CHAPTER 14

Extraction of phenolic compounds

Yassine Benchikh[a,b], Mostapha Bachir-bey[c], Makhlouf Chaalal[a,b], Siham Ydjedd[b,d], Djamel Edine Kati[c]

[a]Laboratory of Biotechnology and Food Quality, Institute of Nutrition, Food and Agro-Food Technologies, University of Constantine 1, Constantine, Algeria
[b]Laboratory of Applied Biochemistry, Faculty of Nature and Life Science, University of Bejaia, Bejaia, Algeria
[c]Department of Food Science, Laboratory of Applied Biochemistry, Faculty of Nature and Life Science, University of Bejaia, Bejaia, Algeria
[d]Department of Nature and Life Science, Faculty of Nature and Life Science and Earth and Universe Science, University 8 May 1945 Guelma, Algeria

14.1 Introduction

Phenolic compounds are ubiquitous molecules found in all plant tissues, either edible or nonedible parts (fruits, leaves, stems, seeds, roots, woods, barks, and peels). Because of their important biological properties, particularly antioxidant activity, phenolic compounds are among secondary substances that have a great interest, especially in last decades (Benchikh et al., 2019; Chaalal et al., 2012; Balasundram et al., 2006).

Phenolic compounds known as monomers or polymers have at least one aromatic phenyl and hydroxyl group. Their structures confer them a possibility to be stable a long time when they neutralize free radicals. These latter are the cause of several diseases worldwide that lead to a considerable rate of death annually (Luna-Guevara et al., 2018; Patil and Masand, 2018; Kyselova, 2011). By their ability to oxidize the organic biological molecules of organs, free radicals can induce DNA mutations, inactivate functional enzymes, and weaken the cell membrane leading respectively to cancers, enzymatic deficiencies, and death of cells (Niki, 2011; Haddad, 2004; Dalton et al., 1999). In our body, all things are right when antioxidants and free radicals are the same in terms of amount, but at a high level of oxidative molecules rate, the situation begins dangerous and the need of exogenous antioxidants from diets, drugs, plants, and other sources is necessary and even mandatory to regulate the deficiency (Suleman et al., 2019; Martins et al., 2011; Haddad, 2004).

On the other hand, as antioxidants, phenolics are used by the food industry in order to prevent oxidation of food constituents and lengthen the shelf-life of products, and also used as an alternative to synthetic additives, like the elaboration of new processed products made from functional food ingredients with health-promoting. In addition, they are used in cosmetic and pharmaceutical industries for the preparation of therapeutic ointments as sun cream, and neutraceuticals as capsules or pills.

In order to extract these phenolic compounds from different sources, several points must be taken into account to obtain an optimal extraction. The nature of phenolic

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compound, its physicochemical characteristics, as its solubility in extraction solvent, and its location in the cell (cell wall or vacuoles) is the first intrinsic factor that can influence its extraction. The extraction conditions of bioactive phytochemicals from vegetables, fruits, flowers, leaves, seeds, algae, and stems or from microorganisms are not similar. The phenolic compounds in solid samples need more time and high temperature to be extracted, but the simple ones do not require these conditions. The second point is the best choice of the appropriate method or technique of extraction, from one technique to another, the recovery of phenolics can highly differ. As reported by the literature, the most methods which are used for phenolic compounds extraction from particularly plants materials are conventional and nonconventional techniques, like maceration, decoction, ultrasound-assisted extraction, microwave-assisted extraction, accelerated solvent extraction, supercritical fluid extraction, enzyme-assisted extraction, and pulsed-electric field extraction. The third point is the extraction factors involving in the recovery of the phenolic compounds. So, several scientific studies have reported the effect of variable conditions on phenolics extraction from different sources such as the nature and concentration of solvent, the solid to solvent ratio, and the time and the temperature of extraction (Benchikh et al., 2014, 2019; Barba et al., 2016; Bachir bey et al., 2014).

In the present chapter, a general overview on phenolic compounds chemistry, the factors influencing their extraction, and finally a report on different conventional and innovative methods frequently employed for phenolic compounds extraction is reported.

14.2 Chemistry of phenolic compounds

Phenolic compounds are known as monomeric or polymeric molecules which have at least one aromatic phenyl and hydroxyl group. Their structure confers them a possibility to be stable a long time when they neutralize free radicals. We find in the literature the name polyphenols given for simple and highly polymerized compounds. However, several scientists prefer to use "phenolic compounds" term in order to avoid confusion between simple phenols as phenolic acids and polymeric molecules like tannins. This group of secondary metabolites presents a high structural diversity, including more than 8000 compounds. The natural structural diversity of phenolics allowed their classification to several classes (de la Rosa et al., 2019; Bravo, 1998). Table 14.1 recapitulates different categories of phenolic compounds found in the nature.

The class of simple phenols (C_6) is not widespread in plants. This group is represented by catechol, phloroglucinol, and hydroquinone. Simple phenols are found in certain medicinal and aromatic leaves such as *Gaultheria* species and *Vaccinium* spp. (blueberry, cowberry, and cranberry). The phenolic acids are subdivided into two subgroups named hydrobenzoic and hydrocinnamic acids, the first and the second subgroups have C_6–C_1 and C_6–C_3 structures, respectively (Fig. 14.1). Gallic, vanillic, syringic, and protocatechic

Table 14.1 Classification of phenolic compounds.

Class	Structure
Simple phenol (catechol, hydroquinone, phloroglucinol…)	C_6
Hydroxybenzoic acids	C_6–C_1
Phenylethanoids (acetophenones, phenylacetic acids, phenethyl alcohol derivatives…)	C_6–C_2
Phenylpropanoids (hydroxycinnamic acids and derivatives, cinnamic aldehydes, monolignols, phenyl propenes, …)	C_6–C_3
Napthoquinones	C_6–C_4
Xanthonoids	C_6–C_1–C_6
Stilbenoids, anthraquinones, and anthrones	C_6–C_2–C_6
Flavonoids, isoflavonoids	C_6–C_3–C_6
Lignans, neolignans	$[C_6$–$C_3]_2$
Biflavonoids	$[C_6$–C_3–$C_6]_2$
Lignins	$[C_6$–$C_3]_n$
Proanthocyanidins (condensed tannins)	$[C_6$–C_3–$C_6]_n$

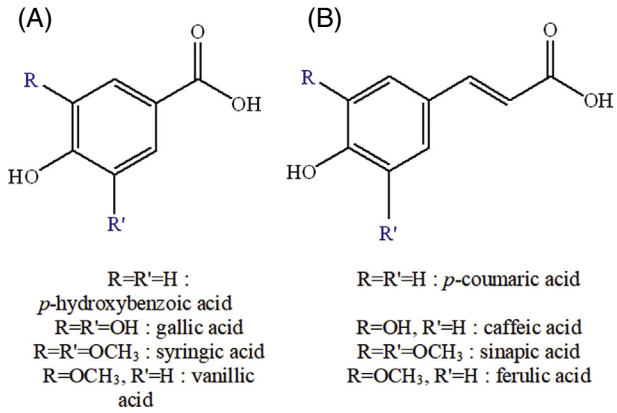

Fig. 14.1 ***Hydroxybenzoic (A) and hydroxycinnamic (B) acids.***

acids are included in hydrobenzoic acids; while in hydrocinnamic acids we find ferulic, sinapic, and caffeic acids (Vuolo et al., 2019; Balasundram et al., 2006; Bravo, 1998). As examples of phenylethanoids (C_6–C_2), it can be cited homogentisic acid and hydroxytyrosol that present in honey and nectar obtained from strawberry and olive trees (leaf and oil), respectively (Gordon et al., 2001; Cabras et al., 1999).

