Analysis of Samples from the Gulf of Mexico Oil Spill by GCxGC-TOFMS

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Key Words: Petroleum, Variable Modulation, GCxGC, ChromaTOF ver. 4.30

1. Introduction

Two petroleum samples from the Gulf of Mexico Oil Spill were obtained: a Well Head Source Oil sample and a sample of Red Mousse. The Well Head Source Oil sample was collected by a Remotely Operated Vehicle (ROV) at the initial leaks in the damaged riser pipe. The Red Mousse sample was collected on the surface in the offshore marine environment. It had not been exposed to the surf zone. The samples provided had already been diluted in dichloromethane and had internal standards added prior to shipment to the lab for GCxGC-TOFMS analysis.

This analysis took advantage of a new feature allowing the analyst to vary the modulation period and hot pulse duration during an acquisition. LECO would like to take this opportunity to thank Prof. Ed Overton for providing the samples analyzed in this project.

2. Instruments and Methods

In this study, measurements were made with a LECO Pegasus® 4D GCxGC-TOFMS system. It was equipped with a GERSTEL MPS2 rail-type auto sampler. Data collection and work-up were performed using ChromaTOF® version 4.30.

For this study, the primary analytical column was a 30.0 m x 0.25 mm ID x 0.25 µm df Rtx-5SilMS. The secondary column was a 1.50 m x 0.10 mm ID x 0.10 µm df BPX-50. The temperature program started at 45°C with a 3 minute hold, and then ramped at 5°C/min to 340°C with a final hold of 15 minutes. The column offset was +5°C with a +20°C modulator offset. Variable modulation period and hot pulse durations were utilized. From time 0 sec to 1280 sec, a 3 sec modulation period with a 500 ms hot pulse was utilized. From time 1280 sec to 2044 sec, a 4 sec modulation period with a 600 ms hot pulse was utilized. From time 2044 sec to 2999 sec, a 5 sec modulation period with a 800 ms hot pulse was utilized. From time 2999 sec to the end of the analysis, a 5 sec modulation period with a 1000 ms hot pulse was utilized.

Acquired data was saved for a range from 45 to 400 m/z at 200 spectra/sec. Helium was used as the carrier gas at a corrected constant flow of 1.0 mL/min. A split/splitless inlet, operated in split mode, was used for sample introduction. The inlet was maintained isothermally at 280°C. An injection size of 1.0 µL was used for each analysis. The Well Head Source Oil was analyzed with a split ratio of 200:1. The Red Mousse sample was analyzed with a split ratio of 50:1.

3. Results

Both of the samples were data processed with a s/n ratio threshold of greater than or equal to 100:1 necessary to be identified as a peak. The peak finding algorithm of the data processing method was not applied in the regions where the solvent tail and column bleed are located. A Contour Plot of the "Well Head Source Oil" sample is shown in Figure 1. The Contour Plot with peak markers is shown in Figure 2. When the data was processed, 2670 peaks were identified in the Well Head Source Oil sample. Four deuterated internal standards were added to this sample—naphthalene-d8, acenaphthene-d10, chrysene-d12, and perylene-d12. The peaks identified in this analysis range from benzene, with a 1st dimension retention time (tr) of 368 sec and a 2nd dimension tr of 1.530 seconds, to dotetracontane (n-C_{42}), which has a 1st dimension tr of 4559 sec and a 2nd dimension tr of 3.315 seconds. The most retained analyte in the 2nd dimension is 2-methyl chrysene, which has a 1st dimension tr of 3114 sec and a 2nd dimension tr of 3.525 seconds. The most retained compound in the 2nd dimension is the internal standard perylene-d12, which has a 1st dimension tr of 3369 sec and a 2nd dimension tr of 4.260 seconds. The four internal standards are highlighted in Figure 3.

The use of three distinct modulation periods is indicated by the "notched" appearance in the upper left corner of the Contour Plot. In the past, a modulation period time of at least as long as that of the analyte with the longest 2nd dimension retention time was required. The duration of the hot pulse was set to provide the best overall 2nd dimension peak shape across the entire chromatogram. Decreasing the modulation period in regions of the analysis, which do not contain analytes which are highly retained on the 2nd dimension, allows for an increase in resolution on the 1st dimension in that region. The use of shorter hot pulse durations allow for increased trapping efficiency in the modulator in regions with more volatile analytes. The use of longer hot pulse durations allow for increased desorption efficiency in the modulator in regions with less volatile analytes. By varying the modulation period and hot pulse duration during the course of an analysis, it is possible to optimize the modulator's performance to provide the best resolution on the 1st dimension column (x-axis) and improved 2nd dimension peak shape throughout the analysis. Figure 4 shows the portion of the Surface Plot where the more volatile components elute. In this segment of the analysis, a 3 second modulation period with a 500 ms hot pulse was utilized to increase trapping efficiency and resolution on the 1st dimension. Figure 5 highlights a section of the Contour Plot where the shorter modulation period provides for increased resolution on the x-axis. Figure 6 shows the portion of the Surface Plot where the less volatile components elute. In this segment of the analysis, a 5 second modulation period was utilized to accommodate the analytes that are highly retained on the 2nd dimension column. A 1000 ms hot pulse was utilized to increase desorption efficiency. The increased desorption efficiency results in improved peak shape and increased signal for the least volatile analytes in this portion of the analysis.

