International Journal of
Agriculture, Environment and Food Sciences

e-ISSN: 2618-5946 https://dergipark.org.tr/jaefs

DOI: https://doi.org/10.31015/2025.2.36 Int. J. Agric. Environ. Food Sci. 2025; 9 (2): 627-637

Effect of encapsulation on aroma and aroma-active components of fresh and black garlic

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Article History
Received: April 26, 2025
Accepted: June 28, 2025
Published Online: June 29, 2025

Article Info
Type: Research Article
Subject: Food Chemistry and Food Sensory Science

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Available at
https://dergipark.org.tr/jaefs/issue/91914/1684706

Abstract

In this study, aroma profiles and aroma-active compounds of fresh garlic (EFG) and black garlic (EBG) samples encapsulated using the complex coacervation method were investigated. Volatile aroma components were analysed by GC-MS (gas chromatography-mass spectrometry) with the HS-SPME (headspace-solid phase microextraction) method. EFG and EBG samples contained 30 and 37 different aroma compounds, respectively. The chemical changes during the fermentation of black garlic caused a significant decrease in the number of aroma compounds. A total of 13 aroma-active compounds were identified in the encapsulated samples. The odor dilution (FD) factors of these compounds ranged from 4 to 1024. Among the 10 identified compounds, 2 were alcohols, 3 were sulfur-containing compounds, 4 were acids, and 1 was a ketone. The remaining 3 compounds were unidentified aroma-active compounds. This study provides an important contribution in terms of expanding the use of encapsulated garlic products in the food industry and developing products suitable for consumer preferences. These findings may lead to the widespread use of encapsulated garlic products in functional food and nutraceutical fields in the future.

Keywords: *Allium sativum* L, black garlic, encapsulation, GC-MS, aroma-active

Cite this article as: Sasmaz, H.K., Sevindik, O., Guclu, G., Selli, S., Kelebek, H. (2025). Effect of encapsulation on aroma and aroma-active components of fresh and black garlic. International Journal of Agriculture, Environment and Food Sciences, 9 (2): 627-637. https://doi.org/10.31015/2025.2.36

INTRODUCTION

Garlic is a plant of the genus Allium belonging to the Liliaceae family and is widely used throughout the world thanks to its unique flavour. From past to present, garlic has been referred to with many titles such as 'nectar of the gods', 'Russian penicillin', 'natural antibiotic' and 'herbal talisman' (Lidiková et al., 2023). Used in many fields such as agriculture, food, cosmetics, personal care, nutraceuticals and traditional medicine, garlic stands out as a valuable product with a wide range of culinary and medicinal uses. In addition, it is reported that garlic is rich in nutrients and functional components and has important medicinal properties such as antimicrobial, antioxidant, hypoglycaemic, anti-hypertension and anti-tumour effects (Sasmaz et al., 2022, 2024a; Banerjee and Maulik, 2002; Eidi et al., 2006; Wang et al., 2012; Casella et al., 2013; Verma et al., 2023; Renu et al., 2023). Black garlic is a functional product obtained by processing fresh garlic. It is usually produced by a controlled process lasting up to 60 days under conditions of 60-90 °C temperature and 60-80% relative humidity (Zhang et al., 2016; Sasmaz et al., 2022, 2025). Spontaneous fermentation and various chemical reactions are involved in the production of black garlic. This process alters the garlic's color, texture, taste, and nutrient profile, yielding a softer texture and sweeter aroma (Kimura et al., 2017). Compared to fresh garlic, black garlic has a significantly different chemical composition, phenolic compounds, the amount of compounds with high antioxidant capacity increases (Chen et al., 2018; Sasmaz et al., 2022). Black garlic contains bioactive components with antioxidant, anticancer, antimicrobial and anti-inflammatory properties (Tomsik et al., 2017; Rios-Rios et al., 2019). Due to their beneficial properties, these ingredients are increasingly used in functional foods (Dordevic, 2015). However, the stability of bioactive ingredients is critical for their successful integration into foods, especially for those derived from natural sources. This is because components such as vitamins, probiotics, minerals, polyphenols, omega fatty acids and phytosterols are sensitive to environmental factors such as light, oxygen, heat and water (Augustin and Sanguansri, 2008; Esfanjani and Jafari, 2016). Therefore, the food industry focuses on developing new methods to minimally affect the organoleptic and quality properties of bioactive ingredients. In this context, encapsulation method is recognised as an effective tool to overcome these problems by protecting bioactive components against environmental and chemical effects (Gouin 2004; Zuidam et al., 2019). Encapsulation is the process of coating bioactive components (core-core) with suitable coating agents. This technology is widely used to improve the stability, specificity and bioavailability of food ingredients. Today, coacervation is an effective micro/nano encapsulation method widely used in the food and pharmaceutical industries. Complex coacervation is a process in which electrostatic interactions occur between two biopolymers with different electrical charges (Timilsena et al., 2019). While previous studies have characterised the aroma of fresh and black garlic (Molina-Calle et al., 2017; Sasmaz et al., 2024b), the effect of complex coacervation on aroma and aroma-active compounds in these products has not been investigated.