The class of flavonoids (C_6–C_3–C_6) is the largest group that represents 2/3 to 3/4 of phenolic compounds that we find in nature. These molecules are generally found conjugated with mono-, di-, or polysaccharides. Chemically, they have two aromatic rings A and B bounded by C3 open or close (ring C) bridge (Fig. 14.2). The bridge C

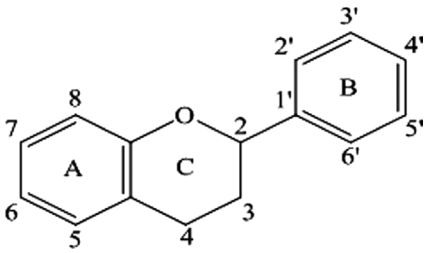

Fig. 14.2 ***Basic flavonoid structure.***

constitutes the base of the flavonoids differentiation; the substitutions on this bridge may lead to the diverse subclasses of flavonoid. It can be distinguished at least six subclasses of flavonoids: flavones, flavanones, flavonols, flavanols, isoflavones, and anthocyanins (Fig. 14.3). The flavones and flavonols are the compounds largely present in nature (Balasundram et al., 2006).

Tannins are considered as polyphenols with a high molecular weight arranged from 500 to 3000 Da. Tannins are represented by two groups, hydrolyzable and condensed tannins. The compounds of the first subgroup are the polymers which can easily be degraded into monomer molecules, constituted generally of gallic and ellagic acids and molecule of glucose. A polymer of tannic acid (pentagalloyl-D-glucoside) is an example of hydrolyzable tannins; this acid is constituted of five molecules of gallic acid conjugated with one molecule of glucose (Fig. 14.4). However, condensed tannins, also known as proanthocyanins, are very solid polymers that require a strong acid treatment, like HCl, in order to hydrolyze them into polyhydroxyflavan-3-ol monomers (Balasundram et al., 2006; Porter, 1989).

14.3 Factors affecting extraction of phenolic compounds

Physicochemical and environmental factors may considerably influence the recovery of phenolics from their original sources. The most factors that affecting the extraction of phenolics are the type and concentration of solvent (nature and polarity), the applied energy (temperature, stirring, amplitude, pressure, and puissance), the time of extraction, and the gradient (sample to solvent ratio). These factors can influence extraction in positive, negative, linear, or quadratic manners and can also express interaction effects. Other factors can also contribute as particle size of the matrix, origin, and nature of matrix (Fig. 14.5).

14.3.1 Nature and concentration of solvent

The first principal factor that must be taken into consideration is the nature of the extraction solvent. Indeed, the choice of appropriate extraction solvent depends on the polarity of phenolic compounds of interest and the nature of the sample matrix. In

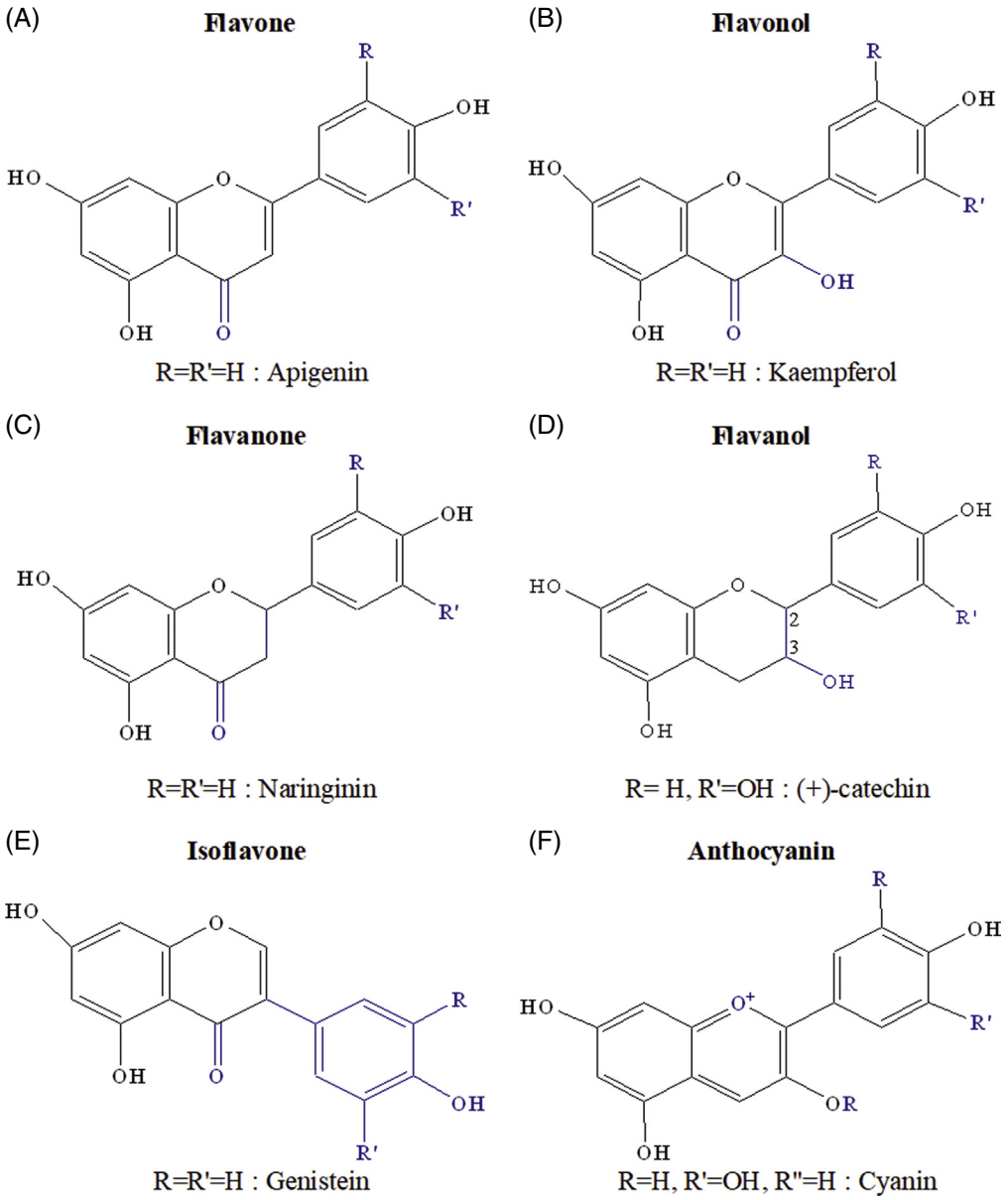

Fig. 14.3 ***Subclasses of flavonoids.***

the large literature, phenolic compounds are generally extracted using aqueous organic systems because some of them are not completely soluble in pure organic solvents and others are highly polar. So, aqueous acetone, ethanol, and methanol are the main solvents used for phenolic compounds recovery (Benchikh et al., 2019; Saci et al., 2018; Bachir bey et al., 2014).

