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Review

Extractions with superheated water

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Abstract

As the temperature of liquid water is raised under pressure, between 100 and 374 °C, the polarity decreases markedly and it can be used as an extraction solvent for a wide range of analytes. Most interest has been in its application for the determination of PAHs, PCBs, and pesticides from environmental samples, where it gives comparable results to Soxhlet extraction but more rapidly and without the use of significant volumes of organic solvents. Unlike SFE, *n*-alkanes are not extracted unless the pressure is reduced and steam is used. Other applications have included the extraction of essential oils from plant material where it preferentially extracts the economically more important oxygenated components compared to steam distillation. The aqueous extract has been concentrated in a number of different methods (solvent extraction, SPE, SPME, extraction disc) or the extraction can be linked on-line to LC or GC. In many cases the superheated water extraction is cleaner, faster and cheaper than the conventional extraction methods.

Keywords: Reviews; Sample preparation; Superheated water; Extraction; Environmental analysis; Pesticides; Essential oils

Contents

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1. Introduction

Water is a unique solvent because of its highly hydrogen-bonded structure, and at room temperature it has a disproportionately high boiling point for its mass, a high dielectric constant and high polarity. However, when heated the properties of water change markedly as the hydrogen-bonded lattice is disrupted as thermal motion increases. As the temperature rises there is a marked and systematic decrease in the permittivity (Fig. 1) [1], an increase in the diffusion rate and a decrease in the viscosity and surface tension [2]. If the pressure is raised so that the water remains in a condensed state, these changes continue above the atmospheric boiling point and up to and beyond the critical point at 374 °C and 218 bar. Over much of this temperature range the density is almost constant so that pressure effects on the properties of the water are minimal [1]. In this review, superheated water is used as a general term to denote the region of the condensed phase between 100 °C and the critical point. Often this phase is described as subcritical water but by analogy with supercritical fluid extraction, this term would probably be preferably employed for the region close to the critical point.

The pressures required to maintain a condensed state of water are moderate, 15 bar at 200 °C and 85 bar at 300 °C. If the pressure drops below the boiling point at any pressure, superheated steam is formed. This has a markedly lower dielectric constant than the liquid state (see Fig. 1) and has gas-like diffusion rates and viscosity properties and consequently behaves quite differently as an extraction solvent to superheated water.

These temperature effects mean that superheated water can have a permittivity very similar to typical organic solvents (for example: water, $\epsilon = 30$ about

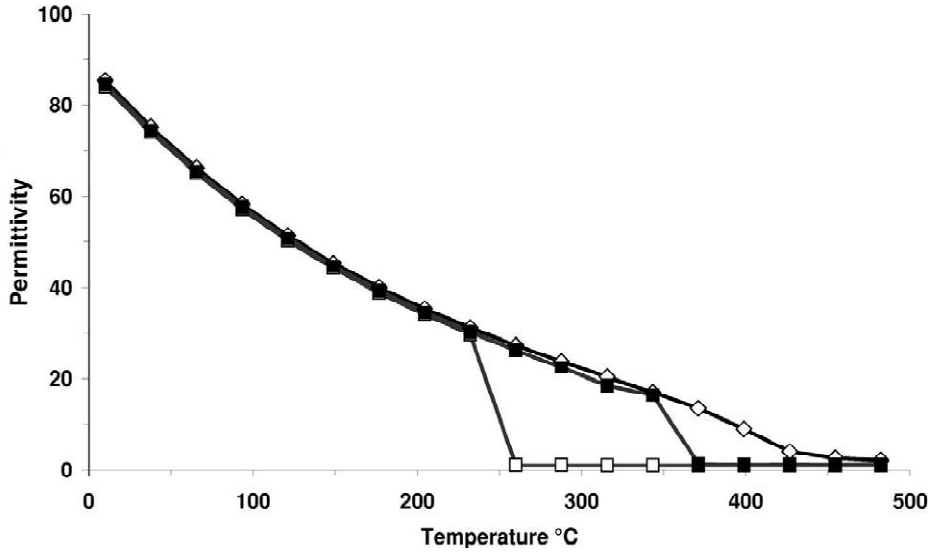

Fig. 1. Changes in the permittivity of water with temperature at three pressures: □, 33 bar; ■, 129 bar; and ◊, 322 bar (adapted from [1]). The drop to low values corresponds to the formation of superheated steam.

220 °C and methanol, $\epsilon = 33$ at room temperature) [1] and it can dissolve a wide range of medium and low polarity analytes. In recent years, superheated water has started to be used widely as an analytical extraction solvent and it is this application that will be considered in the current review. The changes in the polarity of water with increasing temperature have been also exploited in superheated water chromatographic methods [3–5]. In addition superheated water is attracting interest as a solvent for organic synthesis [6] but this is outside the scope of the present review. Under supercritical conditions, particularly if saturated with oxygen, water is highly aggressive and it has been employed for the oxidative degradation of nerve gases and explosives in closed systems (for example [7,8]).

2. Superheated water extractions

Liquid water at elevated temperatures above its boiling point has been used for many years as an industrial solvent and cleaning agent in applications ranging from enhancing the extraction of oil shale [9], the extraction of sulphur from ore bodies in the Frasch process [10], to degreasing. As a vapour, steam is commonly used in hydrodistillation for the isolation of volatile constituents of plant materials to provide essential oils of value in perfumery.

