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Full Length Article

How to obtain a detailed chemical composition for middle distillates via GC × GC-FID without the need of GC × GC-TOF/MS

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ABSTRACT

The method presented in this research allows the development of detailed chemical composition of hydrocarbon mixtures (petroleum and non-petroleum based) in the range of C_6 to C_{33} (69 to 475 °C) via comprehensive two-dimensional gas chromatography (GC × GC) with a flame ionization detector (FID). This method displays the protocol of obtaining a detailed chemical analysis via the classification using only 24 standard compounds without the need for a GC × GC with time-of-flight mass spectrometry (TOF/MS). The column configuration used was a reversed phase, composed of a series of a mid-polar or a polar as the primary column and a non-polar secondary column. Results were expressed as wt% for each main hydrocarbon class divided into each carbon number. Hydrocarbon classes of interest were *n*-paraffins, isoparaffins, mono-, di-, and tricycloparaffins, alkylbenzenes, cycloaromatics (naphthene-containing aromatic compounds), alkylnaphthalenes, biphenyls, three fused benzene rings aromatics (phenanthrenes and anthracenes), and pyrenes. This method was validated by the use of GC-FID, ASTM D1319, D6591, and standard compound mixture.

1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is receiving considerable attention in many research fields, including fuel analysis since it was first described in the literature [1]. GC × GC has two separate columns with two individual stationary phases. A modulator is utilized to inject the effluent from the primary (first dimension) column into the secondary (second dimension) column. In setups with the primary column containing a non-polar stationary phase and the secondary column, a polar stationary phase, the column configuration is called a normal phase. Alternatively, when the primary column contains a polar stationary phase and secondary column non-polar stationary phase, the column configuration is called reversed phase. All the compounds separated in the secondary column consecutively enter the detector. The output yields a retention plane of the 1st dimension separation by 2nd dimension separation [2].

Currently, GC × GC equipped with time-of-flight mass spectrometry (TOF/MS) and flame ionization detector (FID) are the state-of-the-art instruments for qualitative and quantitative analysis of complex fuel mixtures (e.g., aviation and diesel fuels), respectively. Multiple researchers studied the classification of peaks in petrochemical samples using GC × GC-TOF/MS [3–6]. As the TOF/MS provides merely qualitative data, obtaining quantitative data is a challenge. One attempt of developing a tool for obtaining quantitative data from GC × GC-TOF/MS goes through the utilization of Visual Basic Scripting [7]. The ideal option would be to have both detectors on the same instrument. However, TOF/MS is considerably more expensive (up to a 10 times fold) than FID. Therefore, most of the laboratories can afford only GC × GC-FID.

FID does not provide any identification to the peaks; therefore, a further classification in the GC software is necessary. Classification is referred to the process of grouping hydrocarbons into groups with the same carbon number from the same hydrocarbon class. This process has to be completed by the analyst. After the classification is completed, the quantification follows by summing the peak areas of the compounds in each group. Consecutively, the weight percent of each group is calculated by dividing the total peak area of the group by the total peak area of the sample. The procedure of how to create the classification for normal phase column configuration without the need of GC × GC-TOF/MS was described in UOP 990-11 method, Organic analysis of distillate by comprehensive two-dimensional gas chromatography with flame ionization detection [8]. However, normal phase column configuration does not allow as good separation among saturates acyclic paraffins, cycloparaffins, and aromatics as reversed phase column configuration [2,3]. Additionally, the reversed phase column configuration can improve the peak capacity due to the extended separation space [9,10].

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Therefore, reversed phase column configuration is preferred over normal phase for fuel analyses [2,3,11–15]. The primary locations of the main hydrocarbon classes on chromatograms with reversed phase were shown elsewhere [4–6,10]; however, there is a current lack of detailed descriptions on how to create these classes and subgroup them into individual carbon numbers.

This method describes the reversed phase classification development for hydrocarbon mixtures in the range of C_6 to C_{33} using a GC × GC-FID. The method displays the protocol of obtaining a detailed chemical analysis via the classification using only 24 standard compounds without the need for a costly GC × GC-TOF/MS.

2. Experimental

2.1. Materials

2.1.1. Classification

Two samples were used in the development of the classification. The first sample was a commercially available petroleum-based diesel fuel. However, any middle distillate reference material with a wide boiling range and a broad range of all hydrocarbon class constituents can also be utilized. The second sample was composed of the following 24 standard compounds: *n*-octane (1), CAS #: 111-65-9, *n*-dodecane (2), CAS #: 112-40-3, *n*-hexadecane (3), CAS #: 544-76-3, perhydrophenalene (4), CAS #: 2935-07-1, tetradecahydroanthracene (5), CAS #: 6596-35-6, toluene (6), CAS #: 108-88-3, ethylbenzene (7), CAS #: 100-41-4, *n*-propylbenzene (8), CAS #: 103-65-1, *n*-butylbenzene (9), CAS #: 104-51-8, *n*-hexylbenzene (10), CAS #: 1077-16-3, indan (11), CAS #: 496-11-7, 4,7-dimethylindan (12), CAS #: 6682-71-9, 1,1-dimethyltetralin (13), CAS #: 1985-59-7, 1,1,6-trimethyltetralin (14), CAS #: 475-03-6, naphthalene (15), CAS #: 91-20-3, 2-methylnaphthalene (16), CAS #: 91-57-6, 1,8-dimethylnaphthalene (17), CAS #: 569-41-5, biphenyl (18), CAS #: 92-52-4, 4-methylbiphenyl (19), CAS #: 644-08-6, 4,4-dimethylbiphenyl (20), CAS #: 613-33-2, phenanthrene (21), CAS #: 85-01-8, 1-methylanthracene (22), CAS #: 610-48-0, pyrene (23), CAS #: 129-00-0, and 1-methylpyrene (24), CAS #: 2381-21-7. The purity of all standards should be at least the HPLC grade purity. The numbers in parentheses refer to Fig. 1. *n*-Pentane and dichloromethane (DCM) were the solvents used. Acetone was used for syringe wash.

2.1.2. Validation

For validation purposes following samples were used: two commercially available Jet A samples, two commercially available Jet A-1 samples, three hydroprocessed esters and fatty acids (HEFA) samples, 20 different samples of military F-24 aviation fuel, and standard mixture composed of the following 19 standard compounds: *n*-decane (99% pure; Alfa Aesar), *n*-pentadecane (≥99% pure, Sigma-Aldrich), *n*-heptadecane (99% pure, Acros Organics), *n*-octadecane (99% pure, Alfa Aesar), 2,2,4,6,6-pentamethylheptane (> 99% pure, TCI America), 2,2,4,4,6,8,8-heptamethylnonane (98% pure, Acros Organics), 2-methylheptadecane (98% pure, Achemica), 2,6,10,14-tetramethylpentadecane (95% pure, Acros Organics), isopropylcyclohexane (99% pure, TCI America), *trans*-decahydronaphthalene (≥99% pure; Fluka), adamantane (99% pure, Alfa Aesar), *n*-butylcyclohexane (≥99% pure, Sigma-Aldrich), 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene (95% pure, Alfa Chemistry), undecylbenzene (> 99% pure, TCI America), 1,2,3,4-tetrahydronaphthalene (99% pure, Sigma-Aldrich), cyclohexylbenzene (99.5% pure, Acros Organics), 2-ethylnaphthalene (> 99% pure, Sigma-Aldrich), 2,6-dimethylnaphthalene (99% pure, Sigma-Aldrich), and 4-ethylbiphenyl (99% pure, TCI America).

