

Advanced Data Visualization: The Many Dimensions of Petroleomics Using High Resolution Gas Chromatography and Time-of-Flight Mass Spectrometry

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Introduction

With advances in ChromaTOF-HRT® brand software, multi-dimensional chromatographic separations with high-resolution, accurate-mass spectra are easily viewed with chromatograms, mass spectra, Kendrick mass defect plots, van Krevelen plots, and more all within one program. The ability to select a mass defect series based on C#, calculate probable formulas, and then elucidate structure by correlating back to the structured two-dimensional chromatogram with deconvoluted spectral comparison to commercially available libraries allows for quicker and more powerful assignment of peaks. Characterization of complex samples becomes simple, and visualizing the differences between samples is done with side-by-side comparisons of commonly used plots, highlighting heteroatomic species of interest such as sulfur, nitrogen, or oxygen. This poster illustrates the power of these tools by comparing two samples of heavy Venezuelan Crude oil and following the workflow for identification of an unknown component.

Chromatographic Information

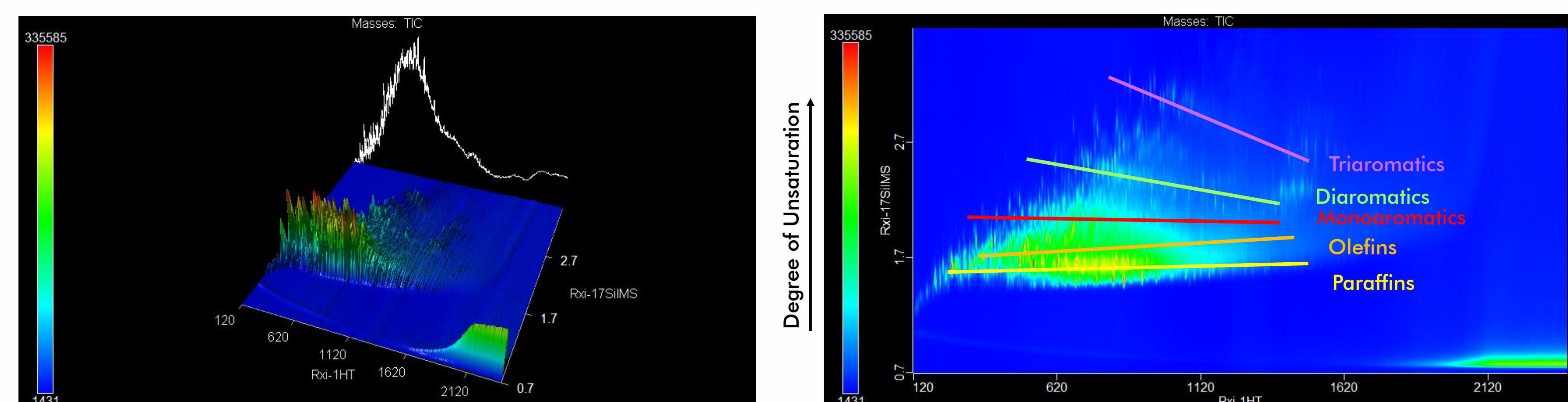


Figure 1: 3D View of GCxGC Chromatogram with reconstructed Linear Trace in background for a sample of Venezuelan Heavy Crude Oil

Figure 2: Contour plot of GCxGC analysis of crude oil with characteristic classification bands marked, illustrating the utility of the structured chromatogram.

