

## QUANTITATIVE EVALUATION OF SULFUR TYPES IN MIDDLE DISTILLATES

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### ABSTRACT

The utilization of fossil fuels in the transportation sector is changing. Due to increasing environmental constraints it is anticipated that changes in transportation fuel specification will be required. It will be necessary to improve diesel fuel quality to address the problems of emission from diesel powered vehicles. A trend in the transportation fuel production indicates an increase of the proportion of diesel fuel produced from oil sands and heavy crude oil. The relatively poor ignition quality of this middle distillate puts pressure on the petroleum industry to produce fuel that is more environmentally clean and yet economically feasible. In the future, knowing which of fuels' physical and chemical properties influence engine exhaust emissions will become very important. Currently, there are several mass spectrometry techniques that can determine the hydrocarbon type composition of diesel fuels. This paper will discuss the results of hydrocarbon type analyses obtained for middle distillate sample by using HVLREI GC-MSD (high voltage low resolution electron impact mass spectrometry) and GC-FIMS (Field Ionization Mass Spectrometry). Comparison of aromatic sulfur types, such as di- and benzothiophenes, calculated by mass spectrometry methods and by GC-FID/SCD (Sulfur Chemiluminescent Detector) will be discussed.

### INTRODUCTION

There are few standardized methods available based on high voltage low resolution electron impact mass spectrometry to perform detailed analyses of complex petroleum mixtures. For fractions boiling in the naphtha range, the ASTM 2789 method is used. For hydrocarbon distillates boiling above the naphtha range, prior chromatographic separation is usually required in order to avoid interference between saturate and aromatic types. The saturate fraction can be analyzed by the ASTM 2786 methods and the aromatic fraction, by the ASTM 3239 method for petroleum fractions boiling within the range from 205 to 540 °C. For fractions boiling within the diesel range (177 to 343°C), the ASTM 2425 method is applied. The Robinson method offers a one-step analysis that does not require the separation into saturate and aromatic fractions. The method, developed by C. J. Robinson in 1971(1), covers the full boiling range and resolves up to 4 saturate and 21 aromatic compound types including 3 thiophenoaromatic types (assuming no olefins are present in the sample).

There is also a GC-FIMS method that identifies the composition of liquid fuel by compound type (z-values) and molecular size (2). The method, developed at SRI, is based on replacing the electron-impact ionizer of an HP GC-MSD system with the SRI volcano-style field ionizer. For most compounds, field ionization produces only the molecular ion. Analysis by FIMS expresses the data as z-series tables giving the composition by compound type (z-values) and molecular size (number of carbon atoms).

This work is a continuation of the GC-FIMS application for compositional analysis of transportation fuels (3). We analyzed light cycle oil (LCO) by GC-MSD and by GC-FIMS for hydrocarbon type composition and found some pronounced differences, especially in the saturate types. The distribution of aromatic types was identical. In order to evaluate the methods, we analyzed one of the samples by GC/FID/SCD (sulfur chemiluminescence detector) in order to quantify the thiophenoaromatic types present in the sample. We compared these results with those obtained by mass spectrometry methods.

### EXPERIMENTAL

Initially, the fuel sample was analyzed by GC-MSD and the hydrocarbon types were calculated using the Robinson method. The sample was then separated into saturate, aromatic and polar fractions using a liquid chromatographic procedure, which was a modified ASTM D2007 method (4). The saturate and aromatic fractions were analyzed separately by both, GC-MSD and by GC-FIMS. The aromatic fraction composition was calculated by ASTM D3239, and the saturate fraction composition was calculated by ASTM D2786. The computer programs for calculation of hydrocarbon types were written by R. Teeter (5) based on modification of the original methods and supplied by PSMASPEC, USA.

