



JSB Nederland
Apolloweg 2B | 8239 DA Lelystad
T +31 (0)320 87 00 18 | F +31 (0)320 87 00 19

JSB Headquarters
Tramstraat 15 | 5611 CM Eindhoven
T +31 (0)40 251 47 53 | F +31 (0)40 251 47 58

info@go-jsb.com | www.go-jsb.com

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Determination of TPH and Ali/Aro split by GCxGC

Report prepared for: Eurofins

1 Objectives

- To evaluate the value added by comprehensive two-dimensional gas chromatography (GC×GC) in removing the requirement for manual splitting during sample preparation.
- Specifically, the following analytical requests have been addressed:
 - Analysis of three samples of differing concentrations
 - Analysis of an RIVM calibration standard at 300ppm
 - Analysis of a RIVM standard + 7 alkanes mix
 - Analysis of a standard consisting of five aromatics and five alkanes to show the retention of these compounds on the system

2 Technical Summary

The instrumental set-up employed to analyze the samples is the following:

Autosampler:	Agilent 7693
Gas Chromatograph:	Agilent 7890B with S/SL injector
Carrier gas:	Hydrogen
Modulator:	Agilent CFT Modulator
Detector:	FID

All data are acquired using *Openlabs Chemstation*.

All 2D data are visualized and processed using the *GC Image* software package (v 2.8r3).



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3 Experimental details

Liquid injection:

Injection volume	2 μ L
Split ratio	2:1

GC:

Inlet temperature	300°C
Inlet Mode	Pulsed Split
Column set	DB-5 (10 m x 0.25 mm x 0.10 μ m) x VF-17 (4 m x 0.25 mm x 0.50 μ m)
Flow (H ₂)	0.25ml/min column 1 constant flow, programmed flow 15.73ml/min to 25.51ml/min column 2
Modulation period	3.46 seconds
Oven temperature program	40°C (hold 2 min), 17°C/min to 260°C, 22°C/min to 360°C (hold 3.5 min)
Detector Temperature	350°C

4 Results and discussion

4.1 Samples 1-3

The results from sample 1 are shown in figure 1 below.

