Journal of Chromatography A, 1217 (2010) 2484–2494

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Review

Pressurized hot water extraction (PHWE)

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ARTICLE INFO

Article history:
Available online 4 January 2010

Keywords:
Pressurized hot water extraction
Temperature
Green extraction
Scaled-up
Pilot-scale
Metabolites

ABSTRACT

Pressurized hot water extraction (PHWE) has become a popular green extraction method for different classes of compounds present in numerous kinds of matrices such as environmental, food and botanical samples. PHWE is also used in sample preparation to extract organic contaminants from foodstuff for food safety analysis and soils/sediments for environmental monitoring purposes. The main parameters which influence its extraction efficiency are namely the temperature, extraction time, flow rates and addition of modifiers/additives. Among these different parameters studied, temperature is described as the most important one. It is reported that the extraction of certain compounds is rather dependent on pressurized water with different applied temperature. Thus, the stability and reduced solubilities of certain compounds at elevated temperatures are highlighted in this review. With some modifications, a scaled-up PHWE could extract a higher amount of desirable compounds from solid and powdered samples such as plant and food materials. The PHWE extracts from plants are rich in chemical compounds or metabolites which can be a potential lead for drug discovery or development of disease-resistant food crops.

Contents

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doi:10.1016/j.chroma.2009.12.050

1. Introduction

In the analysis of solid samples, the method of extraction is regarded as a crucial step in the sample preparation. Classical sample preparation techniques that rely on extraction with solvents such as liquid–liquid extraction (LLE), sonication, Soxhlet extraction and other methods have been used. However, these traditional methods may often be time consuming with low extraction efficiency and also require large volume of non-environmental friendly organic solvents. In recent years, there is steady progress in extraction technology with the development of new and simpler sample preparation methods such as supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), pressurized liquid extraction (PLE) and pressurized hot water extraction (PHWE) which have been described in several earlier reviews [1–20].

To reduce the usage of organic solvents, PHWE is a feasible green solvent extraction method as it utilizes pressurized water at elevated temperature and controlled pressure conditions. Various reports have shown that at certain temperature and applied pressure, the polarity of water can be varied close to those of alcohols. Thus, it can dissolve a wide range of medium and low polarity analytes [21–36]. The major advantage of PHWE is the reduction in the consumption of organic solvents. Moreover, water is easily available, non-toxic and can be recycled or disposed with minimal environmental problems. Hence, PHWE has steadily become an efficient and low cost method of extraction for less-polar organic components from environmental soil, sediments and plant materials [15,16,23–38].

The application of pressurized water as an extraction fluid at elevated temperatures was first reported in the pioneering work of Hawthorne and co-workers for extraction of some polar and non-polar analytes from soil samples in 1994 [39]. Their works have since changed the perception that highly polar water could be transformed into a suitable extraction solvent for organic compounds under certain high temperatures and controlled pressurized conditions. The term "pressurized hot water" is used to denote the region of condensed phase of water between the temperature range from 100 °C (boiling point of water) to 374 °C (critical point of water). Other common terms such as "superheated water", "near critical water", "subcritical water", "high temperature extraction" and "extraction using hot compressed water" have also been used. In the case of PHWE, the density of water remains almost constant over this range of temperature so that the pressure effect on the properties of water is minimal [40]. During the extraction, moderate pressures are needed to keep a condensed phase of water such as 15 bar at 200 °C and 85 bar at 300 °C. If the pressure decreases below the boiling point at any pressure, superheated steam will be formed. The basic principle of PHWE and its feasibility as a green solvent extraction method to extract organic and non-polar compounds from numerous kinds of matrices have been described in earlier reviews [15–20,41–48].

In this review, the fundamental principles of the PHWE are briefly explained. The main parameters affecting its extraction efficiency, namely the temperature, pressure, static or dynamic operation mode in terms of extraction time/flow rate and also modifiers/additives are covered. The current review will evaluate the extraction efficiencies of PHWE applied on different compounds from a variety of sample matrices like environmental soils/sediments, plant and food samples. The PHWE is also used in sample preparation to extract organic contaminants from foodstuff for food safety analysis and soils/sediments for environmental monitoring purposes. It is noted that there is a steady growing trend to use PHWE to extract bioactive and nutritional compounds from plant and food materials (Table 1). Finally, the scaled-up use of PHWE as a green solvent extraction method for industrial application is discussed with reference to a successful pilot-scale project to remove contaminants from soil samples. At the same time, limitations of PHWE are discussed in this review as well.

2. Fundamental principles of PHWE

2.1. Changes in physicochemical properties of water

Water is a highly polar solvent with a high dielectric constant (ε) at room temperature and atmospheric pressure due to the presence of extensive hydrogen-bonded structure. Hence, traditionally water is not considered as a suitable extraction fluid for non-polar or organic compounds at room temperature. When the temperature of water is raised, there is a steady decrease in its permittivity, viscosity and surface tension but an increase in its diffusivity characteristics. With enough pressure to maintain water in the liquid phase at elevated temperature, the initial value of the dielectric constant of 80 at 25 °C decreases to 27 at 250 °C and 50 bar, which falls between those of methanol (ε = 33) and ethanol (ε = 24) at 25 °C. Under these conditions, water behaves like certain organic solvents which can dissolve a wide range of medium and low polarity analytes [21–36].

