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Supercritical Fluid Extraction

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There has been growing interest in supercritical fluid extraction (SFE) in the past few years due to its numerous advantages over liquid extraction (rapidity, low solvent volumes, nontoxicity of carbon dioxide, great selectivity by modifying the fluid density, low dilution of the extracts, possibility of online coupling with chromatographic techniques and automation).

Analytical applications of SFE began in the late 1980s, with particular focus on environmental samples. While early reports were on spiked matrices and/or highly contaminated samples, recent applications deal with samples containing low levels of incurred contaminants. It was soon found that extraction conditions are strongly dependent on both the solutes and the matrix, so that parameters need to be adjusted for every new application.

This article will focus on the main pollutants extracted, showing the important parameters that influence extraction recoveries, and illustrating the great potential of this technique together with its limitations.

Sample Preparation Prior to Extraction

To ensure better desorption of analytes from the matrix, several sample treatments can be performed, either physical (e.g. grinding) or chemical (e.g. addition of derivatization reagents).

Pretreatment of the Sample

This step is of prime importance, as it may greatly enhance the extraction efficiency.

Solids The moderate water solubility in supercritical CO_2 may lead to restrictor plugging; in addition, water can be detrimental to the extraction of nonpolar compounds. Consequently, matrices with a high water content (typically 75%) require the addition of a drying agent to the sample (e.g. hydromatrix, a pelletized diatomaceous earth, magnesium or sodium sulfate). This also enlarges the surface area of the sample. However, the presence of residual water usually favours the extraction of polar compounds.

Grinding the sample should also enhance the extraction but, excessive grinding may lead to a pressure drop within the extraction cell, thereby decreasing the solubility of the analyte at the bottom of the cell. The pressure drop problem may be overcome by mixing the finely ground sample with a coarse dispersing agent.

Finally, the presence of sulfur in some matrices (e.g. sediments or sewage sludges) can cause lack of reproducibility and restrictor blockages. To overcome these problems, it is suggested to mix the sample with copper prior to extraction to act as sulfur scavenger.

Liquids A few studies have been performed on the direct SFE of aqueous matrices using a special extraction vessel. However, such analytes are mainly preconcentrated on to a solid-phase extraction (SPE) disk or cartridge, before being eluted with the supercritical fluid. This SPE-SFE combination offers a greater selectivity compared to elution with an organic solvent (e.g. CO_2 at low density selectively extracts organochlorine pesticides from C_{18} disks, while extraction at a higher density in the presence of methanol is required to elute organophosphorus pesticides).

Derivatization Reactions

Extraction of highly polar compounds may be improved by coupling derivatization reactions with SFE, to convert polar functions into less polar groups for better solubility in the fluid. This procedure affords extracted compounds that are readily amenable to gas chromatography. Besides, the derivatizing agent may react with active sites of the matrix, leading to better desorption of solutes.

The three main reactions are alkylation (with acidic methanol, alkyl halides, tetraalkylammonium salts or Grignard reagents), acylation (mostly with acetic anhydride, in the presence of organic bases such as pyridine) and silylation (with hexamethyldisilazane and trimethylchlorosilane). As the latter requires relatively anhydrous conditions, matrices with moisture contents greater than 0.4% may reduce derivatization efficiency.

Derivatization may be performed prior to extraction or under supercritical fluid conditions (*in situ* derivatization). The latter approach is most common as it reduces sample handling. Pre-extraction derivatization is used for particular applications (e.g. alkylation with Grignard reagents due to their low solubility in CO_2). As complex environmental matrices contain many potential interferences that can be derivatized, excess quantities of reagent should be used.

Ion Pairing

SFE of ionic compounds may be possible by formation of an ion pair, which is soluble in the fluid. The ion-pairing reagent may also react with the matrix active sites, thus favouring the desorption of solute molecules.

Common Pollutants Extracted by SFE

SFE has been successfully applied to the determination of several pollutants from different matrices. The strong solute–matrix interactions usually impose proper modifier selection and elevated temperature. Typical extraction conditions for the main pollutants are given in **Table 1**.

Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons (PAHs) have commonly been extracted from environmental matrices, and SFE has recently been adopted as an official method (US Environmental Protection Agency method 3561).

These analytes are relatively nonpolar and should be extracted with neat CO_2. However, the delocalized π-electron system of PAHs can cause strong interactions with the active sites of the matrix surface, hindering their extraction. Extraction of high molecular weight PAHs from real samples therefore requires high pressure and temperature, as illustrated in **Figure 1** for urban dust particulates. Elevated temperature are suspected to favour analyte desorption from the active sites of the matrix.

PAH solubility in supercritical CO_2 decreases with increasing number of fused aromatic rings, so addition of a modifier is recommended to achieve acceptable recoveries. Methanol is the most common modifier, but satisfactory results can be obtained with other modifiers. For example, toluene-modified CO_2 is efficient in extracting two to six fused aromatic ring PAHs from soil with high carbon content (50%); addition of toluene to the sample also improves the extraction of nitro-PAHs from diesel and air particulates. A combination of toluene, trifluoroacetic acid and triethylamine is an even better modifier for PAHs and nitro-PAHs; the additives are thought to block the matrix active sites, thus preventing possible readsorption of solute molecules. Extraction of PAHs from air particulate matter is also improved in the presence of diethylamine or acetonitrile, as illustrated in **Figure 2**.

The efficacy of the modifier is highly dependent on matrix characteristics. For example, the addition of methylene chloride as a static modifier allowed the quantitative extraction of PAHs from soil with CO_2; this modifier solubilizes the soil aggregates, thus increasing the contact between soil particles and supercritical CO_2.

The effect of increasing the temperature is always advantageous at constant density. Modifier and temperature effects are additive, so that extraction using CO_2 with modifiers at high temperature is usually the most rigorous SFE method for the extraction of particularly difficult samples such as urban air particulates, as shown in **Figure 3**.

Another approach has been the use of *in situ* chemical derivatization to determine PAHs from a harbour sediment. The derivatizing agent (Tri-Sil, a 2:1 (v/v) mixture of hexamethyldisilazane and trimethylchlorosilane) was added to the extraction vessel prior to the extraction step. As shown in **Figure 4**, results were improved compared with extraction with CO_2 or 10% methanol-modified CO_2. As PAHs cannot be derivatized, the effect of the reagent was to help displacement of the analytes from the matrix.

