



Ohmic-assisted hydrodistillation of essential oils from *Mentha piperita*: a comparison with conventional hydrodistillation

Mohsen Gavahian¹, Reza Farhoosh^{2*}, Asgar Farahnaky³, Katayoun Javidnia⁴, Fakhri Shahidi⁵

Received: 2014.03.01

Accepted: 2014.07.21

Abstract

Ohmic-assisted hydrodistillation (OAHD) is an advanced hydrodistillation (HD) technique utilizing ohmic heating process and could be considered as a novel method for the extraction of essential oils. Long extraction time is one of the major problems with traditional methods. OAHD of essential oils from the aerial parts of peppermint was studied and the results were compared with those of the conventional HD. The results showed that OAHD method had the extraction time of 19.71 min while this value was about 55.88 min for HD. Scanning electron micrographs of mint leaves showed a sudden eruption of essential oil glands for OAHD samples. GC-MS analysis did not indicate any noticeable changes in the compounds of the essential oils obtained by OAHD in comparison with HD. The results introduced OAHD as a green technology.

Keywords: Essential oils, GC-MS, Hydrodistillation, Ohmic-assisted hydrodistillation, *Mentha piperita*.

Introduction

Mentha piperita L. (peppermint), a perennial aromatic/medicinal plant belonging to the family Lamiaceae, is a hybrid of *M. spicata* L. (spearmint) and *M. aquatic* (The Wealth of India, 1962). This plant was cultivated by the ancient Egyptians and documented in the Icelandic pharmacopoeia of the thirteenth century. It is widely grown in temperate areas of the world, particularly in Europe, North America and North Africa but nowadays cultivated in other regions of the world including Middle East (Briggs, 1993; The Wealth of India, 1962).

The essential oil of Peppermint is commercially used in food, beverage, pharmaceutical, cosmetics, health and tobacco industries (Carmines, 2002). Tobacco industry consumes about 40% of the total mint essential

oil followed by pharmaceutical and confectionary industries. Usually the major components of peppermint oil include menthol, menthone and menthofuran. Menthol, the main substance that gives the mints their characteristic aromas and flavors, is used as a raw material in toothpaste, toothpowder, chewing tobacco, confectionary, mouth fresheners, analgesic balms, cough drops, perfumes, chewing gums, candies and tobacco industry (The Wealth of India, 1962). The peppermint oil is reported to have anti-oxidant properties (Ribeiro *et al.*, 2002), antibacterial activity (Singh *et al.*, 2011) and is one of the most important constituents of some over-the-counter remedies in Europe for irritable bowel syndrome (Pittler and Ernst, 1998).

Essential oils can be isolated using a number of methods, e.g. hydrodistillation (HD), steam distillation (SD) and organic solvent extraction (Presti *et al.*, 2005). Traditional methods for the extraction of essential oils from medicinal plants/herbs are known to be SD and HD. However, these methods suffer from some disadvantages including losses of volatile compounds and long extraction times and are known to be energy intensive methods. Furthermore,

1, 2 and 5. PhD Student and Professors, Department of Food Science and Technology, Faculty of Agriculture, Ferdowsi University of Mashhad.

3. Associate Professor, Department of Food Science and Technology, School of Agriculture, Shiraz University, Shiraz Iran.

4. Professor, Medicinal & Natural Products Chemistry Research Center, Shiraz University of Medical Sciences Shiraz, Iran.

(* Corresponding author Email: rfarhoosh@um.ac.ir)

elevated temperatures can cause partial or full degradation of natural constituents especially monoterpenes which are vulnerable to structural changes under steam distillation conditions. Conventional solvent extraction method is likely to involve losses of more volatile compounds during removal of the solvent (Presti *et al.*, 2005).

Ohmic heating (also referred to as Joule heating, electroheating and electro conductive heating) is defined as a process wherein an electrical current (usually alternating) is passed through materials and can be used to generate heat within the product (Goullieux & Pain, 2005). The heating occurs in the form of internal energy transformation (from electric to thermal which is due to Joule effect) within the material (Sastry, 2005). Ohmic processing enables to heat materials at extremely rapid rates (generally, from a few seconds to a few minutes) (Sastry, 2005). Electrical conductivity is the main parameter determining the heating rate of an ohmic heating treatment. Ohmic heating only works in water continuous systems (due to necessity of ionic mobility) and materials with low electrical conductivity like oil droplets in mixed systems (i.e. aromatic plant leave) can not be heated directly by ohmic process but oil droplets will be heated almost rapidly thru heat transfer from the direct neighborhood which however is very nearby due to the small dimensions (Goullieux & Pain, 2005). Distilled water is an excellent electrical insulator so in many studies on ohmic technology, salted water is used as the liquid phase for ohmic treatments (Goullieux & Pain, 2005). In the nineteenth century, several patents were filled for the use of direct resistance heating for the sterilization of static liquid foods (Jones, 1897; Roberts, 1900). In 1993, with the Food and Drug Administration (FDA) approval, process of stable low acid foods at ambient temperature became legal. Since then, ohmic heating has been used commercially in Japan, the USA and Europe.

Among novel extraction methods of essential oils, utilizing microwaves for the extraction has been widely studied. Different

extraction methods including HD, microwave-assisted hydrodistillation (MAHD), simultaneous distillation-solvent extraction (SDE) and supercritical fluid extraction (SFE) were reported by Stashenko *et al.* in 2004 for the extraction of essential oils from Colombian *Xylopiya aromatica* (Lamarck) (Stashenko *et al.*, 2004). MAHD was compared with HD in the extraction of essential oils from *Thymus vulgaris* L. (Golmakani & Rezaei, 2008).