2.2. Extraction mechanism

The extraction mechanism in PHWE is proposed to involve four sequential steps which take place in the extraction cell filled with sample materials and a high portion of sands. The first step is the desorption of solutes from the various active sites in the sample matrix under the pressurized and elevated temperature conditions. The second step may involve the diffusion of extraction fluid into the matrix. Next, depending on the sample matrix, the solutes may partition themselves from the sample matrix into the extraction fluid and finally be chromatographically eluted out of the extraction cell to the collection vial [15,18,39]. An earlier theoretical study has suggested that the extraction mechanism in PHWE could fit in a thermodynamic model [49]. In this model, the extraction of any compound from a solid matrix requires two steps: (1) the compound must be desorbed from its original binding sites in (or on) the sample matrix (generally modeled by rate processes such as diffusion) and (2) the compound must be eluted from the sample in a manner analogous to frontal elution chromatography (controlled by the thermodynamic partitioning coefficient, K_D). Hence, a model based solely on the thermodynamic partitioning coefficient K_D, which assumes that analyte desorption from the matrix is rapid compared to elution that is used to describe the extraction profiles obtained with PHWE.

The enhancement on the extraction efficiency of PHWE can be attributed to: (1) an improvement in the solubility and mass transfer effects and (2) an increased disruption of surface equilibria [18]. With the modification of the properties of water at elevated temperatures, the capacity of the fluid to solubilize analytes is increased. There is reduced viscosity but improved diffusivity of water to allow better penetration through the matrix particles. If fresh water is continuously introduced during a dynamic extraction in PHWE, it improves the mass transfer and hence, increases extraction rate. Both the high temperatures and pressures could disrupt the surface equilibria. The increased temperature can overcome the solute–matrix interaction caused by van der Waals forces, hydrogen bonding, dipole attraction of the solutes molecules and active sites in the matrix. Thus, the thermal energy supplied can disrupt cohesive (solute–solute) and adhesive (solute–matrix) interaction by decreasing the activation energy required for desorption process. The transfer of the analytes from matrix to pressurized hot water is achieved by the diffusion and convection processes [16]. However, thermally labile compounds are degraded at elevated

Table 1
Analyses of plants and food materials based on PHWE.

Analyte(s)	Matrix	Temperature (°C)	Pressure	Mode	Flow-rate (ml/min)	Extraction time (min)	Reference method(s)	Sample pre-treatment	Analysis method	Reference
Plants										
Stevioside, rebaudioside A	*Stevia rebaudiana*	100	11–13 bar	Dynamic	1.5	15	Reflux	Nil	HPLC	[22]
Gastrodin, Vanillyl alcohol	*Gastrodia elata*	100	8–10 bar	Dynamic	1.5	20	Reflux	Nil	HPLC	[26]
Phenolic compounds	*Momordica charantia*	150–200	10 MPa	Dynamic	2.0	320	Soxhlet extraction	Nil	Anti-oxidant study	[59]
Tanshinone I and IIA	*Salvia miltiorrhiza*	95–140	10–20 bar	Dynamic	1.0	20, 40	Soxhlet extraction	SPE	HPLC, LC–MS	[53]
Essential oil	*Fructus amomi*	150	50 bar	Dynamic	1.0	5	Recovery and repeatability	SPME	GC–MS	[76]
Essential oil	*Acorus tatarinowii*	150	50 bar	Dynamic	1.0	5	Steam distillation	SPME	GC–MS	[77]
Essential oil	*Fructus amomi*	160	60 bar	Dynamic	1.0	5	Steam distillation	LPME	GC–MS	[78]
Borneol, terpinen-4-ol, carvacrol	*Origanum anites*	100, 125, 150, 175	60 bar	Dynamic	2.0	30	Steam distillation, Soxhlet extraction	SPE	GC × GC/TOF–MS	[79]
Essential oils	*Origanum micrathum*	100, 125, 150, 175	40–80 bar	Dynamic	1.0–3.0	30	Nil	SPE	GC × GC/TOF–MS	[80]
Pulegone, terpinen-4-ol, *trans*-carveol, verbenone	*Ziziphora taurica*	150	60 bar	Dynamic	2.0	30	Steam distillation, direct thermal desorption	SPE	GC × GC/TOF–MS	[81]
Glycyrrhizin	*Glycyrrhiza glabra*	30–120	5 atm	Static	Nil	60–120	Nil	Nil	UV	[85]
Anthocyanins	*Brassica oleracea*	80–120	50 bar	Static	Nil	11	Nil	Nil	HPLC	[86]
Anthraquinones	*Morinda citrifolia*	80, 120	4 MPa	Dynamic	4.0	120	Nil	Nil	HPLC	[87]
Gallic acid, ellagic acid, corilagin	*Terminalia chebula* Retz	120–200	4 MPa	Dynamic	2.0–4.0	150	Soxhlet extraction, Hot water extraction in stirred vessel	Nil	Anti-oxidant study	[88]
Saponins, cyclopeptides	*Vaccaria segetalis* Garcke, *Saponaria vaccaria*	160	750 psi	Dynamic	0.5, 1.0, 2.0, 4.0, 8.0	80	Ultrasonication extraction	Nil	HPLC	[89]
Terpenes (α-pinene, limonene, camphor, citronellol, carvacrol)	Basil and oregano leaves	100, 150, 200, 250	Nil	Static	Nil	30, 300	Sonication extraction	Nil	GC–FID	[91]
Volatile oil	*Cuminum cyminum* L.	100–175	20 bar	Dynamic	2.0,4.0	Nil	Hydrodistillation, Soxhlet extraction	Nil	GC–FID, GC–MS	[92]
Lignans	*Linum usitatissimum*	140	5.2 MPa	Dynamic	0.5	400	Nil	Nil	HPLC	[97]
Rosmarinic acid, carnosic acid	*Rosmarinus officinalis*	60–100	1500 psi	Static	Nil	25	Nil	Nil	CE–ESI-MS	[98]
Anti-oxidants	*Spirulina platensis*	60, 115, 170	1500 psi	Static	Nil	3, 9, 15	Nil	Nil	Anti-oxidant study	[100]
Anti-oxidants	*Spirulina platensis*	115, 170	1500 psi	Static	Nil	9, 15	Nil	Nil	MEKC–DAD	[101]
Cedarwood oil	*Juniperus virginianna*	50, 100, 150, 200	500,750,1500, 3000 psi	Static	Nil	15	Liquid and SFE	LLE	SFC	[103]
1,1-Diphenyl-2-picrylhydrazyl	*Diascorea alata*	100	1.34 MPa	Dynamic	10.0	<180	Nil	Nil	HPLC	[104]
Anthraquinones	*Morinda citrifolia*	100, 170, 220	7 MPa	Dynamic	2.0, 4.0, 6.0	18	Organic solvent extraction	Nil	UV	[106]
Shikimic acid	Chinese star anise (*Illicium verum* Hook. f.)	30–200	5–15 MPa	Dynamic	5.0–15.0 g/min	10	Nil	Nil	HPLC	[107]
Food										
Total sugars, proteins	Defatted rice bran	200	Nil	Static	Nil	5	Nil	Nil	Anti-oxidant study	[69]
Isoflavones	Soybeans	100	1000 psi	Static	Nil	Nil	Vortexing, shaking, stirring, sonication and Soxhlet	Nil	HPLC	[90]
Lignans, proteins and carbohydrates	Defatted flaxseed meal	130,160, 190	750 psi	Dynamic	1.0	400	Nil	Nil	HPLC	[93]
Flavonoids	Knotwood of aspen	150	220 bar	Static	Nil	35	Soxhlet, ultrasonic extraction and reflux in methanol	Nil	GC–FID, GC–MS, HPLC–UV, HPLC–MS	[94]
Catechins, Proanthocyanidins	Grape seed	50, 100, 150	1500 psi	Static	Nil	30	Extraction with 75% methanol	Nil	HPLC	[95]
Capsaicin, dihydrocapsaicin	Peppers	50–200	100 atm	Static	Nil	Nil	Nil	Nil	LC–MS	[96]
Anthocyanins, phenolics	Dried red grape skin	100–160	Nil	Static	Nil	40 s	Conventional hot water, aqueous 60% methanol extraction	Nil	HPLC	[99]
Catechin, epicatechin	Tea leaves, grape seeds	100–200	1500 psi	Static	Nil	5, 10	Ultrasound-assisted extraction	Nil	HPLC	[102]
Isoflavones	Defatted soybean flakes	110	641 psig	Static	Nil	2.3 h	Soxhlet extraction	SPE	HPLC	[105]
Total phenolic content	Citrus pomaces	25–250	0.1–5.0 MPa	Static	Nil	10, 30, 60	Nil	Whatmann No. 1 filter paper	Anti-oxidant study	[108]

