Supercritical fluid extraction as a useful method for pesticides determination

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Supercritical fluid extraction (SFE) has faced a growing interest in the past few years, due to its numerous advantages over classical liquid solvent extractions (mainly rapidity, selectivity, low solvent volumes required). In particular, applications of this technique have been reported for the determination of pesticides in complex matrices, such as soils and sediments, water samples (after a solid-phase extraction), plant materials, animal tissues, and food items. In fact, SFE of pesticides represents quite a challenge due to the wide range of polarity encountered and the variety of matrices that may contain those residues. Consequently, extraction parameters need to be carefully chosen. So, this paper details the main strategies possible for efficient extractions of pesticides from several matrices.

Despite attractive features (rapid extractions, small solvent volumes, non-toxicity of CO_2, potential of selectivity depending on the fluid density, relatively clear and concentrated extracts, possible coupling with chromatography and automation), the use of SFE in routine analytical applications is a rather slow process. Indeed, the major drawback of this recent technique is the large number of parameters to control and optimize, which results in time required for developing a new method. In addition, the extraction conditions are strongly dependent on the matrix to be extracted, so that parameters need to be adjusted for every new application.

Determination of pesticides remains a challenge for mainly three reasons: the wide variety of physicochemical properties and chemical structures of pesticides, the many possible matrices that should be investigated, and the trace concentrations at which pesticides are usually present. Recent papers reviewed environmental applications of SFE [1,2], especially with regards to the extraction of the main classes of pesticides [3-5]. As SFE performances are strongly dependent on the nature of the sample, this article will consider the matrices that have been submitted to SFE for pesticides determination.

Principle of SFE

A fluid is in its supercritical state when both its pressure and temperature are above their critical value (when only one critical value is attained, the fluid is said subcritical). Supercritical fluids possess unique properties, intermediate between gas and liquids properties [6–10]. In particular, their high diffusivity allows for rapid extractions. In addition, the fluid density may be precisely adjusted, by a correct choice of both pressure and temperature.

The key parts of an SFE system are the high-pressure pump which delivers the fluid, and the restrictor which maintains the pressure inside the system. Extraction is performed inside a high-pressure cell (containing the sample), maintained at the correct temperature. The fluid may simply fill the cell (static mode), or continuously flow through the vessel (dynamic mode). The extracted solutes are entrained by the supercritical fluid flow out of the cell; their collection is usually achieved as the fluid is depressurized by passing through the restrictor. The collected solutes are further analyzed using gas or liquid chromatography. Also, a few recent studies report the use of enzyme immunoassay as a rapid screening process [5,11,12]. Alternatively, the SFE system may be coupled on-line with chromatographic systems, gas chromatography (GC), liquid chromatography (LC), or supercritical fluid chromatography (SFC), by means of an interface [5,8]. For example, the coupling of SFE and SFC enabled the determination of thiolcarbamate herbicides (molinate and thiobencarb) from spiked soil samples (with organic content from 1.75 to 12.9%) [13]. Obviously, such a system seems very attractive when traces of pesticides are considered, as it avoids possible losses or contamination; however, it affords less flexibility than the off-line coupling, so its use remains uncommon.

Difficulty in developing a new SFE method is linked to the great number of parameters to take into account, as discussed below. In particular, SFE results are strongly dependent on the physical nature of the matrix and the polarity of the pesticides. Consequently, optimization of the extraction conditions is recommended for every new class of pesticides or new matrix. In addition, whereas spiked samples generally require mild conditions for quantitative extractions, real samples need more drastic conditions due to stronger solute-matrix interactions.

Method development

The success of a SFE method not only depends on the extraction step itself (i.e. nature of the supercritical fluid and choice of extraction parameters) but also on the matrix considered (a pre-treatment may be recommended) as well as on the trapping system [3,14,15]. Consequently, SFE must be regarded as a four-stage process: desorption of the

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compound from the matrix with subsequent diffusion into the matrix; solubilization of the analyte by the supercritical fluid; sweeping out of the extraction cell by the fluid; trapping of the extracted solutes upon depressurization of the fluid. Each part of the process has to be carefully optimized in order to obtain quantitative and reproducible recoveries. Most of the time, the first step remains the most difficult to control, as solute-matrix interactions are very difficult to hinder and to predict. This problem is crucial when dealing with samples that contain native pesticides. The main strategies for improving SFE of pesticides are exposed in figure 1.

Preparation of the sample

The physical structure of the matrix is of prime importance, as the extraction efficiency is strongly related to the ability of the supercritical fluid to diffuse within the matrix. For that reason, the extraction conditions of the same group of pesticides may differ from one matrix to another. As a general rule, decreasing the particle size of solid matrices leads to a higher surface area, so that extraction is more efficient. Yet, excessive grinding may hinder the extraction due to readsorption of the analytes onto matrix surfaces (this could be avoided by increasing the flow-rate) and/or pressure drop inside the extraction chamber.

Presence of water in the sample may aid the extraction process by swelling the matrix (and enabling better diffusion of the supercritical fluid into the matrix) and increasing the polarity of the fluid (which is needed fo extracting polar compounds). However, excess of water is detrimental to the extraction, as polar compounds will rather partition into the water phase than in the fluid; this effect has been observed during the SFE of molinate from soils samples [13]. Besides, the solubility of water in CO_2 (0.3%) causes restrictor plugging by ice upon fluid depressurization as well as water carrying over into the collection system and ultimately into the chromatographic system. Removal of water is usually done by freeze-drying the matrix, as oven drying may result in pesticides volatilization. Alternatively, addition of drying agents to the sample may be used; this treatment is very attractive as it favours the dispersion of the analytes in the matrix and the sample homogeneization. Yet, the drying agent must be correctly chosen (i.e. high absorptivity of water, good sample consistency, no heating upon hydration, inert), and should not retain the pesticides. Several drying agents have been used: Hydromatrix (a pelletized diatomaceous earth material) [16-20], magnesium sulfate [21], sodium sulfate [22-26], celite [24] or cellulose CF–1 [27]; their properties are detailed elsewhere [4]. Sodium and magnesium sulfate possess relatively weak water retention capabilities, and $MgSO_4$ heats upon hydration; besides its fine particles may damage the restrictor, and it forms agglomerates when mixed with water [28]. In fact, Hydromatrix appears as the best drying agent for SFE; it absorbs twice its mass in water, and enables extraction due to sample dispersion and reduced particle size. Alternatively, a combination of $MgSO_4$ and Hydromatrix may be advantageous [28,29]. Nevertheless, drying agents must be used with great care as they may retain some pesticides. For example celite, Hydromatrix and cellulose CF–1 were shown to partially retain polar pesticides, such as methamidophos, acephate and omethoate [18,27,28], while magnesium sulfate reduced the recoveries of non polar pesticides [28].