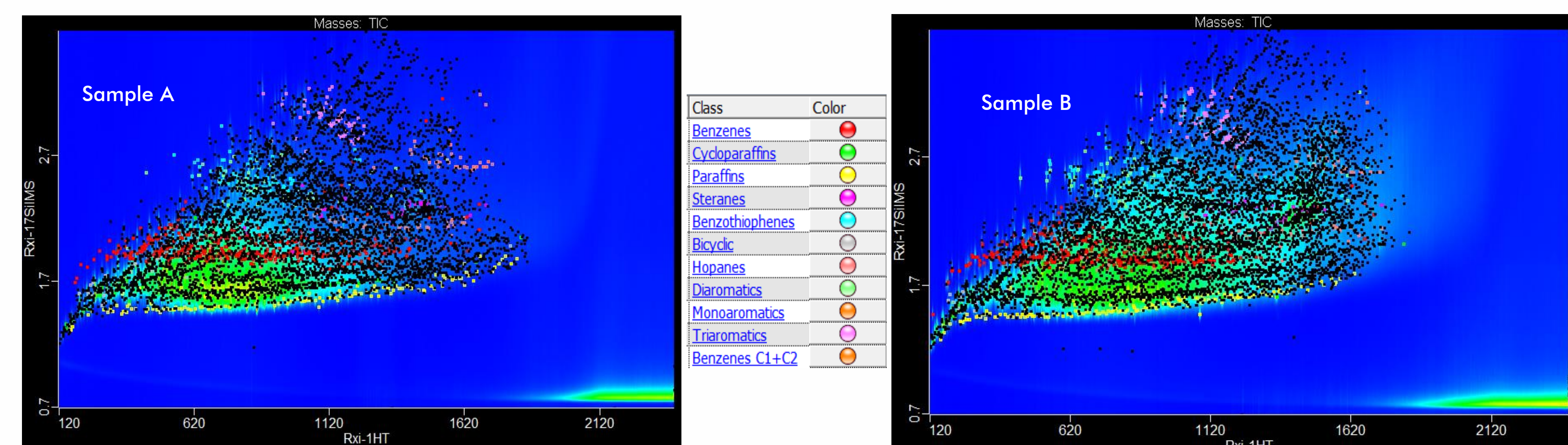


Figure 3: Contour plots of GCxGC analysis of crude oil samples with automatically deconvoluted peak markers shown. Colored markers correspond to peaks that have been filtered and classified according to compound type using advanced Peak Filtering tools. The different classes are defined using spectral information. The color-coded key is shown in the middle.

	Sample A	Sample B
Benzenes	7.308	9.911
Cycloparaffins	9.661	5.823
Paraffins	23.559	16.505
Steranes	0.139	0.893
Benzothiophenes	0.328	0.389
Bicyclic	2.116	1.616
Hopanes	0.547	0.974
Diaromatics	1.131	2.809
Monoaromatics	7.308	9.911
Triaromatics	0.901	2.019
Benzenes C1+C2	0.121	0.569
Unclassified	54.392	59.46
Total	100	100

Figure 4: The table above shows the automatically calculated classification summary for the Peak Area % of each compound class present.