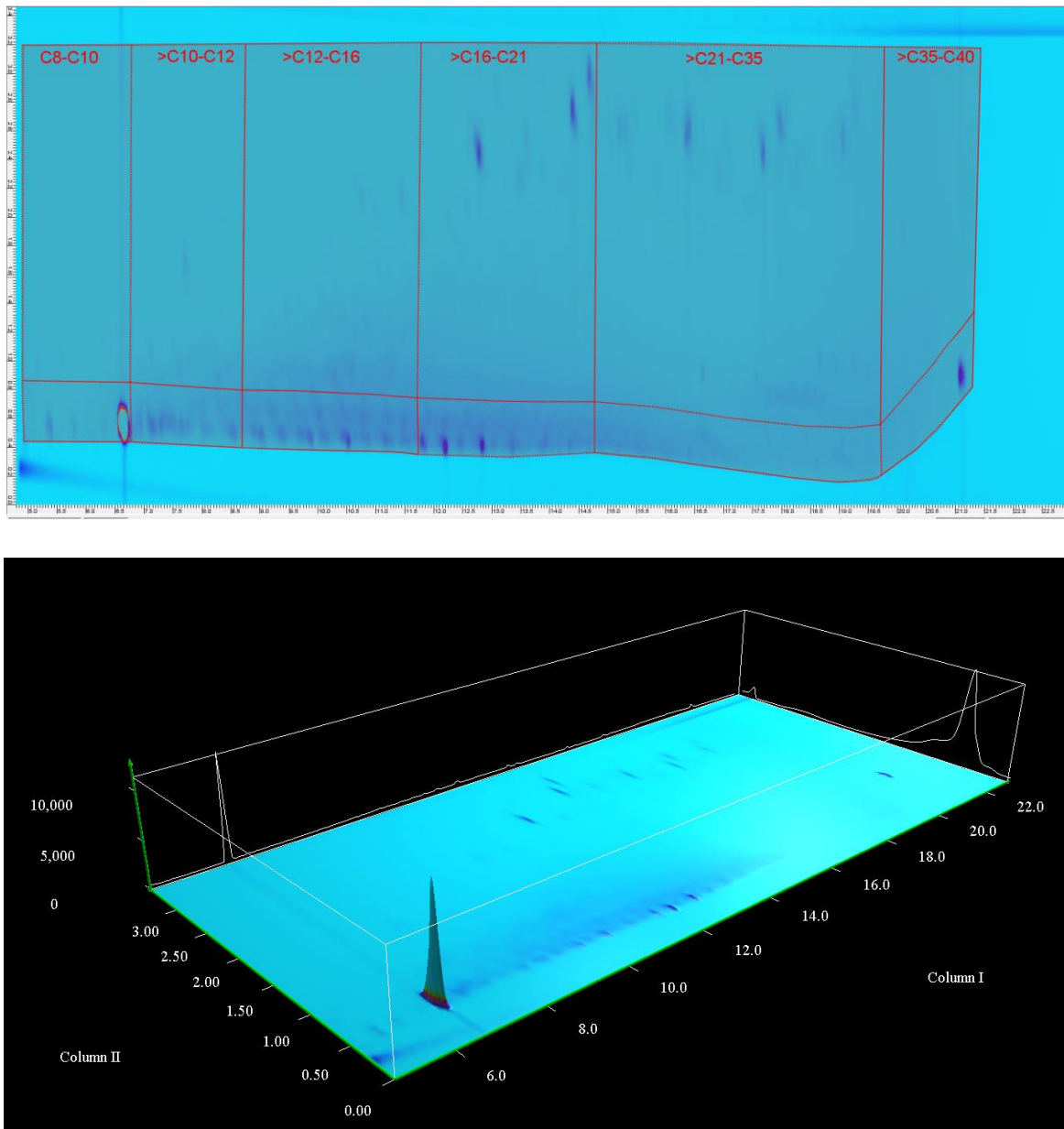


Figure 1. 2d (top) and 3D (bottom) view of Sample 1 showing significant C10 spike. 2D plot (top) and 3D view (bottom)

The results indicate the presence of a significant C10 spike, as well as a C40 spike, with the C10 spike being significantly larger than any of the other peaks. However, good separation of aliphatics and aromatics can also be observed. The detail of the chromatogram is more easily seen if we zoom in on the region between these spikes, as shown in Figure 2 below, which better shows the spread of compounds in the sample.

