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Soxhlet Extraction

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The health of our environment is now a matter of great concern. This has stimulated an intensive search for an understanding of both the ways in which the natural environment works and the anthropogenic actions that bring about environmental changes. A large number of studies have been, or are in the process of being, developed in order to increase our knowledge of the processes causing environmental pollution and to propose clean analytical methods for monitoring and subsequent control. Thus, a high percentage of the studies developed so far fall within the field of analytical chemistry. There are a number of stages involved in any analytical method: definition of the aim, selection and establishment of an appropriate method, sampling plan, sample collection, sample handling and pretreatment, final measurements (detection/determination), method validation, assessment and interpretation of the results and, finally, safety.

In spite of the evolution of analytical techniques involved in some of the above mentioned stages (particularly detection/determination), the development of some of these has not been as great as desirable. These steps constitute 'critical points' of an analytical method and, consequently, the main source of errors. The pretreatment step (including separation techniques) can be considered as a 'critical step'. Conventional Soxhlet extraction is currently one of the most frequently used pretreatment techniques, not only in environmental analysis, but also in many other fields. Its principles, performance, environmental applications and improvements are considered in more detail below.

Principles of Conventional Soxhlet Extraction

Soxhlet extraction is a very useful tool for preparative purposes in which the analyte is concentrated from the matrix as a whole or separated from particular interfering substances. Sample preparation of environmental samples has been developed for decades using a wide variety of techniques. Solvent extraction of solid samples, which is commonly known as solid–liquid extraction (also referred to as leaching or Lixiviation in a more correct use of the physicochemical terminology), is one of the oldest methods for solid sample pretreatment. Conventional Soxhlet extraction remains as one of the most

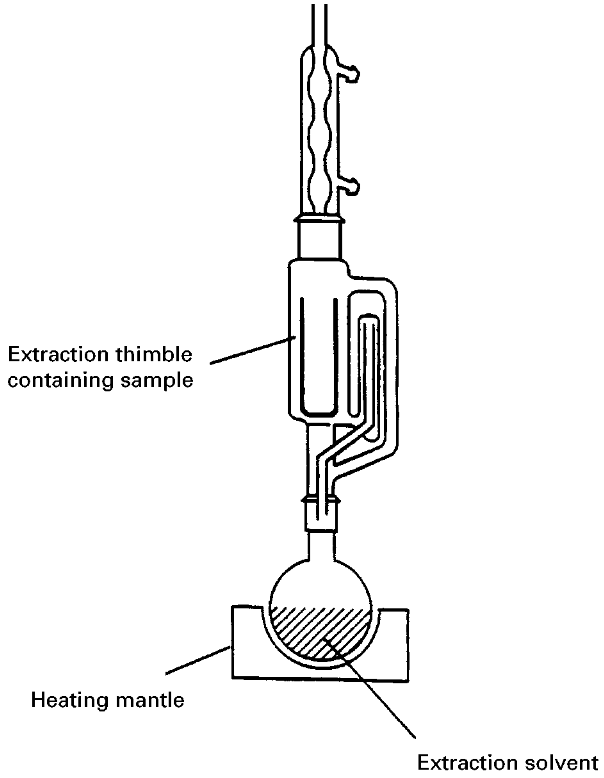

Figure 1 Soxhlet extraction apparatus. (Reproduced from Reeves RN (1994) *Environmental Analysis*. New York: John Wiley.)

relevant techniques in the environmental extraction field. This assertion is supported by the double use of conventional Soxhlet: (1) as an extraction step in a given method, and/or (2) as a well-established model for comparison of new extraction alternatives.

In conventional Soxhlet, the sample is placed in a thimble-holder and during operation is gradually filled with condensed fresh solvent from a distillation flask. When the liquid reaches an overflow level, a siphon aspirates the whole contents of the thimble-holder and unloads it back into the distillation flask, carrying the extracted analytes in the bulk liquid. This operation is repeated until complete extraction is achieved. This performance makes Soxhlet a hybrid continuous–discontinuous technique. Inasmuch as the solvent acts stepwise, the assembly can be considered as a batch system; however, since the solvent is recirculated through the sample, the system also bears a continuous character. **Figure 1** shows a scheme of a conventional Soxhlet device. As can be seen, Soxhlet extraction is a very simple technique. This simplicity makes the procedures for different samples very similar. For this reason, an overview of its extensive application in the environmental field during the last two decades is presented here, which cover the kind of samples, analytes, solvents, etc. used and the role of Soxhlet extraction in the overall analytical process.

