Application note | AN004458

Industrial

Streamlined static headspace GC–MS approach for detection of impurities in recycled PET

Authors

Giulia Riccardino[1], Daniela Cavagnino[1], and Daniel Kutscher[2]

[1]Thermo Fisher Scientific, Milan, Italy

[2]Thermo Fisher Scientific, Bremen, UK

Keywords

Contaminants, acetaldehyde, benzene, limonene, recycled PET, gas chromatography, static headspace, single quadrupole mass spectrometry, TRACE 1610 GC, TriPlus 500 HS, ISQ 7610 GC–MS.

Goal

The aim of this application note is to demonstrate the qualitative and quantitative performance of the Thermo Scientific™ TriPlus™ 500 Gas Chromatography Headspace (HS) autosampler for the determination of common contaminants such as acetaldehyde, benzene, and d-limonene in recycled polyethylene terephthalate (rPET).

Introduction

Polyethylene terephthalate (PET) is a widely used thermoplastic polymer valued for its strength, low weight, durability, and adaptability. Owing to these properties, it is extensively applied in packaging, textile fibers, and electronic components. PET is particularly suitable for recycling because it can be melted and reshaped multiple times with minimal loss of performance, and it is easily recognizable by the recycling code “1” (♺). The recycling of PET involves several stages, including collection, sorting, transport, processing, washing, pelletizing, and remanufacturing into new products [1]. However, during these steps, contaminants such as plasticizers, residual monomers, and degradation byproducts may be introduced. The presence of such substances can pose potential risks to both environmental and human health, making the identification and characterization of contaminants in recycled PET essential for evaluating material quality and safety. Among the non-intentionally added substances (NIAS), benzene, acetaldehyde, and limonene are of particular relevance. Benzene is a recognized carcinogen and represents a serious health concern if present in PET. It may form as a degradation product of PET, with the reaction catalyzed by acidic compounds released at high temperatures by polymer impurities such as polyvinyl

chloride (PVC). Poor temperature control or overheating can increase benzene formation as a degradation byproduct. Acetaldehyde, another degradation product of PET generated during bottle manufacturing, can alter the sensory properties of bottled beverages. Limonene, a flavor compound commonly present in soft drinks, may be absorbed into recycled PET and subsequently migrate into packaged beverages, potentially affecting product quality.

Gas chromatography coupled to headspace sampling is a fast and simple technique that enables the extraction of volatile and semivolatile compounds from solid and liquid samples without the need for time-consuming sample preparation.

In this study, headspace sampling coupled to single quadrupole mass spectrometry was used to assess the overall quantitative performance for analysis of acetaldehyde, benzene, and limonene in recycled PET packaging.

The capability of the Thermo Scientific™ ISQ™ 7610 single quadrupole GC–MS of combining the simultaneous acquisition of both single ion monitoring (SIM) and full scan (FS) allowed for sensitive targeted analysis as well as screening of unknown contaminants possibly present in recycled PET bottles.

Experimental

In all experiments, a TriPlus 500 HS autosampler was coupled to a Thermo Scientific™ TRACE™ 1610 Gas Chromatograph (GC), configured with a Thermo Scientific™ iConnect™ Split/splitless Injector Module (iConnect-SSL), and connected to an ISQ 7610 single quadrupole mass spectrometer.

The separation of the target analytes was achieved using a Thermo Scientific™ Trace GOLD™ TG-624 SILMS capillary column, 60 m x 0.25 mm x 1.4 µm (Part No. 26059-3330). This column provides a low to mid polarity phase with high thermal stability (maximum operating temperatures up to 320 °C) and high inertness, enabling Gaussian peak shapes for analysis of volatile organics. The TriPlus 500 HS autosampler is connected directly to the analytical column, removing the use of a long external transfer line. In this configuration, the SSL injector module is used only for the pneumatic control of the carrier gas and split flow. The operating conditions applied in this study are detailed in Table 1.

Table 1. HS GC–MS operating conditions for determination of acetaldehyde, benzene, and limonene in rPET.

