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Application News

No. M286

Gas Chromatography Mass Spectrometry

Evaluation of Aroma Generated During Cooking

The flavor and smell of food, together with its taste, are important factors in the sales of food products. With heightened interest in diet in recent years, food manufacturers are developing functional, high quality foods, increasing the need for evaluation of the aroma produced by foods in actual use situations such as cooking and eating.

The aroma of foods consists of the intrinsic smell of the food itself and the smell produced by heating the food. Even foods that seem to have an unpleasant fishy smell before cooking lose that smell when heated, and the components responsible for its smell change to an aroma component, for example, giving a unique roast smell. The Maillard (aminocarbonyl) reaction plays a key role in the formation of this unique aroma during heating, and the products also include substances with distinctive smells.

In this Application News, we evaluated the difference in the aroma components of soy sauce when cooked and when unheated. This article introduces the results of a search for the distinctive components of soy sauce when cooked and when unheated by comparing the aroma components detected under these respective conditions using Signpost MS (Reifycs Inc.), a multivariate analysis software program.

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Method of Capturing Aroma Components During Cooking

Pretreatment methods such as headspace (HS) extraction and solid phase microextraction (SPME) are used in evaluating the smell of foods. However, in order to evaluate the smell of foods in actual use situations, for example, during cooking, ingenuity is necessary in the pretreatment method.

When the HS method is used to evaluate the aroma components of liquid samples such as condiments in a condition of higher than 100 °C like during cooking, adequate capture of those components is difficult, as the amount of sample injected in the vial is on the microliter (µL) order. The sample size is limited considering the pressure resistance of the vial because the vaporization volume of the water in liquid food products is extremely large. As an additional problem of the HS method, since the reaction during heating by the HS method occurs in a glass vial, the heating conditions are different from those in actual cooking, and this may cause differences in the aroma components.

MonoTrap monolithic silica adsorbent (GL Sciences Inc.) makes it possible to capture aroma components under a variety of conditions regardless of the limitations of the vial environment and temperature conditions. MonoTrap also has a high capture capacity because its structure has a porous silica skeleton with a large surface area.

A sealable metal pot with MonoTrap DCC18 (active carbon & ODS, disk-type) fixed to the pot lid with MT holder (GL Sciences Inc.) was used to capture the aroma components produced during heating in the cooking utensil. In addition, an aluminum foil guard (Figs. 1 and 2) was devised to prevent direct attachment of scattered droplets from the soy sauce on the MonoTrap during cooking.

The aroma components were captured by fixing two sets of MonoTrap in this manner.

The soy sauce sample was a commercially-available product, and the temperature during cooking was set to 200 °C using an IH cooking heater. The pot was set on the heater, and after confirming adequate heating, 20 mL of the soy sauce was poured into the pot. The pot was then closed with lid with the attached MonoTrap and heated for 20 s, after which the pot was removed from the heater and the aroma components were captured for 1 h. The aroma components of the soy sauce in the unheated sample were captured for 1 h in a metal pot without heating.

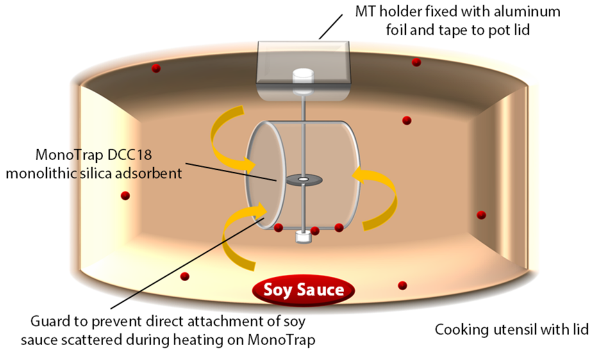

Fig. 1 Method of Setting MonoTrap in Cooking Utensil (Schematic Drawing)
(Round marks : Scattered Droplets of Soy Sauce, Arrows : Aroma Components)

