



The emission levels of terpenes representatives from available on Polish market culinary dried herbs: proposal for a solvent-free and non-destructive solution for the comparative analysis of dried consumer products

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Abstract

In most analytical procedures, quality assessment (type and level of organic compounds) of commercially available herbs (as a plant) as well as dried herbs is carried out using techniques based on the extraction process with the use of an organic solvent. These solutions are not good from the point of view of the assumptions in the implementation of the principles of green analytical chemistry. For this reason, new solutions that are solvent-free and as less intrusive as possible to the studied samples are being developed for comparative analyses of products of natural origin used as food additives. Performed investigations focuses on the role of terpenes in defining the aromatic qualities of five commercially available dried herbs: basil (*Ocimum basilicum* L.), oregano (*Origanum vulgare* L.), thyme (*Thymus vulgaris* L.), rosemary (*Salvia rosmarinus* L.), and marjoram (*Origanum majorana* L.). At the stage of volatile compounds extraction to the gaseous phase the stationary miniature emission chamber system was employed. The method used to investigate the terpene emission level from culinary dried herbs was TD-GC-FID. The dried herb samples were conditioned in two temperature conditions – 25 °C and 50 °C. The calculated values of total volatile organic compounds (TVOCs) emitted from the investigated samples ranged from 0.739 $\mu\text{g}\cdot\text{g}^{-1}$ (for rosemary) to 444 $\mu\text{g}\cdot\text{g}^{-1}$ (for oregano). Sixteen representatives of terpenes emitted into the gaseous phase from the investigated samples were determined. In addition, on the basis of a comparative analysis of the emission of organic compounds into the gaseous phase from commercially available essential oils (derived from the same types of plants as the studied herbs), those compounds that can be considered characteristic and defining of a particular type of herb have been identified. This study introduces a non-invasive, solvent-free method for assessing the quality of dried culinary herbs by analyzing terpene emissions in the gaseous phase. This approach aligns with green analytical chemistry principles and offers a rapid, environmentally friendly alternative to traditional solvent-based extraction techniques.

Keywords Dried herbs · Terpenes · Emission rate · Solventless technique

Introduction

Herbs and spices have played a key role in food preparation process for centuries. In ancient times, they were used both to enhance the flavor of dishes and to protect their freshness. In the cuisines of the world, various mixtures of herbs and spices are used, which give dishes a unique character and distinguish them in taste [1]. The distinctive aroma, flavor, and health benefits of many herbs are primarily due to terpenes and other volatile organic compounds (VOCs) [2, 3]. Terpenes, naturally occurring aromatic molecules found in the essential oils of herbs, fruits, and plants, play a key role in defining a plant's sensory and therapeutic properties. In

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culinary contexts, terpenes and other active VOCs enhance the sensory appeal of food by intensifying flavors and aromas [4, 5]. The balance and presence of active VOCs, particularly terpenes, are thus critical to the culinary and health-related value of herbs. Given their capacity to influence biological systems, the therapeutic potential of terpenes has garnered significant research interest, further highlighting their medicinal applications [6]. Thus, the presence and balance of active VOCs, such as terpenes, are crucial for both the culinary and health-related value of many herbs and plants [7]. Research has focused on the therapeutic potential of terpenes, given their capacity to positively influence diverse biological systems within the human body [8, 9]. For instance, specific terpenes such as limonene, thymol, and carvacrol are recognized for their strong antibacterial and antifungal properties, rendering them effective in combating bacterial and fungal infections [10]. In traditional medicine, several species of *Thymus* (*Thymus vulgaris* L.), particularly thyme, have historically been utilized to treat a range of respiratory conditions, including whooping cough, bronchitis, and asthma. This therapeutic efficacy in managing respiratory issues can be attributed to their anti-inflammatory and antimicrobial properties, which are essential for alleviating symptoms and enhancing respiratory health [11].

To conduct a comprehensive analysis of herbal samples (assessing the concentration level of a given organic compound in the investigated natural samples), it is imperative to employ extraction techniques that facilitate the isolation and preconcentration of organic compounds which occurs in the natural complex samples [12]. In the context of herbal and spice extraction, solvent-based techniques are widely used to effectively isolate bioactive constituents [13]. Typically, the process begins with grinding the plant material into a fine powder, which is then subjected to a solid-liquid extraction (SLE) mainly using classical Soxhlet system [14]. Moreover, a technique for extracting bioactive compounds developed using ultrasound-assisted extraction (UAE) and subsequent reversed-phase high-performance liquid chromatography (RP-HPLC) for separation and quantification can be used. This technique uses the cavitation effect generated by ultrasonic waves to enhance solvent penetration into plant tissues [15]. It can be effectively applied for the extraction and analysis of important phytochemicals in medicinal plants. To enhance the efficiency of different extraction processes, techniques such as ultrasonic or microwave-assisted extraction (USE or MAE) are often employed. These techniques can significantly improve the yield and extraction rates by increasing the interaction between the solvent and the plant material [16, 17]. Additionally, it should be noted that for the extraction of volatile compounds, in particular essential oils that are rich in mono- and sesquiterpenes, hydrodistillation remains one

of the most classical and widely adopted techniques. This method relies on the co-distillation of plant material with water or steam, which facilitates the release and subsequent condensation of thermolabile volatile constituents without substantial degradation. Hydrodistillation is especially suitable for aromatic and medicinal plants, as it allows for the efficient isolation of complex mixtures of volatile secondary metabolites. Despite being a traditional technique, it is still extensively used in both laboratory-scale research and industrial production due to its relative simplicity and effectiveness. In the broader context of phytochemical analysis, hydrodistillation is often combined with subsequent analytical methods, such as gas chromatography coupled with mass spectrometry (GC–MS), to enable the detailed qualitative and quantitative profiling of volatile components [18]. Overall, optimizing extraction conditions—such as solvent choice, temperature, and duration—plays a critical role in maximizing the efficacy of herbal extractions, leading to high-quality products that retain the therapeutic properties of the original plant material [19].

As a result of the increasing demand for more efficient and reliable extraction methods, there is a growing interest in solvent-free extraction techniques. For the VOCs a good solution is the application of headspace analysis (HSA), especially due to the fact that this kind of technique might be automatized and the use of the organic solvents is extremely minimal or even fully solventless. Nevertheless, the main limitation of this technique is the calibration process (appropriate internal standard is needed), ensuring optimal conditions for equilibrium in the vessel and the problem with the determination of organic compounds which might be present in the sample at very low content level [20]. More developed solution is the integration of HS with solid-phase microextraction (SPME) technique using appropriately selected sorption fibers which might selectively collect the defined group of volatile and semi-volatile compounds (SVOCs). This solution is well-known for its high efficiency, requiring minimal sample preparation, might be automatized and eliminating the need for solvents [21]. On the other hand, also in this case there are some limitations associated with the calibration process and preserve the optimal equilibration conditions. The combination of gas chromatography-mass spectrometry (GC-MS) with HS-SPME as well as HS-SPME combined with two dimensional gas chromatography (GC x GC) significantly improves the analysis of volatile compounds, especially in a qualitative analysis – possible identification of primary organic compounds as well as their potential metabolites [22–24]. However, it should be mentioned that classical HAS and the combination of HS-SPME mostly works based on the statical conditions – maintaining the sample in

a sealed vial for a defined time and in the defined temperature conditions, waiting for the equilibrium to be reached.

The primary aim of this study was to introduce a non-destructive, solvent-free method for conducting a comparative analysis of commercially available culinary dried herbs in Poland, specifically basil (*Ocimum basilicum* L.), oregano (*Origanum vulgare* L.), thyme (*Thymus vulgaris* L.), rosemary (*Salvia Rosmarinus* L.), and marjoram (*Origanum majorana* L.). The research focused on evaluating the chemical profiles of these herbs to assess their authenticity and quality without the need for organic solvents. To achieve this, a stationary miniature emission chamber system (Micro-Chamber/Thermal Extractor™) was employed for sample seasoning at two temperature ranges: 25 °C and 50 °C. For analyte extraction from the sorption medium Tenax TA, a solvent-free, two-stage thermal desorption technique combined with gas chromatography (TD-GC) was applied.

The scientific novelty of this study lies in the fact that, to the best of our knowledge, it is the first time that commercially available culinary herbs on the Polish market have been analyzed using a completely solvent-free method – fulfilling the principals of green analytical chemistry. This innovation significantly advances the way we evaluate the authenticity and quality of herbs, as it eliminates the need for organic solvents, which are typically used in conventional analytical methods.

Furthermore, the proposed procedure offers an alternative to the traditional headspace analysis or with the use of SPME technique as a sampling device. Unlike the static approach employed in HSA or HS-SPME, the research presented here is conducted in a dynamic mode. This dynamic approach eliminates the need to wait for equilibrium to be established between the tested substance and the gaseous phase, allowing for faster and potentially more accurate analysis of the herbs' chemical profiles.

By analyzing the emission profiles of these compounds, the study aimed to identify specific chemical markers—primarily terpenes—that could serve as indicators of herb authenticity and quality. Additionally, to establish a reliable database for comparison, commercially available essential oils corresponding to each of the dried herbs were investigated. These oils were used to confirm the typical chemical composition of each herb and were considered as reference materials for identifying key terpenes that are characteristic of each herb. An additional objective was to create a database that facilitates the qualitative comparison of similar products from different suppliers, supporting the verification of product authenticity. The data interpretation focused on identifying groups of similarity (clusters) based on both the chemical composition of the herbs and the sensory characteristics derived from their volatile emissions. To identify

patterns and structures within the data, the study employed both hierarchical cluster analysis and non-hierarchical methods, specifically K-means clustering, alongside factor analysis to uncover latent factors driving the data structure. This approach aimed to reveal specific variables associated with each cluster, contributing to a deeper understanding of the herbs' unique profiles.

Materials and methods

Samples characteristics

Commercially available five types of culinary dried herbs commonly used in food preparation – basil (*Ocimum basilicum* L.), oregano (*Origanum vulgare* L.), thyme (*Thymus vulgaris* L.), rosemary (*Salvia rosmarinus* L.) and marjoram (*Origanum majorana* L.) - were selected as the subject of the study. These herbs are available commercially in ready-made packages and have been subjected to thermal and mechanical processing by their manufacturer. Most packages contained about 15 g of product. The packages were mostly made of paper, although some also have an inner aluminium coating for extra protection against external factors - keeping the herbs fresh for longer time and protecting them from moisture and light. In addition, herbs declared by the producer as organically grown (ecological) were also analyzed for comparison purposes. Detailed information about the types of investigated herbs, type of the packing and the average mass of product taken for emissions investigation was listed in Table 1. Moreover, it was necessary to introduce markings to facilitate the identification of the investigated herbs.

Apart from assessing the herbs, the study also subjected the corresponding essential oils to analysis – essential oils of basil (*Ocimum basilicum* L.), oregano (*Origanum vulgare* L.), thyme (*Thymus vulgaris* L.), rosemary (*Salvia rosmarinus* L.), and marjoram (*Origanum majorana* L.). The essential oils utilized in the study were obtained from commercially available retail store (ETJA, Elbląg, Poland), ensuring accessibility and representative quality for comprehensive analysis. According to the manufacturer of the essential oil, some of the essential oils were produced by steam distillation of fresh or dried parts of the plant. The essential oils corresponded to the types of investigated herbs and constituted a specific reference element and confirmation of the emission of individual compounds from the terpenes characteristic for a given herb.

