



# A Beneficial GCxGC-TOFMS Procedure for Environmental Forensic Fingerprinting Utilizing Structural Classifications to Differentiate Light Crude Oils

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## INTRODUCTION

Crude oil fingerprinting and source identification has become a crucial aspect within the emerging field of environmental forensics. The complex nature of crude oil demands analytical solutions and instrumental methods that will separate and identify the complex chemical profile, as well as differentiate petroleum from distinct geographic regions. Comprehensive two-dimensional gas chromatography (GCxGC) expands the peak capacity of the chromatographic separation thereby increasing resolution and analyte characterization of 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 study illustrates GCxGC-TOFMS data from the comparative analysis of six light crude oil standards from different global regions. A method was developed that utilizes variable modulation to maximize available peak capacity. Comprehensive two-dimensional chromatography facilitates structured separation of functional group classes within the GCxGC chromatographic plane. The comparison of light crude oil highlights the differences of key functional groups by utilizing the "Classifications" feature available in ChromaTOF software. Major Classification regions for alkanes, alkenes, alkynes, alcohols, aldehydes, ketones, alkyl-cyclics, indenes, naphthalenes, thiophenes, dibenzothiophenes, and PAHs are shown. Fingerprinting was accomplished by processing each sample's data with "Classifications" followed by creation of a "Classifications Summary". These features within the ChromaTOF software provide a relative area percentage for each classified region. This software feature is a valuable data analysis tool for comparison of key chemical functional group variations between light crude oils. The data presented in this poster illustrate the advantages of GCxGC-TOFMS and software features which assist in differentiating light crude oils from various global regions.

## EXPERIMENTAL METHODS

### GCxGC-TOFMS Analysis Parameters

- Gas Chromatograph: Agilent 6890 equipped with a LECO dual stage quad jet thermal modulator, secondary oven and GERSTEL MPS2 autosampler (Restek Corp.)
- GC Primary Column: 30 m x 0.25 mm id. x 0.25 µm film thickness Rxi-5SilMS (Restek Corp.)
- GC Secondary Column: 1.1 m x 0.15 mm id. X 0.15 µm film thickness Rxi-17Sil-MS (Restek Corp.)
- Carrier Gas: Helium set @ 1.0 mL/min
- Injection Mode: Split 25:1
- Inlet Temperature: 300°C
- Primary Column Temperature Program: Initial temperature 60°C for 1.0 min ramped @ 2.5°C/min to 260°C then ramped @ 8°C/min to 290°C held for 10 min
- Secondary Column Temperature Program: Initial temperature 65°C for 1.0 min ramped @ 2.5°C/min to 265°C then ramped @ 8°C/min to 295°C held for 10 min
- GCxGC Modulator Temperature Offset: 20°C
- Total Run Time: 94.75 min

### Mass Spectrometer: Pegasus 4D

- Mass range: 35-600 m/z
- Acquisition Rate: 200 spectra/second
- Ion source Temperature: 230°C
- Acquisition Delay: 170 seconds

## FINGERPRINTING BY CLASSIFICATIONS

#	Class	dTIC
1*	Indenes, tetrahydro-Naphthalenes	3.561
2	C1 - ~ C11 Benzenes and misc. alcohols, aldehydes	12.241
3	C1-C4 Naphthalenes	4.029
4	Dibenzothiophenes, PAH's	2.435
5	Benzothiophenes	1.094
6	Alkanes, Alkenes, Alcohols, Aldehydes, Ketones	49.704
7	C1 - ~ C11 Alkyl Cyclics, Alkenes, Alkynes, and misc. Cyclics	37.817
8	Bicyclics, Octa- & Decahydro-Naphthalenes, Alkynes	3.234
	Total	100.000

Figure 1. The figure above is a list of the eight Classification regions used to fingerprint the chemical profile of six light crude oil standards. The "Classifications Summary" assigns the relative peak area percent for each "Class" using the deconvoluted total ion chromatographic (dTIC) peak area percent summation.



