



ASG

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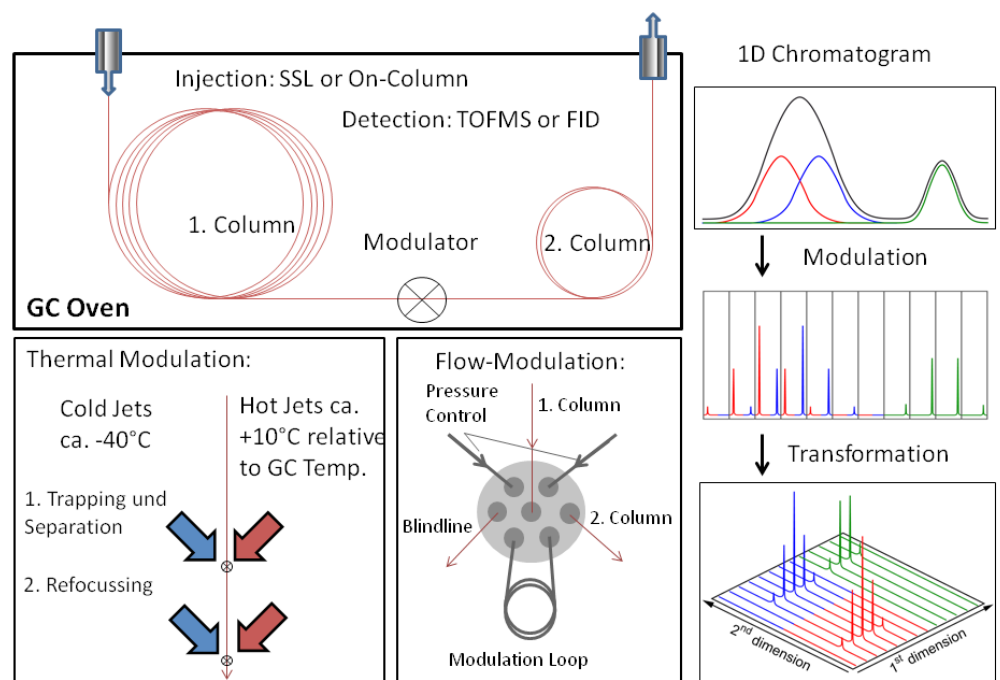
COMPLETE QUANTIFICATION OF MIDDLE DISTILLATES USING ASG 2253 GC×GC-TOFMS AND ASG 2502 GC×GC-FID

Comprehensive two-dimensional gas chromatography (GC×GC) provides an enormously enhanced selectivity compared to conventional gas chromatography. Due to the coupling of capillary columns of different polarity it is possible to separate complex mixtures into single components. The core part of the two-dimensional separation, the so-called modulator, is located between the first and the second dimension.

The function of the modulator is the accumulation of components, which elute from the first column simultaneously, refocusing and injecting them into the second column for further separation. This process can be performed by regular cycles of cold- and hot-jets (thermal modulation), or by adjusting the carrier gas flow in the second dimension (flow modulation). The schematic structure of a GC×GC instrument is given in **Figure 1**.

SCHEMATIC STRUCTURE OF GC×GC

Figure 1: Schematic structure of a GC×GC instrument, comprising an injector, conventional capillary column and detector. Both columns including the modulator are located within a conventional GC oven. For separated heating of the second column, the GC oven can be optionally equipped with an additional smaller oven.





Substances, showing the same boiling point but different polarity, can be separated by the second column. By this, compounds of the same substance class organize in structured groups within the two-dimensional separation space due to their very similar physico-chemical properties. The application of a "reversed-phase column combination" (semi-polar column as 1st dimension and non-polar column as 2nd dimension) provides an optimal utilization of the two-dimensional separation space, compared to the often applied "normal-phase combination" (see **Figure 2**). In this way, a classification of n-/iso-paraffins, naphthenes, mono-, di- and tri+-aromatics by carbon number is possible using FID for detection (see **Table 1**), and supports the identification of unknown compounds using TOFMS for detection.