Table 1 General information about the investigated samples of commercially available dried herbs

Label	Herb type	Average mass $\pm$ SD [g]	Packaging material
Marjoram_a	Marjoram	0,633 $\pm$ 0,027	Paper
Marjoram_b		0,645 $\pm$ 0,032	Multilayer
Marjoram_c		0,629 $\pm$ 0,024	Paper
Marjoram_d		0,633 $\pm$ 0,015	Multilayer
Marjoram_eko		0,6100 $\pm$ 0,0088	Paper
Basil_a	Basil	0,639 $\pm$ 0,018	Paper
Basil_b		0,618 $\pm$ 0,015	Multilayer
Basil_c		0,633 $\pm$ 0,030	Multilayer
Basil_d		0,620 $\pm$ 0,018	Multilayer
Basil_eko		0,637 $\pm$ 0,020	Paper
Oregano_a	Oregano	0,615 $\pm$ 0,012	Paper
Oregano_b		0,649 $\pm$ 0,027	Multilayer
Oregano_c		0,648 $\pm$ 0,021	Multilayer
Oregano_d		0,663 $\pm$ 0,021	Multilayer
Oregano_eko		0,656 $\pm$ 0,016	Paper
Thyme_a	Thyme	0,635 $\pm$ 0,019	Multilayer
Thyme_b		0,635 $\pm$ 0,0052	Multilayer
Thyme_c		0,649 $\pm$ 0,029	Multilayer
Thyme_d		0,659 $\pm$ 0,025	Paper
Thyme_eko		0,645 $\pm$ 0,017	Paper
Rosemary_a	Rosemary	0,638 $\pm$ 0,020	Multilayer
Rosemary_b		0,660 $\pm$ 0,016	Paper
Rosemary_c		0,661 $\pm$ 0,025	Paper
Rosemary_eko		0,621 $\pm$ 0,0069	Paper

SD standard deviation ($n=3$)

Reagents and analytical equipment

During the performed emissions investigations the following reagents and solvents were used: (i) methanol ($\geq 99.9\%$ (GC), anhydrous, Merck KGaA, Darmstadt, Germany); (ii) reference standard solution containing toluene in methanol at content level of $200 \mu\text{g}\cdot\text{mL}^{-1}$ (certified reference material, TraceCERT[®], Merck KGaA, Darmstadt, Germany); (iii) reference standard solution containing 20 representatives of terpenes, dissolved in methanol (content level $2000 \mu\text{g}\cdot\text{mL}^{-1}$ of each - (-)- α -Bisabolol; (+)-Cedrol; (+)-Pulegone; (1R)-(+)-Camphor; (R)-(+)-Limonene; 3-Carene; Camphene; Citronellol; Fenchol; Geranyl acetate; Isoborneol; L-(-)-Fenchone; Menthol; Nerolidol; α -Cedrene; α -Humulene; α -Pinene; α -Terpinene; β -Pinene; γ -Terpinene) (Cannabis Terpene Mix A certified reference material, TraceCERT[®], Merck KGaA, Darmstadt, Germany).

The emission studies of the selected organic compound was carried out using the following devices and equipment: (i) Tenax TA sorption tubes (60/80 mesh, stainless steel TD tube, O.D. $\times$ L 1/4 in. $\times$ 3 1/2 in., preconditioned, Merck KGaA, Darmstadt, Germany); (ii) the stationary emission chambers system containing 4 chambers (114 cm³ capacity

each) fully compliant with ISO 12219-3 (Micro-Chamber/Thermal Extractor[™], μ -CTE[™] 250, Markes International, Inc.); the thermal desorption (TD) unit (Markes Series 2 Thermal Desorption Systems; UNITY/TD-100, Markes International, Inc.), gas chromatography-flame ionization detector (GC-FID) system (Agilent Technologies 7820 A GC System) equipped with GC capillary column (30 m $\times$ 320 μm $\times$ 5 μm , J&W DB-1, USA). Detailed information about the Micro-Chamber/Thermal Extractor[™] potential might be found elsewhere [25–27].

Analytical procedure used to assess the emission of organic compounds from investigated herbs samples

Before analysis, herb samples were weighted on a petri dish (average sample mass listed in Table 1). Herb samples were tested at two temperatures: (i) 25 °C - room temperature, the temperature was chosen to determine the emission of compounds from the terpene group under standard temperature conditions (regular storage); (ii) 50 °C - a high temperature imitating the conditions of adding herbs at the stage of cooking dishes. The selected range of temperatures might be associated with the conditions typically encountered by consumers while utilizing herbs in their culinary endeavours. The general analytical protocol used to assess the emissions of terpenes representatives, with the detailed equipment working conditions and analysis parameters was shown in Fig. 1.

In a case of commercially available essential oils, the samples were prepared by mixing 1 μL of selected type of essential oil in 0.5 mL of methanol. The ready solutions were mixed using a Vortex shaker. To identify the terpenes representatives which might be released to the gaseous phase from the selected essential oil solution, 1 μL of prepared methanol solution was taken and injected on a petri dish placed inside the emission chamber. Next the chamber was closed, the Tenax TA tube was installed at the outlet of the chamber and the gaseous phase was collected for 10 min at flow rate $25 \text{ mL}\cdot\text{min}^{-1}$ in 50 °C. After this, collected samples of analytes were desorbed and determined using the same equipment conditions as in a case of herb samples.

Calibration and quality assurance/quality control

Before using the Tenax TA sorption beds, each tube was conditioned at high temperature (300 °C for 30 min) under a stream of nitrogen (flow rate $50 \text{ mL}\cdot\text{min}^{-1}$; RH 0%). Additionally, according to the good laboratory practice, before each part of analysis (after changing the investigated herb) the blank samples were investigated (investigation of the gaseous phase composition of an empty chamber).

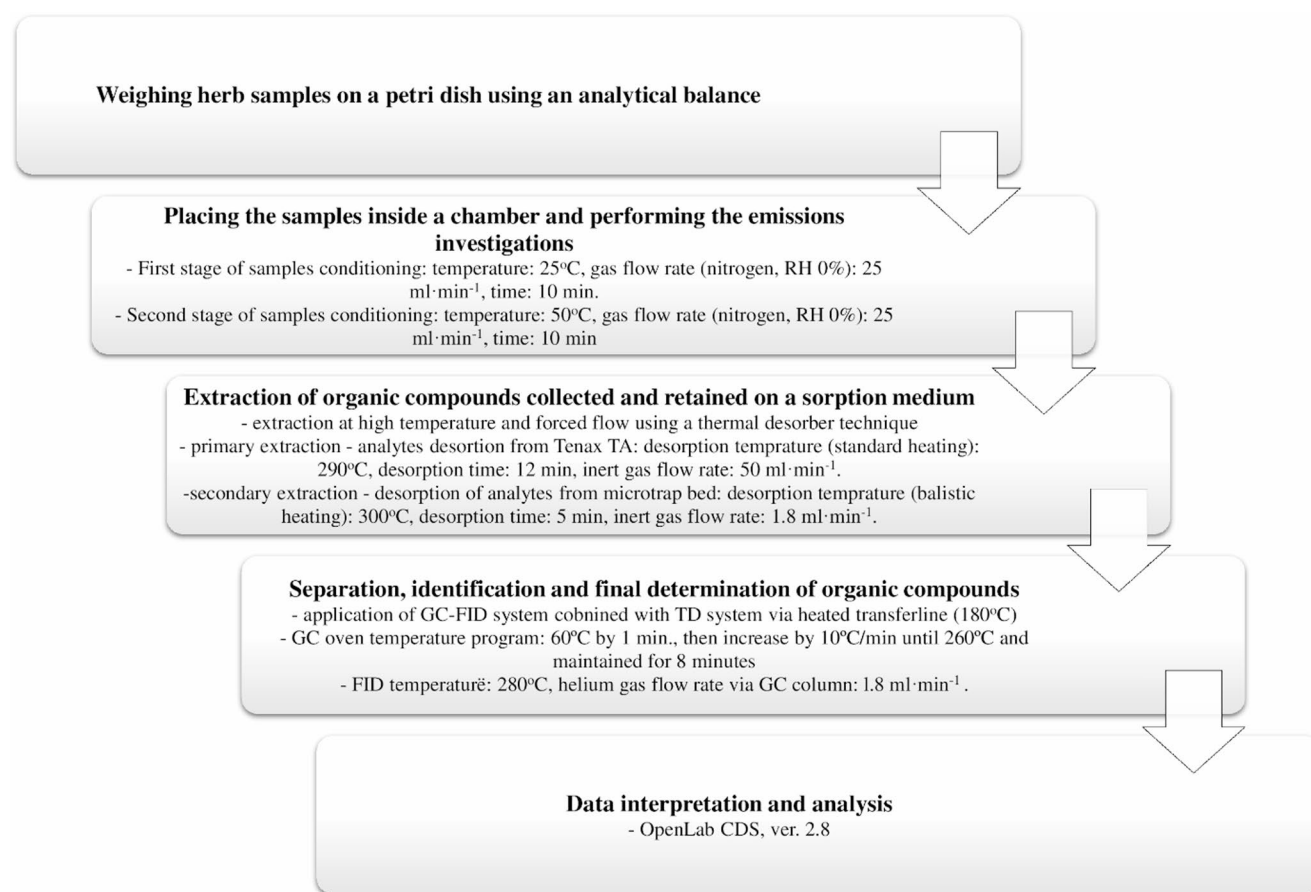


Fig. 1 Analytical protocol used to assess the emission rate of representatives of terpenes compounds from investigated herb samples

The reference standard solution of toluene was used as an internal standard (ISTD) for the calculation of the total concentration of volatile organic compounds (TVOCs parameter) emitted to the gaseous phase from investigated herb samples. Moreover, mentioned reference solution was employed to assess an injection repeatability as well as to estimate the organic compounds recovery (efficiency of the thermal desorption technique).

The amount of terpene representatives emitted from the investigated herbs samples and retained on the Tenax TA sorption bed was performed using calibration by the external standard method (development of calibration curves of analyte mass dependence on peak area). The reference standard solution containing 20 representatives of terpenes, dissolved in methanol was used as an ESTD for calibration of the TD-GC-FID system. For this purpose, calibrations solutions were prepared in 1.8 mL amber glass chromatographic vials. Calibration solutions were prepared in a two ranges: lower from 4 µg·mL⁻¹ to 140 µg·mL⁻¹ (equal to from 4 ng to 140 ng of analyte per sorption bed); higher from 140 µg·mL⁻¹ to 4000 µg·mL⁻¹ (which corresponds to 140 ng to 4000 ng of analyte per sorption bed). Detailed information about the calibration protocol and employed

equipment might be found elsewhere [28–30]. Each calibration range contains 5 calibration solutions. Three repetitions were performed for each point on the curve. The determination coefficient (R^2) for the obtained calibration curves for the lower concentration range was from 0.967 to 0.999. As for the higher concentration range, the value of R^2 parameter was from 0.989 to 0.999. The identification of emitted compounds from the investigated culinary dried herbs was performed by comparing retention times with a certified reference solution of terpenes representatives as well as by comparing chromatograms obtained for the investigated herb and its essential oil analogue. Due to this fact it was possible to select such terpenes which emissions to the gaseous phase are characteristic for a defined type of dried herb.

