

Light Crude Oil Fingerprinting from Six Different Global Regions Using GCxGC-TOFMS with Structural Classifications to Compare Functional Group Differences

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1. Introduction

The complex nature of crude oil demands analytical solutions and instrumental methods that will separate and identify the complex chemical profile as well as characterize key chemical functional group class differences between complex samples. Comprehensive two-dimensional gas chromatography (GCxGC) expands the peak capacity of the chromatographic separation thereby increasing resolution and analyte characterization for complicated samples. Time-of-Flight mass spectrometry (TOFMS) offers continuous full range non-skewed mass spectral information and fast acquisition rates ideal for analyte identification of complex mixtures.



This application note shows GCxGC-TOFMS data from the comparative analysis of six light crude oil standards from different global regions. A GCxGC-TOFMS analysis method was developed that utilizes variable modulation to maximize the available peak capacity of the second dimension. Comprehensive two-dimensional chromatography facilitates structured separation of functional group classes within the GCxGC chromatographic plane.

The comparisons of light crude oil highlight the differences of key functional groups utilizing the Classifications feature available in ChromaTOF software. Major Classification regions such as alkanes, alkenes, alkynes, alcohols, aldehydes, ketones, alkyl-cyclics, indenenes, naphthalenes, thiophenes, and PAHs are shown. The comparison of the chromatographic and peak table data with "Classifications" provides a rapid data analysis technique to evaluate key chemical functional group differences in crude oils from various geographic regions. The data presented in this

note illustrate the advantages and benefits of GCxGC-TOFMS as well as a "Classifications" strategy to accurately compare chemical differences between light crude oils from different global regions.

USING CLASSIFICATIONS FOR SAMPLE PROFILING

The "Classifications" feature available in the ChromaTOF software was utilized to compare and highlight the differences in key chemical functional group classes between the six different light crude oil standards.

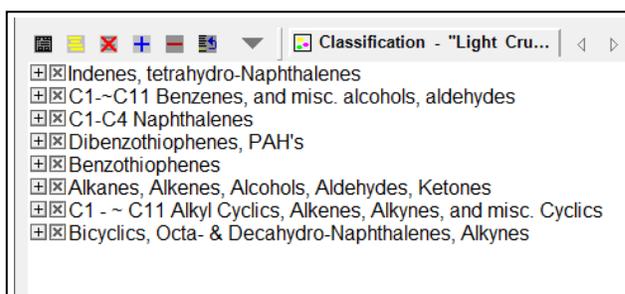


Figure 1. The figure above is a list of the 8 Classification regions used to define the chemical profile of six light crude oil standards.

2. Results

The following two-dimensional contour plots illustrate differences in chemical composition which can be beneficial in differentiation of the light crude oil origin. Table 1 lists the area percent results for each classification that specifically defines each standard.

Eight classifications are shown with colored peak markers and labels that represent different chemical and functional group classes. The orthogonal separation system used in GCxGC, provides very structured chromatograms that generate distinct bands of analytes grouped by specific chemical characteristics. This optimized separation illustrates the advantages of GCxGC-TOFMS to provide an informative profile for the chemical composition of light crude oil.

