

# The Use of GCxGC-TOFMS and Classifications for the Quantitative Determination of Different Compound Classes in Complex Isoparaffinic Hydrocarbon Samples

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## 1. Introduction

One of the important challenges facing hydrocarbon analysts is the accurate determination of the amounts of different classes of compounds in complex samples. For example a typical aliphatic hydrocarbon sample may contain linear hydrocarbons ranging over twenty or more carbon numbers, as well as a plethora of branched and cyclic hydrocarbon isomers over a similar range of carbon numbers. One dimensional gas chromatographic (GC) analysis is inadequate for this task, even when using long specialized columns, and Time-of-Flight Mass Spectrometry (TOFMS), as can be seen in Figure 1.

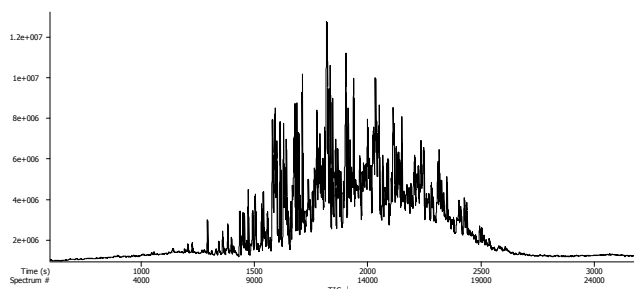


Figure 1. GC-TOFMS Analysis of the Complex Aliphatic Hydrocarbon Sample 1.

The sample complexity precludes accurate assessment of all the different classes of hydrocarbon components, even when using advanced techniques such as GC-TOFMS and the powerful deconvolution algorithm available through the ChromaTOF® software package.

Comprehensive two-dimensional gas chromatography (GCxGC) coupled to Time-of-Flight mass spectrometry (TOFMS) can play a significant role in handling samples where complexity is a key issue. The increased peak capacity of GCxGC, coupled with the powerful deconvolution software available in the ChromaTOF software package used to operate LECO Pegasus® and TruTOF® systems, allows the co-elution always present in complex hydrocarbon samples to be minimized. Where it does occur, the software handles this in such a way that compound identification and quantitation are not compromised. In addition, the Classification feature provides a powerful tool for differentiation and quantitation of compound classes.

## 2. Experimental Conditions

### Samples

Two samples (1 and 2) were used for analysis which contained linear, branched and cyclic alkanes over a significant range of carbon numbers. No aromatic components were present in the samples. Both samples contained over 1000 components.

### Analysis Conditions

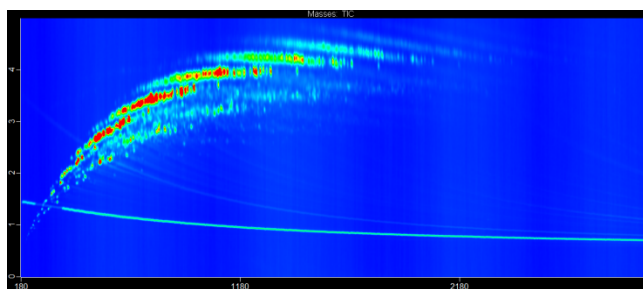
The correct choice of columns is a prerequisite for successful GCxGC analysis of complex hydrocarbon samples. The column set should provide good separation of all the components, it should be thermally robust with the ability to handle the elevated temperatures needed for successful chromatography of the less volatile components, and it should make good use of the total chromatographic space of the analysis. This is of particular importance in the samples used in this analysis. Because of the sample complexity and the extremely large number of branched and cyclic hydrocarbons present in the samples it was found that the customary "non-polar" – "polar" column combination did not provide suitable component separation. The final column set used and the conditions for the analyses are shown in Table 1 below.

**Table 1. GCxGC-TOFMS conditions for complex hydrocarbon analysis.**

<b>Detector</b>	LECO Pegasus® 4D Time-of-Flight Mass Spectrometer
<b>Acquisition Rate</b>	100 spectra/s
<b>Acquisition Delay</b>	3 min
<b>Stored Mass Range</b>	45 to 450 m/z
<b>Transfer Line Temp</b>	240°C
<b>Source Temp</b>	225°C
<b>Detector Voltage</b>	-1700 Volts
<b>Mass Defect Setting</b>	0
<b>Column 1</b>	Rtx-Wax, 30 m x 0.25 mm ID, 0.25 µm film thickness
<b>Column 2</b>	Rtx-5, 1.2 m x 0.1 mm ID, 0.1 µm film thickness
<b>Column 1 Oven</b>	40°C for 1 min, to 140°C at 2°C/min
<b>Column 2 Oven</b>	65°C for 1 min, to 165°C at 2°C/min
<b>Modulation Period</b>	5 s
<b>Modulator Temp Offset</b>	40 °C (Relative to the Primary Oven)
<b>Inlet</b>	Split (100:1) at 225°C.
<b>Injection</b>	0.1 µL
<b>Carrier Gas</b>	Helium, 1 mL/min. corrected constant flow
<b>Data Processing</b>	
<b>1<sup>st</sup> Dim Peak Width</b>	60 s
<b>2<sup>nd</sup> Dim Peak Width</b>	0.15 s
<b>S/N</b>	200
<b>Match Required to Combine</b>	500
<b>Mass for Area Calculation</b>	dt

### 3. Results and Discussion

Using the conditions described above, Sample 1 was analyzed to produce the GCxGC-TOFMS chromatogram shown in Figure 2. As can be seen, the hydrocarbon components present in the sample are separated into different classes within the chromatogram. These are indicated by the coloured bands. Using the TOFMS spectra the different bands can be identified, e.g. C-11 linear, C-11 branched, C-11 cyclic. This can be easily achieved for all the carbon numbers present in the sample. This facile separation of classes can then be used in the Classification Software to define and quantify the different groups within the sample.