For GC-MSD runs, a Hewlett Packard GC-MS with HP 5972 MSD, HP 7673 GC/SFC injector and HP 5890 GC was used. The column was a 30m x 0.25mm x 0.25µm High

Resolution GC Column J122-5532 DB-5MS. The oven was held at 35°C for 3 min and was then heated at 10°C/min to 280°C. The MSD temperature was 280°C. The cool on-column injection technique was employed with helium as the carrier gas at a constant flow rate of 1.2 ml/min.

For the GC-FIMS runs, a 30-m x 0.25mm x 0.25µm HP1-MS non-bonded column was used. The injection (0.2µl; 19:1 split) was made with the oven at 45°C. The oven was heated at 17°C/min to 300°C. Sulphur determination was performed using Hewlett Packard gas chromatograph HP6890 series equipped with cool on-column injector and nonaliter adapter, FID/SCD detector (Sulphur Chemiluminescence Detector) SIEVERS 355. The HP 1909/Z-213, HP-1 Methyl siloxane (30.0m x 320.00µm x 1.00µm) column with the injection volume of 0.5µl was used. The total sulphur content was calculated by using the response factor determined from running the sulphur standard with the known sulphur concentration. For aromatic sulfur speciation, the standards benzothiophene and dibenzothiophene were analyzed. Knowing the retention time for both compounds, the baseline integration was performed separately for benzothiophenes and dibenzothiophenes on the sample chromatogram. Then, each of the sulfur groups was calculated knowing the response factor and assuming the average molecular weight 190 Da for benzothiophenes and 220 Da for dibenzothiophenes. The calculated result was confirmed with the result obtained by using the standard method for sulfur determination such as: ASTM D4294 (Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy).

## RESULTS AND DISCUSSION

### HYDROCARBON TYPES

The GC-MSD and GC-FIMS results are presented in Table 1. The results for separated fractions are presented together with the Robinson results for the total sample. The hydrocarbon type composition of fuels analyzed by GC-FIMS is usually presented as a z-series. All the numbers in a z-table (Table 2) are given as sums of the weight fractions from C<sub>1</sub> to C<sub>20</sub> for z-numbers from -2 to -14. The elemental formula of any hydrocarbon can be generally expressed as C<sub>n</sub>H<sub>2n+2z</sub>, where z is a measure of the unsaturation index. All acyclic alkanes have the general formula of C<sub>n</sub>H<sub>2n+2</sub> (i.e., z-value of +2), and monocyclic alkanes have the general formula of C<sub>n</sub>H<sub>2n</sub> (i.e., a z-value of 0). The z-value decreases by 2 for every degree of unsaturation (ring or double bond). Since the fractions were analyzed separately, it was possible to identify all the saturate types and some of the aromatic types without any interference.

In Table 1, each saturate type in the GC-FIMS column corresponds to a z-series number given in Table 2 for the saturate fraction. It is quite noticeable that the saturate region mainly covers the intensities in z series from +2 to -4, that is from paraffins to tricyclic alkanes. The aromatic region covers mainly the intensities in z series from -6 to -14 corresponding to alkylbenzenes up to naphthocycloalkanes. Some of the peaks detected with z < -6 in the saturate fraction could be attributed to some aromatic impurities due an incomplete separation. The numbers in Table 1 suggest that in this case those impurities are negligible. For the aromatic fraction, the masses detected in the saturate region are also minor and could be due to a small amount of saturates, such as tricycloalkanes, that are left behind after saturate separation and later coeluted with the aromatics.

In Table 1, there are three columns for the results from GC-FIMS analysis. The first column is a direct translation of a z-table into hydrocarbon types. First, comparison of the aromatic types obtained by GC-MSD and FIMS suggested that there was a difference in the polyaromatic types. FIMS showed results about 10% higher for the total mono- and diaromatics. The difference in alkylbenzenes was 11%, in naphthalenes, 17%. Tri- and tetraaromatics were not calculated by FIMS, while they were 9.0% and 2.9% by ASTM D3239. These differences could be explained by the fact that because of the limited number of samples analyzed by GC-FIMS, the response factors for various series have not yet been optimized. Furthermore, at this stage of development, FIMS only calculates the hydrocarbon types for lighter material.

