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Comparison of solid-phase and single-drop microextractions for headspace analysis of herbal essential oils

Research Article

Martin Adam*, Petr Dobiáš, Petra Pavlíková, Karel Ventura

Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic

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Abstract: The analytical microextraction methods of gas chromatography coupled with flame ionisation detector (GC-FID) for determination of selected essential oils in herbs were proposed. Two microextraction methods for the isolation of essential oils from plants such as *Lavandula spica* L., *Melissa officinalis* L., *Mentha piperita* L. and *Salvia officinalis* L. were used. The methods of solid-phase and single-drop microextractions, were optimised and compared. The obtained LOD values for all studied essential oils were found to be within 2.5–20.5 μg for SDME and 57.0-139.8 μg for SPME method per 100 g of dried sample leaves. The appropriate LOQ values were then 8.4-68.4 μg for SDME and 189.8-466.1 μg for SPME of target analytes per 100 g of dried sample leaves.

Keywords: *Solid-phase microextraction • Single-drop microextraction • Gas chromatography • Essential oils • Herbs*

1. Introduction

Aromatic plants and their essential oils have been used since antiquity in flavouring and fragrances, as condiments or spice, in medicines as antimicrobial preservatives [1,2]. Recently, the essential oils are being tried as potential candidates for weed and pest and disease management [3,4]. It is primarily because essential oils are easily extractable, eco-friendly being easily biodegradable and play an important role in plant protection against pests [1,2,5]. All these benign properties of essential oils permit their use even in sensitive areas such as schools, restaurants, hospitals and homes [6]. Essential oils are complex mixtures of volatile substances usually present at low concentrations that are used with great benefit in aromatherapy, both in conjunction with conventional medicine and as an alternative therapy [7,8]. Many authors have reported antimicrobial, anti-fungal, antioxidant and radical-scavenging properties [9,10] of the spices and essential oils. A direct food-related application has been tested [11].

Essential oil can be isolated using a number of isolation methods; *e.g.* hydrodistillation, steam distillation and organic solvent extraction [12]. Because monoterpenes are well known to be vulnerable to chemical changes under steam distillation conditions, and even conventional solvent extraction is likely to involve losses of more volatile compounds during removal of the solvent [13]. Headspace sampling (HS) is an alternative to liquid injection when essential oils must be selectively introduced into a gas chromatograph to avoid transfer of non-volatile constituents which may increase run times or complicate the separation [14].

As a modern alternative to traditional sample preparation technology, solid-phase microextraction (SPME) has been introduced by Pawliszyn and co-workers [15-17]. It eliminates the use of toxic organic solvents and substantially shortens analysis time allowing automation of sample preparation. Important features of SPME are simplicity, low cost, rapidity, selectivity and sensitivity when combined with appropriate detection methods [18,19].

* *E-mail: Martin.Adam@upce.cz*

In 1996, liquid-phase microextraction (LPME), also known as single-drop microextraction (SDME), was introduced by Jeannot *et al*. [20,21]. This technique is based on the distribution effect of the analytes between a microdrop of organic solvent and sample matrix. The organic solvent drop is suspended at the tip of a microsyringe needle and exposed to the sample. After extraction, the microdrop is retracted back into the microsyringe and injected into either gas- or high-performance liquid chromatograph for further analysis [22]. SDME has the advantages of high extraction speed and simplicity. It utilizes inexpensive apparatus and virtually eliminates solvent consumption [23]. Contrary to the SPME procedure, this technique does not require any desorption step.

The main goals of the presented work were to optimise the experimental conditions of solid-phase microextraction in the headspace mode (HS-SPME) when examining herbal essential oils and to compare HS-SPME method with headspace single-drop microextraction method (HS-SDME) developed in our previous study and with the classical steam distillation method in order to analyse selected essential oils in four different herbal samples.

The novelty of this work is the evaluation of the application of two different microextraction methods (*i.e*. SPME and SDME) to the herbal essential oils analysis, their comparison to each other and to the classical steam distillation method.