**Figure 2. Total Ion Chromatogram GCxGC-TOFMS results for Sample 1.**

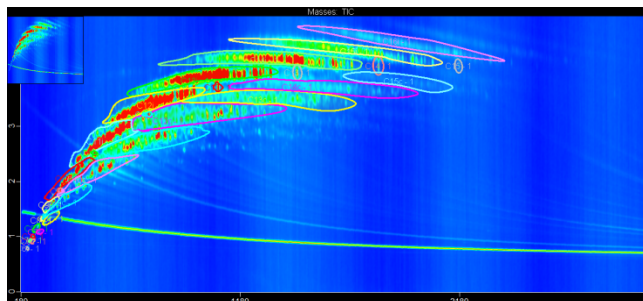
#### Classifications

Comprehensive two-dimensional chromatography separates sample components into different areas in the chromatogram, depending on compound class (or chemical structure). This is especially useful in the analysis of complex hydrocarbon mixtures. In these samples the high degree of similarity between aliphatic hydrocarbon mass spectra make unambiguous structural assignment practically impossible, especially when there are numerous branched or cyclic components of the same carbon number.

Although the individual components cannot always be identified, it is frequently sufficient to be able to determine what percentage each class contributes to the total amount of material present in the sample. The classification software can be used to determine this, and is particularly useful as once a classification template is built, it can be used on all similar samples run with the same column set under identical conditions.

After data processing and library searching, a classification template was constructed for Sample 1. The linear hydrocarbons (C6 – C14) were first identified, and classifications built for these components, and named C6, C7, C8 etc. Once these had been identified the sets of branched hydrocarbons or isoparaffins (C6 – C16) could be defined. These were named C6i, C7i, C8i etc. Finally the cyclic hydrocarbons (C6 – C15) were defined. These were named C6c, C7c, C8c etc. During the building of the classification template mass spectra are cross referenced to library spectra as an additional verification step.

Determination of the branched and cyclic group classification templates was facilitated by using extracted ions. Care was taken to prevent any overlap of the classification regions, as this could lead to sample components with more than one possible identity. The final classification template is shown in Figure 3.

**Figure 3. Classification template for Sample 1.**

### Data Processing

Once the classification template is built it can be used in the data processing method to define the components present in each group. Quantitation is achieved using the TIC or the DTIC. The result after using this approach is shown in a portion of the Peak Table in Table 2.

**Table 2. A Portion of the Peak Table for Sample 1 after using the classification template.**

Name	R.T. (s)	Classifications	Quant Mass	Area
Cyclohexane, 1,3-dimethyl-, cis-	290, 1.240	C8c	Dt	131113
Cyclopentane, 1-ethyl-3-methyl-, trans-	290, 1.280	C8c	Dt	424177
Heptane, 3,5-dimethyl-	295, 1.480	C9i	Dt	2707903
Cyclohexane, 1,2-dimethyl-	305, 1.320	C8c	Dt	1530985
Hexane, 3-ethyl-2-methyl-	305, 1.540	C9i	Dt	101532
Cyclohexane, 1,3-dimethyl-, cis-	315, 1.340	C8c	Dt	221588
Heptane, 2,4,6-trimethyl-	315, 1.690	C10i	Dt	103325
Octane, 2,2-dimethyl-	315, 1.710	C10i	Dt	413670
Cyclohexane, 1,3,5-trimethyl-	320, 1.460	C9c	Dt	374213
trans-1,2-Diethyl cyclopentane	320, 1.510	C9c	Dt	391803
Octane, 4-methyl-	320, 1.620	C9i	Dt	5797279
Octane, 2,2-dimethyl-	325, 1.760	C10i	Dt	658654

The data can now be copied into Excel, and the "SUMIF" function used to calculate total areas and area percents for the different classes and groups.

SUMIF(range,criteria,sum\_range)

Adds the cells specified by a given condition or criteria

Here, range is the full set of cells containing the classes C6, C6i, C6c, etc; criteria is an individual class "C6i"; and sum\_range is the full set of cells containing the area values.

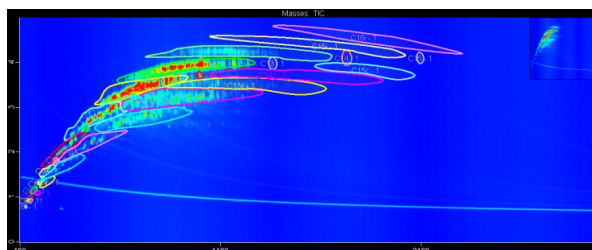
The final set of results for Sample 1 is shown in Table 3.