The numerical values of basic validation parameters such as limit of detection (LOD) and limit of quantification (LOQ) were determined based on the developed calibration curves and by determining the numerical value of the signal-to-noise ratio (S/N, or signal-to-noise ratio). It was estimated that the value of the LOD parameter was 0.5 ng per tube, while the value of the LOQ parameter was assumed to be three times the LOD (LOQ=1.5 ng per tube).

Multivariate statistical methods used for data mining

The methods used for the data mining and interpretation are well-known and documented in the chemometric literature, namely hierarchical and non hierarchical (K-means mode) cluster analysis and factor analysis.

The aim of the monitoring data mining was to reveal hidden relationships between the object of interest or between the variables used by multivariate statistical methods (chemometrics). It was important to find out patterns of similarity among object and/or variables, which could be of help in the correct data interpretation. It was also important to detect those specific descriptors being responsible for the formation of similarity patterns between the objects.

The chemometric methods used in the present study were hierarchical and non-hierarchical (K-means) analysis for detection of similarity patterns and, additionally, factor (principal components) analysis for matrix data structure interpretation. All methods used are well known chemometric techniques thoroughly documented [31, 32]. Hierarchical cluster analysis (HCA) is non-supervised pattern recognition method usually applied to standardized (by z-means) input data aiming formation of clusters of objects or variables specifically located in a multivariate space. The similarity measure was the square of the Euclidean distance and the linkage approach was Ward's method assuring minimal variation of the system. The graphical output is traditional tree-like plot (dendrogram) with test for cluster significance Sneath's index (1/3 or 2/3 of the maximal similarity distance). Non-hierarchical cluster analysis (K-means clustering) is supervised pattern recognition method allowing to organize the objects of interest or their descriptors into a priori selected number of clusters (according a preliminary hypothesis or expert opinion).

Factor analysis (principal components analysis or PCA) is a traditional dimensionality reduction technique based on the decomposition of the input data matrix into matrix of factor loadings (for assessment of the partitioning of the variables) and matrix of factor scores (for assessment of the new objects coordinates in the new factor space). Thus, the data set structure is easier interpreted and visualized. As a chemometrical approach principal components analysis (factor analysis) is a typical display method, which ensures the reduction of the size of the space of the variables. The substitution of a great number of correlated parameters by a small number of independent factors (principal components) is a useful tool for data interpretation and data structure explanation.

Results and discussion

Marjoram analysis

The emission values of the determined representatives of terpenes released into the gaseous phase from the samples of marjoram dried herbs were listed in Table 2. The compounds highlighted in bold in the tables represent the major terpene constituents characteristic of each herb, confirmed through analysis of the corresponding commercially available essential oils. The analysis of marjoram herbs samples (Marjoram_A to Marjoram_Eko) reveals several dependencies and differences in terpene emissions at 25 °C and 50 °C. γ -Terpinene consistently shows the highest emissions across the samples, especially in Marjoram_D and Marjoram_Eko, where it exceeded $4000 \text{ ng} \cdot \text{g}^{-1}$ at 50 °C. This compound also is characterized by substantial emissions in Marjoram_C and Marjoram_B at the higher temperature. The elevated emission levels of γ -Terpinene, particularly in Marjoram_D and Marjoram_Eko, suggest that these samples may offer a more intense aromatic profile, potentially associated with a stronger, citrusy, or herbal scent typical of γ -Terpinene. The emission of γ -Terpinene in these samples suggests a potential varietal or environmental influence, especially considering that both Marjoram_D and Marjoram_Eko consistently exhibited higher emissions of several terpene.

The output of α -Pinene in marjoram illustrates variability among disparate samples, with Marjoram_D indicating the highest emission level at $298 \pm 64 \text{ ng} \cdot \text{g}^{-1}$ when scrutinized at 50 °C. The comparatively elevated presence of α -Pinene in Marjoram_D is likely to impart a fresh, pine-like aroma to its overall aromatic profile, thereby differentiating it from other samples. In contrast, Marjoram_Eko, which emits $122 \pm 20 \text{ ng} \cdot \text{g}^{-1}$, alongside Marjoram_A, exhibiting $20.2 \pm 5.5 \text{ ng} \cdot \text{g}^{-1}$, indicates more subdued α -Pinene characteristics, rendering these samples more appropriate for applications that require a gentler pine-like fragrance.

TVOC levels reveal broad differences in overall emission strength across samples, with Marjoram_B and Marjoram_D exhibiting the highest TVOC at 50 °C ($99.4 \pm 20.5 \mu\text{g} \cdot \text{g}^{-1}$ and $61.3 \pm 9.0 \mu\text{g} \cdot \text{g}^{-1}$, respectively), followed closely by Marjoram_Eko. These elevated TVOC levels correspond to the high individual emissions of compounds like γ -Terpinene, indicating that these samples have a more complex aromatic profile at elevated temperatures.

In summary, each marjoram herbs sample demonstrates unique emission characteristics with temperature-dependent variations. Marjoram_D and Marjoram_Eko showed particularly high emissions of γ -Terpinene at 50 °C, contributing to intense aromatic profiles.

Table 2 Assessed emission values (defined as mean±standard deviation ($n=3$)) of determined representatives of terpenes from marjoram dried herbs

Herb type	Marjoram_A			Marjoram_B			Marjoram_C			Marjoram_D			Marjoram_Eko		
	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]
α -Pinene	13.3±5.2	20.2±5.5	17.53±0.57	4.3±1.7	< LOD	< LOD	< LOD	< LOD	< LOD	298±64	42.4±2.2	122±20	42.4±2.2	122±20	
Camphene	6.54±2.5	6.8±2.6	< LOD	< LOD	< LOD	< LOD	11.7±2.1	< LOD	< LOD	30.3±5.5	4.91±0.72	8.0±2.3	4.91±0.72	8.0±2.3	
β -Pinene	< LOD	7.3±1.0	8.23±0.85	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	312±62	30.8±3.2	91±11	30.8±3.2	91±11	
α -terpinene	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	
D-Limonene	12.6±5.2	57±22	128±38	12.7±3.4	32±12	304±48	32±12	304±48	32±12	382±33	(24.6±3.4)×10 ²	1001±89	172±21	1001±89	
γ -Terpinene	37.6±1.3	(9.3±3.6)×10 ²	(14.5±3.5)×10 ²	73.1±7.9	201±70	(30.0±5.1)×10 ²	201±70	(30.0±5.1)×10 ²	201±70	(16.5±2.6)×10 ²	>4000	>4000	(8.9±1.1)×10 ²	>4000	
L-Fenchone	6.51±0.25	218±54	(3.9±1.0)×10 ²	11.16±0.47	38±15	911±199	38±15	911±199	38±15	261±42	(26.5±6.1)×10 ²	(14.3±1.3)×10 ²	141±18	(14.3±1.3)×10 ²	
Camphor	10.1±3.9	15.5±1.5	< LOD	< LOD	< LOD	< LOD	3.72±0.44	< LOD	< LOD	11.6±3.5	14.1±3.3	38.6±2.9	14.1±3.3	38.6±2.9	
Isoborneol	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	
Citronellol	< LOD	77±28	61±11	6.6±1.3	< LOD	< LOD	< LOD	< LOD	< LOD	9.1±3.0	18.4±7.1	98±17	18.4±7.1	98±17	
Pulegone	46±17	109±40	87±18	8.4±3.2	6.9±1.9	128±32	6.9±1.9	128±32	6.9±1.9	132±52	79±24	(3.5±1.0)×10 ²	79±24	(3.5±1.0)×10 ²	
Geranyl Acetate	14.3±5.5	79.9±7.1	74.9±7.8	15.4±1.6	6.7±1.1	94.2±7.2	6.7±1.1	94.2±7.2	6.7±1.1	28±11	7.3±1.1	96±10	7.3±1.1	96±10	
α -Cedrene	30.8±8.2	(5.4±2.1)×10 ²	203±80	13.0±5.1	25.8±8.5	(4.6±1.3)×10 ²	25.8±8.5	(4.6±1.3)×10 ²	25.8±8.5	69±11	36.2±7.2	(5.6±1.6)×10 ²	36.2±7.2	(5.6±1.6)×10 ²	
α -Humulene	3.03±0.43	29±11	16.8±6.5	9.9±1.5	4.4±1.7	26.7±6.2	4.4±1.7	26.7±6.2	4.4±1.7	11.7±2.5	43±17	46±18	43±17	46±18	
Cedrol	< LOD	< LOD	< LOD	4.9±1.8	< LOD	< LOD	< LOD	< LOD	< LOD	10.6±4.0	8.1±2.9	< LOD	8.1±2.9	< LOD	
alpha Bisabolol	< LOD	< LOD	< LOD	9.9±1.2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	15.6±6.1	< LOD	15.6±6.1	< LOD	
TVOCs	10.6±4.2	21.9±1.7	19.2±4.4	1.44±0.28	1.64±0.37	27.9±4.7	1.64±0.37	27.9±4.7	1.64±0.37	15.8±2.1	11.3±2.7	61.3±9.0	11.3±2.7	61.3±9.0	
[μg·g ⁻¹]															

TVOC – total amount of volatile organic compounds emitted from investigated herb type

LOD – 0.5 ng

LOQ – 1.5 ng

>4000 – emission of the organic compound was above 4000 ng per gram of a herb

Basil analysis

The analysis of various commercial basil herbs samples reveals several notable patterns and dependencies within the emission levels of terpenes at 25 °C and 50 °C (see Table 3). Among the samples, Basil_A and Basil_D exhibited the highest emissions of β -Pinene ($457 \pm 59 \text{ ng} \cdot \text{g}^{-1}$ at 25 °C and $2270 \pm 690 \text{ ng} \cdot \text{g}^{-1}$ at 50 °C for Basil_A; $88.7 \pm 6.8 \text{ ng} \cdot \text{g}^{-1}$ at 25 °C and $516 \pm 37 \text{ ng} \cdot \text{g}^{-1}$ at 50 °C for Basil_D) and D-Limonene ($179 \pm 50 \text{ ng} \cdot \text{g}^{-1}$ at 25 °C and $970 \pm 200 \text{ ng} \cdot \text{g}^{-1}$ at 50 °C for Basil_A; $220 \pm 57 \text{ ng} \cdot \text{g}^{-1}$ at 25 °C and $1560 \pm 610 \text{ ng} \cdot \text{g}^{-1}$ at 50 °C for Basil_D), suggesting that these samples possess a significantly higher emission potential for these compounds. The elevated levels of both D-Limonene and β -Pinene in Basil_A, in particular, indicate a potentially more intense aromatic profile compared to other basil herbs samples.