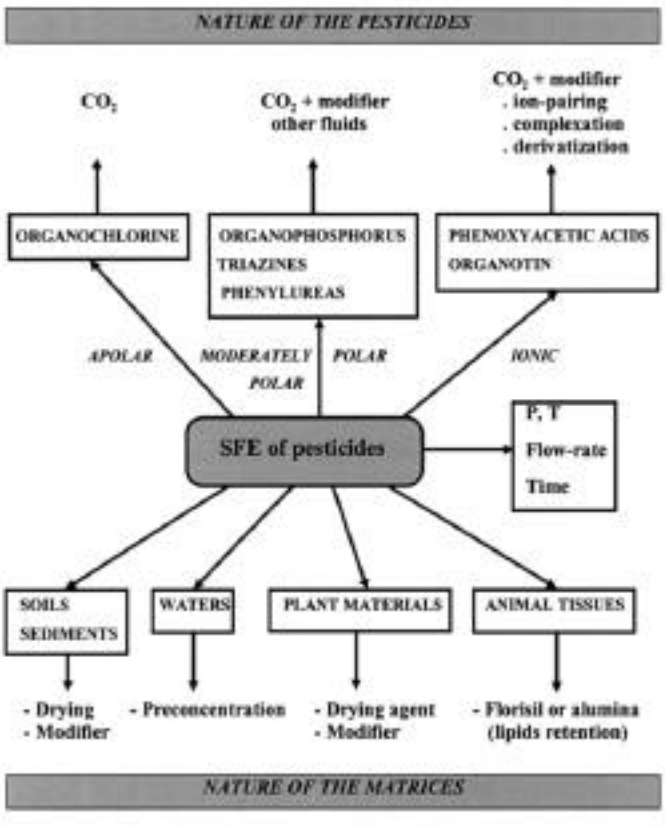

Figure 1. Strategies for improving supercritical fluid extraction of pesticides.

Nature of the supercritical fluid

Due to its attractive features (low critical parameters, non toxicity, non flammability, no reactivity, high purity, low cost, gaseous under atmospheric pressure), CO_2 is by far the most employed supercritical fluid. In fact, it is a good extracting agent for non polar pesticides, such as organochlorine pesticides; several organophosphorus compounds have also shown high solubility [30]. However, its non polar character precludes efficient extraction of most of the pesticides, because of their moderate to high polarity. So, other fluids have been tested, especially nitrogen peroxide and sulfur hexafluoride; despite better extractions of polar compounds, severe drawbacks of these fluids (explosions with N_2O [31], environmental concerns with SF_6) prevent their application. Also, fluoroform was a suitable supercritical fluid for extracting organochlorine pesticides (as well as polychlorinated biphenyls) from biological matrices; in fact, even though slightly lower recoveries than with CO_2 are observed, much less lipids are extracted [32]. Yet, this fluid presents severe drawbacks (high cost and potential environmental hazard) that make its use unviable.

Water has also been investigated as a possible polar supercritical fluid [33]. Very recently, subcritical water (250 °C, 200 bar) has been reported to enable quantitative extraction of a polar pesticide metabolite (trichloropyridinol, a metabolite of chlorpyrifos) from spiked soil, within 15 minutes as compared to 30 minutes with CO_2 [34]. Yet, this fluid requires very high temperatures (due to its high critical temperature), which precludes its common use.

Optimization of the extraction

Numerous factors need to be controlled during the extraction: pressure and temperature inside the cell, static time, flow-rate and dynamic time (or fluid volume), and volume of modifier added. An important feature in the development of a SFE method is the polarity of the pesticides to be extracted as well as the solubility in water. Also, it is now well established that SFE conditions developed for fortified samples often yield low extraction efficiency with real samples, because of much stronger interactions between pesticides and the matrix.

For a given temperature, the fluid density is proportional to the pressure, so that increasing the pressure is beneficial to the solubility of analytes into the fluid. A class of compounds may be characterized by its "threshold pressure" (i.e. the pressure above which they begin to be soluble in the fluid). Consequently, a correct choice of the pressure may lead to selective extractions; thus, it should allow the successive extraction of classes of pesticides, and/or the extraction of pesticides without simultaneous extraction of matrix interferents [35].

Despite a negative effect on the fluid density, elevated temperatures usually increase recoveries of compounds in native matrices, mainly due to a better desorption from the matrix [2,36]. Yet, some pesticides (captan for example) readily degrade at high temperatures; consequently, moderate temperatures should be used whenever possible.

A short period of static time may improve the recoveries, especially for pesticides that are difficult to extract or when a modifier is added to the matrix. The dynamic time is essentially a measure of the total volume of fluid that percolated through the cell (as determined by the flow-rate). Obviously, pesticides that are hardly extracted (i.e. polar pesticides, or compounds that strongly interact with the matrix) require large volumes of extraction fluid (usually more than 4 vessel volumes).

