

# Group-Type Analysis of Jet Fuel Using the Agilent Flow-Modulated GC×GC-FID

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## Abstract

Conventional chromatographic and spectroscopic techniques are not sufficient to fully analyze the composition of jet fuel. Yet, a complete picture of jet fuel compounds is essential in developing and producing safe, efficient fuels. This application note describes a method for the group-type analysis of jet fuel according to China's regulatory standard NB/SH/T 6078-2023<sup>1</sup> using the Agilent 8890 reverse fill/flush flow-modulated two-dimensional gas chromatography system with flame ionization detector (GC×GC-FID). The relative abundance and partial carbon number distribution of monoaromatic and diaromatic species in jet fuel were determined with exceptional repeatability, linearity, sensitivity, and quantitative precision. The system exhibited exceptional retention time (RT) repeatability in both dimensions (%RSD of <sup>1</sup>RT ~0, %RSD of <sup>2</sup>RT ≤ 0.27) and quantitative precision (< 2.0% RSD) for all nontrace compounds across 10 replicates. The linearity of 12 individual aromatic compounds and six aggregate groups of aromatics across eight concentration levels resulted in a linear coefficient (R<sup>2</sup>) exceeding 0.999. These performance characteristics provide the necessary foundation for routine jet fuel analysis in laboratories with limited expertise in GC×GC method development and maintenance.

## Introduction

Jet fuel, also known as aviation kerosene and aviation turbine fuel, is a petroleum product primarily used as fuel for aircraft turbine engines. Characterizing the composition of jet fuel is essential for ensuring safe and efficient aircraft operation and for maintaining the high performance and reliability standards the aviation industry requires. This type of analysis also has significant practical importance for understanding the fuel production process and evaluating catalyst performance and lifetime. The aromatic hydrocarbon content of jet fuel is a crucial quality indicator and is subject to global regulations.

However, the number of unique hydrocarbon structural isomers in jet fuel exceeds the selectivity of conventional one-dimensional chromatographic and spectroscopic methods, which cannot provide the necessary hydrocarbon composition and carbon number distribution information. Comprehensive GC×GC has a number of advantages over conventional chromatographic techniques, such as enhanced resolution, peak capacity, sensitivity, and a highly ordered and structured separation pattern. The analysis procedure of such petroleum products can be significantly simplified, since GC×GC allows direct injection without the need for sample pretreatment. Additionally, the analysis of such petroleum products by GC×GC does not require any sample preparation or pretreatment, making it an attractive method for quality control laboratories.

This application note establishes a group-type quantification method for jet fuel according to China's NB/SH/T 6078-2023 standard<sup>1</sup> using the Agilent 8890 reverse fill/flush flow-modulated GC×GC-FID system.<sup>2-4</sup> The Agilent reverse flow modulator (RFM) is a differential flow modulator. It is based on the Agilent Capillary Flow Technology (CFT) and fractionates the carrier gas by simply directing the carrier gas flow. The system requires no additional footprint (since the modulator is installed within the GC oven), has no moving parts, is cost-effective, robust, and yields highly reproducible results. The system is particularly suited to analyzing middle petroleum distillates like jet fuel, because these mixtures typically have a well-defined beginning and end of elution in GC separations. This application note determined the relative abundance of 1-ring aromatics, 2-ring aromatics, and homologous aromatic series by carbon number in real jet fuel samples. The repeatability, linearity, and quantitative precision of the system was also evaluated.

## Experimental

### Samples

Jet fuel was obtained from two refinery companies in China. A gravimetric blend of chemical standards at various concentration levels was prepared in-house. The chemical standards were purchased from ANPEL Laboratory Technologies (Shanghai) Inc.

The jet fuel was injected directly, without sample preparation.

### Instrumentation

An 8890 GC×GC-FID system with a split/splitless inlet and a reverse fill/flush RFM were used with the configurations listed in Table 1. Three different column sets were evaluated.

