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Supercritical Fluid Extraction (SFE) in Environmental Analysis

Total extraction and study
of pesticide retention in soil

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Abstract

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This thesis deals with the use of supercritical fluid extraction (SFE) in environmental analysis. Traditionally SFE in environmental analysis has been used for quantitative extraction. In this thesis, quantitative extraction as well as other applications of SFE will be discussed.

Studies of SFE extraction efficiency of pesticides from water and soil matrices were performed. Solid phase extraction (SPE) with Empore discs and bulk sorbent in combination with SFE, showed promising results for extraction of pesticides from water samples. With the bulk sorbent, it may also be possible to design effective extraction procedures for specific target analytes, using sorbents with different chemical properties. Sulfonylurea herbicides were extracted from soil with the objective to develop a general SFE procedure for sulfonylureas. The results showed that optimized SFE methods cannot always be directly applied to similar compounds without further method development.

The possibility to fine tune the selectivity of SFE were used for pesticide retention studies on model matrices and soils. Investigation on model matrices with well known properties (sand and silica) gave valuable information for further studies on binding mechanisms. The purpose of such studies would be to characterize different interactions that determine the behaviour of pesticides in complex matrices such as soils. Extraction of soils under moderate SFE condition, *i.e.* nonquantitative extraction, allows the interaction between soil and analyte to influence the recovery. This is useful for pesticide retention studies. The results indicate that nonquantitative extraction can be used to study the relative strength of different types of sorptive sites. The use of SFE to determine pesticide sorption coefficients (K_d) in field-moist soil has the potential to yield better information to model the fate of pesticides in the field than sorption coefficients characterized by traditional batch-slurry techniques.

Keywords: environmental analytical chemistry, pesticides, SFE, soil retention, supercritical fluid extraction

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Papers discussed

This thesis is based on the following papers, which are referred to by their roman numbers.

- I. Solid-phase extraction of pesticides from surface water using discs, bulk sorbents and supercritical fluid extraction (SFE).
Bengtsson, S., Berglöf, T., Granat, S. and Jonsäll, G.
Pestic. Sci. **41** 55-60 (1994).
- II. Supercritical fluid extraction of metsulfuron methyl, sulfometuron methyl, and nicosulfuron from soils.
Berglöf, T., Koskinen, W. C. and Kylin, H.
Intern. J. Environ. Anal. Chem., in press.
- III. Selectivity in supercritical fluid extraction (SFE). Recovery of pesticides from model matrices.
Berglöf, T., Jonsäll, G. and Markides, K. E.
Manuscript. *J. Chromatography*, submitted
- IV. Predicting the leachability of pesticides from soils using Near Infrared Reflectance.
Bengtsson, S., Berglöf, T. and Sjöqvist, T.
J. Agric. Food Chem. **44** 2260-2265 (1996).
- V. Metsulfuron methyl sorption-desorption in field moist soils.
Berglöf, T., Koskinen, W. C., Norberg, K. and Kylin, H.
J. Agric. Food Chem., submitted.

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1 Introduction

The intentional and unintentional dissemination of toxic xenobiotic compounds, such as pesticides, industrial chemicals and combustion products, into the environment has aroused much public and scientific concern over the possible environmental impact and/or health effects. To resolve some of the questions involved, chemical groups, such as polycyclic aromatic hydrocarbons (PAH) and agricultural pesticides, may be included in national monitoring programmes, necessitating hundreds of substances to be measured in a wide range of samples. The efficient handling of these samples is a major challenge to the community of practicing analytical chemists.

Monitoring of residues of pesticides and other substances of environmental interest is costly, time consuming and, in itself, an activity with potentially deleterious environmental impact. Large amounts of "ultra-pure" organic solvents and other reagents are used in the extraction, cleanup and detection of pollutants in environmental and food samples. Traditional extraction and work-up procedures such as soxhlet and liquid-liquid extraction are expensive not only due to the high cost of solvents and reagents, but also due to the labour costs involved. Furthermore, traditional techniques generate hazardous chemicals to be emitted to the environment and work-health problems. Thus, top priority must be given to improvement of analytical procedures to decrease the use of organic solvents, reduce analysis time and cut analytical costs. To meet these goals, several new techniques are pursued in the pesticide residue laboratories.

An promising alternative is supercritical fluid extraction (SFE), with the main advantages being the replacement of organic solvents with environmentally acceptable supercritical fluids such as carbon dioxide (CO₂), high efficiency (high recovery and short extraction time), and high selectivity in the extraction process. SFE is presently gaining increasing acceptance as an alternative to more conventional extraction procedures (Bøwadt and Hawthorne, 1995; Camel et al., 1993; Hawthorne, 1990; Janda et al., 1993).

Traditionally, the primary uses of SFE in environmental analysis has been for quantitative extractions. In this thesis, quantitative extractions as well as other applications of SFE will be discussed.

1.1 Objective

The aim of the studies presented in this thesis was to

- (a) investigate fundamental principles of extraction with supercritical fluids (SFE),
- (b) study the potential of SFE as an extraction technique in environmental analysis (**Papers I-II**).
- (c) use SFE for studies of pesticide retention in model and soil matrices (**Papers III-V**).

2 Supercritical Fluids

A substance reaches its supercritical state above the critical point, i.e. when the pressure is above the critical pressure P_c and the temperature is above the critical temperature T_c of the particular substance, (Figure 1).

