Optimizing GCxGC Parameters for Petroleum Analysis Using a Free Web-Based Tool

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Introduction

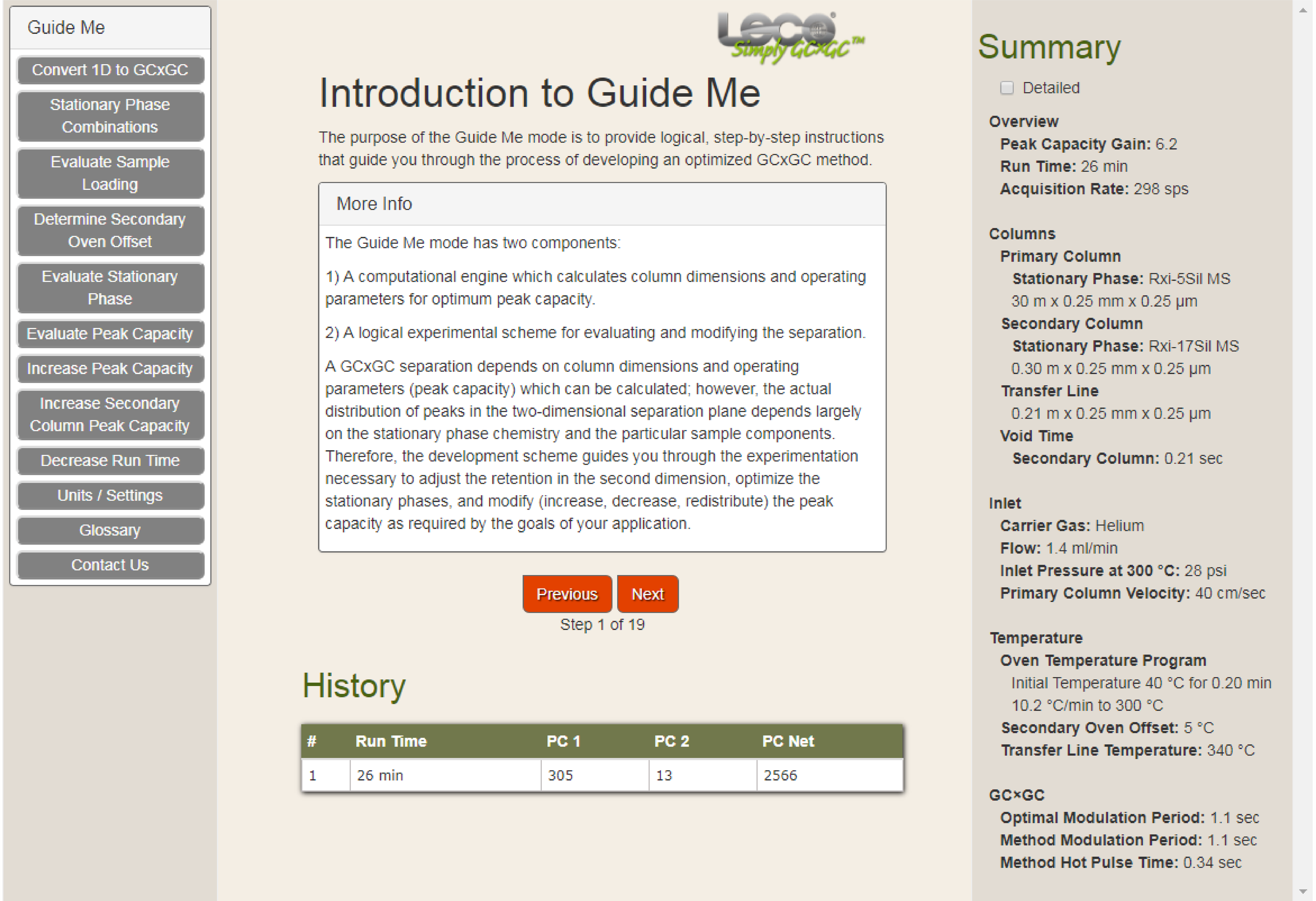
Comprehensive two-dimensional gas chromatography (GCxGC) combined with time-of-flight mass spectrometry (TOFMS) is a well-established technique for characterization of petroleum samples because of the ability to separate structural classes of hydrocarbons into distinct bands of analytes that can then be identified with library-matched mass spectra. However, transferring traditional one-dimensional gas chromatography methods to optimized two-dimensional methods can be daunting because of the sheer number of options available for setting up commercial GCxGC systems—choosing orthogonal column phases, secondary oven temperature offsets, modulator temperatures, and second dimension separation period lengths. Using a new online tool, Simply GCxGC™, the process of translating an existing analysis into an optimized GCxGC method is experimentally determined for a sample of diesel fuel. Calculations that maximize use of two-dimensional space and minimize analyte wrap-around are applied to user-controlled parameters to make the most of peak-capacity increases and further enhance the chromatographic resolution gains from the additional dimension of separation.