Both methods, ASG 2253 (GC×GC-TOFMS) and ASG 2502 (GC×GC-FID), show application-specific advantages and disadvantages. The application of (GC×GC-FID) provides a complete quantitative overview of the composition and can replace with only one measurement the standard methods DIN EN 12916, DIN EN 14103 and DIN EN 14078 and can partly provide more detailed results. A more precise identification of single compounds (e.g. heteroaromatics) or compounds classes within the above mentioned is not possible. Our in-house method ASG 2253 does provide this possibility. By coupling with a time-of-flight mass spectrometer (TOFMS), complete mass spectra (m/z 30 – 700) can be generated with an acquisition rate of up to 200Hz. The real challenge lies in the evaluation of this enormous amount of raw data.

For this purpose, an automated analysis method has been developed based on Visual Basic Script, which provides the possibility of a precise classification of sample components by substance class and carbon number corresponding to the characteristic mass spectra respectively (see **Figure 3**). Furthermore, a method has been developed to quantify all sample components based on several different internal standards (see **Table 2**).

Table 1: Exemplary evaluation of a measurement of common diesel fuel (B7) using GC×GC-FID. Quantification is verified based on exemplary mixtures of standard compounds. A detailed classification of mono-, di- and polyaromatics is not possible with this method.

Figure 2: Two-dimensional chromatogram of common diesel fuel (B7). Separation was achieved using a reversed column combination consisting of a 50% phenyl-substituted column as 1st dimension and 100% polydimethylsiloxane as 2nd dimension

Figure 3: 2D chromatogram of the same EN 590 diesel fuel after data processing and classification using Visual Basic Script. Single peak marker are highlighted in different colors corresponding to the different substance classes respectively.

%(m/m)	n-Paraffins	iso-Paraffins	Naphthenes	FAME	MA	DA	Tri+A	Total
7	0.07%	0.04%	0.02%	-	0.08%	-	-	0.2%
8	0.28%	0.27%	0.16%	-	0.66%	-	-	1.4%
9	1.16%	0.91%	0.68%	-	3.08%	-	-	5.8%
10	1.93%	2.58%	1.67%	-	3.44%	0.17%	-	9.8%
11	1.99%	2.51%	2.51%	-	2.55%	0.62%	-	10.2%
12	1.96%	2.10%	2.57%	-	2.32%	0.98%	-	9.9%
13	2.07%	2.20%	2.02%	-	1.69%	1.07%	-	9.1%
14	2.06%	2.28%	1.88%	-	1.04%	0.76%	0.03%	8.1%
15	1.94%	2.48%	2.06%	-	0.61%	0.43%	0.06%	7.6%
16	1.59%	2.47%	1.21%	0.44%	0.62%	0.31%	0.10%	6.7%
17	1.43%	2.05%	0.92%	-	0.49%	0.20%	0.09%	5.2%
18	1.20%	2.20%	0.54%	6.27%	0.41%	0.09%	0.11%	10.8%
19	1.12%	2.52%	0.46%	-	0.41%	0.05%	0.08%	4.6%
20	0.98%	1.82%	0.38%	0.13%	0.23%	-	0.13%	3.7%
21	0.75%	0.96%	0.27%	-	0.13%	-	-	2.1%
22	0.51%	0.84%	0.10%	0.04%	0.09%	-	-	1.6%
23	0.44%	0.76%	0.05%	-	0.04%	-	-	1.3%
24	0.31%	0.51%	0.05%	-	0.04%	-	-	0.9%
25	0.20%	0.37%	0.02%	-	0.02%	-	-	0.6%
26	0.12%	0.21%	0.02%	-	0.01%	-	-	0.4%
27	0.07%	0.03%	0.01%	-	-	-	-	0.1%
28	0.01%	0.02%	-	-	-	-	-	<0.1%
29	0.01%	0.01%	-	-	-	-	-	<0.1%
Total	22.2%	30.1%	17.6%	6.9%	17.9%	4.7%	0.6%	100%

