

COMBINED APPROACH FOR THE CHARACTERIZATION OF PLASTICS USING SPECTRAL LIBRARIES CREATED FROM BOTH PYROLYSIS-GC-MS AND PYROLYSIS-APGC-QTOF-MS

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INTRODUCTION

Scientific interest is growing in sustainable polymers and natural materials to increase recycling and develop biobased plastics. Polymers derived from natural sources, such as feedstocks, however, are complex and require characterization prior to use. Furthermore, increased use of post-consumer recyclates and biobased plastics may lead to an increase in regulations prescribing the presence of additives and potential contaminants.¹

In the field of polymer research, pyrolysis (py) coupled to gas chromatography-mass spectrometry (GC-MS) has been extensively used for samples that are not amenable to solubilization.^{2,3} However, 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 high resolution mass spectrometry (HRMS) 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 which can help with the confirmation of a molecular formula for identification. APGC can be coupled to a quadrupole time-of-flight mass spectrometer (QToF MS) which can acquire data in MS^E mode. The accurate mass of both precursor and fragment ions are available to provide information for structural elucidation and ultimately aid compound identification.⁴

These results describe a combined approach using spectral polymer libraries, built in-house, to increase confidence in polymer compound identification. Also described is the comparison between classical py-GC with EI-quadrupole MS and py-APGC-QToF MS. The analytical advantages of soft ionization and accurate mass, to aid characterization of plastic products is explored.

METHODS

Sample preparation

A number 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.

Instrument conditions

A pyrolyzer (CDS 5000, CDS Analytical) was installed on a GC-MS with EI (Instrument 1) and on a GC-QToF with APGC (Instrument 2, Figure 1).

| Pyrolysis Conditions | |
|----------------------|----------|
| Initial Temp. | 0 °C |
| Ramp Rate | 20 °C/ms |
| Final Temp. | 750 °C |

| GC Conditions | |
|-------------------|--|
| Inlet Mode | Split |
| Inlet Temp. | 310 °C |
| Septum Purge Flow | 3 mL/min |
| Split Ratio | 75:1 |
| Split Flow | 75 mL/min |
| Column | Rtx-5MS, 30m x 0.25 mm x 0.25 µm (available from RESTEK) |
| Column Flow | 1 mL/min |
| Oven Gradient | 45 °C for 5 min, up to 300 °C at 20°C/min, 10 min final hold |
| Total GC Run Time | 27.75 min |

| MS Conditions | |
|-----------------|-------------|
| Instrument 1 | Xevo™ TQ-GC |
| Ionization Mode | EI+ |
| Electron energy | 70 eV |
| Emission | 300 µA |
| Source Temp. | 250 °C |
| Mass Range | m/z 10-650 |
| Scan Time | 0.1 s |
| GC Interface | 300 °C |

| MS Conditions | |
|----------------------------------|-------------------------|
| Instrument 2 | Xevo G2-XS QToF |
| Ionization Mode | APGC |
| Corona current | 3 µA |
| Sampling cone | 30 V |
| Source Temp. | 150 °C |
| Mass Range | m/z 10-1500 |
| Scan Time | 0.2 s |
| Cone gas | 50 L/h |
| Auxiliary gas | 550 L/h |
| MS ^E collision energy | Low 6 V High 15 to 45 V |
| GC Interface | 280 °C |

Data Acquisition and Processing:

Datasets were acquired and processed using MassLynx™ v.4.2 and MassFragment Software.

Due to the reproducible and characteristic degradation of most polymer standards by pyrolysis² both the py-GC-EI-MS and py-APGC-QToF MS were investigated for pyrolyzates library searching capabilities. However, spectral libraries for pyrolyzates are not freely available. Therefore, to search the pyrograms of plastic samples and help identify any chemical constituents, in-house spectral libraries were created.

A library for each instrument platform was built from the averaged mass spectrum obtained from pure polymer standards and used within an existing NIST spectral library platform (Figure 3). Once created, plastic and biobased plastic samples were analyzed under the same conditions as the polymer standards. Averaged mass spectrum were generated from these pyrograms and then searched against the in-house spectral libraries for matches. Data was collected in full scan on the instruments and both the py-GC-EI-MS and the py-APGC-QToF MS libraries showed comparative results.

Soft ionization is critical when undertaking characterization due to the presence of the molecular ions. On traditional vacuum GC-MS instruments, soft ionization is normally achieved by chemical ionization (CI) in positive or negative ionization mode. This often requires venting the MS, exchanging the ion source with a dedicated CI, conditioning the source, and using additional chemical reagent gases, adding to the analysis cost, time, and complexity. APGC, an ionization technique similar to atmospheric pressure chemical ionization, uses a corona discharge, enabling softer ionization. Higher masses can be seen than with EI due to the reduced ionization-induced fragmentation, as demonstrated in Figure 6 for the tetramer at m/z 416 of polystyrene.

