Waters™

Application Note

Characterization of Plastics Using Mass Spectral Reference Libraries Developed From Pyrolysis-APGC-QToF MS

Rachel Sanig, Rhys Jones, Cristian Cojocariu

Waters Corporation

This is an Application Brief and does not contain a detailed Experimental section.

Abstract

Due to the reproducible and characteristic degradation of many polymer standards by pyrolysis, library searching can be an important tool in the identification of chemical constituents in polymeric materials. Spectral libraries for pyrolyzates, however, are not freely available. Pyrolysis-gas chromatography with soft ionization and high-resolution mass spectrometry is an effective analytical tool for laboratories focusing on compositional analysis of complex polymer materials using gas phase separation. Soft ionization allows for molecular ion detection to assist with the confirmation of chemical elemental composition, structural elucidation, and, ultimately, for compound identification. In this technical note, this analytical platform is investigated for its library searching capabilities using libraries built in-house, to increase confidence in polymer compound identification.

Benefits

- Pyrolysis-APGC-QToF MS is an effective analytical tool for laboratories focusing on compositional analysis of complex materials using gas phase separation.

- Soft ionization using APGC allows molecular ions to be detected from which elemental compositions are derived to aid compound identification.
- Py-APGC-QToF MS can be utilized for library creation from the averaged mass spectrum of polymer standards and applied to real life samples.

Introduction

In the field of polymer research, pyrolysis coupled to gas chromatography-mass spectrometry (py-GC-MS) has been extensively used for samples that are not amenable to solubilization due to the reproducible and characteristic degradation of many polymer standards.[1,2] Spectral libraries for pyrolyzates, however, are not freely available and the high energy of electron ionization (EI) leads to insufficient sensitivity and selectivity making it difficult to undertake the characterization of plastic products, impurities, and additives.

Pyrolysis-GC with soft ionization and quadrupole time of flight high-resolution mass spectrometry (QToF MS) is potentially a useful tool in this field to help address some of the limitations. Atmospheric Pressure Gas Chromatography (APGC) enables softer ionization, resulting in molecular ion detection. The QToF MS can acquire data in MS^E mode, whereby both low and high collision energy spectra are simultaneously acquired. Coupled together, the accurate mass of both precursor and fragment ions are available, both of which aid structural elucidation and, ultimately, compound identification.[3]

The ability to create spectral libraries of pyrolyzates is an important tool for the characterization of polymeric materials, to make identification of chemical constituents easier for the analyst. In this technical note, both py-GC-EI-MS and py-APGC-QToF MS are investigated for pyrolyzates library searching capabilities. These results describe a simple combined approach using spectral polymer libraries, built in-house, to increase confidence in polymer compound identification.

Experimental

Sample Description

A selection of polymer standards were weighed to approximately 0.1 mg and loaded into glass capillaries between two plugs of quartz wool. The glass tubes were then placed into the pyrolyzer autosampler and analyzed in triplicate on the GC-EI-MS and the APGC-QToF MS.

Pyrolysis Conditions

Pyrolyzer:	CDS 5000, CDS Analytical
Inlet temperature:	310 °C
Ramp rate:	20 °C/ms
Final temperature:	750 °C

GC Conditions

Inlet mode:	Split
Split ratio:	75:1
Split flow:	75 mL/min
Inlet temperature:	310 °C
Column:	Rtx-5MS, 30 m x 0.25 mm x 0.25 µm, RESTEK
Column flow:	1 mL/min
Septum purge flow:	3 mL/min
Oven gradient:	45 °C for 5 min, ramp to 300 °C at a rate of 20 °C/min, final hold for 10 min

Total GC run time:	27.75 min

MS Conditions

System 1: Xevo™ TQ-GC

Ionization mode:	EI+
Electron energy:	70 eV
Emission:	300 µA
Source temperature:	250 °C
Mass range:	*m/z* 10–650
Scan time:	0.1 s
GC interface temperature:	300 °C

System 2: Xevo G2-XS QTof*

Ionization mode:	APGC™ +ve ionization
Corona current:	3 µA
Sampling cone:	30 V
Source temperature:	150 °C
Mass range:	*m/z* 10–1500

Scan time:	0.2 s
Cone gas:	50 L/h
Auxillary gas:	550 L/h
GC interface temperature:	280 °C
MS^E collision energy:	Low energy 6 V, High energy 15–45 V

**(Equivalent or better performance is expected with the Xevo G3 QTof).*

Data Management

Data acquisition, processing, and reporting were performed using Waters™ MassLynx™ 4.2. Software. Libraries were created within an existing NIST spectral library platform.

