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**Solvent-Free Microwave Extraction of Essential Oil from Aromatic Herbs.
From laboratory to pilot and industrial scales.**

Aurore Filly¹, Xavier Fernandez², Matteo Minuti³,
Francesco Visinoni³, Giancarlo Cravotto⁴, Farid Chemat^{1*}

¹ Université d'Avignon et des pays du Vaucluse, INRA, UMR408, GREEN extraction team,
F-84000 Avignon, France

² Université de Nice Sophia Antipolis, UMR 7272 CNRS, Institut de Chimie de Nice, Parc
Valrose, 06108 Nice, France

³ Milestone srl, Via Fatebenefratelli, 1/5, I-26010 Sorisole, Bergamo, Italy.

⁴ Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino, Via P. Giuria 9,
10125 Torino, Italy

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 hours. Experiments performed in a 75L pilot microwave reactor prove the feasibility of SFME up scaling and potential industrial applications.

Keywords: Green extraction, Solvent-free microwave extraction, scaling-up, essential oil, rosemary, pilot scale.

Introduction

Solvent-free microwave extraction (SFME) was developed in 2004 by Chemat *et al.* [10]. 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 (Figure 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 [8]. 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 in terms of extraction time, yield, chemical composition and quality of the essential oil as well as how environmentally friendly the approaches are.

2. Experimental

2.1 Plant material

Fresh rosemary plants (*R. officinalis*) were purchased from Midiflore. 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%.

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 900W delivered in 10W increments. During experiments, time, temperature, pressure and power were controlled by the software. The experimental SFME variables were optimised in order to maximize 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 7L of water for 2h (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 litres and contains a removable, rotating PTFE drum that allows up to 75 litres 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 4 sensors placed on the magnetrons' wave guides (please check meaning). 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. 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 µl; split ration 1/100; HP1 column (J&W Scientific), polydimethylsiloxane (10 m × 1 mm i.d., film thickness x 0.4 µm; 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 C₆ to C₂₇ 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-1MSTM (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 mLmin⁻¹; injector temperature, 250 °C; split ratio, 1:150; temperature program, 45 °C to 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); ionization energy, 70 eV; electron ionisation mass spectra were acquired over the mass range 35-400 amu.

2.5.3 Identification of the components

Identification of the components was based on computer matching against commercial libraries (Wiley, MassFinder 2.1 Library, NIST98), laboratory mass spectra libraries built up from pure substances, and MS literature data [4-7-12-14-15-17-19] combined with a comparison of GC retention indices (RI) on apolar and polar columns. RIs were calculated with the help of a series of linear alkanes C₆-C₂₇ on apolar and polar columns (HP-1MSTM and HP-INNOWAX). Compounds available in the laboratory were confirmed by external standard compound co-injection.

3. Results and discussion:

Classic hydrodistillation remains the most common essential oil extraction method both in the laboratory and on an industrial scale. The main drawbacks are the long extraction time

involved and the risk of thermal degradation. A number of studies on solvent-free *in situ* microwave-generated hydrodistillation highlighted the efficiency and the wide applicability of this technique. We have recently compared the ability of traditional hydrodistillation and SFME to extract three common mint species (*Mentha spicata* L. var. *rubra*, *Mentha spicata* L. var. *viridis* and *Mentha x piperita* L.) using either fresh plant or rehydrated material [x]. While the quality of the isolated oils was comparable, SFME was faster and, as such, gave reduced energy consumption and overall process cost. The differences in the oil composition obtained with this environmentally friendly technique are related to the water solubility of the components. The reduction in costs and CO₂ emissions makes the scale-up of this technique extremely appealing. This challenging task could be pursued by means of a new pilot scale SFME apparatus, a multimode microwave reactor (MAC-75) designed for this specific application.

3.1 Preliminary study: Optimization of microwave power

An appropriate microwave irradiation power setting is important in essential oil extraction as high power can degrade volatile compounds and the plant material itself. Thus, the relationship between time and irradiation power in SFME was studied at 50, 150, 250, 500 and 750W power settings (figure b). With the aim of assessing the power setting's influence on essential oil composition, all extracts were collected and analyzed using gas-chromatography with a flame ionization detector GC-FID and gas chromatography coupled with mass spectrometry GC-MS. A microwave irradiation power of 150W for 150g of fresh rosemary plant, or 1W/g was the optimum microwave power density. Essential oil extraction was completed and the loss of volatile compounds avoided after 30min of microwave irradiation. 250, 500 and 750W power settings allow shorter extraction time but these artefacts were found in the essential oil (This is not clear). At power settings of 250W and 500W, there is a loss of oxygenated compounds and the smell of the essential oil is less typical of the plant; aromatic, fruity, slightly camphor. The matrix burns before essential oil is extracted at a power setting of 750W.

