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Application News

MALDI-TOF mass spectrometry

Solvent-Free Preparation for MALDI-MS Analysis of Virgin and Recycled Polyethylene Terephthalate (PET)

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User Benefits

- Simple and quick sample preparation
- Solvent-free preparation for the analysis of poorly soluble polymers
- Avoidance of hazardous solvents

■ Introduction

Polyethylene terephthalate (PET) is a widely used polymer found in everyday applications, most notably in single-use beverage bottles (1). Since 2021, taxes have been imposed on non-recycled PET, increasing the demand for efficient methods to differentiate between virgin and recycled PET (2). This has made rapid and straightforward analytical techniques for PET more relevant than ever. However, PET presents several analytical challenges due to its poor solubility, complicating analysis using techniques like MALDI (Matrix-Assisted Laser Desorption/Ionization) (3). PET can be dissolved in solvents such as 1,1,1,3,3,3-hexafluoropropan-2-ol, but this solvent belongs to the highly controversial PFAS (per- and polyfluoroalkyl substances) class, known for its environmental persistence and potential health risks (4-5). The development of solvent-free analytical methods for PET is highly beneficial, as it eliminates the need for environmentally harmful solvents and aligns with growing sustainability standards.

■ Sample preparation

In the initial step was similar to (6). The PET sample is ground into smaller particles. Subsequently, the sample is weighed along with the matrix (dithranol) and the cation donor (sodium trifluoroacetate (NaTFA)), followed by thorough grinding with a mortar and pestle. After grinding, the sample is melted at 300ºC and applied on a MALDI target. The prepared sample is then analysed on an AXIMA Performance™ instrument.

■ Measurement Conditions

The sample was analyzed on an AXIMA Performance MALDI-TOF mass spectrometer shown in Fig. 1. Table 1 shows the measurement conditions.

Table 1 Analysis conditions for AXIMA Performance

Mode	Reflectron (positive)
Mass range	1000 – 8000
Laser power	120
Profiles	50
Shots per profile	10
Ion Gate (Da)	1000

Fig. 1 AXIMA Performance™ MALDI TOF Mass Spectrometer

■ Results

The spectrum of virgin PET exhibits a series of consecutive peaks with a separation of 192 mass units, corresponding to the repeating monomeric unit of PET (Fig. 2). Additionally, an intense peak is observed in conjunction with a less intense series, separated by 44 mass units. This 44 mass unit difference suggests the presence of an additional carboxyl group within the polymer chain, indicating that the polymer chains possess a carboxyl-functional end group. In the spectrum of recycled PET, the same peaks detected in the spectrum of virgin PET are also present, suggesting that the primary chemical structure of the polymer is largely preserved during the recycling process. However, the spectrum of recycled PET reveals an additional variation in peak distribution, which indicates the presence of different terminal groups. These variations can be attributed to the recycling process, during which polymer chains may undergo scission, resulting in the formation of new end-group functionalities or alterations in the polymer chain structure, as evidenced by the altered peak distribution.

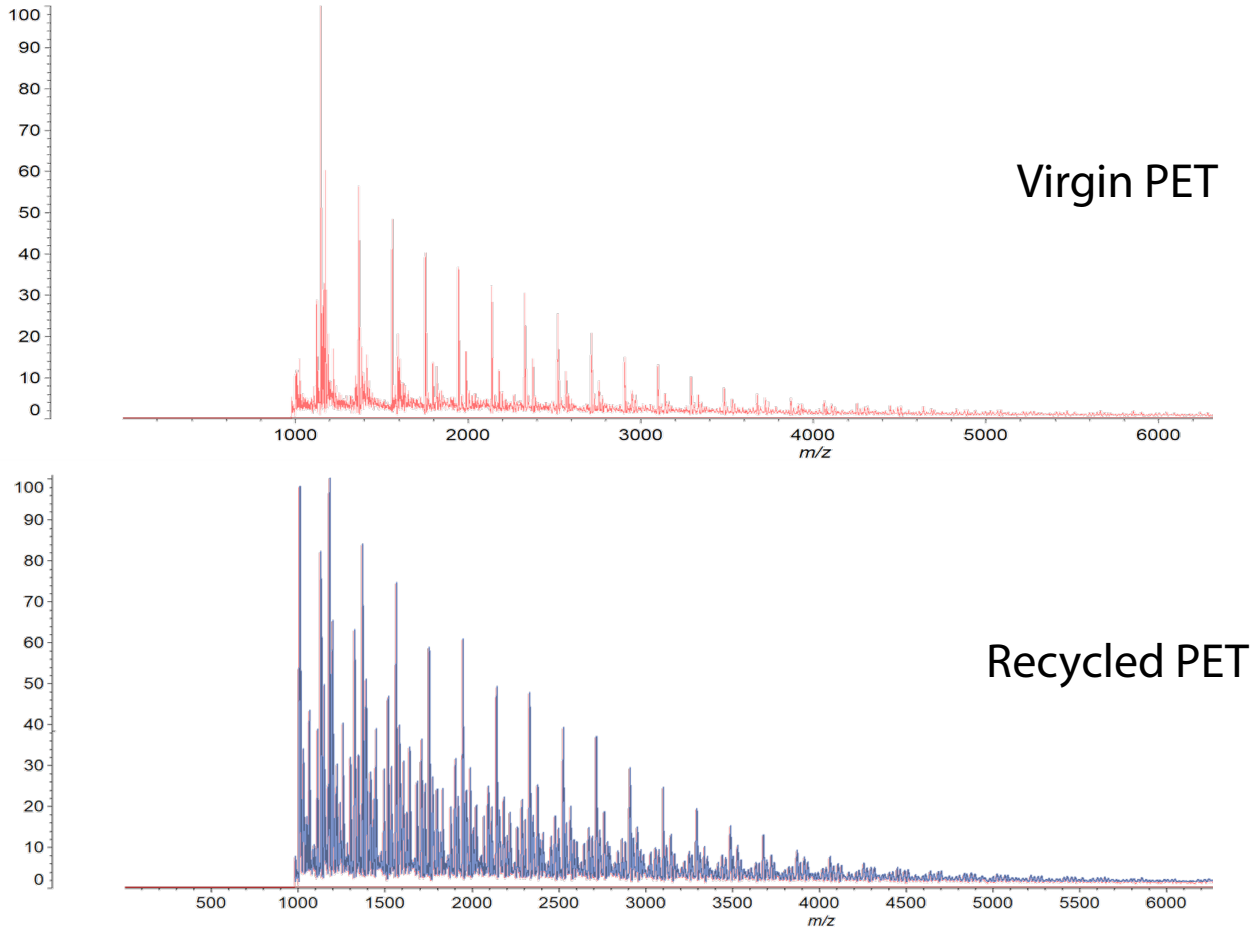

Fig. 2: Comparison of virgin PET spectrum (red) with recycled PET spectrum (blue)

■ Conclusion

Using solvent-free preparation methods, PET could be successfully analyzed in its solid phase. This approach is particularly advantageous because PET is difficult to dissolve, making solvent-free techniques highly effective. Furthermore, it was possible to distinguish between virgin PET and recycled PET, demonstrating the efficacy of this analytical method in differentiating between these materials

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