Table 1 summarizes the main characteristics of Soxhlet extraction, clean up and detection/determination for each group of pollutants discussed below.

Use of Conventional Soxhlet Extraction for Leaching of Organic Pollutants

Organic pollutants present in solid environmental samples from natural or man-made sources are most of the time properly extracted with organic solvents in a Soxhlet device. The following sections show how conventional Soxhlet extraction is used as a technique for separation of the analytes from the solid matrix. The pollutants are classified into three groups depending on the matrices in which they are present: air, solid and liquid samples. It is worth noting that, in spite of the solid character of particulates, the samples are classified as a function of the medium in which they are present. Thus, airborne and water particulates are classified as air and liquid samples, respectively.

Organic Pollutants in Air

Organic pollutants are in the gas phase of the atmosphere and are associated with airborne particulate matter. Sampling of organic pollutants is usually carried out by filters through which a large volume of air is circulated. After filtration, the filter is extracted with an appropriate solvent and the target analytes are removed in the extract. When the extract is not suitable for direct individual separation/determination a prior clean-up stage must be applied. These and other aspects are discussed below.

Polycyclic aromatic hydrocarbons Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are among the most studied environmental pollutants. This is due to both their continuous emissions from combustion and their biological activities, such as toxicity, mutagenicity and carcinogenicity. Determination of PAHs from air requires a suitable sampling device, including an aspiration pump, which retains the air particulates on glass or quartz fibre, cellulose or paper filters. However, the filter is not the sole collection medium for PAH-containing small-size aerosols. Chemicals such as Tenax GC, PUFs (see **Table 2** for abbreviations) or Amberlite XAD-2 resins should provide a back up to these filters by retaining PAHs not trapped by the filter. A layer of activated charcoal between two filters is used for collection of gaseous components.

Table 1 Selection of the most representative characteristics of methods for determination of organic pollutants with Soxhlet extraction as pretreatment step

Compound	*Matrix*	*Sampling*	*Soxhlet features*		*Clean up*	*Detect/Determ.*
			Solvent	*Time*		
PAHs PCDDs/PCDFs PCBs/OCPs Phenols Benzidines Nitrosamines Phthalate esters Etc.	Solid samples (soil, sediment, sludge, biological tissue, etc.) Particulates, vapour, smoke, liquid samples	Homogenization (mix, ground and sieve) Moisture control Filters (glass or quartz fibre) and PUFs, XAD resins, Tenax GC, etc.	*Polar species* Dimethyl formamide Tetrahydrofuran Acetonitrile Acetone Methanol Ethanol *Non-polar species* Hexane Iso-octane Ethers Light petroleum *Aromatics* Benzene Toluene *General use* Dichloromethane Ethyl acetate Isopropyl alcohol Chloroform	From 8 to 48 h depending on the matrix, analyte and solvent	**Sorbents* Alumina (non-polar analytes with polar interferents) Silica gel (strongly polar species) Florisil (aromatic and aliphatic interferents) Activated carbon (non-polar analytes from aqueous samples) **Solid phase extraction* –(non-polar species) C_{18} C_8 Cyclohexyl Phenyl Cyano –(polar species) Amino Diol *Chromatography *Distillation *LLE	*Techniques* GC HPLC TLC SFC Spectroscopy *Detectors* FID (hydrocarbons) NPD (nitrogen and phosphorous) FPD (sulfur and phosphorus) ECD (halogenated) UV/VIS and DAD MS (universal) Flourescence

Table 2 Abbreviations

ASE	Accelerated solvent extraction
CE	Capillary electrophoresis
CIMS	Chemical ionization mass spectrometry
ECD	Electron capture detector
EIMS	Electron impact mass spectrometry
EPA	Environmental protection agency
FID	Flame ionization detector
FMASE	Focused microwave-assisted Soxhlet extraction
GC	Gas chromatography
HPLC	High performance liquid chromatography
HPS	High pressure Soxhlet extraction
LC	Liquid chromatography
LLE	Liquid–liquid extraction
MAE	Microwave assisted extraction
MS	Mass spectrometry
NPD	Nitrogen phosphorus selective detector
OCPs	Organochlorine pesticides
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo-dioxins
PCDFs	Polychlorinated dibenzo-furans
PUFs	Polyurethane foam plugs
SEC	Size-exclusion chromatography
SFC	Supercritical fluid chromatography
SFE	Supercritical fluid extraction
SIM	Selected ion monitoring
TLC	Thin-layer chromatography
UV	Ultraviolet
VOCs	Volatile organic compounds

