

## Pyrolysis-Gas Chromatography-High Resolution Mass Spectrometry with Soft Ionization for Increased Confidence of Polymer Characterization

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### Abstract

This application note highlights a comparison between classical pyrolysis-GC with EI-Tandem Quadrupole MS and pyrolysis-APGC coupled to a QToF MS. The analytical advantages of soft ionization and high resolution accurate mass acquisition were explored for the analysis of polymer standards and biobased plastic bags. Additionally, software tools to assist putative identification of compounds are highlighted. This instrument configuration demonstrates an effective tool for the characterization of complex post consumer, industrial or biobased polymeric materials.

### Benefits

- Pyrolysis-APGC-QToF MS is an effective analytical tool for laboratories focusing on compositional analysis of complex polymer materials using gas phase separation
- Soft ionization using APGC allows for molecular ion detection to assist with the confirmation of chemical

elemental composition, structural elucidation, and ultimately, for compound identification

- The soft ionization can be achieved in a more time efficient workflow than is possible with traditional vacuum GC-MS instruments
- The MS<sup>E</sup> data acquisition mode allows for the collection of both the accurate mass of precursor and fragment ions, key for the structural elucidation of unknowns within a sample

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## Introduction

Scientific interest is growing in sustainable polymers and natural materials to increase recycling and develop biobased plastics to replace single use oil-based 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 around the presence of additives and potential contaminants. This could potentially require more in-depth evaluation of the chemical make-up of the polymer formulations.<sup>1</sup>

In the field of polymer research, pyrolysis coupled to gas chromatography-mass spectrometry (GC-MS) has been extensively used and is becoming increasingly prominent<sup>2</sup> for samples that are not amenable to solubilization.<sup>3</sup>

However, the high energy of electron ionization (EI) leads to insufficient sensitivity and selectivity for undertaking the characterization of polymers and the identification of additives and potential contaminants by this technique. Pyrolysis-GC with soft ionization high resolution mass spectrometry (HRMS) is a complementary technique used in this field to help address some of these limitations. Atmospheric pressure gas chromatography (APGC) is an ionization technique similar to atmospheric pressure chemical ionization, which uses a corona discharge, enabling softer ionization. This results 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<sup>E</sup> mode, whereby both low and high collision energy spectra are simultaneously acquired. Using this technique, the accurate mass of both precursor and fragment ions are available to provide information for structural elucidation and ultimately aid compound identification.<sup>4</sup>

In the experiments described, a comparison between classical pyrolysis-GC with EI-Tandem Quadrupole MS and pyrolysis-APGC coupled to a QToF MS was performed. The analytical advantages of soft ionization and accurate

mass acquisition were explored. Additionally, MassFragment, a software tool to assist putative identification of compounds, is highlighted.

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## Experimental

### Sample Description

A selection of polymer standards and commercially available biobased plastic bags (BIOTEC GmbH & Co. KG) were weighed to approximately 0.1 mg and loaded into glass capillaries between two plugs of quartz wool and placed into the pyrolyzer autosampler. All samples were acquired in triplicate on two instruments: Xevo™ TQ-GC with an EI source and Xevo G2-XS QToF with an APGC™ source.

### Method Conditions

#### Pyrolysis Conditions

Pyrolyzer: CDS 5000, CDS analytical

Inlet temp.: 310 °C

Ramp rate: 20 °C/ms

Final temp.: 750 °C

#### GC Conditions

Inlet mode: Split

Split ratio: 75:1

Split flow: 75 mL/min

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Inlet temp.:	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 temp.:	250 °C
Mass range:	<i>m/z</i> 10–650
Scan time:	0.1 s
GC interface temp.:	300 °C

## System 2: Xevo G2-XS QTof

Ionization mode:	APGC+
Corona current:	3 $\mu$ A
Sampling cone:	30 V
Source temp.:	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 temp.:	280 °C
MS <sup>E</sup> collision energy:	Low energy 6 V High energy 15–45 V

## Data Management

Data acquisition, processing and reporting were performed using Waters MassLynx™ 4.2. Software. Putative identifications were made using MassFragment.

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## Results and Discussion

The total ion pyrograms from the polymer standards acquired with the two different instruments were compared. From an initial appraisal, it was clear that the py-APGC-QToF MS technique was more information rich. This can

be seen here in the case of the polystyrene standard shown in Figure 1. The region highlighted from 12 to 17.5 minutes shows the presence of a greater number of peaks. There are differences in retention times between the two data sets due to the presence of a vacuum at the outlet of the column on the TQ-GC, whereas the APGC source is at atmospheric pressure.