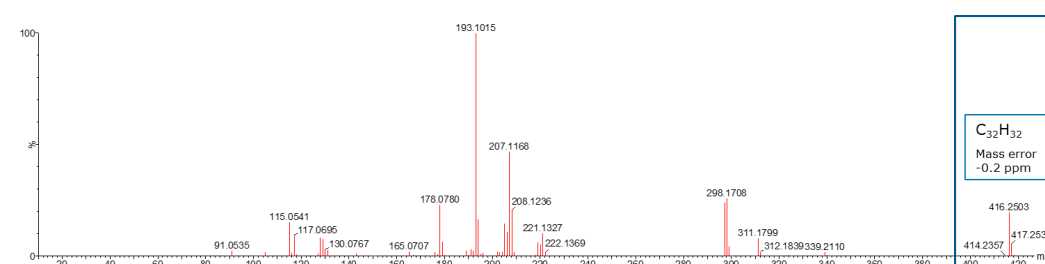


Figure 6. Polystyrene tetramer at m/z 416 for polystyrene.

RESULTS: CHARACTERIZATION

Using APGC-QToF MS for polymers, soft ionization and MS^E can be combined to analyze complex samples where compounds cannot be found in a library. A number of commercially available bioplastic bags (BIOTEC GmbH & Co. KG) were analyzed under the same conditions as the polymer standards. An example pyrogram is shown in Figure 9.

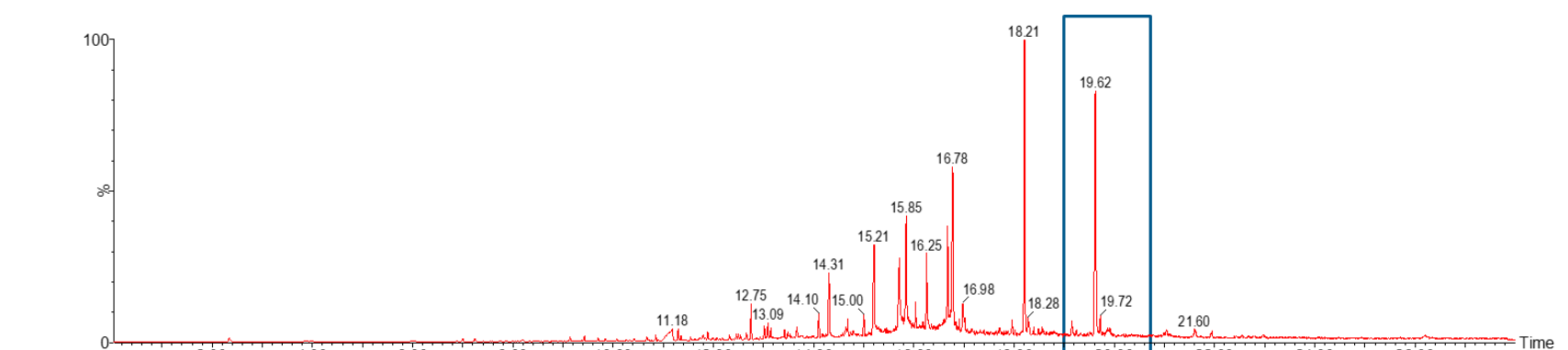


Figure 9. Pyrogram of a biobased plastic bag (Bioplast™ 500 bag).

The high and low energy mass spectrum were created for the peak at retention time 19.62 min (Figure 10). An elemental composition was predicted using the accurate mass of the molecular ion, and the peak was putatively assigned as erucamide. Using MassFragment, the *.mol file for this compound (obtained from Chempidder) was searched against the accurate mass fragments of the high energy spectra, with many matches made, increasing confidence in this identification. MassFragment assigns the proposed *.mol chemical structure of erucamide to the measured fragment ions by applying novel algorithms to known precursor structures.⁵ For a 100% match a reference sample would be needed, however, this tool saves analyst's time in the elucidation process.