Although nitrous oxide modified with 5% methanol may be considered to be the most efficient fluid for extracting PAHs, its use should be avoided due to the possibility of explosion with this combination. Difluorochloromethane is also efficient but environmental concern discourages its common use. Subcritical water (250°C, 50 bar) seems a more viable alternative to CO_2 for the SFE of organic compounds with a wide range of polarities. The dielectric constant of water decreases as the temperature increases so that at moderate temperatures (50–100°C) polar compounds are extracted (e.g. phenols, amines), while nonpolar to moderately polar organics (including

Table 1 Typical applications of SFE to solid environmental matrices

Compounds		*Matrices*	*Reagent added to the matrix*	*Fluid*	*Observations*
Polyaromatic hydrocarbons		Soils, sediments, urban dust, fly ash	None	CO_2–CH_3OH (10%) CO_2–toluene (10%) CO_2–diethylamine (10%) Subcritical H_2O	Strong interactions with the matrix High temperatures recommended, as well as with addition of modifier
			CH_2Cl_2	CO_2	Solubilization of soil aggregates by CH_2Cl_2
			Tri-Sil	CO_2	Tri-Sil displaces the solutes from the matrix
Polychlorinated biphenyls		Soils, sediments, sewage sludge	None	CO_2 CO_2–CH_3OH (1–2%) CO_2–diethylamine Subcritical H_2O	Moderate temperatures (70–100°C)
Dioxins		Fly ash, sediments	None	CO_2–CH_3OH (2%)	Strong interactions with the matrix Better recoveries with a dry matrix
			Strong acid	CO_2	Destruction of the matrix by the acid
Phenols		Soils, house dust	None	CO_2–CH_3OH (2–20%) CO_2–CH_3OH (32%)–H_2O (8%)	High temperatures recommended
			Acetic anhydride and pyridine	CO_2	*In situ* acetylation of phenols
Pesticides	Organochlorine	Soils, sediments	None	CO_2–toluene	Toluene disrupts solute–matrix interactions
	Organophosphorus		None	CO_2–CH_3OH (5%)	
	Triazines		None	CO_2–CH_3OH (10–30%) CO_2–[$CH_3OH + 2\%H_2O$] (10%)	Matrix moisture enhances the extraction
	Phenoxyacetic acids		None	CO_2–CH_3OH (20%)	
			TMPA	CO_2	Ion pairing and methylation
			BF_3/CH_3OH	CO_2	Methylation
Surfactants	Nonionic	Soils, sediments, sewage sludges	None H_2O	CO_2–CH_3OH (27.5%) CO_2	
	Anionic		None	CO_2–CH_3OH (40%)	
			TAA salts	CO_2	Ion pairing
			Methylation reagent	CO_2	Methylation
	Cationic		None	CO_2–CH_3OH (30%)	
Metallic species	Organometallics	Sediments	None	CO_2–CH_3OH (10–20%)	
			Organic ligand[a] Derivatization reagent[b]	CO_2–CH_3OH (5%)	
	Metal ions	Sediments	Organic ligand[c]	CO_2–CH_3OH (5%)	Formation of a metal chelate Methanol increases the chelate solubility

TMPA, trimethylphenylammonium hydroxide; TAA, tetraalkylammonium.

[a] Organic ligands: dithiocarbamates (mainly sodium diethyldithiocarbamate and diethylammonium diethyldithiocarbamate).

[b] Derivatization reagents: hexylmagnesium bromide, thioglycolic acid methylester.

[c] Organic ligands: dithiocarbamates, β-diketones, crown ethers, organophosphorus compounds.

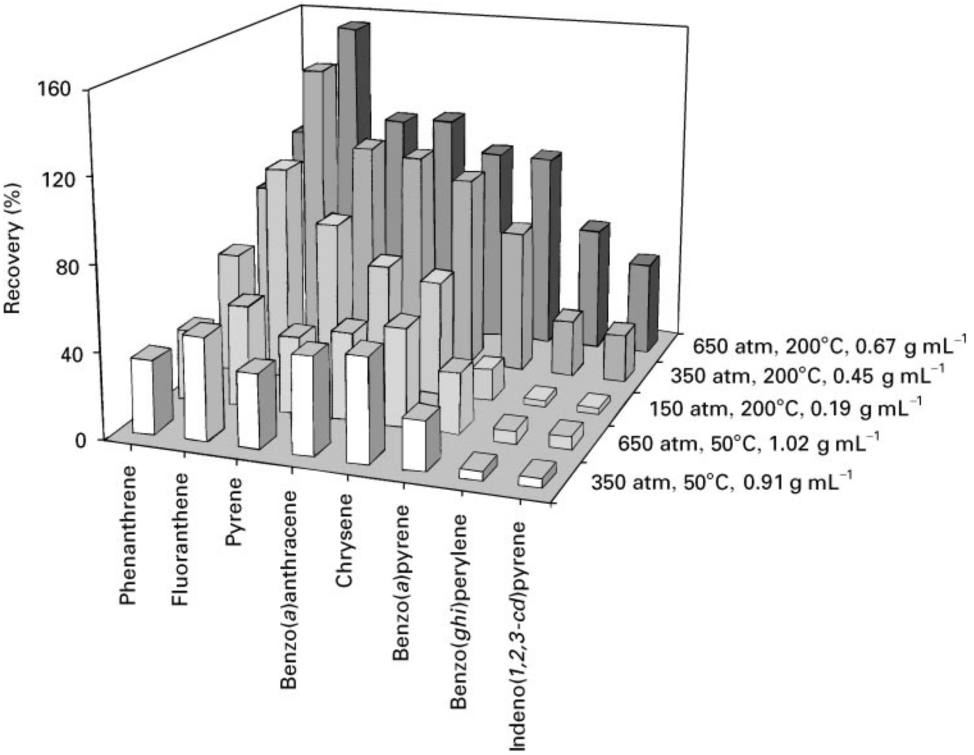

Figure 1 Recoveries of PAHs from urban air particulates (standard reference material SRM 1649) using supercritical CO_2^{a} extraction at different pressures and temperatures. ^{a}40-min extractions. (From Langenfeld JJ, Hawthorne SB, Miller DJ and Pawliszyn J (1993) Effects of temperature and pressure on supercritical fluid extraction efficiencies of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Analytical Chemistry* 65: 338–344. Copyright 1993 American Chemical Society.)