2.2. Two-dimensional gas chromatography

Any gas chromatograph with a split injection system equipped with a capillary injection port with a deactivated glass liner, a flame ionization detector, two-stage thermal modulation system, and a cryo autofill unit can be utilized. In this study, an Agilent 7890B GC with an FID, a thermal modulator (LECO Corporation, Saint Joseph, MI), an Agilent 7683B series injector, and an HP 7683 series autosampler was used. ChromaTOF software optimized for GC × GC-FID (LECO Corporation, Saint Joseph, MI) was used for GC imaging, data processing, and classification development.

LECO Pegasus GC-HRT 4D (EI) High-Resolution TOF/MS (LECO Corporation, Saint Joseph, MI) with an Agilent 7890B gas chromatograph, a thermal modulator cooled with liquid nitrogen, and an Agilent G4513A auto-injector was used for qualitative analysis of the samples. ChromaTOF (Version 1.90.60.0.43266) was utilized for data collection (with an *m/z* of 45-550), processing, and analysis. Identification of the compounds was achieved by matching the measured mass spectra (similarity value of > 800) with Wiley (2011) and NIST (2011) mass spectral databases. GC × GC-TOF/MS was used for validation purposes.

2.3. Chromatographic columns

In the reversed phase column configuration, the polarity of the primary column can have different phases (polar or mid-polar) while the secondary column has always a non-polar phase. The method described in this work was developed and validated for both phases – polar (polyethylene glycol) and mid-polar ((50%-Phenyl)-methylpolysiloxane). The primary column length of 30 or 60 m, with a 0.25 mm ID,

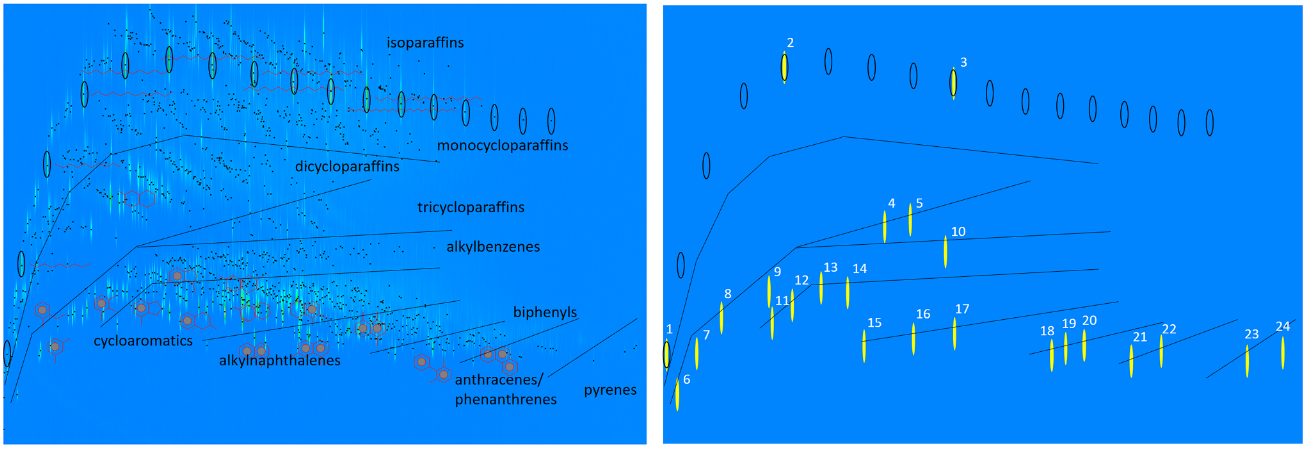


Fig. 1. GC × GC-TOF/MS chromatogram of diesel fuel sample (*m/z* range of 45–550) indicating the main hydrocarbon classes (left) and representative scheme of the standard mixture with the position of all eluted peaks (right).

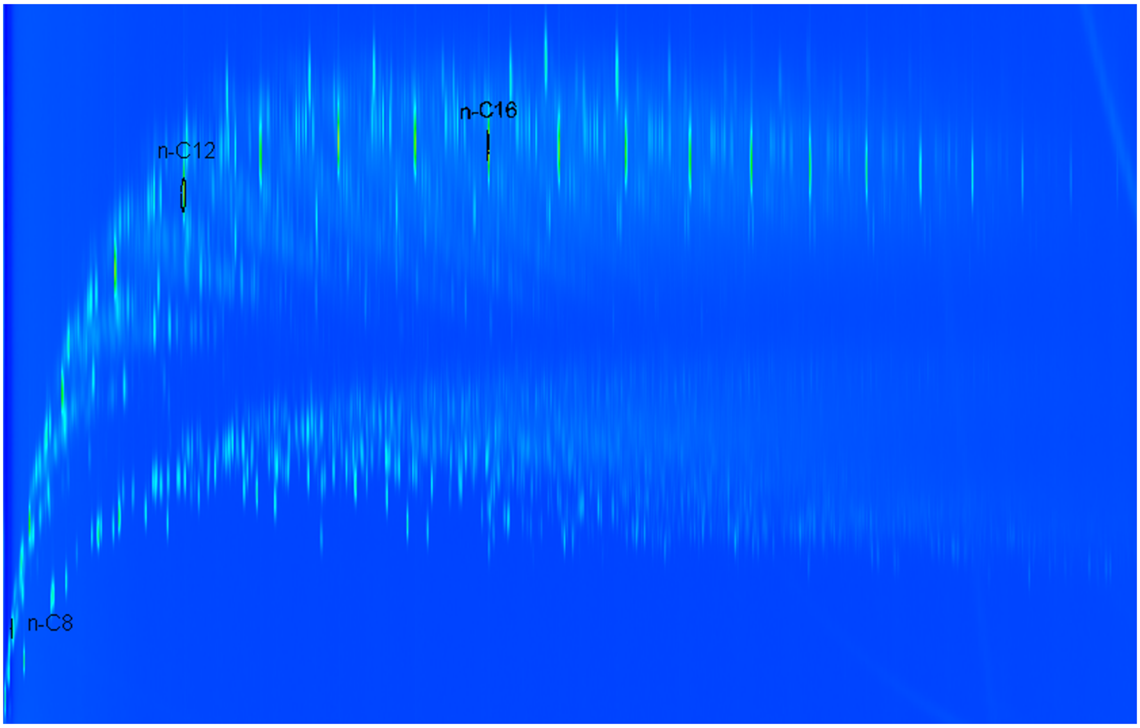


Fig. 2. GC × GC-FID chromatogram of diesel fuel sample with the locations of *n*-octane, *n*-dodecane, and *n*-hexadecane.

and internally coated to a film thickness of 0.25 µm was explored. The following are some examples of polar phase columns that can be used: VF-WAXms, Stabilwax, Rtx-WAX, or DB-WAX. It should be noted here that the temperature limitation of these polar columns is 250 °C. The following are some examples of mid-polar phase columns that can be used: DB-17 ms, VF-17 ms, Rxi-17Sil MS, Rtx-50, or BPX-50. The secondary non-polar column (dimethyl polysiloxane) can have a length of 0.8–1.2 m, with a 0.10 or 0.25 mm ID, and internally coated to a film thickness of 0.10 or 0.25 µm. It should be noted here that the secondary column length has to be adjusted in order to avoid wrap-around effect. The following are some examples of non-polar phase columns that can be used: Rxi-1 ms or DB-1.

