When Single Dimension GC Separations Fail: Exploring Real World Applications for Comprehensive Two-Dimensional GC (GC×GC)

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Background

One of the benefits of GCMS as an analytical tool is its ability to provide data which can be effectively searched against established libraries. This requires resolved or well-defined analytes, or the detection, *inter alia*, of lower abundance analytes which elute under highly abundant analytes. The potential for long analytical runs exists as a solution but these often fail due to retention mechanisms in GC. An approach which addresses this issue is comprehensive two-dimensional gas chromatography (GC×GC) where orthogonal selectivity between two phases facilitates separation of coeluting analytes. This poster will demonstrate several applications in which single dimension gas chromatographic separations fail to provide resolution of components of complex mixtures. In many instances, time-of-flight mass spectrometry, coupled with mathematical deconvolution algorithms, has been successfully utilized to extract pure spectra for coeluting analytes in a complex chromatogram. However, there are instances when math alone cannot solve these challenging problems. One common example is a so-called perfect coelution in which the peaks of two or more analytes apex at the exact same retention time. This leads to a mass spectrum composed of more than one analyte which cannot be mathematically resolved. Instances such as these provide an opportunity for GC×GC to demonstrate the separation power needed to successfully isolate and identify components that are often missed in one-dimensional GC separations.

Examples will be highlighted for food/flavor/fragrance, metabolomic, and petrochemical application markets. The advantage in number of compounds detected and overall quality of their mass spectral library similarity scores, as compared to one-dimensional methods will be clearly demonstrated.

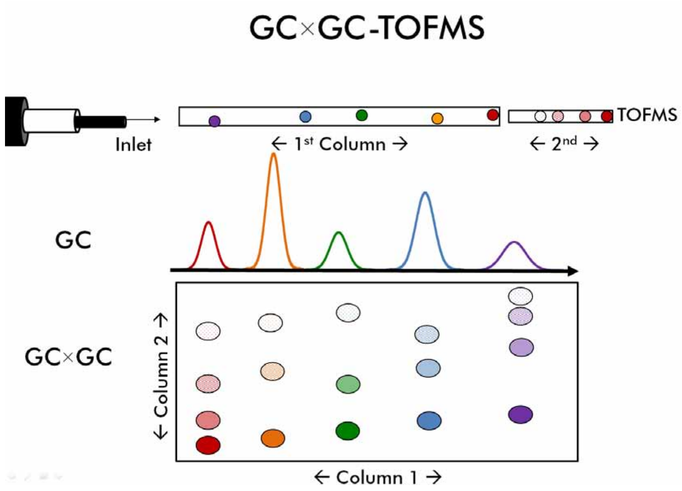

Figure 1. Visual Representation of Benefits of GC×GC Separation

Instrumentation

Figure 2. Pegasus® 4D GC×GC TOFMS

Pegasus 4D Capabilities

- Increased peak capacity over 1D
- Increased s/n values over 1D
- Fast acquisition rates (up to 500 spectra/second)
- Low Maintenance Ion Source
- Seamless software package (ChromaTOF®)

Application Examples

GC & GC×GC Food/Flavor/Fragrance

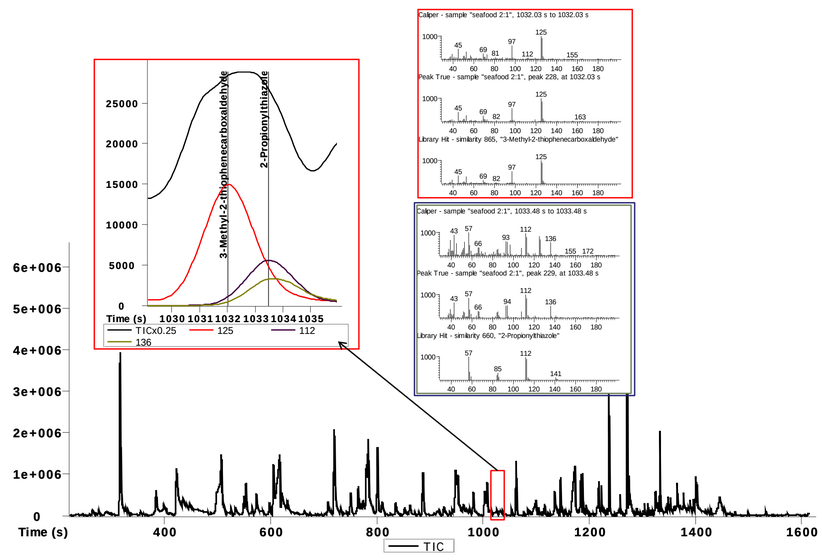

Figure 3. Single dimension separation of flavor and fragrance compounds in a pet food sample. Expanded view shows a region of the chromatogram where only one out of three analytes was successfully identified. In this example, deconvolution alone was unable to resolve all three analytes present in this region of the chromatogram. The GC×GC separation of the same sample is demonstrated in Figure 4 below.