The recent analytical interest in superheated water as an extraction solvent began with the work of Hawthorne and co-workers, who were interested in environmentally friendly extraction methods for soils and environmental solids. In 1994, they reported [11] the superheated water extraction (SWE) of polar and non-polar analytes from soil samples with liquid water over a range of temperatures up to 400 °C. The highest (supercritical $\epsilon = 8$) temperature quantitatively extracted the PAHs, C_{13}–C_{30} *n*-alkanes and all the more polar analytes. Under subcritical conditions at 250 °C ($\epsilon = 29$), the PAHs (and the more polar analytes) were obtained with >97% recovery but the yields of the higher *n*-alkanes decreased markedly. This selectivity makes subsequent GC analysis easier and no degradation of the PAHs was observed. These results contrasted with supercritical fluid extraction (SFE) where the *n*-alkanes were the most readily extracted. On decreasing the temperature to 200 °C and below, the recoveries of spiked PAHs decreased. Altering the pressure from 50 to 600 bar at 250 °C, while maintaining a liquid extraction phase, had virtually no effect on extraction strength, although the results for steam at 5 bar were lower. This work lead to a study of the extraction of PCBs, which were also readily achieved with superheated water at 250 °C [12] and initiated a wide ranging series of studies on the extraction of environmental samples.

The method has since been applied to pesticide residues from soils and plants and for the extraction of flavours and fragrances and these will be considered later. The major advantage of the use of superheated water is that it considerably reduces the use of organic solvents in environmental analysis, which has been a considerable concern as the usage of many of the widely used solvents have been restricted or banned by the Montreal protocol. The alternative method of SFE using carbon dioxide requires much higher pressures and as a weak solvent the yields were often dependent on the matrix

2.1. Sample solubility in superheated water

As a background for the extraction studies, Hawthorne and co-workers the group at North Dakota examined the changes in the water solubility of typical analytes with temperature and studied in detail the interactions between a wide range of polar and non-polar analytes and different potential sorbents [2]. They found that although low temperature water could break inert or dipole bonding between analytes and matrices, higher temperatures were required to break van der Waals forces, and the highest temperatures were needed to break π–π electronic interactions. They examined the solubilities of a number of PAHs [13] and found marked changes in solubility as the temperature increased. For example, the solubilities of anthracene, chrysene and perylene increased by 20 000-fold over the range 25–200 °C. The mole fraction solubility of chrysene increased from 0.63×10^{-9} at 298 K to $75\,800\times10^{-9}$ at 498 K. However, pressure had no effect over limited ranges, which is in contrast to its marked effect in SFE. Further studies by Miller and Hawthorne [14] of hydrophobic organic compounds in superheated water found similar large changes in

solubility with temperature. Increasing the temperature of water from 25 °C to near the normal melting point of the organic solute, resulted in solubility enhancements ranging from 6-fold for naphthalene (at 65 °C) to a 130 000-fold increase for chlorothalonil (at 200 °C) and a 275 000 fold increase for benz[a]pyrene (at 250 °C). Similar but smaller changes in solubility were reported by Curren and King [15] for the triazines over the range 50–125 °C. The absence of a dependence on pressure means that in many of the studies, pressure control led was often limited or only reported as long as a sufficiently high value was maintained to ensure a condensed state of the water.

2.2. Extraction conditions

In most of the extraction studies distilled or deionised water has usually been used alone as the solvent in either static or dynamic extraction modes. Sometimes it is degassed or flushed with nitrogen to remove oxygen to prevent oxidative side reactions. pH control has been employed to enhance the extraction of selected analytes. For example, Crescenzi and co-workers [16] found improved extraction efficiency for a range of polar and medium polar pesticides, if a phosphate buffer at pH 7.5 was employed as the superheated eluent and this seemed to be also able to release sequestered pesticides from aged soils. In a few cases because the extraction power of superheated water can be limited organic solvents have been added to the water to give solvent assisted superheated water extraction. For example, to obtain atrazine from beef kidneys in a matrix solid-phase dispersion, Curren and King [17] used an ethanol–water (30:70 v/v) mixture at 100 °C to obtain high yields but this review will concentrate on methods in which water is the dominant solvent.

In other studies, Fernández-Pérez and Luque de Castro [18] added dodecyl sulfate (SDS) as a micellar agent to the extraction water to enhance the extractability of PAHs and thereby reduce the extraction temperature and time required. The SDS was separated from the PAHs during a subsequent solid-phase extraction (SPE) stage before analysis. It was claimed that the method reduced corrosion of the extraction vessel and prevent deposition of the PAHs as the extraction water solution was cooled.

Almost all the matrices examined have been solids, either soils or environmental solids, such as particulates, or powdered plant materials. In most cases liquid–liquid extraction have not been employed because of the difficulty of handling two liquid phases in a closed pressure system. However, a true liquid–liquid system was reported by Fernández-Pérez and co-workers [19] for the extraction of transition metal ions from a flowing oil sample by mixing it with water, heating to 150 °C and then separating the layers after cooling.

2.3. Comparisons with other extraction methods

Many of the reports have compared SWE with previously reported methods, such as Soxhlet extraction, pressurised solvent extraction (PSE), SFE, or steam distillation for plant materials. For most environmental samples the results were generally similar to previous methods although there were some interesting variations.

In their work, Yang and co-workers [12,20] found comparable results for the PAHs between SWE, Soxhlet and SFE although the first method was often the fastest. In contrast, the behaviour of the *n*-alkanes was markedly different and SWE gave much poorer recoveries. However, on reducing the pressure the *n*-alkanes were released by superheated steam at 250 or 300 °C. It was thought that this was because of the much lower permittivity of the steam (typically $\epsilon = 1$) (Fig. 1), which was more compatible with the polarity of the hydrocarbons.

This observation was confirmed in studies by Hartonen and co-workers [21] who compared the extraction of *n*-alkanes and PAHs from model sand systems by SFE, SWE, steam and solvent extraction followed by collection on a Tenax trap. They found that steam gave >95% of the diesel hydrocarbons but the recovery using superheated water was lower.