## Method settings

**Table 1.** GC×GC-FID experimental conditions.

Agilent 8890 GC Parameters				
Inlet		Split/splitless inlet, 280 °C, injection volume 0.5 µL, split ratio 500:1		
Detector		Analysis FID		Monitor FID (Optional)
	Temperature	300 °C		300 °C
	H <sub>2</sub> Flow	35 mL/min		35 mL/min
	Air Flow	350 mL/min		350 mL/min
	Makeup (N <sub>2</sub> ) Flow	30 mL/min		30 mL/min
	Acquisition Rate	200 Hz		5 Hz
Column Sets		Column Set 1	Column Set 2	Column Set 3
	Primary Column	Agilent DB-1, 20 m × 0.18 mm, 0.4 µm, (p/n 121-1023) Flow rate: 0.5 mL/min	Agilent DB-1, 40 m × 0.18 mm, 0.4 µm, (p/n 121-1043), Flow rate: 0.5 mL/min	Agilent DB-1, 20 m × 0.1 mm, 0.4 µm, (p/n 127-1023), Flow rate: 0.35 mL/min
	Secondary Column	Agilent DB-HeavyWAX, 5 m × 0.32 mm, 0.2 µm, (p/n 123-7157), Flow rate: 25 mL/min	Agilent DB-HeavyWAX, 5 m × 0.32 mm, 0.2 µm, (p/n 123-7157), Flow rate: 25 mL/min	Agilent DB-17ht, 5 m × 0.25 mm, 0.15 µm, (p/n 122-1811), Flow rate: 14 mL/min
	Monitor Column	Deactivated fused silica, 1.9 m × 0.1 mm, (p/n 160-2635-10), Flow rate: 0.63 mL/min	Deactivated fused silica, 1.9 m × 0.1 mm, (p/n 160-2635-10), Flow rate: 0.63 mL/min	Deactivated fused silica, 4.2 m × 0.1 mm, (p/n 160-2635-10), Flow rate: 0.43 mL/min
Carrier Gas		He	He	H <sub>2</sub>
Oven		Initial 50 °C (no hold), 4 °C/min to 260 °C, total 52.5 min	Initial 50 °C (no hold), 2.5 °C/min to 250 °C, total 80 min	Initial 40 °C (no hold), 3 °C/min to 250 °C, total 70 min
Modulator	Modulation Delay	2 min	2 min	2 min
	Modulation Period	4 s	3 s	3 s
	Inject Time	0.12 s	0.1 s	0.12 s
Software		Data acquisition: Agilent OpenLab CDS, version 3.7.189, firmware revision 2.1.0.626, driver version: DSA GC7.7 [189]. 2D-GC Data analysis: GC Image GC×GC Edition software, version 2021r2. (GC Image, LLC., Lincoln, NE, USA)		

GC Image software was used for plotting <sup>2</sup>D chromatograms (Figure 1), generating peak identification templates, GC sequence processing, and data analysis.

## Results and discussion

### Column selection

The success of GC×GC separations relies heavily on the correct selection of GC columns and on the working mechanism of the modulator.<sup>5,6</sup> The Agilent RFM is a differential flow modulator that uses a relatively small primary (<sup>1</sup>D) column flow rate and significantly larger secondary (<sup>2</sup>D) column flow rate to facilitate collection and reinjection of the primary column eluent onto the secondary column. The detailed working mechanism can be found in the references.<sup>2-4</sup> Based on its working mechanism, the general rules of selection of proper column dimensions are:

- A <sup>1</sup>D column with a narrower inner diameter (id = 0.1 to 0.25 mm)
- A shorter <sup>1</sup>D column enables faster analysis, while a longer column provides enhanced resolution and peak capacity
- A <sup>2</sup>D column with a wider inner diameter (id = 0.25 to 0.32 mm)

- <sup>2</sup>D column length could be optimized to meet different resolution needs; the typical length is 2 to 5 m
- <sup>2</sup>D column with thinner film thickness ( $d_f = 0.1$  to  $0.25$  µm)

