Understanding the phenomena of extraction of essential oils by the microwave accelerated distillation process: case of the Washington Navel variety

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ABSTRACT: In this study, two techniques Hydrodistillation (HD) and Microwave-accelerated distillation (MAD), was used to extract essential oils (EOs), from the peels of citrus fruits Washington Navel (Citrus sinensis L. Osbeck) collected from Tipaza province, north Algeria during April 2018. The extraction yield and time of EOs were (0.28% and 180 min) using HD extraction and (0.27% versus 30 min) using MAD extraction. After using gas chromatography analyses (GC-FID) and (GC-MS), 21 aromatic compounds obtained and identified for both extraction approaches. On the other hand, and in order to better comprehension the extraction phenomena, two models of extraction processes were applied, the first one considers the existence of a single site with a constant speed ruled by the equation of the quasi-stationary state, whereas, the second assumes that there are two distinct sites. The first is part of the fraction easily accessible with a very high desorption rate k1 (fast fraction), the second contains the fraction that is difficult to extract, with a low desorption speed k2 (slow fraction). The results showed that, the application of the two sites model can describe accurately the used extraction methods in this study. The data from HD extraction modeling indicate that this method extraction is fast fraction (f equal 0.79), then MAD method (f equal 0.40).

Keywords: Orange peel; Essential oil; Extraction; Microwave; Hydrodistillation.

1. INTRODUCTION

The "Citrus", more commonly known as citrus fruits, originated from subtropical and tropical regions of Asia, were introduced into the Mediterranean basin by Alexander the Great during his great invasion of India [1]. The citrus fruits are part of the family Rutaceae, that contains flowering plants characterize usually with a strong odor. Among Rutaceae family are the genera of oranges, grapefruits, lemons and limes [2].
Oranges considered one of the fruits rich in water which exceed 85% totaled weight, and contain various essential nutrients and bioactive compounds such as carbohydrates, organic acids, aromatic substances, dyes, vitamins (especially), minerals, trace elements and fiber [3]. The peels of oranges have an ancient history of traditional uses, they are widely used to treat several illnesses, especially in Algeria rural communities. The local population used these peels to relieve symptoms of digestive disorders associated with acute or chronic inflammation [4-7].

Several studies have mentioned the use of traditional methods like isotropic distillation and solvent extraction, to recover essential oils and aromas which fits and used in food industry, pharmaceuticals and cosmetics. However, these traditional methods are subject to numerous criticisms including the enormous consumption of energy and solvents (originated generally from petroleum) which are harmful to health and environment [8]. Their for, researchers in the field of extraction and distillation, continue to invent and create a new efficient process “green extraction” in terms to reduce extraction time, solvent consumption, energy, glassware, gases emissions, and in the same yielded higher extracts [9-11].

The innovative of Microwave Assisted Extraction (MAD) was in fact the key process technology to accomplish the mentioned old-style extractions shortcomings. Microwave energy is a non-ionizing form which create an electromagnetic radiation that causes molecular motion by migration of ions and rotation of dipoles, but does not normally cause changes in molecular structure [12]. Energy of microwave has a frequency range from 300 to 300,000 MHz. The majority of the frequencies used for commercial microwave devices are 2450 MHz, which corresponds to a power output of 600-700 Watts [12]. The same wavelengths are used for radar transmission and telecommunication. Not to interfere with these uses, industrial and domestic microwaves heaters are required to operate at either 2450 MHz or 900 MHz.

Two parameters define the dielectric properties of materials. The first is $\varepsilon_r$, the dielectric constant which describes the polarizability of the molecule in an electric field. The dielectric loss factor, $\varepsilon''$, measurement of the efficiency with which the absorbed microwave power able to be converted into heat. The ration of the terms is the dissipation factor, $\delta$.

Usually, the higher the dielectric constant, the greater the degree of microwave absorption. Water has a higher dielectric constant for common solvents. However, the dissipation factor is much lower than other solvents. Therefore, the rate of water absorption of the microwave energy is higher than the rate at which the system can dissipate heat. This phenomenon explains the effects of “superheating” that occurs when there is water in the matrix. Localized superheating may have positive or negative effects, depending on the matrix. In some cases, this may exceed the diffusivity of the analyte in the matrix. In other situation, the intense heating may give rise to degradation of the analyte and/or “explosion” of the solvent. To get maximum heat distributed through the utmost, it is better to choose a solvent that has a high dielectric constant as well as a high dissipation factor.