However, by analyzing the SICs (single ion chromatograms) from the GC-FIMS analysis of LCO, compounds such as fluorenes (z-16), phenanthrenes (z-18), phenanthrocycloalkanes (z-20) and pyrenes (z-22) were found in the spectra. In order to avoid a discrepancy between the actual spectra and the results of a z-table, it was assumed that the amount of phenanthrenes, fluorenes and pyrenes calculated by FIMS would be very close to the ones calculated by other MS methods. According to data in Table 1, there was no significant difference between the aromatic types obtained by ASTM D3239 and the Robinson method. The aromatic compounds tend not to fragment too much when analyzed by both techniques and there is reason to believe that the analysis by FIMS would produce a similar distribution. The amount assumed for phenanthrenes was 9.0%, for fluorenes, 5.0%, and for pyrenes, 3.0% (average from ASTM3239 and Robinson results). Recalculated results are presented in the second column of FIMS analysis (Table 1). Now the comparison was much better with the results from other GC-MS methods with the exception of alkylbenzenes and naphthalenes. These are the groups that overlap with the aromatic sulfur types.

In order to compare two different MS methods, we had to compare results for all hydrocarbon types. When the Robinson and ASTM 2786 methods were compared, the total

amount of cycloparaffins was in a good agreement, however, there were differences within the cycloparaffinic types and between straight chain paraffins. The values for normal paraffins and polycycloparaffins calculated by ASTM 2786 were higher than the corresponding values calculated by the Robinson method while the order was reversed for monocycloparaffins. For samples where the saturates content is high and cycloparaffin content is high, these differences could be much more profound. There is a method, INT 101 (6), that overcomes the discrepancies of the Robinson method, however it still does not answer the question of true saturates distributions. Comparison of saturates distribution measured by the GC-FIMS and GC-MSD also could not answer this question.

If field ionization produced only the molecular ions, then it could be assumed that the results obtained by GC-FIMS would reflect the true distributions. Consequently, the results in Table 1, obtained by the electron impact GC-MSD, especially for the cycloparaffins, would be greatly underestimated. However, at this point the results obtained by FIMS for the saturate fraction do not quite reflect the compound distribution. The isoparaffins tend to fragment and do not produce the molecular ion. They can not be accounted for in the calculation and therefore lower the amount of the calculated total paraffins. It will be our future task to determine the proper response factors for various paraffin mixtures and adjust the calculation. At this point the methods could be evaluated based on aromatics distribution. We looked particularly at the aromatic sulfur distribution and compared it with the results determined by another method rather than mass spectrometry.

As mentioned before, the aromatics distributions for the sample were identical except for the overlapping species in FIMS results. The numbers with the asterisk (Table 1) present the sums of intensities for a particular z-series that have interference within the series, such as alkylbenzenes with benzothiophenes and naphthalenes with dibenzothiophenes. We were able to calculate the values for benzothiophenes and dibenzothiophenes. The calculation was performed by setting the separate time windows for the sulfur and the hydrocarbon types. It was possible since the two species were separated by GC prior to being analyzed by FIMS.

The nominal mass of dibenzothiophene is 184 Da, which is the same as that of a C<sub>4</sub>-naphthalene. Figure 1 shows the selected ion chromatograms (SICs) for m/z 184, 198, 212, 226, 240 and 254 extracted from the TIC of MD2-aromatics. The C<sub>4</sub>-naphthalenes (m/z 184) elute between 9.4 and 10.6 min. The cluster of peaks due to C<sub>4</sub>-naphthalenes is followed by a strong peak at 10.8 min., which is due to dibenzothiophene. The control run of dibenzothiophene is shown in Figure 2. The SIC of mass 198 in Figure 1 shows a similar pattern as that found for m/z 184. Here, the alkyl-naphthalenes are between 9.2 and 11.2 min., and the isomeric methyl-dibenzothiophenes are between 11.3 and 12.4 min. The pattern is repeated for the SICs of other masses up to mass 268. Integration was performed for the dibenzothiophene portion of the SIC for every extracted mass. The integrated area was related to the total area of the SIC. The ratio then was multiplied by a corresponding mass percent taken from a z-table in order to calculate the dibenzothiophene portion (assuming the response factors being the same for both compound types). The same exercise was performed for benzothiophenes (the SICs for m/z 134, 148, 162, 176, 190 and 204 were extracted). The integration was done for benzothiophenes with m/z up to 232.