2.4. Analysis

This paper does not discuss how to develop the best method for optimal separation in the selected GC × GC instrument. Operation conditions to achieve the best separation possible are left to the analyst. Some examples can be found in the literature [3,12,16]. All chromatograms displayed in this work were recorded using DB-17 ms as the primary and DB-1 as the secondary column. The detailed parameters of the method used, GC × GC linearity, and repeatability are listed in previous work [3]. S/N value of 50 was used for data processing in this study. Wrap-around effect is allowed unless it is not a total wrap-around, namely, peaks can elute in void volume region (Supporting Information, Fig. S1). If total wrap-around is present, one of the following remedies can be utilized: trimming the secondary column or increasing the secondary oven temperature offset. Once the instrument is tuned, the analyst can proceed with the following steps.

2.5. Samples preparation

Prepare the middle distillate reference sample by diluting 10 µl of diesel fuel sample in 1 ml of solvent in a 2 ml autosampler vial. Use DCM as a solvent for the mid-polar columns and *n*-pentane for the polar primary column. Prepare the standard mixture by following these steps: place the liquid scintillation vial on the analytical balance, add ∼5 mg (several crystals) of each solid standard compound, add ∼5 mg (about one drop) of each liquid standard compound, then fill the liquid scintillation vial with ∼15 ml of the solvent.

2.6. Sample analyses

The sample injection should follow these steps: rinse the syringe with the solvent, rinse the syringe with the sample, then inject the sample, again rinse the syringe with solvent and then rinse the syringe with acetone. Manual injection is allowed; however, autosampler is recommended. First, run the solvent so the delay can be set up. Then analyze the diesel fuel sample; the chromatogram will look like Fig. S1. Lastly, run the standard mixture; the chromatogram should look like Fig. 1.

3. Classification

Carbon number increases with the increasing primary retention time in every hydrocarbon class (i.e., from the left side of the chromatogram to the right side). The complete chromatogram of the diesel sample without the classification borders is shown in Fig. S1. The complete chromatogram of diesel sample with main hydrocarbon regions obtained from GC × GC-TOF/MS is displayed in Fig. 1.

3.1. n-Paraffins

Open the standard mixture as a background in the ChromaTOF software. The first compound (from the left) in the *n*-paraffin region is *n*-octane, the second one is *n*-dodecane, and the third one is *n*-hexadecane. Draw the borders for these three *n*-paraffins. Then open the diesel sample as the background. The image will be what is displayed in Fig. 2. Adjust the chromatogram colors so just the most abundant compounds are visible (these will be mostly *n*-paraffins) as shown in Fig. 3. Suggestion for such adjusting is to set the colors from 0% to 100% with the ratio of 0.6–0.8. Based on three *n*-paraffin standards, complete the classification for the rest of *n*-paraffins. *n*-Paraffins eluting in a very clear order with the increasing carbon number from the left of

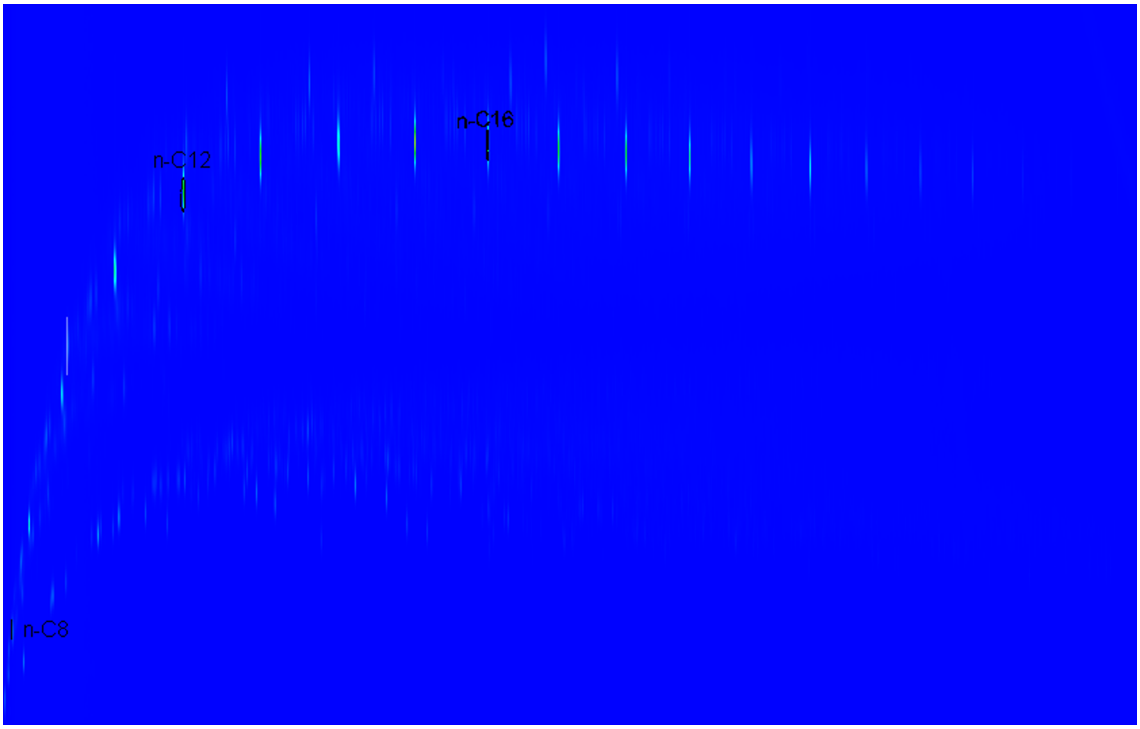


Fig. 3. GC × GC-FID chromatogram of diesel fuel sample with the locations of *n*-octane, *n*-dodecane, and *n*-hexadecane after adjusting the colors.