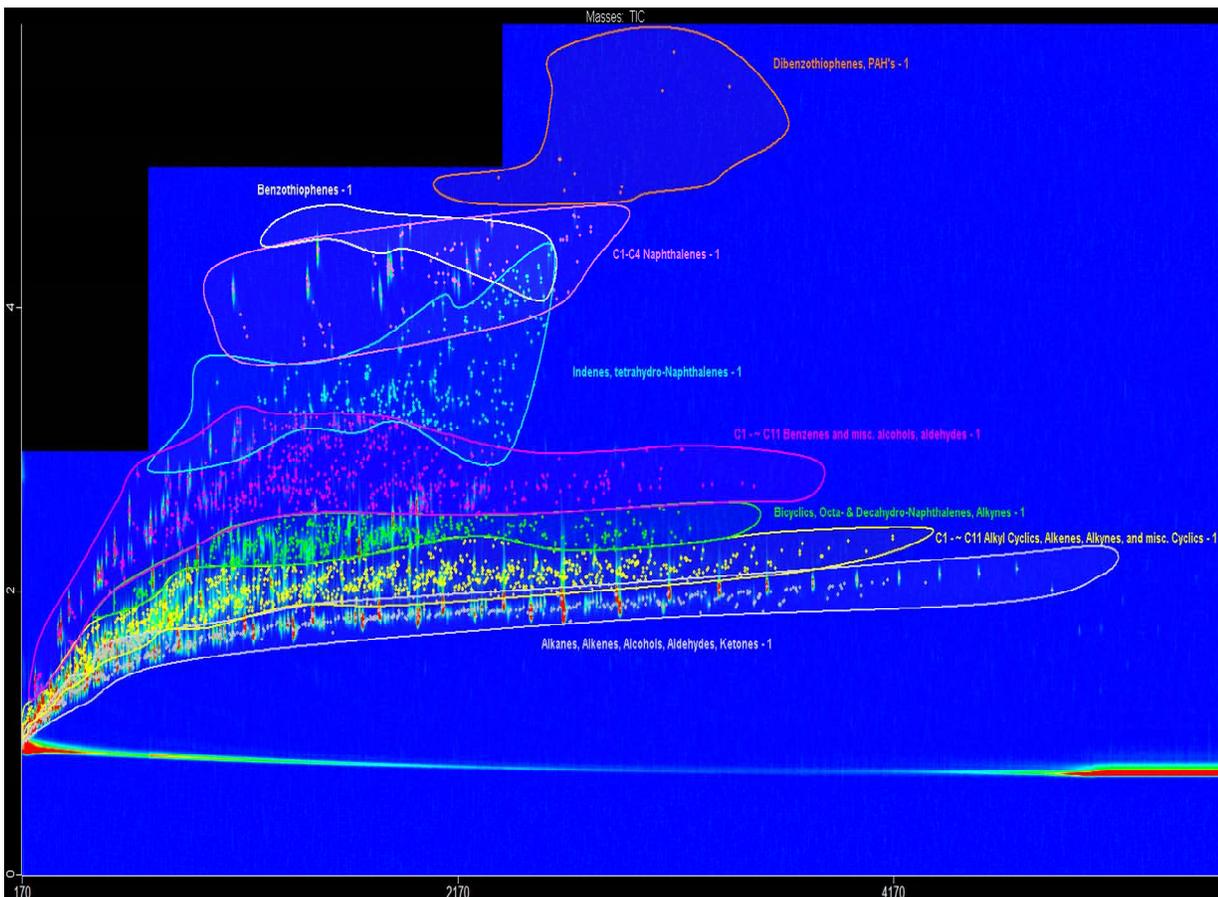


Figure 2. The two-dimensional chromatogram in the figure above shows the GCxGC-TOFMS analysis of a Nigerian light crude oil standard (I Nigerian 1C).