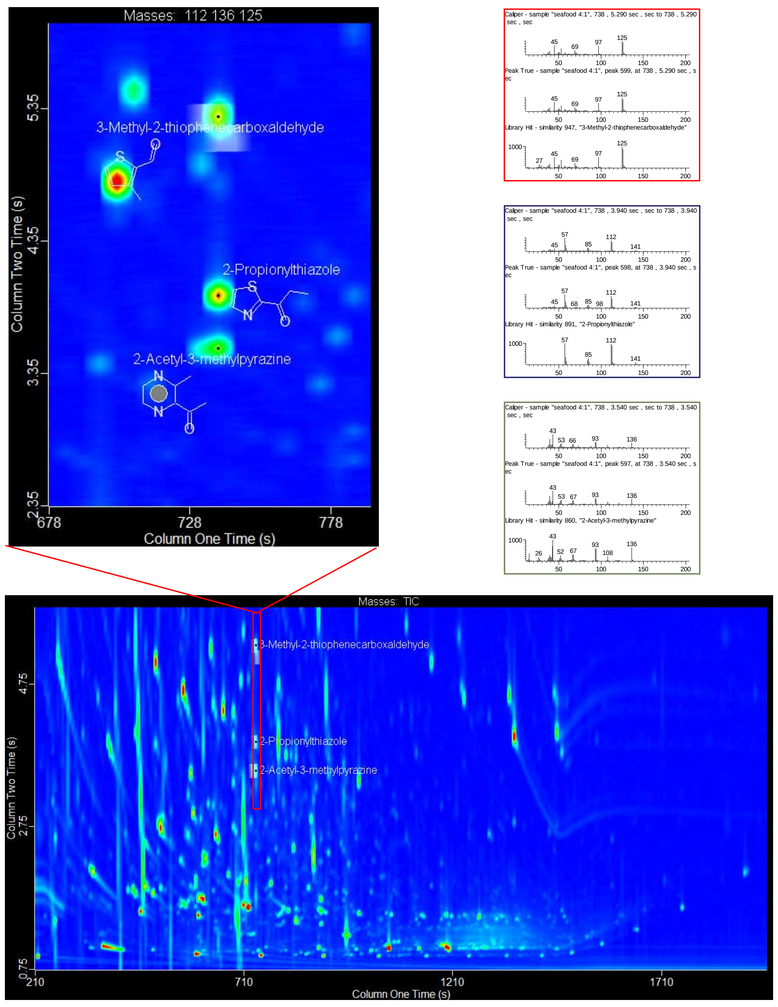

Figure 4. GC×GC separation of flavor and fragrance compounds in a pet food sample. The increased peak capacity led to effective separation and identification of analytes that were not identified effectively using a single dimension separation.

Table I. The table below effectively summarizes a significant advantage of GC×GC over single dimension GC in terms of a demonstrable ability to discover more about what's in your food/flavor/fragrance sample. GC×GC can play a major role in aroma and flavor characterization research in which key compounds could be misidentified or missed entirely.

Number of Compounds Identified with ≥ 800 match	
GC-TOFMS	214
GC×GC-TOFMS	610

GC & GC×GC Metabolomics

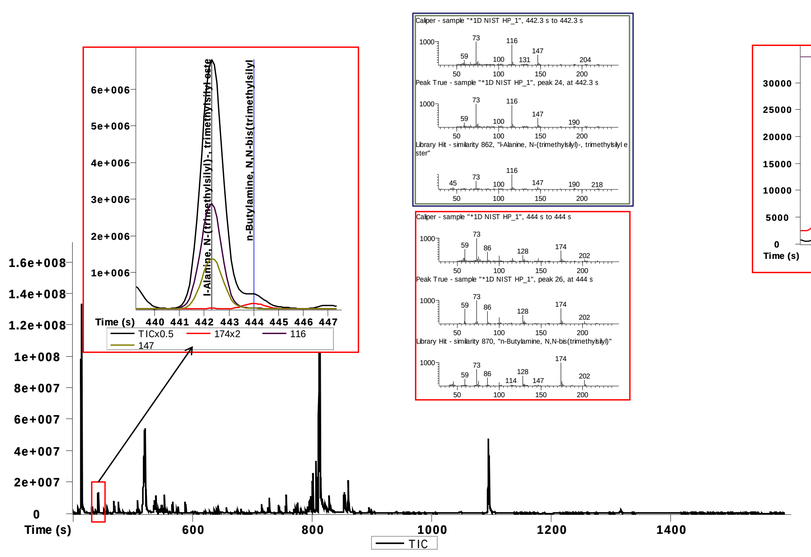

Figure 5. Single dimension separation of compounds present in derivatized extracts from NIST human plasma. Expanded view shows a region of the chromatogram where only one out of three analytes was successfully identified. In this example, deconvolution alone was unable to resolve all three analytes present in this region of the chromatogram. The effectiveness of a GC×GC separation of the same sample is demonstrated in Figure 6 below.