TriPlus 500 HS autosampler parameters	
Vial incubation temperature (°C)	120
Vial incubation time (min)	30
Vial pressurization mode	Pressure
Vial pressure (kPa)	55
Vial pressure equilibration time (min)	1
Loop/sample path temperature (°C)	120
Loop pressure (kPa)	34
Loop equilibration time (min)	1
Injection mode	Standard
Injection time (min)	1
Needle purge flow level	3
Enable standby purge	Enabled

TRACE 1610 GC parameters	
iC-SSL	
Inlet module	SSL
Injection mode	Split
Injection temperature (°C)	100
Split ratio	15:1
Purge flow (mL/min)	5
Carrier gas, flow (mL/min)	He, 1.1
Oven temperature program	
Temperature (°C)	35
Hold time (min)	3
Rate (ºC/min)	40
Temperature 2 (°C)	270
Hold time (min)	5
GC run time (min)	13.875
Oven equilibration time (min)	0.20
Analytical column	
TraceGOLD TG-624SILMS	60 m x 0.25 mm x 1.4 µm (Part No. 26059-3330)

ISQ 7610 mass spectrometer parameters		
Transfer line temperature (°C)	270	
Ion source type	Extractabrite	
Ion source temperature (°C)	280	
Ionization type	EI	
Emission current (µA)	50	
Tuning parameters	SMART tune	
Aquisition mode	FS	SIM
Mass range (m/z)	10-250	Acetaldehyde (RT = 5.33): 15, 19, 43, 44 Benzene (RT = 8.38): 51, 77, 78 d-Limonene (RT = 10.80): 68, 96, 136

Data acquisition, processing, and reporting

The Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) was used for data acquisition, processing, and reporting. Integrated instrument control ensures full automation from instrument setup to raw data processing, with reporting and storage in compliance with modern regulatory guidelines including FDA 21 CFR Part 11 and European Commission (EU) Annex 11.

The Chromeleon CDS Report Designer allows users to create and customize reports using a flexible spreadsheet-based interface enabling efficient data analysis and allowing users to flag and check compliance of the results with the laboratory method validation criteria.

Standard and sample preparation

Calibration curve preparation

Benzene (Sigma Aldrich, puriss., ≥ 99.7%, Part No. 32212-1L), acetaldehyde (Sigma Aldrich , PESTANALTM, Part No. 506788), and d-limonene (Sigma Aldrich, Analytical Standard, Part No. 62118-1ML) were diluted in acetonitrile (Fisher Scientific™, ≥ 99.9%, Part No. 15674740) to prepare a stock solution at a concentration of 3,000 ng/µL. The stock solution was further diluted in acetonitrile to obtain 11 calibration levels ranging from 0.01 to 500 ng/µL. An aliquot of each standard solution (5 µL) was spiked into a 20 mL crimp cap headspace vial (vial Part No. 6ASV20-1, cap Part No. 6PMSC18-ST2) and used to assess linearity, limits of detection, and for quantitative assessment. In the same way, n = 9 vials were spiked with 5 µL of working solutions at 1.0 ng/µL (acetaldehyde) and 0.025 ng/µL (benzene and d-limonene) and used to assess method repeatability.

Sample preparation

Plastic bottles (n = 6) containing drinking water were purchased locally. Samples for analysis were obtained by cutting the bottles into small, consistent chips of a size of 5 x 5 to 8 x 8 mm with minimal friction heating to avoid warming the polymer and losing acetaldehyde. An aliquot (weight: 1 g ± 0.01) of each sample was sealed into a 20 mL crimp cap headspace vial for analysis.

Results and discussion

Chromatography

Plastic is a complex and challenging matrix because of its diverse composition. The capability of simultaneous selected ion monitoring (SIM) and full scan (FS) acquisition enabled high sensitivity and selectivity to distinguish between the target compounds and the matrix, combined with untargeted screening of other contaminants possibly present in the sample. An example of SIM and FS chromatograms from a plastic bottle sample is reported in Figure 1.

