Solutions

Safety. Science. Transformation.™

Assessing the Applicability of Analytical Test Methods for Measuring Polyethylene Terephthalate (PET) Made from Recycled Content

Authors:

Lillian Chen | Principle R&D Scientist
Sunny Chi | Lead R&D Scientist
Helena Chiang | Manager R&D
Dr. Renate Messing | Research Scientist
Michael Savarie | Program Manager
Dr. William Hoffman | Senior Research Scientist
Dr. Anne Bonhoff | Senior Research Scientist
Dr. Carl Wang | Director R&D

LET'S GO

Introduction

Polyester (generally referred to as polyethylene terephthalate, PET) is the most widely used fiber in the global textile market, accounting for around 52% (57 MT) of the total volume of textile fibers produced in 2020.[1] Due to the growth and high materials consumption of the textiles industry, CO2 emissions may be created through production emissions as well as raw material use.[1] The global chemical pollution may also be increased by the release of micro- and microplastics to the environment.[2] To reduce these negative impacts on the environment, the industry has agreed to reduce CO2 emissions and environmental pollution by increasing their use of recycled PET.[3] In 2020, approximately 15% (8.4 MT) of PET in the textile fiber market came from recycled inputs, as shown in Figure 1. Most of the recycled input was from mechanically recycled, post-consumer PET bottles.[1]

However, the demand for using waste to make products is not only from the textile industry. EU Packaging and Packaging Waste Directive (PPWD) has set a target for 30% recycled content in the packaging made from PET by 2030. The results of a NAPCOR Report (Figure 2) indicate an increased consumption of rPET materials and the trend of bottle-to-bottle recycling in North America in recent years[4]. Like the situation in Europe, to prevent the downcycling of bottles, the beverage industry advocates for "priority access" to rPET supply.[5]

Global polyester production (Million tonnes)

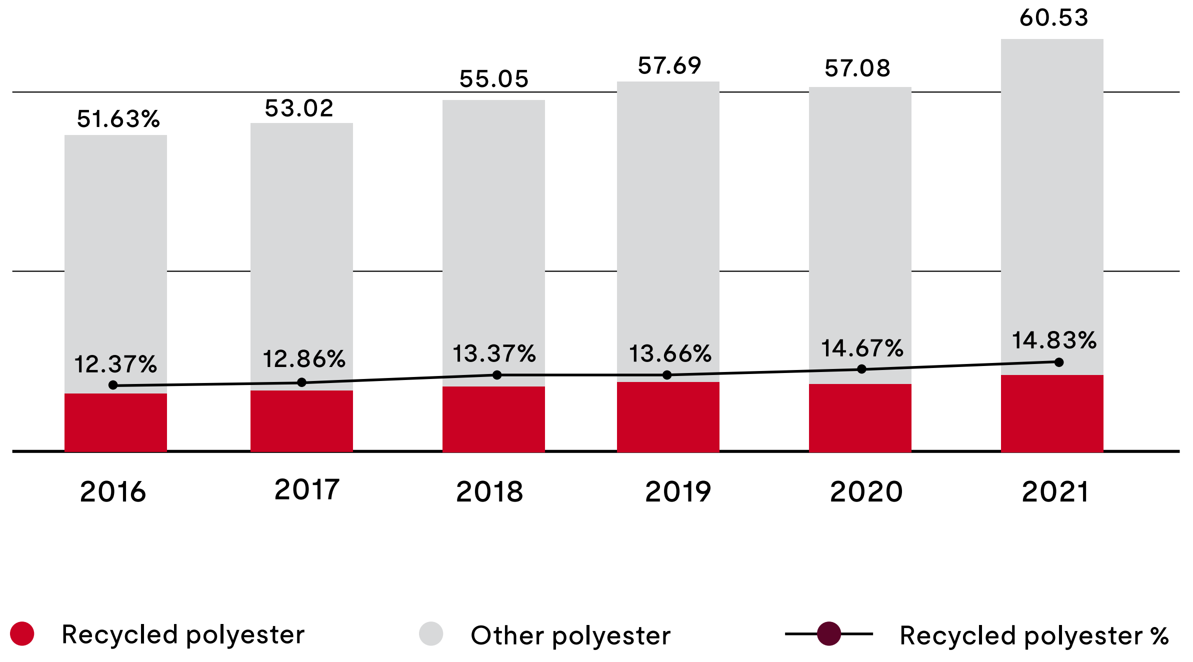

Figure 1: Global production size of polyester fibers and the ratio of recycled polyester[1]

This strong market demand intensifies concerns about a supply shortage and increases the price of rPET flakes/pellets. According to recent reports, some virgin polyester is being sold with a claim of using recycled materials[6], and it is estimated that more than 50% of what is marked and sold as rPET is made of virgin polyester.