Results and Discussion

A library for each instrument configuration was built from the averaged mass spectrum obtained from pure polymer standards and used within an existing NIST spectral library platform (Figure 1).

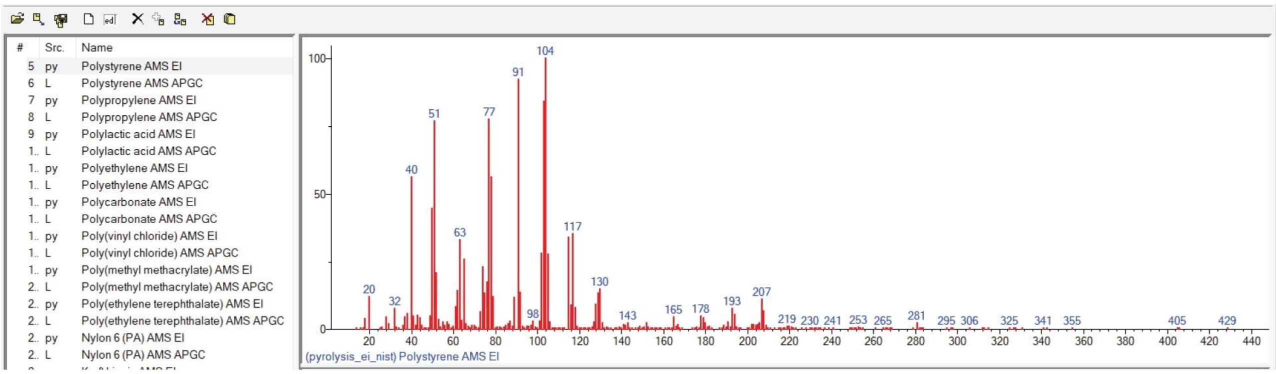

Figure 1. Examples of the NIST library entries created from the analyzed polymer standards for both instrument platforms (py-GC-EI-MS and py-APGC-QToF-MS).

To investigate the libraries for searching capabilities, plastic and biobased plastic samples were then analyzed under the same conditions as the polymer standards. Averaged mass spectra were generated from the pyrograms of these samples and then searched against the in-house spectral libraries for matches. Data were collected in full scan on the instruments and both the py-GC-EI-MS and the py-APGC-QToF MS libraries showed comparative results based on forward match and reversed match scoring. Typically, greater than 800 for a match is considered good and adds to the probability of a correct assignment using the library.[4]

For example, the spectra search of a recycled PET (poly(ethylene terephthalate)) container generated from both instruments showed a primary match for the PET standard. The library forward match and reversed match scores were 865 and 865, respectively, on py-GC-EI-MS (Figure 2) and 818 and 818, respectively, on the py-APGC-QToF MS (Figure 3).