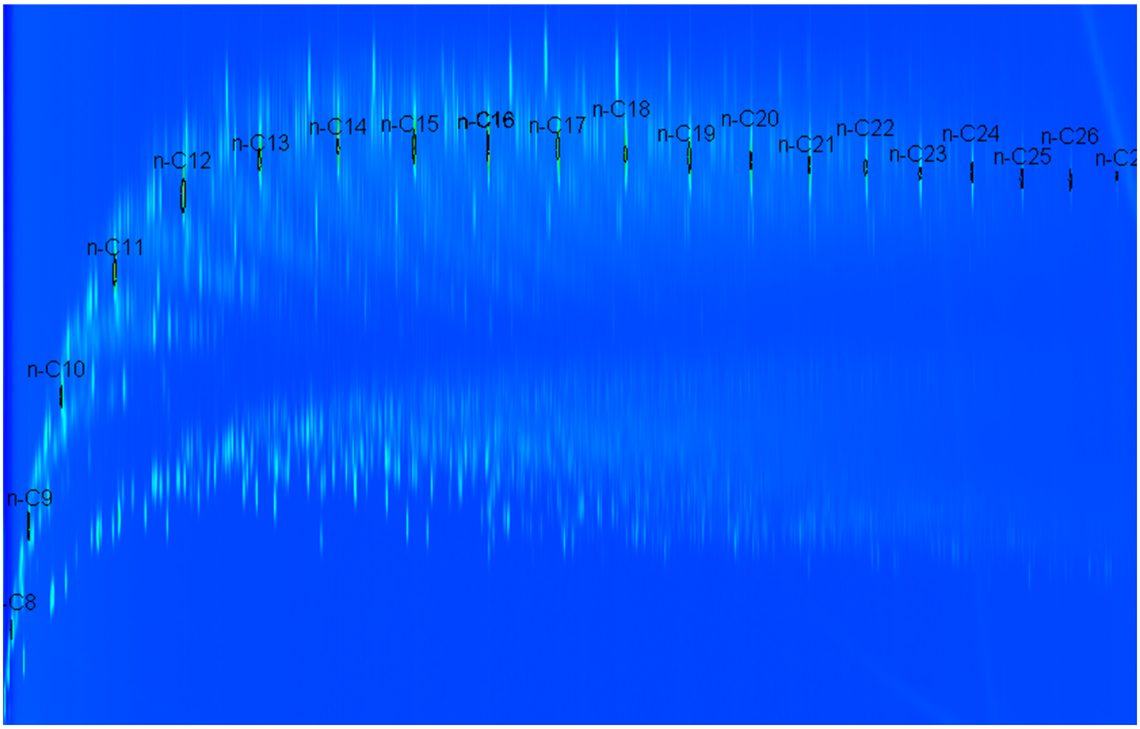
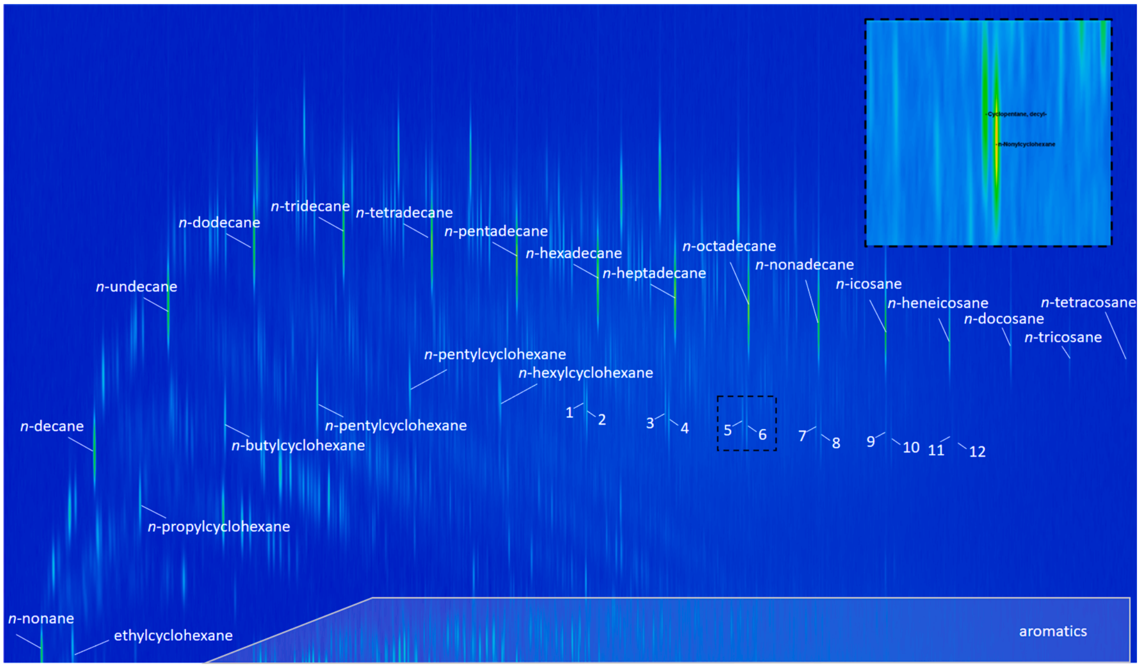


Fig. 4. GC × GC-FID chromatogram of diesel fuel sample with the locations of all *n*-paraffin regions (n-).

the chromatogram to the right, which is making very easy to find them all. If peak markers are turned on, it will help with drawing the borders. When all *n*-paraffins are identified and labeled, the classification will look as displayed in Fig. 4.

3.2. Isoparaffins

Open the diesel sample as a background in ChromaTOF software. The isoparaffins can be seen after adjusting the colors to the normal view (suggestion: from 0% to 100% with a ratio of 1.0–1.5). Draw the borders for isoparaffins. No standards are necessary for drawing the isoparaffin borders. Isoparaffins eluting between and above the *n*-paraffins. Isoparaffins with the same carbon number elute from the *n*-paraffin to the left. After all the borders are drawn, the classification will look as displayed in Fig. 10. Fig. S2 in Supporting Information displays the classification post the current step.



1	*n*-octylcyclopentane	4	*n*-octylcyclohexane	7	*n*-undecylcyclopentane	10	*n*-undecylcyclohexane
2	*n*-heptylcyclohexane	5	*n*-decylcyclopentane	8	*n*-decylcyclohexane	11	*n*-tridecylcyclopentane
3	*n*-nonylcyclopentane	6	*n*-nonylcyclohexane	9	*n*-dodecylcyclopentane	12	*n*-dodecylcyclohexane

Fig. 5. Magnified portion of a GC × GC-TOF/MS chromatogram (*m/z* range of 45–550) indicating the monocycloparaffin landmark peaks in the diesel fuel sample.

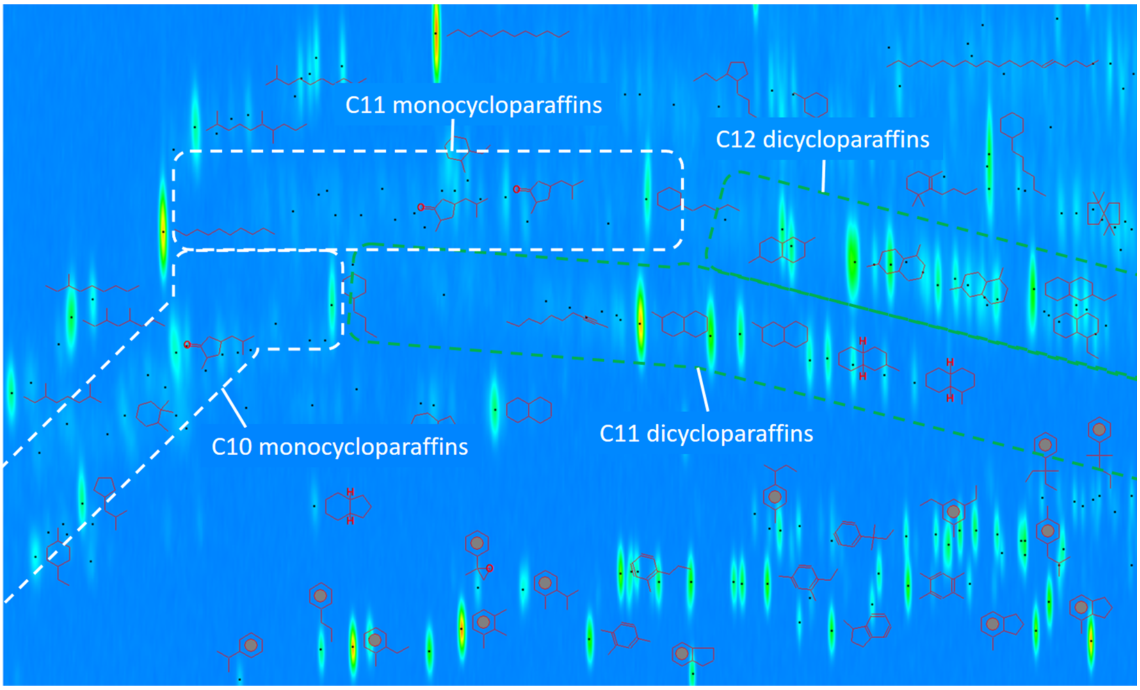


Fig. 6. Magnified portion of a GC × GC-TOF/MS chromatogram (*m/z* range of 45–550) indicating the elution order of mono- and dicycloparaffins in the diesel fuel sample.

