

Deep Eutectic Solvent as a Green Solvent for Fast Analysis of the Volatile Components of *Satureja hortensis* L.

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Deep eutectic solvents (DESs) and ionic liquids have been considered as organic solvents and applied in numerous chemical procedures. DESs usually are produced by combining two or three organic components. DES can be formed in a mixture by combining the hydrogen bond donors such as urea, polyols, and carboxylic acids with the hydrogen bond acceptors. In the present study, deep eutectic solvents as green solvents, and extraction method known as Headspace-solvent microextraction were used. Deep eutectic solvents hydrodistillation single drop microextraction (DES-HS-SDME) was used for extracting the essential oil compounds using DESs as extraction solvents prepared by combining the choline chloride and *p*-chlorophenol. They were used to extract the volatile compounds from *Satureja hortensis* L. leaves. To avoid the traditional and time-consuming hydrodistillation, the volatile components in *Satureja hortensis* L.'s aerial parts were analyzed through a simple distillation using headspace single-drop microextraction along with gas chromatography. According to the experimental findings, DESs-HS-SDME is a rapid, low-cost, simple, and reliable technique to determine the volatile fractions in *Satureja hortensis* L.

Keywords: Deep eutectic solvents, *Satureja hortensis* L., Choline chloride, Microextraction

INTRODUCTION

Satureja hortensis L. belongs to the Lamiaceae group. Traditionally, it was utilized as a stomachic, stimulant, expectorant, aphrodisiac, and carminative treatment of various kinds of infectious illnesses. Some pharmaceutical properties such as anti-diarrheal, antispasmodic, anti-inflammatory as well as antimicrobial properties were reported in the literature. Lamiaceae types are well-known for producing a diverse array of secondary metabolites, including non-volatile and volatile terpenes, hydroxycinnamates, hydroxybenzoates, and flavonoids. Also, many members of the genus *Satureja* have medicinal and aromatic features [1].

Single-drop microextraction (SDME) was established as a microextraction method providing analytic extraction in some microlitres of an organic solvent. By SDME, some

problems related to the solid-phase microextraction (SPME) technique were prevented, including fiber degradation and sample carry-over [2].

Recently, researchers considered a green solvent as one of the key aspects of green chemistry. Today, deep eutectic solvents (DESs) and ionic liquids (ILs) are considered as non-volatile organic solvents and are used in many chemical methods [3].

In many extraction methods, such as liquid-liquid extraction (LLE) and solid phase extraction, a large amount of organic solvents is consumed (SPE). However, DES solvents can be an alternative to some of them.

DES solvents have properties similar to those of ionic liquids, namely, viscosity, surface tensions, high conductivity, thermal stability, polarity, and negligible vapor pressure. Unlike the ionic liquids, DESs can nevertheless be easily prepared at low cost and with high purity.

DESs are normally produced by combining two or three

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organic components. DES can be formed in a mixture by combining hydrogen bond donors (HBD) like urea, polyols, and carboxylic acids with hydrogen bond acceptors (HBA) [3,4]. One of the most extensively utilized HBAs in DESs is choline chloride (ChCl). The DESs contains much lower melting points (lower than those of the individual components) compared to any of its distinct components, which is probably caused by the impact of intermolecular hydrogen bonds [5]. In comparison with ILs, DESs possess numerous advantages, including easy preparation, biodegradability, low cost, environmental friendliness, and pharmaceutically acceptable toxicity [6-9]. They were used for catalysis, organic synthesis, electrochemical material, and dissolution [10-15].

DESs solvents can be used in (micro) extraction of target analytes from complex matrixes followed by quantification using analytical instruments, modification of nanoparticles, sorbents, dissolution or digestion of solid samples. It has been used as eluent after a dispersive solid-phase extraction (DSPE) procedure, as a mobile phase additive/modifier in chromatography [16-19]. Also, DES can be regarded as an alternative to ILs in many applications: stabilization of DNA, electrochemistry, separation processes, CO₂ capture, organic synthesis, nanotechnology, synthesis of polymers, transition metal catalyzed reactions, and biotransformations [20].

Here, DESs were used for extracting the essential oil compounds from *Satureja hortensis* L. using single-drop microextraction. The extraction circumstances were enhanced utilizing the relative peak areas as the index. According to the experimental findings, DESs-HS-SDME is a rapid, low-cost, simple, and reliable technique to determine volatile fraction in *Satureja hortensis* L.

