



Analysis of black pepper volatiles by solid phase microextraction–gas chromatography: A comparison of terpenes profiles with hydrodistillation



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ABSTRACT

Solid phase microextraction (SPME) is widely used in food flavor compounds analysis in majority for profiling volatile compounds. Based on such profiles conclusions are often drawn concerning the percentage composition of volatile compounds in particular food, spices or raw materials. This paper focuses on the usefulness of SPME for the profiling of volatile compounds from spices using black pepper as an example. SPME profiles obtained in different analytical conditions were compared to the profile of pepper volatiles obtained using hydrodistillation in Clevenger apparatus. The profiles of both monoterpenes and sesquiterpenes of black pepper were highly dependent on sample weight (0.1 and 1 g samples were tested), and extraction time (durations from 2 to 120 min were tested), regardless of the SPME fiber used (PDMS and CAR/PDMS coatings were used). The characteristic phenomenon for extraction from dry ground pepper was the decrease of monoterpenes % share in volatiles with increasing extraction times, whereas at the same time the % contents of sesquiterpenes increased. Addition of water to ground pepper substantially changed extraction kinetics and mutual proportions of mono to sesquiterpenes compared to dry samples by minimizing changes in mono- to sesquiterpenes ratio in different extraction times. Obtained results indicate that SPME can be a fast extraction method for volatiles of black pepper. Short extraction times (2–10 min) in conjunction with the fast GC analysis (2.1 min) proposed here may offer fast alternative to hydrodistillation allowing black pepper terpenes characterization.

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1. Introduction

Black pepper (*Piper nigrum* L.) is one of best known and earliest used spices responsible for pungency in food. Its origin is in Malabar in South India. Pepper is grown primarily in India, Malaysia, Brazil, Indonesia and Sri Lanka. Depending on the maturity level and processing method, one may obtain different types of pepper. Black pepper is produced of grown, but still green fruit, which is dried in the sun, while white pepper is ripe fruit which is first removed from the skin, and then sun-dried. The popularity of pepper is caused by its characteristic flavor and pungency. Pepper contains essential oil which is composed of terpene hydrocarbons (89% altogether), oxygenated terpenes and aromatic compounds [1–4]. Recent research conducted with comprehensive gas chromatography–mass spectrometry has identified 273 volatile compounds in pepper. [5].

Pepper's characteristic aroma and flavor are contributed by constituents of pepper essential oil such as (E)- β -caryophyllene, limonene, β -pinene, β -phellandrene, δ -3-carene, sabinene, β -bisabolene, α -pinene, eugenol, terpinen-4-ol, hedycaryol, β -eudesmol, α -humulene, zingiberene, elemicin, bulnesol, cubenol and caryophyllene oxide [1–3,6]. Jagella and Grosch [7] identified (\pm)-linalool, (+)- α -phellandrene, (–)-limonene, myrcene, (–)- α -pinene, 3-methylbutanal and methylpropanal as main odorants in black pepper. 2,3-diethyl-5-methylpyrazine and 2-isopropyl-3-methoxy-pyrazine were linked to musty, moldy off-flavor of black pepper [8].

Various extraction techniques have been used to study essential oils in *Piper nigrum* L. Previously, the volatile compounds of pepper have been identified after hydrodistillation, headspace/solid-phase microextraction (HS–SPME), supercritical fluid extraction (SFE), solvent assisted flavor evaporation (SAFE), and purge-and-trap technique [1,9–13].

Hydrodistillation is one of the oldest methods used to obtain essential oils from plants. It is performed both in lab and on industrial scale. In the latter case, hydrodistillation can be performed in

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apparatuses that differ from the lab types with regard to steam generation. In laboratories Clevenger type apparatuses are used where plant material is placed in water in a round-bottom flask, and essential oils are being condensed while the plant/water material is being boiled for 1–3 h. Essential oil can be collected neat or in xylene added to the apparatus. Such extraction is a standard in essential oil industry as well as in labs controlling essential oil composition of plant materials [4]. Apart from this hydrodistillation is also used as a reference method when other extraction techniques are investigated [14,15].

Solid-phase microextraction (SPME) is a solventless technique developed in 1990 by Janusz Pawliszyn for the purposes of volatile and semivolatile analysis. It proved to be useful for quantitation in food matrices down to ppt levels [16] and been widely used in the analysis of food flavors and off-flavors [17,18]. In food flavor compounds analysis, SPME has been shown to prevail among microextraction techniques. In a recent study that examined 632 manuscripts on the analysis of flavor compounds that were published between 2006 and 2011, it turned out that SPME was used in as many as 549 [18]. Surprisingly, in the majority (70–80%) of its applications in flavor analysis, SPME is used for qualitative, not quantitative work. The use of SPMS for qualitative work, mostly for “profiling” volatile or aroma compounds, is caused by the “convenience” of the technique – its simplicity and ease of operation. In many circumstances SPME is used instead of standard methods such as hydrodistillation for essential oils characterization, although as an extraction method based on partition – it yields different profiles of extracted compounds that are different from those obtained with exhaustive extraction methods.