Currently, the leading verification standards in the market are the Global Recycled Standard (GRS)[7], the Recycled Claim Standard (RCS)[8], UL 2809 Environmental Claim Validation Procedure (ECVP) series for Defined Content[9], and the SCS Recycled Content Standard[10]. These standards set requirements for third-party certification of recycled inputs and chain of custody models for a final product. These methodologies are based on the calculation of defined sources using different chain of custody models[11] to validate the recycled content supply chain and thereby determine the appropriate recycled content claim. Another proposed approach is applying a test-based verification process with the aim to detect the presence of materials originating from recycled PET bottles to enhance the supply chain's transparency and reduce fraud.[12]

This paper summarizes the results of a research study performed by the UL Solutions research team and is intended to evaluate the potential of determining the recycled content in products produced from recycled PET using analytical test methods. Several chemicals have been identified as potential tracing markers[13] and are investigated for their potential to accurately indicate the recycled content in final rPET products and in the processing stages, including the input materials and production process.

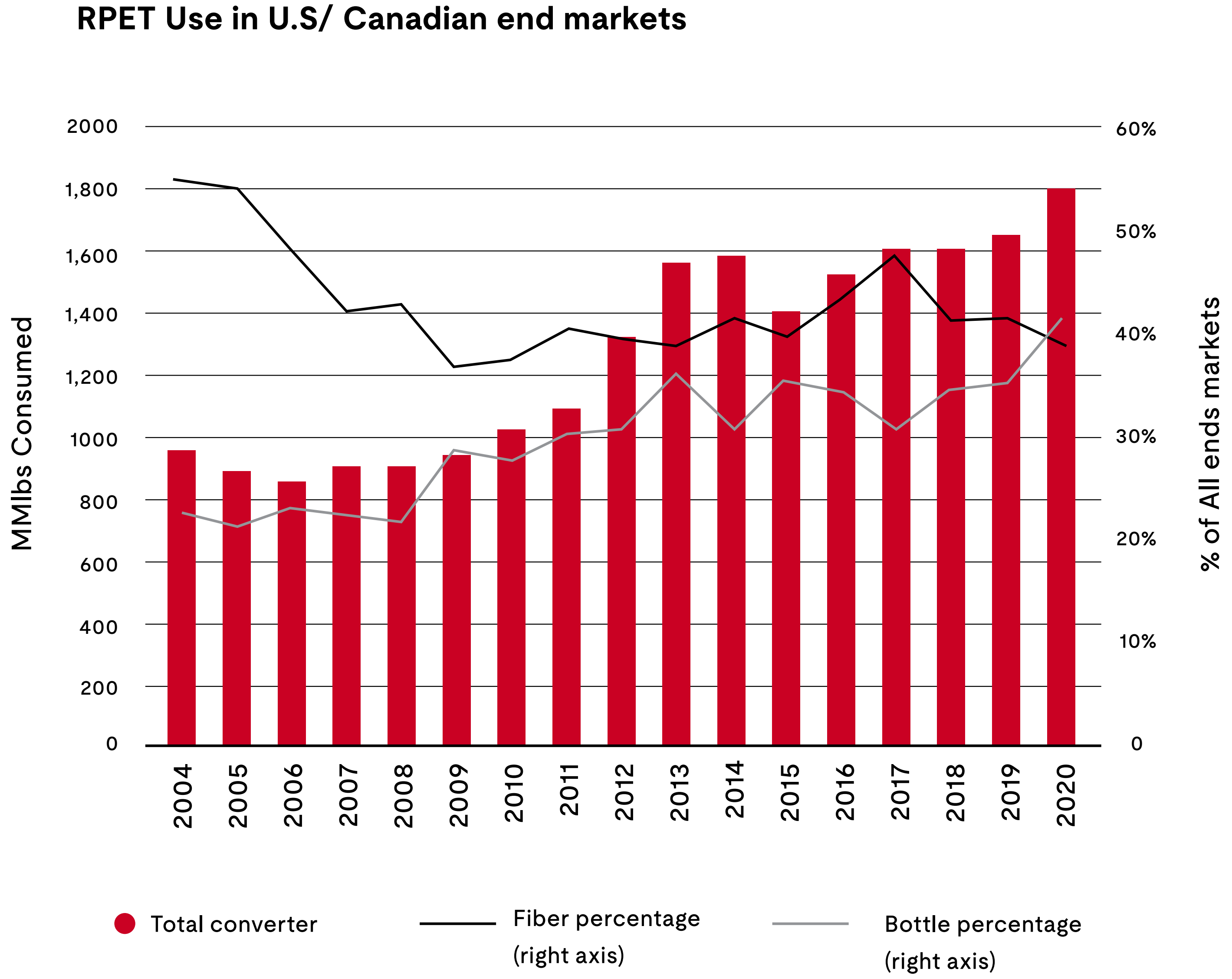

Figure 2: Consumption analysis of rPET materials in North America[5]

Mechanical recycling of PET fibers from PET bottles

