EOID the electrons generated by a microchannel electron multiplier array are converted to photons by a phosphor screen and detected via an array of photodiodes (**Figure 7**). Very high sensitivites have been reported, with benzene being detected at 7.5×10^{-14} g levels.

Multidimensional gas chromatography (MDGC) is another technique that seeks to overcome the problems involved in the analysis of multicomponent mixtures of volatile constituents. It is based on the separation of the constituents via one column and isolating the coeluted species in one or more cryotraps to be separated by a second column of different selectivity. MDGC is usually coupled with detectors such as IR and MS for increased specificity.

GC-MS has emerged as one of the premier methods for the rapid, convenient and sensitive analysis of pollutants. This development is partly a result of the public concern and legislative pressure for reliable monitoring of environmental quality. The commercial availability of relatively inexpensive, computer-interfaced, bench-top instruments has rendered the technique almost routine for cost-effective analysis. Even greater speeds and resolving powers of the future generations of instruments will augment the significance of GC-MS in the environmental field.

See also: **II/Chromatography: Gas:** Detectors: Mass Spectrometry. **Extraction:** Solid-Phase Extraction. **III/Fungicides:** Gas Chromatography. **Herbicides:** Gas Chromatography. **Pesticides:** Gas Chromatography. **Polychlorinated Biphenyls: Gas Chromatography. Polycylic Aromatic Hydrocarbons:** Gas Chromatography.

Further Reading

Berezkin VG and Drugov YS (1991) *Gas Chromatography in Air Pollution Analysis*. Amsterdam: Elsevier.

Black RM, Clarke RJ, Read RW and Reid TJ (1994) Application of gas chromatography–mass spectrometry and gas chromatography–tandem mass spectrometry to the analysis of chemical warfare samples, found to contain residues of the nerve agent sarin, sulphur mustard and their degradation products. *Journal of Chromatography A* 662: 301–321.

Bruner F (1993) *Gas Chromatographic Environmental Analysis*. New York: VCH Publishers.

Claussen FA (1997) Arsenic speciation of aqueous environmental samples by derivatization with thioglycolic acid methyl ester and capillary gas–liquid chromatography–mass spectrometry. *Journal of Chromatographic Science* 35: 568–572.

Jones FE (1994) *Toxic Organic Vapors in the Workplace*. Boca Raton, FL: Lewis Publishers.

Karasek FW, Hutzinger O and Safe S (eds.) (1985) *Mass Spectrometry in the Environmental Sciences*. New York: Plenum Press.

Keith LH (ed.) (1992) *Compilation of E.P.A.'s Sampling and Analysis Methods*. Grand Rapids, MI: Lewis Publishers.

Sinha MP and Gutnikov G (1991) Development of a Miniaturized Gas Chromatograph–Mass Spectrometer with a Microbore Capillary Column and an Array Detector. *Analytical Chemistry* **63**, 2012–2016.

Subramanian G (ed.) (1995) *Quality Assurance in Environmental Monitoring, Instrumental Methods*. Weinheim: VCH Publishers.

Tamilarasan R, Morabito PL, Lamparski L, Hazelwood P and Butt A (1994) Determination of neutral chlorinated extractable organic compounds in water samples using large volume on-column injection capillary gas chromatography–mass spectrometry. *Journal of High Resolution Chromatography* 17: 689–694.

Wang Z, Fingas M, Landriault M *et al.* (1998) Identification and linkage of tarballs from the coasts of Vancouver Island and Northern California using GC/MS and isotopic techniques. *Journal of High Resolution Chromatography* 21(7): 383–395.

Wilkins CL (1994) Multidimensional GC for qualitative IR and MS of mixtures. *Analytical Chemistry* 66(5): 295A–301A.

Winegar ED and Keith LH (eds.) (1993) *Sampling and Analysis of Airborne Pollutants*. Boca Raton, FL: Lewis Publishers.

Pressurized Fluid Extraction

S. R. Sumpter, DuPont Agricultural Products, Wilmington, DE, USA

Introduction

Pressurized fluid extraction (PFE) is used to extract a wide variety of compounds from solid and semi-solid environmental samples. Soil is the predominant environmental solid extracted. Sediment samples are also frequently extracted. Sludge, chimney brick, fly ash and urban dust comprise other materials that are extracted using PFE. There are several reasons to use pressurized fluid extraction for environmental samples. PFE methods are:

- automated
- easy to transfer
- environmentally friendly, consuming little solvent
- relatively fast

- simple, requiring little expertise
- acceptable to regulatory agencies.

Several PFE methods have been developed to extract compounds from environmental samples. These are listed in **Table 1**. These methods are summarized in the sections that follow. One promulgated method in particular has extensive applicability. This method is United States Environmental Protection Agency (EPA) Method 3545. It is suitable for the extraction of several compound classes from environmental solid and semisolid samples. Compound classes listed in Table 1 that are extracted using EPA Method 3545 are noted.