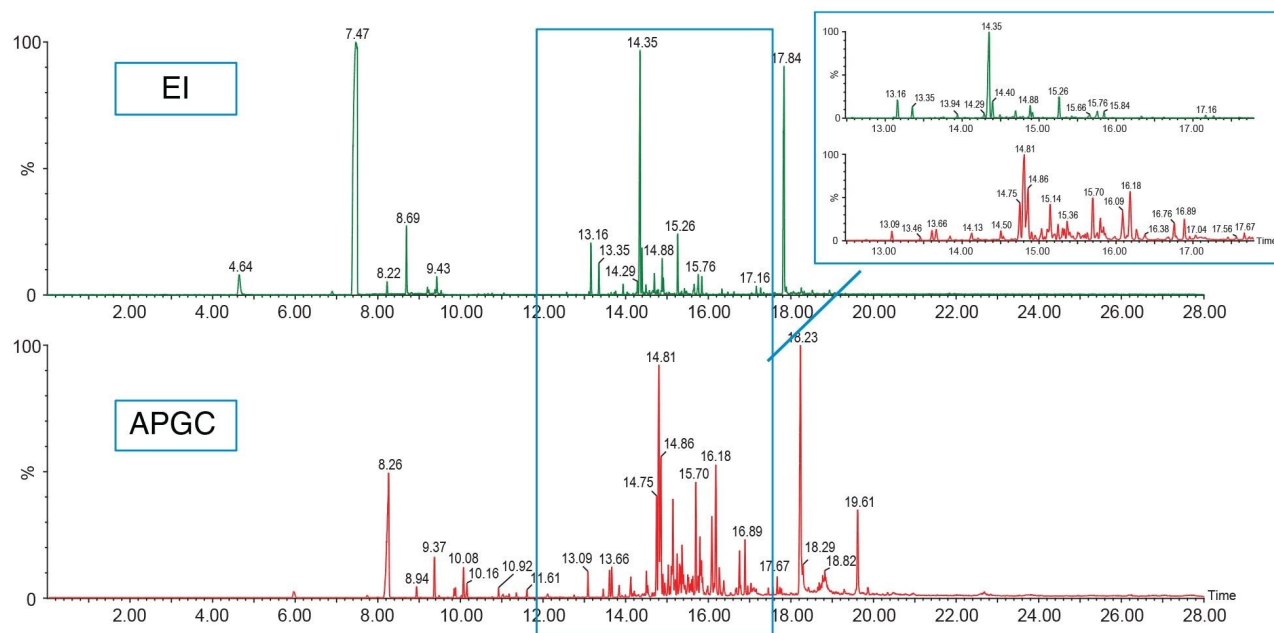


Figure 1. Comparison of total ion pyrograms from EI full scan data (in green) to APGC full scan data (in red) for the polystyrene standard.

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 source followed by conditioning of the source, and using additional chemical reagent gases, which all add to the analysis cost, time, and complexity of the analysis. With APGC, soft ionization can be achieved without these steps, providing a more time efficient workflow.

Interrogation of the peaks within the pyrograms of the two techniques highlighted more benefits of using APGC. In the case of the polystyrene standard, the mass spectrum was investigated for the presence of the masses that should typically be detected by pyrolysis-GC-MS.<sup>1</sup> Whilst the styrene monomer, dimer, and trimer could be

detected via both ionization techniques, the tetramer at  $m/z$  416.2504 could only be detected via APGC (Figure 2) due to the reduced ionization-induced fragmentation.

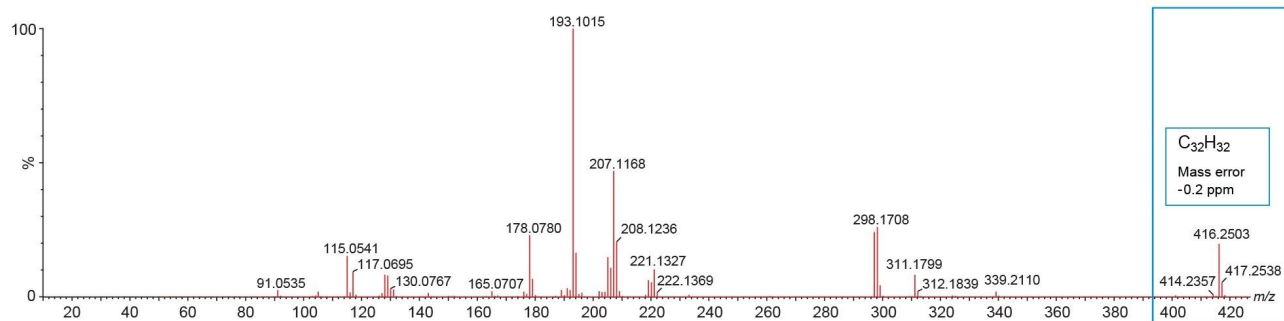


Figure 2. APGC spectrum of the polystyrene tetramer peak eluting at retention time 22.69 minutes with  $m/z$  416.2503 corresponding to the  $[M]_4^+$  cation ( $C_{32}H_{32}$ ).