MATERIALS AND INSTRUMENTS

Materials

The plant substances were gathered in Northeast of Iran in June 2019. The Laboratory of Botanic Ecology of Razi University confirmed the species identification. A voucher sample was deposited at the herbarium of this laboratory with the code 1202 MAR.

The reagents, solvents, and terpenes were obtained from Merck, Aldrich, and Fluka, and used without further

purification. Choline chloride and *p*-Chlorophenol were provided from Merck. All materials were used at analytical-grade.

Isolation of the Essential Oil by Hydrodistillation

To extract the essential oil through conventional hydrodistillation (HD), 100 g dried plant specimen was boiled for three hours in a Clevenger type apparatus. Followed by cooling, transparent yellowish oil gathered over the water surface. Using a syringe, the oil was gathered, transported into a brown vial, and kept at 4 °C.

Preparation of DES

For preparation of deep eutectic solvent, 0.13 g ChCl as hydrogen bond acceptor and appropriate amount of different hydrogen bond donors such as phenol, 4-chlorophenol, and ethylene glycol acids were inserted into a 10 ml screw-cap tube. After closing its cap, it was located over a water bath for 8 min at 90 °C, and vortexed for 12 min. Once more, the heating/vortexing cycle was repeated to obtain a homogeneous liquid.

HS-SDME Extraction

The following process presents the way for DESs-HS-SDME extraction. The weighed herb (3 g) was transferred into a 25 ml round bottom flask containing 1 ml water. Followed by assembling a condenser, a 10 µl microsyringe (Hamilton, USA) with 2 µl DES as an extraction solvent was introduced into the plant sample's headspace. Depressing the syringe plunger, a microdrop of extracting solvent was suspended from the needle tip, and then the microwave power was used. The herb was heated. The plunger was withdrawn after (40 min) extraction, and the microdrop was retracted into the micro syringe. Ultimately, the micro drop was straightly injected into the GC injection port. Using the DESs-HS-SDME technique, the volatile compounds in the *Satureja hortensis* L. were transported to the headspace in a short period. Simultaneously, the components in the headspace were extracted and compacted utilizing a suspended microdrop solvent. A simplex technique was used for the optimization of the effective parameters affecting extraction efficiency in this process. A simplex technique can considerably decrease the number of the tests required to obtain the highest extraction efficiency.

Over optimizing, the relative areas of four main peaks in the GC-MS chromatogram were monitored. Using the simplex process, $(n + 1)$ first tests were designed (n is the number of effective elements that affect the extraction efficiency in SDME technique), the circumstances, consistent with the worst response, were reflected, and the reflection procedure was repeated till observing no more enhancement in the response. The reflections were occasionally modified when required. DESs-HS-SDME is a method based on equilibrium, and a straight association exists between the extracting time and the extracted amount.

Gas Chromatography-mass Spectrometry

An FID detector system and a Hewlett-Packard HP 7890 series GC armed with a split/splitless injector were utilized for determination. Helium (99.999%) was used as a carrier gas with 1.1 ml min^{-1} flow-rate. The column was kept for 2 min at $100 \text{ }^\circ\text{C}$ and incremented to $200 \text{ }^\circ\text{C}$ at a rate of $20 \text{ }^\circ\text{C min}^{-1}$. Then it was elevated to $280 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$ and maintained for 10 min at this temperature. The temperature of the injector was adjusted at $300 \text{ }^\circ\text{C}$, and all injections were performed on the pulse splitless state (sampling time of 10s).

The compounds were separated on a $30 \text{ m} \times 0.25 \text{ mm}$ HP-5 MS column (Agilent Technologies, Palo Alto, CA, USA) with a film thickness of $0.25 \text{ }\mu\text{m}$. The column was maintained at $50 \text{ }^\circ\text{C}$ and incremented to $180 \text{ }^\circ\text{C}$ at a rate of $15 \text{ }^\circ\text{C min}^{-1}$, then it incremented to $280 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$ and maintained at this temperature for 10 min. The injector temperature was adjusted at $300 \text{ }^\circ\text{C}$, and all injections were performed for 2 min on the splitless mode. The ion source, GC-MS interface, and quadrupole temperatures were adjusted at 230, 150, and $280 \text{ }^\circ\text{C}$, respectively. The compounds were recognized using the Wiley 7 N (Wiley, NY, New York, USA) Mass Spectral Library.

The components of the volatile oil with hydrodistillation were recognized by calculating their retention indices at a temperature set for the oil on a HP-5MS column and n -alkanes (C6-C24) under the same circumstances. The singular compounds were recognized by comparing their mass spectra and the internal reference mass spectra library of original compounds, and approved by comparing their retention indices with authentic compounds or the reports in the literature. The Wiley 7 N (Wiley, New York, NY, USA)

mass spectral library and retention indices were used to identify the compounds.