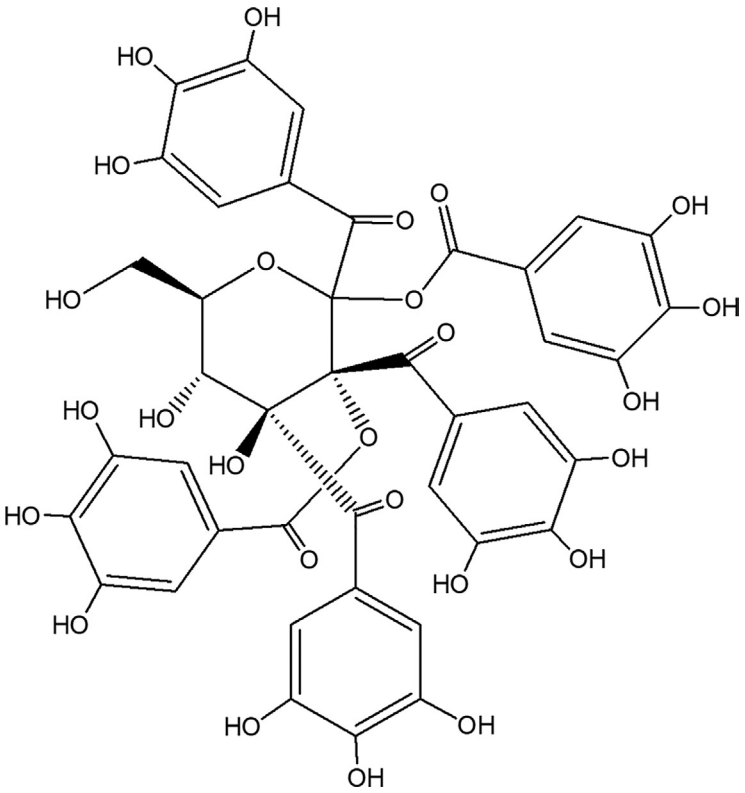

Fig. 14.4 *Tannic acid (1,1,2,2,3-pentagalloyl-D-glucoside).*

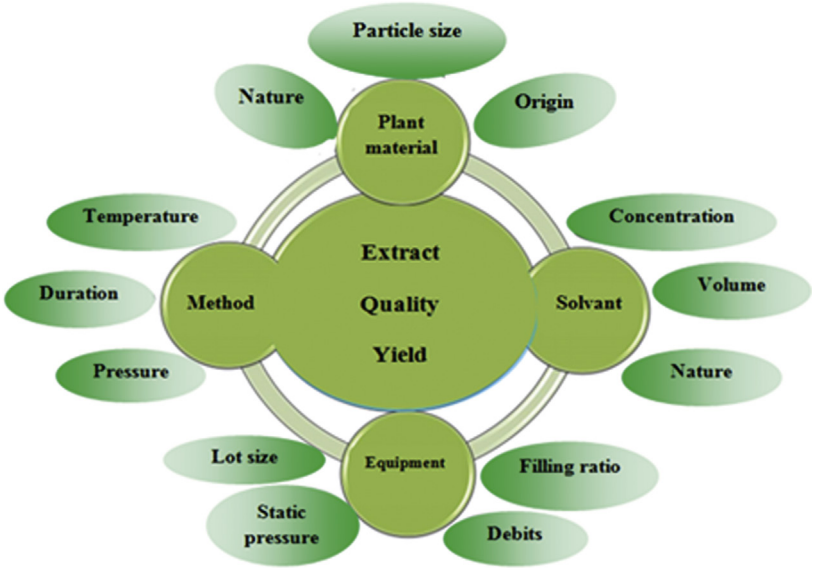

Fig. 14.5 *Factors influencing the extraction of phenolic compounds.*

Numerous studies were optimized the solvent concentration for phenolics extraction from different plant matrices. Acetone/water at 70/30 and 60/40 (v/v) was the best solvent that permits the highest contents of phenolic compounds from carob pulp and figs (Benchikh et al., 2014). The optimal solvent percentage of phenolics extraction from *Cinnamonum cassia* is 60% ethanol (Dvorackova et al., 2015). However, 80% methanol was recommended for grapes of *Vitis vinifera* (Benmeziane et al., 2014).

The extraction using pure organic solvents is not generally adequate for phenolic compounds extraction; these solvents are usually diluted with water in order to obtain appropriate solvent polarity. Binary solvent systems present high efficiency for phenolic compounds extraction relative to pure solvents (Wong et al., 2014). These findings are explained by "like dissolves like" principle; the solvent, with a given polarity, extracts phenolic compounds characterized by similar polarities to solvent polarity. Thereby, the rise of water part in organoaqueous system induces the enhancement of its polarity till to reach the adequate polarity to extract the most phenolic compounds of the given material (Luthria, 2012).

14.3.2 Time

The period of extraction is another factor that can influence the extraction of phenolic compounds process. A more time of contact between particles and solvent could improve the yield of extraction, but a prolongation of extraction time can lead to the oxidation of phenolic compounds already extracted. The time required to maximize extract of phenols changes according to matrix nature and also depends on other extraction factors like the temperature and the extraction energy (agitation, amplitude, pressure, puissance). The second law of Fick predicts that the compounds diffuse from the high concentrated part (matrix) to low concentration part (extraction solvent) till to reach the equilibrium between the two sections and this requires a certain duration related on the factors previously cited. For example, phenolics extraction of *Opuntia ficus-indica* seeds showed their increase with the time till 90 minutes. This duration allows the bioactive compounds to diffuse and move from the particles of the matrix to the extraction solvent. The prolonged extraction duration beyond this optimal time causes a decrease of phenolics concentration. This diminution is the consequence of the decomposition of polyphenols by oxidation induced by oxygen and light (Chaalal et al., 2012).

14.3.3 Temperature

The application of heating during phenolics extraction can increase the extraction yield by increasing the mass transfer after allowing a good diffusion of the solvent into particle matrix, and then improve desorption of target compounds (Benchikh et al., 2014; Vongsangnak et al., 2004; Cacace and Mazza, 2003). By heating, the solvent viscosity diminished allowing to its better infiltration through particles of matrix and also ameliorates

the diffusion of phenolics (Richter et al., 1996). The extraction temperature must be taken into consideration when extracting phenolic compounds; each vegetal matrix requires an optimal temperature. Once this latter is exceeded, a degradation of phenolics can occur. It is also indicated to point out that some phenolics are susceptible to elevated temperature; therefore, the choice of a suitable extraction temperature must be studied.

14.3.4 Solid to solvent ratio

The proper solid to solvent ratio is another necessary factor that can influence phenolics extraction. The choice of low solid to solvent ratio causes oxidation of bioactive compounds due to more dissolved oxygen in the medium particularly with prolonged extraction time and using high temperature (Shi et al., 2003). However, using high ratio causes an incomplete extraction; the solvent arrives to saturation before complete extraction of phenolic compounds and this requires several extraction cycles.