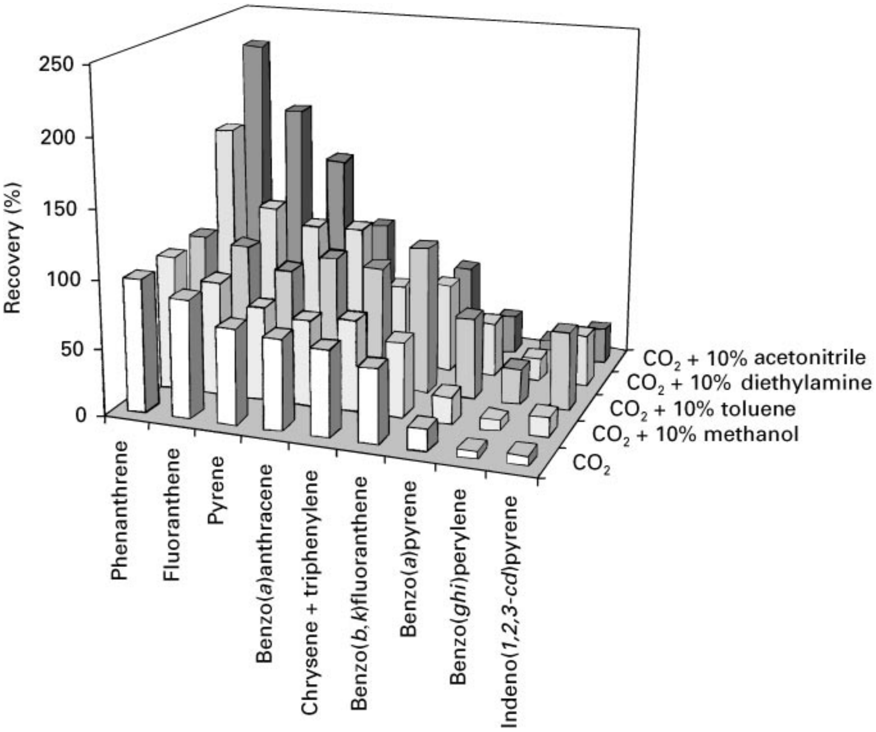

Figure 2 Influence of the presence of a modifier in supercritical CO_2 on the recoveries of PAHs from air particulate matter (standard reference material SRM 1649)^a. ^{a}400 bar, 80°C, 250 μL (10% v/v) modifier added to the sample, 5 min static/10 min dynamic. (From Langenfeld JJ, Hawthorne SB, Miller DJ and Pawliszyn J (1994) Role of modifiers for analytical-scale supercritical fluid extraction of environmental samples. *Analytical Chemistry* 66: 909–916. Copyright 1994 American Chemical Society.)

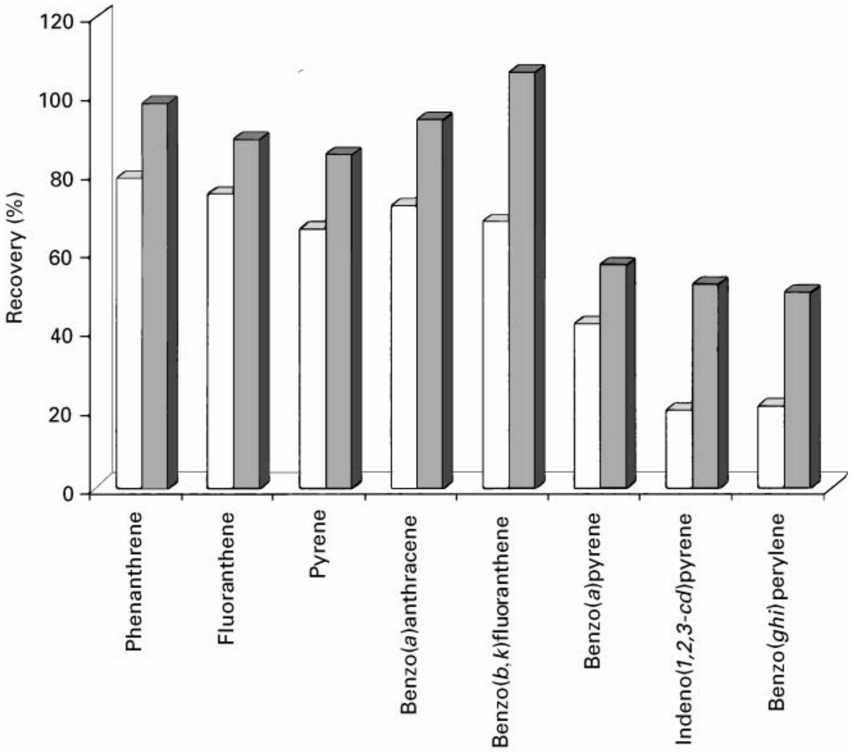

Figure 3 Temperature effect on the recoveries of PAHs from air particulate matter (standard reference material SRM 1649) using methanol modified CO_2[a]. [a]400 bar, 80 μL (10% v/v) methanol added to the sample, 15 min static/15 min dynamic. (From Yang Y, Gharaibeh A, Hawthorne SB and Miller DJ (1995) Combined temperature/modifier effects on supercritical CO_2 extraction efficiencies of polycyclic aromatic hydrocarbons from environmental samples. *Analytical Chemistry* 67: 641–646. Copyright 1995 American Chemical Society.)

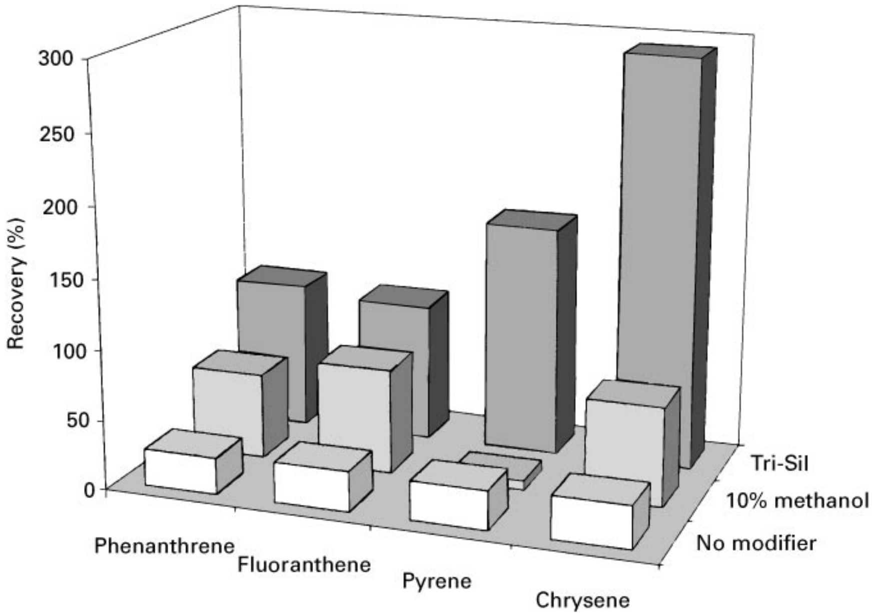

Figure 4 Recoveries of PAHs from a harbour sediment (HS-3) using either supercritical CO_2, 10% methanol modified CO_2, or *in situ* derivatization with Tri-Sil[a] followed by CO_2 extraction. Three sequential extractions were conducted (each at 350 bar and 60°C, 15 min static/15 min dynamic). [a]Tri-Sil is a mixture of hexamethyldisilane and trimethylchlorosilane 2 : 1 (v/v); 0.5 mL of this reagent was added to the cell prior to the extraction. The derivatizing agent was added just prior to each static step. (From Hills JW and Hill HH (1993) Carbon dioxide supercritical fluid extraction with a reactive solvent modifier for the determination of polycyclic aromatic hydrocarbons. *Journal of Chromatographic Science* 31: 6–12. With permission of Preston Publications, a Division of Preston Industries Inc.)

