Enhancing Characterization of Mixed Polymers with a Mass Spectral Processing Software for Py-GC-MS

Author:

Karen Sam

Application Note
General

Abstract
This application note demonstrates a polymer subtraction capability in Py-GC-MS data analysis software.

Introduction

A pyrogram of a pure polymer can often be complex, and interpretation may rely on a mass spectral database of polymers in combination with analyst expertise. Therefore, a mixture of polymers can be even more challenging to interpret. Here, specialized mass spectral processing software, CDS Mnova Plugin, which uses Mestrelab's Mnova MSChrom and a pyrolysis database of polymers, allows for analysis of Py-GC-MS data using a novel compound subtraction function. In this application note, this innovative algorithm was used to subtract one polymer in a two polymer mixture.

Results and Discussion

The CDS Mnova Plugin, which uses Mestralab's Mnova MSChrom and DB plugins, composes of a chromatographic processing software, search engine and database portal (p/n 10A1-3027) to perform searches on unknown pyrograms. A Py-GC-MS database (p/n 10A1-3026) and an EGA database (p/n 10A1-3025) with over 600 entries each, are available. Each database record includes a polymer name, synonyms, description, CAS number, linear formula, molecular structure, mass spectrum and chromatogram (Figure 1).

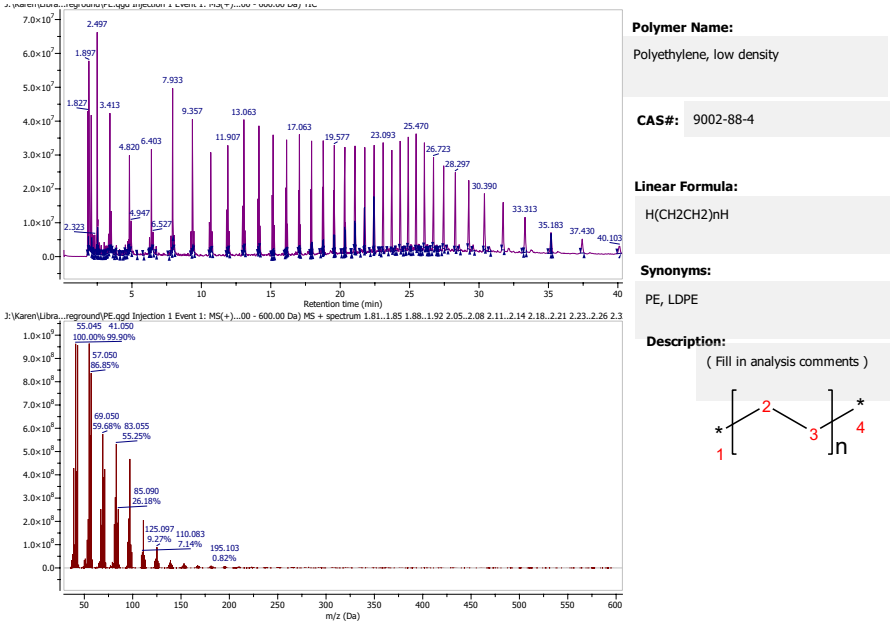


Figure 1. Pyrolysis Database Record

The workflow of analysis to perform a compare a sample against the polymer database is composed of 4 steps. Step 1 is to perform a baseline correction, which can be used to deduct a blank TIC from sample TIC data, therefore minimizing common mass spectra found in a blank chromatogram, like column bleed. Load the pyrogram, select the "Add MS Dataset" icon from the MS browser (Figure 2), then load the blank data into the MS browser (Figure 3). Figure 4 shows the sample and blank data loaded into the MS browser. Next, select "Function 1" of the

