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

Author:

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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 MS processing software, MSChrom, together with a pyrolysis database of polymers, allows for analysis of py-gc-ms data using a novel compound subtraction feature. In this application note, this innovative algorithm was used to subtract one polymer in a two polymer mixture.

Results and Discussion

MSChrom plus py-gc-ms database composes of a chromatographic processing software with search engine that can access a pyrolysis database to perform searches on unknown pyrograms. Each database record includes a polymer name, synonyms, description, CAS number, linear formula, molecular structure, mass spectrum and a chromatogram (Figure 1).
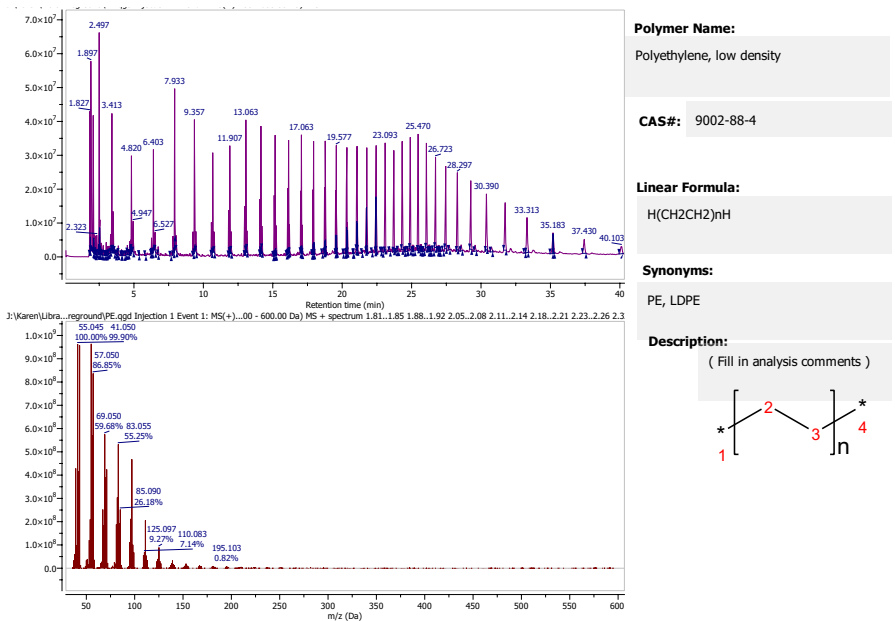

Figure 1. Pyrolysis Database Record

The workflow of analysis for is composed of 4 steps. Step 1 is to perform a batch 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. Three folders are created in Windows; a background, foreground, and output folder (Figure 2). Blank chromatogram data is dragged into the background folder, and sample chromatogram data into the foreground folder. Then the Chromatogram Subtraction function is accessed, which can be found under the Report Icon from the Tools Ribbon in MSChrom (Figure 3). Data pathways for the respective folders, as well as the datafile instrument type (Path

Mask) are inputted into the dialogue box (Figure 4). For the Path Mask, "*." and then the file extension is entered, and Single Background Spectrum, and Arithmetic Precision 1 is selected.
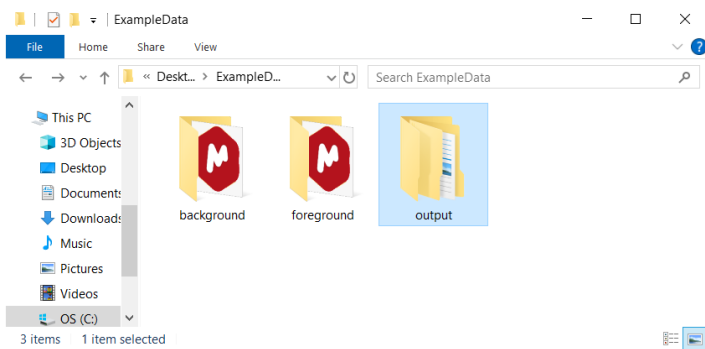

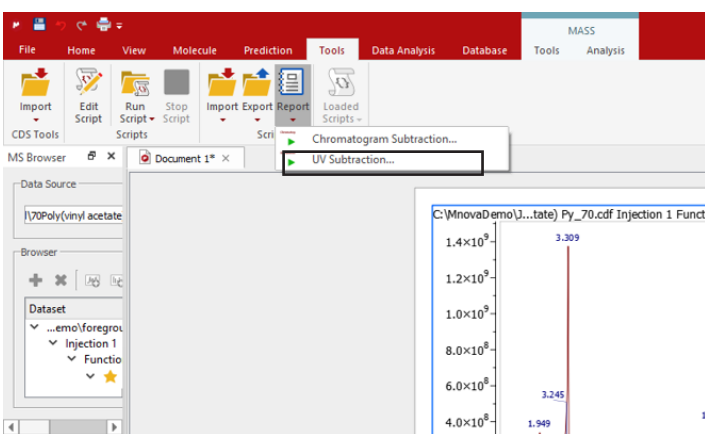Figure 2. Three folders created for corresponding TIC data.