The authors of EPA Method 3545 found the PFE method gives recoveries comparable to those obtained by rigorous Soxhlet extraction and other techniques, such as shaking, supercritical fluid and sonication extraction methods. Compared to these techniques, PFE takes less time (< 30 min) and consumes less solvent (15–30 mL). Using PFE, the method is applicable to the extraction of polychlorinated biphenyls (PCBs), semi-volatile base/neutral/acids (BNAs), organophosphorous pesticides (OPPs) organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and chlorinated herbicides from soil. Of all of the extraction conditions, only the extraction solvent is changed when extracting different compound classes. For example, acetone–hexane is used to extract a sample when analysing for OCPs and PCBs, methylene chloride–acetone is used to extract a sample when analysing BNAs and OPPs, and acetone–methylene chloride acidified with phosphoric acid is used to extract a sample when analysing for chlorinated herbicides. Extraction conditions for Method 3545 are shown in **Table 2**.

Relative recoveries of the PFE method (Method 3545) compared to other methods such as shaking or sonication extraction are summarized in **Table 3**. In this work, relative recoveries are the quotient of PFE recoveries divided by shaking, sonication, or Soxhlet extraction recoveries.

The following sections summarize details of critical sample preparation steps that are necessary before PFE, as well as the conditions used to extract the compounds listed in **Table 1**.

Table 1 Compound classes of environmental importance extracted using pressurized fluid extraction

Compound class
Aliphatic hydrocarbons
Alkylphenols
BTEX
[a]Chlorinated herbicides
Chlorinated hydrocarbons
Ethoxylates
Explosives (HMX, RDX, TNT, DNT)
Gasoline
Linear alkylbenzenesulfonates (LASs)
[a]Organochlorine pesticides (OCPs)
[a]Organophosphorus pesticides (OPPs)
Phenoxyacid herbicides
[a]Polychlorinated bipheyls (PCBs)
Polychlorinated dibenzofurans (PCDFs)
Polychlorinated dibenzo-*p*-dioxins (PCDDs)
[a]Polycyclic aromatic hydrocarbons (PAHs)
[a]Semi-volatile base/neutral/acid (BNAs)
Acids
Alcohols
Amides
Aromatic amines
Aromatic chloroethers
Azobenzenes
Benzidines
Chloroanalines
Chlorobenzenes
Chlorophenols
Methylphenols
Nitroanalines'
Nitrobenzenes
Nitrophenols
Nitrosamines
Phenyl hydrazines
Phthalates
Toluidines
Total petroleum hydrocarbons (TPHs)

[a]Compounds extracted using U.S. EPA Method 3545.

Applications

Aliphatic Hydrocarbons

Aliphatic hydrocarbons are readily extracted by PFE using aqueous and organic extraction solvents. Using organic extraction solvent, pentane, nonane, decane, undecane, tetradecane, and pentadecane are efficiently extracted using the conditions listed in **Table 4**. Due to its volatility, pentane recoveries are the lowest of these analytes. Pentane boils at 36°C, so special precautions are required to keep it from evaporating from the extraction cell before the extraction is performed. To prevent loss of pentane, extraction cells are cooled and aluminium retention discs are added into the tops of the extraction cells.

Water in the form of super-heated steam may also be used to extract aliphatic hydrocarbons. Dodecane, pentadecane, octadecane, heneicosane, tetracosane, heptacosane, triacontane, and tritriacontane are efficiently extracted from solid and semi-solid environmental samples using the conditions listed in **Table 5**.

Table 2 Summary of sample preparation and extraction conditions used in EPA Method 3454 to extract PCBs, semi-volatile BNAs, OPPs, OCPs and chlorinated herbicides from solid and semisolid environmental samples

Extraction conditions	*Extraction analysis conditions*
Sample preparation	Grind sample to 100–200 mesh (150–75 μm particle size)
Dispersing or drying agent	Mix sample with anhydrous sodium sulfate or diatomaceous earth
Sample size	Up to 30 g if a dispersing agent is not used
Extraction cell volume	11, 22, or 33 mL cell, depending on sample size
Extraction solvent	OCPs and PCBs: 1 : 1 acetone : hexane BNAs and OPPs: 1 : 1 methylene chloride : acetone Chlorinated herbicides: 2 : 1 acetone : methylene chloride acidified with phosphoric acid
Temperature	100°C
Heat step	5 min
Static time	5 min
Flow type	Static, dynamic, or mix of both
Number of cycles	1–5
Extraction pressure	2000 psi
Flush volume	60% of cell volume
Purge time	60 s

Extraction conditions from USEPA SW-846, 3rd edn., Update III (July 1995) Test methods for evaluating solid waste, Method 3545, Accelerated solvent extraction. U.S. GPO: Washington, DC.

Alkylphenols

Alkylphenols are metabolites of alkylphenol ethoxylates: a class of non-ionic surfactants that were used as cleaning agents and still find use today. Alkylphenols are monitored in the environment as they pose potential risk to animals. Time, and the amount of organic solvent, are saved in the pressurized fluid extraction of alkylphenols from sediment. For the extraction, CO_2 extraction solvent is modified with organic solvent. Either methanol, ethanol, 1-butanol, 2-propanol, acetone, or dioxane may be used. Sediment spiked with heptylphenol and nonylphenol is extracted with 100% recovery after 15 min extraction times. Longer times are required to extract 100% nonylphenol from the sediment. A dynamic extraction time of 60 min with 27.5% methanol does not completely extract aged nonylphenol from soil. **Table 6** shows a summary of sample preparation and extraction conditions for alkylphenols.

