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Review

Analytical-scale supercritical fluid extraction: a promising technique for the determination of pollutants in environmental matrices

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ABSTRACT

Analytical-scale supercritical fluid extraction (SFE) has become of increasing interest in the last few years because of its efficiency and rapidity concerning the extraction of organic compounds prior to separation and detection by chromatographic techniques. SFE has several advantages over classical solvent extractions such as faster analysis, better selectivity, higher efficiency and the absence of toxic solvent waste, which reduces safety hazards. This paper describes the principles of SFE and its coupling with chromatographic techniques; numerous environmental applications are also reported.

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1. INTRODUCTION

Sample preparation methods generally used by analytical chemists are both time and solvent consuming. According to a recent survey, two thirds of the analysis time are devoted to sample preparation and this step accounts for at least one third of the error generated during the performance of an analytical method [1]. The improvement and automation of sample preparation will therefore lead to a reduction in analysis time and to a greater precision of results.

Recent concern about the hazards associated with most of the solvents used, and the costs and environmental dangers of waste solvent disposal, have led to the development of alternative sample extraction methods such as solid-phase extraction (SPE) and supercritical fluid extraction (SFE). Un-

til recently, SFE has been used mainly for large-scale processing applications (*e.g.*, decaffeinization of coffee) [2]; but for several years the use of SFE methods for analytical applications has attracted considerable interest. The potential advantages of this technique come from the unique properties of supercritical fluids.

2. SUPERCRITICAL FLUID PROPERTIES

A fluid is said to be in its supercritical state when both its temperature and pressure are above their critical values. If only one of these two parameters fulfils this condition, it is said to be in its subcritical state.

Supercritical fluids possess unique physico-chemical properties which make them attractive as extraction solvents (Table 1 [3]). Concerning kinetics,

TABLE 1

APPROXIMATE VALUES OF DENSITIES, VISCOSITIES AND DIFFUSION COEFFICIENTS OF GASES, SUPERCRITICAL FLUIDS AND LIQUIDS

From ref. 3.

Fluid	Density $(g\ cm^{-3})$	Viscosity (Pa s)	Diffusion coefficient $(cm^2\ s^{-1})$
Gas	$(0.6–2) \cdot 10^{-3}$	$(1–3) \cdot 10^{-5}$	$0.1–1.0$
Supercritical fluid	$0.2–0.9$	$(1–3) \cdot 10^{-4}$	$(0.1–5) \cdot 10^{-4}$
Liquid	$0.6–1.6$	$(0.2–3) \cdot 10^{-3}$	$(0.2–3)) \cdot 10^{-5}$

their viscosity is 5–20 times lower than that of ordinary liquids: the diffusion coefficients of solutes are consequently greater. This clearly provides a means for faster and more efficient extractions compared with classical liquid phases, owing to a more rapid and more complete penetration of solid matrices.

From a thermodynamic point of view, supercritical fluids have densities 100–1000 times greater than those of gases, which gives them a solvating power closer to that of liquids. In additon, their density is closely related to the pressure and, to a lesser extent, the temperature (Fig. 1) [4]. As the solvent strength of a supercritical fluid is directly related to its density (it can be described by the empirical correlation $\delta = 1.25P_c^{1/2}(\rho_g/\rho_l)$, where δ is the Hildebrand solubility parameter, P_c is the critical pressure of the fluid, ρ_g is the density of the supercritical fluid, and ρ_l is the density of the fluid in its liquid state), the solvating ability of a supercritical fluid toward a species can easily be modified by changing the extraction pressure and/or the temperature. That allows the adjustment of a large scale of density values and the selective extraction of compounds by varying the extraction pressure. For example, supercritical carbon dioxide can selectively extract alkanes and polyaromatic compounds from diesel exhaust particulates [5]: at 45°C and 75 atm, 85% of the alkanes were removed from the particulates after 5 min (with these operating conditions polyaromatic compounds were not extracted), whereas 300 atm and 90 min were needed to extract 90% of the polyaromatic compounds.

By far the most widely used extraction fluid has been supercritical CO_2. Its preferential use is due to the fact that it is chemically inert, inexpensive, non-toxic, non-flammable and has an easily accessible critical point at 31.1°C and 72.8 bar with a density of 0.468 g ml^{-1}; its low critical temperature allows extraction to be performed under mild thermal conditions. Carbon dioxide is also available in pure form [6,7] and, if desired, can be purified further. In addition, supercritical CO_2 vaporizes on reaching the atmosphere, thereby enabling extracted solutes to be easily isolated for further analysis and/or the direct coupling to analytical techniques such as gas chromatography (SFE–GC), high-performance liquid chromatography (SFE–HPLC) and supercritical fluid chromatography (SFE–SFC).

However, many other supercritical fluids have been used e.g., N_2O, SF_6, CH_3OH, H_2O and $CHClF_2$ (Freon-22). Some of them may be useful for extracting specific compounds (e.g., N_2O has been found to be more efficient than CO_2 for the extraction of amines from contaminated soils (see Fig. 2) [8].

3. CHOICE OF OPERATING CONDITIONS

Supercritical fluid extraction is carried out by placing the sample in contact with a static supercritical fluid in a closed container ("static" mode) or by percolating a supercritical fluid through the sample ("dynamic" mode) [9]. The static mode allows a better penetration of the matrix by the fluid [10], but the latter method permits saturation of the extraction fluid to be avoided, leading to better recoveries and shorter extraction times. Thus, in most instances, extractions combine these two modes: a short period of time is allowed for static equilibration, before enabling the sample to be dynamically extracted [11].
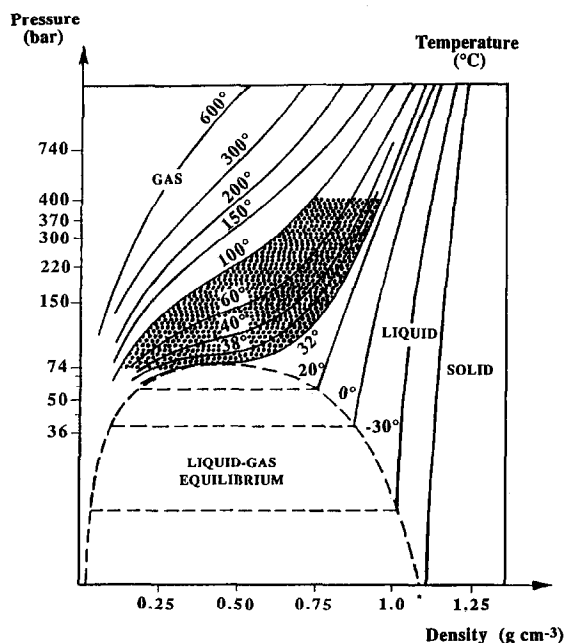
Once extracted from the matrix, the solute of in-