14.4 Extraction techniques of phenolic compounds

Phenolic compounds are used in various fields like chemical, pharmaceutical, and agro-food industries. The obtaining of these bioactive phytochemicals from natural resources needs their appropriate extraction using different methods. This extraction implicated the separation of bioactive molecules from their original location by an adequate solvent with applying a selective technique as well as required factors (Handa, 2008). The selection of appropriate extraction method represents a crucial step for phenolic compounds extraction because it determines the phenolics yield and the degree of purity, the required amount of solvents, and the consumption of energy. There are several methods for phenolic compounds extraction that can be generally divided as conventional and nonconventional techniques.

14.4.1 Conventional extraction techniques

Conventional extraction techniques are widely used to extract bioactive compounds from their natural sources. Extracting power of these methods is based on the type of solvent, the application or not of heating, and the use of certain apparatus and instruments (Azmir et al., 2013). In spite of the simplicity of these extraction methods and their relative cheapness, they present numerous drawbacks and limitations such as a requirement of a long time of extraction, the use of large volumes of toxic solvents, and high consumption of energy. Most classical techniques are (1) maceration, (2) decoction, (3) infusion, (4) Soxhlet, and (5) percolation.

14.4.1.1 Maceration

The maceration comes from the Latin word *maceratus* that means to soften (Singh, 2008). Maceration is among the oldest and widely used methods of extraction, it is

used from daily habits as culinary preparations to the industrial production scale. This simple method presents a great diversity of applications and can be used with variable conditions.

Maceration is based on intimate interaction of a solvent and a solid matrix in order to transfer desired compounds such as phenolic compounds from the matrix inside to the liquid phase. The subsequent step consists of the separation of solvent phase from solid part by filtration, decantation, or centrifugation. Once the solvent is brought into contact with the desired sample, a close interaction is created between the solvent and the particles of the matrix. The molecules of phenolics situated at the surface of particles are rapidly solubilized by solvent (Fig. 14.6). On the other hand, the compounds which are positioned inside the sample particles require more time for their extraction. For this purpose, the solvent diffuses inside the matrix, dissolves the solutes which will subsequently be transferred outside. In order to facilitate the recovery of phenolics, many factors are often considered like the type of solvent, the time, the temperature, the solid-to-solvent ratio, the particle size, and the number of extractions (Petigny et al., 2015; Bachir bey et al., 2014).

Maceration is a good method for phenolic extraction due to its adaptation for variable plant resources, a wide choice of extraction parameters, and does not require a particular instrument. As the temperature can be chosen according to the sensitivity of the desired compounds, this method is suitable for heat sensitive phenolic compounds. This technique remains long, when extending time is necessary for extraction, and is not efficient for extraction of molecules that are firmly bound to other compounds of the matrix such as proteins, sugars, or those contained in the cell well. For this, other steps are necessary such as enzymatic or acid treatments. In some cases, the use of heat is necessary for extraction. Maceration using hot water is called infusion and boiling in water is known as a decoction.

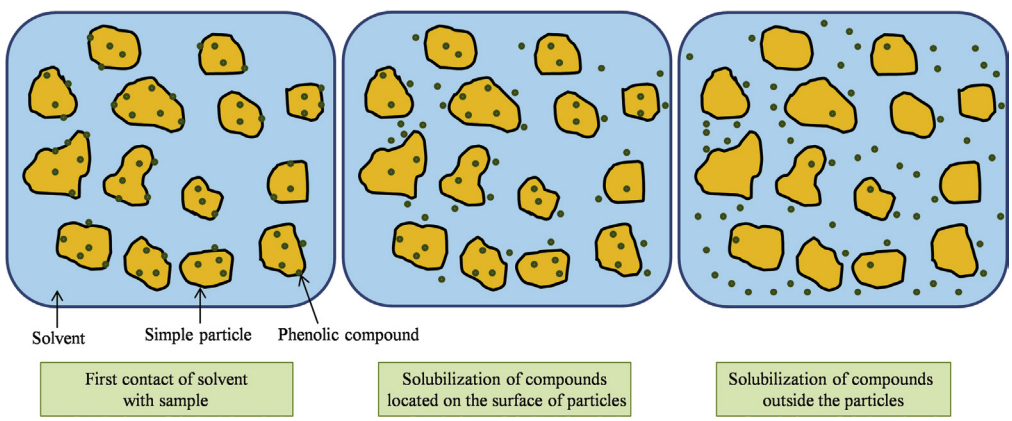

Fig. 14.6 ***Steps of phenolic compounds extraction by maceration.***

14.4.1.2 Decoction

The difference between the simple maceration and decoction extraction technique is that in this later the temperature of extraction is applied at ebullition point of the extraction solvent. The objective of this extraction by heating is to facilitate the diffusion of solvent through particles of material by softening and dilating their cell walls. In this technique, the extraction temperature must be fixed from the beginning to the ending of the decoction.

The decoction is carried out using boiling water during a specified time or till a specific volume is reached. This extraction is often the method of choice for the extraction of polyphenols from hard and more fibrous plants, barks, roots, and wood. Phenolic compounds extracted by this method must be water-soluble and heat-stable. Generally, the initial sample to water ratio is done with 1/4, 1/10, or 1/16 and the treatment lasts for 5 minutes to 2 hours or more. The quantity of water is reduced to reach a specific sample to solvent ratio (e.g., 1/4) or adjusted at the end of extraction to the desired volume. Extraction with this method can enhance and facilitate the extraction recovery but the heat sensitive molecules can be degraded.

14.4.1.3 Infusion

Contrarily to the decoction, the infusion is processed by soaking phenolic resources (in general, from soft tissues like leaves and petals) in hot or boiling water for certain time (15–30 minutes) without maintaining the temperature at the ebullition point of the solvent. The prepared infusion is used freshly, conserved for a short time at cold or by addition of preservatives such as ethanol.

The advantages of extraction by infusion or decoction are the simplicity of the method and the use of water, which is a cheap and nontoxic solvent. The main drawbacks of these two methods are that they are predisposed to microbial (fungus and bacteria) growing due to the presence of a large amount of water. Because water is not specific for phenolics, the use of this solvent of extraction causes the solubilization of other not desired compounds such as sugars and proteins particularly at high temperature that requires many purification steps of phenolic compounds. These are the principal reasons why infusions and decoctions are not really popular for industrial uses. Infusion is more economic than the decoction extraction technique with less degradation of heat sensitive molecules.

14.4.1.4 Soxhlet

The Soxhlet apparatus has been proposed first by Franz Ritter von Soxhlet (German agricultural chemist, 1848–1926) for the determination of milk lipids (Soxhlet, 1879). This method is generalized for the extraction of lipids from different resources, alkaloids, and phenolic compounds (Chin et al., 2013). Soxhlet extractor is considered as the widely used tool for solid–liquid extraction in numerous fields like food (fruits, vegetables, and industrial products), herbal, and phytopharmaceuticals.