If the extractor does not allow the use of CO_2, 100% methanol, ethanol, 1-butanol, 2-propanol, acetone, or dioxan may be used as the extraction solvent. Since the solvent is typically evaporated before analysis, the most volatile solvent should be used.

BTEX (Benzene, Toluene, Ethylbenzene, and Xylene)

BTEX (benzene, toluene, ethylbenzene, and xylene) mixtures are efficiently extracted from solid and semisolid environmental samples by PFE using organic and aqueous solvents. BTEX mixtures are extracted from sand spiked with BTEX by PFE using organic solvent and standard conditions described in Table 4. BTEX mixtures are also quantitatively extracted by subcritical water using the conditions listed in Table 5.

Ethoxylates

Alkylphenol ethoxylates are non-ionic surfactants used for cleaning that are monitored in the environment. Ethoxylates are extracted from sediment by

Table 3 Summary of pressurized fluid extraction validation data for EPA Method 3545. Reported relative recoveries for the various compounds are the results of the PFE method used divided by the U.S. EPA reference methods listed

Compound class	*U.S. EPA reference method*	*% Relative recovery*
Chlorinated herbicides	8150A (shake method)	113
Organochlorine pesticides	3541 (automated Soxhlet)	97
Organophosphorous pesticides	3540 (Soxhlet)	99
Polychlorinated biphenyls	3540 (Soxhlet)	98
Polycyclic aromatic hydrocarbons	3540 (Soxhlet)	105
Semivolatile base/neutral/acids	3541 (automated Soxhlet)	99

Data compiled from the following sources: Ezzell (1998) *American Environmental Laboratory* January/February 24; Ezzell *et al.* (1995) *LC.GC* 13: 390; and Richter *et al.* (1995) *American Laboratory* February, 24.

Table 4 Summary of standard sample preparation and extraction conditions used to extract aliphatic hydrocarbons, BTEX, gasoline and TPH from soil

Extraction conditions	*Extraction/analysis conditions*
Dispersing or drying agent	None used
Sample size	10 g
Extraction cell volume	11 mL
Extraction solvent	Methylene chloride for aliphatic hydrocarbons and BTEX
Temperature	100°C
Heat step	5 min
Static time	5 min
Flow type	Mix of both static and dynamic extraction
Number of cycles	1
Extraction pressure	1500 psi

Extraction conditions from Ezzell JL and Richter BE (1996) *American Environmental Laboratory* February, 16.

PFE. Extraction conditions for octylphenol-9,5-ethoxylate, nonylphenol-13-ethoxylate and decylphenol monoethoxylate are the same as those for alkylphenols (see Table 6). Using the modified CO_2 as the extraction solvent with dynamic extraction, 60 min longer are required.

Explosives

Explosives are another important class of compounds that are monitored in the environment. They are monitored in military site or decommissioned site soil since the explosives can potentially contaminate water supplies. PFE extracts HMX (octohydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), TNT (2,4,6-trinitrotoluene), and DNT (2,4-dinitrotoluene) using the conditions shown in **Table 7**.

Table 5 Summary of sample preparation and extraction conditions used to extract aliphatic hydrocarbons, BTEX, PCBs, and PAHs from soil, sediment, sludge, and urban dust using water as the extraction solvent

Extraction conditions	*Extraction analysis conditions*
Sample preparation	Soil is homogenized
Dispersing or drying agent	None used
Sample size	0.2–0.5 g, cell void volume filled with sand
Extraction cell volume	0.5–0.8 mL (4.6 mm i.d. × 30 mm stainless steel HPLC column or 4.6 mm i.d. × 50 mm stainless steel SFE cell)
Extraction solvent	HPLC grade water purged two hours with nitrogen to remove dissolved oxygen
Temperature	250°C
Extraction time	15 min
Flow type	Dynamic, 1 $\text{mL}^{-1}\,\text{min}^{-1}$
Number of cycles	1
Extraction pressure	73.5 psi for aliphatic hydrocarbons and 735 psi for BTEX, PCBs, and PAHs

Extraction conditions from Yang *et al.* (1997) *Environmental Science and Technology* 31: 430. Reproduced with permission from the American Chemical Society.

Table 6 Summary of sample preparation and extraction conditions used to extract alkylphenols, ethoxylates, and linear alkylbenzene sulfonates from environmental solid and semi-solid samples

Extraction conditions	*Extraction analysis conditions*
Sample preparation	Water was separated from sediment by centrifugation. Sediment was dried at ambient temperature and ground to a particle size of less than 10 μm and water content was adjusted to 10% (w/w). After filling the cells, empty space in the extraction cell was filled with 3 mm diameter glass beads. Any remaining space, 2 mL was filled with modifier solvent.
Dispersing or drying agent	None used
Sample size	1 g
Extraction cell volume	5 mL
Extraction solvent	CO_2, modified with methanol, ethanol, 1-butanol, 2-propanol, acetone, or dioxane.
Temperature	100°C
Heat step	None
Static time	10 min
Flow type	Mix of static (10 min) and dynamic (5–60 min) extraction
Number of cycles	1
Extraction pressure	2200 and 2940 psi

Kreißelmeier and Durbeck (1996) *Fresenius Journal of Analytical Chemistry* 354: 921.