Figure 3. Step 1: Batch Process Baseline Correction.

MSChrom then proceeds with the baseline correction process (Figure 5), then places a folder of newly corrected data in the specified output folder (Figure 6). Each file in this folder can be brought over to MSChrom, by dragging from Windows and dropping into the program.

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 7). 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 8), will display the co-added mass spectrum will be displayed under the chromatogram.

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 9). This will produce a list of search results (Figure 10). Each or all of the records can be examined by highlighting, and selecting "OK", which will open the record in the database browser (Figure 11). The unknown and the record mass spectra can be compared by
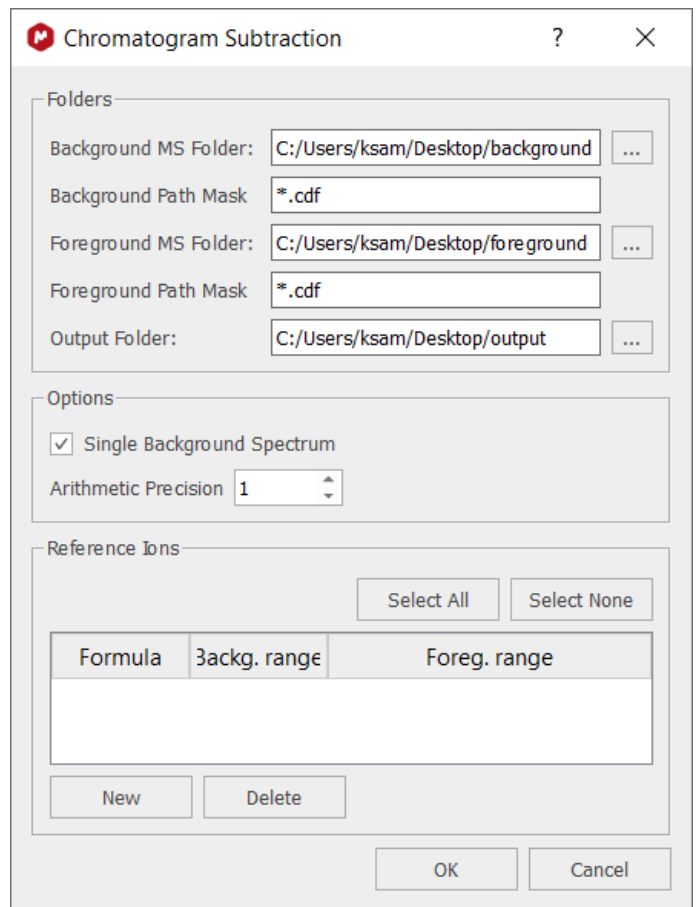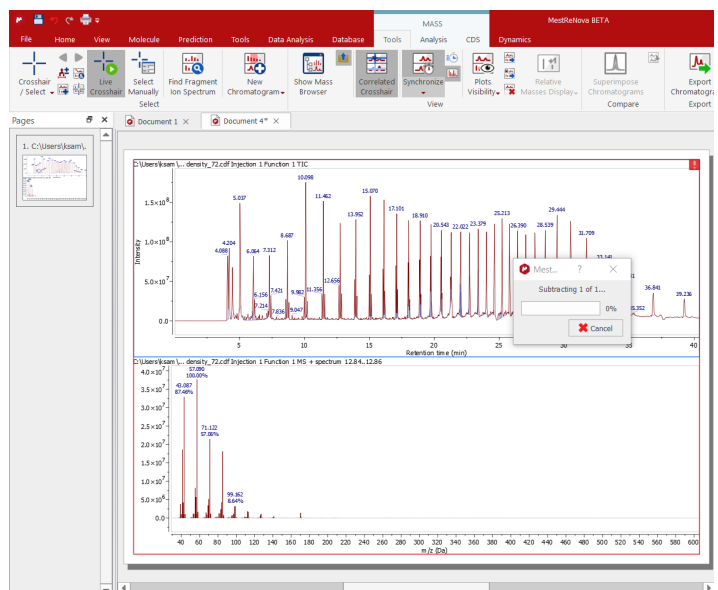

Figure 4. Baseline Correction Dialogue Box

Figure 5. Baseline Correction in Process.