Recent works using microwave extraction (MAD) has undergone profound changes, due to speed, efficiency, selectivity and energy [13-16]. Microwave extraction has become a preferred solution to the problems facing traditional extraction methods. In general, the yields of essential oils obtained by MAD is the same or better than the old style methods [14]. MAD method could be described as a “dry distillation”, which it is obvious that this approach has no need to use water or organic solvent during the extraction, we directly put the plant material in a microwave reactor, and the heated water inside the plant breaks the cells containing the essential oil, at this point, the essential oil is released and then recovered by the water vapor produced by the plant material itself, after a complete extraction (no significant increase in the volume of oil collected) the excess water returned to the distillation flask [16, 17].
The modern distillation process are still in use today as the most important processes for obtaining essential oils from plant sources. Extractions using the MAD are performed at atmospheric pressures so the temperature inside the extraction vessel is normally within +/- 5°C of the solvent boiling point. The heating process is more efficient because all of the energy is focused on one sample instead of being split among several samples [18]. When the temperature of the solvent approaches the boiling point, the solvent vaporized, rises to a reflux condenser where it is condensed and returned to extraction vessel. The heating associated with MAD allows the solvent to rapidly overcome matrix effects and promotes faster desorption of the target analytes and other extractables.

In this paper, a comparative study between Hydro distillation (HD) and Microwave-accelerated distillation (MAD) targeting the essential oils of orange peel "Washington Navel" will be discussed, also we will try to clarify and comprehended the EOs extraction foundations, the mechanism and suggesting a specific extraction mechanism.

2. MATERIALS AND METHODS

2.1. Plant material

In this study, citrus fruits were collected from Tipaza province, north Algeria (36°35’31”N and 2°26’58”E) during April 2018. The samples of Washington Naval (Citrus sinensis L.), a species of orange famous in Algeria, were washed with distilled water to remove the dust. Next, the enough oranges sample were peeled by hand, then the peels were dried in shade at room temperature over three weeks.

2.2. Extraction apparatus and procedures

About 250 g of the samples (peels) were subjected to a Hydro-distillation (HD) using a Clevenger-type apparatus for a duration of 180 minutes. The same amounts of samples (250 g) were oriented to a Microwave accelerated distillation (MAD) process. In MAD extraction, orange peels samples were heated using a constant microwave power of 600 watts for 30 minutes. By the end of the extraction, the resulted essential oils (EOs) were recovered in small test tubes and mixed with anhydrous sodium sulfate (Na₂SO₄) to eliminate any potential water merged with the resulted EOs. Finally, the obtained EOs were stored at 4°C until further analyses.

In the work, hydro-distillation and MAD were used, a process in which the plant material and water are put together in a vessel and the mixture is allowed to boil. The emerging mixture of vaporized water and oil moves through a coil usually cooled with running water, were the steam is condensed. The mixture of condensed water and essential oil is collected and separated by decantation. If necessary, the oil should be freed from dissolved and suspended water by treatment with anhydrous sodium sulphate. This serves to prevent subsequent hydrolysis of esters and other hydrolysable constituents of the oil, hence helping to preserve its odor and properties.

2.3. Gas chromatography and gas chromatography–mass spectrometry identification GC-MS

Essential oil (EOs) obtained by Hydrodistillation (HD) and Microwave-accelerated distillation (MAD) were analyzed using GC–MS (Hewlett–Packard computerized system comprise a 6890 gas chromatograph coupled to a 5973A mass spectrometer). The analyses were carried out on two fused-silica-capillary columns with different stationary phases, the first column was non-polar: HP5MS™ (30 m × 0.25 mm × 0.25 µm film thickness) and the second was polar a Stabilwax™ consisting of Carbowax™-PEG (60 m × 0.25 mm × 0.25 µm film thickness). Helium carrier gas flow rate was of 0.3 mL/min, the temperature was programmed at first
at 60°C for 8 min then increased with 2°C/min until reaches 250°C then fixed at 250°C for 15 min; EOs injection volume was 1 µL. The determination of oil components with their relative percentage was calculated from the peak areas resulted after using the GC-FID chromatography, the components identification, was based on comparing their spectra with those of references in the MS Library (National Institute of Standards and Technology NIST and Wiley), and with mass spectra literature data. To confirm the identification, the corresponding retention indexes (RI), were calculated using the n-alkanes series, C5-C28, and then compared with those reported in the literature [19]. The relative amounts of individual components were calculated based on GC-FID peak area.

