Application Note

Materials

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Analysis of Aldehydes, Benzene, and Limonene in Recycled Polyethylene Terephthalate

Using an Agilent 7697 headspace sampler and 8890/5977C GC/MSD

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Abstract

This application note describes a method for the quantitation of three common contaminants (acetaldehyde, benzene, and d-limonene) in recycled polyethylene terephthalate (PET) using an Agilent 8890/5977C GC/MSD with an Agilent 7697 headspace sampler. The method demonstrated excellent sensitivity, with detection limits of 0.034 ng/µL for acetaldehyde, 0.002 ng/µL for benzene, and 0.006 ng/µL for d-limonene. The limits of quantitation for the three compounds were 0.112, 0.008, and 0.022 ng/µL, respectively. The three compounds were successfully quantified in three PET samples with acetaldehyde from 474 to 975 µg/kg, benzene from 5.5 to 18.6 µg/kg, and d-limonene from 0.42 to 3.21 µg/kg.

Introduction

PET is commonly used in the food and beverage industry, as it is easy to recycle. The quantity of food containers and beverage bottles made from recycled PET materials is on the rise.

Contaminants in recycled PET, including acetaldehyde, benzene, and limonene, can migrate from the packaging into the contents, potentially affecting the safety and quality of the products stored inside.[1] Monitoring these contaminants is crucial for ensuring the quality of recycled PET products, as they can affect the physical, chemical, and sensory properties of recycled PET, potentially leading to product defects or health concerns.

Acetaldehyde is a byproduct resulting from side reactions during the production of PET. If acetaldehyde migrates or leaches into bottled water, it might influence the organoleptic properties of the water. Benzene is a degradation product of polymer impurities in recycled PET. Benzene is a known carcinogen, and its presence in PET materials is a significant health concern. Detecting benzene contamination is essential for preventing exposure to this hazardous substance.

Limonene is a flavoring compound used in soft drinks that has the potential to migrate from the beverage to the bottle wall. As a result, recycled PET soft drink bottles normally contain detectable amounts of limonene. It is crucial to deodorize the pellets produced from recycling, removing any contaminants and flavor compounds, especially when they are used in the production of food packaging.

The U.S. Food and Drug Administration (FDA) has set a limit of 220 µg/kg as the maximum permitted contaminant concentration in recycled PET for use in contact with food.[2]

This application note demonstrates the use of a 7697 headspace sampler and 8890/5977C GC/MSD for the analysis of acetaldehyde, benzene, and d-limonene in recycled PET materials. With the developed method, acetaldehyde, benzene, and d-limonene in three recycled PET samples were successfully quantified.

Experimental

Reagents and samples

- 1 mL of 10,000 µg/mL acetaldehyde and 7,500 µg/mL d-limonene in toluene was purchased from Restek (RT-CS-28342-1)
- 1 mL of 3,500 µg/mL benzene in toluene was obtained from Restek (RT-CS-28342-2)
- Three cryogenic-ground samples (samples 1, 2, and 3) were received from a local customer

Standards preparation

A 600 ng/µL stock solution of acetaldehyde, benzene, and d-limonene was prepared by aliquoting 60 µL of standard 1,140 µL of standard 2, and 800 µL of acetonitrile.

Subsequent working solutions were prepared by serial dilution according to Table 1.

A 5 µL amount of each calibration standard was transferred into a 20 mL headspace vial for analysis.

Table 1. Working solutions prepared by serial dilution.

Calibration Standard Concentration (ng/µL)			Stock Solution Concentration (ng/µL)	Stock Solution Volume (µL)	Acetonitrile Volume (µL)
Acetaldehyde	Benzene	Limonene			
300	245	225	600	500	500
150	123	113	600	100	300
30.0	24.5	22.5	300	100	900
15.0	12.3	11.3	300	50	950
3.00	2.45	2.25	300	10	990
1.50	1.23	1.13	15	100	900
0.300	0.245	0.225	15	20	980
	0.123	0.113	15	10	990
	0.0245	0.0225	0.3	100	900

Sample preparation

The three ground samples were weighed, placed in a headspace vial, and analyzed directly using the same acquisition method as for the calibration standards.

Agilent 7697 headspace sampler and GC/MSD parameters

The analysis parameters of the 7697 headspace sampler are shown in Table 2.