SFE of polar compounds is enhanced by modifiers added to the matrix or the supercritical fluid. These modifiers may be polar organic solvents, derivatizing reagents or ion-pairing reagents [37,38]. In the early stages of SFE, a polar organic solvent was added to improve the solubility of the solutes into the CO_2. For example, methanol was found to increase the solubility in CO_2 of simazine, propazine and trietazine [39], as well as atrazine and 2-hydroxyatrazine [40]; in case of the polar metabolites of atrazine, best results were obtained using methanol containing 2% (v/v) water [40,41]. Yet, it rapidly appeared that the solvent had another effect, that could be much more important: it facilitated the desorption of solute molecules from the active sites of the matrix. Finally, some modifiers (such as water) are suspected to favour the swelling of the matrix, thereby enhancing diffusion of the fluid inside the matrix [11]; for example, recovery of diuron and methyl tribenuron from plant materials and clays was related to the swelling of the matrix caused by the modifier [42]. So, modifier may be added either continuously to the fluid, or just before the extraction directly into the matrix. The second way essentially favours the desorption of the solutes, due to the low solvent volume added (around 0.5 mL); also, to be efficient, this mode of addition requires a static period to allow the solvent to interact with the matrix. Nature of the modifier is strongly dependent on the analytes to be extracted [43]. For example, toluene may be added directly into the cell to overcome interactions between hexachlorocyclohexane (HCH) isomers and soil active sites [22]. It must be pointed out that the percentage of modifier should be as low as possible for three main reasons. Firstly, using a solvent-modified CO_2 changes the critical parameters of the mixture [44]; in particular, it elevates the critical temperature, so that high percentages of solvent lead to a subcritical state, whose properties are slightly less advantageous than those of supercritical fluids. Secondly, presence of the modifier reduces the extraction selectivity, and may requires a clean-up step before analysis. Finally, as discussed below, the modifier may decrease the collection efficiency some times [45].

For very polar pesticides, extraction may be enhanced by performing *in situ* derivatization inside the cell, so that polar functions are converted into less polar groups (such as ether, ester, silyl groups) [38]. The obtained derivatives are thus more soluble into the fluid. Moreover, the derivatizing agent is suspected to also react with active sites of the matrix, leading to the desorption of solutes. Finally, this procedure affords extracted compounds that are readily amenable to gas chromatography. As an example, hexylmagnesium bromide converts the mono-, di- and trisubstituted organotin compounds into their corresponding hexyl derivatives, enabling their SFE with pure CO_2 from sediments [46]. In case of ionic pesticides, SFE may also be possible thanks to the formation of an ion-pair with the solute, in order to improve the solubility in the fluid [38,47]. In addition, the reagent may also react with the sites onto the matrix surface, thus favouring the desorption of solute molecules. For example, sodium diethyldithiocarbamate [48] or diethylammonium diethyldithiocarbamate [49] forms neutral complexes with ionic organotin fungicides, thereby allowing their SFE extraction. Addition of an ion-pair reagent to the CO_2 has also been used to enhance the extraction of a polar metabolite of chlorpyrifos from soil [34].

Trapping of the extracted analytes

Once extracted, the pesticides must be efficiently trapped before their analysis. Depending on the instrumentation, collection is ensured either by bubbling the CO_2 into a solvent, or by trapping onto a solid-phase filled cartridge. When solutes are trapped into a solvent, careful choice of the solvent is needed. Trapping of non polar compounds such as organochlorine pesticides would require a non polar solvent, such as isooctane [50] or toluene [22], while ethyl acetate is a good collection solvent for organophosphorus pesticides [21]. Yet, this system may result in analyte volatilization or aerosol formation, as observed for several pesticides (namely HCH isomers [22], 2,4-D, atrazine and alachlor [11]). For that reason, the second system should be preferred; for example, trapping onto octadecyl-bonded silica was more efficient than solvent collection for atrazine, simazine and alachlor [11]. In addition, it affords the possibility of an enhanced selectivity, by correctly choosing both the packing material and the elution solvent. For example, a Florisil trap has been used to efficiently retain organochlorine and organophosphorus pesticides extracted from grain samples [51]. Also, an alumina trap was demonstrated to separate the fungicide quintozene and its metabolites from chlorophyll and other interferences extracted from several vegetables [16]. Recently, several adsorbent traps (octadecyl-, cyano-,

diol-bonded silica gel, Tenax, and stainless-steel beads) and eluents (hexane, ethyl acetate, acetone and methanol) were investigated for the SFE of different selected pesticides (fenpropimorph, pirimicarb, parathion-ethyl, triallate, and fenvalerate) from soils. Best recoveries were obtained using a combination of a diol trap and ethyl acetate [20]. Yet, in practice, the most commonly used material still remains the octadecyl-bonded silica [11]; a recent comparison of four traps (octadecyl- and diol-bonded silica, Tenax and Porapak-Q) and four elution solvents (acetone, ethyl acetate, acetonitrile and methanol) for 56 pesticides confirmed the general use of this material with acetone elution as the best choice [29].

When an organic modifier is added to the supercritical fluid, trapping onto a solid trap may be less efficient, as the modifier condenses inside the trap and acts as an elution solvent, thereby decreasing the retention of the analytes. This effect is more pronounced for high percentages of modifier. Also, efficiency of any collection system is strongly dependent on the gaseous CO_2 flow-rate coming out of the restrictor, due to possible entrainment of solutes by the CO_2 flow. For that reason, supercritical fluid flow-rates inside the cell should be limited to approximately 2 mL min^{-1} (i.e. around 1 L min^{-1} gaseous CO_2).

The main matrices investigated for pesticides determination

Several recent articles report applications of SFE for pesticides from several matrices [1-5,8,10,52]. With regards to the numerous possible classes, pesticides have a broad range of physical properties and chemical structures; so, their ability to be extracted will differ greatly from one class to another. In fact, their solubility in pure CO_2 could be evaluated from their octanol-water partition coefficient [39,53]. Thus, organochlorine pesticides are highly soluble into pure CO_2, while organophosphorous compounds require a modifier to be added; addition of a polar modifier becomes crucial for triazines and phenylureas. In case of phenoxyacetic acids, an ion-pairing or derivatization reagent may be added to enable their extraction.

Soils and sediments

Environmental matrices such as soils and sediments have been widely investigated as possible applications of SFE. Recent examples are reported in table I. SFE of organochlorine pesticides from spiked sand and soil samples revealed a much cleaner extract than using Soxhlet extraction, so that no additional clean-up step was required [50].