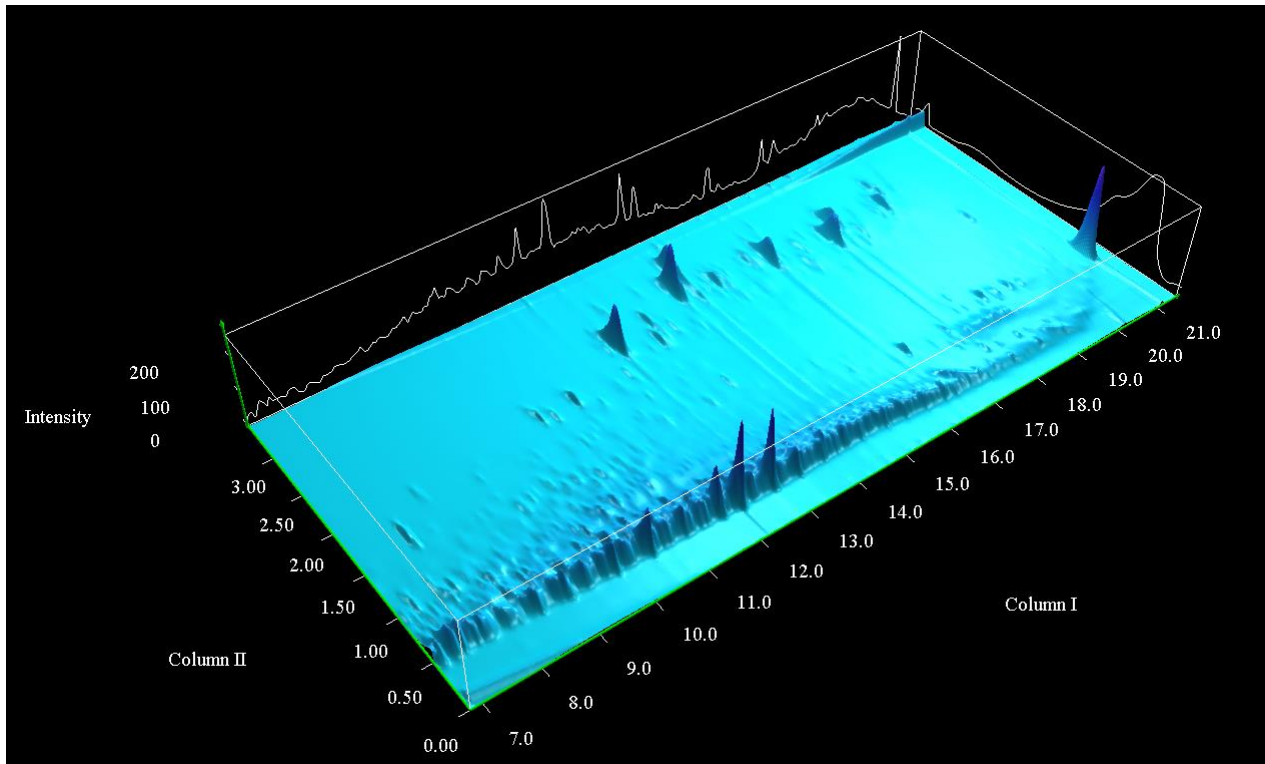


Figure 2. 3D view of Sample 1 showing a zoom between the C10 and C40 spikes.

Sample 2 also appears to contain two large spiking compounds eluting in the C8-C10 