Van Bavel and co-workers [22] compared pressurised water and steam for the extraction of polychlorinated bibenzofurans and naphthalenes from model systems and industrial soil. The optimum conditions were found to be steam at 300 °C at 50 atm when results comparable to Soxhlet extraction were obtained. The advantage over liquid water extraction at the same temperature (at 250 atm) was attributed to the lower permittivity of the steam

($\epsilon = 1$). At a higher temperature (400 °C) some losses were noted but it was thought that these might be due to mechanical problems or oxidation degradation. Their success in removing hydrophobic chlorinated pollutants suggest a potential value in this method for the remediation of contaminated soils.

Pross and co-workers [23] compared the extraction of spiked polychlorinated biphenyl from soils with supercritical carbon dioxide, sulfur hexafluoride and subcritical water. All three had attributes but water was judged the best overall because of its low price, good availability and environmental safety.

Although in some ways similar, different results were obtained with plant materials where the polarity of the analytes of interest is more varied. The comparison here is primarily with steam distillation. The principal difference is that the water is more polar and the extraction is not based on volatility so favours the extraction of oxygenated materials, which potentially are important as they are economically more important than the alkanes favoured by SFE and steam distillation.

2.4. Sample stability

Despite the apparently severe temperatures and potential for oxidation and hydrolysis, most of the analytes examined were stable even up to 250 °C. In most cases SWE showed no decomposition. This confirmed results from superheated water chromatography where functional groups, such as phenols and esters, were generally stable [3]. However, attempts to extract phenylurea herbicides at 120 °C resulted in severe losses but they were stable at 90 °C [24]. In a study by Lou and co-workers [25] hydrolysis was encouraged during the extraction of chlorinated acid and ester herbicides from soils, so all that all the analytes were obtained as the free acids and could be trapped on an ion-exchange resin disk.

In a recent paper Thompson and Carr [26] have examined the thermal stability of a number of analytes on a hot (up to 190 °C) PBD-zirconia column in acetonitrile–water and examined the products for degradation on an ODS-column at 40 °C. Their main conclusion was that many complex analytes can be separated at high temperatures. However, other authors have suggested that stability needs to be tested by recovery and by-product tests before a method is adopted.

2.5. Equipment

Most extractions have employed relatively simple home made equipment but some use has been made of commercial pressurised solvent extraction systems (PSE) (for example [28,29]) or a system based on SFE equipment, which might contain an active valve or fixed restrictor, such as capillary or needle valve. In cases where a fixed restrictor is used the back-pressure can be altered by adjusting the flow-rate. However, because pressure is not a critical factor in SWE due to the low compressibility of water over the typical temperature ranges, the pressure control can be very basic and accurate measurement and control is not required.

One interesting development was to use the vapour pressure of the solvent to generate its own over-pressure. Hageman and co-workers [29] placed a soil sample with water in a closed vessel (a simple pipe with two end-fittings), which was then heated in an oven at 250 °C for 15 min to give a static extraction. (A subsequent warning reminded potential users that some expansion space must be left above the water in the extraction vessel [30]). The cooled aqueous solution was sampled by SPME and analysed by GC. During this study they were surprised to found that d_{10}-anthracene being used as an internal standard was oxidised to anthraquinone but non-deuterated anthracene was stable. None of the other PAHs or their deuterated forms were affected. The deuterated internal standards were needed because the PAHs may partition back onto the soil as the aqueous extraction solution is cooled. More polar analytes, such as anilines, remained in solution on cooling and no internal standards were required. The results compared well with other methods and often yielded analytes that were lost during prolonged Soxhlet extraction. A later paper applied the same technique to the extraction of PCBs from soils and sediment [31]. The authors claimed that the method was cost effective (each extraction vessel only costing $6, the extraction water cost was negligible and the SPME fibre cost $1 per extraction), field portable, simple and rapid.

3. Extraction of the analyte for analytical determination

One disadvantage of SWE is that the extract is a relatively dilute aqueous solution and this has raised concerns about the solubility of analytes and the potential for precipitation and sample loss by re-adsorption onto the original matrix. This is principally a problem when there are marked differences in solubility on cooling as with the PAHs. For large scale separations care must be taken to avoid narrow bore tubing that might be blocked by a precipitate. The dilute extract although free of the matrix often has needed concentration/extraction before any subsequent assay step. However, because the extract solution is a clean matrix, sample handling and concentration is much easier than from the original sample material.

3.1. Solvent trapping/extraction

One method is to collect the total aqueous extraction solvent and to extract it with a small volume of an organic solvent. For example in the extraction of ground oregano the cooled water was extracted with hexane [32]. The extraction took only 15 min and for most of the constituents the yields were higher than after 3 h of conventional steam distillation. However, this method can result in some sample loss but will give a more concentrated solution for subsequent analysis. Ideally, an internal standard should be employed.

3.2. SPE and SPME extraction

As a frequent aim of SWE is to avoid the use of organic solvents, alternative solvent free (or minimal solvent) extraction methods have been used. The aqueous extraction solution can be passed through a solid-phase extraction cartridge and then the analytes can be extracted by solvent elution in a small volume. For example, Crescenzi and co-workers [16] trapped the extract on a C_{18} trap and then eluted it for separation and McGowin and co-workers used a C_{18} cartridge to trap PAHs. When terbuthylazine (CBET) was extracted from soil, di Corcia and co-workers [33] trapped the pesticides and metabolites onto carbon black and then eluted with an organic solvent for LC–MS. Similarly Crescenzi and co-workers [24] trapped a range of neutral and acidic herbicides, including triazines, phenylureas and phenoxyacetic acids, on a carbon cartridge from a hot water extraction. Selective back elution with organic solvents gave a class fractionation of the herbicides.

