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Development of a green innovative semi-industrial scale pilot combined microwave heating and centrifugal force to extract essential oils and phenolic compounds from orange peels

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ABSTRACT

A new process for extraction of essential oils from orange peels (*Citrus sinensis L.*) using microwave and centrifugal (MW/C) force was studied. MW/C is a combination of microwave heating to explode the internal cells of biological material, and centrifugation to intensify diffusion, collection and separation of compounds of interest. MW/C is performed at atmospheric pressure with an injection of water vapor. A detailed study concerning optimization of different operating parameters like microwave power density and centrifugation was performed. MW/C has been compared to the hydrodistillation method. In addition of essential oils collection, in the aqueous phase several phenolic compounds can be obtained and valorized. Influence of the two main parameters was discussed first on essential oils and, in second part, on phenolic compounds recovery. The new combined MW/C process provided reduction in the extraction time compared to hydrodistillation method, with an advantage to collect in a same experiment volatile and nonvolatile compounds with high quality.

Industrial relevance: This work was carried out thanks to the investment of IFTS France, an international technical center worldwide known in the field of solid-fluid separations. Considering the huge amount of plant extracts this new combined system using microwave and centrifugal (MW/C) force may be suitable for scaling up. The results of this investigation on pilot reactors pave the way for the design of an industrial device.

1. Introduction

Nowadays, it is impossible to deny that the excessive use of terrestrial resources for human activity is destroying our planet. More and more ideas are emerging to find solutions to existing problems in order to respect the planet, namely to reduce waste, energy consumption and use of petroleum and to increase the recovery of materials (Cecilia, García-Sancho, Maireles-Torres, & Luque, 2019; Clark & Luque, 2013; Lin et al., 2014).

In the field of plant extraction, this is expressed by the search for new extraction processes meet the six principles of green-extraction. These are based on well-reasoned sourcing (principle 1), reducing the consumption of solvent (principle 2) and energy (principle 3), generating as much as possible low waste production (principle 4) and process extraction time (principle 5) and finally obtained a natural and safe extract (principle 6). In this context, an innovative process combining microwave heating and centrifugal force is studied. The microwave heating in the field of extraction has already proved its worth (Paré, 1992; Périno, Pierson, Ruiz, Cravotto, & Chemat, 2016) and it is used by industrials, for example to flavor vegetable oils with aromatic plants (Ciriminna et al., 2016). The centrifugal force seems to be an advantage for the homogenization of the electromagnetic field and the intensification of the solid liquid separation. In addition, these two elements can be operated simultaneously and they seem to have a synergy in drying processing (Apaolaza, Valat, Ginisty, Sommier, & Jomaa, 2015). This, it would reduce the overall energy consumption of the process compared to two separate unit operations. The pilot Microwave assisted centrifugation (MW/C) has demonstrated with a previous study (Angoy et al., 2018) is efficiency for extraction of non-volatile molecules by this process.

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For this study, we were interested in extracting volatile compounds as essential oils. In this objective, the raw material chosen was orange peels (flavedo with a small part of albedo) from *Citrus sinensis L.*, in order to valorize this waste. In fact, the world citrus production is estimated at 54.3 million tons in 2018 (USDA, 2014). The juice production is the first industrial transformation of *Citrus sinensis L.*. The amount of world industrial waste of citrus, such as peels, seeds and pulp membrane, is estimated at 15 million tons (Marín, Soler-Rivas, Benavente-García, Castillo, & Pérez-Alvarez, 2007). The peel is an important source of essential oils, especially limonoïds which are used for the production of perfumes and other cosmetics. The limonene, $> 90\%$ of the essential oils composition could be used as green solvent instead of hazardous petroleum solvents for fats and oils determination. Essentials oils are used in food and pharmaceutical industries but also as flavoring ingredients to drinks, ice creams and other food products (Bakkali, Averbeck, Averbeck, & Idaomar, 2008; Hanif, Nisar, Khan, Mushtaq, & Zubair, 2019; Raeissi, Diaz, Espinosa, Peters, & Brignole, 2008). Citrus peel represents, also, an important source of bioactive compounds such as phenolic compounds and in particular flavonoïds. Flavonoïds have been found to have health-related properties, which include antioxidant, anticancer, antiviral and anti-inflammatory activities (Barreca et al., 2017; Benavente-Garcia & Castillo, 2008; Mahato, Sharma, Sinha, & Cho, 2018; M'hiri, Ioannou, Ghoul, & Boudhrioua, 2015; Russo, Bonaccorsi, Inferrera, Dugo, & Mondello, 2015). *Citrus sinensis* L. present considerable amounts of flavanones, flavones, flavonols and anthocyanins. The main phenolic compounds are the flavanones such as hesperidin, narirutin and eriocitrin. Others phenolic compounds such as derivate of ferulic and sinapic acids are also present.

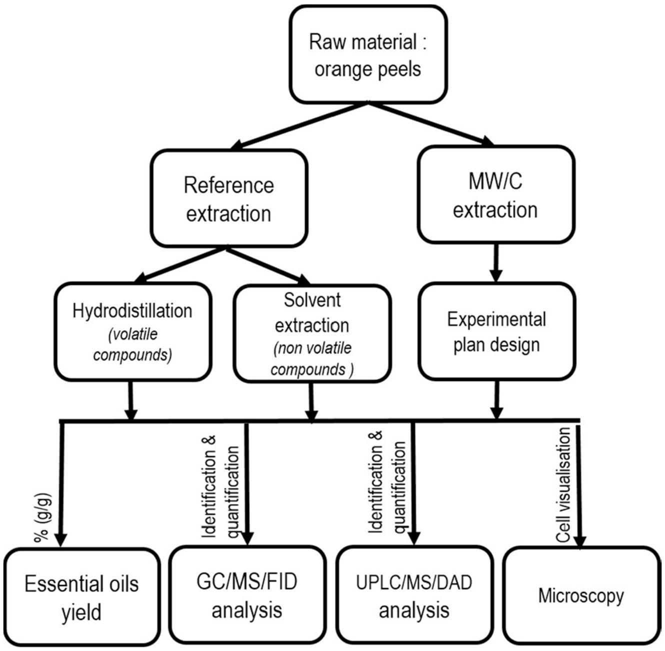
Essentials oils from citrus peel are traditionally extracted by cold pressing. Used only for citrus, because of the location of their essential oils, this method is done without heating: it involves subjecting the whole fruit to a high pressure using a hydraulic press. The essential oil contained in small glands of the peel is then separated from the juice by a mechanical system such as centrifugation. Distillation is also used in some countries as an economical way to recover the oils with a better yield than cold pressing but can degrade components such as linalool due to its high temperature processing (Gavahian, Chu, & Mousavi Khaneghah, 2019).

In this study, the innovative process microwave and centrifugal force (MW/C) has been used for extraction of essential oils from orange peels using less solvent and energy. Comparison has been made for conventional hydrodistillation and solvent extraction in term of extraction time, yield and composition. The extraction parameters were optimized and chemical composition was studied. To highlight the physical action of extraction systems, scanning electron microscopy supplemented the chemical analysis study. This operating procedure is described in Fig. 1.

2. Materials and methods

2.1. Plant material and chemicals

The orange fruit (*Citrus sinensis L.*) was cultivated in Spain. The peel has been separated from the inside of the fruit and purchased cut into peel strips and frozen. Its initial moisture was 75%. Orange peel was defrosted 24 h at room temperature before extraction. Sodium carbonate anhydrous, chlorogenic acid (caffeoylquinic acid C3878 (Purity $> 95\%$) HPLC grade) and tangeritin were purchased from Sigma-Aldrich (Saint-Quentin Fallavier, France), hesperidin, and ferulic acid from Extrasynthèse (Genay, France), sodium disulfite and n-alkanes (C7–C30) from Merck (Lyon, France). Ethanol and acetonitrile LC-grade were from Fisher Chemicals. Glutaraldehyde, osmium tetroxyde, hexamethyldisilazane and sodium cacodylate were from electron microscopy sciences. Other chemicals such as *N*,*N*-Dimethylformamid and Dimethylsulfoxide (DMSO) were analytical reagent grade and purchased from Sigma-Aldrich (Saint-Quentin Fallavier, France).



