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Technical Report

New Approach for Off-Flavor-Complaint Product Analysis Using GC/MS Off-Flavor Analyzer

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Abstract:

Identification of components causing off-flavor requires experience and knowledge. The GC/MS Off-Flavor Analyzer includes a database containing parameters required for analysis and information (such as types and threshold values) about primary components that cause off-flavor. As a result, even less experienced analysts can use the system to easily start analyzing off-flavor components. This report introduces a case where we analyzed a packaged food product with a complaint about an off-flavor using a GC/MS Off-Flavor Analyzer. We were able to narrow down the substances that may have caused the off-flavor to four components by comparing the questionable product to the normal product. We also checked the off-flavor with a sniffer using sensory information contained in the GC/MS Off-Flavor Analyzer and successfully identified that the off-flavor was caused by anisoles. To ascertain the cause of the off-flavor, we separately measured each part of the product (package and food parts) and compared the concentration of anisoles. Results show that the package contained a higher concentration of anisoles, which caused the off-flavor. The system is expected to be used to identify the causes of off-flavors in foods, containers, and packages.

Keywords: GC/MS, off-flavor, odor, food, complaint, SPME, MonoTrap

1. Introduction

In recent years, there have been numerous food-related accidents and scandals. For example, there was an incident where off-flavor-causing components were detected from confections and pesticides were detected in frozen foods. In both cases, all the affected items were recalled from the market. In most incidents involving food, the problem is discovered when a consumer reports an issue. Therefore, to prevent incidents involving food, it is important to analyze the food for off-flavor. One of the key points of off-flavor analysis is that only a few chemical substances are responsible for most cases.

For the last 15 years, Daiwa Can Company has been offering off-flavor analysis, sensory evaluation, off-flavor trial kits, off-flavor-related evaluation testing, and other services. The number of incidents caused by the top ten components identified as causing off-flavor over the past 15 years was counted and their ratio to all detected components was calculated. These ten components were responsible for 25 % of all cases. Furthermore, the top 30 substances were encountered in 50% of the cases, meaning that understanding off-flavor problems requires simply learning about the top 30 substances. To carry out off-flavor analysis, knowing primary off-flavor-causing components is necessary.

There are generally two basic methods for evaluating off-flavor.

(1) Sensory Evaluation

Sensory evaluation involves human assessors actually using their five senses to evaluate the intensity and differences between flavors. Components causing off-flavor can be identified based on the results of sensory evaluation and sensory information of compounds. This approach gives results that are directly linked to the sensations of humans. Therefore, proper evaluation requires maintaining a consistent ability to smell off-flavor, determining how to eliminate bias, and so on. Consequently, the assessors that perform sensory evaluations must have smelling sensitivity and skills higher than a given level, and it is important that off-flavor assessors pass a smell sensitivity test at least once a year to confirm that their sense of smell is adequately sensitive.

(2) Instrumental Analysis

This allows objective identification and quantification of the components causing off-flavor using analytical instruments. Typically, gas chromatograph mass spectrometer (GC/MS) systems are used. GC/MS allows you to investigate (i) what components the sample contains (qualitative analysis), and (ii) how much of the components of interest the sample contains (quantitative analysis). Based on the qualitative analysis results, sensory information about the detected components is checked to determine whether it is consistent with the off-flavor from the reported sample. The quantitative analysis results can then be used to calculate the concentration of the detected components in the sample to determine whether the concentration is greater than the threshold for off-flavor.

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When analysts without knowledge or experience in off-flavor analysis carry out off-flavor analysis, instrumental analysis using a GC/MS system is mainly performed. However, identification of components causing an off-flavor requires sensory information of compounds and their off-flavor threshold values. If analysts do not have knowledge about primary off-flavor-causing components, they need to search for candidates from a vast number of compounds.

The GC/MS Off-Flavor Analyzer we developed already includes a database containing parameters required for analysis and information (such as types and threshold values) about primary compounds that cause off-flavor. That means even less experienced analysts can use the system to easily start analyzing off-flavor components.

This report introduces a case where we measured a packaged food for which there was a complaint about an off-flavor using the GC/MS Off-Flavor Analyzer and confirmed that the system was applicable to investigations for causes of off-flavor.

