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Application News

GC-MS GCMS-QP™ 2020 NX/HS-20 NX

Analysis of Acetaldehyde and Limonene in Recycled PET Using an HS-GC/MS System

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User Benefits

- By using a headspace sampler (HS), acetaldehyde and limonene in plastic can be measured without dissolving the plastic in solvent.
- Using an HS-GC/MS system, target components that are otherwise difficult to identify due to high contaminant levels can be analyzed qualitatively and quantitatively.
- Using an HS-20 NX unit, low to medium-boiling point components can be analyzed with high sensitivity.

■ Introduction

One environmental problem threatening the Earth is plastic waste. Packaging waste accounts for 20 to 30 percent of household waste by weight and 60 % by volume.

In particular, due to the light weight and durability of polyethylene terephthalate (PET), which is widely used for beverage bottles and various other containers, various methods for reusing PET are being considered. In Japan, 96.7 % of PET bottles are collected and 88.5 % are recycled, on the other hand, only about 40 % are recycled in Europe and about 20 % in the United States.[1)]

For recycling PET, recycling companies in Japan have been implementing their own quality measurements. One example is a method based on using a gas chromatograph mass spectrometer (GC-MS) system.

Gas chromatograph mass spectrometer (GC-MS) systems can be used to identify component peaks for qualitative and quantitative analysis of target substances, even for samples that contain many contaminants that make identification difficult.

It is known that acetaldehyde can easily remain in PET containers that contained water beverages, and limonene that contained citrus-based beverages. This article describes an example of using a GCMS-QP™ 2020 NX system with a HS-20 NX unit (Fig. 1) for qualitative and quantitative analysis of acetaldehyde and limonene in PET bottles.

Fig. 1 GCMS-QP™ 2020 NX + HS-20 NX System

■ Sample Preparation

Six types of samples with different pretreatment states were prepared. Sample types included pellets and freeze-ground pellet powder obtained from a recycler, two types of PET bottles that contained commercially marketed bottled water, and one PET bottle type each that contained lemon tea and orange juice. Each type of sample was sealed inside an HS vial.

The state and quantity of each sample are indicated in Table 1.

Table 1 Information about Each Pretreated Sample

Sample	State	Qty
Pellets*1	Pellets	5 g
Powder*1	Powder	0.5 g
Water 1*2	Cut into pieces with scissors	1 g
Water 2*2	Cut into pieces with scissors	1 g
Lemon Tea*2	Cut into pieces with scissors	1 g
Orange Juice*2	Cut into pieces with scissors	1 g

*1 PET sample provided by a recycling company
(identical samples in pellet and powder state)
*2 PET bottles for commercial beverages
(lightly washed with water and cut with scissors)

■ Analytical Conditions

The conditions for analysis are listed in Table 2.

Table 2 Analytical Conditions

GC-MS Analytical Conditions	
Model:	GCMS-QP2020 NX
Column:	SH-PolarWax (0.25 mm I.D. × 30 m, d.f. = 0.5 µm)
Column Temp.:	40 °C – 10 °C/min – 250 °C Total 21 min
Injection Mode:	Split 1 : 20
Carrier Gas Controller:	Constant linear velocity mode (He)
Linear Velocity:	30 cm/sec
Ion Source Temp.:	200 °C
Interface Temp.:	250 °C
Measurement Mode:	Scan/SIM (Simultaneous Measurements)
Scan Range:	*m/z* 10 to 250
SIM:	*m/z* 43, 29, 42 (Acetaldehyde) *m/z* 136, 68, 93 (D-Limonene)
Event Time:	0.3 sec
HS Analytical Condition	
Oven Temperature:	80 °C
Sample Line Temp.:	150 °C
Transfer Line Temp.:	150 °C
Vial Stirring:	Off
Vial Volume:	20 mL
Vial Heat-Retention Time:	30 min
Vial Pressurization Time:	0.5 min
Vial Pressure:	80.0 kPa (He)
Loading Time:	0.5 min
Needle Flush Time:	5 min
Injection Volume:	1 mL
Load Equilib. Time:	0 .1 min

■ TIC Chromatogram

Fig. 2 shows a TIC chromatogram of the powder sample as a typical sample.