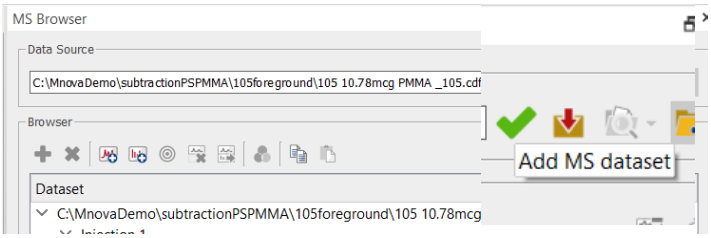


Figure 2. Add MS Dataset

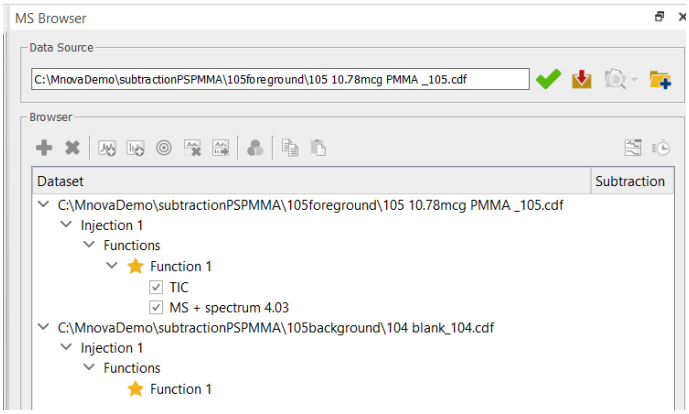


Figure 3. Blank data added to MS browser.

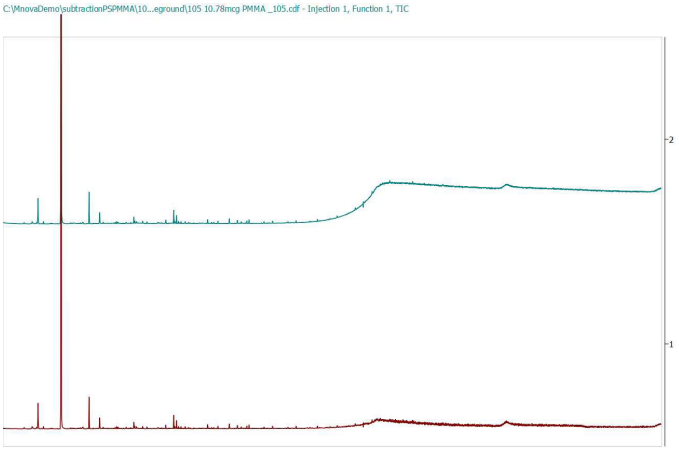


Figure 4. Before (top) and after (bottom) baseline correction.

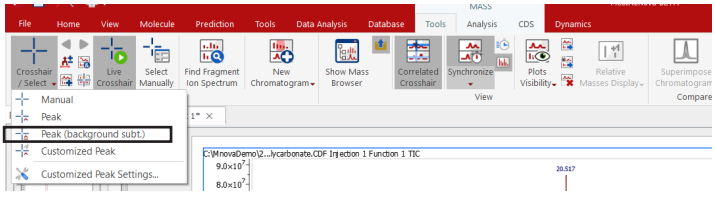


Figure 5. Step 2: Choose Peak (background subt.) tool.

sample data, and then the MS Subtraction Icon. In the dialogue box that opens, select the data to dialogue box that opens, select the data to be subtracted (function 1). MSChrom then calculates a new, baseline subtracted chromatogram (Figure 4).

Step 2 is to co-add the mass spectra of each peak with each other in the TIC. This is done by selecting Peak (background subt.) under the Crosshair Select Icon of the Mass Tools Ribbon (Figure 5). The Peak (background subt.) tool allows a user to select mass spectra of peaks to display, in which the tails of each peak are not included in the mass spectrum, to provide cleaner data. After selecting this option, left-clicking, holding and dragging across the chromatogram (Figure 6), will display the co-added mass spectrum will be displayed under the chromatogram.

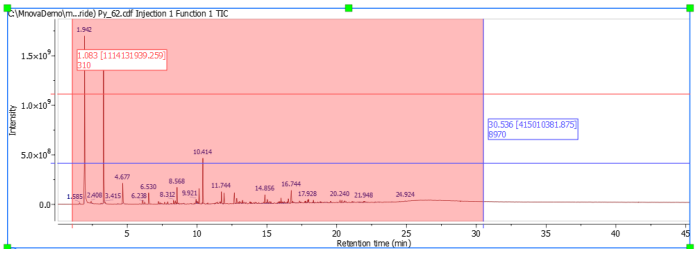


Figure 6. Co-adding integrated peaks to create a composite mass spectrum.