Peak True Spectral Information

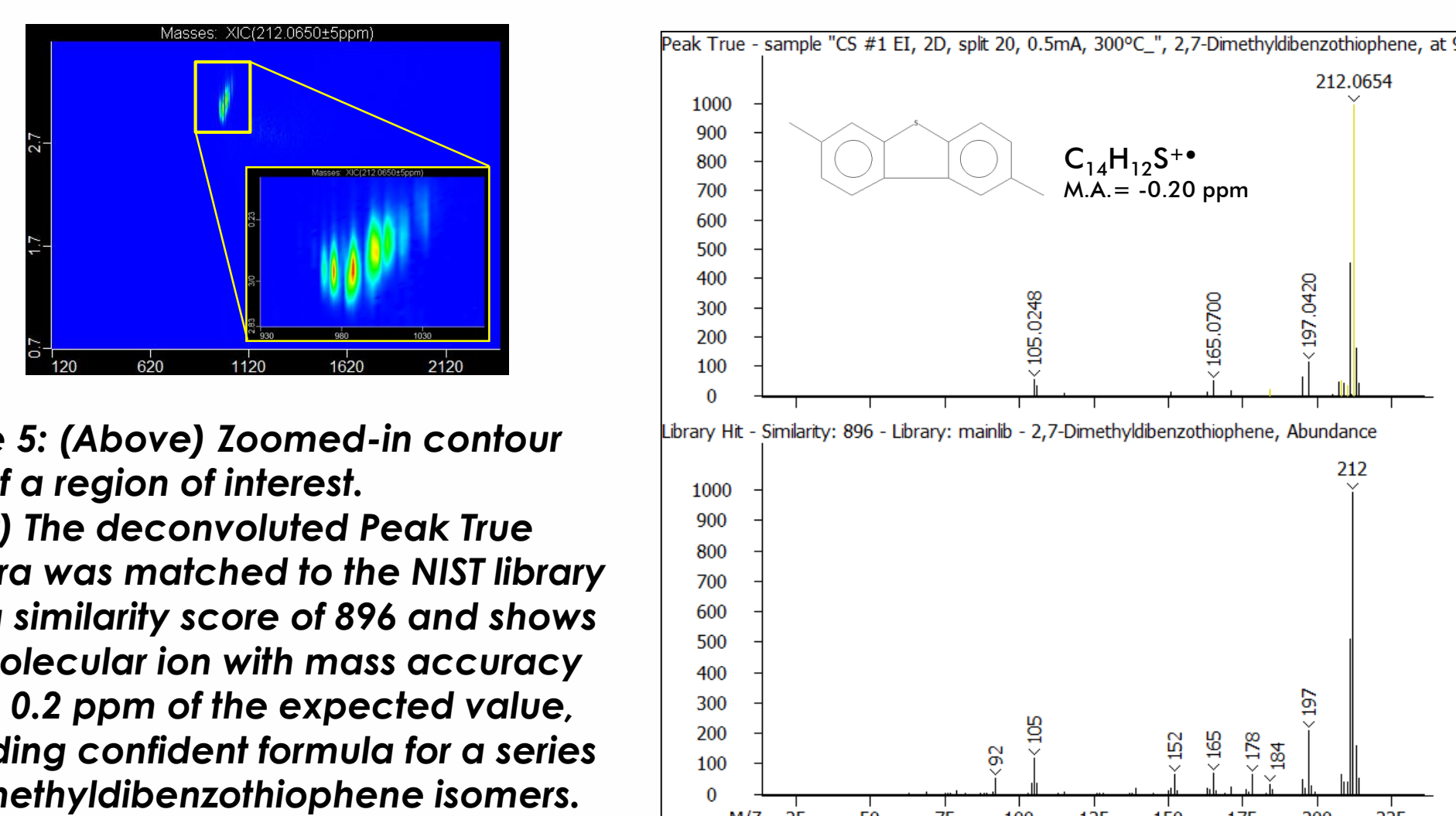


Figure 5: (Above) Zoomed-in contour plot of a region of interest. (Right) The deconvoluted Peak True spectra was matched to the NIST library with a similarity score of 896 and shows the molecular ion with mass accuracy within 0.2 ppm of the expected value, providing confident formula for a series of dimethyldibenzothiophene isomers.

