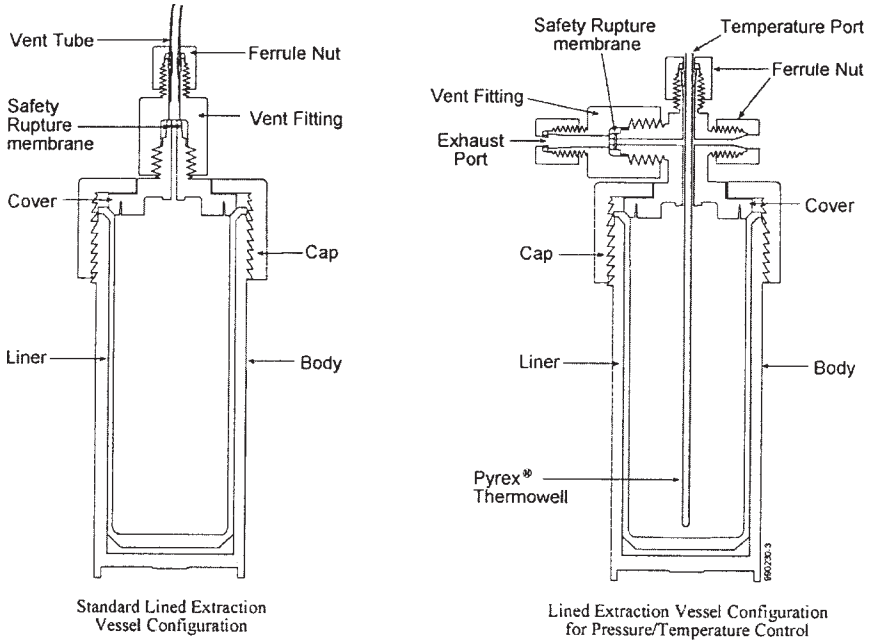

FIGURE 4. Schematic diagram of CEM's lined digestion vessel with and without temperature and control.

* Specific applications of MAE are given in Table 7.

water in the soil matrix (to prepare a representative aged soil sample, water was added to the soil matrix to bring its water content to 30%).

Other successful microwave-assisted extractions of PAHs from soils, sediments, and fly ash have been reported with hexane-acetone (1:1),[53,54,57,58,61,63,64,91] acetone alone,[56,62,75] dichloromethane alone,[56,57,59,60,63,64,67] dichloromethane-toluene(50:50),[57,64] acetone-petroleum ether (1:1),[63] methanol-toluene (9:1),[63] and toluene-water.[72]

Dean et al.[56] reported on a direct comparison between Soxhlet, MAE, and SFE for PAHs and concluded that the major advantage of MAE is the speed of extraction, but they also acknowledged that without additional cooling after extraction it takes approximately 30 min until the vessels will be opened and extracts processed. Barnabas, Dean, and co-workers[62] also investigated effects of pressure, temperature, extraction time, and percent of methanol modifier added to the extraction solvent in order to optimize the extraction.

Chee et al.[63] reported a 5-min heating at 115°C with 30 mL hexane-acetone (1:1) as the optimum extraction conditions for a 5-g sample, conditions that are very similar to those reported by Lopez-Avila et al.[52,53]

Optimization of MAE of PAHs using open-vessel technology was conducted by Budzinski et al.,[64] who reported that the optimum conditions are 30% water, 30 mL dichloromethane, and 10 min heating at 30 W power. When considering that the time needed to reach the boiling point is about 2 min (for dichloromethane), a heating time of 10 min is more than sufficient to extract PAHs quantitatively from the matrix, especially when adding water that is supposed to cause swelling of the matrix.

b. Organochlorine pesticides (OCPs)

MAE of OCPs was reported by Onuska and Terry,[65] Lopez-Avila et al.,[52,53,66] Fish and Revesz,[55] Chee et al.,[67] and Vetter et al.[68,69]

Onuska and Terry[65] extracted aldrin, dieldrin, and DDT from soils and sediments using acetonitrile, isooctane, or a mixture of isooctane-acetonitrile (1:1, v/v) and achieved quantitative recoveries using five or seven 30-s irradiations with microwave energy. They also reported that MAE recoveries increase as the moisture content of the soil increases up to 15%. Fish and Revesz[55] used hexane-acetone as extraction solvent and reported that OCP recoveries improved when changing from 1:1 hexane-acetone to 2:3 hexane-acetone. The latter solvent has a composition similar to the azeotropic vapor in the Soxhlet extractor.

Lopez-Avila et al.[66] extracted 45 OCPs from freshly spiked and 24-h aged soil samples with hexane-acetone (1:1, v/v). For the freshly spiked soil, 38 compounds had recoveries between 80 and 120%, six compounds had recoveries between 50 and 80%, and the recovery of captafol was above 120%. For the spiked soil samples aged for 24 h, 28 compounds had recoveries between 80 and 120%; 12 compounds had recoveries between 50 and 80%; compounds, including captafol, captan, and dichlone, were poorly recovered; and chloroneb and 4,4′-DDT had recoveries above 120%.

When recoveries from freshly spiked soil were compared with those from aged spiked soil, it was found that the recovery of captafol dropped from 122 to 36%, the recovery of captan dropped from 106 to 21%, and the recovery of dichlone dropped from 78 to 10%. Captafol and captan appear to be quite stable after irradiation of soil/solvent suspensions, but dichlone was found to disappear after irradiation of the solvent (the recovery of dichlone from solvent was only 5.5% after heating at 145°C for 5 min and 2.6% after 20 min at the same temperature). Microbial degradation may be responsible for the low recoveries of captafol and captan, whereas in the case of dichlone, it is quite likely that this compound is not stable under the conditions used. Nonetheless, these recoveries are higher than those obtained by Soxhlet or sonication extraction.