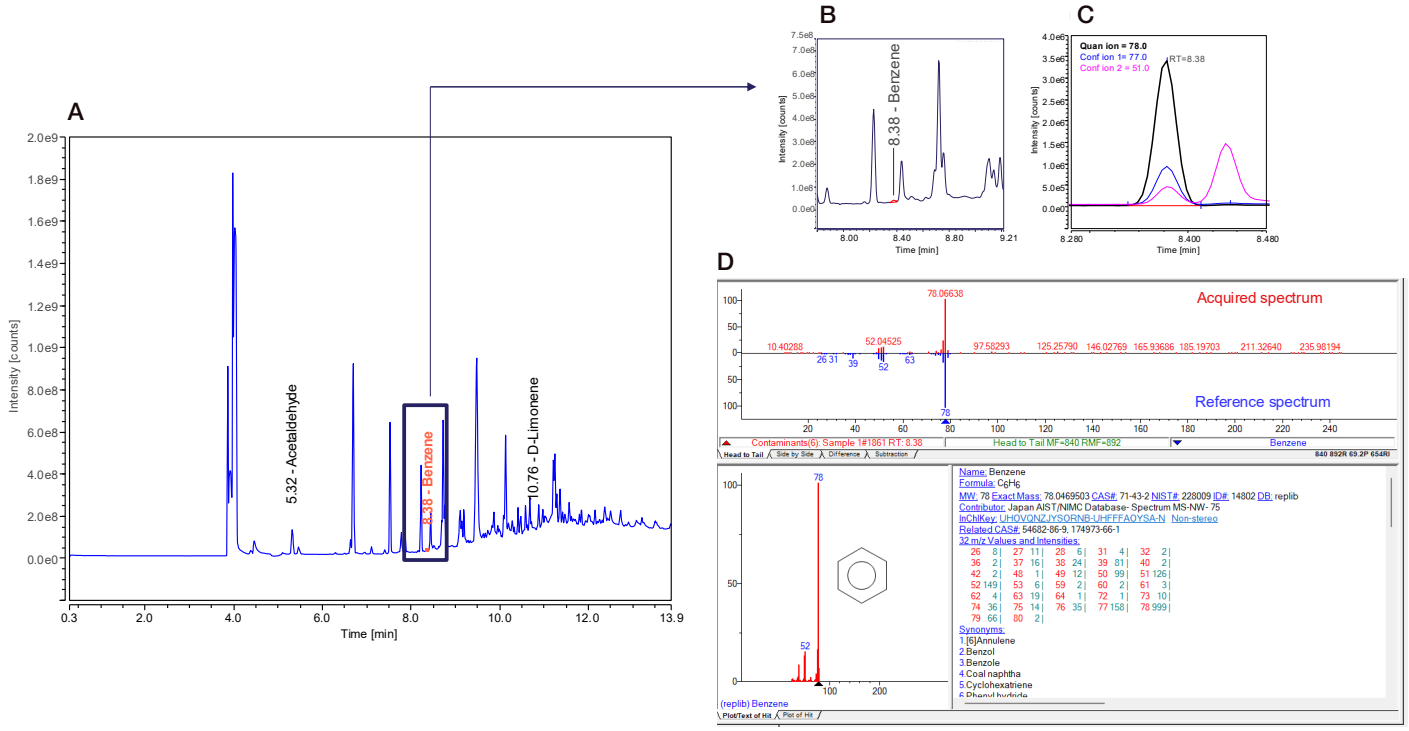

Figure 1. Example of data results for a plastic bottle sample. (A) FS acquisition with (B) zoomed view for benzene allows for a complete overview of the sample composition. (C) SIM acquisition enables higher sensitivity and selectivity for target compounds. (D) Confirmation or putative identification of analytes based on spectral matching with commercial libraries.

Linearity and limits of detection (LODs)

Linearity was assessed by injecting eleven calibration levels ranging from 0.01 to 500 ng/µL (corresponding to 0.05 – 2,500 ng in vial) in total evaporation mode. The generated calibration curves were fitted using a linear type and weighted 1/amount to nearly equal weighting for low and high concentrations. Each calibration level was prepared and analyzed in duplicate and the response values were averaged before curve fitting. The coefficient of determination (R^2) showed linear trend with values ≥ 0.997, calculated amounts ± 20% the expected values, and ion ratio (IR) deviation across the calibration levels < 15%. Full range calibration curves as well as zoomed details of the lowest calibration levels are reported in Figure 2.