The extraction solvent used depends on the analytical technique preferred. Acetone is the best choice for GC and methanol is the best solvent for LC analysis. For the results shown in **Figure 1**, methanol was used as the extraction solvent. The extraction step takes 12 min per sample, resulting in 45 mL of extract.

Gasoline

Gasoline is extracted from spiked sand using the standard PFE conditions listed in Table 4. The average recovery of gasoline using these conditions is 94.4%, as determined by IR detection.

Linear Alkylbenzenesulfonates

Anionic surfactants are widely used for industrial as well as household cleaning and for pesticide formulations. Of the anionic surfactants, biodegradable

Table 7 Summary of sample preparation and extraction conditions used to extract explosives from soil

Extraction conditions	*Extraction analysis conditions*
Sample preparation	Soil is homogenized
Dispersing or drying agent	None used
Sample size	30 g
Extraction cell volume	33 mL
Extraction solvent	Methanol or acetone
Temperature	100°C
Heat step	5 min
Static time	5 min
Flow type	Mix of both static and dynamic
Number of cycles	1
Extraction pressure	1500 psi
Flush volume	60% of cell volume
Purge time	90 s

Extraction conditions from Ezzell (1998) *American Environmental Laboratory* January/February 24.

linear alkylbenzenesulfonates (LAS) are the most common and can be found in waste water systems and river water. From these water sources, anionic surfactants partition to sediment. LAS are selectively extracted from sediment by PFE allowing simple quantitation by high performance liquid chromatography. Extraction conditions for linear LAS [linear decyl- up to tridecylbenzenesulfonate (LAS-10 to LAS-13)] are the same as those for alkylphenols listed in **Table 6**. Methanol is the best CO_2 modifier (at 2200 psi) for these compounds.

Pesticides

Pesticides including herbicides, insecticides and fungicides are broadly applied throughout the world to generate greater harvests and to protect food supplies. As pesticides are present in soil, sediment and water, they are an important class of environmental compounds. Pesticides are extracted by PFE using organic and aqueous solvents.

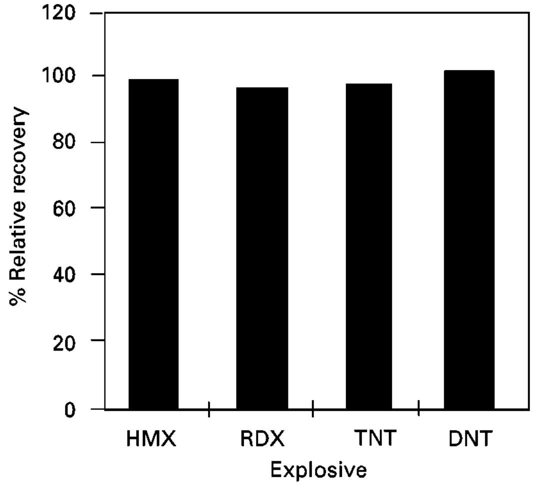

Figure 1 Average percent relative recovery data of explosives extracted from soil spiked at 3 mg kg^{-1} level. (Reprinted from Ezzell 1998. Copyright 1998 by International Scientific Communications, Inc.)

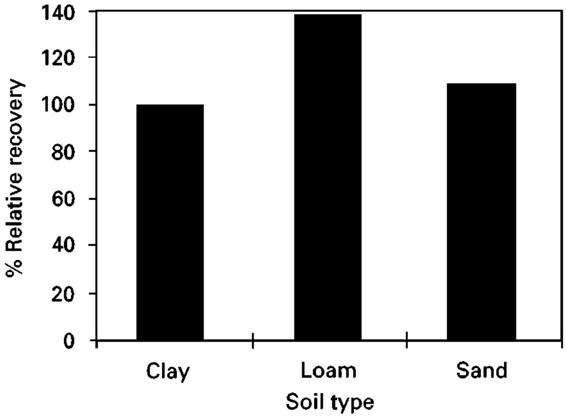

Figure 2 Average percent relative recovery data of herbicides extracted from three soil types. Soils were fortified with 50–500 and 500–5000 μg kg^{-1}. (Data from Ezzell *et al.* 1995.)

Sample preparation and extraction conditions for chlorinated herbicides, OCPs, OPPs in soil using EPA Method 3545 are shown in **Table 2**. The method (Method 3545) specifies the use of mixtures of organic solvents to extract a wide variety of organochlorine and organophosphate pesticides and chlorinated herbicides.