Water samples can also be extracted by MAE; however, they have to be preconcentrated first on a membrane disk or some adsorbent material. Chee et al.[67] used C_{18}-membrane disks and then extracted the disks with 20 mL solvent (acetone and dichloromethane) in a closed-vessel MAE system at 80°C, 100°C, and 120°C for 1, 3, 5, and 10 min. Acetone was found to give higher recov-

eries than dichloromethane.[67] This approach would allow extremely low detection limits because several disks generated by processing a large volume of sample can be extracted in one vessel.

Vetter and co-workers[68,69] extracted OCPs from fatty tissues (e.g., seal blubber) with solvents such as hexane[68] and ethyl acetate (1:1).[69] To transfer heat to hexane, which is microwave transparent, disks of Weflon (2.5 cm in diameter × 0.3 cm thickness) were used in the extraction vessel. The yield of extractable fat and recoveries of OCPs after seven irradiation cycles were comparable to those obtained by Soxhlet extraction. Because ethyl acetate-cyclohexane (1:1, v/v) seems to extract more fat than hexane, a gel permeation chromatography step after extraction is a must.

c. PCBs

MAE of PCBs was reported by Lopez-Avila et al.,[90] Onuska and Terri,[91] Chee et al.,[67] Pastor et al.,[72] Dupont et al.,[70] and Kodba and Marsel.[71] Lopez-Avila et al.[90] used hexane-acetone (1:1, v/v) and reported that the average recoveries from typical soil matrices were greater than 70% for the Aroclors 1016 and 1260 and the method precision was better than 7%. Furthermore, there was no degradation of PCBs after heating of solvent/soil suspensions with microwave energy. Three reference materials and 24 soils from a Superfund site, most of which contained Aroclors, were extracted by MAE and analyzed by both GC/ECD and enzyme-linked immunosorbent assay (ELISA). Because ELISA is very sensitive and its detection range is quite narrow, the hexane-acetone extracts were first diluted with methanol and subsequently with the assay buffer (which contained 50% methanol) to bring the Aroclor concentrations to less than 5 ng/mL. These data[90] indicate excellent agreement between the certified Soxhlet/GC/ECD data and the MAE-ELISA data (correlation coefficient 0.9986; slope 1.0168) and the MAE-GC/ECD data and the MAE-ELISA data (correlation coefficient 0.9793; slope 1.0468).

Other solvents used to successfully extract PCBs from environmental samples include isooctane,[91] acetone and dichloromethane,[67] and toluene-water.[72]

d. Phenols

MAE of phenolic compounds was reported by Lopez-Avila et al.,[52,53,54,90] Llompart et al.,[73,74] Chee et al.,[75] and Egizabal et al.[76] Acetone-hexane seems to be the preferred solvent for 16 phenolic compounds and dichloromethane,[75] acetone-petroleum ether (1:1)[75] were reported to work well for extraction of nonyl phenol.[75] The only compounds found to degrade during MAE are 2,4-dinitrophenol and 4,6-dinitro-2-methylphenol.[52,90] MAE recoveries for phenolic compounds are usually higher than the classic extraction method recoveries, and the method precision is significantly better for MAE (e.g., coefficient of variation of 3% for MAE when compared with 15% for Soxhlet and 20% for sonication).[50]

e. Herbicides

Immidazolinones (e.g., imazapyr, imazmetapyr, imazethapyr, imazaquin, etc.) are extracted from soil with 0.1 *M* ammonium acetate/ammonium hydroxide (pH 9-10) in a 10-min extraction.[77–79] A variety of soil samples fortified at 1 to 50 ppb exhibited an average recovery of 92% (standard deviation 13%).

Triazine herbicides have been extracted successfully from soil by MAE with water,[80,81,84] methanol,[81] acetone-hexane (1:1),[81] dichloromethane,[81] acetonitrile-0.5% ammonia in water (70:30),[82,83] dichloromethane-water (50:50),[83] methanol-dichloromethane (10:90).[83] Water seems to be preferred because it is a very polar solvent and can interact strongly with polar matter in soils to enhance the desorption of triazines;[81] it is a cheap, safe, and environmentally friendly solvent; and it heats up very quickly when irradiated with microwave energy. Xiong et al.[84] reported that direct heating of soil with water gave a 73.4% recovery for atrazine from soil, and therefore stated that "MAE is not only a simple heating".

f. Organotin and Organomercury Compounds

Methods reported in the literature for the determination of organotin compounds in soils use

extraction with organic solvents in the presence of a complexing agent or leaching with acetic or hydrochloric acid assisted by sonication or some sort of shaking. Open-vessel MAE was recommended to accelerate the leaching with 50% acetic acid aqueous solution, and the data showed that a 3-min irradiation at 60 W was sufficient to recover tributyl tin from certified reference sediments.[85] Ethanoic acid (0.5 *M* in methanol) was also reported.[86] When dealing with biological matrices (e.g., tuna tissue, mussel tissue), solubilization with tetramethyl-ammonium hydroxide (TMAH) for 3 min at 90°C, 115°C, and 130°C in a closed vessel was demonstrated to be as efficient as the hot-plate procedure.[87] Schmitt et al.[88] reported on the integration of the solubilization step with the derivatization/extraction step by using 11 *M* acetic acid and $NaBEt_4$.