Composite Spectral Information

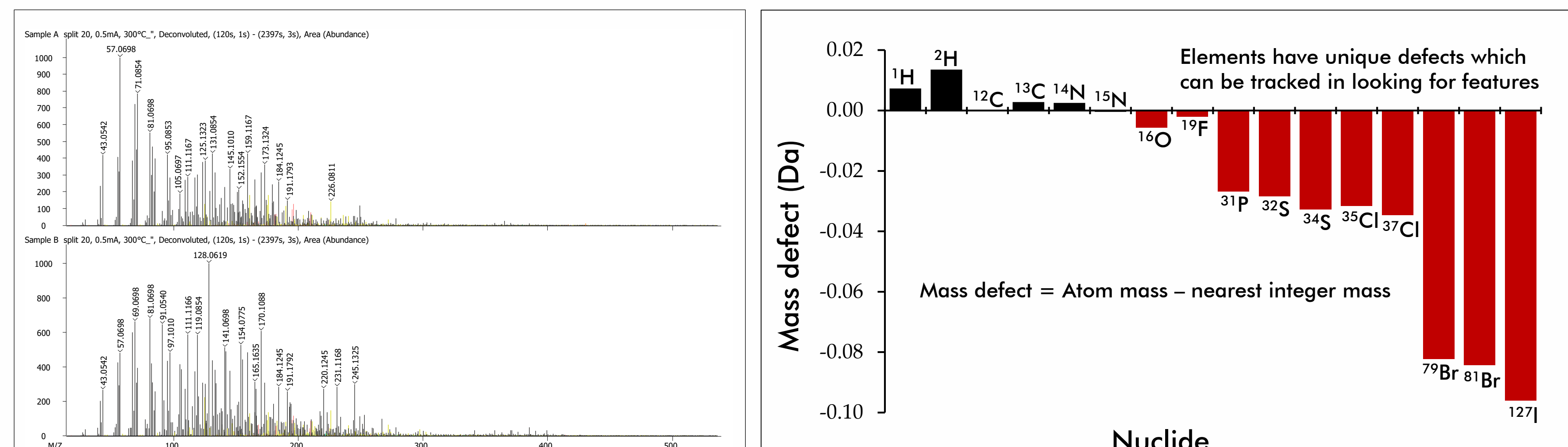
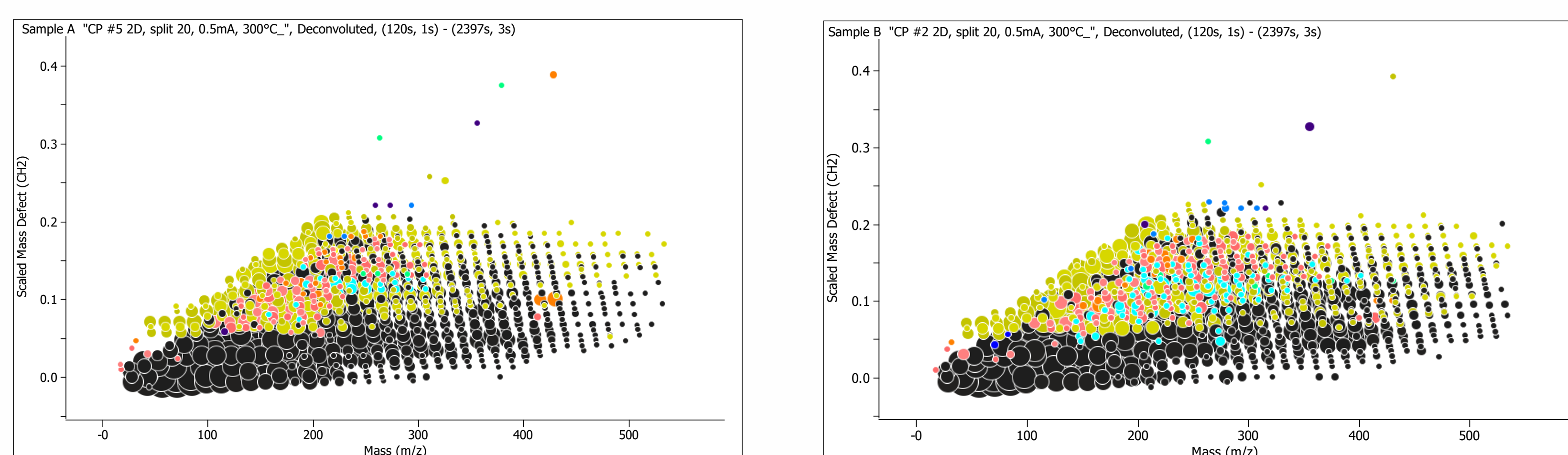


Figure 6: Composite spectra for each sample generated by summing all mass signals present in the GCxGC chromatogram.

Figure 7: Chart of Mass Defects for common heteroatomic substitutions. No two elements have the same mass defect so every (C_nH_mN_pO_qS_rCl_tBr_u) is unique, if the instrument is capable of measuring the difference.



#	Class	Region	Area	Area % In-Class	Area % In-Sample
1	HC		126999811	100.00	17.00
2	N		89730	100.00	0.01
3	O		1972889	100.00	0.26
4	O2		45681	100.00	0.01
5	NO		0	100.00	0.00
6	NO2		0	100.00	0.00
7	S		9743742	100.00	1.30
8	SO		2031	100.00	0.00
9	SO2		0	100.00	0.00
10	SO3		86285	100.00	0.01
11	SO4		0	100.00	0.00
12	Unassigned		608026686		81.40
13	Total		746966855		100.00

Figure 8: Mass defect plots generated for Sample A and Sample B with spectral filters applied. Colors correspond to heteroatom-containing species, as shown in the key in the middle, while size of dots corresponds to intensity in the composite spectra. Automatically calculated spectral classification summary tables are shown with area % for each heteroatomic class within the sample.