The adsorbed compounds are extracted by Soxhlet into different organic solvents such as toluene, benzene, cyclohexane, tetrahydrofuran, dichloromethane and liquid CO_2. Clean-up extract procedures are mainly performed by the use of silica gel (SFC, LLE and LC are also used), and the individual separation/determination stage involves HPLC-UV and GC-MS. A less common technique for PAH determination is TLC-UV.

Polychlorinated dibenzo-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) Analysis of dioxins has become an issue of major importance because of their carcinogenic nature. The main source of dioxin emission is combustion (in waste incineration and the steel industry). In comparison with the wide variety of methods used for the determination of PAHs from air, the method for determination of PCDDs and PCDFs is well established and only some minor modifications are found in the literature. These compounds are sampled by splitting the air into two phases. The split involves glass fibre filters, which retain airborne particulates, and PUF solid sorbents, which retain vapours. The PUF sorbents are fortified with a range of ^{13}C-labelled PCDDs and PCDFs before sampling (sometimes spiking precedes the sampling step). The same spiked procedure is applied to particulate phases before extraction. The filter and foam are then extracted by Soxhlet with toluene (benzene/ethanol and dichloromethane have also been used but less frequently than toluene), followed by an acid–base clean-up step, then drawing of the extract through micro-columns of silica gel, alumina and carbon (sometimes a chromatographic clean up is applied before). Individual separation of the analytes and determination are performed by high-resolution GC–EIMS-SIM.

Polychlorinated biphenyls (PCBs) and other chlorinated compounds A wide variety of pollutants other than PCDDs and PCDFs contain chlorine. This makes them very harmful due to their activity in the atmosphere. PCBs and other compounds (chlorinated solvents, halogenated methoxybenzenes (halogenated anisoles), polychlorinated naphthalenes, etc.) are the most representative chlorinated compounds in addition to OCPs (alpha and gamma hexachlorocyclohexane (HCHs), chlorothalonil, dichlofluanid, toxaphene, chlorpyrifos, alachlor, etc.).

Sampling of these compounds is similar to that described in the previous two sections and either the adsorbent used or the extraction solvent and post-extraction procedures applied are widely documented in the literature. Thus, the performance of different sorbents, such as Chromosorb 102, Porapak R, Supelpak-2, Amberlite XAD-2, Amberlite XAD-4, Carbonaceous Ambersorb XE-340 and polyurethane foam, has been evaluated with use of atmospheres containing known concentrations of OCPs. The most efficient trap for HCH and PCBs was found to be two cartridges containing PUFs-Tenax-GC sandwich traps, connected in series. Halogenated anisoles and hexachlorobenzene (HCB) have been sampled from air using a high volume sampling technique in which air was pumped through two layers of solid sorbent: the upper sorbent layer was a mixture of silica gel 60/ENVI-Carb or ANGI-Sorb 5B/ANGI-Sorb 10B and the lower sorbent layer was silica gel 60/ENVI-Carb or ANGI-Sorb 2.5B. These solid sorbents are Soxhlet extracted with organic solvents, mainly dichloromethane (but also with others such as petroleum ether, ethyl ether, hexane, acetone and mixtures) and, after the appropriate clean up, the detection/determination step is developed mainly by GC-ECD.

Other pollutants usually determined in air In addition to PAHs and chlorinated pollutants from the atmosphere, there are some other families of pollutants that have a significant effect on the environment. Thus, alcohols and phenols, organophosphorous compounds, anilines and benzidines, aliphatic hydrocarbons, etc., can be included in this classification. The procedures for determination and the general characteristics of the chemicals and instruments used (solid sorbents, extractant, extraction time, clean up and detection/determination) are similar to those discussed in previous sections.

