

## Review

# Supercritical fluid extraction in environmental analysis

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### ABSTRACT

Supercritical fluid extraction (SFE), usually with carbon dioxide and often with a modifier, is a rapid, selective and convenient method for sample clean-up in environmental analysis. Three inter-related factors influence analyte recovery in SFE: solubility in the fluid, diffusion through the matrix and adsorption in the matrix. SFE may be coupled on-line to various analytical methods: gas, liquid and supercritical fluid chromatography. A wide range applications of SFE from environmental samples is described: hydrocarbons, chlorobenzenes and chlorobiphenyls, dioxins and chlorinated pesticides, herbicides and ionic surfactants. Organic compounds may be concentrated from air and water and extracted from adsorbents by SFE. Direct SFE from water is also possible.

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## 1. INTRODUCTION TO SUPERCRITICAL FLUID EXTRACTION

Supercritical fluid extraction (SFE) is a novel sample preparation method which promises to have a profound influence on environmental analytical chemistry, since it affords rapid, selective and convenient sample clean up [1-4]. The main advantage of a supercritical fluid over an extracting liquid is that its properties, *viz.* density, solvating power, viscosity and solute diffusivity, can all be controlled by varying the applied pressure and temperature. This leads to greater selectivity, rapid mass-transfer and higher flow-rates as compared with liquids. Further, the separation of solvent from solute is simply achieved by decompression, since the solvent is usually gaseous at ambient temperature. SFE also has considerable advantages over liquid extraction in terms of sample size, cost and volume of solvent

and analysis time. Extraction can be performed either off-line or on-line; coupling of SFE to gas, liquid and supercritical fluid chromatography (SFC) have all been demonstrated.

In this review, we outline some of the principles of SFE in the context of environmental analysis and describe some illustrative applications.

## 2. PRACTICE OF SFE

Carbon dioxide has so far been the most widely used extraction solvent because of its convenient critical properties [5], non-toxicity, cheapness and non-flammable character. It is usually classified as a non-polar solvent, but its large quadrupole moment leads to some affinity with polar solutes and many large polar organic molecules are soluble in it.

For the extraction of more polar molecules, polar modifiers such as those listed in Table 1 are usually

TABLE 1  
MODIFIERS FOR CARBON DIOXIDE IN SFE

Modifier	$T_c$ (°C)	$P_c$ (atm)	Molecular mass	Dielectric constant at 20°C	Polarity index
Methanol	239.4	79.9	32.04	32.70	5.1
Ethanol	243.0	63.0	46.07	24.3	4.3
Propan-1-ol	263.5	51.0	60.10	20.33	4.0
Propan-2-ol	235.1	47.0	60.10	19.3	3.9
Hexan-1-ol	336.8	40.0	102.18	13.3	3.5
2-Methoxyethanol	302	52.2	76.10	16.93	5.5
Tetrahydrofuran	267.0	51.2	72.11	7.58	4.0
1,4-Dioxane	314	51.4	88.11	2.25	4.8
Acetonitrile	275	47.7	41.05	37.5	5.8
Dichloromethane	237	60.0	84.93	8.93	3.1
Chloroform	263.2	54.2	119.38	4.81	4.1
Propylene carbonate	352.0		102.09	69.0	6.1
N,N-Dimethylacetamide	384		87.12	37.78	6.5
Dimethyl sulphoxide	465.0		78.13	46.68	7.2
Formic acid	307		46.02	58.5	
Water	374.1	217.6	18.01	80.1	10.2
Carbon disulphide	279	78.0	76.13	2.64	

added to the CO<sub>2</sub> [6]. The modifier–phase diagram must be considered to ensure that there will be only one phase under the conditions of the extraction. Thus for methanol–CO<sub>2</sub> at 50°C, there is only one phase above 95 atm (1 atm = 1.01 · 10<sup>5</sup> Pa) whatever the composition, but below this pressure, two phases are possible. A comprehensive compilation of phase data for CO<sub>2</sub> mixed with numerous modifiers has been published [7].

Experimental SFE is conceptually simple [4]: a pump is used to supply a known pressure of the extraction fluid to an extraction cell held at a temperature above the critical temperature of the fluid, which then flows through the sample and out through a pressure restrictor to a collecting device at atmospheric pressure (Fig. 1).

The pump is either a syringe or a reciprocating type with a cooled head. Modifier, if required, is introduced either by means of a separate pump via a mixing device, or from a pre-mixed cylinder; it should be remembered however, that if using a cylinder, the modifier composition changes slightly as the contents are consumed. Alternatively, modifier may be added directly to the matrix. An on-off valve is located between pump and extraction vessel, and often a length of tubing in the cell oven to ensure that the fluid is at the correct temperature.

The solid sample to be extracted is held between frits in an extraction cell usually fabricated from

stainless-steel and available from a number of suppliers. The extraction cell dimensions may affect the rate of extraction [8], perhaps because of turbulence effects; diffusers and ultrasonic irradiation have also been employed. Cell orientation and fluid flow direction is important if the cell is not full, but less important if it is. A commercial SFE instrument allowing eight parallel extractions is available. Liquid or wet samples may be mixed [9] with an adsorbent such as pelletised Celite (“Hydromatrix”) or a drying agent (*e.g.*, magnesium sulphate). Organic water pollutants may be adsorbed onto a solid adsorbent (either solid-phase extraction cartridges or filter discs) from which they are removed for chromatographic analysis by SFE [10]. Direct SFE of aqueous solutions has also been demonstrated [11].

The restrictor maintains the pressure within the cell. It may be, most simply, a length of fused-silica capillary tubing with an internal diameter between 20 and 50 μm or a crimped stainless-steel tube. More elaborate devices include back-pressure regulators and micrometer valves. The extracted material may be collected in a vial containing solvent or by direct cooling. The restrictor is usually heated to prevent blockage when extracting materials containing water which freezes as the supercritical fluid evaporates. This arrangement also prevents deposition of extracted material in the restrictor; during extraction of sediments containing elemental sulphur, locating a copper scavenge column between cell and restrictor is also recommended [12]. Solid traps containing glass beads, silica gel or a liquid chromatographic stationary phase have also been used to collect analytes. Alternatively, SFE equipment is directly coupled to an analytical instrument and such systems are discussed in Section 4.

### 3. FACTORS AFFECTING EXTRACTION FROM ENVIRONMENTAL SAMPLES

Three interrelated factors influence recovery during SFE as is shown in the so-called SFE triangle [13]. For successful extraction, the solute must firstly be sufficiently soluble in the supercritical fluid. This is particularly important at the start when extraction is occurring rapidly. The onset of extraction in a graph of % recovery in a given time against fluid pressure or density (Fig. 2a) is referred to as the

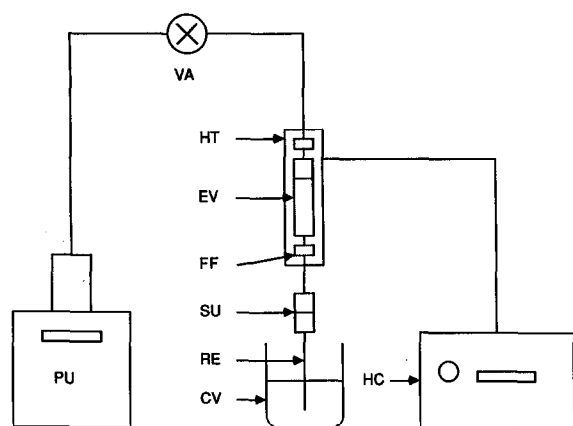


Fig. 1. Off-line SFE system. PU = CO<sub>2</sub> pump; VA = on/off valve; HT = thermostatted heating tube; FF = fingertight connectors; CV = collection vial; SU = swagelok union; RE = restrictor; HC = heater controller; EV = extraction vessel.