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 12).

In step 4, the database record can be transferred to MSChrom by selecting the record in the Scores Section, right-clicking, and chosing "Paste Record to Mnova" (Figure 13).
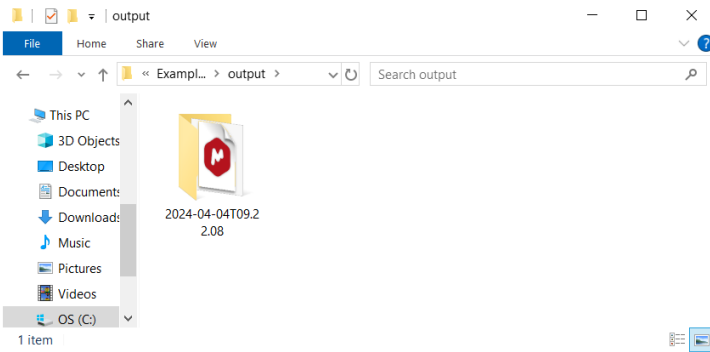
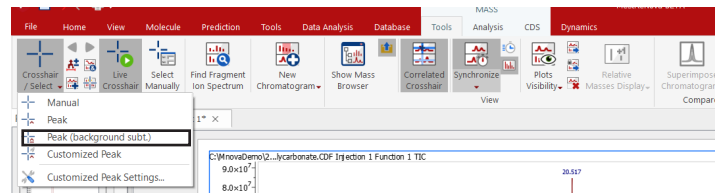Figure 6. New Baseline Corrected Data Folder Created in Output Folder.

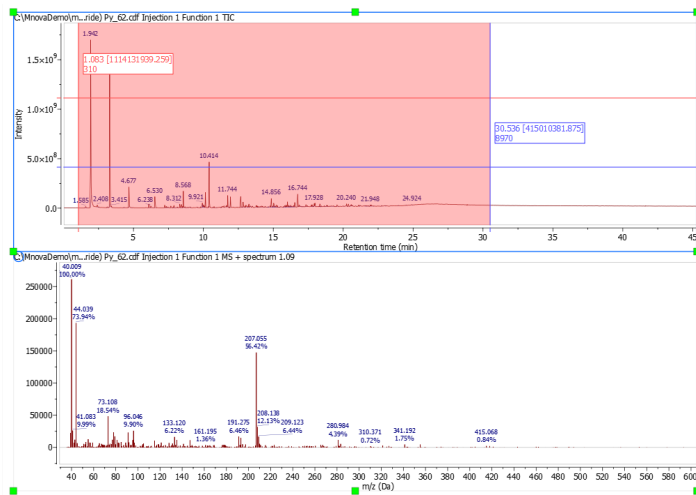Figure 7. Step 2: Choose Peak (background subt.) tool.

Figure 8. Co-adding integrated peaks (top) to create a composite mass spectrum (bottom).
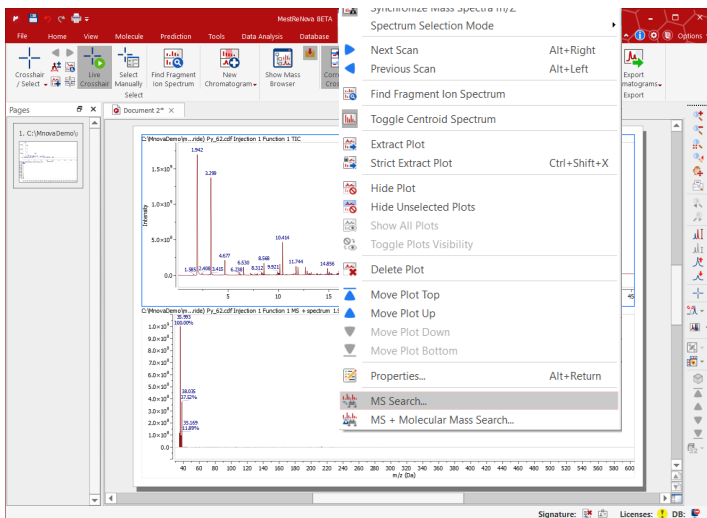

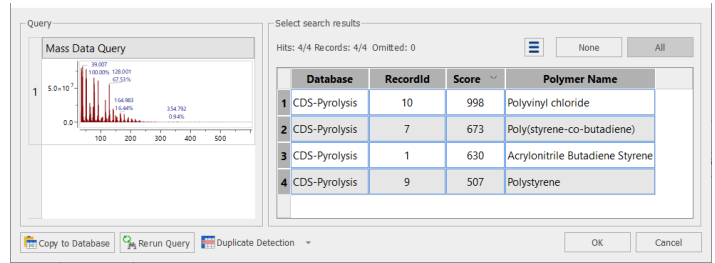Figure 9. Step 3: Searching the Co-added mass spectrum.

