

## Chapter 2

# Solvent-Free Extraction: Myth or Reality?

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**Abstract** One of the many environmental challenges faced by Extraction field is the widespread use of organic solvents. With a solvent based extraction the solvent necessarily has to be separated from the final extract. A large number of these solvents are toxic that pose a risk to workers and community members and virtually all of them are classified as volatile organic compounds (VOCs) that contribute to smog. In this context, the development of solvent-free extraction processes is of great interest in order to modernize classical processes making them cleaner, safer and easier to perform. This chapter presents a picture of current knowledge on innovative solvent-free methods of natural products extraction. It provides the necessary theoretical background and some details about extraction using the most innovative, rapid and green techniques such as microwaves, instant controlled pressure drop (DIC) process and Pulsed Electric Field (PEF): the technique, the mechanism and some applications.

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## 2.1 Introduction

In a typical chemical or extraction process, solvents are used extensively for dissolving reactants, solvating molecules, extracting products, separating mixtures. However the major part of the organic solvents currently found in industry, in spite of a large number of well-known advantages, are characterized by several dangerous effects for the human health and the environment. Many organic solvents are Volatile Organic Compounds (VOCs), and it means that they are highly volatile, very useful for industrial applications, contribute both to increase the risks of fire and explosion, and to facilitate the release in the atmosphere in which these solvents can act as air pollutants causing ozone depletion and global warming. Moreover, many conventional solvents are highly toxic for human beings, animals and plants, and often their toxicological properties are completely unknown.

For example, *n*-hexane, solvent of choice for extraction of oils, can be emitted during extraction and recovery; it has been identified as an air pollutant since it can react with other pollutants to produce ozone and photochemical oxidants [1, 2]. Precautions to minimize the effects of these solvents by improved recycling have limited success and cannot avoid some losses into the environment. Moreover, the risk connected to potential accidents is still present.

During the last years, a central objective in extraction field of natural products has been set to develop greener and more economically competitive processes for the efficient extraction of natural substances with potential application in the cosmetic or agrochemical industries. In this context, the development of solvent-free alternative processes is of great interest in order to modernize classical processes making them cleaner, safer and easier to perform.

Therefore the following benefits could be mentioned for solvent-free conditions: (1) Avoid large volumes of solvent which reduces emission and needs for distillation; (2) The absence of solvents which facilitates scale-up; (3) Extracts are cleaner without residues; (4) Safety is enhanced by reducing risks of overpressure and explosions.

Extraction of olive oil using mechanical pressing is recognized as a solvent-free alternative. Virgin olive oils are extracted from olive fruits by using only physical methods, which include crushing of olives, malaxation of resulting pastes and separation of the oily phase. Because of its location in mesocarp of cells and the use of purely mechanical pieces of apparatus for its extraction, virgin olive oil does not require further treatment before its consumption (Fig. 2.1).

This chapter presents a picture of current knowledge on innovative solvent-free methods of natural products extraction. It provides the necessary theoretical background and some details about extraction using the most innovative, rapid and green techniques such as microwaves, instant controlled pressure drop (DIC) process and Pulsed Electric Field (PEF): the technique, the mechanism and some applications.



Fig. 2.1 Solvent free olive oil extraction process

## 2.2 Solvent-Free Microwave-Assisted Extraction

The use of microwave energy was described for the first time in 1986 simultaneously by Gedbye [3] in organic synthesis and by Ganzler [4] for extraction of biological samples and analysis of organic compounds. Since then, numerous laboratories have studied the synthetic and analytical possibilities of microwaves as a non-classical source of energy. Several classes of compounds such as essential oils, aromas,

pigments, antioxidants, and other organic compounds have been extracted efficiently from a variety of matrices mainly and plant materials. Advances in microwave extraction have given rise to solvent-free microwave technique namely Microwave Hydrodiffusion and Gravity.

