Subcritical Water Extraction Laboratory Plant Design and Application

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Abstract: The demand for different green extraction techniques, which provide shortened extraction time and reduced organic solvent consumption, constantly increase. Subcritical water is a green, cheap and non-toxic processing medium, which makes treatments inexpensive, ecofriendly, more selective and less time consuming. Furthermore, lower viscosity and higher values of diffusion coefficient and thermal conductivity at subcritical temperatures improve mass and heat transfer rates. All these properties make subcritical water a satisfactory replacement for organic solvents in extraction processes.

The subcritical water extraction (SWE) technology continuously increases its application in different fields. Thus, the aim of this work was to give an overview of two types of the SWE design: dynamic (continuous flow) and static (batch) systems. The design and development of one SWE static system used for laboratory procedures is given in detail. Some applications together with the optimal extraction parameters of this SWE technology are also shown.

Keywords: subcritical water extraction, plant design, green technology, application

Introduction

The green processes represents an attractive topic in the past few decades. One of environmentally friendly technologies is subcritical water extraction (SWE) with many advantages compared to conventional techniques which is confirmed in our

recently published review articles (Cvjetko Bubalo et al., 2015; Cvjetko Bubalo et al., 2018). The use of these new green processes opens the possibility to achieve better product qualities and/or even to allow the development of completely new products for the use in the food, beverage, cosmetic and pharmaceutical industries as a natural ingredient. Water is probably the best-known and most widely used solvent. When water is used as a solvent, the SWE technology could also be designated as pressurized hot water extraction (PHWE), superheated liquid extraction (SHLE), pressurized liquid extraction (PLE), accelerated solvent extraction (ASE), superheated water extraction (SHWE) or hot water extraction (HWE) (Plaza, Turner, 2015).

Subcritical water extraction

Subcritical water is water at temperatures above its normal boiling point (100°C) and below its critical point (374°C) at a pressure at which it remains in the liquid state. It represents a cheap, safe and non-toxic processing fluid (Ramos et al., 2002). At these conditions, water becomes less polar and therefore it is a suitable replacement for organic solvents. At a temperature above 374 °C and a pressure above 220 bar, water is considered to be in the supercritical state. Water properties in normal conditions, subcritical/near critical state and supercritical state are presented in Table 1 in which it can be seen that with a change of extraction temperature and pressure main water properties change.

Table 1 – Properties of water at different conditions and in different state (Brunner, 2014)

Property	Water at normal conditions	Near-critical water	Supercritical water
T (°C)	25	350	400
P (bar)	1	250	500
ρ (kg m^{-3})	997.45	625.45	577.79
ε (–)	78.5	14.86	12.16
pKw (–)	14.0	11.5	11.5

At ambient conditions water is considered an extremely polar solvent, and its polarity is characterized by a dielectric constant of around 80. In this state, water is suitable for the extraction of highly polar compounds. But, at a temperature between 100 and 374°C, and under a high and sufficient pressure to keep water in the liquid state, the polarity of water considerably decreases and it becomes suitable

for the extraction of both, polar and non-polar compounds. This is caused by a dramatical drop of the dielectric constant with increasing temperature. At elevated temperatures in the subcritical state, surface tension, water viscosity and density, aside from polarity, are significantly lowered too. At elevated temperatures the surface tension of water decreases; this enables enhanced water wetting of the extracting material and the dissolution of targeted compounds in the solvent much faster. Decreased water viscosity enhances its penetration inside the extracting material and thus improves the diffusion rate. The improved diffusion rate enables accelerated extraction as well (Plaza, Turner, 2015).

The advantages of the SWE could be summarized in the following tasks (Cvjetko Bubalo et al., 2018):

- SWE use water as an extraction solvent, which is safe, non-toxic, non-flammable and environmentally friendly;
- Water is easily available and cheap.
- Obtained extracts are safe, without a trace of any toxic solvents;
- SWE is characterized by higher diffusion into the plant matrix and increased mass-transfer properties in comparison to other extraction techniques;
- SWE can be applied for extraction of low-polar as well as non-polar compounds;
- Application of a low cost and easily available extraction solvent and short extraction times minimize the cost of the extraction process.