Surprisingly little information is available in the literature on the influence of SPME extraction parameters on the profiles of different classes of volatile compounds in plants rich in essential oils. In order to verify the usefulness of SPME to characterize the volatile compounds of black pepper and – especially – to investigate the conditions influencing the profile of extracted compounds, the current study was performed. Here special attention was paid to two groups of volatiles that are common for the majority of essential oils bearing plants: monoterpenes and sesquiterpenes. As a reference method of volatiles extraction, employed usually in essential oils analysis, hydrodistillation was used.

2. Materials and methods

Black pepper was bought at the local store with spices. A batch of pepper (approx. 100 g) was ground in a laboratory mill so as to obtain a uniform portion of ground pepper to be used in all experimental procedures. During the time between the experiments, the ground pepper was stored in darkness in a 300 ml Erlenmeyer flask with glass stopper in refrigerator (at 4 °C).

2.1. SPME extraction

SPME fibers of two types were chosen for experiments: polydimethylsiloxane (PDMS) liquid phase coating was selected for absorption of volatiles, whereas Carboxene/polydimethylsiloxane (CAR/PDMS) was selected to represent the adsorption mechanism. Portions of the ground pepper were weighted using laboratory scales and placed in 44 ml vials (Supelco, Bellefonte, PA) closed with PTFE-lined silicon septa and screw caps with a hole enabling SPME sampling. Each vial was used only once to avoid the adsorption of volatiles on a pierced membrane with silicone rubber exposed. For the different experimental trials, different amounts (1 g and 0.1 g) of pepper were used; also, 0.1 g of ground pepper mixed with 1 ml of bi-distilled water was used. The sampling of the volatiles was performed at 20 ± 1 °C (room temperature, maintained by air

condition system) and at 50 °C – heating vials was performed in an in-lab made aluminum block. The block, as high as the vials, was placed on an IKA heater with temperature control. The temperature was equilibrated in the block for 5 min prior to the extraction process. The extraction time for analyzed samples ranged from 2 to 120 min; the samples were analyzed after 2, 5, 10, 20, 30, 60 and 120 min. All samples were run in triplicates.

2.2. Hydrodistillation of black pepper volatiles

Clevenger type apparatus (Deryng apparatus, WPL s.c. Gliwice, Poland) was used for hydrodistillation process. A 20 g portion of ground pepper was placed in a 500 mL round bottom flask with 200 mL of water, and boiled for 2 h. Collected neat essential oil was used for subsequent chromatographic analyses.

2.3. Analysis of volatiles by gas chromatography–mass spectrometry (GC/MS)

Oil extracted after hydrodistillation, as well as all SPME samples were run on a GC/MS system. 7890A gas chromatograph coupled to 7000A triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA) was used for the analyses. A triple quadrupole instrument was run as a single quadrupole one with the first quadrupole set for ion transmission; the collision gas was switched off. The compounds were separated on a Restek RTX-5 column (10 m × 0.18 mm × 0.25 μm) using helium as a carrier gas (0.5 ml/min, constant flow). Desorption temperature for both SPME fibers was 250 °C. The SPME samples were analyzed in split mode (1:150) at programmed temperature (40 °C for 1 min, then increased by 10 °C every minute until 240 °C). The transfer line temperature was set to 290 °C, while the ion source (EI) temperature was set to 230 °C. Mass spectra (EI) were registered in a SCAN mode using a range of 33–333 amu at 107 ms/cycle (9.3 cycle/s). The obtained compounds were identified tentatively by comparing the obtained spectra with that from NIST 05 library of mass spectra and by comparing their retention indices calculated for DB-5 type of columns with those available in the literature.

2.4. Analysis of volatiles by fast gas chromatography with FID detection

To evaluate the possibilities of accelerating chromatographic separation a narrowbore chromatographic column was used in an Agilent Technologies 7890A gas chromatograph equipped with split/splitless injection port and flame ionization (FID) detector. SPB-5 column (5 m × 0.050 mm × 0.1 μm), Supelco, Bellefonte, PA, was used for analyses with H₂ as a carrier gas (at a constant pressure of 68.8 psi – 0.4 mL/min). The desorption temperature was the same as in the GC/MS experiments. The split value due to a small capacity of column was 1:1000. SPME 0.75 mm liner (Supelco, Bellefonte, PA) was used for the extraction. The analyses were performed at a programmed temperature. Different experimental conditions were run with temperature ramp rates ranging from 10 °C to 80 °C/min. The final program was 40 °C, then increased by 80 °C each minute until reaching 200 °C and 40 °C each minute until reaching 280 °C. The total duration of the analysis for the selected parameters was 4 min, and the elution of the compounds took place within 2.1 min.

3. Results and discussion

3.1. Volatile compounds of black pepper analyzed by hydrodistillation

The GC/MS analysis of essential oil obtained after hydrodistillation process revealed 22 main volatile compounds, which can be

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