Ohmic heating technology presents a large number of actual and potential future applications, including its use in blanching, evaporation, dehydration, fermentation, extraction (USA-FDA, 2000), sterilization, pasteurization and heating of foods to serving temperature in the military field or long-duration space missions (Sastry *et al.*, 2009). Ohmic extraction is one way of using ohmic heating in an extraction process. Ohmic heating as an alternative extraction technique of medicinal plants was first reported by Sensoy and Sastry (2004). Since then, numerous studies have sought the applicability of this new approach for the extraction of materials (Lakkakula *et al.* 2004). Gavahian *et al.* (2011) used a combination of ohmic heating and distillation for separation of essentials oils from *Zataria multiflora* Boiss. (Shirazi thyme) and found significant reductions in extraction time and consumed energy for ohmic-assisted hydrodistillation (OAHD) compare to traditional hydrodistillation method. This research team also reported similar results on OAHD for *Thymus vulgaris* and *Myrtus communis* (Gavahian *et al.* 2012-2013). Nonetheless, due to the lack of enough information it seems that more research is needed to fully explore advantages and disadvantages of OAHD for extraction of essential oils from other medicinal plants.

Despite many studies reported on the different methods of extraction of essential oils from *M. piperita*, there is no report on the extraction of essential oils from this medicinal plant using OAHD. Therefore, the aim of this work was to use OAHD technique for the extraction of essential oils from dried

peppermint areal parts and to compare the extraction parameters and composition of the extracted essential oils with those obtained by conventional HD as the reference method.

Materials and methods

Plant materials

Fresh aerial parts of *Mentha piperita* when the plant has enough foliage (before flowering stage) were collected from an indigenous crop in Noor-Abad (Mamasani, Southern Iran), in July 2013.

The identity of the genus *Mentha* was certified by plant taxonomy experts from Biology Department of the Shiraz University, Shiraz, Iran. The herbs were then dried in a dark room under ambient conditions (30-40°C) for four days on a large screened tray, packed in high density poly ethylene (HDPE) bags, put in a cardboard box and kept in a dark and cool place for further experiments. The moisture content of the plants was measured in triplicate using a laboratory oven by drying until constant weight and was about 12.4±0.2%.

OAHD

OAHD was performed using an ohmic distillator device with platinum electrodes as designed and developed by Farahnaky *et al.*,

2010, in the Department of Food Science and Technology of Shiraz University. Processing parameters (e.g. processing time, temperature and power consumption), were precisely monitored using a software developed and coupled with a Wattmeter to record the input power of ohmic apparatus to double check the data given by the software. OAHD was performed at 220 V, 50 Hz and variable current values depending on the process time. Figure 1 shows the schematic representation of the procedure.

As shown in Figure 1 in OAHD procedures, 30 g of dried peppermint aerial parts and 0.5 L salted water (1 NaCl%, w/v) were heated in the apparatus flask for up to 2 h from initial temperature of 27±1°C (similar to initial temperature of material in HD method). The extraction process continued until no more essential oils were obtained. During the first 12 min, the amount of collected essential oils was recorded at 1 min intervals. After the first 12 min of extraction, recording of the amount of essential oils continued at 5 min intervals up to 1 h and afterwards at 15 min intervals. To remove water, the extracted essential oils were then dried over anhydrous sodium sulfate and stored in amber vials at 4°C for further experiments.

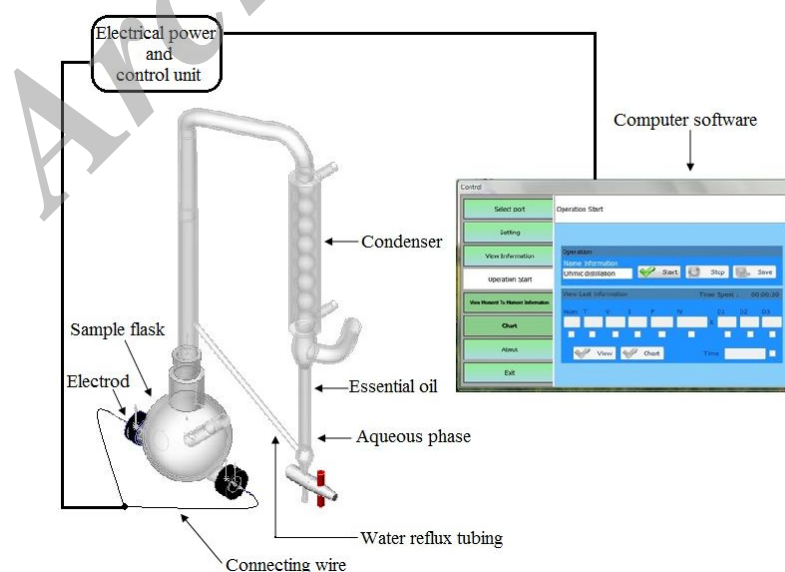


Fig. 1. Schematic representation of the ohmic-assisted hydrodistillator apparatus used in this study

Hydrodistillation

HD is an approved method that is used as a reference for the quantification of essential oils (Stahl-Biskup, 2002). HD was carried out in a similar way as OAHD, using a laboratory heater (MAG-K; Gerhardt Ltd., Germany; and 500 W) instead of ohmic distillator. The volume and dimensions of the utilized container were exactly similar to that used for the ohmic distillator device. In addition, processing parameters (*i.e.* temperature and energy consumption) were monitored using the designed software. Alternatively, the input power consumption was monitored using a separate Wattmeter at the entrance of electrical heater power supply (*i.e.* at the entrance of ohmic apparatus power supply). Thirty grams of dried peppermint aerial parts with 0.5 L distilled water were put into HD with a Clevenger-type apparatus, and essential oils were extracted for 2 h, after which no more essential oils were obtained. During the first 1 h, the collected essential oils were decanted from the condensate at 2.5-min intervals followed by decanting of the essential oils every 30-min. As OAHD can only be operated for electrically conductive solutions (*i.e.* salted water should be used instead of distilled water) (Goullieux & Pain, 2005) and to study the effect of the presence of salt in water on the mint extraction, another extraction treatment, *i.e.* salted hydrodistillation (SHD), was performed at the described conditions for HD, except for SHD 1% NaCl was dissolved in distilled water before the extraction. Removal of water from essential oils was performed as described for OAHD samples. The extracted essential oils were then stored in a cool (4 °C) and dry place for further experiments.