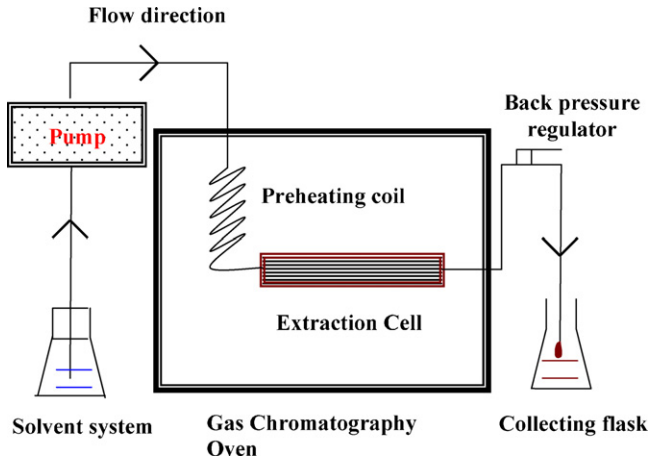

Fig. 1. A schematic diagram of a laboratory self-assembled PHWE system [54].

temperatures. Sufficient pressure is required to be exerted on water when temperature above its boiling point is used. The presence of pressure could facilitate extraction from samples where analytes are trapped in the matrix pores. This pressure forces the water into areas of the matrices which are not normally covered if water at atmospheric pressure is used [50].

2.3. Instrumentation

The basic experimental set-up for PHWE is similar to that used in Accelerated Solvent Extraction (ASE) as reported in an earlier review [16]. PHWE can extract wet samples directly as compared to SFE with carbon dioxide (CO_2) as an extraction fluid. It is easier to operate with water than liquefied CO_2. In a laboratory self-assembled system, degassing of water is needed to prevent potential oxidative corrosion of extraction cell and delivery lines due to the presence of dissolved oxygen in water. Most published studies have described a similar construction of the PHWE system [21,16,19,20,51–53]. Typically, it consists of a water supply, a pump for transporting the solvent, a heater for heating solvent, a pressure vessel where the extraction occurs, a means to control the pressure in the system and a collection vessel for the extract. Thus, a general instrumentation set-up can be described by the following laboratory assembled system in Fig. 1 adapted from Ong et al. [54]. The set-up consists of a stainless steel preheating coil to ensure that water is at its operating temperature before entering into the stainless extraction cell. A pump is used and the extraction is carried out at an elevated temperature maintained by a gas chromatography oven. The extraction processes is operated in pressures of between 10 and 60 bars. The outlet flow is controlled by a miniature back pressure regulator to generate the back pressure. PHWE using commercially available system like the Dionex ASE 200 has been reported [55,56]. For certain set-ups, a second pump is used to deliver chloroform/dichloromethane into a fused silica-lined tee placed in the oven between extraction cell and collection valve to prevent deposition of analytes when water cools during collection. Depending on its applications, a cooling trap may be used to cool fluid coming out of the extraction cell to room temperature [18]. With quality data and determination of scaled-up factors, the design of pilot or industrial PHWE equipment has been reported [57].