Organic pollutants in solid samples Organic pollutants are present in a wide range of environmental solid samples. Thus, soil, sediment, sewage sludge and ash are the most commonly studied matrices in the environmental field. All these matrices can be leached by conventional Soxhlet extraction. There are two criteria that solid samples must meet before extraction: (1) they must be finely divided (in order to improve the sample–solvent contact), and (2) sample moisture must be carefully controlled. After the extraction step by an organic solvent, a clean-up procedure is necessary due to the co-extraction of both fat residues and other interferent substances. The usual procedures for analytical processing of the most representative organic pollutants are as outlined below.

Polycyclic aromatic hydrocarbons Soil or sediment samples are dried to constant weight, ground, sieved and mixed with anhydrous Na_2SO_4. Soxhlet extraction is performed with dichloromethane (chlorobenzene, benzene, cyclohexane and hexane/acetone are less common for this purpose) and the extract is reduced in a Kuderna–Danish concentrator, a rotary-evaporator or under a N_2 stream. Clean up (if needed) involves: (1) passing the extract through one or more microcolumns containing silica gel, alumina, C_{18}, Florisil, Amberlite XAD-2, etc., and/or (2) fractionation by semi-preparative normal-phase LC. The PAHs are determined either by HPLC (with UV, MS or fluorimetric detection) or GC (with FID or MS detection).

Fly ash is Soxhlet extracted with toluene (or benzene) and the extract is cleaned up by TLC on a plate coated with silica gel. Detection/determination involves the same techniques as those used in soil.

Sewage sludge is Soxhlet extracted with toluene. The extract is evaporated and then, liquid–liquid partitioned between cyclohexane, dichloromethane and H_2O. The cyclohexane extract is purified on a silica column. Separation of neutral and polar PAHs is performed by HPLC-UV with individual separation/determination by GC-FID.

Polychlorinated dibenzo-dioxins and polychlorinated dibenzo-furans As could be seen in the previous section, the extraction of PCDDs and PCDFs is usually performed in a single step. The special characteristics of these compounds makes it mandatory to study them apart from the rest of the chlorinated pollutants. Despite the existence of papers on determination of dioxins and furans from solid matrices such as soil or sediment, the main source of emission in the literature is combustion processes. Here, the most important solid matrix is fly ash from incinerators. However, the procedure followed for fly ash could be applied to other matrices with minor changes of the sample preparation step. Fly ash samples are collected at the bottom of the electrostatic precipitators of the incinerator (this is why they are considered as solid pollutants; however, when ashes are in the atmosphere they are considered as air pollutants). The fly ash is treated with 1 N HCl, filtered, washed with H_2O and air-dried at room temperature. After addition of ^{13}C-labelled PCDD and PCDF internal standards, the sample is Soxhlet-extracted with toluene (benezene and hexane/acetone have also been used) and the extract is concentrated, then subjected to clean up involving partitioning with concentrated H_2SO_4 and sequential LC on multi-layered silica gel (containing acid-modified, base-modified, $AgNO_3$-modified and neutral forms of silica gel), acid alumina and Celite/Carbopack stationary phases as described in US EPA Method 8280A. A portion of the resulting solution is analysed by high resolution GC-EIMS-SIM.

Polychlorinated biphenyls and other chlorinated compounds The large number of chlorinated pollutants in solid samples present in the environment makes their classification and study very difficult. However, it has been clearly demonstrated that there are three groups (PCBs, OCPs and polychlorinated phenols), which are the subject of most of the papers found in the literature. Despite that the following paragraphs are devoted to these groups of organic pollutants, the procedures described are also applicable to the rest of the chlorinated compounds (particularly with regard to Soxhlet extraction).

The first step of the analysis of chlorinated phenolic compounds in polluted soils is wetting of the sample with H_2SO_4, followed by Soxhlet extraction with hexane/acetone or diethyl ether/petroleum ether. Different techniques can be used for subsequent treatment of the extract, the most representative being acetylation and LLE. After evaporation, the acetates are cleaned up on a deactivated silica gel column and subjected to GC (with ECD or MS detection). The chlorophenols are also individually separated/determined by LC-atmospheric-pressure-CIMS.

PCBs are among the most studied pollutants in solid samples in recent years. Their properties (resistance to oxidation, acids, bases, and other chemicals, high thermal stability, dielectric behaviour, etc.) make them the most frequently used organic compounds and, consequently, the greatest environmental pollutant.