At the critical point, the densities of the two phases become identical and the distinction between gas and liquid disappears, the substance becomes a supercritical fluid. The fluid is neither a gas nor a liquid but possesses properties of both. Viscosity is low and diffusivity is high as for a gas, while the solvating power is liquid-like.

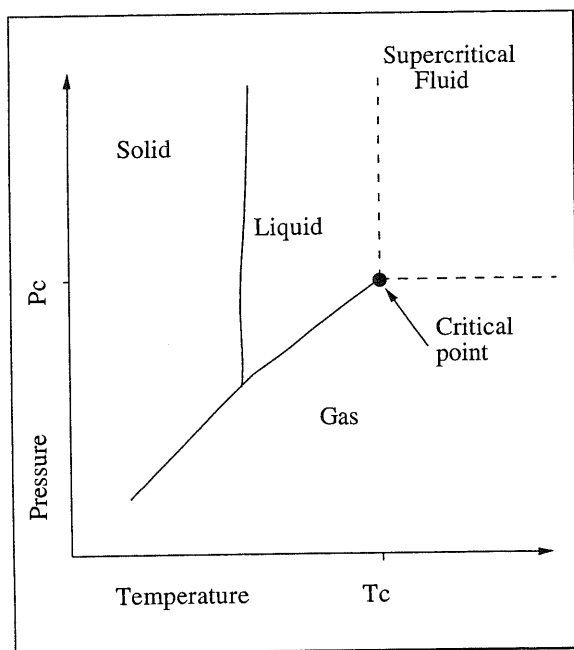


Figure 1. Phase diagram of a substance.

Using supercritical fluids for extraction provides several advantages. The solubilizing power, and thus the selectivity, can be adjusted in SFE by varying the density (i.e. pressure and temperature) of the supercritical fluid. This selectivity of the SFE process offers considerable advantages, such as cleaner extracts than liquid solvent extraction which frequently contain large amounts of matrix organics. This reduces the need for cleanup and facilitates quantification of target analytes. Excluding a cleanup step minimizes both the analysis time and the number of error sources (Papilloud and Haerdi, 1994).

A number of compounds has been used as supercritical fluids in SFE applications: CO_2 , N_2O , NH_3 , SF_6 , chlorofluorocarbons (CFCs, "freons") (Lee and Markides, 1990), and recently even water (Hawthorne et al., 1994). Most of them have some kind of disadvantage, such as being reactive, toxic, explosive or expensive or having high critical temperature and/or pressure.

The most frequently used extraction fluid is supercritical carbon dioxide CO_2 . CO_2 has relatively low critical pressure and temperature, low toxicity and reactivity, and can be obtained in high purity at low cost. CO_2 is an excellent extraction medium for nonpolar analytes, reasonably good for moderately polar analytes, while the solubility of polar analytes is poor but can be enhanced by addition of modifiers.

3 Supercritical fluid extraction

3.1 The SFE process

The SFE process involves three steps (Hawthorne et al., 1993).

1. Extracting the analytes out of the matrix and into the supercritical fluid.
2. Moving the solution of supercritical fluid with extracted analytes away from the extraction cell.
3. Collection of the extracted analytes by removing the supercritical fluid.

It is important in particular to understand the first step, the breaking of bonds between matrix and analyte. Three interrelated factors influence recovery of the extraction step. Knowledge about these factors, diffusion (analytes must be transported sufficiently rapidly from the matrix by diffusion), solubility (analytes must be sufficiently soluble in the supercritical fluid) and the matrix constitution, is necessary to obtain a better understanding of the extraction process. The second step is dependent on factors such as fluid flow and sample size. The third step depends mainly on instrumental factors such as the restrictor and collecting system.

Several theoretical models for the SFE process have been discussed (McNally, 1995).

King (1989), discussed a method for predicting optimum SFE conditions for analyte solubility, including four basic parameters.

1. Miscibility pressure (pressure where the solubility starts, threshold pressure).
2. Pressure at which the analyte reaches its maximum solubility in the supercritical fluid.
3. Pressure region between miscibility and maximum solubility pressures (pressure range for fractionation of the sample).
4. Knowledge about the analytes physical properties.

In general, supercritical fluids are more effective extraction agents at temperatures above the melting point of the analyte. These principles can be used in method development.

Pawliszyn (1993), suggested a model based on mass transfer kinetics, where the matrix particles are assumed to consist of an organic layer on an impermeable core, and the analyte is adsorbed onto the core surface. The analyte must first be removed from the matrix into the supercritical fluid, and then be swept from the extraction cell (compare chromatographic elution). One or both of these processes can be slow and rate determining. (see also section 3.5.7, *Flow*). Several factors are included in the model (desorption kinetics, swelling, analyte diffusion in the organic component of the sample, and fluid/matrix distribution coefficients) that could potentially contribute to slow extraction rates. The model was used to describe extraction differences between native and spiked samples (Langenfeld et al., 1995).

Bartle and Clifford, developed several ideal case models, and assumes that the matrix particles all are spherical and of the same size, the analyte is uniformly distributed throughout the matrix, the flow-rate is rapid enough so that the concentration of the analyte is close to zero, and that the analytes move through the matrix by a process similar to diffusion (Clifford et al., 1995).

The models consists of four steps (Figure 2).