MW/C: MicroWave / Centrifugation with water vapor injection (high rotational speed)

Fig. 1. Protocol treatment of orange peels by microwave and centrifugal force (MW/C) and reference extractions.

2.2. Extraction procedures

2.2.1. Reference methods

Each reference extraction was performed at least three times.

2.2.1.1. Solvent extraction: phenolic compounds. This extraction allowed to evaluate the total quantity of phenolic compounds present in the orange peel. Orange peel was lyophilized and grinded in powder during 2 min with a multimoulinette compact (Moulinex®). With a solvent/solid ratio of 10, the powder was solubilized in N·*N*-Dimethylformamide to extract flavanones, flavones, flavonols and hydroxycinnamic acids (Polidori, Dhuique-Mayer, & Dornier, 2018). The extracts were stirred in presence of zirconium beads in a SPEX MiniG™ mill for 1 min at 1200 rpm. After 5 min of centrifugation at 13,000 G-force and 5 °C, the supernatant was recovered and two cycles of extraction (solvent + homogenization + centrifugation) were carried out on the pellet. The whole supernatant was collected, adjusted in an accurate volume and filtered through syringe filter 0.45 µm RC-membrane (Phenomenex). The samples were stored at −18 °C until UPLC analysis.

2.2.1.2. Hydrodistillation: essential oils. Two hundred and fifty grams of orange peels was submitted to hydrodistillation using a florentin flask according to the European Pharmacopeia, and extracted with two liters of distilled water for 2 h at 100 °C (until no more essential oils were obtained). The essential oils were collected, dried under anhydrous sulphate, weighed and stored at −18 °C before analysis.

2.2.2. Microwave centrifuge (MW/C) pilot extraction

Extraction was performed using MW/C (Fig. 2), a modified semi-industrial pilot combining centrifugal force and microwave heating available at IFTS (Agen, France). This system is a multimode microwave reactor (2.45 GHz) with a maximum delivered power of 1200 W adjustable in 10 W increments. The basket rotational speed is variable from 1000 to 4000 rpm (179 to 2870 G-force) and rotation can be maintained during all the microwave heating procedure. Inspired by Périno et al. (2016), the procedure begins with 500 g of orange peels defrosted, drained and placing in the basket. During extraction by MW/

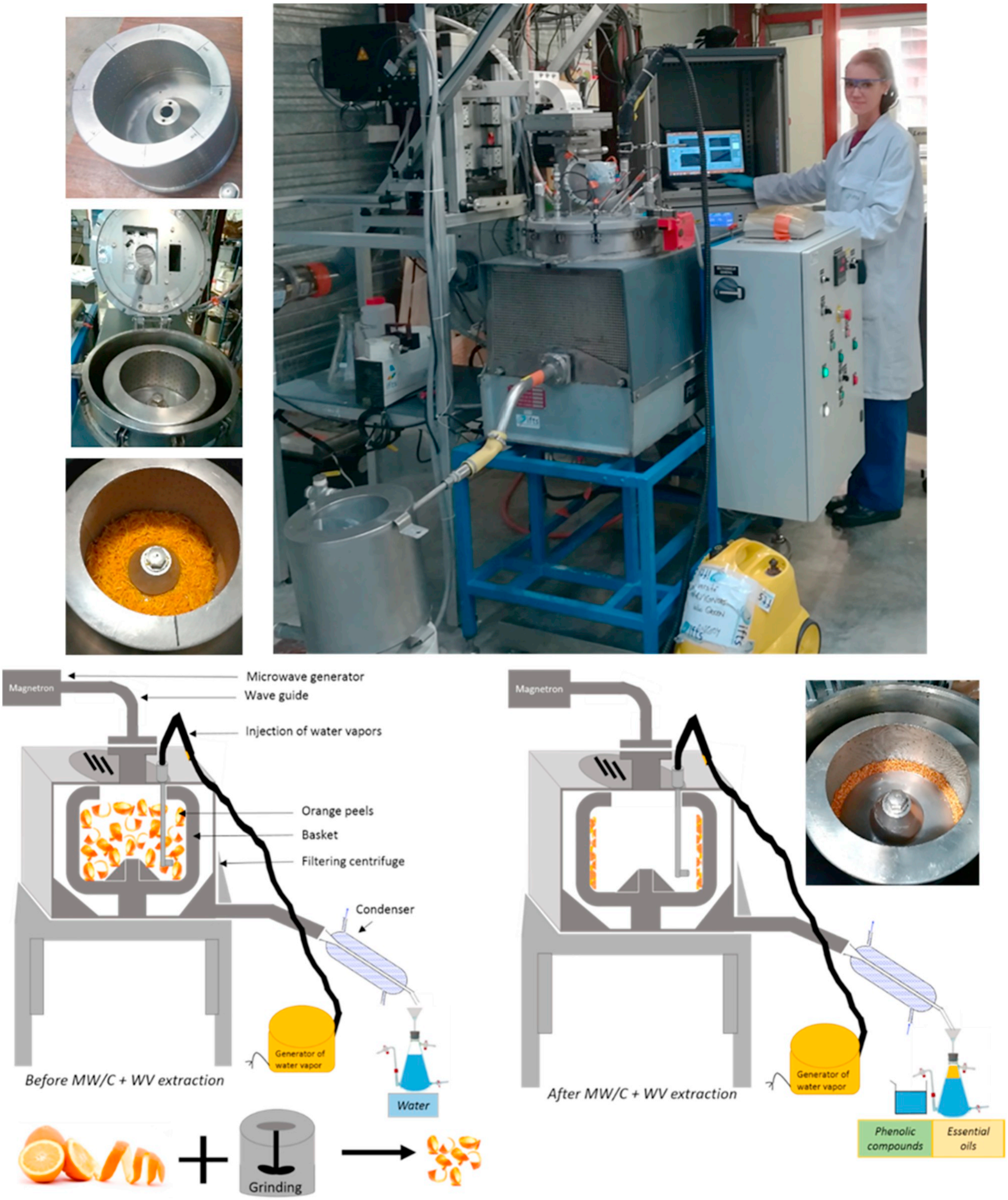


Fig. 2. Microwave-assisted dynamic extraction by combination with centrifugal force and water vapor before and after extraction.

C, an injection of water vapor (Kärcher® SC 1702) was added to promote the collect of volatile and non-volatile compounds. The extract was generated by internal heating of the cells of orange peels and injected steam. Then the liquid was expulsed from the basket by centrifugal force and carried away by gravity driven flow into a condenser that was cooled to 4 °C and collected through the florentin flask in order to separate by density difference essentials oils and aqueous phase. Fractions were stored at −20 °C until gas chromatography (GC) and ultra-high performance liquid chromatography (UPLC) analysis. The orange peels after extraction (residual orange peels) are collected at the end of the extraction to carry out a hydrodistillation to assess the residual essential oil content. MW/C extraction, with a power density of 2.4 W/g and a centrifugal force of 196 G-force (i.e. 1046 rpm) during 30 min (which corresponds to optimal conditions) was compared to hydrodistillation. The minimum speed of 1000 rpm is required to protect the centrifuge motor (i.e. a minimum frequency of 10 Hz).

Temperatures were measured using Thermo-buttons Plug & Track 22 T placed in contact with vegetable matrix.