### **2.2.1 Principle**

Microwave hydrodiffusion and gravity (MHG) [5] is a new and green technique for the extraction of biomolecules patented in 2008. MHG was conceived for laboratory and industrial-scale applications in the extraction of pigments, aroma components, and antioxidants from different kind of plants. Based on a relatively simple principle, this method also involves placing the plant material in a microwave reactor, without adding any solvent or water. The internal heating of the *in situ* water within the plant material distends the plant cells and leads to the rupture of cells. The heating action of microwaves thus frees secondary metabolites and *in situ* water, which are transferred from the inside to the outside of the plant material. This physical phenomenon, known as hydrodiffusion, allows the extract, diffused outside the plant material, to drop by gravity out of the microwave reactor and fall through the perforated Pyrex disk.

A cooling system outside the microwave oven cooled the extract continuously. The crude extracts are collected in a receiving flask for further analysis (Fig. 2.2). MHG not only appeared as an efficient and economical technology but its chief advantage is its environmental friendly approach as it works without using any solvent just under effect of microwaves and earth gravity at atmospheric pressure.

### **2.2.2 Instrumentation**

A Milestone NEOS-GR microwave laboratory oven (900 W maximum), as shown in (Fig. 2.2), is used to perform the microwave hydrodiffusion and gravity (MHG) extraction: this is a multimode microwave reactor of 2.45 GHz. Temperature is monitored by an external infrared (IR) sensor. MHG could also be used to produce larger quantities of extracts by using existing large-scale microwave extraction reactors called “MAC-75” (Fig. 2.3).

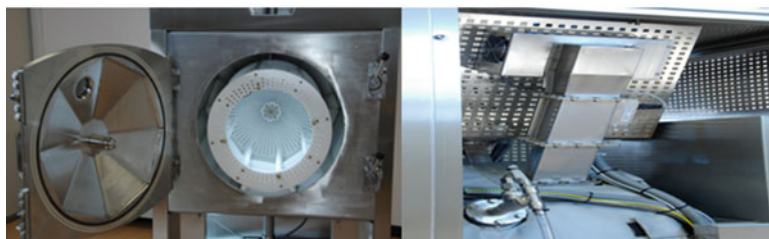
### **2.2.3 Application**

The feasibility of microwave process in the preparation of samples has been investigated on different matrices, as shown in the Table 2.1. This process was applied to many kinds of plants such as aromatic plants and citrus for an essential

**Fig. 2.2** Solvent free microwave extraction laboratory system (NEOS-GR)



oil extraction [6–8]. The first example is the *menthe pulegium L.* extraction [6], where 0.95 % of essential oil was obtained by the heating of 500 g of matrix at 500 W during 20 min at atmospheric pressure. For *Citrus limon L.* [7], 500 g of matrix were also treated at 500 W for 15 min and two respective yields of 0.7 and 1.6 % of essential oil were obtained at atmospheric pressure. Another example with *Rosmarinus Officinalis L.* [8] was tested by taking 500 g of plant at 500 W during 15 min, which provided 0.33 % of essential oil.



**Fig. 2.3** Pilot scale Solvent free microwave extraction ‘MAC 75’

**Table 2.1** MHG application in extraction of natural compounds

Material	Analytes	Ref.
M. spicata L., M. pulegium L.	Essential oil	[6]
Rosemary leaves	Essential oil	[7]
Citrus peels	Essential oil	[8]
Onion ( <i>Allium cepa</i> L.)	Phenolic compounds	[9]
Red, yellow, white and grelot onion	Phenolic compounds	[10]
Sea buckthorn ( <i>Hippophaë rhamnoides</i> )	Phenolic compounds	[11]

Zill-e-Huma et al. reported MHG as a novel technique for extracting flavonoids from onion. The plant tissues were strongly disrupted by microwave irradiation through the microscopic observation of extracts, so that target compounds could be efficiently extracted and detected by HPLC and other analysis [9, 10]. MHG was also applied to extraction of flavonoids from sea buckthorn by-products, producing a little lower yield of flavonol in a very short time (15 min) in comparison to classic methods but a higher content of reducing compounds contained in MHG extracts [11].