1. Rapid supercritical fluid entry into the matrix.
2. Reversible release process (sorption/desorption).
3. Transport by diffusion or otherwise to the edge of the matrix particle.
4. Removal by solvation in the fluid.

Different models involve some or all of these processes. In the first model (hot-ball) only process 3 was considered to be slow and rate determining (Bartle et al., 1990). Model 2 involves both process 3 and 4 to be rate determining (Clifford, 1993). In the latest model, processes 2, 3 and 4 are all considered to be rate determining (Clifford et al., 1995). The models have been used to

compare experimental SFE data with theoretical data in an attempt to further understand the SFE process. Influence of parameters such as desorption, readsorption, rate of diffusion and solubility on the extraction process have been studied.

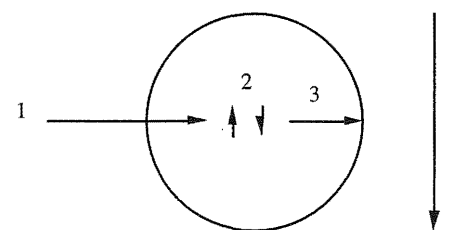


Figure 2. A model for SFE.

3.2 Applications

SFE have been exploited for quantitative extraction of organic compounds such as pesticides, from a variety of environmental matrices (Barnabas et al., 1994; Stuart et al., 1996). Several investigations have been published regarding the use of SFE for the analysis of organophosphorous and organochlorine pesticides (Lopez-Avila et al., 1990; Snyder et al., 1993), triazine herbicides (Robertson and Lester, 1994; Steinheimer et al., 1994), phenoxyacetic acids herbicides (Lopez-Avila et al., 1993; Rochette et al., 1996), phenylurea herbicides (Robertson and Lester, 1994), and sulfonylurea herbicides (Berdeaux et al., 1994; **Paper II**).

Systematic optimization of instrumental parameters and physical/chemical variables are necessary to establish quantitative and reproducible extraction procedures. There are many experimental variables which may affect SFE efficiencies: analyte concentration and type, collection method, extraction cell size, dimensions and dead volume, extraction fluid, extraction time, modifier type and concentration, pressure/density, restrictor type, sample (amount, particle size and moisture), static/dynamic extraction, temperature, total volume of extraction fluid.

Instrumental variables, matrix related variables, and SFE parameters will be discussed in the following sections (3.3-3.5).

3.3 Instrumentation

A pump is used to supply a supercritical fluid of a known pressure to the extraction cell. The critical temperature of the fluid is attained by placing the cell in an oven. A restrictor maintains the pressure in the system and allows transport of fluid to the collection vial (Figure 3).

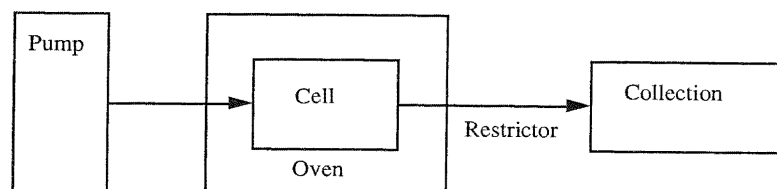


Figure 3. SFE instrument.

Two main types of extraction can be performed, static and dynamic extraction. Usually a period of static extraction is followed by dynamic extraction, during which time the analytes are collected. The restrictor is closed during the static extraction step. A period of static extraction is necessary to allow the modifier or reagent to equilibrate and interact with the sample if a modifier is added directly into the extraction cell.

SFE can be performed either off-line or on-line. Off-line extractions, where the analytes are collected in a vial, yield extracts that can be further concentrated, diluted, cleaned and analyzed. SFE in an on-line system e.g., coupled to an analysis instrument such as a gas chromatograph (GC) or a supercritical fluid chromatograph (SFC), constitutes both an extraction technique and injection system for further analysis (cleaning, separation or detection). Only off-line applications were studied in the present work.

Extraction cell dimensions may affect the extraction rate because of turbulence effects. Cylindrical extraction cells are normally used for SFE. If the volume of the cell is larger than that of the sample, the remaining volume should be filled with an inert material such as sand. Decreasing the dead volume in this way will improve extraction efficiency (Hawthorne et al., 1993).

Sometimes a precipitate will clog the restrictor. Methods to prevent restrictor clogging were investigated by Burford et al. (1992). Heating the entire length of the restrictor to 50-250 °C, can eliminate the restrictor clogging problem (Porter et al., 1992). SFE of high sulphur containing samples such as soils and sediments can cause restrictor clogging by extracted elementary sulphur.

Addition of copper powder has been shown to solve this problem (Bøwadt and Johansson, 1994). However, organic analytes which contain sulphur may not survive this copper treatment (Tilio et al., 1994). The copper powder should be placed at the outlet of the cell (rather than being mixed with the sample) to obtain higher recoveries of sulphur containing analytes (Peterson, M., Swedish University of Agricultural Sciences, personal communication). Extraction of sediment samples with heated restrictor (80 °C), but without the addition of copper powder was impossible, due to almost immediate restrictor clogging (Johansson et al., 1995).