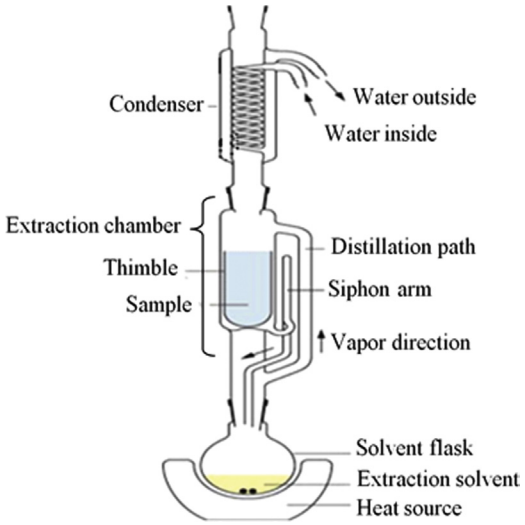

Fig. 14.7 ***Soxhlet extractor.***

The Soxhlet apparatus consists of three compartments: solvent flask, extraction chamber, and condenser (Fig. 14.7). The solvent located on solvent flask was subjected to heating to its boiling point leading to its evaporation. The generated vapor passes through the distillation path to reach the condenser where it will be condensed then returned in the form of droplets to the extraction chamber. The latter contains a cellulose thimble filled with the sample. Once the extraction solvent reaches the level of the siphon top, it will be spilled completely and the solution go back into the extraction flask. Then, the solvent can be evaporated again to achieve the number of cycles necessary for the extraction of desired bioactive compounds. These latter accumulate progressively in the extraction flask until their complete extraction (Azmir et al., 2013; Zougagh et al., 2004).

The advantages of the Soxhlet method are easy to operate and gave a good extraction yield; besides, it is a reference method for the quantification of many compounds. Moreover, this method permits the use of one portion of the solvent which is renewed for each cycle of extraction instead of several different volumes of solvent.

On the other hand, the Soxhlet method has several disadvantages. Indeed, phenolic compounds extraction using Soxhlet apparatus requires considerable volumes of organic and nonorganic toxic solvents, which makes the extraction not only expensive but causes problems for the manipulator and the environment. In the steps of isolations and purifications of phenolics, the elimination of the solvent is essential and the removal of residual solvents and impurity is difficult, this requires the use of good quality solvents which makes extraction more expensive. In addition, this method needs numerous extraction cycles that needed a long time of extraction up to 24 hours or more. The use

of heating during extraction leads to the degradation of certain heat sensitive phenolic compounds, especially with using long extraction time and the exposition of extracted compounds to light (Easmin et al., 2015).

The time of extraction by Soxhlet apparatus varied considerably between authors and according to used phenolic resource. The period of 30 minutes was used by Pan et al. (2008) to extraction phenolic compounds from longan (*Dimocarpus Longan* Lour.) peel; 1–4 hours were used to extract these compounds from *Vernonia cinerea* leaves (Alara et al., 2018). Two extraction hours were chosen for Horseradish roots (*Armoracia rusticana*) (Tomsone et al., 2012) and *Terminalia chebula* fruits (Rangsriwong, 2007). However, a long time (14 and 24 hours) was used for the extraction of phenolic compounds from *Maclura pomifera* fruits and *Phaleria macrocarpa* (Easmin et al., 2015; Altuner et al., 2012).

Different solvents with variable polarities were used to extract phenolic compounds from variable plant resources like water, methanol, ethanol, acetone, 2-propanol, diethylether, ethylacetate, and n-hexane, or a combination of solvents like ethanol/water/acetic acid (80/20/1 v/v/v), ethanol (20%, 40%, 60%, and 80%), and water/ethanol/methanol/acetone/dichloromethane (1/2.5/2.5/2/2) (Alara et al., 2018; Altuner et al., 2012; Tomsone et al., 2012; Rangsriwong, 2007).

14.4.1.5 Percolation

Percolation is another method used for the extraction of phenolic compounds. This technique used for the recovery of phenolic compounds the unique equipment called percolator. This instrument is a flask with the conical form open in both sides with the presence of a lid on the broad top side and a tap on the narrow bottom side. Percolation processed by maceration of the sample with extraction solvent (water, alcohol…, or their mixtures), flowed by draining of extract by the outlet of the percolator.

The sample is first imbibed with a suitable volume of solvent and allowed to stand for an appropriate time (2–4 hours) in a well-closed container. Subsequently, the mixture is transferred to the percolator, an appropriate quantity of solvent is added, and the device is allowed to macerate in the closed percolator for 24 hours. Once the maceration is over, the outlet tap of the percolator is then opened and the extract is allowed to drip slowly with a flow rate of 1 mL/min. Additional solvent is added as required, the marc is then pressed. After that, sufficient solvent is added to perform a final wash and reach the required extract volume. The abstained extract is clarified by filtration and concentrated or dried.

14.4.2 Nonconventional extraction techniques

These techniques are known as nonconventional extraction techniques because they are recent. These techniques are similar in that they work at high pressures and temperatures, which positively led to ameliorate the speed of the extraction process (Björklund et al., 2000; Sparr Eskilsson and Bjorklund, 2000). Some of the most developing techniques

are (1) microwave-assisted extraction; (2) ultrasound-assisted extraction; (3) accelerated solvent extraction; (4) supercritical fluid extraction; (5) pulsed-electric field-assisted extraction; and (6) enzyme-assisted extraction. These techniques considerably reduce the consumption of solvents and increase the speed of the extraction process (Biesaga and Pyrzynska, 2013).

14.4.2.1 Microwave-assisted extraction

Microwaves are electromagnetic fields in the frequency ranges from 300 MHz to 300 GHz. Their oscillating fields are perpendicular, which are electric and magnetic fields (Azmir et al., 2013; Kaufmann and Christen, 2002). Microwave-assisted extraction is promised on the microwave energy absorption by polar compounds (Romanik et al., 2007).

Industrial and domestic microwaves are generally operated at 2.45 GHz because the interferences can occur (Pangarkar, 2008; Kaufmann and Christen, 2002). In microwave-assisted extraction, microwave energy is used to heat a solvent which allows penetrating in sample particles and releases the bioactive compounds from the matrix into the solvent (Fig. 14.8) (Sparr Eskilsson and Bjorklund, 2000).