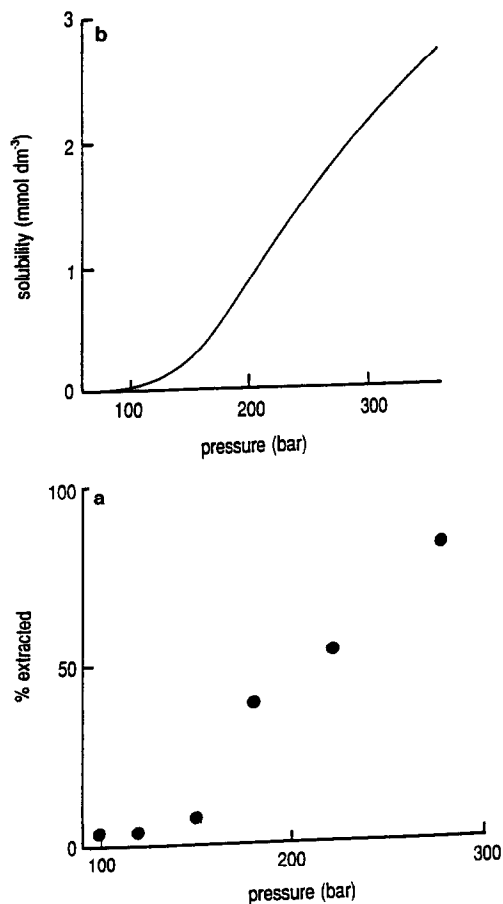


Fig. 2. (a) Percentage recovery of atrazine from soil by SFE with carbon dioxide at different pressures after 15 min at 80°C and constant flow-rate, compared (b) with calculated solubility at the same temperature.

“threshold” pressure. Control of solubility via applied pressure may allow stepwise extraction; for example [14] the extraction of two- and three-ring polycyclic aromatic hydrocarbons (PAHs) from a coal-derived solid occurred at a CO<sub>2</sub> pressure of 100 atm whereas five-ring PAHs required a pressure of 200 atm (Fig. 3). These observations have been correlated with calculated solubilities [15]. It is thus important to know the conditions under which the analyte is sufficiently soluble. In fact solubility of a substance in a supercritical fluid is the sum of two factors: the volatility of the substance and the solvating effect of the supercritical fluid, which is a

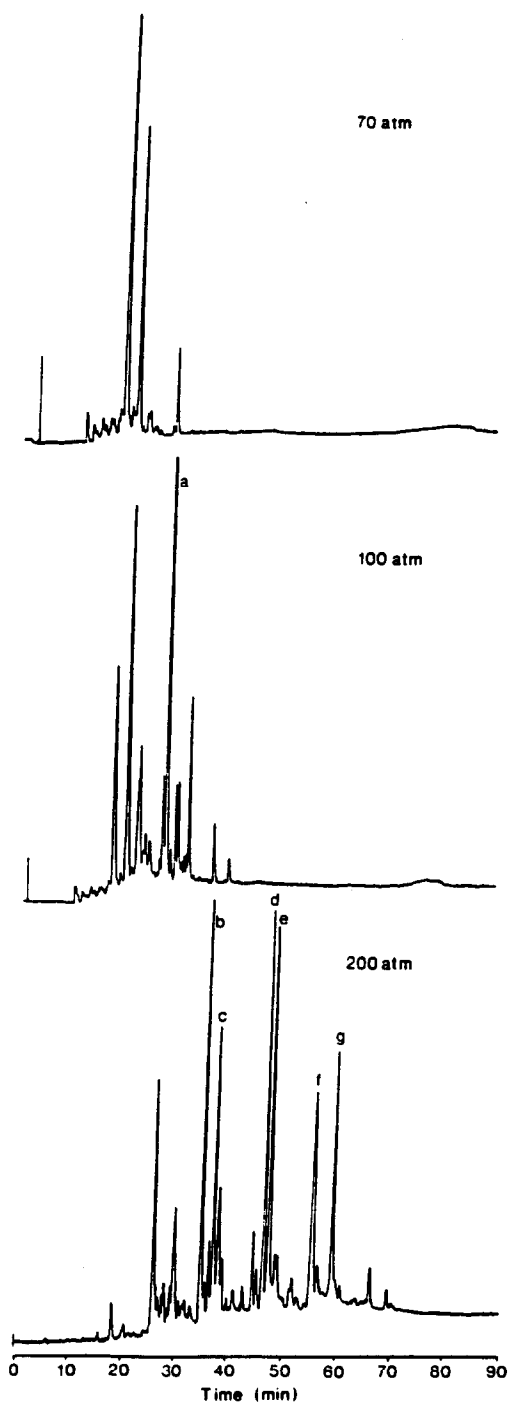


Fig. 3. SFC chromatogram of coal tar pitch extracted at different pressures. From ref. 14. Selected peak identities: a = phenanthrene; b = fluoranthene; c = pyrene; d = benz[a]anthracene; e = chrysenes; f = benzofluoranthenes; g = benzopyrenes.

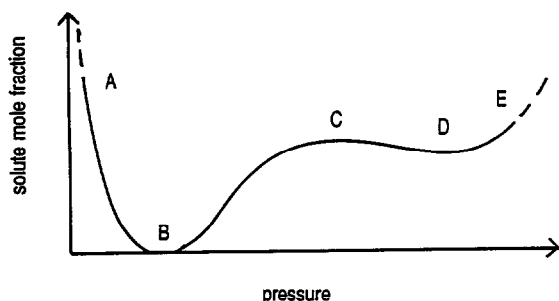


Fig. 4. Schematic diagram of solubility versus pressure at constant temperature.

function of fluid density [13]. The solubility has the general form shown schematically in Fig. 4; it is noteworthy that a decrease in solubility may occur (regions A–B and C–D) as a consequence of repulsive forces “squeezing” the solute out of solution. A number of compilations of solubility data for supercritical fluids have appeared (e.g., ref. 16), from which the threshold pressure can be determined; such data are generally obtained by gravimetric measurements, although a more rapid chromatographic procedure has been used with some success [17]. Alternatively, supercritical fluid solubilities may be predicted either by use of an equation of state such as the Peng–Robinson equation [18], or by means of various empirical correlations so as to extend existing data. The solubility data for atrazine (Fig. 2b) thus obtained [19] correlates well with experimental extraction behaviour (Fig. 2a): predicted solubilities begin to rise at 100 atm in agree-

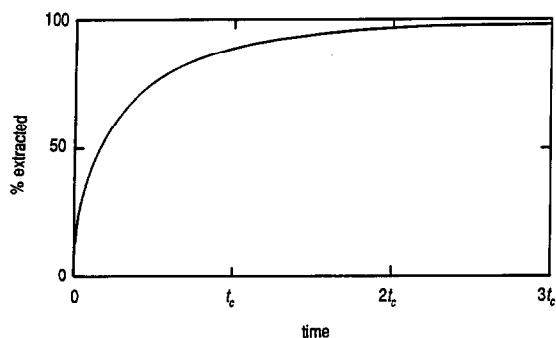


Fig. 5. Theoretical curve of percentage extraction versus reduced time.

ment with the experimentally observed “threshold” solubilities. Janda *et al.* [20] observed that simazine was much less efficiently extracted from sediment than was atrazine. Calculated solubility curves [19] for these compounds are in quantitative agreement with these results; simazine is predicted to be much less soluble than atrazine in supercritical CO<sub>2</sub>.