Conversely, it was observed that the basil varieties identified as Basil_B and Basil_C exhibited generally lower emission levels of most terpenes compared to other varieties, suggesting a potential difference in the production of aromatic compounds. Furthermore, within these specific samples, even in the face of an increase in temperature, the growth rate of emissions was notably less pronounced when compared to the emissions observed in Basil_A and Basil_D, suggesting that the aromatic characteristics may differ significantly. This notable observation cultivates the chance of subtler aromatic features or essential compositional distinctions that may be apparent among these assorted basil herbs specimens.

In tandem with the previously mentioned findings, several specific compounds, such as α -Terpinene, were regularly observed at emission levels that were consistently lower than the LOD value across the majority of samples in both temperature conditions, which indicates that their presence in the samples is only detectable in trace amounts, regardless of the basil's herbs source. Isoborneol emissions in basil samples are minimal or below quantifiable levels at both 25°C and 50°C, indicating that this compound contributes little to the overall aromatic profile of basil across temperature variations. This lack of Isoborneol emission suggests that basil's scent profile leans more heavily on other VOCs, particularly those associated with fresh, herbal, and sweet notes, making it suitable for applications where these characteristics are desired without a prominent Isoborneol influence.

The basil herbs from organic farming sample, Basil_Eko, was distinctive for its elevated emission of D-Limonene at 50 °C ($1172 \pm 234 \text{ ng} \cdot \text{g}^{-1}$). The similarities between Basil_D and Basil_Eko, particularly their higher emissions of D-Limonene at 50 °C and the shared emissions below

LOD for compounds such as α -Humulene, suggest a comparable aromatic profile.

The assessment of TVOC emission levels further illuminates these differences. Basil_A demonstrated the most elevated TVOC concentrations at both temperature conditions ($13.2 \pm 3.1 \mu\text{g} \cdot \text{g}^{-1}$ at 25 °C and $87.1 \pm 20.6 \mu\text{g} \cdot \text{g}^{-1}$ at 50 °C), which is consistent with its heightened individual terpene emissions, signifying a more intricate and potent aroma profile. Conversely, Basil_C, exhibiting the lowest TVOC concentrations ($3.5 \pm 1.3 \mu\text{g} \cdot \text{g}^{-1}$ at 25 °C and $24.0 \pm 6.6 \mu\text{g} \cdot \text{g}^{-1}$ at 50 °C), reveals a markedly diminished aromatic intensity in comparison to the other specimens.

Oregano analysis

The examination of data derived from the oregano samples (Table 4) uncovers various significant patterns in their emissions of terpenes representatives, which are modulated by temperature and potentially by origin of investigated herbs (unfortunately on the pakings there was no information about the origin of defined type of herb).

Oregano_B and Oregano_D stand out with very high γ -Terpinene emissions at 50 °C, each exceeding $4000 \text{ ng} \cdot \text{g}^{-1}$. These two samples also show significant emissions of D-Limonene, with Oregano_B reaching $>4000 \text{ ng} \cdot \text{g}^{-1}$ and Oregano_D at approximately $(25.3 \pm 6.2) \times 10^2 \text{ ng} \cdot \text{g}^{-1}$. This suggests a possible correlation between γ -Terpinene and D-Limonene emissions, potentially indicating a shared biosynthetic pathway or similar temperature response in these samples.

Both Oregano_D and Oregano_Eko demonstrate considerable emissions of γ -Terpinene at a temperature of 50 °C. While α -Cedrene emissions vary across samples, Oregano_Eko and Oregano_D have particularly high levels at 50 °C ($992 \pm 87 \text{ ng} \cdot \text{g}^{-1}$ and $195 \pm 77 \text{ ng} \cdot \text{g}^{-1}$, respectively). This suggests that α -Cedrene levels may be influenced by temperature and potentially by organic cultivation, as seen in Oregano_Eko.

Isoborneol emissions vary significantly across oregano samples at 50 °C, with Oregano_D showing the highest level at $(19.3 \pm 1.8) \times 10^2 \text{ ng} \cdot \text{g}^{-1}$, followed by Oregano_Eko at $694 \pm 95 \text{ ng} \cdot \text{g}^{-1}$. Oregano_B and Oregano_A also emit pivotal levels of Isoborneol but are lower in comparison to Oregano_D, indicating that Oregano_D may provide a particularly strong aromatic profile at elevated temperatures. In contrast, Oregano_C displays a moderate Isoborneol emission, which could suggest a more subdued scent profile suitable for milder aromatic applications.

The emission of α -Pinene at 50 °C is exceptionally high in Oregano_B, exceeding $4000 \text{ ng} \cdot \text{g}^{-1}$, and moderately elevated in Oregano_A and Oregano_D, at $864 \pm 67 \text{ ng} \cdot \text{g}^{-1}$ and $(5.5 \pm 1.4) \times 10^2 \text{ ng} \cdot \text{g}^{-1}$, respectively. This indicates that

Table 3 Assessed emission values (defined as mean±standard deviation ($n=3$)) of determined representatives of terpenes from Basil dried herbs

Herb type Emitted compound	Basil_A		Basil_B		Basil_C		Basil_D		Basil_Eko	
	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]
α -Pinene	230±29	(11.2±3.1)×10 ²	18.44±7.2	37.6±1.3	21.8±5.0	79.2±5.2	53.3±4.1	262±47	19.8±8.1	90.0±7.7
Camphene	52.1±4.9	222±83	5.3±1.9	11.5±3.9	< LOD	13.73±2.6	7.9±1.2	35.8±9.5	4.41±0.95	27.5±8.6
β -Pinene	457±59	(22.7±6.9)×10 ²	< LOD	22.40±8.6	15.8±6.2	108.8±6.2	88.7±6.8	516±37	25.0±8.6	110±19
α -terpinene	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ
D-Limonene	179±50	(9.7±2.0)×10 ²	94±24	(7.2±2.5)×10 ²	54±16	(4.7±1.1)×10 ²	220±57	(15.6±6.1)×10 ²	84±13	(11.7±2.3)×10 ²
γ -Terpinene	78±10	268±68	24.1±1.9	52±19	13.7±3.6	15.6±6.1	47.6±5.9	182±52	18.3±5.4	70.5±9.2
L-Fenchone	33±14	< LOQ	15.5±6.0	< LOQ	13.4±2.1	82±15	23.2±4.5	< LOQ	14.7±4.6	82±31.1
Camphor	51±17	(4.9±1.9)×10 ²	38±15	350±35	< LOD	< LOD	42.7±9.9	(7.9±1.8)×10 ²	25.4±4.9	282±64
Isoborneol	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOQ
Citronellol	9.0±2.3	236±59	9.9±3.7	265±35	3.2±1.1	57±19	28.4±8.5	714±17	16.6±1.2	240±8.5
Pulegone	29±11	63.6±5.4	34±12	274±74	18.2±7.1	122±42	24.0±9.2	283±69	31.3±4.5	(5.2±1.4)×10 ²
Geranyl Acetate	8.3±3.1	129±51	20.7±6.3	163±38	18.2±7.0	155±61	23.6±9.3	190±74	< LOD	103±25
α -Cedrene	9.4±3.5	128±51	19.9±7.6	263±96	< LOD	53.2±6.4	20.5±8.0	(6.1±2.4)×10 ²	10.1±2.4	132±50
α -Humulene	3.8±1.8	30±11	< LOD	128±50	2.9±1.0	11.8±4.3	< LOD	128±50	< LOD	44±17
Cedrol	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ
alpha Bisabolol	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ
TVOCs [μg·g ⁻¹]	13.2±3.1	87.1±20.6	8.8±3.0	74.5±14.1	3.5±1.3	24.0±6.6	12.8±3.6	12.6±3.5	5.89±0.84	70.9±12.5

TVOC – total amount of volatile organic compounds emitted from investigated herb type

LOD – 0.5 ng

LOQ – 1.5 ng

>4000 – emission of the organic compound was above 4000 ng per gram of a herb

Oregano_B may be best suited for applications requiring a dominant piney aroma. The considerably lower α -Pinene emission in Oregano_Eko and Oregano_C, especially the minimal presence in Oregano_C ($232 \pm 78 \text{ ng} \cdot \text{g}^{-1}$), suggests that these varieties may serve applications where a subtler α -Pinene note is preferred. This variability reflects the potential for customization in aromatic formulations depending on the strength of the α -Pinene emission needed.

Diaz-Maroto et al., 2002 used the HS-SPME-MS system to perform the isolation of volatile compounds from oregano (not dried herb) acquired from a local store. The authors manage to identify 22 volatile compound e.g. α -Pinene, γ -Terpinene, Borneol and α -Humulene [33].

TVOC levels reveal each sample's aromatic potential. Oregano_B and Oregano_D display high TVOC values at 50°C ($444 \pm 18 \mu\text{g} \cdot \text{g}^{-1}$ for Oregano_B and $99.2 \pm 7.1 \mu\text{g} \cdot \text{g}^{-1}$ for Oregano_D), aligning with their elevated individual terpene emissions. In contrast, Oregano_C has low TVOC values at both temperatures, suggesting a milder aromatic profile overall. Certain compounds, including α -Terpinene, exhibit emissions below the LOQ value across most samples and at various temperatures.

Thyme analysis

The emission values of the determined representatives of terpenes released into the gaseous phase from the samples of thyme dried herbs were listed in Table 5. At an elevated temperature of 50°C , the emissions of γ -Terpinene exhibit remarkably high concentrations, with the samples Thyme_B and Thyme_Eko particularly distinguishing themselves by demonstrating values that significantly exceed $4000 \text{ ng} \cdot \text{g}^{-1}$, while the sample designated as Thyme_A reveals emissions that are notably quantified at $(27.2 \pm 6.7) \times 10^2 \text{ ng} \cdot \text{g}^{-1}$. In contrast, the samples Thyme_C and Thyme_D, which present γ -Terpinene emissions measured at $994 \pm 83 \text{ ng} \cdot \text{g}^{-1}$ and $(3.2 \pm 1.2) \times 10^2 \text{ ng} \cdot \text{g}^{-1}$ respectively, exhibit considerably lower values under these thermal conditions, thereby indicating a substantial degree of variation among the different samples analyzed. The emission of γ -Terpinene in Thyme_B and Thyme_Eko displays considerable sensitivity to temperature alterations, possibly increasing their aromatic efficacy in elevated temperatures.

The observation of significant emission level of γ -Terpinene in the samples Thyme_B and Thyme_A implies the existence of a potential synergistic interaction between these volatile compounds, which may serve to enhance specific aromatic notes, particularly those that are characteristic of herbaceous and subtly citrus-like fragrances. The emissions of γ -Terpinene in Thyme_B and Thyme_Eko suggest their applicability in contexts where robust herbal and citrus

scent are essential, notably in essential oils or culinary flavorings.

The emission of Isoborneol is notably highest in the Thyme_Eko sample, reaching $308 \pm 82 \text{ ng} \cdot \text{g}^{-1}$ at 50°C , significantly surpassing the other thyme samples, which indicates a pronounced temperature sensitivity of this compound in this variety. In contrast, Thyme_C and Thyme_D exhibit comparatively lower and more consistent levels of Isoborneol emissions, suggesting a more uniform aromatic profile within these samples under elevated temperature conditions.