2. Procedures

2-1. Preparation of Measurement Samples

Contents of the packaged food product for which an off-flavor was reported (off-flavor product) and a normal product were divided into inside and outside parts respectively and then shredded using a kitchen knife. 2.020 g each of both the inside and outside contents were then weighed, placed in a 20 mL vial, and then sealed immediately with a screw cap. The packages of each product were also shredded using scissors and approximately 0.010 g each were used as the measurement sample with the same procedure as above.

2-2. Analytical Conditions

For the GC/MS unit, the TQ-8040 triple quadrupole mass spectrometer with a sniffer was used. To inject the sample, the solid phase micro extraction method (SPME method) was used with the AOC-5000 Plus multifunctional autosampler. For the SPME fiber, DVB/Carboxen/PDMS was used. Measurement samples were extracted while being heated at 80 °C for 30 minutes.

SPME and GC-MS/MS analytical conditions registered to the GC/MS Off-Flavor Analyzer were used and scan/MRM simultaneous measurement was performed. Table 1 shows detailed analytical conditions.

Table 1 GC-MS/MS Analytical Conditions

System Configuration	
Pretreatment unit	: AOC-5000 Plus
GC/MS	: GCMS-TQ8040
Sniffer	: Sniffer-9000
Software	: GCMSsolution Ver. 4.31 AOC-5000 Plus Control Software
Database	: GC/MS Off-Flavor Analyzer
AOC-5000 Plus	
Sample injection	: Solid phase micro extraction (SPME) method
SPME fiber	: 1 cm DVB/Carboxen/PDMS StableFlex (SUPELCO)
Sample extraction	: Vapor phase extraction
Sample quantity	: Contents 2.020 g, Packages 0.010 g
Preheat time	: 5 min
Equilibrium temperature	: 80 °C
Shaking speed	: 250 rpm
Shaking ON time	: 5 sec
Shaking OFF time	: 2 sec
Vial needle position	: 22 mm
Extraction time	: 30 min
Inlet port needle position	: 54 mm
Desorption time	: 2 min
Bake-out	: 5 min (270 °C)
Vial	: 20 mL screw vial (Thermo)
Screw cap	: 10/20 mL magnet screw cap (Thermo)

GC	
Insert liner	: SPME Liner (SGE)
Column	: InertCap 5MS/Sil (30 m × 0.32 mm I.D., df = 0.5 μm) (GL Sciences)
Injection unit temperature	: 250 °C
Injection mode	: Split (1:5)
Carrier gas	: Helium
Control mode	: Pressure (90 kPa)
Purge flowrate	: 3 mL /min
Column oven temperature	: 50 °C (5 min) → (10 °C /min) → 250 °C (10 min)
MS	
Ion source temperature	: 200 °C
Interface temperature	: 250 °C
Measurement mode	: Scan/MRM simultaneous measurement
Scan mass range	: *m/z* 45–500
Scan event time	: 0.1 sec
Scan speed	: 5000 u/sec
MRM event time	: 0.3 sec
MRM transition	: Use the GC/MS Off-Flavor Analyzer transition.
Sniffer	
Split ratio	: MS:Sniffer (0.5:1)
Make-up pressure	: 20 kPa
Air pressure	: 200 kPa

3. Analysis Results

3-1. Comparison Between Off-Flavor Product and Normal Product

To narrow down candidates of off-flavor-causing components, we measured the outside parts of the contents of both the off-flavor product and normal product, and then compared the results. Since the GC/MS Off-Flavor Analyzer includes calibration curve information of registered off-flavor components, approximate quantitative values of detected components are automatically calculated without requiring the measurement of standard samples. Then the concentration of detected components was calculated by dividing the obtained quantitative values by the weight of the measurement sample.

Table 2 shows the results of the comparison of detected components between the two products. Larger amounts of four compounds; *p*-dichlorobenzene, pelargonic acid, 2,4-dichloroanisole, and 2,4,6-trichloroanisole were detected in the off-flavor product.

By analyzing the off-flavor product and the normal product using the GC/MS Off-Flavor Analyzer, we were able to narrow down the candidates of off-flavor-causing components to four.