Instrumentation

Pegasus® BT 4D
High-Performance TOFMS

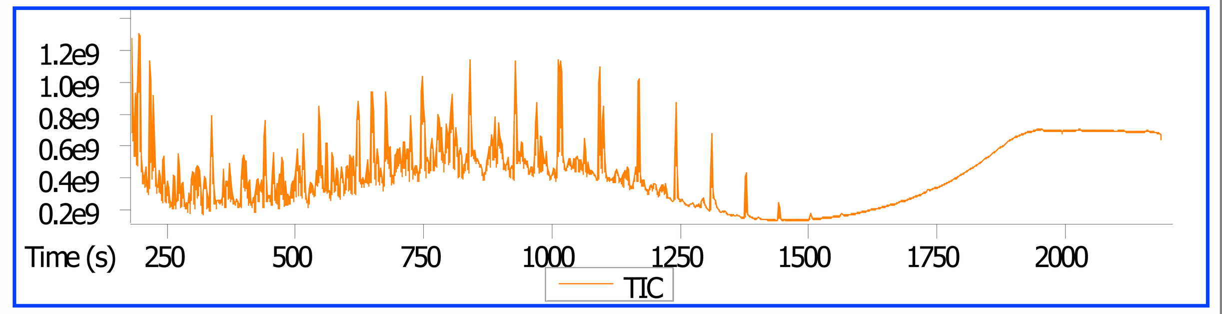
- Dual-Stage Thermal Modulator
- Acquisition rates up to 500 spectra/s
- Mass precision within 0.1 Da
- Benchtop size

Simply GCxGC



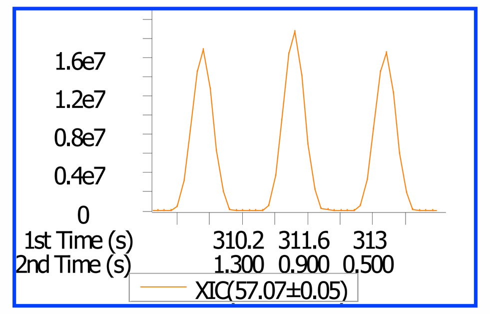
Workflow

Convert 1D to GCxGC

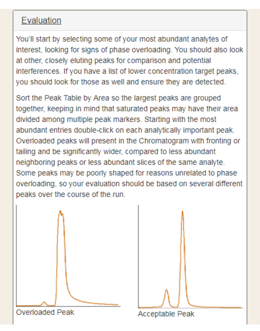


1D Diesel Sample on Rxi-5MS 30 m x 0.25 mm x 0.25 µm column chromatogram is pictured above. The process for "Guide Me" conversion from this 1D run to a GCxGC sample is shown below.