Table 1

2D-CHROMATOGRAMS

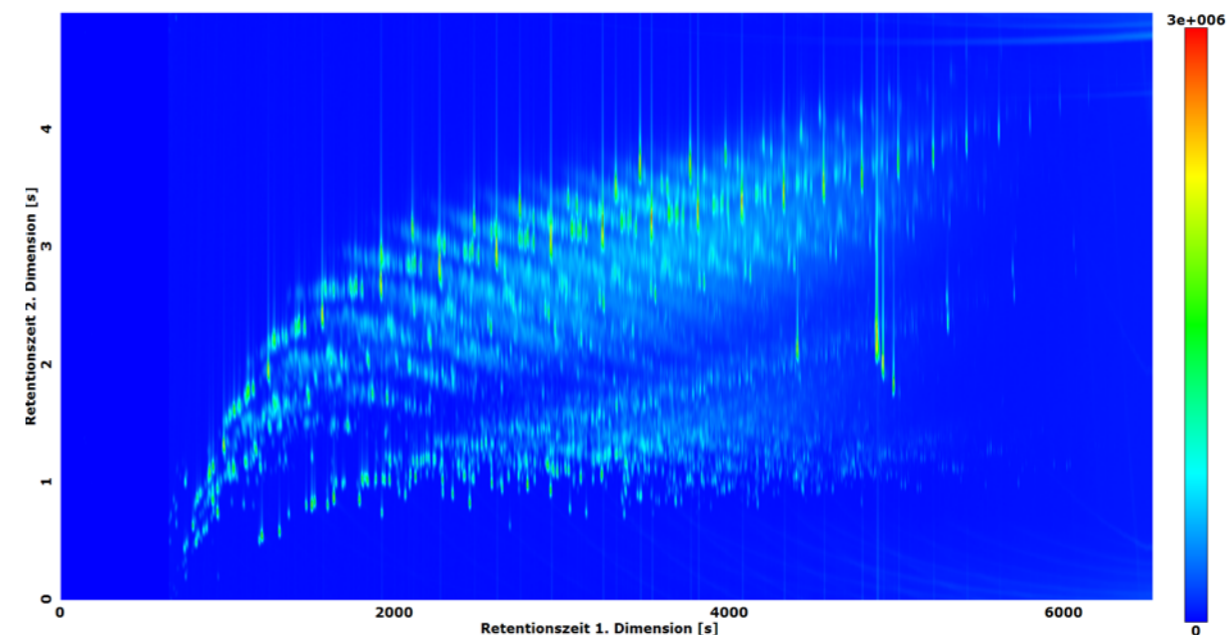


Figure 2

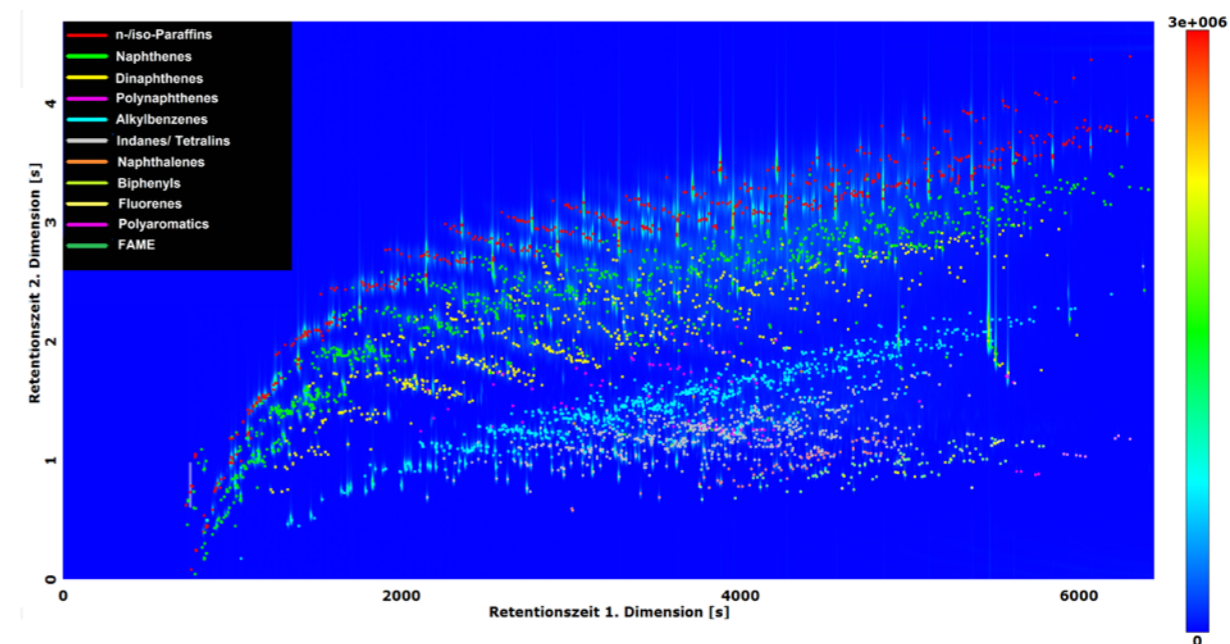


Figure 3

QUANTIFICATION RESULTS OF AN EN 590 DIESEL FUEL

Carbon number	n-Paraffins	iso-Paraffins	Naphthenes	Dinaphthenes	Polynaphthenes	Alkylbenzenes	Naphthenobenzenes	Naphthalenes	Biphenyls/Diphenylmethanes/Acenaphthenes	Fluorenes	Phenanthrenes/Anthracenes	Pyrenes/Fluoranthenes	FAME				Total
													0	1	2	3	
7	0.01%	-	0.03%	-	-	0.03%	-	-	-	-	-	-	-	-	-	-	0.07%
8	0.14%	0.07%	0.25%	0.01%	-	0.19%	-	-	-	-	-	-	-	-	-	-	0.66%
9	0.75%	0.30%	1.06%	0.09%	-	0.64%	0.16%	-	-	-	-	-	-	-	-	-	3.00%
10	1.32%	0.89%	2.61%	0.76%	<0.01%	0.93%	1.20%	0.07%	-	-	-	-	-	-	-	-	7.78%
11	1.58%	0.91%	1.85%	0.69%	0.01%	0.91%	1.77%	0.17%	-	-	-	-	-	-	-	-	7.89%
12	1.45%	0.56%	2.00%	0.86%	0.02%	0.77%	1.99%	0.31%	0.04%	-	-	-	double bonds				8.00%
13	1.56%	0.94%	2.85%	0.73%	0.02%	0.82%	2.59%	0.34%	0.17%	0.01%	0.03%	-	0	1	2	3	10.06%
14	1.64%	0.92%	3.01%	0.71%	0.01%	0.81%	2.11%	0.34%	0.44%	0.06%	0.11%	-	0.02%	-	-	-	10.16%
15	2.12%	1.21%	2.99%	0.46%	-	0.58%	0.94%	0.28%	0.35%	0.08%	0.14%	-	-	-	-	-	9.15%
16	2.12%	1.33%	3.40%	0.38%	-	0.37%	0.76%	0.09%	-	0.11%	0.08%	0.04%	0.84%	0.04%	-	-	9.56%