3.3. Cycloparaffins

Cycloparaffins elute between *n*-paraffins and aromatic compounds. In the middle distillates, mono-, di-, and tricycloparaffins can be found.

3.3.1. Monocycloparaffins

Open the diesel sample as a background in ChromaTOF software. Adjust the chromatogram colors from 0% to 100% with a ratio of 0.6–0.8. Draw the borders for monocycloparaffins. Monocycloparaffins elute between *n*-paraffins and dicycloparaffins. The borders between mono- and dicycloparaffins are well defined by *n*-alkyl cyclohexanes, which are very well seen on chromatogram following the path of *n*-paraffins. These are displayed on GC × GC-TOF/MS chromatogram in Fig. 5. With increasing carbon number, two peaks close to each other can be observed – the left peak is alkyl-cyclopentane, the right peak is alkyl-cyclohexane. All the peaks between *n*-paraffin and alkyl-cyclopentane are alkyl-methylcyclohexanes. This observation is in a good agreement with the literature [6]. At lower carbon numbers these two peaks might be very close to each other or might even coelute. However, all these peaks belong to monocycloparaffins group. The borders of the *n*-paraffins and the monocycloparaffins of the same carbon number should intercept. After all the borders are drawn, the classification will look as displayed in Fig. 10. Fig. S3 in Supporting Information displays the classification post the current step.

3.3.2. Dicycloparaffins

Open the diesel sample as a background in ChromaTOF software. Adjust the colors to the normal view (suggestion: from 0% to 100% with a ratio of 1.0–1.5). Find the borders between dicycloparaffins and tricycloparaffins as outlined in the next chapter. The beginning of tricycloparaffins is the end of dicycloparaffins. Draw the borders for dicycloparaffins. Dicycloparaffins elute between monocycloparaffins and tricycloparaffins. Dicycloparaffin borders are directly connected to monocycloparaffins; however, the carbon number of dicycloparaffins is one carbon number higher than that of monocycloparaffins. Dicloparaffins start with carbon number 8. GC × GC-TOF/MS chromatogram (Fig. 6) validates this statement. After all the borders are drawn, the classification will look as displayed in Fig. 10. Fig. S4 in Supporting Information displays the classification post the current step.

3.3.3. Tricycloparaffins

Open the standard mixture as a background in ChromaTOF software. The first compound from the left in tricycloparaffins region is perhydrophenalene and the second one is tetradecahydroanthracene. These tricycloparaffin peaks elute at the border between di- and tricycloparaffins. Therefore, these peaks can serve as the visual landmarks for drawing the border between di- and tricycloparaffins. GC × GC-TOF/MS chromatogram with a designated tricycloparaffin region can be seen in Fig. 7. Open the diesel sample as a background in ChromaTOF software with the normal view. Draw the borders for tricycloparaffins. Tricycloparaffins elute between dicycloparaffins and aromatics. Tricycloparaffin borders are directly connected to dicycloparaffins; however, the carbon number of tricycloparaffins is one carbon number higher than that of dicycloparaffins. Tricloparaffins start with carbon number 10. After all the borders are drawn, the classification will look as displayed in Fig. 10. Fig. S5 in Supporting Information displays the classification post the current step.

3.4. Aromatics

In reversed phase column configuration, the primary column can have either a polar or midpolarity phase. Columns with polar phase allow better separation between aromatic compound classes; however, the operating temperature range is very limited. Here, the classifications using both phases are discussed. For jet fuel, aromatics are basically divided into four hydrocarbon classes – alkylbenzenes, cycloaromatics (i.e., naphthene-containing aromatic compounds such as indans, tetralins, and their alkyl-isomers), naphthalenes, and biphenyls. For diesel fuels, aromatics can contain additional classes with three fused benzene rings (anthracenes and phenanthrenes) and four fused benzene rings (pyrenes). The procedure described here was developed and validated for both types of primary columns (polar and midpolar). However, if the polar primary column (VF-WAXms) was used, the borders between aromatic classes were easier to distinguish than the case where the midpolar column was used.

3.4.1. Alkylbenzenes

Open the standard mixture as a background in ChromaTOF software. The compounds in alkylbenzene region from the left elute in the following order: toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, and *n*-hexylbenzene. Mark these peaks. Open the diesel sample as the background. Use the above-mentioned standards and Fig. 8 to draw the borders for alkylbenzenes. First four alkylbenzene compounds will help to orient better at the beginning of the alkylbenzene group. *n*-Hexylbenzene will serve as a landmark for higher carbon numbers. Alkylbenzenes elute between saturates and cycloaromatics. The first compound in this group is benzene (serves as a landmark, shown in Fig. 8). After all the borders are drawn, the classification will look as displayed in Fig. 10. Fig. S6 in Supporting Information displays the classification post the current step.

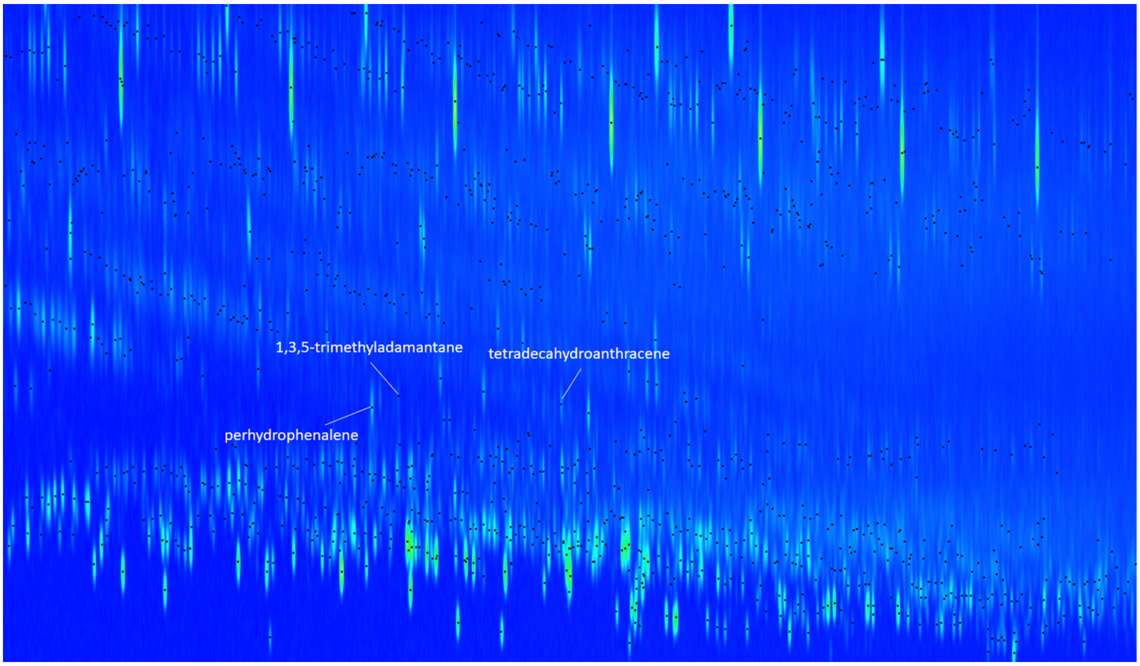


Fig. 7. GC × GC-TOF/MS chromatogram of diesel fuel sample (*m/z* range of 45–550) with the location of tricycloparaffin region.