For some compounds, the use of the softer ionization of APGC results in the presence of the molecular ion, which is critical when detection and confirmation of the molecular ion is required. This is demonstrated here for the polymer, polycapraamide (Nylon 6). In Figure 3, a compound identified at  $m/z$  194.2374, (assigned as N-(5-cyanopentyl)pent-4-enamide,  $C_{11}H_{18}ON_2$ )<sup>2</sup> was found in the APGC pyrogram 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.

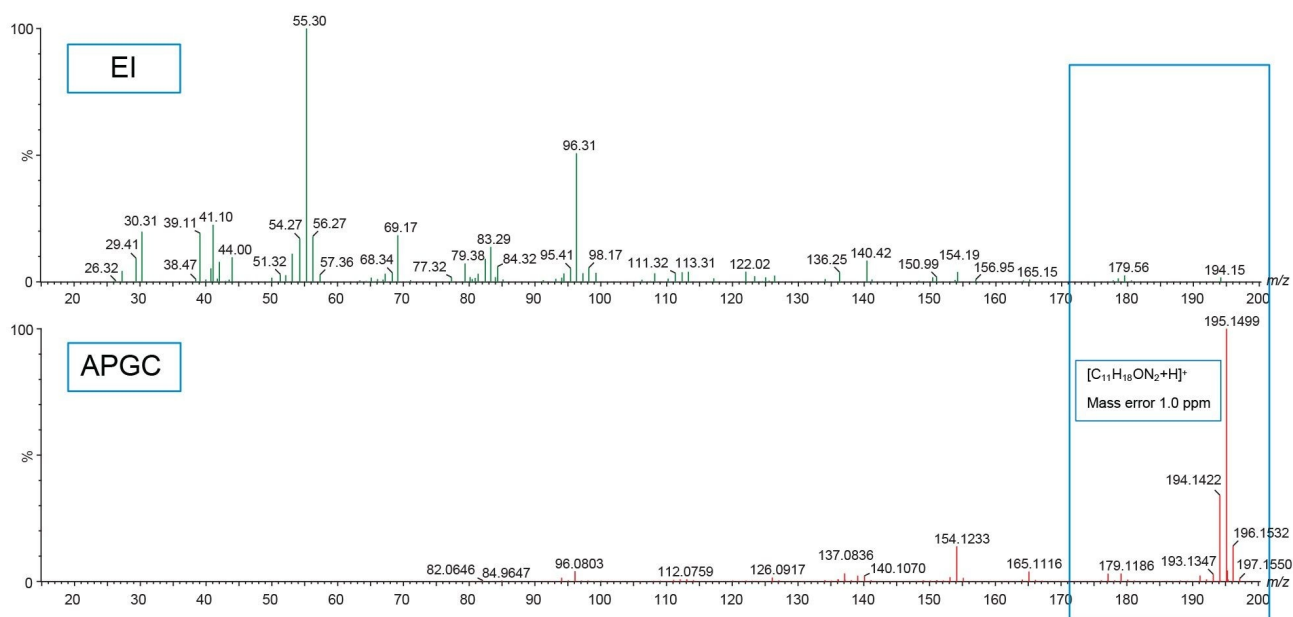


Figure 3. Comparison of Nylon 6 spectra from EI and APGC highlighting the presence of the protonated molecular ion in APGC.

Another advantage of the APGC-QToF MS is the use of MS<sup>E</sup> where high and low collision energies are alternated so that the accurate mass of both precursor and fragments ion can be simultaneously acquired. This assists with the structural elucidation of unknowns. For the compound identified at  $m/z$  194.2374, Figure 4 demonstrates the high and low energy spectra for the peak, showing increased fragmentation with the higher collision energy.