Organomercury compounds can be extracted from sediments with 6 *M* hydrochloric acid at 120°C for 10 min in closed vessel[89] or 2 *M* nitric acid and 2 *M* hydrochloric acid after 3 min irradiation at 60 W in open vessel.[88] Pure acetic acid and 1 *M* sulfuric acid could only extract 85 and 55%, respectively. Microwave-assisted digestion of the biological tissue with 25% TMAH for 2 to 4 min at 40 to 60 W gave quantitative recovery of both organomercury and inorganic mercury.[88]

C. Accelerated-Solvent Extraction (ASE)

1. Theoretical Considerations and Equipment

Accelerated-solvent extraction (ASE), known as EPA Method 3545, uses organic solvents at high temperature (50 to 200°C) and pressure (1500 to 2000 psi) to extract organic compounds from environmental samples. The higher temperature at which the extraction is conducted, when compared with the conventional Soxhlet extraction, increases the capacity of solvent to solubilize the analyte and the higher pressure increases the diffusion rate into the pores of the matrix, thus facilitating the mass transfer of the analyte into to the extracting solvent. Increased temperature is also known to weaken the bonds between the analyte and the matrix and to decrease the viscosity of the solvent (lower viscosity means improved penetration into the matrix and thus increased extraction yield). This technique uses much smaller volumes of solvent than the Soxhlet extraction (see Table 2), is relatively fast, and does not require filtration of the extract after extraction. The technique is automated (as many as 24 samples can be extracted in unattended operation), but costs are high. The instrument (manufactured by Dionex) is shown in Figure 5. Three different extraction cell sites (e.g., 11, 22, and 33 mL) are available to accommodate small to large samples, and typical extraction times are 10 to 20 min per sample.

Each vessel is fitted with finger-tight removable end caps with compression seals. The instrument is operated via computer control; an autoseal actuator places the extraction vessel in line for extraction and then returns it to the original location after the extraction. The computer also monitors the level of solvent in the collection vial via an infrared sensor. Should the system fail to extract or get plugged, then an automatic shut-off procedure will occur.

The ASE procedure is presented below in six steps:

1. Load sample into cell
2. Fill cell with solvent (0.5 to 1 min)
3. Heat and pressurize cell (5 min)
4. Hold sample at pressure and temperature (static extraction for 5 min)
5. Pump clean solvent into sample cell (0.5 to 1 min)
6. Purge solvent from cell with nitrogen (1 to 2 min)

2. Applications of ASE

Specific applications of ASE are given in Table 8.

PAHs have been extracted from marine sediments, urban dust, and reference materials with dichloromethane-acetone (1:1, v/v) at 100°C and 2000 psi.[92] There was excellent agreement between the ASE results and the Soxhlet extraction data in the Richter et al. study,[92] but in a study by Dean the ASE results were quite different than the Soxhlet extraction data (extraction solvent

TABLE 6
Features of Commercially Available MAE Systems

Model/ Manufacturer	Power (watts)	Sensors	Max. Pressure (bar)	Vessel Volume (mL)	Vessel Material	Number of Vessels	Max. Temp. (C)
Multiwave/ Anton Paar GmbH, Austria	1000	Pressure control in all vessels Infrared temperature measurement in all vessels	70	100	TFM/ceramics	12	230
			70	100	TFM/ceramics	6	260
			130	50	TFM/ceramics	6	260
			130	50	Quartz	6	300
			130	20	Quartz	6	300
MARS-6/ CEM, USA	1500	Infrared temperature measurement in all vessels	36	100	TFM	14	300
			100	100	TFM	12	300
Ethos 900/1600, Milestone, USA	1600	Pressure control in all vessels Temperature control in all vessels	30	120	TFM or PFA	10	240
			100	120	TFM	6	280
			30	120	TFM or PFA	12	240
			100	120	TFM	10	280
Model 7195/ O.I. Corp. USA	950		13	90	TFM	12	200
			40	90	TFM	12	200
Soxwave 100/ 3.6 Prolabo, France	250	Temperature control	Open vessel	250	Quartz	1	
			Open vessel	100 or 250	Quartz	6	

was dichloromethane). Acetone-hexane (1:1, v/v) at 100°C and toluene (175°C/200°C) were also reported for the extraction of PAHs from soils and other environmental solid matrices.[98,101,102] Toluene gave the highest extraction yields of PAHs from contaminated soils.[98]

PCBs were extracted from certified reference materials with acetone-hexane (1:1, v/v) at 100°C, and the results were in good agreement with the certified values. The particle size seems to influence the extraction efficiency with higher extraction efficiency for smaller particles.[93] Extraction of PCBs from soils with acetone-hexane (75:75, v/v) was optimized by Zuloaga et al.[103] A temperature of 100°C, pressure of 2100 psi, and static extraction time of 13 min were the optimum conditions for that solvent combination.

Polychlorinated dibenzo-*p*-dioxins and furans were extracted from soil, sediment, fly ash with toluene at 180°C[100] or acetone-hexane (1:1, v/v) or dichloromethane-acetone (1:1, v/v).[98] Pretreatment with 6 *M* HCl prior to extraction is required in the case of fly ash sample.[100]

Determination of pesticides was investigated by Pyle and Marcus,[96] Ezzell et al.,[95] and Obana et al.[99] Obana utilized ASE to extract organophosphorus pesticides from foods (e.g., flour, grapefruit juice, orange juice, broccoli) and reported that the precision of ASE was always better than the hexane extraction.

Other compound classes that were investigated include phenols,[94] chlorophenoxy acid herbicides,[95] and diflufenican — a herbicide compound.[97]

The number of applications for ASE is somewhat limited because this technique is relatively new.

II. SAMPLE PREPARATION FOR LIQUID MATRICES

The most common techniques employed with liquid samples include liquid-liquid extraction, purge-and-trap, solid-phase extraction (SPE), and solid-phase microextraction. Table 9 gives a description of each technique and lists the sample size, extraction time, solvent usage, costs, ease of

TABLE 7
Selected MAE Applications Reported in the Literature.