Fig. 1. Pressure–density diagram (P, ρ) for carbon dioxide. The shaded area corresponds to the experimental domain of supercritical phase extraction and chromatography. From ref. 4.
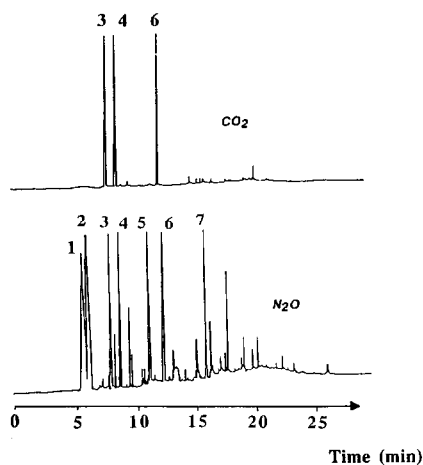
Fig. 2. Supercritical fluid extraction and on-line analysis by gas chromatography of amines from spiked soil using supercritical N_2O and CO_2 for extraction. Peaks: 1 = heptylamine; 2 = N-methylheptylamine; 3 = 2-ethylaniline; 4 = tributylamine; 5 = dodecylamine; 6 = diphenylamine; 7 = octadecylamine. Extraction conditions: 400 bar, 60°C, 20 min static followed by 20 min dynamic (130 μl min^{-1} of compressed fluid through the cell). Chromatographic conditions: HP-1 cross-linked methylsilicone capillary column (20 m × 0,32 mm I.D.); column temperature, 0°C during the extraction, then increased to 300°C at 15°C min^{-1} and held at 300°C for 10 min; flame ionization detection. From ref. 8.

terest needs to be trapped prior to analysis. The success of SFE depends on these two independent steps.

3.1. Optimization of extraction conditions

The two basic parameters in SFE are the extraction recovery (the proportion of the amount of solute extracted with respect to its initial amount, usually expressed as a mass percentage) and the extraction rate (extraction recovery per unit time at a given velocity of the supercritical fluid through the cell), the latter decreasing exponentially with time.

The realization of the extraction of a specified solute from a matrix necessitates the optimization of several parameters, mainly the pressure, temperature, the possible addition of an organic modifier to the fluid and flow-rate.

3.1.1. Influence of pressure

Four parameters are extremely helpful in the understanding of solute behaviour in supercritical

media, and thus in executing successful analytical supercritical fluid extractions [12,13]: (i) the miscibility or threshold pressure [14,15], which corresponds to the pressure at which the solute partitions into the supercritical fluid; (ii) the pressure at which the solute reaches its maximum solubility; (iii) the fractionation pressure range, which is the pressure region between the miscibility and solubility maximum pressures (in this interval it is possible to extract selectively one solute by choosing the correct pressure); and (iv) a knowledge of the physical properties of the solute, particularly its melting point (in fact most solutes dissolve better when they are in their liquid state, *i.e.*, above their melting point).

To illustrate the difference between the threshold pressure and the solubility maximum pressure, the solubility–pressure curve of naphthalene is given in Fig. 3 [13]: this solute is slightly soluble in CO_2 at 75 bar (threshold pressure); as the pressure increases the solubility rises, especially around 90 bar, up to its maximum value.

The fluid pressure is the main parameter that influences the extraction recovery. An elevation of this pressure at a given temperature results in an increase in the fluid density (Fig. 1), which means a better solubility of the solutes. Consequently, the
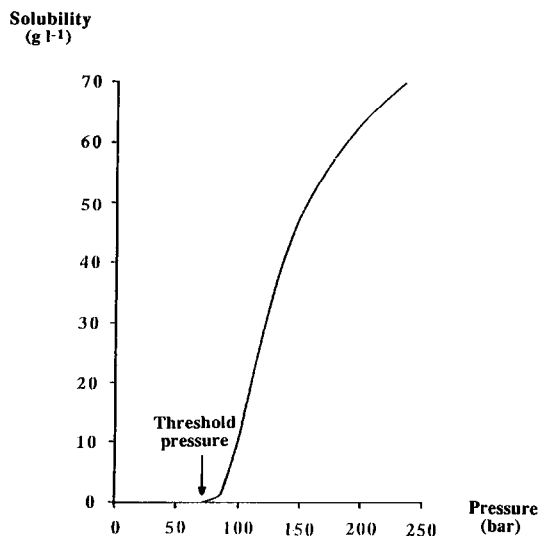

Fig. 3. Variation of the solubility of naphthalene with the pressure of supercritical CO_2 at 45°C. From ref. 13.

higher the extraction pressure, the smaller is the volume of fluid necessary for a given extraction; for example, one needs to double the volume of CO_2 in order to extract 70% of diuron herbicide from a contaminated soil when working at 110 bar instead of 338 bar (Fig. 4) [16]. However, high pressure is not always recommended for complex matrices owing to the higher solubility of solutes when the pressure is elevated; thus the extract can become very complex and, consequently, its analysis becomes very difficult. On the other hand, it must be borne in mind that the presence of co-extracted solutes can dramatically change the solubility level of the solute of interest.

3.1.2. Influence of temperature

At a constant pressure the density of CO_2 decreases when the temperature rises. This effect becomes more pronounced as the compressibility increases, as shown in Fig. 1. The temperature also affects the volatility of the solute. Hence the effect of a temperature elevation is difficult to predict because of its dependence on the nature of the sample. For a non-volatile solute, a higher temperature would result in lower extraction recovery owing to a decrease in solubility; thus the distribution coefficient of phenol between water and supercritical CO_2 decreases when the fluid temperature rises from 25 to 30°C [17]. On the other hand, for a volatile solute, there is a competition between its solu-

bility in CO_2 (which decreases as the temperature increases) and its volatility (which rises with increasing temperature). For example, when the temperature increases from 80 to 120°C, the extraction recovery of diuron from soil with methanol-modified CO_2 is enhanced from 75% to 99% [9].

3.1.3. Addition of a modifier

The low polarity of CO_2 limits its use to the extraction of relatively apolar or moderately polar solutes. Thus, a small amount of a polar organic solvent (methanol, acetonitrile, water, etc.), called a "modifier" or "entrainer", is usually added to the supercritical fluid for the extraction of more polar solutes. The nature of the modifier depends on the nature of the solute to be extracted [18]; for example, the extraction of diuron is greatly enhanced with methanol instead of acetonitrile as a modifier, probably because of hydrogen bonding which could exist between diuron and methanol [16]. A reasonable starting point consists of selecting a modifier that is a good solvent in its liquid state for the target analyte.

It should be noted that the addition of large amounts of modifier will considerably change the critical parameters of the mixture [19,20], as shown in Fig. 5 for methanol–carbon dioxide mixtures [19]. As a result, binary mixtures of carbon dioxide and an organic solvent are often used in a subcritical state, where the diffusion coefficients are smaller than in a supercritical state.