Step 3 is to search the database using the composite mass spectrum which is performed by right clicking on the displayed mass spectrum, and selecting MS Search (Figure 7). This will produce a list of search results (Figure 8). Each or all of the records can be examined by highlighting, and selecting “OK”, which will open the record in the database browser (Figure 9). The unknown and the record mass spectra can be compared by dragging the Mass Spectrum Mass Data entry in the Scores Section to the Spectral View section. The unknown, or Query, will be shown at the bottom and the database record will be shown at the top, in the Spectral View Section (Figure 10).

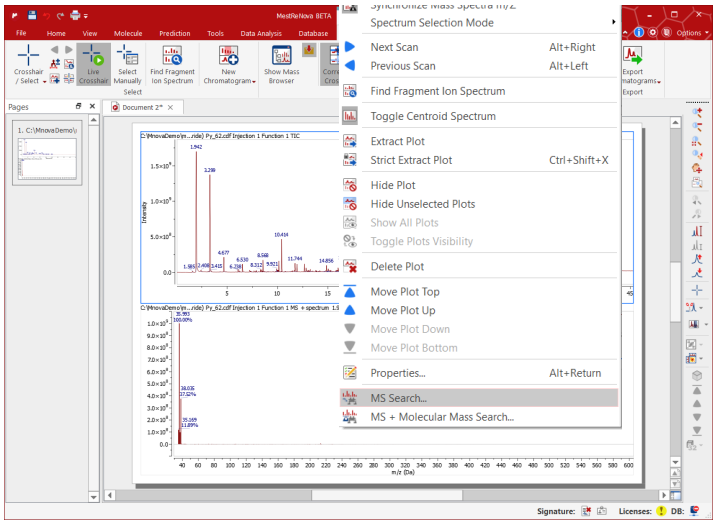


Figure 7. Step 3: Searching the Co-added mass spectrum.

Step 4 is to transfer the database record to MSChrom by selecting the record in the Scores Section, right-clicking, and chosing “Paste Record to Mnova” (Figure 11). A second page will open in MSChrom that will contain the database record.

Chromatograms of both the unknown and the record can be put on the same page for comparison by pressing “shift”, and selecting both pages in the “Pages” Field, then choosing “Export and Stack All Chromatograms” from the “Export Chromatograms” Icon in the “Tools” Ribbon (Figure 12). This will create a new page in the document that has the unknown chromatogram and the database record chromatogram on the same page (Figure 13). This can be an excellent way of confirming a match result.

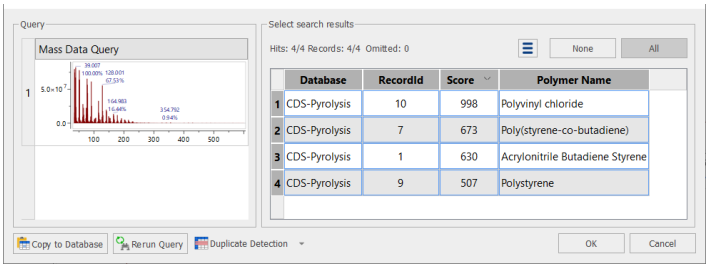


Figure 8. Database Search Results.

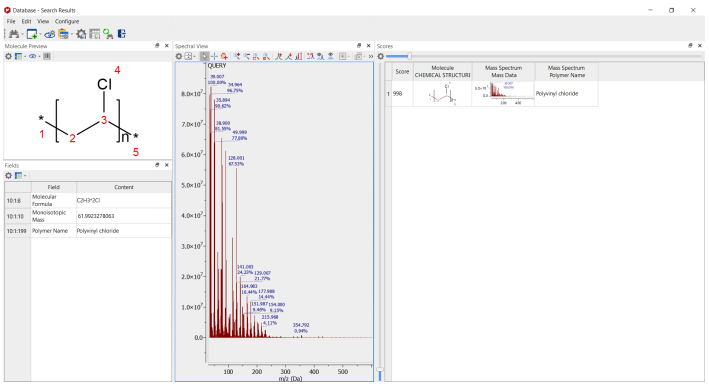


Figure 9. Database Record in Database Browser.