The encapsulation process offers the possibility of expanding the use of encapsulated garlic products in the food industry due to its potential to partially suppress the pungent aroma of fresh garlic and delay the release of characteristic aroma compounds that occur during fermentation of black garlic.This study aims to characterize the aroma profiles and aroma-active compounds of encapsulated fresh and black garlic using HS-SPME (headspace-solid phase microextraction) with GC-MS (gas chromatography-mass spectrometry), elucidating the impact of encapsulation on sensory properties. To our knowledge, this is the first study in the literature to investigate the aroma characteristics of both encapsulated fresh and black garlic in this context.

MATERIALS AND METHODS

Material

In our previous study, black garlic encapsulation was optimised by central composite design (CCD) based on response surface methodology on the basis of encapsulation efficiency (EE, %) considering three parameters: core/coating ratio, extract concentration and coacervate/maltodextrin (MD) ratio. As a result of this study, the optimum conditions in terms of EE (%) were determined as 4.0 for coating material/core ratio, 50% for extract concentration and 6.0 for MD/coacervate ratio (Sasmaz et al., 2023). In this study, both black and fresh garlic were encapsulated using these optimum parameters. For the preparation of fresh and black garlic extracts, 30 g of garlic was homogenized with 30 mL of distilled water (1:1 ratio, 50% w/v) using a blender (Waring 8011 EB SET2). The resulting mixture was then subjected to ultrasonic-assisted extraction in a water bath for 10 minutes to enhance extraction efficiency. Subsequently, the samples were centrifuged at 5500 rpm for 20 min at 25°C to separate the solid residue. Finally, the supernatant was filtered through coarse cellulose filter paper to obtain clear extracts (Sasmaz et al., 2023). The encapsulation process was finalized after adjusting the solution pH to 3.2, followed by phase separation achieved by maintaining the solution at 4°C for 30 minutes. Prior to lyophilization, the samples were stored in a freezer at -40°C. The freeze-drying procedure was conducted for approximately 48 hours using a laboratory-scale lyophilizer.

Aroma Compounds Analysis

The method used for aroma analyses was a compact system combining analytical techniques such as solid phase micro-extraction (SPME), gas chromatography (GC, Agilent 7890B) and mass spectrometry (MS, Agilent 7010B), which is a kind of dynamic headspace (HS) method. For aroma analyses, 3 g of encapsulated black and fresh garlic samples were placed in a 20 ml glass vial with 5 µl of internal standard solution (IS:4-nonanol, 40 µg) in an autosampler (Gerstel Inc., Linthicum, MD; USA). The vial was sealed using a screw cap containing a PTFE-silicone septum. The sample vial, which is then taken into the pretreatment chamber by the autosampler, is pre-conditioned (incubated) at 50°C for 15 minutes. After preconditioning, a syringe with a 2 cm fibre (Supelco, Bellefonte, PA, USA) coated with 50/30 µm divinylbenzene/carboxylate/polydimethylsiloxane (DVB/Car/PDMS) absorbent materials was used, 33 mm inserted into the vial and collected the trapped aroma compounds volatilised in the environment for 30 minutes at 50°C and brought to the desorption block at 250°C by the autosampler and injected the trapped aroma compounds into the DB-Wax (60 m x 0. 25 mm i.dx 0.25 µm, J&W Scientific-Folsom, USA) column. In the analysis, the oven temperature was gradually heated from 90°C to 140°C and then to 240°C. Helium was used as carrier gas at a flow rate of 1 mL/min. In the GC-MS system, the interface temperature was set to 250°C and the ionisation source temperature to 180°C. Identification of aroma compounds was carried out by comparing the mass spectra obtained with Wiley 11.0 and NIST 14 mass spectral data libraries and retention times determined using alkane standards in the C8-C32 range. The amount of aroma compounds was calculated quantitatively (microgram/kg) using the internal standard method (Sevindik, 2020). Analyses were conducted in triplicate for each sample.

