The Use of Resample to Improve Data Processing for GCxGC-TOFMS

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1. Introduction

Comprehensive two-dimensional Gas Chromatography (GCxGC) peaks generally range from 100 to 200 ms wide. A Time-of-Flight Mass Spectrometer (TOFMS) is the only mass spectrometer capable of proper GCxGC peak definition because it can acquire data at up to 500 spectra/second. Also with TOFMS, a full mass spectrum from 5 to 1000 u can always be acquired if necessary. With fast acquisition rates, full mass range acquisition, and the longer GC runs sometimes seen in GCxGC, file sizes can be rather large (up to 500 MB or more), and automated and flexible data handling is necessary. ChromaTOF®, LECO's fully automated instrument control and data processing software for the Pegasus® 4D, contains many features necessary to handle GCxGC data. Some of these features (all automated) include baseline, peak find, spectral deconvolution, Combine of peak slices, library search, calculate area/height, quantify, Compare, and reporting of data. Recently, a new feature called Resample was added to ChromaTOF that provides additional flexibility for GCxGC data processing.

Resample is a way to create a new data file that is reduced in size from an Acquired Sample File. Often this can lead to faster and more efficient data processing. This note will demonstrate the use of Resample for GCxGC-TOFMS data.

2. Experimental Conditions

Samples

A petroleum standard containing paraffins, iso-paraffins, aromatics, naphthenes, and olefins (PIANO mix) was used to demonstrate Resample with GCxGC-TOFMS, in addition to another standard containing polybrominated diphenyl ethers (PBDEs).

Petroleum—GCxGC-TOFMS

GCxGC:
Agilent 6890 Gas Chromatograph equipped with a LECO GCxGC thermal modulator and secondary oven
Column 1:
100 m x 0.25 mm x 0.50 µm Rtx-1 PONA (Restek)
Column 2:
2 m x 0.25 mm x 0.10 µm Rtx-50 (Restek)
Carrier:
Helium at 2.3 mL/minute, constant flow
Injection:
0.05 µL split at 250°C, split ratio 250:1
Oven 1 Program:
40°C (0.2 min), 2°/min to 200°
Oven 2 Program:
5°C offset from oven 1
Modulation Time:
2 seconds

MS:	LECO Pegasus TOFMS
Ionization:	Electron ionization at 70 eV
Source Temperature:	200°C
Stored Mass Range:	35 to 450 u
Acquisition Rate:	100 spectra/second

PBDE Standard—GCxGC-TOFMS

GCxGC:
Agilent 6890 Gas Chromatograph equipped with a LECO GCxGC thermal modulator and secondary oven
Column 1:
9.5 m x 0.18 mm x 0.20 µm Rtx-5 (Restek)
Column 2:
1 m x 0.25 mm x 0.25 µm Rtx-Dioxin 2 (Restek)
Carrier:
Helium at 1.5 mL/minute, constant flow
Injection:
1 µL direct injection at 250°C, 4 mm Uniliner (Restek)
Oven 1 Program:
120°C (1 min), 10°/minute to 340° (2 min)
Oven 2 Program:
20°C offset from oven 1
Modulation Time:
3 seconds

MS:	LECO Pegasus TOFMS
Ionization:	Electron ionization at 70 eV
Source Temperature:	225°C
Stored Mass Range:	200 to 1000 u
Acquisition Rate:	50 spectra/second
Data Processing:	LECO ChromaTOF software.

3. Results and Discussion

To reduce processing time for GCxGC-TOFMS data, it is often desirable to process only part of the chromatogram. Figure 1 is a contour plot, or GCxGC chromatogram, of a PIANO mix that is marked with yellow lines to illustrate an example of limited data processing. The only area of interest in this example is the first dimension retention time region, approximately 1850 to 3550 seconds, which contains the C3-C6 benzenes. ChromaTOF already contains segmented processing capability that allows peak finding for only this region (Figure 2), which can reduce the overall processing time.