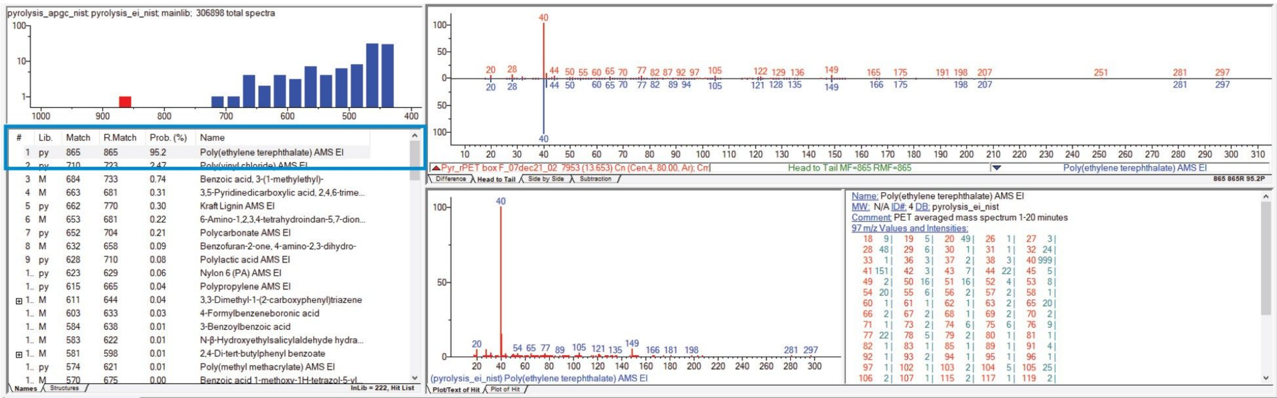

Figure 2. Library forward match and reversed scores for PET in the py-GC-EI-MS library.

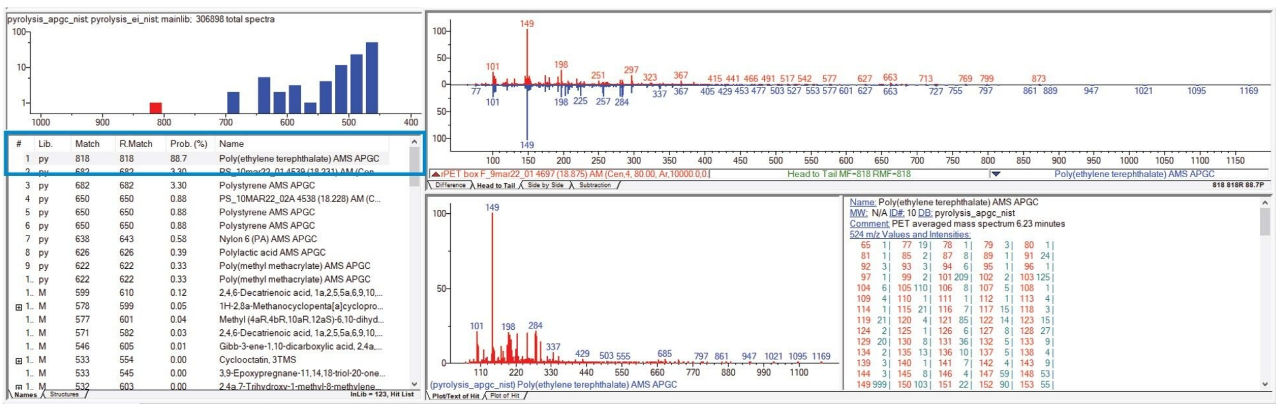

Figure 3. Library forward match and reversed scores for PET in the py-APGC-QToF MS library.

The spectra search of a biobased plastic straw generated from py-GC-EI-MS showed it to be made primarily from poly(lactic acid) (PLA), with the library forward match and reversed match scores being 863 and 868, respectively (Figure 4). This was sufficient to identify PLA as the main constituent of this sample. The py-APGC-QToF MS full scan library was also used to search the pyrograms of plastics samples with comparative results. The biobased plastic straw showed matches for PLA of 851 and 852, respectively (Figure 5).