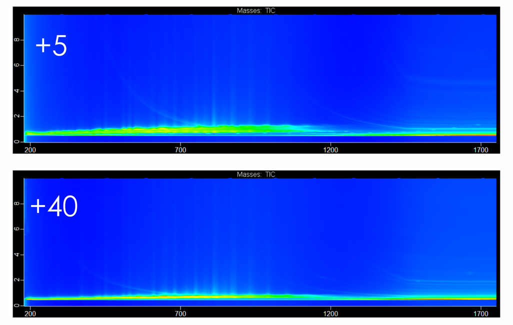
Evaluate Sample Loading

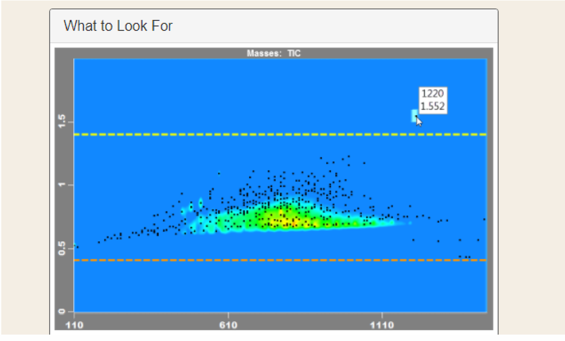


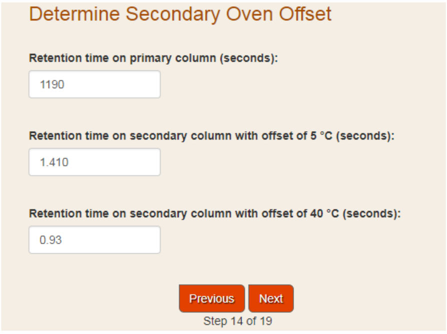
A zoomed view of the chromatogram of diesel sample collected with experimental GCxGC values for evaluation of sample loading is shown on the left. The mass trace for m/z 57.07, a characteristic mass for alkanes expected to be present in diesel in high concentrations, is displayed. To the right, a screenshot of the evaluation criteria as explained in the Simply GCxGC app is shown. Sample loading is shown to be acceptable with Split 100 injection.



Determine Optimum GCXGC Parameters

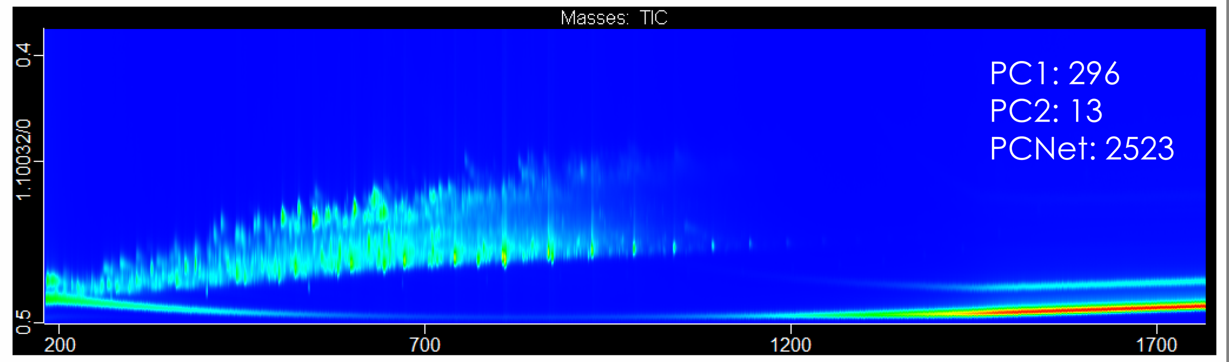






Two injections of the diesel sample with +5 ºC and +40 ºC secondary oven offset are run to determine optimum secondary oven offset and 2nd dimension separation time, so that all peaks of interest are maintained in the sections between the void time line (orange dotted line), and the void time+optimum 2nd dimension separation time line (yellow dotted line). Elution times of the last eluting peak are entered into the Simply GCXGC app, which then returns optimum secondary oven temperature offset, 2nd dimension separation time, and hot pulse values for the current column configuration and primary oven temperature ramp. This step can be repeated multiple times as other configurations are explored when the user desires more peak capacity.