3. Parameters affecting the extraction process in PHWE

The main parameters that influence the selectivity and extraction efficiency of PHWE include temperature, pressure, extraction time, flow rates and modifiers/additives. The geometry of the extraction cell and flow direction have little effect on the recovery of the analytes from sample materials [58]. For the validation of analytical methods, the extraction efficiency of PHWE is often compared with other reference methods such as heating under reflux, Soxhlet extraction, sonication and others which rely on pure or aqueous mixture of organic solvents [3,22,24–27,59–62]. In botanicals, the bioactive or marker compounds are present naturally and significant analyte–matrix interaction will be present. Hence, spiking of the target compounds into the plant matrix will not mimic the real environment of the matrix [22,26,51–53,62–64].

3.1. Temperature

Temperature is the main factor which could affect the extraction efficiency and selectivity in PHWE. It could influence the physicochemical properties of water and also subject thermally labile analytes to their decomposition or hydrolytic attack. In PHWE, the applied extraction temperature is usually above the normal boiling point of the fluid used. The physical advantages such as high diffusion, low viscosity and low surface tension are achieved at elevated temperature condition. The increased vapour pressures and rapid thermal desorption of target compounds from matrices could enhance the extraction efficiency of PHWE [16]. The high temperatures have also changed the properties of water and thus making the polarity of water closer to those of non-polar compounds. This will enhance the solubility of less-polar compounds in water for extraction from different matrices [22,29,54,56,59,62,65–71]. However, degradation of compounds and the intensity of reactions such as hydrolysis and oxidation can occur with increased temperature. The amount of PAHs extracted from sediments did not increase beyond 250 °C but there was a degradation phenomenon at higher temperature [28,72]. For non-polar organic pollutants, pressurized water at temperature higher than 300 °C could enhance the solubility and extraction efficiencies of these compounds by PHWE due to its decreasing dielectric constant [39,73,74]. Thus, a systematic optimization on temperature has to be carried out for the respective classes of compounds.

Herbicides such as phenoxy acids were found to degrade at relatively low temperature above 120 °C [75]. Thus, PHWE has an important impact on the extraction efficiencies of compounds present in plants [22,24,26,59–62,76–81]. The bioactive and marker compounds in plants may be non-polar or polar and can also be thermally labile and/or prone to hydrolytic attack. To extract non-polar compounds from plant matrix, an increase in applied temperature up to 200 °C (Table 1) may be needed. However, the degradation of target compounds at higher applied temperature beyond 250 °C was observed in the extraction of marker compounds such as stevioside, rebaudioside A, berberine, aristolochic acids, baiclein, glycyrrhizin, tanshinone I and IIA and others in medicinal plants [22,26,59–62,51–53,76–82].

It was noted that the behaviour of marker compounds from *Radix Codonopsis pilosula* by PLE with methanol and PHWE were rather different under elevated temperature conditions [52]. It was proposed that the presence of dissolved gases such as oxygen and nitrogen in the compressed dense water at higher temperature might reduce the solubility of certain target compounds. At the same time, PLE with methanol showed better recovery of stevioside from *Stevia rebaudiana* leaves than PHWE within the temperature range of 110–160 °C [83]. Another observation showed that under increasing temperature and extraction time conditions, PHWE enhanced the recovery of flavonoids but had a lower recovery of carotenoids from yellow Thai silk waste compared to PLE with ethanol at 50–79 °C [84].

3.2. Pressure

The effect of adjusting pressure could change the phases of water. Moderate pressures such as 15 bar at 200 °C and 85 bar at 300 °C are required to maintain the liquid phase of water. Pressure is usually varied from 10 to 80 bars to maintain water in its liquid phase at extraction temperature and often has little effect on the extraction efficiency of PHWE. The recovery of organic pollutants from solid environmental samples was suggested to have little dependence on pressure [39,74]. Similarly, varying pressure did not improve the recovery of essential oils from medicinal plants and ginsenosides from American ginseng [77,78].

3.3. Dynamic or static extraction mode

PHWE can be performed in either static or dynamic mode. In the dynamic extraction mode, both extraction time and flow rate are important parameters for the optimization of PHWE. The extraction time strongly depends on the extraction temperature, nature of matrix and analytes. Using PHWE, it was observed that an extraction time of 20 min at 100 °C gave higher yields of stevioside and rebaudioside A from *Stevia rebaudiana* as compared to heating under reflux for 60 min [22]. Dynamic PHWE enhances the extraction compared to boiling in a flask (static type pf extraction). In PHWE, the water is forced through a narrow sample cell at high pressure which generally enhances the extraction. However, prolonged heating may result in compound degradation and thus optimization of extraction time is very important [22,26,59–62,51–53,76–82]. Using the dynamic extraction mode, the equilibrium is displaced to completion as fresh solvent is continuously pumped through the sample. Thus, it requires more volume of fluid compared to the static mode. A flow rate of 1 or 1.5 ml/min is usually used in the dynamic extraction mode (Tables 1–4). However, a higher flow rate will generally improve extraction efficiencies of highly concentrated samples because the total volume of water is increased and also its enhancement in physical mass transfer of analytes from matrix [15,39]. Hence, the extraction time or flow rate in PHWE need to be determined during validation process.

In the static extraction mode, its extraction efficiency strongly depends on the partition-equilibrium constant and solubility of compounds at elevated temperatures. Thus, highly concentrated samples or low solubility analytes may lead to incomplete extraction due to limited volume of water used.