## 2.3 Instant Controlled Pressure Drop Process (DIC, “Détente Instantanée Contrôlée”)

The instant controlled pressure drop process, abbreviated DIC for ‘Détente Instantanée Contrôlée’, was developed by Allaf et al. in 1988 [12]. DIC extraction is based on fundamental studies with respect to the thermodynamics of instantaneity [13].

### 2.3.1 Principle

It consists of a thermo-mechanical process induced by subjecting the product to a fast transition from high temperature/high pressure to a vacuum. DIC extraction usually starts by establishing this high temperature/high pressure by injecting steam, microwaves, hot compressed air, etc. for some seconds, proceeding then to an abrupt pressure drop toward a vacuum (about 5 kPa with a rate higher than  $0.5 \text{ MPa}\cdot\text{s}^{-1}$ ). By instantly dropping the pressure, rapid autovaporization of the moisture inside the material will occur. It will swell and lead to texture change which results in higher porosity as well as a greater specific surface area and reduced mass-transfer resistance through Darcy’s vapor transfer instead of Fick’s similar law. The short time – high temperature operation (few seconds) and the immediate drop in temperature (to be lower than  $30^\circ\text{C}$ ) thanks to the pressure drop prevent further thermal deterioration and provide a final extract of great quality.

### 2.3.2 Instrumentation

DIC equipment is in the main part divided in three components: (1) the autoclave with heating jacket also named the processing vessel where the product is placed, (2) the vacuum tank linked to a vacuum pump, and (3) the instant valve enabling the abrupt connection between (1) and (2). The vacuum tank is cooled through a double jacket in order to condensate the extracts. Other devices are part of the DIC process such as a steam generator, an air compressor (for the electro-pneumatic actions) and the vacuum pump. A schematic diagram of the DIC apparatus and the pressure profile are presented in Figs. 2.4 and 2.5.

In order to undergo a DIC cycle, the raw material is placed within the autoclave where a vacuum is subsequently applied. This will facilitate the contact between the steam and the product enabling a homogenous heating of the product. It is afterward filled with saturated steam set and maintained at a required pressure for an optimized time. After this thermal treatment the steam is cut off and the spherical instant valve is opened in less than 0.2 s inducing an abrupt pressure drop towards a vacuum in the autoclave. After a vacuum period, the atmospheric pressure established in order to recover the solid material. The extracts are collected from the vacuum tank.

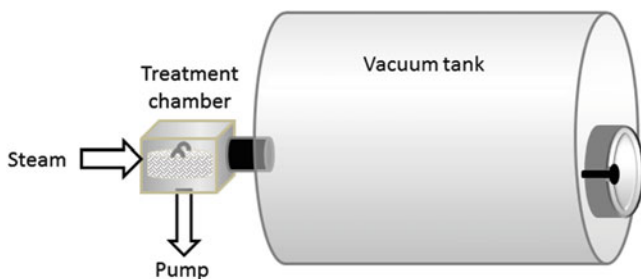


Fig. 2.4 Schematic diagram of the instantaneous controlled pressure-drop

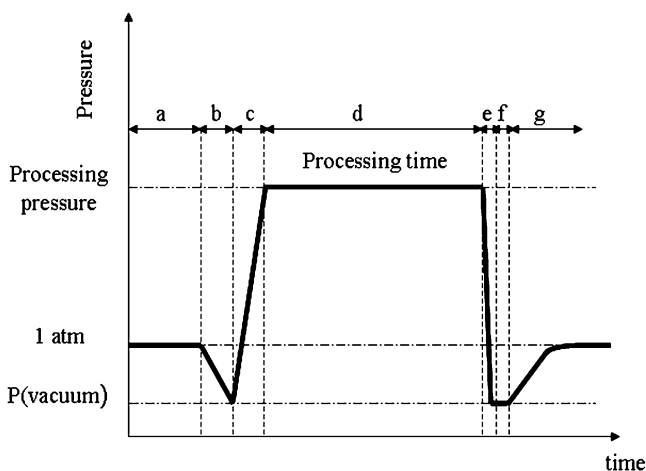


Fig. 2.5 Pressure-time profile of DIC processing cycle

Table 2.2 Instant controlled pressure drop applications

Material	Analytes	Ref.
Malaysian Roselle	Anthocyanins	[14]
Seeds of <i>Tephrosia purpurea</i>	Oligosaccharides	[15]
Myrtle leaves	Essential oil	[16]
Lavender	Essential oil	[17]
Ylang-ylang	Essential oil	[18]
Rapeseed	Oil	[19]

### 2.3.2.1 Applications

The feasibility of DIC process in the preparation of samples has been investigated on different matrices (Table 2.2).