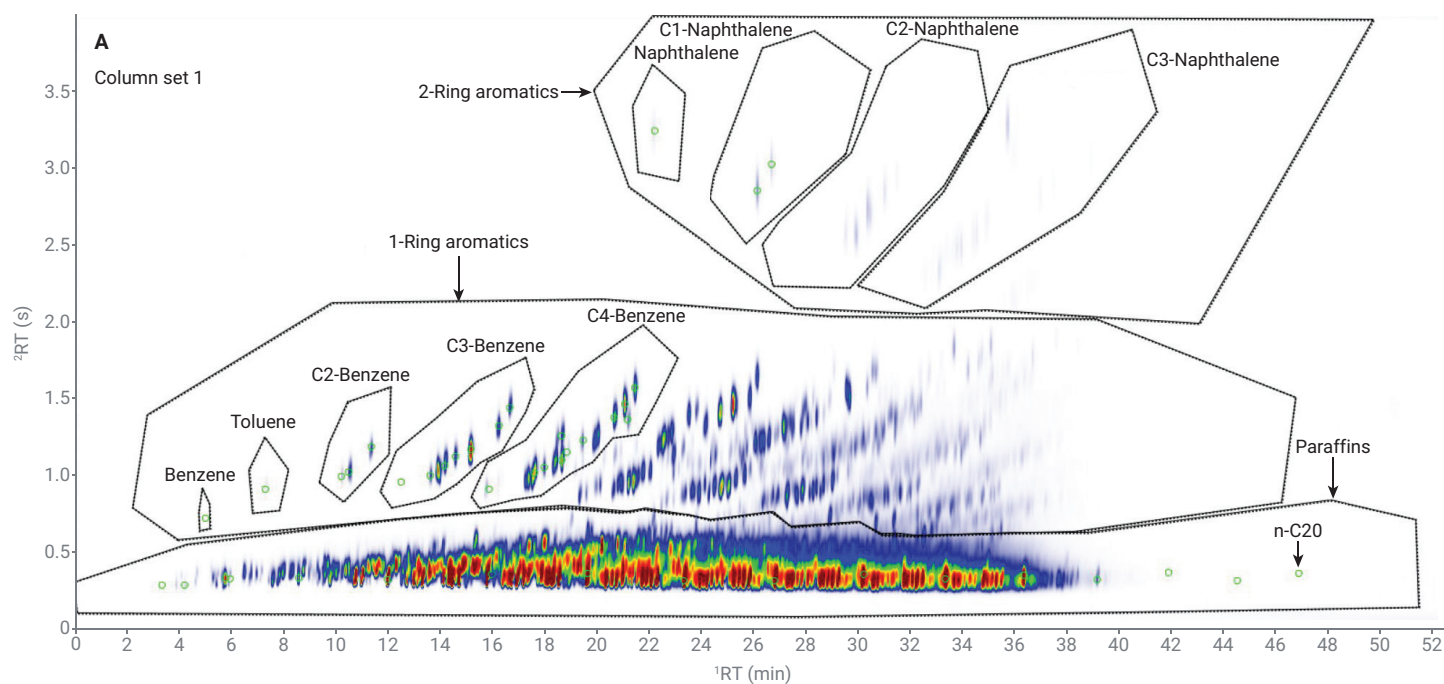
In the context of targeting aromatics in this study, a normal phase configuration was chosen, with a nonpolar column as the primary column and a midpolar or polar column as the secondary column. Two popular choices, the Agilent J&W DB-HeavyWAX (polyethylene glycol, with a maximum temperature of 280 °C) and the Agilent J&W DB-17ht ((50%-phenyl)-methylpolysiloxane, with a maximum temperature of 365 °C), were assessed as potential secondary columns. The DB-HeavyWAX column offers enhanced orthogonality, whereas the DB-17ht column may be better suited for a broader range of compounds with less polar characteristics. In group-type analysis, the separation in the second dimension is more demanding than separation in the first dimension; therefore, a relative long secondary column (5 m) was used.