Modifiers can be introduced as mixed fluids in the pumping system with a second pump and a mixing chamber [21], or by simply injecting the modifier as a liquid into the sample before extraction [9,22] (the latter way being less successful because it leads to concentration gradients within the matrix). Alternatively, one may use directly a cylinder tank of modified CO_2, but this is much more expensive; besides, as the tank gets empty, the content of modifier tends to increase.

Fig. 4. Variation of the extraction yield of diuron from a polluted soil with the volume of CO_2 percolated at different pressures: ● = 110; ■ = 235; ◆ = 338 bar. Extraction conditions: extractant, CO_2–CH_3CN (90:10, v/v); extraction cell, 25 cm × 4.6 mm I.D.; temperature, 100°C; flow-rate of liquid CO_2, 16.5 ml min^{-1}. From ref. 16.

3.1.4. Influence of fluid velocity

The speed of the supercritical fluid flowing through the cell has a strong influence on the extraction efficiencies. The slower the fluid speed, the deeper it penetrates the matrix. The fluid speed can be expressed by the linear velocity, which is strongly dependent on the flow-rate and the cell geometry.
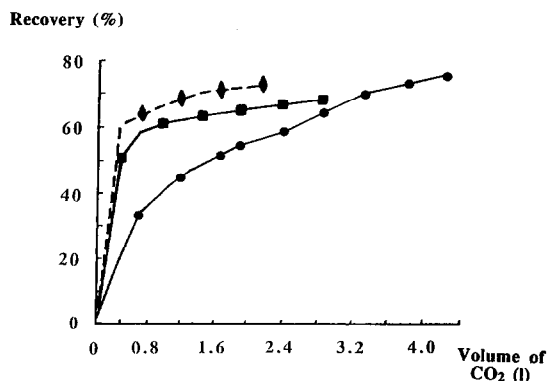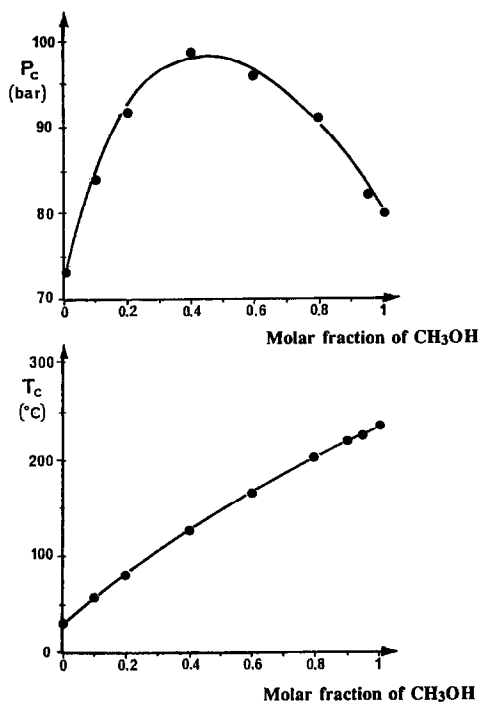
Fig. 5. Variations of the critical pressure and temperature of CO_2–CH_3OH mixtures with the molar fraction of methanol. From ref. 19.

3.1.4.1. Influence of flow-rate. For a given extraction cell, the flow-rate can be easily changed by using a new restrictor with a different inside diameter. Decreasing the flow-rate results in a lower linear velocity and usually in increased extraction recoveries (as a result of an extended contact between the supercritical fluid and the sample); for example ^{14}C-labelled linear alkylbenzenesulphonates were better extracted by supercritical CO_2 modified with methanol (40 mol%) (at 380 bar and 125°C) from a sludge-amended soil with a liquid CO_2 flow-rate of 0.45 ml min^{-1} (mean recovery 90.8 ± 1.3%) instead of 1.2 ml min^{-1} (mean recovery 75.6 ± 1.1%), the same volume of fluid being used in each instance [23]. However, this entails longer extraction times. On the other hand, high flow-rates can result in a decrease in the recovery either by inducing an elevated pressure drop through the extraction cell {this phenomenon probably occurred during the extraction of diuron from a contaminated soil with a CO_2–methanol mixture (90:10, v/v) [16]}, or by increasing analyte loss during decompression

of the fluid. Thus an optimum flow-rate has to be found. Typical values range around 1 ml min^{-1} of compressed fluid (with extraction cells of I.D. *ca.* 1 cm), which corresponds to *ca.* 500 ml min^{-1} of gas after decompression.

3.1.4.2. Influence of cell geometry. For a given flow-rate, the fluid linear velocity can be changed by using several cells having the same volume but different inside diameters. Higher extraction efficiencies are expected with short, broad cells because the fluid linear velocity decreases as the cell diameter increases.

This has been observed during the extraction of polychlorinated biphenyls (PCBs), spiked onto octadecylsilane (C_{18}) sorbents, by supercritical CO_2 at 60°C and 140 bar (density 0.549 g ml^{-1}), with a flow-rate of 0.075 ml min^{-1} and a total fluid volume of 1.5 ml [24]. Two different cells containing 0.510 g of the standard packing were investigated in this study: a long, narrow cell with dimensions 4.4 × 50.0 mm (I.D. × length of bed) having a 1:11 diameter to length ratio, and a short, broad cell with dimensions 9.9 × 9.9 mm (I.D. × length of bed) having a 1:1 diameter to length ratio. Changing the cell geometry from 1:11 to 1:1 resulted in an average relative increase in the extraction recovery of nearly 50%; in addition, the recoveries decrease with increasing chlorine content, which correlates with chromatographic data obtained employing similar sorbents.

Similar results have been obtained for polycyclic aromatic hydrocarbons (PAHs) from a C_{18} sorbent using two different cells containing a 0.8-ml sorbent bed [a long, narrow cell with dimensions 0.37 × 7.3 cm (I.D. × length of bed) having a 1:20 diameter to length ratio, and a short, broad cell with dimensions 1.0 × 1.0 cm (I.D. × length of bed) having a 1:1 diameter to length ratio] [25–27]. Using supercritical CO_2 at 100°C and 315 bar (density 0.675 g/ml), with a flow-rate of 0.6 ml min^{-1} and a total fluid volume of 7.5 ml, the average recoveries ± standard deviations for the analytes pyrene, perylene, benzo[*ghi*]perylene and coronene using the 1:20 cell were 60.4 ± 0.9, 17.1 ± 0.6, 6.5 ± 0.7 and 1.7 ± 0.2%, respectively. With the 1:1 cell they were 80.4 ± 1.6, 35.8 ± 0.8, 15.4 ± 1.4 and 5.2 ± 0.3%, respectively [25–27].

On the other hand, neither the extraction cell dimensions nor the chlorine content had any signif-

icant effect on the recoveries of PCBs from the common adsorbent Florisil [24]. Considering the extraction by supercritical CO_2 of native PAH from railroad bed soil, neither the flow-rate nor the cell geometry had a significant influence on the extraction efficiency [28]. These results show the importance of the matrix effect in SFE; an adsorbent matrix such as Florisil behaves similarly to soil matrices because the analyte–matrix interactions are the same (solutes are primarily adsorbed on the surface or within the pores of the solid material).

