



ELSEVIER

Journal of Chromatography A, 761 (1997) 231–247

JOURNAL OF
CHROMATOGRAPHY A

Molecular analysis of the sulphur components in a light cycle oil of a catalytic cracking unit by gas chromatography with mass spectrometric and atomic emission detection

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Received 5 June 1996; revised 30 September 1996; accepted 1 October 1996

Abstract

This paper presents a detailed characterization of the sulphur components present in a light cycle oil of a catalytic cracking unit. The sulphur is distributed over the benzothiophene (BT), dihydrobenzothiophene, dibenzothiophene (DBT) and naphthothiophene families. All monosubstituted BT and DBT isomers are identified next to most components of the C₂-BT and C₂-DBT subfamilies. A correlation was developed for the prediction of the retention times of polymethylBTs. This correlation was applied to the identification of trimethylBT and tetramethylBT. The sulphur components were quantified using gas chromatography with an atomic emission detector.

Keywords: Oils; Sulphur compounds; Thiophenes

1. Introduction

Complex hydrocarbon mixtures in the gasoil range are mostly characterized in two ways, group type analysis and boiling range determinations. Molecular characterization of gasoils, in contrast with gasolines, is not frequently done because of the large number of components, particularly the isomers of saturated components. However, the content of isoparaffins, naphthenes and aliphatic sulphur components in light cycle oil (LCO), the gasoil fraction of the effluent of a catalytic cracking unit, is limited. Substituted aromatics are partly dealkylated or the length of the alkyl side chains is reduced during the catalytic cracking process, thereby decreasing the importance of higher substituted aromatics in the LCO. For this

type of complex mixture, molecular identification, using high-resolution capillary gas chromatography combined with mass spectrometry, is possible. This paper focuses on the sulphur-containing components of a LCO of a catalytic cracking unit. This molecular based analysis can be used for more detailed kinetic modeling of hydrodesulphurization (HDS) [1] and for the calculation of physical and thermodynamic properties of the mixture.

2. Experimental

A quadrupole mass spectrometer, part of the Hewlett-Packard 5989A system was used for the identification. Electron impact ionisation mass spectra were obtained at 70 eV at a rate of 1.6 scans/s. The quadrupole temperature was 100°C, the ion

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source temperature was 250°C and the transfer line temperature was 250°C. The GC separation was performed with a Hewlett-Packard 5890 Series II instrument on a 50-m \times 0.2 mm fused-silica capillary column coated with a 0.5- μ m film of cross-linked 100% dimethylsiloxane (HP-PONA). Helium was used as the carrier gas (0.645 ml/min at 35°C). The column was temperature programmed from 35°C (5 min) to 80°C (15 min) at a rate of 2.5°C/min and then to 200°C (5 min) at a rate of 2.0°C/min and finally to 250°C at a rate of 1°C/min. The injector temperature was 250°C. A 1- μ l volume of undiluted LCO, with a boiling range of 225–370°C, was injected at a split ratio of 63:1.

Atomic emission detection (AED) is element specific and has a high dynamic range for C, H, N and S. GC-AED (HP 5921A) was used for the quantification of the sulphur components. The gas chromatograph of the GC-AED unit was equipped with a 25.0 m \times 0.20 mm HP-1 column with a 0.17- μ m film of 100% dimethylpolysiloxane. Helium was used as the carrier gas (1.1 ml/min at 40°C). The column was temperature programmed from 40°C (5 min) to 260°C (6 min) at a rate of 1.0°C/min. The

injector temperature was 250°C and 1 μ l of undiluted sample was injected at a split ratio of 59:1. The reference components, with the exception of benzo-thiophene (BT) and dibenzothiophene (DBT) (Aldrich), were synthesized by Total (Harfleur, France).

3. Results and discussion

The sulphur chromatogram of the LCO obtained with GC-AED is shown in Fig. 1. The LCO sulphur chromatogram does not show humps of poorly resolved groups of peaks like those found in a straight run gasoil sulphur chromatogram, since most aliphatic sulphur components are converted during catalytic cracking and since the number and length of the alkyl side chains of the aromatic sulphur-containing components is reduced. The total sulphur content of the LCO (1.28%, w/w) was determined with AED using hydrogen linearization. Identical response factors were obtained for BT and DBT with a calibration mixture containing both components. The distribution of the total sulphur content over different classes is shown in Table 1.

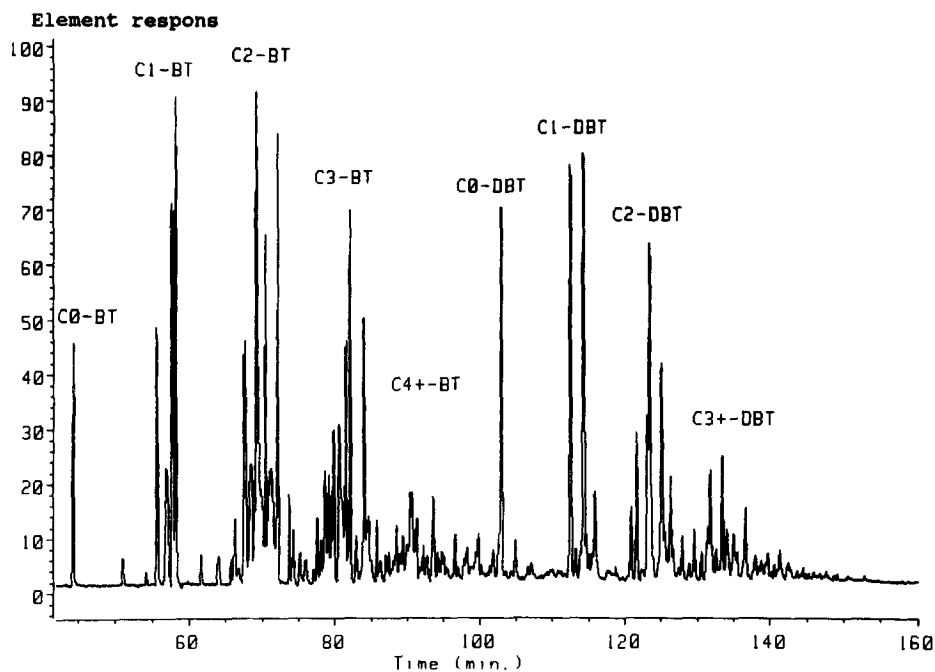


Fig. 1. Sulphur chromatogram of the LCO using GC-AED.

Table 1
Distribution of sulphur in LCO over different classes defined by the retention time intervals

Class number	Main sulphur subfamily present	Retention time interval (min)	Sulphur (%)
1	C ₀ -BT	44–45	1.5
2	C ₁ -BT	45–59	10.2
3	C ₂ -BT	59–73	19.1
4	C ₃ -BT	73–85.5	16.2
5	C ₄₊ -BT	85.5–102.5	13.1
6	C ₀ -DBT	102.5–103.5	3.3
7	C ₁ -DBT	103.5–117	12.5
8	C ₂ -DBT	117–130	11.8
9	C ₃₊ -DBT	130–160	12.4

These classes correspond only roughly with the BT and DBT sulphur subfamilies, because of overlap between the higher boiling sulphur subfamilies and the presence of some components of the dihydroben-

zothiophene (DHBT) and naphthothiophene (NT) families. The non-substituted parent components are shown in Fig. 2. Classes 3 and 4, corresponding to the C₂- and C₃-BT subfamilies, contain most sulphur. Classes 1 to 5, with the substituted BT and DHBT, contain 59.3% of all sulphur. The other part, 40.7%, is spread out over the DBT and NT families. The identification of the sulphur components was done with a combination of various techniques, GC-MS, matching of the increases of the HDS products to the decreases in the sulphur components after hydrotreatment, comparison of the retention times with literature data and by an understanding of the elution order of the isomers.