Results and discussion

Compound identification and retention time confirmation

The 600 ng/µL stock solution was analyzed in full scan data acquisition mode and the total ion chromatogram (TIC) is shown in Figure 1.

The data file for the 600 ng/µL sample was processed using Agilent MassHunter Unknowns Analysis software. Automatic deconvolution of the data was performed using Unknowns Analysis to identify the components present in the sample. From the resulting list of components, the three target compounds were identified through library matching against the NIST23 spectral library, achieving match scores above 95. The retention times of the three compounds were determined to be 5.296, 8.416, and 11.119 minutes, respectively (Figures 2 to 5).

Table 2. Agilent 7697 headspace autosampler and GC/MSD parameters for PET analysis.

Headspace	
Incubation Temperature	120 °C
Loop Temperature	120 °C
Transfer Line Temperature	130 °C
Incubation Time	30 min
Gas Chromatograph	
Model	Agilent 8890 GC
GC Column	Agilent DB-VRX, 60 m × 0.25 mm, 1.4 µm (p/n 122-1564)
Column Pneumatics	Constant flow
Carrier Gas	Helium
Injection Mode	Split (10:1)
Inlet Temperature	240 °C
Injector Liner	Agilent Ultra Inert liner (p/n 5190-6168)
Flow Rate	1.0 mL/min
Oven Temperature	40 °C hold for 3 min
	40 °C/min to 240 °C, hold 5.0 min
Equilibration Time	3 min
Mass Spectrometer	
Model	Agilent 5977C GC/MSD
Ionization Mode	EI, 70 eV
Acquisition Mode	SIM
SIM Ions	Acetaldehyde (42, 44), benzene (78, 77), d-limonene (136, 68)
GC Transfer Line Temperature	250 °C
Ion Source Temperature	230 °C
Quad Temperature	150 °C

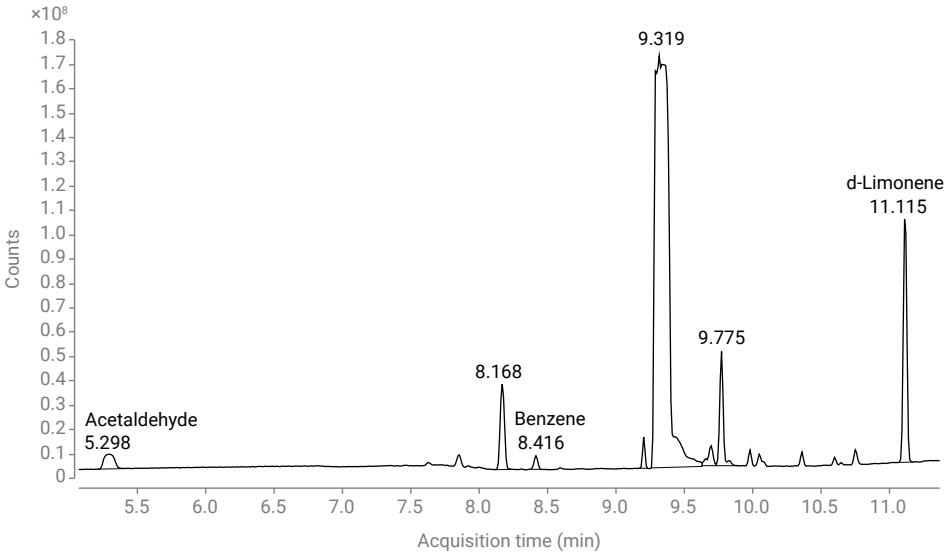

Figure 1. Total ion chromatogram of 600 ng/µL acetaldehyde, benzene, and d-limonene.