band as shown below in figure 3, but zooming in on the rest of the chromatogram reveals more detail about the sample.

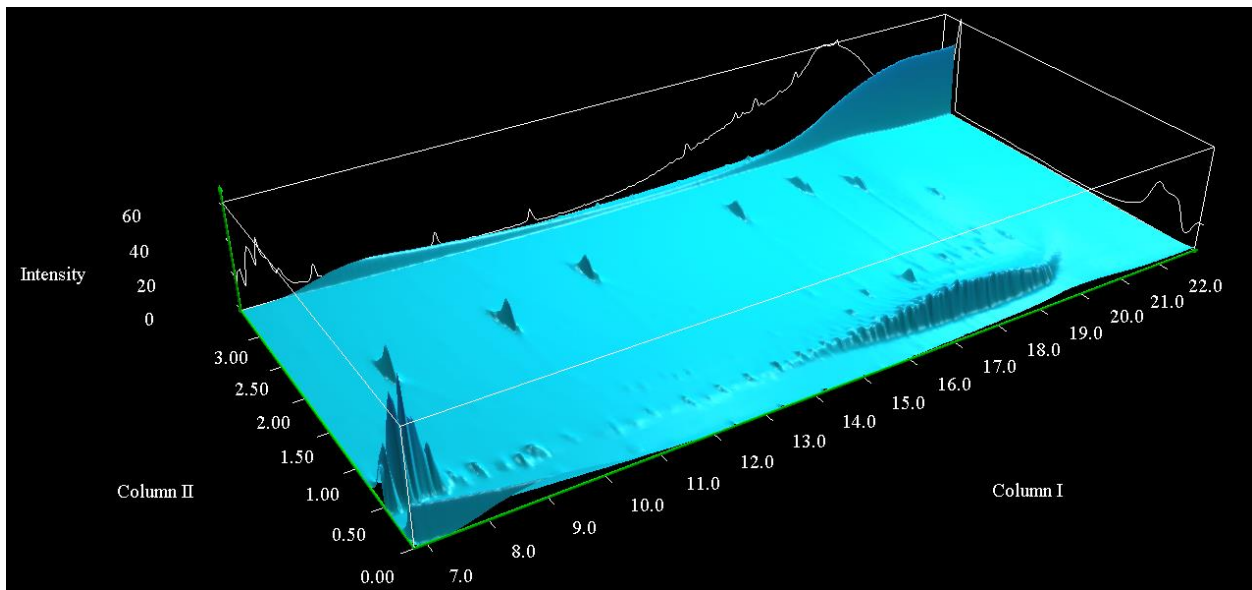
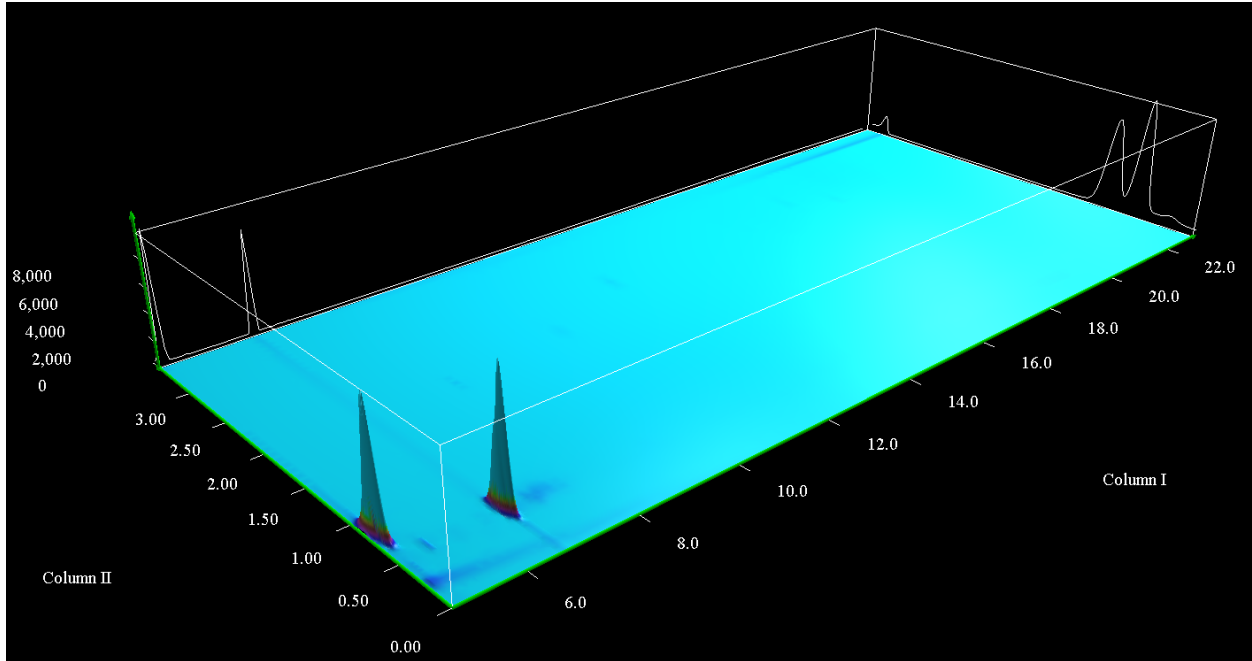