Another alternative approach has been to assay the aqueous extraction solutions using solid-phase micro extraction (SPME) [27,34] from dynamic or from static extraction [31] followed by GC analysis. Additional steps can also be introduced, for example in the isolation of the group of natural pyrethoids, the original analytes were deliberately hydrolysed to the free acids by Krappe and co-workers [35] in the presence of basic alumina as a catalyst and were extracted using superheated water at 200 °C. The acids were trapped by SPME on a PDMS fibre and examined by GC using octanoic acid as the internal standard.

Because the small size of the extraction medium in SPME means that extraction is often incomplete, the alternative stir bar extraction method has also been examined. Wennrich and co-workers [28] compared the use of SPME and stir bar extractions followed by thermal desorption and GC–MS of organohalogen pesticides from strawberries. They later extended the method to other vegetables (apples, kohlrabi, lettuce and tomatoes) [36]. The stir bar extraction gave a significant higher sensitivity of the overall assay compared to SPME but both methods had similar reproducibility.

3.3. In-situ trapping

Because of the much lower solubility of very non-polar analytes in cold water there is a danger that they might be deposited back onto the sample matrix or into the connecting tubing as the extraction solution cools. A successful method in these cases has been to add a trapping agent to the extraction vessel so that the extracted materials are trapped out of the cooling aqueous phase within the extraction vessel. For example, in an extension of their earlier static extraction followed by SPME [29], Hawthorne and co-workers [37] carried out a static extraction but placed a styrene–divinyl benzene extraction disc in the extraction vessel. As the aqueous solution

cooled down, about 95% of the extracted PAHs partitioned into the disc. This had potentially great advantages for fieldwork as only the disc (in an autosampler vial) needed to be brought back to the analytical laboratory. The disc was subsequently extracted with acetone/methylene chloride for GC. The results were quantitatively very similar to Soxhlet extractions.

A similar technique but using a SAX extraction disc was used by Field and co-workers [38] to trap acid metabolites of Dacthral directly from the aqueous extraction solution. The extraction was as efficient as passing the solution through the disc after the extraction. For example, if ODS-silica was added to a sample of municipal waste, it increased the recovery of PAHs and of triazine pesticides at higher extraction temperatures [39].

In a related study by Lou and co-workers [25], a strong anion-exchange disc was used to trap chlorinated acid herbicide as free acids, which were then eluted and silylated before GC.

3.4. Linked systems

Rather than extracting or isolating the analytes of interest, an alternative approach has been to link the extraction system directly to the assay procedure. Yang and Li [40] indirectly coupled SWE to LC by trapping the initial extract on a C_{18}-cartridge, which was then removed and placed in the sample loop position of an LC so that the extract was flushed with the HPLC mobile phase directly onto the column. They demonstrated that this method could be used for the extraction and determination of BTEX alkylbenzenes and polycyclic aromatic hydrocarbons from sand and contaminated soils. The inclusion of the trap caused no band broadening and did not require a separate flushing step to isolate the extracted materials. Li and co-workers [41] then described an integrated system using the same concept. By switching the mobile-phase flows, the extract was first obtained using SWE and trapped on a cold cartridge. The cartridge was then washed directly with the LC eluent onto a column. This hyphenated system was evaluated by the extraction and determination of caffeine, nitrotoluenes, polychlorinated biphenyls, chlorophenols and anilines. A similar system was used by Crescenzi and co-workers [16], who linked a C_{18} cartridge on-line before a LC–MS detection.

This method was taken a stage further by Hyötläinen and co-workers [42]. In their study a superheated water extract of polyaromatic hydrocarbons from sediments was trapped on a Tenax cartridge. The trap was dried in situ and was then washed with pentane and then with pentane–ethyl acetate (9:1), which was transferred directly to a GC column for analysis.

In a subsequent study, Kuosmanen and co-workers [43] applied a similar method to a superheated water extract of a brominated flame retardant from a sediment. In this case, the extract from the Tenax trap was eluted using a normal phase eluent onto a cyanobonded silica LC column. A selected fraction was then passed on-line to a GC and separated on a capillary column with FID detection. This method enabled the low levels of brominated analytes to be separated from alkanes and PAHs before GC.

These methods employed conventional LC mobile phases, however, since superheated water can also be used as a reversed-phase chromatographic eluent it should be possible to completely eliminate the use of organic solvents. Early studies directly linking SWE and aqueous LC were carried out by Young and co-workers [44]. They carried out a dynamic SWE of a series of aromatic analytes and sampled the flowing extraction stream at intervals by switched aliquots to a specially designed LC column. The column contained bonded solid particles with a very low retentivity and would elute the alkylbenzene analytes using a water mobile phase at room temperature. However, most of the extract was lost and could not be passed to the LC system.

More recently Bone and Smith [45] demonstrated that a superheated water extract could be trapped on a cooled cartridge and then released with an aqueous eluent as a concentrated fraction simply by raising the temperature of the trap (and thus decreasing the polarity of the water). More recently, Smith and Tajuddin [46] have shown that an extracted sample of pharmaceuticals and antioxidants can be passed on-line to a superheated water chromatograph using a conventional RP-column and separated using a thermal gradient. By increasing the release temperature in steps, successively less polar fractions can be analysed sequentially. This system enabled the ex-

traction, trapping, and chromatographic stages to be carried out without sample loss and without requiring any organic solvent simply by using an aqueous mobile phase and temperature generated changes in elution strength.