3.2 Kinetics:

An SFME extraction time of 30 min on the laboratory and pilot scale provides yields (0.54% and 0.50 %, respectively) which are comparable to HD (0.57%) after 2h. Fig c.1 and c.2 show the variation in extraction yield according to extraction time. Four phases are observed: step 0 represents the heating phase, ranging from room temperature to 100°C; step 1 is represented by an increasing line which indicates the first quantities, located at the surface of vegetable

particles, extracted. This is followed by a second increasing line, step 2, representing the internal diffusion of the essential oil from the middle of the particles towards the external medium caused by the internal warming of the water located in the plant cells. The last step corresponds to a horizontal line which marks the end of the extraction process. 80 % (after step 1) of final yield is obtained within 24 min using the SFME process (laboratory and pilot scale) and the same proportion is collected after 60 min using the conventional method. The end of the extraction process is reached after 30 min for the microwave process and 90 min using HD.

3.3 Quality and quantity of essential oil

A total of 45 major compounds (in agreement with the literature) were identified in rosemary essential oil extracted using the two techniques. The principal volatile compounds are limonene and α -pinene followed by camphor, camphene, bornyl acetate, β -pinene, borneol, eucalyptol, α -terpineol, β -caryophyllene and terpin-4-ol, however, their proportions depend on the isolation technique used (Table b). The oxygenated compounds are more odoriferous than monoterpene hydrocarbons and, hence, the most valuable. They are the most abundant oxygenated component in the SFME oil 36.2%, whereas the HD oil contains 33.9% oxygenated compounds (please check meaning). The higher proportion of oxygenated compounds obtained using SFME is probably due to the fact that it causes less intense thermal and hydrolytic effects than HD which uses a large quantity of water. Furthermore, oxygenated compounds have a high dipolar moment and will interact more vigorously with microwaves and can therefore be extracted more easily than monoterpene hydrocarbons which have low dipolar moments.

Essential oils obtained using the MAC-75 were quantitatively and qualitatively (aromatic profile) similar to those obtained by SFME. Only the most minor compounds present in the SFME oil are not found in the up-scaled sample.

3.4. Up-scaling, cost and environmental impact

While conventional procedures such as Hydro-distillation are often highly time and/or energy consuming, microwave extraction provides numerous advantages from an industrial point of view. Microwaves have wide-ranging large scale commercial applications as a processing technology and can provide high returns on capital investment. Improvements in product efficiency, process enhancement and low maintenance costs are achievable on a commercial scale.

30 min, and no solvent or water, are all that is needed to recover essential oil from fresh rosemary with yields comparable to conventional extraction procedures. It is a rapid technique and one that consumes less energy and is advantageous from an environmental point of view. For this purpose, a pilot study has been performed with 3 kilograms of fresh rosemary plant; microwave irradiation power was 3 kW over 30 minutes. Essential oil yields in the MAC-75 were relatively comparable to the lab scale experiments. The first experiment in a large scale microwave reactor appears to be promising. Thus the important role and the real potential of microwaves in industry begin to become clear.

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 4.5kW.h per gram of essential oil for HD and 0.25kW.h per gram of essential oil for SFME. At the same time, the calculated quantity of carbon dioxide released into the atmosphere is dramatically higher in HD (3600 g CO₂/ g of essential oil) than in SFME (200g CO₂/ g of essential oil). Hydro-distillation requires an extraction time of 120 minutes to heat the water and plant material to the extraction temperature, followed by evaporation of water and essential oil, while the SFME method requires only 30 minutes of fresh aromatic herb heating and the evaporation of the *in situ* water and essential oil of the plant material.

Conclusion:

SFME offers important advantages over traditional hydro-distillation. It is quicker, more effective and has a more environmentally friendly approach, making SFME a promising tool for the extraction of essential oils from aromatic plants. When compared to conventional hydro-distillation, optimised microwave treatment shows an increase in oxygenated compound content which are more odoriferous than monoterpene hydrocarbons. This was again found in large scale experiments (MAC-75), showing the potential applicability of the technique in industry.

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