2.3. Experimental design

Box–Wilson design, also called central composite design (CCD), was used to achieve optimal conditions of the process with a minimal number of experiments (Allaf, Tomao, Besombes, & Chemat, 2013). The type of CCD used in this study was central composite face-centered (CCF) experimental design to determine the optimal conditions of MW/C process. The application of a CCF design is a convenient way to optimize a process with five levels ($-\alpha$, -1, 0, $+1$, and $+\alpha$) for each factor. This design is needed to evaluate the effects and interactions of two independent variables, namely microwave power density (MWPD), varied between 0.19 and 2.31 W/g, and centrifugal force (CF), varied from 196 to 2583 G-force (i.e. 1450 to 3400 rpm). The other parameters such as mass of vegetable matrix, injection of water vapor and time were kept constant. A total of 14 different combinations, including 4 factorial design ($-1/-1$; $-1/+1$; $+1/-1$; $+1/+1$), four star points ($-\alpha/0$; $0/-\alpha$; $+\alpha/0$; $0/+\alpha$) and six replicates at center point (0/0), chosen in random order, were employed for response surface modelling. The selected optimization response was the essential oils yield (EOY) after 30 min processing time:

$$EOY = \frac{Essential\ oils\ mass\ collected\ by\ MW/C\ extraction}{Essential\ oils\ mass\ collected\ by\ Hydrodistillation} \times 100$$

The experimental results were processed by using the software Statgraphics® (Version 18 × 64, Statistical Graphics Corporation, Rockville, USA). Variance analysis (ANOVA) was performed to determine significant differences between independent variables ($P \leq 0.05$) and Pareto charts were introduced, as well as general trends, response surface, empirical model coefficients and R^2 were determined.

2.4. Gas chromatography

2.4.1. Compounds identification of essential oils

1 µL of diluted essential oil (10 µl in 1 mL hexane) was injected in GC/MS QP2010 (Shimadzu, Kyoto, Japan) using two fused silica capillary columns with different stationary phases (apolar phase: TG-5MS 30 × 0,25 mm × 0,25 µm and polar phase: TG-WAX 30 m × 0,25 mm × 0,5 µm). Chromatographic conditions were as follow: injector at 250 °C in split (split ration 20); oven temperature program: initial temperature 50 °C, then increased at 2 °C/min to final temperature 240 °C. Carrier gas was Helium at 35 cm/s. the spectra were recorded in ionization electronic at 2 scans/s (70 eV) between 29 and 300 *m/z*.

The identification of the compounds was performed by comparison of mass spectrum and the retention index (Kovats Indices) with the commercial libraries (Mass spectra database: NIST08; Retention index database: http://www.pherobase.com). The retention indices are calculated from a series of linear alkanes (C7-C30) at 100 µg/mL per compound injected on the two columns.

The calculation of the linear retention indices (Retention Index) is given by the following relation:

$$R = 100 \times \left(\frac{t_{IR} - t_{ZR}}{t_{(z+1)R} - t_{ZR}} + z \right)$$

with IR, retention index; t_{IR}, peak sample retention time; t_{ZR}, retention time of the alkane eluted before the peak; $t_{(z+1)R}$, retention time of the alkane eluted after the peak and z, number of carbon of the alkane eluted before the peak.

The results for the polar column (TG-WAX) allowed one to confirm the identification carried out using the nonpolar column TG5.

2.4.2. Composition of essential oil

Composition of the essential oil was determined by CG/FID using the same chromatographic conditions as GC/MS analysis. The composition was determined by calculating the ratio between the area of a peak of a compound considered and the sum of the areas of all the peaks of compounds present in the extract according to the following formula:

$$(\%)\ i = \frac{i\ area}{\sum areas\ of\ all\ the\ peaks\ of\ compounds\ present\ in\ the\ sample}$$

with i, a sample compound.

This calculation was performed for each compound identified in the essential oils of orange peel.

2.5. Ultra-high performance liquid chromatography (UPLC) analysis and identification of phenolic compounds

For quantitative studies, phenolic extracts of orange peels were analyzed by Ultra-high performance Liquid Chromatography (UPLC) using an ACQUITY UPLC® system (Waters Corp., Milford, MA, USA) linked simultaneously to both a diode array detector 190–800 nm (UPLC DAD, Waters, Milford, MA, USA) with a ACQUITY UPLC® C18T3 HSS column (50 mm × 2.1 mm, i.d., 1.8 µm; Waters Corp., Milford, MA, USA). The column temperature was set at 35 °C. The analysis was achieved with a gradient elution using water containing 0.05 mL of HCOOH/100 mL (solvent A) and CH_3CN (solvent B) as the mobile phase at a flow rate of 0.4 mL/min. The phenolic compounds were separated according to the appropriate gradient composed of A and B. Gradient conditions of the mobile phase were: B, 0–30%, 0–15 min; B, 30–70%, 15–20 min; B, 70–100% 20–21 min; B, 100% 21–22 min; B, 0%, 22–25 min to return to the initial conditions. The injection volume was 3 µL with partial-loop with needle overfill injection. Phenolic compounds were detected at 280, 330 and 360 nm. Empower™ 2 software (Waters) was used for instrument control and integration of the peaks at obtained chromatograms. Total time of UPLC analyze was 24 min.

Compounds were identified by their UV–vis spectra and retention time, as well as by comparison with the bibliographic data. The content of phenolic compounds in extracts was quantified by UPLC DAD analysis with detection wavelength at 330 nm for hydroxycinnamic acid, 280 nm for flavanones and flavones and 360 nm for flavonols. Calibration curve obtained from dilution series of ferulic acid for hydroxycinnamic acid, tangeritin for flavones and hesperidin for flavanones allow to quantify phenolic compounds present in extracts. Stock solutions of the standard (1 mg/mL) were prepared in methanol as well as dilutions from 10 to 100 µg/ml for ferulic acid and in DMSO for tangeritin and hesperidin. Results were expressed in µg standard equivalent/g of fresh material (µg/g of FM).

All the studied phenolic compounds were identified by their UV–vis analysis in comparison with the bibliographic data.

2.6. Scanning electron microscopy (SEM)

The microstructures of the orange peel before and after extraction using different techniques were analyzed using a scanning electron microscope (XL30, FEI Philips, France). The techniques studied are microwaves (2 W/g), centrifugation (200 G-force), microwaves coupled to centrifugation (2 W/g and 200 G-force) and hydrodistillation. For observations, the samples were carefully collected after being subjected to the extraction technique. Then, in order to fix their structure, they were soaked in 2.5% (*v/w*) of glutaraldehyde prepared in a buffer solution of 0.1 M sodium cacodylate, pH 7.2 for 1 h. They were then washed three times for 30 min each time with the same buffer solution. They were stored at 4 °C before being post-fixed with osmium tetroxide (diluted to 1% (*v*/v)) and 0.1 M sodium cacodylate buffer, pH 7.2 for 1 h. Then they were rinsed with distilled water three times for 3 min. Then, the samples underwent a series of graduated dehydration in the presence of absolute ethanol (30%, 50%, 70%, 90% for 5 min each and

Table 1
Experimental conditions of experiments and yields obtained in a preliminary study with MW/C.

Experiment n°	Water vapor injection (4 L/h) (Yes/No)	Microwave power density (W/g)	Rotational Speed (G-force)	Essential oils yield %
1	No	1	200	28
2	Yes	1	200	59
3	Yes	0	200	0
4	Yes	1	2500	4

100% for 2 times 10 min) and hexamethyldisilazane (HDMS) - Ethanol (1/1 by volume) for 10 min, then dehydration with HDMS for 5 min. The final step in the dehydration process was to soak in an HDMS bath until complete evaporation.

The samples were then mounted on aluminum end caps, and covered with a thin layer of gold (SCS 004, BALZERS) by sputtering.

They were observed by high vacuum scanning electron microscopy at 10 kV. A secondary electron detector was used. The observation conditions are given on the images taken, in particular the scale and the magnification used.

3. Results and discussions

3.1. Preliminary study

First experiments were carried out to determine the potential of MW/C pilot for extraction of volatile compounds such as essential oils and the influence of water vapor injection (4 L/h), during extraction, on the yield (Table 1). Three parameters were observed as microwave power density, rotational speed and water vapor injection.