Aroma Extract Dilution Analysis (AEDA)

The AEDA methodology was employed to characterize the potent aroma compounds of the samples. A purge and trap extraction was employed beforehand and the liquid extract representative of sample's original aroma was used for AEDA procedure. The purge and trap system comprised a nitrogen source that was regulated by a flow meter and connected to a splitter system that divided the flow into multiple channels to purge three samples concurrently. A standard 20-mL vial, sealed with a crimp cap and a septum, was utilized to contain the solid sample. The needle of the N_2 source and the cartridge were installed through the septum to purge and trap the aroma compounds. The details of this extraction process was explained in detail in our previous work (Sasmaz et al., 2024b). AEDA was performed by gradually diluting the aroma extracts with dichloromethane, with the ratio of extract to solvent initially set at 1:1, then gradually increasing to 1:2, 1:4, 1:8, 1:16, and so forth, until the desired ratio was reached. Three panelists with extensive experience in the field utilization an olfactometric port within a GC-MS-O device to assess the aromatic extracts. The dilution and sniffing procedure was methodically executed until no odor was perceptible. During this procedure, each odor perceived from the olfactometric port was represented as a flavor dilution (FD) factor comprising 4, 8, 12, and so forth. The ratio previously cited indicated that the higher the FD factor of a key aroma compound, the more effective it was on the aroma profile (Sasmaz et al., 2024b).

Statistical Analysis

Statistical analysis was performed using the independent samples t-test in SPSS 22.0 (version 22, SPSS Inc., Chicago, IL, USA). Differences in the content levels were evaluated, and means with p-values less than 0.05 were considered statistically significant.

RESULTS AND DISCUSSION

Aroma Profiles of Encapsulated Samples

In order to observe the effects of encapsulation process on the aroma components of fresh and black garlic, two samples prepared as encapsulated fresh garlic (EFG) and encapsulated black garlic (EBG) were examined in terms of aroma profiles. For this purpose, analyses were performed on encapsulated garlic samples by HS-SPME method with GC-MS device and the results obtained are given in Table 1. Significant differences were observed in the aroma components between the EFG and EBG samples ($p< 0.05$). 30 aroma compounds in the EFG sample and 37 in the EBG sample were detected. The sulfurous compounds group dominated with 12 compounds in both samples, and apart from these compounds, a total of 45 different aroma compounds were identified and quantified, including four thiols, five aldehydes, five ketones, four alcohols, six volatile acids, one furan, one volatile phenol, two terpenes and five other compounds. When the total concentration of aroma compounds of EFG and EBG samples were analysed, the total concentration of aroma compounds in EBG sample was considerably lower than that of EFG sample (EFG: 41170 µg/kg; EBG: 1353 µg/kg). This finding is thought to be a reflection of the effect of the degradation reactions of flavour precursor amino acids on flavour during black garlic fermentation. There are several studies in the literature on both the minimisation of the release of flavour compounds by the encapsulation process and the loss of important flavour compounds that give garlic its pungent odour by the fermentation process (Lotfy et al., 2015; Molina-Calle et al., 2017). Chromatograms highlighting differences between EFG and EBG samples are shown in Figure 1..

Organosulfur compounds

Black garlic is formed as a result of natural reactions and biochemical transformations of the constituents, without the involvement of microorganisms and without the addition of preservatives, only by the action of enzymes naturally present in the raw material (Molina-Calle et al., 2017; Najman et al., 2022; Sasmaz et al., 2024b). During prolonged controlled heating, garlic is subjected to enzymatic and non-enzymatic browning reactions (such as oxidation, caramelisation and Maillard reactions). These reactions alter the physicochemical properties, bioactive components and nutritional value of garlic, as well as leading to significant transformations in its aromatic structure (Molina-Calle et al., 2017; Najman et al., 2022; Sasmaz et al., 2024b). Aroma compounds such as furfural, furanones and pyrazines formed during Maillard reactions are effective in the formation of sweet, fruity and caramelised tones characteristic of black garlic. In addition, unstable organosulfur compounds such as allicin, which is mainly responsible for the pungent odour in fresh garlic, are degraded by heat treatment into derivatives such as S-alylcysteine and S-alylmercaptocysteine, which are more stable structures. These compounds shape the biological effects of black garlic and form the basis of its characteristic aroma (Najman et al., 2022; Kilic-Buyukkurt et al., 2024; Sasmaz et al., 2024b). Considering the findings obtained, although the total concentrations of aroma compounds were approximately 40 times higher in the EFG sample than in the EBG sample, the number of aroma compounds detected in the EBG sample was higher. When Table 1 is analysed, a total of 14 compounds including seven disulphides, five trisulphides and two other organosulfur compounds were detected in the samples. Organosulfur compounds, which are known to be the most dominant compounds in the flavour profiles of both fresh and black garlic, have also played an important role in the formation of the characteristic odours of encapsulated garlic. Among these compounds, alkenyl sulphates are known to be the characteristic flavour components of garlic. Alkenyl sulfides have been reported to inhibit both the initial and developmental stages of tumourigenesis in an experimental carcinogenesis model for various cancer types (Ariga et al., 2006). In the literature, it has been found that garlic contains more than thirty organosulfur compounds, and it has been observed that the encapsulation process applied in encapsulated fresh and black garlic samples traps or suppresses many of these compounds. One of the important findings obtained while determining the flavour profiles of encapsulated fresh and encapsulated black garlic is that the total concentration of organosulfur compounds is approximately 180 times more dominant in fresh garlic than in black garlic. The same situation was similarly observed in the flavour profiles of fresh and black garlic whose flavour profiles were examined within the scope of this project and in the flavour table of fresh and black garlic added bread. While the total concentration of disulphides in the EFG sample was 5709 µg/kg, the total disulphide concentration in the encapsulated black garlic samples was only 64.0 µg/kg.