Physical constants

Specific gravity and the refractive index of the essential oils from the mint samples were measured according to Food Chemical Codex (FCC) (FCC, 1996) at 25 and 20 °C, respectively. The color parameters of the oils (L: lightness, a: redness-greenness and b: blueness-yellowness) were determined according to the method described by Afshari-

Jouybari & Farahnaky (2011). In addition, the color of the oils was determined visually as directed in FCC (FCC, 1996).

Scanning electron microscopy (SEM)

SEM images of dried peppermint leaves were obtained for the untreated samples as well as for those extracted by OAHD (for 30 min) and HD (for 60 min) after two different extraction methods: using salted water or salted hydrodistillation method (SHD) and using distilled water or normal hydrodistillation method (NHD). The leaves were freeze-dried using a freeze drier (Armfield, UK) and fixed on the aluminum sample holder and then sputtered with gold in a sputter coater (Polaron SC7640, UK). All the samples were examined with a scanning electron microscope (Cambridge, UK) under high-vacuum condition and at an accelerating voltage of 20.0 kV and at a working distance of 7.5–9.5 mm (*i.e.* the distance between the surface of the sample and the microscope lens).

Gas chromatography-Mass spectrometry (GC-MS)

GC-MS analysis of the essential oils was performed using an Agilent 7890A chromatograph, coupled with Agilent 5975C mass spectrometer (Agilent Technologies, USA), operating at 70 eV ionization energy, 0.5 s/scan and the mass range: 35-400, equipped with a HP-5MS capillary column (phenyl methyl siloxane, 30 m×0.25 mm; 0.25 μm film thickness). The oven temperature increased from 60 to 240°C at a rate of 3°C/min, the injector and detector temperatures were 240°C and 250°C, respectively. Helium was used as the carrier gas with a flow rate of 0.9 mL/min and a split ratio of 1:50. Relative percentage data were obtained from electronic integration of peak areas without the use of correction factor. The software adopted to handle mass spectra and chromatograms was ChemStation.

Retention indices were determined by using retention times of normal alkanes that had

been injected after the oil under the same chromatographic conditions according to the Van Den Dool & Kratz method (Van Den Dool & Kratz, 1963). The compounds were identified by comparison of their mass spectra with the Wiley library or with the published mass spectra.

Statistical analysis

All extractions with HD and OAHD were performed in triplicates. Analysis of variance (ANOVA) was performed to determine significant differences between the means and Duncan multiple range tests was used to compare among the means using SPSS (version 19.0.0; IBM Institute Inc., USA).

Results and discussion

Comparison of temperature profiles of the extraction methods

The temperature profiles during OAHD,

NHD and SHD extractions are shown in Figure 2a. To reach extraction temperature (about 100 °C) and thus obtain the evaporation of the first essential oil droplets with steam, it was necessary to heat the mix for 6.10 ± 0.19 min in OAHD while it was more than 30 min for HD (30.76 ± 2.84 min for NHD and 30.52 ± 3.88 for SHD).

The rate of temperature raise was obtained from the slope of the linear part of temperature profile (Figure 2a). Table 1 shows that this parameter in OAHD was almost 5.5 times greater than that of HD. These data also indicate that there was no significant difference between NHD and SHD in terms of rate of temperature increase. This finding was in line with previous reports (Gavahian *et al.*, 2011, 2012).

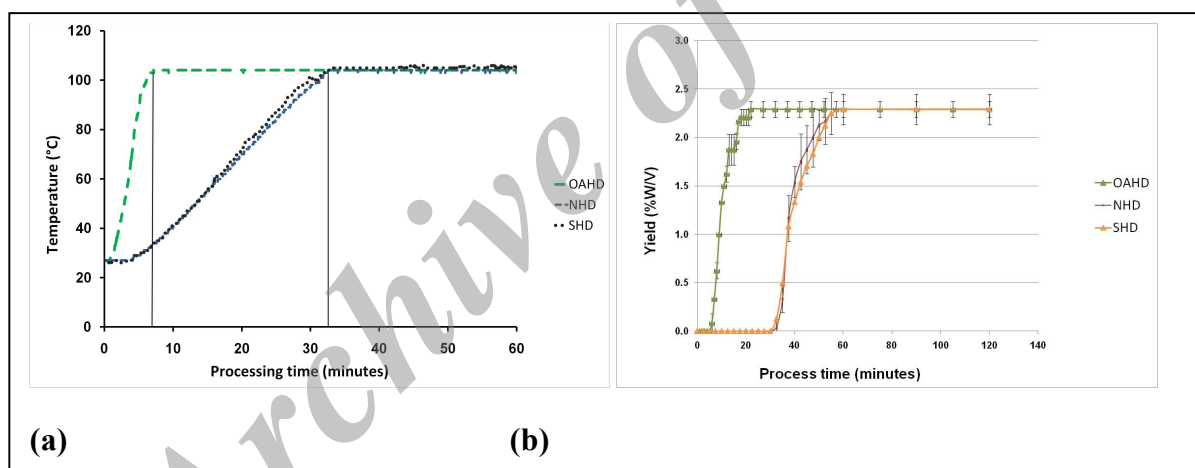


Fig. 2. (a) Temperature-time profile of materials and (b) Extraction yield (ml essential oils/100 g dried herb) as a function of time for HD (NHD and SHD) and OAHD of essential oils from peppermint aerial parts.