As the overall procedures followed for the determination of PCBs and OCPs are similar, both groups are usually determined together. Solid sample preparation is similar to that shown for the determination of pollutants from solid samples (see PAHs from soils). Soxhlet extraction is performed with either a single solvent (toluene or dichloromethane) or a mixture of solvents such as, hexane/acetone, pentane/dichloromethane, etc. Clean up usually involves sulfur removal by reaction with Cu or tetrabutylammonium sulfite and the use of silica gel, Florisil and fractionation by SEC if required. The most usual way for individual separation/determination of PCBs and OCPs is GC-ECD.

Other pollutants in solid samples There are some other pollutants that are frequently determined in solid samples. These compounds (in general, the same as those covered in Organic Pollutants in Air) are usually in trace amounts in the environment. Thus, organic pollutants such as aliphatic hydrocarbons, aldehydes, non-chlorinated phenols, cresols, anilines and benzidines, VOCs (mainly organic solvents), phthalates, amines, non-chlorinated pesticides, etc., are also determined due to their importance in the environment. Soxhlet extraction has shown its suitability as a technique for separation of these pollutants from solid environmental matrices.

Organic Pollutants in Water

Water is the most important liquid in the environment. A wide range of human activities, such as mining, coal and fuel combustion, industrial and agricultural processes, domestic sewage, etc, contribute to the pollution of the aquatic environment. However, the key contribution to water pollution is the solubilization of pollutants. Thus, the study of pollutants in water can be divided into pollutants that are solubilized in water (mainly inorganic pollutants) and those present as the solid phases of the aquatic medium, such as sludge, sediment, particulates and biological species (organic and inorganic pollutants).

The way in which sludge and sediment are Soxhlet extracted in order to isolate the analytes from the solid matrix has been discussed in previous sections. This section is therefore devoted to the analysis of organic pollutants (mainly PCBs and pesticides) from water and associated particulates. In spite of the fact that biological samples are also a part of the environment, they are considered to be a matter concerning biochemistry and toxicology and, therefore, beyond the scope of this article.

It is obvious that Soxhlet extraction is not a suitable method for direct separation of analytes from liquid sample, but that it must be used after a previous filtration step. This procedure is very similar to that followed for air samples. The two phases existing in water within suspension matter samples (liquid and particulate) are split by filters (paper, glass-fibre or quartz-fibre) and solid sorbents (PUFs, granular activated carbon, Aquapak 440A, Separon SE, ODS gel and Amberlite XAD-2, -4 or -7 resins). The solid sorbents and the particulate matter constitute the solid sample to be subsequently extracted by Soxhlet. Collection of the solid matter by centrifugation is an alternative to filtration. Some of the procedures found in the literature are discussed below.

PCBs and OCPs are Soxhlet extracted from solid particulate matter with dichloromethane. After silica gel or Florisil clean up in the presence of activated Cu, analyses are developed by GC-ECD (or GC-MS). The determination of organophosphorus and organonitrogen pesticides in solid particulate matter from surface water is developed by dichloromethane Soxhlet extraction and GC-NPD. The determination of PAHs from water samples requires hexane/acetone Soxhlet extraction, cleanup on both an Al_2O_3–Na_2SO_3 column and silica column, and finally, individual separation by HPLC and fluorimetric detection.

Many aquatic organisms accumulate pollutants inside their tissues by bioaccumulation. This behaviour is used in pollution surveillance programmes, due to the following advantages it provides: (1) the analyses of soil, air, water, etc. yield levels of pollutants present at the time the samples were taken, whereas those observed in bioaccumulator species reflect the level over a period of time; and (2) pollutants concentrate in biological species at high levels, and can therefore be monitored by analytical techniques with relatively high detection limits.

The most relevant field in which biological samples are used is in the analysis of the aquatic environment. Fish, mussels and a number of other species are studied in order to evaluate pollution levels in the surrounding environment. The pollutants studied are the same as in previous sections, and Soxhlet extraction has great relevance as a pretreatment technique due to the solid character of the matrix. In spite of this, one of the most relevant drawbacks in Soxhlet extraction of these samples is their high water content (the presence of water in samples subjected to Soxhlet extraction constitutes a shortcoming whose importance is a function of the amount of water). Thus, it is necessary to macerate the sample initially with anhydrous Na_2SO_4. After this, a conventional Soxhlet extraction of the mixture with an organic solvent (depending on the nature of the analytes) is performed.