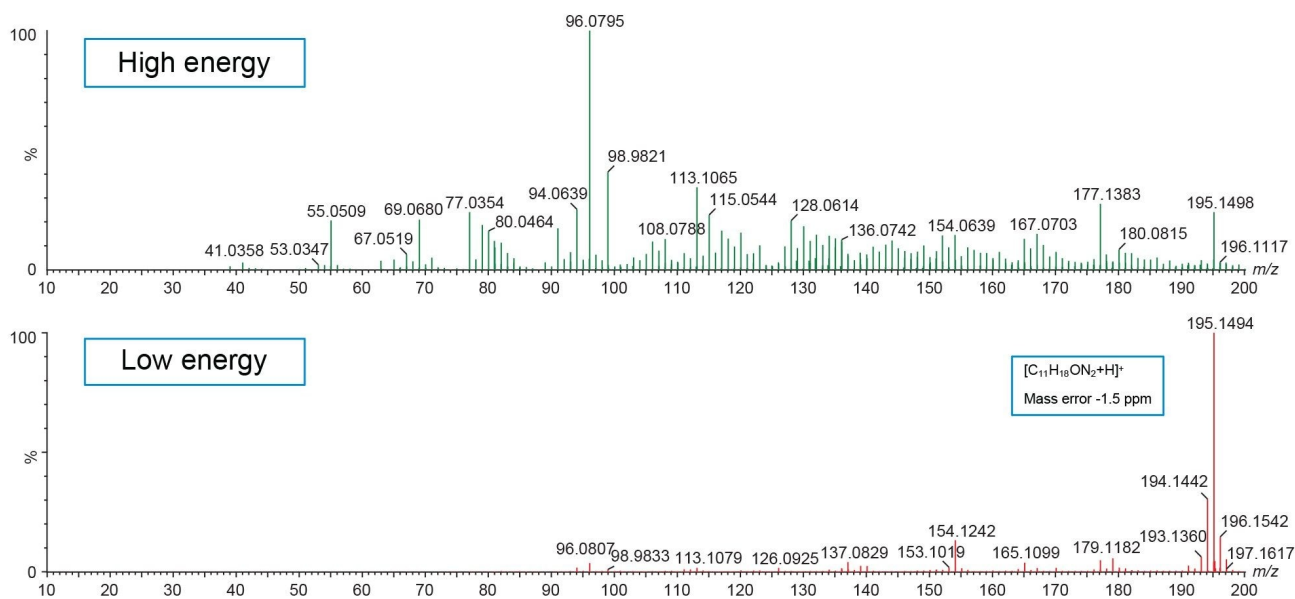


Figure 4. Example of high and low energy spectra for the protonated ion of *N*-(5-cyanopentyl)pent-4-enamide using  $MS^E$ .

## Identification

Using APGC-QToF MS for polymers, soft ionization results in detection of higher masses and gives rise to the presence of the molecular ion which assists with elemental composition prediction. Additionally, if  $MS^E$  is implemented, the accurate mass of both the precursor and fragment ions are acquired. Combining these tools is critical for the elucidation of unknowns where compounds cannot be found in a library. Commercially available bioplastic bags (BIOTEC GmbH & Co. KG) were analyzed. An example pyrogram for a plastic bag sample (Bioplast 500) is shown in Figure 5 using the using the APGC-Xevo G2-XS QToF with  $MS^E$ .

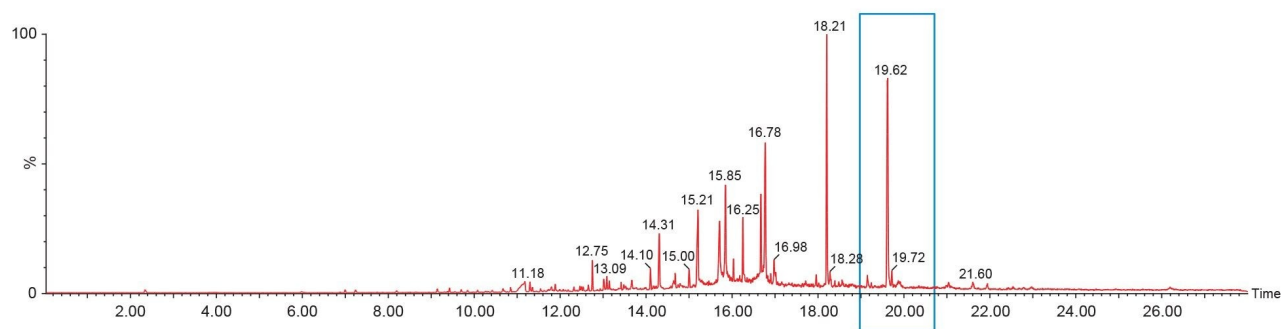


Figure 5. Pyrogram of a biobased plastic bag (Bioplast 500).