2.4. Scanning electron micrographs (SEM)

In this study the samples Washington Naval peel were freezed, then fixed on a holder using aluminum tape and then sputtered with gold in order to be examined by a TOPCON ABT60, under vacuum condition and accelerating voltage of 15 kV, with a spot size 5 and a working distance of 15 mm.

3. RESULTS AND DISCUSSION

3.1. Chemical composition

The quantitative study has brought out the efficiency of both methods MAD (Microwave-accelerated distillation known as ‘MAD’ or ‘DryDist’ is an original combination of microwave heating and dry distillation at atmospheric pressure) [20-22], and traditional hydro-distillation (HD), for the extraction of essential oil (EOs) from the samples of Washington Naval peel. The yield of EOs was 0.28% and 0.27% (v/w) for Hydrodistillation (HD) and microwave-assisted distillation (MAD), respectively and also the results showed that 21 components were identified (See Table 1) and presented about 96% of the total detected constituents.

In fact, it has been observed that the maximum amount of essential oil can be extracted by MAD in 30 minutes compared to 180 minutes in the HD method, and this is very clear that the time of extraction with MAD is lower than HD. One of the advantages of solvent-free extraction, assisted by microwaves MAD, is using less time extraction, energy, and the more important none solvent was used. In addition to these advantages, we have paid attention to factors influencing the MAD extraction in order to propose a mechanism of extraction and identify the characteristics on which we can play, to optimize or anticipate the extraction by MAD. In this purpose, we have studied the morphology of the Washington Naval peel extracted by MAD, and tried to modelling the extraction by applying two kinetics models. At last, we tried to understand the differences between the composition of the resulted essential oils extracted by MAD and HD, on the basis, in one hand, on the theories of distillation related to the boiling temperatures, and in other hand, on the theories of diffusion based on the solubility of compounds in aqueous environment.

3.2. Effects of microwaves on the morphology of the orange peel cells

Scanning electron micrographs were done on the samples before extraction (MAD and HD), orange peel cells as shown in Figure 1-(a-c), it is obvious that the cells contained a significant amount of water, in the presence of microwave energy can undergo “superheating” because the bulk solution are not able to dissipate the heat as rapidly as it is generated. So, the microwaves interact with the bulk solution and the free water molecules; causing localized super-heating.

They show damaged cell walls because of the explosion produced at the cell walls level, consequence of the sudden temperature increasing explained by Paré and Bélanger [23]. These damages are generated by some hot points produced at the interface of the walls, at the irradiation by microwaves. In fact, when the
glands are subjected to a very major thermic stress and at high located pressures induced by the specific heating by microwaves, the internal pressure into the glands can exceed their extreme capacity of expansion. Therefore, a faster break arises linked to the realized one, by traditional abrasion or by heating. Besides, the presence of polar compounds as water and oxygenated compounds can cause a sudden increase of the temperature furthering the process of des-hydratation located, with a very high heating speed into the cell, the latter phenomenon increases the transfer speed of cells components through the cells walls.

Table 1. The chemical composition and yields of essential oil Washington Naval peel obtained by HD and MAD extractions, where RI, retention indices.

