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HS-20 NX (Loop Model) Headspace Autosampler
GCMS-QP™2050 Single Quadrupole Gas Chromatograph Mass Spectrometer

Application News

Acetaldehyde, Benzene, and Limonene in Recycled PET (rPET) Bottles by Headspace-GCMS

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User Benefits

- HS-20 NX headspace autosampler with short and inert transfer line allows for the measurement of acetaldehyde, benzene, and limonene in rPET without the need for complex solvent extraction.
- With an industry-leading max scan speed of 30,000 u/sec and Fast Automated Scan/SIM Type (FASST) functionality in GCMS-QP2050, it enables both qualitative and quantitative analysis of target contaminants in rPET.

■ Introduction

Polyethylene terephthalate (PET) is widely used in various applications, particularly in the production of beverage bottles, due to its advantageous properties such as high strength, transparency, and recyclability. With growing environmental concerns related to plastic waste, recycled PET (rPET) has received increasing attention, especially in the context of food-contact materials (FCMs). Ensuring the chemical safety and overall quality of rPET has gained a significant attention for both manufacturers and regulatory authorities. One of the critical aspects of rPET safety evaluation is the presence of volatile organic compounds (VOCs) that may migrate or leach into food or beverages, thereby affecting both consumer safety and product sensory attributes.

Among the VOCs of concern, acetaldehyde, benzene, and limonene are commonly monitored by manufacturers. Acetaldehyde is a byproduct of the thermal degradation of PET that can occur during the production process. Benzene, a carcinogenic compound, is sometimes found in rPET due to contact with polyvinyl chloride (PVC) during the recycling process of PET bottles[1]. Limonene, a flavor compound, may also be present in rPET, resulting from post-consumer contamination, such as using soft drink PET bottles as feedstock. While limonene is not toxic, its presence in rPET could affect the flavor profile of the food or drink packaged in the bottles. These compounds are of particular concern as non-intentionally added substances (NIAS) in recycled materials[2].

The current application news utilizes headspace technique with single quadrupole GCMS to accurately identify and quantify the concentrations of acetaldehyde, benzene, and D-limonene in rPET samples.

Fig. 1 GCMS-QP2050 (with Nexis GC) and HS-20 NX Headspace Autosampler (Loop Model)

■ Experimental

Instrumental and Analytical conditions

In this experiment, a headspace autosampler system, HS-20 NX (Loop Model) (Shimadzu Corporation, Japan) and a single quadrupole GCMS system, GCMS-QP2050 (Shimadzu Corporation, Japan) were used (Fig. 1). The details of the system and analytical conditions for the static headspace coupled with GCMS are shown in Table 1. Data acquisition and data processing were performed using LabSolutions™ GCMS software.

Table 1 Analysis Conditions

Instrumentation	
GCMS system	: GCMS-QP2050 (with Nexis™ GC)
TMP Capacity	: 255 L/sec
Auto sampler	: HS-20 NX (Loop Model)
Column	: SH-PolarWax (30 m x 0.32 mm I.D. x 1.0 µm)*1
Headspace Parameters	
HS Oven Temperature	: 80 ˚C (30 min)
Pressurizing Gas Pressure	: 80.0 kPa (nitrogen)
Gas Chromatograph Parameters	
Injection Mode	: Split (Split Ratio = 20)
Carrier Gas	: Helium
Flow Control Mode	: Linear velocity (62.3 cm/s)
Column Temperature Program	: 35 ˚C (2 min) - 10 ˚C/min - 230 ˚C (1 min) Total 22.50 min
Mass Spectrometer Parameters	
Ion Source Temperature	: 200 ˚C
Interface Temperature	: 230 ˚C
Acquisition Mode	: FASST (Scan/SIM Simultaneous Measurements)

*1 P/N：227-36252-01

Standards and Sample Preparation

Acetaldehyde was obtained from Sigma-Aldrich, while D-limonene was sourced from TCI Co., Ltd. Benzene and acetone were purchased from Kanto Chemical Co., Inc.

Calibration standard stock solutions were prepared by mixing the three target compounds in acetone, followed by serial dilution to generate seven calibration levels (Table 2). Subsequently, 2µL of each calibration stock solution was added to individual 20-mL headspace vials. Each was sealed with crimp cap immediately after adding the standard. Assuming 1.0 g of matrix was present in each vial, the final concentration of each compound was calculated and was expressed in ng/g, as shown in Table 2.

Table 2 Stock and Calibration Concentrations of Acetaldehyde, Benzene, and D-Limonene

Calibration Level	Stock Solution in ppm (µg/mL)			Calibration Range in ppb (ng/g)		
	AA*	Benzene	D-Limonene	AA*	Benzene	D-Limonene
Cal. 1	62.50	6.25	1.25	125.0	12.5	2.5
Cal. 2	125.00	12.50	2.50	250.0	25.0	5.0
Cal. 3	250.00	25.00	5.00	500.0	50.0	10.0
Cal. 4	500.00	50.00	10.00	1000.0	100.0	20.0
Cal. 5	1000.00	100.00	20.00	2000.0	200.0	40.0
Cal. 6	2000.00	200.00	40.00	4000.0	400.0	80.0
Cal. 7	4000.00	400.00	80.00	8000.0	800.0	160.0

*AA = acetaldehyde

Six different brands of rPET bottle samples were obtained from the market. Each sample was cut into smaller pieces (~5-8 mm), then 1.00 g of each sample was weighed into a 20-mL headspace vial and sealed with a crimp cap.