Analyte	Matrix	Solvent	MAE Conditions	Reference
17 PAHs, 14 phenols, 20 organochlorine 13 miscellaneous compounds (e.g., chlorinated benzenes nitroaromatic compounds and phthalate esters	3 Reference marine sediments 3 Reference soils Topsoil	Hexane-acetone (1:1)	Closed-vessel extraction at 80°C, 115°C for 5, 10, 20 min	52, 53, 54, 91
PAHs	Soil	Acetone Dichloromethane	29 min at 120°C in closed vessel	56
PAHs	Marine Sediments	Dichloromethane	5 to 40 min irradiation at 30 to 90 watts in open vessel, 10 min irradiation at 30 watts in open vessel	57
	Mussel tissue Air particles	Dichloromethane-toluene (50:50) Acetone-hexane (50:50)		
PAHs	Reference marine sediments	Hexane-acetone (1:1)	5 min at 115°C in closed vessel	58
PAHs	Reference marine sediments	Dichloromethane	5 to 10 min at 35°C in open vessel	59, 60
PAHs	Fly ash	Hexane acetone (90:10)	70°C in closed vessel	61
PAHs	Soil	Acetone	20 min at 120°C, closed vessel	62
PAHs	Marine sediments	Dichloromethane Acetone-hexane (1:1)	5 and 15 min at 115° and 135°C, closed vessel	63
PAHs	Reference marine sediment Reference soil Reference river sediment Reference sewage sludge Industrial soil Marine sediment	Dichloromethane Dichloromethane-toluene (50:50) Acetone-hexane (50:50, 60:40) Acetone	10 min, 30 watts, open vessel	64
Organochlorine pesticides	Sediment saturated with distilled water (1g sample and 2 mL water)	Acetonitrile Isooctane Isooctane-acetonitrile (1:1)	30 sec irradiation in open vessel; repeat up to 5 times	65

TABLE 7 (continued)
Selected MAE Applications Reported in the Literature.

Analyte	Matrix	Solvent	MAE Conditions	Reference
16 Phenols, 20 organochlorine pesticides	Topsoil Claysoil Sand Reference soil	Hexane-acetone (1:1)	Closed-vessel extraction at 115°C for 10 min	66
16 PAHs 10 Organochlorine pesticides 4 Aroclors 6 Phthalate esters 7 Organophosphorus pesticides 5 Fungicides/herbicides	Water samples preconcentrated on C18 membrane disks	Acetone Dichloromethane	1,3,5,10 min at 80°C, 100°C, 120°C, closed vessel	67
PCB 153 PCB 180 PCB 138 p.p'-DDE Hexachlorocyclohexane Hexachlorobenzene	Seal blubber Pork fat Cod liver	n-Hexane	Several 30 sec extractions at 1000 watts	68
		Ethyl acetate-cyclohexane (1:1)	Several irradiations at 250 to 1000 watts in increments of 100 watts	69
PCBs	Municipal sewage sludge	Hexane-acetone (1:1)	10 min, 30 watts, open vessel	70
PCBs	River sediments	Acetone-hexane (1:1)	15 min, closed vessel	71
C_{16}-C_{32} hydrocarbons 20 PAHs 4 Organochlorine pesticides PCBs	Marine sediments	Toluene-water (1:5 to 1:2)	6 min, closed vessel	72
Phenol Methyl phenols	Soils	Hexane and hexane-acetone (2:8) with pyridine and acetic anhydride for in-situ derivatization	130°C in closed vessel	73, 74
Nonyl phenol	Water samples preconcentrated on C18-packed cartridge, C18 packed disk Sediments	Dichloromethane Acetone-petroleum ether (1:1)	5 and 15 min at 100°C to 120°C, closed vessel	75

Analyte	Matrix	Solvent	MAE Conditions	Reference
Phenol 2-chlorophenol 2-Methylphenol 2-Nitrophenol 2,4-Dichlorophenol	Soil	Acetone-hexane (various ratios)	Closed vessel	76
Imidazolinone herbicides	Soil	0.1 M ammonium acetate/ammonium hydroxide (pH 9-10)	3 to 10 min irradiation at 125°C in closed vessel	77-79
Atrazine and degradation products	Lupin seeds Rat feces	Water followed by 0.35N HCl	Closed vessel, 95-98°C	80
Atrazine Simazine Prometryne	Sandy loam Clay Bentonite Florisil	Methanol Acetone-hexane (1:1) Dichloromethane Water		81
Atrazine Simazine Metazachlor Desisopropyl atrazine Desethyl atrazine	Sand Peat Clay	Dichloromethane with water, methanol, and acetonitrite Acetonitrite-0.5% ammonia in water (70:30)	5 to 45 min at 30° to 130°C, 20 min at 115°C	82, 83
Atrazine	Soil	Water	3, 4, and 5 min closed vessel	84
Organotin compounds (mono-, di- and tributyltin; mono-, di-, and triphenyltin	2 Reference sediments	50% acetic acid Isooctane Methanol Water Artificial sea water	1 to 7 min irradiation in open vessel, up to 160 watts	85
Organotin compounds	Sediments	0.5M ethanoic acid in methanol	3 min, open vessel	86
Butyl and phenyl organotin	Reference marine biological matrix Tuna tissue Mussel tissue	25% tetramethyl-ammonium hydroxide in water	3 min at 90°C, 115°C, and 130°C, closed vessel	87
Organotin compounds	Sediments	11M acetic acid $NaBEt_4$	3 min at 50 to 60 watts, open vessel	88

TABLE 7 (continued)
Selected MAE Applications Reported in the Literature.

