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Solvent-free microwave extraction of essential oil from aromatic herbs: From laboratory to pilot and industrial scale

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ABSTRACT

Solvent-free microwave extraction (SFME) has been proposed as a green method for the extraction of essential oil from aromatic herbs that are extensively used in the food industry. This technique is a combination of microwave heating and dry distillation performed at atmospheric pressure without any added solvent or water. The isolation and concentration of volatile compounds is performed in a single stage. In this work, SFME and a conventional technique, hydro-distillation HD (Clevenger apparatus), are used for the extraction of essential oil from rosemary (*Rosmarinus officinalis* L.) and are compared. This preliminary laboratory study shows that essential oils extracted by SFME in 30 min were quantitatively (yield and kinetics profile) and qualitatively (aromatic profile) similar to those obtained using conventional hydro-distillation in 2 h. Experiments performed in a 75 L pilot microwave reactor prove the feasibility of SFME up scaling and potential industrial applications.

1. Introduction

Solvent-free microwave extraction (SFME) was developed in 2004 by Chemat et al. Lucchesie Chemat Smadja (2004a), (2004b). Based on a relatively simple principle, this process consists of the microwave-assisted dry distillation of a fresh plant matrix without adding water or any organic solvent. SFME is neither a modified microwave-assisted extraction (MAE) which uses organic solvents, nor a modified hydro-distillation (HD) which use a large quantity of water (Fig. 1). The selective heating of the *in situ* water content of plant material causes tissues to swell and makes the glands and oleiferous receptacles burst. This process thus frees essential oil, which is evaporated by azeotropic distillation with the water present in the plant material (Li et al., 2013). The water excess can be refluxed to the extraction vessel to restore the original water to the plant material. This process has been applied to several kinds of fresh and dry plants, such as spices (ajowan, cumin and star anise), aromatic herbs (basil, mint and thyme) and citrus fruits. Table 1 summarises the most important essential oils that have been extracted by SFME.

More efficient SFME can be attained on samples that show higher dielectric loss (high water content), because of the strong interaction that microwaves have with the, salt and nutrient containing, physiological water. Thus, the matrix undergoes dramatic swelling and subsequent tissue rupture, enabling the essential oil to flow towards the water layer. This mechanism (I) is also based on the ability of essential oil components to dissolve in water. In fact, solubilisation is the limiting step and solubility becomes the essential parameter in SFME selective extraction. Essential oils contain organic compounds that strongly absorb microwave energy (mechanism II). Compounds with high and low dipolar moments can be extracted in various proportions by microwave extraction. Organic compounds that have a high dipolar moment will interact more vigorously with microwaves and can be extracted more easily in contrast with aromatic compounds which have low dipolar moments.

The purpose of the present study is to optimise the SFME recovery of essential oil from rosemary on a laboratory scale and apply the same conditions to a pilot scale.

Comparisons have been made between SFME (on laboratory and pilot scales) and conventional HD as well as in terms of extraction time, yield, chemical composition and quality of essential oil that environmentally friendly.

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Table 1
most important products extracted by SFME.

Common name	Scientific name	SFME operating conditions	Refs.
Orange	*Citrus sinensis* L.	T = 30 min, m = 200 g, P(atm) = 200 W	Ferhat, Meklati, Smadja, and Chemat (2006)
Marjoram	*Origanum vulgare* L.	T = 35 min, m = 150 g soaked in water during 1 h, P(atm)= 500 W	Bayramoglu, Sahin, and Sumnu (2008)
Laurel	*Laurus nobilis* L.	T = 85 min, m = 150 g soaked in water during 1 h, P(atm)= 622 W	Bayramoglu, Sahin, and Sumnu (2009)
Orange	*Citrus sinensis* L.	T = 10 min, m = 200 g, P(atm)= 200 W	Ferhat, Meklati, Visinoni, Abert Vian, and Chemat (2008)
Lemon	*Citrus limon* L.	T = 30 min, m = 200 g, P(atm) = 200 W	Ferhat, Meklati, and Chemat (2007)
Basil	*Ocimum basilicum* L.	T = 30 min, m = 250 g, P(atm) = 500 W	Lucchesie et al. (2004a), (2004b)
Mint	*Mentha crispa* L.	T = 30 min, m = 250 g, P(atm) = 500 W	
Thyme	*Thymus vulgaris* L.	T = 30 min, m = 250 g, P(atm) = 500 W	
Caraway	*Carum ajowan* L.	T = 60 min, m = 250 g soaked in water during 1 h, P(atm) = 500 W	Lucchesie et al. (2004a), (2004b)
Cumin	*Cuminum cyminum* L.	T = 60 min, m = 250 g soaked in water during 1 h, P(atm) = 500 W	
Anise or star anise	*Illicium verum*	T = 60 min, m = 250 g soaked in water during 1 h, P(atm) = 500 W	
Cardamom	*Elletaria cardamomum* L.	T = 75 min, m = 100 g soaked in water, P(atm) = 390 W	Lucchesie, Smadja, Bradshaw, Louw, and Chemat (2007)
Rosemary	*Rosmarinus officinalis* L.	T = 40 min, m = 250 g, P(atm) = 500 W	Okoh, Sadimenko, and Afolayan (2010)
Rosemary	*Rosmarinus officinalis* L.	T = 30 min, m = 200 g, P(atm) = 200 W	Tigrine-Kordjani, Meklati, and Chemat (2006)
Laurel	*Laurus nobilis* L.	T = 50 min, m = 140 g soaked in water during 1 h, P(atm) = 85 W	Uysal, Sozmen, and Buyuktas (2010)
Lemon balm	*Melissa officinalis* L.	T = 50 min, m = 280 g soaked in water, P(atm) = 85 W	