SFE usually exhibits [13] the time dependence shown in Fig. 5. If the concentration of analyte in a continuous flow of fluid is well below the solubility limit, the rate determining process is diffusion out of the matrix. An effective diffusion coefficient ( $D$ ) and a particular matrix geometry are assumed, along with no solubility limitation; the solutions of the appropriate differential equations are obtained by the same methods as those applied to heat conduction. For a sphere, the solution is therefore described as the “hot-ball” model [21]. If the mass of solute, initially  $m_0$ , is  $m$  after time  $t$ , the ratio  $m/m_0$  is given by

$$\frac{m}{m_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 \frac{Dt}{r^2}\right) \quad (1)$$

where  $n$  is an integer. Making the substitution  $\pi^2 \cdot \frac{D}{r^2} = a$ , where  $r$  is particle radius

$$\frac{m}{m_0} = \frac{6}{\pi^2} \cdot \left[ \exp(-at) + \frac{1}{4} \exp(-4at) + \frac{1}{9} \exp(-9at) + \dots \right] \quad (2)$$

representing a sum of exponential decays and reproducing (Fig. 6a) observed behaviour. At long times, the later (faster decaying) terms decrease in importance in comparison with the first term; a graph of  $\ln(m/m_0)$  versus  $t$  becomes linear (Fig. 6a). Although the initial steeper fall appears as a small feature, it represents the extraction of the majority of the material. Eqn. 1 shows a squared dependence on  $r$ , rationalising the well known fact that speed of extraction is increased by crushing or grinding solids, or coating liquids on a finely divided substrate. Real samples will contain particles of irregular shape and the curve has a large intercept compared with the value of  $-0.5$  for spheres (Fig. 6b).

Fig. 7 shows experimental results [21] for the extraction of phenanthrene from rail-road bed soil at 50°C using CO<sub>2</sub> at 400 atm. The curve of  $\ln$

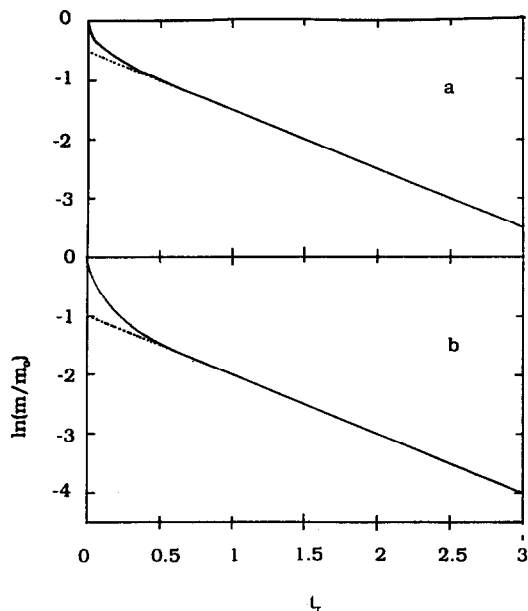


Fig. 6.  $\ln(m/m_0)$  versus scaled time for the hot-ball model: (a) basic model; (b) with effect of irregular particle shape.

$(m/m_0)$  versus  $t$  has the form of the "hot-ball" model although the intercept is close to  $-2$ , indicating irregular shapes for the soil particles. Similar curves have been found for the SFE of numerous analytes from environmental matrices, e.g., PAH with molar mass 128 to 252 [20] and atrazine [19] from soils, and alkylbenzenesulphonates from organic digester sludge [21].

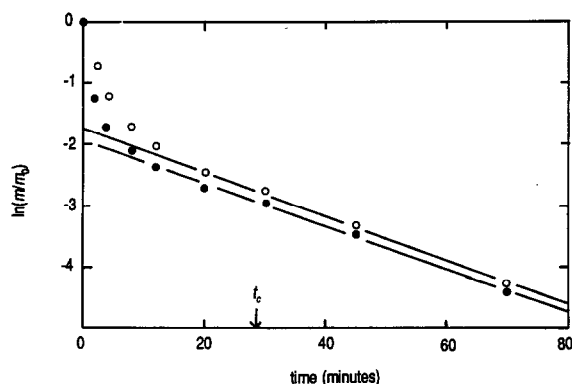


Fig. 7. SFE of phenanthrene from railroad soil with  $\text{CO}_2$  at  $50^\circ\text{C}$ , two different pressures and constant flow-rate. From ref. 21.  $\circ$  = 180 atm;  $\bullet$  = 400 atm.

TABLE 2

USE OF THE EXTRAPOLATION PROCEDURE DURING SFE OF VOLATILE ORGANICS FROM SOIL

	Measurement (arbitrary units)			
	$m_1$	$m_2$	$m_3$	$m_0$
	726	248	116	1190
	888	208	68	1200
	771	176	64	1050
	762	208	84	1110
	720	212	92	1100
	753	188	80	1080
	861	200	76	1180
	768	192	80	1100
	813	224	88	1180
Mean	785	206	83	1130
Standard deviation	58	21	15	55
R.S.D. (%)	7.4	10	18	4.9

The exponential behaviour of the extraction after the initial period means that extrapolation may be used to obtain quantitative analytical information without exhaustive extraction. If  $m_1$  is the mass extracted in the initial non-exponential period and  $m_2$  and  $m_3$  are the masses extracted in two subsequent equal time periods, then the total mass,  $m_0$  is given by

$$m_0 = m_1 + \frac{m_2^2}{m_2 - m_3} \quad (3)$$

This method has been tested by Liu *et al.* [22] by coupled SFE-GC of volatile organic compounds at sub- $\mu\text{g/g}$  levels in soil. Table 2 contains results of repeated runs during which extraction was carried out for approximately 20 min but not to completion. An overall R.S.D. of 4.9% was observed. Table 3 compares the effect of different time intervals on the values of  $m_0$  for the extraction of three compounds from soil. The calculated  $m_0$  values were not affected as long as the first time period covers the entire non-linear region.

Solubility affects the kinetics of SFE since, as already stated, the "hot-ball" [21] model assumes no solubility limitations. If the concentration of solute in the fluid is finite (assumed to be proportional to the concentration in the matrix at the surface), and

TABLE 3  
EFFECT OF TIME INTERVAL USED IN COMPUTING  $m_0$

Time intervals used (s)			Measured value of $m_0$ (arbitrary units)		
$\Delta t_1$	$\Delta t_2$	$\Delta t_3$	Toluene	<i>p</i> -Xylene	Benzylamine
0–200	200–400	400–600	116	196	251
0–400	400–600	600–800	116	196	279
0–400	400–800	800–1200	116	197	266
0–300	300–800	800–1300	116	197	262
0–300	300–700	700–1100	116	196	263
0–500	500–1000	1000–1500	116	198	262
Mean $m_0$			116	197	266
Standard deviation (S.D.)			–	0.82	7.2
R.S.D. (%)			–	0.42	2.7

the partition coefficient is proportional to the solubility of the solute in the fluid ( $S$ ), a new version of eqn. 1 can be written [23]

$$\frac{m}{m_0} = 6 \sum_{n=1}^{\infty} \frac{\left(\frac{hr}{ar}\right)^2}{[hr(hr-1) + a_n^2] \exp(-a_n^2 D H r^2)} \quad (4)$$

where  $a_n$  are the roots of the equation

$$a \cot(a) = 1 - hr \quad (5)$$

and

$$h = \frac{KSF}{AD} \quad (6)$$

$K$  is a constant for a particular matrix,  $A$  is its surface area and  $F$  is the volume flow-rate of fluid. Plots of  $\ln(m/m_0)$  against time now form a family of curves (Fig. 8) for which the gradients of the linear portions become increasingly steep as solubility increases, with a limiting value for infinite solubility—the previously mentioned “hot-ball” model.