At least eight chlorinated herbicides (2,4-D; 2,4-DB; 2,4,5-T; 2,4,5-TP; dalapon, dicamba, dichloroprop and dinoseb) are extracted using this method. Extraction takes 12 min per sample, generating 15 mL of extract. Average relative recoveries for the

Table 8 Summary of sample preparation and extraction conditions used to extract pyrithiobac sodium from soil

Extraction conditions	*Extraction analysis conditions*
Sample preparation	Remove sticks and rocks and break up clumps of soil
Dispersing or drying agent	Mix 10 g soil with 7 g of silica gel
Sample size	10 g
Extraction cell volume	22 mL cell
Extraction solvent	Water
Temperature	100°C
Heat step	5 min
Static time	5 min
Flow type	Mix of both static and dynamic extraction
Number of cycles	1
Extraction pressure	200 psi
Flush volume	60% of cell volume
Purge time	60 s

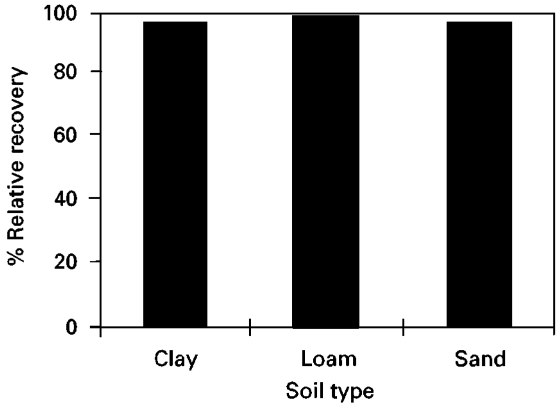

Figure 3 Average percent relative recovery data of organochlorine pesticides extracted from three soil types. Soils were fortified at 5, 50 and 250 μg kg^{-1}. (Data from Richter *et al.*, 1995. Copyright 1995 by International Scientific Communications, Inc.)

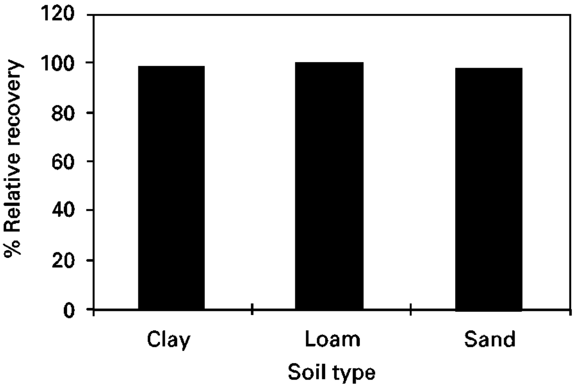

Figure 4 Average percent relative recovery data of organophosphorous pesticides spiked at low and high levels on three soil types and then extracted using EPA Method 3545. Soils were fortified with 250 and 2500 μg kg^{-1}. (Data from Ezzell *et al.,* 1995.)

eight chlorinated herbicides are shown in **Figure 2**. Relative recoveries are the quotient of PFE recoveries divided by shaker extraction recoveries.

Organic acids are extracted using organic solvents and by subcritical water. The advantages of using aqueous extraction solvent are (1) purchase and disposal costs are low and (2) it is environmentally friendly. Conditions used to selectively extract pyrithiobac sodium (the active ingredient in Staple® herbicide, used to control broadleaf weeds in cotton) are listed in **Table 8**.

Organochlorine pesticides (OCPs) are extracted using the conditions listed in **Table 2**. Average relative recoveries for the 20 OCPs are shown in **Figure 3**. Relative recoveries are the quotient of PFE recoveries divided by automated Soxhlet extraction recoveries.

Organophosphate pesticides (OPPs) listed in **Table 9** are extracted from soil using the conditions listed in **Table 2**. Average relative recoveries for the 24 OPPs are shown in **Figure 4**. Relative recoveries are the quotient of PFE recoveries divided by Soxhlet extraction recoveries.

Table 9 Twenty-four organophosphate pesticides extracted by EPA Method 3545

Azinphos methyl
Chlorpyrifos
Coumaphos
Demeton-O,S
Diazinon
Dichlorovos
Dimethoate
Disulfoton
EPN
Ethoprop
Fensulfothion
Fenthion
Mevinphos
Monocrotphos
Naled
Parathion ethyl
Parathion methyl
Phorate
Ronnel
Sulfotepp
Sulprofos
TEPP
Tetrachlorvinphos
Tokuthion

Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are significant environmental pollutants that are routinely monitored in soil, sediment and sludge. PCBs are extracted from these matrices using organic and aqueous extraction solvents. PFE conditions using organic solvents are listed in Table 2; PFE conditions used for aqueous solvents are listed in Table 5. Although not listed in Table 2, acetonitrile and methylene chloride also provide adequate extraction of PAHs in environmental solid and semi-solid samples. Concentrations of PCBs extracted from soil, sediment, urban dust and sludge using PFE and exhaustive Soxhlet extraction are similar. This is true for both organic and aqueous extraction solvents in PFE.

Table 10 Summary of sample preparation and extraction conditions used to extract dioxins and furans from chimney brick, urban dust, fly ash and sediments

Extraction conditions	*Extraction analysis conditions*
Sample preparation	Grind soil to 100–200 mesh (150–75 μm particle size)
Dispersing or drying agent	Mix with anhydrous sodium sulfate or Hydromatrix™
Sample size	4–10 g
Extraction cell volume	11, 22 or 33 mL cell, depending on sample size
Extraction solvent	Toluene, 15 mL
Temperature	180°C
Heat step	9 min
Static time	5 min
Flow type	Static, dynamic, or mix of both
Number of cycles	1–2
Extraction pressure	2000 psi

Extraction condition reproduced from Richter *et al.* (1997) *Chemosphere* 34: 975, with permission from Elsevier Science.