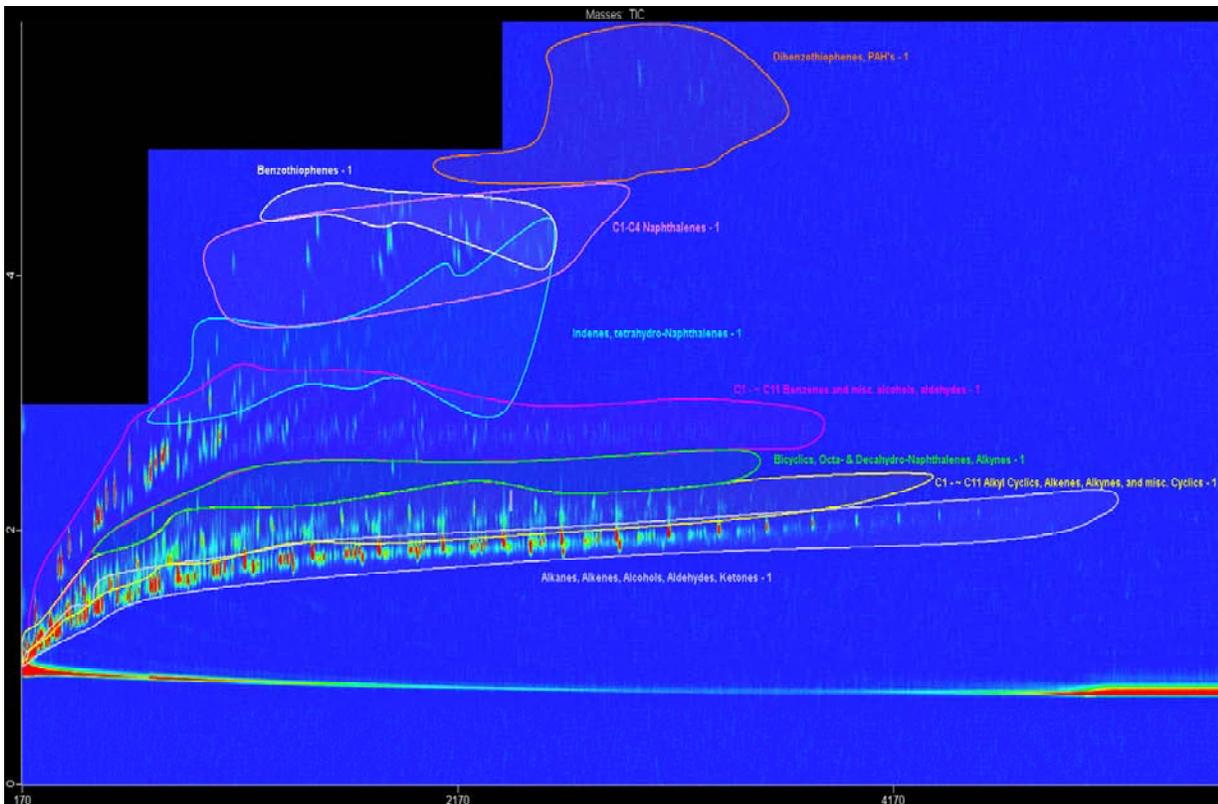


Figure 3. The figure above shows the GCxGC-TOFMS analysis of an Arabian Light crude oil standard (II Arabian Light 2B) without the peak markers. The contour plot shows the efficient two-dimensional chromatographic separation of the different structured chemical classes. The peaks in the contour plot are scaled by the color intensity with red as the most intense peaks and blue as the baseline.