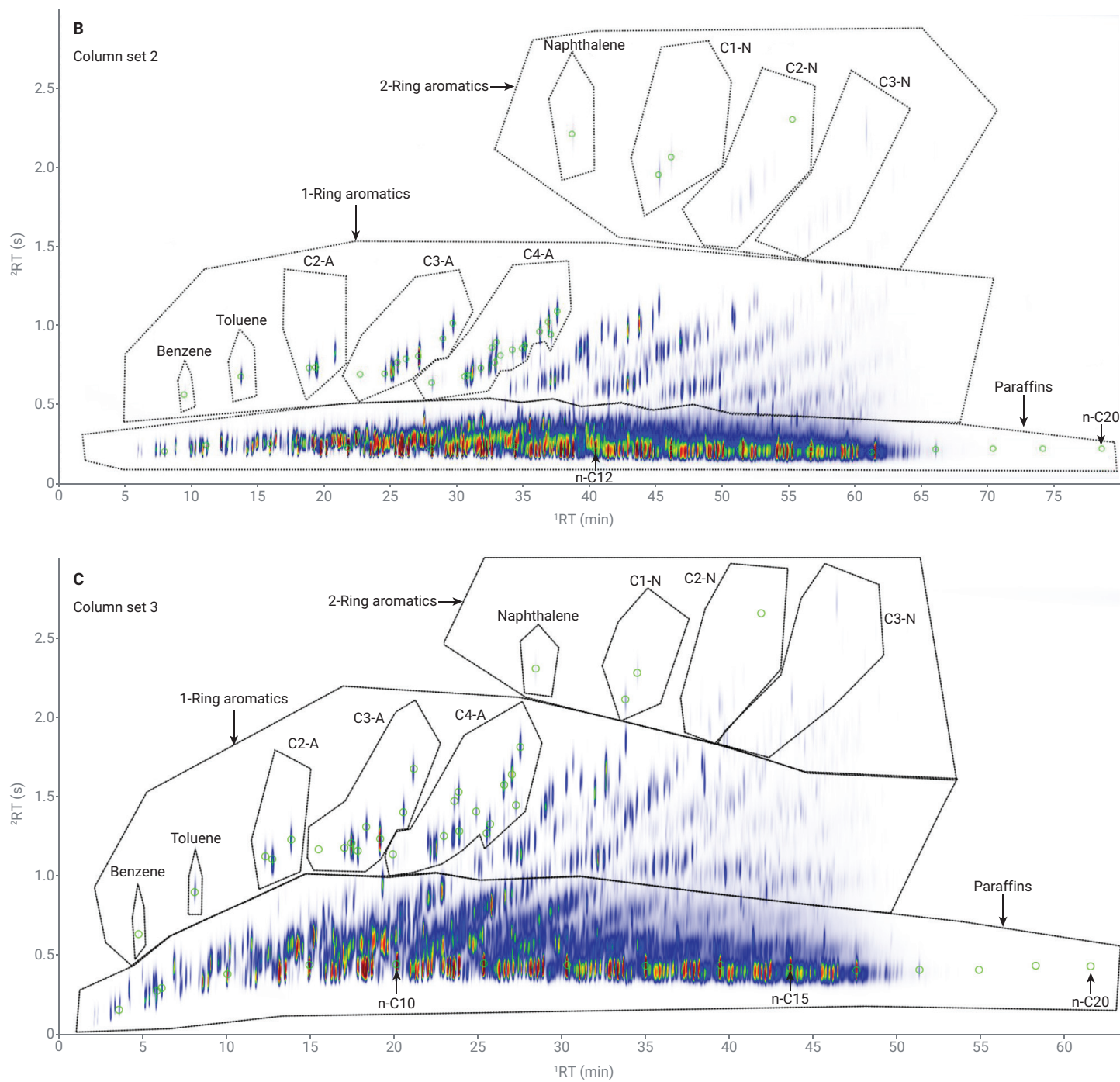
To shorten overall analysis time, one can use a short primary column and a relatively fast temperature programming rate. The first method used a 20 m × 0.18 mm primary column and a 4 °C/min heating rate. As shown in Figure 1A, the saturates (paraffins, isoparaffins, and cycloparaffins), 1-ring aromatics, and 2-ring aromatics are well separated from each other and grouped into three horizontal bands. Within each band (molecular class), individual compounds with a given number of carbon atoms exhibit a "roof-tile" separation pattern. To further enhance the separation, a longer primary column combined with a slower oven ramp is advised.