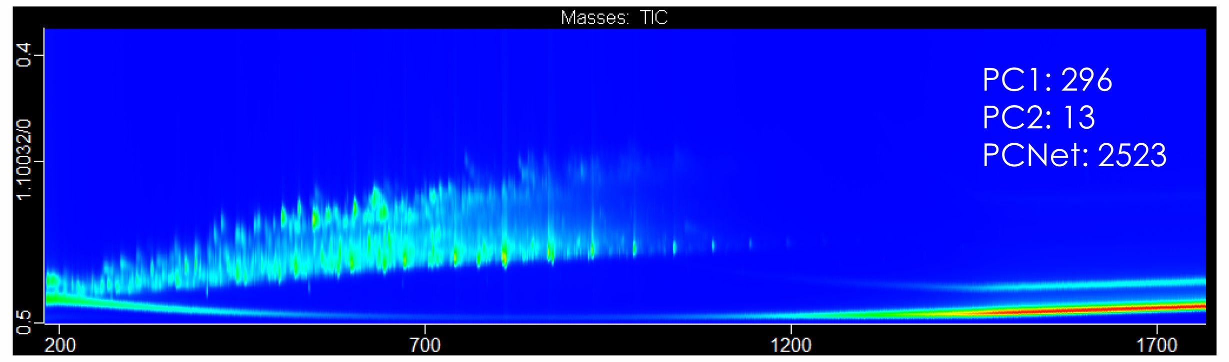
Evaluate Peak Capacity



GCxGC Diesel Sample on Rxi-5MS 30 m x 0.25 mm x 0.25 µm coupled to Rxi-17SilMS 2 m x 0.25 mm x 0.25 µm column using calculated optimal GCxGC parameters of 0.3 m in secondary oven, 10.3 ºC/min ramp rate from 50 ºC to 300 ºC, carrier gas flow rate of 1.4 mL/min, +16 ºC secondary oven offset, 2nd dimension separation time of 1.1 s with 0.33 s hot pulse, and spectral acquisition rate of 309 spectra/s.

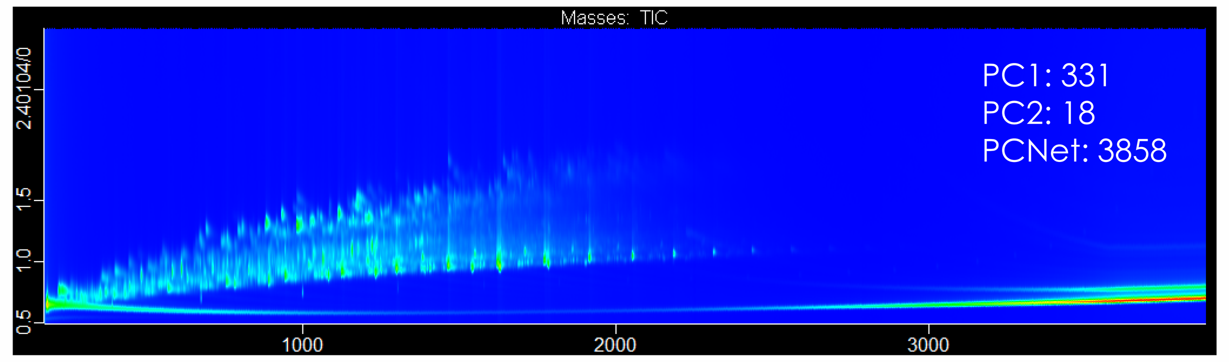
Normal Phase

Rxi-5MS 30 m x 0.25 mm x 0.25 µm coupled to
Rxi-17SilMS 2 m x 0.25 mm x 0.25 µm



Optimal GCxGC parameters of 0.3 m in secondary oven, 10.3 ºC/min ramp rate from 50 ºC to 300 ºC, carrier gas flow rate of 1.4 mL/min, +16 ºC secondary oven offset, 2nd dimension separation time of 1.1 s with 0.33 s hot pulse, and spectral acquisition rate of 309 spectra/s. Total peak capacity calculated at 2523.