Figure 3. 3D view of Sample 2 showing two large spiking compounds (top) and zoom after C10 (bottom)

Sample 3 was clearly the most concentrated sample, and also contained the two large peaks in the C8-C10 band as shown below in figure 4.

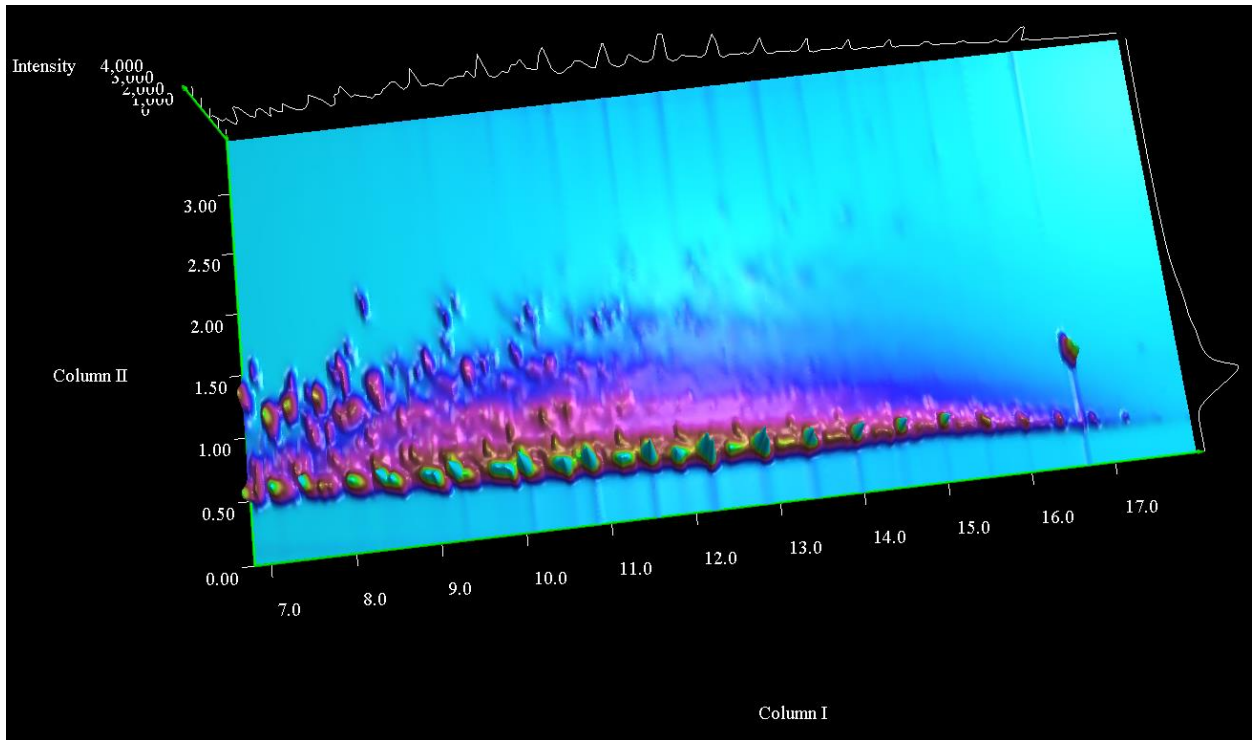
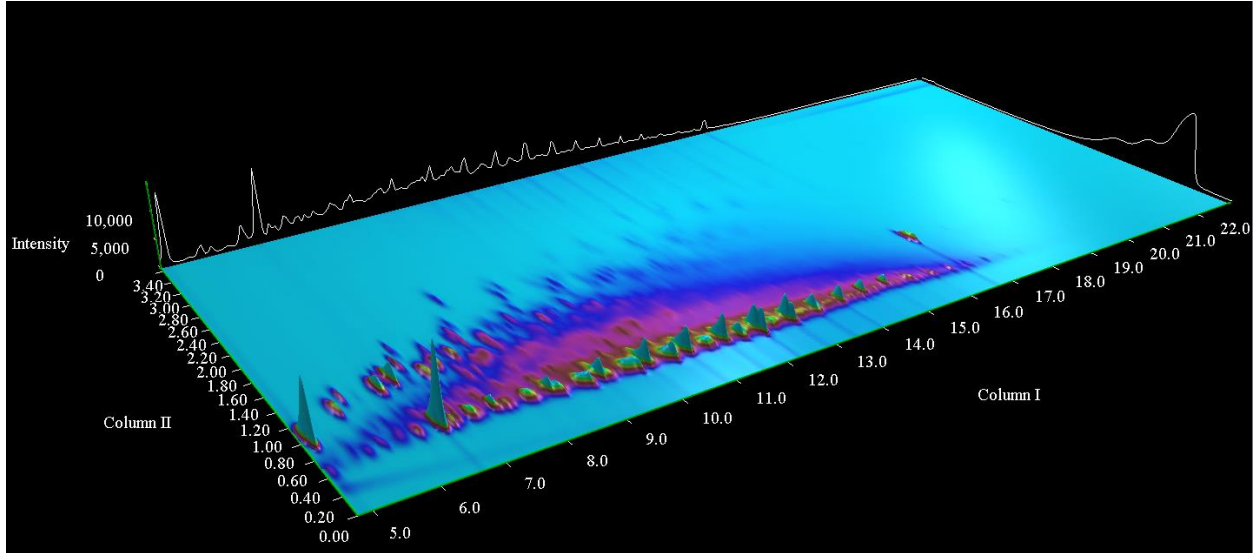


Figure 4. 3D view of Sample 3 showing two large peaks in the C8-C10 band (top) and a close-up view of the central region (bottom)

Again, these results show clear separation of aliphatic and aromatic compounds. The samples were not analysed against a calibration, but the suspected presence of spiking compounds would significantly

affect the results in any case. The observed responses of the three samples indicate that sample 3 contained the highest concentration of hydrocarbons, with sample 2 containing the lowest concentration. The linear response of the system has long been established and published. The split between the bands is shown in table 1.

Area Name	Group Name	Sample 1		Sample 2		Sample 3	
		Volume	TPH %	Volume	TPH %	Volume	TPH %
1. Ali C8-C10	Ali	202085.78	25.07	227155.46	46.56	408383.87	5.59
1. Aro C8-C10	Aro	5152.33	0.64	48209.63	9.88	278139.62	3.81
2. Ali >C10-C12	Ali	29064.20	3.61	9327.76	1.91	609273.77	8.34
2. Aro >C10-C12	Aro	12028.00	1.49	835.31	0.17	549667.91	7.52
3. Ali >C12-C16	Ali	74620.36	9.26	852.70	0.17	1537865.42	21.05
3. Aro >C12-C16	Aro	61417.90	7.62	1527.51	0.31	1133054.71	15.51
4. Ali >C16-C21	Ali	81552.10	10.12	1515.13	0.31	1207733.00	16.53
4. Aro >C16-C21	Aro	89478.90	11.10	1368.47	0.28	819403.08	11.22
5. Ali >C21-C35	Ali	61346.87	7.61	29206.36	5.99	340515.95	4.66
5. Aro >C21-C35	Aro	124711.37	15.47	33002.39	6.76	289791.62	3.97
6. Ali >C35-C40	Ali	16967.28	2.11	6318.74	1.30	4590.42	0.06
7. Aro >C35-C40	Aro	47016.90	5.83	21885.01	4.49	20460.59	0.28
TPH	TPH	805950.33	100.00	487849.35	100.00	7305905.07	100.00