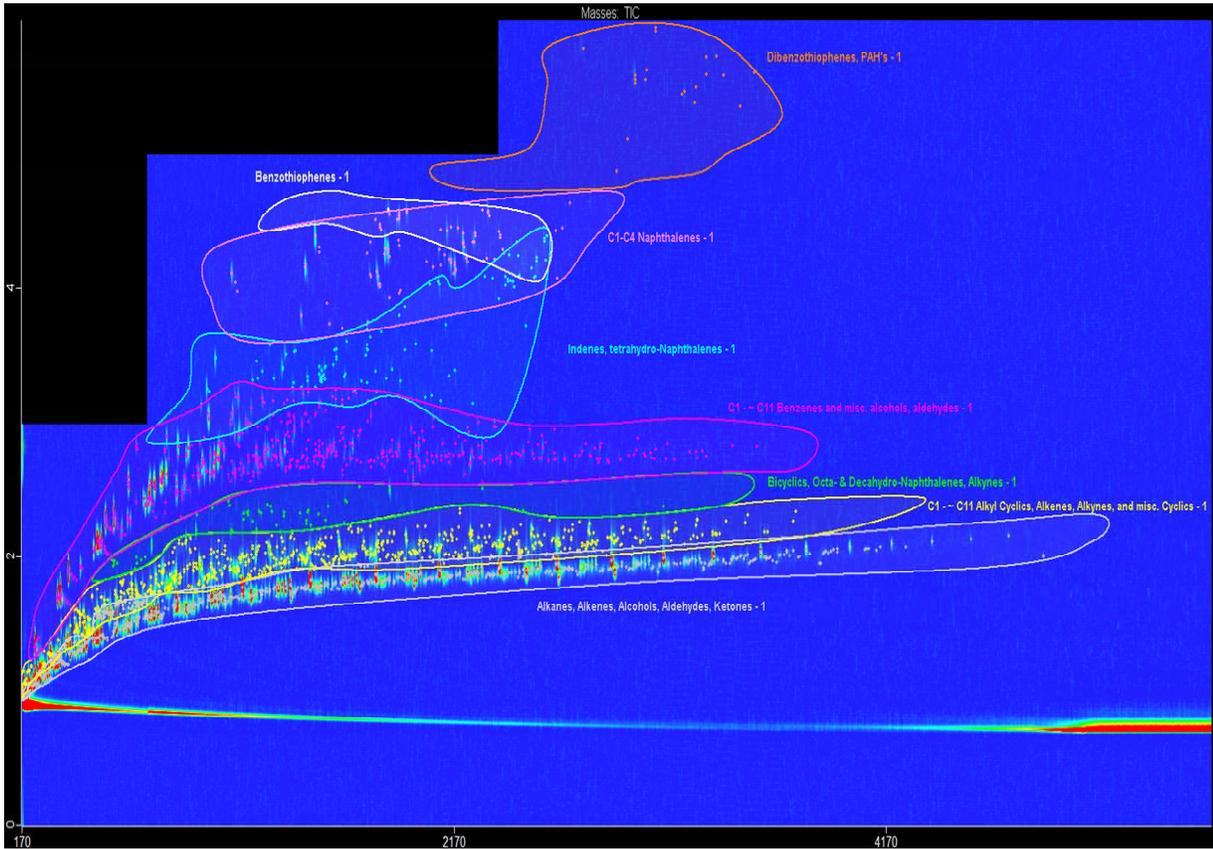


Figure 4. The two-dimensional chromatogram in the figure above shows the GCxGC-TOFMS analysis of an Arabian light crude oil standard (III Arabian Light 1B). Notice that by comparison of the Arabian light crude oils in Figures 4, 5, and 6, the chemical class composition of the "Classification" regions appear very similar