3.4 Sample and sample preparation (the matrix)

3.4.1 Sample pretreatment

Pretreatment of the sample is important, since such factors as sample condition, sample size, particle size and shape, all have an influence on the extraction performance. A correlation between matrix swelling and extractability was shown by Fahmy et al. (1993). They hypothesized that water acts as swelling agent for the matrix, while other modifiers such as methanol act as solubilizing agents for the analytes once the matrix is swelled.

3.4.2 Moisture

The water content of the sample can influence the extraction behaviour in either a positive or negative manner. Low amounts of water can act as a modifier and enhance the recovery. Low water contents (1-2%) may also be advantageous by covering sorptive sites on the matrix (Burford et al., 1993a). Higher amounts of water often complicates the extraction process, since water is immiscible with or poorly soluble in most extraction fluids, or can cause restrictor plugging, thus necessitating the use of a drying agent. Snyder et al. (1993), showed a dramatic increase in polar organophosphorous pesticides recoveries at moisture contents greater than 10%, probably due to limited solubility of water in the supercritical fluid, and a formation of a two phase system, while 5% moisture increased the recoveries. Sorption sites on the solid matrix might also be removed by moisture (Yarita et al., 1996). Recoveries decreased (higher sorption coefficients) when soil moisture content was increased from 11 to 17% (Paper V). An alternative to using a drying agent is drying the sample prior to extraction. However, drying the sample can lead to losses of even relatively non volatile analytes, and mixing with a drying agent is often a better alternative.

3.4.3 Drying agents

Examples of drying agents used in environmental analysis are, Hydromatrix (pelletized diatomaceous earth) which adsorbs twice its weight of water (Hopper and King, 1991) and magnesium sulphate (Reimer et al., 1995). Burford et al. (1993a) suggested that the drying agent should be placed at the outlet of the cell

(rather than being mixed with the sample) to obtain highest recoveries of volatile species while avoiding restrictor plugging. They also showed that some drying agents could selectively retain certain analytes.

3.4.4 Spiking

During methods development or testing of environmental parameters, it is often necessary to create artificial samples by addition of the analytes to a sample matrix. These spiked (fortified) analytes can not interact with the same type of active sites in the matrix as do analytes in authentic samples. Spiked analytes are situated on the surface of sample matrices and have little time to migrate to strong binding sites. Natively introduced pollutants have often been in contact with the matrix for long times and have the potential to be associated with much stronger binding sites than recently spiked chemicals (Burford et al., 1993b). Therefore, SFE conditions developed with spiked samples often yield poor recoveries from authentic samples.

Spike recovery studies are best used to evaluate the collection efficiencies of an extraction method, and should not be used to determine quantitative extraction conditions (Hawthorne et al., 1993). Different spiking techniques are described in the literature. In the spot spiking method a small volume of standard is added directly to the sample in the extraction cell prior extraction. For the simulation of real samples slurry spiking methods are used, where the sample is mixed with a solution containing the standard, and the solvent is then evaporated prior extraction.

The uses of radiolabeled compounds (^{14}C) throughout the experiments provide a simple method to test the extraction procedure by determining the losses at each extraction step with scintillation counting. It also facilitates investigations of bound residues and pesticide retention in soil, where low amounts of pesticides are measured.

A spiking method used in **Paper IV** involved mixing of the soil samples with water prior to the addition of spiking solution. Water was added in order to hydrate active sites in the soil matrix, thus allowing the analytes to distribute evenly over the soil and interact with active sites in the matrix.

To mimic naturally occurring pesticide binding to soils, fortified soil samples were prepared by spraying a pesticide solution on a soil sample. The samples were aged for two months at 20 °C under daily irrigation. This way, the pesticides were expected to bound to the soil matrix by mechanisms occurring under natural conditions (Berglöf et al., 1997).

3.4.5 Water samples

Extraction of analytes from water samples usually involves trapping the analytes on solid phase extraction (SPE) media, such as SPE cartridges (Furton and Lin, 1993), discs (Howard and Taylor, 1992; **Paper I**) or bulk sorbents (**Paper I**), prior to extraction with supercritical fluids. SFE of Empore discs was found to be more effective than elution with ethyl acetate (established SPE procedure, Hagen et al., 1990). Furthermore, SFE gave more reproducible results than ethyl acetate elution (see table 1 and 3 in **Paper I**). Solid phase extraction (SPE) with Empore discs and bulk sorbent in combination with SFE, showed promising results for extraction of pesticides from water samples. With the bulk sorbent, it may also be possible to design effective extraction procedures of specific target analytes, using sorbents with different chemical properties (**Paper I**).

3.5 Important SFE parameters

3.5.1 Fluids

Different extraction fluids were investigated by Hawthorne et al. (1992a). Carbon dioxide, methanol modified carbon dioxide, N_2O and Freon-22 (CHClF_2), were used for extraction of PAHs and PCBs from environmental samples, and the results showed that Freon yielded the highest recoveries and pure carbon dioxide the lowest, probably due to the high dipole moment of Freon-22. However, the use of CFCs (freons) is not recommended because of their negative effect on the environment. Sulphur hexafluoride (SF_6) is a very nonpolar molecule and can selectively extract aliphatic hydrocarbons from a mixture of both aliphatic and aromatic hydrocarbons (Levy et al., 1991). The use of N_2O should be avoided due to its strong oxidizing properties and risk of explosions even under mild SFE conditions (Raynie, 1993). Carbon dioxide cylinders are often pressurized with a helium headspace. The carbon dioxide can, therefore, contain a small amount of helium which reduces the solubilizing power of the supercritical fluid (King et al., 1995).