Name	Included Volume (Total)	TPH % (Total)	Included Volume (Total)	TPH % (Total)	Included Volume (Total)	TPH % (Total)
Ali	465636.60	57.77	274376.16	56.24	4108362.43	56.23
Aro	339805.41	42.16	106828.32	21.90	3090517.53	42.30
TPH	805950.33	100.00	487849.35	100.00	7305905.07	100.00

Table 1. Summary of ali/aros split in samples 1, 2 and 3.

4.2 Standards

4.2.1 RIVM Calibration Standard

The results from the RIVM standard are shown in figure 5 below. This standard contains a spread of compounds across the bandings, and good separation of aliphatic and aromatic compounds was observed.

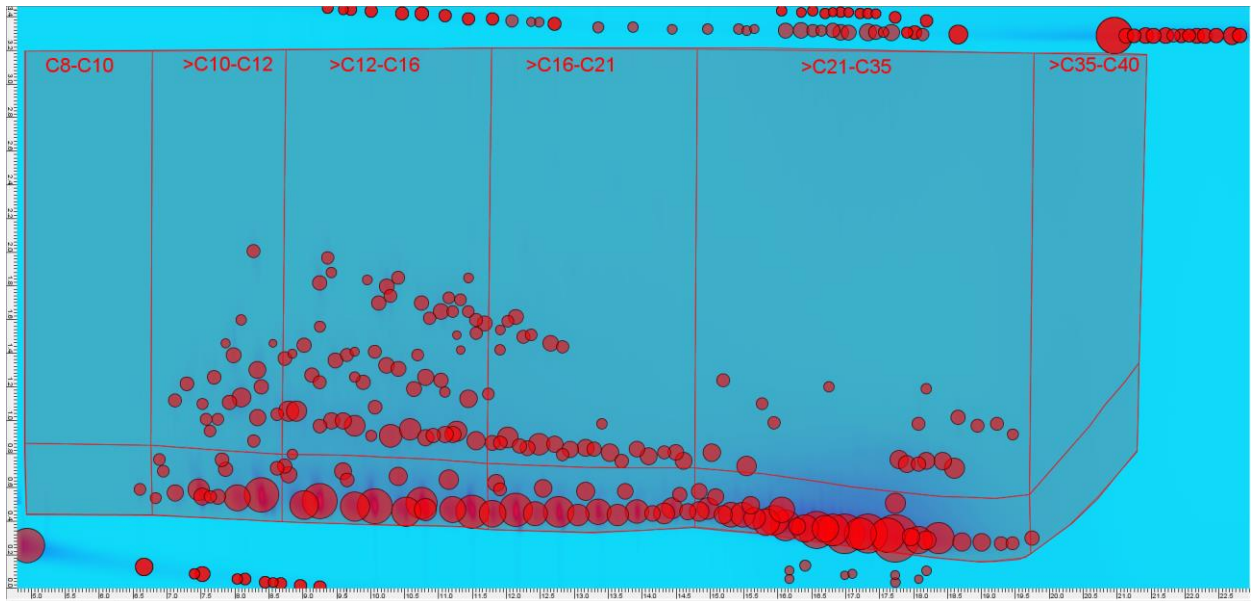
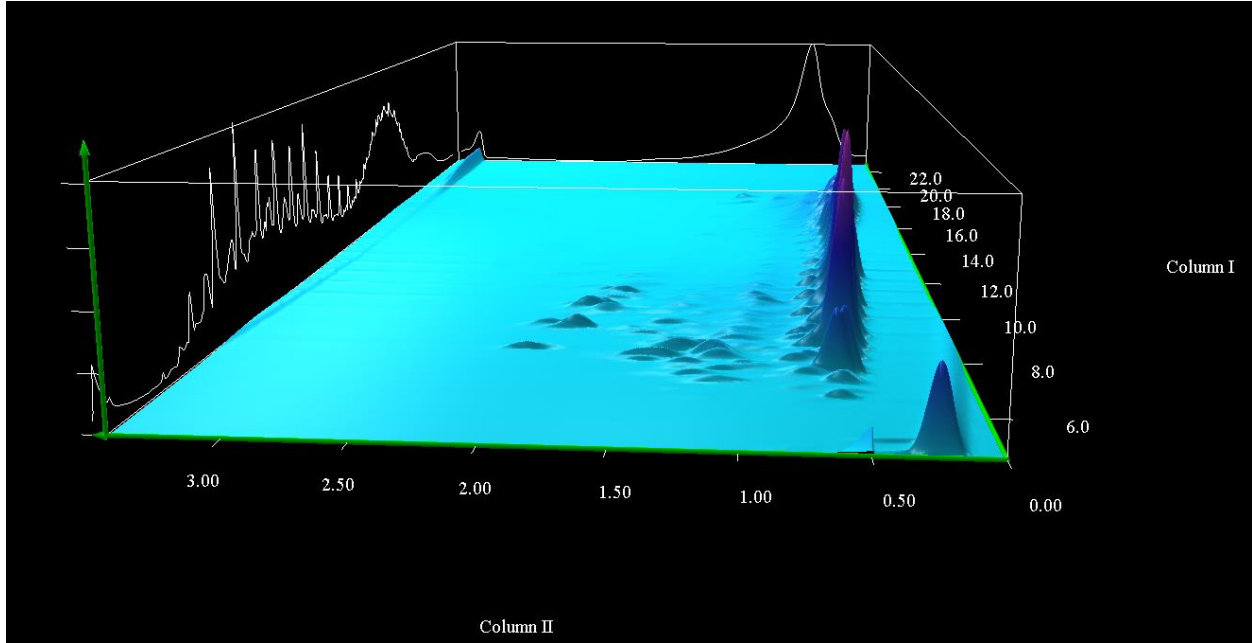