Resample is a recently added ChromaTOF feature that allows segmented processing by creating a new file for the desired retention time region, with the added benefits of choosing a sample reduction rate (acquisition rate), and/or restricting the mass range for the new file. The sample reduction rate allows a user to create a file of, for example, 50 spectra/second acquisition rate from one of 100 spectra/second, which cuts the file size in half and can speed processing. The nice thing about this part of the

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feature is that the "extra" spectra are not thrown away, but are instead summed to produce a signal-to-noise enhancement. Mass range restriction, in addition to decreasing file size which leads to processing time improvement, may have the added benefit of improving spectral deconvolution when lower (or higher) m/z ions are discarded that are only from matrix interferences.

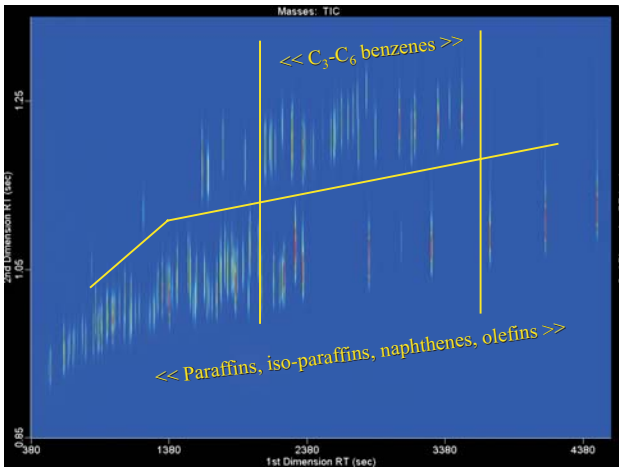

Figure 1. Contour plot of PIANO mix analyzed with GCxGC-TOFMS. The vertical yellow lines denote the first dimension retention area for processing the C_3-C_6 benzenes. The horizontal yellow line is used only to mark the second dimension separation of aliphatics and aromatics.

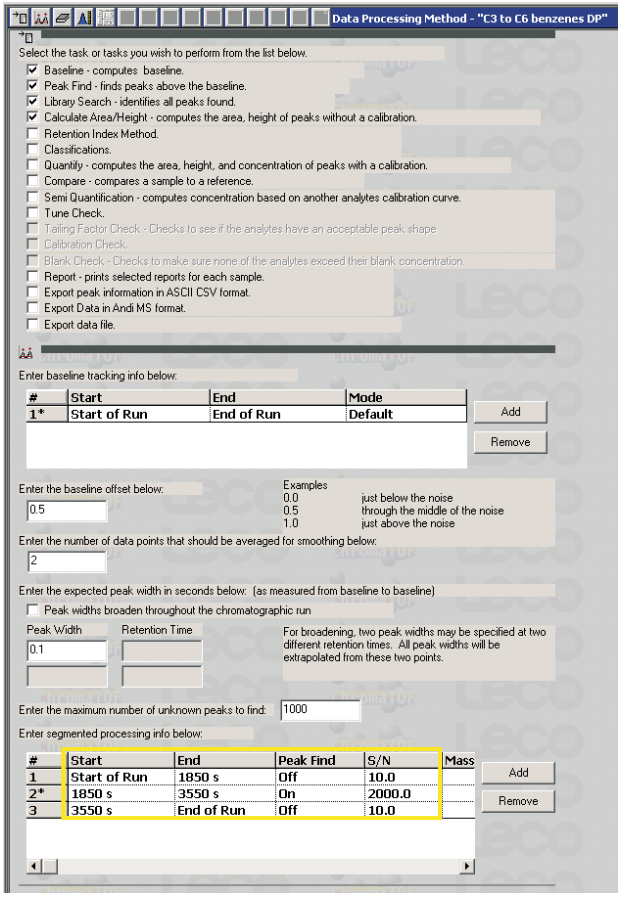

Figure 2. Segmented processing capability of ChromaTOF where peak finding can be restricted across a narrow retention time range.

Figure 3, a meld of screen captures from ChromaTOF, shows the Resample dialog boxes with new entries for the C3-C6 benzene retention time region of the PIANO mix. And Figure 4 shows the process of Resample occurring, where the new file (peg file extension) is created. After creating the new file in the directory of the user's choice, it can be returned to the Acquired Sample Files database by using Import for peg files.