Analyte	Matrix	Solvent	MAE Conditions	Reference
Organomercury compounds	Sediments	2M nitric acid 2M hydrochloric acid	3 min at 60 watts, open vessel	88
	Reference biological materials	25% tetramethyl-ammonium hydroxide	2 to 4 min at 40 to 60 watts, open vessel	
Methylmercury	Aquatic sediments Certified reference sediments	Digestion with 6M HCl (methylmercury is extracted at room temperature by complexation with cysteine acetate and toluene)	10 min at 120°C, closed vessel	89

TABLE 8
Environmental Applications of ASE

Analyte	Matrix	Ase Conditions	Reference
PCBs PAHs Pesticides	Marine sediment Urban dust Reference materials	Acetone-hexane (1:1, v/v) Dichloromethane - acetone (1:1, v/v) 100°C 1,500-2,000 psi 5 min equilibration followed by 5 min static pretreatment with HCl	92, 94, 101, 102
PAHs Chlorinated pesticides Dioxins and dibenzofurans	Soils Scrubber dust slurry Fly ash	Acetone-hexane (1:1, v/v) Toluene Dichloromethane-acetone (1:1, v/v) 100°C (acetone-hexane, dichloromethane-acetone) 175°C/200°C (toluene) 10/14 MPa	98
Dioxins	Soil, sediment, dust, fly ash	Toluene 180°C 2000 psi 9 min equilibration 5 min static	100
Phenols	Soil	Dichloromethane 30-70°C 600-3,000 psi time 5-25 min	94
PCBs	Reference materials (sediments, sludge)	Acetone-hexane (1:1, v/v) 100°C 5 min equilibration 5 min static	93
PCBs	Soil	Acetone-hexane (75:25, v/v) 70°C, 95°C, 125°C, 155°C, 180°C 1,000 psi; 1,300 psi; 1,700 psi; 2,100 psi; 2,400 psi 2 min; 5 min; 9 min; 13 min; 16 min (static extraction time)	103
Organophosphorus pesticides	Clay soil Loam soil Sand	Dichloromethane-acetone (1:1, v/v) 100°C 2,000 psi 5 min equilibration 5 min static	95
Organophosphorus pesticides	Foods	Cyclohexane-acetone (1:1, v/v) Dichloromethane-acetone (1:1, v/v) Ethyl acetate-acetone (1:1, v/v) 100°C 1,500 psi	99
Chlorophenoxy acid herbicides	Clay soil Loam soil Sand	Dichloromethane-acetone (1:2, v/v) with 4% H_3PO_4-water (1:1) 100°C 2,000 psi 5 min equilibration 5 min static	95
Diflufenican	Soil	Acetonitrile 100°C 2,000 psi 5 min equilibration 4 min static 60 sec purge	97

TABLE 9
Extraction Techniques for Liquid Matrices

	Liquid-liquid	Purge and trap	SPE	SPME
Description of System	Analyte is partitioned between two immiscible solvents; continuous and discontinuous operation possible	Aqueous sample is purged with a gas followed by trapping on a suitable adsorbent. Analytes desorbed using heat and transferred directly to GC.	Analyte retained on a solid adsorbent; extraneous sample material washed from sorbent. Desorption of analyte using organic solvent.	Analyte retained on a fiber coated or bonded with a polymeric material. Analyte desorbed using heat and transferred directly to GC or solvent and analyzed by HPLC.
Sample size	1 L	5 to 25 mL	1 mL to 1 L	1 mL to 1 L
EPA Method	EPA Methods 3510 and 3520	EPA Method 5030	EPA Method 3535	-
Extraction time	Discontinuous: 20 min and continuous: up to 24 hours	10-20 min	10-20 min	10-60 min
Solvent usage	3 x 60 mL for discontinuous; up to 500 mL for continuous	None	Organic solvent required for wetting sorbent and elution of analyte (10-20 mL)	None
Cost	Low cost	Moderate cost	Relatively low cost (use of an SPE manifold) Cartridges are disposable	Relatively low cost (replacement fiber and syringe-barrel holders)
Ease of operation	Easy	Automated systems available	Automated and robotic systems available for routine operation	Relatively easy to use; care required because of fragility of fiber. Automated systems available.
Disadvantages	Concentration of sample required after extraction	Applicable to volatile organic compounds only; selection of adsorbent required	Method development required; choice of sorbent and optimization of sorbent selectivity	Method development required; choice of fiber and optimization of procedure required

Adapted from Reference 108.

operation, and disadvantages. The liquid-liquid extraction and the purge-and-trap techniques will not be addressed in this article. The reader should refer to other literature citations for these subjects.

A. Solid-Phase Extraction

SPE is now a recognized alternative to the conventional liquid-liquid extraction. The EPA methods using SPE cleanup are listed in Table 10. The SPE sorbents (Table 11) can be classified into nonpolar phases, polar phases, and iso-exchange phases. The nonpolar sorbents have methyl, octyl, octadecyl functional groups bonded to the surface of silica to alter their retentive properties. Polar sorbents have cyano, amino, and diol, but unmodified silica is also included in this category. The ion-exchange phases have either cationic or anionic functional groups, such as SCX, DEA, or SAX. Specialty phases have also been introduced for specific applications. They include selective extraction of radioactive radium, strontium, and technetium using the Empore Rad disks and of anionic species from aqueous solutions using sulfonated polystyrene-DVB cationic resins treated with metallic counterions that form complexes with these anions.