RESULTS AND DISCUSSION

Hydrodistillation is a time-consuming technique requiring large quantities of a plant substance. In this work, decent findings were obtained by combining the incessant hydrodistillation with deep eutectic solvents headspace single drop microextraction (DESs-HS-SDME) within a short period (few minutes) and using a small quantity of plant.

Table 1 represents the circumstances used for the preliminary tests and the consequently designed tests for DESs-HS-SDME. Using a modified reflection technique, the experimental circumstances were attained. The modifications were mainly carried out based on the practical restriction of some factors like microdrop volume (manipulation of the larger drops is difficult). The findings clearly show the positive effects of sample weight, microdrop volume, and extraction time on the extraction efficiency of the DESs-HS-SDME method.

Characterization of the DESs

In the present work, DES was prepared from 4-chlorophenol and ChCl. Figure 1 shows the Fourier transform infrared spectroscopy (FT-IR) for the synthesized DES. The important part in this spectrum is the hydrogen bonding between the 4-chlorophenol and the ChCl.

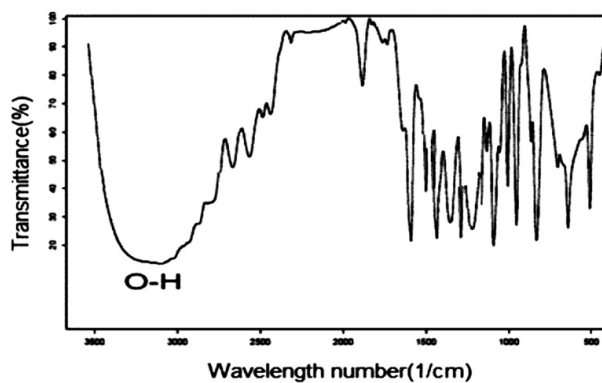


Fig. 1. FT-IR spectrum of the DES synthesized from 4-chlorophenol and ChCl.

Table 1. The Experimental Conditions and the Obtained Results for the DES-HS-SDME Experiments Performed in the Simplex Optimization Procedure

Exp. no	Sample weight (g)	Extraction time (min)	Temperature (°C)	Droplet volume (μl)
1	1	35	80	1
2	2	45	80	1
3	2	35	90	1
4	2	35	80	2
5	2	35	80	1
6 (Refl.) ^a	3	40	85	1.5
7 (Refl.)	2.25	43	89	2
8 (Refl.)	2.62	32	92	1.25
9 (Refl.)	3	40	83	1.5
10 (Refl.)	3	43	94	1

^aReflection.

Therefore, it is expected that the wavelength number of the OH group is altered in the DES compared to that in 4-chlorophenol. According to the FT-IR spectrum, the broad band at 3282 cm⁻¹ related to the stretching vibration of the O-H group in 4-chlorophenol was changed to 3180 cm⁻¹ in the DES.

DESs-HS-SDME Optimization

To attain high extraction efficiency of the analytes through DESs-HS-SDME for extracting essential oils from *Satureja hortensis* L., various factors related to the quantities of the extracted essential oils were investigated. So, to establish the SDME method for determining the essential oils by DESs, different parameters control the optimal performance, such as the type of extraction phase, optimization of sampling time and temperature, and DESs volume.

DES Type

Before optimizing the extraction factors, the effect of the DES type on the extraction of the gathered analytes in the GC was investigated. The selection of the proper solvent is vital for the SDME technique depending on the extraction of the target compounds in this medium. Because of the critical effect of the solvent on DESs-HS-SDME, three various DESs including ChCl as an HBA and 4-chlorophenol, phenol, and ethylene glycol as the HBDs

were prepared and evaluated. Figure 2 represents a comparison of the peak heights obtained for the four major components. The most intense signals and the least overlap were obtained by use of ChCl: 4-chlorophenol deep eutectic solvent. Figure 2 indicates that the DES created from ChCl: 4-chlorophenol is the most effective extraction solvent with the maximum peak areas and extraction efficiencies for the selected analytes among the examined DESs. Hence, it was chosen as the solvent for further experiments. A comparison of the two methods (DESs-HS-SDME and HD) is shown in Table 2).