Supercritical water has extremely high solubilizing power and the supercritical temperature and pressures are high (374 °C, 218 atm). All these properties makes it instrumentally difficult to use supercritical water for extraction purposes. However, subcritical water has been shown to be an effective fluid for the extraction of several classes of environmental pollutants (Hawthorne et al., 1994).

3.5.2 Modifiers

Since CO₂, the most common extraction fluid, is relatively nonpolar, addition of a polar modifier to the extraction fluid or sample can increase the solubility (modifier-analyte interactions) of polar substances and increase the ability of the supercritical fluid to displace analytes from matrix active sites.

Modifiers frequently used include, alcohols, acetone, water, ethyl acetate (Lee and Markides, 1990). Modifiers can be added by including a small amount of modifier when filling the fluid delivery system or with a separate modifier pump. The modifier can also be added directly to the sample in the extraction cell, and in this case, a static extraction step must be performed to allow the modifier to be distributed in and contact the sample properly.

Different types and concentrations of modifiers were investigated by Langenfeld et al. (1994). For many environmental analytes, a low concentration of modifier (1%) is as effective as a higher concentration (10%), indicating that the modifier acts by competing with the target analytes for the active sites on the sample matrix (modifier-matrix interactions) rather than increasing analyte solubility (Langenfeld et al., 1994). Modifier identity generally had a larger impact on the extraction efficiency than did the concentration of the modifier. Addition of a modifier can swell the matrix, and thereby expose internal structures of the matrix to the supercritical fluid, increasing extraction rates (Fahmy et al., 1993).

One drawback is that the use of modifiers generally produces dirtier extracts than does pure carbon dioxide, due to co-extraction of the matrix. This often necessitates additional clean up steps prior to analysis.

Effects of modifier addition on the recoveries of pesticides added to silica was studied. The results showed good correlation of extraction efficiency with the polarity of investigated compounds (Figure 4). The most water soluble analytes could not be extracted at all without addition of modifier (**Paper III**).

3.5.3 Derivatization

The extraction efficiency of polar analytes such as phenoxy acetic acids (Hawthorne et al., 1992b; Lopez-Avila et al., 1993) can be increased by addition of a derivatization agent to the sample prior to SFE. Extraction efficiency of nonderivatizable analytes can be increased by reducing the polarity of the matrix sorption sites, thus facilitating the release of sorbed analytes (Hills and Hill, 1993).

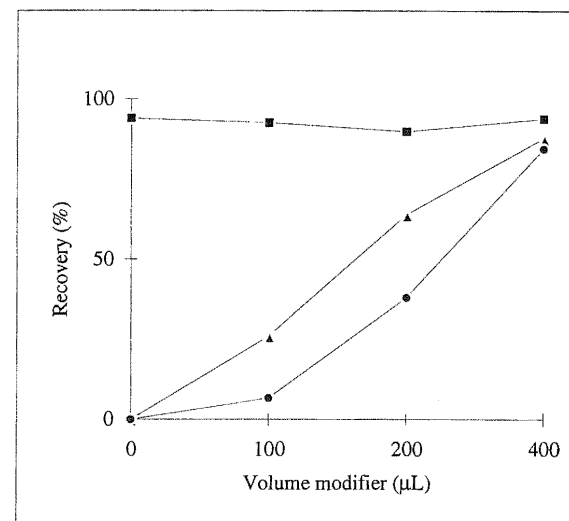


Figure 4. Effect of methanol addition on the recoveries of pesticides extracted from silica. ■=lindane (0.007) ▲=dimethoate (24) ●=hexazinone (33) (water solubility, g/L, Tomlin, 1994)

3.5.4 Pressure

Pressure and temperature are among the most important physical parameters in SFE, and together they determine the density of the supercritical fluid.

Instrumental characteristics and the influence of five basic variables (temperature, pressure, extraction time, static/dynamic extraction, restrictor i.d.) were investigated and pressure and temperature could be identified as key parameters (Berglöf and Jonsäll, 1993). These results correspond to results obtained by other investigators (Ho and Tang, 1992; Kane et al., 1993).

3.5.5 Temperature

SFE at higher temperatures has been investigated by Hawthorne and Miller (1994). High temperatures can be important for the release of analytes which interact strongly with the sample matrix. Positive effect of increased temperature probably results from an increase in volatility and/or an easier desorption of the solute molecules from the active sites of the matrix (Camel et al., 1995).

Johansson et al. (1995) studied optimization of SFE conditions and the effect of temperature and pressure on the recoveries of ionic alkyllead compounds from spiked sediment samples. The recoveries increased for trimethyllead at higher temperatures, with similar results being observed for the ethyllead compounds. This indicates easier desorption of analytes with increasing temperature (Camel et al., 1995).

3.5.6 Density

Solvent strength of a supercritical fluid is directly related to its density (Giddings et al., 1968): $\delta = 1.25 P_c^{1/2} (\rho_g / \rho_l)$

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 phase.

SF-Solver (Software from Isco) equates the solvent polarity (strength) of a supercritical fluid via the Hildebrand solubility parameter. Solubility of a substance in a supercritical fluid is affected by volatility of the substance and the solvating power (which is a function of fluid density) of the supercritical fluid (Clifford, 1993).