These considerations are in keeping with effects observed during the SFE at 50°C and constant flow-rate of phenanthrene from soil (Fig. 7). At 180 atm (open circles) the  $\ln(m/m_0)$  versus time curve falls less steeply initially than the 400 atm curve (closed circles) and the linear portion is displaced upwards. The lower rate of extraction at

180 atm can be explained by the difference in solubility at the two pressures. At 50°C, the saturated mole fraction of phenanthrene in CO<sub>2</sub> is 0.0015 at 180 atm but 0.003 at 400 atm. Although the two curves appear similar, the amount extracted after 4 min differs by over 10%. The effect of adsorption on active sites in the matrix may be overcome by adding modifier to the CO<sub>2</sub> to increase the rate; spiked samples may be a poor guide to the necessary conditions (Fig. 9).

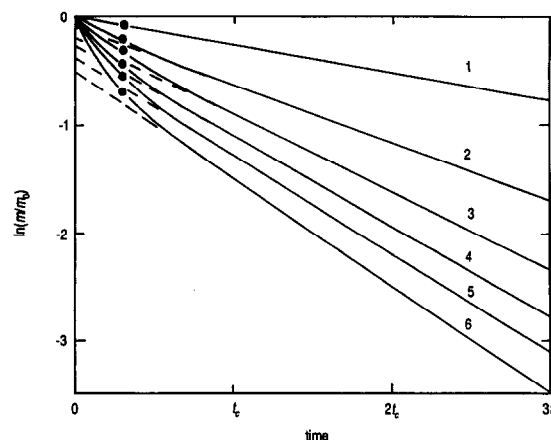


Fig. 8. Solubility-limited hot-ball model plots. Solubility increases from curve 1 to curve 6.

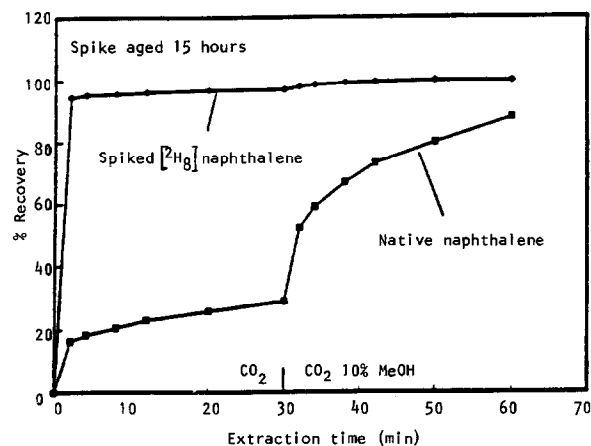


Fig. 9. SFE recovery rates of naphthalene and spiked  $[^2\text{H}_8]$ naphthalene from the same sample of air particulates at 400 atm and 80°C. From ref. 49.

#### 4. ON-LINE COUPLING OF SFE TO CHROMATOGRAPHIC ANALYSIS

Since the extraction solvent is easily removed, the analyte may be trapped for subsequent separation, and trace analysis is possible with on-line GC, SFC and HPLC. In direct coupling, the solvent peak is eliminated and the analysis of compounds which may elute with the solvent becomes possible. On-line coupling also reduces sample handling, the possibility of sample loss and contamination. The process is attractive if only limited amounts of sample are available since all of the analyte can be transferred.

A number of application areas of SFE-GC and SFE-SFC have been described [1,4]. If analytes are both thermally stable and volatile, then GC is the preferred separation technique; thus fuels, polychlorinated biphenyls and PAH in environmental samples can all be analysed by on-line SFE-GC. When the sample contains thermally unstable or reactive compounds, SFE-SFC is recommended; SFE-SFC is particularly attractive [24] since the extracting fluid may be the same as the mobile phase. SFE-SFC can be applied to the analysis of soils and sediments for compounds such as thermally unstable pesticides.

#### 4.1. SFE-GC

On-line SFE-GC has the following steps: extraction, depressurisation and venting of the supercritical fluid, collection and focusing of the extract on to a GC column and GC analysis. Two broad methods of collection and focusing have been reported. In the first, the extract is collected in an external device, *e.g.*, by depressurising into a cold trap located before the GC; the trap is heated in a flow of carrier gas to transfer the extract to the column. Alternatively, the GC system may be used as the trap by depressurising into a retention gap before the column or depositing the extract directly inside the column [4,24] (Fig. 10).

The cold trapping procedure prevents any deleterious effects of the supercritical fluid on the GC column or detector but is limited by the efficiency of collection of volatiles in the extract. Use of a suitable adsorbent, *e.g.*, Tenax, with thermal desorption may be used. SFE-GC with column collection is more efficient since the stationary phase helps concentrate the extract in a narrow band; both on-column and split injection versions have been reported for quantitative analysis. The former permits ng/g detection limits for milligram amounts of sample extracted. Split injection is preferred if the sample is wet, since freezing and plugging of the restrictor outlet or GC column may occur with on-column injection.

The coupling of SFE with GC provides a rapid and convenient method for the analysis of air and water matrices. Trace components in air may be

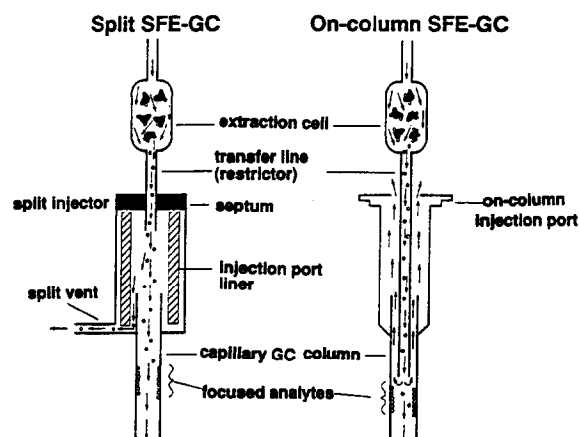


Fig. 10. On-line coupling of SFE to GC. From ref. 3.



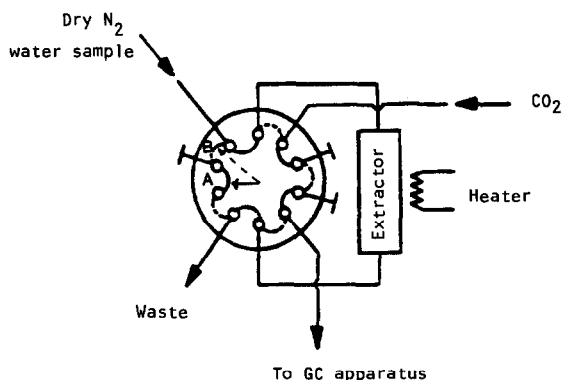


Fig. 11. Apparatus for automated SFE-GC analysis of water. From ref. 25.

concentrated onto adsorbents such as Tenax, polyurethane foam, charcoal or silica/alumina, from which they may be extracted by SFE and transferred quantitatively to the GC via an SFE-GC interface. Similarly, pollutants in water may be concentrated on polyurethane foam or solid-phase extraction cartridges and Empore discs and then analysed by SFE-GC.

An automated version of the latter equipment has been described [25] (Fig. 11), in which water is passed through a Tenax column which, after drying, is subjected to SFE. Contaminants are transferred to the capillary GC column via a length of small internal diameter fused-silica capillary. The whole isolation process is controlled by a single ten-port valve.

#### 4.2. SFE-SFC

The instrumentation [24] for on-line SFE-SFC ranges from relatively simple systems to more complex arrangements involving switching valves and multiple pumps. Most systems include an extraction cell which is temperature controlled or held in an oven, a switching valve, a cryogenically cooled trap and a chromatographic oven housing the column—usually a capillary—and a detector. The fluid may be delivered to both the cell and column using a single pump. When different conditions are required for simultaneous extraction and chromatography, a dual pumping system is required.