Table 1. Effect of extraction method on rate of temperature raise, come up time to reach 100 °C, starting time of oil accumulation, extraction duration, total extraction time, rate of essential oils accumulation, yield and energy consumption.

	OAHD	HD	
		NHD	SHD
Rate of temperature increase (°C/min)	$15.7^a \pm 0.8$	$2.8^b \pm 0.7$	$2.9^b \pm 0.6$
Come up time to reach 100 °C (min)	$6.10^b \pm 0.19$	$30.76^a \pm 2.84$	$30.52^a \pm 3.88$
Starting time of oil accumulation (min)	$6.17^b \pm 0.50$	$34.16^a \pm 1.93$	$33.33^a \pm 1.17$
Extraction duration (min)	$13.33^b \pm 2.05$	$21.72^a \pm 4.52$	$21.83^a \pm 2.68$
Total extraction time (min)	$19.71^b \pm 2.58$	$55.88^a \pm 3.30$	$55.17^a \pm 3.25$
Rate of essential oils accumulation (ml/min)	$0.061^a \pm 0.015$	$0.048^b \pm 0.006$	$0.046^b \pm 0.004$
Yield (%V/W)	$2.29^a \pm 0.08$	$2.29^a \pm 0.16$	$2.29^a \pm 0.08$
Electric consumption (kWh/ml essential oils)	$0.135^{b*} \pm 0.011$	$0.689^a \pm 0.081$	$0.677^a \pm 0.041$
CO ₂ rejected (g/ ml essential oils)	$108.3^b \pm 8.7$	$551.8^a \pm 64.8$	$541.7^a \pm 32.9$

* The same letters in each row indicate that the means are not significantly different ($p < 0.05$).

Comparison of extraction kinetics and extraction yield

The extraction kinetics of essential oils from peppermint using OAHD was compared with that of HD (NHD and SHD) (Figure 2b). Extraction with OAHD started much earlier than HD methods (about 6 min for OAHD and more than 34 min for HD). This is due to the more efficient heating in the ohmic system. Unlike the classical conductive heating methods, ohmic heating can heat the entire sample almost simultaneously and at a higher rate, therefore it is able to generate heat deep inside products rapidly (Goullieux & Pain, 2005; Sastry, 2005). In addition, no significant difference was observed between NHD and SHD methods in terms of starting time of extraction. This means that the addition of sodium chloride (1% w/v) did not affect the starting time of extraction of the mint in the traditional heating system.

Table 1 shows the effect of extraction method on yield, starting time of oil accumulation, extraction duration, total extraction time and rate of essential oils accumulation. As the data shows, by the time the extraction of essential oils with HD started (i.e. about 34 min), almost all of extractable essential oils had been extracted with OAHD. After extraction time of 20 min, OAHD resulted in a similar oil recovery to that obtained by HD after more than 55 minutes.

The rates of essential oils accumulation of OAHD and HD are shown in Table 1. This parameter was obtained from the slope of linear part of each graph in Figure 2b by dividing the amount of extracted oils (ml) to its corresponding time (min), which is equal to the mean rate of essential oils accumulation (ml/min). The results show that OAHD isolates essential oils almost 27% faster than the conventional HD method. On the other hand, in terms of the rate of essential oils accumulation there was not any significant difference between NHD and SHD. This data illustrates that the rate of extraction in OAHD was greater. In addition, OAHD method has shorter extraction duration time (i.e. the

difference between total needed extraction time and starting time of oil accumulation). This is due to higher extraction rate in OAHD. As can be seen in Figure 2b, extraction graphs of OAHD method are steeper than HD graphs. Because of low electrical conductivity of essential oils and dry material (such as dried mint leaves), OAHD is only enable to heat the vicinity of this material rapidly i.e. ohmic heating only works in water continuous phase (due to necessity of ionic mobility) and the materials with low electrical conductivity like oil droplets in mixed systems (i.e. aromatic plant leave) cannot be heated directly by ohmic process. Despite this restriction, the glands which contain oil droplets will be heated almost rapidly thru the heat transferring from the direct neighborhood which however is very nearby due to the small dimensions (Goullieux & Pain, 2005). These phenomena (direct ohmically heating of aqueous phase which containing plant material without direct ohmically heating of jailed essential oils in glands) can be considered as an advantage of OAHD. If oil droplets were capable to be heated ohmically, they may undergo thermal degradation during OAHD. So the volatile mint oils can be isolated faster and approximately same oil properties are prospected (i.e. no structural change or chemical degradation of isolated oil is expected due to direct thermal effect of ohmic heating).

The essential oil content of medicinal plants can be influenced by harvest time, ecological and climatic conditions (i.e. Clark *et al.*, 1980; Tabatabaie & Nazari, 2007; Khorasaninejad *et al.*, 2010; Baranauskiene, 2003). It was previously reported that the oil content of peppermint can vary by harvest time from 0.72% to more than 3% and oil yield of peppermint depends on growing stage (White *et al.*, 1987). Similarly, Tabatabaie & Nazari (2007) reported that the essential oil content of peppermint can vary from less than 2% to more than 4% by changing farming conditions (soil nutrient solutions and salinity).