Pesticides adsorbed to silica and extracted at various densities of supercritical carbon dioxide showed a pronounced density dependent recovery (Figure 5). None of the pesticides can be extracted quantitatively from silica at the lowest density (0.25 g/mL). Probably due to hydrogen bonds between the analytes and the matrix, addition of a modifier was necessary to break the bonds (**Paper III**).

Similar results with density dependent recoveries were obtained for extraction of metsulfuron methyl from soils (**Paper II**).

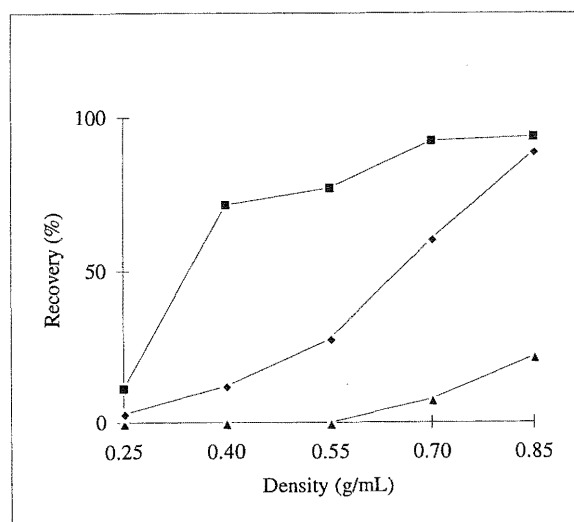


Figure 5. Solubility profiles of pesticides extracted from silica, varying the density of supercritical carbon dioxide at 55 °C. ■=lindane, ◆=parathion-methyl, ▲=linuron.

3.5.7 Flow

Extractions performed with varying flow rates can give information about the limiting process in SFE. If changing the extraction flow rate changes the extraction rate proportionally, then the extraction is primarily limited by analyte solubility and chromatographic retention of analytes on active sites in the matrix. Samples that are controlled by the kinetics of the initial transport of bound analytes from the matrix into the extraction fluid, show no changes in extraction rate with varying SFE flow rate, and large samples will be extracted at a similar rate as a smaller sample (Hawthorne et al., 1993).

3.5.8 Time/Volume fluid

Extraction time or volume of a supercritical fluid (often expressed as numbers of cell volumes) used during the extraction are important parameters, because the recoveries are volume dependent. Numbers of cell volumes needed for quantitative recovery is highly dependent on the matrix-analyte pair. The bulk of the analytes usually elutes during the first part of the extraction.

3.5.9 Collection

The collection step should always be optimized before investigation of other SFE parameters, otherwise poor trapping efficiency could easily give the impression that the extraction is incomplete. Analytes extracted in off-line SFE can be trapped in a solvent or on an adsorbent. Significant losses of analyte can occur during the collection step. Various collection solvents with different solvent polarity and temperature have been investigated (Langenfeld et al., 1992). The results showed that solvent properties, including polarity and temperature are more important than solvent volume in obtaining minimum analyte losses.

Losses that occur with collection in a liquid solvent may occur both because a particular analyte molecule is never trapped in the solvent, or because trapped molecules are purged from the collection solvent by the high gas flow of the depressurized extraction fluid (Langenfeld et al., 1992). Collection solvent temperature, as well as volume influence trapping of the extracted analyte (Porter et al., 1992).

A trapping study involving two collection modes (I and II) was performed by Johansson *et al.* (1995). One vial was used in mode I, while two collection vials in series were used in mode II. The first vial was sealed with a septum, the restrictor outlet being immersed below the surface of the collection fluid. A capillary protruded into the headspace above the collection fluid in the first vial, and into the solvent in the second open-top collection vessel. When using collection mode II, recoveries in the first vessel were good and no analytes could be detected in the second vessel. However, when using collection mode I,

recoveries decreased at higher densities, owing to poor trapping efficiency and losses from the collector at the higher decompressed gas flow rates. For example, the recovery for trimethyllead decreased from 95 to 40% when extracted at 0.85 g/mL.

Octadecylsilane-bonded (C-18) silica was used as a trapping material in the study presented in **Paper II**. Extractions were performed with modifier (methanol, 4% w/w). Recoveries were shown to be time dependent, but a decrease in extraction recovery could be found after longer extraction times, probably due to poor trapping efficiency and losses of analytes from the trapping sorbent by methanol rinsing during extraction. Methanol becomes a liquid when the pressure drops and can itself rinse analytes from the sorbent trap (Mulcahey and Taylor, 1992). No traces of analytes could be found in the second methanol filled trap. The methanol trap was checked for losses due to purging by adding metsulfuron methyl directly to the solvent, followed by a 30 minutes extraction (of thimble filled with soil) under normal conditions, the results showed no losses due to purging and it , therefore would seem that the analyte was transported out of the sorbent trap in a form that could not be trapped by the liquid trap. Burford et al (1992) showed that most of the loss of analytes during the collection step depends on poor trapping in the liquid, not purging of trapped analytes away from the liquid. A third trap containing methanol, dichloromethane or water as collecting solvents was connected to the second trap, but no traces of analyte could be found in the solvent. This trapping problem was circumvented by using a lower modifier concentration (2%, w/w). Recovery then increased with extraction time and a 30 minute extraction was necessary to obtain quantitative recovery (85%).