The Red Mousse is a weathered product created when the oil has been exposed to water and air, forming a stable emulsion. The Red Mousse sample analyzed in this project was collected on the surface offshore. Figure 7 shows the Contour Plot for the Red Mousse sample. The Contour Plot with peak markers is shown in Figure 8. When the data was processed, 992 peaks above the s/n threshold were identified in the Red Mousse sample. The most noticeable difference from the Well Head Source Oil sample is the absence of analytes in the more volatile portion of the plot. The most volatile peak identified in the Red Mousse is 2,4,6-trimethyloctane, which has a 1st dimension tr of 1560 sec and a 2nd dimension tr of 1.490 seconds. The most retained analyte in the 2nd dimension is 2-methyl chrysene, which has a 1st dimension tr of 3114 sec and a 2nd dimension tr of 3.535 seconds.

4. Conclusions

To date, the oil spill off the coast of Louisiana, in the Gulf of Mexico, is the largest oil spill in US history. The environmental and economic consequences of this event will continue well into the future. The ability to identify the chemical make-up of these incredibly complex samples, including the source oil as well as the changes in composition resulting from weathering and additional chemicals used in response to the spill will be an important tool utilized by those responding to this event. These samples contain components over a wide range of volatilities and functionalities. When analyzed by GCxGC-TOFMS, the large number of individual components can be resolved and identified in a single analysis, providing an efficient means for the analyst to obtain a large amount of information about the sample with a minimum amount of effort. LECO's Pegasus 4D GCxGC-TOFMS system and ChromaTOF software are an excellent choice for the analysis of highly complex samples such as those demonstrated in this work.