LCO was analyzed also by another technique, GC/SCD (gas chromatograph/ sulfur chemiluminescence detector). The GC/SCD chromatogram of this run is presented in Figure 3(a). The chromatograms of benzothiophene (retention time 19.520 min.) and dibenzothiophene (retention time 32.686 min.) standards are presented in Figures 3(b) and 3(c) respectively. The total sulfur was calculated using the total area and the factor as was explained earlier. The sulfur obtained by this method was 1.38wt.%. This number was verified by the ASTM 4294 method (Dispersive x-Ray Fluorescence Spectroscopy) which reported sulfur of 1.45wt.%. Knowing the retention time for benzothiophene and dibenzothiophene, part of the chromatogram was integrated between 19.52 and the beginning of peak at 32.686 min. for benzothiophenes, and between start of peak at 32.686min to the end for dibenzothiophenes. The calculation was performed according to a procedure described above. The results of sulfur determination are summarized in Table 3.

Total sulfur determined by GC/SCD was in a good agreement with the result from ASTM 4294. The result obtained by the GC-FIMS was the closest to the SCD result, especially in terms of distribution between di- and benzothiophenes. This comparison favors the GC-FIMS method for calculation of other hydrocarbon types in fuels with a high degree of accuracy provided that the response factors for the paraffins would be adjusted.

## CONCLUSION

The results presented in this paper demonstrate the ability of various GC-MS methods to provide rapid and detailed group-type analysis of middle distillates. Analysis of data from each method suggests a discrepancy, particularly for saturates distribution, between the Robinson method for unseparated sample and between ASTM D2786 and ASTM D3239 for separated fractions. The difference was even greater when these results were compared with GC-FIMS

results. Comparison of di- and benzothiophenes content in one of the samples calculated by different methods indicates that analysis by GC-FIMS may offer more reliable distribution of hydrocarbon types compared to the other two methods, provided that the results would be corrected for the isoparaffins fragmentation. The GC-FIMS combination allowed the overlapping species in the same z-series to be separated by time and thus accurately calculated. By creating separate time windows for the GC-separated species and determining their response factors it could be possible to analyze the samples having a full boiling range without prior separation.

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Table 1 – Comparison of hydrocarbon type analyses results for Light Cycle Oil by different GC-MS methods