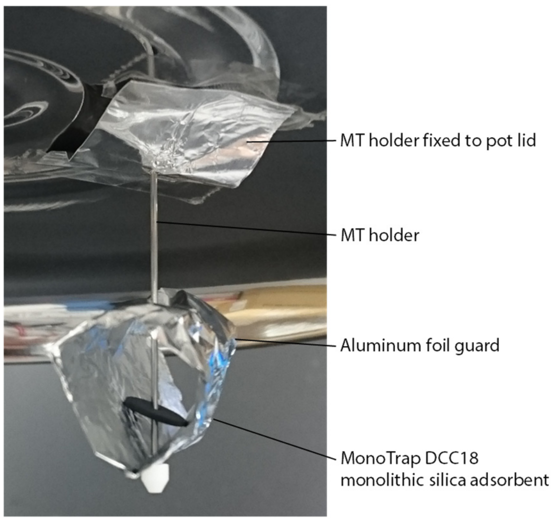

Fig. 2 View of MonoTrap Attached to Pot Lid

Sample Preparation and Analysis Conditions

The MonoTrap used to capture the aroma components was subjected to solvent extraction with 1 mL of diethyl ether and sonicated for 5 min, followed by dewatering with anhydrous sodium sulfate and concentration by nitrogen purge to obtain a final volume of 100 µL. Table 1 shows the GC/MS analysis conditions.

Table 1 Analysis Conditions

GC-MS	: GCMS-QP™ 2020 NX
Autoinjector	: AOC™-20i+s
Column	: SUPELCOWAX®10 (Length: 30 m, 0.25 mm I.D., df = 0.25 µm)
[GC]	
Vaporizing chamber temp.	: 280 °C
Column oven temp.	: 50 °C ⇒ (3 °C/min) ⇒ 230 °C (5 min)
Injection mode	: Split (1 : 5)
Carrier gas	: He
Carrier gas control	: 30.0 cm/s (Constant linear velocity)
Injection volume	: 2 µL
[MS]	
Ion source temp.	: 200 °C
Interface temp.	: 250 °C
Ionization method	: EI
Data acquisition mode	: Scan
Event time	: 0.3 s

Results

Fig. 3 shows the results of the analysis of the soy sauce aroma components captured when heated and when unheated.

Tables 2 to 4 show the distinctive components captured during heating, the distinctive components of the unheated sample, and the components detected in common under both conditions, respectively. The components that were detected under only one of the capture conditions were regarded as distinctive components of that condition. Among the components detected under both conditions, when the peak area values differed by one order of magnitude (roughly 10 times or more), that component was regarded as a distinctive component of the condition under which the larger amount was detected. When the peaks were on the same order (difference of peak area values is 5 times or less), the component was regarded as a common component.

When classified by the method described above, the aroma of the heated soy sauce contained 26 distinctive components, the aroma of the unheated soy sauce contained 6 distinctive components, and 6 components were regarded as common.

From the aroma of the heated soy sauce, mainly, alcohols, aldehydes, and pyrazines were detected as distinctive components. Among these, furfuryl alcohol, pyrazines, furfural, pyrrole, and aldehydes are known to be products formed by the Maillard reaction. Components characterized as fragrant burnt smells were detected, as furfuryl alcohol has a burnt smell, pyrazines have a roast smell, and furfural has an almond smell.

The main components detected in the aroma of the unheated soy sauce were alcohols. Butyl alcohol and isobutyl alcohol are known to be favorable aroma components of soy sauce, and these components decreased remarkably in the heated soy sauce. These results suggested that the character of "soy sauce" decreases and fragrant smells increase in its place as a result of cooking.