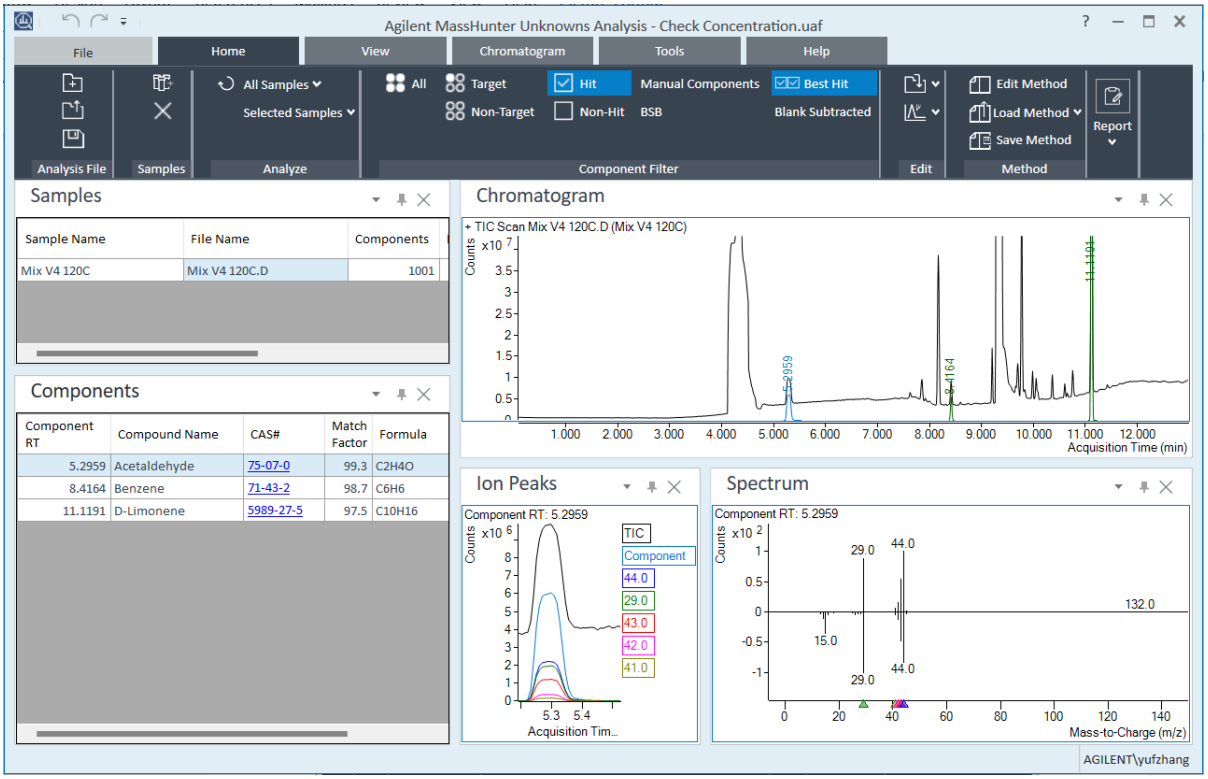

Figure 2. Acetaldehyde, identified with a retention time of 5.296 minutes.