Pegasus 4D GCxGC-TOFMS

## GCxGC-TOFMS RESULTS

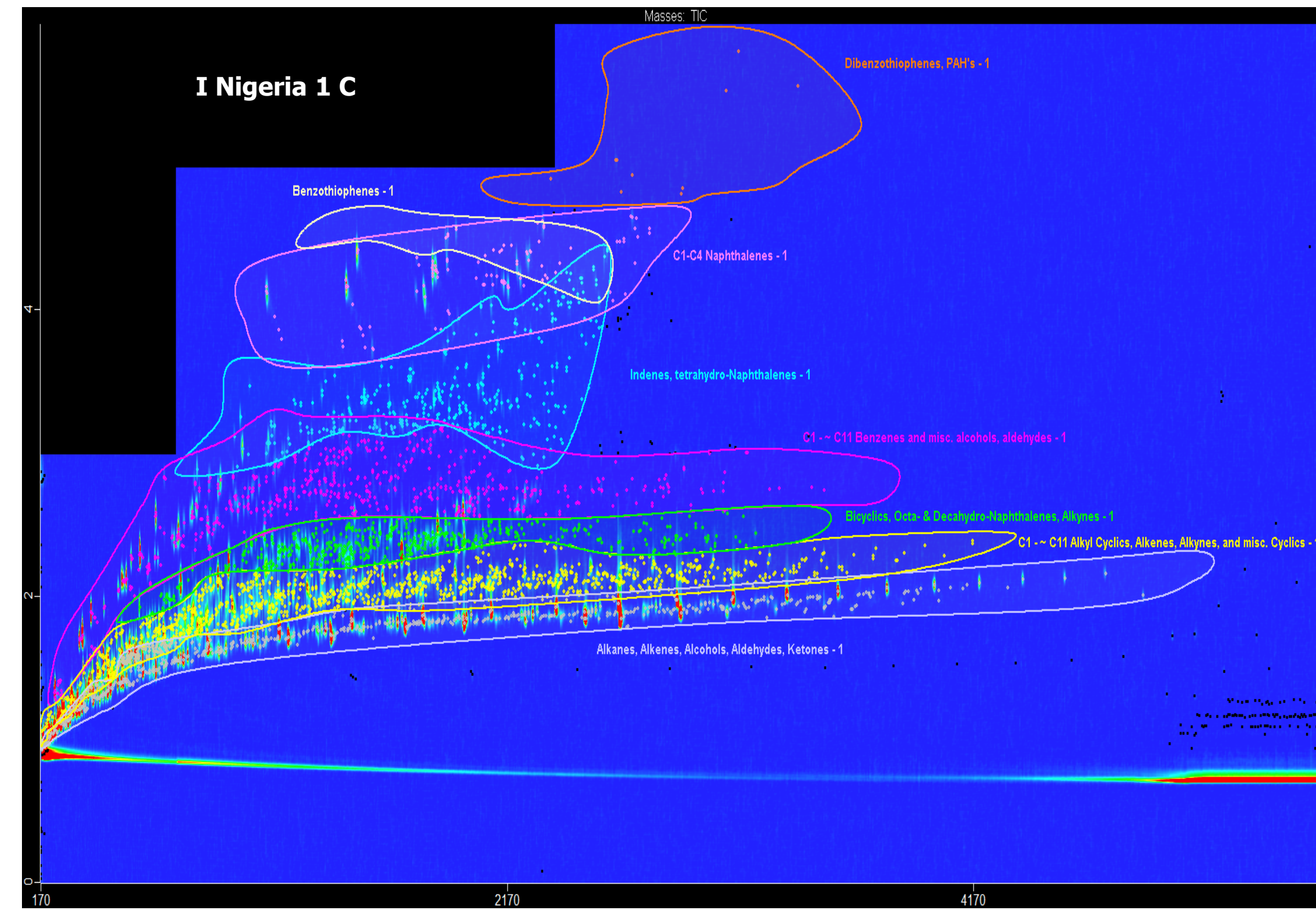


Figure 2. The two-dimensional chromatogram in the figure above shows the GCxGC-TOFMS analysis of a Nigerian light crude oil standard. Eight different classification regions are shown with colored peak markers and labels that represent different chemical and functional group classes. The orthogonal separation system used in GCxGC provides 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 excellent fingerprint of the chemical composition of light crude oil.

