

Short communication

# Solvent-free microwave extraction of essential oil from aromatic herbs: comparison with conventional hydro-distillation

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## Abstract

Solvent-free microwave extraction (SFME) is a combination of microwave heating and dry distillation, performed at atmospheric pressure without added any solvent or water. Isolation and concentration of volatile compounds are performed by a single stage. SFME has been compared with a conventional technique, hydro-distillation (HD), for the extraction of essential oil from three aromatic herbs: basil (*Ocimum basilicum* L.), garden mint (*Mentha crispa* L.), and thyme (*Thymus vulgaris* L.). The essential oils extracted by SFME for 30 min were quantitatively (yield) and qualitatively (aromatic profile) similar to those obtained by conventional hydro-distillation for 4.5 h. The SFME method yields an essential oil with higher amounts of more valuable oxygenated compounds, and allows substantial savings of costs, in terms of time, energy and plant material. SFME is a green technology and appears as a good alternative for the extraction of essential oils from aromatic plants.

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## 1. Introduction

Herbs and spices are invaluable resources, useful in daily life as food additives, flavours, fragrances, pharmaceuticals, colours or directly in medicine. This use of plants has a long history all over the world, and over the centuries, humanity developed better methods for the extraction of essential oils from such materials. Essential oils are complex mixtures of volatile substances generally present at low concentrations. Before such substances can be analysed, they have to be extracted from the matrix. Various different methods can be used for that purpose, e.g. hydro-distillation (HD), steam distillation, Soxhlet extraction, and simultaneous distillation–extraction. Nevertheless, these molecules are well known to be thermally sensitive and vulnerable to chemical changes [1–4]. Losses of some volatile compounds, low extraction efficiency, degradation of unsaturated or ester compounds through thermal or hydrolytic effects

and toxic solvent residue in the extract may be encountered using these extraction methods. These shortcomings have led to the consideration of the use of new “green” technique in essential oil extraction, which typically use less solvent and energy, such as supercritical fluids, ultrasound and microwave [5–7]. Indeed, for an extract to be classified as an essential oil, on heat and water may be used in its extraction from the plant.

There has recently been widespread interest in the application of microwave heating in solvent extraction. Several classes of compounds such as essential oils, aromas, pesticides, phenols, dioxins, and other organic compounds have been extracted efficiently from a variety of matrices (mainly soils, sediments, animal tissues, food and plant material). All the reported applications have shown that microwave assisted solvent extraction (MAE) is a viable alternative to conventional techniques for such matrices. The main benefits are the reduction of extraction time [8–11].

Historically, dry distillation was used by alchemists for sublimation and extraction [12]. Nowadays, this technique is largely used either for the extraction of inorganic materials from soils or for organic compounds from wood and coke

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[13]. Nevertheless, it is not known how the combination of dry distillation and microwave heating affects extraction. It is expected that not only would the kinetics of extraction be increased but also the quantity of solvent used could be reduced or eliminated.

A recent patent describes a new method for extracting natural products without added any solvent or water by using microwave energy [14]. The solvent free microwave extraction apparatus is an original combination of microwave heating and dry distillation at atmospheric pressure. SFME was conceived for laboratory scale applications in the extraction of essential oils from different kind of aromatic plants. Based on a relatively simple principle, this method involves placing plant material in a microwave reactor, without any added solvent or water. The internal heating of the in situ water within the plant material distends the plant cells and leads to rupture of the glands and oleiferous receptacles. This process thus frees essential oil which is evaporated by the in situ water of the plant material. A cooling system outside the microwave oven condensed the distillate continuously. The excess of water was refluxed to the extraction vessel in order to restore the in situ water to the plant material. The SFME is neither a modified microwave assisted extraction (MAE) which use organic solvents, or a modified hydro-distillation which use a large quantity of water.

In this paper, the potential of the SFME technique has been compared with a conventional method, hydro-distillation, as the current technique and commercial situation call for research into new extracts and new extraction techniques. We have applied SFME and HD techniques to extract essential oils from aerial parts of three aromatic herbs: basil (*Ocimum basilicum* L.), garden mint (*Mentha crispa* L.), thyme (*Thymus vulgaris* L.) belonging to the *Labiatae* family which is a highly advanced and homogeneous family, largely used in food preparation, perfumery and medicine. We make appropriate comparisons in term of extraction yields and rates, essential oil composition, and energy consumption.