PAHs) are extracted at higher temperatures (200–250°C), as illustrated in **Figure 5**.

PAHs have also been determined in water samples after their preconcentration on to C_{18} disks and their further elution with supercritical CO_2.

Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are lipophilic and thereby highly soluble in CO_2. Hence, CO_2 alone or modified with a small amount of methanol (typically 1–2%) is efficient for their extraction. **Figure 6** illustrates the effects of both pressure and temperature on the recovery of PCBs from river sediment using neat CO_2. Best recoveries are obtained at high temperature, whatever the pressure. Surprisingly, high molecular weight PCBs are more efficiently extracted, despite their expected reduced solubilities; in fact, this is in agreement with the tighter binding of low molecular weight PCBs to the sediment matrix.

Recovery rates may be improved by addition of modifiers, especially methanol, as illustrated in **Figure 7**. Thus, methanol-modified CO_2 allowed the SFE of PCBs and organochlorine pesticides at the part-per-trillion level in marine sediments. Water under subcritical conditions is also an effective extractant for PCBs.

Recently, a single SFE method for field extraction of PCBs and PAHs in soils has been developed with neat CO_2 (150°C, 400 bar) to avoid co-extraction of matrix material, allowing direct gas chromatography. The simultaneous extraction and clean-up of mussel samples can be achieved by adding Florisil on top of the sample, enabling the direct determination of 11 PCBs (as well as 15 organochlorine pesticides).

Dioxins

Dioxins (polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)) are of great environmental concern owing to their acute toxicity. Like PCBs, they are readily amenable to extraction by SFE. As these pollutants have been mainly detected in emissions from municipal incinerators, their extraction from fly ash matrices has been investigated. SFE gave satisfactory results, as compared to Soxhlet extraction. Despite the high solubility of these compounds in pure CO_2, it gave almost no extraction due to the strong matrix adsorption of the dioxins. Upon addition of 2% methanol to the CO_2, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin was efficiently extracted from a dry sediment; the presence of water in the matrix hindered its extraction. The suitability of nitrous oxide for the SFE of PCDDs and PCDFs

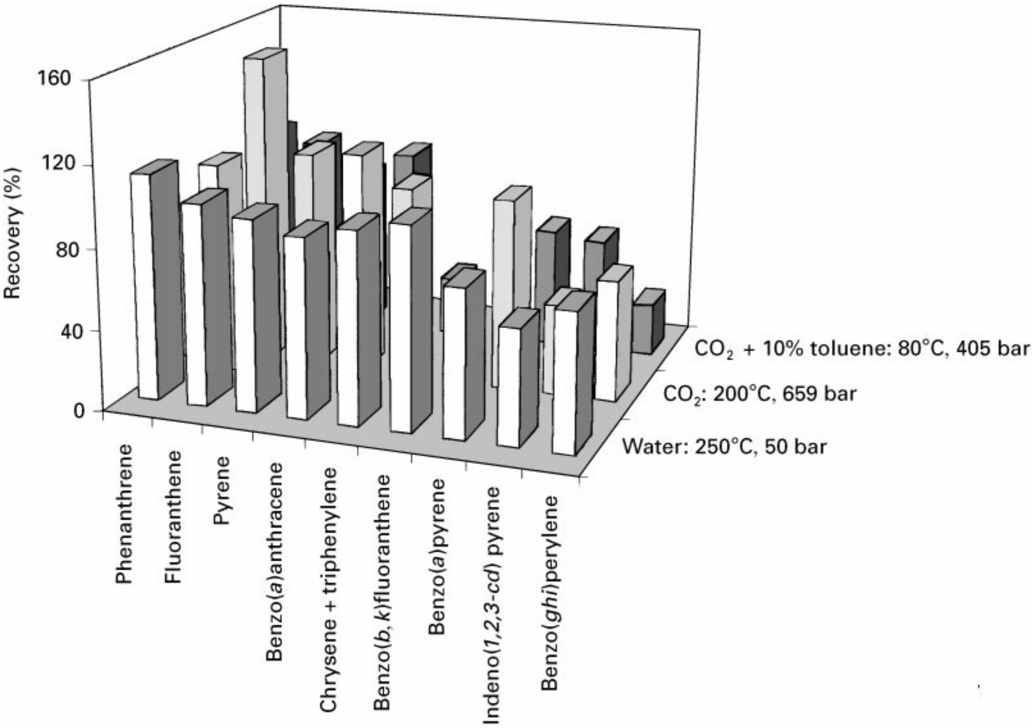

Figure 5 Recoveries of PAHs from urban air particulate (National Institute for Standards and Technology NIST 1649) using either supercritical $CO_2{}^a$ (200°C, 659 bar), 10% toluene modified $CO_2{}^b$ (80°C, 405 bar) or subcritical water (250°C, 50 bar). ^{a}40-min extractions. ^{b}20-min extractions (10 min static/10 min dynamic). (From 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. Copyright 1994 American Chemical Society.)