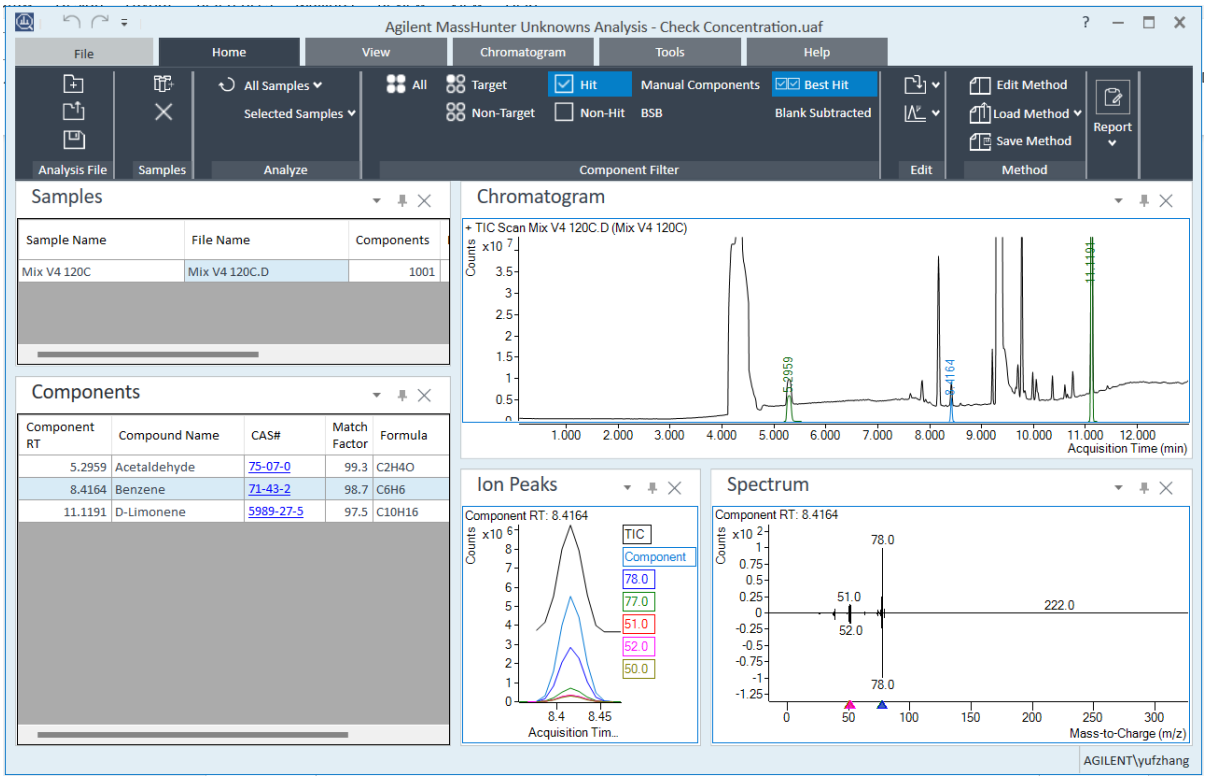

Figure 3. Benzene, identified with a retention time of 8.416 minutes.

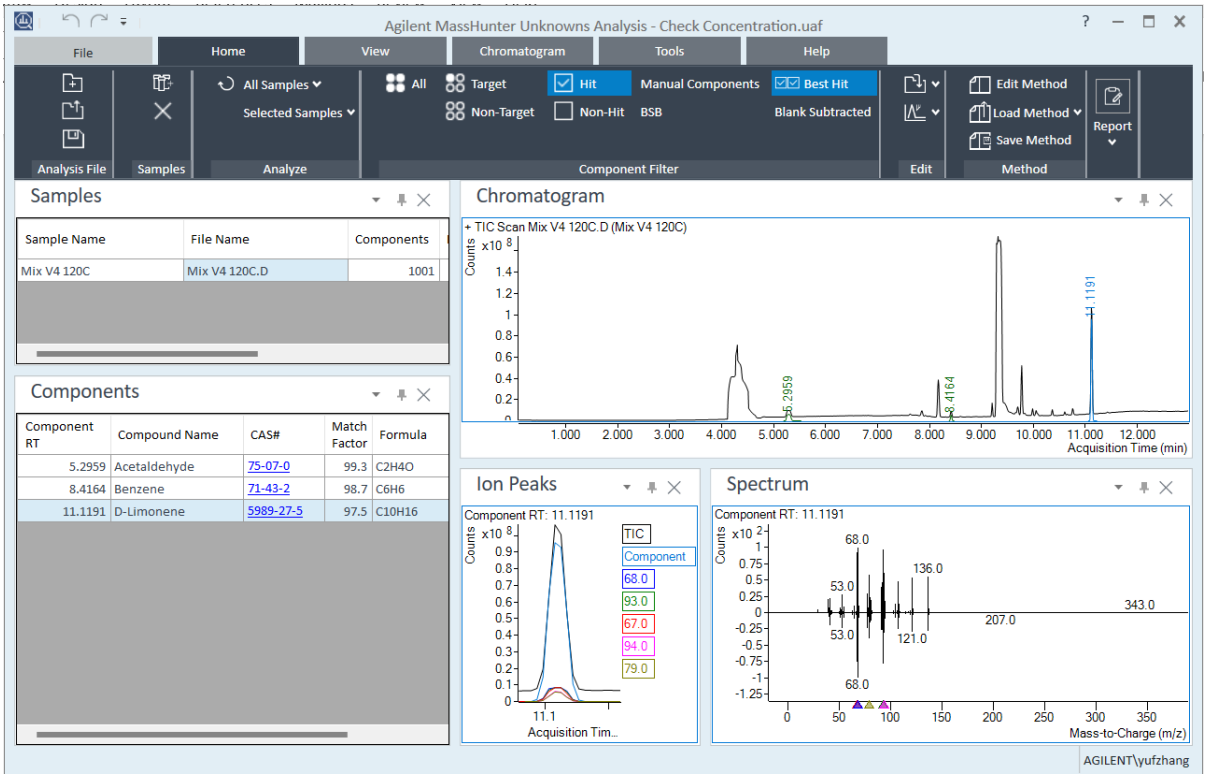

Figure 4. d-limonene, identified with a retention time of 11.119 minutes.