4. Pesticide retention

4.1 Model matrices

By studying the adsorption of a pesticide on a model matrix with well known properties, such as silica, information of different possible retention mechanisms for particular pesticides in soil can be gained (Koskinen and Harper, 1990). Silica and sand spiked with pesticides were used as model matrices in a study of matrix effects on recovery (**Paper III**). Compounds of low polarity did elute, while compounds of higher polarity interact more strongly with the matrix and could not be extracted even at the highest density (0.85 g/mL) without enhancing the polarity by the addition of a modifier. SFE from matrices with well know properties can give information about different retention mechanisms. The investigation presented in **Paper III** can be extended further by studying binding mechanisms on other model matrices with well known properties. The purpose would be to characterize different interactions that determine the behaviour of organic compounds in complex matrices as soils.

4.2 Soil

Soils consist of three phases, a solid phase (about 50%), a liquid phase (about 25%) and a gas phase (about 25%). The solid phase, in particular the soil organic matter, is the primary site for adsorption and transformation processes, while transport of soluble and volatile chemicals in the soil take place primarily in the liquid and gas phase (Koskinen and Harper, 1990). Adsorption varies depending on differences in organic matter composition. Organic matter is typically less than 5% of a productive soil. One part of the organic matter, soil humus is composed of a base-soluble fraction called humic and fulvic acids, and an insoluble fraction called humin. The difference in the nature of humic acids can affect soil organic matter and the pesticide retention. Humic substances in soil have a strong affinity for organic compounds with low water solubility such as DDT or atrazine (Manahan, 1994).

4.3 Pesticides and pesticide retention in soil

Pesticides can be divided into different classes depending on structure, properties or uses. Some common classes are organochlorine, organophosphorous and carbamate insecticides, and triazine and phenoxyacetic acid herbicides. The chemical characteristics of pesticides are largely responsible for their behaviour in soil. Among important chemical properties are, volatility, pK_a , polarity, water solubility, $\log K_{ow}$ (distribution octanol/water), K_d (sorption coefficient, distribution between soil and water),

$K_{oc} = K_d \cdot 100$ divided by % organic carbon (K_d is generally normalised by the organic carbon content). K_{oc} is assumed to be independent of soil properties.

Retention is defined as the ability of the soil to retain a pesticide or other organic molecule and to prevent the molecule from moving either within or being leached out of the soil matrix. Adsorption depends upon physical and chemical properties of the pesticide, nature of the organic matter, and properties of the soil system such as pH, moisture, temperature and clay mineral composition, the organic matter and clay being key factors in the behaviour of many pesticides in soil (Kördel et al., 1993; Stevenson, 1994; **Papers II, IV, V**).

Soil sorption is usually described with sorption equations such as the Freundlich isotherm (**Paper V**). Unequal slopes of the sorption and desorption isotherms, usually with the slope of the sorption isotherm being the steeper, is known as hysteresis effect. Hysteresis was shown for metsulfuron methyl using batch and SFE techniques (**Paper V**).

Analytes in environmental samples may be associated with a variety of inorganic and organic active sites, each with different binding strengths. The presence of certain functional groups, such as -OH, -NH₂, -NHR, -CONH₂, -COOR, and -NR₃, in the molecular structure of the analyte encourages adsorption, especially to soil humus. An understanding of the binding mechanisms involved in the retention process can help to develop more effective and selective extraction procedures for removing pesticides in the matrix.

Another, perhaps less obvious, advantage of highly selective extraction is the possibility to obtain information about the different binding mechanisms and interactions between analyte and matrix components. This relation between extraction efficiency and matrix interaction was noted by Cheng (1990), who suggested the use of combinations of solvents of varying polarities to exhaustively extract pesticides from environmental matrixes.

Influence of soil-pesticide interactions on SFE efficiency have been studied (Dean, 1996; Dean et al., 1996). It is now suggested that SFE offers better opportunities to study such interactions than traditional extraction methods, since a large number of parameters can be varied continuously to achieve the necessary extraction conditions. For example, SFE was used for extraction of atrazine from soils. The results indicate that different binding mechanisms were involved in the retention process and that the binding mechanisms changed with time (Koskinen et al. 1995). The influence of ageing of the sample on extraction behaviour was also studied by Camel et al. (1995), who showed that extractions generally became more difficult with increasing age, i.e. longer time for

binding to occur. Pignatello et al. (1993) suggested that both slow and fast sorptive sites exist in a matrix. Native pollutants are often much harder bound to the matrix than spiked, due to a slow sorption process (Pignatello et al., 1993). Björklund et al. (1997) studied sorption processes of PCBs, the results show the existence of sorption sites of various strength.

Compounds covalently bound to humic matter, largely through the action of microbial enzymes, are known as bound residues and are highly resistant to biological and chemical attack (Manahan, 1994). SFE has also been used to recover bound pesticide residues (nonextractable residues) from aged soil samples (Capriel et al., 1986; Khan, 1995). Harsh SFE conditions were used to extract radiolabeled pesticides strongly bound to the matrix and not accessible by the use of liquid solvent extraction.

Adsorption by soil is also a key step in the degradation of a pesticide. Degradation of a pesticide can take place by biodegradation, chemical degradation or photochemical degradation. Therefore, it is of great interest to be able to characterize the binding of pesticides to a soil matrix, as this will influence what type of degradation the pesticide can undergo.