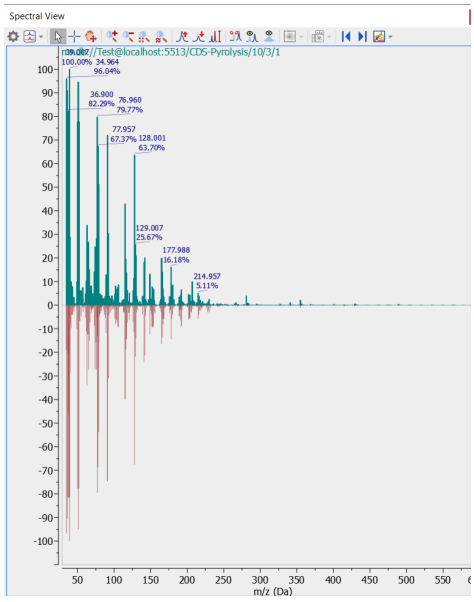


Figure 10. Database Match (top) and Unknown(bottom) Mass Spectrum in Spectral View of Database Browser.

However, a lot of Py-GC-MS analyses involve more than one polymer, so a simple mass spectral search may not provide a complete solution. Here, CDS Mnova Plugin’s Compound Subtraction function was used to subtract one polymer from a two polymer mixture. An example polymer mixture was pyrolyzed at 700°C. The database search’s top record was revealed as Polypropylene (Figure 14). When the two pyrograms were compared, peaks not seen in the record confirm the presence of additional material (Figure 15). A pyrogram of polypropylene was added to the MSChrom document, and the Compound Subtraction Icon, which allows for peak alignment and subtraction, was then selected under the CDS ribbon, shown in Figure 16. Using the interface, polypropylene’s largest peak, 2,4-dimethyl heptene at 5.59 minutes, was aligned on the x-axis (retention time) to the same peak in the mixture by graphically selecting them in each plot; a normalization factor was calculated to allow the background pyrogram to match the intensity of the mixture, and selecting “OK” performed the subtraction. Figure 17 shows that

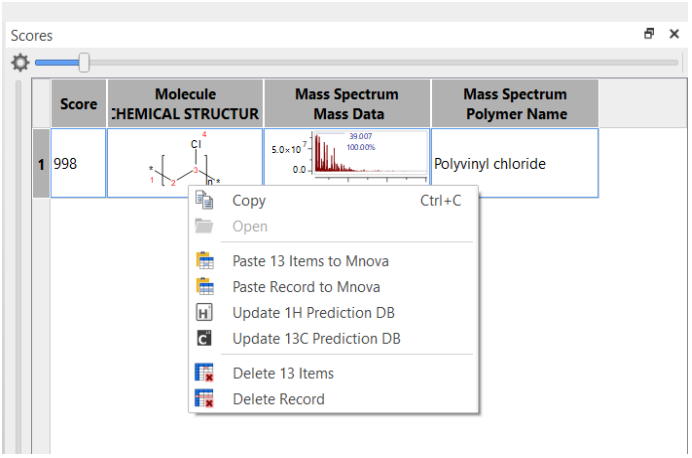


Figure 11. Step 4: Bringing Record to MSChrom, right click and select “Paste Record to Mnova”.

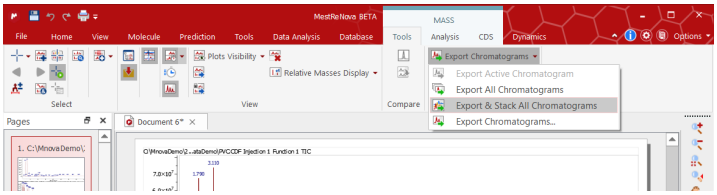


Figure 12. Exporting and Stacking Chromatograms from Unknown and Record.

the aligned peak had been removed after Compound Subtraction. When the compound subtracted pyrogram was searched against the pyrolysis database a new top match of polyethylene replaced the polypropylene hit (Figure 18). The compound subtracted mixture pyrogram now more closely resembles a polyethylene pyrogram (Figure 19), indicating the unknown is a mixture of polyethylene and polypropylene.