2. Experimental Procedures

2.1. Chemicals

Analysed plant samples were purchased from Botanicus Ltd. (Ostrá, Czech Republic). These were *Lavandula spica* L., *Melissa officinalis* L., *Mentha piperita* L. and *Salvia officinalis* L. All plants were collected during the time period between May to July 2007. The leaves were separated from the rest of the plants, dried at room temperature and then stored in dark, wide mouthed, glass bottles at 4°C prior to use. Before analysis, the plant samples were pre-treated by grinding in a mortar to maximize surface area. Standards of essential oils, such as borneol (99%), camphor (95%), carvacrol (98%), 1,4-cineole (98%), eucalyptol (98%), limonene (98%), menthol (99%), menthone (99%), myrcene (90%), nerol (98%), α-pinene (99%) and α-thujone (96%) used for the identification and quantification of target compounds were purchased from Sigma–Aldrich (Prague, Czech Republic). *p*-Xylene (analytical grade) used as an extraction solvent was obtained from Merck (Darmstadt, Germany).

2.2. Instrumentation

All extracts were analysed by a GC-FID system HP5890 (Hewlett-Packard, Avondale, PA, USA) equipped with a capillary column Ultra No. 2 (25 m × 0.32 mm I.D. 0.52 µm film thickness of phenylmethylsilicone). Chromatograms were evaluated using the CSW integration software (Data Apex, Prague, Czech Republic).

Three different coated SPME fibers, 100 µm Polydimethylsiloxane (PDMS), 50/30 µm Divinylbenzene/Carboxen/Polydimethylsiloxane StableFlex (DVB/CAR/PDMS) and 65 µm Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) were used. The commercially available SPME device for manual sampling and all fibers were purchased from Supelco (Bellefonte, PA, USA). The extraction temperature was adjusted by a Julabo thermostat EC-5 (Julabo Labortechnik, Seelbach, Germany).

2.3. Single-drop microextraction procedure

All extractions were performed in 10 mL glass vials sealed with PTFE-faced septum caps (Supelco, Bellefonte, PA, USA). Prior to extraction, the sample (0.5 g) was transferred into the sampling vial and preheated at the extraction temperature for 10 min. SDME was performed with a commercially available 5 µL GC microsyringe with the skew needle Hamilton Syringe (75N; Hamilton Bonaduz AG, Bonaduz, Switzerland).

Before each extraction, the microsyringe was washed several times with the solvent in order to eliminate the bubbles in the barrel and the needle. After passing through the septum, the needle tip had to be kept about 0.5 cm above the surface of the sample (headspace – HS). The syringe was clamped and the plunger depressed to cause the solvent to form a drop (2.0 µL) suspended at the tip. The sample was maintained at the same temperature as that of the water bath during extraction which was 70°C. When the extraction was terminated after a period of time (90 s), the acceptor drop was retracted into the microsyringe. After extraction, the microsyringe was removed from the sample vial and immediately inserted into the gas chromatograph.

2.4. Solid-phase microextraction procedure

Before its first use, all SPME fibres were reconditioned in order to remove contaminants by warming in the heated injection port of a gas chromatograph at 220°C for 30 min. All extractions were performed in 10 mL glass vials sealed with PTFE-faced septum caps (Supelco, Bellefonte, PA, USA). Prior to extraction, the analysed sample (0.5 g) was transferred into the sampling vial and preheated at the extraction temperature for

10 min. The appropriate SPME fibre (50/30 µm DVB/CAR/PDMS) was exposed to the headspace above the dried sample. After preliminary optimisation experiments, the exposition time of 25 min and a temperature of 70°C were selected as the suitable extraction conditions. After extraction, the SMPE fibre was removed from the sample vial and immediately inserted into the gas chromatograph where the thermal desorption at the injector (temperature 220°C) was carried out.

2.5. Steam distillation procedure

For the steam distillation procedure 20 g of analysed sample was distilled for 4 hours and the target essential oils were extracted into 1 mL of *p*-xylene. The obtained essential oils solution was then analysed by GC/FID.