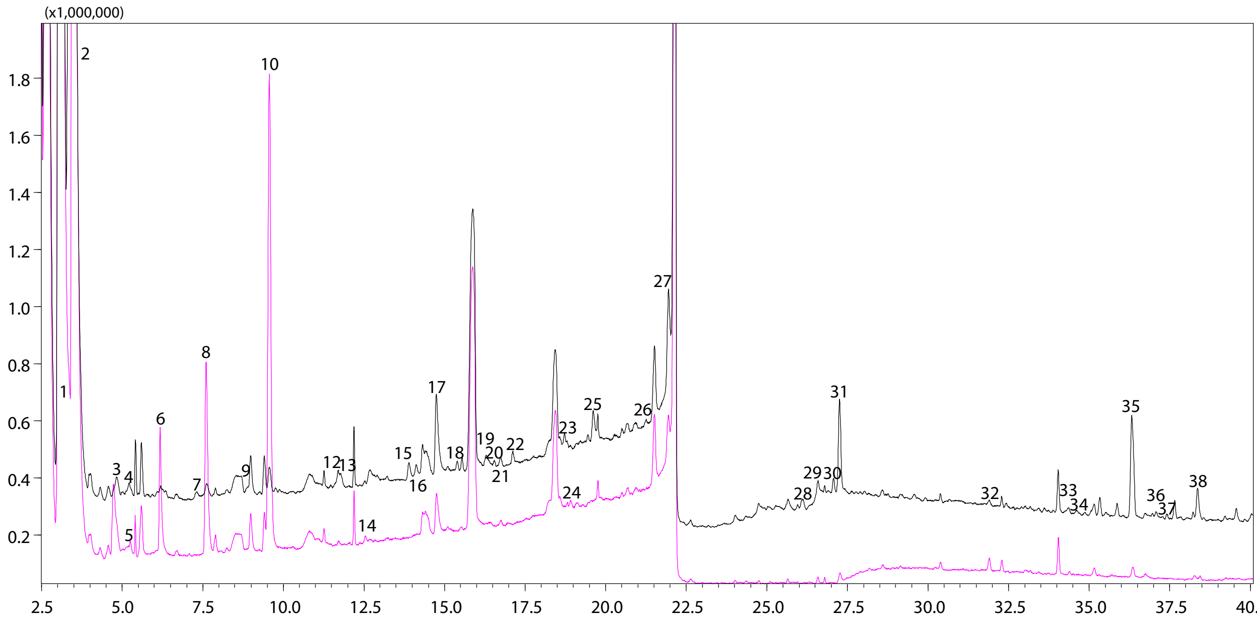

Fig. 3 Results of Analysis of Aroma Components in Cooked and Unheated Soy Sauce
Black: Cooked, Pink: Unheated

Table 2 Distinctive Aroma Components of Cooked Soy Sauce

ID.	Alcohols	R.T.	*m/z*
3	2-Butanol	4.82	55
9	2,4-Dimethyl-1-penta-2,4-dienol	8.88	112
12	1-Heptanol	11.71	69
31	Furfuryl alcohol *	27.25	98
35	Phenethyl alcohol *	36.32	91
	Aldehydes		
1	2-Methylbutanal	3.36	57
18	2-Isopropyl-5-methyl-2-hexenal	15.40	69
25	Furfural	19.62	96
27	Benzaldehyde	21.96	106
29	Phenylacetaldehyde	26.59	91
36	2-Phenyl-2-butenal	37.07	117
37	4-Methyl-2-phenyl-2-pentenal	37.41	174
	Pyrazines		
13	2-Methyl pyrazine	11.78	94
15	2,5-Dimethyl pyrazine	13.90	81
16	2,6-Dimethyl pyrazine	14.12	67
19	2-Ethyl-6-methyl pyrazine	16.29	121
20	2-Ethyl-5-methyl pyrazine	16.55	121
22	2,3,5-Trimethyl pyrazine	17.12	122
23	2-Ethyl-3,6-dimethyl pyrazine	18.72	135
28	2,5-Dimethyl-3-isoamylpyrazine	26.11	122
30	2,5-Dimethyl-3-isopentyl pyrazine	27.07	122
	Others		
7	Methyl propenyl ketone	7.31	84
11	n-Propylbenzene	9.75	91
26	2-Acetylfuran	21.26	95
34	Guaiacol	34.60	109
38	2-Acetylpyrrole	38.36	94

Table 3 Distinctive Aroma Components of Unheated Soy Sauce

ID.	Alcohols	R.T.	*m/z*
6	Isobutyl alcohol *	6.17	74
8	Butyl alcohol *	7.62	56
10	3-Methyl-1-butanol *	9.56	55
24	1-Octen-3-ol	18.91	57
	Esters		
14	Furfuryl ethyl ether	12.55	126
	Others		
5	2-Oxopentanedioic acid	5.25	101