17	1.79%	1.20%	3.22%	0.36%	-	0.29%	0.18%	-	-	-	-	0.01%	-	-	-	-	7.05%
18	1.61%	1.46%	2.72%	0.67%	-	0.26%	0.13%	-	-	-	-	-	0.18%	3.67%	1.31%	0.53%	12.54%
19	1.81%	1.54%	1.68%	0.47%	-	0.16%	-	-	-	-	-	-	-	-	-	-	5.66%
20	1.16%	0.59%	1.13%	0.18%	-	0.21%	-	-	-	-	-	-	0.07%	0.02%	-	-	3.36%
21	1.20%	0.59%	0.60%	0.01%	-	0.08%	-	-	-	-	-	-	-	-	-	-	2.48%
22	0.58%	0.22%	0.25%	-	-	0.04%	-	-	-	-	-	-	0.01%	-	-	-	1.10%
23	0.35%	0.36%	0.01%	-	-	-	-	-	-	-	-	-	-	-	-	-	0.72%
24	0.13%	0.18%	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31%
25	0.06%	0.09%	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.15%
26	0.03%	0.02%	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.05%
27	0.02%	0.01%	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.03%
28	0.01%	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01%
29	0.01%	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01%
Total	21.45%	13.42%	29.66%	6.32%	0.07%	7.09%	11.83%	1.60%	1.01%	0.25%	0.36%	0.05%	1.10%	4.79%	3.31%	3.53%	99.80%

Table 2: Quantitative results given in %[m/m] and organized by substance class and carbon number.

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