Evaluation of reversed phase versus normal phase column combination for the quantitative analysis of common commercial available middle distillates using GC×GC–TOFMS and Visual Basic Script

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Abstract

Normal and reversed phase column combinations for comprehensive two-dimensional gas chromatography time-of -flight mass spectrometry were evaluated concerning their suitability for the analysis of common commercial available middle distillates. Compound classes were identified and quantified by applying a previously developed data evaluation method [1] for middle distillates based on GC×GC-TOFMS using "normal phase" column combination and Visual Basic Scripting (VBS). The GC×GC-TOFMS methodology was transferred to a "reversed phase" column combination and it could be found that this kind of column combination provides advantages for the quantification of petrochemical samples in terms of precision of the results. Special improvements were observed for the quantification for aromatics and paraffin.

1. Introduction

Since the introduction of comprehensive two-dimensional gas chromatography in analytical chemistry a rapid development of the underlying hardware and software took place. An often mentioned fundamental principle of comprehensive separation techniques is the orthogonality of the separation. Early publication postulated an orthogonal separation could only be achieved using a non-polar column in the first dimension [2]. Later publications come to the conclusion, that a maximum in orthogonality is not an mandatory requirement, but the most efficient utilization of the separation space and non-orthogonal solutions can be more adequate for certain cases [3,4,5]. The application of reversed phase column combination has recently been evaluated for the analysis of petrochemical samples regarding the utilization of the two-dimensional separation space and the formation of compound groups [6,7,8] and especially Adam et al. performed an extensive study on different column combinations focused on the analysis of FAME [9]. Two aspects of the inverse elution order can be mentioned. The first one is the more dispersed distribution of saturated compounds especially in the case of cycloalkanes, also including adamantanes, sesqui-, tri- and teraterpanes [6,8]. The second is the reduced separation of aromatic compounds, which are “compressed” to a smaller region of the total separation space [6]. The late one could be a disadvantage when FID is used for detection and quantification. Nevertheless, the separation of these classes is still sufficient in case of mass spectrometry detection, which provides enough selectivity for a clear classification, especially when classification tools based on spectrum information are applied [1, 10 – 14].

In a previous work a comprehensive quantification method for commercial available middle distillates using GC×GC-TOFMS was presented for jet A1 fuel, light heating oil and diesel fuel. [1] The application of a normal-phase column combination allowed a full absolute quantification and classification of the compounds in the matrix according compound class and carbon number. The presented study focuses on a modification of this normal-phase approach, which was already applied by the author in an earlier study for the analysis of the aromatic fraction within middle distillates [14]. The reversed-phase approach was now extended for a full and absolute quantification of common commercial available middle distillates and the effects and benefits of the phase selection for the separation and quantification are discussed.

2. Experimental

The quantification method, presented in a previous work [1] was implemented on a reversed phase column combination with inverted polarities. For the first dimension a medium-polar 50% Phenyl Polysilphenylene-siloxane column (BPX50, SGE) was applied since it represents the best compromise between polarity and temperature stability. The classification method were adjusted, to account for the new elution order of the compound groups and carbon number distribution. A scheme is shown in Figure 1. The GC×GC-TOFMS analysis for both approaches were performed on a LECO Pegasus 4D equipped with a four jet dual stage modulator amd Data acquisition anddata processing including the application of Visual Basic Scripting is described in a previous work [1]. The parameters of the applied column combinations and further instrumental parameters are listed in Table 1. The fuel samples and blends were diluted 1:1 with dichloromethane and spiked with internal standard solution [1]. 1µl of each sample was injected with a split ratio of 1:300 and 1:400, respectively.