In some particular instances, the extraction recovery can also be improved by decreasing the extraction cell diameter (i.e., by increasing the linear velocity). This result can be explained by a better mass transfer within the cell due to an increase in turbulence in the fluid flow pattern inside the extraction cell. As an example, larger peak areas have been obtained for n-octadecane and n-eicosane using a 4 mm I.D. cell ($610 \cdot 10^3$ and $202 \cdot 10^3$ counts, respectively) instead of a 6 mm I.D. cell ($478 \cdot 10^3$ and $140 \cdot 10^3$ counts, respectively) [13].

3.1.5. Influence of the nature of the matrix

Factors such as the particle size, shape, surface area, porosity, moisture, level of extractable solutes and the nature of the matrix will affect the analytical results and are considered later. In the same way the interactions between solutes and active sites of the matrix can necessitate strict extraction conditions.

3.2. Efficiency of the solute trapping system

Once the compounds of interest are in the supercritical extraction fluid, the next step is to isolate them for further analyses. Generally, this is accomplished by decompression of the fluid through a restrictor (often heated to prevent the formation of pieces of ice that could plug the restrictor). Trapping becomes more difficult when either the solute is more volatile or the flow-rate is higher. The collection technique therefore needs to be efficient.

Most often, SFE is coupled to chromatographic techniques, either "off-line" or "on-line" [29]. The former coupling is much simpler to perform and gives an extract available for other analyses, whereas the latter provides the means to achieve maximum accuracy and sensitivity and to minimize losses.

3.2.1. Trapping systems for off-line SFE

Two different methods are commonly used for collecting the extract on depressurization of the CO_2, using a liquid trap or a solid surface.

With a liquid trap, the restrictor is simply placed in a vial containing a suitable liquid. The analyte is gradually dissolved in the solvent while the CO_2 is being discharged to the atmosphere. Sometimes the large volume of gas on decompression results in violent bubbling of the solvent, thus leading to analyte losses.

In the solid surface method, the extracted analytes are trapped on a solid surface (glass vials, stainless-steel beads or glass beads) cryogenically cooled either by the expanding supercritical fluid or by another source (CO_2 or liquid N_2); they are then rinsed from the surface for further analysis. In some instances, the trapping may involve a solid-phase sorbent (usually chromatographic packing material): after being cryogenically and chemically trapped, the solutes are eluted from the sorbent with a small volume of solvent. The latter system provides two trapping mechanisms: cryogenic trapping and adsorption; hence it presents the inconvenience of giving relatively slow desorption rates for some polar solutes from adsorptive materials [30].

3.2.2. Systems for coupling SFE on-line to chromatographic techniques

Very often SFE is coupled to gas chromatography (SFE–GC) or supercritical fluid chromatography (SFE–SFC) [29,31]. The success of such on-line couplings depends on the efficiency of the extract collection and of the quantitative transfer inside the chromatographic column within a narrow band (otherwise it would affect the chromatographic performances). Several interfaces have been tested.

For on-line SFE–capillary GC, the simplest method involves and on-column injector: the restrictor is inserted directly into the GC column through the injector [5,32–36]. This gives the best sensitivity with diluted samples. For concentrated or larger sized samples, the supercritical fluid is depressurized into a conventional split–splitless injection port, via a heated transfer line [8,37–40]. Other interfaces have been used: a T-piece between the restrictor and the column (with possibly a short retention gap) [41,42], a thermodesorption–cold trap injection system [43], a programmed-temperature

vaporizer injector [44,45] and a six-port valve [46–48].

SFE has also been coupled with both capillary and packed-column SFC (SFE–CSFC and SFE–PSFC).

With capillary columns, the simplest method involves an injector loop: part of the extract is injected directly into the column [9,49]. This enables the precipitation of the solutes or other related problems to be avoided. Other interfaces usually require a preconcentration of the analytes after depressurization of the supercritical fluid. This is carried out in an injector loop [50,51], either in a cryogenically cooled capillary [52,53] or in a column [54].

With packed columns, the injector loop has been successfully used, as it allows part of or all the extract to be injected into the column [55–58]. Other methods require a preconcentration step which is carried out in the chromatographic column itself [59], in a precolumn [60,61] or in a cryogenic trap [62,63].

4. ENVIRONMENTAL MATRICES EXTRACTED BY SFE

SFE has been applied to a broad range of environmental samples. The efficiency of this technique depends both on the nature of the solute to be extracted an on the characteristics of the matrix. Several pollutants have been successfully extracted using this technique, including PAHs, PCBs, dioxins, furans, phenols, pesticides and herbicides [64].

Polar solutes generally require modified carbon dioxide as the extractant. In some instances they can be derivatized *in situ* by the addition of a reagent directly to the sample matrix prior to extraction [65–67].

Although SFE is best suited for solids, other matrices (air samples and liquids) have also been investigated.

4.1. Air samples

Classical methods for the identification and determination of organic compounds from fumes involve two independent steps. Pollutants are first trapped on a solid-phase sorbent; then they are either thermally desorbed and analysed by GC, or eluted with a suitable liquid solvent before their sep-

aration by HPLC. Both methods may result in incorrect quantification: thermal desorption can entail the decomposition of thermally unstable volatile solutes, whereas solvent elution produces a dilute sample which hinders the determination of trace components. SFE has been applied as an alternative in order to overcome these problems.

Few studies have shown the efficiency of supercritical fluids in extracting compounds with different volatility from solid-phase sorbents [68–71]. These supports provide an easy way to collect volatile toxicants presents in gases before desorbing them by SFE for further analysis. Several samples have been successfully extracted following this procedure; some examples are presented in Table 2. Fig. 6 illustrates the on-line SFE–GC analysis (with flame ionization detection) of hardwood smoke phenolics collected from a residential chimney on a polyurethane foam sorbent plug (identification of individual species was based on a SFE–GC–mass spectrometric (MS) analysis of a replicate sample); quantitative recovery was obtained after a 10-min extraction with supercritical CO_2 at 300 bar and 45°C and a cryogenic trapping temperature of -30°C [35].

4.2. Liquids

The SFE of solutes in liquid samples has been confronted with technological complications related to the insulation of the matrix itself and the CO_2–liquid miscibility, like the design of a special extraction cell [74–76]. As a consequence, only a few studies have dealt with the direct SFE of liquids (Table 3). Most of the time liquid samples are first adsorbed on a solid material before being extracted by the supercritical fluid (Table 4). For example, Fig. 7 shows the chromatogram obtained after on-line SFE–GC (flame ionization detection) of a polyurethane foam sorbent resin that had been soaked in a coal gasification wastewater [37].