<table>
<thead>
<tr>
<th>No</th>
<th>Compoundsa</th>
<th>RI b</th>
<th>HD (%)</th>
<th>MAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>α-Thujene</td>
<td>920</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>α-Pinene</td>
<td>926</td>
<td>0.50</td>
<td>0.40</td>
</tr>
<tr>
<td>3</td>
<td>Sabinene</td>
<td>961</td>
<td>0.33</td>
<td>0.74</td>
</tr>
<tr>
<td>4</td>
<td>β-Myrcene</td>
<td>988</td>
<td>1.76</td>
<td>1.65</td>
</tr>
<tr>
<td>5</td>
<td>α-Phellandrene</td>
<td>1001</td>
<td>0.12</td>
<td>0.19</td>
</tr>
<tr>
<td>6</td>
<td>Limonene</td>
<td>1030</td>
<td>92.49</td>
<td>91.39</td>
</tr>
<tr>
<td>7</td>
<td>Terpinolene</td>
<td>1120</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>8</td>
<td>Linalool</td>
<td>1125</td>
<td>0.42</td>
<td>1.86</td>
</tr>
<tr>
<td>9</td>
<td>Citronellal</td>
<td>1167</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>10</td>
<td>Terpin-4-ol</td>
<td>1191</td>
<td>0.35</td>
<td>0.13</td>
</tr>
<tr>
<td>11</td>
<td>α-Terpineol</td>
<td>1203</td>
<td>0.27</td>
<td>0.23</td>
</tr>
<tr>
<td>12</td>
<td>Nerol</td>
<td>1237</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>13</td>
<td>Neral</td>
<td>1268</td>
<td>0.06</td>
<td>0.14</td>
</tr>
<tr>
<td>14</td>
<td>Geraniol</td>
<td>1271</td>
<td>0.04</td>
<td>0.07</td>
</tr>
<tr>
<td>15</td>
<td>Geranial</td>
<td>1284</td>
<td>0.02</td>
<td>0.22</td>
</tr>
<tr>
<td>16</td>
<td>(E)-Caryophyllene</td>
<td>1391</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>17</td>
<td>Valencene</td>
<td>1488</td>
<td>0.39</td>
<td>0.09</td>
</tr>
<tr>
<td>18</td>
<td>Nootkatone</td>
<td>1799</td>
<td>0.26</td>
<td>0.33</td>
</tr>
<tr>
<td>19</td>
<td>ν-Octanol</td>
<td>1102</td>
<td>0.05</td>
<td>0.13</td>
</tr>
<tr>
<td>20</td>
<td>Decanal</td>
<td>1210</td>
<td>0.27</td>
<td>0.24</td>
</tr>
<tr>
<td>21</td>
<td>Geranyl Acetate</td>
<td>1366</td>
<td>0.05</td>
<td>0.54</td>
</tr>
</tbody>
</table>

| Extraction time (min) | - | 180 | 30 |
| Yield (%)            | - | 0.28 | 0.27 |

a: Compounds are identified based on the comparison of their mass fragmentation pattern and their retention indices.

b: (RI) Retention indices calculated on non-polar HP5MS™ capillary column.

The result is sudden non-uniform rise in temperature with more pronounced effects where the water is in larger proportions. The temperature excess quickly to the boiling point of water and sometimes higher. The result is a dramatic expansion in the volume of the system [23, 24]. The cells cannot accommodate the high internal pressures that are created as a result of the microwave energy. They rupture allowing the contents to flow freely toward the relatively cool surrounding solvent that solubilizes them rapidly besides, the micrography of hydro-distillation reports that the cells walls are much damaged because of the long-term of extraction.

During MAD, a polar solvent with a high dielectric constant surrounds the matrix. The generated microwave waves are applied in a magnetron in a pulsed manner. The solvent molecules absorb the
microwave power and become polarized. When the microwave field is removed, the thermal disturbance is restored. This procedure heats the bulk solution and can cause localized superheating effects (only in matrices that contain water). Finally, the thermal equilibrium is established within the system because the heat is transferred from the bulk solution and the “pockets affected by superheating effects” by collision so that the energy is distributed uniformly throughout the system.

The final temperature of the extraction is proportional to the power (watts), time, and initial temperature; it is inversely proportional to the heat capacity of the solvent, and the mass of sample in grams [25]. The heat produced by the interaction of the microwaves with the solvent subsequently increases the diffusivity of the solvent and hopefully that of the analyte. The solvent is then able to diffuse into the matrix and extract the analytes; and then diffuse out of the matrix carry along the soluble components.

![Figure 1. Variety Washington Navelbark, observed at the electronic microscope by scanning (a) non treated; (b) treated by HD (180 min); (c) treated by MAD (30 min).](image)

3.3. Modelling of kinetic data

In order to enhance the experimental data obtained and for a best comprehension of extraction phenomena, we tried to modelling of extraction by applying two kinetic models. These models are assuming that the extraction is only limited by the speed of desorption of the compound of the matrix and not by the molecular diffusion, ruled by the model based on the thermodynamic coefficient of sharing. The first model is considering the existence of a sole site with a permanent speed ruled by the equation of the quasi-stationary state.

\[ k_0 = (1/10)^n \ (\ln(Y_\infty / (Y_\infty - Y_t)), \ (Equation \ of \ order \ 1), \]

The above equation derivation leads to the following expression:

\[ \frac{Y(t)}{Y_\infty} = 1 - e^{-k_0 t} \]

\(Y(t)\): Obtained efficiency, after time \(t\)