A typical SFE-SFC system is illustrated in Fig. 12. The outlet of the cell is connected to a flow restrictor which is in turn connected to an accumulating trapping system; this may be a coated or more usually uncoated fused-silica retention gap or transfer line, or an adsorbent trap housed in a cryogenically cooled tee. During extraction, the tee is vented to atmosphere and the extract is concentrated within the transfer line or trap. After extraction is complete, the valve is switched and supercritical fluid is introduced into the side arm of the tee to transfer the extract on to the SFC column. If uncoated fused-silica tubing is used for the retention gap, the extract is rapidly transferred to the analytical column and there concentrated by phase-ratio focusing. The process is aided by keeping the mobile phase at low density. Other more complicated systems have been reported, using on-off and multipoint switching

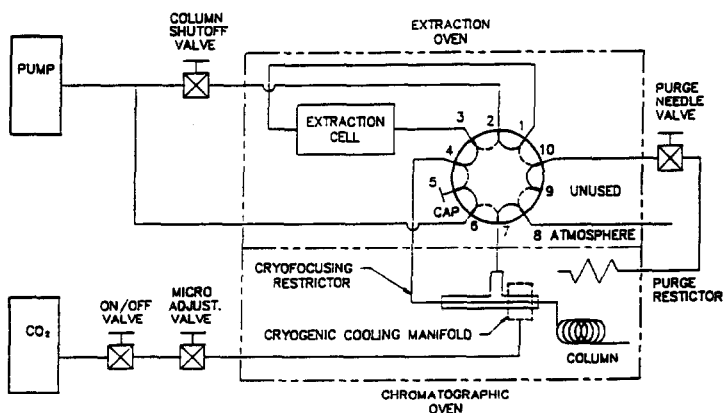


Fig. 12. On-line coupling of SFE to SFC.

valves to allow continuous extraction or to permit venting of the extraction cell during simultaneous chromatographic analysis.

#### 4.3. SFE–HPLC

Coupled SFE–HPLC has also been described [26]. For example, a system for the determination of chlorinated phenols in various solid matrices permits direct introduction of supercritical fluid extracts into an HPLC, allowing quantitative determinations down to the sub- $\mu\text{g/g}$  level without clean-up.

### 5. APPLICATIONS

#### 5.1. Purgeable halocarbons

Eleven purgeable halocarbons were isolated from a sediment matrix by on-line SFE with carbon dioxide [27]. The restrictor from the SFE apparatus was directly inserted into a split/splitless injector (Fig. 10). The injector was kept at 250–325°C to minimise cooling when supercritical fluid decompressed. To focus the analytes, it was necessary to cryogenically cool the gas chromatographic oven during the SFE. The halocarbons deposited in the capillary chromatographic column were then analysed by GC–electron-capture detection (ECD). The SFE was performed at 250 atm and 40°C for 10 min. Volume of the extraction cell with the sediment was 2 cm<sup>3</sup>. Recovery of the purgeable halocarbons from the sediment was in the 90% region at low  $\mu\text{g/g}$  levels.

#### 5.2. Chlorobenzenes and chlorophenols

Hong-Xu [28] described SFE of ten chlorobenzenes from sediment samples. The SFE was performed off-line. After the SFE, the analytes were concentrated in the trap packed with C<sub>18</sub> reversed-phase. Chlorobenzenes were then eluted from the trap by isooctane and after a clean-up procedure analysed by GC–ECD. Optimum SFE conditions were as follows: extraction temperature 80°C, extraction time 20 min, sample amount 1 g placed in 7 cm<sup>3</sup> extraction chamber, extraction pressure of pure CO<sub>2</sub> 168 atm, flow-rate of liquid CO<sub>2</sub> 2 cm<sup>3</sup>/min. The method was tested using sediments with certified concentrations of chlorobenzenes and by

comparisons with Soxhlet extraction. In the concentration range 5–200 ng/g for the different chlorobenzenes, the SFE provided results coincidental with the certified values and/or Soxhlet extraction.

Richards and Campbell [29] investigated recovery of some priority pollutants from spiked soil samples by SFE, Soxhlet extraction and sonication liquid extraction. They found that SFE is more efficient than other extraction methods for 13 of 16 compounds tested. SFE averaged 80.2% and individual values ranged from 70.4 to 95%. Only phenolic and chlorophenolic compounds had equivalent recoveries in the SFE and Soxhlet extraction. Sonication was less efficient than the SFE for all compounds studied except 2,4-dichlorophenol, which was recovered in equal amounts by both extraction methods. Groups of compounds tested were: phenols and chlorophenols, chlorobenzenes and naphthalene. The best results were obtained by using carbon dioxide with 2% of methanol as a supercritical fluid. The extraction was performed at 39.5 MPa and 80°C. The spiked soil (2 g) (spiking level 25  $\mu\text{g/g}$  for each compound) was extracted in a 1.67 cm<sup>3</sup> chamber for 30–40 min (20 cm<sup>3</sup> of the extraction fluid was consumed; measured as a liquid using pump displacement). The SFE was performed off-line; the compounds extracted by the SFE were trapped at the outlet of the restrictor into methylene chloride. The methylene chloride solution was concentrated to 1 cm<sup>3</sup> under gentle stream of nitrogen and analysed by GC–MS.

Recovery of chlorophenols from spiked sediment was also measured in other work using off-line SFE [30]: supercritical fluid CO<sub>2</sub> at 23 MPa and 48°C, amount of sediment 0.5 g, time of the SFE 15 min, restrictor used was 20 cm long, 25  $\mu\text{m}$  I.D. Analytes leaving the restrictor were trapped in 0.5 cm<sup>3</sup> of methanol. After derivatisation to chlorophenol acetates, the compounds were analysed by capillary GC. Recoveries of *o*- and *p*-chlorophenol, 3,4-dichlorophenol, 2,4,5-trichlorophenol and pentachlorophenol were equal to or higher than 90%. Under the SFE conditions described there were no differences between recoveries from dry and wet (20% of water) sediment except *o*-chlorophenol and *p*-chlorophenol, which were partially lost during the drying.

### 5.3. Polychlorinated biphenyls

The possibility of isolation of polychlorinated biphenyls (PCBs) from sediment using simple off-line SFE apparatus was shown already in 1986 [31]. More recent papers deal with on-line coupled techniques, where SFE is directly coupled usually to GC-ECD.

Hawthorne and Miller [32] accomplished coupling SFE to GC-ECD by inserting the SFE restrictor outlet through the on-column injection port. The GC oven was cooled during the extraction. Extracted analytes were thermally focused inside the capillary chromatographic column at the outlet of the restrictor. Since nitrous oxide, which was used as a supercritical fluid, gives a relatively high ECD response, after the extraction period and withdrawing the restrictor from the injector the chromatographic column was flushed for 2–3 min with a carrier gas still at low temperature (5°C). PCBs were then analysed using a temperature program. Parameters of the SFE were as follows: extraction period 10 min, extraction pressure 300 bar, temperature 45°C, extraction fluid nitrous oxide. A restrictor with 25  $\mu\text{m}$  I.D. (corresponding to a flow-rate of the gaseous nitrous oxide of *ca.* 240  $\text{cm}^3/\text{min}$ ) was used. This restrictor provided good SFE recoveries, but required wide-bore thick-phase GC columns to provide good low-temperature focusing. The amount of the sediment taken for one analysis was 10 mg. The on-line SFE-GC-ECD analysis of the spiked sediment (8  $\mu\text{g}/\text{g}$  of Aroclor 1254) gave essentially quantitative extraction and recovery of the PCBs.