Calibration curve

Based on the response of the calibration standard solutions, calibration curves were plotted for the three compounds. The calibration ranges are set up to cover a wide concentration range of the three compounds in the recycled PET samples. The results are shown in Table 3, and in Figures 6 to 8.

Table 3. The calibration range and R^2 for the three compounds.

No.	Compound Name	Calibration Range (ng/µL)	R^2
1	Acetaldehyde	0.3 to 600	0.999
2	Benzene	0.0245 to 24.5	0.999
3	d-Limonene	0.0225 to 112.5	1.000

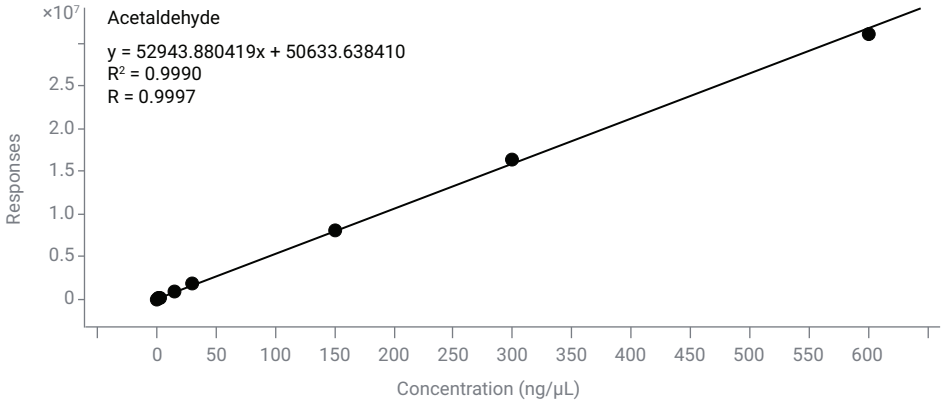

Figure 6. Calibration curve for acetaldehyde, 0.3 to 600 ng/µL.

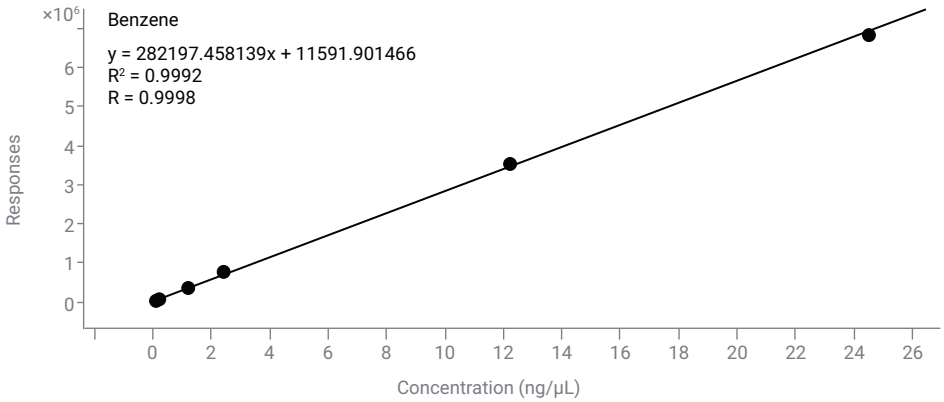

Figure 7. Calibration curve for benzene, 0.0245 to 24.5 ng/µL.

