LAAN-A-MS-E023

SHIMADZU

Application News

Gas Chromatography Mass Spectrometry No.M256

Analysis of Aroma in Frozen Shrimp Using Thermal Desorption-GC/MS

The smell of food is an important characteristic related to its taste, aroma, and freshness. The headspace technique, in which the gas released during heating of the sample is analyzed, has typically been used in the aroma analysis of foods. The headspace technique usually relies on heating of the sample to transfer the target substances to the vapor phase. However, in the case of perishable foods, there is always a danger that heating will cause sample degeneration. Although the headspace technique can be conducted using a lower heating temperature, this approach would normally result in reduced sensitivity. An alternate approach when analyzing samples which could be affected by thermal degradation involves concentrating the volatilized gas at or near room temperature using the thermal desorption technique. This Application News introduces an example of analysis of trace quantities of substances volatilized from frozen shrimp at room temperature.

■ Analysis Outline

1. Sampling
   Volatile substances were collected.

2. Sample introduction
   Volatile substances were introduced into GC/MS.

3. Data analysis
   3.1 Qualitative analysis
   Volatile substances were identified from their mass spectra.
   3.2 Quantitative analysis of the generated gas
   For each substance identified, a calibration curve was generated using standard samples of known concentration. The volatilized compounds in the shrimp samples were calculated using the calibration curves.

■ 1. Sampling Method

The frozen sample (5 g) was enclosed in a container and set aside for 30 min to defrost at room temperature. Nitrogen gas was then passed through the container at 100 mL/min. A total of 500 mL of the expelled gas was passed through the collection tube containing adsorbent packing for trapping the target substances, thereby concentrating the volatile aroma substances. Since this analysis targets trimethylamine, a collection tube packed with CarbotrapB+ Carboxen1000 (SHIMADZU PN 223-57474-91) was used. TENAX-TA, which is a frequently used packing for thermal desorption analysis, was not used in this case due to its weak retention of trimethylamine. Weak retention is cause for concern due to the possible breakthrough and loss of the analyte. The type of collection tube must be selected according to the chemical properties of the analytes.

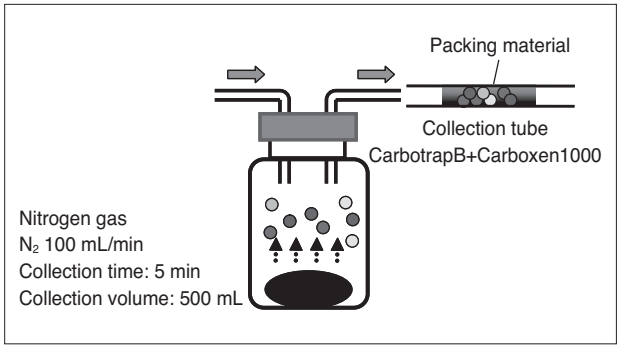

Fig. 1 Schematic Diagram of Sampling Method

■ 2. Sample Introduction

Analysis of the volatile aroma substances of frozen shrimp was conducted using the thermal desorption technique. The thermal desorption technique uses a collection tube which is connected to the instrument; the collection tube, containing volatile substances collected from the sample, is thermally desorbed and introduced into the GC/MS. Since the sample width (bandwidth) of the volatile substances widens at the time of desorption from the collection tube, typically, a secondary trap tube is installed and the volatile substances are cooled and re-concentrated to narrow the bandwidth, thus achieving higher chromatographic resolution. The analytical conditions are shown in Table 1. Sample introduction when using thermal desorption is as illustrated in the schematic diagram of Fig. 2.