In the paper published by Onuska and Terry [33], the PCBs extracted from the sediment by SFE were collected in an “accumulator” (2 m  $\times$  0.32 mm I.D. fused-silica capillary coated with cross-linked SE-54 stationary phase). The analytes emerging from the restrictor are partitioned in the accumulator, which is kept at lower temperature (5°C). Desorption from the accumulator is achieved by a rapid temperature ramp to 140°C and with hydrogen as a carrier gas. Direct on-line coupling of the accumulator to the analytical capillary column is made by switching a six-port valve to another position (the first position of the six-port valve is utilised during the SFE). Recommended parameters of the SFE were: supercritical fluid  $\text{CO}_2$  + 2% methanol (kinetics of SFE with pure  $\text{CO}_2$  were proved to be slower), pressure

20.7 MPa, temperature 40°C. The restrictor was 10 cm long, 25  $\mu\text{m}$  I.D. (flow-rate of the supercritical fluid 0.35 g/min). The SFE was performed in static mode: the extraction cell was pressurised and the pressure was maintained in the cell for 2 min to reach equilibrium. Extracted analytes were then transferred to the accumulator by opening a valve in the extraction cell outlet for 30 s. The valve was then closed and the cycle was repeated five times. After the fifth step the six-port valve was switched to another position, residual methanol in the accumulator was flushed by the carrier gas at 5°C, and GC-ECD analysis started. From 10 to 100 mg of the sediment with a certified value of 2.02  $\mu\text{g}/\text{g}$  of PCBs were extracted and analysed. Statistic comparison of the certified and determined values revealed excellent coincidence.

Recent data provided by Onuska and Terry [34] show that difluorochloromethane (freon-22) is the most efficient fluid for SFE of PCBs from sediment (most likely because of its high dipole moment) in comparison with pure  $\text{CO}_2$ . Methanol-modified  $\text{CO}_2$  yielded also acceptable recoveries. The off-line SFE using freon-22 was performed mostly at 100°C and 400 atm and PCBs were trapped by inserting the restrictor outlet into several  $\text{cm}^3$  of acetone in a vial. Although the widespread use of freons for industrial purposes is being reduced, which would affect their future analytical uses, the hydrogen-containing fluorochlorohydrocarbons have much lower influence on ozone depletion, and are more suitable for SFE.

### 5.4. Tetrachlorodibenzo-*p*-dioxins

Onuska and Terry [35] tested SFE for isolation of tetrachlorodibenzodioxin (2,3,7,8-TCDD) from sediment matrix. They used off-line SFE. The extraction cell had a volume of 0.5  $\text{cm}^3$  and 50 mg of the sediment were extracted. The sediment was spiked by the tested compound to a concentration of 0.2  $\mu\text{g}/\text{g}$ . The SFE extracts were collected in hexane, which was, after the procedure completion and concentration of the hexane solution, analysed by GC-MS. The results of the study showed, that pure  $\text{CO}_2$  is not able to extract tetrachlorodibenzodioxin effectively. After 30 min of extraction at 310 atm and 40°C the recovery was only about 50%. Much better results were obtained using pure nitrous oxide (91% recovery). The best results involved modification of

the fluids by 2% of methanol. During 30 min of SFE, recovery by carbon dioxide + 2% methanol of over 93%, and by nitrous oxide + 2% methanol of 100% was achieved. Moisture content in the sediment dramatically decreased the recovery by 10–15%. To achieve the same recovery with wet sediment the time of SFE must be doubled. For comparison, classical Soxhlet extraction of 1 g of the sediment by a hexane–acetone–trimethylpentane mixture for 18 h provided only 65% recovery of TCDD.

The SFE was also used for enrichment and isolation of TCDD from municipal incinerator fly ash [36]. For the SFE pure nitrous oxide and its mixtures with methanol and toluene were used. Experiments were carried out at 45°C with 25 mg sample. The best recovery was obtained with nitrous oxide + 2% methanol at 400 bar. Under these conditions the SFE was more efficient than the Soxhlet technique.

Suitability of nitrous oxide for the SFE of dibenzo-*p*-dioxins and dibenzofurans from incinerator fly ash was also described by Alexandrou *et al.* [37]. They found also that carbon dioxide + 10% benzene is able to provide high recoveries of these compounds. For the fractionation and clean-up of the complex organic mixtures in an organic solution obtained after the off-line SFE of the fly ash sample, a further SFE step can be used (instead of the usual clean-up procedure by column liquid chromatography). For example, the liquid extract can be collected in a Florisil column. The column is then extracted for 15 min with CO<sub>2</sub> at 40°C and 200 atm. During this extraction over 75% of PCBs and chlorobenzenes are removed from the column. Full recoveries of polychlorodibenzo-*p*-dioxins are obtained by extracting of the column with nitrous oxide for 90 min at 400 atm [38].

### 5.5. Organochlorine pesticides

More than 20 organochlorine pesticides were isolated from sediment matrix by off-line SFE [39]. Spiked sediment (1–10 g) was extracted at 60°C and 250 atm for 5 min in static mode and 20 min in dynamic mode. Flow-rate of supercritical fluid (CO<sub>2</sub>) was 0.5 cm<sup>3</sup>/min. Methanol was used as polarity modifier. Recovery of chlorinated pesticides under these conditions was higher than 90%. It

was also shown that the SFE with carbon dioxide is inefficient for extracting elemental sulphur from environmental solids [40]. Elemental sulphur is a serious problem when an electron-capture detector or a flame photometric detector is used for the gas chromatographic analysis. The extracts of environmental solids after liquid extraction usually require treatment with metallic mercury or copper, which results in conversion of soluble sulphur to insoluble sulphides. The method is effective; however the treatment leads to degradation of a number of pesticides. In contrast to Soxhlet extracts, less than 2% of the elemental sulphur was present in the SFE extracts, while the majority of pesticides from the spiked sediments were recovered. Thiophosphate and chlorinated pesticides were used in this work [41].

### 5.6. *s*-Triazine herbicides

SFE recoveries higher than 90% from sediment can be achieved by pure CO<sub>2</sub> for propazine, terbutilazine, atrazine and cyanazine [42]. Simazine, as a very poorly soluble compound in pure CO<sub>2</sub>, requires addition of methanol to the supercritical fluid. The entrainer can be added directly to the sediment in the extraction chamber [43]. The SFE was performed under the following conditions: off-line SFE, amount of the spiked sediment 0.5 g, spiking level 4 µg/g–40 ng/g, extraction pressure 230 atm and temperature 48°C, time of the SFE 30 min, consumption of the liquid CO<sub>2</sub> during the extraction period 18 cm<sup>3</sup>. Compounds leaving the restrictor from the SFE apparatus were trapped into a few cm<sup>3</sup> of methanol. Methanolic solution was (after concentration under gentle stream of nitrogen) analysed by capillary GC–flame ionization detection (FID) and/or HPLC–diode-array detection (DAD) at 225 nm. Due to background of natural hydrocarbons in the sediment, which are easily recovered by SFE and interfere with *s*-triazines during the GC, the HPLC method was found to be more suitable for the final analysis than GC–FID. It was also confirmed in another study with actual soil samples [44], that presence of methanol or acetone in supercritical CO<sub>2</sub> improved recovery of atrazine.

### 5.7. Phenoxy-carboxylic acid herbicides

Experiments on the solubility of some pesticides in supercritical carbon dioxide [39] and model experiments with their SFE from a glass wool [40] showed the potential of the method for environmental samples containing phenoxy-carboxylic acids or their derivatives.

Soil spiked with 1.8–7.5  $\mu\text{g/g}$  of isooctyl ester of 2,4,5-trichlorophenoxyacetic acid was extracted in off-line apparatus under the following conditions [41]: sample amount 10 g (before the SFE the soil was mixed with water and methanol, 5% and 3% (w/w), respectively, in order to increase polarity of the passing supercritical fluid), pressure 100–316 atm, temperature 40–45°C, extraction time 40 min, flow-rate of the liquid  $\text{CO}_2$  2–2.5  $\text{cm}^3/\text{min}$ . It was shown that the higher the pressure, the higher the recovery of the herbicide. However, at the highest pressure the recovery did not exceed 80%.