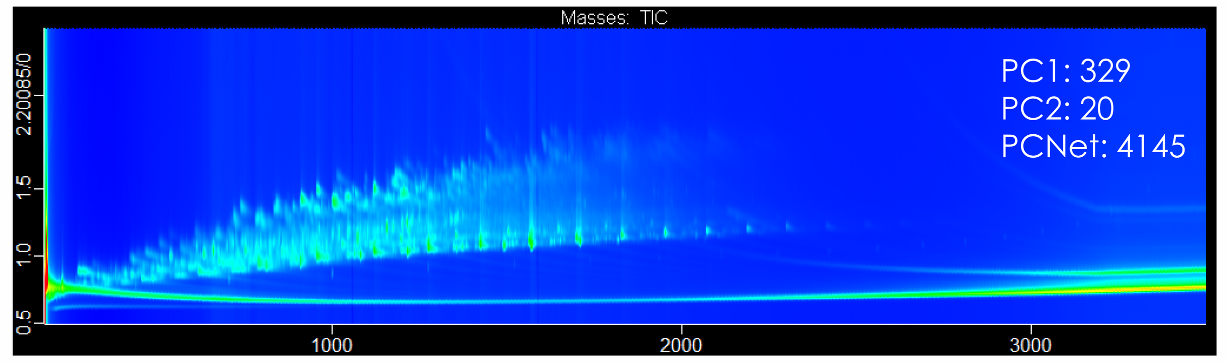
Slow Down Ramp Rate → More Peak Capacity



Optimal GCxGC parameters of 0.3 m in secondary oven, 4.2 ºC/min ramp rate from 50 ºC to 300 ºC, carrier gas flow rate of 1.4 mL/min, +9 ºC secondary oven offset, 2nd dimension separation time of 2.4 s with 0.73 s hot pulse, and spectral acquisition rate of 192 spectra/s. Total peak capacity calculated at 3858.

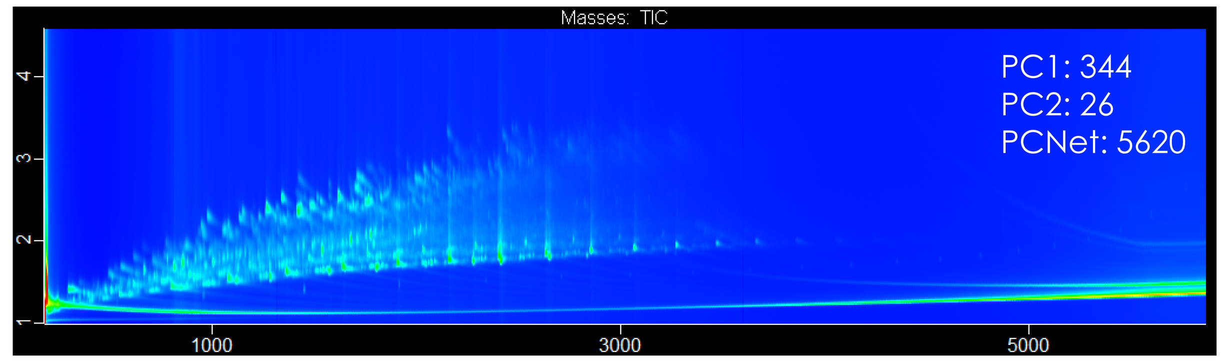
Change 2D Column ID → More 2D Peak Capacity

Rxi-5MS 30 m x 0.25 mm x 0.25 µm coupled to
Rxi-17SilMS 2 m x 0.18 mm x 0.18 µm



Optimal GCxGC parameters of 0.3 m in secondary oven, 4.7 ºC/min ramp rate from 50 ºC to 300 ºC, carrier gas flow rate of 1.4 mL/min, +10 ºC secondary oven offset, 2nd dimension separation time of 2.2 s with 0.60 s hot pulse, and spectral acquisition rate of 234 spectra/s. Total peak capacity calculated at 4145.