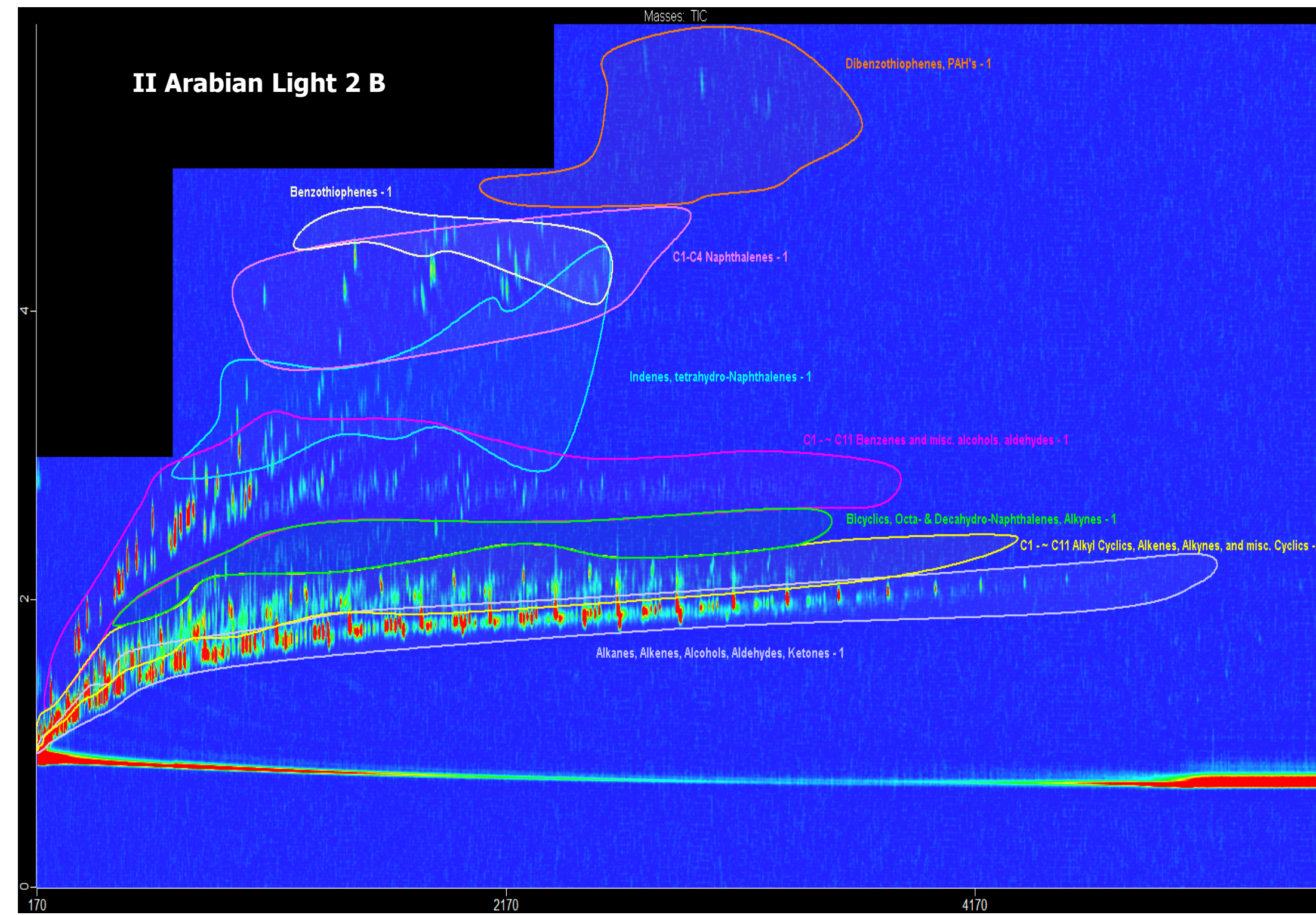


Figure 4. The figure above shows the GCxGC-TOFMS analysis of an Arabian light crude oil standard without the peak markers. Eight different classifications are shown and labeled representing different chemical structures and functional group classes. The contour plot shows the efficient two-dimensional chromatographic separation of the different structured chemical classes. The peaks in the contour plot are scaled by color intensity with red as the most intense peaks and blue as the baseline.