Soils and sediments represent particular matrices considering the strong interactions occurring between their active sites and the pesticides [39]. For that reason, modifiers are generally added, either to the fluid or directly into the sample. Thus, addition of methanol to the cell was required to overcome interactions between several organophosphorus pesticides and spiked soil [30]; the extraction became more difficult as the soil samples aged, due to diffusion of the solute in the matrix and stronger interactions with the soil. In fact, methanol (5% added to the CO_2), as compared to hexane and acetone, appeared as the best modifier for the extraction of several pesticides (fenpropimorph, pirimicarb, parathion-ethyl, triallate and fenvalerate) from spiked soil samples [20]. Also, methanol modified CO_2 enabled the extraction of atrazine, deethylatrazine and deisopropylatrazine from spiked sediment samples [23], while methanol containing 2% (v/v) water was efficient for atrazine and 2-hydroxyatrazine in a spiked soil (4% organic matter) [40]. However, more stringent conditions were required for bound residues; for example, 30% methanol was needed to efficiently extract bound atrazine from a mineral soil, along with high pressure (350 bar) and temperature (125 °C) [56]. Another study reported methanol or the mixture acetone-water-triethylamine (90/10/1.5 v/v/v) to enhance extraction of 2,4-D from soils [11,12,56].

In case of highly polar pesticides (such as phenoxyacetic acids or organotins) stronger modifications of the fluid should be used, allowing complex formation or *in situ* derivatization prior to the extraction [38,59]. For example, addition of diethylammonium diethyldithiocarbamate or sodium diethyldithiocarbamate as a complexing reagent to methanol-modified CO_2 was successful for extracting di-, tri- and tetra-substituted organotin compounds from soils and sediments [48,49]. However, only partial extraction of monobutyltin could be achieved. Also, addition of a complexing reagent (HCl) to methanol-modified CO_2 (20% v/v) enabled extraction of tributyltin from spiked sediments [58].

Alternatively, hexylation of organotin compounds allowed extraction using pure CO_2; this led to less matrix material extracted as compared to methanol-modified CO_2 [46]. Yet, poor recoveries (15 and 40%) were observed with monosubstituted organotin compounds, possibly due to stronger interactions with the matrix. Chemical derivatization has also been reported for acidic herbicides. Hence, the ion-pairing methylating reagent trimethylphenylammonium hydroxide (TMPA) converted 2,4-D and dicamba into their methyl ester derivatives, thereby allowing their extraction with pure CO_2 from a real agricultural soil [47]. Besides, the correct choice of the reagent may provide selectivity to the SFE; thus, only 2,4-D was derivatized in presence of BF_3/methanol [39,47].

Several studies have been conducted to elucidate the solute-soil interactions. As a general rule, the higher the organic content, the more difficult the extraction; besides, this effect is more pronounced as the solute is polar, due to stronger interactions with the matrix [54]. As an example, the recoveries of organochlorine pesticides from soil samples decreased for the soil with the highest organic content [39]. Also, the SFE of hexaconazole (a systemic triazole fungicide) was less efficient as the soil organic content increased from 1.5% to 5.7%, due to strong matrix-solute interactions [57]. Extractions of 2,4-D from selected spiked model soil components (gibbsite, goethite, calcite, illite, silica gels, humic materials) confirmed that organic matter was the main component limiting extraction of 2,4-D from soils [60].

Recently, a multivariate optimization scheme has been applied to the SFE of pesticide residues (atrazine, diuron and bensulfuron-methyl) from soils, using a quadratic model and a central composite design, and considering two groups of independent variables (soil environmental variables and SFE parameters) [55]. The analyte residence time in the soil was the most significant environmental factor. Then, for aged

Table I . Applications of SFE to pesticides from soils and sediments.

Class of pesticides	*Matrices*	*Sample preparation*	*Extraction*	*Collection/ analysis*	*Ref.*
ORGANOCHLORINE					
α-HCH, HCB, β-HCH, γ-HCH, β-heptachlor epoxide, 4,4'-DDE, dieldrin, TDE, 1,4'-DDT, 4,4'-DDT	*Spiked* sand Peat soil	-----	CO_2 50 °C, 200 bar	Isooctane GC/ECD	[50]
HCH isomers	Contaminated soil	Mixing with Na_2SO_4 Addition of sand and copper powder Toluene addition	CO_2 70 °C 150 to 400 bar	Toluene GC/ECD	[22]
Lindane, aldrin, dieldrin, heptachlor, isodrin	*Spiked* soils	-----	CO_2 50 °C, 250 bar	CH_2Cl_2 GC/MS	[39]
ORGANOPHOSPHOROUS					
Diazinon, malathion, chlorfenvinphos	*Spiked* soils	-----	CO_2 + 5% CH_3OH 50 °C, 250 bar	CH_2Cl_2 GC/MS	[39]
Diazinon, disulfoton, dimethoate, malathion, parathion ethyl, carbofenthion, azinphos methyl, coumaphos	*Spiked* soil	-----	CO_2 + 2% CH_3OH 50 °C, 250 bar	Ethyl acetate GC/FID	[30]
Parathion-ethyl	Soils	Mixing with Hydromatrix	CO_2 + 5% CH_3OH 60 °C, 380 bar	Diol silica Ethyl acetate elution GC/NPD	[20]
TRIAZINES					
Atrazine, prometon	Agricultural soil	-----	CO_2 200 °C, 400 bar	$CHCl_3$ GC/FID	[36]
Simazine, propazine, trietazine	*Spiked* soils	-----	CO_2 +10% CH_3OH 50 °C, 250 bar	CH_2Cl_2 LC/UV	[39]
Atrazine, HA, DEDIHA	*Spiked* soil	Non polar washing (toluene + hexane)	CO_2 +CH_3OH/H_2O 65 °C, 300 bar	CH_3OH LC/UV	[40]
Atrazine, DEA, DIA	*Spiked* sediments	Mixing with silica sand and Na_2SO_4	CO_2 + 4% CH_3OH 43 °C, 100 bar	CH_3OH GC/MS	[23]
Atrazine, DEA, DIA, cyanazine	*Spiked* soils	-----	CO_2 + 5% CH_3OH or H_2O, 40 °C 105 to 345 bar	Stainless steel beads LC/UV	[54]
Atrazine	*Spiked* soil	-----	CO_2 + 5% CH_3OH 80 °C, 400 bar	CH_3OH Enzyme immunoassay	[12]
Atrazine, HA, DEA, DIA, HDIA, HDEA, DEDIA, DEDIHA	*Spiked* sediments	Homogeneization	CO_2 +10% CH_3OH containing 2% H_2O 65 °C, 300 bar	CH_3OH LC/MS	[41]
Atrazine, simazine	*Spiked* soils	-----	CO_2+15% acetone/ H_2O/triethylamine 90:10:1.5 v/v/v 66 °C, 200-345 bar	C_{18} silica Enzyme immunoassay	[11]
Atrazine	Soils	Air-dried	CO_2 + 17.5% CH_3CN/H_2O+HCl/ Triton X-100 80/10/10 v/v/v 150 °C, 350 bar	Solvent LC/UV	[55]