### 5.8. Fuels and crude oil

Fuel and crude oil contamination of environmental solids can be relatively easily isolated from the environmental solids by SFE using pure  $\text{CO}_2$ . It was, for example, shown [45], that recovery of  $\text{C}_5$ – $\text{C}_{40}$  *n*-hydrocarbons from spiked alumina by the SFE approached 100% ( $\text{CO}_2$  at 325 atm; extraction temperature 60°C and time 20 min). The method was also used for the determination of biomarkers (pristane and phytane) and carbon number distribution in crude oil source rocks (extraction pressure 400 bar, time 20 min, temperature 60°C, amount extracted 200 mg, on-line SFE–GC–FID).

It was shown [46] for the example of a wet sediment (20% water) contaminated by fuel, that  $\text{C}_8$ – $\text{C}_{30}$  *n*-hydrocarbons, alkylbenzene and alkyl-naphthalene isomers were removed from the sample (1.3 g) by pure  $\text{CO}_2$  (380 atm and 50°C) in 10 min completely. It is important, that the SFE is efficient also for wet samples, because lower *n*-alkanes otherwise disappear during the drying procedure. Quantitative analysis was performed using on-line SFE–capillary GC–MS with a conventional split/splitless injector. The SFE–GC coupling was achieved by inserting the restrictor (10 cm long, 25  $\mu\text{m}$  I.D.) directly into the split/splitless injector.

Pure supercritical  $\text{CO}_2$  was also found to be an

excellent fluid for extraction of diesel fuel from clay and soil [47] (similar results are also described in ref. 48). A range of hydrocarbons from  $\text{C}_{14}$  to  $\text{C}_{20}$  was monitored. The off-line SFE was performed at 314 atm and 70°C. Matrix sample size was 1 g and flow-rate of the liquid  $\text{CO}_2$  was 2  $\text{cm}^3/\text{min}$ . Up to 100 volumes of the SFE cartridge of the liquid  $\text{CO}_2$  were used for the SFE. The analytes extracted were then trapped in the small  $\text{C}_{18}$  column and after the SFE eluted with 3  $\text{cm}^3$  of methylene chloride. The eluate was analysed by GC–FID.

### 5.9. Polycyclic aromatic hydrocarbons

PAHs are one of the most troublesome group of compounds, because they are poorly soluble in supercritical fluids, especially the compounds with more condensed benzene rings (also for ordinary liquid solvents). Their recovery also strongly depends on the type of matrix. Recovery of the PAHs also usually decreases with increasing molecular mass (decreasing solubility). At matrices such as fly ash and sediments they are adsorbed very strongly and their release by a supercritical fluid is sometimes difficult to obtain complete recovery. One should take care about the type of matrix to be analysed for PAHs. For example, it was shown [42], that PAHs were not completely recovered from urban dust by  $\text{CO}_2$  at 80 atm (density 0.23  $\text{g}/\text{cm}^3$ ), whilst the SFE of glass beads spiked with the PAHs removed a significant amount of analytes.

Different solubilities of various groups of hydrocarbons in supercritical fluids can be used for removal of compounds, which could interfere during final chromatographic analysis. The SFE thus provides a certain selectivity. It was shown by Hawthorne and Miller [43], that the major portion of *n*-alkanes (nonadecane–hexacosane) was removed from diesel exhaust particulates by  $\text{CO}_2$  at 75 atm, while PAHs were not significantly extracted. The PAHs were then extracted at 300 atm with recovery mostly above 90%.

There has not been yet established an unambiguous analytical scheme for SFE of PAHs from various matrices. However, probably the best results were obtained with nitrous oxide with 5% methanol as a supercritical fluid. Recovery of PAHs using this fluid is much higher than recoveries obtained with  $\text{CO}_2$  or ethane and even higher than with  $\text{CO}_2$  with

TABLE 4  
SFE OF PAHs FROM ENVIRONMENTAL SOLIDS

Matrix, amount	Fluid	Time of SFE	Temp. (°C)	Pressure (MPa)	Conc. order	SFE setup	Ref.
Carbon black, 450 mg	CO <sub>2</sub>	Static 5 min	50	32.8	µg/g	On-line	27
Urban dust, 6 g	CO <sub>2</sub>	4 h	40	36.2	µg/g	Off-line	31
Sediment, 10 mg	N <sub>2</sub> O	10 min	45	30.6	µg/g	On-line	32
Urban dust, 15 cm <sup>3</sup> SFE cell	CO <sub>2</sub>	Static and 1 min dynamic	50	20	µg/g	On-line	42
Dust, 5–30 mg	CO <sub>2</sub>	90 min	45	30.6	µg/g	Off-line	43
	CO <sub>2</sub> -CH <sub>3</sub> OH	30 min	65	30.6	µg/g	Off-line	43
Dust, sediment, fly ash, 20–50 mg	Ethane, N <sub>2</sub> O, CO <sub>2</sub> , N <sub>2</sub> O-CH <sub>3</sub> OH	30 min	45–65	30.6	µg/g	On-line	44
Petroleum waste sludge, 310 mg	CHClF <sub>2</sub>	40 min	100	40	µg/g	Off-line	49

5% methanol [44]. It is probably due to higher polarity of the nitrous oxide-methanol and resulting higher solubility of the PAHs in this fluid. Typical conditions which were used for the SFE of PAHs from various matrices are given in Table 4.

A very promising supercritical fluid for the SFE of PAHs is difluorochloromethane (freon-22) [49]. It has been recently shown that extraction rates of individual PAHs from a petroleum sludge were similar with freon-22, whilst the rates decreased with increasing molecular mass using CO<sub>2</sub> and nitrous oxide. The SFE with difluorochloromethane for 40 min was much more efficient than methylene chloride sonication for 18 h, especially for higher PAHs. Also trifluoromethane provides good recoveries of PAHs from soil [50].

#### 5.10. Linear alkylbenzenesulphonates

Quantitative extraction of anionic surfactants from soil, sediment, and municipal waste water treatment sludge was achieved by supercritical CO<sub>2</sub>, whose polarity was increased by high content (*ca.* 40 mol%) of methanol [51]. Recovery of alkylbenzenesulphonates was higher than 90% after 30 min of the SFE at 380 atm and 125°C. Amount of the sample extracted was usually 1 g. Flow of the extraction fluid through the extraction cartridge was 1.2 or 0.45 cm<sup>3</sup>/min, using 10 cm lengths of either 30 or 25 µm I.D. fused-silica tubing as a restrictor. The compounds extracted by the SFE were collected in a vial containing 5 cm<sup>3</sup> of ethanol. For the recovery

measurement <sup>14</sup>C-labelled compounds were used. The native alkylbenzenesulphonates were analysed by HPLC with fluorescence detector. The off-line SFE apparatus used comprised a simple vessel for the preparation of high content of polarity modifier in the supercritical fluid.

#### 5.11. SFE of organic compounds from adsorbent materials

SFE can be also used for extraction of organic compounds from Tenax, XAD resins, reversed-phase based sorbents, charcoal or polyurethane foams after previous enrichment of organic compounds from water, air, etc.

It was shown [43] that PAHs can be effectively removed from Tenax by CO<sub>2</sub>: 80 mg of Tenax, which was used for enrichment of PAHs from diesel exhaust, were extracted by CO<sub>2</sub> at 45°C and 20 MPa for 5 min. Naphthalene, 9-fluorenone, phenanthrene, pyrene, benz[*a*]anthracene, benzo[*ghi*]perylene and coronene provide recoveries higher than 90%. Similar results were obtained for XAD-2 resin and polyurethane foam [52]. On the other hand, PAHs were not recovered from Sphero carb. However, nor was Soxhlet extraction successful in this case [52].

