

Group-type Analysis of Petroleum Products by GCxGC



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Introduction

Precise characterization of petroleum-derived fuels is important for the oil industry and environmental monitoring alike. However, it is a tedious and difficult task to identify each of the thousands of individual components present in these complex samples.

Group-type analysis using complementary two-dimensional gas chromatography (GCxGC) offers significant advantages over conventional chromatography with its vastly expanded separation space and the added benefit of highly structured groupings of compounds for simple classification of hydrocarbons.

To separate complex species by GCxGC, it is essential to have a highly efficient column dimension and a complementary column selectivity. High temperature resistance and flexibility of the GC column tubing are an added advantage for GCxGC.

In addition, complementary selectivities like Zebron™ ZB-1HT Intorno™, which is a non-polar 100% dimethylpolysiloxane based stationary phase and Zebron ZB-50, which is a higher-polar 50% phenyl phase, offer improved separation for group-type analysis.

Here we demonstrate the use of reverse fill/flush flow modulation with complementary set of column chemistry for robust, repeatable and affordable GCxGC, combined with simple, yet effective, data processing workflows for group-type analysis.

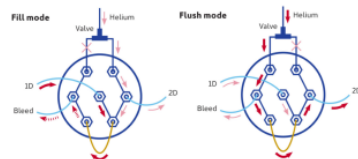
Experimental Conditions

- Sample: Crude oil (industrial)
- GCxGC: INSIGHT™ flow modulator (SepSolve Analytical)
- Column set: Zebron ZB-1HT Intorno and ZB-50 (Phenomenex) in both "normal" and "reversed" phase configurations
- Software: Instrument control and data processing was performed using ChromSpace®

Materials and Methods

GCxGC Normal Phase		GCxGC Reversed Phase	
Column 1	Zebron ZB-1HT	Column 1	Zebron ZB-50
Column 2	Zebron ZB-50	Column 2	Zebron ZB-1HT
Detector: FID			
Carrier Gas: Hydrogen			
Flow: 40 mL/min, Air Flow: 400 mL/min, Temperature: 300 °C			

FIGURE 1.
The valve-based INSIGHT modulator



The valve-based INSIGHT modulator uses reverse fill/flush dynamics, which provides increased peak capacity and improved peak symmetry compared to forward fill/flush devices

FIGURE 2.
GCxGC-FID colour plots for the separation of the same crude oil using two different column sets

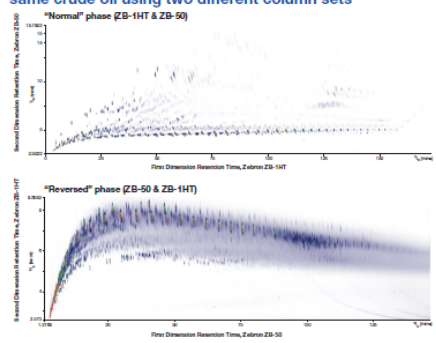
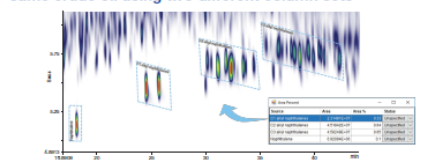


FIGURE 3.
GCxGC-FID colour plots for the separation of the same crude oil using two different column sets



Results and Discussion

Figure 2 shows the GCxGC-FID separations achieved for the crude oil. Note the wide volatility range from C₁₀-C₄₄ with excellent peak shape throughout.

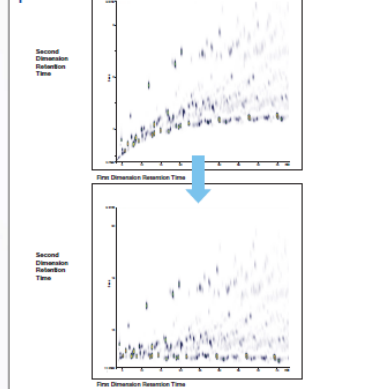
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and then the ChromSpace software draws the image on a graph. The chromatogram in Figure 2 shows great distribution of peaks across both sets.

The Zebron ZB-1HT Intorno is a non-polar and separation by boiling points on one dimension and the Zebron ZB-50 is a polar, slow phenyl phase that separates with p-pi interactions in the other dimension. As illustrated in Figure 2, they can be run in "normal" phase with the non-polar ZB-1HT Intorno as the first column separating by boiling points and then separating by p-pi interactions on the second phase with the ZB-50. Or they can be set in "reversed" phase in the opposite arrangement. Reversed phase is popular for the complex oil matrices with many similar boiling point aromatics; components since it does a great job in separating them first group-type. ChromSpace incorporates a range of other processing tools which are beneficial for GCxGC analysis of petrochemicals, including an alignment tool to allow a homologous series of landmark peaks to be used to "correct" all t_R positions. As you can see from Figure 4 this can simplify the application of standards.

FIGURE 4.
Alignment tool to allow a homologous series of landmark peaks to be used to "correct" all t_R positions



Conclusion

- Fast and efficient group-type analysis of complex petrochemicals is possible using flow-modulated GCxGC-FID
- INSIGHT flow modulator offers consumable-free, robust and repeatable GCxGC for a wide range of analyses
- Streamlined data processing workflows in ChromSpace software
- Using two Zebron GC columns, ZB-1HT Intorno and ZB-50, provides complementary orthogonal selectivity to address individual aromatics and aromatics from each other
- Reversed phase GCxGC works well to separate the higher boiling point large molecular compounds into group types

The best published method for the analysis of complex petrochemicals is possible using flow-modulated GCxGC-FID. Copyright © 2023 Phenomenex, Inc. All rights reserved. This document is the property of Phenomenex, Inc. and is not to be distributed outside of the company.