	Normal-Phase Column Combination		Reversed-Phase Column Combination	
	1st dimension	2nd dimension	1st dimension	2nd dimension
Phase	BPX1	BPX50	BPX50	BPX1
Length	60m	3m	60m	2.8m
Inner Diameter	0.25mm	0.1mm	0.25mm	0.1mm
Film thickness	0.25µm	0.1µm	0.25µm	0.1µm
Temperature Program	70 – 300°C; 2°C/min	+10°C Offset; 2.2°C/min*	60 – 300°C; 2°C/min	+20°C Offset 2°C/min
Injection temperature	300°C			
Carrier Gas	He			
Flow	1 ml/min			
Modulation	6s		8s	
Mass range	30 – 500 m/z			
Frequency	200 Spectra/s			

Table 1: GCxGC Parameters for normal and reversed phase.

3. Results and Discussion:

Diesel fuel on normal phase column combination:

The principle of a complete quantitative group-type analysis of middle distillates using GC×GC-TOFMS and Visual Basic Scripting has been published in detail recently [1]. In this previous study, a non-polar×medium polar column combination was used. To prevent very high retention times and/or wrap around for aromatic compounds like PAHs an advanced temperature program had to be applied. Nevertheless, peak broadening for late eluting polar compounds (e.g. tri+aromatics) were observed and wrap around becomes more likely with increasing size of the conjugated π system. This is a known issue since the second dimension is operating quasi-isothermal. As a consequence the S/N of these compounds will decrease compared to early eluting non-polar compounds with equal abundance. Regarding the much smaller concentrations compared to e.g. n-alkanes, it cannot be ruled out that significant amounts will be discriminated during data processing caused by this effect. Especially aromatics are effected since it’s amount in fuel have been continuously decreased due to legal regulations.

Furthermore, the most abundant compounds, especially n-paraffins, show strong tailing in the 2nd dimension into the elution regions of lower abundant other compound classes. This effect impeded the data processing and thus the qualitative and quantitative analysis. An example for an NP separation of Diesel fuel is shown in Figure 1a.

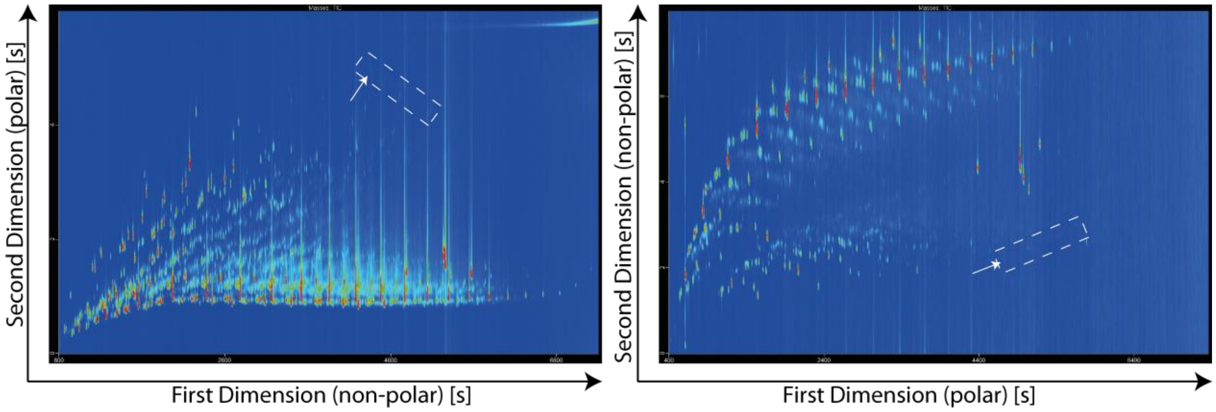

Figure 1: Exemplary chromatograms of a common diesel fuel (B7), blended with 7% biodiesel (FAME) using normal-phase (left) and reversed-phase (right) column combination. For the given examples, the elution order of the groups for the second dimension will invert. The position of tri+aromatics are indicated. The arrow indicated the position of phenathrene/anthracene. The separation parameters are given in Table 1.