**Table 3. Results obtained for Sample 1 after processing with Classifications.**

Carbon Number	Linear	Branched	Cyclic	TOTAL	AREA %
6	0	344216	235602	579818	0.01
7	737956	489025	699890	1926871	0.04
8	976487	1826022	4403223	7205732	0.16
9	10091344	13606694	17317348	41015386	0.93
10	10827199	119384548	115621994	245833741	5.59
11	12317329	567526739	212649029	780175768	18.01
12	9924108	933306396	266372392	1209602896	27.49
13	7611541	877100967	138562056	1023274564	23.26
14	2215921	603118072	71269239	676603232	15.38
15	0	307022162	3351034	310373196	7.05
16	0	90763044	0	90763044	2.06
<b>TOTAL</b>	<b>54701885</b>	<b>3514487885</b>	<b>830481807</b>	<b>4399671577</b>	
<b>AREA %</b>	<b>1.24</b>	<b>79.88</b>	<b>18.88</b>		

The classification template, as developed for Sample 1, may now be applied to any samples run on the same column set and under identical conditions. To test the validity of this approach, Sample 2 was analysed and processed using the same classification template.

The chromatogram after data processing, with the classifications from the template, is shown in Figure 4. The results obtained after processing are shown in Table 4.



**Figure 4. Chromatogram of Sample 2 after application of Classification template.**

**Table 4. Results obtained for Sample 2 after processing with Classifications.**

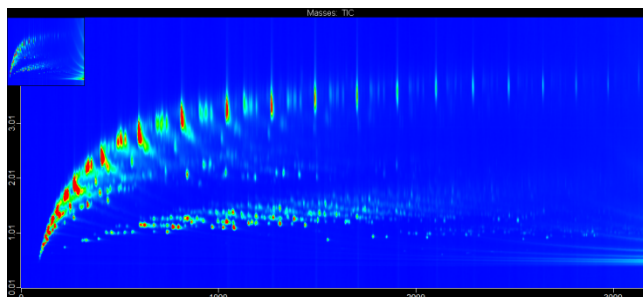
CARBON NUMBER	Linear	Branched	Cyclic	TOTAL	AREA %
6	0	85308	422607	507915	0.01
7	732295	720980	1096495	2549770	0.05
8	1339417	3540088	3341728	8221233	0.16
9	4232035	17146599	9768966	31147600	0.61
10	8409078	101436197	76162432	186007707	3.63
11	15168968	472317126	343859738	831345832	16.23
12	15675067	1538778074	627038677	2181491818	42.58
13	1372614	1470762256	141394910	1613529780	31.49
14	0	262544784	5862235	268407019	5.24
15	0	0	0		
16	0	0	0		
<b>TOTAL</b>	<b>46929474</b>	<b>3867331412</b>	<b>1208947788</b>	<b>5123208674</b>	
<b>AREA %</b>	<b>0.92</b>	<b>75.49</b>	<b>23.60</b>		

This approach to group selection and quantitation is extremely useful, and easy to apply. Firstly, the unambiguous identification of all the components of the sample is not necessary. Because we are defining groups in terms of their position in the chromatogram, the actual compound name does not matter. This is a great benefit when dealing with complex hydrocarbon samples, where it is not possible to positively identify all of the sample components.

Secondly, the GCxGC approach provides a far more accurate picture of the sample than can be obtained by 1D GC. In the 1D case, there is frequent overlap of classes and the complexity of the chromatogram (Figure 1) makes it impossible to selectively separate and quantify different groups. However, because of the added peak capacity provided by GCxGC the groups can be completely separated with the correct choice of column combination, giving better quantitation and a clearer understanding of the sample components.

The ChromaTOF software can also be used to do this type of calculation using the Classification Summary Tables. This is described in Classification Summary Table Tutorial v1.0 obtainable from LECO Corporation. The only disadvantage to this approach is that only individual classification sums are obtainable, and the results then still have to be taken into Excel for group calculations.

Finally, the approach can easily be extended into even more complex samples. An examination of the diesel sample chromatogram in Figure 5 shows that, not only can the aliphatic components be easily grouped as has been done above, but the aromatic and higher aromatic classes are also easily separated to allow a complete picture of the sample to be obtained. This is more time consuming to produce the initial template but once this has been constructed it can be applied to numerous diesel samples and provides a quick, accurate sample characterization.



**Figure 5. Chromatogram of a Diesel Sample, showing aromatic components in addition to aliphatic components, suitable for Classification.**

#### 4. Conclusions

Classifications provide a convenient and simple approach for the determination of the amounts of different classes of compounds present in complex hydrocarbon samples. Templates are easy to build, and the results should be much more accurate than those obtained by 1D GC. Once the template is constructed it can be used without further modification on other samples recorded under identical conditions.

This Application Note is also available in electronic format on the LECO Africa website ([www.lecoafrika.co.za](http://www.lecoafrika.co.za)) in the Application Notes section.

#### 5. Acknowledgments

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