Structural changes during the extraction of essential oil

The images of mint glands on the leaves obtained by scanning electron microscopy before and after the extraction process are shown in Figure 3. Figure 3a is a micrograph of the untreated gland (*i.e.* before the extraction). Figure 3b, c and d show the SEM images of peppermint glands that had undergone NHD (60 min), SHD (60 min) and OAHD (30 min), respectively. The three extraction methods resulted in clear physical changes in the glands. The glands that had undergone HD (NHD and SHD) were wrinkled while those that had undergone OAHD were not and presented smoother surfaces. The mint leaves that had undergone OAHD showed eruption of essential oil glands and their surrounding area. This phenomenon can be related to the high rate of heat transfer resulting from the extraction method. In OAHD, the heat is generated rapidly inside the sample; in contrast, in HD the heat transfer is mainly performed slowly by conduction and convection only (Goullieux & Pain, 2005). As a result, in OAHD, heat is generated very rapidly all over the sample with adequate electrical conductivity (*i.e.* in surrounding area of the glands) and penetrates suddenly to other areas (like glands) according to Fourier's law (mainly because of high local temperature gradient and small dimension of particles which lead to high local heat flux). This event may be one of the reasons for sudden eruption of the glands which undergo OAHD. Ferhat et al. (2006) studied the solvent-free microwave extraction of fresh orange peels, and reported that when the glands were subjected to more severe thermal stresses and localized high

pressures, as in the case of microwave heating, the pressure build-up within the glands could exceed their capacity for expansion and as a result it causes their rupture more rapidly than in conventional extraction using HD. Similar results were obtained for the extraction of essential oils from *Zataria multiflora* Boiss. and *Thymus vulgaris* L. using OAHD (Gavahian *et al.*, 2011, 2012).

Physical constants evaluation

The physical properties (specific gravity, refractive index and color) of mint essential oils extracted by OAHD and HD (NHD and SHD) are shown in Table 2. There is no significant difference between OAHD and HD for the specific gravity and refractive indices. Every essential oil has a typical range of refractive indexes and densities at specified temperatures. Generally, the densities of essential oils range from 0.780 to 0.970 g.cm⁻³ (Bowles, 2003). Similarly, sensory color perceptions of all samples were similar and within the range indicated by FCC.

From the physical tests of the extracted essential oils, it can be concluded that OAHD, as a new extraction technique, did not introduce any considerable changes to the studied physical properties of the essential oils extracted from the aerial parts of mint.

GC-MS

The identified components in the extracted essential oils of peppermint aerial parts by OAHD and HD (NHD and SHD) are given in Table 2. The 34 components presented in Table 2 comprise more than 98.6% of the total GC peak areas.

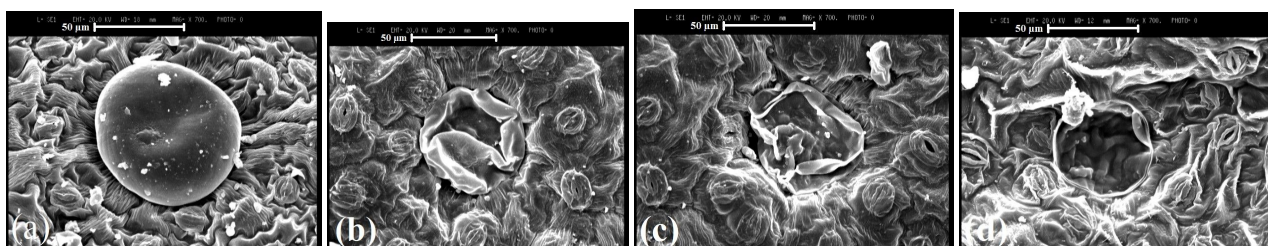


Fig. 3. Scanning electron micrographs of the glands from mint leaves: (a) untreated, (b) after NHD for 60 min, (c) after SHD for 60 min and (d) after OAHD for 30 min.

Table 2. Physical properties and chemical compositions of essential oils of mint aerial parts extracted by OAHD, NHD and SHD using GC-MS.