Use of Conventional Soxhlet Extraction for the Leaching of Inorganic Pollutants

The application of conventional Soxhlet extraction in the field of inorganic pollutants has been developed to a much less extent than that of organic pollutants. There are in the literature only a few applications of Soxhlet extraction to inorganic compounds. Soxhlet extraction is used mainly as a clean up step prior to the determination of inorganic pollutants with the aim of removing organic substances in the extract. As an exception to this, metals have been determined in the extract after a Soxhlet step. This is possible either when metals are forming organometal compounds or are concentrated by sorption on PUFs impregnated with an organic substance. However, the suitability of Soxhlet extraction for the isolation of inorganic pollutants is poor and some other techniques such as hydrolysis, digestion, distillation, etc. are recommended for this purpose.

Improvements in Soxhlet Extraction

Soxhlet extraction has been the most frequently used technique for isolation of organic pollutants from environmental samples for the last twenty years. However, the use of new extraction techniques that overcome the drawbacks associated with Soxhlet is, today, one of the most promising research lines in the field of solid sample treatment.

The most significant drawbacks of Soxhlet extraction are the long time required for the extraction and the large amount of organic solvent wasted, which is not only expensive to dispose of but which can cause environmental pollution itself. Moreover, the conventional device is not easily automated. There are two different ways in which to circumvent the drawbacks of conventional Soxhlet extraction, namely: (1) the use of one of the new alternatives (such as SFE, MAE, ASE, etc.); and (2) the improvement of conventional Soxhlet. As this article is devoted to Soxhlet extraction, the following sections discuss only the latter way, that is, improving the shortcomings of the conventional device while keeping its positive characteristics.

High-pressure Soxhlet extraction

High pressure in Soxhlet devices is achieved by placing the extractor in a cylindrical stainless-steel autoclave or by the use of either commercial or laboratory-made supercritical fluid-Soxhlet extractors. Thus, PAHs and PCBs and be removed from environmental samples using HPS with liquid CO_2 in working conditions close to those corresponding to the supercritical state of the extractant. The main drawback of this alternative is the change from supercritical to liquid state of the extractant, which affects Soxhlet performance.

Automated Soxhlet (Soxtec HT and Büchi B811)

Commercial automated Soxhlet devices perform the extraction with similar precision to conventional Soxhlet but with a significant saving of time and extractant. The most relevant characteristic of a Soxtec system is the possibility of developing three different steps, namely, boiling, rinsing and recovery of the solvent, by switching a lever. The B811 extractor is able to perform the same steps as a Soxtec device but it can also work as a conventional Soxhlet. The overall performance of the B811 extractor is computer controlled. The analysis of organic pollutants from soil and sediments is an example of the methods developed for use with this device.

Focused microwave-assisted Soxhlet extraction (Soxwave and FMASE)

The Soxwave is a commercial system with an operational performance similar to that of Soxtec HT. The system performs the same three steps but with two significant differences: (1) a different heating source (microwave instead of electricity) is used; and (2) the sample is also irradiated with microwave energy, making it easier to rupture the analyte–matrix bonds. The main drawback of Soxwave is its dependence on the extractant dielectric constant. Thus, efficient extractions are only obtained with polar solvents (due to the characteristics of microwave irradiation) and, consequently, this device is not as universal as a conventional Soxhlet is. Moreover, the energy the analytes receive is at least as high as that necessary to reach the boiling point of the solvent, which can cause degradation of thermolabile analytes. Some applications of Soxwave have been developed in the environmental field and, due to its suitability for water-based extractions, quantitative extractions have been achieved in the isolation of metals from solid samples such as coal or soils.

FMASE is the last of the improvements carried out on the conventional Soxhlet extractor. In fact, the FMASE device works as a conventional Soxhlet, but the cartridge zone, where the extractant and sample are in contact, is placed in the microwave cavity of a specially designed focused microwave oven.