Microwave-assisted extraction is based on heating up the molecules of water in the particle cells, which causes the elevated of cell wall pressure from the inside and then conduct to its destruction (Wójciak-Kosior et al., 2013). Mechanism of microwave-assisted extraction consists of five steps: (1) The energy of microwaves is absorbed by

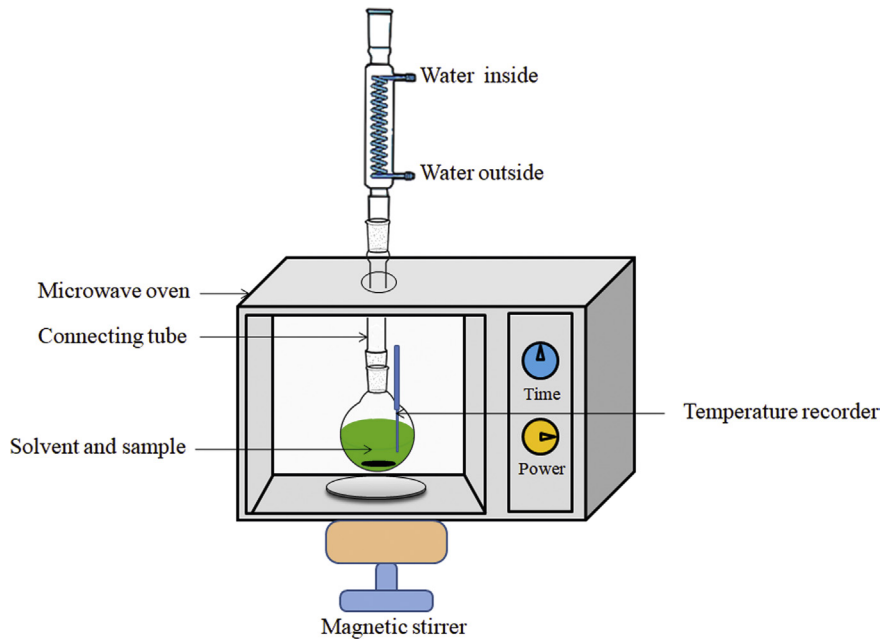

Fig. 14.8 *Microwave-assisted extraction apparatus.*

sample, (2) the waves interact with the polar part of the material which is the molecules of water, causing their vibration then a considerable increase of the temperature, (3) this causes the evaporation of water and a generation of a great pressure of steam, (4) leading to the rupture of the cell walls of the material, and (5) the released bioactive compounds can be easily moved outside the cells. In the last decade, microwave-assisted extraction is proposed as an alternative extraction technique due to its easy and fast of use (Saci et al., 2018; Silva, 2017; Barba et al., 2016).

Many studies have mentioned the advantages of this extraction technique comparing with others (Hiranvarachat et al., 2013). Its main advantages are: extraction time is shortened, sample heating is easily controlled, and the amount of the used solvent is reduced (Romanik et al., 2007). Furthermore, it increases the diffusion of phenolics from matrix to solvent which leads to enhancing extraction recovery (Silva, 2017; Garofulić et al., 2013; Liazid et al., 2011).

The possibility to use microwave-assisted extraction at the industrial scale has been taken great attention in last decades for the extraction of natural compounds, particularly phenolic compounds, from plant matrices and industrial by-products (Barba et al., 2016; Filly et al., 2014; Petigny et al., 2014; Li et al., 2013). The extraction of phenolic compounds from grape waste and by-products has been mostly investigated by several studies (Yu et al., 2014; Al Bittar et al., 2013; Liazid et al., 2011). The optimal extraction conditions of anthocyanins from grape skins by using microwave-assisted extraction were 2 g of sample, 500 W, 100°C, 40% methanol in water as extraction solvent, and the extraction time is reduced from 5 hours to 5 minutes compared to conventional solid–liquid extraction technique (Liazid et al., 2011). Yu et al. (2014) have studied the factors influencing the extraction of phenolic compounds from grape peels, and they noticed that extraction requires less time to obtain the higher phenolic content at just 3 minutes instead of more than 10 minutes.

14.4.2.2 Ultrasound-assisted extraction

As a modern technique, ultrasound-assisted extraction is recently developed in order to improve the extraction of phenolic compounds (Saci et al., 2018; Barba et al., 2016; Karabegović et al., 2011). Ultrasounds are waves of elevated sound with frequency arranged from 20 kHz to 100 MHz (Azmir et al., 2013).

The extraction of bioactive compounds from phenolic resources using ultrasounds consists of the transduction of sound waves with higher frequency than those audible by the human ear. After introducing the ultrasonic probe, the energy emitted by ultrasounds penetrates into particles. This energy can be enough to destruct the cells of matrices, and this leads to improving the extraction of phenolic compounds. There are two ultrasound-assisted extraction systems: ultrasonic probe system extraction and ultrasonic bath extraction using a solvent. When the ultrasounds waves are diffused in the extraction solvent (containing the sample), the cavitation bubbles begin to be generated

causing by successive compression and expansion in the solvent. These bubbles are gradually increased their volume, and just achieving a great pressure, these bubbles implode and then create the breaking of cell walls matrix by generating porosities, this facilitates the access of extraction solvent in particles and, after this, the release of bioactive molecules from inside to outside of the matrix occurs. The mechanic effect of ultrasounds induces a great penetration of solvent in the cell matrix and improves the phenomenon of mass transfer (Azmir et al., 2013; Santos et al., 2009).

Food and chemical industries have to use ultrasounds for the extraction of bioactive molecules in many processes. Ultrasound-assisted extraction consumes less solvents and energy (Pingret et al., 2012). This technique is commonly used in laboratory scale (Fig. 14.9). It is generally applied to ameliorate the extraction of bioactive compounds from many biological sources, particularly through the cavitation phenomenon (Saci et al., 2018; Cares et al., 2010). This latter is based on the generation of heating which is provided from the conversion of kinetic energy (Azmir et al., 2013).

The mechanism of this extraction technique consists of two physical phenomena: (1) the solvent diffuses through the cell walls and (2) the solvent inside particles makes soluble bioactive molecules and drains with it these molecules once the cell walls are destructed. These types of phenomena are significantly influenced by radiation of ultrasounds (Cares et al., 2010).

However, as already mentioned, this technique generates energy which could increase extraction temperature and distorts some heat sensitive molecules, so the installation of a condenser, around the utensil containing solvent and sample, is needed after extraction in order to control extraction temperature (Rial-Otero, 2009; Santos et al., 2009).

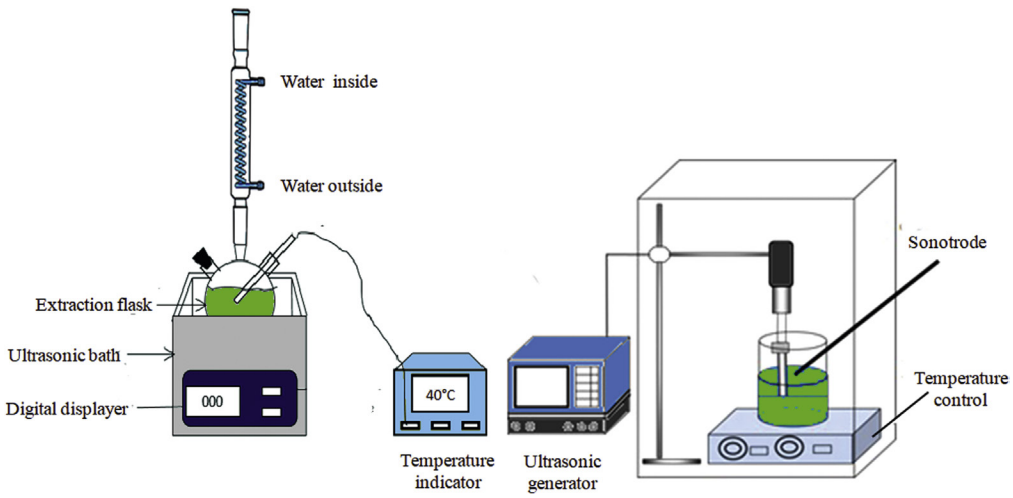

Fig. 14.9 ***Ultrasound apparatus.***

In the recent results reported by Saci et al. (2018), the extraction conditions of phenolic compounds from carob pulp by using ultrasound-assisted extraction were investigated. The solvent concentration, ultrasound amplitude, and extraction time influenced significantly on the extraction of phenolic compounds from carob pulp, and the optimal extraction conditions were 59.30%, 85.86%, and 53.24 minutes, respectively, and the maximized total phenolic compounds content was 30.75 gallic acid equivalents per 100 g of dry matter.