Classes 1 and 2 contain BT, the 6 MeBT isomers, DHBT and some MeDHBTs. A single ion chromatogram (*m/z* 148) for the MeBTs is shown in Fig. 3. The C₆-benzene peak corresponds to 1,3,5-trimethyl-

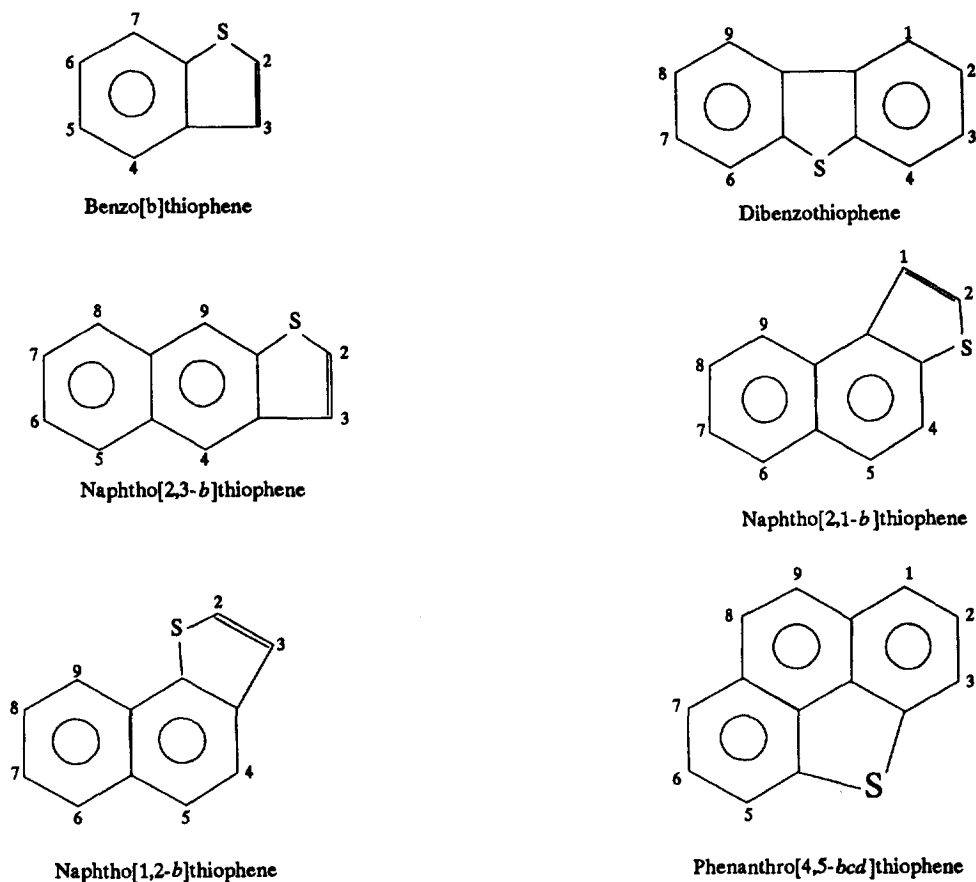


Fig. 2. Molecular structures of the sulphur-containing parent components present in LCO.

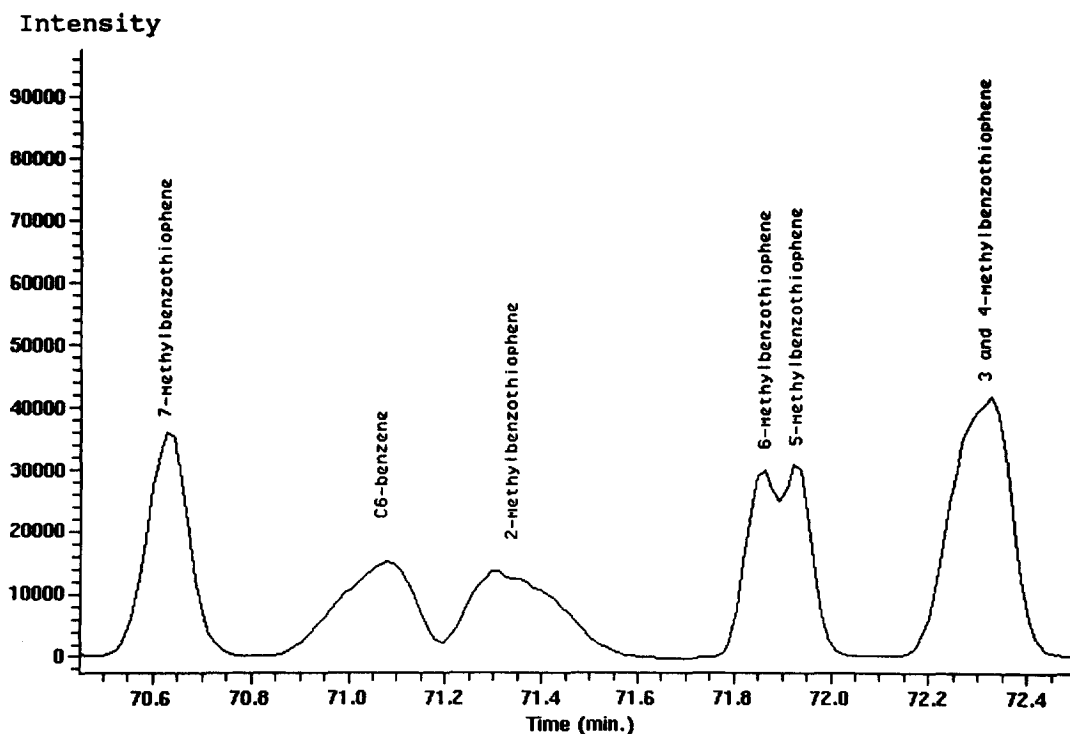


Fig. 3. Part of the single ion chromatogram (m/z 148) of the LCO showing the peaks corresponding to the C_1 -BT isomers.

2-propylbenzene. The identification of the MeBTs was based on literature retention indices [2] for non-polar columns. The peaks corresponding to 5- and 6-MeBT are partly separated, as seen in Fig. 3, and those corresponding to 3- and 4-MeBT coelute.

In Fig. 4 Fig. 5 a part of the total ion chromatogram with the peaks corresponding to the C_1 -BT desulphurization products are shown before and after HDS on a $CoMo/Al_2O_3$ catalyst in a completely mixed flow reactor at 310°C, 80 bar and a space time of 326 $kg_{cat} h/kmol S$. The C_1 -BT isomers were completely converted under these conditions. The desulphurization of the six C_1 -BT isomers results in the five C_3 -benzenes shown in Table 2.

The decrease in the molar flow of each C_1 -BT isomer as a percentage of the decrease in the molar flow of all C_1 -BT isomers and the increase in the molar flow of each desulphurization product as a percentage of the increase in the molar flow of all reaction products is shown in Table 2. These normalised decreases of 5- and 7-MeBT are added in column 2, since both of these have 1-Et-3-MeBenzene as the reaction product. The normalised in-

creases of the HDS products of 3- and 4-MeBT are added in column 4, since both C_1 -BT isomers coelute. The integrated abundances of each of the most important fragments of every isomer are added for the quantitative interpretation of the MS data. The C_1 -DHBT isomers that have the same HDS reaction products as the C_1 -BT isomers interfere little, as the former are only present in small quantities. There is a good similarity between the corresponding normalised increases and decreases (Table 2, columns 2 and 4), showing that the proposed elution order is correct. The normalised increases of the products of 3- and 4-MeBT HDS (isopropylbenzene and 1-ethyl-2-methylbenzene) can be used to determine the ratio of the abundances of both sulphur components. The peak 3+4-MeBT consists of $17.7/(17.7+16.7)=51.4\%$ 3-MeBT and 48.6% 4-MeBT. These results also indicate that there is no important isomerization of the MeBTs before the sulphur removal reactions take place. A single ion chromatogram (m/z 150) with the molecular ion peaks of the C_1 -DHBT and a small fragment of the C_1 -BT isomers is shown in Fig. 5. The C_1 -DHBT