2.6. Chromatographic analysis

The separation conditions were as follows: initial column temperature 60°C, increased to 150°C at 5°C min^{-1} then increased to 280°C at 30°C min^{-1} (hold for 2 min). The injector and detector temperatures were maintained at 220 and 290°C, respectively. The nitrogen (purity 5.0, Linde Gas, Prague, Czech Republic) was used as the carrier gas with 50 kPa column head pressure (split ratio 1:10). Hydrogen and air (both Linde Gas) passed at 30 and 300 mL min^{-1} were used in the FID mode. The extracted analytes were identified and quantified using the standard addition method. In the case of microextraction methods, the appropriate amounts of standards were added to the sample before the extraction process started.

3. Results and discussion

Before both microextraction techniques (*i.e*. SPME and SDME) could be compared to each other to analyse herbal essential oils, it was necessary to optimise individual extraction parameters. The SPME optimisation procedure is described in more detail.

3.1. Solid-phase microextraction method optimisation

To develop a SPME procedure for the determination of essential oils, optimisation of several variables related to extraction and desorption steps was required in order to achieve maximum efficiency of extraction of the compounds studied and to resolve the selectivity of the different coatings *vs*. other components present in the matrix. SPME fibre coating selection, sample mass together with the size of sampling vial, extraction time and temperature as well as the desorption time at the injector temperature were optimised for the comparison of the procedures.

Three different SPME fibres (*i.e*. 100 µm PDMS, 65 µm PDMS/DVB and 50/30 µm DVB/CAR/PDMS StableFlex) were tested. Although the whole optimisation process was performed for all tested coatings, only results obtained for DVB/CAR/PDMS are discussed in this article.

First, the appropriate sample amount / headspace volume ratio, and therefore, the influence of sample weight on the composition of the extracted compounds was studied. It was determined that an increased amount of sample in the vial produced a higher concentration of target volatile compounds in the headspace. But, after the fibre was saturated with volatile analytes, an increase of sample amount had no further effect on the mass transfer. Thus, based on these observations, the optimal sample weight was chosen to be 0.5 g of dried herbal leaves per a 10 mL dosage of sample vial. At these amounts, the headspace volume is equal to one half of the sampling vial.

The effect of the extraction temperature on the HS-SPME efficiency was tested. In this investigation, temperatures varied every 10°C from 40 to 90°C with the DVB/CAR/PDMS fiber, and the mixed herbal sample was used to evaluate the amounts of α-pinene, myrcene, α-thujone and menthone sampled. For these evaluations, the extraction time was set at 30 min to obtain equilibrium. All experiments were performed in triplicate. Dependencies of GC–FID peak areas on extraction temperature for four components listed above are shown in Fig. 1A.

It was observed that the peak areas of interest increased with the temperature until 70°C. At higher temperatures the peak areas of target compounds become lower. This effect could be explained by the competition between increasing concentration of analytes in the headspace and predominant desorption processes at higher temperatures. Thus, the temperature 70°C was selected and used for further extractions.

HS-SPME is considered complete when the analyte concentration has reached equilibrium between the sample matrix and the fibre coating. In this case, a three phase system including sample matrix, headspace and fibre surface is occurred. Determination of adsorption equilibrium times was carried out using the DVB/CAR/PDMS. In this investigation, adsorption times were varied from 10 to 60 min at 70°C using a different (from previous experiments) mixed herbal sample. All experiments were performed in triplicate. The extraction time profiles for α-pinene, myrcene, α-thujone and menthone used as test references are shown on Fig. 1B.