No.	Compound Name	KI*	KI**	Relative peak are [%]***		
				OAHD	NHD	SHD
1	(2E)-Hexenal	854	855	t ^a	t ^a	t ^a
2	α -Thujene	928	930	t ^a	t ^a	t ^a
3	α -Pinene	937	939	0.8 ^a ±0.0	0.7 ^b ±0.0	0.7 ^b ±0.0
4	Camphene	954	954	t ^a	t ^a	t ^a
5	Sabinene	973	975	0.5 ^a ±0.1	0.5 ^a ±0.0	0.5 ^a ±0.1
6	β -Pinene	977	979	1.3 ^a ±0.1	1.3 ^a ±0.1	1.3 ^a ±0.2
7	Myrcene	989	990	0.2 ^a ±0.0	0.2 ^a ±0.0	0.2 ^a ±0.1
8	p-Mentha-1(7),8-diene	1006	1008	t ^a	t ^a	t ^a
9	α -Terpinene	1018	1017	0.1 ^a ±0.0	0.1 ^a ±0.0	0.1 ^a ±0.0
10	Limonene	1029	1029	t ^a	t ^a	t ^a
11	1,8-Cineole	1033	1031	8.5 ^a ±0.4	7.5 ^a ±0.7	8.1 ^a ±0.4
12	(Z)- β -Ocimene	1037	1037	2.8 ^a ±0.2	3.1 ^a ±0.6	2.7 ^a ±0.1
13	(E)- β -Ocimene	1048	1050	0.1 ^a ±0.0	0.1 ^a ±0.0	0.1 ^a ±0.0
14	γ -Terpinene	1059	1059	1.6 ^a ±0.0	0.9 ^b ±0.0	0.8 ^b ±0.1
15	Terpinolene	1087	1088	t ^b	0.1 ^a ±0.0	0.1 ^a ±0.0
16	trans-Sabinene hydrate	1099	1098	0.2 ^a ±0.0	0.2 ^a ±0.0	0.2 ^a ±0.1
17	iso-Menthone	1164	1162	26.1 ^{ab} ±0.3	26.4 ^a ±0.0	25.6 ^b ±0.5
18	Menthofuran	1166	1164	16.3 ^a ±0.0	15.5 ^b ±0.0	16.2 ^a ±0.3
19	neiso-Menthol	1188	1186	28.7 ^c ±0.3	30.3 ^b ±0.1	30.9 ^a ±0.3
20	Pulegone	1239	1237	5.5 ^a ±0.1	5.4 ^a ±0.0	5.6 ^a ±0.2
21	Piperitone	1254	1252	0.3 ^a ±0.0	0.2 ^b ±0.0	0.3 ^{ab} ±0.1
22	neo-Menthyl acetate	1274	1273	0.3 ^b ±0.0	0.4 ^a ±0.0	0.4 ^a ±0.1
23	Menthyl acetate	1293	1295	2.6 ^b ±0.0	2.9 ^a ±0.0	2.2 ^c ±0.2
24	iso-Menthyl acetate	1306	1305	0.1 ^b ±0.0	0.2 ^b ±0.0	0.2 ^a ±0.1
25	β -Bourbonene	1387	1388	0.1 ^a ±0.0	0.2 ^a ±0.0	0.2 ^a ±0.0
26	β -Elemene	1389	1390	t ^a	t ^a	t ^a
27	(E)-Caryophyllene	1416	1419	1.1 ^a ±0.1	1.2 ^a ±0.0	1.2 ^a ±0.2
28	β -Copaene	1430	1432	t ^a	t ^a	t ^a
29	(E)- β -Farnesene	1454	1456	0.1 ^a ±0.0	0.1 ^a ±0.0	0.1 ^a ±0.0
30	Germacrene D	1486	1485	0.9 ^a ±0.0	0.8 ^b ±0.0	0.8 ^b ±0.1
31	Bicyclgermacrene	1498	1500	0.1 ^a ±0.0	0.1 ^a ±0.0	0.1 ^a ±0.0
32	Germacrene A	1506	1509	t ^a	t ^a	t ^a
33	δ -Amorphene	1515	1512	t ^a	t ^a	t ^a
34	Caryophyllene oxide	1580	1583	0.1 ^b ±0.0	0.1 ^b ±0.0	0.2 ^a ±0.0
Total		-	-	98.6	98.7	98.7
Physical properties						
Specific gravity				0.9089 ^a ± 0.0069	0.9089 ^a ± 0.0071	0.9091 ^a ± 0.0059
Refractive index				1.4377 ^a ± 0.0300	1.4377 ^a ± 0.0391	1.4324 ^a ± 0.0468
Appearance				Plae yellow	Pale yellow	Pale yellow
L [#]				62.0 ^a ± 3.6	61.0 ^a ± 3.6	62.7 ^a ± 2.5
a				-1.3 ^a ± 0.6	-3.3 ^a ± 1.5	-1.0 ^a ± 1.0
b				10.0 ^a ± 3.6	10.7 ^a ± 3.5	11.3 ^a ± 2.5

* Experimentally determined Kovats retention index (KI) relative to C19-C18 n-alkanes on the DB-5MS column (Kovats, 1965).

** Literature Kovats retention index (Adams, 2007)

[#] L: lightness, a: redness-greenness and b: yellowness-blueness.

*** t=trace (<0.05), Mean ± SD (n=3), The same letters in each row indicate that the means are not significantly different ($p < 0.05$).

The compositions of the essential oils obtained by HD and OAHD were almost similar and as a result, components extracted by NHD were also found in OAHD. Also, there were slight but significant differences between the quantities of some components extracted by HD and those extracted by OAHD (for example compound No. 3, α -pinene). This theme is also observed for NHD

and SHD (for example compound No. 17, iso-Menthone). Similar results were obtained for the extraction of essential oils by MAHD (Stashenko *et al.*, 2004) and OAHD (Gavahian *et al.*, 2011, 2012). In the current study, the main compounds of all three essential oils were neiso-Menthol (compound No. 19), iso-menthone (compound No. 17) and menthofuran (compound No. 18). The

essential oil composition of many aromatic plants can be influenced by harvest time, ecological and climatic conditions (Baranauskiene, 2003). Many reports have already confirmed the main components reported in this survey to be the most abundant components in *Mentha piperita* L. essential oil (i.e. Clark *et al.*, 1980; Tabatabaie & Nazari, 2007; Khorasaninejad *et al.*, 2010)

Cost, cleanliness and scale-up

In terms of time and energy, the reduced cost of extraction is clearly an advantage for the proposed OAHD method (Table 1). As shown in Figure 2b, the traditional method (HD) requires an initial time of 34 min for heating 0.5 L of water containing 30 g of mint before the extraction begins while OAHD required less than 20 min for complete the extraction process, resulting in a significant reduction in the extraction time. The energy requirement to perform the extraction, based on the power consumptions of the electromantle for 1 ml of extracted oils, was 0.7 kWh for HD (NHD and SHD) while this value was 0.1 kWh for OAHD. This indicates a substantial saving in the extraction cost by OAHD compared to the conventional extraction technique, HD.