\(Y_\infty\): Maximal efficiency obtained

\(k_0\): Speed constant at the initial stage

\(t\): time

Chen and Spiro [23], have tried to model the extraction by microwaves of secondary metabolites from mint leaves and rosemary leaves. After using the equation of the quasi-stationary state, The obtained results were quit wandered, The second model proposed on 1977 by Cerf and Coll [26] surviving bacterial spores, is assuming that two distinct sites are existing. The first one is rising from the fraction easily accessible with the desorption speed very big \(k_a\) (fast fraction) and the second one, contains the fraction extractible with
difficulty, with a low speed of desorption \( k_2 \) (slow fraction). The equation can be written as follows:

\[
\frac{Y(t)}{Y_\infty} = 1 - f.e^{-k_1t} - (1 - f).e^{-k_2t}
\]

According to Kubátová and Coll [27], the extraction by supercritical fluid tends, generally made in two distinct stages: the first one, called fast stage, is regarding the compound mass weakly attached to the matrix and the second one, called slow stage, is associated to the compound mass strongly linked to the matrix. They have also noticed that the models of both sites, based on the kinetics, perfectly, describes the extraction of the compounds of essential oils from the Satura savory (Satureja hortensis) with the help of a supercritical fluid (CO\(_2\)). Moreover, the model based on the coefficient of thermodynamic of sharing is not satisfactory by the look of extraction of these compounds and of polyaromatic hydrocarbons (HPAs) by supercritical fluid.

Besides, the obtained results by Chemat and Coll [28], studying the model of both sites, showed, that this one can perfectly describe the methods of extraction by microwaves used for the two secondary metabolites (carvone and limonene) from the caraway seeds).

In order to apply these two models, the functions pre-introduced within (the Microcal Origin software) have enabled to adapt our experimental data to this model and to draw it, the results were shown in Table 2.

**Table 2. Results of the modelling of the kinetic of extraction,**

<table>
<thead>
<tr>
<th>Method</th>
<th>Sole site</th>
<th>Both sites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k ) (min(^{-1}))</td>
<td>( f )</td>
</tr>
<tr>
<td>HD</td>
<td>0.0894</td>
<td>0.79</td>
</tr>
<tr>
<td>MAD</td>
<td>0.0817</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Where:

- \( f \): fraction quickly extracted
- \( k \): rate constant of extraction (model of sole site)
- \( k_1 \): rate constant of extraction of the fast fraction (model of both sites)
- \( k_2 \): rate constant of extraction of the slow fraction (model of both sites).

The model of sole site, shown by the Figure 2 indicates that this model can be applied to our experimental data, the essential oils either hydro-distillated or extracted by microwaves, has the same speed extraction as shown in Table 2.

Figure 3 representing the application of the model of both sites which shows that this one can describe both methods of extraction. The data issued from the modelling of the HD extraction indicated efficiency of 79%, are found in the fast fraction (\( f = 0.79 \)); while less than 40% (\( f = 0.40 \)) is observed in MAD. After analysing the constants of extraction speed, described in Table 1, we noticed the presence of two periods:

- The first period when the constant of extraction speed of the fraction quickly extracted \( K_1 \) is maximal (0.22 for MAD against 0.089 for the HD). This one is corresponding to the extraction of the superficial oil, the recovery of the oil, is made by mere evaporation.
- The second period where the constant of extraction speed of the fraction slowly extracted \( k_2 \), gradually decreases (0.09 for HD against 0.143 for the MAD). This one could be attributed to the extraction of the essential oil located in the endogen sites.

Therefore, the assisted procedure by microwaves is showing a significant increase of efficiency during the prior 20 minutes of extraction, knowing that more 87% of the compounds are extracted at this stage.
3.4. Effect of the temperature

The collected information of the morphological study and the modelling of the kinetic of extraction, can explain the speed of extraction by MAD, comparing to the technique of HD; but they cannot explain, nor anticipate the chemical compounding of the extracted essential oil, and why, are we getting a rate of oxygenated compounds more important by MAD.

Table 3 showing the structure, the boiling temperature and the contents of principal molecules, outnumbered in each one of the essential oils in Washington Navel peel, in this study, when extracting in MAD and HD methods, the boiling temperature of the compounds was evaluated by the software of specific calculation “ACD boiling point” [29], a natural question occurs when reading this table, “Why do we get more oxygenated compounds by MAD at Although the distillation is more rapid and although these products have a higher boiling temperature?
Another question is arising: "why are we obtaining less limonene (175°C) by MAD even though we are distilling more quickly and even though the boiling temperature of this hydrocarbon is lower than the other oxygenated compounds (220-250°C)?" This study is enabling to clarify these observations.