^{14}C Atrazine, ^{14}C prometryn	Soils	Grinding	CO_2 +30% CH_3OH 120 °C, 150 bar 125 °C, 350 bar	CH_3OH Radioassay analysis GC/TSD	[56]
THIOLCARBAMATES					
Molinate, thiobencarb	*Spiked* soils	Air-dried	CO_2 60 °C, 200 bar	On-line SFC	[13]
SUBSTITUTED UREAS					
Diuron, bensulfuron-methyl	Soils	Air-dried	CO_2 + 17.5% CH_3CN/H_2O+HCl/ Triton X-100 80/10/10 v/v/v 70−100 °C, 350 bar	Solvent LC/UV	[55]
TRIAZOLES					
Hexaconazole	Soils	Air-dried (48 h) Sieved (2-3.5 mm)	CO_2 +30% CH_3OH 55 °C, 250 bar	CH_3OH Cyano- and C_{18} silica clean-up GC/ECD	[57]
PHENOXYACETIC AND BENZOIC ACIDS					
2,4-D, dicamba	*Spiked* sediment Agricultural soil	Derivatization with TMPA (20%) or BF_3 in CH_3OH (12%)	CO_2 80 °C, 400 bar	CH_3OH GC/ECD	[47]
2,4-D	*Spiked* soil	Silylation, methylation, ionpairing, or ionic displacement	CO_2, 80 °C 300 or 380 bar	Hexane GC/ECD	[37]
2,4-D	*Spiked* soil	-----	CO_2 + 5% CH_3OH 80 °C, 400 bar	CH_3OH Enzyme immunoassay	[12]
2,4-D	*Spiked* soils	-----	CO_2+15% acetone/ H_2O/triethylamine 66 °C, 200-345 bar	C_{18} silica Enzyme immunoassay	[11]
^{14}C 2,4-D	Soil	Grinding	CO_2 +30% CH_3OH 120 °C, 150 bar 125 °C, 350 bar	CH_3OH Radioassay analysis GC/TSD	[56]
ORGANOTINS					
Monobutyl-, dibutyl-, tributyl-, monophenyl-, diphenyl-, triphenyltin	Sediments	Hexylmagnesium bromide addition	CO_2 40 °C, 350 bar	Hexane GC/FPD	[46]
Tributyltin	Sediments	HCl addition	CO_2 +20% CH_3OH 60 °C, 350 bar	Isooctane	[58]
Tributyl-, dibutyl-, monobutyltin	Sediments	Sodium diethyl-dithiocarbamate addition	CO_2 +10% CH_3OH 70 °C, 250−500 bar	CH_2Cl_2-CH_3OH 1:1 Derivatization GC/AED	[48]
Dimethyl-, diethyl-, dibutyl-, diphenyl-, trimethyl-, triethyl-, tributyl-, triphenyl-, tetrabutyl-, tetracyclohexyl-, tetraphenyltin	Soils and sediments	Diethylammonium diethyldithio-carbamate addition	CO_2 + 5% CH_3OH 45 or 60 °C 350 to 450 bar	CH_2Cl_2 or C_{18} silica (CH_2Cl_2 elution) Derivatization GC/AED	[49]

samples (12 months), the soil organic matter and clay minerals content had a negative effect on the recoveries due to stronger analyte-matrix interactions (especially for bensulfuron-methyl). Considering the SFE parameters, solubility of the pesticides in the fluid was crucial with freshly spiked soils. On the opposite, the diffusion processes were the limiting factor for aged soils; in that case, the extraction was favoured upon elevation of the temperature or addition of a modifier. In particular, a surfactant (Triton X–100) was more efficient than acetonitrile or methanol as a modifier, possibly because of a better swelling of the matrix and/or the formation of non-ionic reverse-micelle [61].

Water

SFE is unapplicable to water samples directly, for several reasons. Firstly, the entrainment of some water by the CO_2 would result in ice formation upon depressurization, leading to constant blocking. Also, due to the high difference in polarities of the fluid and the matrix, very low efficient extractions could be obtained. So, water samples are pre-extracted using solid-phase extraction. In that way, pesticides are trapped onto a solid material, which is further extracted using SFE [35,62,63]; few applications are presented in table II.

Table II. Applications of SFE to pesticides from water samples.