Table 4 Common Aroma Components of Unheated and Cooked Soy Sauce

ID.	Alcohols	R.T.	*m/z*
2	Ethanol	3.45	45
	Aldehydes		
21	Nonanal	16.74	57
	Esters		
17	Ethyl lactate	14.75	75
32	Ethyl phenylacetate	31.90	91
	Others		
4	Toluene	5.22	91
33	trans-Geranylacetone	34.40	69

* : Common aroma component of unheated and cooked soy sauce, but peak area values are remarkably different.
ID. : Shown in Fig. 3.
m/z : Value used in analysis by Signpost MS.

Visualization by Multivariate Analysis Software

Signpost MS (Reifycs Inc.), a multivariate analysis software is capable of extracting ionic information detected from the data obtained by GC-MS in the form of spots, aligning the results on the basis of retention time, and comparing the differences between samples (Fig. 4). Visual evaluation of the differences between data is also possible by various techniques such as pairwise plots (comparison of two groups), hierarchical clustering, principal component analysis (PCA), and transition chart.

The qgd files (scan data only) obtained by GCMSsolution™ can be imported directly into Signpost MS.

The aroma components of the heated soy sauce and unheated soy sauce were analyzed by designating 38 spots by the *m/z* and retention time (R.T.) shown in Tables 2 to 4. The comparison of the amounts of aroma components detected in the heated and unheated soy sauce was displayed as a heat map (Fig. 5) by hierarchical clustering on Signpost MS.

As mentioned above, furfuryl alcohol is a characteristic soy sauce aroma during cooking, while butyl alcohol is remarkable in unheated soy sauce. The ratio of the detected amounts of compounds such as furfuryl alcohol and butyl alcohol can be understood visually from the heat map. In addition, the ratio of the detected amounts of the aroma components detected commonly under both conditions can also expressed visually.

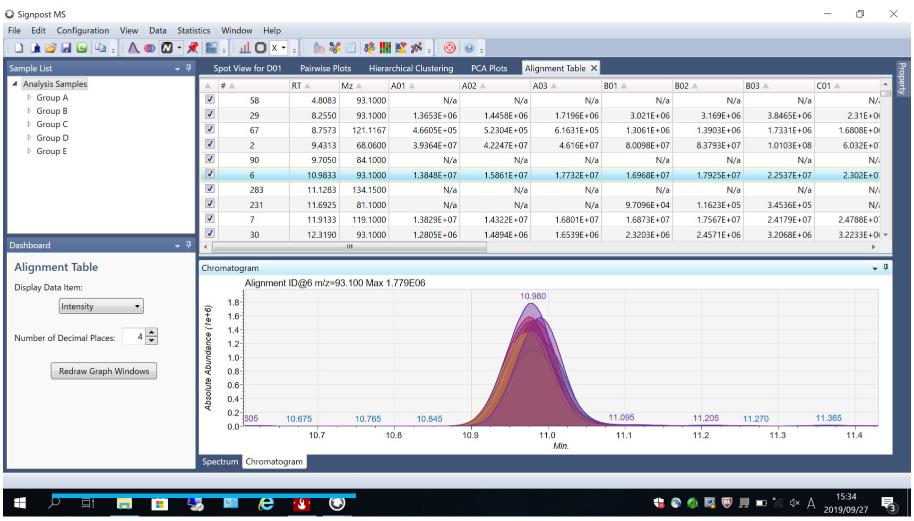

Fig. 4 Signpost MS Analysis Screen

Fig. 5 Comparison of Detected Amounts under Two Conditions by Heat Map on Signpost MS

Conclusion

The aroma components formed by cooking soy sauce were captured by the monolithic silica adsorbent MonoTrap, and the differences between those aroma components and the aroma components of unheated soy sauce were clarified.

The smells generated in situations for the actual purpose of food products can be evaluated by using MonoTrap.

In addition, the differences between data can be judged visually by utilizing multivariate analysis.

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