The assessment of TVOCs emission levels provides additional evidence supporting the diverse aromatic potentials that exist among the various thyme samples examined. Thyme_B distinctly exhibits the highest levels of TVOCs at the elevated temperature of 50°C , attaining a measurement of $185 \pm 11 \mu\text{g} \cdot \text{g}^{-1}$, which is consistent with its substantial emissions of both γ -Terpinene and L-Fenchone, thereby indicating a concentrated and rich aroma profile. Following closely is Thyme_A, which presents a TVOCs level of $118 \pm 25 \mu\text{g} \cdot \text{g}^{-1}$, further suggesting the presence of a strong and pronounced aromatic profile. In stark contrast, both Thyme_C and Thyme_D reveal relatively low emission levels of TVOCs, a finding that is in harmony with their diminished individual compound emissions, suggesting the existence of a milder and less intense aroma overall. The moderate TVOCs emission level recorded in Thyme_Eko at $68 \pm 13 \mu\text{g} \cdot \text{g}^{-1}$ suggests a more balanced aromatic quality, which may prove advantageous for applications wherein a subtler and less overpowering scent profile is specifically desired.

In addition to the aforementioned compounds, other compounds such as α -Cedrene, D-Limonene, and Geranyl Acetate reveal significant trends that contribute to the overall aromatic complexity associated with thyme. Notably, both Thyme_A and Thyme_B demonstrate increased emissions of α -Cedrene when evaluated at the temperature of 50°C , with Thyme_A attaining a measurement of $(15.9 \pm 6.3) \times 10^2 \text{ ng} \cdot \text{g}^{-1}$, while Thyme_B reaches a value of $340 \pm 89 \text{ ng} \cdot \text{g}^{-1}$. This particular compound is likely to impart woody and balsamic undertones to the overall aroma profile, thereby particularly enhancing Thyme_A's suitability for applications where a more intricate and multifaceted fragrance is sought. The elevated levels of D-Limonene, particularly pronounced in Thyme_B at 50°C , which measures at $3157 \pm 176 \text{ ng} \cdot \text{g}^{-1}$, contribute bright citrus and fresh notes that serve to complement the herbal scent imparted by γ -Terpinene, thus enriching the overall aromatic profile. Although Geranyl Acetate emissions are comparatively lower across the various samples, they nonetheless peak in Thyme_A at a level of $80.2 \pm 4.4 \text{ ng} \cdot \text{g}^{-1}$ at the temperature

Table 4 Assessed emission values (defined as mean $\pm$ standard deviation ($n=3$)) of determined representatives of terpenes from oregano dried herbs

Herb type	Oregano_A			Oregano_B			Oregano_C			Oregano_D			Oregano_Eko		
	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]
α -Pinene	108 $\pm$ 14	864 $\pm$ 67	(8.7 $\pm$ 3.3) $\times 10^2$	(8.7 $\pm$ 3.3) $\times 10^2$	> 4000	232 $\pm$ 78	2.34 $\pm$ 0.26	232 $\pm$ 78	64 $\pm$ 17	(5.5 $\pm$ 1.4) $\times 10^2$	82 $\pm$ 19	453 $\pm$ 21	82 $\pm$ 19	453 $\pm$ 21	453 $\pm$ 21
Camphene	46 $\pm$ 7.1	422 $\pm$ 28	(4.4 $\pm$ 1.7) $\times 10^2$	(4.4 $\pm$ 1.7) $\times 10^2$	> 4000	18.4 $\pm$ 7.2	6.62 $\pm$ 0.97	18.4 $\pm$ 7.2	24 $\pm$ 7.3	233 $\pm$ 67	50 $\pm$ 12	392 $\pm$ 33	50 $\pm$ 12	392 $\pm$ 33	392 $\pm$ 33
β -Pinene	25.1 $\pm$ 3.7	1.59 $\pm$ 0.59	211 $\pm$ 82	211 $\pm$ 82	1120 $\pm$ 83	24.6 $\pm$ 4.4	< LOD	24.6 $\pm$ 4.4	69 $\pm$ 17	253 $\pm$ 23	32.1 $\pm$ 8.7	78.2 $\pm$ 4.6	32.1 $\pm$ 8.7	78.2 $\pm$ 4.6	78.2 $\pm$ 4.6
α -terpinene	< LOD	< LOQ	< LOD	< LOD	< LOQ	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOQ
D-Limonene	109 $\pm$ 12	833 $\pm$ 75	(4.3 $\pm$ 1.0) $\times 10^2$	(4.3 $\pm$ 1.0) $\times 10^2$	> 4000	(2.8 $\pm$ 1.1) $\times 10^2$	3.9 $\pm$ 1.0	(2.8 $\pm$ 1.1) $\times 10^2$	246 $\pm$ 58	(25.3 $\pm$ 6.2) $\times 10^2$	116 $\pm$ 16	953 $\pm$ 91	116 $\pm$ 16	953 $\pm$ 91	953 $\pm$ 91
γ -Terpinene	(20.9 $\pm$ 1.5) $\times 10^2$	> 4000	> 4000	> 4000	> 4000	59 $\pm$ 22	8.6 $\pm$ 2.8	59 $\pm$ 22	(11.9 $\pm$ 2.5) $\times 10^2$	> 4000	559 $\pm$ 116	(26.2 $\pm$ 2.2) $\times 10^2$	559 $\pm$ 116	(26.2 $\pm$ 2.2) $\times 10^2$	(26.2 $\pm$ 2.2) $\times 10^2$
L-Fenchone	54.1 $\pm$ 8.2	603 $\pm$ 66	190 $\pm$ 49	190 $\pm$ 49	(31.4 $\pm$ 1.6) $\times 10^2$	28.8 $\pm$ 6.1	< LOD	28.8 $\pm$ 6.1	56 $\pm$ 13	(6.3 $\pm$ 1.4) $\times 10^2$	22.0 $\pm$ 5.9	316 $\pm$ 39	22.0 $\pm$ 5.9	316 $\pm$ 39	316 $\pm$ 39
Camphor	20.6 $\pm$ 3.4	133 $\pm$ 42	11.41 $\pm$ 4.3	11.41 $\pm$ 4.3	54 $\pm$ 17	24.3 $\pm$ 9.1	< LOD	24.3 $\pm$ 9.1	41 $\pm$ 13	674 $\pm$ 69	16.6 $\pm$ 3.9	100.3 $\pm$ 4.8	16.6 $\pm$ 3.9	100.3 $\pm$ 4.8	100.3 $\pm$ 4.8
Isoborneol	83 $\pm$ 33	(7.7 $\pm$ 3.1) $\times 10^2$	86 $\pm$ 33	86 $\pm$ 33	(6.0 $\pm$ 2.3) $\times 10^2$	(3.5 $\pm$ 1.3) $\times 10^2$	6.4 $\pm$ 2.5	(3.5 $\pm$ 1.3) $\times 10^2$	94 $\pm$ 36	(19.3 $\pm$ 1.8) $\times 10^2$	27.5 $\pm$ 1.9	694 $\pm$ 95	27.5 $\pm$ 1.9	694 $\pm$ 95	694 $\pm$ 95
Citronellol	< LOD	37 $\pm$ 13	14.3 $\pm$ 5.6	14.3 $\pm$ 5.6	265 $\pm$ 58	35 $\pm$ 13	< LOD	35 $\pm$ 13	< LOQ	55 $\pm$ 13	< LOD	67.5 $\pm$ 5.1	< LOD	67.5 $\pm$ 5.1	67.5 $\pm$ 5.1
Pulegone	128 $\pm$ 38	(11.3 $\pm$ 4.6) $\times 10^2$	49 $\pm$ 19	49 $\pm$ 19	(27.4 $\pm$ 10.9) $\times 10^2$	260 $\pm$ 67	8.8 $\pm$ 2.9	260 $\pm$ 67	72 $\pm$ 28	(10.6 $\pm$ 1.0) $\times 10^2$	115 $\pm$ 19	614 $\pm$ 29	115 $\pm$ 19	614 $\pm$ 29	614 $\pm$ 29
Geranyl Acetate	28 $\pm$ 8.0	174 $\pm$ 68	27 $\pm$ 10	27 $\pm$ 10	108 $\pm$ 34	63 $\pm$ 19	6.401 $\pm$ 0.060	63 $\pm$ 19	12.7 $\pm$ 3.8	206 $\pm$ 37	18.2 $\pm$ 6.8	80.2 $\pm$ 7.8	18.2 $\pm$ 6.8	80.2 $\pm$ 7.8	80.2 $\pm$ 7.8
α -Cedrene	58 $\pm$ 17	(8.3 $\pm$ 3.3) $\times 10^2$	191 $\pm$ 75	191 $\pm$ 75	> 4000	195 $\pm$ 77	12.3 $\pm$ 2.3	195 $\pm$ 77	48 $\pm$ 19	(13.7 $\pm$ 2.4) $\times 10^2$	65 $\pm$ 22	(9.8 $\pm$ 1.9) $\times 10^2$	65 $\pm$ 22	(9.8 $\pm$ 1.9) $\times 10^2$	(9.8 $\pm$ 1.9) $\times 10^2$
α -Humulene	5.2 $\pm$ 2.0	< LOQ	8.5 $\pm$ 3.2	8.5 $\pm$ 3.2	(2.7 $\pm$ 1.0) $\times 10^2$	26 $\pm$ 10	7.60 $\pm$ 0.90	26 $\pm$ 10	6.7 $\pm$ 2.5	40 $\pm$ 10	19.2 $\pm$ 7.5	90 $\pm$ 32	19.2 $\pm$ 7.5	90 $\pm$ 32	90 $\pm$ 32
Cedrol	< LOD	< LOQ	2.12 $\pm$ 0.80	2.12 $\pm$ 0.80	< LOQ	< LOQ	8.5 $\pm$ 1.3	< LOQ	2.231 $\pm$ 0.016	< LOQ	6.6 $\pm$ 1.4	< LOQ	6.6 $\pm$ 1.4	< LOQ	< LOQ
alpha Bisabolol	< LOD	< LOQ	4.7 $\pm$ 1.7	4.7 $\pm$ 1.7	< LOQ	< LOQ	< LOD	< LOQ	13.6 $\pm$ 0.47	< LOQ	5.7 $\pm$ 2.2	< LOQ	5.7 $\pm$ 2.2	< LOQ	< LOQ
TVOCs	11.77 $\pm$ 0.72	78.1 $\pm$ 22.4	66.9 $\pm$ 2.1	66.9 $\pm$ 2.1	444 $\pm$ 18	18.3 $\pm$ 2.4	1.2 $\pm$ 0.51	18.3 $\pm$ 2.4	10.5 $\pm$ 2.7	99.2 $\pm$ 7.1	9.9 $\pm$ 1.6	69 $\pm$ 12	9.9 $\pm$ 1.6	69 $\pm$ 12	69 $\pm$ 12

TVOC – total amount of volatile organic compounds emitted from investigated herb type

LOD – 0.5 ng

LOQ – 1.5 ng

> 4000 – emission of the organic compound was above 4000 ng per gram of a herb

of 50 °C, thereby enhancing floral and fruity characteristics that contribute to the multi-dimensional nature of the aroma.