2. Experimental

2.1. Plant material

Fresh rosemary plants (*Rosmarinus officinalis*) were purchased from Midiflore (Aromatic plant, Hyeres, France). They were composed of stems, leaves and flowers. Only fresh plant material was used in all of the extractions. The initial moisture of this rosemary was 70%. In fact the dry mass ratio (DMR) was determined through the use of a moisture analyser (OHAUS MB35). 5 g of sample were heated 45 min at 110 °C to obtain the mass stability. This method gives us the water content of the sample.

$$\text{DMR} = 100 - \text{moisture percent of sample}$$

2.2. Laboratory SFME apparatus and procedure

SFME was performed in a laboratory microwave oven (NEOS, Milestone, Italy). This is a 2.45 GHz multimode microwave reactor with a maximum power of 900 W delivered in 10 W increments. During experiments, time, temperature, pressure and power were controlled by the software. The experimental SFME variables were optimised in order to maximise the essential oil yield. In a typical SFME procedure performed at atmospheric pressure, 150 g of fresh plant material was heated using a fixed power of 150 W without adding any solvent or water. Essential oil and aromatic water was simply separated by decantation. The essential oil was collected, dried under anhydrous sodium sulphate and stored at 4 °C until subsequent analysis.

2.3. Hydro-distillation apparatus and procedure

One kilogram of fresh rosemary was submitted to hydrodistillation using Clevenger-type apparatus, (Clevenger, 1928) according to the European Pharmacopoeia, and extracted with 7 L of water for 2 h (until no more essential oil was obtained). The essential oil was collected, dried under anhydrous sodium sulphate and stored at 4 °C until used.

2.4. Pilot scale SFME apparatus and procedure

The MAC-75 apparatus is a multimode microwave reactor. It contains 4 magnetrons (4 × 1500 W, 2450 MHz) with a maximum power of 6000 W delivered in 500 W increments. The stainless steel microwave cavity has a capacity of 150 L and contains a removable, rotating PTFE drum that allows up to 75 L of plant material to be loaded. The rotation ensures a homogeneous microwave distribution to the material inside the drum. The drum circumference is entirely perforated to allow the vapour and liquid to pass. The cavity has 6 external tube connections (one in the top, one in the bottom and 4 in the sides) and is wrapped in removable thermal insulation. The absorption of microwave power is controlled by sensors placed on wave guides. The system automatically adjusts the power delivered if absorption is too low. The temperature is monitored by a Resistance Temperature Detector (PT-100) inserted into the cavity. The cavity is able to work in deep vacuum or as an open vessel. The functional deep vacuum is need with plant material particularly. Interlocks on the door prevent accidental opening during the process or when the cavity contains liquid. The device is controlled by an industrial touch screen control terminal with an intuitive graphic user interface.

2.5. GC and GC–MS identification

2.5.1. Gas chromatography by flame ionic detector (FID)

GC analysis was carried out using an Agilent 6850 gas chromatograph, under the following operation conditions: vector gas, Helium; injector and detector temperatures, 250 °C; injected volume, 1 l; split ration 1/100; HP1 column (J&W Scientific), polydimethylsiloxane (10 m × 1 mm i.d., film thickness × 0.4 m; constant flow 0.3 mL/min). Temperature program 60–250 °C at 4 °C/min and 250 °C for 80 min. Retention indices were determined with C_6–C_{27} alkane standards as reference. Relative amounts of individual components are based on peak areas obtained without FID response factor correction. Three replicates were performed for each sample. The average of these three values and the standard deviation were determined for each component identified.

2.5.2. Gas chromatography–mass spectrometry analysis

GC–MS analysis was carried out using an Agilent 6890N coupled to an Agilent 5973 MS (Agilent, Massy, France). Samples were analysed on a fused-silica capillary column HP-1MS™ (polydimethylsiloxane, 50 m × 0.25 mm i.d. × film thickness 0.25 μm; Interchim, Montluçon, France) and INNOWAX (polyethyleneglycol, 50 m × 0.20 mm i.d. × film thickness 0.4 μm; Interchim, Montluçon, France). Operation conditions: carrier gas, helium; constant flow 1 mL min^{-1}; injector temperature, 250 °C; split ratio, 1:150; temperature program, 45–250 °C or 230 °C, at 2 °C/min then held isothermal (20 min) at 250 °C (apolar column) or 230 °C (polar column), ion source temperature, 230 °C; transfer line temperature, 250 °C (apolar column) or 230 °C (polar column), ionisation energy, 70 eV; electron ionisation mass spectra were acquired over the mass range 35–400 amu.