3.4. Modifiers and additives

The addition of some organic, inorganic modifiers and additives may enhance the solubility of analytes in water and increase the interactions of target analytes with water. They can also alter the physicochemical properties of water at elevated temperature. It was reported that a higher amount of natural sweetener from licorice (*Glycyrrhiza glabra*) roots could be achieved by PHWE with dissolved ammonia (0.01%, w/v) [85]. PHWE with extraction fluids containing 5% ethanol was also reported to enhance the extraction of anthocyanins in red cabbage [86]. The degradation of compounds could be reduced by micelle-mediated extraction (MMPHWE) with Triton X-100 compared with PHWE without the use of surfactant [87].

4. Applications of PHWE

PHWE has been mainly applied on solids and powdered samples because these matrices are more compatible with a flow extraction system. Methods using PHWE have been applied successfully on food and plant materials for the extraction of their flavours and fragrances, and also for their bioactive compounds (Table 1). In addition, methods using PHWE have also used in the extraction of organic contaminants from foodstuff for the food safety analysis (Table 2). The changes in the physicochemical properties of water have enabled the extraction of non-polar organics such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) from environmental soil and sediment samples (Table 3). Due to its green nature and feasibility to extract a wide range of compounds under certain extraction conditions, PHWE is noted to aid in bioremediation processes by recovering pesticides and herbicides from soils/sediments (Table 4).

4.1. Extraction of bioactive and nutritional compounds from plant and food materials

In recent years, PHWE has gradually become a useful option for the isolation of bioactive and nutritional compounds from plants and food materials. PHWE is a direct method to recover analytes without the need to cleanup. This will reduce costs, as the analytes extracted are safe for further testing, processing and human consumption. The nature of these materials is soft and thus can be easily reduced into smaller sizes to improve the extraction efficiency. As seen in Table 1, the studies on the plant materials concentrate on the extraction of bioactive compounds and also volatile essential oils at optimized extraction conditions. The usage of pure water mimics the tradition herbal preparations which usually involve sequential steps with boiling in water. The extraction efficiencies of the marker compounds from *Gastrodia elata* and *Stevia rebaudiana* using PHWE were found comparable or higher than heating under reflux using water [22,26]. The chromatograms in Fig. 2 showed that both marker compounds GA and VA present in *Gastrodia elata* could be extracted by PHWE as an alternative extraction method to the traditional heating under reflux [26].

Table 1 demonstrated the feasibility of PHWE for the extraction of volatile components from botanicals at optimized conditions. The extraction of volatile essential oil from *Cuminum cyminum* L. at a higher temperature of 150 °C by PHWE gave comparable yields with reference to Soxhlet extraction and steam distillation (hydrodistillation) [92]. Comparable results were also reported for PHWE, hydrodistillation and Soxhlet in the extractions of Borneol [79] and Pulegone [81] in plant materials. Thus, PHWE is offered as a fast, clean and high efficiency extraction method for volatile components present in plants.

PHWE is also a common method to extract compounds from food materials (Table 1) [69,90,93–96,99,102,105]. The stability of these compounds at elevated temperature and their extraction efficiencies compared with other methods of extraction were studied. The total sugar present in defatted rice bean was determined to be the highest using PHWE at 200 °C [69]. The extraction of catechins and proanthocyanidins from dried grape seeds was found to be comparable to conventional extraction with 75% methanol [95]. Using PHWE, five different capsaicinoids (nordihydrocapsaicin, capsaicin, dihydrocapsaicin, an isomer of dihydrocapsaicin, and homodihydrocapsaicin) present in peppers were successfully isolated at 200 °C and quantified by HPLC before they the extraction yield decreased at higher applied temperatures [96]. The feasibility of PHWE as a green method to extract natural compounds from food materials was also validated with reference to other methods such as Soxhlet extraction, ultrasonic extraction and heating under reflux with pure or aqueous mixture of alcohols (Table 1).

4.2. Removal of organic contaminants in foodstuff

The analysis of chemical contaminants in food has grown considerably in recent years. These chemical contaminants can be broadly classified into 4 main categories: (1) pesticides, (2) vet-

Table 2
Analyses of organic contaminants in foodstuff.

Analyte(s)	Matrix	Temperature (°C)	Pressure	Mode	Flow-rate (ml/min)	Extraction time (min)	Reference method(s)	Sample pre-treatment	Analysis method	Reference
Sulfonamide (SAs)	Cattle and fish muscle tissue	80	Nil	Dynamic	1.0	4	Nil	Cellulose filter	LC–MS	[110]
Carbamates (carbamate insecticides)	Bovine milk	90	Nil	Dynamic	1.0	5	Nil	Cellulose filter	LC–MS	[111]
Sulfonamides (SAs)	Pork meat	160	1500 psi	Static	Nil	5	Nil	Oasis HLB cartridge	CE–MS	[112]
Antibiotics	Cattle and pig meat samples	70	1500 psi	Static	Nil	10	Nil	Nil	LC–MS	[61]
Herbicides (Chlormequat and mepiquat)	Wheat flours and flour-based baby foods	120	100 atm	Static	Nil	15	Nil	Filter	LC–MS-MS	[113]
Cholesterol	Solid food	135	10 bar	Dynamic	3.0	5	Nil	C_{18} cartridge	UV–vis	[114]
Fluorescent whitening agents (FWAs) and azo dyes (AZOs)	Paper used for wrapping food	250	100 atm	Static followed by Dynamic	0.5	201	Dynamic Sonication-assisted extraction, Soxhlet extraction	Nil	HPLC	[115]
Insecticides: (i) Carbofuran (ii) Imidacloprid	Seed-pellet	(i) 150 (ii) 100–150	Nil	Static	Nil	30	Nil	SPE	HPLC	[116]
Pesticides	Skin of grapes	120	Nil	Dynamic	1.0	40	Nil	Microporous membrane liquid–liquid extraction (MMLLE)	GC–MS	[73]
Pesticides (Atrazine)	Beef kidneys	100	50 atm	Static (30% Ethanol)	Nil	10 per cycle	Nil	SPME	GC–MS	[117]
Pesticides (Atrazine)	Water	50–125	50 atm	Static (Modified with ethanol and urea)	Nil	Nil	Nil	Nil	On-line LC	[118]

Table 3
Analyses of environmental samples based on PHWE.