In summary, the findings suggest that Thyme_B and Thyme_Eko, characterized by their high emissions of γ -Terpinene and considerable TVOCs emission levels, are exceptionally well-suited for applications where a strong, herbaceous fragrance is particularly desirable. Conversely, Thyme_A's aromatic profile, which highlights its notable emissions of α -Cedrene and Geranyl Acetate, indicates a complex and rich aromatic blend that may hold significant appeal for specialized fragrance formulations or unique culinary applications.

Rosemary analysis

The information about the emission levels of determined terpenes from investigated rosemary dried herbs samples was listed in Table 6. Both Rosemary_A and Rosemary_B were characterized by high levels of α -Pinene, exceeding 4000 ng·g⁻¹ at 50 °C, while Rosemary_C reaches 734±230 ng·g⁻¹. The α -Pinene, a compound often linked with fresh, woody, and pine-like scents, is present at levels that could enhance the aromatic intensity of rosemary dried herbs, particularly in samples Rosemary_A and Rosemary_B.

In the analysis of rosemary herbs samples, the emissions of β -Pinene demonstrate significant variability, particularly when subjected to a temperature of 50 °C. Rosemary_A showcases the highest concentration of β -Pinene at 2824±789 ng·g⁻¹, indicating a substantial capacity for introducing fresh, woody, and subtly spicy characteristics to its aromatic composition at elevated thermal conditions. Meanwhile, Rosemary_B also reveals notable β -Pinene emissions, achieving levels of 2170±380 ng·g⁻¹ at 50 °C, which implies a comparably vigorous profile that could augment rosemary's utility in contexts necessitating a distinct β -Pinene presence.

Conversely, Rosemary_C presents a markedly lower emission of β -Pinene, quantified at 128±41 ng·g⁻¹ at 50 °C, which signifies a more subdued β -Pinene profile that may be appropriate for formulations where a more nuanced aromatic influence is desired.

The elevated emission of Camphene further amplifies the fresh and woody profile, with Rosemary_B also surpassing 4000 ng·g⁻¹ at 50 °C, and Rosemary_A showing a substantial emission of 1735±680 ng·g⁻¹. This pattern indicates a sensitivity of these compounds to thermal variations, potentially augmenting the sensory attractiveness of rosemary herbs samples in elevated temperature settings. The rosemary herb samples display substantial variation in Isoborneol emissions at 50 °C, with Rosemary_B reaching over 4000 ng·g⁻¹ and Rosemary_C emitting 1297±508 ng·g⁻¹. This indicates a pronounced aromatic

intensity for Isoborneol in higher temperatures, particularly in Rosemary_B, which may enhance its potential applications in fragrance and flavor formulations. For Camphor, all rosemary samples show higher emissions at 50 °C, with both Rosemary_A and Rosemary_B exceeding 4000 ng·g⁻¹, and Rosemary_C closely following with emissions also exceeding 4000 ng·g⁻¹.

TVOCs emission levels at 50 °C reinforce these findings, with Rosemary_B reaching the highest value of 263±45 μ g·g⁻¹, followed by Rosemary_A at 103±47 μ g·g⁻¹, while Rosemary_C remains lower at 20.0±7.8 μ g·g⁻¹. These high TVOCs levels indicate that Rosemary_B, in particular, has an intense aromatic potential, likely due to the combined effects of elevated α -Pinene, Camphene, D-Limonene, and Camphor emissions. Garzoli et al., 2021 investigated essential oils and hydrolates of *Rosmarinus officinalis* L. The volatile composition of vapor phase essential oils and hydrolates was performed by HS-GC-MS system [34]. The authors find out that the most abundant components in both phases for investigated *Rosmarinus officinalis* L were α -Pinene, 1,8-Cineole, Camphene, Borneol and Camphor – similar to the results listed in Table 6.

Statistical evaluation of obtained research results - hierarchical and Non hierarchical (K-means mode) cluster analysis

The input data set was associated with the five types of culinary dried herbs from different manufacturer. For this reason each type of herb was included in versions A, B, C, D, Eco and it makes the total number of objects 24. In a case of variables, the input data for statistical evaluation contained information about the emissions of TVOCs and different type of terpenes obtained at two different temperatures (25 and 50 °C). For this reason it gives the total number of variables equal 34.

The major goal of the data interpretation is to identify groups of similarity (clusters) either between the objects or between the variables. Further, the determination of the data structure by identification of latent factors related to that structure is sought as well as identification of specific variables for each group of identified clusters of objects. The methods used for the data mining and interpretation are well-known and documented in the chemometric literature, namely hierarchical and non hierarchical (K-means mode) cluster analysis and factor analysis.

Preliminary remarks concerning the specificities of the data set: it is obvious and logic that the emissions at the higher temperature are higher than those at the lower temperature; a quick check of the correlations between the variables of interest are quite significant and it generally

Table 5 Assessed emission values (defined as mean±standard deviation ($n=3$) of determined representatives of terpenes from thyme dried herbs

Herb type Emitted compound	Thyme_A		Thyme_B		Thyme_C		Thyme_D		Thyme_Eko	
	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]
α -Pinene	62.9±8.6	(10.6±2.7)×10 ²	220±15	994±61	224±19	n.m.	5.6±2.1	27.2±9.1	45.4±5.3	130±50
Camphene	37.8±4.4	(7.6±2.9)×10 ²	119±26	760±66	152±15	n.m.	8.0±1.9	14.7±3.8	19.4±1.6	189±73
β -Pinene	48.6±7.7	377±23	135±26	279.6±8.9	76.85±8.5	n.m.	< LOD	7.0±2.7	19.5±1.1	54.6±1.3
α -terpinene	< LOD	< LOQ	< LOD	< LOQ	< LOD	n.m.	< LOD	< LOQ	< LOD	< LOQ
D-Limonene	230±38	(27.7±6.4)×10 ²	472±47	3157±176	274±41	n.m.	7.8±3.1	41±13	95±15	(12.6±2.6)×10 ²
γ -Terpinene	257±35	(27.2±6.7)×10 ²	790±92	> 4000	447±66	n.m.	51±12	(3.2±1.2)×10 ²	994±83	> 4000
L-Fenchone	35.7±5.9	(6.1±2.1)×10 ²	55±14	504±61	36.0±6.4	n.m.	3.73±0.24	14.0±4.9	18.3±2.0	362±96
Camphor	38.5±8.5	(8.5±2.8)×10 ²	84±23	(4.7±1.0)×10 ²	65.9±6.5	n.m.	28.3±7.9	35.0±8.2	48±17	292±47
Isoborneol	29.0±9.9	(10.9±4.2)×10 ²	39±12	(3.0±1.1)×10 ²	60±19	n.m.	51±15	82±23	40±12	308±82
Citronellol	19.4±3.0	42±11	< LOD	< LOQ	< LOQ	n.m.	< LOQ	< LOQ	< LOD	< LOQ
Pulegone	38±15	244±95	24.4±5.6	81±26	59±22	n.m.	20.1±4.2	70±25	112±18	(8.8±1.6)×10 ²
Geranyl Acetate	8.5±2.6	80.2±4.4	8.2±1.3	< LOQ	< LOD	n.m.	10.1±2.0	88±33	9.2±4.2	< LOQ
α -Cedrene	59±17	(15.9±6.3)×10 ²	64±12	340±89	47±17	n.m.	21.1±7.2	143±51	53±18	(7.3±1.8)×10 ²
α -Humulene	6.1±1.1	39±11	6.5±2.2	4.2±1.8	6.3±2.1	n.m.	6.4±1.8	9.2±3.1	53±19	< LOQ
Cedrol	2.75±0.25	< LOQ	5.26±0.97	< LOQ	< LOD	n.m.	4.22±0.85	< LOQ	4.5±1.3	< LOQ
alpha Bisabolol	< LOD	< LOQ	14.4±5.1	< LOQ	12.5±2.8	n.m.	6.79±0.99	< LOQ	8.4±3.1	< LOQ
TVOCs	12.9±2.1	118±25	22.4±8.8	185±11	31.0±5.1	n.m.	2.7±0.80	7.8±2.1	14.8±6.9	68±13

TVOC – total amount of volatile organic compounds emitted from investigated herb type

LOD – 0.5 ng

LOQ – 1.5 ng

>4000 – emission of the organic compound was above 4000 ng per gram of a herb

n.m. – not measured

excludes “temperature” as possible factor influencing the overall data structure. Besides several variables (9, 10, 32 and 34) lack any variation (all registered values are below LOD) and they should be excluded from the variables list.

In a case of hierarchical and non-hierarchical (K-means) of variables, both clustering approaches give one and the same partitioning of the variables into totally four clusters. It should be reminded that the hierarchical clustering is an unsupervised pattern recognition method forming the clusters spontaneously without preliminary conditions since K-means clustering is a supervised pattern recognition method based on a priori requirement for the number of clusters that should be obtained by the partitioning procedure (*a priori* hypothesis and expert opinion).

In Fig. 2 the hierarchical dendrogram for clustering of 30 variables was presented with notification of the identified clusters at significance level of $2/3D_{\max}$ (test of Sneath). Cluster 1 contains following 12 members: alpha-Pinene_1, alpha-Pinene_2, Camphene_1, Camphene_2, D-Limonene_1, D-Limonene_2, beta-Pinene_1, beta-Pinene_2, Camphor_1, Camphor_2, Isoborneol_1, Isoborneol_2. As for Cluster 2, it contains following 18 members: TVOC_1, TVOC_2, alpha-Cedrene_1, alpha-Cedrene_2, alpha-Humulene_2, gamma-Terpinene_1, Pulegone_2, L-Fenchone_1, L-Fenchone_2, gamma-Terpinene_2, Pulegone_1, alpha-Humulene_1, Cedrol_1, alpha Bisabolol_2, Citronellol_1, Citronellol_2, Geranyl Acetate_1, Geranyl Acetate_2. In this big cluster 1 all members are included with their labeling 1 and 2 for low and high temperature. Exceptions are only those variables which are left without respective matches due to the elimination of them (lack of variability) – (+)-Cedrol and (-)-alpha Bisabolol. It confirms the statement that the temperature is only a relative factor of the system in consideration. Again, the temperature indices are together for the members in the second cluster. It could be assumed that the separation of the variables is due to the physical or chemical or structural differences between the characteristics of the emissions measured (volatility, bond saturation, cycles in the molecule, structural or functional groups, reactivity). The non hierarchical (K-means) clustering for clustering into 2 *a priori* predetermined clusters gave the same result as the hierarchical mode.

In Fig. 3, the hierarchical and non-hierarchical (K-means) of 24 cases was presented. Considering the data shown in the Fig. 3 it might be observed the occurrence of three clusters defined as: C1 (Oregano_B, Rosmarin_A, Rosmarin_B) – 3 members; C2 (Oregano_A, Oregano_D, Oregano_EKO, Majoran_D, Majoran_EKO, Thyme_A, Thyme_B, Thyme_C, Thyme_EKO) – 9 members and C3 (Basil_A, Basil_B, Basil_C, Basil_D, Basil_EKO, Majoram_A, Majoram_B, Majoram_C, Oregano_C, Thyme_D, Rosmarin_C, Rosmarin_EKO) – 12 members. It might

be observed that cluster C2 is combination of dominantly Oregano and Thyme and cluster C3 of Basil, Majoram and Rosmarin. This partitioning is probably due to some specific properties of the investigated herbs and their ability to act in a symbiotic way on the humans [35].