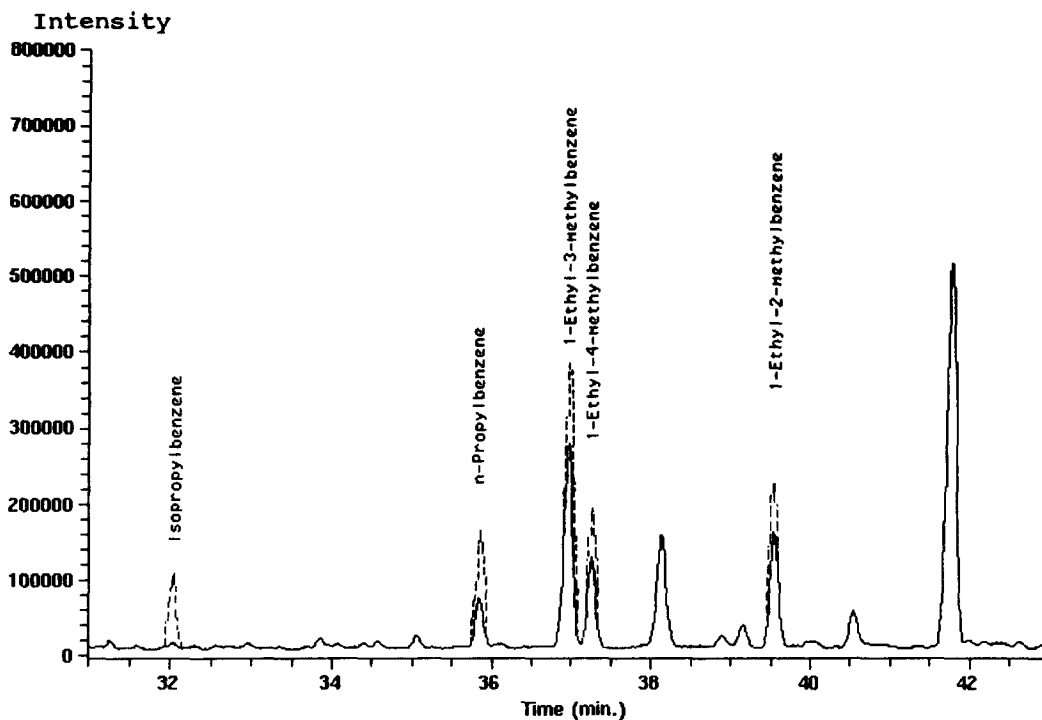


Fig. 4. Part of the total ion chromatogram of a LCO showing the peaks corresponding to the C₁-BT desulphurization products before (—) and after (---) hydrodesulphurization.

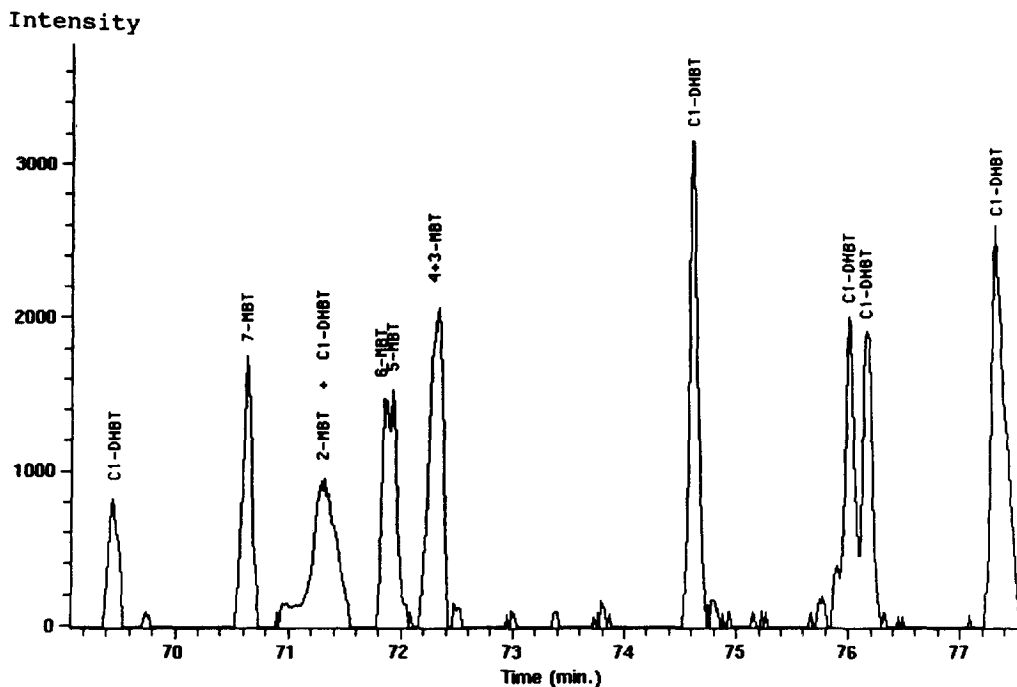


Fig. 5. Part of the single ion chromatogram (*m/z* 150) of the LCO showing the peaks corresponding to the C₁-DHBT and C₁-BT isomers.

Table 2

Normalised decreases in the C₁-BT isomers and the corresponding normalised increases in the C₁-BT desulphurization products

C ₁ -BT isomer	Normalised decrease in the C ₁ -BT isomers		HDS reaction products of the C ₁ -BT isomers	Normalised increases in the reaction products	
	1	2		3	4
2-MeBT	18.39	18.39	<i>n</i> -PrBenzene	19.60	19.60
3-MeBT	36.22	36.22	iso-PrBenzene	17.66	37.34
4-MeBT	36.22	36.22	1-Et-2-MeBenzene	16.68	37.34
5-MeBT	12.20	33.42	1-Et-3-MeBenzene	29.91	
7-MeBT	21.22	33.42	1-Et-3-MeBenzene	29.91	29.91
6-MeBT	11.95	11.95	1-Et-4-MeBenzene	13.13	13.13

peaks elute over a wider interval than the C₁-BT peaks. One C₁-DHBT coelutes with 2-MeBT and cannot be seen as a single peak on Fig. 5. A C₁-DHBT fragment with a mass of 135 was used to discriminate between the C₁-BT and the C₁-DHBT isomers.

Class 3 contains mainly C₂-BTs. There are 21 C₂-BT isomers, i.e. fifteen DiMeBTs and six EtBTs.

A single ion chromatogram (*m/z* 162) showing these isomers is shown in Fig. 6. The fragmentation spectra are used to determine the type of the substituents. The identification was based on the retention indices of [2]. All fifteen DiMeBT isomers are identified, except 4,7-DiMeBT and 3,7-DiMeBT. The elution order was again confirmed by matching the increases in the HDS products to the decreases in

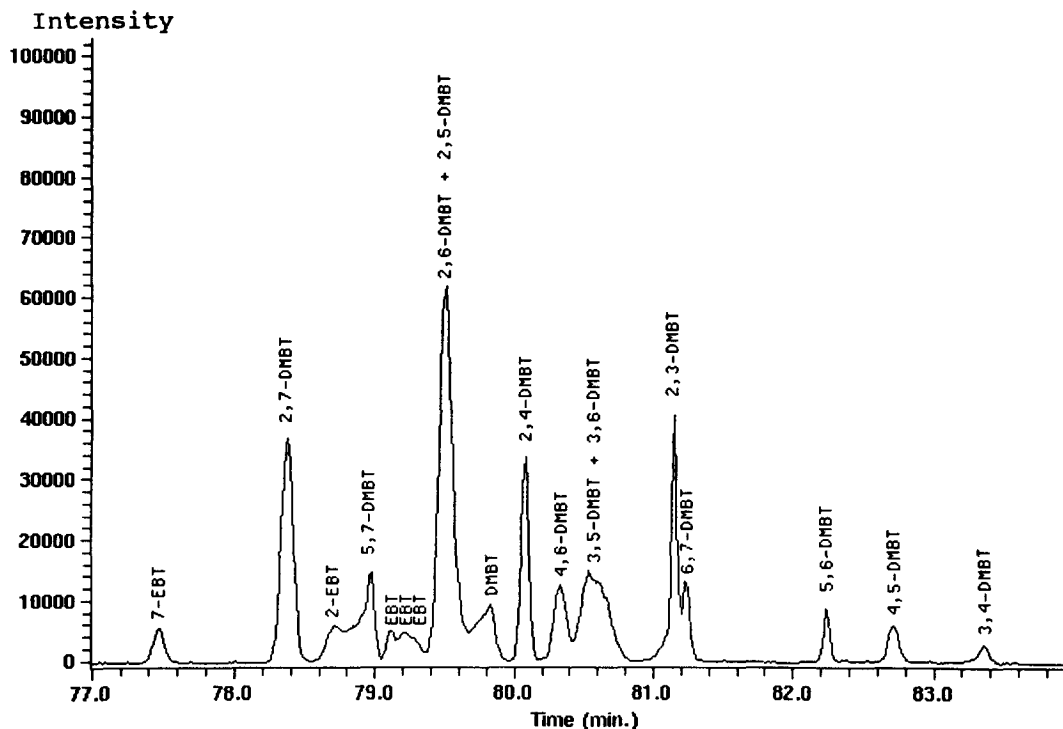


Fig. 6. Part of the single ion chromatogram (*m/z* 162) of the LCO showing the peaks corresponding to the dimethylbenzothiophene (DMBT) and ethylbenzothiophene (EBT) isomers.

the sulphur components after hydrotreating the LCO. The 2-substituted components are more abundant. These are also present, to a greater extent, in straight run gasoil.