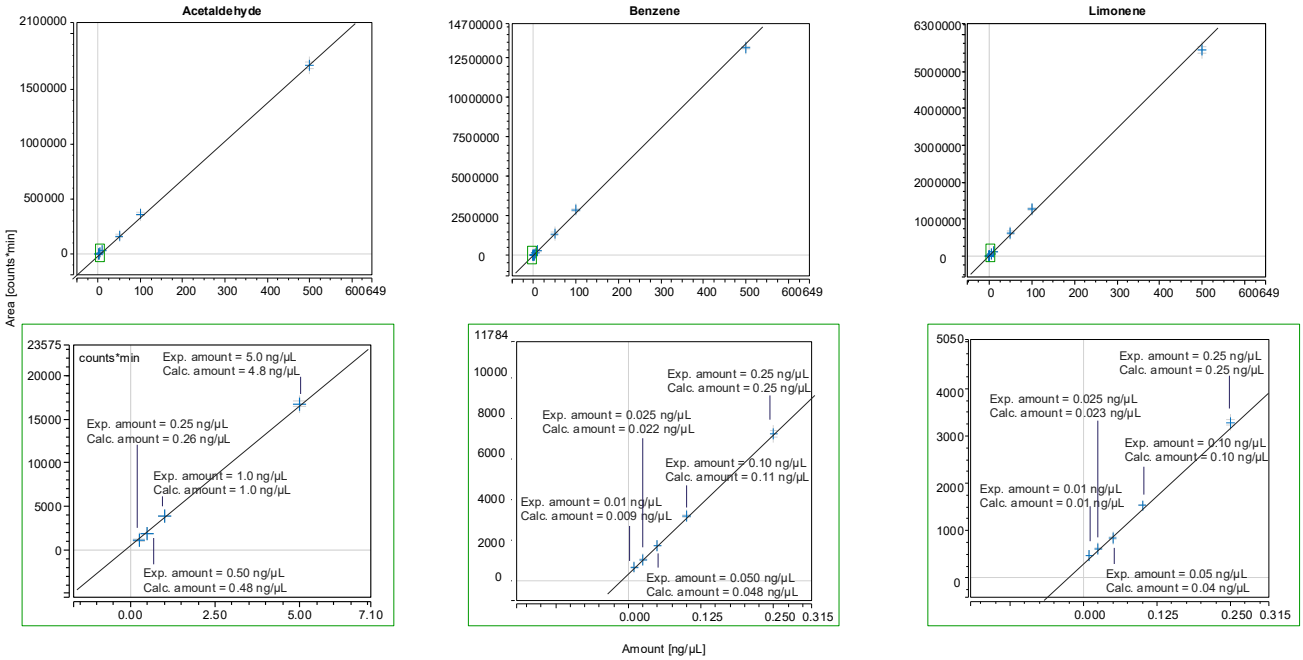

Figure 2. Full range calibration curves and details of the lowest calibration range for the investigated contaminants.

LODs were calculated based on the standard deviation of the responses and the slope of the calibration curve. Table 2 summarizes some method characteristic parameters, such as linearity ranges, calculated R^2, average IR deviation across the calibration curve, average amount deviation (%) from expected, and calculated LODs.

Table 2. Calibration ranges, calculated R^2, average IR deviation, average amount deviation from expected, and LODs for the target compounds.

Target analyte	RT (min)	Quantitation range (ng/µL)	Coefficient of determination (R^2)	Average IR deviation (%)	Average amount deviation (%)	Calculated LODs (ng/µL)
Acetaldehyde	5.32	0.25–500	0.999	1.3	5.1	0.02
Benzene	8.38	0.01–500	0.999	1.4	5.4	0.01
d-Limonene	10.77	0.01–500	0.997	3.0	5.9	0.03

Repeatability

The repeatability of the analytical system was evaluated by analyzing n = 9 calibration standards spiked with 5 µL of working solution at 0.025 ng/µL for benzene and limonene, and 1.0 ng/µL for acetaldehyde. The highly efficient pneumatic control and the inert sample path of the TriPlus 500 HS autosampler ensure reliable and reproducible analyte injection and transfer with an absolute peak area relative standard deviation (RSD) of < 5%, as reported in Figure 3.

Targeted and untargeted analysis of contaminants in rPET samples

Samples were prepared as described and analyzed using the method conditions reported in Table 1. Full scan data were used to confirm the identity of target contaminants acquired in SIM as well as to assign a putative identification to other unknown peaks found in the sample. Peak identification was based on spectral comparison with the NIST 2023 library.

The concentration of the target contaminants in the samples (expressed in µg/kg or ppb) was calculated using SIM acquisition data. The results were consistent with typical rPET values reported in the literature [2-5], as reported in Table 3.