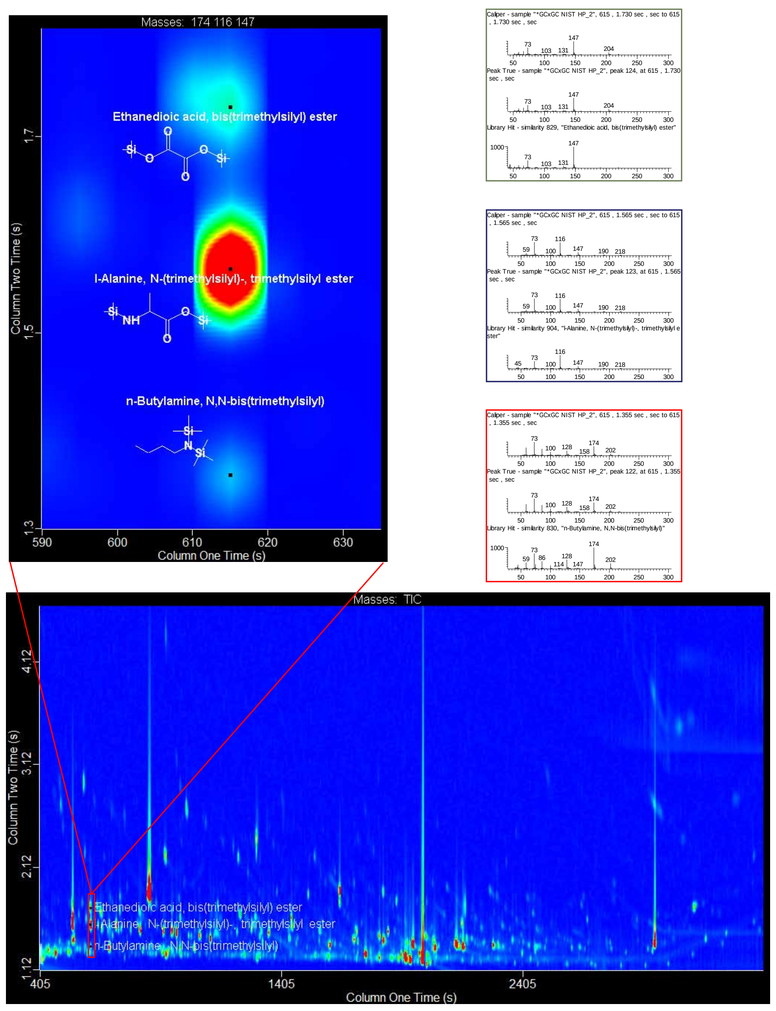

Figure 6. GC×GC separation of compounds present in derivatized extracts from NIST human plasma. The increased peak capacity led to effective separation and identification of analytes that were simply missed using a single dimension separation. The expanded view shows the power of the second dimension separation and its ability to obtain high quality spectral matches to commercially available libraries as a result.

Table II. The table below effectively summarizes a significant advantage of GC×GC over single dimension GC in terms of a demonstrable ability to discover more metabolites in a given study. This is of paramount importance when attempting to identify important biochemical pathways.