According to market research in 2021, recycled polyester is mainly made from PET bottles by mechanically recycling with an estimated share of 99% of all recycled polyester.[14] A typical mechanical recycling process is shown in Figure 3 and includes several steps, starting from the post-consumer waste collection, sorting, crushing, washing, shredding, and sifting to obtain PET flakes. Then, the flakes are classified into different grades according to the intrinsic viscosity, color, impurity, water content, size, and bulk density of the recyclates[15]. A critical factor affecting the post-consumer PET flakes suitable for recycling is the level and nature of contaminants present. Contaminants can be a problem because they may cause deterioration of physical and chemical properties during reprocessing.

In the textiles industry, PET is generally blended with other fibers and recycling PET from mixed fabrics is still challenging and costly. Therefore, the rPET generated from textiles or clothes is still small in proportion to the market.[16, 17]

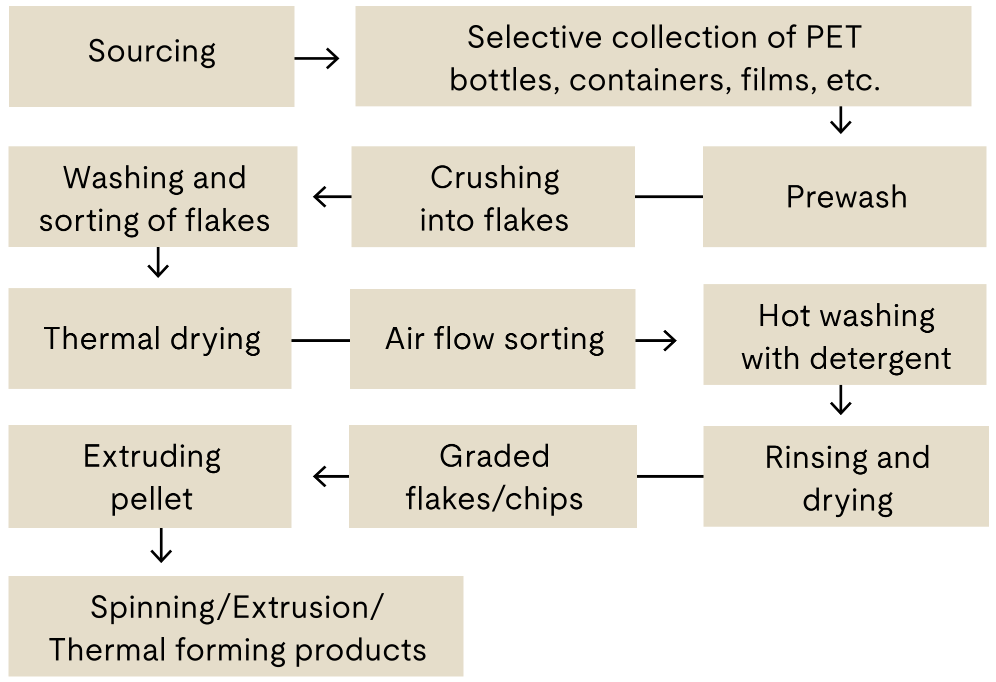

Figure 3: Typical PET bottle recycling process – mechanical recycling

Research on an alternative approach using analytical test methods

A variety of test methods to detect tracing markers associated with rPET are proposed to verify the presence and quantity of recycled content in a product or raw material.[18] The potential tracing markers considered are as follows:

- Comonomers to PET, like diethylene glycol (DEG) and isophthalic acid (IPA), are commonly used to modify PET's matrix for better clarity, processability, ductility, and gas barrier in keeping with the needs of bottles.
- Additives like 2-Aminobenzamide, an acetaldehyde scavenger used for water or beverage bottles only.
- Degradation compounds of PET that are generated during the processing of the material (e. g. extrusion, molding, etc.) such as acetaldehyde-2-methyl-1,3-dioxolane, etc.

Sample No.	Sample Designation	PET Source	PET Usage and Shape
1	VBottle-Used-1	Virgin PET	Water/Soft Drink Bottle
2	VBottle-Used-2		
3	VBottle-Used-3		
4	VBottle-Used-4		
5	VBottle-Used-5		
6	VBottle-Used-6		
7	VBottle-Used-7		
8	VBottle-Used-8		
9	VBottle-Used-9		
10	VBottle-Used-10		
11	VBottle-Used-11		
12	VBottle-Used-12		
13	VBottle-Used-13		
14	VBottle-Used-14		
15	VBottle-Used-15		
16	VBottle-Used-16		
17	VBottle-Pellet-1	Virgin PET	Virgin PET Pellet for Bottle
18	RBottle-Shred-2	rPET	Recycled PET Bottle Shred

Sample No.	Sample Designation	PET Source	PET Usage and Shape
19	VFiber-Pellet-1	Virgin PET	Virgin PET Pellet for Fiber
20	VFabric-1	Virgin PET	100% Fabric PET
21	RFabric-1	rPET	Recycled Fabric PET
22	RFiber-2		
23	RFabric-3		
24	RFabric-5		
25	RFabric-6		
26	RFabric-7		
27	RFabric-8		
28	RFabric-9		
29	VTrays-1	Virgin PET	Food Trays PET
30	VTrays-2		
31	RTrays-Shred-1	rPET	Recycled Trays PET (Shred)
32	RTrays-Pellet-2		Recycled Trays PET (Pellet)

Table 1: Overview of PET samples collected from the market

- Flavorings in drinks or beverages, such as limonene, p-cymene, etc.

To measure these potential markers of rPET, the following analytical test methods are applied accordingly. Chemical identification and quantification are performed using Fourier-Transform Infrared Spectroscopy (FTIR), Gas Chromatography–Mass Spectrometry (GC/MS), Nuclear Magnetic Resonance (NMR) Spectroscopy, and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Material characterization was performed using Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and a Viscometer. A total of fourteen analytical methods were used to verify the correlation between specified markers and the recycled PET content. To conduct a comprehensive investigation of these markers in the stream of PET recycling, a total of thirty-two samples were collected from the market and examined. The samples include different virgin and recycled PET products, such as pellets for bottles and yarn, used bottles, and textile products, as shown in the overview in Table 1.

The suitability of test methods evaluated in this research study are summarized in Table 2 below. Four different detection items were identified with their corresponding test method, and each test method is judged according to six criteria, and ranked according to their applicability.

Detection Item	Method	Quantification	Detection limit	Easy to approach	Sample differentiation	Matrix Effect (ex. Dyes)	Sample preparation	Ranking
Comonomer (IPA or DEG)	NMR	+++	++	+	+++	+++	+	1
	FTIR	+	-	+++	---	--	++	3
	TGA	+	-	+++	---	--	++	3
Migratable additives or decomposed compounds of PET	Thermal desorption GC/MS	++	+++	++	---	+	+	3
	Extraction GC/MS	++	+++	++	---	+	--	3
Melting point	DCS	-	-	+++	+++	-	+++	2
Intrinsic Viscosity	Viscosimeter	+	-	+	+	-	+	3

Table 2: Summary of analytical methods for tracers in PET

Among the test results, the technique of NMR spectroscopy shows a promising capability to quantify the IPA and DEG content in PET. Figure 4 shows the IPA content for the test samples, indicating a trend between bottle and non-bottle samples. Figure 5 shows the results for DEG content detected, with no significant trend between the samples. IPA is commonly used as a comonomer to control the physical and optical properties of virgin PET by impacting the crystallization of semi-crystalline PET.[19] This applies to bottles and other applications, which is supported by the results of this research study, as in most bottle samples IPA is detected, while fewer fabric samples have IPA content detected, and those that do have it in lower amounts.