Drawbacks of SWE (Cvjetko Bubalo et al., 2018):

- High investments costs;
- At elevated temperatures, the risk of unwanted reactions (caramelization, Maillard reactions) increases and toxic compounds can be formed;
- At elevated temperatures possible degradation of temperature sensitive compounds can be expected.

These unique properties of subcritical water, as well as the fact that water as a solvent is easily available, safe, cost-effective, non-toxic, non-flammable, and environmentally friendly, lead to a number of studies on the possibility of the SWE application for the extraction of various compounds, bioactive and many others. The SWE was firstly used in 1994 for extracting polar and non-polar compounds from soils. Since that time, the SWE has been used mainly as an extractant of compounds such as PAHs, PCBs, pesticides and polychlorinated benzofurans from environmental solid samples (Hyotylainen et al., 2000; McGowin et al., 2001). It is also an efficient method for the extraction of antioxidants (phenols and flavonoids), essential oils, fatty acids, oils, carotenoids, sugars, mannitol, pectin, resorcinol, etc. Some of these applications are given in Table 2.

Table 2 – Some applications of the SWE in the last 5 years

Material for extraction/ resource	Targeted compound	SWE operating conditions	Reference
Pistachio (*Pistacia vera* L.) hulls	Polyphenols; gallic acid; pentagalloyl glucose; quercetin; anacardic acid	**Investigated range:** Temperature: 110–190 °C Flow rate: 4 mL/min Pressure: 69 bar **Optimal conditions/highest recovery:** Total gallotannin yields:150-170°C Flavonols: 110-150°C	Erşan et al. (2018)
Red ginseng	Ginsenoside Total phenols	**Investigated range:** Temperature: 150-200 °C Extraction time: 5-30 min **Optimal conditions/highest recovery:** 200°C, 20 min	Lee et al. (2018)
Wood	Hemicellulose	**Investigated range:** Temperature: 160°C Pressure: 9 bar Extraction time: 5-80 min **Optimal conditions/highest recovery:** 80 min	Gallina et al. (2018)
Black mulberry (*Morus nigra* L.)	Gallic acid, protocatechuic acid, catechin, chlorogenic acid, caffeic acid, β-resorcylic acid, p-coumaric acid, naringin, rutin	**Investigated range:** Temperature: 60–200 °C Pressure: 10 bar Extraction time: 30 min **Optimal conditions/highest recovery:** 160°C	Nastić et al. (2018)
Wild geranium (*Geranium macrorrhizum* L.)	Gallic acid, protocatechuic acid, catechin, chlorogenic acid, vanillic acid, p-coumaric acid, ferulic acid	**Investigated range:** Temperature: 60–200 °C Pressure: 10 bar Extraction time: 30 min **Optimal conditions/highest recovery:** 160°C	Nastić et al. (2018)
Comfrey (*Symphytum officinale* L.)	Gallic acid, protocatechuic acid, caffeic acid, β-resorcylic acid, p-coumaric acid, ferulic acid, sinapic acid, naringin, rutin, cinnamic acid, naringenin	**Investigated range:** Temperature: 60–200 °C Pressure: 10 bar Extraction time: 30 min **Optimal conditions/highest recovery:** 160°C	Nastić et al. (2018)
Wild garlic (*Allium ursinum* L.)	Total phenols and total flavonoids	**Investigated range:** Temperature: 120-200 °C Extraction time: 10-30 min Added acidifier, HCl: 0-1.5% **Optimal conditions/highest recovery:** 180.92 °C, 10 min, added acidifier 1.09%	Tomsik et al. (2017)