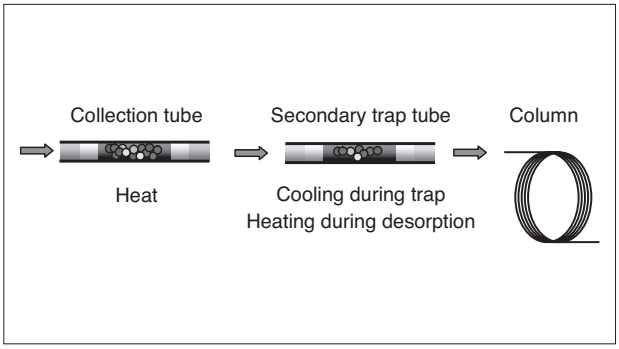

Fig. 2 Schematic Diagram of Thermal Desorption

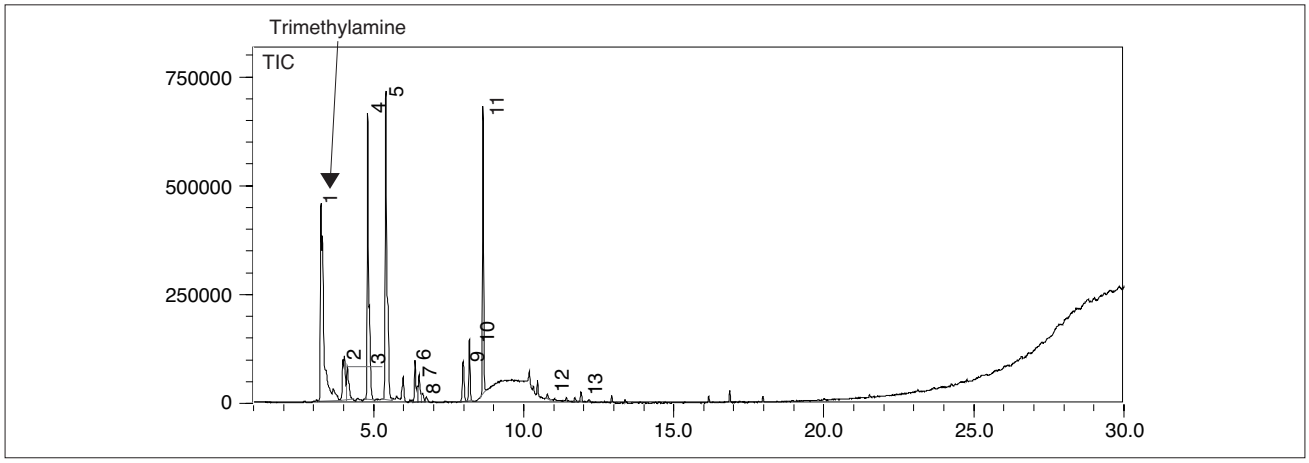

Fig. 3 TIC of Frozen Shrimp

■ 3. Data Analysis

3.1 Qualitative Analysis

The total ion chromatogram obtained from analysis of the frozen shrimp is shown in Fig. 3.
The principle peak was identified by conducting a similarity search with the NIST08 Mass Spectral Library. The identification results are shown in Table 2. Trimethylamine, carbon disulfide and dimethyl sulfide, etc. were confirmed.

Table 1 Analytical Conditions

-TD-	
Model	: TD-20
Desorp Temp.	: 250 ˚C
Desorp Flow Rate	: 60 mL/min
Desorb Time	: 10 min
1st Trap Tube	: CarbotrapB+Carboxen1000 (SHIMADZU PN223-57474-91)
2nd Trap	: TENAX-TA (SHIMADZU PN223-54144-91)
Trap Low Temp.	: -20 ˚C
Trap High Temp.	: 250 ˚C
Valve Temp.	: 230 ˚C
Line Temp.	: 250 ˚C
IF Temp.	: 230 ˚C
Model	: GCMS-QP2010 Plus
-GC-	
Column	: RESTEK Stabilwax (60 m × 0.32 mm I.D. df = 0.5 µm)
Column Temp.	: 40 ˚C (2 min) – 8 ˚C/min – 250 ˚C (15 min)
Carrier Gas	: He (Constant Linear Velocity Mode)
Linear Velocity	: 36 cm/s
Injection Method	: Split
Split Ratio	: 15:1
-MS-	
Interface Temp.	: 230 ˚C
Ion Box Temp.	: 200 ˚C
Ionization Method	: EI
Scan Range	: *m/z* 35 - 550
Scan Interval	: 0.5 s

Table 2 Results of Similarity Search

Peak	compound name
1	Trimethylamine
2	Carbon disulfide (CS_2)
3	Dimethyl sulfide
4	Acetone
5	Tetrahydrofuran(THF)
6	Isopropyl alcohol
7	Chloromethoxymethane
8	Ethanol
9	Acetonitrile
10	Chloroform
11	Toluene
12	1-Butanol
13	Pyridine

3.2 Quantitative Analysis of Generated Gas

Quantitative analysis was conducted to determine the amount of generated gas associated with the detected peak number 1, trimethylamine (retention time at approximately 3 minutes).
A trimethylamine standard substance was diluted with methanol, and quantities corresponding to 0.1, 0.3 and 1 µg were added to the collection tube. Analyses were then conducted using the same procedure as with the actual sample. Fig. 4 shows the calibration curve generated using the area values of the mass chromatogram of *m/z* 58. For the quantitative calculation results, quantities added to the collection trap were assumed to correspond to the collected headspace volume of 500 mL.

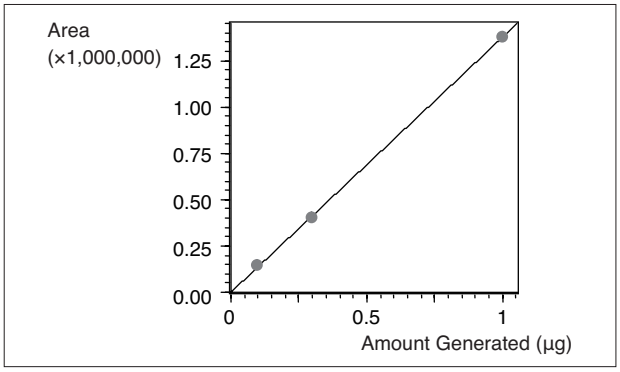

Fig. 4 Calibration Curve of Trimethylamine (*m/z* 58)

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