For recovery study, 1.00 g of one rPET sample was weighed into a 20-mL headspace vial, followed by the addition of 2uL of Calibration Level 3 (Cal. 3) stock solution. The vial was then sealed with a crimp cap immediately.

■ Result

Sensitivity and Repeatability

Calibration Level 1 (Cal. 1) was analyzed using the proposed system, and the SIM chromatogram for each compound is presented in Fig. 2. The signal-to-noise ratios (S/N) for all target compounds at Cal. 1 are presented in Table 3. The Limit of Quantitation (LOQ) was determined based on a S/N of 10, while the Limit of Detection (LOD) was calculated at a S/N of 3.3. The calculated LOD (Calc. LOD) and calculated LOQ (Calc. LOQ) are summarized in Table 4.

In terms of repeatability, the %RSD was assessed based on the Cal. 3 standard with six repeat injections. The %RSD for all compounds were less than 3.5% (Table 5), demonstrating the excellent repeatability of the method and the stability of the proposed system.

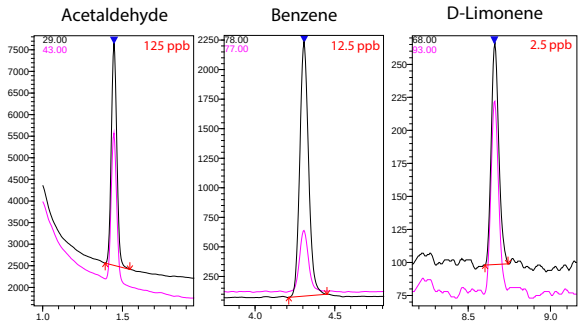

Fig. 2 SIM Mass Chromatograms of Acetaldehyde, Benzene, and D-Limonene at Cal. 1

Table 3 S/N of all compounds at Cal. 1 and calculated LOQ and LOD

	Acetaldehyde	Benzene	D-Limonene
Cal. 1 (ppb)	125	12.5	2.5
S/N (*n*=2)	16.93	233.57	17.62

Table 4 Calculated LOQ and LOD for all compounds

	Acetaldehyde	Benzene	D-Limonene
Calc. LOQ* (ppb)	73.83	0.54	1.42
Calc. LOD* (ppb)	24.37	0.18	0.46

*Calculated based on Cal 1 S/N

Table 5 Area repeatability %RSD of all compounds at Cal. 3

Injection	Area		
	AA*	Benzene	D-Limonene
1	53,119	35,636	2,044
2	53,843	36,716	2,090
3	50,940	34,174	2,009
4	49,953	33,875	2,001
5	49,743	34,499	2,045
6	50,197	34,409	1,978
%RSD	3.42	3.09	1.97

*AA = acetaldehyde

Calibration Curves

Fig. 3 presents the calibration curves constructed based on seven calibration level as detailed in Table 2. All target compounds exhibited excellent linearity, with correlation coefficient (R^2) values greater than 0.999.

Fast Automated Scan/SIM Type (FASST)

In FASST mode, data acquisition was performed by scan and SIM in a single run, allowing quantitation and confirmation simultaneously. This helps user to check for false positives from unknown contaminants. As shown in Fig. 4, this enables both mass spectral matching via NIST library and quantification using SIM mass chromatograms in one data.