In the second approach, a 40 m × 0.18 mm primary column and a heating rate of 2.5 °C/min were used. Despite the longer total analysis time, the second method demonstrates significantly enhanced separation efficiency. This is visible in the improved resolution of the saturates region and in the

congested area of the 1-ring aromatics region, revealing a more detailed "roof-tile" effect (Figure 1B). Further reducing the heating rate and increasing the modulation period can lead to greater separation enhancement, albeit at the cost of increased analysis time.

Given the lower polarity of the DB-17ht column, it cannot provide the distinct separation between paraffins and aromatics as well as the DB-HeavyWAX. Opting for a 20 m × 0.1 mm primary column and employing a slow heating rate allows for effective 2D separation, as illustrated in Figure 1C. The narrower id column enables higher linear velocity at lower flow rates, improved separation efficiency, and enhanced resolving power. Additionally, using hydrogen instead of helium in the third approach improves separation efficiency and resolution.





**Figure 1.** GCxGC separation using different column sets. For the method details, see Table 1.

## Repeatability

RT stability is a critical characteristic for GC×GC-FID analysis, as peak identification relies on their position in the 2D chromatogram. The flow modulator, which does not involve any moving parts or cold/hot jets, achieves modulation by controlling the flow direction through a collection channel using an electronic pressure control module. By controlling the modulation process using the Agilent sixth-generation electronic pneumatics control technology, exceptionally stable RTs were achieved. Table 2 presents the primary retention time (<sup>1</sup>RT) and secondary retention time (<sup>2</sup>RT) data of various common aromatic species identified in jet fuel

(n = 10). The <sup>1</sup>RT remains almost constant. The %RSD of <sup>2</sup>RT is less than 0.27% for all compounds, and near 0.0000% for most. The exceptional RT stability allows the user to generate a data template and use it for peak identification routinely without much concern about mismatch. The FID response in a GC×GC-FID system is also highly repeatable; the absolute area %RSD of each identified blob was typically below 2%, except in cases of very low concentrations such as benzene at 0.0033% mass, where it reached 2.95%. The normalized area %RSD is mostly below 1%, with a few exceptions falling between 1 and 3%.