Material for extraction/ resource	Targeted compound	SWE operating conditions	Reference
Uva ursi herbal dust	Total phenols and total flavonoids	**Investigated range:** Temperature: 120–220 °C Extraction time: 10–30 min Pressure: 30 bar Added acidifier, HCl: 0-1.5% **Optimal conditions/highest recovery:** 151.2 °C, 10 min, 1.5% HCl	Naffati et al. (2017)
White grape pomace	Total phenols	**Investigated range:** Temperature: 170–210°C Extraction time: 30 min Pressure: 100 bar **Optimal conditions/highest recovery:** 210°C, 100 bar, 30 min	Pedras et al. (2017)
Winter savory (*Satureja montana* L.)	Total phenols and total flavonoids	**Investigated range:** Temperature: 79.15-220.5 °C Extraction time: 5.9-34.1 min Pressure: 30 bar **Optimal conditions/highest recovery:** 220°C, 20.8 min, 30 bar	Vladic et al. (2017)
Ginger (*Zingiber officinale*)	Gingerol	**Investigated range:** Temperature: 130-140 °C Extraction time: 10-40 min Pressure: 2 bar **Optimal conditions/highest recovery:** 130°C, 20 min, 2 bar	Yulianto et al. (2017)
Mandarin (*Citrus unshiu* Markovich) peel	Flavonoids (Narirutin, Hesperidin, Naringin, Naringenin)	**Investigated range:** Temperature: 110–190 °C Extraction time: 5–15 min **Optimal conditions/highest recovery:** 130°C, 15 min	Ko et al. (2016)
Tumeric rhizomes (*Curcuma longa* L)	Curcumin	**Investigated range:** Temperature: 120-160°C Extraction time: 6-22 min Particle size: 0.6-2 mm Pressure: 10 bar **Optimal conditions/highest recovery:** 140°C, 10 bar, 14 min, 0.71 mm	Kiama-halleh et al. (2016)
Spent coffee grounds (*Coffea arabica* L.)	Total phenols	**Investigated range:** Temperature: 110-190 °C Extraction time: 15-75 min Pressure: 50 **Optimal conditions/highest recovery:** 177 °C, 55 min, 50 bar	Xu et al. (2015)

Material for extraction/ resource	Targeted compound	SWE operating conditions	Reference
Black tea	Myrcetine and Quercetin* Kampherol**	**Investigated range:** Temperature: 110-200°C Extraction time: 5-15 min Pressure: 101 bar **Optimal conditions/highest recovery:** 170°C, 15 min, 101 bar* 200°C, 15 min, 101 bar**	Cheigh et al. (2015)
Ginseng leaf	Myrcetine and Quercetin* Kampherol**	**Investigated range:** Temperature: 110-200°C Extraction time: 5-15 min Pressure: 101 bar **Optimal conditions/highest recovery:** 170°C, 10 min, 101 bar* 200°C, 15 min, 101 bar**	Cheigh et al. (2015)
Citrus peel	Pectin	**Investigated range:** Temperature: 100-140 °C Extraction time: 5 min **Optimal conditions/highest recovery:** 120 °C, 5 min	Wang et al. (2014)
Apple pomace	Pectin	**Investigated range:** Temperature: 130-170 °C Extraction time: 5 min **Optimal conditions/highest recovery:** 150 °C, 5 min	Wang et al. (2014)

Process parameters of the SWE

The main factors affecting the extraction efficiency during the SWE include extraction temperature, time, and solute characteristics. Temperature represents an extremely important parameter due to the fact that at different temperatures different components are formed. A higher temperature of the water leads to the improved wetting of the sample. Further, increasing the temperature also favors mass-transfer kinetics, and results in faster diffusivity. When the temperature increases during the SWE, the strong solute-matrix interactions caused by van der Waals forces, hydrogen bonding, and dipole attractions of the solute molecules and active sites on the matrix can be disrupted, and hydrogen bonding is weakened with increasing temperature. Thermal energy can overcome the cohesive (solute-solute) and adhesive (solute-matrix) interactions by decreasing the activation energy required for desorption (Richter et al., 1996). In addition, the viscosity and surface tension of subcritical water decrease at higher temperatures, hence promoting better penetration

of water into the matrix particles to enhance extraction. There are three main draw-backs in using elevated temperatures in the SWE: decreasing selectivity of the extraction, degradation of some analytes, and other chemical reactions in the sample matrix.