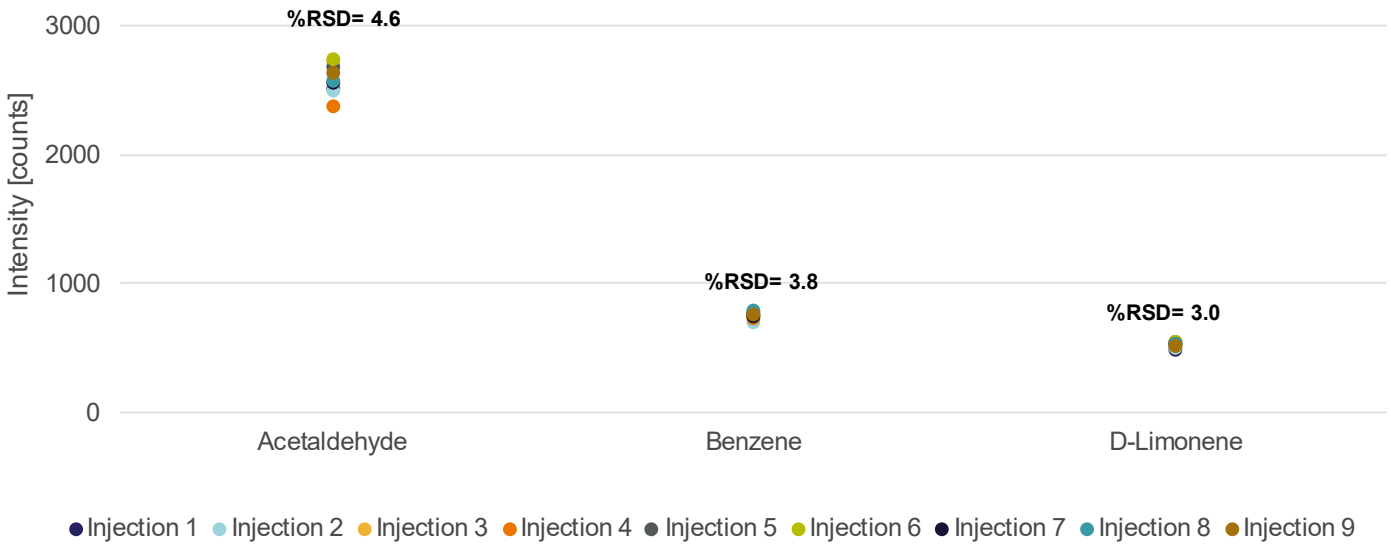

Figure 3. Absolute peak area repeatability (%RSD) obtained for n = 9 calibration standards spiked at 0.025 ng/µL for benzene and limonene, and 1.0 ng/µL for acetaldehyde.

Table 3. Quantitative analysis of contaminants in rPET bottles used for drinking water.

Sample	Weight (g)	Acetaldehyde	Benzene	d-Limonene
		µg/kg	µg/kg	µg/kg
1	1.009	1,985	16.4	41
2	1.003	2,301	1.2	54
3	1.004	2,324	11.6	42
4	1.001	1,399	10.4	22
5	1.006	1,623	1.2	23
6	1.005	1,164	1.0	24

The analysis of the FS acquisition allowed for the identification of other NIAS components typically found in rPET, such as 2-methyl 1,3-dioxolane, which originates from the reaction of acetaldehyde and the monomer ethylene glycol and was also identified in the analyzed samples. The identification of those additional analytes was confirmed by extracting the characteristic ions and comparing the acquired spectra with the ones contained in the NIST 2023 library. An example of analyte putative identification in sample 4 is reported in Figure 4.