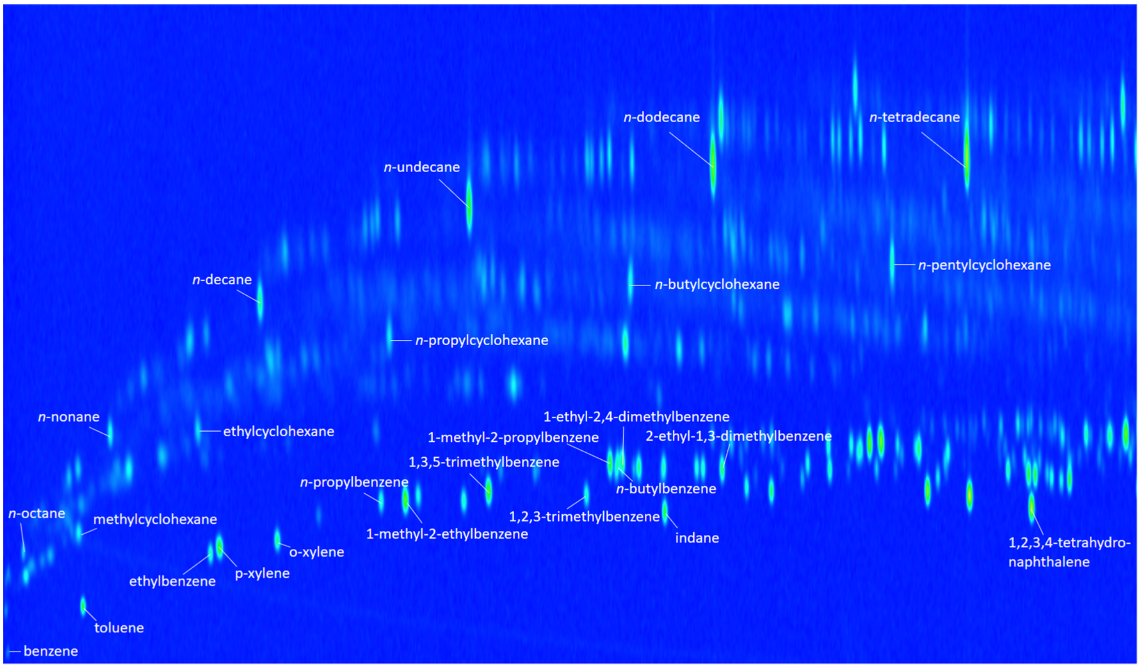


Fig. 8. Magnified portion of a GC × GC-TOF/MS chromatogram (*m/z* range of 45–550) indicating the aromatic landmark peaks in the diesel fuel sample.

3.4.2. Cycloaromatics

Open the standard mixture as a background in ChromaTOF software. The compounds in cycloaromatics region from the left eluting in the following order: indan, 4,7-dimethylindan, 1,1-dimethyltetralin, and 1,1,6-trimethyltetralin. Mark these peaks. These peaks will serve as landmarks for the beginning of cycloaromatic regions. Open the diesel sample as the background. Use the above-mentioned standards to draw borders for cycloaromatics. Cycloaromatics elute between alkylbenzenes and alkylnaphthalenes. The first cycloaromatic compound is indan (serves as a landmark, shown in Fig. 8). Cycloaromatics and alkylbenzenes borders of the same carbon number are directly connected to each other. After all the borders are drawn, the classification will look as displayed in Fig. 10. Fig. S7 in Supporting Information displays the classification post the current step.

3.4.3. Alkynaphthalenes

Open the standard mixture as a background in ChromaTOF software. The compounds in alkylnaphthalene region from the left elute in the following order: naphthalene, 2-methylnaphthalene, and 1,8-dimethylnaphthalene. Mark these peaks. These peaks will serve as landmarks for the beginning of alkylnaphthalene regions. Open the diesel sample as the background. Use the above-mentioned standards and Fig. 9 to draw borders for alkylnaphthalenes. Alkylnaphthalenes elute between cycloaromatics and biphenyls. The first compound in this group is naphthalene (serves as a landmark, shown in Fig. 9). The end of alkylnaphthalene region is defined by the beginning of the biphenyl region, which is discussed in the next chapter. Alkylnaphthalenes and cycloaromatics borders of the same carbon number are directly connected to each other. After all the borders are drawn, the classification will look as displayed in Fig. 10. Fig. S8 in Supporting Information displays the classification post the current step.

3.4.4. Biphenyls

Open the standard mixture as a background in ChromaTOF software. The compounds in biphenyl region from the left elute in the following order: biphenyl, 4-methylbiphenyl, and 4,4-dimethylbiphenyl. Mark these peaks. These peaks will serve as landmarks for the beginning of biphenyl regions. Open the diesel sample as the background. Use the above-mentioned standards and Fig. 9 to draw borders for biphenyls. Biphenyls elute between alkylbenzenes and anthracenes and phenanthrenes. The first compound in this group is biphenyl (serves as a landmark, shown in Fig. 9). The end of biphenyl region is defined by the beginning of the anthracenes and phenanthrenes region, which is discussed in the next chapter. Biphenyl borders are directly connected to alkylnaphthalenes; however, the carbon number of biphenyls is one carbon number higher than that of alkylnaphthalenes. After all the borders are drawn, the classification will look as displayed in Fig. 10. Fig. S9 in Supporting Information displays the classification post the current step.

3.4.5. Anthracenes and phenanthrenes

Open the standard mixture as a background in ChromaTOF software. The compounds in anthracene and phenanthrene region from the left elute in the following order: phenanthrene and 1-methylanthracene. Mark these peaks. These peaks will serve as landmarks for the beginning of anthracene and phenanthrene regions. Open the diesel sample as the background. Use the above-mentioned standards and Fig. 9 to draw borders for anthracenes and phenanthrenes. Anthracenes and phenanthrenes elute between biphenyls and pyrenes. The first compound in this group is phenanthrene (serves as a landmark, shown in Fig. 9). The end of anthracene and phenanthrene region is defined by the beginning of the pyrene region discussed in the next chapter. Anthracene and phenanthrene borders are directly connected to biphenyls; however, the carbon number of anthracenes and phenanthrenes is one carbon number higher than that of biphenyls. After all the borders are drawn, the classification will look as displayed in Fig. 10. Fig. S10 in Supporting Information displays the classification post the current step.