SFE was also used for determination of semi-volatile mutagens in air using solid adsorbents [53]. Adsorbents (finally XAD-4 resin was utilised), which were used for the trapping of the mutagens from air, were extracted by pure and entrainer-modified car-

bon dioxide. Mutagens, such as 4-nitrobiphenyl, 2-nitrofluorene and fluoranthene, were recovered from the XAD-4 trap in 180 min with efficiency 88.5, 92.3 and 60.6%, respectively, by using CO<sub>2</sub> with 12% of hexane at 400 atm and 50°C [53].

Chlorinated benzenes (tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene) can be isolated from water by solid-phase extraction (Amberlite XAD resins, Tenax GC and reversed-phase HPLC C<sub>18</sub> were used). The analytes can be, after drying of the sorbent by means of a stream of nitrogen at 60°C, released from the adsorbent material by supercritical fluid extraction. In this work [25], carbon dioxide with 10% of methanol at 400 atm and 60°C was used. The restrictor used was a piece of 20 µm I.D. fused-silica capillary. Time of the SFE was 45 min. Overall recovery of chlorobenzenes was over 97% for their concentration of 1 µg/dm<sup>3</sup> in water.

Sulphonyl urea herbicides can be isolated from water samples by solid phase extraction [54]. The analytes were then eluted from the extraction disk by SFE using 5% methanol + CO<sub>2</sub>. For the final analysis HPLC–UV (235 nm) was used. Compounds tested were: sulphachloropyridazine, thifensulphuron methyl, metsulphuron methyl, sulphometuron methyl, chlorsulphuron, tribenuron methyl, benz-sulphuron methyl and chlorimuron ethyl. Recovery of the herbicides was mostly higher than 80%. Only tribenuron methyl and chlorimuron ethyl had recoveries lower than 80%. Recoveries were measured for 1 dm<sup>3</sup> water sample and concentration level 50 µg/dm<sup>3</sup>.

Solid-phase extraction with SFE elution was also tested for analysis of explosives in water [55]. 2,6-Dinitrotoluene, 2,4-dinitrotoluene, and trinitrotoluene were adsorbed on phenyl stationary phase. After the nitrotoluenes were trapped on the solid sorbent, they were eluted by supercritical CO<sub>2</sub>. Before the SFE, the sorbent was doped with toluene. After the off-line experiments, on-line SPE–SFE–GC–ECD was used for analysis of water samples. Recovery of the SFE (400 atm, 75°C) achieved 100%. The method was tested for low µg/dm<sup>3</sup> and ng/dm<sup>3</sup> levels.

### 5.12. Direct SFE of organics from water solutions

There are several problems associated with the

SFE of compounds from water solution. Probably the main problem is relatively high solubility of water in the supercritical CO<sub>2</sub> (approximately 0.3% [56]). For a dynamic SFE, which is commonly used for the extraction of solids, the removal of water phase and enrichment of the supercritical fluid by water can cause “principal” (the water phase is transferred through the restrictor into the collection vessel or accumulator in off-line methods; and/or would enter the chromatographic system, which is not desirable in most cases) and technical (plugging of the restrictor by ice during the supercritical fluid expansion) problems. The problems have been recently partly solved, but the present state-of-art of the SFE of organics from water is not as acceptable for routine analysis as the SFE of environmental solids.

The first papers about the SFE of water samples probably appeared in late eighties [11,57]. The first method [11] is based on “closed-loop stripping” principle, when the supercritical fluid is (after pressurising of the system) recycled by a pump from the outlet of the extraction cell back into the water sample. After equilibrium in the whole system is achieved, a sample of the supercritical phase is taken by means of a valve with loop. The content of the loop is then analysed by supercritical fluid chromatography.

The system described above was tested for analysis of diisopropyl methylphosphonate (concentration 834 µg/dm<sup>3</sup>–834 mg/dm<sup>3</sup>) in water. Volume of water sample was 8 cm<sup>3</sup>. Time necessary to reach the equilibrium was 1.5 h. When 0.1 mg of NaCl was added to the water sample before the extraction, the equilibrium time was reduced to less than 5 min. The relative standard deviation was 15% for concentration 834 µg/dm<sup>3</sup> and 1.5% for concentration higher than 8.34 mg/dm<sup>3</sup>. The method was also used for SFE of phenol from aqueous solutions [58].

The other system [57] is based on a sandwich type phase separator, in which supercritical CO<sub>2</sub> and water phase, after passing extraction coil, are separated by means of a hydrophobic membrane. Two membranes were able to withstand higher pressure: PVDF [(-CH<sub>2</sub>-CF<sub>2</sub>-)<sub>n</sub>] and Delrin [(-CH<sub>2</sub>-O-)<sub>n</sub>]. A sample of the separated supercritical fluid was taken by a valve with loop for SFC analysis. Phenol and 4-chlorophenol were utilised as test compounds.

Water solutions can be also extracted by a super-

critical fluid when a smaller amount of water is added to the inert material (sand, glass beads, etc.). The film of the water phase on the surface of the carrier material can be subjected to SFE. In this case the restrictor has to be attached in the upper part of the extraction chamber, to prevent liquid water entering the restrictor. This method was used for the SFE of phenol from water [45].

### 5.13. Simultaneous SFE and derivatisation

The *in-situ* derivatisation of the polar compounds is quite challenging. Under the SFE conditions (especially at higher pressures) the derivatisation reactions of highly polar compounds could take place easily [59,60], resulting in less polar products, which are more suitable for the SFE and subsequent chromatographic analysis.

An interesting paper has been recently published by Hawthorne and co-workers [45,61]. For the derivatisation of polar compounds (2,4-dichlorophenoxyacetic acid and Dicamba, phospholipid fatty acids in the whole cells and phenolics in waste water) trimethylphenylammonium hydroxide and boron trifluoride in methanol were used. The procedure consists of four steps: (1) the sample is placed into the extraction cell together with the derivatising reagent, (2) the cell is placed into the heater and pressurised by CO<sub>2</sub> to 400 atm, (3) the derivatisation takes place for 5–45 min under static conditions (the outlet of the extraction cell is closed), and (4) the outlet of the cell is opened and the sample is extracted dynamically for 5–15 min. Derivatised compounds —methyl esters and/or anisoles— were trapped at the outlet of the restrictor into a small amount of methanol or dichloromethane. The solutions were analysed by GC–FID, –ECD and –MS. Recovery for all compounds is >90%.

*In-situ* derivatisation–SFE was also used for acetylation of phenols isolated by solid-phase extraction from water samples [62]. The pH value of the water sample was adjusted to 12. The water sample was then passed through the conditioned anion-exchange disk. Anionic form of the phenols was thus trapped in the exchanger. After the solid-phase extraction, 0.5 cm<sup>3</sup> of acetic anhydride was added and the derivatisation to the acetylated phenols took place under the static SFE conditions (400 atm, 50°C). After the derivatisation, the phenolic acetates

were eluted with 30 cm<sup>3</sup> of supercritical CO<sub>2</sub>. The SFE extract was trapped in 2 cm<sup>3</sup> of acetone and analysed by GC–MS. Recovery of all phenols tested (2- and 4-nitrophenol and 1-naphthol) was higher than 75% at 25–50 µg/dm<sup>3</sup> level. Total time for the derivatisation–SFE was about 30 min.

## 6. CONCLUSIONS

Supercritical fluid extraction is rapidly becoming an important technique in the preparation of samples for analysis. Much of the work published is related to environmental problems. It has been shown to be rapid, less laborious and usually less toxic and hazardous but more environmentally friendly than liquid extraction.

A problem remaining with this technique is the effect of the matrix on extraction. This can sometimes result in a large fraction of the solute being slowly extracted after a rapid initial extraction. Further efforts are required in the understanding of this phenomenon and in the development of techniques to overcome it.

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