Some general remarks can be made on the elution order of peaks corresponding to the MeBTs and DiMeBTs. Substituents on the 2 and 7 positions, closest to the sulphur atom, increase the rate of elution, while substituents on positions 3 and 4 retard it. Two neighbouring substituents increase the retention time. Three types of neighbour interactions are present in BT; one with the two substituents on the benzene moiety, one with both substituents on the thiophene moiety (pair 2,3) and one with a substituent on both moieties (pair 3,4). The DiMeBT retention times were fitted with the following linear model:

$$t_R = t_a + p_2\delta_2 + p_7\delta_7 + p_3\delta_3 + p_4\delta_4 + p_B\delta_B \\ + p_{2,3}\delta_{2,3} + p_{3,4}\delta_{3,4}$$

where t_R is the retention time (min); t_a is the reference time (min); p are the parameters of the model (min); δ_i equals 1 if a methyl substituent is present at position i , otherwise it equals 0; δ_B equals 1 if two neighbouring methyl substituents are present on the benzene moiety; and $\delta_{i,j}$ equals 1 if a methyl substituent is present at the i and j positions

The parameter values obtained by linear regression are given in Table 3. The correlation coefficient is 0.9984. The accelerating effect of methylsubstituents on the 2 and 7 position is reflected in the negative values for the corresponding parameters. Position 7 (−0.927 min) has a more pronounced advancing effect than position 2 (−0.394 min). The retarding

Table 3
Parameter values for the retention time prediction model and the reference time t_a for the C_2 -BT subfamily

Parameter	Parameter value (min)
p_2	−0.394
p_7	−0.927
p_3	0.818
p_4	0.574
p_B	2.342
$p_{2,3}$	0.881
$p_{3,4}$	2.112
t_a	79.84

effect of two neighbouring methyl substituents on the benzene moiety is important (+2.342 min). Two methyl substituents on positions 3 and 4 have a similar effect (+2.112 min), while a pair of methyl groups on positions 2 and 3 retard the elution to a lesser extent (+0.881 min). A plot of the fitted versus experimental retention times is given in Fig. 7.

A single ion chromatogram (m/z 176) with the C_3 -BT isomers is shown in Fig. 8. The model for DiMeBT was used with the same parameters and with a reference time of 0 min for the identification of the TriMeBT isomers. The fit between the experimental and predicted retention times is good (Fig. 9). The reference retention time, t_a , was determined for the TriMeBT isomers with the experimental retention time of 2,4,6-TriMeBT. Two sets of six and two TriMeBT isomers with almost equal abundances and elution times could not be determined unequivocally. The elution order of the other TriMeBTs was confirmed by matching them with the desulphurization product peaks. The TriMeBT isomers with substituents on the 2 and 3 positions are the most abundant, as expected by the type of synthesis mechanism of substituted BTs in crude oils. Next to the twenty TriMeBT isomers, there are 30 EtMeBT, six PrBT and six IsoPrBT isomers. The characteristic ions used to discriminate between the isomer types are shown in Table 4. The distribution of sulphur within the C_3 -BT subfamily is shown in Table 5.

The C_4 -BT subfamily consists of 174 isomers. The different isomer types and their characteristic ions are shown in Table 4. Discrimination between the C_4 -BT isomer types was possible for the TetraMeBTs with m/z 189 and for DiEtBTs with m/z s 175 and 161. The fragmentation patterns of the ethyldimethylBTs and the methylisopropylBTs are similar as are the methylpropylBTs and the *sec*-butylBTs. The presence of components with non-linear substituents in a LCO is limited compared to that of components with linear substituents. This was concluded on the basis of an analysis of the C_3 -benzenes, C_3 -naphthalenes and C_4 -benzenes. Therefore, peaks consisting of m/z s 175 and 190 and of m/z s 161 and 190, respectively, were considered to be ethyldimethylBTs and methylpropylBTs. The single ion chromatogram (m/z 190) corresponding to

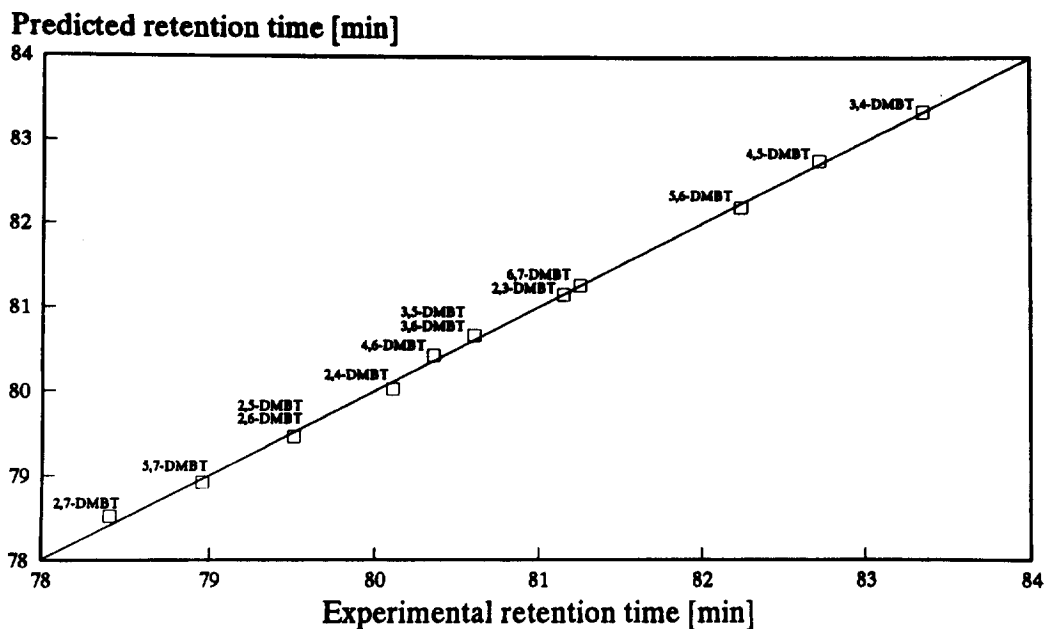


Fig. 7. Fitted versus experimental retention times for the dimethylbenzothiophenes (DMBT).