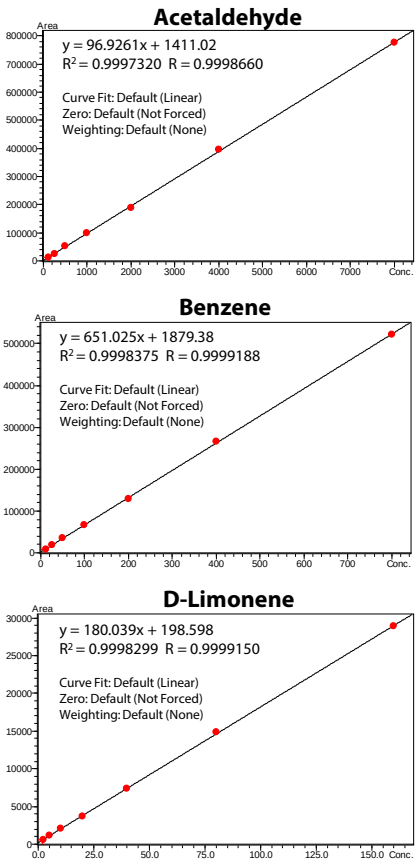

Fig. 3 Seven-Point Calibration Curves of Acetaldehyde, Benzene, and D-Limonene

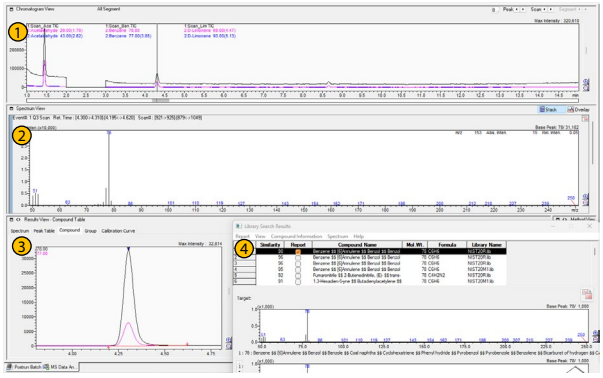

Fig. 4 A Single Data Contains Scan and SIM Results: (1) Chromatogram view, (2) Scan Mass Spectrum, (3) SIM chromatograms, and (4) Library Search Results

Analysis Results

Six different brands of rPET bottle samples were analyzed using the proposed system. Table 6 summarizes the concentrations of acetaldehyde, benzene, and D-limonene per gram of rPET sample. Acetaldehyde was detected in all samples at low levels, less than 120 ng/g, which is well below the EU SCF specific migration limit (SML) of 6 mg/kg (equivalent to 6000 ng/g)[3]. Benzene was not detected in any of the samples. D-limonene was detected in some samples but only at very low concentrations, typically below 1 ng/g.

Table 6 Quantitative Analysis Results for Each Analyzed rPET Sample

No.	Sample	Acetaldehyde (ng/g)	Benzene (ng/g)	D-Limonene (ng/g)
1	rPET Bottle Brand A	26.8*	N.D.	0.2*
2	rPET Bottle Brand B	35.5*	N.D.	0.6*
3	rPET Bottle Brand C	76.8*	N.D.	0.1*
4	rPET Bottle Brand D	80.9*	N.D.	0.3*
5	rPET Bottle Brand E	167.1	N.D.	N.D.
6	rPET Bottle Brand F	115.7*	N.D.	N.D.

*Detected value is lower than Cal 1
N.D. = Not Detected

Table 7 Recovery Results of Target Compounds in rPET Bottle Samples Spiked with Cal 3

Sample		Concentration (ng/g)			% Recovery		
		Acetaldehyde	Benzene	D-Limonene	Acetaldehyde	Benzene	D-Limonene
rPET Bottle Brand A	Non-spiked	26.8*	N.D.**	0.2*			
	Spiked with Cal 3	516.5	55.8	11.9	98	112	117
rPET Bottle Brand B	Non-spiked	35.5*	N.D.**	0.6*			
	Spiked with Cal 3	519.8	53.0	11.6	97	106	110

*Detected value is lower than Cal 1
**N.D. = Not Detected

Recovery

For the recovery study, two rPET samples (Brand A and Brand B) were spiked with Cal. 3 standard (500 ng/g of acetaldehyde, 50 ng/g of benzene, and 10 ng/g D-limonene). %Recovery for the spiked samples are calculated using the formula below:

$$\%\ Recovery = \frac{Conc.\ of\ Spiked - Conc.\ of\ Non\text{-}spiked}{Actual\ Spiked\ Conc.} \times 100$$

As shown in Table 7, the recoveries for all target compounds in both spiked samples fell within 80% to 120%. These results confirm that the proposed method using HS-20 NX headspace autosampler coupled with the GCMS-QP2050 is suitable for the accurate analysis of acetaldehyde, benzene and D-limonene in rPET samples.

■ Conclusion

The analysis of acetaldehyde, benzene, and D-limonene in rPET using the HS-20 NX headspace autosampler coupled with the GCMS-QP2050 system demonstrated excellent analytical performance. The method achieved good recovery rates (80%–120%) and allowed for the acquisition of both Scan and SIM data in a single run. Good repeatability was observed, with %RSD values below 3.5%, with excellent linearity of R^2 exceeding 0.999. The approach offers practical advantages for manufacturers and regulatory bodies in ensuring the safety and quality of rPET used in food packaging applications.

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■ References

1) Thoden van Velzen, E. U., Brouwer, M. T., Stärker, C., & Welle, F. (2020). Effect of recycled content and rPET quality on the properties of PET bottles, part II: Migration. Packaging Technology and Science, 33(9), 359-371.
2) Coniglio, M. A., Fioriglio, C., & Laganà, P. (2019). Non-Intentionally Added Substances in PET-Bottled Mineral Water. SPRINGERBRIEFS IN MOLECULAR SCIENCE, 1-66.
3) European Commission, 2011. Commission regulation (EU) No 10/2011.

<Related Applications>

1. Analysis of Acetaldehyde and Limonene in Recycled PET Using an HS-GC/MS (GCMS-QP™ 2020 NX/HS-20 NX), Application News No. 01-00311-EN

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