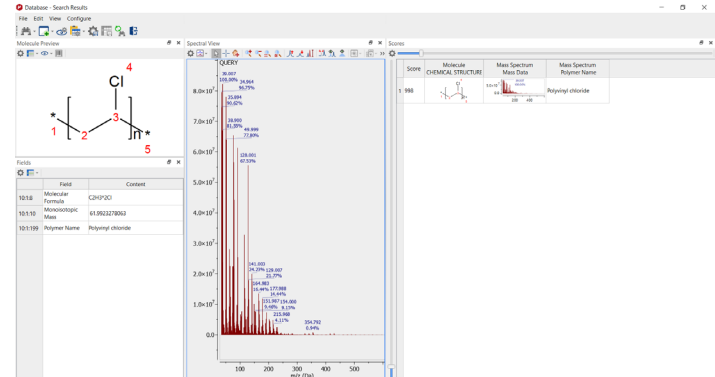Figure 10. Database Search Results.

Figure 11. Database Record in Database Browser.

A second page will open in the MSChrom Document 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 14). This will create a new page in the document that has the unknown chromatogram and the database record chromatogram on the same page (Figure 15). This can be an excellent way of confirming a match result.

However, a lot of pyrolysis-gc-ms analyses involve more than one polymer, so a simple mass spectral search may not provide a compete solution. Here, MSChrom's Compound Subtraction feature 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 16). When the two pyrograms were compared, peaks not seen in the record confirm the presence of additional material (Figure 17). 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 18. 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 19 shows that the aligned peak had been removed after Compound Subtraction.
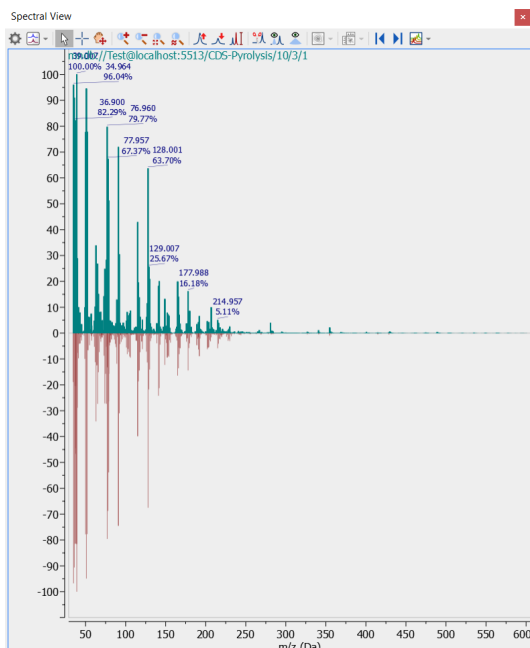
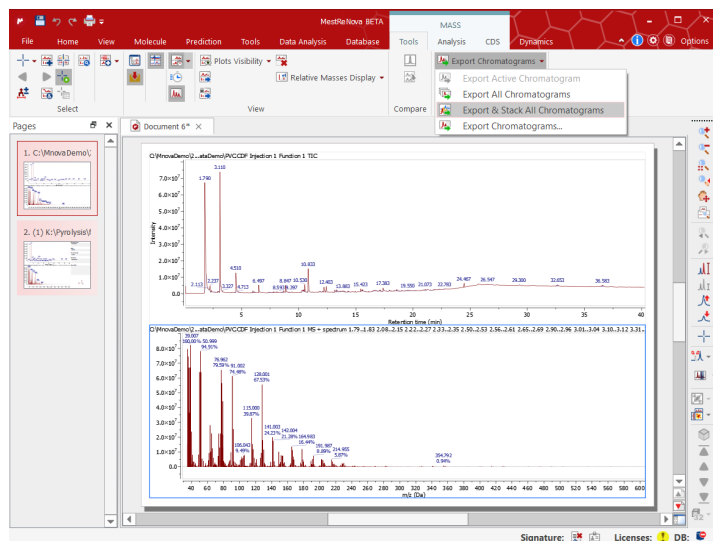Figure 12. Database Match (top) and Unknown(bottom) Mass Spectrum in Spectral View of Database Browser.

