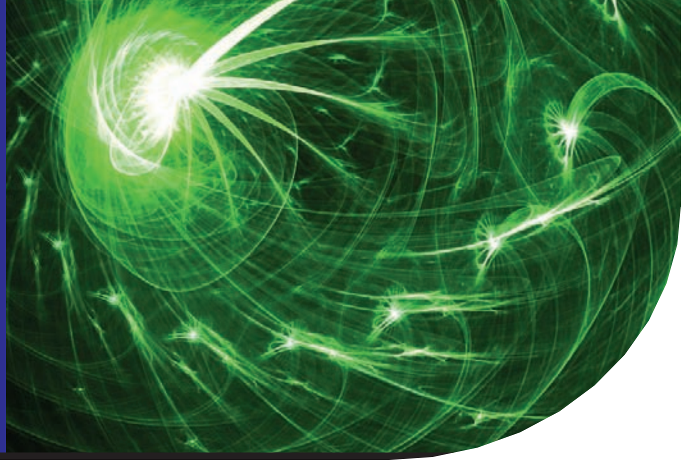

Analysis of Samples from the Gulf of Mexico Oil Spill by GCxGC-TOFMS

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 Professor Ed Overton for providing the samples analysed in this project.

> ***"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 utilised by those responding to this event"***

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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 30.0m x 0.25mm ID x 0.25µm df Rtx-5SilMS. The secondary column was a 1.50 m x 0.10mm ID x 0.10µm 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 utilised. From time 0 seconds to 1280 seconds, a 3 second modulation period with a 500 ms hot pulse was utilised. From time 1280 seconds to 2044 seconds, a 4 seconds modulation period with a 600 ms hot pulse was utilised. From time 2044 seconds to 2999 seconds, a 5 seconds modulation period with a 800 ms hot pulse was utilised. From time 2999 seconds to the end of the analysis, a 5 seconds modulation period with a 1000 ms hot pulse was utilised.

Acquired data was saved for a range from 45 to 400 m/z at 200 spectra/seconds. Helium was used as the carrier gas at a corrected constant flow of 1.0mL/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 1.0µL was used for each analysis. The Well Head Source Oil was analysed with a split ratio of 200:1. The Red Mousse sample was analysed with a split ratio of 50:1.

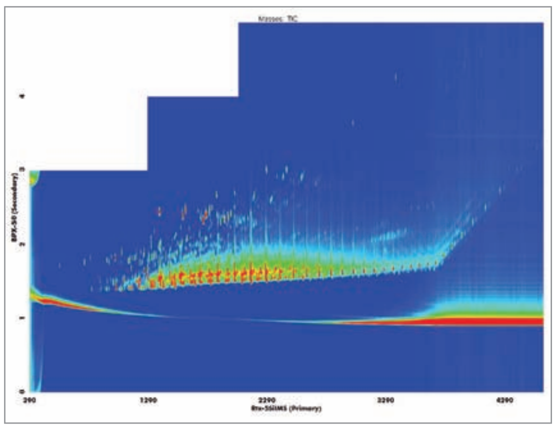


Figure 1: A contour plot of the Well Head Source Oil sample. The use of three distinct modulation periods is indicated by the 'notched' appearance in the upper left corner of the contour plot.

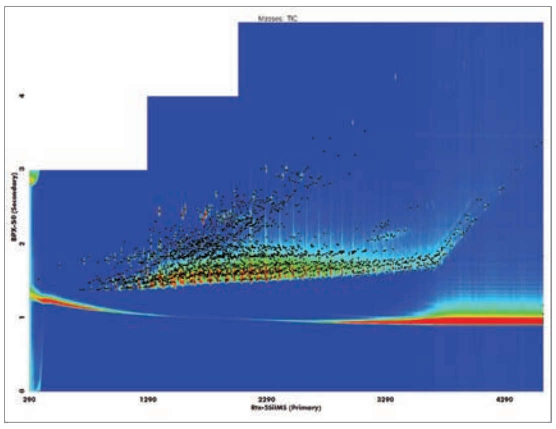


Figure 2: A contour plot of the Well Head Source Oil sample showing peak markers for the 2670 peaks with a s/n ratio of ≥ 100. The 4 peaks indicated by white peak markers are the deuterated internal standards.