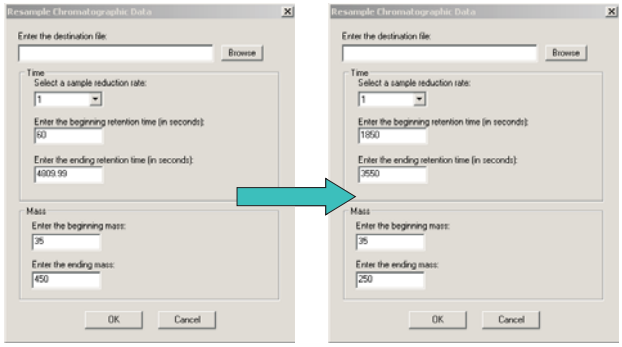

Figure 3. Example of Resample of a PIANO mix Acquired Sample File where a new file will be created for the retention time range of 1850 to 3500 seconds and the mass range of 35 to 250.

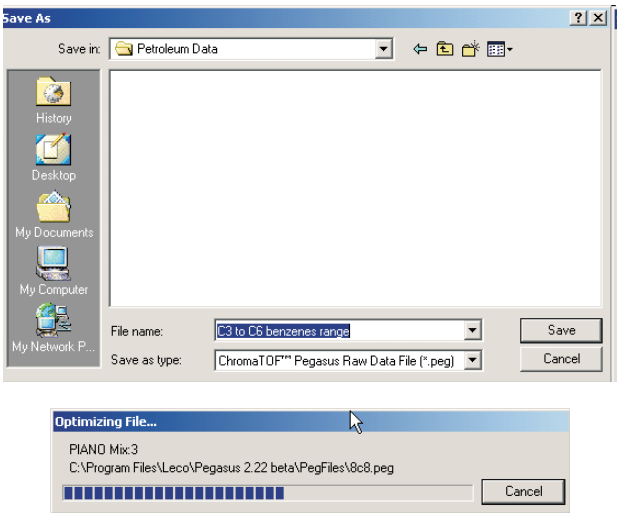

Figure 4. File being created from Resample parameters seen in Figure 3.

Table 1 contains the information used to construct the new file from Resample and illustrates the resulting file size reduction. It is important to note that the original file is completely intact and could even be used again to construct a new file with different Resample parameters.

Table 1. Resample parameters and reduced file size.

Resample Parameter	Old File	New File
Sample reduction rate	1	1
Beginning retention time (sec.)	60	1850
Ending retention time (sec.)	4810	3550
Beginning mass	35	35
Ending mass	450	250
File size (Mb)	377.9	70.4

For the previous example of Resample, it was not necessary to use the sample reduction rate parameter, as the peak widths generated for GCxGC of the PIANO mix mandated the 100 spectra/second acquisition rate. During a GCxGC-TOFMS analysis for PBDEs though, decabromodiphenyl ether (BDE 209), which is notoriously tough to chromatograph, showed very broad peaks (slices) that were over-sampled at the 50 spectra/second rate that was appropriate for other PBDEs (Figure 5).

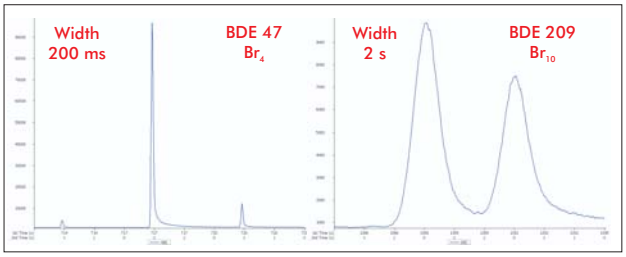

Figure 5. Linear chromatograms showing modulated peaks for BDEs 47 (tetrabromo) and 209 (decabromo). 50 spectra/second is an appropriate acquisition rate for the 200 ms wide peaks of BDE 47, but the rate is too fast for the broad peaks of BDE 209 (which results in a sensitivity decrease).

Using Resample with sample reduction rates of 2, 5, and 10 (a dialog box demonstrating this, with retention time and mass range reductions, is shown in Figure 6) better peak responses are seen for BDE 209 (Figure 7). As mentioned earlier, this enhanced peak response is due to spectral summing.