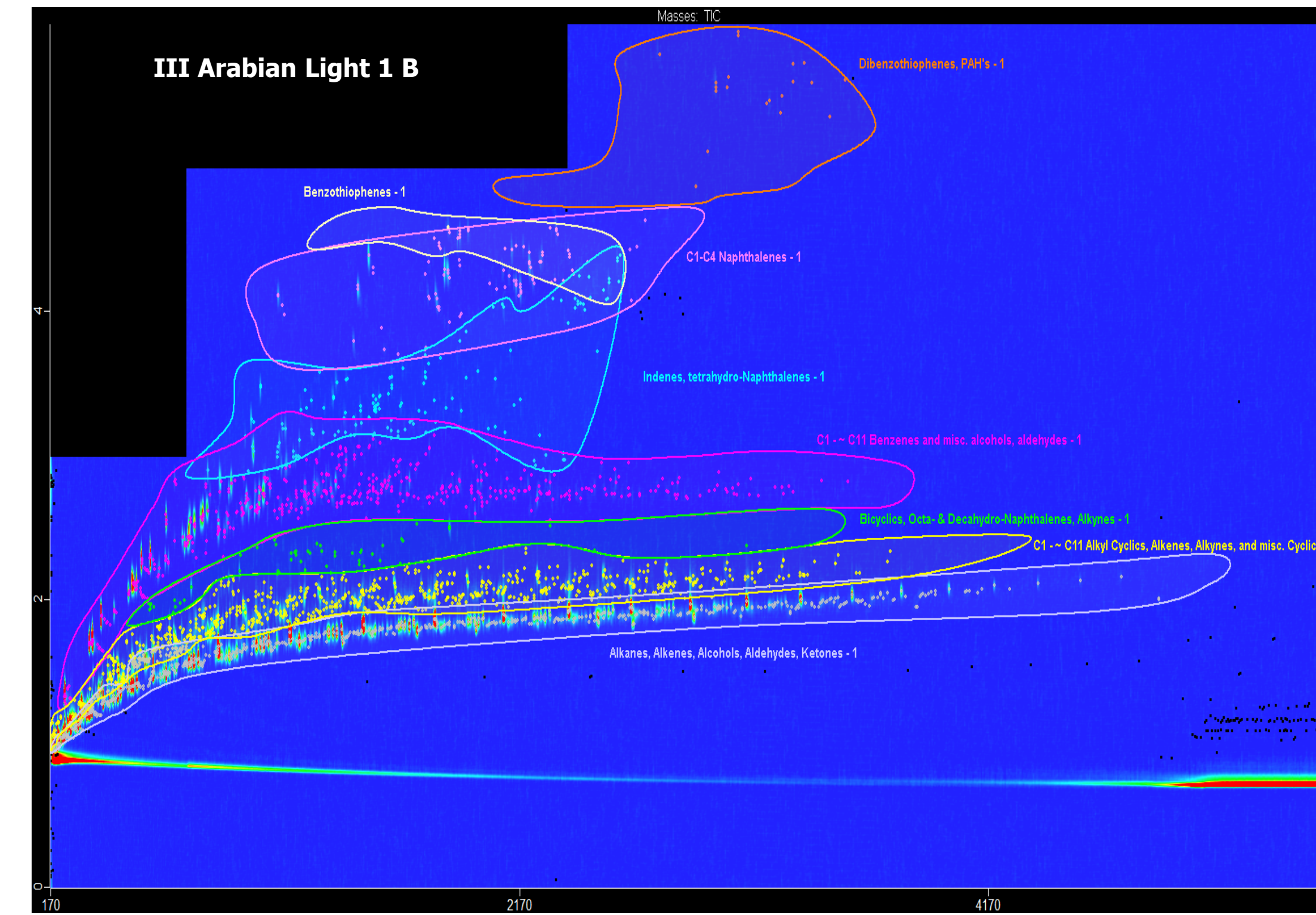


Figure 6. The two-dimensional chromatogram in the figure above shows the GCxGC-TOFMS analysis of an Arabian light crude oil standard. Notice that by comparison, the Middle Eastern light crude oils in Figures 3, 4, and 6, the chemical class compositions of the Classification regions appear very similar. This is reinforced in the tabular data shown in Table 1.