Hydrocarbon C <sub>n</sub> H <sub>2n</sub> +Z	Z No.	Robinson	ASTM 2786	ASTM 3239	GC-FIMS	GC-FIMS	GC-FIMS	GC-FIMS
		Total	Saturates	Aromat.	Saturates	Aromat.1	Aromat.2	Aromat.3
<b>SATURATES</b>		<b>21.90</b>	<b>22.70</b>		<b>22.70</b>			
Paraffins	2	11.90	12.40		5.96			
Cycloparaffins		<b>10.00</b>	<b>10.30</b>		<b>16.74</b>			
Monocycloparaffins	0	6.40	4.10		7.92			
Dicycloparaffins	-2	3.60	2.50		1.76			
Polycycloparaffins	-4	0.00	3.70		7.06			
<b>AROMATICS</b>		<b>78.10</b>		<b>73.70</b>		<b>73.70</b>	<b>73.70</b>	<b>73.70</b>
Monoaromatics		<b>21.50</b>		<b>20.40</b>		<b>29.70*</b>	<b>22.90*</b>	<b>19.60</b>
Alkylbenzenes	-6	9.50		8.60		21.10*	16.20*	12.90
Benzocycloalkanes	-8	9.70		9.60		7.10	5.50	5.50
Benzo-dicycloalkanes	-10	2.30		2.20		1.50	1.20	1.20
Diaromatics		<b>35.20</b>		<b>33.40</b>		<b>44.00</b>	<b>38.80*</b>	<b>32.30</b>
Naphthalenes	-12	21.20		21.30		38.80*	29.80*	23.30
Naphthocycloalkanes	-14	7.60		6.80		5.20	4.00	4.00
Fluorenes	-16	6.30		5.30		0.00	5.00	5.00
Triaromatics		<b>10.70</b>		<b>9.00</b>		<b>0.00</b>	<b>9.00</b>	<b>9.00</b>
Phenanthrenes	-18	9.10		7.80		0.00	7.80	7.80
Phenanthro-cycloalkanes	-20	1.60		1.20		0.00	1.20	1.20
Tetraaromatics		<b>3.30</b>		<b>2.90</b>		<b>0.00</b>	<b>3.00</b>	<b>3.00</b>
Pyrenes/Benzofluorenes	-22	2.70		2.60		0.00	3.00	3.00
Chrysenes	-24	0.50		0.30		0.00	0.00	0.00
Pentaaromatics		<b>0.00</b>		<b>0.20</b>		<b>0.00</b>	<b>0.00</b>	<b>0.00</b>
Chrysocycloalkanes	-26	0.00		0.20		0.00	0.00	0.00
Benzyrenes/Perylenes	-28	0.00		0.00		0.00	0.00	0.00
Dibenzanthracenes	-30	0.00		0.00		0.00	0.00	0.00
Unidentified		<b>0.00</b>		<b>0.00</b>		<b>0.00</b>	<b>0.00</b>	<b>0.00</b>
C <sub>n</sub> H <sub>2n</sub> -32/C <sub>n</sub> H <sub>2n</sub> -46	-32	0.00		0.00		0.00	0.00	0.00
C <sub>n</sub> H <sub>2n</sub> -36/C <sub>n</sub> H <sub>2n</sub> -26S	-36	0.00		0.00		0.00	0.00	0.00
C <sub>n</sub> H <sub>2n</sub> -38/C <sub>n</sub> H <sub>2n</sub> -28S	-38	0.00		0.00		0.00	0.00	0.00
C <sub>n</sub> H <sub>2n</sub> -42/C <sub>n</sub> H <sub>2n</sub> -32S	-42	0.00		0.00		0.00	0.00	0.00
C <sub>n</sub> H <sub>2n</sub> -44/C <sub>n</sub> H <sub>2n</sub> -34S	-44	0.00		0.00		0.00	0.00	0.00
<b>Aromatic Sulfur</b>		<b>7.50</b>		<b>7.80</b>		<b>0.00</b>	<b>0.00</b>	<b>9.80</b>
Benzothiophenes	-10S	3.40		3.60		0.00	0.00	3.30
Dibenzothiophenes	-16S	3.90		4.00		0.00	0.00	6.50
Benzonaphthothiophenes	-22S	0.20		0.20		0.00	0.00	0.00

Arom.1- Original data from z-table

Arom.2- Data adjusted for polyaromatics

Arom.3- Data adjusted for aromatic sulfur

Table 2 - FIMS results for saturate and aromatic fractions of LCO by z-series

Sample ID	2	0	-2	-4	-6	-8	-10	-12	-14	
Aromatics(%of Ar.)	0.02	0.08	0.05	0.12	28.65	9.61	2.03	52.72	6.72	100.00
Aromatics(%of Total)	0.01	0.05	0.04	0.09	21.10	7.07	1.50	38.84	5.00	73.70
Aromatics(%of Ar.)*	0.01	0.06	0.04	0.09	22.06	7.40	1.57	40.60	5.17	77.00
Aromatics(%of Total)*	0.01	0.03	0.03	0.06	16.25	5.45	1.16	29.91	3.80	56.70
Saturates(%of Sat.)	26.28	34.92	7.82	24.04	0.42	2.89	3.34	0.35	0.16	100.24
Saturates(%of Total)	5.96	7.92	1.76	5.45	0.10	0.64	0.75	0.08	0.04	22.70