3.4.6. Pyrenes

Open the standard mixture as a background in ChromaTOF software. The compounds in pyrene region from the left elute in the following order: pyrene and 1-methylpyrene. Mark these peaks. These peaks will serve as landmarks for the beginning of pyrene regions. Open the diesel sample as the background. Use the above-mentioned standards and Fig. 9 to draw borders for pyrenes. Pyrenes elute under anthracenes and phenanthrenes. The first compound in this group is pyrene (serves as a landmark, shown in Fig. 9). Pyrenes borders and anthracene and phenanthrene borders of the same carbon number are

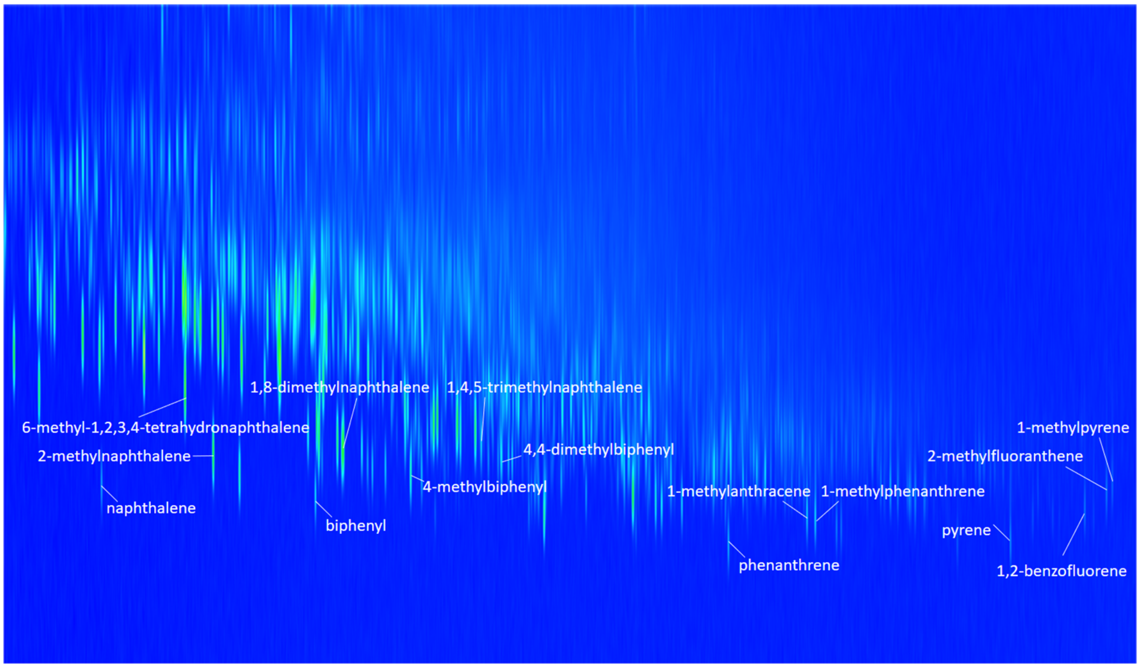


Fig. 9. Magnified portion of a GC × GC-TOF/MS chromatogram (*m/z* range of 45–550) indicating the aromatic landmark peaks in the diesel fuel sample.

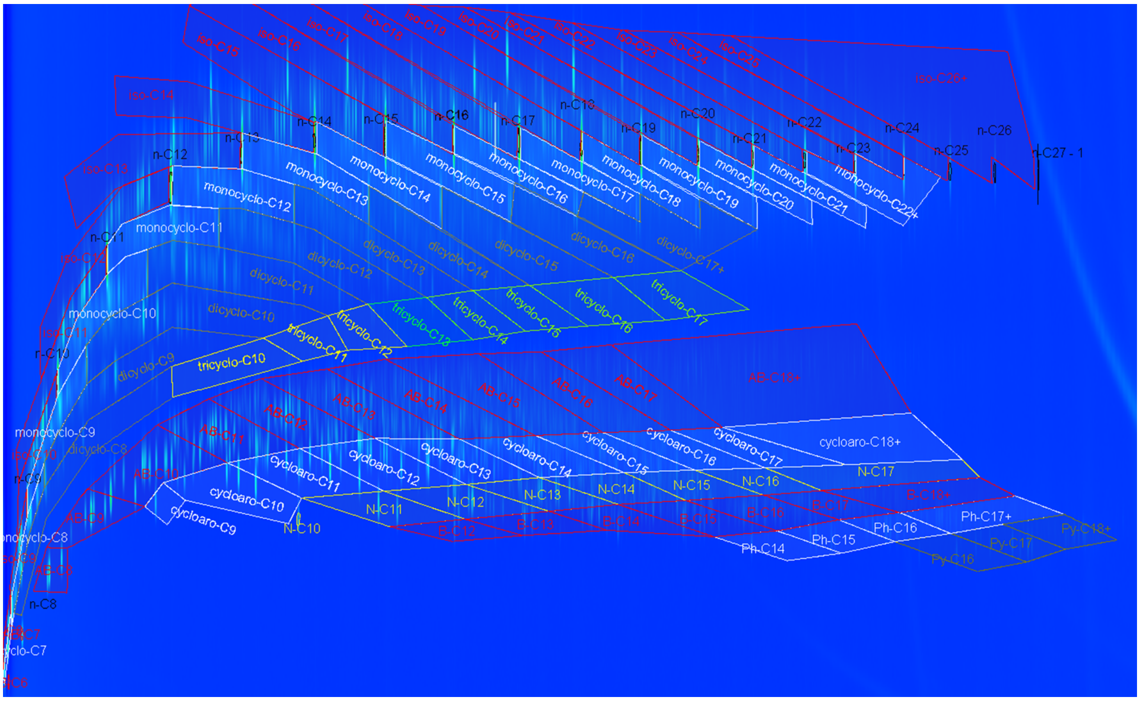


Fig. 10. GC × GC-FID chromatogram of diesel fuel sample with the locations of all pyrene regions (Py-).

directly connected to each other. After all the borders are drawn, the classification will look as displayed in Fig. 10.

4. Results and discussion

4.1. Quantification

Once the classification is completed in ChromaTOF software (or any other software such as GC Image), include the classification into the Data Processing Method. Process the sample of interest. Export the ChromaTOF Peak Table into Excel. Sum all peak areas belonging to the same group and all peak areas belonging to the sample. This summation can be done manually or using Excel macros or functions. The response factors of all hydrocarbon compounds are equal to 1 [17]. Therefore, in order to obtain wt% for each group, divide the total peak area of the group by the total peak area of the sample. Olefins are lumped with cycloparaffins and compounds containing heteroatoms are lumped with aromatics.

4.2. Method validation

One challenge in finding a suitable method of validating the

Table 1

Comparison between *n*-paraffin content obtained from GC-FID (A) following D5442 method and GC × GC-FID (B) using the classification described here.