Number of Compounds Identified with ≥ 800 match	
GC-TOFMS	119
GC×GC-TOFMS	359

GC & GC×GC Petroleum

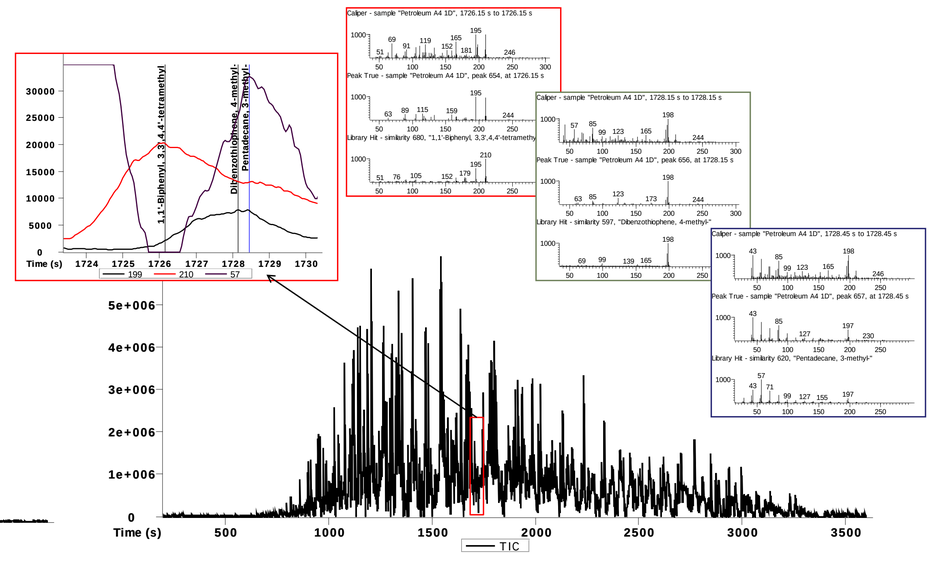

Figure 7. Single dimension separation of compounds present in African Crude Oil. Expanded view shows a region of the chromatogram where none of the analytes were confidently identified. In this example, deconvolution alone was unable to resolve all three analytes present in this region of the chromatogram. The power of a GC×GC separation of the same sample is demonstrated in Figure 8 below.

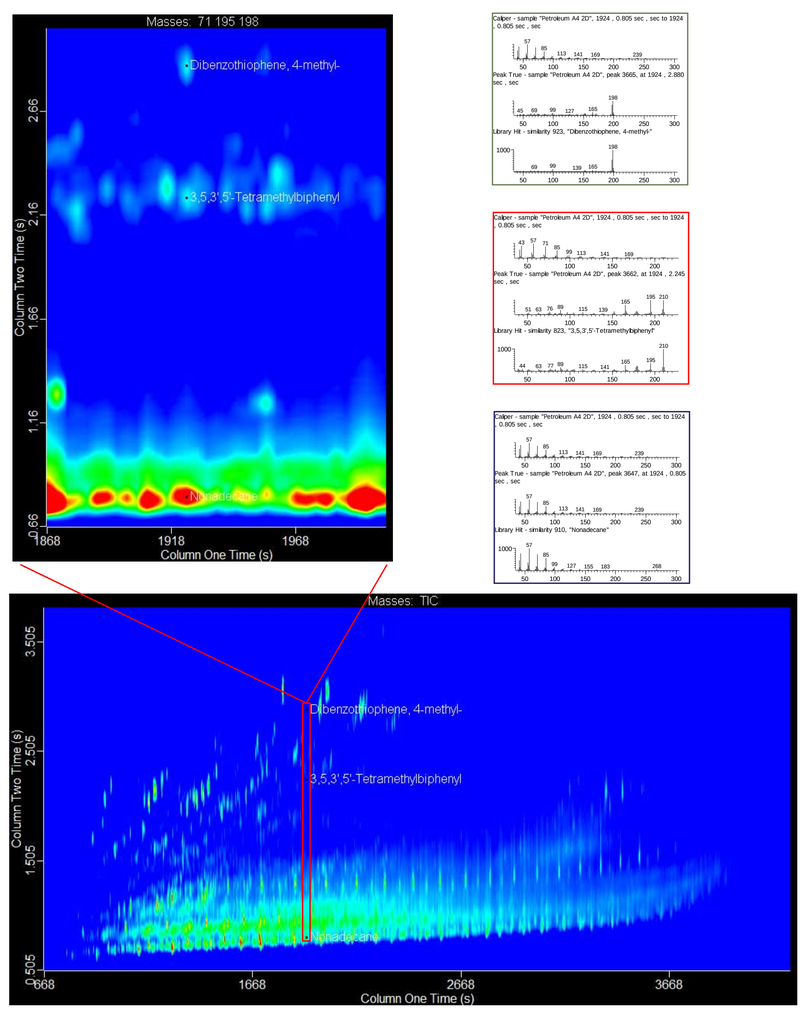

Figure 8. GC×GC separation of compounds present in African Crude Oil. The increased peak capacity led to effective separation and identification of analytes that were not confidently identified in a single dimension separation. The expanded view shows the power of the second dimension separation and its ability to obtain high quality spectral matches to commercially available libraries as a result. The structured nature of GC×GC chromatograms also aid in identification of compound classes since they tend to align in distinct bands in the two-dimensional display. In this example, the cryofocusing effects of thermal modulation significantly enhanced the signal-to-noise ratio of the example analytes, which also improved the ability to detect and identify them with added confidence.

Table III. The table below effectively summarizes a substantial advantage of GC×GC over single dimension GC in terms of a more complete characterization of petroleum samples.

Number of Compounds Identified with ≥ 800 match	
GC-TOFMS	163
GC×GC-TOFMS	1150