Firstly, hydrodistillation was carried out to know the initial composition of orange peels in essential oils. The yield found was 0.9 ± 0.1% (g/g of fresh matrix). Experiments n°1 and n°2 (Table 1) were carried out with the same parameters, a microwave power density of 1 W/g of fresh matrix and a low rotational speed (200 G-force, i.e.1100 rpm), the only difference was an addition of injection of water vapor during the process. The most important essential oils yield (EOY), 59%, was obtained with water vapor injection (experiment n°2 twice as high as experiment n°1). Experiment n°3 revealed that without application of microwave power density, neither essential oils were collected. During experiment n°4 with a high rotational speed (2500 G-force, i.e. 3750 rpm), only 4% of essential oils were recovered. Microwave power density appears like a limiting factor, and centrifugal force would have a negative influence on EOY.

In this preliminary study, the maximum of essential oils yield is obtained with injection of water vapor, a microwave power density of 1 W/g and a centrifugal force of 200 G-force. These parameters allow essential oils extraction in only 30 min. The parameters found were not optimized but allowed to know about the influence of each parameters on extraction of essential oils and to carry out the experimental design.

3.2. Central composite design

Essential oils yields (EOY) obtained for different trials of the experimental design protocol and the two independent variables (decoded and coded) are shown in Table 2. ANOVA gave a R^2 coefficient of 0.97.

A Pareto chart of standardized effects presented in Fig. 3a shows significant effects of microwave power density (MWPD) and centrifugal force (CF) variables (linear, quadratic and interactions between variables). The bar length of each parameters characterizes the absolute importance of the estimated effects. The vertical line represents the limit between the significant and insignificants effects with a 5% risk of error.

Four effects are significant at 95% confidence level in the studied experimental domain ($P < 0.05$): the linear effects of the variables CF and the interaction between MWPD and CF are the most significant (Fig. 3a). They have a negative influence on the EOY while linear MWPD effect has a positive influence and appears as the limiting factor and confirms preliminary study results obtained on a different matrix.

Table 2
Different trials for MW/C extraction from orange peels with an extraction time of 30 min and injection of water vapor (4 L/h).

Trial number	Decoded variables		Coded variables		Essential Oils Yield (% g/g)
	A: Microwave power density (W/g)	B: Centrifugal force (G-force)	A	B	
1	0.5	376	−1	−1	9 ± 3
2	0.5	2068	−1	+1	3 ± 3
3	2.0	376	+1	−1	66 ± 3
4	2.0	2068	+1	+1	31 ± 3
5	1.25	196	0	−α	33 ± 3
6	1.25	2583	0	+α	10 ± 3
7	0.19	1052	−α	0	2 ± 3
8	2.31	1052	+α	0	54 ± 3
9	1,25	1052	0	0	33 ± 3
10	1.25	1052	0	0	37 ± 3
11	1.25	1052	0	0	40 ± 3
12	1.25	1052	0	0	33 ± 3
13	1.25	1052	0	0	28 ± 3
14	1.25	1052	0	0	33 ± 3

Experimental data treated with the Statgraphics® software-based CCD enabled us to determine an empirical relationship between the response studied (EOY) and the key variables involved in the model. Thus, a second order polynomial equation is obtained which describes the quantitative effect of process variables and their interactions on the measured response:

$$\mathrm{EOY}\,(\%) = 49,2051 \times MWPD + 0,0155856 \times CF - 4,22118 \times MWPD^2 \\ - 0,0107555 \times MWPD \times CF - 5,01732 \times 10^{-6} \times CF^2 - 17,8408$$

where EOY (%) is Essential Oils Yield % (g/g), MWPD is microwave power density (W/g) and CF is centrifugal force (G-force).

The optimized experimental conditions, with the goal of optimizing EOY, were achieved for a MWPD of 2.4 W/g and 196 G-force for centrifugal force. The experimental EOY obtained was 60 ± 3%. It was compared to the EOY, 71 ± 3%, calculated by the experimental design. The experimental EOY does not reach the theoretical EOY. However, this yield confirms a good performance of the pilot in its current configuration. The low centrifugal effect (196 G-force) to obtain this yield can be explained by the fact that essential oils are volatile compounds and their extraction is directly affected by the circulation of steam and air in the pilot system. It is less the case for non-volatile compounds such as phenolic compounds (Angoy et al., 2018) where a MWPD of 1.2 W/g is used with a high centrifugal force 2585 G-force to obtain an optimal yield.

Nevertheless, the pilot MW/C can extract 60% of essentials oils present in orange peels in 30 min against 2 h by hydrodistillation. From the energy consumption point of view, record of energy consumption leads to the following values for MW/C with optimum parameters during 30 min:

- microwave energy consumption: 4.3 MJ/kg of fresh matrix (FM),
- centrifuge energy consumption: 1.8 MJ/kg of FM,
- energy consumption for vapor injection: 10.4 MJ/kg of FM.

For a total of 16.4 MJ/kg of FM. It is important to note that these values and particularly the one related to vapor injection can still be optimized with technical modification of the pilot. In comparison hydrodistillation requires 20.9 MJ/kg of FM just to heat and vaporize additional water, namely about 25% more than MW/C.

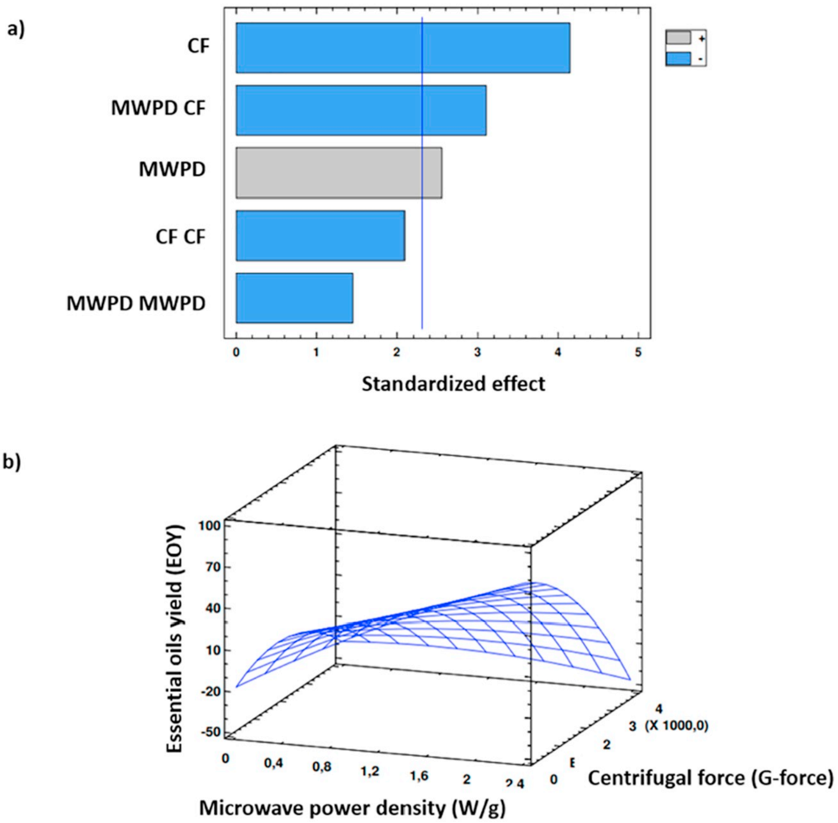


Fig. 3. a) Global yields standardized by Pareto chart with in blue color negative effect and gray color positive effect, and b) estimated response surface as a function of microwave power density (MWPD) and centrifugal force (CF).