3-2. Checking Off-Flavor Based on Sensory Information

We sniffed the components using a sniffer in order to identify the component that caused the off-flavor.

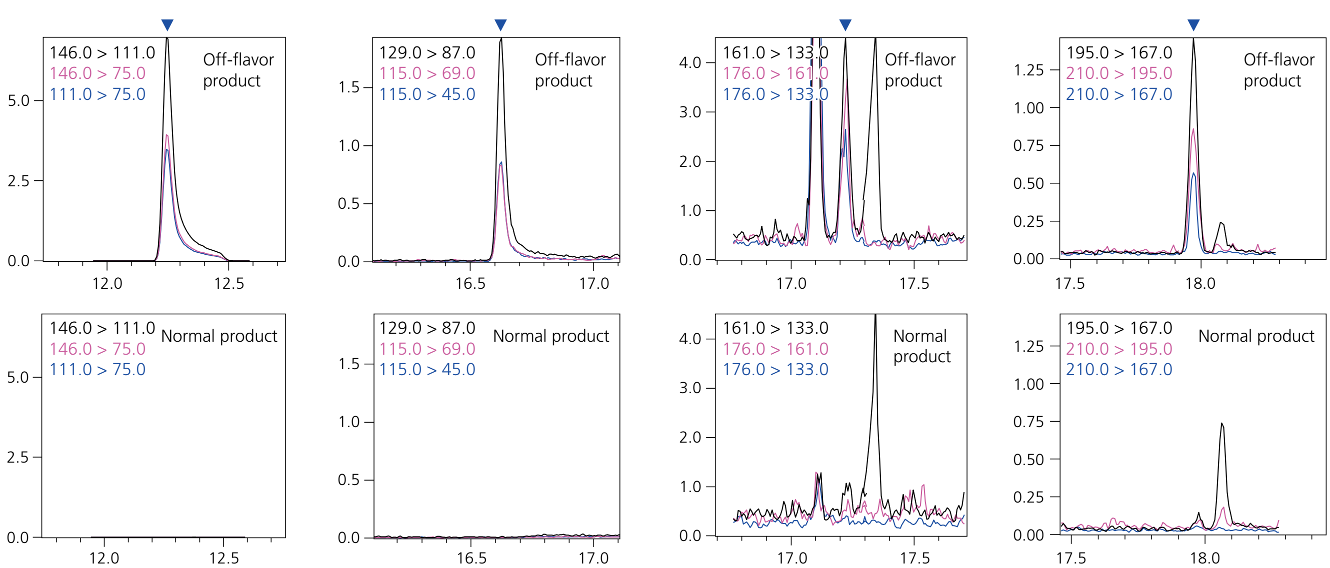
The GC/MS Off-Flavor Analyzer contains sensory information and off-flavor threshold values of registered compounds. This enables even analysts who do not have sensory information of detected components to judge the smell. In addition, since the GC/MS unit automatically narrows down the components detected and displays their elution time, analysts are able to check the smell of the components only when they are detected. Since they do not need to keep sniffing, efforts spent on sniffing can be reduced.

As a result of checking the smell of the off-flavor product, we confirmed the smell of 2,4,6-trichloroanisole. Since the concentration of this component was greater than its off-flavor threshold value, we were able to conclude that it was the cause of the off-flavor. The concentrations of *p*-dichlorobenzene, pelargonic acid, and 2,4-dichloroanisole detected were less than their off-flavor threshold values and we did not actually smell them. Therefore, we concluded that they were not the cause of the off-flavor.

Table 2 Concentration Comparison Between Off-Flavor Product and Normal Product

Compound Name	Concentration (pg/mg)		Off-Flavor Threshold (pg/mg)	Off-Flavor Threshold (pg/mg)
	Normal Product	Off-Flavor Product		
p-Dichlorobenzene	0.052	66.558	1000	Insect repellent
Pelargonic acid	N.D.	0.851	100	Dried fruit-like acid off-flavor
2,4-Dichloroanisole	N.D.	0.003	10	Mold
2,4,6-Trichloroanisole	N.D.	0.009	0.001	Mold