4.3. Solids

The properties of supercritical fluids make them very useful for the rapid and quantitative extraction of organic pollutants from environmental solids. In addition to solubility considerations, several characteristics exert a powerful influence and need to be taken into account.

TABLE 2

EXAMPLES OF SUPERCRITICAL FLUID EXTRACTIONS OF FUMES COLLECTED ON DIFFERENT SOLID-PHASE SORBENTS

| Air samples collected on different adsorbents	Extracted solutes	Super- or subcritical fluid or fluid mixture	Off-line coupling		On-line coupling			Ref.
			Collection	Analysis	GC	CSFC	PSFC	
Polyurethane foam								
Urban air	Alkanes and aromatic hydrocarbons	CO_2			*			35
Diesel exhaust	Alkanes and PAHs	CO_2	Solvent	GC	*			36, 72
Roofing tar volatiles	Alkanes, benzenes, PAHs, phenols, S-heterocyclic compounds	CO_2			*			36, 72
Polyimide 109								
Air of a laboratory building	Organic compounds	CO_2	Adsorption	GC				73
Tenax								
Vehicle exhaust	Alkanes, benzenes, PAHs, oxy-PAHs	CO_2			*			5, 36
Glass-fibre filter								
Diesel exhaust	PAHs	CO_2	Solvent	GC				5
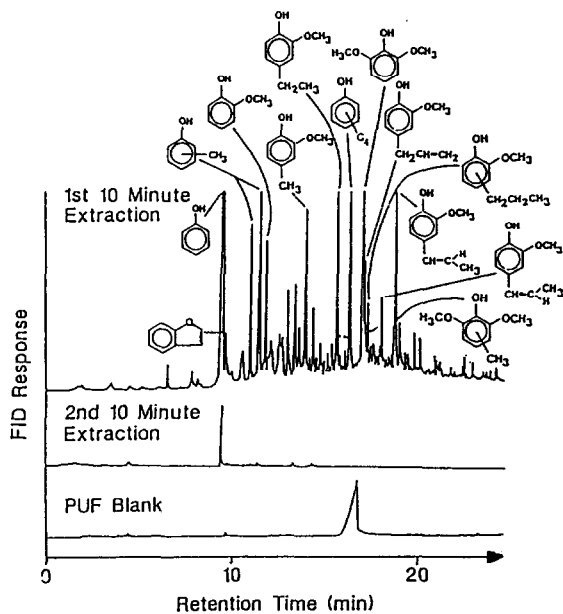
Fig. 6. Supercritical fluid extraction and on-line analysis by gas chromatography of hardwood smoke phenolics collected from a residential chimney on a polyurethane foam (PUF) sorbent plug. Extraction conditons: CO_2, 400 bar, 45°C, 10 min, on-column deposition at -30°C. Chromatographic conditions: DB-5 fused-silica capillary column (30 m × 0.32 mm I.D.) (1 μm film thickness); column temperature, -30°C during the extraction, before being rapidly elevated to 30°C at 30°C min^{-1}, then to 320°C at 8°C min^{-1}; carrier gas, hydrogen; flame ionization detection. Identification of individual species was based on the SFE and on-line analysis by GC–MS of a replicate sample. From ref. 35.

4.3.1. Influence of physical nature of the matrix

Very often, grinding solid samples before use enhances extraction due to an increase in the surface area exposed to the supercritical fluid and thereby allowing better diffusion of the solute out of the sample matrix. Nevertheless, precautions must be taken in order to avoid large pressure drops in the extraction cell due to sample compaction (thus, fine grinding of the matrix is not recommended) and plugging (very often the addition of either small pieces of filter-paper or glass-wool or layers of glass beads at both ends of the cell prevents particles from being swept out).

4.3.2. Influence of chemical nature of the matrix

Extraction of an analyte depends on its distribution between the supercritical fluid and the sorptive sites of the sample matrix. The recovery rate is therefore a function of both the chemical nature of the solute and of the matrix itself. A solid with numerous active sites will highly adsorb polar solutes, resulting in a poor extraction rate. For example, the recovery of explosive from soil samples decreases when the organic content of the soil increases [52]. Some matrices are particularly difficult to extract (fly ash probably being one of the best known [80]).

The presence of organics inside the material can also affect the extraction as they could be more eas-

TABLE 3

EXAMPLES OF SUPERCRITICAL FLUID EXTRACTIONS OF LIQUIDS

Liquid matrix	Extracted solutes	Super- or subcritical fluid or fluid mixture	Off-line coupling		On-line coupling			Ref.
			Collection	Analysis	GC	CSFC	PSFC	
Standard in carbon disulphide or methylene chloride	Alkanes	CO_2					*	62
Contaminated water	Phenol	CO_2, CO_2–CH_3OH	Solvent	GC				17, 66
Municipal waste water treatment	Linear alkylbenzenesulphonates	CO_2, CO_2–CH_3OH, N_2O	Solvent	HPLC				77
Aqueous media	N-containing bases	CO_2	Adsorption	GC, HPLC			*	74, 76
	Phosphonate	CO_2					*	74
Viscous engine oil	Phenol	CO_2	Solvent, adsorption	HPLC			*	75
	Aromatics	CO_2					*	57

TABLE 4

EXAMPLES OF SUPERCRITICAL FLUID EXTRACTIONS OF LIQUIDS COLLECTED ON DIFFERENT SOLID-PHASE SORBENTS

Liquids adsorbed on different sorbents	Extracted solutes	Super- or subcritical fluid or fluid mixture	Off-line coupling		On-line coupling			Ref.
			Collection	Analysis	GC	CSFC	PSFC	
Polyurethane foam								
Coal gasification wastewater	Phenolics and N-containing aromatics	CO_2			*			37
Tenax								
Standard in acetone	PCBs	CO_2			*			43
Glass-wool								
Standard in methanol	Pesticides	CO_2	Adsorption	HPLC				78
Glass beads								
Standard in methylene chloride	PAHs, pesticides	CO_2	Solvent	GC				79
Mixture of a coal tar and a coal liquid	PAHs	CO_2			*			41
Alumina beads								
Standard in carbon disulphide	Alkanes, aromatics	CO_2, N_2O, SF_6			*			38, 39
Standard	*n*-Alkanes	CO_2			*			40
Octadecyl-bonded silica								
Standard in chloroform	PAHs, pesticides	CO_2	Solvent	GC				25–27
Standard in cyclohexane	*n*-Alkanes, nicotine, dicyclohexylamine	CO_2–C_2H_5OH			*			44

ily extracted than the solute of interest and/or plug the restrictor. This was evidenced during the extraction of PAHs from a reference sample (marine sediment SRM 1941) containing 2% (w/w) of elemental sulphur: the deposition of elemental sulphur as S_8 plugged the restrictor [19].