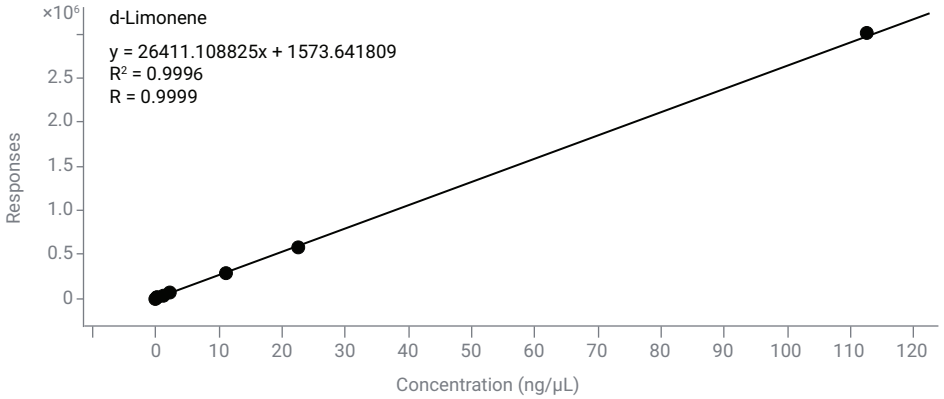

Figure 8. Calibration curve for phenylacetaldehyde, 0.0225 to 112.5 ng/µL.

Quantification results of PET samples

Based on the calibration curve setup, quantification was performed for the three compounds in the three recycled PET samples. The quantification results are summarized in Tables 4 to 6 and the chromatogram is shown in Figure 9. Acetaldehyde was quantified to be in the range of 474 to 975 µg/kg. Benzene was in the range of 5.5 to 18.6 µg/kg, and d-limonene was quantified to be in the range of 0.42 to 3.21 µg/kg in the three samples.

The concentration calculation was based on the following:

Amount in 5 µL (ng) = calculated concentration (ng/µL) × 5 µL

Final concentration (µg/kg) = amount in 5 µL/sample weight

Table 4. Quantification results of acetaldehyde in the three recycled PET samples.

Sample	Sample Weight (g)	Acetaldehyde		
		Calculated Concentration (ng/µL)	Amount in 5 µL (ng)	Concentration in Sample (µg/kg)
S1	1.80	351	1,753	975
S2	1.62	240	1,201	740
S3	1.59	151	755	474

Table 5. Quantification results of benzene in the three recycled PET samples.

Sample	Sample Weight (g)	Benzene		
		Calculated Concentration (ng/µL)	Amount in 5 µL (ng)	Concentration in Sample (µg/kg)
S1	1.80	1.97	9.84	5.48
S2	1.62	6.03	30.1	18.57
S3	1.59	3.73	18.7	11.73

Table 6. Quantification results of d-limonene in the three recycled PET samples.

Sample	Sample Weight (g)	d-Limonene		
		Calculated Concentration (ng/µL)	Amount in 5 µL (ng)	Concentration in Sample (µg/kg)
S1	1.80	0.150	0.750	0.42
S2	1.62	0.182	0.910	0.56
S3	1.59	1.02	5.11	3.21