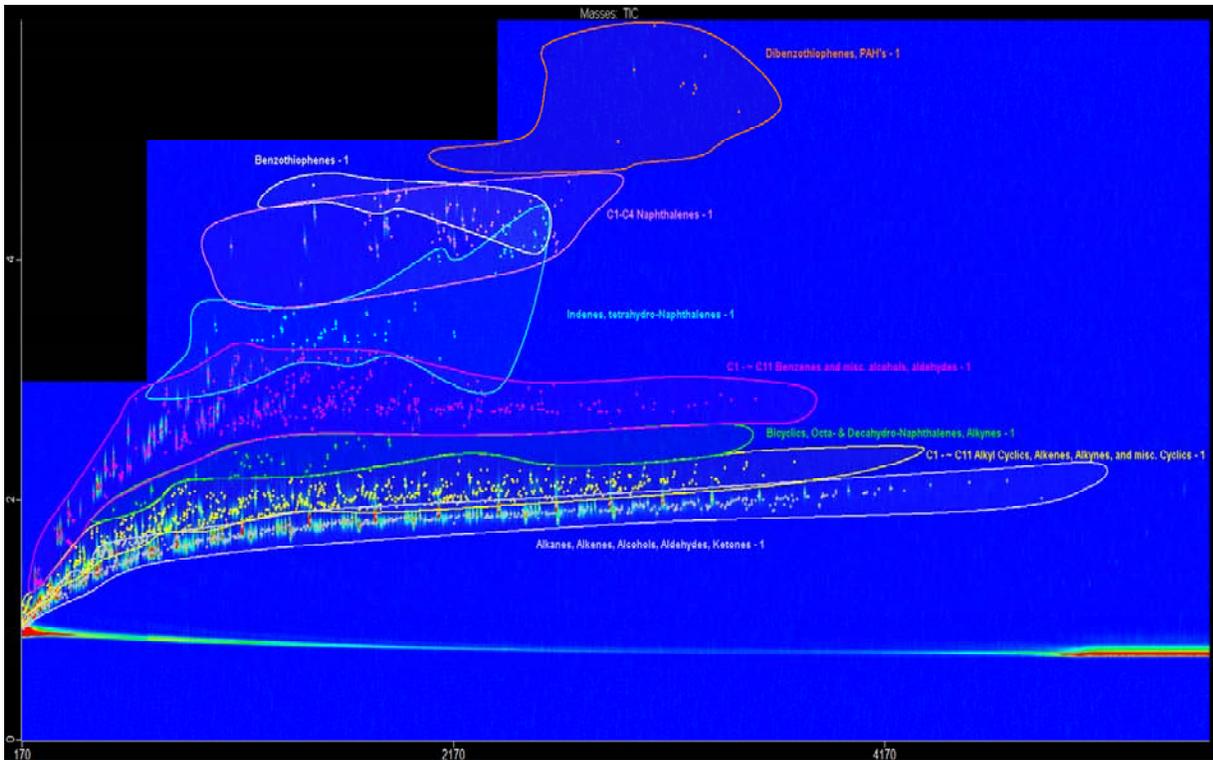


Figure 5. The two-dimensional chromatogram in the figure above shows the GCxGC-TOFMS analysis of an Arabian light crude oil standard (IV Basrah Light 2A). Notice the expanded peak capacity and isomeric resolution of the C1-C4 Naphthalenes classification.