4.3.3. Influence of moisture

Depending on the nature of the solute, the presence of water affects the extraction efficiency. For example, the removal of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin from a wet spiked sediment [19.8% (w/w) water content] by modified carbon dioxide (containing 2% of methanol) requires twice the time for achieving the same extraction recovery compared with a dry spiked sediment [0.3% (w/w) water content] [81]. Similar results have been obtained during the carbon dioxide extraction of PAHs from petroleum waste sludge [82]. Water usually hinders the extraction of apolar compounds by sheathing the

surface of the matrix and acting as a barrier to CO_2 penetration. This assumption is supported by the recent comparison between $CHClF_2$ (Freon-22) and CO_2 used as a supercritical fluid for the extraction of PAHs from petroleum waste sludge: $CHClF_2$ removes much more water from the sample than CO_2, thus increasing the amount of analytes exposed to the supercritical fluid and thereby leading to higher extraction efficiencies [82].

In contrast, water helps to bring polar compounds into solution owing to competition for active matrix sites.

Moisture also exerts an influence on the action of a modifier as illustrated in Table 5 [83]: methanol facilitates the extraction of phenol from a dry soil sample owing to an increase in the polarity of the supercritical fluid mixture (hydrogen bondings occur between phenol and methanol); however, this organic solvent has no effect when a wetted soil is considered, probably as a result of dissolution of
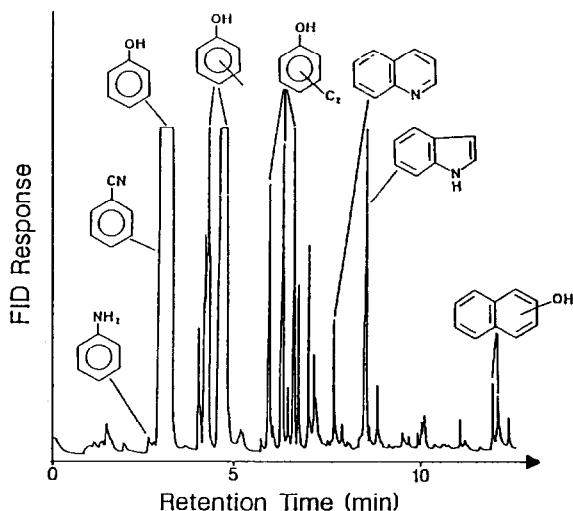
Fig. 7. Supercritical fluid extraction and on-line analysis by gas chromatography of coal gasification wastewater impregnated on polyurethane foam sorbent. Extraction conditons: CO_2, 300 bar, 45°C, 10 min, on-column deposition at 10°C. Chromatographic conditions: DB-5 fused-silica capillary column (30 m × 0.32 mm I.D.) (1 μm film thickness); column temperature, 10°C during the extraction, then rapidly increased to 70°C and subsequently to 320°C at 8°C min^{-1}; carrier gas, hydrogen; splitting ratio, 1:50; flame ionization detection. Identifications were based on the SFE and on-line analysis by GC–MS of a duplicate sample. From ref. 37.

TABLE 5

INFLUENCE OF POLAR MODIFIER ADDITION (2 mol%) TO SUPERCRITICAL CO_2 ON THE DISTRIBUTION COEFFICIENT OF PHENOL

Extraction conditions: extraction cell, 300 ml; initial mass, 100 g + 1% (w/w) phenol; pressure, 150 bar; temperature, 25°C; extraction time, 60 min (static); extractant: CO_2, CO_2–benzene or CO_2–CH_3OH (reprinted from ref. 83).

Nature of supercritical fluid	Distribution coefficient of phenol	
	Dry soil	Wetted soil
CO_2	0.35	0.35
CO_2 + benzene (2 mol%)	0.8	>7
CO_2 + methanol (2 mol%)	>7	0.35

methanol in the water contained in the soil, so the supercritical phase polarity is no longer increased. In contrast, as benzene is virtually insoluble in water, it favours the supercritical phase over the wetted soil phase; hence almost all the phenol can be extracted from the wetted soil owing to π–π interactions between benzene and phenol.

4.3.4. Influence of contamination

The way in which analytes are incorporated within the matrix is of prime importance. The longer a solute stays in a solid, the better it will diffuse through its pores and react with the eventual active sites contained in it. Spiked solute often resides superficially in the matrix, and it is therefore extracted more easily by the supercritical fluid; besides, if the spiking solvent is not removed before extraction (to minimize the loss of volatiles) it could act as a modifier and affect the extraction conditions [84].

In real contaminated samples, chemical reactions

may also take place between the solute and other organic materials or active sites of the matrix, resulting in other pollutants that could be more difficult to extract. For example, parathion (an organophosphate pesticide) tends to form toxic products such as 4-nitrophenol, aminoparathion and diethyl thiophosphate [85]. In addition, some solutes may be hardly extracted from real contaminated samples because of associations between the solute molecule and matrix components; thus pesticides often lead to unextractable or "bound" pesticide residues in plant matrices and soils.

To optimize the SFE conditions for a specific sample, an analytical chemist needs to follow logically ordered steps [10]. Very often, standard solutions of the analytes must be first deposited on a non-sorptive matrix such as filter-paper, sand or deactivated glass beads. As there is no solute–matrix interaction in that case, this step provides the analyst with the minimal extraction conditions before extracting the solutes from more difficult matrices. For example, Fig. 8 shows the chromatogram obtained after the on-line SFE–GC of deactivated glass beads (45–150 μm I.D.) spiked with a small amount (0.5 ppm) of PAH compounds [41]. The extraction was conducted for 2 min with CO_2 at 50°C and 250 bar (density 0.83 g ml^{-1}). All the solutes were quantitatively recovered, except naphthalene (its high volatility probably entailed losses during sample preparation).

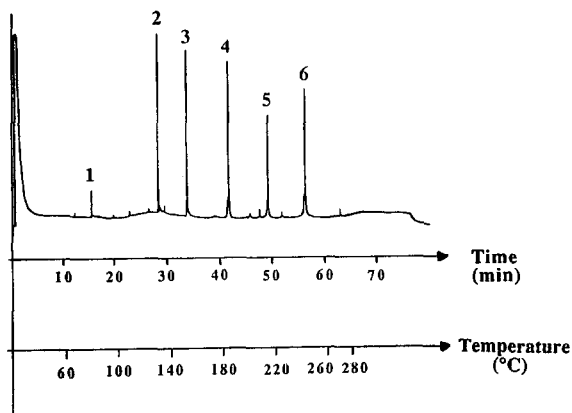Matrix effects can then be studied by performing

Fig. 8. Supercritical fluid extraction and on-line analysis by gas chromatography of PAHs deposited on deactivated glass beads (45–150 μm diameter) at a low level (0.5 ppm). Peaks: 1 = naphthalene; 2 = fluorene; 3 = phenanthrene; 4 = pyrene; 5 = chrysene; 6 = benzo[e]pyrene. Extraction conditions: CO_2, 250 bar, 50°C, 2 min, on-column deposition. Chromatographic conditions: SE-54 fused silica-capillary column (15 m × 0.25 mm I.D.) (0.25 μm film thickness) with a short retention gap of deactivated fused-silica tubing (30 cm × 0.53 mm I.D.); column temperature, increased from 30 to 280°C at 4°C min⁻¹; carrier gas, helium (linear velocity ca. 40 cm s⁻¹); flame ionization detection. From ref. 41.