Analyte(s)	Matrix	Temperature (°C)	Pressure	Mode	Flow-rate (ml/min)	Extraction time (min)	Reference method(s)	Sample pre-treatment	Analysis method	Reference
PAHs	Environmental solids	50–400	5–600 bar	Static	Nil	Nil	Nil	Nil	GC–FID, GC–MS	[39]
TNT (2,4,6-trinitrotoluene)	Soils	150, 175, 200, 225	Nil	Static	Nil	Nil	Nil	Nil	HPLC	[27]
PAHs	Sediments	150	2000 psi	Static	Nil	5	Nil	SPME	GC–MS	[28]
PAHs	Sediments	100, 150	15 MPa	Static	Nil	10	Soxhlet extraction, MAE	Nil	GC–MS	[71]
PAHs	Soils	250	17.2 MPa	Dynamic	0.20	Nil	Soxhlet extraction	Nil	UV	[72]
Heterocyclic analogs of anthracene, phenanthrene and fluorene	Solids	313 K	5 MPa	Dynamic	0.017 g/s	Nil	Nil	Nil	Nil	[120]
Phenanthrene, PAHs	Environmental solids	100–350	Nil	Static	Nil	30	Nil	Nil	GC–MS	[121]
PAHs	Environmental solids	313–498 K	0.1 MPa	Static	Nil	Nil	Nil	Nil	GC–MS	[122]
PAHs	Soil	250	1000 psi	Dynamic	265.0, 132.5, 121.24, 242.13, 253.57 ml/h	1, 2 h	Nil	Nil	GC–FID, GC–MS	[123]
PAHs	Environmental solids	100–185	100–160 bar	Static	Nil	8	Nil	Nil	GC–MS	[124]
Organics	Sediments	120, 200	Nil	Static	Nil	3	Nil	SPE	GC–MS	[125]
Semivolatile organics	Sediments	120, 200	Nil	Static	Nil	3	Nil	SPE	GC–MS	[126]
Acenaphthene, anthracene, and pyrene	Environmental solids	300	5 MPa	Dynamic	0.10	Nil	Nil	Nil	GC–MS	[127]
Linear alkylbenzene sulfonates	Sediments	100	20–30 bar	Dynamic	2.0	70	Soxhlet extraction	Nil	HPLC–UV	[128]
PAHs	Sediments	22, 100, 200	Nil	Static	Nil	30, 60, 90	Nil	Nil	GC–MS	[129]
Dioxins, PCBs	Soil	25–350	0.2–25 MPa	Static	Nil	Nil	Nil	Nil	GC–MS	[130]
Phenolic compounds (phenol, 3-methylphenol, 4-chloro-3-methylphenol and 3,4-dichlorophenol)	Sands	50, 100, 200, 300	Nil	Static	Nil	20	Nil	Nil	CZE, GC–MS	[131]
PAHs	Sea sand and soil	300	290 bar	Dynamic	1.0	20	Soxhlet extraction	Nil	GC–MS	[135]
Brominated flame retardants (BFRs)	Sediments	250–350	118 bar	Dynamic	1.0	40	Soxhlet extraction	Solid-phase trap	GC–MS	[136]
Brominated flame retardants (BFRs)	Sediments	325	118 bar	Dynamic	1.0	40	Nil	Phase-phase trap	LC–GC–FID	[137]
Polychlorinated dibenzofurans and naphthalenes	Industrial oil and seasand	200–400	10–250 atm	Dynamic	1.0	30	Soxhlet extraction	Nil	GC–MS	[138]
PAHs	Airborne particulate matter samples	250	5.5 MPa	Dynamic	2.0	18	Nil	Poly(styrene divinyl-benzene)membrane	GC–FID, GC–MS	[139]
Organic liquid products	Fossil fuels	300–400	Nil	Static	Nil	Nil	Nil	Nil	CHN analyzer	[140]
Oxygenated materials	Humic soils	150 and 250	3–120 atm	Dynamic	0.5–1.0	0.5, 3, 10 h	Nil	Nil	GC–MS HPLC	[141]
Surfactants and some of their metabolites	Sewage sludge	150–230	100 bar	Static/Dynamic	1.0	1017	Soxhlet extraction	SPE	LC–MS	[142]
Reductive dechlorination of PCBs	Oils	150–300	10 MPa	Static	Nil	Nil	Nil	Nil	GC–ECD/FID	[143]
Amino acids	Soil	150–250	17.2 MPa	Static	Nil	10	Nil	Nil	GC–MS	[144]
Organophosphate triesters (OPs)	Sediments	90	1500 psi	Static	Nil	5	Nil	Oasis HLB cartridge	GC–MS	[145]

Table 4
Analyses of pesticides and herbicides in soils and sediments based on PHWE.