The fact that the S-CH_3 bond is easily broken with heat treatment is accepted as an indicator that organosulfur compounds are not resistant to heat treatment (Plano et al., 2009). In the light of this information, it is expected that the amount of organosulfur compounds that give the garlic its pungent specific odour will decrease considerably with the heat treatment applied during the fermentation of black garlic, such as the result obtained in our study. It has been reported that the diallyl disulphide compound, which was determined in both EFG and EBG samples and is the most dominant compound among the disulphides of EFG, has many protective effects against colon, kidney, skin, breast and oesophageal cancers (Bansal et al., 2018). In previous studies, it has been reported that allinase enzyme degrades cysteine sulfoxides such as alliin in heat treatment applications, releasing characteristic aroma compounds such as thiosulfanes, diallyl sulfide and diallyl disulfide (Puccinelli et al., 2017).

(1E)-1-Propenyl disulphide compound, known in the literature as one of the fastest oxidising compounds of garlic and onion when chopped or crushed, was the second most dominant compound determined in fresh garlic (1440µg/kg). This compound was also found to be greatly reduced by being oxidised by black garlic fermentation and almost disappeared with the encapsulation process (8.3µg/kg). In addition to disulphides, five different trisulphide compounds were determined in the EFG sample and three different trisulphide compounds in the EBG sample, and the total aroma concentrations of these compounds were found to be 13353.3 and 42.1 µg/kg, respectively. As in the case of disulphides, trisulphide compounds were observed to undergo a great loss in quantity by fermentation and encapsulation processes. It has been reported in the literature that allyl trisulfide, the most dominant trisulfide compound detected, and other trisulfide compounds give effective results in the treatment of many diseases, especially cancer (Seki et al., 2008). Many trisulfide compounds were determined in studies on the flavour profiles of garlic and it was determined that most of these compounds were lost during the fermentation and encapsulation processes of black garlic. In the studies conducted in the literature, considering the flavour profiles of fresh and black garlic, in parallel with the results obtained in our study, it was reported that heat treatment degraded the trisulfide compounds predominantly found in garlic and many trisulfide compounds were lost (Abe et al., 2020).

In addition to disulphide and trisulphide compounds, two organosulfur compounds, which are among the most dominant compounds of encapsulated garlic, especially EFG samples, were detected. 3-Vinyl-1,2-dithi-4-ene and 2-vinyl-1,3-dithi-4-ene were the compounds that gave EFG samples their characteristic flavours. It has been emphasised in the literature that these compounds are the compounds that give the pungent odours of fresh garlic (Mangoba et al., 2019).

Thiols

The second important aroma group identified in the aroma profiles of EFG and EBG samples were thiols. 3H-1,2-Dithiol is the most dominant compound among these compounds and was found at a high concentration of 5361 µg/kg in the EFG sample, while this compound was not detected in the EBG sample. In the study conducted by Sasmaz et al. (2024), this compound was detected in black garlic, the fact that it was not detected in encapsulated samples is another proof that the encapsulation process has a direct effect on the flavour profile of black garlic. In addition, it was observed that thiols, which are known as one of the aroma groups that persist in human breath when fresh garlic is consumed, were suppressed by the encapsulation process. This situation shows that the usage areas of encapsulated garlic products have the potential to expand. It has been reported in previous studies in the literature that 3H-1,2-dithiol compound has a negative aroma in garlic (Yang et al., 2019). In the literature, Ikram et al. (2019) determined *Allium fistulosum* in the green onion variety known as winter onion and reported that it contributes to the bitter characteristic odour of green onion.