3.2. Diesel Fuel on reserved phase column combination:

The presented reverse phase combination mitigates most of these effects and will also enhance the separation of the n- and iso-paraffin isomers due to a longer retention on the second dimension [6,8].

For the shown middle distillates, the limits of the separation space in the second dimension will be clearly defined by the row of alkanes. Saturated compounds now remain longer on the non-polar second dimension with slight differences regarding carbon number, alkyl-chain length and branching. Applying a reversed-phase column combination, supplementary heating or shortening of the second dimension was not necessary. These effects could be explained due to a higher retention of aromatic compound on the first dimension resulting in a higher elution temperature of these compounds. Non-polar compounds are almost not effected by the additional interaction. Consequently, sharp peaks for aromatic compounds can be achieved even for minor components like phenanthrenes or pyrenes. and the median peak width for e.g. phenanthrene (widths at half high of the peak) will degrease of about 18% form 0,14 sec to a median of 0,11 sec for the given column sets. Although the separation of aromatic compounds worsens with increasing carbon number especially in the case of di-aromatic compounds, an outstanding separation of all aromatics is not necessary as long as mass spectrometry and scripting tools based on mass spectra are applied for classification. Consequently, the choice of a reversed-phase column combination is recommendable when it comes to comprehensive analysis and full quantification of middle distillates.

The situation is different for n- and iso-paraffins where mass spectra are similar, resulting in a misclassification even if very sophisticated data processing is applied. Using a normal phase column combination, this misclassification manifests when insufficient separation concerning the first or second dimension separation occurs and the processing algorithms fail in distinguishing the different peaks. This deficiency could also be overcome using a reversed phase column combination. As mentioned before, saturated compounds elute from the middle polar second dimension with slight differences leading to well-defined elution profiles. Furthermore, the tailing of highly abundant compounds like n-paraffins does not longer affect the qualitative or quantitative analysis of other compounds. Regarding the increasing use of hydrogenated vegetable oils (HVO) as share of biogenic origin and thus a higher amount of n- and iso-paraffins, the application of reversed column combinations are further gaining in importance.

This improvement of data analysis is reflected when the quantification results of the same samples, measured with both GC×GC setups, are compared directly concerning the standard deviation of the single measurements. After the developed quantification method was adapted completely to the reversed-phase setup, the overall quantification showed similar results as the GC×GC system equipped with the normal phase column combination. Moreover, the single measurements showed less deviation among each other and regarding the separation of n- and iso-paraffins and naphthenes a higher accuracy could be achieved. . The comparisons of the quantitative results using both GC×GC systems are given in table 2 exemplary for diesel fuel B7 as summarized values of the superordinate compound groups. Data for light heating oil and jet fuel could be found in [15] suppl. information.

	Normal Phase System		Reversed Phase System	
	Amount	Std dev	Amount	Std dev
Paraffins	34,72%	0,80%	34,87%	0,18%
Naphthenes	36,10%	0,66%	36,25%	0,10%
Monoaromatics	18,90%	0,46%	18,36%	0,11%
Diaromatics	2,88%	0,07%	2,70%	0,03%
Polyaromatics	0,41%	0,02%	0,49%	0,03%
FAME	6,83%	0,06%	6,84%	0,06%

Table 2: Comparison of the quantitative results of diesel fuel B7 using GC×GC-TOFMS equipped with a reversed phase and a normal phase column combination .

4.Conclusion

In this work, a reversed-phase column combination for comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS) was applied for the quantitative analysis of middle distillates showing significant advantages compared to the utilization of a normal-phase approach. The results were compared to previously published data using a normal-phase approach and evaluated regarding the efficiency of the group-type separation and the accuracy of the quantification. Quantification will become more precise by a reversed-phase column combination in combination with Visual Basic Scripting for an automated identification of different mass spectra. In addition, also a better separation of n- and iso-paraffins and different kinds of naphthenes can be achieved. The sensitivity for the quantification of aromatic compounds will also improve due to smaller peak width of these compounds.

Acknowledgments

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