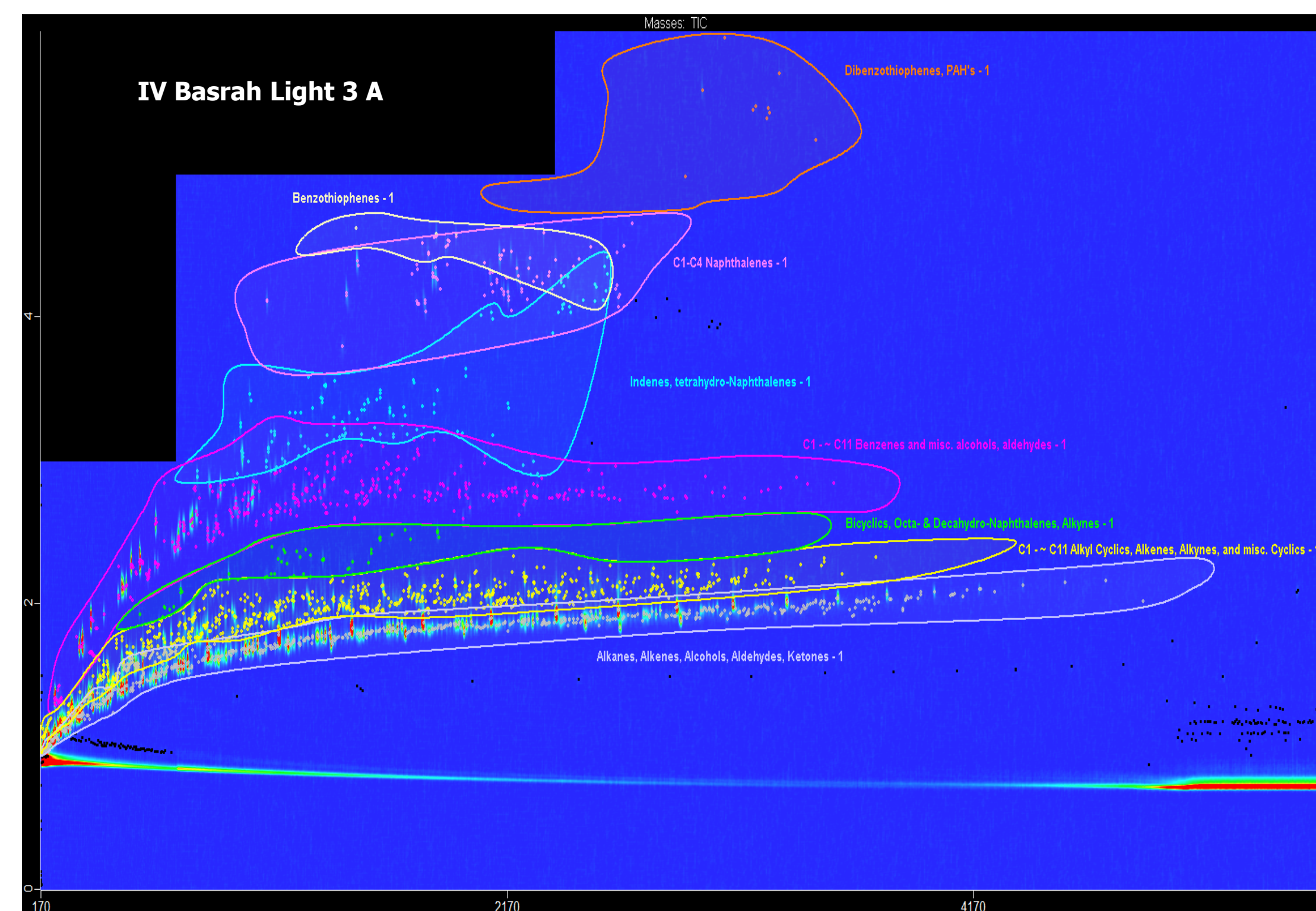


Figure 3. The two-dimensional chromatogram in the figure above shows the GCxGC-TOFMS analysis of an Arabian light crude oil standard. Notice the expanded peak capacity and isomeric resolution of the C1-C4 Naphthalenes classification. The orthogonal separation system used in GCxGC provides structured chromatograms that generate distinct bands of analytes grouped by specific chemical characteristics. This optimized separation illustrates the advantages of GCxGC-TOFMS to provide an excellent fingerprint of the chemical composition of light crude oil.