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 data 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 (t_r) of 368 seconds and a 2nd dimension t_r of 1.530 seconds, to dotetracontane (n-C_{42}), which has a 1st dimension tr of 4559 seconds and a 2nd dimension t_r of 3.315 seconds. [The most retained analyte in the 2nd dimension is 2-methyl chrysene, which has a 1st dimension t_r of 3114 seconds and a 2nd dimension t_r 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 seconds and a 2nd dimension t_r of 4.260 seconds]. The four internal standards are highlighted in *Figure 3*.

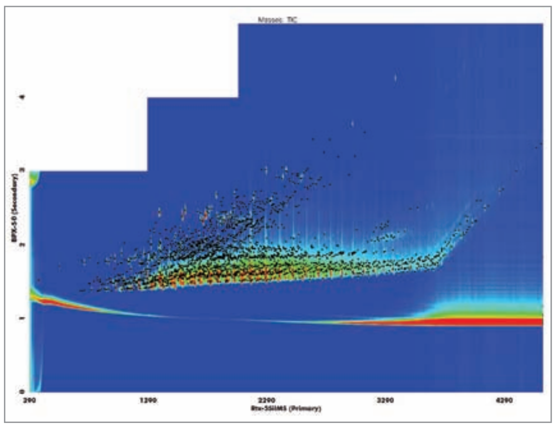


Figure 3: A contour plot highlighting the retention plane locations of the four internal standards, naphthalene d-8, acenaphthene-d10, chrysene-d12 and perylene-d12.

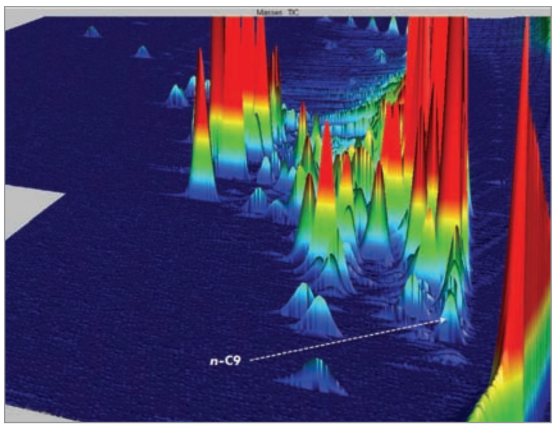


Figure 4: A surface plot of the Well Head Source Oil sample showing peak shape of the early eluting compounds.

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 that do not contain analytes that are highly retained on the 2nd

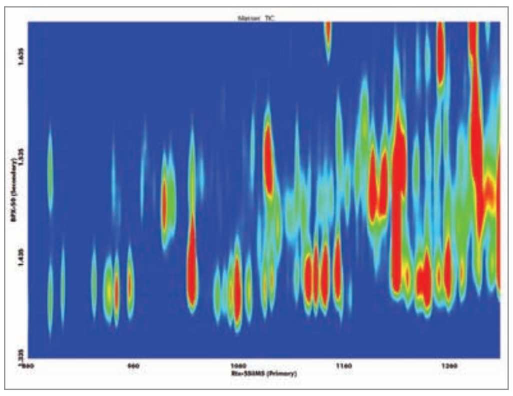


Figure 5: A highlighted section of the Contour Plot where the shorter modulation period (3 sec) provides for increased resolution on the x-axis.

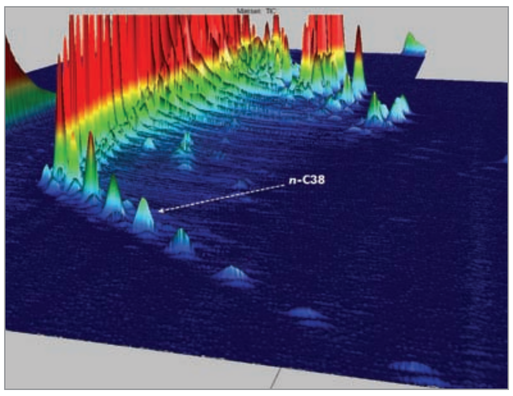


Figure 6: A surface plot of the Well Head Source Oil sample showing peak shape of the late eluting compounds.

dimension, allows for an increase in resolution on the 1st dimension in that region. The use of shorter hot pulse durations allows for increased trapping efficiency in the modulator in regions with more volatile analytes. The use of longer hot pulse durations allows 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 optimise 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 utilised 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 utilised to accommodate the analytes that are highly retained on the 2nd dimension column. A 1000 ms hot pulse was utilised 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.