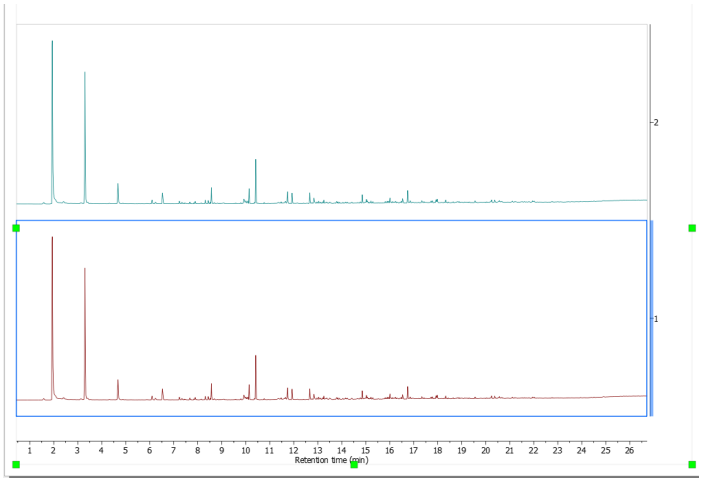
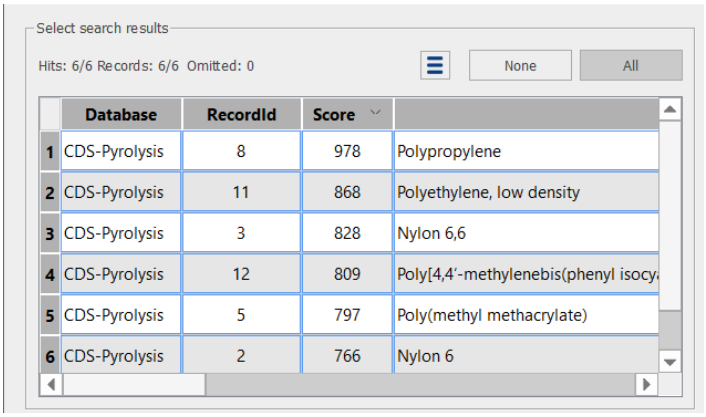


Figure 13. Unknown and Record Chromatograms Stacked for Comparison.



	Database	RecordId	Score	
1	CDS-Pyrolysis	8	978	Polypropylene
2	CDS-Pyrolysis	11	868	Polyethylene, low density
3	CDS-Pyrolysis	3	828	Nylon 6,6
4	CDS-Pyrolysis	12	809	Poly[4,4'-methylenebis(phenyl isocy
5	CDS-Pyrolysis	5	797	Poly(methyl methacrylate)
6	CDS-Pyrolysis	2	766	Nylon 6

Figure 14. Polymer Mixture Search Results.

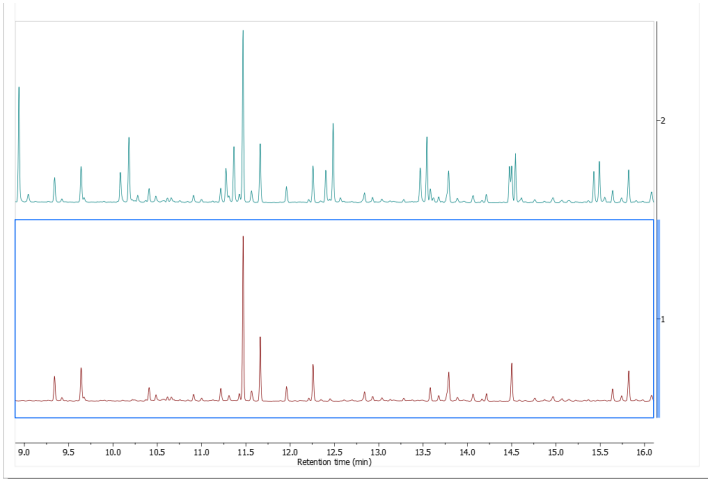


Figure 15. Unknown (top) vs. Polypropylene (bottom).

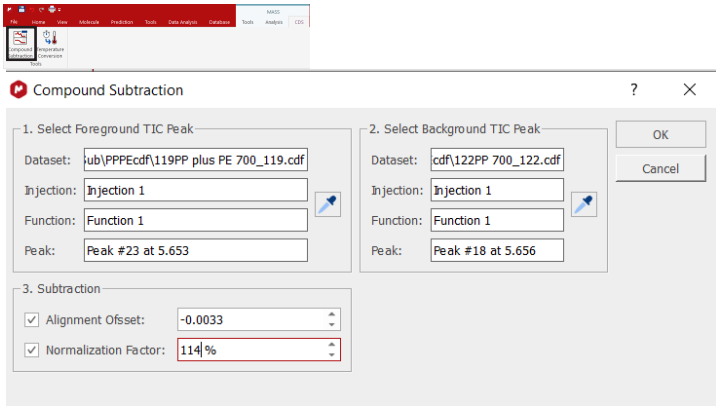


Figure 16. Compound Subtraction Interface.