N.D.: less than detection limit



p-Dichlorobenzene
Concentration: 66.558 pg/mg

Pelargonic acid
Concentration: 0.851 pg/mg

2,4-Dichloroanisole
Concentration: 0.003 pg/mg

2,4,6-Trichloroanisole
Concentration: 0.009 pg/mg

Fig. 1 MRM Chromatograms of Four Components with Quantitative Values Higher in the Off-Flavor Product than in the Normal Product

3-3. Prediction of Where the Off-Flavor Occurred

Measuring each part of off-flavor products separately is helpful to ascertain the cause of the off-flavor. Therefore, we measured the package, as well as the internal and external contents. Fig. 2 shows MRM mass chromatograms of *p*-dichlorobenzene, pelargonic acid, 2,4-dichloroanisole, and 2,4,6-trichloroanisole detected in each sample. Table 3 shows the comparative results of their concentrations.

Concentration values of *p*-dichlorobenzene, pelargonic acid, 2,4-dichloroanisole, and 2,4,6-trichloroanisole were the highest in the off-flavor of the package, the internal contents, and external contents. Thus, we were able to conclude that the off-flavor-causing component got on the package and then spread to the contents inside the package.

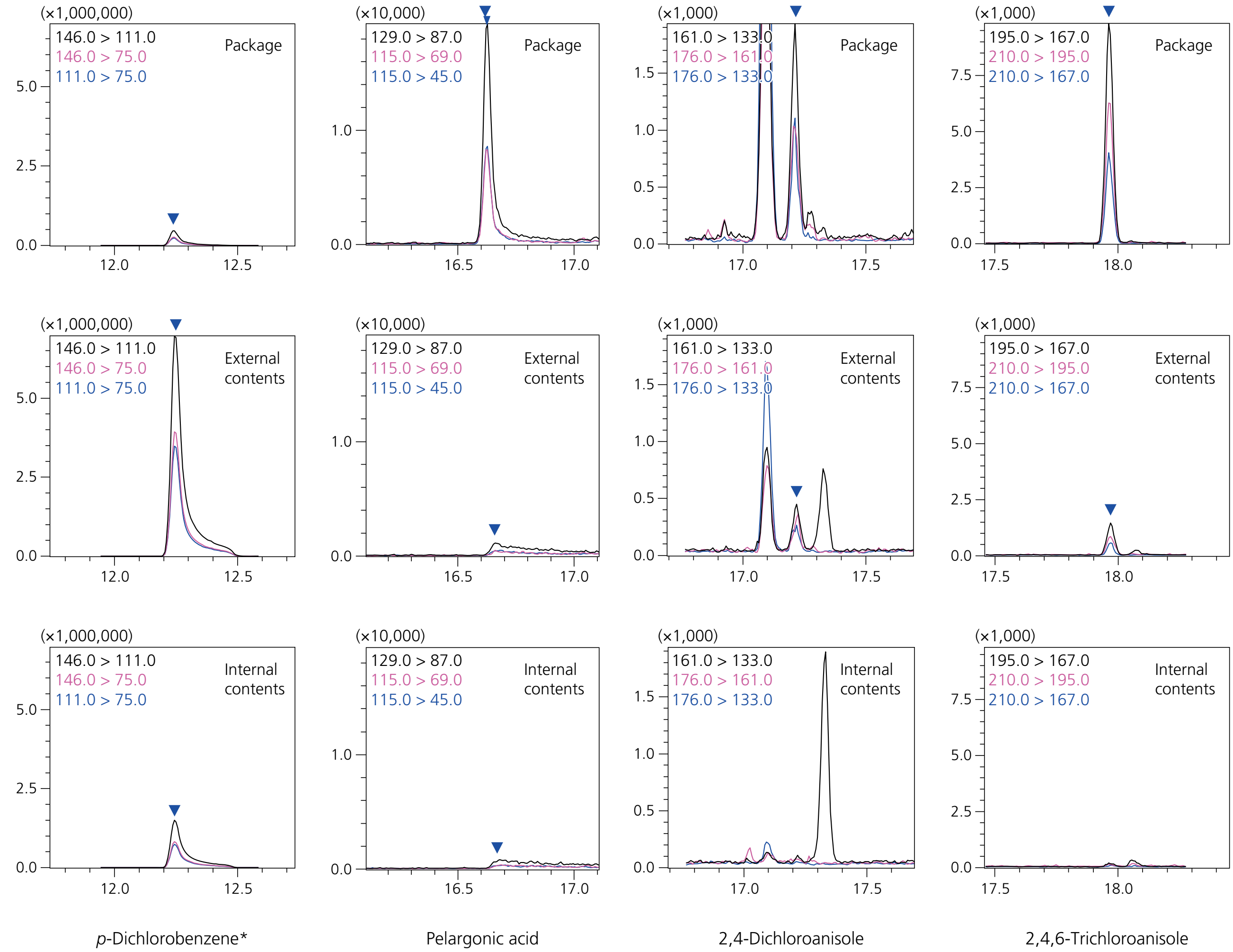


Fig. 2 MRM Chromatograms of Off-Flavor Components in Each Part

* Since the weight of package and external contents are different, peak area values of *p*-dichlorobenzene in the package is less than the external contents.

Table 3 Comparison of Area Values of Off-Flavor Components in Each Part

Compound Name	Concentration (pg/mg)		
	Package	External contents	Internal contents
p-Dichlorobenzene	1097.891	66.558	18.420
Pelargonic acid	599.069	0.851	0.766
2,4-Dichloroanisole	2.121	0.003	N.D.
2,4,6-Trichloroanisole	12.990	0.009	0.001

N.D.: less than detected limit

4. Conclusion

We measured a packaged food product with an off-flavor using the GC/MS Off-Flavor Analyzer. We were able to narrow down off-flavor-causing components to four. We then checked the smell of the four detected components using a sniffer and confirmed the off-flavor of 2,4,6-trichloroanisole. We compared the detected concentration of 2,4,6-trichloroanisole against its off-flavor threshold value registered with the off-flavor analyzer. Since the detected concentration was higher than the off-flavor threshold value, we were able to conclude that it was the cause of the off-flavor.