The commercially available SPE formats are listed below:

- Syringe-barrel cartridges (cartridge body made of polypropylene, has polythylene frits, 40 μm particles sandwiched between two frits)

TABLE 10
EPA Methods Using SPE Cleanup[a]

EPA Method	Analytes	Matrix	SPE Phase
506	Phthalates and adipate esters	Drinking water	C_{18}-bonded silica
513	Tetrachlorodibenzo-*p*-dioxin	Drinking water	C_{18}-bonded silica
508.1	Chlorinated pesticides, herbicides, and organohalides	Drinking water	C_{18}-bonded silica
515.2	Chlorinated acids	Drinking water	PS-DVB*
525.1	Organic compounds (extractable)	Drinking water	C_{18}-bonded silica
548.1	Endothall	Drinking water	Anion exchange
549.1	Diquat and paraquat	Drinking water	C_{18}-bonded silica
550.1	Polycyclic aromatic hydrocarbons	Drinking water	C_{18}-bonded silica
552.1	Haloacetic acids and dalapon	Drinking water	Anion exchange
553	Benzidines and nitrogen-containing pesticides	Drinking water	C_{18}-bonded silica or PS-DVB
554	Carbonyl compounds	Drinking water	C_{18}-bonded silica
555	Chlorinated acids	Drinking water	C_{18}-bonded silica
548	Endothall	Drinking water	C_{18}-bonded silica
525.2	Organic compounds	Drinking water	C_{18}-bonded silica
3535	Organochloropesticides, phthalate esters, TCLP leachates	Aqueous samples	C_{18} or PS-DVB
1658	Phenoxy-acid herbicides	Wastewater	C_{18}-bonded silica
1656	Organohalide pesticides	Wastewater	C_{18}-bonded silica
1657	Organophosphorus pesticides	Wastewater	C_{18}-bonded silica
3600	Organochlorine pesticides and polychlorinated biphenyls	Wastewater	Florisil, alumina, silica gel
8440	Total recoverable petroleum hydrocarbons	Sediment, soil, sludge	Silica gel
8325	Benzidines and nitrogen-containing pesticides	Water, wastewater	C_{18}-bonded silica
TO13	Benzo[a]pyrene and other polynuclear aromatic hydrocarbons	Air	XAD-2 resin or polyurethane foam

[a] Reprinted with permission from Ref. 104.

TABLE 11
Commonly Available Silica-Bonded Sorbent

Sorbent	Phase
Nonpolar Phases	C_1, methyl C_8, octyl C_{18}, octadecyl
Polar Phases	Si, silica CN, cyanopropyl OH, diol NH_2, amino
Ion-exchange phases	SCX, benzenesulfonic acid DEA, diethylamino-propyl tertiary amine SAX, trimethylamino-propyl quaternary amine

- Membrane disks (packing-impregnated PTFE disks; fiberglass-support disks)
- Disk cartridge (membrane disk is placed in a syringe barrel)
- 96-well plate (SPE disks or cartridges)

The syringe-barrel type cartridges are the most popular format. The barrels are inexpensive and they fit conveniently into the vacuum manifolds that are available commercially.

The membrane disks are also very popular and exist in 8-, 12-, 47-, and 99-mm-diameter formats. The disks can be either as packing-impregnated, PTFE disks or as fiberglass-support disks. The latter is more rigid, has a high area-to-volume ratio, and allows gravity flow. Variations of the disk technology include the disk cartridge in which an SPE disk is placed in a syringe barrel and the 96-well SPE extraction plate. The 96-well plate is a great solution for high sample throughput but is prone to cross-contamination. When the plate is operated with a vacuum manifold, a clogged wall can overflow if the robotic liquid level sensor feature is off.[104]

B. Solid-Phase Microextraction

Historical developments and the fundamentals behind the SPME technique as well as numerous applications are the subject of a book written by J. Pawliszyn.[105] This section discusses one relevant application in SPME and gives a brief summary of the most relevant parameters that can affect extraction efficiency of the analyte from the matrix.

SPME is a direct, solventless extraction technique in which the analytes are absorbed directly from an aqueous or gaseous matrix onto a fused-silica fiber to which a stationary phase has either been bonded or been applied as a coating. The absorbed analytes are subsequently thermally desorbed into the injection port of a gas chromatograph/mass spectrometer. Analytes can be detected at parts-per-billion levels using GC with element selective detectors or MS, and the precision of this technique was determined to be 1.5 to 6% RSD. A new interface for coupling SPME to HPLC was also reported.[106] The main difference between SPME-GC and SPME-HPLC is in the desorption procedure. In the SPME-HPLC, the analytes are desorbed from the fiber with a minimum amount of solvent to avoid band broadening contributed by a large solvent volume.

To date, several coating materials are available from Supelco, and they have been summarized in Table 12. They include polydimethylsiloxane (PDMS) of 100 and 7 μm thickness, polyacrylate (85 μm thickness), PDMS/DVB (65 μm thickness), Carboxen (50 μm thickness), Carboxen/DVB (65 μm thickness), and Carboxen/PDMS (75 μm thickness). In selecting the fiber, the principle "like dissolves like" applies. PDMS-coated fibers are typically the first choice because they can withstand temperatures up to 300°C. When mixed with other materials, such as DVB, this fiber works very well for volatile-chlorinated solvents.