Aldehydes

Another group found in the aroma profile of encapsulated fresh and black garlic was aldehydes. The compounds furfural, which is known to be formed by Maillard reactions of certain components subjected to heat treatment and is responsible for burnt caramel-like odours, and *(E,E)*-2,4-decadienal, which has a toasted oily odour, were only detected in EBG samples. However, nonanal, *(E)*-2-octenal, known for its pleasant, citrusy and soap-like odours, and benzaldehyde compounds with almondy and caramel odours were detected in both samples. In previous studies, it was reported that aldehydes are the compounds that characterise the specific aroma of black garlic and furfural was the most prominent aldehyde compound in black garlic (Ding et al., 2021). In our study, it was observed that aldehyde compounds, which are predominant in the flavour profile of black garlic and released by the Maillard reaction of fructans under the influence of heat treatment and humidity, were significantly reduced by the effect of encapsulation process.

Table 1. Aroma profiles of encapsulated fresh garlic (EFG) and encapsulated black garlic (EBG) (µg/kg)

No	RT	LRI	Compounds	EFG (µg/kg)	EBG (µg/kg)	Sig
			Thiols			
1	30,03	1494	3H-1,2-Dithiol	5360.5 ± 126.1	Nd	*
2	34,86	1628	*(Z)*-5-(Methylthio)-4-penten-2-ol	680.1 ± 55.3	21.6 ± 2.0	*
3	35,79	1636	1,5-Pentanethiol	Nd	7.1 ± 0.2	*
4	38,09	1712	3-methyl 3H-1,2-dithiol	891.1 ± 92.0	10.4 ± 0.8	*
			Total	6931.7 ± 273.4	39.1 ± 3.0	*
			Organosulfur compounds			
			Disulfides			
5	20,61	1283	Allyl methyl disulfide	125.8 ±10.2	Nd	*
6	28,11	1454	*(Z)*-1-Allyl-2-(prop-1-en-1-yl)disulfane	166.8 ±1.5	Nd	*
7	28,62	1463	Diallyl disulfide	3671.0 ±28.7	24.9 ± 1.4	*
8	28,92	1485	Allyl *(E)*-1-propenyl disulfide	Nd	9.6 ± 0.9	*
9	31,29	1516	*(1Z)*-1-propen-1-yl propyl disulfide	Nd	11.4 ± 0.1	*
10	39,20	1780	*(1E)*-1-propenyl disulfide	1439.7 ± 456.3	8.3 ± 0.5	*
11	46,00	2030	Pentyl propyl disulfide	305.7 ± 27.1	9.9 ± 0.6	*
			Total	5708.9 ± 523.7	64.0 ± 3.5	*
			Trisulfides			
12	24,79	1370	Dimethyl trisulfide	86.7 ± 0.2	Nd	*
13	32,48	1592	Allyl methyl trisulfide	2818.9 ± 29.1	18.2 ± 0.6	*
14	40,06	1789	Allyl trisulfide	9680.3 ± 243.5	14.0 ± 1.3	*
15	46,96	2005	Allyl *(E)*-prop-1-enyl trisulfide	601.7 ± 66.0	9.8 ± 0.7	*
16	48,69	2124	Diallyl trisulfide	165.8 ± 41.8	Nd	*
			Total	13353.3 ± 380.6	42.1 ± 2.5	*
			Total sulphides	19062.3 ± 904.3	106.1 ± 6.1	*
			Other organosulfur compounds			
17	38,22	1714	3-Vinyl-1,2-dithi-4-en	6615.7 ± 316.5	Nd	*
18	41,63	1842	2-Vinyl-1,3-dithi-4-en	5393.8 ± 434.6	52.4 ± 1.8	*
			Total	12009.5 ± 751.1	52.4 ± 1.8	*
			Aldehydes			
19	25,53	1390	Nonanal	37.6 ± 1.6	28.2 ± 1.0	*
20	26,65	1429	(*E*)-2-Octenal	62.9 ± 1.0	38.4 ± 0.1	*
21	27,77	1439	Furfural	Nd	33.4 ± 0.7	*
22	29,93	1492	Benzaldehyde	173.7 ± 7.9	105.0 ± 15.4	*
23	40,62	1792	*(E,E)*-2,4-Decadienal	Nd	33.0 ± 3.8	*
			Total	274.2 ± 10.5	237.9 ± 20.9	*
			Ketones			
24	31,57	1570	(*E,E*)-3,5-Octadien-2-one	147.4 ± 1.4	64.8 ± 5.8	*
25	34,75	1624	Acetophenone	87.2 ± 8.0	239.3 ± 5.5	*
26	41,05	1796	3-methyl-1,2-cyclopentanedione	Nd	12.0 ± 0.8	*
27	45,69	2001	Furyl hydroxymethyl ketone	Nd	7.3 ± 0.2	*
28	55,16	2470	Benzophenone	Nd	69.2 ± 7.2	*
			Total	234.6 ± 9.4	392.7 ± 19.4	*
			Carboxylic acids			
29	27,32	1429	Acetic acid	36,2 ± 1,8	107,5 ± 0,6	*
30	35,86	1647	3-Methyl-butanoic acid	288,8 ± 8,5	Nd	*