Polychlorinated Dioxins and Furans

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are environmental pollutants that are extracted from chimney brick, urban dust, fly ash, soil and sediment using PFE. Conditions for the extraction of PCDDs and PCDFs are listed in **Table 10**.

PFE and Soxhlet extraction results of PCDDs and PCDFs levels found are essentially equivalent for the matrices tested. PFE required less time and solvent than Soxhlet extraction.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are important environmental compounds being carcinogenic and mutogenic. They are extracted by organic solvents and by subcritical water. Using organic solvents, PAHs are extracted from urban dust, sediment and soil using the PFE conditions listed in **Table 2**. Subcritical water extraction requires the conditions listed in **Table 5**. Results from certified reference materials indicate that PFE efficiently extracts PAHs from these matrices. **Figure 5** shows a comparison of the amounts of PAHs found in PFE extracts and certified values.

The following organic solvents also provide adequate extraction of PAHs in environmental samples: toluene/methanol 1 : 1 (v : v), toluene, methylene chloride, acetonitrile, hexane/acetone 1 : 1 (v : v) and water. **Figure 6** shows the amounts of PAHs found in urban dust (SRM 1649) extracts comparing various organic and aqueous extraction solvents.

Semi-Volatile Base/Neutral/Acid Compounds

Semi-volatile base/neutral/acid compounds (BNAs) are extracted from solid and semi-solid environmental samples using the conditions listed in **Table 2**. Average relative recoveries for the 56 US EPA priority pollutants list (PPL) and target compound list (TCL) are shown in **Figure 7**. Relative recoveries are the quotients of PFE recoveries divided by Soxhlet extraction recoveries.

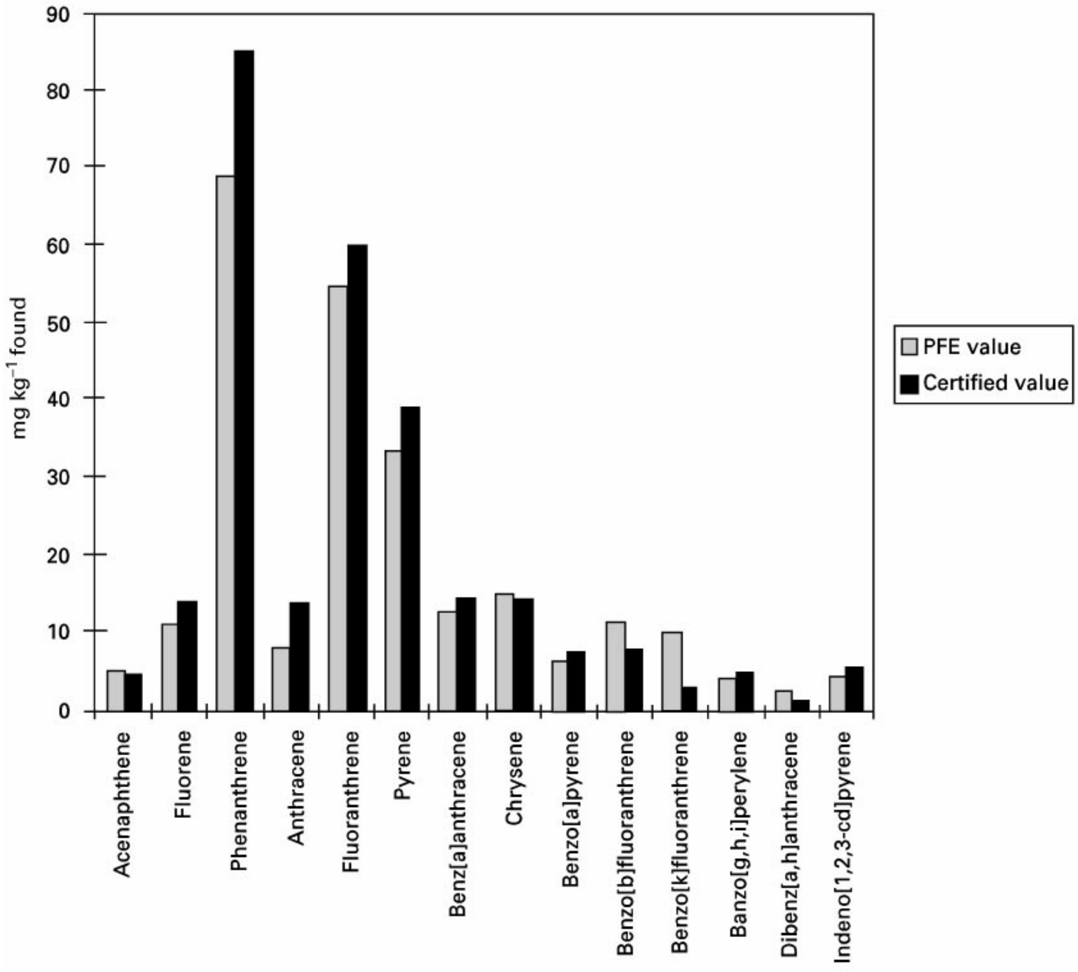

Figure 5 Comparison of amounts of PAHs found in PFE extracts and certified values. (Data from Richter, Jones, Ezzell *et al.* 1996.)