3.3. Composition of essentials oils

Processes hydrodistillation (reference) and MW/C with optimal parameters (2.4 W/g; 196 G-force) were compared in terms of detailed composition of essential oil collected from orange peels which are reported in Table 3. There is no qualitative difference according to the technique used, a total of 42 compounds were identified and categorized according to their family such as monoterpenes and sesquiterpenes oxygenated or not oxygenated and aldehydes and carboxylic esters. Amounts of non-oxygenated compounds are largely higher than oxygenated compounds due to the limonene quantity. Limonene is the major component of orange peels essential oils with an average percentage of 94–95% for both HD and MW/C process in agreement with published reports (Del Bosco et al., 2013). However, its contribution to the organoleptic quality of the essential oil of orange is not very important with regard to its high perception threshold (minimum concentration for which an odor is perceptible) (Plotto, Margaría, Goodner, Goodrich, & Baldwin, 2004). Aldehydes are major contributors to the characteristic aroma of essential oils of oranges (Chisholm et al., 2003; Högnadóttir & Rouseff, 2003), even if their quantity is low compared to monoterpenes (Plotto et al., 2004). Linalool with an important floral odor contributes to the total aroma of oils. By comparing the contents of decanal, octanal, geranial and linalool, it can be seen that their concentrations are similar whatever the technique used. The proportion of 4-terpineol is higher in the HD extract (0.10 ± 0.01%) than in the optimum MO/C extracts 0.02 ± 0.01%. Indeed, linalool in acidic medium and in the presence of water tends to degrade into 4-terpineol (Filly, Fabiano-Tixier, Louis, Fernandez, & Chemat, 2016). It dehydrates, cyclizes and rehydrates to 4-terpineol. These are concerted reactions and with transfer of chirality. In hydrodistillation, the contact between the plant matrix and water and the exposure to high temperature is long enough (2 h) to generate the differences observed.

Table 3
Chemical composition of *Citrus sinensis* L. peels essential oils by Hydrodistillation and MW/C process obtained via gas chromatography analysis.

N°	Compounds[a]	R.I.[b]	HD(%)[c]	MW/C(%)[d]
Monoterpenes				
1	Alpha pinene	929	0.40 ± 0.04	0.34 ± 0.01
2	Sabinene	968	0.24 ± 0.03	0.58 ± 0.02
3	Beta pinene	972	0.53 ± 0.03	0.56 ± 0.05
4	Beta myrcene	987	1.82 ± 0.05	1.73 ± 0.02
5	Limonene	1024	95.0 ± 0.2	94.7 ± 0.1
6	Gamma terpinene	1054	0.5 ± 0.1	0.41 ± 0.06
7	Terpinolene	1082	0.14 ± 0.01	0.11 ± 0.01
Oxygenated monoterpenes				
8	Linalool	1099	0.15 ± 0.01	0.14 ± 0.03
9	4-Terpineol	1175	0.10 ± 0.01	0.02 ± 0.01
10	Geranial	1264	0.04 ± 0.01	0.05 ± 0.01
Other oxygenated compounds				
11	Octanal	1002	0.02 ± 0.04	0.06 ± 0.06
12	Decanal	1204	0.35 ± 0.01	0.31 ± 0.01
	Total		100.00	100.00

Olfactory active compounds (Chisholm, Jell, & Cass Jr, 2003; Högnadóttir & Rouseff, 2003).

[a] Essential oils compounds sorted by chemical families and percentages calculated by GC-FID on ZB-5MS capillary column.

[b] Retention indices relative to C7–C30 n-alkanes calculated on non-polar ZB-5MS capillary column.

[c] Hydrodistillation.

[d] MicroWave/Centrifugation process (2.4 W/g; 196 G).

These results showed that microwaves strongly accelerate the extraction process. Indeed, the extraction time for MW/C is 30 min against 2 h in hydrodistillation, and without considerably modifying the composition of the essential oil, a phenomenon which is already described in the literature (Paré & Bélanger, 1997; Sahraoui, Vian, El Maataoui, Boutekedjiret, & Chemat, 2011). The new technique therefore makes it possible to obtain a yield of 60% in essential oils with an equal or even slightly higher quality compared to those obtained by hydrodistillation with an extraction time reduced by 4.

3.4. Identification of phenolic compounds in orange peels

During the MW/C extraction, water vapor is injected to intensify the yield of essential oils. The mixture of water vapor (injected water vapor and in situ water vapor from orange peels) with essential oils is condensed and collected using a florentine vase. The recovered mixture is in the form of two phases: the upper lipophilic phase containing essential oils and the lower aqueous orange phase containing different molecules including phenolic compounds. Once essential oils have been collected, the second objective of this study is to enhance this aqueous phase and therefore to characterize it by physicochemical analyzes.

Three families of phenolic compounds are identified in orange peels such as flavanones, flavones and hydroxycinnamic acids at 280 nm, 280 nm and 330 nm, respectively. In total forty, compounds were identified (Fig. 4). Compounds 1 to compounds 6, Retention Times (RT) from 3.1 min to 6.1 min, are hydroxycinnamic acids derivatives, the first two are coumaroyl glucarate and the last three feruloyl glucarate. They absorb at 330 nm. Compound 7 and 8 at RT = 6.9 min and (λ_{max} = 326 nm) RT = 7.2 nm (λmax = 340 nm) were identified, respectively, as vicenin II (apigenin 6,8 –di–C– glucoside) and eriodictyol-7-rutinoside caffeoyl. Compounds 9 and 10 as a derivated of hydroxycaffeic acid (RT = 7.8; λmax = 322 nm) and apigenin-7-O-(6″malonyl-apiosyl-glucoside) (RT = 8.6; λmax = 326 nm) respectively. Compound 11 at RT = 9.6 min (λmax = 283 nm), and compound 12 at RT = 10.3 min (λmax = 287 nm) were identified, respectively, as naringenin-7-O-rutinoside and hesperidin. Compounds 13, 14 and 15 were identified as neohesperidin (RT = 11.6 min; λmax = 285 nm), obacunone glucoside (RT = 12.2 min; λmax = 351 nm) and luteolin 7-O-rutinoside (RT = 12.8 min; λmax = 283 nm). Finally, compounds 16, 17, 18, 19 and 20 were identified as nobiletin (RT = 16.6 min; λmax = 331 nm), sinensetin (RT = 17.0 min; λmax = 332 nm), nobiletin (RT = 17.4 min; λmax = 338 nm), 3-methoxynobiletin (RT = 17.6; λmax = 339 nm) and tangeritin (RT = 17.8 min; λmax = 331 nm), respectively. This identification was confirmed in comparison with data found in literature (Kelebek, Canbas, & Selli, 2008; M'hiri, Ioannou, Ghoul, & Boudhrioua, 2015; Nakajima, Macedo, & Macedo, 2014).

Chromatographic profile of the extract obtained by MW/C process is almost similar qualitatively to that obtained after solvent extraction of orange peel at wavelengths of 280 and 330 nm, but it can see that the major compound for pilot extraction is the n°4, feruloyl glucarate, and for solvent extraction the n°12, hesperidin. Hesperidin, a representative citrus flavanone with a water solubility of 0.02 g/L, is not extracted with the MW/C extraction which uses only water to collect phenolic compounds. However, this technique seems to be effective for the extraction of hydroxycinnamic acids, more hydrophilic molecules compared to flavanones.

3.5. Quantification of phenolic compounds in orange peels

UPLC-DAD analysis allows to quantify the extracted phenolic compounds expressed in standard equivalent µg/g of fresh material (FM). To compare the quantities obtained according to the extraction techniques carried out, in the remaining tests, the surfaces of the three peaks of compounds (4, 12 and 20, Fig. 4) will be exploited representing the three phenolic compounds families. The quantification will be determined with three standards chosen for each family namely hesperidin (H), tangeritin (T), and ferulic acid for feruloyl glucarate (FG). The MW/C extractions presented come from the experimental design previously carried out; they were selected to observe influence of two parameters on the yield of phenolic compounds, then results will be compared to the solvent extraction.