Class of pesticides	*Matrices*	*Sample preparation*	*Extraction*	*Collection/ analysis*	*Ref.*
ORGANOCHLORINE					
Lindane, dieldrin, aldrin	*Spiked* water	Preconcentration onto a C_{18} disk	CO_2 50 °C, 135 bar	Hexane GC/MS	[62]
α-HCH, γ-HCH, β-HCH, δ-HCH, heptachlor, heptachlor epoxide, α-chlordane, β-chlordane, endosulfan I, endosulfan II, dieldrin, endrin, endrin aldehyde, methoxychlor, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT	*Spiked* reagent water	Preconcentration onto a C_{18} disk or cartridge	CO_2 60 °C, 300 bar	Acetone GC/MS	[63]
α-HCH, γ-HCH, β-HCH, δ-HCH, heptachlor, heptachlor epoxide, α-chlordane, γ -chlordane, oxychlordane, trans-nonachlor, endosulfan I, endosulfan II, endosulfan sulfate, aldrin, dieldrin, endrin, endrin aldehyde, 4,4'-DDE, 4,4'-DDT	*Spiked* drinking water, wastewater	Preconcentration onto a C_{18} disk	CO_2 60 °C, 400 bar	Hexane GC/MS	[64]
ORGANOPHOSPHOROUS					
Dichlorvos, diazinon, malathion	*Spiked* water	Preconcentration onto a C_{18} disk CH_3OH addition	CO_2 50 °C, 350 bar	Hexane GC/MS	[62]
Fenitrothion, fenamiphos, parathion	*Spiked* water	Freeze drying	CO_2 50 °C, 200 bar	Ethyl acetate LC/UV or GC/NPD	[65]
TRIAZINES					
Atrazine, simazine	*Spiked* water	Freeze drying	CO_2 50 °C, 200 bar	Ethyl acetate GC/NPD	[65]
PHENOXYACETIC ACIDS					
2,4-D, 2,4,5-T	*Spiked* water	Retention onto an anion exchange resin Methylation with methyl iodide	CO_2 80 °C, 200 bar	Solvent GC/AED	[66]

Yet, a drying agent should be packed into the cell to retain residual water and avoid restrictor plugging [64]. Hence, several organochlorine pesticides could be extracted from water samples using octadecyl-bonded silica materials [62-64]. For the determination of 2,4-D and 2,4,5-T in aqueous samples, retention onto an anion exchange resin has been proposed [66]; the solutes were further recovered by methylation with methyl iodide and subsequent SFE with CO_2.

Plant materials

As numerous pesticides may be found in plant tissues, several studies have been conducted in order to optimize SFE conditions. They have been recently reviewed [4]. Recent studies are reported in table III.

Due to the high moisture of most of the plant tissues (80 − 95% in fruits and vegetables), water must be removed or controlled before the SFE. As lyophilization is time consuming and may cause the loss of volatile analytes [26], addition of a drying agent to the sample is highly recommended. For example, Hydromatrix efficiently absorbed the high moisture of fruits and vegetables, enabling the extraction of numerous organochlorinated pesticides with pure CO_2 [16–18]. Addition of dry ice to the sample-Hydromatrix mixture may favour the formation of an homogeneous powder, and reduce the degradation of several pesticides (espe-

Table III . Applications of SFE to pesticides from plant materials.

Class of pesticides	*Matrices*	*Sample preparation*	*Extraction*	*Collection/ analysis*	*Ref.*
ORGANOCHLORINE					
^{14}C Dieldrin	Radishes	Grinding	CO_2+30% CH_3OH 120 °C, 150 bar 125 °C, 350 bar	CH_3OH Radioassay analysis GC/TSD	[56]
Pentachloronitrobenzene, pentachlorobenzene, HCB, tetrachloronitrobenzene, pentachloroaniline, pentachloroanisole, pentachlorothioanisole	*Spiked* green beans, potatoes, celery, radishes, carrots	Grinding Mixing with Hydromatrix	CO_2 40 °C, 200 bar	Alumina trap Isooctane elution GC/ITD	[16]
ORGANOPHOSPHOROUS					
Chlorpyrifos	Grass	----	CO_2+2% CH_3OH 100 °C, 400 bar	On-line LC/GC	[67]
Diazinon, Pyrimiphos-methyl, fenitrothion, chlorpyriphos, ethion	Rice grains	-----	CO_2 +5% CH_3OH 45 °C, 315 bar	CH_2Cl_2 GC/AED	[68]
Methamidophos, acephate	Green beans	Frozen sample Mixing with $MgSO_4.H_2O$ and Hydromatrix CH_3OH addition	CO_2 60 °C, 320 bar	C_{18} silica CH_3CN elution GC/ITD	[28]
^{14}C Fonofos, ^{14}C pirimiphos methyl	Onion, wheat	Grinding	CO_2+30% CH_3OH 120 °C, 150 bar 125 °C, 350 bar	CH_3OH Radioassay analysis GC/TSD	[56]
TRIAZINES					
^{14}C Atrazine	Canola	Grinding	CO_2+30% CH_3OH 120 °C, 150 bar 125 °C, 350 bar	CH_3OH Radioassay analysis GC/TSD	[56]

cially organophosphorus) [17]. Anhydrous magnesium sulfate was also efficient in removing water from fresh vegetables [21].

The SFE of pesticides from plant materials generally require the addition of a solvent modifier to overcome strong solute-matrix interactions. Methanol has been widely used: extraction of dieldrin from radishes [56], chlorpyrifos from grass field samples [67], methamidophos from spiked vegetables [21], organophosphorus compounds from rice [68], carbendazime from lettuce leaves [69], fonofos from onions [56], pirimiphos methyl from wheat and beans [56], atrazine from canola [56]. Acetone was also efficient for the extraction of carbofuran and carbaryl from tobacco [70]. Alternatively, pesticide residues may be released upon hydrolyze of plant tissues prior to SFE; for example, an acid pre-treatment (17% H_3PO_4, 100 °C, 4 h) allowed the CO_2 extraction of 2,4-dichlorophenoxy butanoic acid, a plant metabolite of 2,4-dichlorophenol from spiked samples [71]. Yet, extraction of field-treated straw matrices was more difficult (possibly due to the association of the pesticide residue with lignin).

The viable use of SFE in laboratories requires the development of multiple pesticide residues applications. So, several multi-residue methods have been developed for the determination of pesticides in fruits, vegetables and cereals, as indicated in table IV. The best strategy should be to use pure CO_2 in order to minimize extraction of interferences from the matrix. In that way, extraction of 92 pesticides from fortified apples could be achieved [24]; even though the more polar compounds (acephate, omethoate and vadimothion) were slightly recovered during the first extraction, performing a second extraction under the same conditions enabled their extraction. Yet, the mild conditions reported (i.e. 45 °C, 189 bar, 10 min) should reveal insufficiency in case of real samples. Similarly, pure CO_2 (60 °C, 320 bar) allowed satisfactory extraction for most of the 40 or 46 pesticides considered from fruits and vegetables; low recoveries of polar compounds (especially omethoate and metamidophos) might be improved by a second extraction [17,18].