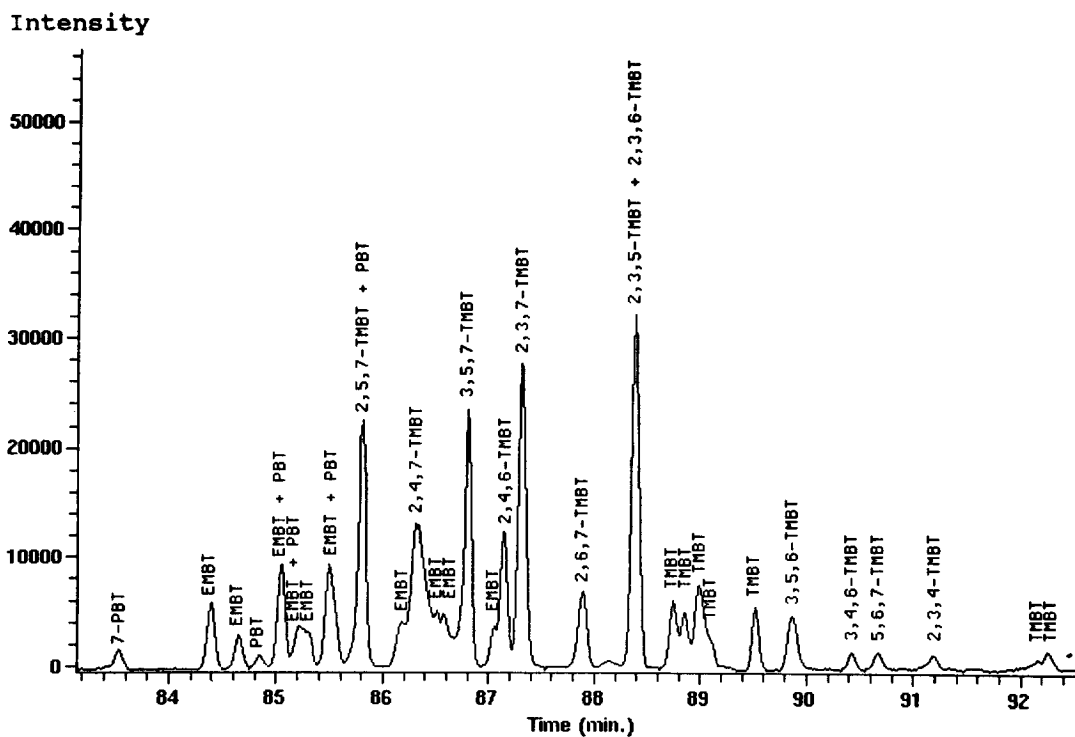


Fig. 8. Part of the single ion chromatogram (m/z 176) of the LCO showing the peaks corresponding to the propylbenzothiophene (PBT), ethylmethylbenzothiophene (EMBT) and trimethylbenzothiophene (TMBT) isomers.

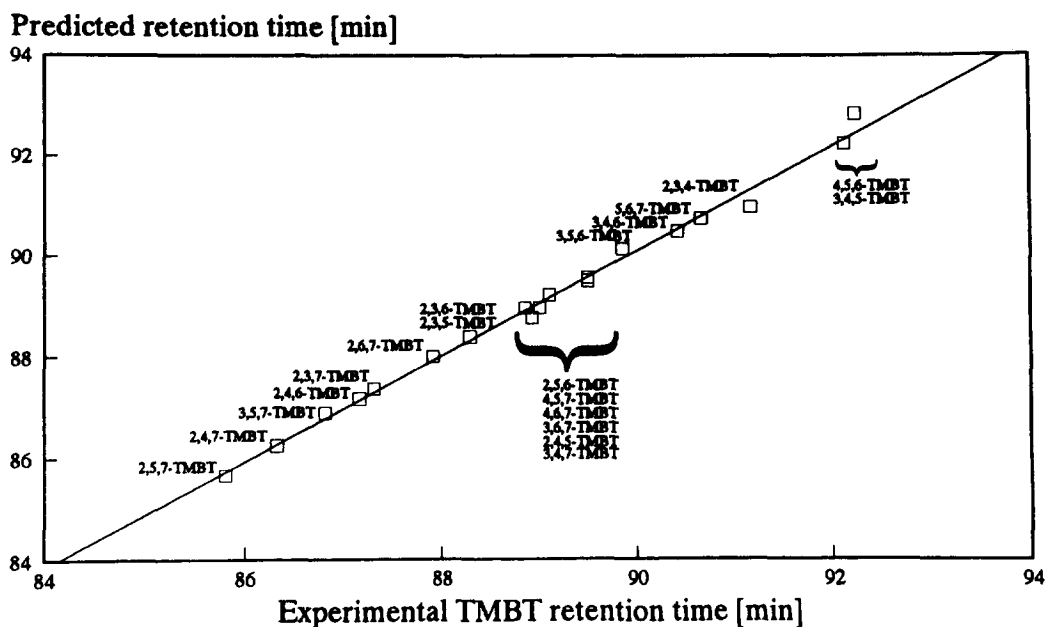


Fig. 9. Predicted retention times versus experimental retention times for the trimethylbenzothiophenes (TMBT) with the corresponding identification results.

Table 4
Types of C₃-BT and C₄-BT isomers and the corresponding characteristic ions

Type of substituent(s)	Number of isomers	Characteristic ions in order of importance
<i>n</i> -Propyl	6	147,176
Isopropyl	6	161,176
Ethylmethyl	30	161,176
Trimethyl	20	161,176,175
<i>n</i> -Butyl	6	147,190
<i>sec.</i> -Butyl	6	161,190
<i>tert.</i> -Butyl	6	175,147,190
Isobutyl	6	147,190
Methylpropyl	30	161,190
Methylisopropyl	30	175,190
Ethylidimethyl	60	175,190
Diethyl	15	175,190,161
Tetramethyl	15	175,190,189

Table 5
Distribution of sulphur within the C₃-BT isomers

Type of substituent(s)	Sulphur (%)
Trimethyl	69.8
Ethylmethyl + isopropyl	24.3
Propyl	5.9

the C₄-BTs is shown in Fig. 10. Only five tetra-MeBTs were detected in the LCO. These were identified with the model presented before. The predicted versus the experimental retention times are given in Fig. 11. The reference retention time, t_a , was determined for the tetraMeBT isomers with the

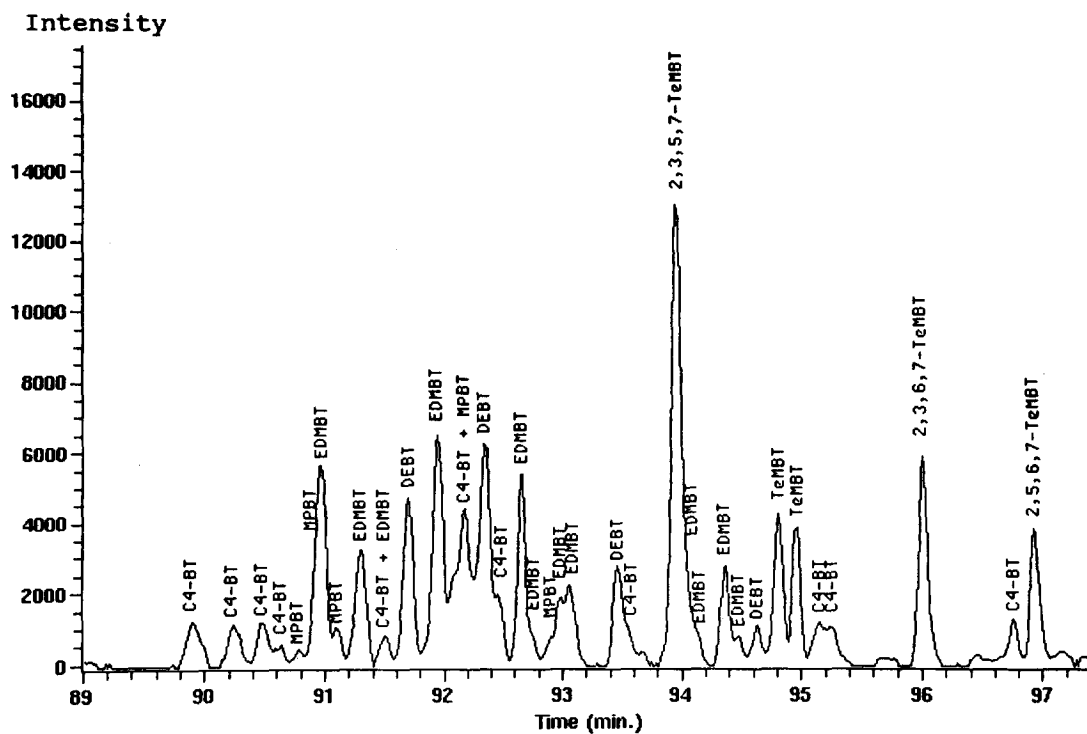


Fig. 10. Part of the single ion chromatogram (m/z 190) of the LCO showing the peaks corresponding to the methylpropylbenzothiophene (MPBT), diethylbenzothiophene (DEBT), ethyldimethylbenzothiophene (EDMBT) and tetramethylbenzothiophene (TeMBT) isomers.