Figure 5. 3D (top) and 2D (bottom) views of the RIVM Chromatogram highlighting good separation of aliphatic and aromatic compounds.

4.2.2 RIVM Standard + 7 alkanes mix.

The results from the RIVM standard spiked with 7 alkanes are shown in figure 6 below. The 7 large alkanes are easily identified.

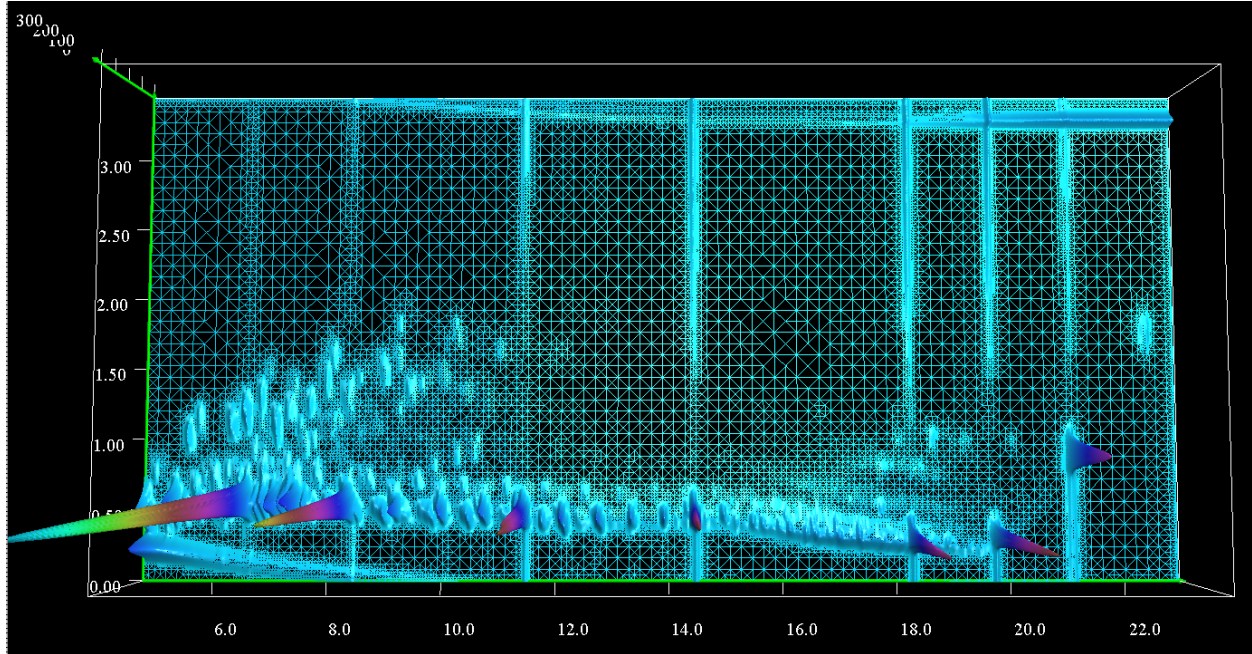


Figure 6. 3D view (wireframe view) of the RIVM + 7 alkanes standard.