31	41,81	1852	Hexanoic acid	250,5 ± 3,9	103,1 ± 2,3	*
32	44,53	1914	2-Ethyl-hexanoic acid	Nd	4,5 ± 0,3	*
33	47,22	2070	Octanoic acid	768,0 ± 11,2	33,0 ± 2,1	*
34	49,44	2144	Nonanoic acid	240,2 ± 17,2	Nd	*
			Total	1583,6 ± 42,6	248,1 ± 5,3	*
			Alcohols			
35	18,24	1170	3-Penten-2-ol	85.4 ± 1.5	13.9 ± 1.3	*
36	19,79	1238	2-Hexanol	91.9 ± 1.7	41.1 ± 3.8	*
37	34,26	1621	*(E)*-p-Menta-2,8-dienol	402.1 ± 22.5	20.8 ± 0.3	*
38	41,94	1859	Furaneol	Nd	10.8 ± 0.8	*
			Total	579.4 ± 25.7	86.6 ± 6.1	*
			Terpenes			
39	30,87	1512	Linalool	190.0 ± 16.2	58.7 ± 3.6	*
40	50,31	2228	α-Bisabolol	305.0 ± 1.5	32.2 ± 2.9	*
			Total	495.0 ± 17.7	90.9 ± 6.6	*
			Phenols			
41	47,43	2081	3-Methyl-phenol	Nd	26.4 ± 0.2	*
			Total	0.0	26.4 ± 0.2	*
			Furans			
42	29,28	1489	Acetylfuran	Nd	36.1 ± 2.5	*
			Total	Nd	36.1 ± 2.5	*
			Other compounds			
43	27,55	1435	1,3-Dimethylpyrazole	Nd	10.7 ± 1.1	*
44	30,51	1496	Diethyl oxalate	Nd	21.0 ± 2.2	*
45	39,37	1785	3-Acetopyridine	Nd	5.4 ± 0.4	*
			Total	0.0	89.4 ± 5.5	*
General Total				***41170.2 ± 2034.6***	***1353.3 ± 75.5***	*

(*) The symbol in the row indicates statistical differences ($p<0.05$*). Nd: Not detected. EBG:Encapsulated black garlic, EFG: Encapsulated fresh garlic. LRI: Linear retention indexes calculated in DB-Wax column.

Furans

Furans, another aroma group identified with heat treatment, were not found in encapsulated fresh garlic samples as expected, while the only furan compound found in EBG samples was acetylfuran. Acetylfuran compound, which gives black garlic its sweetness and unique flavour, is known to be released by the Maillard reaction of S-alk(en)il-l-cysteine amino acid under high temperature (Molina-Calle et al., 2017).

Alcohols

Another aroma group detected in the encapsulated garlic samples in the study was alcohols (Table 1). 3-Penten-2-ol, 2-hexanol and *(Z)-p*-menta-2,8-dienol were the three volatile alcohol compounds that could be detected in EFG samples, while in EBG samples, especially furfuryl alcohol, alpha kumyl alcohol and furaneol compounds were formed due to the effect of heat treatment. In studies conducted in the literature, Setiyoningrum et al. (2022) reported that the furfuryl alcohol released with the heat treatment applied especially in black garlic makes an important contribution to the aroma of black garlic.

Ketones

When the table of aroma compounds obtained was examined, another important aroma group was ketones. Among the five ketone compounds identified in the samples, *(E,E)*-3,5-octadien-2-one and acetophenone compounds were detected in both EFG and EBG samples, while 3-methyl-1,2-cyclopentanedione, furyl hydroxymethyl ketone, benzophenone compounds were detected only in EBG samples.

Volatile acids

When the results given in Table 1 are considered, it is seen that another aroma group detected in encapsulated garlic samples is volatile acids. Acetic acid, 3-methyl-butanoic acid, hexanoic acid, 2-ethyl-hexanoic acid, octanoic acid and nonanoic acid were the acid compounds detected in encapsulated garlic samples, while 2-ethyl-hexanoic acid was not detected in EFG, 3-methyl-butanoic acid and octanoic acid were not detected in EBG samples. When the results are considered, it is thought that the encapsulated garlic products in the present study do not have a great contribution to the total aroma in terms of acids, since the detection threshold values of volatile acids, which generally give garlic oily odours, are high.