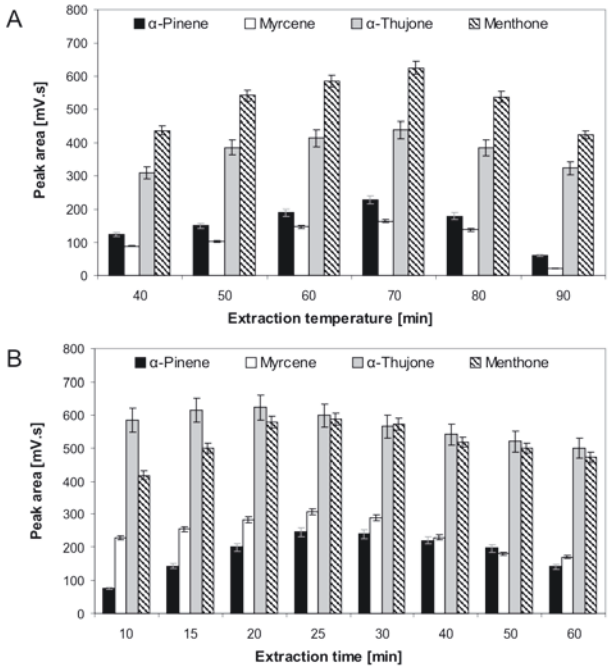

Figure 1. Effect of extraction temperature (A) and extraction time (B) upon the HS-SPME efficiency of target essential oils for mixed herbal sample (DVB/CAR/PDMS fibre, sample amount 0.5 g).

For the selected SPME fibre, the optimum extraction time was 25 min with no significant improvement in the extraction obtained at longer times. In subsequent studies, the time period 25 min was selected as the extraction time.

The same procedure as described above for 50/30 µm DVB/CAR/PDMS fibre was repeated for other tested SPME fibres (*i.e.* 100 µm PDMS and 65 µm PDMS/DVB, respectively). It was found that the optimum conditions for PDMS fibre were 90°C for 30 min and for PDMS/DVB were 50°C and 20 min.

Finally, all tested SPME fibres were compared to each other. All evaluations of the fibers were performed the same day using the same mixed herbal sample. Fig. 2 displays the comparison of GC-FID chromatograms obtained for each of the fibres tested. All extractions were performed at the optimum conditions for each appropriate SPME fibre. Because these chromatograms were obtained for the same sample and with the same detector sensitivity, the peak heights for each fibre were compared. The highest peaks were observed for 50/30 µm DVB/CAR/PDMS fibre; so this fibre was determined to be the best for the herbal essential oils analysis.

Suitable desorption conditions were the last optimised parameters. For this purpose, different time periods at the injection temperature (220°C) were tested to determine the optimum time all analytes were desorbed from the fibre coating and minimizing the "carryover effect" to the following analysis. For the DVB/CAR/PDMS fibre, desorption time varying between 1 and 10 min was optimised. Stabilisation of the chromatograms and reproducible peak areas were observed using desorption time of 5 min at 220°C. These values of temperature and desorption time were selected for subsequent studies.

3.2. Single-drop microextraction method application

Different factors that may affect the extraction process are the selection of a suitable solvent, solvent volume, temperature and time. Thus, it is crucial to perform the respective optimisation in order to obtain the good recovery. Because this optimisation has already been performed and published [24], in this work only final extraction conditions are presented. So it was found that 2 µL of *p*-xylene at 70°C for 90 s using 0.5 g of sample in a 10 mL sampling vial are suitable conditions for the HS-SDME method. However, contrary to the majority of the literature sources, we decided to use different method for extraction solvent selection. Usually, solvents with low volatility which enables the application of longer extraction times are used. But, our decision was to select a solvent with higher volatility compared to the volatility of target analytes (*i.e.* essential oils). Thus, p-xylene was tested and successfully produced peaks with shorter retention times than those of the target compounds.