## 2. Experimental

### 2.1. Plants material

Fresh plant material was purchased at the end of the humid season (March) from the Chaudron market in Reunion Island (France D.O.M.). Reunion Island is situated in the Indian Ocean, close to Madagascar, and located at 21°S55°E.

The initial moisture of each plant was respectively 90% for basil, 95% for garden mint, and 80% for thyme.

### 2.2. SFME apparatus and procedure

Solvent free microwave extraction has been performed in a Milestone “DryDist” microwave laboratory oven. This is a multimode microwave reactor 2455 MHz with a maximum delivered power of 1000 W variable in 10 W increments. The

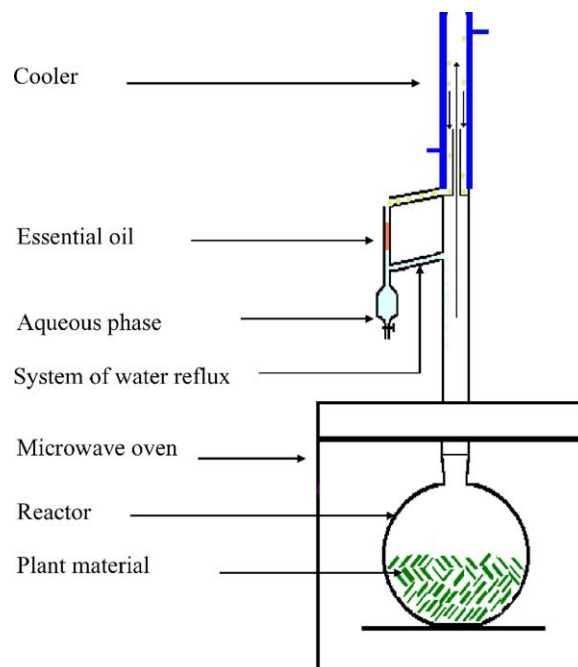


Fig. 1. SFME system.

dimensions of the PTFE-coated cavity are 35 cm × 35 cm × 35 cm. During experiments, time, temperature, pressure, and power can be controlled with the “easy-WAVE” software package. Temperature was monitored by a shielded thermocouple (ATC-300) inserted directly into the sample container and by an external infrared (IR) sensor. Temperature was controlled by a feedback to the microwave power regulator. The SFME apparatus is illustrated in Fig. 1.

The experimental SFME variables have been optimised by the univariate method in order to maximize the yield of essential oil. In a typical SFME procedure performed at atmospheric pressure, 250 g of fresh plant material was heated using a fixed power of 500 W for 30 min without added any solvent or water. A cooling system outside the microwave cavity condensed the distillate continuously. Condensed water was refluxed to the extraction vessel in order to provide uniform conditions of temperature and humidity for extraction. The extraction was continued at 100 °C until no more essential oil was obtained. The essential oil was collected, dried under anhydrous sodium sulphate and stored at 0 °C until used.

### 2.3. Hydro-distillation apparatus and procedure

Five hundred grams of each aromatic herb were submitted to hydro-distillation with a Clevenger-type apparatus [15] according to the European Pharmacopoeia and extracted with 6 L of water for 4.5 h (until no more essential oil was obtained). The essential oil was collected, dried under anhydrous sodium sulphate and stored at 0 °C until used.

#### 2.4. Gas chromatography–mass spectrometry identification

The essential oils were analysed by gas chromatography coupled to mass spectrometry (GC–MS) (Hewlett-Packard computerized system comprising a 5890 gas chromatograph coupled to a 5971A mass spectrometer) using a fused-silica-capillary column with an apolar stationary phase SBP5<sup>TM</sup> (60 m × 0.32 mm × 1 μm film thickness). GC–MS were obtained using the following conditions: carrier gas He; flow rate 0.7 mL/min; split 1:20; injection volume 0.1 μL; injection temperature 250 °C; oven temperature progress from 60 to 130 °C at 1 °C/min, from 130 to 200 °C at 2 °C/min, from 200 to 250 °C at 4 °C/min and holding at 250 °C for 40 min; the ionisation mode used was electronic impact at 70 eV. Identification of the components was achieved from their linear retention indices on SBP5<sup>TM</sup> column, determined with reference to an homologous series of C<sub>8</sub>–C<sub>22</sub> *n*-alkanes, and by a comparison of their mass spectral fragmentation patterns with those stored in the data bank (Wiley/NBS library) and the literature [16,17].