We divided the packaged food product into multiple parts: the internal and external parts of the contents and the package itself, and measured each separately in order to ascertain the cause of the off-flavor. Since the components were most prevalent in the package, we were able to conclude that the off-flavor transferred from the package to the content of the packaged food.

Identification of off-flavor requires pretreatment for extraction of off-flavor-causing components, information about off-flavors, such as sensory information of components and threshold values, and techniques and expertise to check the actual off-flavor. The GC/MS Off-Flavor Analyzer contains sensory information of primary off-flavor-causing compounds, including their GC/MS information, types of off-flavor, and off-flavor threshold values. Using this system allows even less experienced analysts to easily identify the cause of off-flavor. This system can be used to investigate the cause of off-flavor from foods and packaging.

Models Compatible to GC/MS Off-Flavor Analyzer

GC/MS	: GCMS-QP2020, GCMS-QP2010 Ultra, GCMS-TQ Series
Multifunctional autosampler	: AOC-6000 or AOC-5000 Plus
Sniffer	: Phaser (GL Sciences B.V.), Sniffer-9000 (Brechbuhler)
Multifunctional inlet	: OPTIC-4 (GL Sciences B.V.) Note: The system does not support the OPTIC-4 LINEX function.
OPTIC-4 workstation	: Evolution Workstation Ver. 4.5 or later
GC/MS workstation	: GCMSsolution Ver. 4.31 or later
Compatible columns	: InertCap™ 5MS/Sil (30 m, 0.32 mm I.D., df = 0.5 µm) InertCap™ 17MS (30 m, 0.25 mm I.D., df = 0.25 µm) InertCap™ Pure-WAX (30 m, 0.25 mm I.D., df = 0.25 µm) Note: InertCap is a trademark of GL Sciences Inc.

GC/MS

GCMS-TQ8040

GCMS-QP2020

Pretreatment Unit

Dedicated for liquid injection
AOC-20i/s Auto Injector

For liquid injection, headspace and SPME
AOC-6000 Multifunctional Autosampler

MonoTrap - thermal desorption
OPTIC-4 Multifunctional Inlet

Note: MonoTrap is a trademark of GL Sciences Inc.

Sniffer

Phaser

Sniffer-9000

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