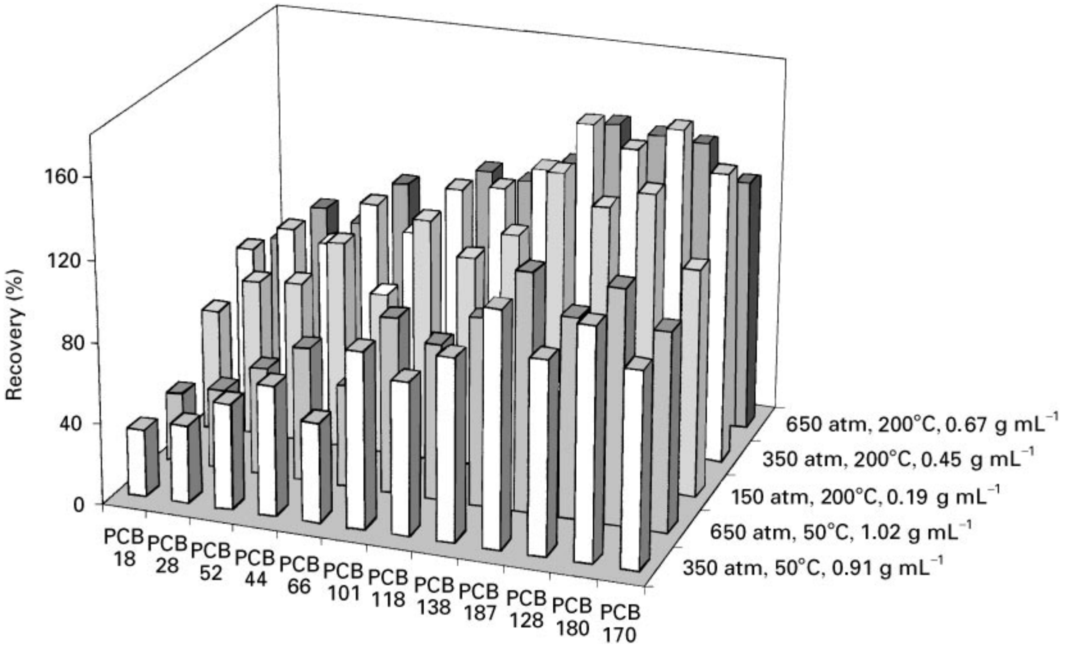

Figure 6 Recoveries of PCBs from river sediment (standard reference material SRM 1939, containing 3% water and 10% organic matter) using supercritical $CO_2{}^a$ extraction at different pressures and temperatures. ^{a}40-min extractions. (From Langenfeld JJ, Hawthorne SB, Miller DJ and Pawliszyn J (1993) Effects of temperature and pressure on supercritical fluid extraction efficiencies of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Analytical Chemistry* 65: 338–344. Copyright 1993 American Chemical Society.)

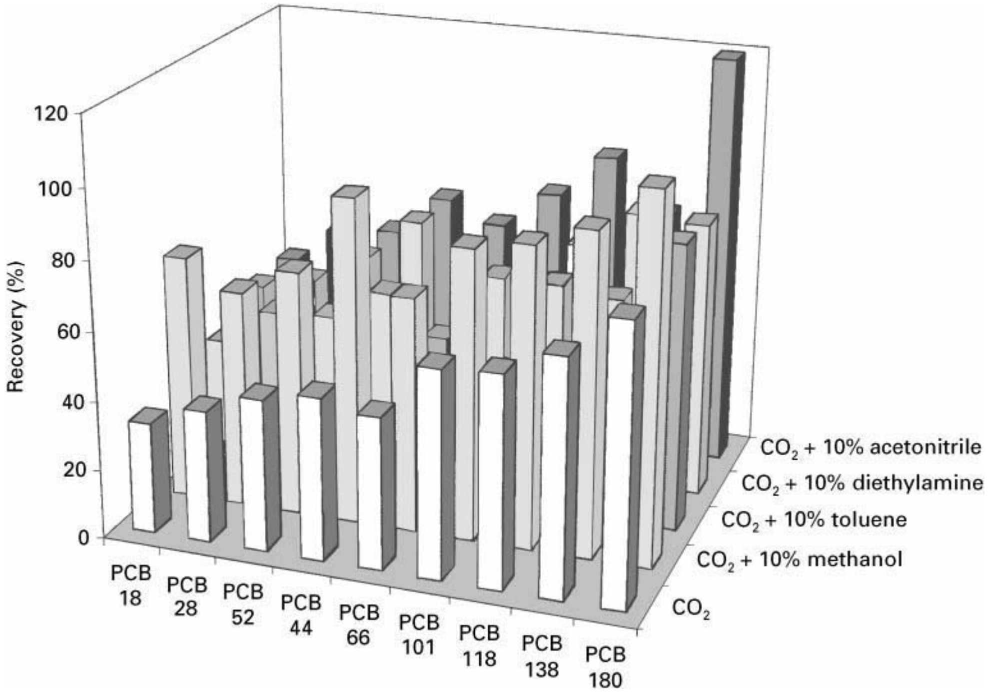

Figure 7 Influence of the presence of a modifier in supercritical CO_2 on the recoveries of PCBs from river sediment (standard reference material SRM 1941)^a. ^{a}400 bar, 80°C, 250 μL (10% v/v) modifier added to the sample, 5 min static/10 min dynamic. (From Langenfeld JJ, Hawthorne SB, Miller DJ and Pawliszyn J (1994) Role of modifiers for analytical-scale supercritical fluid extraction of environmental samples. *Analytical Chemistry* 66: 909–916. Copyright 1994 American Chemical Society.)

has also been described. Alternatively, the matrix may be destroyed by exposure to a strong acid, and further extracted with neat CO_2.

Phenols

Phenols are moderate to highly polar compounds. Thus, several approaches have been used for their SFE: direct addition of a polar modifier (e.g. water, acetonitrile, methanol) to the matrix, dynamic addition of the modifier to the CO_2, or *in situ* acetylation.

For example, addition of 2% methanol improved their extraction from soil. Enhanced-fluidity liquid extraction (CO_2 with 20% methanol) improved the recovery of phenols from house dust. Further improvements could be achieved using a methanol–water–CO_2 mixture (32.1/7.9/60 mol %), as water is supposed to swell the matrix material, allowing more efficient penetration and interruption of matrix–analyte interactions. Similar results have been obtained with sediments.

As illustrated in **Figure** 8, phenols are efficiently acetylated during SFE by means of direct reaction with acetic anhydride. Even though recoveries of phenols decrease as the activated charcoal content of the soil increases due to stronger solute–matrix interactions, improvement upon derivatization is evident. In addition, extracts are cleaner because of milder extraction conditions.

Similarly, the SFE of pentachlorophenol and related compounds from soil samples can be achieved using *in situ* acetylation (with acetic anhydride and triethylamine at 80°C) followed by CO_2 extraction. Increasing the extraction temperature from 50 to 200°C resulted in higher recoveries of chlorophenols from an industrial soil.

Pesticides

Pesticides have a broad range of physical properties and chemical structures. Their solubility in pure CO_2 may be evaluated from their octanol–water partition coefficients. Organochlorine pesticides are highly soluble in pure CO_2, while organophosphorous compounds require a modifier; addition of a polar modifier becomes crucial for triazines. In the case of phenoxyacetic acids, an ion-pairing or derivatization reagent needs to be added.