RESULTS: LIBRARIES

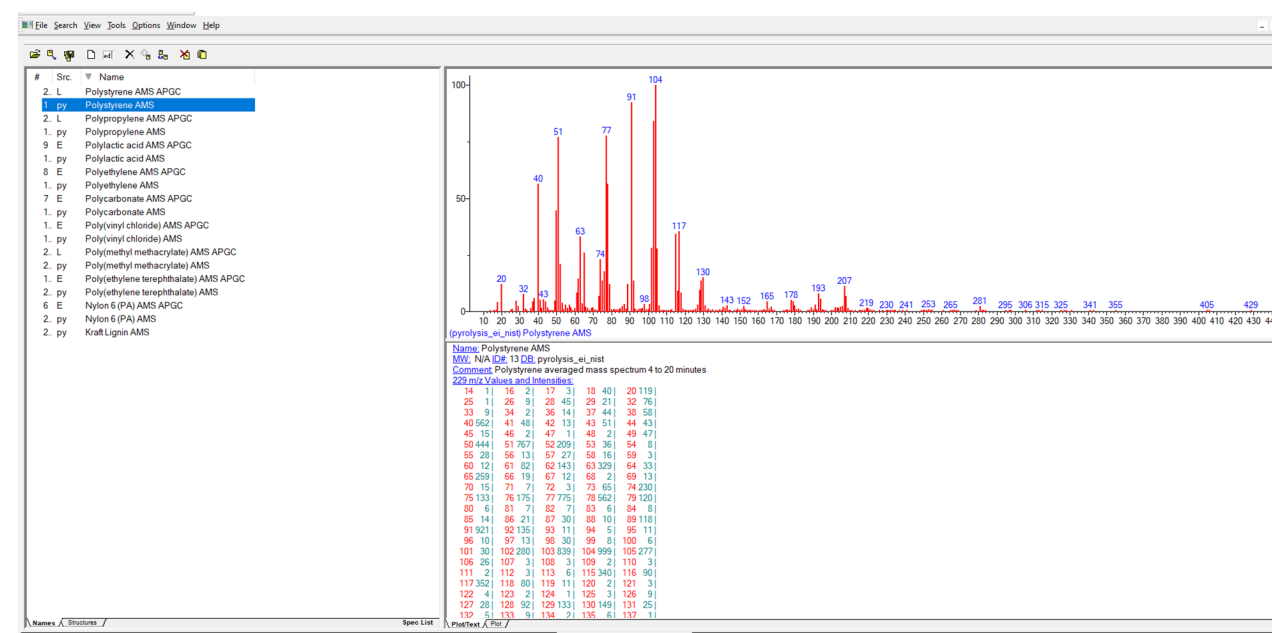


Figure 3. Library entries created from the polymer standards analyzed.

RESULTS: COMPARISON

In Figure 7, a compound identified at m/z 194.2374, (assigned as N-(5-cyanopentyl)pent-4-enamide, C₁₁H₁₈ON₂)² was found in the APGC pyrogram of the polymer, polycapraamide (Nylon 6), with the protonated molecular ion present. The corresponding chromatographic peak in the EI pyrogram had the appropriate mass fragments but without the presence of the molecular ion.

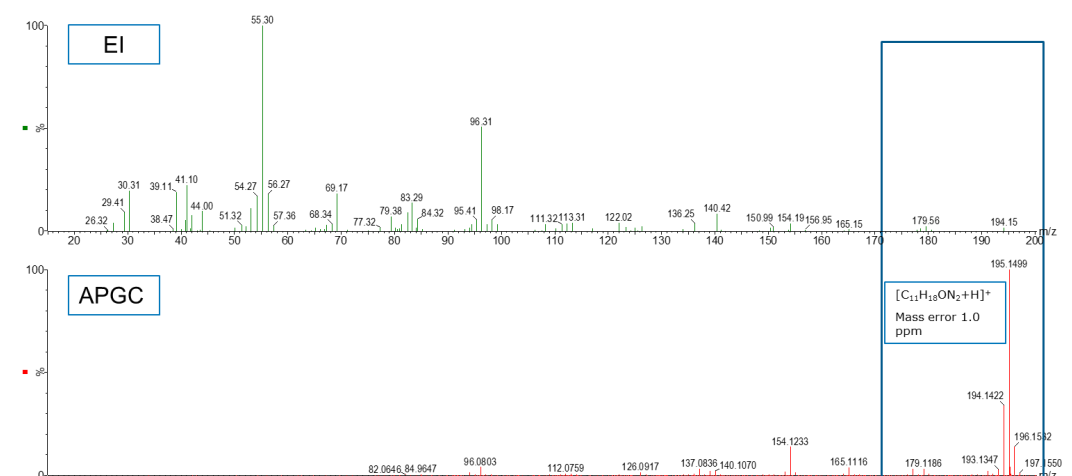


Figure 7. Comparison of Nylon 6 spectra from EI and APGC highlighting the presence of the protonated molecular ion in APGC.

For example, the spectra search, Figure 4, 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 match and reversed scores being 830 and 834, respectively. 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 866 and 866, respectively (Figure 5).