n-	Jet A #1		Jet A #2		Jet A-1 #1		Jet A-1 #2		HEFA #1		HEFA #2		HEFA #3	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
C7	0.12	0.12	0.07	0.08	0.03	0.02	0.16	0.11	0.01	0.00	0.00	0.00	0.30	0.00
C8	0.49	0.54	0.52	0.64	0.58	0.61	0.65	0.76	1.44	1.56	0.12	0.12	0.60	0.73
C9	1.64	1.84	3.94	4.05	1.30	1.42	2.81	2.75	2.09	2.15	1.91	1.98	0.94	1.13
C10	3.48	3.72	4.24	4.46	4.54	4.68	6.12	6.13	1.55	1.38	1.79	1.73	1.36	1.50
C11	4.71	4.70	2.95	3.06	6.84	6.82	6.17	6.44	0.96	0.96	1.47	1.56	1.37	1.55
C12	3.28	3.91	2.31	2.37	4.77	4.70	2.50	2.60	0.80	0.83	1.26	1.42	1.32	1.46
C13	2.48	3.60	2.00	1.90	2.97	3.05	1.14	1.38	0.57	0.65	1.03	1.04	1.12	1.14
C14	1.69	1.95	1.16	1.27	0.51	0.58	0.52	0.57	0.33	0.25	0.69	0.69	1.68	1.75
C15	0.79	0.81	0.64	0.76	0.03	0.04	0.11	0.12	0.43	0.51	0.34	0.32	0.15	0.14
C16	0.28	0.38	0.30	0.36	0.00	0.00	0.01	0.01	0.15	0.13	0.00	0.00	0.67	0.71
C17	0.10	0.11	0.10	0.10	0.00	0.00	0.01	0.00	0.11	0.10	0.00	0.00	0.03	0.02
C18	0.04	0.03	0.02	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00

proposed classification process is the novelty of comprehensive two-dimensional gas chromatography. Hence efforts were focused on utilizing an array of widely utilized techniques such as GC-FID, fluorescent indicator adsorption (ASTM D1319), high-performance liquid chromatography (HPLC) with refractive index detector (RID), GC × GC-FID, and GC × GC-TOF/MS (discussed previously).

4.2.1. GC-FID

Quantitative analysis of *n*-paraffins via GC-FID is a commonly trusted method in the literature. Therefore, this method was chosen to be reliable for validation. HP 5890 GC equipped with FID was used for the qualitative and quantitative *n*-paraffin analysis. The method followed the ASTM standard D5442. First, the standard mixture of C_7–C_{30} *n*-paraffins was used for calibration and then the *n*-paraffins were identified based on their individual retention times. The wt% was calculated as a relative ratio of the peak area of each *n*-paraffin to the total peak area integrated on the chromatogram. Detailed GC-FID parameters can be found in a previous paper [18]. Table 1 below displays the results obtained from both GC-FID (A) and GC × GC-FID (B). *n*-Paraffin peaks are easy to observe on the chromatogram; however, their area (Gaussian and/or Lorentzian shape that overextends to infinite horizontal asymptotes parallel to the positive and negative x-axes) is very dependent on the separation efficiency of the column and the GC method. GC × GC-FID can achieve better separation when compared to GC-FID, thus the integration of *n*-paraffins may be more precise. Therefore, the reason why GC-FID yielded slightly lower values can be the systematic under-reporting of the GC output due to the column efficiency.

4.2.2. ASTM D1319

ASTM D 1319 is the method that uses a glass adsorption column packed with activated silica gel to measure the total aromatics content. This method enables the determination of aromatics from 5 to 99 vol%. Reproducibility of this method is 2.5 vol% [19]. For validation purposes, aromatic contents of 20 samples of F-24 aviation fuels were measured via D1319 as well as via GC × GC-FID. To compare the two techniques, wt% reported by GC × GC-FID was converted to vol% utilizing the densities of each group. Density values were taken from the literature [8]. Fig. 11 shows good agreement between the two techniques for total aromatics content. All samples fell within the reproducibility of D1319 method.

4.2.3. HPLC-RID

The ASTM method for calculating the aromatics (mono-, di-, and poly-) content for middle distillates via HPLC is D6591. This method was used in this work to compare aromatic contents obtained from HPLC (Shimadzu LC-10 CE) and GC × GC-FID. The results are displayed in Table 2.

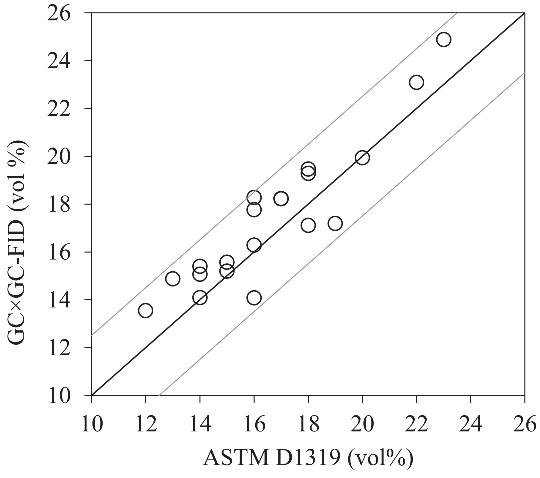


Fig. 11. Comparison between ASTM D1319 and GC × GC-FID total aromatic content (vol%).

Table 2

Comparison between hydrocarbon group content obtained from HPLC (A) following D6591 method and GC × GC-FID (B) using the classification described here.

Hydrocarbon group	Jet A #1		Jet A #2		Jet A-1 #1		Jet A-1 #2	
	A	B	A	B	A	B	A	B
Saturated hydrocarbons	82.2	82.3	75.6	76.0	78.7	79.3	82.0	82.4
Monoaromatics	15.6	15.5	22.6	22.4	20.1	19.6	17.3	16.9
Diaromatics	2.2	2.2	1.7	1.7	1.2	1.1	0.7	0.7
Polyaromatics	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

4.2.4. GC × GC-FID

Due to the fact, there are no other methods, which can be used for the validation, an additional pathway to further validate the quantitative results between different carbon numbers for the same hydrocarbon class was used. For this purpose, a mixture of 19 compounds (different than those used for classification) with known wt% composition was prepared. This mixture was measured via GC × GC-FID with the classification described. The results (Table 3) obtained via GC × GC-FID were compared to known concentrations.

5. Conclusion

The flame ionization detector (FID) does not provide any identification to the peaks; therefore, further classification is necessary. Classification refers to the process of grouping hydrocarbons into

Table 3
Comparison of known and measured concentrations (wt%) via GC × GC-FID.

Name	Concentration	GC × GC-FID
n-decane	5.98	5.97
n-pentadecane	5.63	5.60
n-heptadecane	2.46	2.44
n-octadecane	5.36	5.32
2,2,4,6,6-pentamethylheptane	5.19	5.23
2,2,4,4,6,8,8-heptamethylnonane	6.09	6.06
2-methylheptadecane	5.83	5.81
2,6,10,14-tetramethylpentadecane	5.23	5.19
isopropylcyclohexane	5.45	5.41
trans-decahydronaphthalene	6.77	6.77
adamantane	2.46	2.48
n-butylcyclohexane	5.98	6.00
1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene	5.57	5.59
undecylbenzene	8.61	8.63
1,2,3,4-tetrahydronaphthalene	9.05	9.08
cyclohexylbenzene	5.39	5.41
2-ethylnaphthalene	5.71	5.74
2,6-dimethylnaphthalene	1.41	1.40
4-ethylbiphenyl	1.85	1.86

groups with the same carbon number from the same hydrocarbon class. This process has to be completed by the analyst in GC × GC software. After the classification is completed, the quantification follows by summing the peak areas of the compounds in each group. Consecutively, the weight percent of each group is calculated by dividing the total peak area of the group by the total peak area of the sample. In this work, a method for obtaining a detailed classification of middle distillates using two-dimensional gas chromatograph (GC × GC) with FID without the need of GC × GC with mass spectrometry (MS) was presented. A reversed phase column configuration with a primary mid-polar or polar column and a secondary non-polar column was explored. This method was validated by comparing the chromatogram outputs to those obtained from the GC × GC-TOF/MS. Additional methods utilized for further validation were: GC-FID, ASTM D1319 and D6591, and a standard mixture of 19 compounds.

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Appendix A. Supplementary data

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