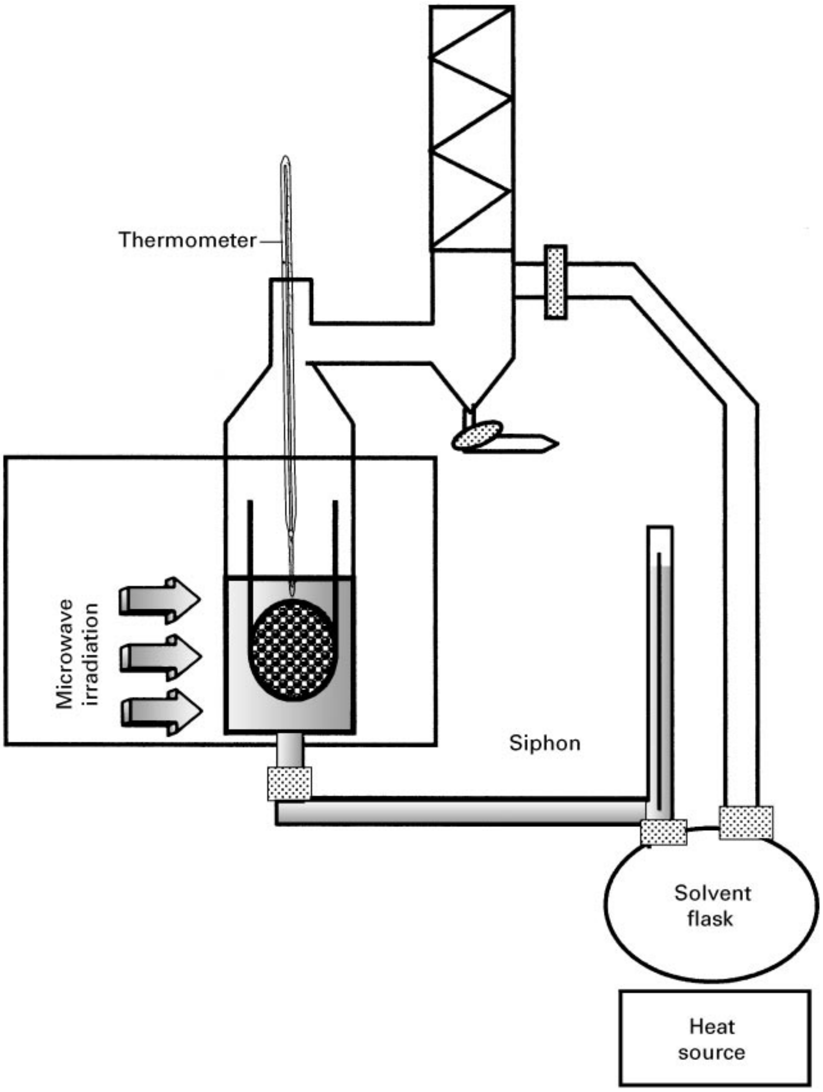

Figure 2 Scheme of the FMASE device. (Reproduced with permission from García-Ayuso LE and Luque de Castro MD (1999) *Analytica Chimica Acta* 382: 309.)

Figure 2 shows a scheme of the FMASE device. The similar performance with respect to its conventional counterpart makes FMASE a suitable alternative for almost all the applications developed in a conventional Soxhlet, that can be developed without changes, except in the time required for quantitative extraction.

FMASE maintains the advantages of conventional Soxhlet extraction while overcoming the limitations, such as the long extraction time, non-quantitative extraction of strongly retained analytes and unsuitability for automation. Solvent distillation in FMASE is achieved by electrical heating, which is independent of the extractant polarity, and recycling saves 75–85% of the total extractant volume. The main drawback in FMASE is the difficulty of using water as extractant due to its design, as both thermal insulation and shortening of the present distillation device is mandatory for reception of water vapour on the sample-cartridge vessel, condensation there and dropping on the sample. A comparison between conventional Soxhlet and FMASE for leaching of PAHs, herbicides and n-alkanes from soil shows the advantages of the latter when compared with the conventional design. FMASE provides efficiencies similar to those obtained by conventional Soxhlet with extraction times at least eight times shorter.

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Supercritical Fluid Extraction

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

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

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

Sample Preparation Prior to Extraction

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

Pretreatment of the Sample

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

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

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

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

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

Derivatization Reactions

Extraction of highly polar compounds may be improved by coupling derivatization reactions with SFE, to convert polar functions into less polar groups for better solubility in the fluid. This procedure affords extracted compounds that are readily amenable to