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

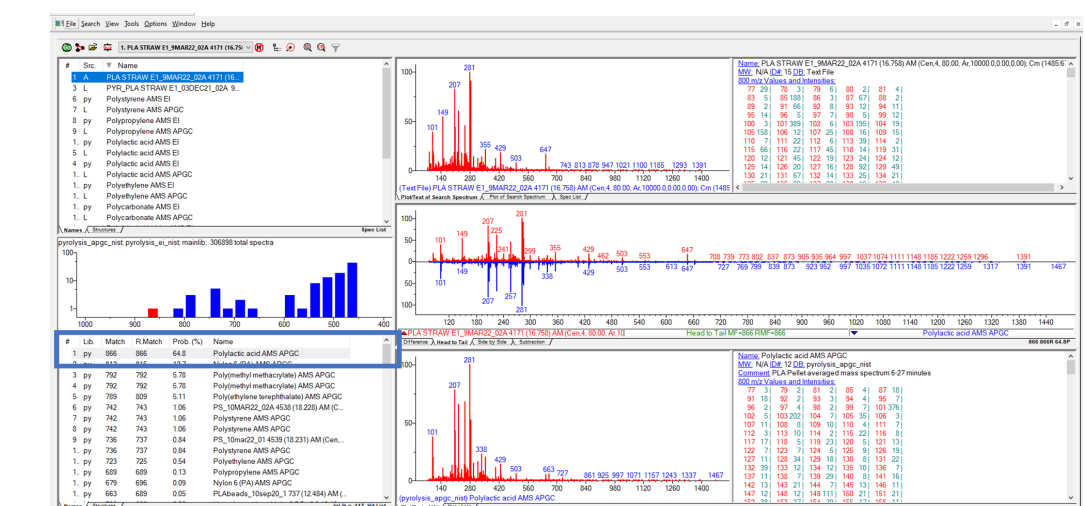


Figure 5. Library match and reversed scores for PLA in the py-APGC-QToF MS library

Another advantage of the APGC-QToF MS is the use of MS^E where high and low collision energies are alternated so that the accurate mass of both precursor and fragments ion can be simultaneously acquired. For the compound identified at m/z 194.2374, Figure 8 demonstrates the high and low energy spectra for the peak, showing increased fragmentation with the higher collision energy.

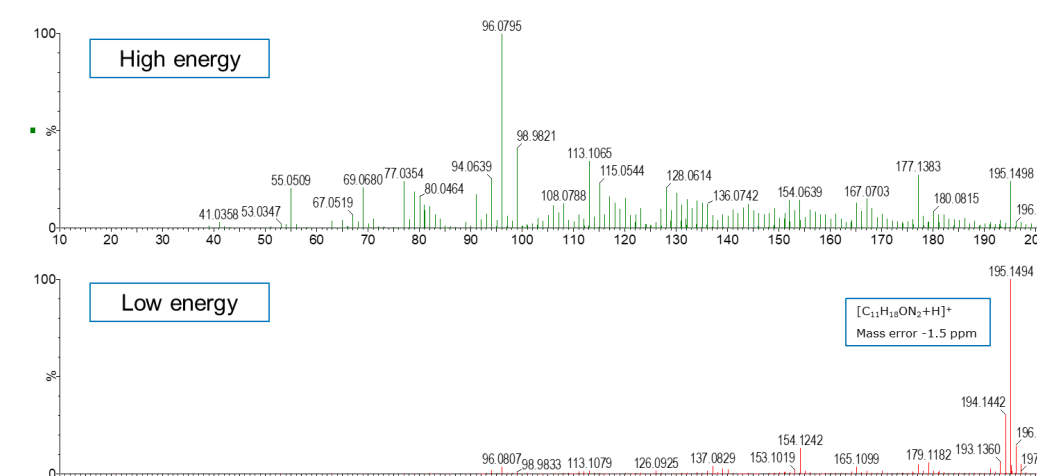


Figure 8. The high and low energy spectra for the protonated ion of N-(5-cyanopentyl)pent-4-enamide using MS^E.

CONCLUSION

- These preliminary results are indicative of promising analytical tools to combine the identification of polymers present within a sample with further characterization of plastic products.
- Due to the reproducible and characteristic degradation of most polymer standards² both py-GC-EI-MS and py-APGC-QToF MS can be utilized for library creation from the averaged mass spectrum of polymer standards.
- Furthermore the results obtained indicate that pyrolysis-APGC-QToF MS is a useful tool for laboratories focusing on compositional analysis of complex polymer materials.
- APGC uses soft ionization reducing fragmentation and promoting the presence of the molecular ion assisting with the identification of unknowns.
- MS^E enabled MS allows for the collection of both the accurate mass of precursor and fragment ions which is key for the structural elucidation of unknowns within a sample.
- Both platforms described can be utilized when library searching is needed. Where further characterization of plastic products impurities, and additives is required then py-APGC-QToF MS provides the necessary tools

References

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Figure 1. Pyrolyzer coupled to the APGC QToF mass spectrometer.

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