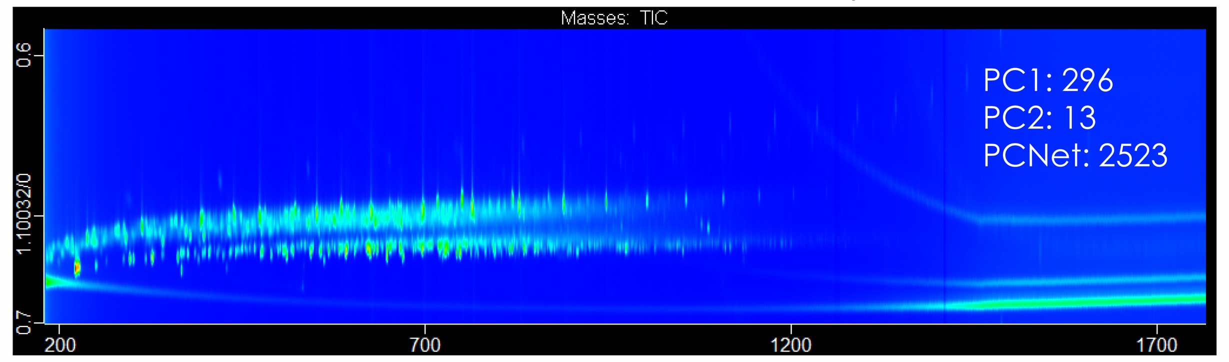
Slow Down Ramp Rate
Add Loop in 2D Oven → More Peak Capacity



Optimal GCxGC parameters of 0.45 m in secondary oven, 2.7 ºC/min ramp rate from 50 ºC to 300 ºC, carrier gas flow rate of 1.4 mL/min, +15 ºC secondary oven offset, 2nd dimension separation time of 3.6 s with 1.10 s hot pulse, and spectral acquisition rate of 178 spectra/s. Total peak capacity calculated at 5620.

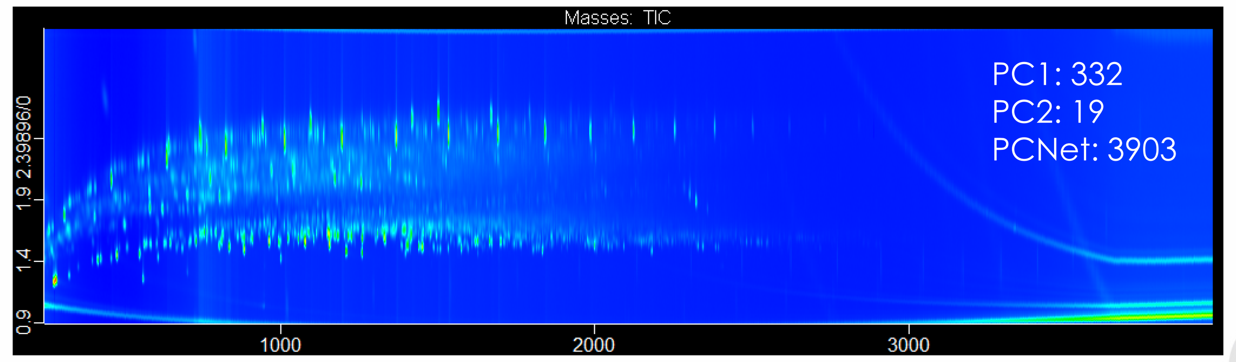
Reverse Phase

Rxi-17SilMS 30 m x 0.25 mm x 0.25 µm coupled to
Rxi-5MS 2 m x 0.25 mm x 0.25 µm



Optimal GCxGC parameters of 0.3 m in secondary oven, 10.3 ºC/min ramp rate from 50 ºC to 300 ºC, carrier gas flow rate of 1.4 mL/min, +32 ºC secondary oven offset, 2nd dimension separation time of 1.1 s with 0.33 s hot pulse, and spectral acquisition rate of 309 spectra/s. Total peak capacity calculated at 2523.