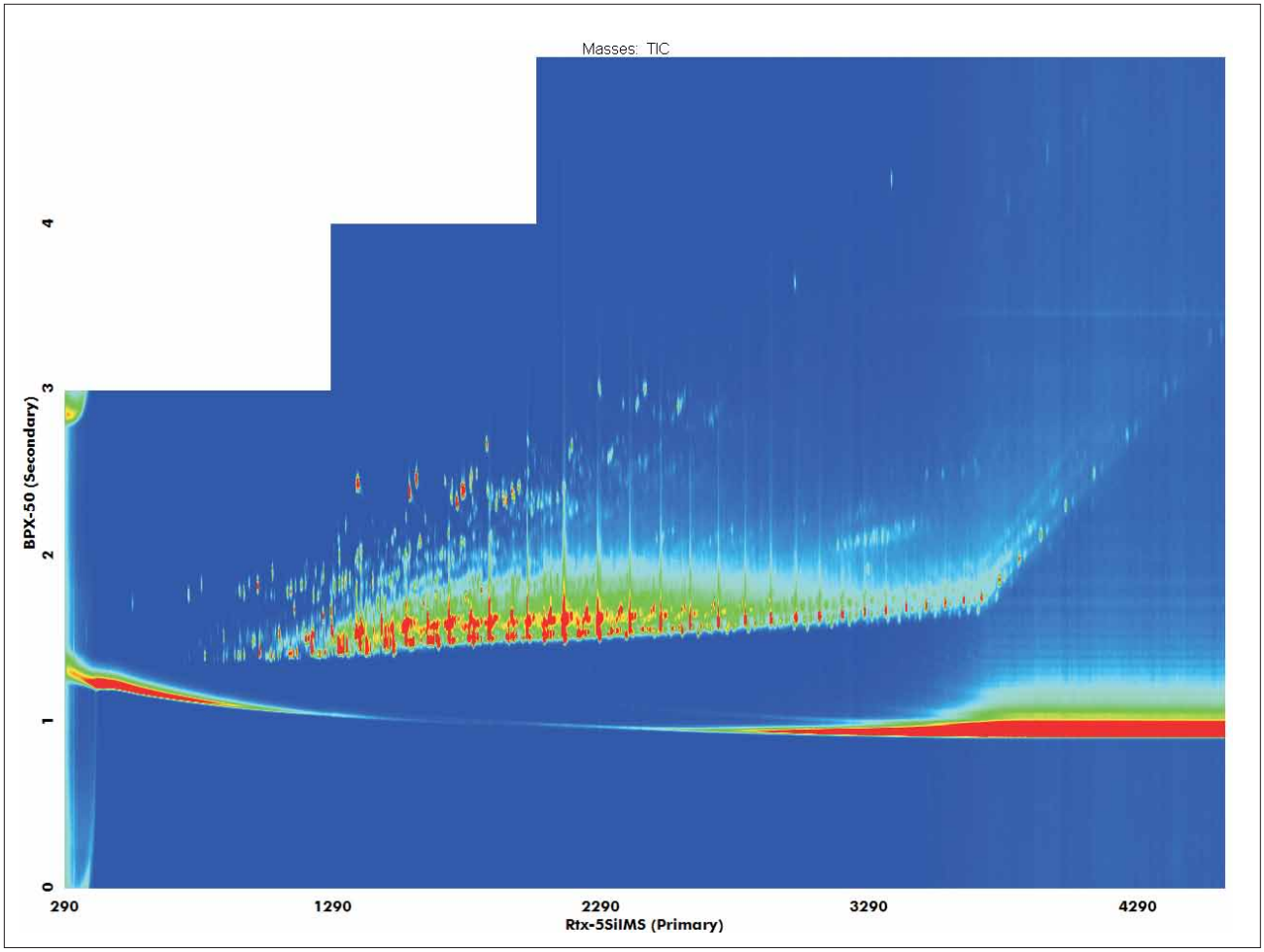

Figure 1: A contour plot of the Well Head Source Oil sample. The use of three distinct modulation periods is indicated by the "notched" appearance in the upper left corner of the contour plot.

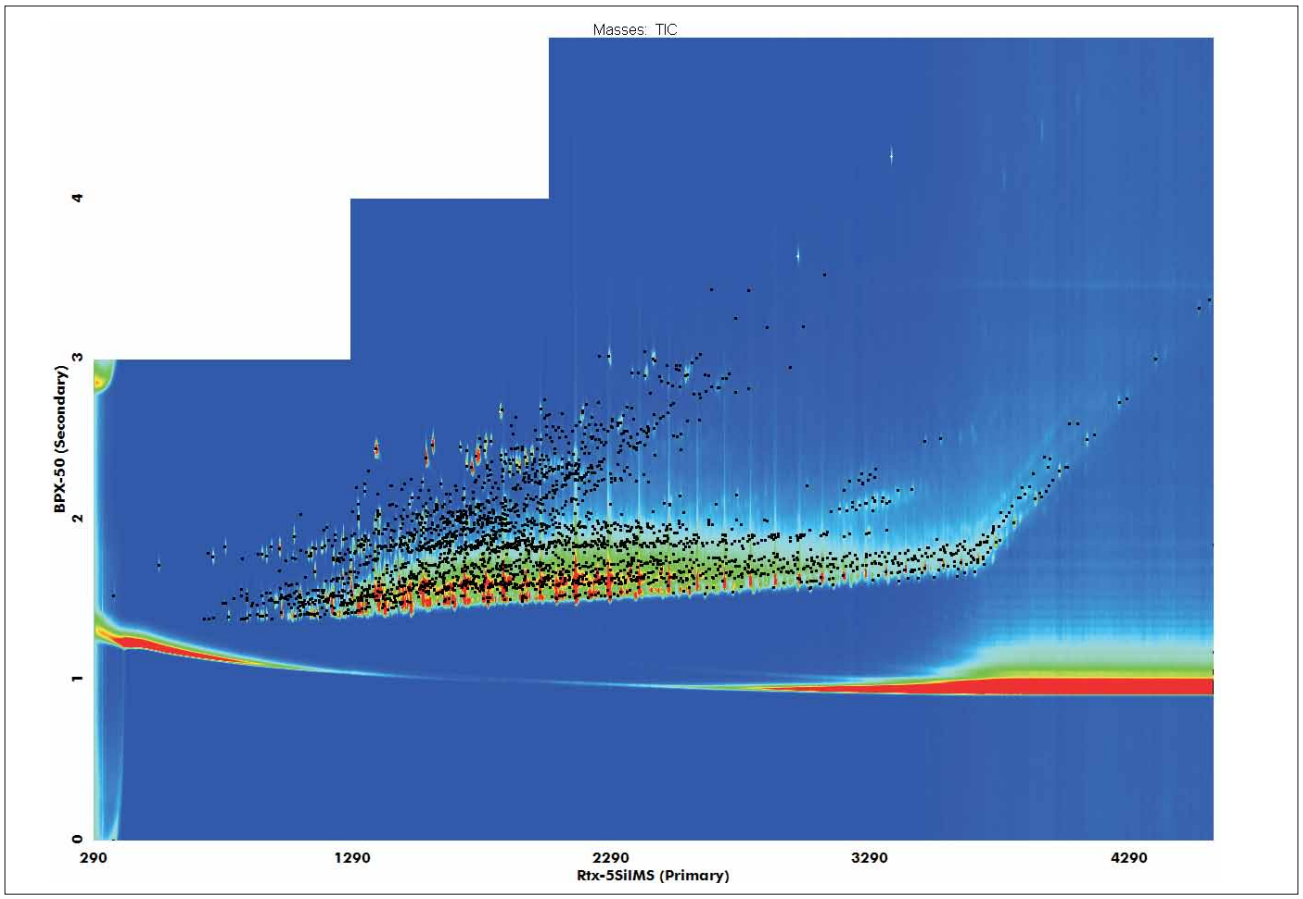

Figure 2: A contour plot of the Well Head Source Oil sample showing peak markers for the 2670 peaks with a s/n ratio of ⩾ 100. The 4 peaks indicated by white peak markers are the deuterated internal standards.