Another useful parameter is the soil–water partition coefficient, as it is indicative of the pesticide's soil adsorption; recoveries have been shown to decrease

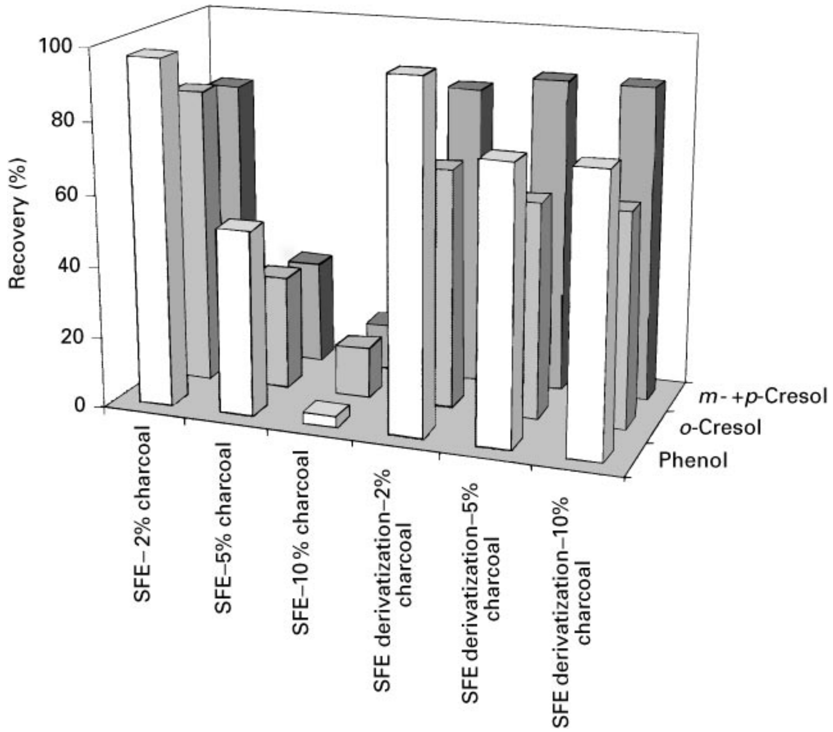

Figure 8 Recoveries of phenolic compounds from three garden soils with 2, 5 and 10% activated charcoal content, using SFE alone[a] or SFE-derivatization[b]. [a]CO_2, 90°C, 382 bar, 0.77 g mL^{-1}, addition of 100 μL methanol to the sample, 10 min static/15 min dynamic[b]. CO_2, 115°C, 0.4 g mL^{-1}, addition of 20 μL pyridine and 115 μL acetic anhydride to the sample, 5 min static/15 min dynamic. (From Llompart MP, Lorenzo RA, Cela R, Li K, Belanger JMR and Pare JRJ (1997) Evaluation of supercritical fluid extraction, microwave-assisted extraction and sonication in the determination of some phenolic compounds from various soil matrices. *Journal of Chromatography A* 774:243–251. With permission from Elsevier Science.)

as the soil organic content is increased, due to strong analyte–matrix interactions.

Nonpolar pesticides Despite their high solubility in CO_2, the solute–matrix interactions may yield lower recoveries than expected from solubility alone. Thus, extractions of organochlorine pesticides from spiked soils were unsatisfactory, especially for soils with a high organic content. Modifiers have been tested to enhance the SFE of organochlorine pesticides from different matrices. For example, toluene added to a contaminated soil improved the extraction with CO_2 of hexachlorocyclohexane isomers.

Several organochlorine pesticides were also efficiently extracted from aqueous matrices using a combination of SPE (on to C_{18} disks and cartridges) and pure CO_2 SFE.

Moderately polar and polar pesticides Methanol-modified (5%) CO_2 is a common extractant for organophosphorus pesticides. The polar triazine herbicides require a higher percentage of methanol (10%) in CO_2 to increase their solubility and disrupt solute–matrix interactions. Methanol (10%) containing 2% water may also be used. The ternary mixture acetone–water–triethylamine (90/10/1.5 v/v/v) is also efficient. Water is suspected of increasing the surface area of clay containing soils by swelling. Thus, a direct correlation between diuron extraction from montmorillonite clay and the percentage swelling of the matrix (due to the modifier) was observed at different pressures and temperatures. In contrast, triethylamine should compete with solute molecules on to the active sites of the soil. Also, soil moisture has been reported to enhance triazine extraction, as well as addition of a surfactant (Triton X-100), which probably leads to the matrix swelling and the formation of nonionic reverse micelles.

Extraction of bound pesticide residues in soils may require more severe conditions (for example, extraction of triazine from a mineral soil entailed 30% methanol, 350 bar and 125°C).

Ionic pesticides Specific SFE conditions are required to improve their solubility and/or to overcome strong solute–matrix interactions. Addition of 20% methanol to CO_2 allowed the extraction of four herbicides (dicamba, 2,4-dichlorophenoxyacetic acid (2,4-D), 2-(2,4,5-trichlorophenoxy)propionic acid (2,4,5-TP) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)) from house dust (440 bar and 100 or 150°C). Pre-extraction of extraneous matrix material was achieved with CO_2 after hexane was added to the sample. The mixture acetone–water–triethylamine (90/10/1.5 v/v/v) also enhanced extraction of 2,4-D from soil.

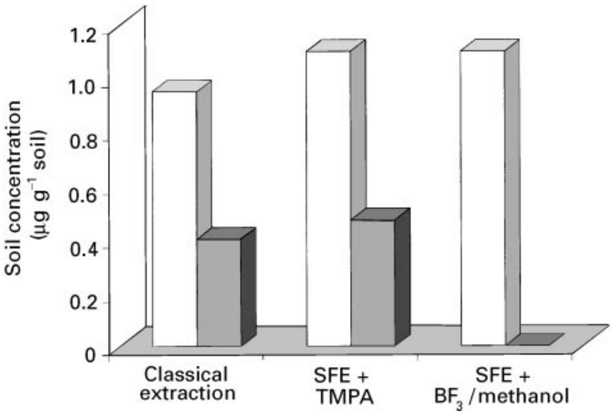

Figure 9 Extraction of native pesticides from an agricultural soil using either classical extraction (two sequential extractions with 0.5 mol L^{-1} KOH in 10% KCl/water) or SFE (with TMPA (three sequential extractions (each 15 min static/15 min dynamic), CO_2, 400 bar, 80°C) or BF_3–methanol (a single extraction (15 min static/15 min dynamic), CO_2, 400 bar, 80°C) as derivatization reagents). Open bars, 2,4-D; filled bars, dicamba. (Reproduced with permission from Hawthorne *et al.*, 1992. Copyright 1992 American Chemical Society.)

The ion-pairing methylating reagent TMPA facilitated the CO_2 extraction of 2,4-D and dicamba from sediments. The presence of methyl iodide improved the recoveries of 2,4-D and 2,4,5-T from soil. Alkylation with methanol and BF_3 as a catalyst is also promising for the preferential extraction of 2,4-D over dicamba, as illustrated in **Figure 9**.