Figure 13. Step 4: Bringing Record to MSChrom, right click and select "Paste Record to Mnova".

When the compound subtracted pyrogram was searched against the pyrolysis database a new top match of polyethylene replaced the polypropylene hit (Figure 20). The compound subtracted mixture pyrogram now more closely resembles a polyethylene pyrogram (Figure 21), indicating the unknown is a mixture of polyethylene and polypropylene.
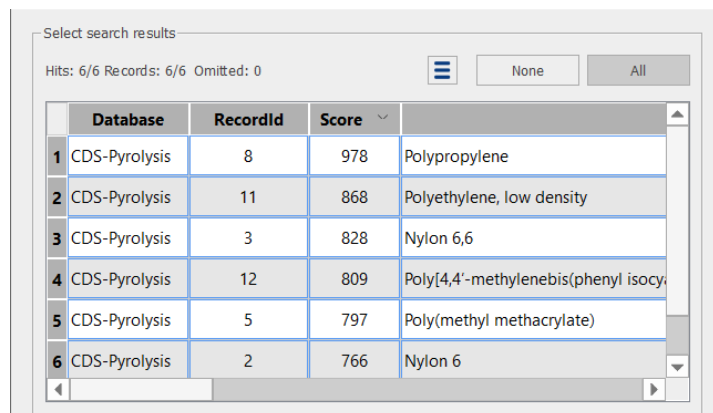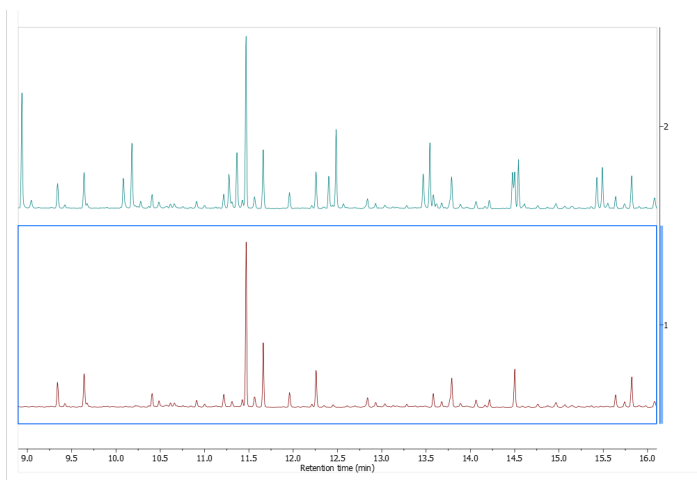

Figure 14. Exporting and Stacking Chromatograms from Unknown and Record.

Figure 15. Unknown and Record Chromatograms Stacked for Comparison.

Figure 16. Polymer Mixture Search Results.

Figure 17. Unknown (top) vs. Polypropylene (bottom).

Figure 20. New Search on Compound Subtracted Data reveals new top Record (Polyethylene).

	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)
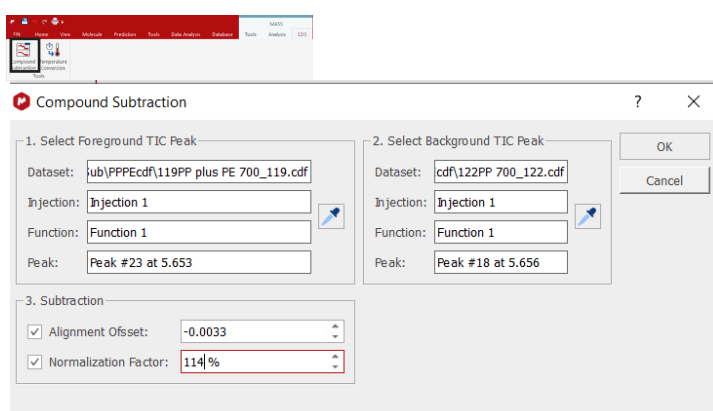
Figure 18. Compound Subtraction Interface.

Figure 19. Mixture before (top) and after (bottom) chromatogram subtraction was performed.

Figure 21. Polyethylene Pyrogram (top) and Compound Subtracted Pyrogram (bottom).

Conclusion

Pyrolysis-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, Compound Subtraction in MSChrom, together with a pyrolysis database of polymers helps to deconvolute a polymer mixture of polyethylene and polypropylene.