As IPA is used as a common comonomer to control the optical and physical performance of PET in several applications, it is found in various concentrations in the samples selected from the market, supported by the results of the research study in Figure 4. Furthermore, it is found that the IPA content in PET can vary by regions and products. The situation results in variations in actual IPA content in rPET from batch to batch.

Due to the high variation of the IPA content in virgin PET, the approach of determining the recycled content in PET by comparing the measured IPA content of a sample would require the establishment of an IPA content reference indicator. To establish such a reference indicator, enormous efforts for continuous and seamless monitoring of the of IPA content in virgin PET in various regions, markets, and applications is required.

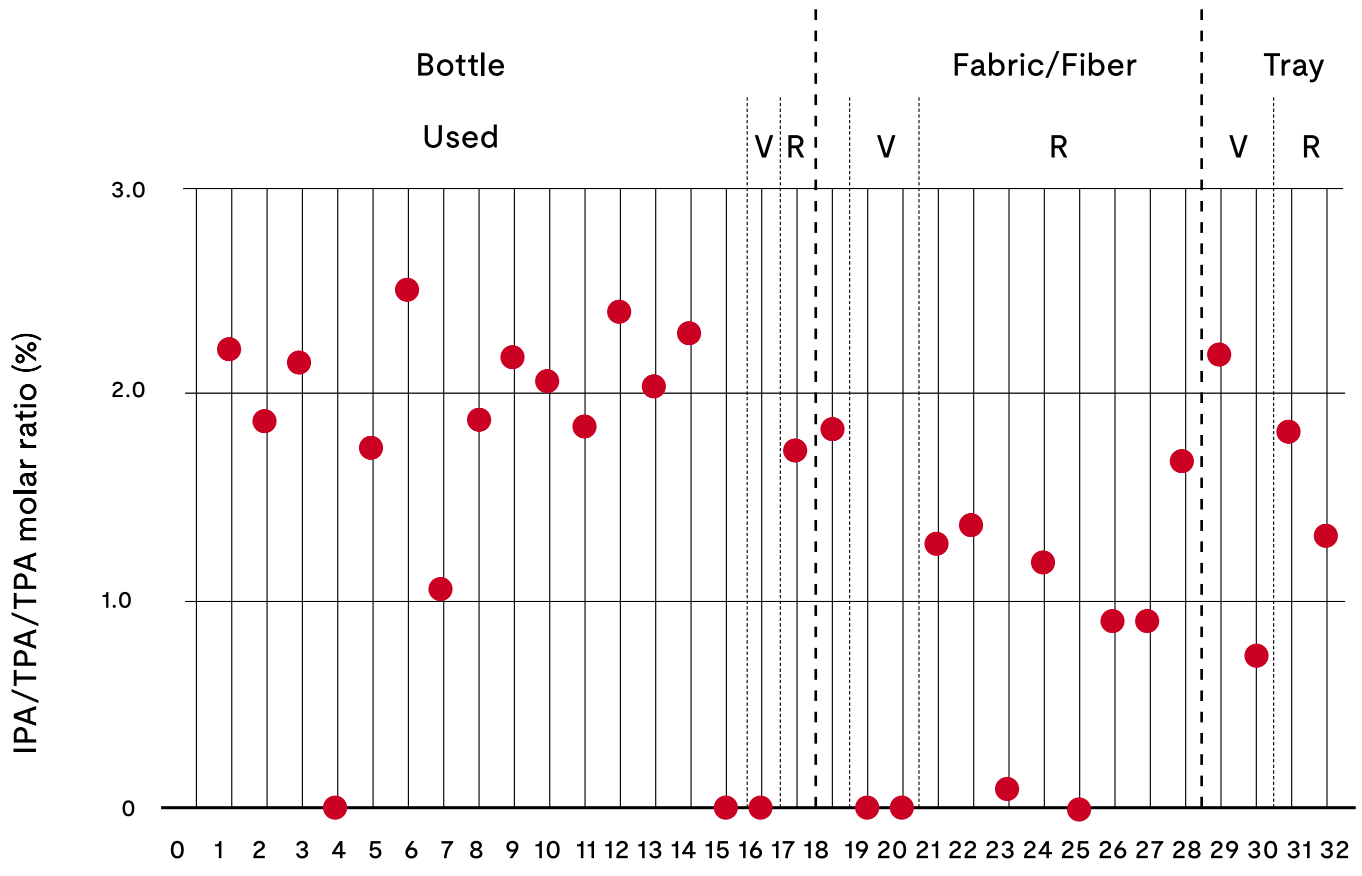

Figure 4: Analyzed IPA content in molar ratio, measured by NMR spectroscopy on all samples.

The main concern is the variation of such reference indicators, bearing the risk of a false estimation of the recycled content.

The proposed methodology using NMR to monitor and quantify the IPA content is probably suitable for validating the origin of materials from a controlled recycling source or a closed-loop recycling process, in which the IPA content is known and/or controlled, enabling the establishment of the required reference indicator.

Beside the NMR results discussed above, a significant correlation between the melting point and the IPA content in PET was also discovered, because IPA impacts the crystallization of PET, but the quantification using the melting point measured by DSC is insufficient. Hence, to determine the content of IPA in PET, NMR is the preferred analytical technique, and DSC can be the additional method for process control due to ease of operation.

The test results from other potential tracing markers in PET, like acetaldehyde, 2-methyl-1,3-dioxolane and 2-aminobenzamide using GC/MS do not indicate the ability to distinguish between different types of PET. For some other tracing markers, analysis by GC/MS is a shortfall because insufficient sample differentiation is observed, leading to inconclusive results.