**Table 2.** RT repeatability and response repeatability of jet fuel (n = 10).

Compound Name	<sup>1</sup> RT			<sup>2</sup> RT			Peak Volume (Area)			Normalized Mass Content%		
	Mean (min)	St. Dev. (min)	%RSD	Mean (s)	St. Dev. (s)	%RSD	Mean	St. Dev.	%RSD	Mean	St. Dev.	%RSD
Benzene	5.0001	0.0000	0.00	0.7450	0.0000	0.00	87.2299	2.5731	2.95	0.0033	0.0001	2.80
Toluene	7.3334	0.0000	0.00	0.9335	0.0024	0.26	1,087.8271	21.2996	1.96	0.0412	0.0007	1.67
Ethylbenzene	10.2667	0.0000	0.00	1.0200	0.0000	0.00	856.3498	11.7349	1.37	0.0325	0.0004	1.11
<i>p</i> -Xylene	10.5334	0.0000	0.00	1.0400	0.0000	0.00	4,036.2063	45.6758	1.13	0.1530	0.0014	0.88
<i>o</i> -Xylene	11.4001	0.0000	0.00	1.2050	0.0000	0.00	2,287.3705	24.0038	1.05	0.0867	0.0007	0.80
Cumene	12.5334	0.0000	0.00	0.9730	0.0026	0.27	49.5900	0.9225	1.86	0.0019	0.0000	1.60
Propylbenzene	13.6667	0.0000	0.00	1.0200	0.0000	0.00	1,283.0731	13.0481	1.02	0.0487	0.0004	0.82
1,3,5-Trimethylbenzene	14.2001	0.0000	0.00	1.0900	0.0000	0.00	3,624.7463	21.0544	0.58	0.1374	0.0003	0.25
1,2,4-Trimethylbenzene	15.2001	0.0000	0.00	1.1800	0.0000	0.00	13,428.6688	78.0989	0.58	0.5092	0.0015	0.30
sec-Butyl benzene	15.8001	0.0000	0.00	0.9355	0.0016	0.17	423.1998	2.1827	0.52	0.0161	0.0001	0.31
1,2,3-Trimethylbenzene	16.2667	0.0000	0.00	1.3395	0.0016	0.12	2,281.7724	12.4335	0.54	0.0865	0.0002	0.27
Indane	16.7334	0.0000	0.00	1.4950	0.0000	0.00	1,834.6467	10.6057	0.58	0.0696	0.0002	0.30
1-Methyl-2-propylbenzene	18.0001	0.0000	0.00	1.0650	0.0000	0.00	888.4991	3.8292	0.43	0.0337	0.0000	0.12
1,2-Dimethyl-4-ethylbenzene	18.6667	0.0000	0.00	1.1100	0.0000	0.00	4,160.3922	17.0717	0.41	0.1577	0.0001	0.07
2-Methylindane	18.7334	0.0000	0.00	1.3100	0.0000	0.00	2,091.4703	11.4373	0.55	0.0793	0.0003	0.39
5-Methylindane	20.7334	0.0000	0.00	1.4250	0.0000	0.00	3,509.8385	13.9533	0.40	0.1331	0.0001	0.07
Tetraline	21.4667	0.0000	0.00	1.5850	0.0000	0.00	3,057.1203	11.6302	0.38	0.1159	0.0000	0.03
Naphthalene	22.2001	0.0000	0.00	3.2915	0.0024	0.07	177.7303	1.3303	0.75	0.0067	0.0000	0.59
2-Methylnaphthalene	26.2001	0.0000	0.00	2.9040	0.0032	0.11	608.5432	2.4912	0.41	0.0231	0.0000	0.13
1-Methylnaphthalene	26.7334	0.0000	0.00	3.0715	0.0034	0.11	255.4166	1.6593	0.65	0.0097	0.0000	0.41

### Linearity and recovery

A series of aromatic standards with various concentrations were prepared to assess the linearity of individual aromatics and aggregate groups (Table 3). The recovery of these standards at each concentration level was also determined.

The standards contain 0.15 to 21.3% 1-ring aromatics and 0.015 to 2.1% 2-ring aromatics by mass. The  $R^2$  for each component and group exceeded 0.999 (Figure 2). The recovery for each component and group at all concentration levels was within a range of 98 to 114%.