As well as chromatographic determinations, because a solvent-free aqueous extract is obtained, SWE is directly compatible with immunoassay determinations. Jiménez-Carmona and co-workers [47] reported that the superheated water extraction of trichloropyridinol (TCP) was much simpler, faster and cheaper (15 min, at 250°C and 200 bar) than a SFE extraction method as the latter method required the use of a methanol co-solvent and ion pair reagent (30 min at 40 °C and 383 bar). The TCP was determined directly on the extract using an ELISA immunoassay, however, the extract from the SWE was more dilute and for some samples might need an additional concentration step before the determination. In a similar approach, Kipp and co-workers [48] used an enzyme immunoassay for PAHs to examine superheated water extracts from soil and sediment samples. By eliminating organic solvents the method can be used in field studies.

4. Applications of superheated water extraction

The main areas of application of SWE have been for solids and powdered samples, most commonly soils and environmental solids and for plant material, largely because these matrices are compatible with a flow extraction system. So far there have been no reports of the applications of SWE in pharmaceutical analysis probably because liquid biological fluid matrices are difficult to handle in a closed system.

4.1. PAHs and halogenated residues in soils and environmental solids

Although the use of a polar solvent for non-polar analytes might seem anomalous, this is probably the main application area of SWE (Table 1) and a degree of selectivity can be obtained between different non-polar analyte groups.

A comparison of the extraction of PAHs from the soil from a gas plant site by Soxhlet, SWE, SFE and PSE extraction by Hawthorne and co-workers [49], reported that there was quantitative agreement between the different methods but the qualities of the extracts were very different. The solvent extracts by PSE and Soxhlet were dark brown, the superheated water extract was orange and the SFE extract was pale yellow. The first three also gave more unwanted peaks in GC–MS and a larger proportion of the matrix was dissolved compared to SFE. When applied to urban particulates, SWE preferentially extracted the PAHs relative to the *n*-alkanes, which were more readily extracted by SFE or solvent extraction (Fig. 2). Selectivity for the PAHs suggested that this method of extraction might usefully indicate the bioavailable PAHs as opposed to sequestered PAHs, which pose a lesser environmental problem.

Yang and co-workers [21] showed that class selective extractions (of phenols, alkylbenzenes (BTEX) at (50–150 °C) and PAHs at 250–300 °C) with superheated liquid water from soils or sludges could be obtained by steadily increasing the temperature of the superheated water but that *n*-alkanes $>n=20$ required superheated steam at 250–300 °C and 5 atms.

4.2. Pesticide residues in soils

This has again proved to be a popular application area (Table 2) probably because of the compatibility of the technique with solid samples. An interesting contrast was a comparison by Krieger and co-workers [55] of the extraction of the herbicide cloransulam-methyl (*N*-(2-methoxycarbonyl-6-chloro-phenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo[1,5c]pyrimidine-2-sulfonanilide) from soil samples with supercritical carbon dioxide or superheated water. SFE with carbon dioxide was relatively inefficient but SWE gave a similar recovery to organic solvents. The aqueous extraction was preferred as it gave a cleaner extract that could be examined directly by HPLC without additional clean-up steps. The recovery increased with water temperature but problems were encountered above 125 °C as cloransulam-methyl was hydrolysed. Pressure had little effect from 65 to 500 atm.

As with other extraction methods more severe conditions are needed for aged samples. Kreiger and co-workers [54] found that tricyclazole could be

Table 1
Application of SWE to the determination of alkylbenzenes, PAHs and PCBs in environmental samples

Analytes	Matrix	SWE Conditions	Assay method	Ref.
Benzene, ethylbenzene and naphthalene	Sand matrix	200 °C	Aqueous LC-UV	[44]
Polychlorinated benzofurans and naphthalene	Industrial soil and sea sand	300–350 °C as water or steam	GC–MS	[22]
PAHs	Environmental solids	250–400 °C 50 bar	GC–MS	[11]
Polar, moderately polar and non-polar organic	Soil, catalyst and sludges	50–300 °C	GC–MS	[20]
PAHs/pesticides	Municipal waste solid compost	110 °C pesticides 150 °C PAH	GC–MS or HPLC	[39]
Polychlorinated biphenyls	Soil and sediments	250–300 °C	GC–MS	[12]
PAHs	Soil	150 °C with micelles	LC-F	[18]
PAHs	Environmental solids	250 °C	GC–MS	[49]
PAHs	Environmental solids	250 °C/Extraction disc	GC–MS	[37]
PAHs	Sediment	300 °C	LC-GC	[42]
Alkanes and PAH	Spiked sea sand	250 °C	GC	[21]
Remediation PAH	Soil	275 °C	GC–MS	[50]
Polychlorinated benzofurans and naphthalenes	Soil	200–400 °C and steam	GC–MS	[22]
Polychlorinated biphenyl	Spiked soils	140 °C	GC–MS	[23]
Oxygenated materials	Humic soils	150 or 250 °C	GC–MS and LC	[51]
PCBs	Soil	250 °C	GC–ECD	[31]
Semi-volatile organics	Environmental solids	250 °C	SPME GC–ECD	[30]
PAHs	Sand and urban air particulates	250–300 °C	SPME/GC	[34]
Semi-volatile organics	Environmental solids	250 °C	SPME	[29]
PAHs	Native soil and sediment	SWE	Enzyme Immunoassay	[48]
Pyrene	Model matrix	300 °C	FIA-Fluorescence	[52]
Hydrocarbons	Oil shales	400–450 °C		[9]
Dechlorination of PCBs	Oils	250 °C plus iron powder	GC–ECD	[53]
BTEX and PAHs	Sand and soils	100–200 °C	On-line LC	[40]