The high and low energy mass spectrum were generated for the peak at retention time 19.62 minutes (Figure 6). An elemental composition was predicted using the accurate mass of the molecular ion, and the peak was putatively assigned as erucamide. MassFragment, a software tool to assist identification of compounds, was employed directly from the spectra. The \*.mol file for this compound (obtained from Chemspider) 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.<sup>5</sup> This approach is based on systematic bond disconnection of the precursor structure instead of the traditional rule-based approach. For a 100% match a reference sample would be needed, however, this tool saves analyst's time in the elucidation process.

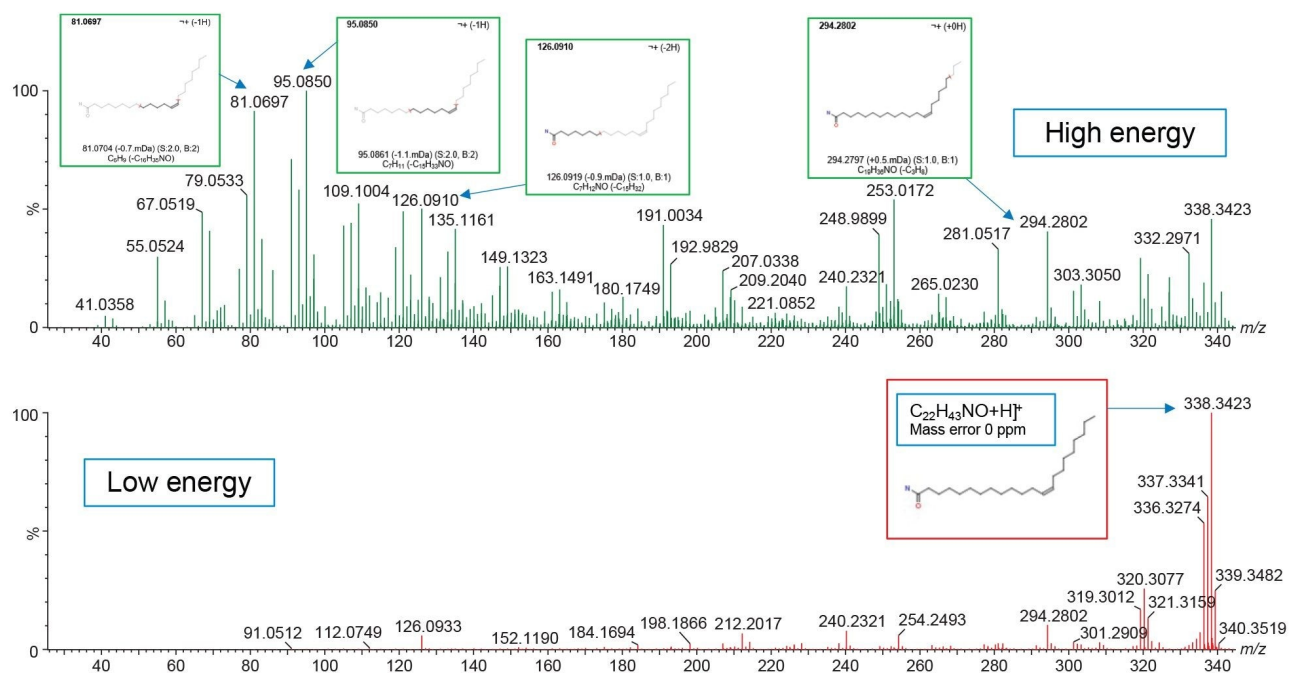


Figure 6. High and low energy spectra for  $m/z$  338.3423 corresponding to the protonated ion of erucamide using  $MS^E$ . Mass fragments assigned by MassFragment.

## Conclusion

The results obtained in the experiments described in this application note demonstrate that pyrolysis-APGC-QToF MS is an effective analytical tool for laboratories focusing on compositional analysis of complex polymer samples using gas phase separations and for materials that are not amenable to solubilization.

Typical py-GC-EI-MS is challenged by insufficient sensitivity and selectivity to undertake characterization of polymers and the identification of additives and potential contaminants. APGC uses soft ionization reducing fragmentation and promoting the presence of the molecular ion assisting with elemental composition prediction. This technique eliminates the need for time consuming chemical ionization that is usually employed by dedicated vacuum GC-MS systems, a necessary step that would be needed to confirm the molecular ions of fragmented electron ionization compounds. This will require instrument venting, source replacement and conditioning, and

optimization of reagent gas, all adding to the time and cost of the analysis.

Further to this, MS<sup>E</sup> data acquisition 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. Together this technology offers a unique solution for increasing confidence in the data for the characterization of unknowns in post consumer, industrial or biobased polymeric materials.

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## References

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