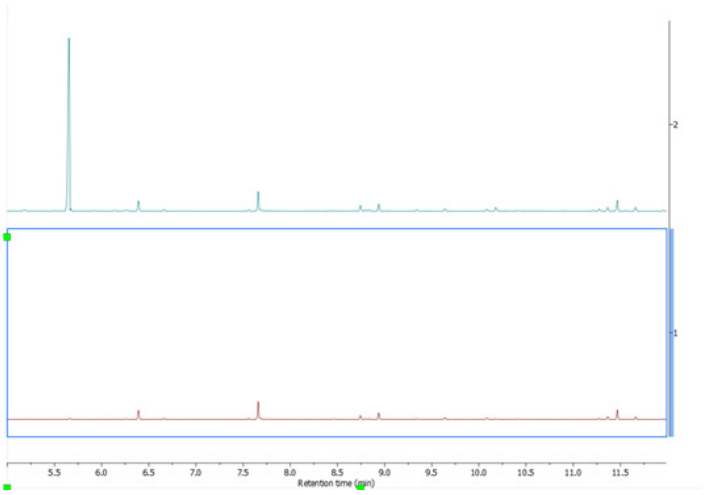
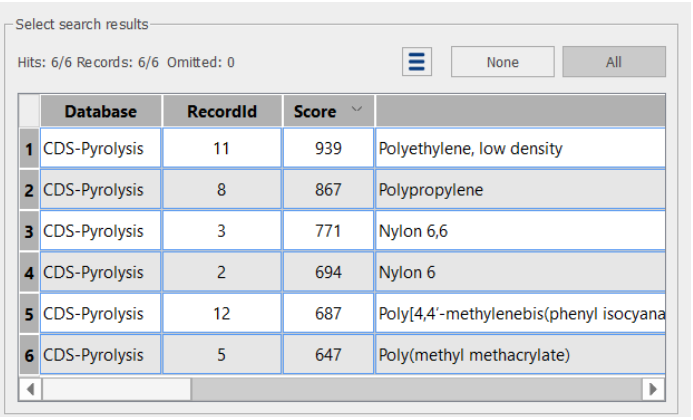


Figure 17. Mixture before (top) and after (bottom) chromatogram subtraction was performed.



	Database	RecordId	Score	
1	CDS-Pyrolysis	11	939	Polyethylene, low density
2	CDS-Pyrolysis	8	867	Polypropylene
3	CDS-Pyrolysis	3	771	Nylon 6,6
4	CDS-Pyrolysis	2	694	Nylon 6
5	CDS-Pyrolysis	12	687	Poly[4,4'-methylenebis(phenyl isocyana
6	CDS-Pyrolysis	5	647	Poly(methyl methacrylate)

Figure 18. New Search on Compound Subtracted Data reveals new top Record (Polyethylene).

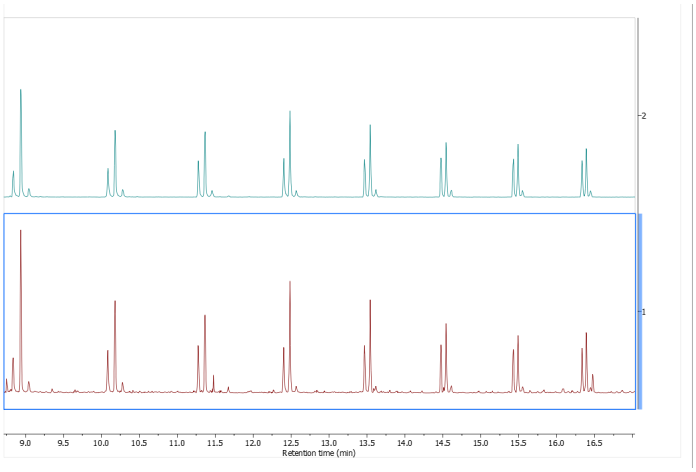


Figure 19. Polyethylene Pyrogram (top) and Compound Subtracted Pyrogram (bottom).

Conclusion

Py-GC-MS data interpretation comes with challenges; tools used include mass spectral databases and analyst knowledge. In addition, co-polymer mixtures may be more challenging to interpret. Here, the CDS Mnova Plugin enables deconvolution of a polymer mixture of polyethylene and polypropylene via compound subtraction together with a pyrolysis database of polymers.