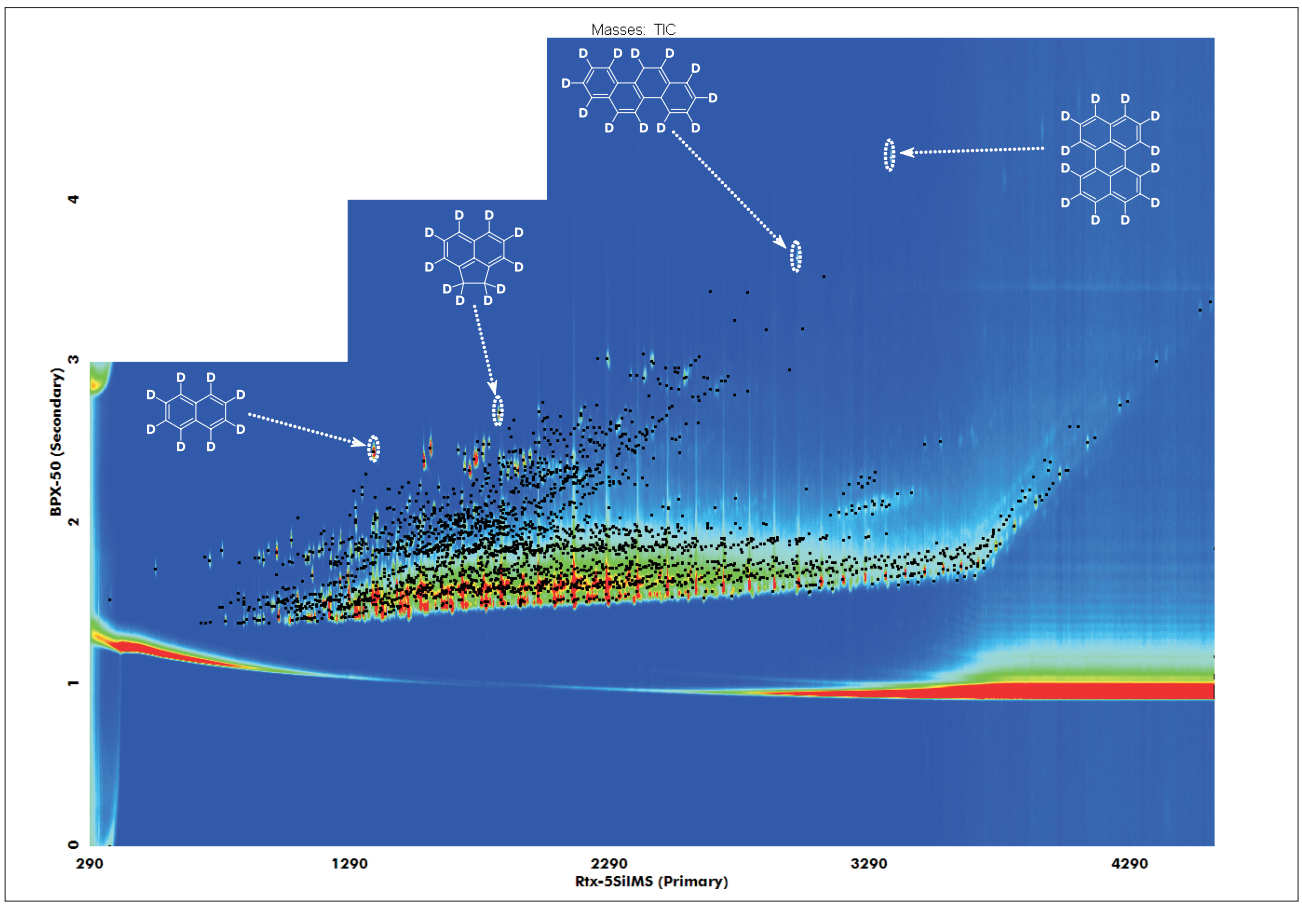

Figure 3: A contour plot highlighting the retention plane locations of the four internal standards, naphthalene d-8, acenaphthene-d10, chrysene-d12 and perylene-d12.