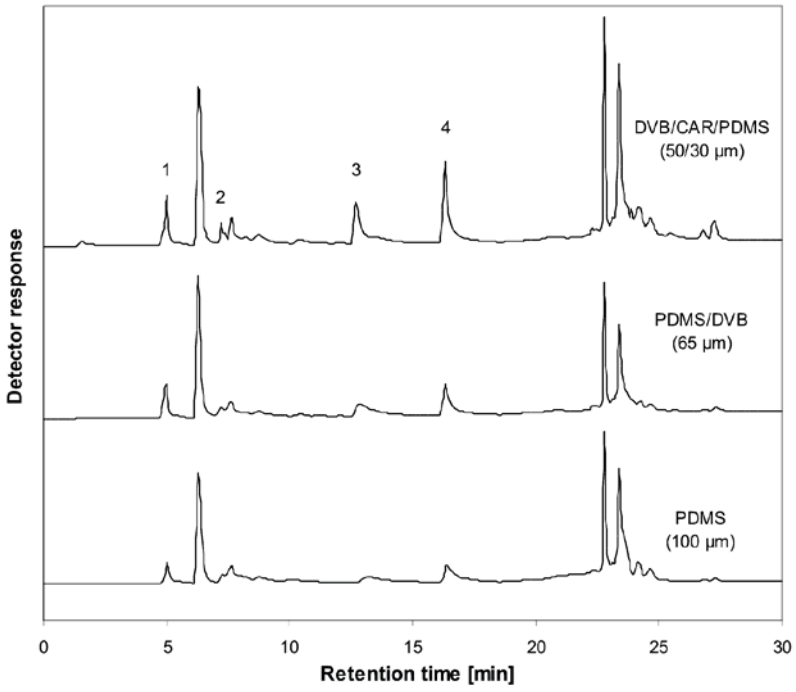

Figure 2. Comparison of chromatograms obtained for tested SPME fibres 1 – α-pinene, 2 – myrcene, 3 – α-thujone, 4 - menthone

3.3. Methods validation

In our study, analytical performance of the method was evaluated within the limits of quantification (LOQ) and detection (LOD), and precision was expressed as the mean relative standard deviations (RSD) when using the optimised conditions described above. The validation was performed for twelve essential oil compounds (listed in the Experimental part). To the LOD and LOQ evaluation, the plant material without target analyte (*i.e*. *Melissa officinalis* L. for α-pinene, myrcene, limonene, camphor, borneol, menthol and carvacrol; *Salvia officinalis* L. for eucalyptol, α-thujone, menthone and nerol; *Mentha piperita* L. for 1,4-cineole, respectively) was used as blank. The results concerning limits of detection (LOD) and quantification (LOQ) for both microextraction methods and all target compounds are summarised in Table 1.

Appropriate chromatograms of target essential oils standard mixture are depicted in Fig. 3. The differences between SPME (part A) and SDME (part B) in retention times of individual compounds are caused by the peak of extraction solvent (*p*-xylene).

The LODs for all studied essential oils, estimated with the aid of the "3:1 signal-to-noise (S/N) ratio" criterion, were found to be within 2.5–20.5 µg per 100 g of dried sample leaves for SDME method; whereas in the case of SPME method, the LOD values were then 57.0-139.8 µg per 100 g of dried sample leaves. The relevant LOQ values, calculated as the S/N = 10, were 8.4-68.4 µg for SDME and 189.8-466.1 µg for SPME of target analytes per 100 g of dried sample leaves. During the LOD and LOQ experiments, appropriate correlation coefficients were evaluated as well. Obtained results varied in the range between 0.9912 and 0.9998 for menthol and limonene, respectively.

Finally, the precision of both microextraction methods under the optimised conditions were determined by analysing the samples in triplicate, and, when expressed as the RSD, typical results were between 2.64 and 8.81 % for SDME, whereas in the case of SPME the appropriate RSD values were in the range 0.15-6.08 (see Tables 2 and 3).

3.4. Real samples results

Finally, both microextraction methods under their optimised conditions were applied for the analysis of essential oils in real samples of *Lavandula spica* L., *Melissa officinalis* L., *Mentha piperita* L. and *Salvia officinalis* L. Obtained results are summarised in the Tables 2 and 3. All extractions were performed in triplicate. The typical GC-FID chromatograms for *Mentha piperita* L. are depicted on Fig. 4A (SPME method) and Fig. 4B (SDME method). In addition, the results obtained by classical steam distillation method are presented in the Tables 2 and 3 as well.