\* - Results are recalculated for the presence of fluorenes, phenanthrenes and pyrenes

Table 3 – Aromatic sulfur types determined by different methods

Aromatic sulfur types Wt.% of total	ASTM 4294	GC-SCD	GC-FIMS	GC-MS ASTM D3239	GC-MS Robinson
Benzothiophenes	-	2.7	3.3	3.6	3.4
Dibenzothiophenes	-	6.0	6.5	4.0	3.9
Naphthobenzothiophenes	-	N/D	N/D	0.2	0.2
Total aromatic sulfur	-	8.7	9.8	7.8	7.5
Total sulfur	1.45	1.38	1.50	1.19	1.14

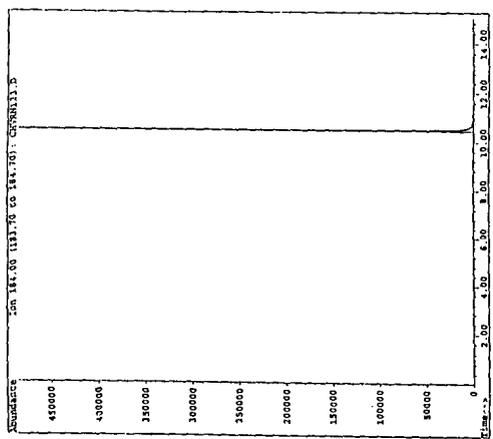


Figure 2. Selected Ion Chromatogram of  $m/z$  184 extracted from GC-FIMS. Analysis of dibenzothiophene

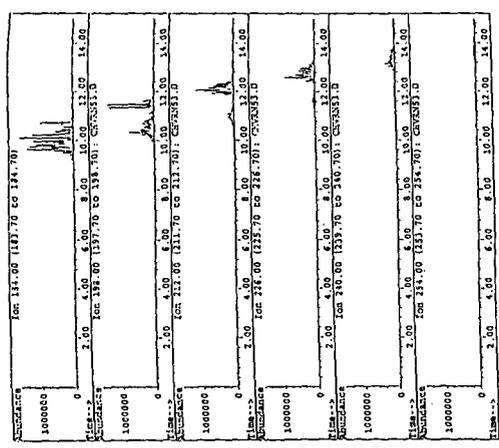


Figure 1. Selected Ion Chromatogram of  $m/z$  184, 198, 212, 226, 240, 254 Extracted from GC-FIMS analysis of LCO

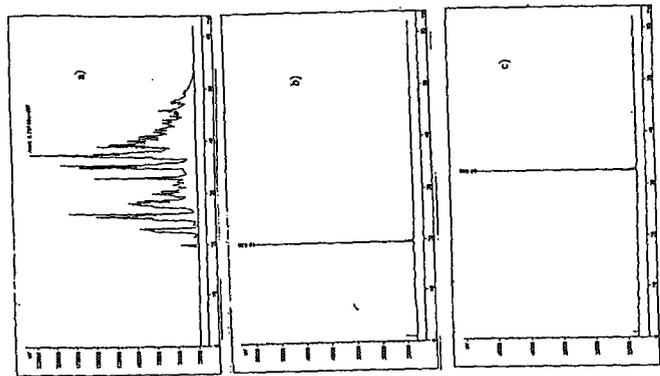


Figure 3. GC-FID/SCD chromatogram of LCO  
 a) GC-FID/SCD chromatogram of the total sample  
 b) GC-FID/SCD chromatogram of benzothiophene  
 c) GC-FID/SCD chromatogram of dibenzothiophene