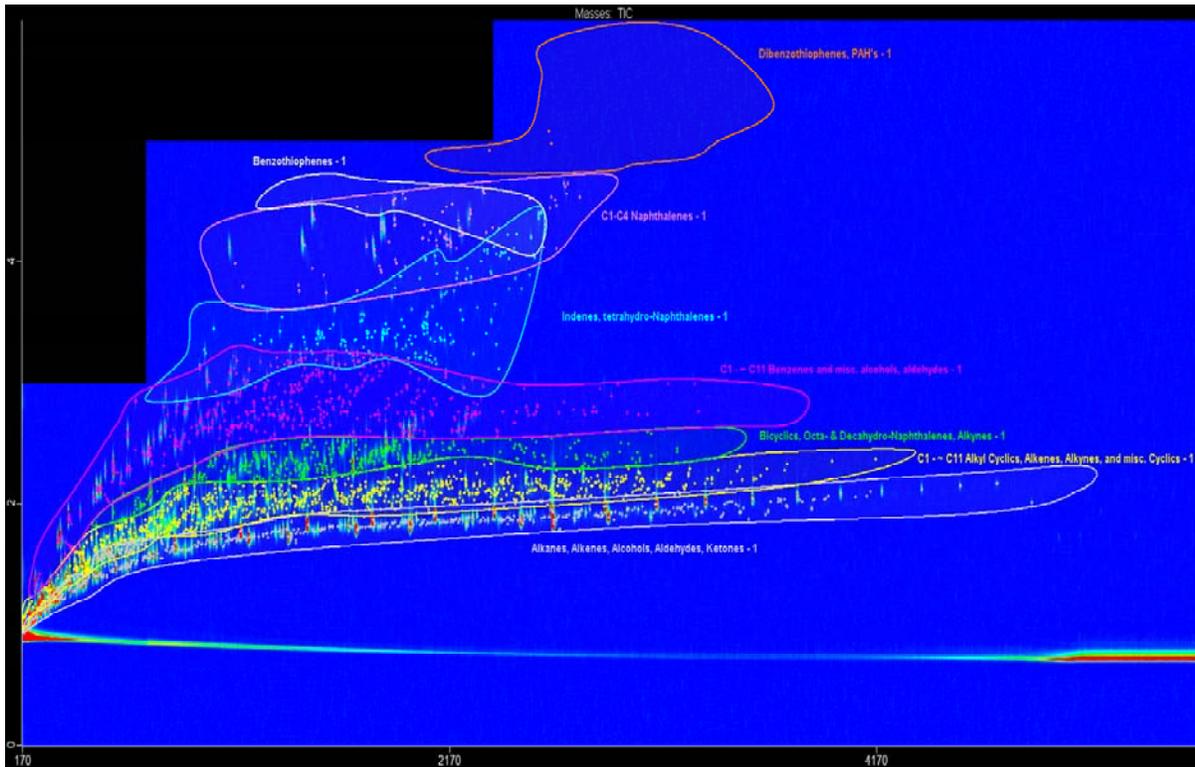


Figure 6. The two-dimensional chromatogram in the figure above shows the GCxGC-TOFMS analysis of Nigerian light crude oil standard (V Nigerian Qua Iboe 2A). Notice that significant regional chemical composition differences can be visually observed between the Nigerian and Arabian Light crude oil standards. Specifically, the green classification highlighting the bicyclic, octa-, and deca-hydro naphthalenes and alkynes region shows that both the Nigerian and Louisiana light crude oil standards contain significantly higher percentages of peaks in this specific "Classification" region.

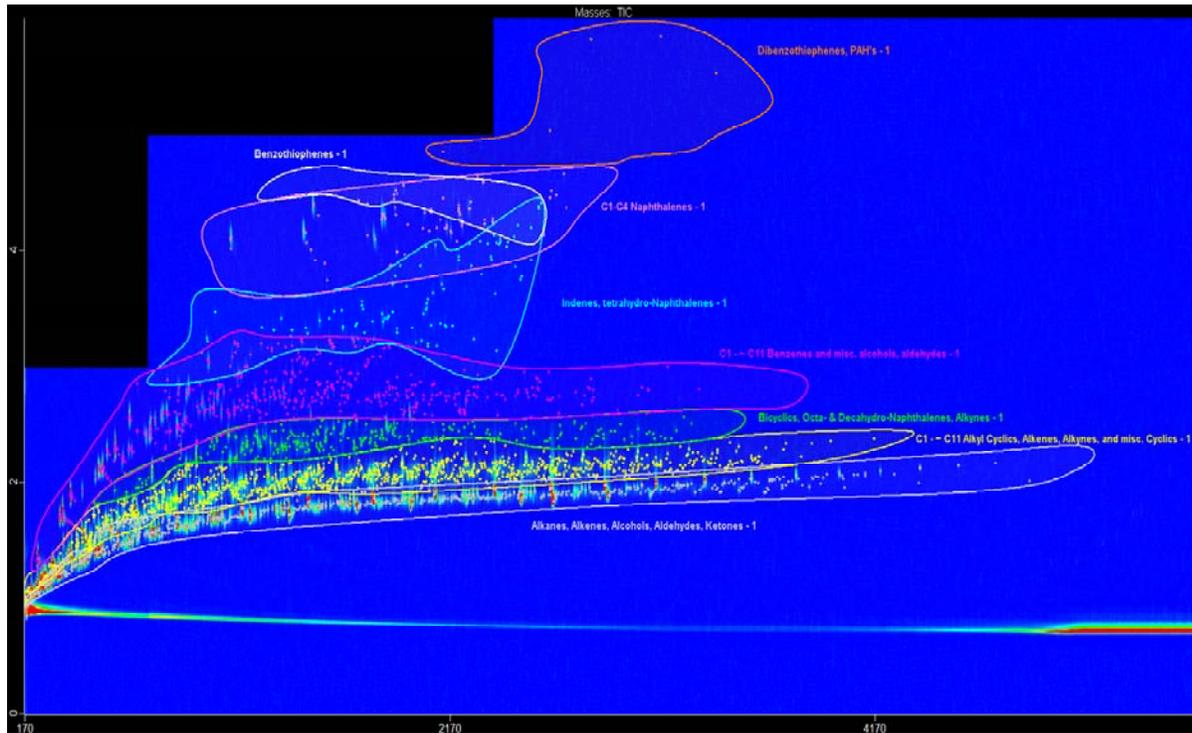
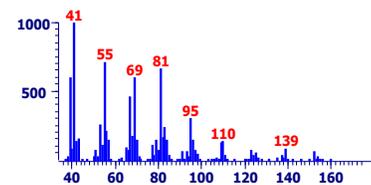