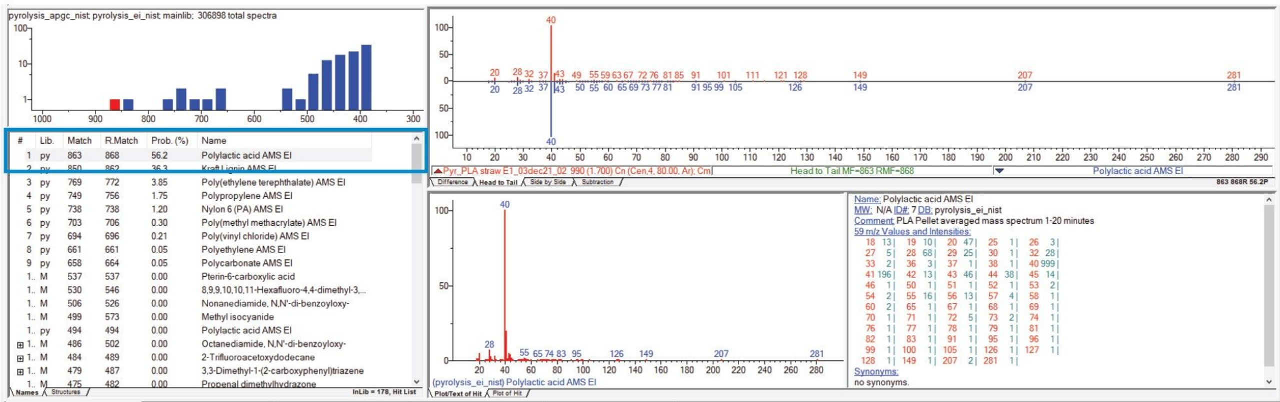

Figure 4. Library forward match and reversed scores for PLA in the py-GC-EI-MS library.

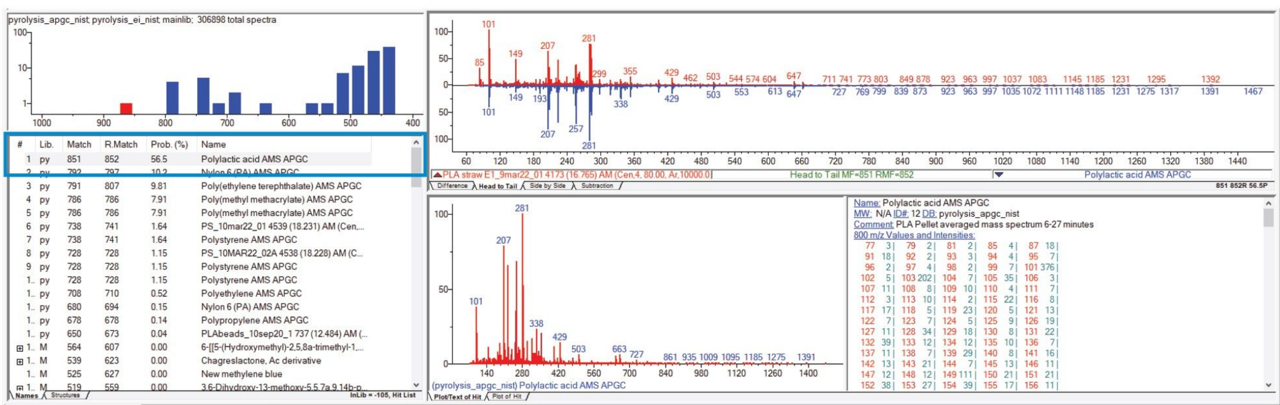

Figure 5. Library forward match and reversed scores for PLA in the py-APGC-QToF MS library.

Conclusion

Both py-GC-EI-MS and py-APGC-QToF MS can be utilized for library creation from the averaged mass spectrum of polymer standards. The mass spectra for plastic and biobased plastic samples can be easily integrated in existing commercial libraries such as NIST and used to search against real samples for fast putative identification of the plastic constituents. Where further characterization of plastic products is required, py-APGC-QToF MS provides additional benefits, such as soft ionization which reduces fragmentation and promotes the presence of the molecular ion, increasing the confidence in identification of unknown compounds.[3]

References

1. Suge S., Ohtani H., Watanabe C. Pyrolysis-GC/MS Data Book of Synthetic Polymers. 2011.
2. Peacock P. M., McEwen C. N. Mass Spectrometry of Synthetic Polymers. ***Anal. Chem.*** 2006;78(12): 3957–3964.
3. Sanig R., Cojocariu C., Jones R. Pyrolysis-gas chromatography-high resolution mass spectrometry with soft ionization for increased confidence for polymer characterization. Waters Application Note 720007599, April 2022.
4. NIST/EPA/NIH Mass Spectral Library Compound Scoring: Match Factor, Reverse Match Factor, and Probability, Jordi Labs.

Featured Products

Xevo TQ-XS Triple Quadrupole Mass Spectrometry <https://www.waters.com/134889751>

Xevo G2-XS QTof Quadrupole Time-of-Flight Mass Spectrometry <https://www.waters.com/134798222>

MassLynx MS Software <https://www.waters.com/513662>

720007849, January 2023