In order to clarify the impact of the different variable on the objects of interest and, vice versa, the impact of the objects on the clustering of variables, following plots (Fig. 4A and B) has to be discussed. It is important also to mention that K-means clustering showed the same results as the hierarchical clustering. It can be seen that the outlying cluster 3 differs substantially for the average of many variables from the other two clusters. It is characterized by the highest variable values (except for Geranyl Acetate_2) for one oregano and two rosmarin objects (might be caused by the manufacturing and drying process, storage method or or arise from the characteristics of the plant and how it was grown before drying out). The other two clusters of objects show relatively homogeneity with respect to the average values of most of the tested variables (emission levels). Exceptions are some enhanced emissions of gamma-Terpinene_2, Pulegone_1, and alpha Bisabolol_1 for basil/majoram cluster 3. Again, manufacturing and drying process as well as raw material specificities could be the reason. In Fig. 4 one could observe the impact of the groups of variables on the dried herbs used. For basil, oregano and thyme both groups of variables (both clusters) do not differ significantly by their impact. It might mean that the emissions of determined terpenes are not affected by the dried herb type. There are some specificities for majoram and rosmarin, which are probably, more sensitive in the emission process. For basil, oregano, and thyme, no significant differences were observed between clusters in terms of terpene emissions, indicating that the dried herb type may not strongly influence the emission profiles of these compounds. In contrast, marjoram and rosemary showed some variability between clusters, suggesting that these species may be more sensitive to factors affecting terpene release during drying or analysis. This variability should be considered when evaluating the quality and authenticity of these herbs.

In Table 7 the factor loadings for two latent factors are presented (marked loadings are statistically significant). Two latent factors explain more than 75% of the total variance of the system. In general, these factors correspond to the two identified clusters of variables. The first latent factor with more than 40% explanation of the total variance. It includes variable with high factor loadings – alpha and beta-Pinene, Camphene, D-Limonene, Camphor and Isoborneol. The conditional name of this factor could be “strong aromatic emissions” and corresponds entirely to cluster 1 of variables. The second latent factor explains over 35% of the

Table 6 Assessed emission values (defined as mean±standard deviation ($n=3$)) of determined representatives of terpenes from Rosemary dried herbs

Herb type Emitted compound	Rosemary_A		Rosemary_B		Rosemary_C		Rosemary_Eko	
	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]	Emission at 25 °C [ng·g ⁻¹]	Emission at 50 °C [ng·g ⁻¹]
α -Pinene	1169±196×10 ²	>4000	1424±106×10 ²	>4000	73±24	734±230×10 ²	8.6±1.3	42±10
Camphene	355±58	1735±680×10 ²	410±28	>4000	78±25	240±89	5.0±1.7	37.7±1.6
β -Pinene	720±103×10 ²	2824±789×10 ²	104.0±5.1	2170±380×10 ²	10.8±4.1	128±41	4.61±0.32	61.9±6.0
α -terpinene	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ
D-Limonene	1404±262×10 ²	>4000	695±57	>4000	84±23	205±72	19.0±1.2	376±41
γ -Terpinene	125±44	321±118×10 ²	29.8±7.1	373±54	10.8±3.5	41.5±1.8	9.3±1.2	39±12
L-Fenchone	46±11	302±110×10 ²	35±11	747±80	16.0±5.3	28.2±3.6	< LOD	11.7±3.1
Camphor	2116±243×10 ²	>4000	1752±360×10 ²	>4000	1022±390×10 ²	>4000	15.06±0.35	147±18
Isoborneol	105±38	589±221×10 ²	136±16	>4000	267±96	1297±508×10 ²	7.8±2.8	96±20
Citronellol	7.1±2.5	50±15	9.7±3.4	156±29	3.98±0.55	34±11	< LOD	25.5±9.8
Pulegone	39.2±6.1	164±55	20.7±5.9	47.9±9.3	18.6±2.9	38±14	10.4±1.3	93±26
Geranyl Acetate	8.9±3.3	59.5±7.5	11.2±1.4	57.2±6.9	7.2±2.6	47.4±1.9	9.06±0.67	82±28
α -Cedrene	75±25	1017±307	45±10	1421±513×10 ²	50±15	621±220×10 ²	7.8±2.1	83±22
α -Humulene	11.9±4.1	< LOQ	5.02±0.38	67±19	5.93±0.19	122±39	17.4±5.8	38±12
Cedrol	< LOD	< LOQ	7.0±2.3	< LOQ	3.89±0.48	< LOQ	4.47±0.61	< LOQ
alpha Bisabolol	7.2±1.5	< LOQ	< LOD	< LOQ	12.9±2.1	< LOQ	4.8±1.5	< LOQ
TVOCs	26.8±3.6	103±47	15.90±0.42	263±45	5.1±1.9	20.0±7.8	0.739±0.028	6.1±2.1
[$\mu\text{g}\cdot\text{g}^{-1}$]								

TVOC – total amount of volatile organic compounds emitted from investigated herb type

LOD – 0.5 ng

LOQ – 1.5 ng

>4000 – emission of the organic compound was above 4000 ng per gram of a herb

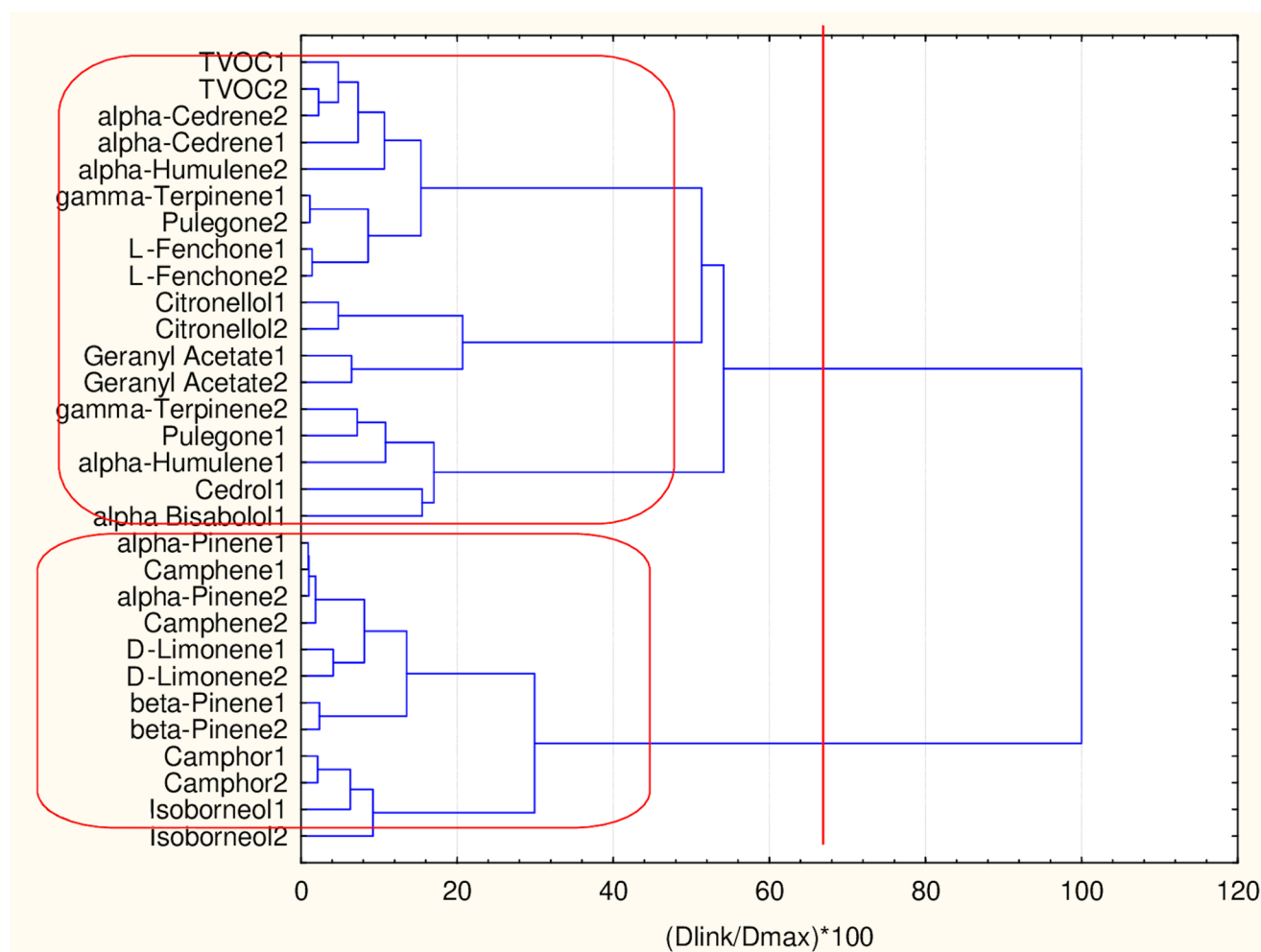


Fig. 2 Hierarchical dendrogram for clustering of 30 variables

total variance and indicates high factor loadings for TVOC, gamma-Terpinene, L-Fenchone, alpha-Cedrene, Pulegone (at high temperature) – part of the members of cluster 2 of variables. Many variables remain with low factor loadings in this factor and do not contribute to explanation of the data structure. The conditional name of this factor could be “non aromatic emissions”.

Conclusions

The obtained results lead to the conclusion that the proposed solvent-free and non-destructive solution can be successfully used in the screening analysis of culinary dried herbs, taking into account the emission levels of determined terpenes. Using selected terpenes as an example, it was confirmed that the same type of dried herb from different manufacturers can differ in the emission profile (type and amount of compounds emitted into the gas phase from a given type of herb). Consequently, it

can be concluded that it can affect the intensity of flavor of the food to which it will be added. In addition, the proposed solution of using pure essential oils derived from a particular plant allowed better identification of potentially characteristic terpenes emitted from the tested dried herb. However, it should be highlighted that it applies only when the same species are analysed (essential oils and dried herbs) and if the chemotype is taken into account in cases where it is relevant.