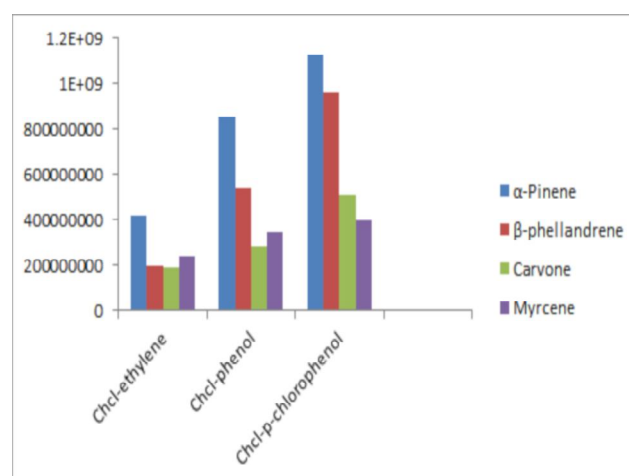
**Fig. 2.** Effect of solvents on extraction efficiency.

Table 2. Constituents of the Oil of *Satureja Hortensis* L.

Compounds	RI ^a	HD ^b Area%	DES ^c Area%	RSD ^d
Thujene	930	0.30	0.21	4.2
α -Pinene	936	6.34	5.21	6.1
α -Fenchene	950	0.06	0.04	3.5
Camphene	952	0.07	0.03	4.5
Verbenene	963	0.09	0.02	3.7
Heptanol-n	966	0.07	0.05	3.2
<i>Trans</i> -pinene	974	0.05	0.02	4.6
Sabinene	977	0.73	0.41	6.2
β -Pinene	981	0.06	0.03	7.8
Myrcene	992	1.23	0.72	6.3
α -Phellandrene	1005	31.65	14.38	6.5
<i>ortho</i> -Cymene	1021	8.34	6.42	8.5
β -Phellanderne	1029	5.72	3.57	7.4
Z-beta-Ocimene	1037	29.60	18.30	7.8
γ -Terpinene	1058	0.33	0.17	7.6
Terpinolene	1088	0.36	-	-
Linalool	1098	1.65	-	-
<i>Cis</i> -Thujone	1100	0.49	-	-
Allo-ocimene	1127	0.18	-	-
<i>Cis</i> -beta-terpineol	1142	0.20	0.04	9.1
Terpin-4-ol	1176	0.15	0.07	8.3
<i>Cis</i> -sabinene hydrate acetate	1219	0.84	0.22	7.5
Carvone	1239	3.03	2.91	5.6
Geraniol	1252	0.31	0.13	8.2
Thymol	1290	4.28	3.45	7.8
Carvacrol	1298	1.41	0.60	9.1
Z-jasmone	1392	0.21	0.07	8.4
Phenyl-hexan-3-one	1421	0.45	0.18	7.3
Germacrene D	1480	0.26	0.10	6.5
Cadina-1,4-diene	1532	0.12	0.05	9.5
Caryophyllene alcohol	1568	0.07	0.02	8.6
Spathulenol	1576	1.02	0.03	9.2

^aRetention indices using a DB-5 column. ^bRelative area (peak area relative to total peak area) for hydrodistillation method. ^cRelative area (peak area relative to total peak area except for the solvent peak) for DES-SDME method. ^dRSD values for DES-SDME method (relative peak area).

DES Volume

The influence of micro drop volume on the extraction efficiencies for the target analytes was investigated. It is obvious that using a big organic drop leads to an increased analytical response. Nevertheless, it is difficult and unreliable to operate larger drops. Also, the larger injection volumes lead to the band broadening in capillary GC. Hence, a micro drop volume of 2 μ l was used to ensure the creation of a reproducible and stable micro drop, although it has shortcomings such as the sensitivity loss.

Sample Temperature

It was recognized that the temperature has dual effect on SDME space. An increase in temperature increases the vapor pressure of the analyte; hence increasing their concentrations in the headspace. However, the analytes' partition coefficients within the headspace and extraction solvent are reduced by the enhanced temperature. The impact of the temperature was investigated within the 80–94 °C range by applying a hanging drop for 40 min in the headspace. Increasing the temperature over 90 °C increased the extraction ability; it is due to an increase in the analytes' distribution constant between the headspace and aqueous phase. Nevertheless, for most of the compounds, by further increasing the temperature over 90 °C, a small reduction in adsorption capacity was found. It is most likely due to the reduced partition coefficients of analytes within hanging drop and headspace, since adsorbing is normally an exothermic procedure. Thus, 90 °C was chosen as the optimal temperature.