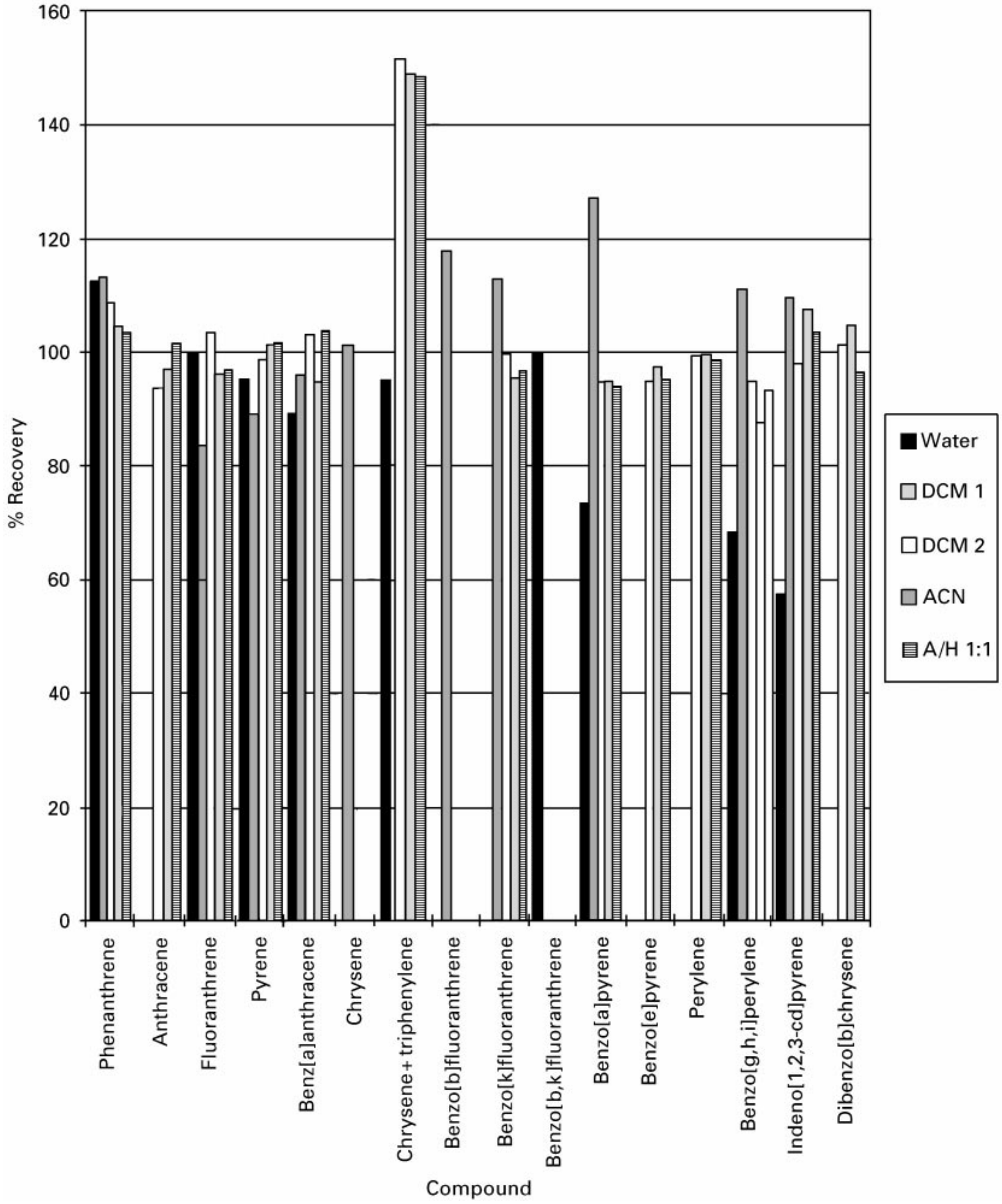

Figure 6 Recovery of PAHs from urban dust (certified reference NIST SRM 1649) extracted by PFE. Extraction solvents were water (250°C, 725 psi) and methylene chloride/acetone 1 : 1. (Data for water extraction from Hawthorne *et al.*, 1994.) Data for methylene chloride extraction (DCM 1) from Richter *et al.*, 1995. Data for methylene chloride extraction (DCM 2) from Schantz *et al.*, 1997.)

Total Petroleum Hydrocarbons

Total petroleum hydrocarbons (TPHs) are extracted from soil samples using the standard PFE conditions listed in **Table 4**. Levels of TPHs extracted by PFE and Soxhlet extraction are typically similar.