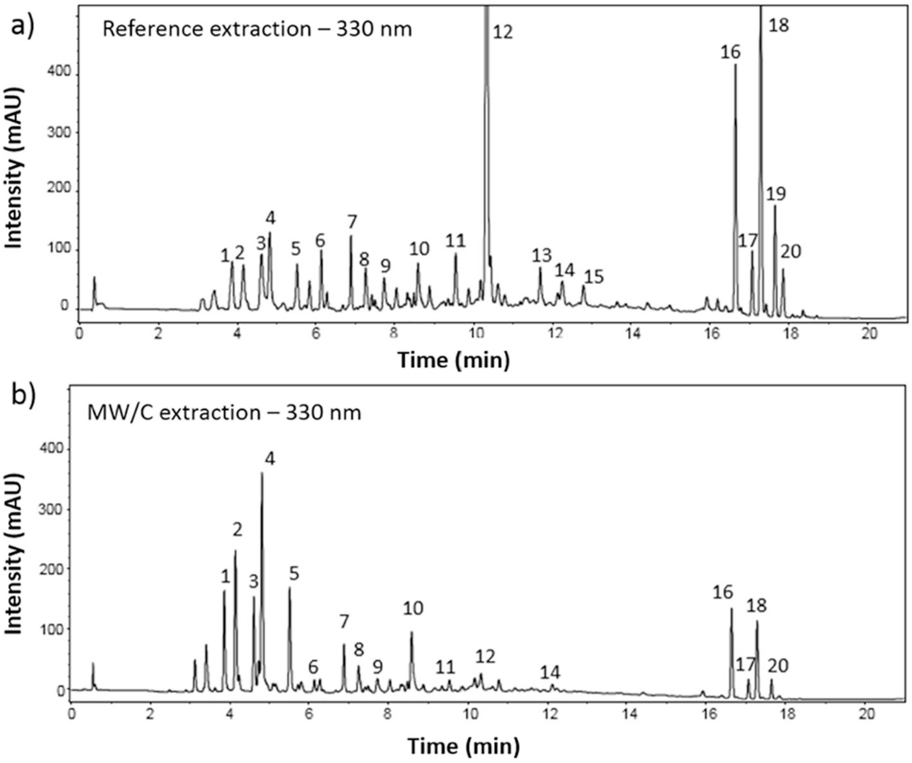


Fig. 4. Identification of the phenolic compounds present at 330 nm in orange peels extract obtained by a) solvent extraction b) MW/C extraction.

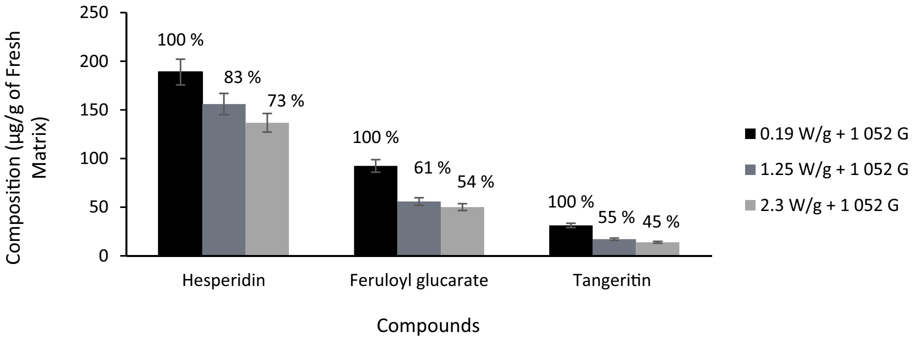


Fig. 5. Content of three phenolic compounds (µg/g FM) during MW/C extraction at 1052 G, with water vapor injection, 30 min treatment time and microwave power density of 0.19 W/g (black), 1.25 W/g (dark gray) and 2.3 W/g (gray).

3.5.1. Microwave power density influence on phenolic compounds yield

The influence of microwave power density is studied on the content of three phenolic compounds extracted from orange peel. Fig. 5 presents three experiments selected for the same G effect (1052 G) but with a microwave power density different from 0.19, 1.25 and 2.3 W/g. The extraction at 0.19 W/g is considered as the reference since it allows to obtain the highest content of the three selected phenolic compounds and will therefore constitute 100%.

The experiment carried out with a microwave power density of 0.19 W/g makes it possible to extract 92 ± 6 µg/g of FM for the FG while 56 ± 3 µg/g of FM are extracted for a higher power density 1.25 W/g, a gain of 39% in this compound. A gain is also obtained, for the two other compounds, of 17% for H and 45% for T between 0.19 W/g and 1.25 W/g. The quantitative difference between the results obtained at microwave power densities of 1.25 W/g and 2.3 W/g is less marked. The highest amount of phenolic compounds was extracted with the lowest microwave power applied for a centrifugal effect of 1052 G. Yield differences can be linked to extraction temperature with a thermal degradation when microwave power density is high.

3.5.2. Comparison between reference extraction and MW/C and centrifugal force influence

The results concerning the selected phenolic compounds obtained using a reference extraction and to the two MW/C extractions from the experimental design at 2 W/g with distinct centrifugal effects: 376 G and 2068 G are presented in Table 4. The comparison with the reference extraction is carried out as well as the influence of the centrifugal effect on the three phenolic compounds considered.

Solvent extraction (SE) obtained 9857 ± 278 µg/g of FM for H while MW/C extractions extracted a maximum of 116 ± 8 µg/g of FM, for the operating conditions considered. For T, 622 ± 4 µg/g FM is extracted by the SE and only 13 ± 1 µg/g FM at most by MW/C. On the other hand, for FG, MW/C extraction (2068 G) allows 72 ± 5 µg/g of FM to be obtained. And SE, 106 ± 1 µg/g FM. If the factors between the two techniques are calculated, the SE extracted 85 times more H, 48 times more T and 1.5 times more FG than MW/C (2 068 G), for the operating conditions considered. The difference between the two techniques for FG is therefore much smaller compared to the other two compounds H and T.

Table 4
Comparison of the content of phenolic compounds obtained by the reference extraction and by MW/C extractions at 2 W/g and 376 G or 2068 G, expressed in µg/g of fresh material (FM).

Extraction technique	Solvent extraction	MW/C, 2 W/g and 376 G	MW/C, 2 W/g and 2068 G
Hesperidin	9857 ± 278	82 ± 6	116 ± 8
Feruloyl glucarate	106 ± 1	28 ± 2	72 ± 5
Tangeritin	622 ± 4	4.2 ± 0.3	13 ± 1

The extraction MW/C (2 068 G) does not allow to extract H and T but permit to obtain a good yield for FG, this observation can be explained by the log (P) relative to each of the molecules studied. The log (P) estimate the lipophilic or hydrophilic nature of the molecules, the closer it is to 0, the more the molecule is hydrophilic. The log (P) of FG is 1 for FG, that of T is 2.66 and that of H is 1.78 (ACDlab data). FG therefore has a more hydrophilic character than that of T and H. Its extraction is therefore facilitated during MW/C unlike H and T which are more lipophilic which cannot be extracted solely by steam or in situ water from orange peels.

Regarding the influence of the centrifugal effect, the results are expressed as a percentage of compounds extracted with the method which allows the best extraction, i.e. 2 W/g and 2068 G. The experiment at 376 G extracted 28 ± 2 µg/g FM for FG compared to 72 ± 5 µg/g FM at 2068 G. The difference between these two experiments, when the centrifugal effect goes from 376 G to 2068 G, represents a gain of 61% for FG and the latter is also observed for the two other compounds H and T evaluated at 29% and 67%, respectively.

In conclusion, the MW/C technique does not extract the highly lipophilic non-volatile compounds H and T, but achieves a good yield for the FG, more hydrophilic molecule which is only little surprising because of the fact that extraction is carried out without organic solvent. MW/C extraction at 2068 G and 2 W/g leads to a relative efficiency of 68% for FG compared to solvent extraction, which is a promising result because the pilot can still be optimized. In addition, the influence of the centrifugal effect is positive for the extraction of the three phenolic compounds considered. These results are consistent with those of the previous study conducted on salad (Angoy et al., 2018).