### 3. Results and discussion

Solvent free microwave extraction is an original combination of microwaves and dry distillation. The apparatus is relatively simple. The isolation and concentration of essential oils are performed in a single stage. This process thus frees essential oil which is evaporated by the in situ water of the plant material. Once the essential oils have been extracted they can be analysed directly by GC–MS without any preliminary clean-up or solvent exchange steps. Table 1 lists the yields, extraction time, oxygenated fraction and chemical composition of the essential oils of basil, garden mint and thyme extracted by SFME and HD.

#### 3.1. Extraction yield and time

One of the advantages of the SFME method is rapidity. The extraction temperature is equal to the boiling point of water at atmospheric pressure (100 °C) for both the SFME and HD extraction methods. Fig. 2 shows the temperature

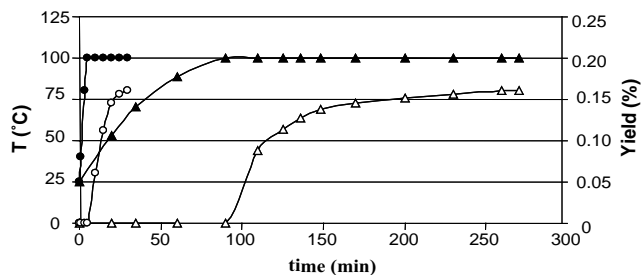


Fig. 2. Temperature profiles (● SFME ▲ HD) and yields (○ SFME △ HD) as a function of time for the SFME and HD extraction of essential oil from thyme.

profiles during SFME and HD of essential oil from aromatic herbs. To reach the extraction temperature (100 °C) and thus obtain the first essential oil droplet, it is necessary to heat for only 5 min with SFME compared with 90 min for HD. As is shown in Table 1 and Fig. 2, an extraction time of 30 min with SFME provides yields comparable to those obtained after 4.5 h by means of HD, which is the reference method in essential oil extraction. The ultimate yields of essential oils obtained by SFME from the three aromatic herbs were 0.029% for basil, 0.095% for crispate mint and 0.160% for thyme. The ultimate yields obtained by HD were 0.028%, for basil, 0.095% for crispate mint and 0.161% for thyme.

#### 3.2. Composition of essential oil

Substantially higher amounts of oxygenated compounds and lower amounts of monoterpenes hydrocarbons are present in the essential oils of the aromatic plants extracted by SFME in comparison with HD. Monoterpenes hydrocarbons are less valuable than oxygenated compounds in terms of their contribution to the fragrance of the essential oil. Conversely, the oxygenated compounds are highly odorous and, hence, the most valuable. The greater proportion of oxygenated compounds in the SFME essential oils is probably due to the diminution of thermal and hydrolytic effects, compared with hydro-distillation which uses a large quantity of water and is time and energy consuming. Water is a polar solvent, which accelerates many reactions, especially reactions via carbocation as intermediates. The greatest difference between the chromatograms for the two methods can be noted for basil as it is shown by Fig. 3.

Linalol and eugenol were the main components in the essential oil extracted from basil but the relative amounts dif-