The EOs of the Washington Navel peel is clearly prevailed by the limonene whichever the extraction technique used. The other outnumbered compound of this oil, is the β-myrcene, a non-oxygenated compound, indeed, but which boiling point (167°C) is clearly lower than the linalool (220°C), oxygenated compound found in low quantity within this essential oil, this is due to their simple and light structure compared to another structures in essential oil.

Table 3. Outnumbered compounds into the essential oil Washington Navel peel samples.

<table>
<thead>
<tr>
<th>Essential oil</th>
<th>Outnumbered compounds</th>
<th>Structure</th>
<th>Teb (°C)</th>
<th>MAD (%)</th>
<th>HD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washington navel</td>
<td>Limonene</td>
<td><img src="image1" alt="Limonene Structure" /></td>
<td>175</td>
<td>91.39</td>
<td>92.49</td>
</tr>
<tr>
<td></td>
<td>β-Myrcene</td>
<td><img src="image2" alt="β-Myrcene Structure" /></td>
<td>167</td>
<td>1.65</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>Linalool</td>
<td><img src="image3" alt="Linalool Structure" /></td>
<td>220</td>
<td>1.86</td>
<td>0.42</td>
</tr>
</tbody>
</table>

On the whole, the MAD enables a best extraction of oxygenated compounds compared with aromatic non oxygenated compounds, like, in the case of linalool and limonene into the essential oil of Washington Navel, although their boiling temperature is the most higher. The MAD is running in 30 minutes while the HD needs a minimum of 3 hours. Taking into account these times, we can imagine that the oxygenated compounds, at a boiling point generally higher (Ex: Teb linalool = 220 °C), will not have enough time for being completely distilled from the fast system of extraction without solvent assisted by microwave. The most of extracted compounds are assumed to be in non-oxygenated nature with boiling temperatures much lower (Ex: Teb limonene = 175°C).

The microwaves enable to free more quickly, the essential oil contained into the vegetable matrix thanksgiving to a quasi instantaneous opening of the releasing glands. At a MAD or HD extraction, the quantity of aromatic molecules oxygenated or not, is lower than the quantity of water being into the vegetable matrix. The boiling temperature of the mixture water + aromatic compounds, which is, thus, required by the boiling temperature, that is to say, 100°C and which is, in no way, dependent from the boiling temperature of essential oil compounds.

The explanation of the difference of chemical composition between the extraction processes by HD and MAD cannot be supported, only by the boiling temperatures of oxygenated compounds or non oxygenated extracts.

3.5. Effect of the solubility

In 1910, Von Rechenberg [30], has published worken titled "Theorie der gewinnung und trennung der ätherischen öle". This work has never been translated; these theories have remained rather unknown. In 1982, Koedam [31], took again the theories of Von Rechenberg and explained by taking the caraway case, that the boiling point of an organic compound, does not explain, only by itself, the phenomenon of distillation, and that it is needed to introduce the notion of solubility.
In fact, the carvone being water-soluble, contrary to limonene, from the moment that one start to heat the reactional middle, it solubilizes and it is carried away by the first water steams. As the middle is exhausted from carvone, and more generally from soluble molecules into water, the limonene and the other terpenes start then to be carried away by the steam. The duration of HD being important, each molecule has time to be distilled quasi completely. Due to the short duration of extraction by MAD, the extraction phenomenon will lean upon more on the solubility than on the boiling temperature. Although the carvone has a boiling point higher, this product is distilled previously because of the high solubility in the water. For the limonene, its insolubility in the water is an obstacle for carrying away this product although its boiling point is lower.

The vaporization phenomenon would be thus, guided neither by the boiling temperature of compounds but by their solubility, which is named by Von Rechenber "the hydrodiffusion phenomenon". Practically at the implementation of a MAD, we will not add, in any case, some water to the vegetable matter; only the internal water of the plant; (to the maximum of 95% on mass of the vegetable matter for the fresh plants); is going to come into play. While for the HD, in order to treat 250 g of vegetable matter, 1 liter of water approximately has been added at the middle, The aromatic compounds that comprise the essential oil are contained within the bark that is found directly, in case of the HD or indirectly, in case of the MAD in aqueous middle. These aromatic compounds, as soon as released from the matrix, are going, after, being solubilizes in order to form a mixture of water-aromatic compounds which will be turned in vapor, condensed and separated.