Paper IV is partly an investigation of the possibilities to use SFE in a nonquantitative mode to characterize the binding of pesticides to soils. The recoveries obtained correlate well with the content of soil organic matter. There is much evidence that an NIR (near infrared reflectance) spectrum contains information about the amount and quality of soil organic matter, clay fractions, cation exchange capacity and base saturation (Al-Abbas et al., 1972; Morra et al., 1991, Stenberg et al., 1995). The potential usefulness of NIR as a tool to predict the leachability of pesticides was shown in **Paper IV**. The method developing step is usually very labour intensive with construction of a large calibration matrix, containing representative samples that cover all the variation of all interesting parameters. Multivariate statistical procedures such as principal component analysis (PCA) or partial least squares regression (PLS) (Joliffe, 1986; Geladi and Kowalski, 1986; Martens and Naess, 1989), can be used to estimate the sorption coefficients and leachability. After that, analysis can normally be performed with routine NIR-instruments with high repeatability and sample capacity. SFE studies were performed at moderate extraction conditions, and thus allowed the soil analyte interactions to influence the recoveries. The results support the hypothesis that nonquantitative extraction methods can be used to access the relative strength of these interactions (**Paper IV**).

Leachability of pesticides in a soil is most accurately determined in lysimeter studies (Führ, 1985; Bergström, 1990). Usually these experiments run for one year or longer. Thus, it is not possible to specifically determine the leachability of every pesticide in every soil. An alternative is to estimate the environmental fate of a pesticide using models. Accurate determination of the parameters needed for modeling is therefore of importance. One such parameter is K_d .

Most commonly K_d values have been determined using batch slurry, column or centrifugation techniques. These techniques suffer from a number of drawbacks:

- * They require soils with water contents above field-capacity, so that soil and soil solution can be separated before analysis.
- * The experiments are usually carried out after drying the soils, while soil water content is expected to have a great influence on the sorption of organic pollutants in soil.
- * The extraction procedure usually alters the physical and chemical characteristics of the soil, resulting in changes in properties of the binding sites during the experiment.

Therefore, developing techniques where K_d can be determined in field-moist soils is of profound importance.

The selectivity of SFE has recently been used to extract atrazine (Koskinen and Rochette, 1996; Rochette and Koskinen, 1996, 1997) and sulfonylurea herbicides (**Paper V**) from the soil solution without also extracting residues bound to the soil particles. Methods were developed where sorption mechanisms can be characterized in intact soils, i.e. with the soil water still present. The application of SFE to determine pesticide sorption coefficients (K_d) in field-moist soil should give a more accurate overall perspective of pesticide fate in field than should sorption characterized by batch slurry techniques. Preliminary results show that leaching models using batch sorption data for atrazine has overpredicted atrazine movement in Minnesota soils. However, the greater K_d values determined using the SFE method gave better prediction of field leaching of atrazine (Koskinen, W. C., USDA, personal communication). Obviously, correctly determined sorption coefficients are of utmost importance for a correct understanding of the behaviour of pesticides in the environment.

5. Future research

The properties of SFE (low solvent consumption, and high extraction efficiency and selectivity) give SFE the potential to serve as an ideal extraction technique in environmental analysis. However, each new analytical problem requires extensive methods development, and a universal extraction strategy for all analyte-matrix combinations will never be possible. Results presented in **Paper II** show the difficulties of developing general SFE methods, and that an SFE method optimized for specific analyte cannot always be directly applied to other similar analytes or to the same analyte extracted from a different matrix without further methods development. The power of the SFE technique lies in the selectivity. The papers discussed in this thesis demonstrate the potential power of using SFE in environmental analysis, both for total extraction (**Papers I-II**) and as a technique for studies of pesticide retention (**Papers III-V**).

The future area of SFE is probably in using the techniques selectivity for specific analytical problems, such as difficult analyte-matrix combinations. One possible research area is to further study and identify bound residues in the matrix, performing SFE under harsh extraction conditions (total extraction).

Another promising application is retention studies as described in **Paper V**. The technique described in **Paper V** is new and still in a basic research stage. So far only sorption coefficients for a limited number of pesticides in a few North American soils have been determined. Further studies regarding optimization of the method are needed. It is also necessary to broaden the scope by including soils from other climatic regions and other pesticides and organic pollutants such as persistent organic pollutants (POPs). Among parameters of interest are analyte concentration and characteristics, soil characteristics such as, water content and water potential, soil clay and organic carbon contents, and pH.

Our future work will focus mainly on the studies of pesticide retention in complex environmental matrices (soils) using SFE techniques, and comparing the effects on models of pesticide mobility in soil by using sorption coefficients determined by SFE and sorption coefficients determined by traditional techniques. In addition to use NIR spectra of the soils in combination with the above techniques as a predictive tool to estimate the leachability of pesticides from soils. The goal of our work is to further characterize and understand the processes involved in the binding of organic pollutants to field moist soils, and to determine K_d -values for organic pollutants in Nordic soils with a varying content of clay and organic matter, and also to expand the methods to include other groups of pesticides and POPs as well.

I am convinced that new environmental applications of the SFE technique other than quantitative extractions will turn up in the near future. Determination of pesticide sorption coefficients is just one example.

SFE has the potential, all that is needed is scientist with new ideas.

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