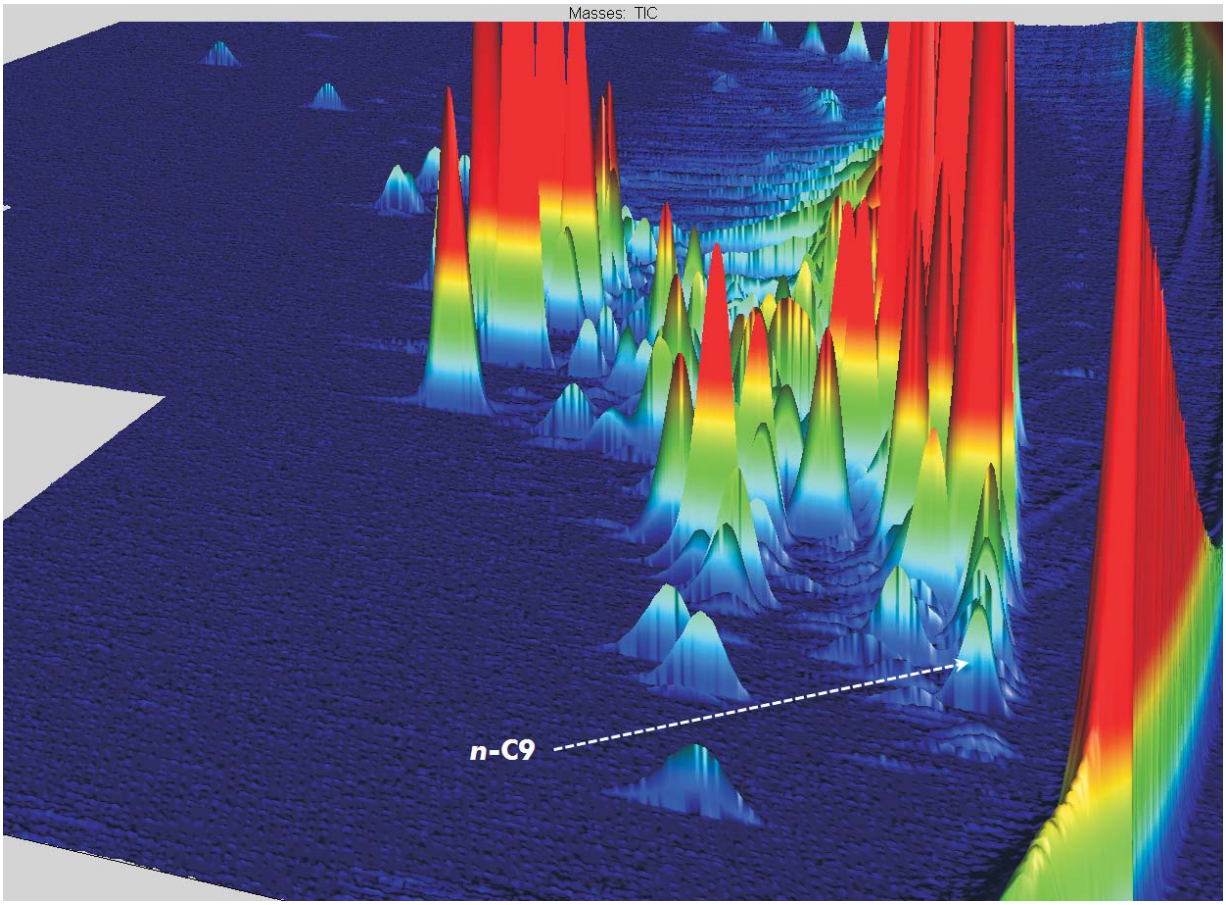

Figure 4: A surface plot of the Well Head Source Oil sample showing peak shape of the early eluting compounds.