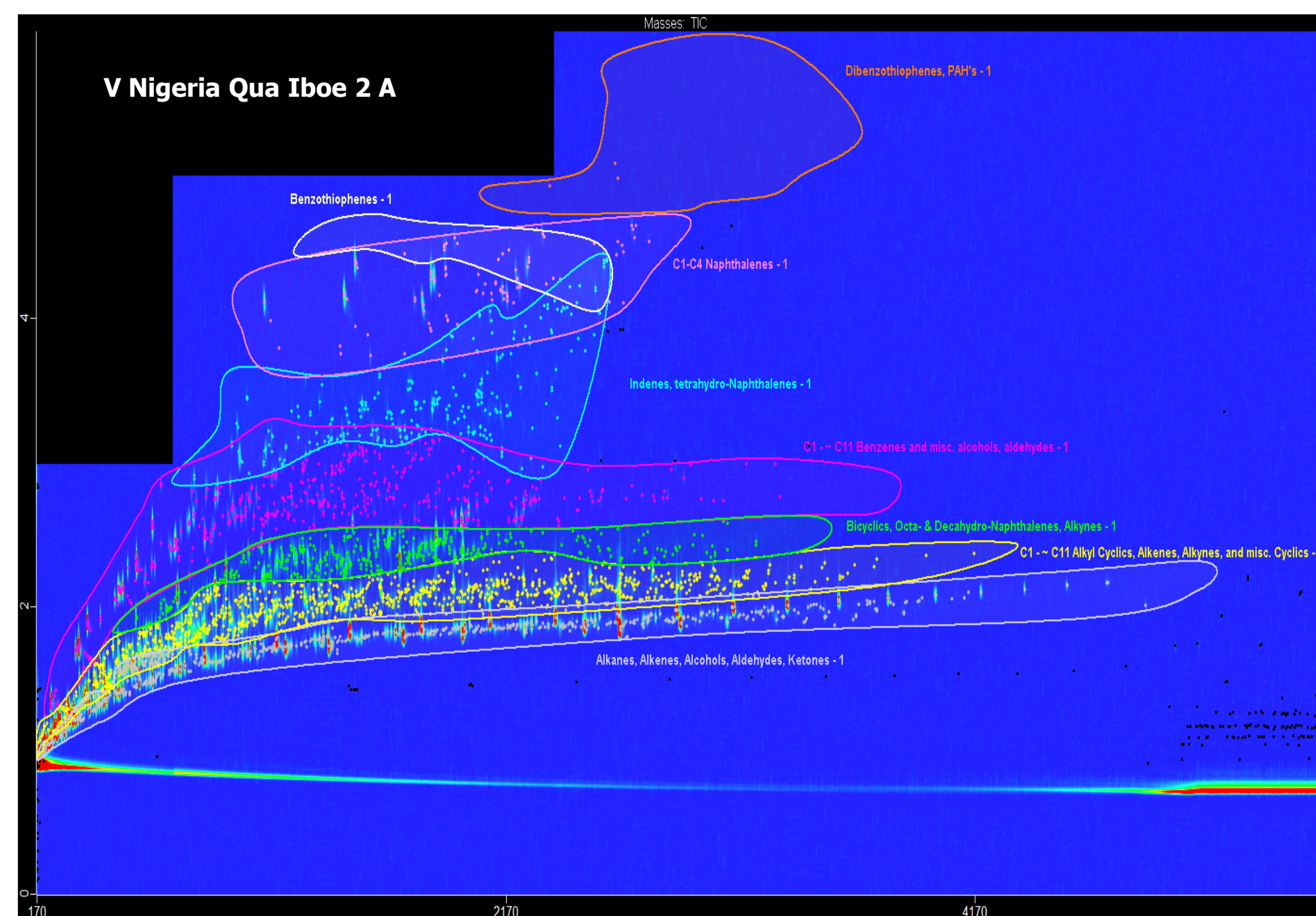


Figure 5. The two-dimensional chromatogram in the figure above shows the GCxGC-TOFMS analysis of a Nigerian light crude oil standard. Notice that significant analyte class differences can be visually observed between the Nigerian and Arabian Light crude oil standards. Specifically, the contents of the green classification region highlighting the bicyclic, octa- and deca-hydro naphthalenes, and alkynes differ significantly for these two samples. The results indicate that GCxGC-TOFMS can successfully differentiate light crude oil from different geographic regions.