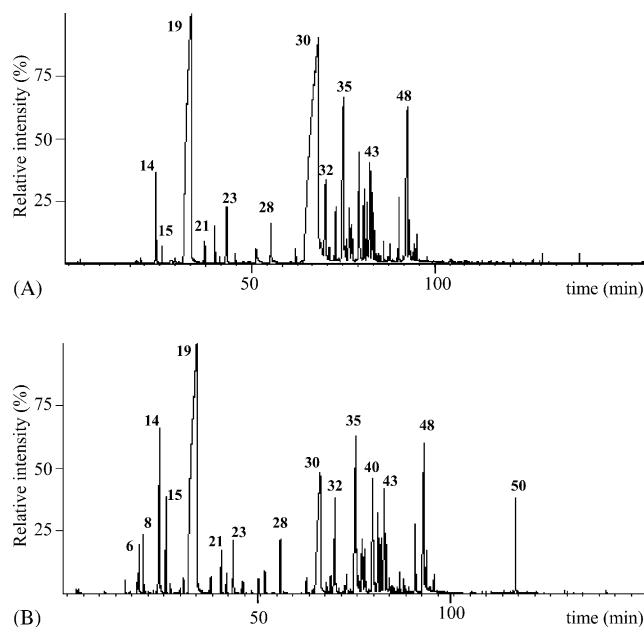


Fig. 3. Comparison of gas chromatograms of the basil essential oil obtained by SFME (A) and HD (B).

Table 1  
 Yields, extraction time, and chemical compositions of basil, garden mint, and thyme essential oils obtained by SFME and HD

Number	Compounds <sup>a</sup>	L.R.I.	Basil		Garden mint		Thyme	
			SFME	HD	SFME	HD	SFME	HD
1	$\alpha$ -Thujene	908	–	–	–	–	0.6	1.7
2	$\alpha$ -Pinene	916	–	0.2	0.1	0.8	0.3	0.8
3	Camphene	934	–	–	–	–	0.1	0.4
4	Sabinene	964	–	0.4	0.3	1.0	–	0.2
5	Octen-3-ol	968	–	–	–	–	2.9	2.5
6	$\beta$ -Pinene	970	–	1.1	0.4	1.4	–	–
7	Octan-3-one	977	–	–	–	–	0.2	–
8	$\beta$ -Myrcene	986	0.1	1.0	0.5	1.3	1.8	2.8
9	Octan-3-ol	991	–	–	1.0	1.8	0.2	0.2
10	$\alpha$ -Phellandrene	1004	–	–	–	–	0.2	0.3
11	$\alpha$ -Terpinene	1014	–	–	–	–	1.7	2.7
12	<i>p</i> -Cymene	1022	–	–	–	–	7.5	11.1
13	Limonene	1025	–	–	<b>9.7</b>	<b>20.2</b>	0.6	0.9
14	1,8-Cineole	1027	1.3	5.8	1.5	–	0.5	0.7
15	<i>trans</i> - $\beta$ -Ocimene	1040	0.2	2.0	–	–	–	–
16	$\gamma$ -Terpinene	1055	–	0.2	0.2	0.8	<b>17.1</b>	<b>22.8</b>
17	<i>cis</i> -Sabinene hydrate	1060	0.1	–	2.5	1.2	2.8	0.9
18	Terpinolene	1079	–	0.3	–	0.1	–	0.2
19	Linalool	1091	<b>25.3</b>	<b>39.1</b>	0.4	0.4	4.6	4.0
20	Camphor	1139	0.3	0.3	–	–	–	–
21	Borneol	1159	0.6	0.9	–	1.2	1.1	1.2
22	Terpin-4-ol	1171	0.1	0.4	0.4	2.6	0.5	1.4
23	$\alpha$ -Terpineol	1189	1.3	1.4	0.5	2.1	0.2	0.2
24	Thymol methyl ether	1229	–	–	–	–	–	0.2
25	Carvacrol methyl ether	1239	–	–	–	–	1.0	1.0
26	Geraniol	1251	0.5	0.5	–	–	–	–
27	Carvone	1258	–	–	<b>64.9</b>	<b>52.3</b>	–	–
28	Bornyl acetate	1282	0.7	1.1	–	–	–	–
29	Thymol	1296	–	–	5.2	1.9	<b>51.0</b>	<b>40.5</b>
30	Eugenol	1352	<b>43.2</b>	<b>11.0</b>	1.2	0.2	1.5	0.3
31	<i>b</i> -Bourbonene	1384	–	–	1.9	2.1	–	–
32	$\beta$ -Elemene	1391	2.4	3.2	1.7	1.7	–	–
33	Methyl eugenol	1397	–	0.1	–	–	–	–
34	$\beta$ -Caryophyllene	1418	1.0	–	3.5	3.4	2.2	1.8
35	<i>trans</i> - $\alpha$ -Bergamotene	1448	6.0	7.6	–	–	–	–
36	$\alpha$ -Humulene	1459	0.8	1.0	0.3	0.2	–	–
37	Neryl propanoate	1462	–	0.8	–	–	–	–
38	Sesquiterpene 1	1469	–	0.9	0.5	0.4	–	–
39	Geranyl <i>N</i> -propanoate	1479	–	–	–	–	0.3	0.2
40	$\gamma$ -Muurolene	1488	2.8	4.2	2.4	2.1	0.8	1.0
41	Bicyclogermacrene	1508	1.4	1.8	0.6	0.5	–	–
42	$\delta$ -Guaiene	1517	0.9	1.0	–	–	–	–
43	$\gamma$ -Cadinene	1526	2.2	3.1	–	–	–	–
44	Sesquiterpene 2	1529	–	1.0	–	0.3	–	–
45	Calamenene <i>cis</i>	1529	–	1.4	0.3	–	–	–
46	Eugenyl acetate	1533	1.6	–	–	–	–	–
47	Oxygenated sesquiterpene 1	1617	0.9	–	–	–	–	–
48	$\tau$ -Cadinol	1652	5.6	6.7	–	–	0.3	–
49	Oxygenated sesquiterpene 2	1661	0.7	0.6	–	–	–	–
50	<i>cis</i> -Phytol	2116	–	0.9	–	–	–	–
Extraction time (min)		–	30	270	30	270	30	270
Yield (%)		–	0.029	0.028	0.095	0.095	0.160	0.161
Oxygenated fraction (%)		–	82.2	69.6	77.6	63.7	67.1	53.1