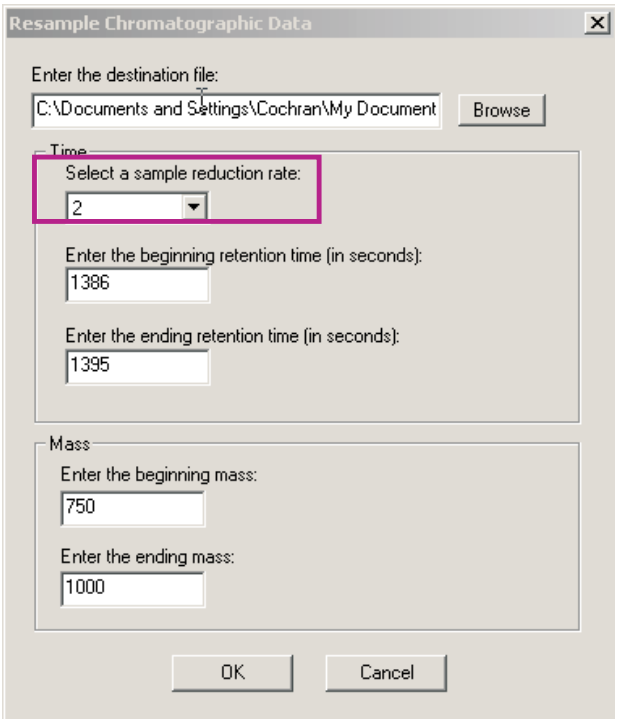

Figure 6. Dialog box showing Resample for BDE 209. Because the data acquisition rate was too fast for the broad peaks, a sample reduction rate of 2 was used for the retention time range for where BDE 209 eluted.

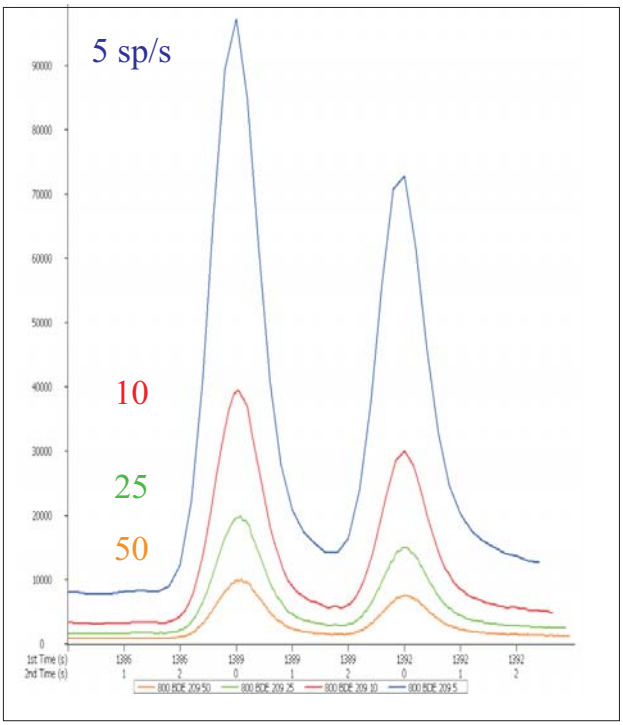

Figure 7. Linear chromatograms for modulated BDE 209 at original acquisition rate of 50 spectra/second (orange) and when sample reduction rates (of 2, 5, and 10) were used in the ChromaTOF Resample feature to produce new files at 25 (green), 10 (red), and 5 (blue) spectra/second. The enhanced peak responses are due to spectral summing.

4. Conclusions

Resample is a new ChromaTOF feature that adds flexibility to GCxGC-TOFMS data processing. New files can be created that reflect sample rate reductions, restricted retention time regions, and narrower mass ranges. The resulting smaller file sizes speed up automated processing routines. In addition, spectral deconvolution may be better due to elimination of low or high m/z matrix ions. When Resample is used to match peak widths properly to acquisition rates through the sample rate reduction, a sensitivity enhancement can occur. No matter how Resample is used, the original data file is still intact.

5. Acknowledgment

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