It should be emphasized that a different type of sample will be commercially available herbs (like in described case), which are the final product (without information on the conditions of its preparation), than plants that have been dried under laboratory conditions (known drying conditions) and then analyzed. Moreover, differences in quantitative and qualitative composition may also depend on the analytical technique that was used at the stage of sample preparation for analysis. Adam et al., 2009 describes research using solid-phase and single-drop microextractions (SDME) for headspace analysis of herbal essential oils

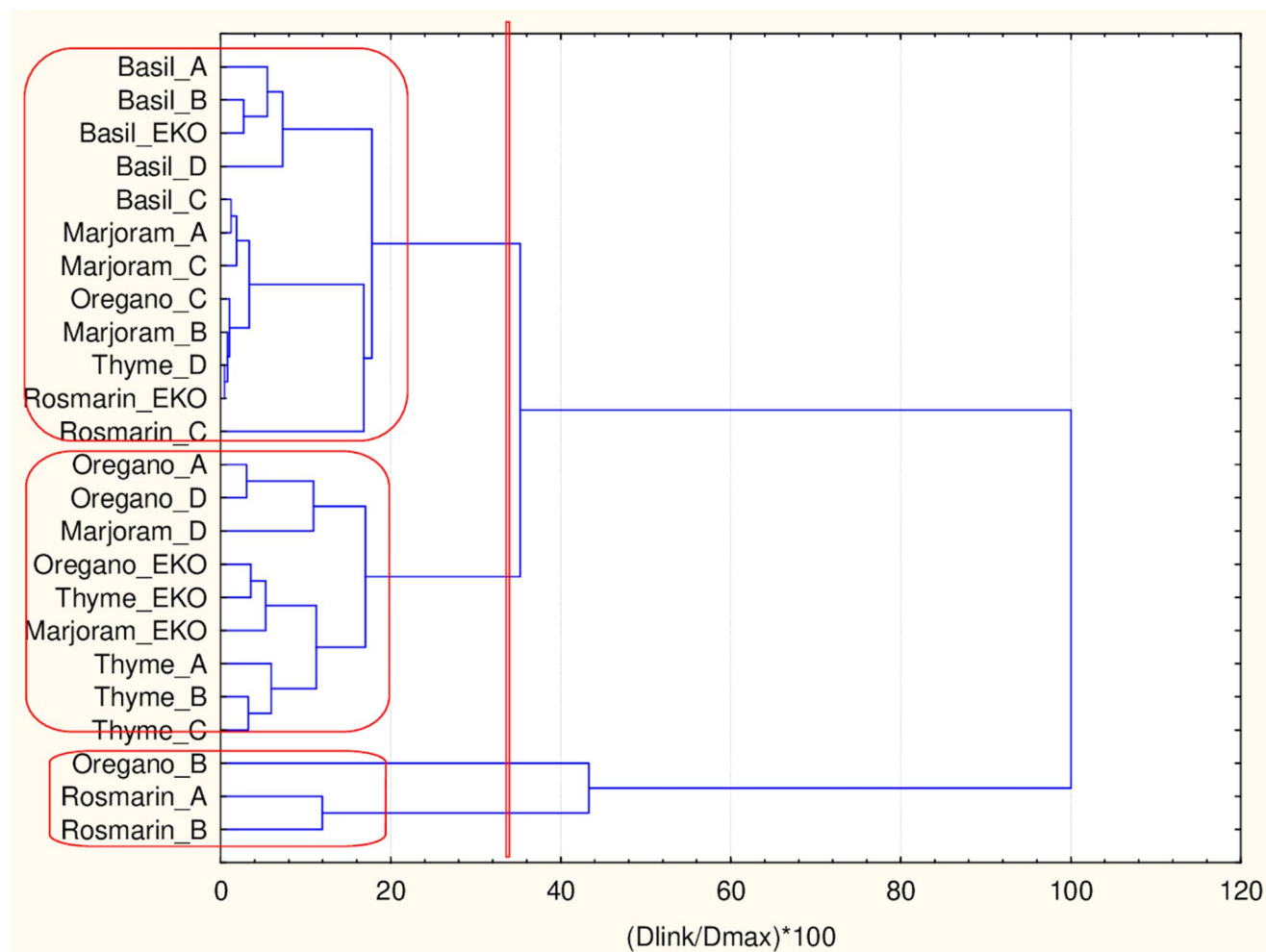


Fig. 3 Hierarchical dendrogram for clustering of 24 cases

from several plants: *Lavandula spica* L., *Melissa officinalis* L., *Mentha piperita* L. and *Salvia officinalis* L. After entire analytical protocol it was concluded that both techniques are good for the analysis, but only for the semi-quantitative determination of herbal essential oils [36].

Morover, considering the same type of herb (but probably from different origin) it might be found several differences in the final results. Sgorbini et al., 2015 perform the investigations on several types of herbs and spices including rosemary (*Rosmarinus officinalis* L.) and thyme (*Thymus vulgaris* L.) using HS-SPME-MS system to search the biologically-active markers. For this reason the authors only focused on the thymol and carvacrol in thyme samples and linalool, bornyl acetate, α -terpineol, and borneol in rosemary [37]. However, mentioned above investigations were performed with a different sampling technique (static conditions) than described in this paper (dynamic conditions) as well as the final determination was performed by MS system using target ion and qualifier ions for quantitation.

No organic solvents were used at any of the stages (except the calibration stage, where methanol was used), so the proposed solution significantly meets the requirements for green analytical chemistry. Importantly, it was also noted that, although the herbs were organically grown according to the manufacturer (herbs defined as eco-friendly), this was not directly associated with significantly higher levels of measured compounds, relative to other herb producers. Performed investigations on dried herbs can provide a solid basis for assessing the authenticity of dried natural products (based on their emission profiles), allowing for precise differentiation between natural and modified aromas. A shortcoming of the study was the lack of any information on the packages regarding the storage time of the herbs in the packages and how they were dried. The lack of these information significantly hinders the interpretation of the obtained research results. For this reason, it seems necessary in the future to expand the research to include the analysis of another group of compounds classified as volatile organic compounds, which can be considered as markers of

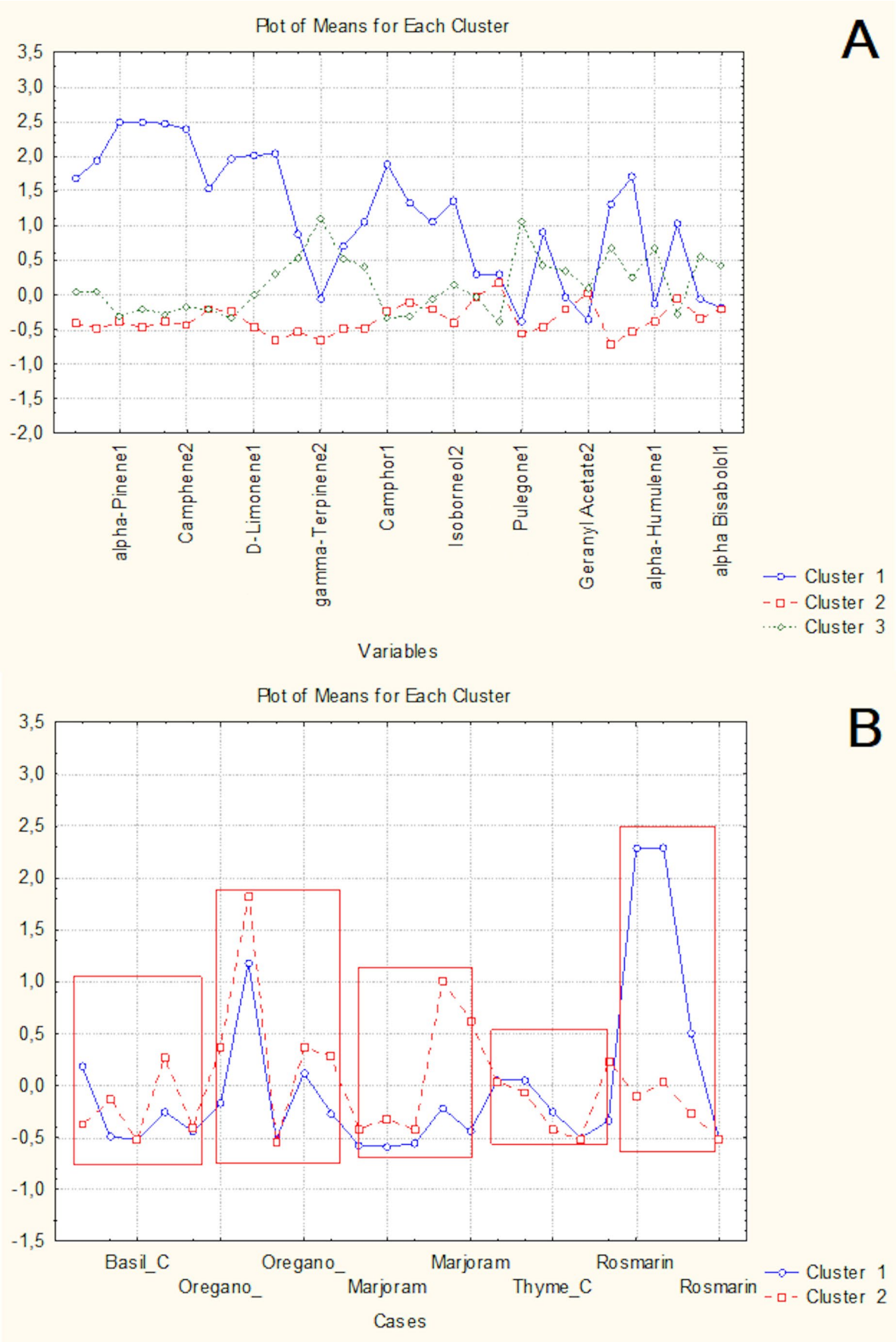


Fig. 4 Plot of averages (standardized values) of each variable for each identified cluster of objects (A) and Plot of averages (standardized values) for each object for each identified cluster of variables (B)

the general term “product quality.” For this type of study, more sophisticated analytical equipment, such as high-resolution gas chromatography combined with tandem mass spectrometry (HRGC-MS/MS), would need to be used. In addition, it will be desirable in the future to expand this type of research to include a comparative analysis of studies related to the emission of organic compounds into the gaseous phase and the level of these compounds in samples of dried herbs - conducting the organic solvent extraction process in a Soxhlet apparatus, ultrasound extraction, hydrodistillation or steam distillation technique.

Table 7 General information about the numerical values of factor loadings (marked loadings are statistically significant)

Factor loadings (varimax normalized) extraction: principal components (marked loadings are significant)		
	Factor – 1	Factor – 2
TVOC_1	0,509	0,702
TVOC_2	0,597	0,705
alpha-Pinene_1	0,949	0,145
alpha-Pinene_2	0,934	0,297
Camphene_1	0,901	0,299
Camphene_2	0,820	0,415
beta-Pinene_1	0,703	-0,017
beta-Pinene_2	0,851	-0,026
D-Limonene_1	0,844	0,094
D-Limonene_2	0,754	0,491
gamma-Terpinene_1	0,091	0,936
gamma-Terpinene_2	-0,182	0,774
L-Fenchone_1	0,086	0,813
L-Fenchone_2	0,149	0,890
Camphor_1	0,883	-0,274
Camphor_2	0,760	-0,301
Isoborneol_1	0,708	-0,036
Isoborneol_2	0,709	0,026
Citronellol_1	0,126	0,160
Citronellol_2	0,070	0,185
Pulegone_1	-0,219	0,471
Pulegone_2	0,069	0,928
Geranyl Acetate_1	-0,172	0,490
Geranyl Acetate_2	-0,243	0,314
alpha-Cedrene_1	0,463	0,711
alpha-Cedrene_2	0,476	0,794
alpha-Humulene_1	-0,158	0,224
alpha-Humulene_2	0,253	0,549
Cedrol_1	-0,071	0,207
alpha-Bisabolol_1	0,031	-0,005
Expl.Var %	41.8	35.3

Explanation: TVOC – total volatile organic compounds; number 1 is associated with the temperature 25°C; number 2 is associated with the temperature 50°C

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Data availability The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare no competing interests.

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

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