Extraction time is notably influenced by temperature and the nature of the sample matrix and solutes. In many works as published in reviews of Plaza and Turner (2015) and Okiyama et al. (2017), a higher antioxidant capacity was observed in the extracts obtained at temperatures of over 175 °C and at longer extraction times, compared to the extracts obtained at lower temperatures and shorter extraction times. The most active antioxidants from rosemary, including carnosol, rosmanol, carnosic acid, methyl carnosate and some flavonoids, were recovered in the extracts using SWE with high antioxidant activity (Ibáñez et al., 2003).

Pressure has very little influence on the properties of water, as long as the water remains in the liquid state. However, a specific minimum pressure is required to maintain the water in the liquid state at the extraction temperature. Pressures elevated from 1 to 10 MPa at treatment temperatures ranging from 100 to 300□ are generally used to maintain water in the liquid state during subcritical water treatment (Wagner, Pruß, 2002).

The particle size of the sample influences the extraction kinetics since a smaller particle size leads to increasing the contact surface between the sample and the extractant.

Solvent-solid ratio is an important parameter in the SWE. It is important that the solvent-solid ratio is as small as possible but at the same time big enough to provide the highest possible extraction yield (Ravber et al., 2015).

All these parameters are important when analyzing the SWE, so the optimization of this process is desirable.

Design of the SWE system

There are two types of equipment for the SWE: dynamic (continuous flow) systems (Fig. 1a) and static (batch) systems (Fig. 1b). The main parts of the dynamic SWE are pump (6.), extractor (4.) and pressure restrictor valves (2.). The pump delivers water through the heating coil to the extraction vessel. On that way water is preheated on the temperature of extraction. The water passes through the extractor. After the extractor the water passes through the cooling coil and can be collected. The pressure of the system is very finely controlled by the air driven liquid pump with a pressure range from 0.2 MPa to 20 MPa. Heating is very finely controlled
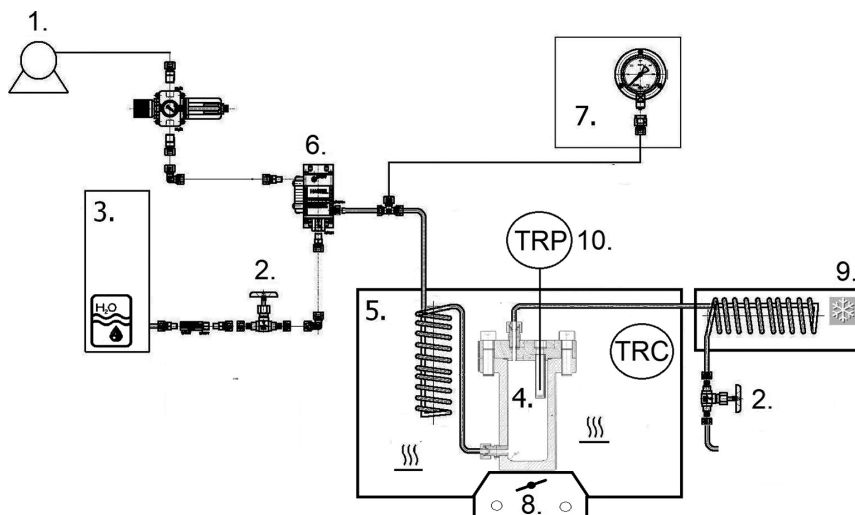
Fig. 1a – The main parts of a dynamic SWE system 1. Compressor, 2. Valves, 3. Water tank, 4. Extractor, 5. Oven, 6. Pump, 7. Manometer, 8. Magnetic stirrer (Optional), 9. Cooling coil (bath), 10. TRP and TRC