The example shown below is for the analysis of a group of halogenated solvents in the presence of various amines (e.g., butyl amine, propyl amine), and acetone and isopropyl alcohol. When the 65-μm PDMS/DVB fiber was immersed into 3 mL water sample (amended with 600 mg NaCl and 150 mg Na_2HPO_4 and adjusted to pH 11 with

TABLE 12
Commonly Available SPME Fibers

Stationary phase	Thickness (μm)	Maximum exposure temperature (°C)	Recommended desorption temperature (°C)	Comments
Polydimethylsiloxane (PDMS)	100	220	200	For volatile, low boiling point (<220°C) and nonpolar compounds (e.g., VOCs)
	7	340	220-320	For semivolatile, high boiling (>200°C) and nonpolar compounds (e.g., PAHs)
Polyacrylate	85	310	220-300	For both polar semivolatile compounds (e.g., pesticides and phenols)
PDMS/DVB	65	270	200-250	For volatiles, amines, nitroaromatic compounds
Carboxen	50	260	200-250	For surfactants
Carboxen/DVB	65	260	200-250	For alcohols and polar compounds
Carboxen/PDMS	75	270	200-250	For gases and low-molecular weight compounds

1N NaOH), as shown in Table 13, the detection limits for the chlorinated solvents were about 5 μg/l, whereas the amines were at 10 to 1000 μg/l and the acetone and isopropyl alcohol at 10,000 μg/l (see Table 14). To achieve detection limits of a few micrograms per liter, a 75-μm Carboxen/PDMS was used for acetone and isopropyl alcohol and the fiber sampled the 1.5-mL headspace of a 4-mL vial filed with 2.5 mL water (amended with 800 mg NaCl) and heated at 45°C. The SPME-GC operating conditions for acetone and isopropyl alcohol analysis are shown in Table 15. Likewise, to lower the detection limit for the determination of trimethylamine, the fiber sampled the headspace instead of being immersed into the sample (see Table 16).

From the example shown, it is evident that headspace sampling is fast (e.g., 10 min) and although magnetic stirring does not affect the diffusion of analytes from the headspace to the fiber, it had to be used to enhance the mass transport of the analyte between the aqueous solution and the headspace due to depletion of the analyte in the headspace during fiber sampling.

The increase in extraction temperature from 20 to 45°C increased the concentration of the analyte in the headspace and thus lowered the detection limit of the technique. Addition of salt to "salt out" the analyte, as in the case of acetone and isopropyl alcohol, was necessary because these compounds are very soluble in water. Finally, in the case of the amines, the sample pH had to be adjusted to 11 to suppress the ionization of these compounds since the PDMS/DVB fiber can only retain the analyte if in neutral form.

Soil samples can also be analyzed by SPME-GC/MS, but the analytes have to be preconcentrated first by a headspace technique. To improve the sensitivity of the technique, the headspace volume above the soil layer should be kept as low as possible and the soil volume should be as large as possible.

C. Matrix Solid-Phase Dispersion

Matrix solid-phase dispersion is recommended in case of viscous samples or nonhomogenous fat and tissue samples.[107] The sample to be extracted

TABLE 13
SPME-GC/MS Operating Conditions

Instrument	Hewlett Packard 5890 Series II gas chromatograph equipped with 5971A MSD
Type of fiber	PDMS/DVB (65-μm film thickness)
Sample volume	3 mL containing 600 mg NaCl and 150 mg Na_2HPO_4 (adjusted to pH 11 with 1N NaOH)
Extraction time	60 min (fiber immersed in the sample); with magnetic stirring
Sampling position	Liquid
Desorption temperature	220°C
Desorption time	5 min
Column	30-m length x 0.25 mm i.d. x 3-μm film SPB-1 fused silica open-tubular column
Temperature Program 1	45°C (2-min hold) to 200°C (5-min hold) at 10°C/min
Injector temperature	220°C
Detector temperature	280°C
Carrier gas	Helium at 39 cm/s

TABLE 14
Method Accuracy, Precision, and Detection Limits for SPME technique

Analyte	Fortified concentration (μg/L)	Mean recovery (percent)	Estimated method detection limit (μg/L)[a]
Group 1			
Acetone	66,600	97.4	10,000
Isopropyl alcohol	53,800	104	10,000
t-Butyl amine	1,200	100	100
n-Propyl amine	10,500	117	1,000
Diethyl amine	400	132	50
N-methyl pyrrolidine	100	109	10
Group 2			
1,1-Dichloroethylene	5	58.0	4.3[b]
trans-1,2-dichloroethylene	5	94.0	6.0[b]
cis-1,2-Dichloroethylene	5	105	6.8[b]
Bromodichloromethane	5	129	7.8[b]
Dibromochloromethane	5	134	6.0[b]
Group 3			
1,1-Dichloroethane	333	77.4	5
Bromochloroethane	333	62.7	5
Chloroform	333	90.8	5
1,1,1-Trichloroethane	333	91.2	5
Carbon tetrachloride	333	89.6	5
Dibromomethane	333	83.2	5
Tetrachloroethylene	333	97.4	5
Bromoform	333	93.1	5

[a] Estimated values based on the instrument response.
[b] Calculated values based on the analysis of seven replicate samples

TABLE 15
SPME-GC/MS Operating Conditioins for Acetone and IPA

Instrument		Hewlett Packard 5890 Series II gas chromatograph equipped with 5971A MSD	
Type of fiber		Carboxen/PDMS (75-μm film thickness)	
Sample volume		2.5 mL containing 800 mg NaCl	
Extraction time		10 min (fiber sampling headspace); with magnetic stirring	
Sampling position		Headspace	
Extraction temperature		45°C	
Desorption temperature		300°C	
Desorption time		3 min	
Column		30-m length x 0.25 mm i.d. x 3-μm film SPB-1 fused silica open-tubular column	
Temperature program I		50°C (2-min hold) to 150°C at 5°C/min	
Injector temperature		300°C	
Detector temperature		280°C	
Carrier gas		Helium at 39 cm/s	
SIM parameters:			
	Dwell time (msec)	Group start time (min)	Ions in group (m/z)
Acetone[a]	100	0	58
Isopropyl alcohol[a]	100	0	45

[a] These two compounds coelute.