3.5.3. Assumptions on the influence of the phenomena involved in the MW/C extraction on the quantity of phenolic compounds

The variability in the contents of phenolic compounds can be explained by oxidation phenomena as already observed on salad extracts (Angoy et al., 2018), by the temperature and the extraction time. Temperature measurements of the plant matrix for 20 min during the extraction using thermo-buttons were carried out. Two extractions (MW/C curves) are carried out at 2.4 W/g and two separate centrifugal effects: 216 G and 2318 G. They are compared with two other extractions (centrifugation curves) in the absence of microwave application but with two different centrifugal effects applied 216 G and 2318 G, respectively. Each extraction was carried out with injection of steam and in triplicate (Fig. 6).

The temperature evolution is similar for the different experiments but the values leading to the highest temperature level are obtained when applying microwaves at 2.4 W/g and a weak centrifugal effect of 216 G, with average temperatures between 95 °C and 100 °C instead of 85 °C and 95 °C for a centrifugal effect of 2318 G. In the absence of microwave field, the high temperatures are between 60 °C and 75 °C for a weak centrifugal effect and between 75 °C and 80 °C for a high centrifugal effect. The higher is the centrifugal effect, the lower is the temperature of the plant matrix.

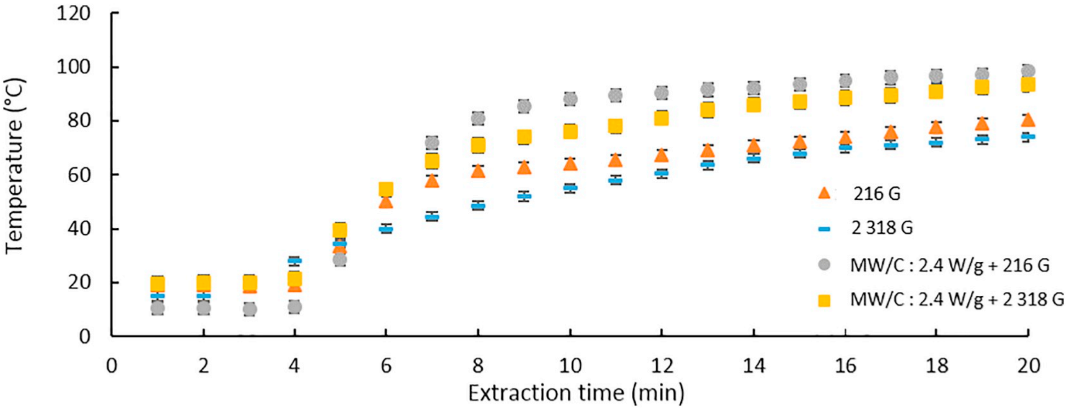


Fig. 6. Temperature evolution within the plant matrix during MW/C extraction at 2.4 W/g and 216 G (gray), 2318 G (yellow) and during centrifugation at 216 G (orange) and 2318 G (blue) (orange peel), all extraction were carried out with injection of water vapor (4 L/h).

The centrifugal effect contributes to heat exchanges, either by inducing air renewal in the machine or by intensifying heat losses and also reduces the exposure time of the extract to the overall system temperature through to efficient liquid drainage. The extraction of essential oils is favored by a high extraction temperature, which therefore explains that the parameters optimized for MW/C refer to a weak centrifugal effect 196 G. On the other hand, the phenolic compounds are likely to be degraded by a high temperature relative to the utilization of microwave energy. To moderate the elevation of temperature, a high speed of rotation (> 1610 G) can be applied simultaneously during extraction and would help, also, to expulse as quickly as possible the liquid out of the system.

3.6. SEM study

3.6.1. Anatomy of orange peels

Orange peels surface and its inner structures under different extraction techniques were investigated using Scanning Electron Microscope (SEM). Through to a schematic representation of orange peel (Fig. 7a), different observations are presented in Fig. 7.

Microscopic examination (70 ×) showed that orange peels comprise several distinct tissues (Fig. 7a). A prominent structure is the oil gland that appears in tissue sections as a large hollow space because a strip orange peels is studied, so a part of essential oils were released during the cutting. Oil glands (OG) are surrounded by a thin wall (Matas, Agustí, Tadeo, Talón, & Rose, 2010) and cover a region from near the surface of the fruit to deep into the albedo, a tissue that is characterized by numerous intercellular airspaces and a characteristic white appearance. By contrast, the flavedo is composed of tightly appressed chromoplast-rich parenchyma cells (PC) that contribute the typical orange color to the citrus fruit. Finally, the epidermis is formed by a single continuous layer of conical cells (CC) covered on the outer periclinal wall by a hydrophilic cuticle.

SEM observations provided more informations on OG, PC and CC characteristics. As shown in Fig. 7c, the inside of OG is very complex with cells films and essential oils drops hidden. PC are very airy near the OG and the peel is crackless.

3.6.2. Process impact on orange peel structures

Microscopic investigation of untreated and treated orange peels is presented in Fig. 7. A lot of structural changes were observed after centrifugation, microwaves, microwaves/centrifugation and conventional treatments (Hydrodistillation) compared to untreated orange peel. As for orange peels subjected to centrifugation, the peel is cracked, the parenchyma cells in the albedo area are compressed, squeezed and the OG are smooth and oval with essential oils drops (Fig. 7d). Peels subjected to microwaves are heterogeneous with airy zone in the center of peel piece and tight on the side unstructured, OG are spherical, very deep and not smooth (Fig. 7e). After the process microwaves/centrifugation, peels are pleated, wrinkly and split, OG are elongated, albedo area compressed and compacted (Fig. 7f). For conventional extraction, peel is pleated, split and wrinkly, cells were compacted and OG were elongated (Fig. 7g) but it appears very different from the other treatments. These observations and experimental data allowed us to propose a mechanism of MW/C extraction at cellular scale.

3.7. Proposal of mechanism

In the orange peels, two very distinct types of cells are present: the essential oil glands and the cells containing phenolic compounds. Essential oils, overall, do not heat up by microwave because they are made up of > 90% of limonene (Farhat et al., 2011; Sahraoui et al., 2011) which does not have a dipole moment. But the use of microwaves facilitates the release of limonene compared to traditional heating by increasing the temperature of the water in situ of the plant matrix.

One possible explanation would be that microwaves would act on all the cells surrounding the essential oil glands because they mainly contain water. These cells rise in temperature (100 °C) and in pressure then explode releasing their contents. They would exert pressure on the essential oil glands which then take a spherical shape under these constraints and explode in turn (Fig. 8). Essential oils would diffuse from the inside to the outside of the plant matrix. The water released as vapor would form an azeotrope with the aromatic molecules contained in essential oils (terpenes, oxygenated compounds, etc.). The injection of additional water vapor would promote the formation of the azeotrope during extraction and therefore the extraction of essential oils.

Simultaneously, the application of centrifugal force allowed exerting pressure on the orange peels favoring the overall compaction of the plant matrix. It helps to intensify the solid-liquid separation and