SFE on a simulated or spiked sample. The actual sample should be the last to be extracted as the extraction conditions in real samples are more severe than in spiked samples.

SFE has been successfully applied to numerous environmental matrices. Some of these applications are summarized in Table 6.

For example, several chemical warfare agent simulants have been extracted from a spiked soil with supercritical CO_2 modified with methanol (5%); these are dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate (DIMP), diisopropyl fluorophosphate (DIFP) and chloroethyl ethyl sulphide (CES). DMMP is the simulant for O-ethyl-S-2-(diisopropylaminoethyl methylphosphonothioate) (VX), DIFP and DIMP are the simulants for O-isopropylmethyl phosphonofluoridate (GB) and CES that for bis(2-chloroethyl) sulphide (HD). Fig. 9 shows that a single SFE is sufficient for extracting all the simulants. However, diethylaminoethanethiol hydrochloride (DEAT · HCl), a by-product

from VX manufacture, is hardly extracted because of its low solubility and/or strong sorption by the soil [102].

SFE also permits class-selective extractions, as illustrated in Fig. 10 [51]. Different PAHs are extracted from coal tar pitch, depending on the supercritical CO_2 pressure. At 70 bar, the two solutes that are mainly extracted are assumed to be dibenzofuran and fluorene. As the pressure is increased, PAHs of higher molecular mass (lower solubility in supercritical CO_2) are extracted; hence the three-ring compounds appear in the 100-bar extract and the four-and five-ring PAHs require a pressure of 200 bar.

5. COMPARISON BETWEEN SFE AND LIQUID–LIQUID EXTRACTION

SFE compares favourably with classical solvent extraction methods such as Soxhlet extraction or sonication [80, 84, 116]; Table 7 gives a comparison of the three methods for the recovery of PAHs from river sediment and fly ash [80]. Indeed, the extraction times involved using SFE are considerably lower (typically, less than 1 h instead of several hours) and the concentration step that is usually required with liquid–liquid extractions when dealing with trace analytes is eliminated or at least reduced to only a few minutes [88]. In addition, SFE requires the use of only a few millimetres of solvent or no solvent at all in some instances.

Sometimes, better recoveries of analytes could be even obtained with supercritical fluids. For example, almost 100% of 2,3,7,8-tetrachlorodibenzo-p-dioxin could be extracted from a sediment spiked with 200 μg kg⁻¹ in 30 min with a supercritical CO_2 methanol (2%) mixture, compared with the standard Soxhlet method which took 18 h and extracted only 65% of the dioxin [81].

6. CONCLUSIONS

There is great concern regarding environmental pollution, especially the exposure of laboratory personnel to toxic solvents and the disposal costs associated with organic solvents. These two major concerns have given importance and preference to the use of supercritical fluids (mainly carbon dioxide) as an extractant medium. They allow the quantita-

TABLE 6

EXAMPLES OF SUPERCRITICAL FLUID EXTRACTIONS OF SOLID MATRICES

Solid matrix	Extracted solutes	Super- or subcritical fluid or fluid mixture	Off-line coupling		On-line coupling			Ref.
			Collection	Analysis	GC	CSFC	PSFC	
Soils and sediments	PAHs	CO_2, CO_2–CH_3OH, N_2O, N_2O–CH_3OH, C_2H_6, $CHClF_2$	Solvent	GC	*			29,32,34, 37,77,80, 82, 86–89
	Pesticides	CO_2, CO_2–CH_3OH, CH_3OH	Solvent, adsorption	GC, HPLC	*		*	52, 56, 66, 79, 85, 87
	Herbicides	CO_2, CO_2–CH_3OH, CO_2–C_2H_5OH, CO_2–CH_3CN, N_2O, N_2O–CH_3OH, C_2H_6	Solvent, adsorption	GC, PSFC, HPLC		*	*	9, 16, 22, 66, 88, 93–96
	PCBs	CO_2, CO_2–CH_3OH, CO_2–toluene, N_2O, $CHClF_2$	Solvent, adsorption	GC	*			30, 32, 48, 82, 92, 97, 98
	Phenols	CO_2, CO_2–CH_3OH, CO_2–benzene	Solvent adsorption	GC, HPLC	*			67, 83, 85, 86, 99
	Alkanes, alkylbenzenes	CO_2, CO_2–CH_3OH, H_2O	Adsorption	CSFC	*	*		35–37, 46, 47, 50, 100
	Linear alkylbenzenesulphonates	CO_2–CH_3OH	Solvent	HPLC				23
	Halocarbons	CO_2			*			40
	Condensed polyaromatics	CO_2, CO_2–CH_3OH	Solvent	GC				78, 89
	Polychlorinated dioxin	CO_2, CO_2–CH_3OH, N_2O, N_2O–CH_3OH	Solvent	GC				81
	Amines	CO_2, N_2O	Adsorption	GC	*			8
	Fatty acids	CO_2–CH_3OH–HCO_2H	Adsorption	GC				101
	Chemical warfare agent simulants	CO_2, CO_2–CH_3OH	Solvent	GC				102
Rocks	Explosives	CO_2	Solvent	HPLC				52
	Hydrocarbons	CO_2, SF_6	Solvent	GC, SFC	*			39, 40, 88, 103