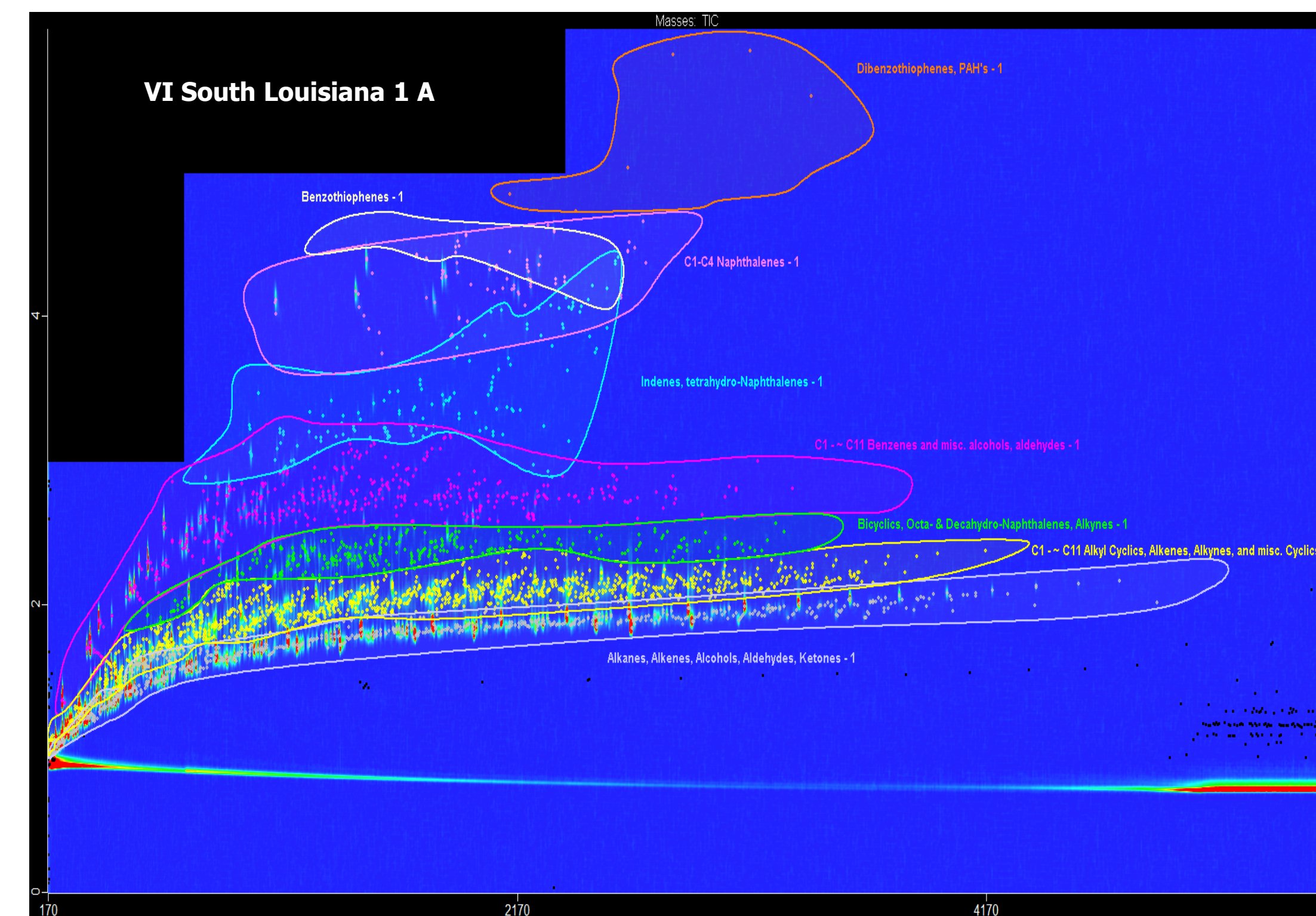


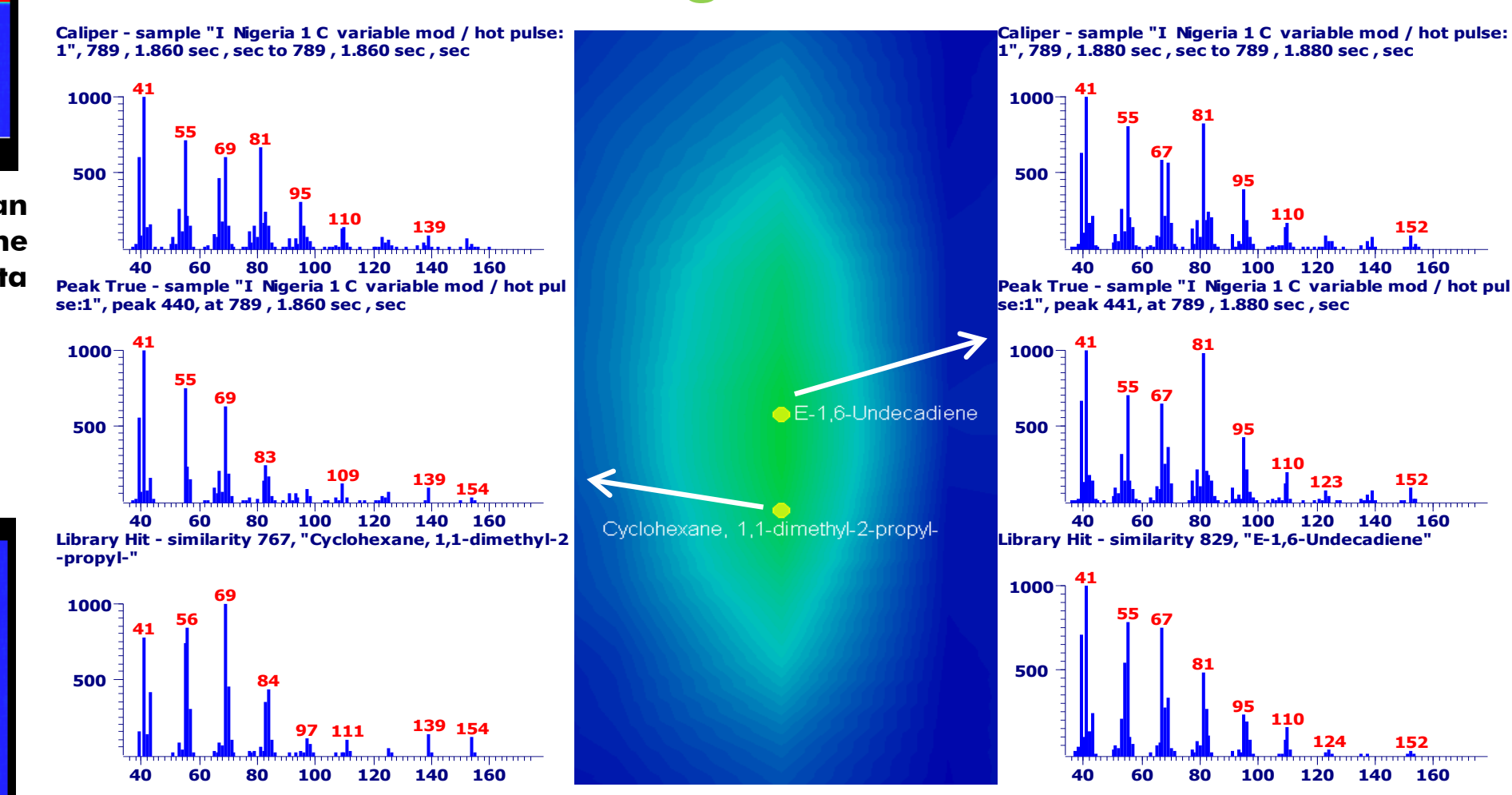
Figure 7. The two-dimensional chromatogram in the figure above shows the GCxGC-TOFMS analysis of Louisiana light crude oil standard. Eight different classifications are shown with colored peak markers and labels that represent different chemical and functional group classes. The orthogonal separation system used in GCxGC provides 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 excellent fingerprint of the chemical composition of light crude oil.