Regarding environmental impacts, the calculated quantity of carbon dioxide (the primary greenhouse gas) emitted to the atmosphere is higher in the case of NHD (552 g CO₂/ml of essential oils) and SHD (542 g CO₂/ml of essential oils) than for OAHD (108 g CO₂/ml of essential oils). In other words, the emitted carbon dioxide by OAHD is about 24 percent of HD for extraction of equal volume of essential oils. These calculations have been made according to the literature: to obtain 1 kWh from coal or fuel, i.e. 800 g of CO₂ will be emitted to the atmosphere during combustion of fossil fuels (Ferhat *et al.*, 2006).

Based on the findings of this research and the previously reported data on OAHD by this group, OAHD is therefore suggested as an “environmentally friendly” extraction method

(from energy consumption view point), which also avoids the use of organic solvents typical to solvent extraction methods. In addition, unlike the novel extraction technique of MAHD, OAHD lacks the risk of radiation leakage and its hazards to the operators. OAHD can also be proposed for the production of larger quantities of essential oils by scaling up of the equipment to be used instead of the conventional HD apparatus.

Conclusion

In this study, OAHD was presented as an “environmentally friendly” extraction method suitable for essential oils extraction. OAHD resulted in a reduced extraction time and a substantial energy saving compared to the conventional HD technique. After 20 min of OAHD extraction, it was possible to collect almost all the existing essential oils of the mint, whereas HD provided the first drops of essential oils after 34 min and almost all the existing essential oils was collected after 56 min. SEM images of mint leaves having undergone OAHD and HD indicated that ohmic heating causes a quick rupture of essential oil glands, resulting in accelerating extraction process. Essential oils obtained by HD and OAHD were almost similar in their compositions. In addition, the results indicate that using 1% NaCl did not have any adverse effects on the extractions parameters and quality of obtained essential oils. Compared to many other solvent extraction techniques, OAHD can be considered as a green technology since it consumes significantly less energy to operate and, in addition, it does not require any organic solvent for the extraction. Such advantages could make OAHD an excellent alternative extraction method for extraction of essential oils. The findings of this research were in line with the previous papers on the application of OAHD. Further investigations are required on large scale ohmic assisted hydrodistillation.

References

- Afshari-Jouybari, H., & Farahnaky, A., 2011, Evaluation of Photoshop software potential for food colorimetry. *Journal of Food Engineering*, 106, 170-175.
- Baranauskienė, R., Venskutonis, P. R., Viskelis, P., & Dambrauskienė, E., 2003, Influence of nitrogen fertilizers on the yield and composition of thyme (*Thymus vulgaris*). *Journal of Agricultural and Food Chemistry*, 51, 7751–7758.
- Bowles, E. J., 2003, The chemistry of aromatherapeutic oils. Allen & Unwin.
- Carmines, E.L., 2002, Evaluation of the potential effects of ingredients added to cigarettes. Part 1: cigarette design, testing approach, and review of results. *Food and Chemical Toxicology*, 40 (1), 77–91.
- Clark, R. J., & Menary, R. C., 1980, Environmental effects on peppermint (*Mentha piperita* L.). I. Effect of day length, photon flux density, night temperature and day temperature on the yield and composition of peppermint oil. *Functional Plant Biology*, 7(6), 685-692.
- Farahnaky, A., Gavahian, M., & Mehraban-Jahromi, M. H., 2010, Design and development of ohmic distillatory device with ability of process monitoring and controlling. Iran patent NO. 63627.
- FCC: *Food Chemical Codex*. 1996. 4th Ed., Pp. 413. Washington, DC USA: National Academic Press.
- Ferhat, A. M., Meklati, Y. B., Smadja, J., & Chemat, F., 2006, An improved microwave Clevenger apparatus for distillation of essential oils from orange peel. *Journal of Chromatography A*, 1112, 121–126.
- Gavahian, M., Farahnaky, A., Javidnia, K., & Majzoobi, M., 2013, A novel technology for extraction of essential oil from *Myrtus communis*: ohmic-assisted hydrodistillation. *Journal of Essential Oil Research*, 25 (4), 257-266.
- Gavahian, M., Farahnaky, A., Javidnia, K. & Majzoobi, M., 2012, Comparison of ohmic-assisted hydrodistillation with traditional hydrodistillation for the extraction of essential oils from *Thymus vulgaris* L. *Innovative Food Science and Emerging Technologies*, 14, 85-91.
- Gavahian, M., Farahnaky, A., Majzoobi, M., Javidnia, K., Saharkhiz, M. J., & Mesbahi, G. R., 2011, Ohmic-assisted hydrodistillation of essential oils from *Zataria multiflora* Boiss (Shirazi thyme). *International Journal of Food Science & Technology*, 46, 2619–2627.
- Golmakani, M. T., & Rezaei, K., 2008, Comparison of microwave-assisted hydrodistillation with the traditional hydrodistillation method in the extraction of essential oils from *Thymus vulgaris* L. *Food Chemistry*, 109, 925-930.
- Goullieux, A., & Pain, J. P., 2005, Ohmic Heating. In: D.W. Sun (Eds.), *Emerging Technologies for Food Processing*. (pp. 469-505). London, UK: Elsevier Academic Press.
- Khorasaninejad, S., Mousavi, A., Soltanloo, H., Hemmati, K., & Khalighi, A., 2010. The effect of salinity stress on growth parameters, essential oil yield and constituent of peppermint (*Mentha piperita* L.). *World Applied Sciences Journal*, 11(11), 1403-1407.
- Lakkakula, N. R., Lima, M., & Walker, T. (2004). Rice bran stabilization and rice bran oil extraction using ohmic heating. *Bioresource Technology*, 92(2), 157–161.
- Pittler, M. H., & Ernst, E., 1998, Peppermint oil for irritable bowel syndrome: a critical review and metaanalysis. *The American Journal of Gastroenterology*, 93(7), 1131-1135.
- Presti, M., Ragusa, S., Trozzi, A., Dugo, P., Visinoni, F., Fazio, A., Dugo, G. & Mondello, L., 2005, A comparison between different techniques for the isolation of rosemary essential oil. *Journal of Separation Science*, 28(3), 273-280.
- Ribeiro, M.A., Martins, M.M., Esquivel, M.M. & Bernardo-Gil, M.G., 2002, Peppermint supercritical CO₂ extraction. Influence of extraction conditions on the antioxidant activity of the residues. *Informacion Tecnologica*, 13 (3), 185–190.
- Sastry, S. K., 2005, Advances in ohmic heating and moderate electric field (MEF) processing. In G. V. Barbosa-Cánovas, M. S. Tapia, & M. P. Cano (Eds.), *Novel food processing technologies* (pp. 491–500). Boca Raton, FL, USA: CRC Press.
- Sensoy, I., & Sastry, S. K., 2004, Extraction using moderate electric fields. *Journal of Food Science*, 69(1), FEP7-FEP13.
- Singh, R., Shushni, M. A., & Belkheir, A., 2011, Antibacterial and antioxidant activities of *Mentha piperita* L. *Arabian Journal of Chemistry*. (In Press, Corrected Proof)
- Stashenko, E. E., Jaramillo, B. E., & Martinez, J. R., 2004, Analysis of volatile secondary metabolites from Colombian *Xylopiya aromatica* (Lamarck) by different extraction and headspace methods and gas