Analyte(s)	Matrix	Temperature (°C)	Pressure	Mode	Flow-rate (ml/min)	Extraction time (min)	Reference method(s)	Sample pre-treatment	Analysis method	Reference
Pesticides	Soil and sediments	120–200	5.0 MPa	Dynamic	1.0	20	Nil	Nil	GC–FID	[146]
Organochlorine pesticides	Soils	130	100 bar	Static	Nil	10	Stir bar extraction	Nil	GC–MS	[148]
Pesticides	Marine sediments	120	50 bar	Dynamic	2.5	25	Nil	Nil	GC–MS	[149]
Triazine herbicides	Spiked compost samples	170–250	Nil	Dynamic	1.0	Nil	Nil	Nil	UV	[150]
Pesticides and herbicides	Soil	90–130 pH 7.5 (phosphate buffered)	<20 bar	Dynamic	0.5	8	Soxhlet extraction	C-18 trap	On-line coupled to LC–MS	[63]
Herbicide cloransalum-methyl	Soil	50–150	65–500 atm	Dynamic	0.4–3.5	30	Organic extraction	Nil	HPLC–UV	[151]
Tricyclazole	Soil and sediments	50–150	75–300 atm	Dynamic	1.0	30	Nil	Nil	HPLC	[152]
Chlorophenoxy acid herbicides	Soils	50–200	Nil	Dynamic and Static–dynamic	1.0–2.0	60	Nil	C-18 trap	HPLC	[153]
Pesticides	Soils	50–300	8 MPa	Dynamic	2.0	90	Soxhlet extraction	Liquid–liquid	GC–MS	[154]
Pesticides	Soils	105	120 kPa	Dynamic	Varies for study	Nil	Soil desorption method	SPE	HPLC	[155]
Naphthalene (PAH)	Soils	260, 280	Nil	Dynamic	1.0 and 1.6 g/min	90, 180, 270, 360	Nil	Nil	GC	[147]

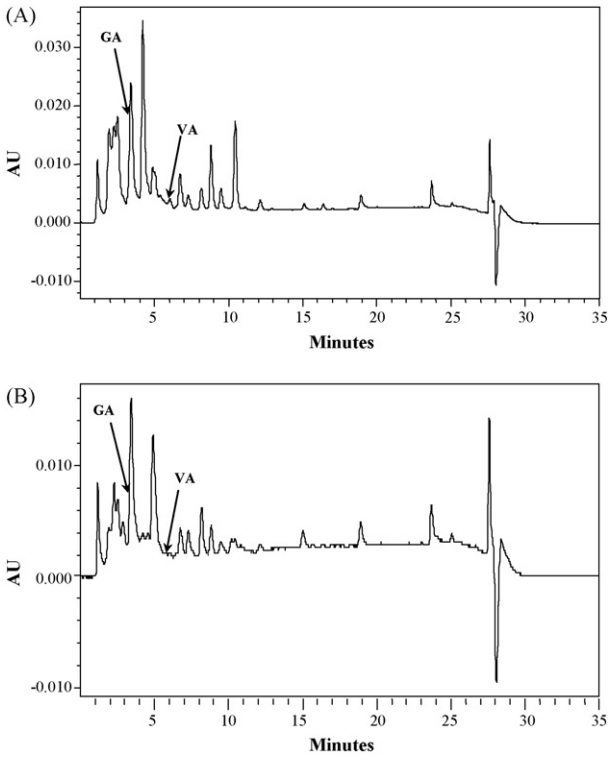

Fig. 2. Chromatograms obtained for GA and VA in *Gastrodia elata* by (A) PHWE at 100 °C and (B) heating under reflux with 60 ml pure water for 60 min. HPLC conditions: 0.1% formic acid in water (solvent A) and 0.1% formic acid in methanol (solvent B) as mobile phase. At initial condition, gradient of pump B was set at 10% and increased to 100% in 25 min and then returned to initial condition for 10 min. UV detection was at 270 nm. Oven temperature was at 40 °C and flow rate was set at 0.7 ml/min [26].

erinary drugs, (3) persistent environmental chemicals and (4) naturally occurring toxicants as described in a review [109]. The extraction of pollutants in food is usually associated with long extraction and cleanup procedures based on the use of Soxhlet method and/or saponification [41,45]. These procedures are laborious and time consuming and usually employ large volumes of toxic organic solvents. From Table 2, the applications of this green PHWE method can aid to extract various chemical constituents present in the food matrices.

In Table 2, sulfonamides (SAs) are bacteriostatic compounds routinely used in veterinary medicine to treat a variety of bacterial and protozon infections in poultry. However, they can be carcinogenic and thus pose human health risk. The recovery of SAs from meat samples was successfully achieved by PHWE using dynamic and static modes [110,112]. Water was the extraction fluid of choice because of its low affinity towards fats and the polar character of the analytes. In the static mode, a higher temperature of 160 °C was needed for the recovery of SAs compared to the dynamic mode with 4 ml of water at 1.0 ml/min passed through the extraction cell heated at 80 °C [110]. There were also the pesticides and herbicides residues on food and animal feeds due to pest and fungal control (Table 2). These harmful chemicals can enter the human system through direct consumption of contaminated food or through milk, meat and other products obtained from animals that feed on contaminated feed and fodder [109,111]. PHWE has proved to be feasible to extract these harmful chemicals from the skin of grapes at 120 °C at a flow rate of 1.0 ml/min for 40 min [73], carbamate insecticides in bovine milk at 90 °C at a flow rate of 1.0 ml/min for 5 min [111] and herbicides in wheat flours and their products under static extraction for 15 min at 120 °C [113]. Hence,

PHWE has gradually increased its role in the sample preparation for food safety analysis.