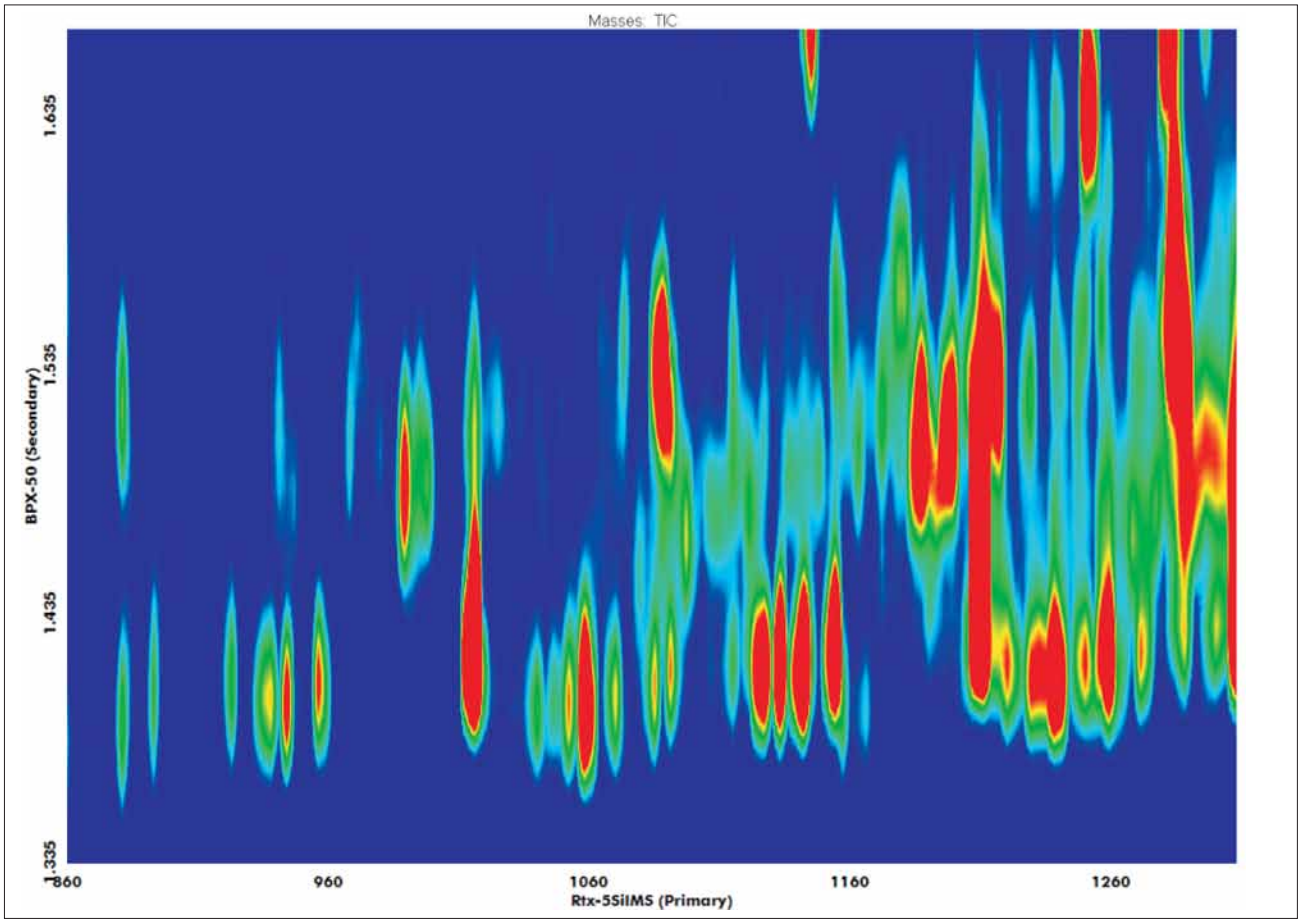

Figure 5: A highlighted section of the Contour Plot where the shorter modulation period (3 sec) provides for increased resolution on the x-axis.