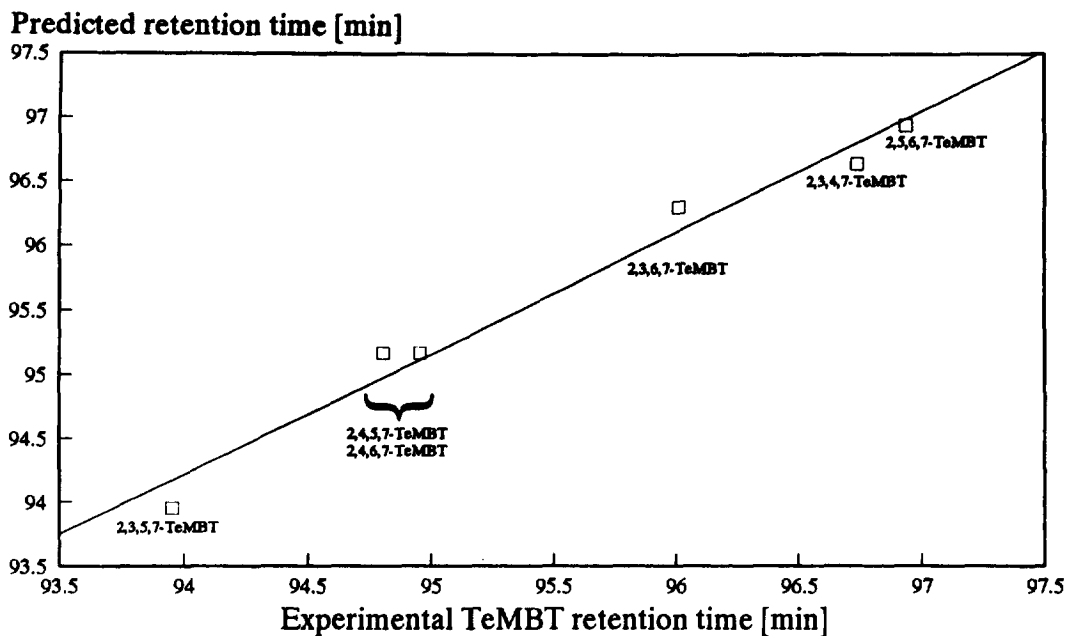


Fig. 11. Predicted retention times versus experimental retention times for the tetramethylbenzothiophenes (TeMBT) with the corresponding identification results.

experimental retention time of 2,3,5,7-tetraMeBT. The C₅-BTs and C₆-BTs, with 474 and 1179 isomers, respectively, are only present in small amounts in this LCO.

Single ion chromatograms with DBT and two NTs (m/z 184), C₁-DBT and C₁-NT isomers (m/z 198) are shown in Fig. 12 Fig. 13, respectively. The NTs and MeDBTs are identified using the retention time data of [3]. The fronting of the DBT peak is probably caused by coelution with naphtho[1,2-*b*]thiophene (Fig. 12). 2-MeDBT and 3-MeDBT coelute on non-polar columns (Fig. 13). The elution order of the C₁-DBT isomers is similar to the elution order of the C₁-BTs. A substituent near the sulphur atom (position 4 for DBT and positions 2 and 7 for BT) accelerates the elution, while a substituent at the top of the molecule (position 1 for DBT and positions 3 and 4 for BT) retards elution with respect to the elution times of the other isomers (positions 2 and 3 for DBT and positions 5 and 6 for BT). The 2- and 3-MeDBTs and the 5- and 6-MeBTs elute in a short time interval or else coelute. None of the 24 MeNT isomers was identified.

Some of the sixteen DiMeDBTs (Fig. 14) were identified using literature retention time data [4], others were identified by co-injection of pure DiMeDBTs (2,4-DiMeDBT, 1,3-DiMeDBT, 2,3-DiMeDBT and 1,2-DiMeDBT). The fragmentation pattern of DiMeDBTs gives further information on the position of the two methyl groups. The 197 fragment is more abundant than the 211 fragment, if one benzene moiety has two substituents. The 211 fragment is most important if each benzene moiety has only one methyl substituent. By comparison with samples that do not contain components of the naphthothiophene family, e.g. Arabian Light straight run gasoil, but do contain the C₂-DBT isomers, the C₂-NTs could be distinguished from the C₂-DBTs. The C₂-NTs are more easily removed by hydrotreatment than the C₂-DBT isomers.

A single ion chromatogram (m/z 226) with the C₃-DBTs is shown in Fig. 15. Three (1,4,6-TriMeDBT, 2,4,6-TriMeDBT and 3,4,6-TriMeDBT) of the 24 TriMeDBT isomers were identified by co-injection of the pure TriMeDBT. These three refractory components have high abundances in LCO

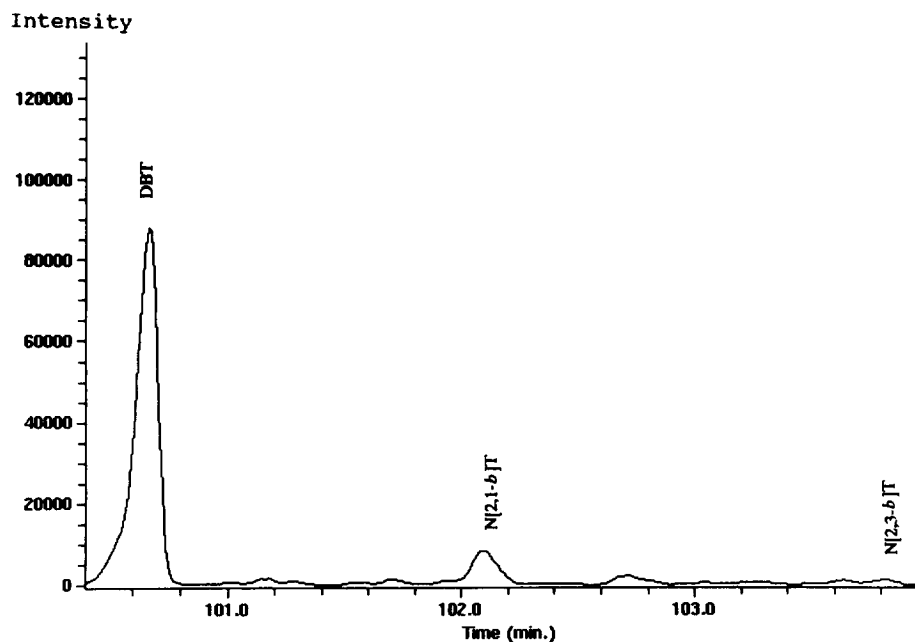


Fig. 12. Part of the single ion chromatogram (m/z 184) of the LCO showing the peaks corresponding to the DBT and the NT isomers.

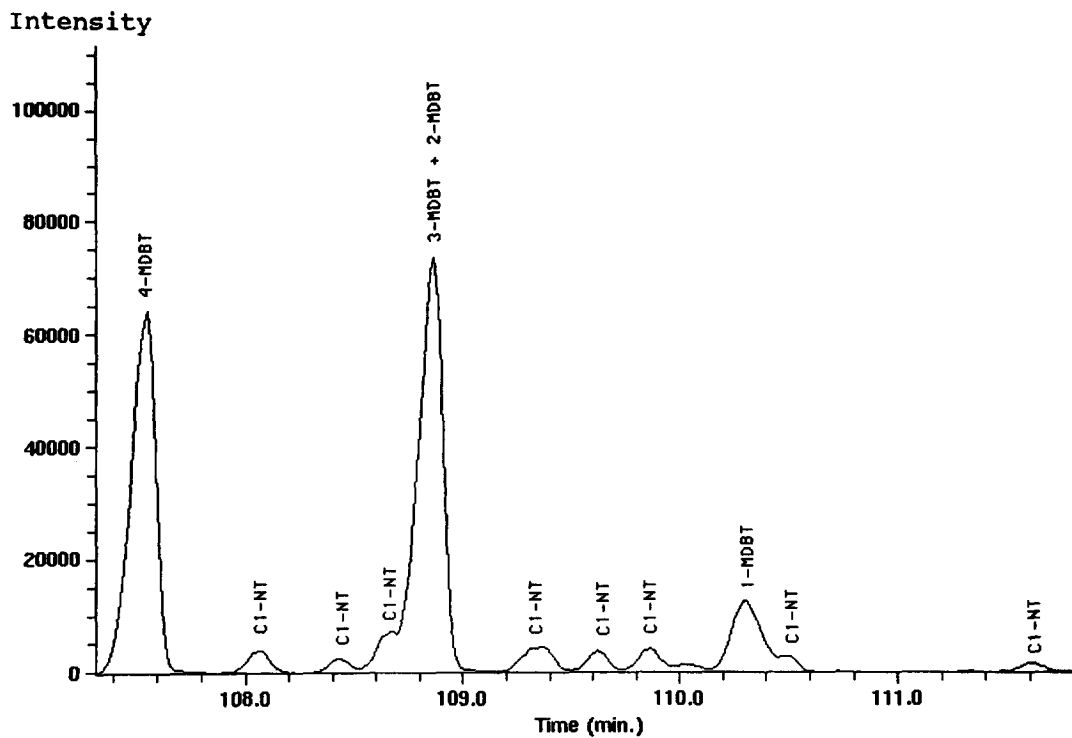


Fig. 13. Part of the single ion chromatogram (m/z 198) of the LCO showing the peaks corresponding to methylbenzothiophene (MDBT) and the C₁-NTs.