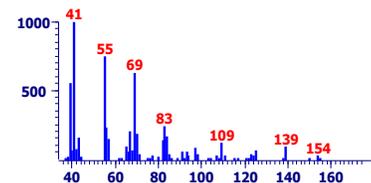
Figure 7. The two-dimensional chromatogram in the figure above shows the GCxGC-TOFMS analysis of a Louisiana light crude oil standard (VI South Louisiana 1A).

TOFMS True Signal Deconvolution®

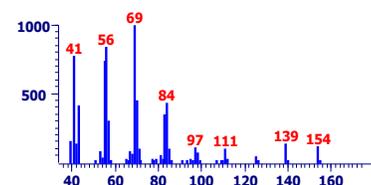
Caliper - sample "I Nigeria 1 C variable mod / hot pulse: 1", 789, 1.860 sec, sec to 789, 1.860 sec, sec



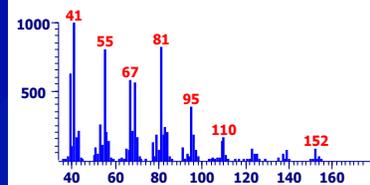
Peak True - sample "I Nigeria 1 C variable mod / hot pulse: 1", peak 440, at 789, 1.860 sec, sec



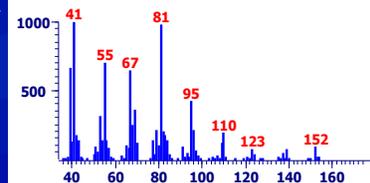
Library Hit - similarity 767, "Cyclohexane, 1,1-dimethyl-2-propyl-"



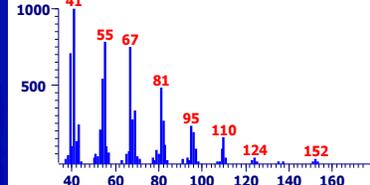
Caliper - sample "I Nigeria 1 C variable mod / hot pulse: 1", 789, 1.880 sec, sec to 789, 1.880 sec, sec



Peak True - sample "I Nigeria 1 C variable mod / hot pulse: 1", peak 441, at 789, 1.880 sec, sec



Library Hit - similarity 829, "E-1,6-Undecadiene"



Peak #	Name	R.T. (s)	Similarity	Area	Height	UniqueMass	S/N	Library
440	Cyclohexane, 1,1-dimethyl-2-propyl-	789, 1.860	767	476012	13883	55	869.01	mainlib
441	E-1,6-Undecadiene	789, 1.880	829	702897	24212	81	1295.5	mainlib

Figure 8. The deconvolution of two analytes in the Nigerian 1C light crude oil sample separated at their peak apices by 20 milliseconds. TOFMS provides fast acquisition and full range non-skewed mass spectral data which allows for effective deconvolution of nearly coeluted peaks.

Table 1. Light crude oil classifications.