(see Figure 6) is placed in a mortar containing a bonded phase solid support (e.g., C_{18}-bonded silica) and blended with this support; thus, the sample is distributed evenly over the surface of the support. Following blending with the support, the coated material is then poured into a syringe column and processed as if it were an SPE cartridge. The difference is in the fact that in SPE, much of the sample is retained in the first few milliliter of the column bed, whereas in matrix solid-phase dispersion the sample is dispersed evenly throughout the bed.

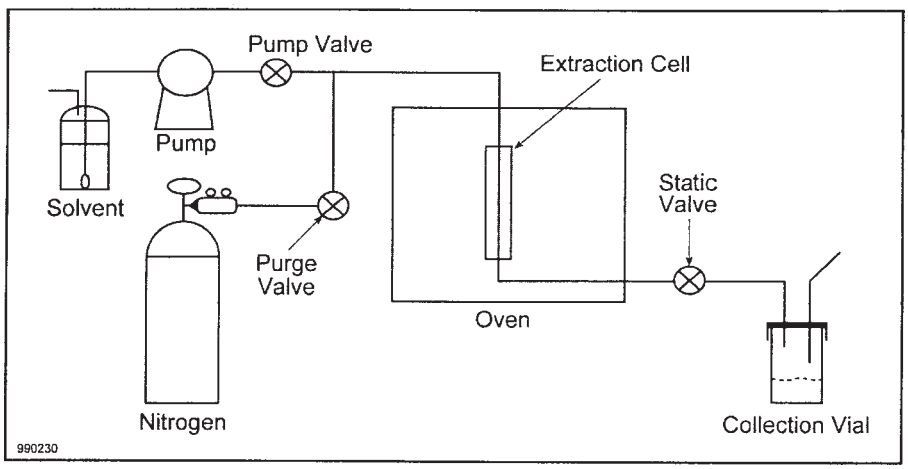

FIGURE 5. Schematic diagram of the ASE system from Dionex Corporation, USA.

TABLE 16
SPME-GC/MS Operating Conditions for Trimethylamine (TMA)

Instrument		Hewlett Packard 5890 Series II gas chromatograph equipped with 5971A MSD	
Type of fiber		PDMS/DVB (65-μm film thickness)	
Sample volume		2.5 mL containing 125 mg Na_2HPO_4 (adjusted to pH 11 with 1 N NaOH)	
Extraction time		10 min (fiber sampling headspace); with magnetic stirring	
Sampling position		Headspace	
Extraction temperature		45°C	
Desorption temperature		300°C	
Desorption time		3 min	
Column		30-m length x 0.25 mm i.d. x 3-μm film SPB-1 fused silica open-tubular column	
Temperature program I		80°C (2-min hold) to 220°C at 20°C/min	
Injector temperature		300°C	
Detector temperature		280°C	
Carrier gas		Helium at 39 cm/s	
SIM parameters:			
	Dwell time (msec)	Group start time (min)	Ions in group (m/z)
TMA	100	0	58 59 57

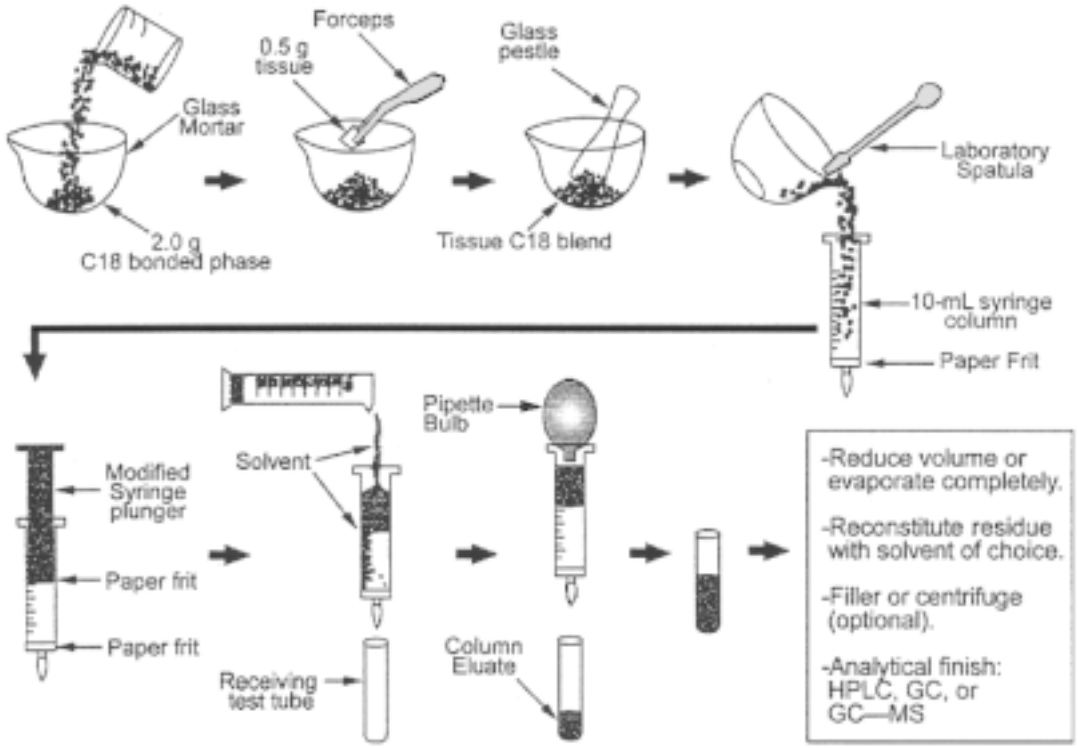

FIGURE 6. Schematic diagram of the matrix solid-phase dispersion process. (Reprinted with permission from Ref. 107.)

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