Extraction Time

Extraction time is an important factor affecting the efficiency of the method. Extraction was conducted at 35–45 min for determining the impact of the extracting time on the effectiveness of the technique. The results, shown in Fig. 3, represent the peak area against extracting time profiles. As shown, at first, the extraction efficiency increased by increasing the extraction time. After about 40 min, the equilibrium was obtained for all the investigated analytes. Based on these findings, a period of 40 min was selected for succeeding tests. The chromatograms are shown in Fig. 4.

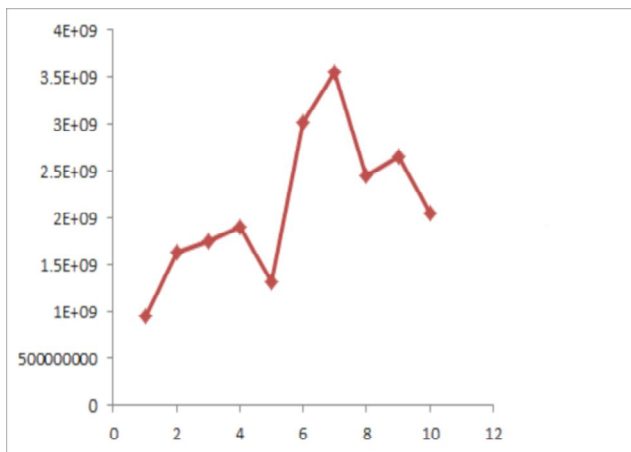


Fig. 3. The response (sum area of the four main peaks) for the designed experiments mentioned in Table 1.

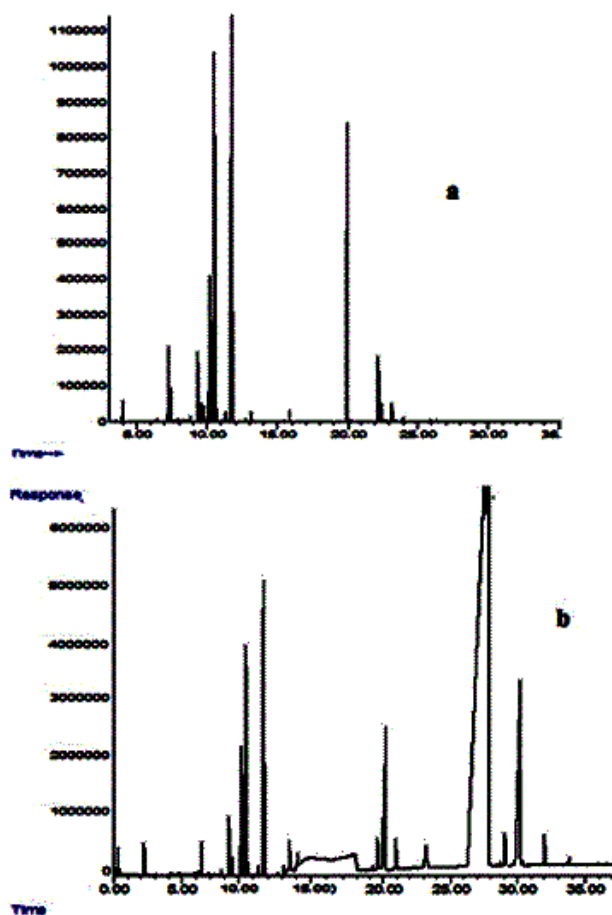


Fig. 4. The chromatograms of the essential oil *Satureja hortensis* L. by (a) hydrodistillation and (b) DES.

In this work, the extraction of volatiles from the plant was investigated with of ChCl: 4-chlorophenol deep eutectic solvent. The retention times of the main compounds were compared with the retention times of the injected standards and essential oils of HD, under the same conditions. The RSDs for the proposed method are low. According to the results, the proposed method is a rapid, sensitive, and repeatable technique that can be used for the preconcentration and determination of the target analytes in different samples.

CONCLUSIONS

In general, DESs-HS-SDME was more rapid and easier than conventional hydrodistillation and required a small amount of samples. Using the DESs-HS-SDME, the isolation, extraction, and concentrating of volatile constituents in *Satureja hortensis* L. can be performed in a single step. In the present work, an SDME process was applied using DESs for extracting and preconcentrating some essential oils in plants, followed by a GC-FID determination. The suggested process is very rapid and simple. The total extraction time (specimen pre-treatment plus chromatography) is around 40 min. For microextraction, the solvent, the dedicated and expensive device is not required. No considerable differences were found between the various kinds of tested samples for quantifying the analytes. The relative standard deviation (RSD) was assessed by four consecutive extraction with each target analyte in the range of 3.2-9.5% (Table 2).

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