Virot et al. (2010) have studied the extraction of phenolic compounds from apple pomace, as a potential source of phenolic compounds which have a great interest for the industry, and they noticed that the phenolic yields were more than 20% compared to the conventional procedure. The authors conclude that ultrasound-assisted phenolic compounds extraction from apple pomace appears to be a relevant, rapid, sustainable alternative to conventional procedure, and that scale-up of the process is possible. Otherwise, Pingret et al. (2012) have also studied the influence of solid to solvent ratio, extraction time and temperature on phenolic compounds extraction, and the optimal extraction conditions were 150 g/mL, 40 minutes, and 40°C, respectively. These authors recommended that these extraction conditions could be applied at the industrial scale.

The extraction of the phenolic compounds of resveratrol from grapes by using ultrasound-assisted extraction showed a significant yield (about 26%) and a reducing of extraction time compared to traditional solvent extraction at 60°C for 30 minutes (Cho et al., 2006). Corrales et al. (2008) have observed a significant increase in extraction yield of phenolic compounds from grape by-product after using ultrasound-assisted extraction compared with maceration extraction. Phenolic compounds extraction of grapes seed oil by using ultrasound-assisted extraction (150 W, 20 kHz) has demonstrated a great efficiency compared to Soxhlet extraction with decreasing time extraction from 6 hours to 30 minutes. The same authors have reported that 15 minutes of phenolic extraction from grape by ultrasound-assisted extraction was required against 12 hours by using the maceration. Corrales et al. (2008) have reported that 1 minute and 35 kHz at 70°C are sufficient to extract the phenolic compounds from grape by-products by using the ultrasound-assisted extraction.

The designs of ultrasound processing equipment have been advanced to be performed and adapted at the industrial scale, as reported by Vilkhu et al. (2008). For industrial extraction phenolic compounds especially from plant tissue, some ultrasound reactor designs have been described by Vilkhu et al. (2008), Chisti (2003), and Vinatoru (2001), and as reported by Vilkhu et al. (2008), these extractors contained (1) stirred sonotrode of ultrasounds immersed into reactor or bath, (2) the reactor contains vessels walls, and (3) the extractor is coupled with external flow-cell where the product can be recycled.

The same authors reported that sophisticated ultrasonic systems have an automated frequency scanning which controls ultrasounds transmission in order to maximize the

extraction of bioactive compounds, and for the food industry, the use of ultrasound-assisted extraction allows, (1) enhancement of extraction rate, (2) increasing the processes of aqueous extraction as juice concentrate processing, and (3) permitting the use of alternative green solvents recognized as safe by ameliorating their extraction yield.

14.4.2.3 Accelerated solvent extraction

This method is known by several names; high-pressure solvent extraction (HSPE), enhanced solvent extraction (ESE), pressurized fluid extraction (PFE), or generally accelerated solvent extraction (Nieto et al., 2010; Björklund et al., 2000). Accelerated solvent extraction is a modern solid–liquid extraction method where aqueous and/or organic solvents are used at elevated pressures and temperatures (Khattab and Zeitoun, 2013; Tandon and Rane, 2008). It can be performed at pressures around 600–2900 psi and temperatures from 37°C to 190°C (Wójciak-Kosior et al., 2013; Tandon and Rane, 2008; Wang et al., 2007). Heating enhances the acceleration of the extraction rate, while elevated pressure avoids denaturation of bioactive compounds above the boiling point of the solvent at the atmospheric conditions. Time and solvent consumption are thus significantly reduced compared to the other solvent extraction techniques (Khattab and Zeitoun, 2013; Tandon and Rane, 2008; Kaufmann and Christen, 2002). Consumption of solvent and time are generally decreased comparing to other solvent extraction methods (Khattab and Zeitoun, 2013; Tandon and Rane, 2008; Kaufmann and Christen, 2002). The amount of solvent added to samples, the cycle of extraction, and temperature are the important factors that influence considerably the extraction efficiency of bioactive compounds by this technique (Wójciak-Kosior et al., 2013; Wang et al., 2007).

Accelerated solvent extraction is operated by introducing the desired product into the extraction cell which is placed on the carousel. Then, the sample is transferred to the oven where the cell is sealed under pressure. After applying the pressure and temperature, the solvent is automatically added. The analytes drained by the solvent are recovered in collection vial, and the extraction cell is flushed and the remained solid particles are expulsed by nitrogen gas, or the new solvent can be added again in the extraction cell to repeat the same steps several times in order to ensure the extraction of remained analytes in sample, and a good highly significant extraction yield. The extraction time depends on the sample used and generally ranges from 10 to 44 minutes (Nieto et al., 2010; Romanik et al., 2007). Fig. 14.10 illustrates the apparatus of accelerated solvent extraction technique. Accelerated solvent extraction has been used successfully for the extraction of analytes from natural plant products, food, and pharmaceuticals (Romanik et al., 2007; Breithaupt, 2004).

14.4.2.4 Supercritical fluid extraction

Extraction with supercritical fluid is one of newer extraction techniques that can offer very good extraction yield (Romanik et al., 2007; Vinatoru, 2001). A supercritical fluid extraction can be summarized in two principal processes: (1) extraction of analytes by

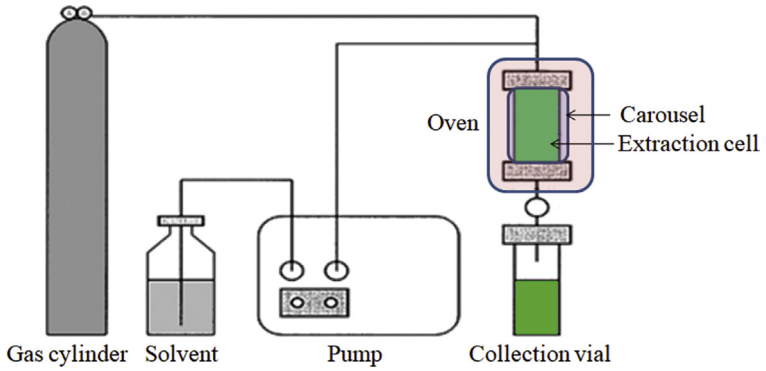

Fig. 14.10 ***Accelerated solvent extraction apparatus.***

using the supercritical fluids, and (2) separation of analytes from them. Because of low viscosity and a high diffusion coefficient of supercritical fluids, these latter can easily penetrate into sample particles and drain with them the soluble analytes (Romanik et al., 2007).