- chromatography. *Journal of Chromatography A*, 1025, 105–113.
- Tabatabaie, S. J., & Nazari, J., 2007, Influence of nutrient concentrations and NaCl salinity on the growth, photosynthesis, and essential oil content of peppermint and lemon verbena. *Turkish Journal of Agriculture and Forestry*, 31(4), 245.
- The Wealth of India., 1962, A dictionary of Indian raw materials and industrial products. Raw material series, (Vol. 5, pp. 342–343.). Publication and information directorate, New Delhi: CSIR.
- White, J. G. H., Iskandar, S. H., & Barnes, M. F., 1987, Peppermint: effect of time of harvest on yield and quality of oil. *New Zealand Journal of Experimental Agriculture*, 15(1), 73-79.
- Yadegarinia, D., Gachkar, L., Rezaei, M. B., Taghizadeh, M., Astaneh, S. A., & Rasooli, I., 2006, Biochemical activities of Iranian *Mentha piperita* L. and *Myrtus communis* L. essential oils. *Phytochemistry*, 67(12), 1249-1255.
- Zhang, H., Feng, C. & Wang, X., 2006, Evaluation of Antioxidant Activity of Parsley (*Petroselinum crispum*) Essential Oil and Identification of Its Antioxidant Constituents. *Food Chemistry*, 39, 833-839.

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تقطیر مقاومتی اسانس از گیاه نعنای فلفلی: مقایسه با روش‌های رایج تقطیر آبی

محسن گواهیان^۱ - رضا فرهوش^{۲*} - عسگر فرحناکی^۳ - کتایون جاویدنیا^۴ - فخری شهیدی^۵

تاریخ دریافت ۱۳۹۲/۱۲/۱۰

تاریخ پذیرش ۱۳۹۳/۴/۳۰

چکیده

تقطیر مقاومتی نوعی روش تقطیر با آب پیشرفته است که از حرارت دهی مقاومتی استفاده نموده و می‌تواند به عنوان روشی نوین جهت استخراج اسانس در نظر گرفته شود. زمان طولانی استخراج یکی از مشکلات اصلی روش‌های سنتی است. در این پژوهش، استخراج اسانس از گیاه نعنای فلفلی به روش تقطیر مقاومتی انجام شد و نتایج حاصله با نتایج مربوط به روش سنتی تقطیر با آب مقایسه گردید. یافته‌ها نشان داد که زمان استخراج در روش تقطیر مقاومتی ۱۹/۱۷ دقیقه بود در حالی که این پارامتر برای روش تقطیر با آب ۵۵/۸۸ گزارش شد. بررسی تصاویر میکروسکوپ الکترونی برگ‌های نعنای بیانگر تخریب ناگهانی غدد در بر گیرنده اسانس در روش تقطیر مقاومتی بود. نتایج مربوط به کروماتوگرافی گازی-طیف سنجی جرمی نشان داد که روش تقطیر مقاومتی تغییر قابل ملاحظه‌ای در ترکیب شیمیایی اسانس‌های استخراجی در مقایسه با روش تقطیر با آب ایجاد نکرد. یافته‌های این پژوهش، روش تقطیر مقاومتی را به عنوان یک روش دوست دار محیط زیست معرفی نمود.

واژه‌های کلیدی: اسانس، تقطیر با آب، تقطیر مقاومتی، نعنای فلفلی، کروماتوگرافی گازی-طیف سنجی جرمی

۱، ۲ و ۵ - به ترتیب دانشجوی دکتری و استادان گروه علوم و صنایع غذایی، دانشکده کشاورزی، دانشگاه فردوسی مشهد.

۳- دانشیار، گروه علوم و صنایع غذایی، دانشکده کشاورزی، دانشگاه شیراز.

۴- استاد، مرکز تحقیقات شیمی دارویی و گیاهی، دانشگاه علوم پزشکی شیراز.

*- نویسنده مسئول : (Email: rfarhoosh@um.ac.ir)