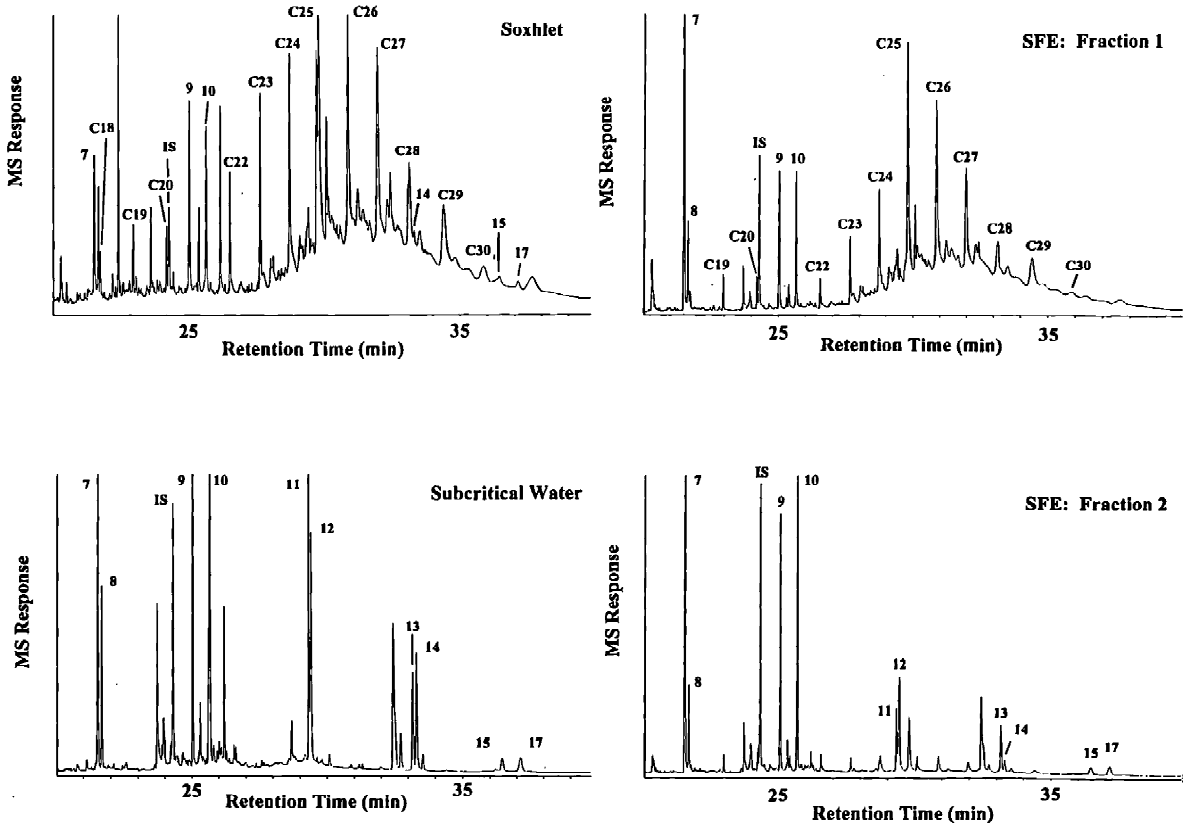

Fig. 2. Comparison by GC–MS of the selectivity of SFE with carbon dioxide (upper right 200 bar 50 °C and lower right 400 bar 150 °C), Soxhlet extraction (dichloromethane–acetone 18 h), and SWE (250 °C) for the extraction of urban air particulates. (C_n, chain length of *n*-alkanes, numbers refer to PAHs) [49].

extracted from freshly spiked soils at 100 °C but required 150 °C for aged samples (200 days).

For some pesticides, which are readily degraded, the determination of the metabolites is as important as the original compound because they can be more readily transported to ground water, but the starting materials and metabolite materials may have very different polarities. Field and co-workers [38] reported a rapid method in which the native non-polar herbicide Dacthal (dimethyl tetrachloroterphthalate) was extracted with SFE and then its mono and di-acidic metabolites were extracted from the same soil sample with hot water at 50 °C. The acids were directly trapped from the extraction solvent by using a SAX extraction disc. Elution gave a concentrated extract, which was readily ethylated for GC analysis. When the terbuthylazine (CBET) and metabolites were extracted from soils SWE, SWE gave 1.4–2.1 times higher yields from aged soils than conventional assays [33].

4.3. Soil remediation studies

As an extension of extraction studies, there has also been an interest in using superheated water for soil remediation. A pilot plant study by Lagadec and co-workers [50] found that the extraction of PAHs and pesticides with superheated water at 250–275 °C for 35 min could convert infertile soils into fertile soils capable of sustaining growth more efficiently than SFE. In another study, superheated water in the presence of zero-valent iron was used to dechlorinate PCBs in soils as part of a remediation study [53].

Johnson and co-workers [51] showed that super-

Table 2
The application of SWE to environmental analysis of pesticides

Analyte	Matrix	SWE conditions	Assay	Ref.
Trichloropyridinol	Soil	250 °C and 200 atm	Immunoassay	[47]
Dacthral and acid metabolites	Soil	50 °C and 200 bar (SAX disc)	Ethylation and GC	[38]
16 neutral and acidic herbicides	Soil	90 °C	Carbograph cartridge LC–MS	[24]
Terbuthylazine (CBET) and metabolites	Soil	100 °C phosphate buffered	LC–MS	[33]
Hydrolysed pyrethins	Soils	200 °C 30 min	SPME/GC–MS	[35]
Chlorinated acid herbicide as acids	Soil	100–150 °C -anion-exchanger disc	Silylation and GC	[25]
Tricyclazole	Soil and sediment	150 °C for aged samples	LC-radioactivity	[54]
Chloransulam-methyl	Soil	<150 °C		[54]
Pesticides and herbicides	Soil	90 °C pH 7.5	LC–MS	[16]
PAH/pesticides	Municipal waste solid compost	110 °C pesticides 150 °C PAH	GC–MS or HPLC	[37]
Remediation pesticides	Soil	Pilot scale 250–275 °C	GC–MS	[50]
Chlorophenols	Soils	125 °C/SPME	GC–MS	[27]

heated water can be used to remove the carboxylic, aliphatic, and carbohydrate types of organic carbon from a humic soil. This treatment has also been used to artificially age peat soils [56]. These studies suggested that superheated water effects the deoxygenation/aromatization reactions of soil organic