Future Applications

There are several reasons why analysts use PFE to extract analytes of interest from solid and semisolid environmental samples. In comparing PFE to Soxhlet, sonication and shaking extraction methods, researchers find that the amounts of analyte extracted from solid and semi-solid samples are similar, but PFE requires less extraction time and less extraction solvent. PFE methods are easy to develop and to transfer. PFE provides automated sample extraction, allowing increased productivity of laboratory personnel. Finally, PFE methods are being accepted by regulatory agencies. Given these advantages, researchers

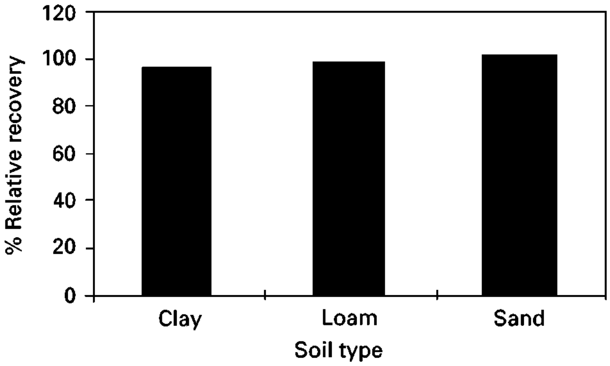

Figure 7 Average percent relative recovery data of 56 semi-volatile base/neutral/acid components extracted from three soil types using PFE. Soils were fortified at 250, 2500, and 12 500 μg kg^{-1}. (Data from Richter *et al.* (1995) reproduced with permission from International Scientific Communications Inc.)

will continue to use PFE to develop many more environmental sample applications.

See also: **II/Extraction:** Supercritical Fluid Extraction. **III/Environmental Applications:** Supercritical Fluid Extraction; Soxhlet Extraction. **Superheated Water Mobile Phases: Liquid Chromatography.**

Further Reading

Ezzell J (1998) The Use of SW-846 Method 3545 for automated extraction of environmental samples. *American Environmental Laboratory*. 10: 24–25.

Ezzell JL and Richter BE (1996) Automated sample preparation for environmental laboratories using accelerated solvent extraction. *American Environmental Laboratory*. 16–18.

Ezzell J, Richter BE, Felix WD, Black SR and Meikle JE (1995) A comparison of accelerated solvent extraction with conventional solvent extraction for organophosphorus pesticides and hebicides. *LC.GC* 13: 390–398.

Hawthorne SB, Yang Y and Miller DJ (1994) Extraction of organic pollutants from environmental solids with sub- and supercritical water. *Analytical Chemistry*. 66: 2912–2920.

Kreißelmeier A and Durbeck H-W (1996) Determination of alkylphenols and linear alkylbenzene sulfonates in sediments applying accelerated solvent extraction (ASE). *Fresenius Journal of Analytical Chemistry*. 354: 921–924.

Richter BE, Ezzell JL, Felix D, Roberts KA and Later DW (1995) An accelerated solvent extraction system for the rapid preparation of environmental organic compounds in soil. *American Laboratory* 27: 24–28.

Richter BE, Jones BA, Ezzell JL, Porter NL, Avdalovic N and Pohl C (1996) Accelerated solvent extraction: a technique for sample preparation. *Analytical Chemistry* 68: 1033–1039.

Richter BE, Ezzell JL, Knowles DE, Hoefler F, Mattulat AKR, Scheutwinkel M, Waddell DS, Gobran T and Khurana V (1997) *Chemosphere* 34: 975–978.

Schantz MM, Nichols JJ and Wise SA (1997) Evaluation of pressurised fluid extraction for the extraction of environmental matrix reference materials. *Analytical Chemistry* 69: 4210–4219.

USEPA SW-846, 3rd Edn., Update III (July 1995) *Test Methods for Evaluating Solid Waste, Method 3545, Accelerated Solvent Extraction*. Washington. U.S. GPO.

Yang Y, Bowadt S, Hawthorn SB and Miller DJ (1995) Subcritical water extraction of polychlorinated biphenyls from soil and sediment. *Analytical Chemistry*. 67: 4571–4576.

Yang Y, Hawthorne SB and Miller DJ (1997) Class-selective extraction of polar, moderately polar, and nonpolar organics from hydrocarbon wastes using subcritical water. *Environmental Science and Technology*. 31: 430–437.

Solid-Phase Microextraction

T. Nilsson, Technical University of Denmark, Lyngby, Denmark

Solid-phase microextraction (SPME) is a technique for the extraction of organic compounds from gaseous, aqueous and solid matrices such as many environmental samples. It is rapid and simple, which makes it ideal for automation and *in situ* measurements, and no harmful solvents are used. The principle of SPME is equilibration of the analytes between an organic polymeric phase coated on to a fused-silica fibre and the sample matrix. The parameters of importance for the equilibration process are described below and various environmental applications are discussed. Traditionally, SPME has been combined with analysis by gas chromatography (GC), and mainly aqueous samples have been analysed. This combination has proved to be sensitive, accurate and precise for the quantitative analysis of volatile organic compounds and different classes of pesticides. Solid samples can also be analysed by SPME in spite of the stronger matrix effects, and recently SPME has been coupled with liquid chromatography (LC) for the analysis of polar pesticides.

Principle

The principle of SPME is that a fused-silica fibre is coated with an organic polymer and exposed to the