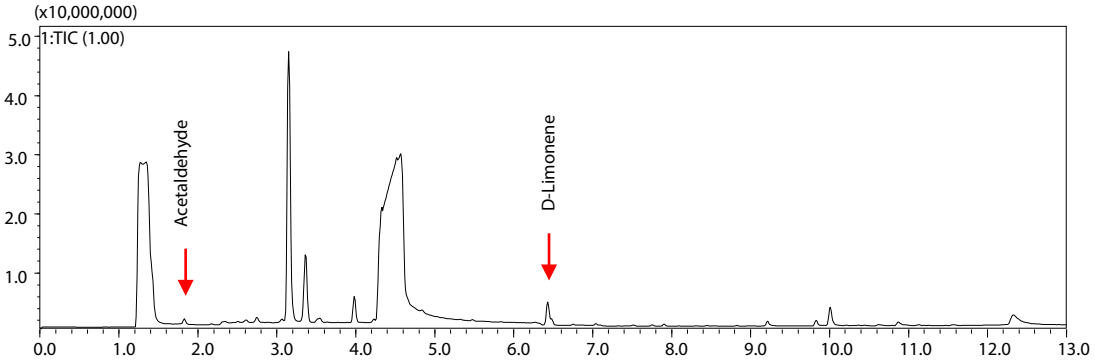

Fig. 2 TIC Chromatogram of Powder Sample

■ Calibration Curves

Calibration curves were prepared by successively diluting samples with acetone solution to seal 2, 20, 100, and 200 µg quantities of acetaldehyde and 20, 100, and 200 ng quantities of limonene in headspace sample vials, and analyzing them based on the analytical conditions indicated in Table 2.
Calibration curves for acetaldehyde and limonene are shown in Figs. 3 and 4 respectively.

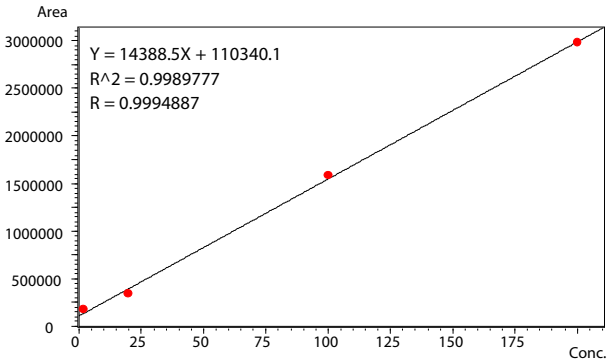

Fig. 3 Acetaldehyde Calibration Curve

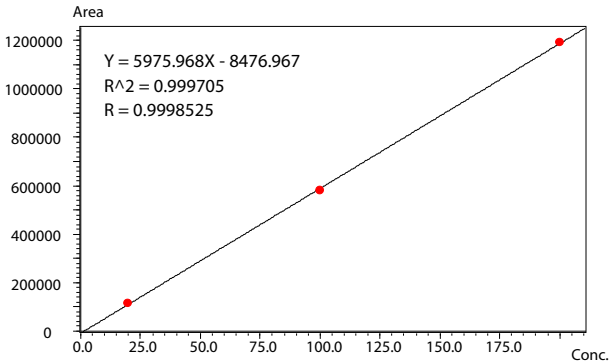

Fig. 4 Limonene Calibration Curve

■ Analysis Results

Table 3 lists the quantities of acetaldehyde and limonene per gram of sample that resulted from analyzing the sample quantities sealed in the respective vials.

Table 3 Quantitative Analysis Results for Each Sample

Sample	Calculated Quantity of Acetaldehyde (µg/g)	Calculated Quantity of Limonene (ng/g)
Pellets	2.3	96
Powder	25	140
Water 1	63	N.D.
Water 2	8.7	N.D.*1
Lemon Tea	23	N.D.*1
Orange Juice	15	N.D.*1

*1 Though limonene was not detected, terpinene, a substance similar to limonene, was detected at an adjacent retention time.

■ Conclusion

Acetaldehyde and limonene in recycled PET material were successfully analyzed qualitatively and quantitatively using an HS-GCMS system. From some of the commercial PET bottle samples, terpinene, a substance similar to limonene, was detected by qualitative analysis at a retention time adjacent to that of limonene.
The results show that the freeze-ground powdered state generally extracted a larger quantity of components into the headspace than the pellet state due to the larger surface area of powder.
Thus, the results indicated that HS-GC/MS analysis offers an effective technique for confirming the quality of recycled PET plastics.

1) The Council for PET Bottle Recycling
https://www.petbottle-rec.gr.jp/english/

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