4.2.3 Fract Standard

This standard contained 5 aliphatic peaks and 5 aromatic compounds. The aim of analyzing this standard was to determine the retention of these compounds on the system. The results are shown below in Figure 7 and table 2. Good separation was observed in both dimensions.

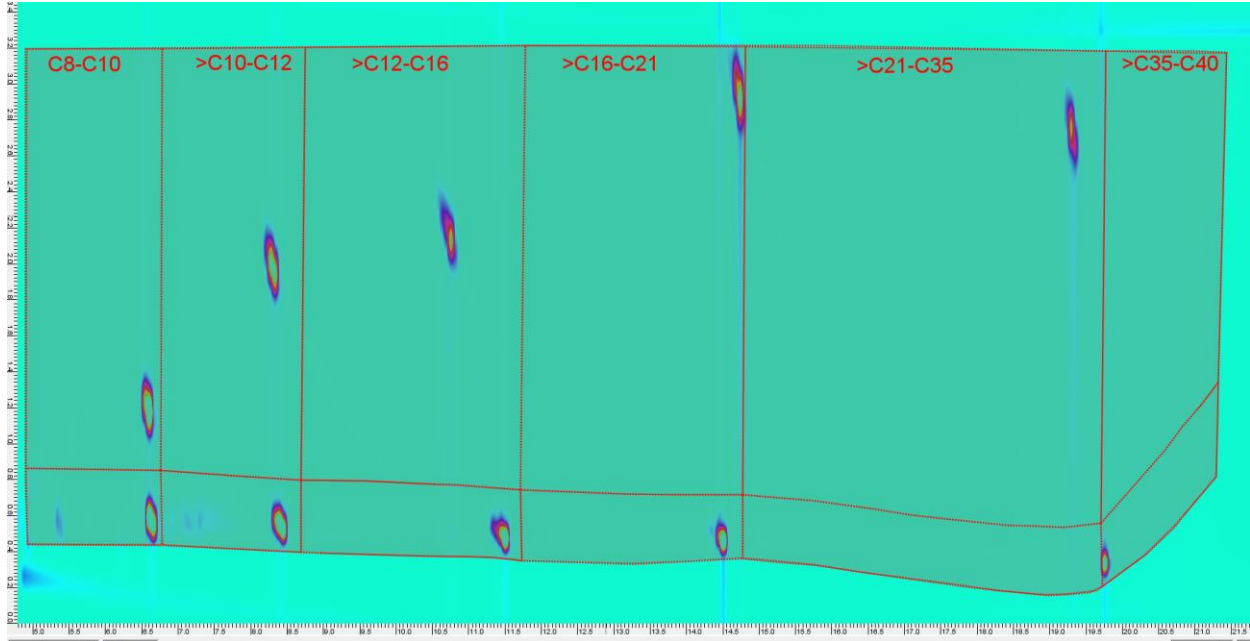


Figure 7. 2D view of the 'Fract Std' showing good separation in both dimensions.

	Retention I (mins)	Retention II (secs)
Aliphatic peak 1	6.574	0.57
Aliphatic peak 2	8.632	0.54
Aliphatic peak 3	11.476	0.47
Aliphatic peak 4	14.474	0.45
Aliphatic peak 5	19.722	0.33
Aromatic peak 1	6.574	1.19
Aromatic peak 2	8.246	1.98
Aromatic peak 3	10.726	2.11
Aromatic peak 4	14.705	2.9
Aromatic peak 5	19.261	2.75

Table 2. Retention times of peaks in 'Fract Std'.



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5 Conclusions

- GC×GC with flow modulation provides significantly enhanced chromatographic resolution and peak capacity, allowing in depth characterization of highly complex samples
- The results presented here demonstrate that the system is fit for purpose for the determination of aliphatic and aromatic TPH compounds in environmental samples, including bands grouped by carbon number
- This technique has been adopted by and achieved accredited status in several environmental laboratories in the UK
- The analytical parameters used to generate this data are typical for this application, with a run time of around 23 minutes to measure up to C40. These parameters can be adjusted and accredited laboratories are using differing parameters - some are measuring from C8 to C44 with GC cycle times of around 25 minutes, whilst others are starting from C10 in order to further reduce the runtime.