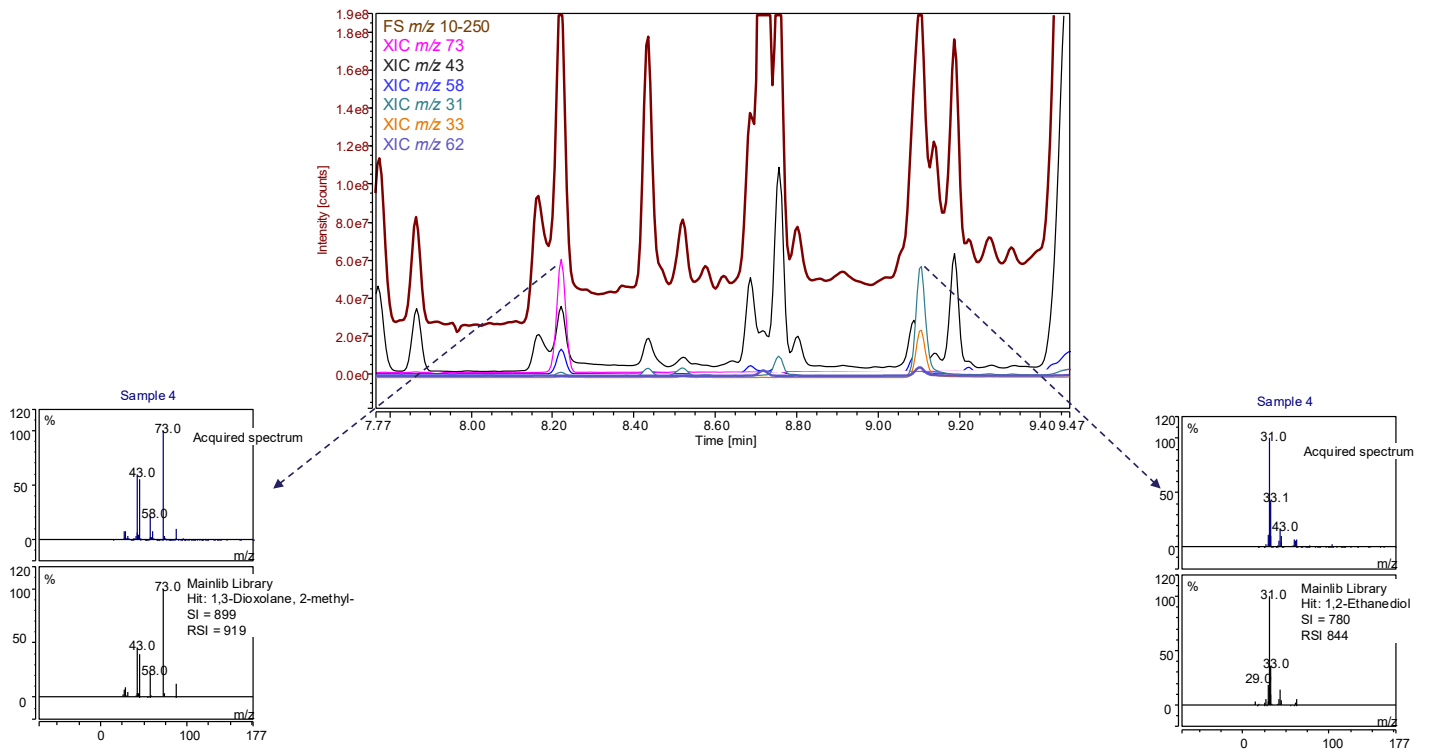

Figure 4. Overlaid FS (brown trace) and extracted ion chromatogram (XIC, colored traces) for sample 4. XICs for 2-methyl 1,3-dioxolane (pink, black, and blue traces) and ethylene glycol (dark green, orange, and purple traces) were used to determine the retention times of the unknown peaks whereas their spectra were used for putative identification based on comparison with NIST 23 library.

Conclusions

The results presented in this work demonstrate that headspace coupled to GC–MS provides a suitable and simple solution for analysis of contaminants in rPET, with no complex sample preparation required.

- The capability of combining FS with SIM acquisition allows for qualitative and quantitative analysis, increasing confidence in compound identification through spectral comparison with NIST library and allowing for the detection of possible analyte co-elution.
- The TriPlus 500 HS autosampler provides highly repeatable solventless extraction from solid samples with absolute area counts RSD < 5%, permitting reliable and consistent quantitative data.
- The ISQ 7610 single quadrupole GC–MS demonstrates an extended linear response (≥ 4–5 orders of magnitude) with R^2 ≥ 0.997, calculated amounts within ± 20% the expected value, and ion ratio deviation ≤ 15% across the calibration curve.
- Sensitivity was demonstrated with overall calculated LOD ≤ 0.03 ng/µL.
- Chromeleon CDS helps ensure data integrity, traceability, and effective data management from instrument control to the final report streamlining analysis and data review processes.

References

1. How does PET plastic recycling work? Recycle the One.
2. U.S. Food and Drug Administration. Use of Recycled Plastics in Food Packaging (Chemistry Considerations): Guidance for Industry: Use of Recycled Plastics in Food Packaging (Chemistry Considerations)
3. Welle F. Maximum concentrations of limonene in mineral water bottles containing postconsumer PET recyclates without organoleptic deterioration. Fraunhofer Institute for Process Engineering and Packaging (IVV). ivv.fraunhofer.de
4. Shen X., Hed Y., Annfinsen S., Singh N., Anwar H., Mylvaganam B., T., Emmer A. (2025) Investigating polyethylene terephthalate beverage packaging: impact of recycled content on acetaldehyde, benzene, and other contaminants. J Polym Environ 33:2362–2370. Investigating Polyethylene Terephthalate Beverage Packaging: Impact of Recycled Content on Acetaldehyde, Benzene, and Other Contaminants | Journal of Polymers and the Environment | Springer Nature Link
5. Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food

Learn more at **thermofisher.com/gcsystems**