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

Sonja Wischnewsky, Shimadzu Europa

One environmental problem threatening the Earth is plastic waste. Packaging waste accounts for 20-30% 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 gaschromatograph massspectrometer (GC-MS) system. 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™ 2020NX system with a HS-20 NX unit *(Figure 1)* for qualitative and quantitative analysis of acetaldehyde and limonene in PET bottles.

Figure 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.
**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)*

Sample	State	Quantity
Pellets *1	Pellets	5 g
Powder *1	Powder	0.5 g
Water *2	Cut into pieces with scissors	1 g
Water *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

Analytical conditions

The conditions for GCMS analysis with HS are listed in *Table 2*.

Table 2: Analytical Conditions.

Analytical Conditions	
[HS-20 NX]	
Oven Temperature	80°C
Sample Line Temperature	150°C
Transfer Line Temperature	150°C
Vial Stirring	Off
Vial Volume	20 mL
Vial Heat-Retention Time	30 min
Vial Pressurization Time	0.5 min
Vial Pressure	80 kPa (He)
Loading Time:	0.5 min
Needle Flush Time	5 min
Injection Volume	1 mL
Load Equilib. Time:	0.1 min
[GC]	
Model	GCMS QP 2020 NX
Column	SH-PolarWax (0.25 mm ID x 30 m x d.f. = 0.5 µm)
Column Temp	40°C with 10°C/min to 250°C (21 min)
Injection Mode	Split
Split Ratio	1:20
Carrier Gas Control	Constant linear velocity mode (He)
Linear Velocity	30 cm/sec
[MS]	
Ion Source Temperature	200°C
Interface Temperature	250°C
Acquisition Mode	SCAN/SIM (Simultaneus)
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

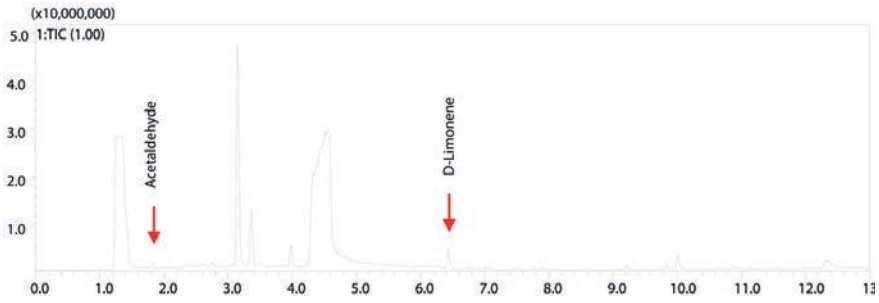

Figure 2. TIC Chromatogram of Powder Sample

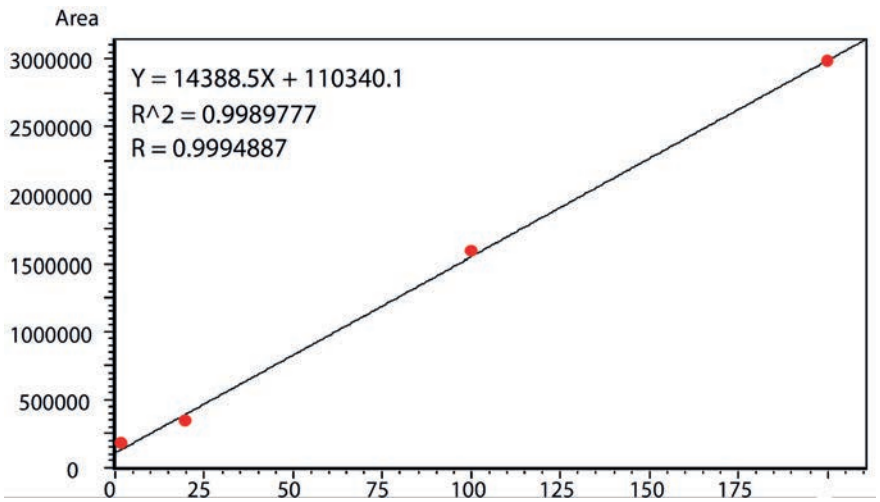

Figure 3. Acetaldehyde Calibration Curve

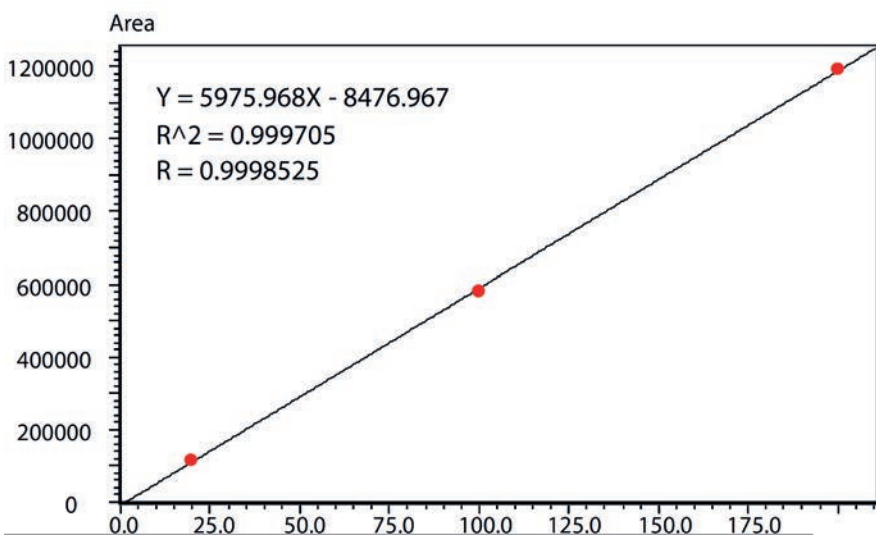

Figure 4. Limonene Calibration Curve

Table 3. Quantitative Analysis Results for Each Sample.

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

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

Sample Preparation

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 analysing them based on the analytical conditions indicated in *Table 2*. Calibration curves for acetaldehyde and limonene are shown in *Figures 3 and 4* respectively.

Analysis results

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

Conclusion

Acetaldehyde and limonene in recycled PET material were successfully analysed 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-GCMS analysis offers an effective technique for confirming the quality of recycled PET plastics.

References

1. The Council for PET Bottle Recycling

https://www.petbottle-rec.gr.jp/english/