Animal tissues

Occurrence of organochlorine compounds in animal tissues (especially fishes and mussels) has been evidenced. These pesticides represent of potential health hazard, as these lipophilic pesticides may concentrate in the fat tissues. For that reason, application of SFE to such matrices has been investigated, as reported in table V. For example, heptachlor epoxide, dieldrin and endrin were determined in chicken tissues; due to strong solute-matrix interactions, relatively drastic SFE conditions were required (i.e. 80 °C, 700 bar) [72].

One major problem when dealing with animal tissues is the co-extraction of lipid materials; so, a further clean-up step may be required before the chromatographic analysis. Another attractive strategy is to add an adsorbent inside the cell; thus, activated basic alumina [74] and Florisil [73] were found to successfully retain lipid material. This allowed the determination of several organochlorinated pesticides (along with polychlorinated biphenyls) from fishes and mussels.

Food items

Applications of SFE to food matrices have been recently reviewed [4]. As an example, SFE has been applied to the determination of organochlorine and organophosphorus pesticides in fatty foods [75]. The procedure involved mixing the fatty foods with Hydromatrix, extraction with acetonitrile-modified CO_2 (3%), and subsequent clean-up of pesticides from extracted fats using an in-line reusable preparative C_1 silica-based column (clean-up occurred under supercritical conditions). Application to the SFE of incurred pesticide residues in french fries, corn chips, blueberry muffins, a chicken potpie, pancakes, and a hamburger was satisfactory, as results were reproducible and comparable with results obtained with the reference method used by the U.S. Food and Drug Administration.

Other matrices

Pesticides may be encountered in a great variety of matrices. Few examples are illustrated in table VI.

Hence, SFE was applied to the extraction of chlorinated pesticides from postconsumer recycled plastics used as agricultural soil covers [25]. These plastics were a mixture of low-density polyethylene (approximately 90% w/w) and ethylene-vinyl acetate copolymer (around 10% w/w). The physical nature of the matrix had a strong influence on the recoveries: plastic films enabled quantitative recoveries, while lower efficiencies were found from plastic pellets due to a more difficult diffusion of the fluid into this matrix. As a consequence, to achieve satisfactory extractions, more drastic conditions were required for pellets (i.e. 400 atm instead of 200 atm for films); besides, the addition of toluene was proved to enhance the recoveries from pellets, possibly by enhancing the accessibility of CO_2 through the polymeric chains.

Also, the SFE of atrazine and two metabolites, hydroxyatrazine (HA) and deethyl-deisopropyl-hydroxyatrazine (DEDIHA), from spiked octadecyl-bonded silica has been reported [40]. Addition of 10% methanol to the CO_2 (250 bar, 50 °C) resulted in acceptable recoveries for atrazine (90%) and hydroxyatrazine (94.5%). On the opposite the more polar metabolite was hardly extracted (20%); the use of methanol containing 2% (v/v) of water as a modifier enhanced its recovery (52%). Similarly, the SFE of atrazine, simazine, deethylatrazine (DEA) and deethylsimazine (DES) from granular activated carbon (GAC) has been investigated, as GAC filters are frequently used in potable water treatment for the removal of traces of pesticides [76]. Almost no extraction occurred using pure CO_2, due to very strong interactions between active sites of the carbon and pesticides. Addition of acetone (50% molar) led to quantitative recoveries for atrazine and simazine, and acceptable results for the two metabolites (around 70% recovery), due to increased solubility in the fluid, along with easier desorption of solute molecules from the matrix.

The extraction of acidic herbicides (2,4-D, dicamba, 2,4,5-T and 2,4,5-TP) from house dust has been reported [77]. This matrix is particularly difficult due to its high water and organic content (3.7 and 30.6% by weight respectively). Addition of methanol (20%) to the CO_2 was required to achieve acceptable recoveries (83 to 95%), as the modifier both enhanced the solubility in the fluid and partially disrupted solute-matrix interactions. Nevertheless, methanol-modified CO_2 resulted in co-extraction of matrix material which further interfered during the derivatization of analytes prior to their analysis. This major drawback could be

Table IV. Multiresidue SFE methods for the determination of pesticides in fruits, vegetables and cereals.

Pesticide residues	*Matrices*	*Sample preparation*	*Extraction*	*Collection/ analysis*	*Ref.*
92 pesticides (organochlorine, organophosphorus, organonitrogen, pyrethroid, others)	*Spiked* apples	Celite and Na_2SO_4 addition	CO_2 45 °C, 189 bar	C_{18} silica Hexane/acetone 1:1 elution	[24]
71 pesticides (organochlorine, organophosphorus, organonitrogen, pyrethroid, others)	*Spiked* apples	Frozen sample mixed with $MgSO_4.H_2O$ and Hydromatrix CH_3OH addition	CO_2 60 °C, 320 bar	C_{18} silica CH_3CN elution GC/ITD	[28]
58 pesticides (organochlorine, organophosphate, organonitrogen, carbamate, imidazole, pyrethroid)	Tomatoes	Freezing Cellulose CF-1 addition	CO_2 50 °C, 350 bar	C_{18} silica Acetone elution GC/ITD	[27]
56 pesticides (organochlorine, organophosphate, organonitrogen, carbamate, imidazole, pyrethroid)	*Spiked* oranges, sweet potatoes, green beans	Frozen sample mixed with $MgSO_4.H_2O$ and Hydromatrix	CO_2 50 °C, 350 bar	C_{18} silica Acetone elution GC/ITD	[29]
46 pesticides (organochlorine, organophosphate, carbamate, pyrethroid, others)	Grapes, carrots, potatoes, broccoli	Grinding Mixing with Hydromatrix	CO_2 60 °C, 320 bar	C_{18} silica CH_3CN elution GC/MS	[18]
40 pesticides (organochlorine, organophosphate, carbamate, pyrethroid, others)	Peaches, oranges, potatoes	Grinding Mixing with Hydromatrix and dry ice	CO_2 60 °C, 320 bar	C_{18} silica CH_3CN elution GC/MS	[17]
11 pesticides (organochlorine, organophosphate)	*Spiked* strawberries	Grinding Mixing with Na_2SO_4	CO_2+10% acetone/CH_3OH 75 °C, 440 bar	Silanized glass beads - hexane elution GC/ECD	[26]
8 pesticides (parathion methyl, pirimiphos methyl, malathion, chlorpyriphos, methoxychlor, dimethoate, dieldrin, carbofuran)	*Spiked* wheat grains	Grinding	CO_2 40 °C, 350 bar	Florisil Acetone elution GC/FPD	[51]
4 pesticides (methamidophos, chlorpyrifos, endosulfan, procimidone)	Peppers, tomatoes, cucumbers	Mixing with $MgSO_4$ CH_3OH addition	CO_2 50 °C, 300 bar	Ethyl acetate GC/FPD or GC/ECD	[21]