Table 3
Application of SWE to miscellaneous environmental analytes

Analyte	Matrix	SWE conditions	Assay	Ref.
Se^{IV}, Se^{VI} and organoselenium compounds	Sludge samples	250 °C 200 bar	Atomic fluorescence spectroscopy	[57]
As, Se and Hg	Coal	180 °C acidified water	Atomic fluorescence spectroscopy	[58]
Ash forming elements	Coal	Acidified HNO_3 180 –300 °C	AAS	[59]
Alkyl mercury	Solid matrices		SPE/GC–MS	[60]
Brominated flame retardants	Sediment	325 °C	GC	[61]
Brominated flame retardants	Sediment	325 °C for 40 min	Trap and normal-phase LC	[42]
Transition metal ions	Engine oils	liquid–liquid flow 150 °C	GF-AAS	[19]

Table 4
Applications of SWE the extraction of flavours and fragrances from plant material and food

Analyte	Matrix	SWE conditions	Assay	Ref.
Kava lactones	Piper methysticum	175 °C for 40 min	GC off line	[62]
Eucalyptus oil	*E. Globus* leaves	150 °C	GC–FID/GC–MS	[32]
Essential oil	Oregano leaves	125 °C then extract hexane	GC–MS	[63]
Essential oils	Savory and peppermint	100–150 °C	GC–MS	[64]
Eugenol and eugenol acetate	Clove buds	150 °C	GC–FID	[65]
Eugenol and eugenol acetate	Cloves	ODS trap then 250 and 300 °C		[66]
Essential oil	Laurel	150 °C	GC and GC–MS	[67]
Essential oil	Marjoram	150 °C	GC–MS	[68]
Oil	Peppermint	125 or 150 °C		[69]
Essential oil	Rosemary	125–175 °C	GC–FID	[70]
Essential oil	Fennel	150 °C	GC–MS	[71]

matter that mimic those of the geologically slow, natural diagenesis processes.

4.4. Miscellaneous environmental samples including transition metal ions

As well as the extraction of organic pollutants there have been a number of studies on the extraction of transition metal ions and toxic metals for subsequent ICP or AAS analysis (Table 3). Jiménez-Carmona and co-workers [59] found that by using mild (180 °C 4 h, Al, Ca, Mg, Na, and K) or more drastic conditions (300 °C 2 h, Fe, Al, Ca, Mg, Na, and K) the yield and speed of extraction was changed. Methyl mercury was also extracted by SWE followed by in-solution derivatisation with sodium tetraethylborate and headspace SPME-GC [61].

4.5. Food and plant materials

Studies on plants materials have concentrated on two areas, the extraction of naturally occurring plant products, principally essential oils (Table 4), and

Table 5
Applications of SWE to the analysis of pesticides from plant material and food

Analyte	Matrix	SWE conditions	Assay	Ref.
Organochlorine pesticides and chlorobenzenes	Strawberries	120 °C	GC–MS	[28]
Organochlorine pesticides and chlorobenzenes	Fruit and vegetables	120 °C	GC–MS	[36]
Atrazine	Beef kidneys	100 °C (30% ethanol)	SPME GC–MS	[17]
Thiabendazole and carbendazim	Food including bananas, lemons, oranges, rice and mushrooms	75–100 °C	LC-UV/F	[72]