by the TRC oven. To prevent sample flow, loss and potential clogging of tubes, the extractor vessel should have sintered stainless steel filters at least at the exit of water from the extractor. Dynamic and static SWE are very similar regarding oven, tubing and valves.
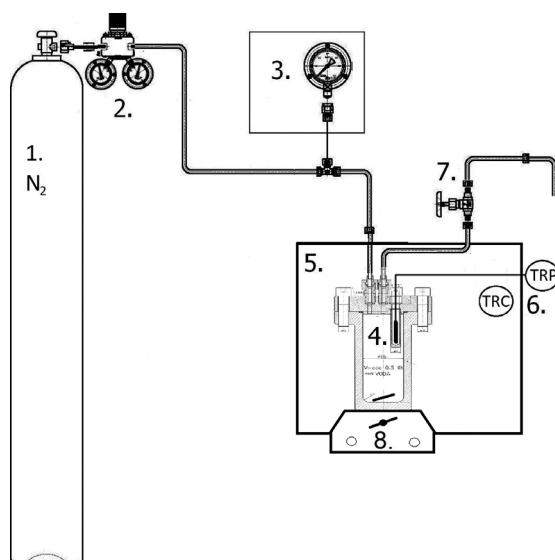
Fig. 1b – The main parts of a static SWE system (Faculty of Food Technology of Osijek): 1. N_2 tank (150/40), 2. Pressure reducing valve (200/50), 3. Manometer, 4. Extractor, 5. Oven, 6. TRC and TRP, 7. Valve, 8. Magnetic stirrer

In contrast to the dynamic SWE the static SWE doesn't have a pump and is pressurized trough N_2 to prevent sample oxidation. The retention time of subcritical water in the dynamic SWE is shorter than in the static SWE resulting in a lower degradation of the thermolabile components which is more preferably. The only disadvantage of the dynamic SWE is that it is more expensive than the static SWE.

At the Faculty of Food technology Osijek the authors of this paper designed and built one plant for the high pressure extraction process using supercritical CO_2 (Jokić et al., 2015; Horvat et al., 2017); so the next step was to design of a new subcritical water extractor.

Handmade subcritical water extraction (HM-SWE) system

The schematic diagram of the newly constructed apparatus for the SWE at the Faculty of Food Technology Osijek is presented in Figure 1b. This is a static SWE system.

Materials used for the HM-SWE system

Materials used for the construction of the HM-SWE system were stainless steel AISI 304. All additional connection tubing parts were also of the same material grade. The extraction vessels were properly tested with a safety factor of 1.5. The extraction vessel was tested at a working pressure of 30 MPa.

Construction of the HM-SWE system

The construction and assembling of the HM-SWE system was performed by Đuro Đaković Aparati d.o.o. (Slavonski Brod, Croatia) which provided material durability tests and pressure test for vessels. Working pressure calculations for the extractor and seamless tubes are given in Eq. (1):

$$P = \frac{2 \cdot S \cdot T}{(O.D. - 2 \cdot T) \cdot SF}$$

where:

P – fluid pressure (MPa)
T – wall thickness (extractor and seamless tube) (m)
$O.D.$ – outer diameter (m)
SF – safety factor (usually 1.5)
S – yield tensile strength of material

Extraction vessel, manometers, pipes and magnetic stirrer

The extraction vessel was made from stainless steel bar (AISI 304) O.D. 90 mm and with a height of 230 mm. A stainless steel rod was drilled (center hole) with a Ø 65 mm bore for 155 mm, so the extractor volume is ca. 500 mL. The extraction vessel is closed with a flange type (Ø 154 mm) closure using eight M16 screws. Sealing is provided with a high temperature O-ring Viton type. In the center of the flange closure there are two quick connectors sealed also with Viton O-rings and one place for a PT temperature probe. High-pressure valves are used to control intake pressure of N2. High pressure pipes AISI 316Ti 6x1mm are used to connect the extraction vessel, gas cylinder and control manometer. The control manometer used is WIKA 0-25MPa with 0.5 MPa division.

The pressure and inert state during the extraction time is provided with N_2 from a cylinder and the desired pressure is achieved using a pressure reducing valve (20/5 MPa).

The magnetic stirrer is placed below the extractor vessel to obtain adequate stirring of water and material.

Conclusions

The SWE emerged in the last few decades as a promising green technology due to its unique properties and a wide variety of possible applications in processing food and natural products. The handmade static system proposed in this paper offers a cost effective solution for small scale research SWE systems. By presenting uniform and simple guidelines for the construction of a laboratory SWE system an adequate scale-up from laboratory to industrial design purposes becomes a simple task.

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