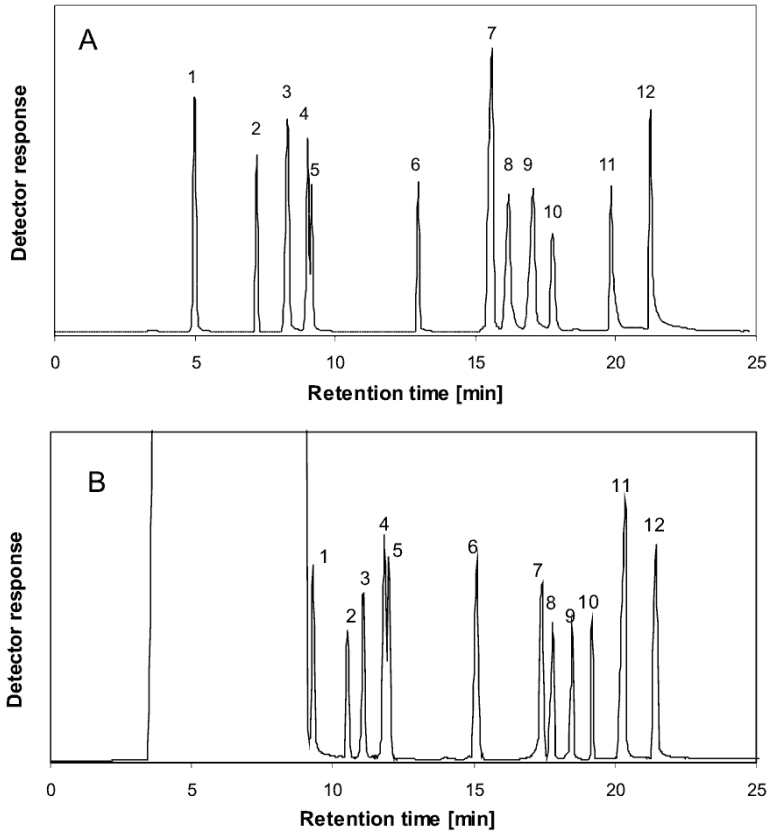

Figure 3. GC-FID chromatograms of standard mixture of analysed essential oils after SPME (A) and SDME (B) extraction step. 1 - α-pinene, 2 – myrcene, 3 – 1,4-cineole, 4 – eucalyptol, 5 - limonene, 6 – α-thujone, 7 – camphor, 8 - menthone, 9 – borneol, 10 – menthol, 11 – nerol, 12 - carvacrol

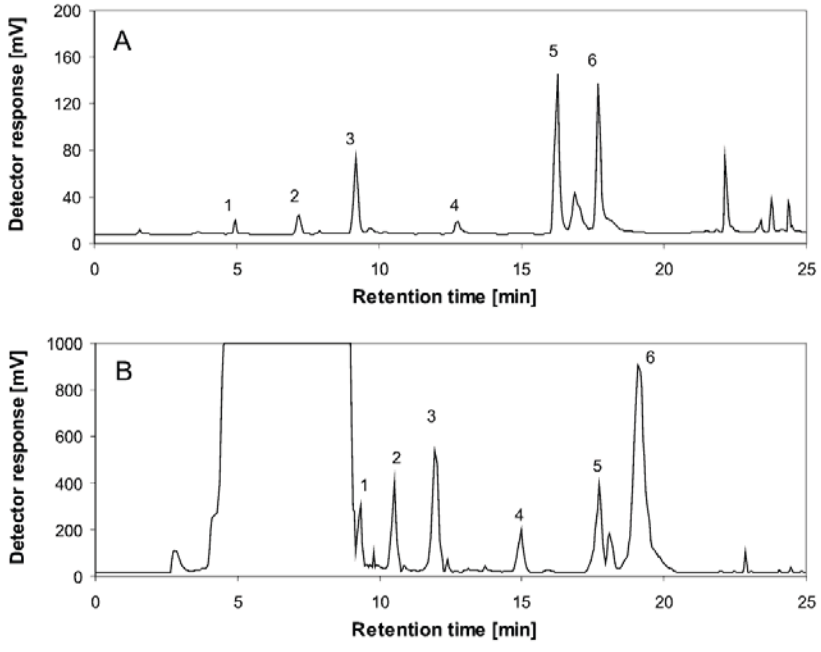

Figure 4. GC-FID chromatograms of *Mentha piperita* L. real extract gained by SPME (A) and SDME (B) method 1 – α-pinene, 2 – myrcene, 3 – limonene, 4 – α-thujone, 5 – menthone, 6 – menthol.