Table 4 showing the structure, the solubility into the water, the boiling temperature and the contents of the two main outnumbered molecules (oxygenated and non oxygenated) of the essential oil from the Washington Navel peel samples extracted by MAD and by HD. The solubilities of the compounds have been assessed theoretically, by using quantic software of specific calculation.

The solubility of some compounds, especially the oxygenated compounds, is higher. In the case of the Washington Navel while the linalool has got a solubility of 0.57g by liter of water, the one of the limonene is nearly zero. So, the difficulty of some molecules to solubilizes is going, therefore to lead to some selectivity. It seems to be that this available water being lower in MAD is furthering, mainly the carrying away of the most soluble molecules, while in HD, the water quantity being more important, is enabling, to each type of molecules, to distillate in equitable manner.

**Table 4.** Characteristics of outnumbered compounds of EOs Washington Navel extracted by MAD and HD.

<table>
<thead>
<tr>
<th></th>
<th>Linalool</th>
<th>Limonene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Solubility into the water (g/l)</td>
<td>0.57</td>
<td>0.00042</td>
</tr>
<tr>
<td>Teb (°C)</td>
<td>220</td>
<td>175</td>
</tr>
<tr>
<td>Dipolar moment (D)</td>
<td>22</td>
<td>14</td>
</tr>
<tr>
<td>Dielectric constant (έ)</td>
<td>2.11</td>
<td>0.75</td>
</tr>
<tr>
<td>MAD (%)</td>
<td>1.86</td>
<td>91.39</td>
</tr>
<tr>
<td>HD (%)</td>
<td>0.42</td>
<td>92.49</td>
</tr>
</tbody>
</table>
3.6. Effect of the polarity of molecules

The experience of using domestic microwaves oven indicates that the foods are being heated up, generally, very quickly under the microwaves effect. At the molecular level, these materials are found globally as neutral entities, at the electrical point of view, but with disymmetric dispatching of their ionic partial loads. In other words, one part of the molecule is positively loaded, the other part negatively. These molecules are therefore, forming some electrical dipoles [32].

The mechanism of dielectric heating leans upon the fact that the polar molecules, such as the water, have got negative and positive terminations: that are dipoles. In the absence of electrical field, the dipoles of dielectric middle are found oriented by chance under the effect of the thermal agitation at the middle. Under the continuous effect of the electrical field, the molecules tend to be oriented towards the direction of electrical field. The more, the electrical field is intense, the less, the thermal agitation tends to disorganize the alignment, which has got importance. When all the molecules are oriented, an induced global dipolar moment is appearing. Under the alternating electrical field of frequency $f$, the dipolar are directed towards the field of half alternating; disarray while the field is cancelled and re-oriented in the other sense during the second half alternating: this is the rotation of dipoles.

The electrical energy is, in part, by the rotation of the dipoles. The electrical energy is partially converted to heat: the alignment of dipoles comparing with the electrical field is impeded by the interactions strengths between the molecules (the bond strengths by bridge of hydrogen and the bond strengths of Van der Waals). These strengths can be compared to the strengths of internal friction that existing in the solid-solid contacts. They, therefore, go against the free rotation of molecules. From the produced friction, appears the clearance of heat as shown on Figure 4.

![Figure 4. Rotation of dipoles subjected to microwave irradiation.](image)

The energy dissipation by the product can be maximal if the frequency of the electrical field is equal to the frequency of relaxation. The phenomenon of relaxation is corresponding to the appearance of a phase displacement between the flicker of the electrical field and the one of dipoles. The frequencies of microwaves being imposed, the heating of a product with a maximal effectiveness, becomes special [33]. In this case, a major part of molecules subjected to the action of the microwaves field, does not rotate with the alternating change of field, but shivers.

The aptitude of a material being heated under the action of microwaves radiation is qualified by the factor of dielectric losses $\varepsilon'$. The products being a factor of losses higher to 1, is being easily heated by microwaves. Among these compounds of dielectric higher losses, we can mention the water at the liquid state.
In practice, the main parameter in order to assess if a natural product can be heated by microwaves is its content of water. When this one is higher to 20% on mass, the product is going to heat easily under the effect of microwaves.

The losses factor $\varepsilon''$ represents the global behavior of material subjected to microwaves irradiation. It can be decomposed into two phenomena, the polarization and the friction. The related permittivity to $\varepsilon'$, or dielectric constant, translates the ability of dielectric to polarize, in other words, being oriented towards the sense of electrical field. The friction appears by a light delay taken by the polarized materials in order being oriented after the application of electrical field. This phase displacement is represented by the corner of losses $\delta$ [32]. The factor of electrical losses $\varepsilon''$ is equal to the electrical constant multiplied by the tangent of losses corner $\varepsilon'' = \varepsilon' \tan \delta$.