The most often used supercritical fluid is carbon dioxide (CO_2). It is excellent and the most used supercritical fluid in the food industry to extract analytes from vegetables. Supercritical fluid extraction is an alternative to conventional solvent extraction because supercritical fluids are nontoxic, cheap, relatively inert, recyclable, nonflammable, and favorable critical parameters (Tc = 1°C, Pc = 74.8 atm) (Romanik et al., 2007; Zougagh et al., 2004). Thus, this technique reduces the volume of solvent, shortens the time of extraction, allows the possibility of coupling with the separation and determination techniques (supercritical fluid extraction/GC, supercritical fluid extraction/HPLC), and facilitates separation of heat sensitive compounds (Sarmento et al., 2008; Romanik et al., 2007). A typical diagram of supercritical extraction process from solids is given in Fig. 14.11.

14.4.2.5 Pulsed-electric field extraction

In this technique, the electrical energy is used to accelerate the extraction process and improve the extraction yield. Pulsed-electric field extraction is an alternative technique for nonthermal processing of food. It is a good alternative to conventional cell membrane permeabilization methods such as thermal treatments and the addition of chemicals as well as of enzymes. During a pulsed-electric field-assisted extraction, the sample is placed between two electrodes and high voltage repetitive pulses are applied in order to achieve membrane breakdown (Boussetta et al., 2009).

The pulsed-electric field-assisted extraction is based on the denaturation of the cell membrane structure for enhancing extraction yield. The sample containing in the cell receives an electric potential where the bioactive compounds are separated according to their charge (Azmir et al., 2013). Fincan et al. (2004) reported that pulsed-electric field-assisted extraction treatment of the plant material was applied either before or during mechanical pressing. Luengo et al. (2013) were investigated the influence

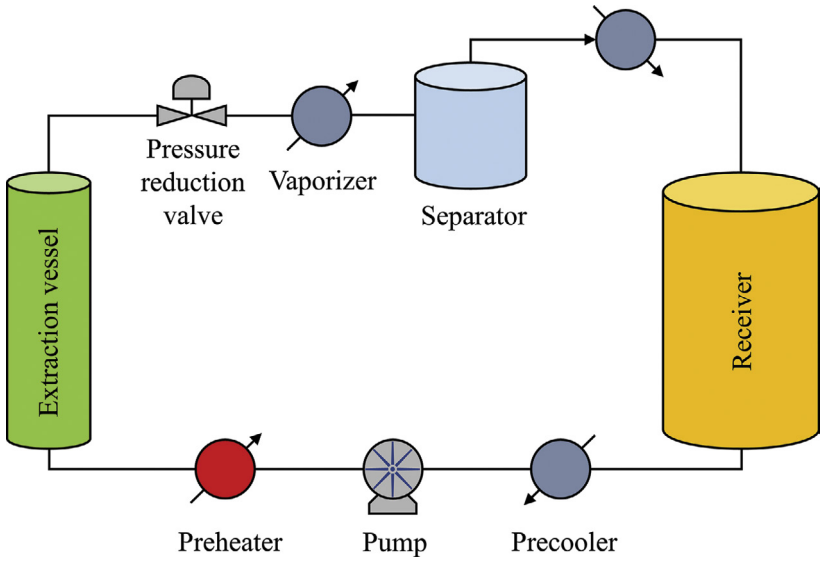

Fig. 14.11 ***Supercritical extraction system.***

of pulsed-electric field-assisted extraction technique on the extraction by pressing of phenolic compounds and flavonoids (naringin and hesperin) from orange peel. Chalermchat et al. (2004) have also used pulsed-electric field-assisted extraction technique for solid–liquid extraction of red beetroot pigment.

14.4.2.6 Enzyme-assisted extraction

Phenolic compounds can be extracted by several previous techniques, but some phenolics remained in sample particles, as those linked to polysaccharides, proteins, and lignins. As an alternative technology, enzyme-assisted extraction technique is an effective way to breakdown these bounds and release the phenolic compounds linked with enhancing extraction yield (Azmir et al., 2013; Rosenthal et al., 1996).

There are two approaches for enzyme-assisted extraction: (1) enzyme-assisted aqueous extraction and (2) enzyme-assisted cold pressing. An aqueous enzymatic extraction method was developed to obtain free oil and protein (Latif and Anwar, 2009; Zhang et al., 2007). Li et al. (2006) showed that enzyme-assisted aqueous extraction has some advantages and can be considered as a feasible technology to extract phenolic compounds from plant materials.

Wang et al. (2010) showed that enzyme-assisted extraction was effective in enhancing the recovery of phenolic compounds and other hydrophilic antioxidant compounds from *Palmaria palmate*.

Table 14.2 recapitulates the advantages and inconveniences of the most common extraction techniques for solid matrices.

Table 14.2 Advantages and inconveniences of classical and modern extraction techniques.

Extraction techniques		Advantages	Inconveniences
Classical	Soxhlet	- No filtration required	- Increasing in extraction time - Agitation is not possible in the Soxhlet device
	Maceration	- Low quantities of plant material are required - Simple application process - Can be designed on a small scale in a laboratory - Efficient Extraction	- Extraction time rather long
Modern	Microwave-assisted extraction	- Fast and repeated extractions - Less solvent used - Elevated temperatures	- Clean-up step needed - Waiting time for the vessels to cool down
	Ultrasound-assisted extraction	- Multiple extractions	- Clean-up step needed - Large solvent volumes - Repeated extractions may be required
	Accelerated solvent extraction	- Fasten the extraction time - Low consumption of solvent - No filtration needed - No manipulation needed	- Clean-up step needed
	Supercritical fluid extraction	- Fast extractions - Low solvent volumes - Elevated temperature - Automated systems - Concentrated extracts - No filtration and clean-up required - Relatively selective interferences	- Several factors should be optimized

14.5 Conclusion

To summarizing the results of a host of investigations outlined in this chapter, it is particularly important to note that phenolic compounds have wide impacts on human activities in the different commercial sectors, particularly chemical, pharmaceutical, cosmetic and food, exerting either positive or negative influence on the processes or on the quality of the products and these characteristics have motivated specific research programs. The interest in natural phenolic compounds has led to the investigation of many plant extracts for their activity.

Each extraction technique has its advantages and inconveniences, and it can be adequate or not to extract the typical phenolic compounds from any sources, this is generally due to the nature of the sample where the compound is found. For this purpose,

the nature of the matrix and phenolic compound should be studied before choosing the adequate extraction technique. Furthermore, the study of extraction conditions influencing the extraction yield must be done in order to recover the most phenolic compounds from the matrix. Intrinsic or extrinsic factors or parameters can easily affect the extraction yield of phenolics, some of them have the highest influence which may interact with other factors to enhance the recovery of phenolic compounds, but with others, we assist to the most decrease. So, it is not just advice to study the influencing factors independently, because, generally, the interaction effect can change the yield of the extraction.

Classical extraction techniques are mostly used till now due to their simplicity, however, in most cases, they do not extract enough of phenolic compounds and the extraction yield is the lowest. Fortunately, with the development of novel technologies, sophisticated and modern techniques recently appeared belong alternative to the classical techniques and with enhancing the extraction yield, reducing the extraction time, and solvent consuming.

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