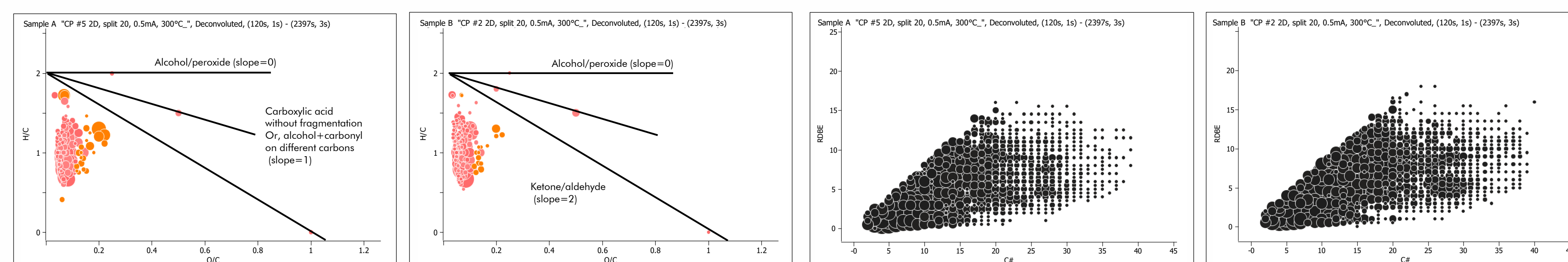


Figure 9: Van Krevelen plots for each sample are shown above, with only masses corresponding to oxygenated species shown. The plots can be used to indicate thermal maturity of sample by evaluating the distribution of oxidative states.

Figure 10: C# vs RDBE plots for each sample are shown above, with only masses corresponding to hydrocarbon species shown, revealing distribution of heavy vs. light compounds and structural complexity.

Identifying an Unknown Compound

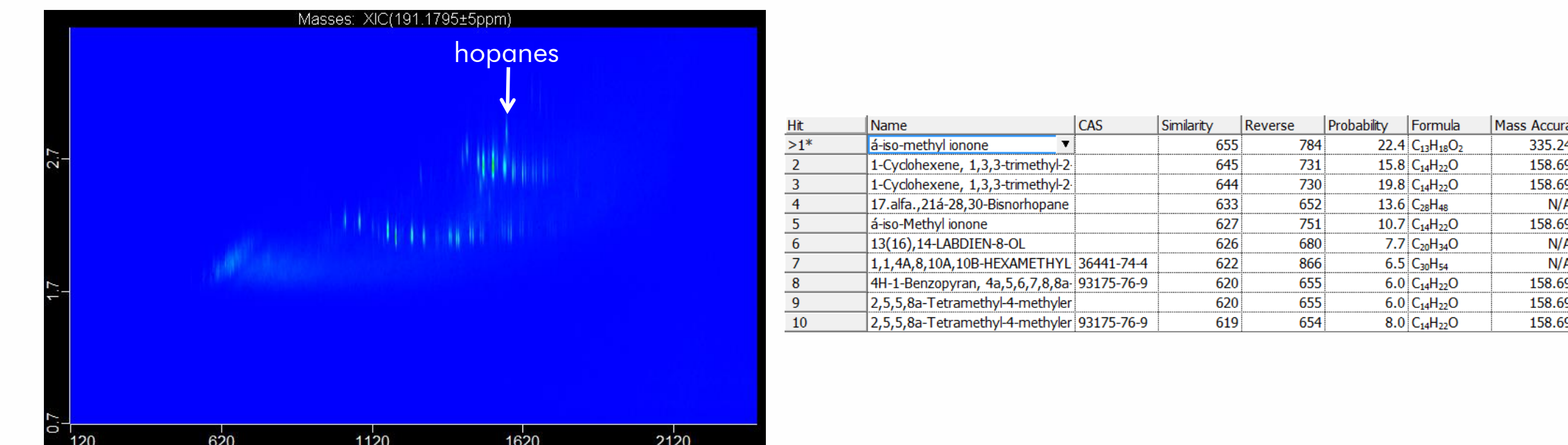


Figure 11: A characteristic mass of hopanes (m/z 191.1795) is plotted in the chromatogram of Sample B above, showing a band of peaks that should correspond to that class of compound. However, the first library hit for the indicated peak has a low similarity score and very high mass accuracy, leading to doubts of this initial attempt at identification.