Benamor et al. [14] have studied extraction of anthocyanins from Roselle calyces using DIC. This work has demonstrated that DIC increases kinetics and extraction yield of these compounds. The same authors have also noticed the impact of DIC treatment on the oligosaccharides (stachyose and ciceritol) extraction from the seeds



of the Indian *Tephrosia purpurea* plant [15]. DIC was shown to be an effective extraction method in terms of processing time (1 h of extraction time instead of 4 h for conventional processes). DIC could be also used for the extraction of oil from various plants. One of its advantages compared to other extraction processes is the short-time contact of the oil with the apparatus heated zones to avoid the harmful thermal reactions of the different molecules, combined to an abrupt pressure variation that allows a rapid release of essential oil due to the rupture of the oil-containing glands. The DIC process is more efficient in terms of rapidity (several minutes versus several hours), essential oil yield (comparable even higher), and higher content of oxygenated compounds.

## 2.4 Pulsed Electric Field (PEF)

Pulsed Electric Field (PEF) technology was invented in the 1960s in order first to offer the possibility to preserve food by replacing traditional pasteurization. Electrotechnologies based on effects of PEF are currently gaining a real interest regarding food processing especially in the field of extraction [20–23].

### 2.4.1 Principle

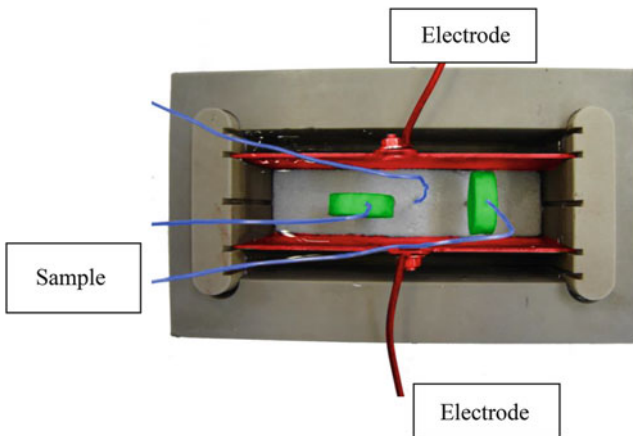
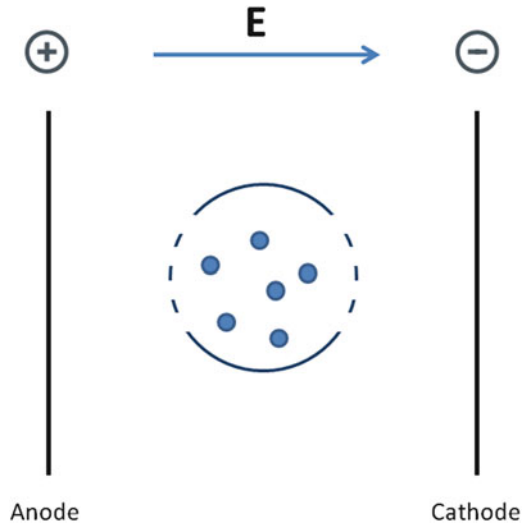
Exposing a biological cell (plant, animal and microbial) to a high intensity electric field (kV/cm) in very short pulses ( $\mu\text{s}$  to ms) induces the formation of temporary or permanent pores on the cell membrane [24]. The cell membranes are charged and pores are formed in the membranes fostering the extraction. This phenomenon, named electroporation, causes the permeabilization of cell membrane i.e. an increase of its permeability and if the intensity of the treatment is sufficiently high, cell membrane disintegration occurs [25] (Figs. 2.6 and 2.7).