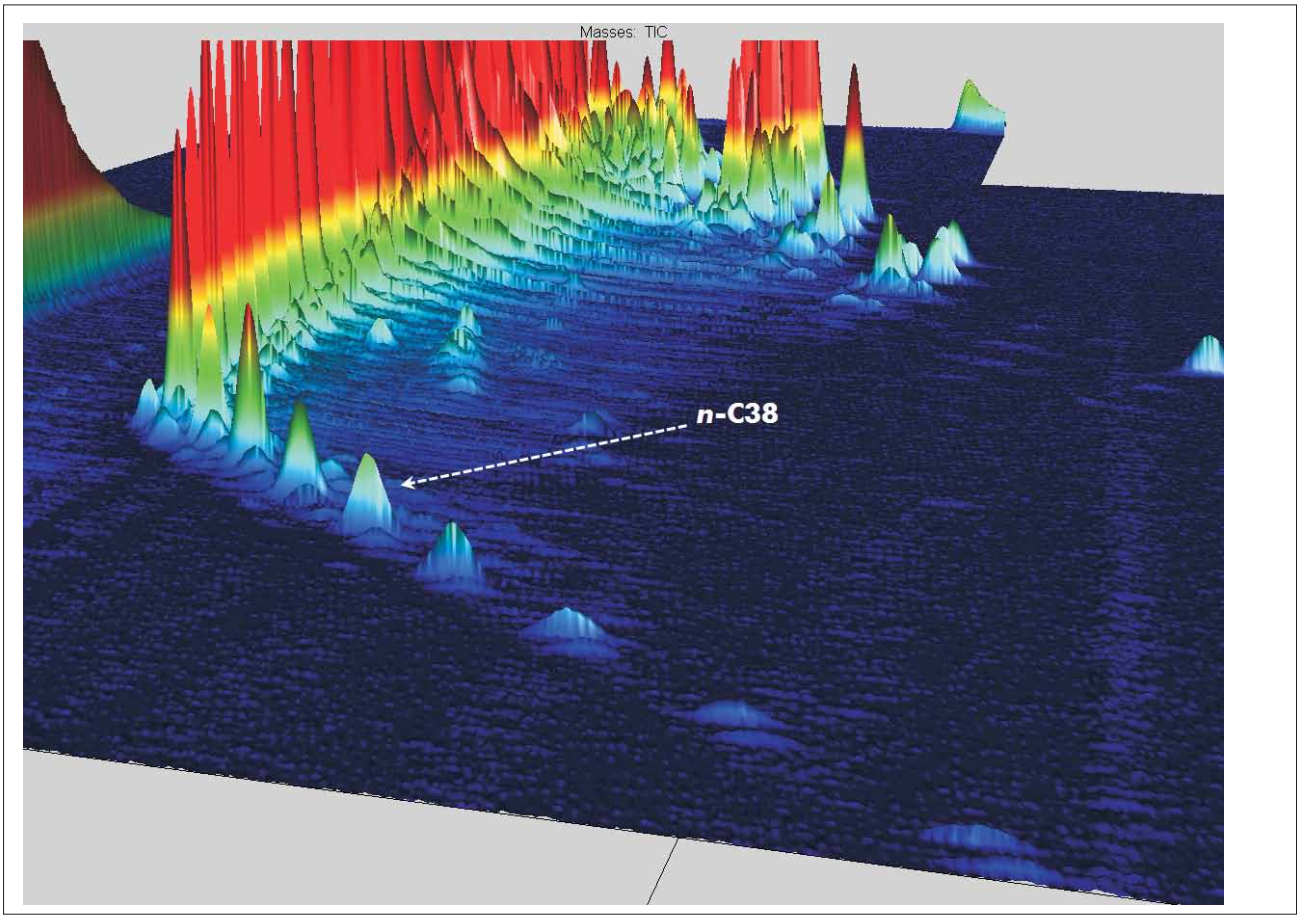

Figure 6: A surface plot of the Well Head Source Oil sample showing peak shape of the late eluting compounds.