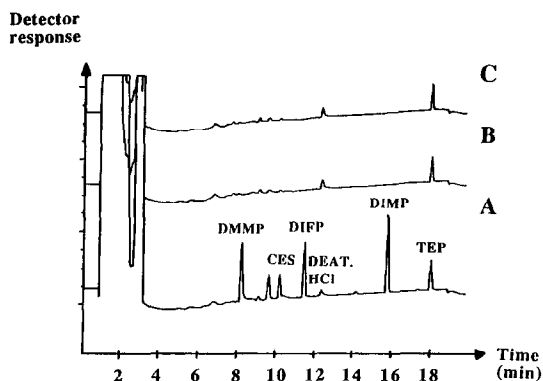| Matrix	Compounds	Fluid	Mode	Technique			Ref.
Air-dried biosludge, generated during the treatment of a coal gasification wastewater	n-Alkanes, PAHs	CO_2	Solvent	GC			5
Digester sludge from a municipal wastewater treatment facility	Linear alkyl-benzenesulphonates	CO_2, N_2O	Solvent	HPLC			23
Petroleum waste sludge	PAHs	CO_2, N_2O, $CHClF_2$	Solvent	GC		*	82
Air particulate matter (urban dust)	Alkanes, PAHs	CO_2, N_2O, N_2O–CH_3OH, C_4H_{10}	Solvent, adsorption	GC	*	*	32, 34, 38, 41, 80, 97, 104
Internal combustion engine valve deposit	PAHs	CO_2	Adsorption	GC			105
Coal, coal tar, carbon black, lampblack, hydrocarbon waste, treated wood, fly ash	PAHs	CO_2, CO_2–CH_3OH, N_2O, N_2O–CH_3OH, CH_3OH, C_2H_6	Solvent, adsorption	GC, HPLC	*	*	32, 34, 35, 40, 51, 57, 72, 80, 106–108
	Hydrocarbons	CO_2, CO_2–$HCOOH$				*	38, 46, 60
	Sesquiterpenes	CO_2				*	34
	Polychlorinated dioxins and furans	CO_2, CO_2–CH_3OH, CO_2–benzene, CO_2–toluene, N_2O, N_2O–CH_3OH, N_2O–toluene	Solvent	GC			109, 110
Semtex (plastic explosive)	Alkanes, nitrates, triazane	CO_2	Solvent	GC			111
Propellants	Stabilizers	CO_2			*		62, 112
Plant tissues	Pesticides	CO_2	Solvent, adsorption	GC, PSFC			113, 114
	2,4-Dichlorophenol	CO_2–CH_3OH,	Solvent	HPLC	*	*	115
	Herbicides	CO_2–C_2H_5OH					9, 94

Detector
response

Fig. 9. Off-line analysis by gas chromatography of (A) first 10-min supercritical fluid extraction of spiked soil, (B) second 10-min supercritical fluid extraction of soil and (C) third 10-min supercritical fluid extraction of soil. DMPP = dimethyl methyl-phosphonate; CES = chloroethyl ethyl sulphide; DIFP = diisopropyl fluorophosphate; DEAT·HCl = diethylaminoethane-thiol hydrochloride; DIMP = diisopropyl methylphosphonate; TEP = triethyl phosphate (internal standard). Extraction conditions: CO_2–CH_3OH (95:5), 300 bar, 60°C, 10 min, 1 g of soil, collection in methanol. Chromatographic conditions: DB-5 fused-silica capillary column (30 m × 0.53 mm I.D.) (1.5 μm film thickness); column temperature, 70°C for 4 min, then increased to 150°C at 8°C min^{-1}; carrier gas, helium (flow-rate 7 ml min^{-1}); injector held at 120°C; flame ionization detector held at 200°C. From ref. 102.

tive extraction of numerous pollutants in a very short time, and the addition of a small percentage of an organic solvent could extend the scope of SFE applications.
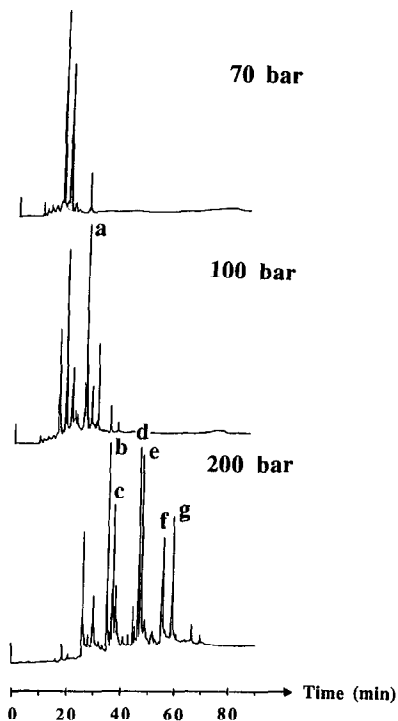

Fig. 10. On-line supercritical fluid chromatography of coal tar pitch extracted with supercritical carbon dioxide at different pressures. Peaks: (a) phenanthrene; (b) fluoranthene; (c) pyrene; (d) benz[a]anthracene; (e) chrysene; (f and g) benzofluoranthenes and benzopyrenes. Extraction conditions: CO_2, 43°C, 60 min, flow-rate 3 ml min^{-1} of gaseous CO_2 at 150 bar, 10 μg of coal tar pitch. Chromatographic conditions: SB-biphenyl-30 fused-silica capillary column (10 m × 0.05 mm I.D.) (0.25 μm film thickness); column temperature, 110°C; supercritical CO_2; initial density of 0.25 g ml^{-1} for 10 min, then increased to 0.74 g ml^{-1} at 0.006 g ml^{-1} min^{-1}; flame ionization detector held at 400°C. From ref. 51.

TABLE 7

COMPARISON OF SONICATION, SOXHLET AND SUPERCRITICAL FLUID EXTRACTION FOR THE EXTRACTION OF PAH COMPOUNDS FROM SPIKED RIVER SEDIMENT AND FLY ASH

Extraction conditions: sonication, 10 ml of CH_2Cl_2, 100 W, 4 h, 0.5 g of spiked sediment; Soxhlet extraction, 50 ml of CH_2Cl_2, 8 h, 1 g of spiked sediment; SFE, N_2O–CH_3OH (5 vol. %), 350 bar, 65°C, 30 or 60 min, total volume of fluid 20 or 40 ml of liquid, 50 mg of spiked sediment or fly ash, 25 μm I.D. outlet restrictor, collection in CH_2Cl_2, analysis by GC–MS (reprinted from ref. 80). Results are means ± standard deviation (n = 3).

Matrix	Compounds extracted	Recovery using different extraction methods (%)			
		Sonication (4 h)	Soxhlet (8 h)	SFE (30 min)	SFE (60 min)
River sediment	Phenanthrene	79 ± 5	98 ± 3	102 ± 4	103 ± 7
	Pyrene	77 ± 5	96 ± 3	95 ± 2	101 ± 8
	Perylene	61 ± 6	86 ± 6	92 ± 10	97 ± 6
Fly ash	Phenanthrene	30 ± 1	60 ± 1	72 ± 5	89 ± 8
	Pyrene	33 ± 1	71 ± 1	48 ± 8	67 ± 4
	Perylene	23 ± 1	77 ± 6	19 ± 5	28 ± 5

Analytical SFE is currently an evolving technique in which many experimental parameters and problems have yet to be properly defined. The influence of some parameters such as the pressure and the temperature of the extraction fluid are now well mastered; others (extraction cell configuration, fluid flow-rate through the extraction cell, period of extraction, sample matrix effects, etc.) need further studies. Similarly, the sample size needs to be optimized. Very often, a small sample size is used; unfortunately it may not be a true representative of the overall sample and, hence, may result in wrong analytical results.

In spite of the above-mentioned precautions, analytical-scale SFE has been successfully applied to a wide range of environmental samples and numerous interesting results have been obtained. This new technique, still in its development stage, will therefore without doubt become a routine sample preparation technique. Nevertheless, one needs to always bear in mind the advice of Bartle and Clifford, who say "SFE must not be considered as a magic technique but as an important weapon in the analyst's armory" [93].

7. ACKNOWLEDGEMENT

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