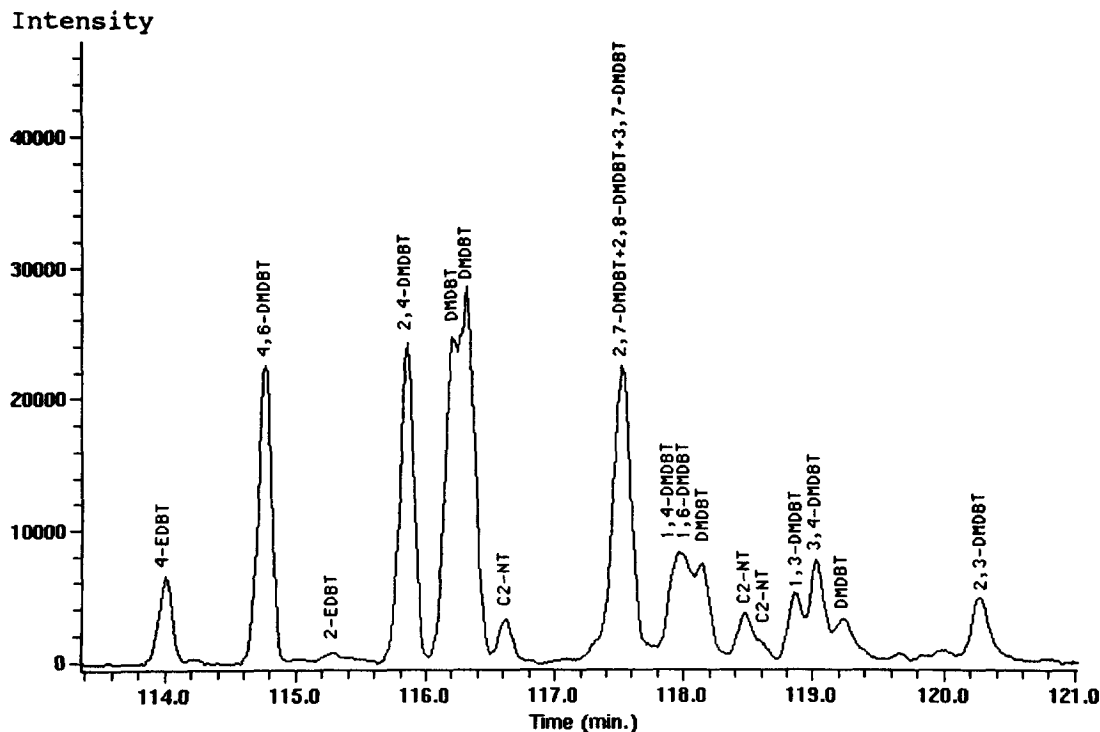


Fig. 14. Part of the single ion chromatogram (m/z 212) of the LCO showing the peaks corresponding to ethyldibenzothiophenes (EDBT), dimethyldibenzothiophenes (DMDBT) and the C₂-NT isomers.

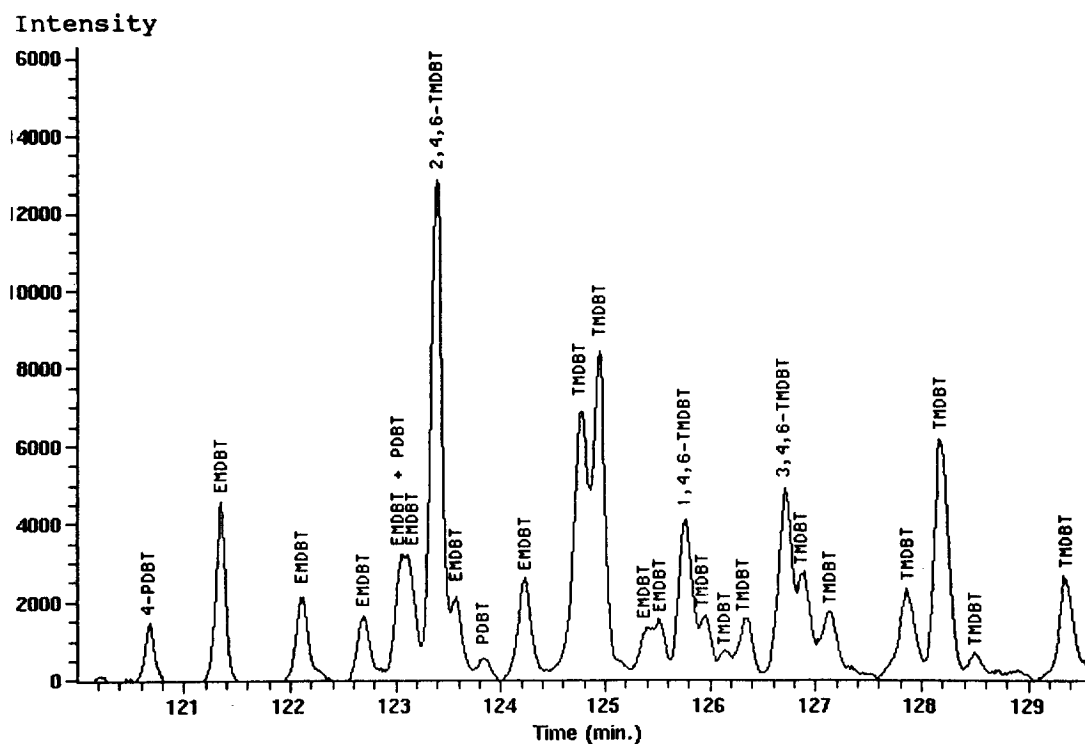


Fig. 15. Part of the single ion chromatogram (m/z 226) of the LCO showing the peaks corresponding to propyldibenzothiophene (PDBT), ethylmethylidibenzothiophene (EMDBT) and the trimethylidibenzothiophene (TMDBT) isomers.

with respect to the other C_3 -DBTs. The distribution of sulphur within the C_3 -DBT subfamily is shown in Table 6. The distribution of sulphur within the C_3 -BT subfamily (Table 4) is similar. Phenanthro[4,5-*bcd*]thiophene elutes together with the C_3 -DBTs. The C_4 -DBTs are only present in small amounts in this boiling fraction of the effluent of the catalytic cracking unit.

A listing of the retention times, obtained on the HP-PONA column, of 180 sulphur components, from which more than 70 are fully identified, and the corresponding ppm (w/w) of sulphur is given in

Table 6
Distribution of sulphur within the C_3 -DBT isomers

Type of substituent(s)	Sulphur (%)
Trimethyl	66.5
Ethylmethyl + isopropyl	27.7
Propyl	5.8

Table 7. The chromatograms obtained on the non-polar columns of the GC-AED and GC-MS systems were compared to determine the ppm (w/w) S of each component. In case of peak overlap on the GC-AED sulphur chromatogram, the determination of the ppm (w/w) S was restricted to a group of components.

Acknowledgments

This work was partly funded by the European Commission under the Joule program contract No. JOU2-0121. G.A.D. is also grateful for a contribution from the Center of Excellence Grant awarded to the Laboratorium voor Petrochemische Techniek by the Belgian Ministry of Science. Fina Research and Total kindly provided several samples and Esso Belgium provided financial support.