Table 1. Analysed essential oils and their retention times (T_R) together with the LOD and LOQ values for both microextraction methods.

Compound	SPME[a]			SDME[b]		
	T_R [min]	LOD [μg] [c]	LOQ [μg] [c]	T_R [min]	LOD [μg] [c]	LOQ [μg] [c]
α-pinene	5.0	57.0	189.8	9.3	2.5	8.4
Myrcene	7.2	82.4	274.6	10,5	3.6	12.0
1,4-Cineole	8.3	124.2	414.0	11.1	3.3	11.1
Eucalyptol	9.0	135.4	451.3	11.9	15.8	52.7
Limonene	9.1	93.4	311.3	12.0	11.3	37.6
α-Thujone	12.9	139.8	466.1	15,1	16.6	55.3
Camphor	15.7	135.9	453.0	17.4	7.7	25.8
Menthone	16.3	131.3	437.6	17.8	14.3	47.7
Borneol	17.1	113.4	378.0	18.5	11.3	37.7
Menthol	17.7	138.8	456.1	19.1	18.3	61.1
Nerol	19.9	128.9	429.7	20.4	20.5	68.4
Carvacrol	21.2	128.8	429.4	21.5	17.9	59.7

[a] – *SPME conditions: 0.5 g of sample in 10 mL vial, fibre 50/30 μm DVB/CAR/PDMS, 70 °C, 25 min*
[b] – *SDME conditions: 0.5 g of sample in 10 mL vial, microdrop 2 μL of p-xylene, 70 °C, 90 s*
[c] – *Calculated as content per 100 g of dried leaves.*
The correlation coefficients varied in the range 0.9912 (menthol) - 0.9998 (limonene).

Table 2. Essential oils contents (per 100 g of dried leaves) of *Lavandula spica* L. and *Melissa officinalis* L. obtained by various methods

Compound	*Lavandula spica* L.						*Melissa officinalis* L.					
	SDME [mg][a]	RSD [%]	SPME [mg][b]	RSD [%]	St.dist. [mg][c]	RSD [%]	SDME [mg]	RSD [%]	SPME [mg]	RSD [%]	St.dist. [mg]	RSD [%]
α-Pinene	11.1	7.63	3.2	3.30	6.5	1.84	n.d.	---	n.d.	---	n.d.	---
Myrcene	8.3	7.78	2.6	5.63	28.0	2.79	n.d.	---	n.d.	---	n.d.	---
1,4-Cineole	9.1	6.65	4.0	5.48	5.5	1.27	4.8	3.24	2.7	1.86	3.9	2.31
Eucalyptol	191.6	3.13	64.6	0.84	36.4	2.64	96.3	5.36	6.7	3.78	10.5	1.46
Limonene	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---
α-Thujone	6.7	8.54	8.4	2.03	8.9	4.23	15.6	3.27	3.4	4.23	3.8	3.22
Camphor	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---
Menthone	14.5	5.94	12.7	5.98	15.8	1.31	129.5	4.70	73.3	0.15	33.1	7.18
Borneol	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---
Menthol	86.5	7.95	18.6	4.68	17.5	1.70	n.d.	---	n.d.	---	n.d.	---
Nerol	62.5	3.11	21.5	5.41	44.2	0.51	62.4	3.45	31.1	3.46	34.2	5.25
Carvacrol	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---

[a] – *SPME conditions: 0.5 g of sample in 10 mL vial, fibre 50/30 μm DVB/CAR/PDMS, 70 °C, 25 min*
[b] – *SDME conditions: 0.5 g of sample in 10 mL vial, microdrop 2 μL of p-xylene, 70 °C, 90 s*
[c] – *Steam distillation method conditions: 20 g of sample, distillation time 4 hours, 1 mL of p-xylene as the essential oils solvent*
RSD – Relative standard deviation, n = 3
n.d. – not determined, values lower than LOQ

3.5. Comparison of used microextraction methods

There are several points of view that could be used for methods comparison. First, based on the LOD and LOQ values presented in the Table 1, the SDME method was found to be more sensitive. In the case of SDME, both the detection and the quantification limits were lower than those obtained by SPME method. But the method precision was found to be better for the SPME method because of the lower RSD values.