L.R.I.: linear retention indices relative to C<sub>8</sub>–C<sub>22</sub> *n*-alkanes on SBP5<sup>TM</sup> capillary column.

<sup>a</sup> Compounds listed in order of elution.

ferred for the two extraction methods. Eugenol is the most abundant component of the SFME extract (43%) and linalool the second most abundant (25%), whereas the HD extract is dominated first by linalol (39%) and then by eugenol (11%). The essential oil of garden mint isolated both by SFME and HD is characterized by an important content in the oxygenated compound carvone respectively, 65% and 52%. Limonene, a monoterpene which is the second most abundant compound, is present at 9.7% and 20%, respectively for SFME and HD. The essential oil of thyme isolated either by SFME and HD contains the same three dominant components: thymol (51% and 41%),  $\gamma$ -terpinene (17% and 23%), and *p*-cymene (7.5% and 11%).

There are slightly fewer compounds present in the chromatograms of essential oils extracted by SFME compared with those obtained by HD. Essential oil from basil extracted by HD and the essential oil from thyme extracted by SFME are the richest in terms of the number of organic compounds. Relatively few new compounds were found as a result of SFME extraction but these were present in very small amounts. The loss of some compounds in SFME compared with HD is probably not that these compounds are not extracted but rather that the reduction in extraction time and the amount of water in the SFME method reduces the degradation of compounds by hydrolysis, *trans*-esterification or oxidation, and hence there are fewer degradation products noted in the analysis.

### 3.3. Cost, energy, and environment ecology

The reduced cost of extraction is clearly advantageous for the proposed SFME method in terms of energy and time. The energy required to perform the two extraction methods are respectively 4.5 kWh for HD, and 0.25 kWh for SFME. At the same time, the calculated quantity of carbon dioxide rejected in the atmosphere is dramatically more in the case of HD (3600 g CO<sub>2</sub> per gram of essential oil) than for SFME (200 g CO<sub>2</sub> per gram of essential oil). Hydro-distillation required an extraction time of 270 min for heating 6 kg of water and 500 g of plant material to the extraction temperature, followed by evaporation of water and essential oil. The SFME method required heating for 30 min only of the plant matter and evaporation of the in situ water and essential oil of the plant material.

## 4. Conclusion

The proposed method of solvent free microwave extraction is an original combination of microwave heating and

dry distillation. It provides more valuable essential oils and allows substantial saving of energy. Additionally, the SFME method offers important advantages over traditional alternatives, namely: shorter extraction times (30 min for SFME method against 4.5 h for hydro-distillation), substantial savings of energy, and a reduced environmental burden (less CO<sub>2</sub> rejected in the atmosphere). All these advantages make SFME a good alternative for the extraction of essential oil from aromatic plants.

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