4.3. Environmental samples

The analysis of environmental samples is always challenging due to the diversity and complexity of sample matrices with a variety of trace level organics [119]. The earlier successful application of PHWE by Hawthorne and co-workers has demonstrated the feasibility of using polar solvent such as water to extract some PAHs from soil under appropriate controlled experimental conditions [39]. A comparison on the recoveries of PAHs by the conventional Soxhlet extraction, PHWE, SFE and PFE methods showed that the qualities of the extracts were rather different. The colour of the PHWE extracts was lighter than the extracts obtained from the other methods. This observation was due to n-alkanes which were more readily extracted by other methods as compared to PHWE [39]. The solubility behaviour of three PAHs, namely the acenaphthene, anthracene, and pyrene, in superheated water was studied at temperatures from 50 to 300 °C to understand the mechanisms of extraction in PHWE [127]. As seen in Table 3, PHWE could recover PAHs from the environmental samples at a temperature less than 250 °C. The extraction yields of PAHs were also found to be comparable to the other reference methods such as Soxhlet extraction [71,72,128]. The kinetic removal of PAHs from soils was also studied by PHWE designed for semi-continuous experiments with residence times of 1 and 2 h at 250 °C [123]. A review on the usage of high temperature pressurized water (both in sub- and supercritical conditions) in the presence of oxidants such as hydrogen peroxide, oxygen, persulfate was reported for the extraction, destruction and oxidation of PAHs from soil samples [132,133]. The subcritical fluid extraction method was also highlighted as one of the remediation technologies specifically for PAH-contaminated soils in a recent review [134].

Apart from its wide applicability to recover the PAHs, PHWE is also shown as feasible option for other classes of compounds such as nitrogen-based pollutants [27], dioxins [131], brominated based compounds [136,137], chlorinated organic pollutants [138], organic liquid products [139] and surfactants [142] present in environmental samples (Table 3). At 200–400 °C, PHWE can extract these analytes which are usually bound tightly to the sample matrix in either dynamic or static mode (Table 3). There was also an attempt to optimize PHWE to extract alanine, aspartic acid, glutamic acid, glycine, serine and valine in soil samples over the temperature range of 30–325 °C at pressures of 17.2 or 20.0 MPa [144]. None of the amino acids was extracted at 30 °C (at 17.2 MPa) as they might be too strongly bounded by the soil matrix to be extracted at such a low temperature. The extraction efficiencies of glycine, alanine, and valine were increased with increasing extraction temperatures from 150 to 250 °C (at 17.2 MPa). The increased solubility of these acids at higher temperatures could be due to the decreasing dielectric constant of water. However, amino acids were not detected in extracts collected at 325 °C (at 20.0 MPa) due to amino acid decomposition at this temperature.

4.4. Pesticides and herbicides in soil and sediments

Agricultural consumption of chemicals, in the form of pesticides and herbicides for pest and fungal control, has been viewed as a source of potential adverse environmental impact. The recovery of these chemicals from the soils/sediments is usually achieved with organic solvents such as acetone, ethyl acetate, or methanol. These procedures are labour intensive, of low extraction efficiency and also involve high consumption of hazardous organic solvents. Under certain optimized conditions, PHWE was proposed as a feasible alternative method to extract different classes of pesticides and herbicides from environmental soil and sediment samples to allow for remediation [15,16,146–156]. As seen in Table 4, PHWE is a suitable method for the recovery of pesticides/herbicides because of its compatibility with the solid samples. PHWE could recover pesticides from the environmental samples at a temperature less than 300 °C (Table 4). The optimization of extraction temperature was required to improve the selectivity of the PHWE to extract different classes of compounds from the environmental specimens. It was found that pesticides such as malathion, heptachlor, aldrin, dieldrin, butachlor, metalaxyl and propiconazole were extracted at 160 °C while chlordane and thiobencarb were recovered at 120 °C and 180 °C respectively from sand [146]. A combination of stir bar sorptive extraction (SBSE) with PHWE was shown as a compatible alternative to recover organochlorine pesticides (OCPs) and chlorobenzenes in soils [148]. An on-line method of extraction using PHWE was developed for the analysis of five triazine herbicides from a spiked complex compost matrix with inclusion of cleanup steps [150]. Hence, PHWE can also aid in the soil/sediment remediation effort for environmental monitoring and safety.

5. Future outlooks

Other than the wide ranging analytical applications of PHWE illustrated in Tables 1–4, it is noted that the likely future trend for this technology is towards scaled-up operation so as to extract large volume of samples. The design of industrial-scale equipment is usually preceded by laboratory (bench) and pilot-scale systems after obtaining sufficient preliminary data and the process is similar to existing one [156]. The key parameters such as temperature, pressure, flow rate or pH are usually fixed to achieve desirable extraction efficiency or rate [157]. The feasibility of PHWE as a green solvent extraction method for industrial applications has been established in a pilot-scale project to recover compounds from highly contaminated soils. The capacity of a laboratory unit was scaled-up by a factor of 1000 to handle an increased amount of soil processed from 8 g to 8 kg [57]. With some modifications, PHWE could be scaled-up to extract high volume of desirable compounds from other solid and powdered samples such as plant and food materials. The botanical extracts are rich in chemical compounds or metabolites which can be a potential lead for drug discovery or development of disease-resistant food crops. The scaled-up PHWE could remove more organic contaminants from larger amount of foodstuff samples to increase the productivity in food safety analysis. This potential application could also treat more environmental soil and sediment samples for remediation purposes.

6. Conclusions

Despite the certain limitations discussed as compared to certain classical method of extraction, PHWE is a feasible green extraction method to be exploited in the future technologies for more anlaytes to be used on a bigger scale. This simple technique utilizes the cheap and non-toxic water as an extraction fluid which is environmentally friendly with little disposal issue. Under optimized conditions, PHWE could be a suitable technique for scale up to handle larger sample sizes for industrial applications. Other potential applications include the coupling of PHWE with chemical fingerprints and pattern recognition tools to aid in quality control of medicinal plants, improve the nutritional value of food crops or produce a potential lead for drug discovery purposes.

Acknowledgement

The authors would like to acknowledge the financial support from Nanyang Technological University (NTU), Singapore.

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