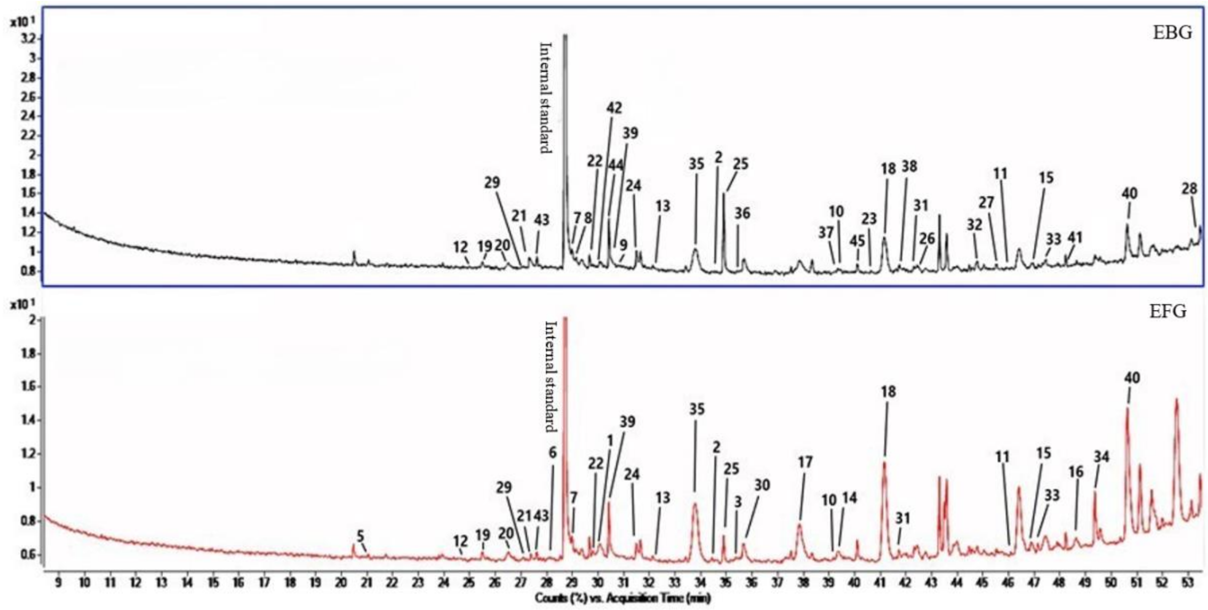

Figure 1. GC chromatograms of encapsulated fresh garlic (EFG) and encapsulated black garlic (EBG). The numbering refers to the order in table 1.

Aroma-active compounds of encapsulated samples

The aroma-active compounds, odours given by these compounds and odour dilution factors (FD) of the products obtained by encapsulating fresh and black garlic samples are given in Table 2. A total of 13 aroma-active compounds were determined in encapsulated samples. Significant differences were observed in the aroma-active compounds between the EFG and EBG samples ($p< 0.05$). The FD factors of the aroma-active compounds varied between 4-1024. Of the 13 aroma-active compounds, 10 were identified and 3 were unidentified (unknown) aroma-active compounds. Unknown odorants (LRI: 1134, 1356, and 1510) were detected by GC-MS-O, but could not be identified by GC-MS due to their low concentration or to limited spectral matches. Of the identified compounds, 2 were alcohols, 3 were sulfur compounds, 4 were acids and 1 was a ketone compound. When the aroma activities of encapsulated garlic samples were compared with unencapsulated fresh and black garlic samples in our previous study by Sasmaz et al. (2023), it was clearly observed that the FD values of encapsulated samples were lower. Osorio et al. (2011) encapsulated guava fruit using maltodextrin, arabic gum and spray dryer and compared the flavour of the encapsules with fresh fruit. It was determined that the encapsules obtained had an aroma very close to the odour of guava fruit when dissolved in water. However, it was also reported that no compounds were detected when the encapsules were analysed for aroma in solid form without dissolving in water. Researchers have explained this situation as the compounds are effectively transferred to the encapsulated structure. In our study, the FD values of encapsulated and non-encapsulated fresh and black garlic samples were analysed.

The highest FD values in encapsulated garlic samples were determined as organosulfur compounds (allyl methyl trisulfide, diallyl disulfide, *(1Z)*-1-propen-1-yl propyl disulfide) as in non-encapsulated samples. It is known that organosulfur compounds formed by the degradation of alliin and its derivatives are very important for both fresh and black garlic flavour and are responsible for the characteristic odours of garlic. In encapsulated fresh and black garlic samples, these two compounds have higher FD values in encapsulated fresh garlic samples. It was determined that these data were also compatible with the aroma compounds of the samples.