**Table 3.** Linearity and recovery of aromatic standards.

Compound	Nominal Mass Content (%)								Recovery of All Levels (Approximate %)
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	
Toluene	0.022	0.044	0.087	0.175	0.350	0.708	1.400	3.066	98 to 101
<i>p</i> -Xylene	0.022	0.043	0.087	0.175	0.349	0.705	1.395	3.057	101 to 104
Ethylbenzene	0.023	0.046	0.092	0.186	0.371	0.749	1.482	3.247	103 to 107
Propylbenzene	0.021	0.043	0.086	0.172	0.344	0.694	1.374	3.009	105 to 110
1,3,5-Trimethyl Benzene	0.011	0.021	0.042	0.085	0.169	0.342	0.676	1.481	105 to 113
Indene	0.010	0.021	0.042	0.084	0.168	0.340	0.672	1.471	107 to 110
1,3-Diethyl Benzene	0.010	0.021	0.042	0.084	0.168	0.340	0.672	1.471	105 to 108
Butylbenzene	0.021	0.042	0.084	0.169	0.337	0.681	1.348	2.952	106 to 112
Tetralin	0.011	0.022	0.044	0.089	0.177	0.357	0.706	1.547	106 to 111
Naphthalene	0.008	0.015	0.030	0.061	0.122	0.246	0.487	1.067	108 to 112
Acenaphthylene	0.006	0.013	0.025	0.051	0.101	0.204	0.404	0.884	109 to 114
Acenaphthene	0.001	0.002	0.005	0.009	0.019	0.038	0.075	0.164	109 to 114
C2-A	0.045	0.089	0.179	0.360	0.720	1.454	2.877	6.303	102 to 106
C3-A	0.032	0.064	0.128	0.257	0.513	1.036	2.050	4.490	105 to 111
C4-A	0.042	0.085	0.170	0.341	0.682	1.378	2.725	5.971	106 to 110
C2-N	0.007	0.015	0.030	0.060	0.120	0.242	0.479	1.048	109 to 114
1-Ring Aromatics	0.151	0.302	0.606	1.218	2.434	4.915	9.723	21.301	104 to 108
2-Ring Aromatics	0.015	0.030	0.060	0.121	0.242	0.488	0.965	2.115	110 to 113