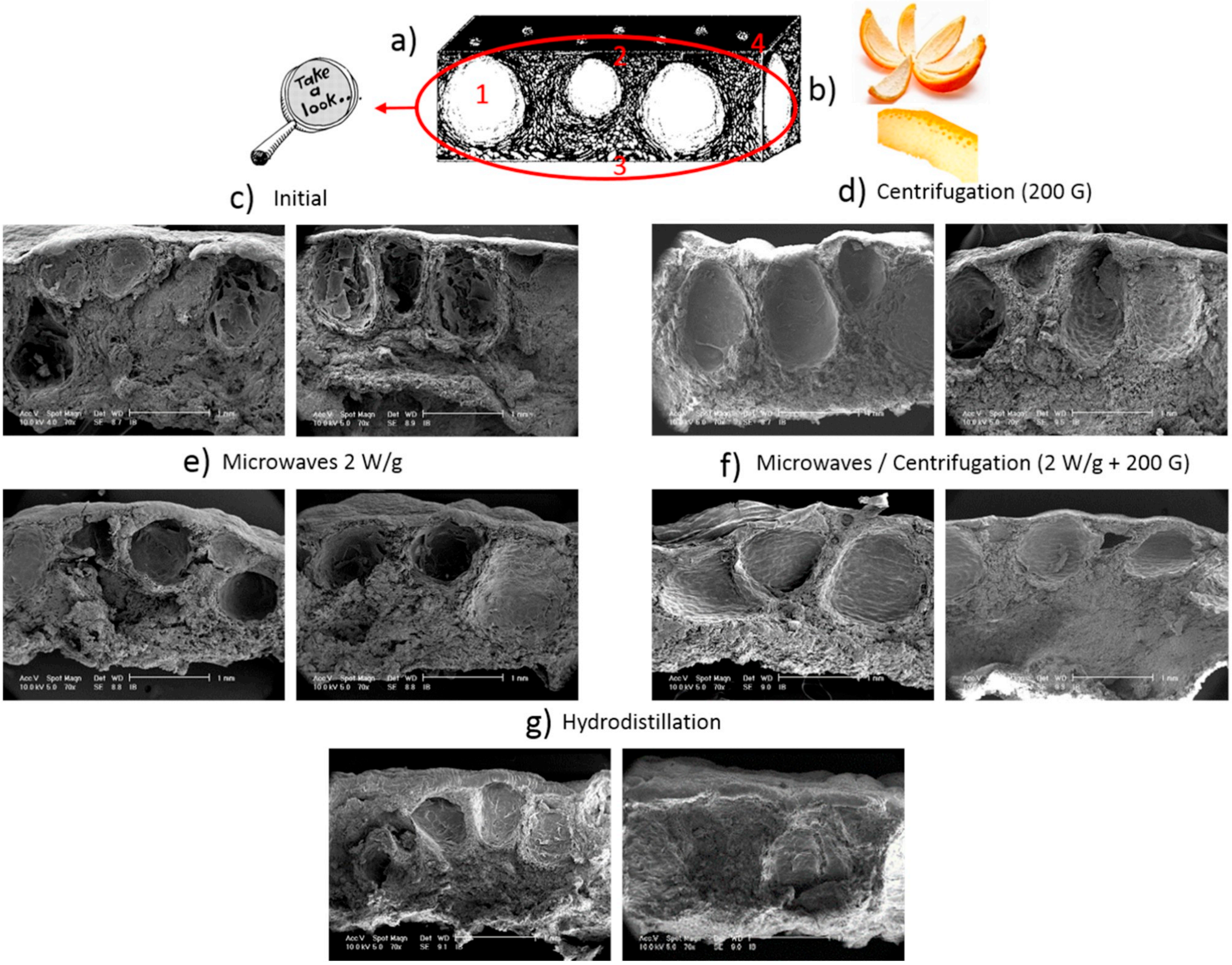


Fig. 7. a) and b) Schematic representation of an orange peel strip ×70. 1: oil glands; 2: Flavedo area; 3: Albedo area; 4: Epidermis. SEM observations of orange peel strips under different processes: c) orange peels untreated; d) Centrifugation (200 G); e) Microwave (2 W/g); f) Microwave/Centrifugation (2 W/g and 200 G); g) Hydrodistillation.

increase the extraction yield by draining the liquid-vapor mixture out of the plant matrix and then out of the system. Centrifugal force would permit to homogenize the electromagnetic field and thus avoid hot spots. Several publications have shown that the application of centrifugal force can damage plant cells by reaching chloroplasts and/or membranes (Kato, Lum, Légeret, Li-Beisson, & Ndathe, 2018; Peterson, Sharma, van der Mei, & Busscher, 2012). This observed cellular damage would depend on both the time and the acceleration applied to the cells, for a G-Force > 600 G (Molina-Miras, Sánchez-Mirón, García-Camacho, & Molina-Grima, 2018).

4. Conclusion and perspectives

The semi industrial pilot MW/C which combines microwaves heating and centrifugal force was adapted to extract essential oils from orange peels. An injection of water vapor during extraction showed the increase of yield of molecules of interest. The rotational speed allows the system to homogenize the temperature field and to intensify the exhausting of the vegetal matrix. In addition the centrifugation reveals to be an advantage to extract phenolic compounds in the aqueous phase from orange peels. The process offers a gain of time and the extraction of volatile and nonvolatile compounds in one experiment without utilization of organic solvent. However, the process is not yet optimized and can be improved to extract efficiently both essentials oils and phenolic compounds with an adequate centrifugal force. At the end of this extraction, natural extract obtained could be used as ingredient in food processing industry for their preservative, coloring or texturing properties and as active compounds in cosmetics, perfume industries, pharmaceuticals or food supplements. Furthermore, MW/C process is environmentally respectful. A numerical model is in progress to better understand physical mechanisms during extraction at cellular scale.

Author statement

All authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript.

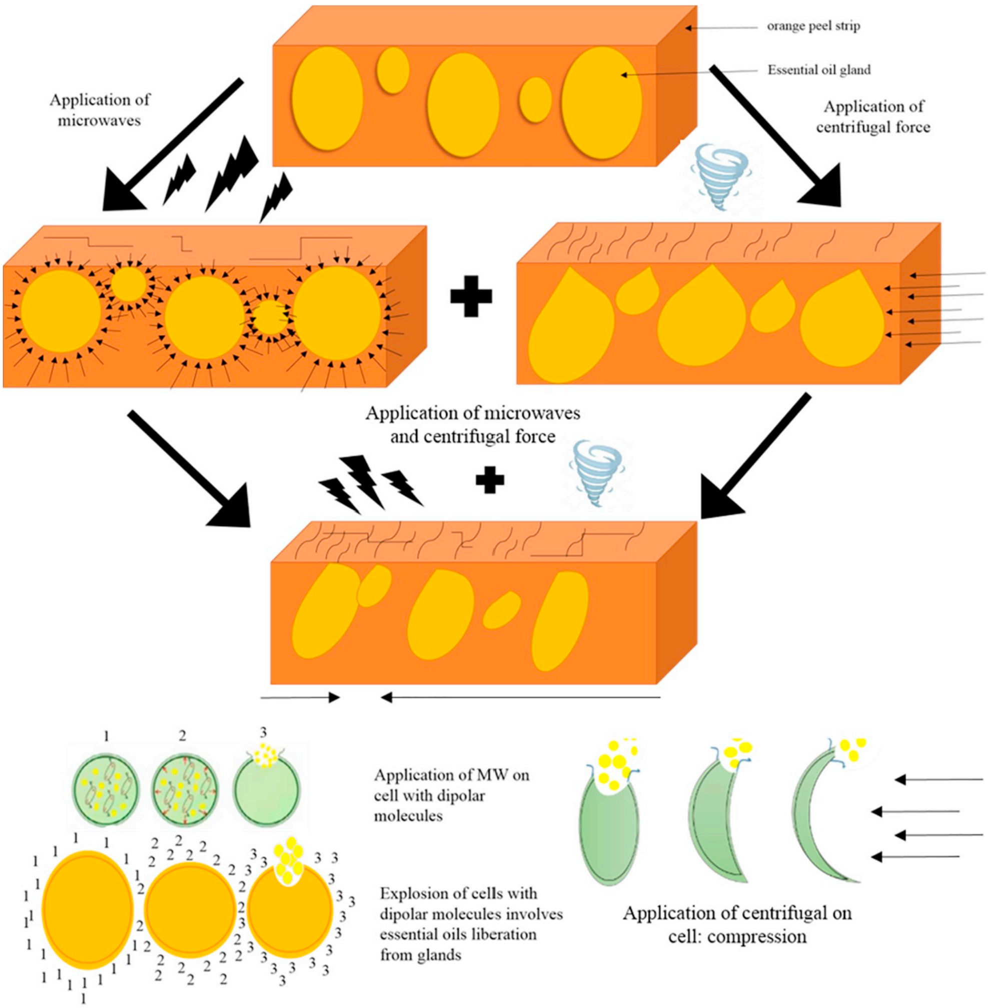


Fig. 8. Proposal of mechanism during MW/C process for extraction of essential oils from orange peels.

Declaration of competing interest

There is no conflict of interest.

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