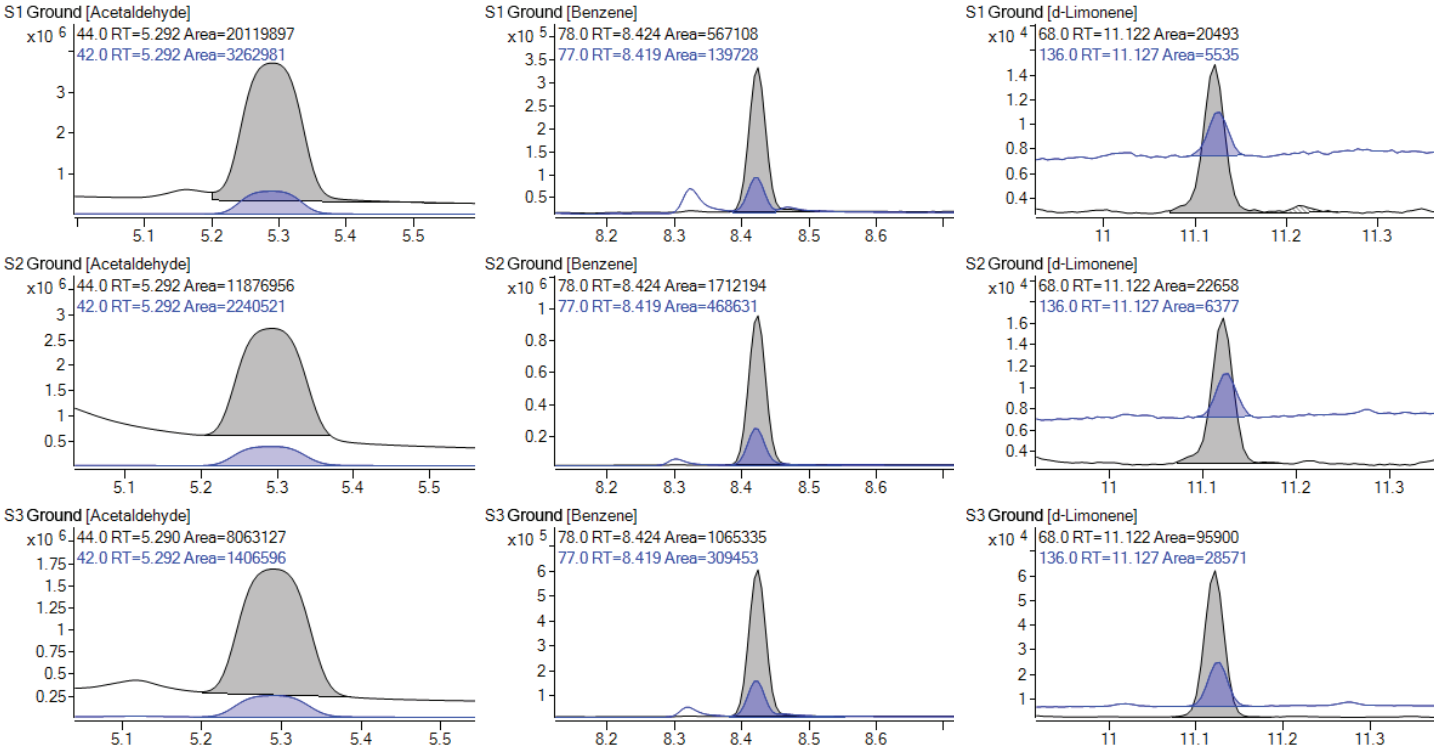

Figure 9. Extracted ion chromatogram of the three compounds in the three samples.

Determination of detection limits

Based on the response of the lowest concentration calibration standard of each compound, the signal-to-noise ratio (S/N) was calculated. The limit of quantification (LOQ) was determined at a S/N of 10, and the limit of detection (LOD) was determined at a S/N of 3. A summary of the LOQ and LOD results is presented in Table 7.

Table 7. LOQ and LOD of the three compounds.

Compound	Concentration (ng/µL)	S/N	LOD (ng/µL)	LOQ (ng/µL)
Acetaldehyde	0.300	26.79	0.034	0.112
Benzene	0.0245	30.68	0.002	0.008
d-Limonene	0.0225	10.39	0.006	0.022

Conclusion

This application note describes the quantitative analysis of acetaldehyde, benzene, and d-limonene using an Agilent 8890/5977C GC/MSD with an Agilent 7697 headspace sampler. This method offers the advantages of full automation, rapid analysis, and minimum sample preparation. With this automated workflow solution, excellent sensitivity was demonstrated with an LOD of 0.034 ng/µL for acetaldehyde, 0.002 ng/µL for benzene, and 0.006 ng/µL for d-limonene. Good linearity was demonstrated, with R^2 above 0.999 for all three compounds over wide concentration ranges. Three recycled PET samples were analyzed, with a detection of acetaldehyde from 474 to 975 µg/kg, benzene from 5.5 to 18.6 µg/kg, and d-limonene from 0.42 to 3.21 µg/kg.

References

1. Benyathiar, P.; Kumar, P.; Carpenter, G.; Brace, J.; Mishra, D. K. Polyethylene Terephthalate (PET) Bottle-to-Bottle Recycling for the Beverage Industry: a Review. *Polymers* **2022**, *14(12)*, 2366.
2. U.S. FDA. Use of Recycled Plastics in Food Packaging (Chemistry Considerations): Guidance for industry. U.S. Department of Health and Human Services Food and Drug Administration Center for Food Safety and Applied Nutrition. **2021**. https://www.fda.gov/media/150792/download.

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