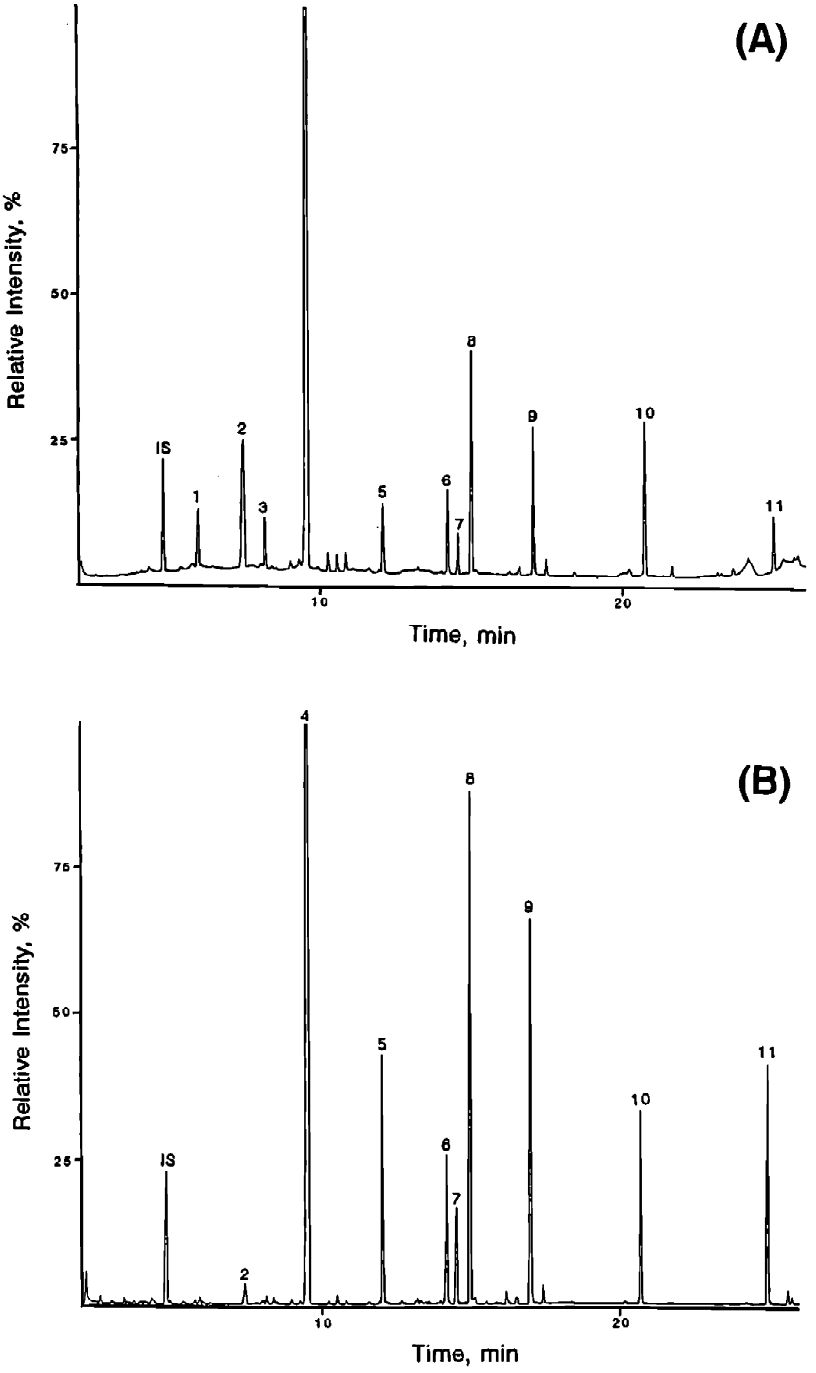

Fig. 3.. Comparison by GC of the extracts obtained by hydrodistillation (A) and SWE (B) of marjoram leaves under optimal working conditions. Peak identification; 1, α-pinene; 2, β-pinene; 3, β-myrcene; 4, eucalyptol; 5, linalool; 6, 2-methyl-6-methylen-7-octen-2-ol; 7, terpinen-4-ol; 8, α-terpineol; 9, geraniol; 10, geranyl acetate; 11, 4-ethenyl-α,α-4 trimethyl-3-(1-methyethenyl) cyclohexanemethanol [68].

secondly on the determination of pesticide residues (Table 5). A recent review of methods for essential oils from plants, compared SFE, SWE, microwave extraction and steam distillation [73]. The authors suggested that SWE was preferable to SFE as it avoids the extraction of cuticular waxes and lipids and the need for the plant material to be dried before extraction. A review specifically of the SFE of herbs and natural products has also been recently reported by Lang and Wai [27].

The contrast is usually with steam distillation (hydrodistillation). The extraction of ground marjoram leaves by Jiménez-Carmona and co-workers [68] by SWE for 15 min gave 5 times as much oil as hydrodistillation for 3 h. The economically more important oxygenated terpenes, such as eucalyptol and geraniol, were preferentially extracted in comparison to the monoterpene hydrocarbons, α-and β-pinene and β-myrcene (Fig. 3). As a result the SWE oil was a better representation of the natural aroma of the herb.

The extraction of rosemary at 150 °C similarly favoured the oxygenated constituents [70] and gave higher yields than steam distillation and required less energy because the water is not vaporised. Comparable results were reported in a comparison of extractions of laurel [67] and fennel [71] by SWE, hydrodistillation and solvent extraction with dichloromethane. The first method was faster, cleaner and gave a higher overall yield with a higher proportion of oxygenated terpenes.

When the SWE of savory and peppermint was compared with steam and SFE extraction by Kubátová and co-workers [64], they reported that, although yields increased with temperature, there was substantial degradation of linalool and γ-terpinene at temperatures >150 °C. However, in contrast to steam distillation, the water appeared to protect the sample from aerial oxidation and thus prevented the oxidation of some analytes, such as thymoquinone. As with the other plant extractions, SWE preferentially extracted oxygenated compounds, whereas the SFE extracts also contained plant alkane waxes. When Ammann and co-workers [69] examined the extraction of peppermint, they found that sabine hydrate was lost compared to SFE or steam distillation. They also reported that on raising the pressure from 10 to 20 atm resulted in an increased yield which they attributed to a mechanical breakdown of the oil-containing cells on the leaf surface rather than a change in solubility. Overall, steam distillation was considered to give the most efficient extraction. In contrast, the extraction of Eucalyptus essential oil gave a much higher yield than from steam distillation [32].

On extraction of powdered kava, the yield of the kava lactones, obtained by superheated water in 20 min at 175 °C, was approximately twice the yield by conventional Soxhlet for 6 h or solvent extraction [62]. The extraction was similar to 18 h of sonication with acetone, methylene chloride or methanol.

SWE can again be combined with SPE and has been used for the extraction of organohalogens from fruit and vegetables [36], although the optimum was found to be PSE with a methanol–water 10:90 mixture.

SWE thus frequently provides a viable alternative to the proposal that SFE [27] should be seriously considered as a good method for the extraction of herbs and natural products. Both provide a clean solvent free method, acceptable as a food product, with few side effects and may even provide alternative mixtures with different compositions.

5. Conclusions

Superheated water extractions have been shown to be feasible with particular interest in avoiding the need for organic solvents in environmental extractions or in food samples. The method is thus environmentally friendly, cheap and non-toxic. The equipment required is relatively simple and avoids the need for the high pressures employed in SFE. A further advance has been linkage to other chromatographic systems and unlike carbon dioxide there is no problems with cooling and condensation. Most samples have been solid matrices, such as soils and plant materials.

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