Surfactants

Nonionic surfactants (e.g. alkylphenolethoxylates) have been extracted from sediments with 27.5% methanol-modified CO_2 (450 bar and 100°C). Water-modified CO_2 (350 bar and 80°C) was also efficient in extracting nonylphenol polyethoxylates from dried sewage sludge, yielding recoveries higher than traditional techniques.

Quantitative extraction of anionic surfactants (linear alkylbenzenesulfonates) from soil, sediment and sludge can be obtained using 40% methanol-modified CO_2 (380 bar and 125°C). Also, TAA salts have been used as ion-pairing reagents to extract linear alkylbenzenesulfonates and linear alkylsulfonates from sewage sludge. Finally, derivatization of anionic surfactants into their methyl esters may also be performed to enhance their extraction.

The ditallowdimethylammonium cation was extracted from anaerobically stabilized sewage sludge and marine sediment using 30% methanol-modified CO_2 (380 bar, 100°C). No improvement could be obtained in the presence of ion pair reagents. Due to the ionic character of this surfactant, it was assumed that high concentrations of anionic surfactants initially present in the matrix allowed the formation of ion pairs with the cationic surfactant, thereby enabling its extraction.

Surfactants (e.g. alcohol phenol ethoxylate) were also extracted from aqueous samples with either direct SFE (by means of a modified extraction cell) or SPE-SFE. In the latter case, methanol-modified CO_2 was required for efficient elution from the C_{18} discs.

Metallic Compounds

Metals exist in the environment as organometallic compounds, ionic species or inorganic compounds. Organometallic compounds are usually soluble in supercritical fluids and may be extracted directly. On the other hand, ionic species require the addition of a ligand to be extracted. Consequently, speciation can be achieved by SFE using sequential extractions (with proper selection of ligands). As an example, methylmercuric chloride and dimethylmercury could be extracted with neat CO_2 and 100 bar (50°C) from solid materials; a dithiocarbamate reagent was further introduced into the matrix to extract Hg^{2+} ions.

Organometallic compounds Several studies have investigated the use of SFE for extracting organometallic compounds from environmental samples. Thus, tributyltin has been successfully extracted from sediments using methanol (20% v/v)-modified supercritical CO_2. Methanol as a modifier provided the most favourable recovery of trimethyllead, triethyllead and diethyllead from sediment and urban dust, as compared to water and acetone (446 bar and 80°C, 10% modifier).

Other approaches have been tested: binding to an organic ligand, formation of an ion pair and *in situ* derivatization. Thus, with the addition of diethylammonium diethyldithiocarbamate as a ligand, di-, tri- and tetra-substituted organotin species could be extracted from soils and sediments using 5% methanol-modified CO_2 (while recoveries of monoalkyltins remained low). Monobutyltin was efficiently extracted from a reference sediment on addition of sodium diethyldithiocarbamate in the extraction vessel (**Figure 10**); increased extraction efficiencies of trimethyllead, trimethyltin, dibutyltin and tributyltin were also observed in this way.

Hexylmagnesium bromide as a derivatizing agent assisted the CO_2 extraction of monophenyltin, diphenyltin and triphenyltin from sediment. Dimethylarsenic acid and monomethylarsenic acid could be extracted from a solid sample by supercritical CO_2 after *in situ* derivatization with thioglycolic acid methyl ester.

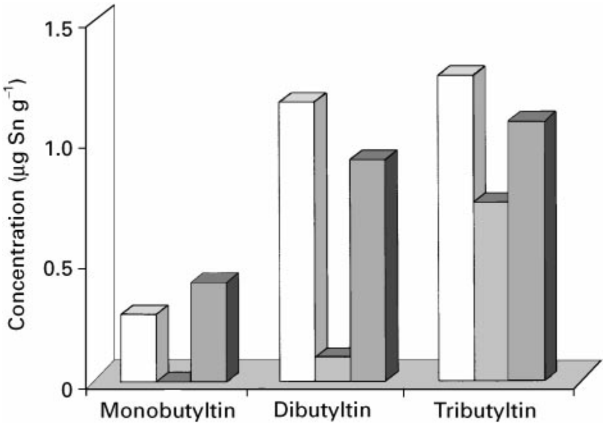

Figure 10 Comparison of extraction efficiencies of organotin compounds from a reference sediment (PACS-1) using SFE with or without the addition of sodium diethyldithiocarbamate (NaDCC). Open bars, certified value; grey bars, no NaDCC; black bars, with NaDCC. (Reproduced with permission from Chau *et al.*, 1995, and with permission from Elsevier Science.)

Organotins in aqueous matrices were ethylated with sodium tetraethylborate, enriched on C_{18} disks and further extracted with acid-modified supercritical CO_2. Alternatively, aqueous matrices containing butyl-, phenyl- and cyclohexyltin compounds were collected on a C_{18} disk, before being derivatized via Grignard ethylation and extracted using supercritical CO_2.

Metal ions Extraction of free metal ions by supercritical CO_2 requires charge neutralization. This can be achieved by binding the metal ion to organic ligands, thereby resulting in neutral stable complexes that are soluble in CO_2. Obviously, rapid complexation kinetics and a high stability constant for the neutral complex will enhance the extraction process. A key factor is the solubility of the complex in the supercritical fluid.

Different organic ligands (dithiocarbamates, β-diketones, crown ethers and organophosphorus reagents) have been tested for their ability to extract heavy metals, lanthanides and actinides from several matrices. In particular, fluorinated ligands yield metal complexes with higher solubility in supercritical CO_2, making them more effective for the extraction of metal ions. In addition, alkyl substitutions in ligands may enhance the solubility of metal complexes in CO_2. As an example, diethyldithiocarbamates and fluorinated β-diketones are effective chelating agents for extracting transition metal ions from solid matrices, as shown in **Figure 11** for Cd^{2+}. Recoveries are improved with methanol (5%)-modified CO_2, as the solubility of the metal chelate is enhanced. As dithiocarbamates tend to decompose in supercritical