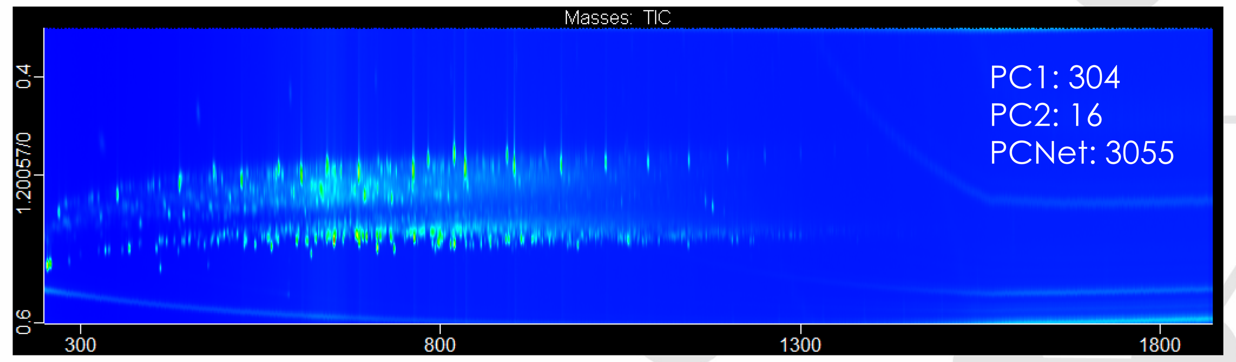
Slow Down Ramp Rate → More Peak Capacity



Optimal GCxGC parameters of 0.3 m in secondary oven, 4.1 ºC/min ramp rate from 50 ºC to 300 ºC, carrier gas flow rate of 1.4 mL/min, +9 ºC secondary oven offset, 2nd dimension separation time of 2.4 s with 0.73 s hot pulse, and spectral acquisition rate of 193 spectra/s. Total peak capacity calculated at 3903.

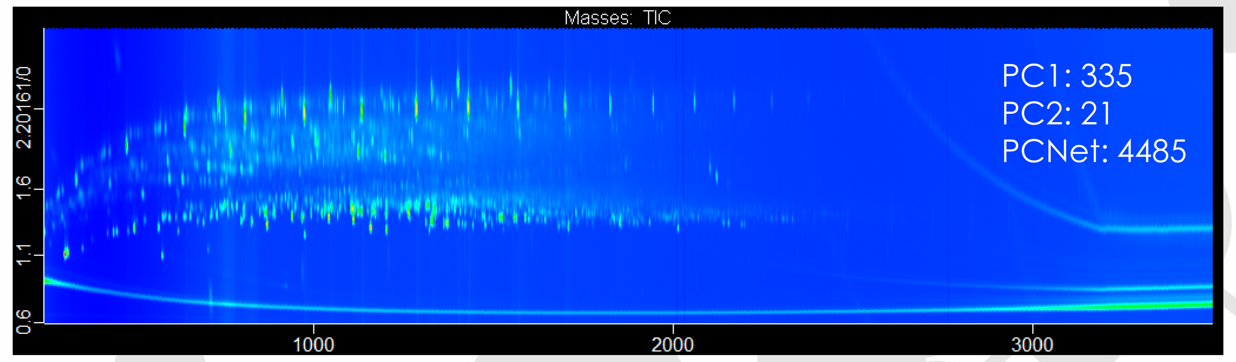
Change 2D Column ID
Add Loop in 2D Oven → More 2D Peak Capacity

Rxi-17SilMS 30 m x 0.25 mm x 0.25 µm coupled to
Rxi-5MS 2 m x 0.18 mm x 0.18 µm



Optimal GCxGC parameters of 0.45 m in secondary oven, 9.6 ºC/min ramp rate from 50 ºC to 300 ºC, carrier gas flow rate of 1.4 mL/min, +9 ºC secondary oven offset, 2nd dimension separation time of 1.2 s with 0.30 s hot pulse, and spectral acquisition rate of 349 spectra/s. Total peak capacity calculated at 3055.

Slow Down Ramp Rate → More Peak Capacity



Optimal GCxGC parameters of 0.45 m in secondary oven, 4.7 ºC/min ramp rate from 50 ºC to 300 ºC, carrier gas flow rate of 1.4 mL/min, +9 ºC secondary oven offset, 2nd dimension separation time of 2.2 s with 0.65 s hot pulse, and spectral acquisition rate of 248 spectra/s. Total peak capacity calculated at 4485.

Conclusions

Using the Simply GCXGC tool to set up experiments yields excellent two-dimensional separations. While initial parameters may not result in the highest peak capacity, Simply GCxGC provides a helpful guide for the next steps that lead to greater peak capacity results and better chromatographic resolution for any given sample, regardless of the initial column phase used.

Delivering the Right Results