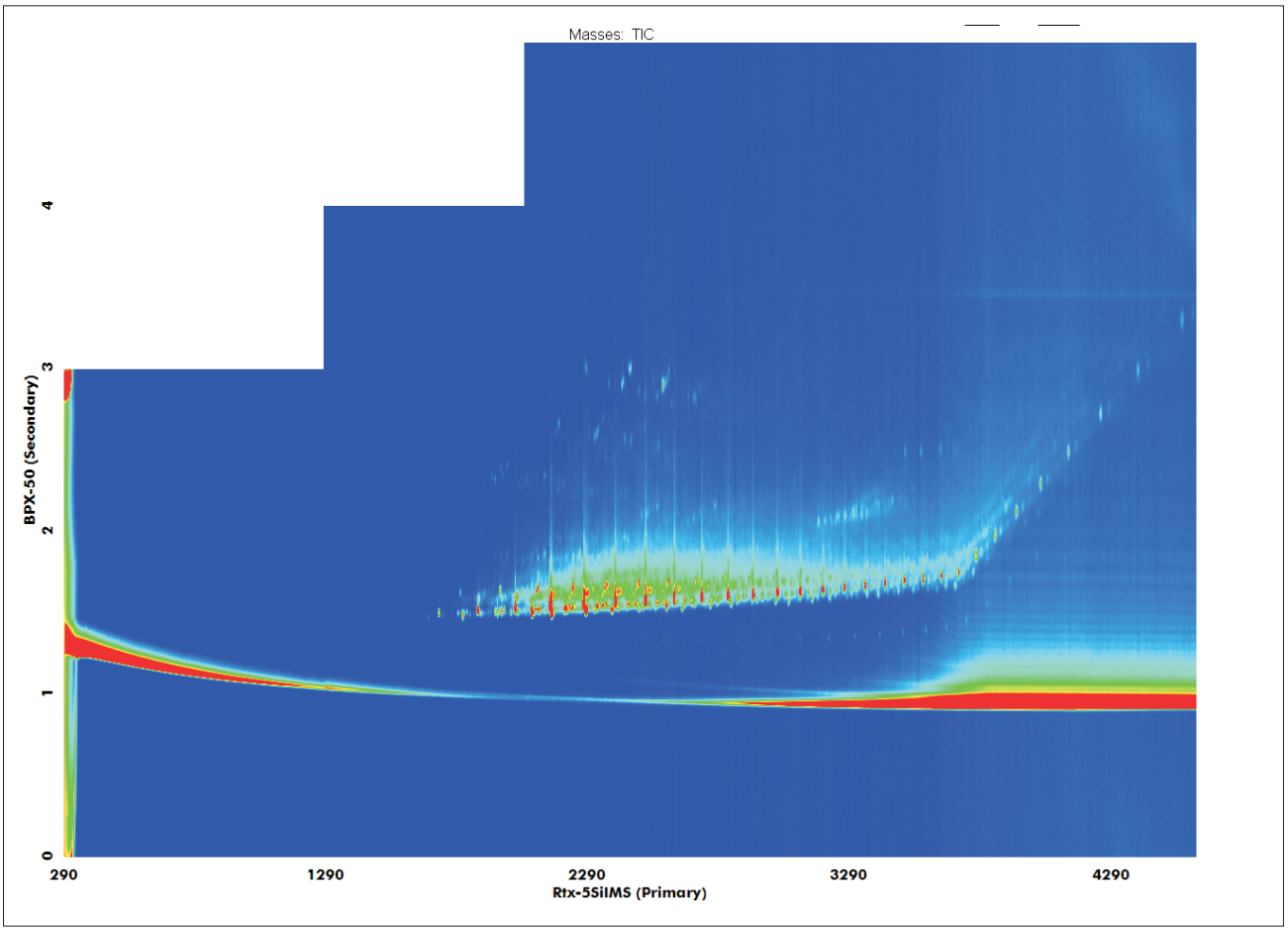

Figure 7: A contour plot of the Red Mousse sample.

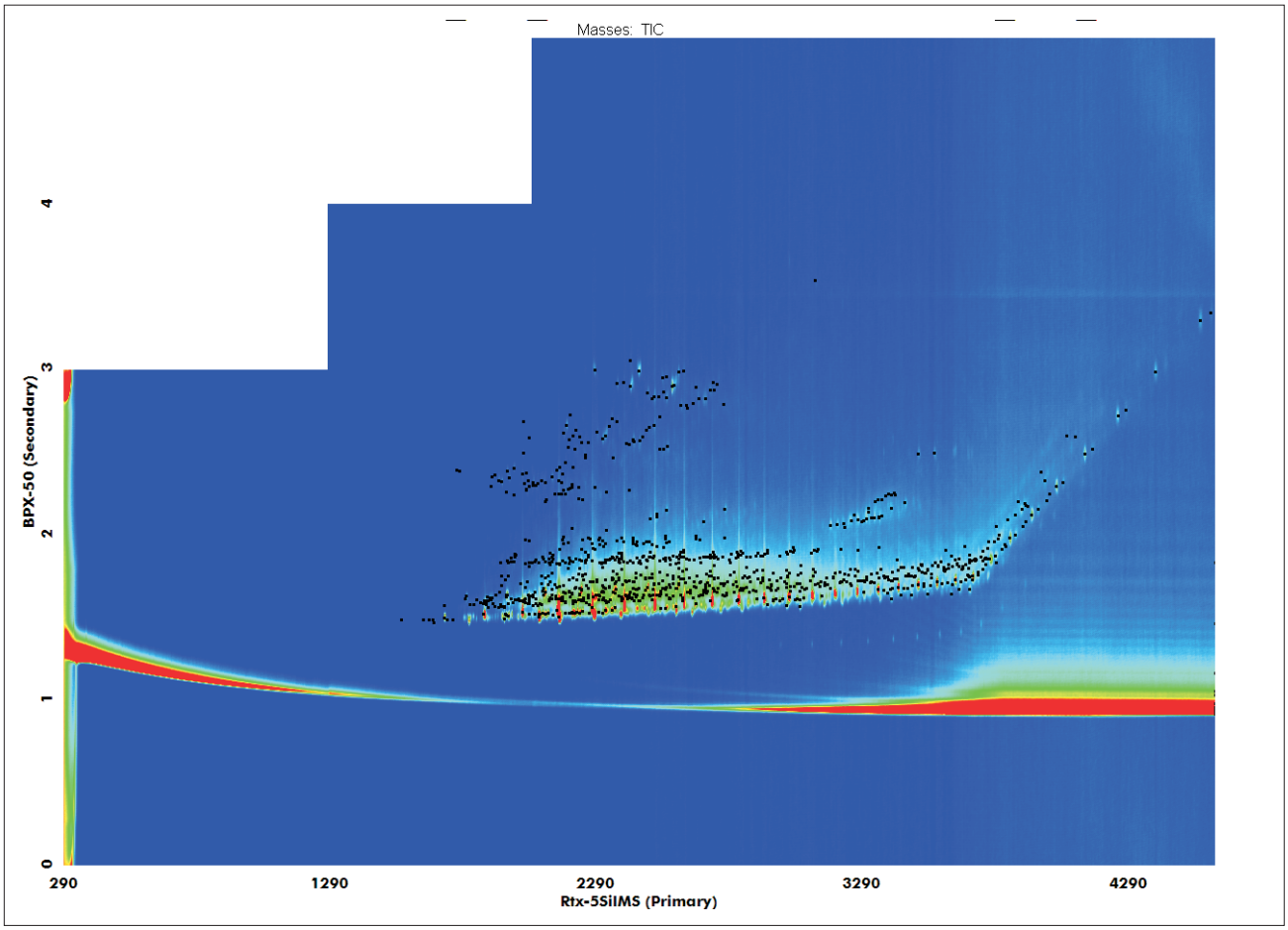

Figure 8: A contour plot of the Red Mousse sample showing peak markers for the 992 peaks with a s/n ratio of ⩾ 100.

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