The essential oils are composed from aromatic molecules getting a great diversity of structure and which can be divided into two main groups: the terpenic hydrocarbons and the oxygenated compounds. In the case of essential oil from the Washington Navel issued from the MAD where the linalool and the limonene are, actually, the outnumbered compounds, we are observing a greater content in oxygenated compounds, mainly the linalool: (dipolar moment equal to 22) compared with the terpenic hydrocarbons, the limonene (dipolar moment equal to 14). The dipolar moment, the dielectric constant, the structure, the water solubility, the boiling temperature and the proportions of linalool and of the limonene main molecules and outnumbered in essential oil of the Washington Navel variety extracted by MAD and HD, are shown in Table 3. These dielectric properties have been calculated thanksgiving to a chemical software quantic hyperchem.

4. PROPOSED MECHANISMS

The synthesis of these various studies of the microwaves effect on the morphology, on the modelling of the kinetic extraction, combined together to the one of factors intrinsic to the target molecule as the boiling temperature, the solubility or the polarity and the dielectric constants, has enabled the upshot of two possible mechanisms specific to the MAD (Figure 5).

4.1. Mechanism I

For a sample of high dielectric losses (constant of water higher to 20%) the extraction can be ensured by microwaves without adding water or organic solvent. The presence of polar compounds such as water and the oxygenated compounds can induce a sudden increase of temperature furthering a process of a located deshylratation with a speed of heating very high at the interior of the cell. This latter phenomenon increases
the speed of transfer of the components of the cell through the cell walls. Due to the short duration of extraction by MAD, this mechanism seems to react as a priority, by some phenomenon of solubility: the non adding of water within the reactor is going to further the selectivity at the level of carrying away the most soluble molecules, which are, furthermore, the molecules making up the oxygenated fraction, from a greater value added as regards to olfactive.

4.2. Mechanism II

The mechanism of dielectric heating is leaning upon the dipolar moment of essential oil. The compounds with high dipolar moments are easily heating their selves by microwaves and are extracted with high proportions compared to the aromatic compounds having low dipolar moments.

5. CONCLUSION

In this study it can be concluded that the Microwave distillation process MAD is one of the "soft" procedures allowing a considerable saving of time and energy and the reduction of the rejections, among the advantages of MAD are shorter extraction times (typically 30 min), shorter cooling times and less use of solvent.

The quantitative study has brought out the efficiency of the MAD (Fast microwave-accelerated distillation or microwave ‘dry’ distillation, known as ‘MAD’ or ‘DryDist’ is an original combination of microwave heating and dry distillation at atmospheric pressure) for the extraction of essential oils of citrus fruit varieties We have thus, been able to observe that it is possible to extract as much essential oil in 30 minutes by MAD as 180 minutes by HD. The qualitative study has enabled us to notice the significant differences in the essential oils composition according to the extraction procedure, At first, the essential oils zest of Citrus studied are outclassed by the limonene while an important variability has been observed within the proportions of the oxygenated fraction according to the technique of extraction used. The oxygenated fraction, made up of olfactive molecule, highly enhanceable, is always higher into the essential oils obtained by MAD [34]. One of the advantages of the extraction without solvent, assisted by microwaves, is undeniably the saving times and therefore, consequently, energy savings.

To enhance the experimental data obtained and for a best comprehension of the extraction phenomenon, we have paid attention to factors influencing the extraction by MAD in order to propose a mechanism of extraction and identify the characteristics on which we can play, to optimize or anticipate the extraction by MAD, For this, we have studied the morphology of the bark of citrus fruit extracted by MAD, and tried the modelling of extraction by applying two kinetics models.

At last, we have tried to understand the differences met, in the composition of the essential oils extracted by MAD and HD, on the basis, in one hand, on the theories of distillation related to the boiling temperatures, and in other hand, on the theories of diffusion based on the solubility of compounds in aqueous environment.

Hence, based on the results obtained in this study, we can conclude that the MAD extraction has very good reproducibility of the results and it also proves to be more profitable from an economic point of view than conventional HD method. Also, this original method could therefore be thought to use as a routine analysis to chemical and food industry laboratories or private analysis and analysis laboratories and the quality control.
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Conflict of Interest: The authors declare that they have no conflict of interest.

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