## LIGHT CRUDE OIL CLASSIFICATIONS COMPARISON

Table 1. Shown below in Table 1 are the calculated peak area percent summations from the "dTIC" for the chemical functional group "Classes" developed in the ChromaTOF software. The similarities and differences in the light crude oils from various geographic regions provide a unique fingerprint for each sample. The table below shows relative area percentages calculated from the "Classifications Summary" for the various chemical classes. This provides a tabular fingerprint of the light crude oil standards from various global regions.

LIGHT CRUDE OIL STANDARD SAMPLES	V Nigeria Qua Iboe 2 A	I Nigeria 1 C	VI South Louisiana 1 A	II Arabian Light 2 B	III Arabian Light 1 B	IV Basrah Light 3 A
CLASSIFICATIONS	dTIC area %	dTIC area %	dTIC area %	dTIC area %	dTIC area %	dTIC area %
Alkanes, Alkenes, Alcohols, Aldehydes, Ketones	43.731	45.674	49.704	56.770	54.796	54.200
C1 - ~ C11 Alkyl Cyclics, Alkenes, Alkynes, and misc. Cyclics	42.108	42.290	37.817	29.105	27.835	28.971
Bicyclics, Octa- & Decahydro-Naphthalenes, Alkynes	5.535	5.882	3.234	1.991	2.156	2.556
C1-C11 Benzenes, and misc. alcohols, aldehydes	11.796	11.066	12.241	15.256	16.782	14.578
Indenes, tetrahydro-Naphthalenes	3.512	3.348	3.561	3.921	4.265	4.805
C1-C4 Naphthalenes	4.294	3.650	4.029	4.121	4.497	5.147
Dibenzothiophenes	1.123	0.940	1.094	1.211	1.294	1.356
Dibenzothiophenes, PAH's	2.406	1.843	2.435	2.525	2.835	3.407
TOTAL PERCENTAGE	100	100	100	100	100	100

## TOFMS True Signal Deconvolution



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. Figure 8 above shows the deconvolution of two analytes separated at their peak apices by 20 milliseconds. TOFMS provides full range non-skewed mass spectral data which allows for effective deconvolution of coeluted peaks. This example shows that even with the increased chromatographic separation power of GCxGC, there are still complex sample types that demand mass spectral deconvolution capabilities.

## CONCLUSIONS

These analyses compared 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 illustrates 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 the ChromaTOF software was utilized to compare and highlight the differences in key chemical functional group classes between the six different standards. Eight "Classification" regions representing various functional groups were created to provide a tabular fingerprint in the form of a "Classifications Summary" for each crude oil standard. This procedure demonstrated the ability to effectively differentiate light crude oils by geographic region.

This experimental work presents the advantages of GCxGC-TOFMS to separate, characterize, and classify the chemical composition of light crude oils. Comprehensive two-dimensional gas chromatography provides structured separation and enhanced resolution capabilities not possible by single dimension chromatography. GCxGC offers the expanded peak capacity and increased detectability needed for the analysis of extremely complex samples. Time-of-flight mass spectrometry (TOFMS) offers continuous full range non-skewed mass spectral information, and fast acquisition rates ideal for characterization of petrochemical mixtures. An example of mass spectral deconvolution and NIST library matched identifications of two nearly coeluted components was illustrated. Utilization of "Classifications" and "Classification Summary Tables" to effectively compare crude oils from various geographic regions was effectively demonstrated.

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