LIGHT CRUDE OIL STANDARD SAMPLES	V Nigerian Qua Iboe 2 A	I Nigerian 1 C	VI South Louisiana 1 A	II Arabian Light 2 B	III Arabian Light 1 B	IV Basrah Light 3 A
CLASSIFICATIONS	Normalized %	Normalized %	Normalized %	Normalized %	Normalized %	Normalized %
Alkanes, Alkenes, Alcohols, Aldehydes, Ketones	43.845	44.521	51.380	58.437	58.741	59.358
C1 ~ C11 Alkyl Cyclics, Alkenes, Alkynes, and misc. Cyclics	39.786	38.553	36.317	27.766	18.093	28.400
Bicyclics, Octa- & Decahydro-Naphthalenes, Alkynes	5.362	5.640	2.209	0.318	0.209	0.339
C1 ~ C11 Benzenes, and misc. alcohols, aldehydes	8.120	8.000	8.487	11.114	20.270	9.740
Indenes, tetrahydro-Naphthalenes	1.184	1.430	0.482	0.909	1.156	0.739
C1 - C4 Naphthalenes	1.407	1.531	0.964	1.039	1.171	0.996
Benzothiophenes	0.263	0.267	0.149	0.334	0.272	0.367
Dibenzothiophenes, PAH's	0.004	0.012	0.011	0.024	0.087	0.042
Miscellaneous Unclassified	0.028	0.047	0.001	0.059	0.001	0.019
TOTAL PERCENTAGE	100.000	100.000	100.000	100.000	100.000	100.000

3. Experimental

The GCxGC-TOFMS analysis was carried out with an Agilent 6890 gas chromatograph equipped with a LECO dual-stage quad jet thermal modulator and a GERSTEL MPS2 autosampler. The GC primary column used a 30 m x 0.25 mm id. x 0.25 μ m film thickness Rxi-5SilMS (Restek Corp.). The secondary column used a 1.1 m x 0.15 mm id. X 0.15 μ m film thickness Rxi-17Sil-MS (Restek Corp.) A 1 μ L split injection was made with a split ratio of 25:1 and an injection port temperature of 300°C. The helium carrier gas flow was set to 1.0 mL/min. A parallel dual temperature ramp program was conducted with a column offset of 5°C. The primary column temperature program began with an initial temperature of 60°C for 1.0 min, ramped @ 2.5°C/min. to 260°C then ramped @ 8°C/min to 290°C and held for 10 min. The parallel secondary column temperature ramp program was carried out simultaneously at a temperature 5°C higher than the primary column temperature program. The LECO Pegasus[®] 4D Mass Spectrometer method used a mass range of 35–600u. The acquisition rate was set at 200 spectra/s. The ion source temperature was set to 230°C with a detector voltage of 1635V. The total run time for the GCxGC-TOFMS analysis was 94.75 min

4. Conclusions

This study compared GCxGC-TOFMS data results of six light crude oil standards from different geographic regions. An optimized GCxGC method was developed using a conventional non-polar and mid-polarity column set. The GCxGC method utilized variable modulation which aids in optimization of the available peak capacity and chromatographic resolution of the first and second dimension separation. The chromatographic data clearly illustrate the capability of comprehensive two-dimensional chromatography to facilitate structured separation of functional group classes within the two-dimensional chromatographic plane. The "Classifications" feature available in ChromaTOF software was utilized to compare and highlight the differences in key chemical functional group classes between the six different standards. Eight classifications representing various functional group classes were employed to develop an approximate estimate by area percentages providing a fingerprint profile for each light crude oil standard. The normalized area percents from Table 1 highlight the differences and similarities between the chemical compositions of the six different light crude oils. This application presents the advantages of GCxGC-TOFMS to separate, characterize, and classify the chemical composition of light crude oils. Comparison of the chromatographic and peak table data with "Classifications" provides a rapid data analysis technique to evaluate key chemical functional group differences in crude oils from various geographic regions. The data presented illustrate the advantages and benefits of GCxGC-TOFMS as well as a data mining "Classifications" strategy to characterize and compare the chemical profiles of light crude oils from different global regions.