Many fields are developing cell membrane disintegration such as biotechnology, medicine and food industry [24, 26–28]. Cell membrane acts as a physical barrier in removing the intracellular substances from plant food tissues in solid–liquid extraction. The disintegration or permeabilization of the cell membrane in a plant food tissue causes the release of intracellular water and solutes (secondary metabolites) to migrate in an external medium. Thus, this method enables enhancing extraction from food plants; it enhances mass transport out of the cell.

### 2.4.2 Instrumentation

A PEF treatment chamber consists of at least two electrodes and insulation that forms the treatment volume (i.e. volume where the foods receive pulses). The final

**Fig. 2.6** Cell in an electric field generating electroporation



**Fig. 2.7** Treatment chamber – lab scale device

distance between the electrodes can be optimized and fixed. The product exposure to a pulsed voltage can hence be done in a batch or continuous treatment chamber. Different pulse-forming networks can be used; their main components include selected voltage power supply, one or several capacitor banks, inductors or/and resistors [24]. Besides pulses of different shape can be generated, including simplest exponential decay pulses and square wave pulses should be limited for exclusion of any significant temperature elevation.

Electric field treatment is applied by a PEF generator which power is also determined depending on the needs. Shape and polarity are criterion of the generator itself. Trains of pulses are usually used for PEF treatment. An individual train consisted of  $n$  pulses with pulse duration  $t_i$  and pulse repetition times  $\Delta t$ . A pause  $\Delta t_1$  can be set after each train,  $N$  being the number of trains. The total time of electrical treatment during PEF treatments are calculated as  $t_1 = N_{\text{tot}} t_i$  where  $N_{\text{tot}}$  is the total number of pulses  $N_{\text{tot}} = Nn$ .

These different parameters, whether temperature  $T$ , electric field strength  $E$  (V/cm), electric energy  $W$  (kJ/kg), number of impulsion  $n$  and duration of an impulsion  $t_i$  can be modified regarding the needs.

Some indications regarding PEF parameters:

- Permeabilisation of plant cells 0.3–1.5 kV/cm 1–10 kJ/kg
- Inactivation of microorganisms 10–30 kJ/cm 50–200 kJ/kg

### 2.4.3 Applications

PEF whether direct treatment or as a pre-treatment facilitate the extraction of vegetable oil, active molecules such as anthocyanins, flavonoids, etc. The application of electroporation through PEF offers a great potential for extraction purposes. It improves kinetics extraction and enhances extraction yields. PEF treatment is suitable for thermolabile fragile molecules since the extraction can be done at low temperature.

Temperature contribution to electroporation efficiency is important, which reflects the synergetic effect of the simultaneous thermal and PEF treatment and it increases at small fields [29].

PEF treatment, or pre-treatment noticeably accelerates diffusion even at low temperature (20–40 °C), which enable the “cold” soluble matter extraction [30].

When PEF is employed it is possible to regain antioxidant substances from plant processing residual material, potential of pectin recovery is enabled [31]. Regarding juice pressing with high polyphenol content, the choice of appropriate regime of pressing is required. PEF application allowed decreasing of the applied pressure and pressing time. PEF is very promising for enhancing juice and polyphenol extraction [31–33]. PEF is a promising enological technology to obtain wines with the high phenolic content necessary for the production of high quality oak aged red wines [34].

For extraction both membrane of the cell and the vacuole have to be opened. The releasing efficiency of ionic components, enzymes, proteins and other bio-products can dramatically depend on the applied method of disruption. The PEF treatment removes membrane barriers and accelerates release of the extract contents; it

**Table 2.3** PEF applications

Material	Analytes	Ref.
Apple mash	Apple juice	[33]
Grape by-products	Phenolic compounds	[34]
Sugar beets	Sucrose	[35]
Inonotus Obliquus	Betulin	[36]
Soybean/Olive	Oil	[37]
Red beetroots	Betalains	[38]

however has practically no influence on the cell walls. As regards to electroporation, pores resealing is possible after the pulse application. If sufficient energy is applied, the pores are electroporated irreversibly (Table 2.3).

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