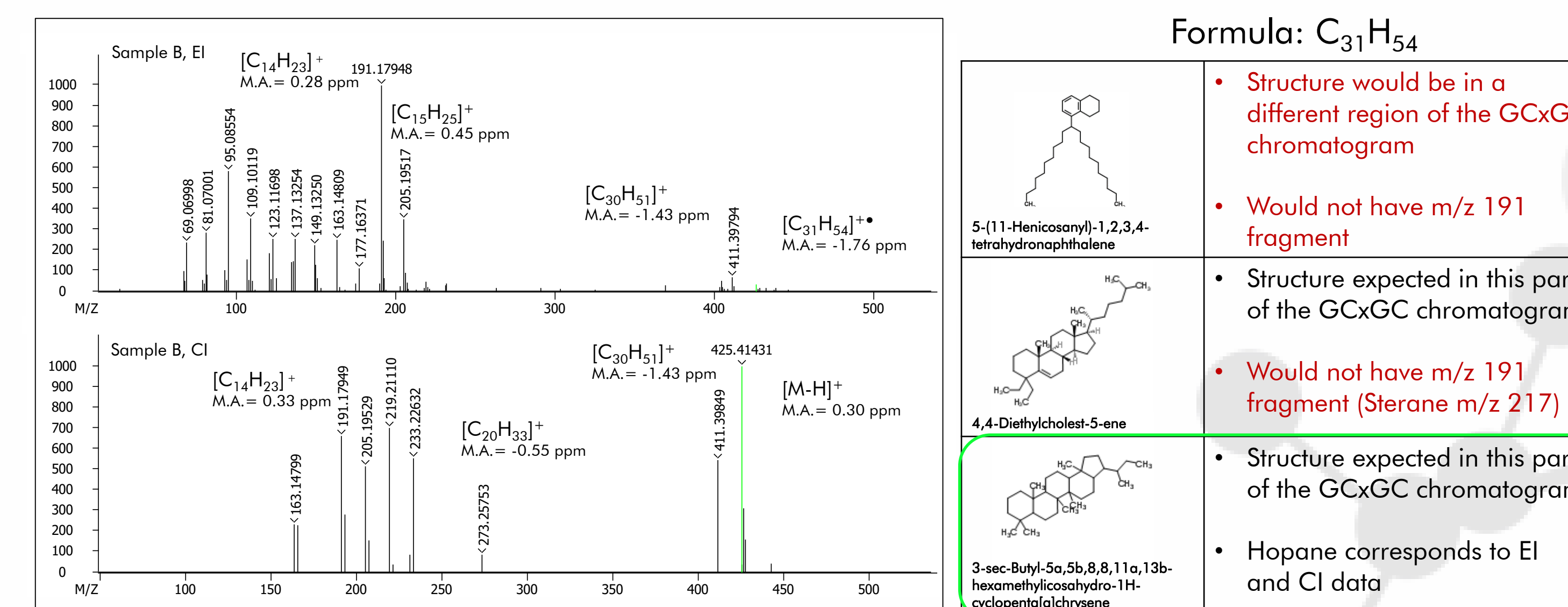


Figure 12: The EI and CI spectra of the peak indicated in Figure 11 are shown with the calculated formula and mass accuracies for major fragments. Note that the molecular ion is present in the EI spectra, and that the [M-H]⁺ present in the CI spectra corresponds to a fully saturated hydrocarbon structure.

Figure 13: The molecular formula for the unknown compound was sent to ChemSpider and the top three hits are shown. Using a combination of chromatographic and spectral information, a tentative identification can be made, as indicated by the green box.



Conclusion

The Spectral Analysis Tools options in ChromaTOF-HRT allow for easy qualitative and quantitative evaluation of samples. In addition, the linked information between spectral masses and the chromatographic space allow for confident identification of not only classes of compounds, but also specific peaks. Integration with internet databases like ChemSpider allow for searching when no commercial library hits are available. The combination of comprehensive two-dimensional gas chromatography with high-resolution mass spectrometry creates powerful data visualization and interpretation tools for further explorations in petroleomics.