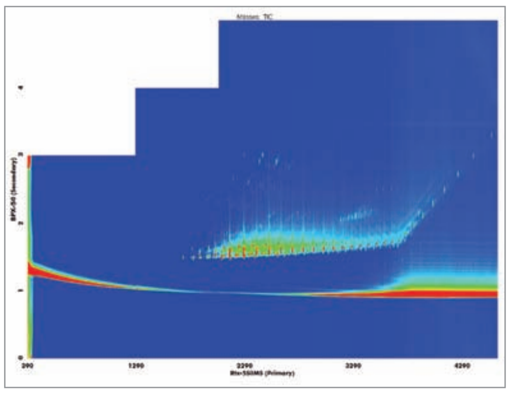


Figure 7: A contour plot of the Red Mousse sample.

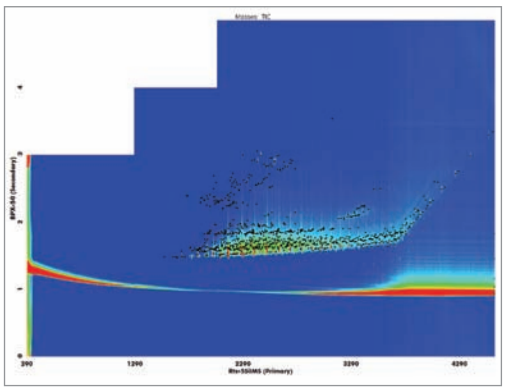


Figure 8: A contour plot of the Red Mousse sample showing peak markers for the 992 peaks with a s/n ratio of ≥ 100.

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 analysed 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 data 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 seconds and a 2nd dimension t_r of 1.490 seconds. The most retained analyte in the 2nd dimension is 2-methyl chrysene, which has a 1st dimension t_r of 3114 seconds and a 2nd dimension tr of 3.535 seconds.

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 utilised by those responding to this event. These samples contain components over a wide range of volatilities and functionalities. When analysed 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 Pegasus4D GCxGC-TOFMS system and ChromaTOF software are an excellent choice for the analysis of highly complex samples such as those demonstrated in this work.

Neutralised Temperature Conditions for Accurate Spectrometer Measurement

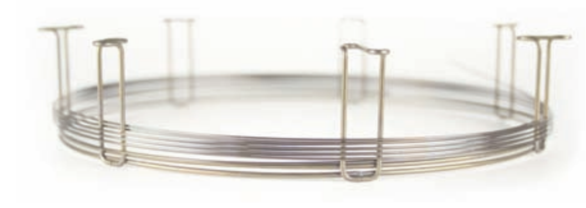
A new accessory from **Ocean Optics** is broadening the range of applications for its field-portable spectrometers. The SteadiQ provides a temperature controlled atmosphere, helping to stabilise temperature effects and eliminate temperature drift in inclement conditions or extreme temperatures from -20C to 50°C. The rugged, portable device assures more accurate, reliable results in field applications including solar irradiance, volcanic observation, greenhouse monitoring, and industrial environments such as cold food storage.

Available in both UV (200-1100nm) and Vis-NIR (400-2500nm) versions, the SteadiQ interfaces directly with Ocean Optics' USB2000+, USB4000, HR2000+, HR4000, Maya2000, Maya2000 Pro, QE65000, and NIRQuest spectrometers. In extreme hot or extreme cold conditions, the unit operates independently from outside temperatures. It connects easily to the spectrometer with preconfigured plug-ins and communicates via the spectrometer's USB port.

Circle no. 19

New Metal GC Columns Deliver Higher Reproducibility for Petrochemical Testing

Phenomenex, Inc introduces the Zebron™ ZB-1XT SimDist – a metal GC column specially designed for simulated distillation analyses in petrochemical applications. The new column features Phenomenex's unique Glass Infusion™ technology, which ensures consistent phase coating and reproducibility. Zebron ZB-1XT SimDist are rugged and provide documented efficiency gains of up to 70% over other comparable metal columns on the market. Every column is individually tested to guarantee quality.



Simulated boiling point methods are commonly used in petrochemical analysis to determine the range of hydrocarbons in a sample. These high-temperature distillation methods require resolution greater than 2.0 of C50 and C52, posing a challenge for most columns used in this application. The new Zebron ZB-1XT SimDist column exhibits less than 3.5% loss in resolution after 90 hours at 430°C.

"Traditional metal GC columns used in these applications have exhibited uneven stationary phase bonding, which negatively affects performance and reproducibility," explained Kory Kelly, GC Product Manager for Phenomenex. "Our proprietary bonding technology ensures consistent quality and each of our new columns is tested individually, rather than in batches."

Circle no. 20