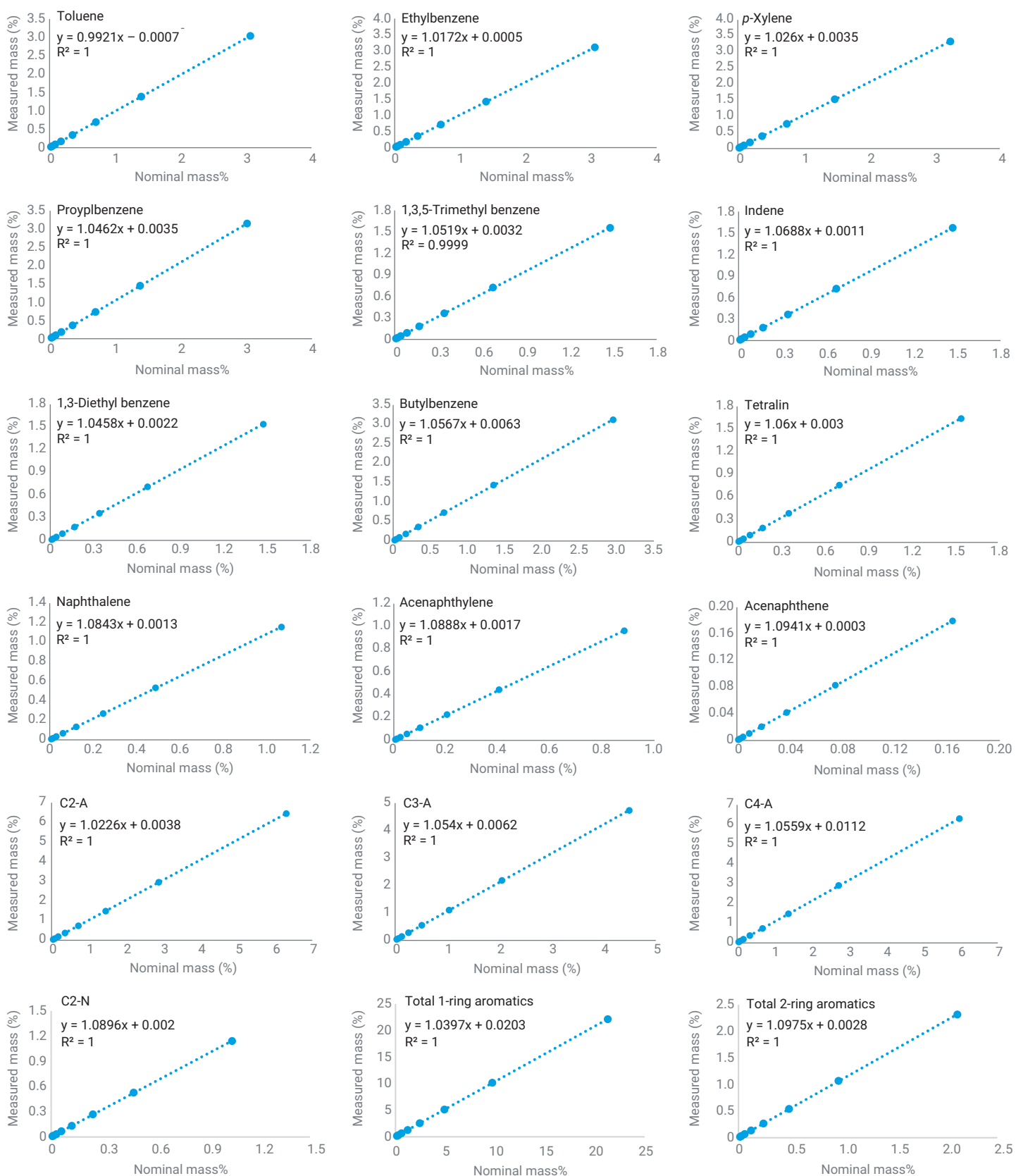


Figure 2. Linearity of individual aromatic compounds and groups.



## Group-Type Analysis

The group-type analysis determines the relative abundance of different chemical groups by normalizing the summed area within each group. Theoretical or experimentally derived relative response factors (RRFs) are typically used for normalization to achieve accurate quantification. A gravimetric blend was prepared to ascertain the RRFs of diverse components. A high level of consistency was found between the measured and theoretical values. This study conforms to the NB/SH/T 6078-2023 standard.<sup>1</sup> After verifying that the RRFs of 1,2,4-trimethylbenzene and naphthalene in relation to ethylbenzene fall within the range of 0.9 to 1.1, the area normalization method was applied, assuming each sample component had an equal detector response (RRF = 1). The quantification results of two jet fuel samples are presented in Table 4. Distinct differences in aromatic composition distribution were observed between the samples from the two sources. Excellent repeatability (n = 10) was demonstrated even at very low concentration levels, such as 0.001% mass content of benzene.

**Table 4.** Group quantification of two types of jet fuel.

Target	Jet Fuel 1		Jet Fuel 2	
	Group Content (w%)	%RSD (n = 10)	Group Content (w%)	%RSD (n = 10)
Benzene	0.001	4.00	0.003	2.33
Toluene	0.068	1.11	0.041	1.67
C2-Benzenes	0.768	0.54	0.272	0.90
C3-Benzenes	3.007	0.23	1.313	0.36
C4-Benzenes	4.377	0.10	1.565	0.09
Naphthalene	0.125	0.12	0.007	0.59
C1-Naphthalenes	0.330	0.15	0.033	1.40
C2-Naphthalenes	0.172	0.18	0.050	0.24
C3-Naphthalenes	0.032	0.65	0.054	0.93
1-Ring aromatics	16.214	0.11	10.22	0.06
2-Ring aromatics	0.661	0.15	0.152	0.49

## Conclusion

The Agilent RFM flow-modulated GC×GC-FID system has been successfully applied to the group-type analysis of jet fuel. This system has proven it can provide high repeatability (both retention time and response), sensitivity, robustness, and quantitative precision. The exceptional retention

time stability and precision in quantitation facilitate the ease of using the RFM for routine peak identification and quantitation. GC×GC-FID is a powerful tool that provides routine compositional analysis to further standardize jet fuel product quality.

## Acknowledgement

All the GC×GC data shown in this application note were generated or analyzed by GC×GC Edition software from GC Image, LLC (Lincoln, NE, USA).

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