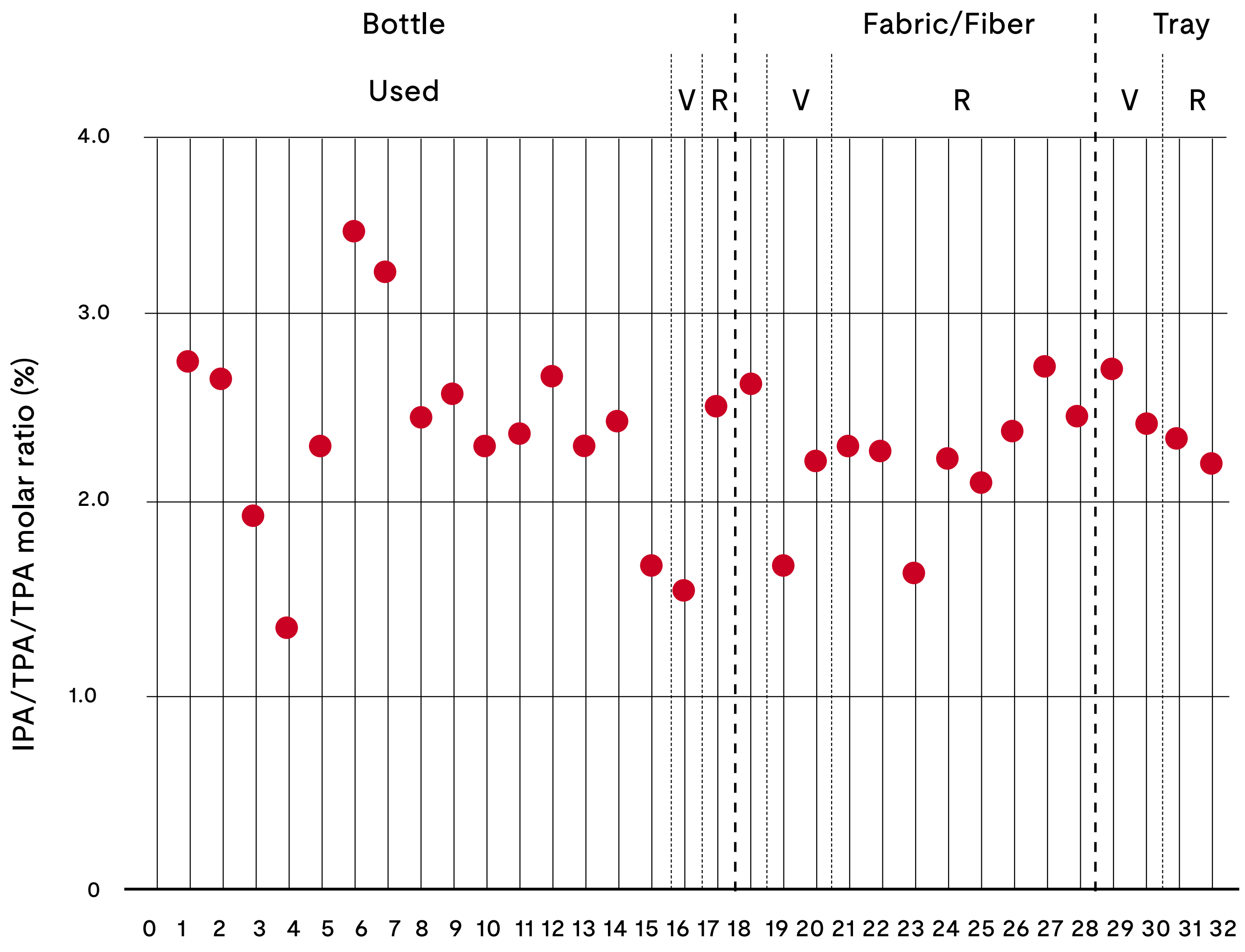

Figure 5: Analyzed DEG content in molar ratio, measured by NMR spectroscopy on all samples.

Conclusion

The method of quantifying IPA with NMR for verifying the rPET content has shown some limitations. IPA alone is not a suitable marker to distinguish recycled PET from virgin PET, due to the high variation found in different virgin PET products. Additionally, IPA can possibly be added during the production process to falsely indicate a material is recycled. Thus, relying on IPA-only analysis may lead to false identification of PET as recycled. While NMR spectroscopy is identified as suitable to quantify the IPA content in PET, the IPA content level in PET appears to be an unreliable method to determine if a PET product contains recycled content.

End notes

1. Preferred Fiber & Materials Market Report, Textile Exchange, 2022
2. The global apparel industry is a significant yet overlooked source of plastic leakage, Nature Communication, June 2024
3. 2025 Recycled Polyester Challenge, First Annual Report, 2022
4. NAPCOR Report Shows US Demand for rPET Grew, as Collection Dipped, in 2020
5. Fair is fair: EU beverage industry demands rPET priority access amid cross-industry "free-riding", Packaging Insights, 03 May 2022
6. Lab tests expose recycled polyester fraud