A total of 4 aroma-active acid compounds, namely acetic acid (vinegar smell, sour), hexanoic acid (sweat smell), octanoic acid (pungent, mouldy) and nonanoic acid (waxy) were detected in encapsulated garlic samples. The FD factors of these compounds ranged from 4 to 16 and generally had higher values in encapsulated black garlic. 3-Penten-2-ol and 2-hexanol were the aroma-active alcohol compounds identified in the encapsulated garlic and gave the samples oily, green and pungent odours, respectively. It has been reported that these compounds were determined as aroma-active compounds in many products such as passion fruit, mussel meat, olive oil and contributed to the odour in previous studies (Hui et al., 2010; Kesen et al., 2013, 2014).

The only ketone compound identified in encapsulated samples was acetophenone, which is responsible for sweet, pungent odours. In the literature, it has been reported that ketones are generally produced from the peroxidation of lipids and amino acids through the Maillard reaction as a result of heat treatment and have significant effects on food odour (Wang et al., 2019). Acetophenone compound has been reported to be one of the important aroma-active compounds responsible for sweet, pungent, floral odours in various samples such as yeast extract (Wang et al., 2019), dried figs (Yao et al., 2021), yoghurt (Liu et al., 2022) in previous studies.

Table 2. Aroma-active compounds of EFG and EBG samples (FD≥4)

No	LRI	Compounds	Odour Descriptions	FD		
				EFG	EBG	Sig
1	1134	Unknown	Garlic	128	Nd	*
2	1170	3-Penten-2-ol	Oily, green	32	4	*
3	1238	2-Hexanol	Pungent	16	4	*
4	1356	Unknown	Popcorn	256	Nd	*
5	1429	Acetic acid	Vinegar smell, sour	4	128	*
6	1463	Diallyl disulfide	Garlic	1024	64	*
7	1510	Unknown	Green, grass	4	Nd	*
8	1629	Acetophenone	Sweet, fruity	8	256	*
9	1516	*(1Z)*-1-propen-1-yl propyl disulfide	Sulfurous, umami	64	32	*
10	1592	Allyl methyl trisulfide	Umami, garlic	16	128	*
11	1852	Hexanoic acid	Buttery	16	64	*
12	2070	Octanoic acid	Ripe fruit	4	32	*
13	2144	Nonanoic acid	Waxy, buttery	4	32	*

(*) The symbol in the row indicates statistical differences (p<0.05*). Nd: Not detected. EFG: Encapsulated fresh garlic, EBG:Encapsulated black garlic,

CONCLUSION

In this study, the aroma profiles and aroma-active compounds of fresh garlic (EFG) and black garlic (EBG) samples encapsulated using the complex coacervation method were investigated, demonstrating for the first time the method's ability to modulate garlic's aroma profile by reducing pungent organosulfur compounds while retaining key aroma-active components.The findings revealed that the encapsulation process had significant effects on the characteristic aroma components of garlic. While 30 different aroma compounds were detected in the EFG sample, this number reached 37 in the EBG sample. However, the concentration of total aroma compounds was about 40 times higher in EFG samples compared to EBG samples. This result reveals that the chemical reactions that take place during the fermentation of black garlic cause a significant reduction in aroma compounds. In particular, organosulfur compounds were found to be much more predominant in fresh garlic than in black garlic. The encapsulation process partially suppressed the pungent flavour of fresh garlic and delayed the release of the characteristic aroma compounds arising during the fermentation process of black garlic. Moreover, encapsulation was observed to reduce the odour dilution factors (FD) of flavour-active compounds. These findings reveal the potential of encapsulation technology to preserve and provide controlled release of aroma components of garlic. This study provides an important contribution in terms of expanding the use of encapsulated garlic products in the food industry and developing products suitable for consumer preferences. Future research should focus on sensory evaluation and encapsulation stability to further optimize garlic-based functional foods.

Compliance with Ethical Standards

Peer-review

Externally peer-reviewed.

Declaration of Interests

Statement of the conflict of interest to the manuscript should be specified in this section.

Author contribution

Hatice Kubra Sasmaz: conceptualization, data curation, formal analysis, funding acquisition, writing - first draft, writing - review & editing, Onur Sevindik: Conceptualization, data curation, formal analysis, funding acquisition, writing (original draft), writing (review & editing). Gamze Guclu: Conceptualization, data curation, formal analysis, funding acquisition, writing (original draft), writing (review & editing). Serkan Selli: Conceptualization, data curation, formal analysis, funding procurement, original draft writing, review, and editing. Hasim Kelebek: Conceptualization, data curation, formal analysis, funding acquisition, writing (original draft), writing (review & editing).

Funding

This study was financially supported by the Scientific and Technological Research Council of Turkey (TUBITAK, Project number: TOVAG-219O174).

Acknowledgments

This study was supported by TUBITAK (The Scientific and Technological Research Council of Turkey) within the scope of the 1001 project with project number "219O174". We would like to thank TUBITAK

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