In order to qualitatively analyse herbal essential oils both microextraction methods are fully comparable both to each other as well as to the classical steam distillation method. This is illustrated in the Tables 2 and 3. Comparing the quantitative results, the values obtained by various methods are different. This could be explained by the different functional mechanisms of both microextraction methods as well as by steam distillation methods.

It is a bit controversial to evaluate which results are accurate. Because of this, analysis of certified reference material (CRM) should be performed; however, no appropriate CRM sample was found resulting in no possibility of evaluation of the extraction yield.

Table 3. Essential oils contents (per 100 g of dried leaves) of *Mentha piperita* L. and *Salvia officinalis* L. obtained by various methods

Compound	*Mentha piperita* L.						*Salvia officinalis* L.					
	SDME [mg][a]	RSD [%]	SPME [mg][b]	RSD [%]	St.dist. [mg][c]	RSD [%]	SDME [mg]	RSD [%]	SPME [mg]	RSD [%]	St.dist. [mg]	RSD [%]
α-Pinene	5.2	3.41	3.6	2.47	3.5	2.10	16.3	5.69	11.9	1.94	15.4	3.48
Myrcene	17.7	7.78	4.0	0.95	29.4	0.36	n.d.	---	n.d.	---	n.d.	---
1,4-Cineole	n.d.	---	n.d.	---	n.d.	---	0.6	2.92	0.4	6.08	1.1	1.54
Eucalyptol	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---
Limonene	248.0	3.00	331.5	2.10	118.0	4.55	54.9	8.73	44.9	5.49	72.2	4.58
α-Thujone	22.8	8.81	3.4	1.13	13.5	1.15	n.d.	---	n.d.	---	n.d.	---
Camphor	n.d.	---	n.d.	---	n.d.	---	221.0	2.76	91.7	0.63	131.4	6.84
Menthone	308.7	8.51	888.5	0.93	187.7	0.71	n.d.	---	n.d.	---	n.d.	---
Borneol	n.d.	---	n.d.	---	n.d.	---	32.6	6.08	11.4	5.43	25.2	4.87
Menthol	828.0	2.64	790.0	2.25	888.3	0.30	n.d.	---	n.d.	---	n.d.	---
Nerol	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---
Carvacrol	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---	n.d.	---

[a] – *SPME conditions: 0.5 g of sample in 10 mL vial, fibre 50/30 µm DVB/CAR/PDMS, 70 °C, 25 min*
[b] – *SDME conditions: 0.5 g of sample in 10 mL vial, microdrop 2 µL of p-xylene, 70 °C, 90 s*
[c] – *Steam distillation method conditions: 20 g of sample, distillation time 4 hours, 1 mL of p-xylene as the essential oils solvent*
RSD – Relative standard deviation, n = 3
n.d. – not determined, values lower than LOQ

A reference material is usually used in the steam distillation method. But the quantitative results of both microextraction methods were found to be different from steam distillation as well. Based on these results, the proposed microextraction methods (*i.e.* SPME and SDME) could be successfully used for qualitative and semi-quantitative determination of herbal essential oils.

4. Conclusions

Essential oils isolation and quantification were performed using the leaves of four plants *Lavandula spica* L., *Melissa officinalis* L., *Mentha piperita* L. and *Salvia officinalis* L. There were two microextraction methods, SPME and SDME, as well as steam distillation method used in these experiments. First, both microextraction methods were optimised and then compared to each other. Obtained extracts were analysed by GC-FID method. Based on the obtained LOD and LOQ values the SDME method seems to be more sensitive, but the RSD values makes the SPME method more precise. The proposed microextraction methods were found to be simple, feasible and suitable for qualitative and semi-quantitative determination of herbal essential oils.

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