7. Global Recycled Standard (GRS), Version 4.0, 2017
8. Recycled Claim Standard (RCS), Version 2.0, 2017
9. UL 2809-1 Environmental Claim Validation procedure (ECVP) for Defined Source Content, Ed. 2, 2023
10. SCS Certification Standard for Recycled Content, SCS-103, version 8.0, 2024
11. ISO 22095 - Chain of custody — General terminology and models, 2020
12. Waste2Wear
13. Develop a post-market test for recycled food contact materials, Smithers Rappa & Smithers Pira Limited, 11.03.2014
14. Preferred Fiber & Materials Market Report, Textile Exchange, 2021
15. ISO 12418 - Plastics — Post-consumer PET bottle recyclates — Part 1 & Part 2
16. Polyethylene terephthalate (PET) recycling: A review, Case Studies in Chemical and Environmental Engineering 9 (2024), 100673
17. Tackling critical challenges in textile circularity: A review on strategies for recycling cellulose and polyester from blended fabrics, Journal of Environmental Chemical Engineering, Volume 11, Issue 5, October 2023, 110482
18. CEN/TS 16861 - Plastics - Recycled plastics - Determination of selected marker compounds in food grade recycled polyethylene terephthalate (PET), 2015
19. Crystallization of Poly(ethyleneterephthalate): A Review Polymers, 2024, 16, 1975. https://doi.org/10.3390/polym16141975

UL.com/Solutions

1690440