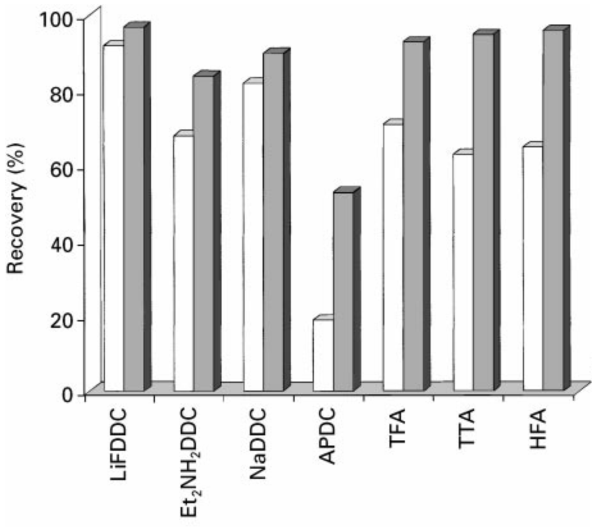

Figure 11 Recoveries of Cd^{2+} from spiked sand samples using SFE with dithiocarbamates or β-diketones as chelating agents. Open bars, CO_2; filled bars, 5% methanol-modified CO_2; 45°C, 250 bar; 15 min static/15 min dynamic. LiFDDC; bis(trifluoroethyl)dithiocarbamate; Et_2NH_2DDC; diethylammonium diethyldithiocarbamate; NaDDC; sodium diethyldithiocarbamate; APDC, ammonium pyrrolidinedithiocarbamate; TFA, trifluoroacetylacetone; TTA, thenoyltrifluoroacetone; HFA, hexafluoroacetylacetone. (Reproduced with permission from Wai *et al.*, 1996, and with permission from Elsevier Science.)

CO_2 in the presence of water, an excess of reagent is recommended to achieve good metal extraction efficiencies.

Addition of a proton-ionizable crown ether (*tert*-butyl-substituted dibenzobistriazolocrown ether) in methanol (5%)-modified CO_2 allowed the selective extraction of Hg^{2+} from sand if a small amount of water was present in the matrix (200 bar and 60°C). Other divalent metal ions (Cd^{2+}, Pb^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}) remained in the sand under these conditions.

Very recently, fluorinated hydroxamic acids have been used for the SFE of Fe(III) with unmodified CO_2. Toxic metals (As, Cd, Cr, Cu, Pb) have been extracted from real contaminated soil and wood samples using the Cyanex reagent (*bis*(2,4,4-trimethylpentyl)-monothiophosphinic acid) as an extractant in supercritical CO_2 modified with 5% methanol.

Up to the present, most of the experiments conducted have focused on spiked samples and future studies need to be conducted with real environmental samples. In such samples, the active sites and natural ligands present may bind strongly to certain metal ions, thereby hindering their complexation with added ligands. Native metals can also be in highly insoluble forms (such as oxides and sulfides), leading to a fraction of the metals that may not be extractable by SFE. It seems that SFE may be used to evaluate the amounts of leachable metals in solid matrices.

Metal ions have also been directly extracted from aqueous samples. First, the supercritical CO_2 is passed through a vessel filled with the ligand. Next, the fluid saturated with the ligand passes through the aqueous phase. For example, CO_2 containing thenoyltrifluoroacetone and tributyl phosphate

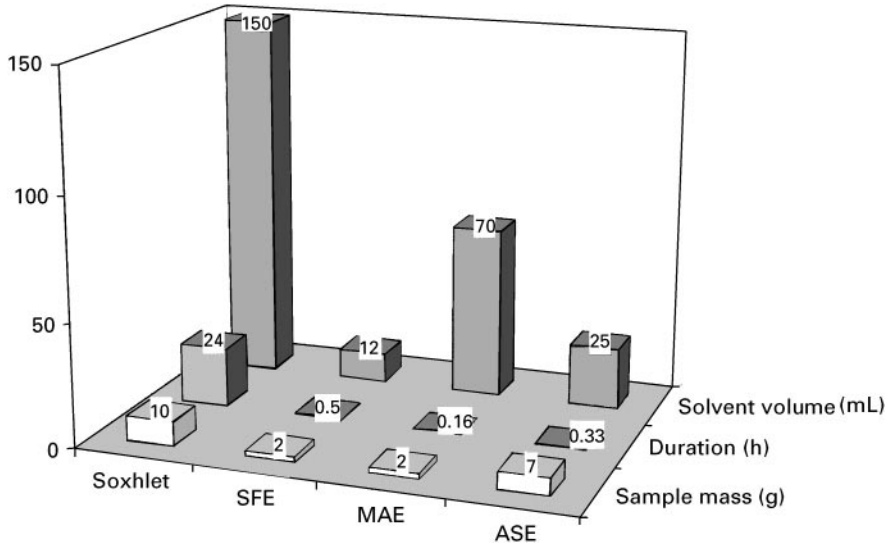

Figure 12 Comparison of extraction techniques for the determination of PAHs from contaminated soil: Soxhlet extraction (10 g sample mixed with 10 g anhydrous sodium sulfate; 150 mL dichloromethane; heating 24 h), SFE (2 g sample; 20% methanol-modified CO_2; 70°C, 250 kg cm^{-2}, 30 min), atomspheric microwave-assisted extraction (MAE) (2 g sample; 70 mL dichloromethane; heat 297 W; 20 min) and accelerated solvent extraction (ASE) (7 g sample; dichloromethane–acetone 1:1 (v/v); 100°C, 2000 psi; 10 min). (Reproduced with permission from Saim *et al.*, 1997, and with permission of Elsevier Science.)

extracted lanthanides (La^{3+}, Eu^{3+} and Lu^{3+}) from a buffered acetate solution.

Future Trends

Despite rapid growth in the past few years, SFE is still rarely used for routine applications. This is mainly because of the large number of parameters to control, as well as the influence of the matrix. The strong matrix–analyte interactions that may occur in environmental matrices frequently make the development of quantitative extraction conditions based solely on solubility considerations and spike recoveries invalid for real samples. In addition, its development is also limited by the high capital cost required.

Yet SFE has several advantages over other techniques (especially rapidity and low solvent volumes, as shown in **Figure 12**). It is successful in extracting a broad range of pollutants from numerous matrices. In particular, polar compounds and ionic species can be extracted through addition of a polar modifier, a derivatization reagent, an ion-pairing reagent or a ligand. These recent applications will be more thoroughly studied in the next few years, especially the possible speciation, due to selective extraction, of metallic compounds.

Subcritical water appears to be a very promising fluid, as it offers the opportunity to extract polar to nonpolar compounds by simply increasing the temperature. No doubt this fluid will be more common in future SFE applications.

Finally, extraction conditions will be optimized for numerous real environmental samples, including certified reference materials, thereby leading to wider use of this technique.

See also: **II/Chromatography: Gas:** Derivatization. **Chromatography: Liquid:** Ion Pair Liquid Chromatography; Mechanisms: Ion Chromatography. **Extraction:** Solid-Phase Extraction; Solvent Based Separation. **III/Metal Complexes:** Ion Chromatography.

Further Reading

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