avoided by pre-extracting once the matrix with pure CO_2 and hexane added to the cell, in order to extract those matrix interferences.

Conclusion

SFE remains an attractive technique, with great potentials for the selective determination of pesticides in complex matrices, as supported by several reported applications. A major feature of SFE is the high quality of the extracts, due to few interferences extracted and a low dilution, enabling further analysis with minimal clean-up and concentration. This is of prime importance for pesticides, due to their trace concentrations frequently encountered whatever the matrix. Yet, SFE faces two major limitations. Firstly, polar compounds require the addition of a modifier to either the fluid or the matrix, thereby decreasing the selectivity of the extraction; also, the range of pesticides that can be quantitatively extracted under the same conditions is limited. Secondly, results are strongly dependent on the matrix, which leads to new optimizations each time a new matrix is considered.

Table V. Applications of SFE to organochlorine pesticides from animal tissues.

Pesticides	*Matrices*	*Sample preparation*	*Extraction*	*Collection/ analysis*	*Ref.*
Heptachlor epoxide, dieldrin, endrin	Chicken	Freezing Grinding Drying (50 °C)	CO_2 80 °C, 700 bar	Glass flasks Alumina clean-up GC/ECD	[72]
α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, endrin aldehyde, endosulfan I, endosulfan sulfate, 4,4'-DDT, 4,4'-DDE, 4,4'-DDD	Mussels	Lyophilization Grinding Florisil addition	CO_2 50 °C, 250 bar	Deactivated fused-silica beads (–30 °C) Hexane elution Concentration GC/ECD	[73]
4,4'-DDE, 2,4'-DDE, c-chlordane, t-nonachlor, 2,4'-DDD, 4,4'-DDD, 2,4'-DDT, 4,4'-DDT	Mussels	Freeze-drying	CHF_3 97 °C, 0.91 g mL^{-1}	C_{18} silica Isooctane elution GC/ECD or GC/MS	[32]
HCB, 4,4'-DDE, mirex	Fishes	Mixing with Na_2SO_4 Activated basic alumina addition	CO_2 100 °C, 350 bar	C_{18} silica Isooctane elution Florisil clean-up GC/ECD	[74]

Table VI. Applications of SFE to pesticides from other matrices.

Class of pesticides	*Matrices*	*Sample preparation*	*Extraction*	*Collection/ analysis*	*Ref.*
ORGANOCHLORINE AND ORGANOPHOSPHORUS					
Chlorobenzilate, endosulfan II, 1,4-DDE, malathion, chlorpyrifos, toclofos-methyl	Recycled plastics (films or pellets)	Addition of Na_2SO_4	75 °C Film: CO_2, 200 bar Pellet: CO_2 +12% toluene, 400 bar	Cryogenic trap (−15 °C) Hexane elution GC/ECD	[25]
TRIAZINES					
Atrazine, simazine, DEA, DES	*Spiked* GAC	-----	CO_2 +50% acetone 150 °C, 500 bar	Solid trap GC/NPD	[76]
Atrazine, HA, DEDIHA	*Spiked* C_{18} bonded silica	-----	CO_2 +10% CH_3OH containing 2%H_2O 50 °C, 250 bar	CH_3OH LC/UV	[40]
PHENOXYACETIC AND BENZOIC ACIDS					
2,4-D, dicamba, 2,4,5-TP, 2,4,5-T	House dust	----	CO_2 +20% CH_3OH 100 or 150 °C 440 bar	CH_3OH Derivatization GC/ECD	[77]

So, future development of SFE will necessitate a better understanding of the interactions between analyte, matrix and modifiers; in that way, SFE methods could be established for several types of matrices. At the present time, SFE suffers from the emergence of other techniques that require less investment costs, along with several attractive features. In particular, the accelerated solvent extraction (ASE) is very promising as it seems to be less prone to matrix dependence than SFE [57,78].

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Glossary

AED: Atomic emission detector
ASE: Accelerated solvent extraction
2,4-D: 2,4-Dichlorophenoxyacetic acid
4,4'-DDE: 2,2-bis(p-chlorophenyl)-1,1-dichloroethene
DEA: Deethylatrazine
DEDIA: Deethyl-deisopropylatrazine
DEDIHA: Deethyl-deisopropyl-hydroxyatrazine
DES: Deethylsimazine
DIA: Deisopropylatrazine
ECD: Electron capture detector
FID: Flame ionization detector
FPD: Flame photometric detector
GAC: Granular activated carbon
GC: Gas chromatography
HA: Hydroxyatrazine
HDEA: Hydroxy-deethylatrazine
HDIA: Hydroxy-deisopropylatrazine
HCB: Hexachlorobenzene
HCH: Hexachlorocyclohexane
ITD: Ion trap detector
LC: Liquid chromatography
MS: Mass spectrometry
NPD: Nitrogen phosphorus detector
P: Pressure
SFC: Supercritical fluid chromatography
SFE: Supercritical fluid extraction
T: Temperature
2,4,5-T: 2,4,5-Trichlorophenoxyacetic acid
TDE: 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane
TMPA: Trimethylphenylammonium hydroxide
2,4,5-TP: 2-(2,4,5-Trichlorophenoxy)propionic acid
TSD: Thermoionic detector
UV: Ultra-violet.