Table 7

Retention time table for the sulphur components, obtained on the HP-PONA column under the conditions described for this column in Section 2

t_R (min)	Subfamily	Type of substituent	Component	Sulphur (ppm, w/w)
62.35	C ₀ -BT	None	Benzothiophene	194
67.41	C ₀ -DHBT	None	Dihydrobenzothiophene	25
69.44	C ₁ -DHBT	Methyl		12
70.63	C ₁ -BT	Methyl	7-Methylbenzothiophene	256
71.16	C ₁ -DHBT	Methyl		}266
71.34	C ₁ -BT	Methyl	2-Methylbenzothiophene	
71.85	C ₁ -BT	Methyl	6-Methylbenzothiophene	}308
71.93	C ₁ -BT	Methyl	5-Methylbenzothiophene	
72.33	C ₁ -BT	Methyl	4-Methylbenzothiophene	}485
72.33	C ₁ -BT	Methyl	3-Methylbenzothiophene	
74.63	C ₁ -DHBT	Methyl		25
75.90	C ₂ -DHBT			}47
76.02	C ₁ -DHBT	Methyl		
76.18	C ₁ -DHBT	Methyl		
77.32	C ₁ -DHBT	Methyl		26
77.45	C ₂ -BT	Ethyl	7-Ethylbenzothiophene	62
77.60	C ₂ -DHBT			}27
77.74	C ₂ -DHBT			
78.4	C ₂ -BT	Dimethyl	2,7-Dimethylbenzothiophene	283
78.7	C ₂ -BT	Ethyl	2-Ethylbenzothiophene	}279
78.8	C ₂ -BT	Ethyl		
78.95	C ₂ -BT	Dimethyl	5,7-Dimethylbenzothiophene	
79.1	C ₂ -BT	Ethyl		
79.25	C ₂ -BT	Ethyl		
79.5	C ₂ -BT	Dimethyl	2,6-Dimethylbenzothiophene	}889
79.5	C ₁ -BT	Dimethyl	2,5-Dimethylbenzothiophene	
79.53	C ₂ -BT	Dimethyl	4,7-Dimethylbenzothiophene	
79.8	C ₂ -BT	Dimethyl	3,7-Dimethylbenzothiophene	
80.1	C ₂ -BT	Dimethyl	2,4-Dimethylbenzothiophene	168
80.35	C ₂ -BT	Dimethyl	4,6-Dimethylbenzothiophene	91
80.53	C ₂ -BT	Dimethyl	3,5-Dimethylbenzothiophene	}308
80.6	C ₂ -BT	Dimethyl	3,6-Dimethylbenzothiophene	
81.15	C ₂ -BT	Dimethyl	2,3-Dimethylbenzothiophene	}325
81.25	C ₂ -BT	Dimethyl	6,7-Dimethylbenzothiophene	
82.24	C ₂ -BT	Dimethyl	5,6-Dimethylbenzothiophene	41
82.29	C ₂ -DHBT			}61
82.72	C ₂ -BT	Dimethyl	4,5-Dimethylbenzothiophene	
82.95	C ₂ -DHBT			}<10
83.05	C ₂ -DHBT			
83.15	C ₃ -DHBT			}37
83.35	C ₂ -BT	Dimethyl	3,4-Dimethylbenzothiophene	
83.51	C ₃ -BT	Propyl	7-Propylbenzothiophene	}44
83.6	C ₂ -DHBT			
84.05	C ₃ -DHBT			14
84.38	C ₃ -BT	Ethylmethyl		64
84.63	C ₃ -BT	Ethylmethyl		}48
84.82	C ₃ -BT	Propyl	2-Propylbenzothiophene	
85.03	C ₃ -BT	Ethylmethyl		}307
85.04	C ₃ -BT	Propyl		

Table 7 (continued)

t_R (min)	Subfamily	Type of substituent	Component	Sulphur (ppm, w/w)
85.16	C ₃ -BT	Propyl		
85.2	C ₃ -BT	Ethylmethyl		
85.25	C ₃ -BT	Ethylmethyl		
85.30	C ₃ -BT	Ethylmethyl		
85.5	C ₃ -BT	Ethylmethyl		
85.53	C ₃ -BT	Propyl		
85.68	C ₃ -BT	Propyl		}188
85.79	C ₃ -BT	Trimethyl	2,5,7-Trimethylbenzothiophene	
86.16	C ₃ -BT	Ethylmethyl		}335
86.31	C ₃ -BT	Trimethyl	2,4,7-Trimethylbenzothiophene	
86.43	C ₃ -BT	Ethylmethyl		
86.50	C ₃ -BT	Ethylmethyl		
86.57	C ₃ -BT	Ethylmethyl		
86.74	C ₃ -BT	Ethylmethyl		
86.80	C ₃ -BT	Trimethyl	3,5,7-Trimethylbenzothiophene	202
87.05	C ₃ -BT	Ethylmethyl		}318
87.15	C ₃ -BT	Trimethyl	2,4,6-Trimethylbenzothiophene	
87.3	C ₃ -BT	Trimethyl	2,3,7-Trimethylbenzothiophene	
87.9	C ₃ -BT	Trimethyl	2,6,7-Trimethylbenzothiophene	59
88.38	C ₃ -BT	Trimethyl	2,3,5-Trimethylbenzothiophene	}249
88.38	C ₃ -BT	Trimethyl	2,3,6-Trimethylbenzothiophene	
88.75	C ₃ -BT	Trimethyl		}163
88.85	C ₃ -BT	Trimethyl		
89.0	C ₃ -BT	Trimethyl		
89.1	C ₃ -BT	Trimethyl		
89.5	C ₃ -BT	Trimethyl		39
89.85	C ₃ -BT	Trimethyl	3,5,6-Trimethylbenzothiophene	}44
89.90	C ₄ -BT			
90.19	C ₄ -BT			}101
90.24	C ₄ -BT			
90.42	C ₃ -BT	Trimethyl	3,4,6-Trimethylbenzothiophene	
90.45	C ₄ -BT			
90.62	C ₄ -BT			
90.66	C ₃ -BT	Trimethyl	5,6,7-Trimethylbenzothiophene	
90.76	C ₄ -BT	Methylpropyl		
90.92	C ₄ -BT	Methylpropyl		}66
90.96	C ₄ -BT	Dimethylethyl		
91.08	C ₄ -BT	Methylpropyl		
91.17	C ₃ -BT	Trimethyl	2,3,4-Trimethylbenzothiophene	}45
91.29	C ₄ -BT	Ethylidimethyl		
91.46	C ₄ -BT			
91.50	C ₄ -BT	Ethylidimethyl		
91.68	C ₄ -BT	Diethyl		54
91.94	C ₄ -BT	Ethylidimethyl		}270
92.07	C ₄ -BT	Methylpropyl		
92.14	C ₃ -BT	Trimethyl		
92.15	C ₄ -BT			
92.24	C ₃ -BT	Trimethyl		

(Continued overleaf)

Table 7 (continued)

t_R (min)	Subfamily	Type of substituent	Component	Sulphur (ppm, w/w)
92.33	C ₄ -BT	Diethyl		
92.44	C ₄ -BT			
92.65	C ₄ -BT	Ethyldimethyl		}101
92.74	C ₄ -BT	Ethyldimethyl		
92.86	C ₄ -BT	Methylpropyl		20
92.95	C ₄ -BT	Ethyldimethyl		}41
93.06	C ₄ -BT	EthylDimethyl		
93.45	C ₄ -BT	Diethyl		}47
93.53	C ₄ -BT			
93.95	C ₄ -BT	Tetramethyl	2,3,5,7-Tetramethylbenzothiophene	}128
94.04	C ₄ -BT	Ethyldimethyl		
94.12	C ₄ -BT	Ethyldimethyl		
94.36	C ₄ -BT	Ethyldimethyl		29
94.46	C ₄ -BT	EthylDimethyl		18
94.62	C ₄ -BT	Diethyl		<10
94.8	C ₄ -BT	Tetramethyl		31
94.95	C ₄ -BT	Tetramethyl		27
95.15	C ₄ -BT			}36
95.25	C ₄ -BT			
96.01	C ₄ -BT	Tetramethyl	2,3,6,7-Tetramethylbenzothiophene	61
96.75	C ₄ -BT			}88
96.93	C ₄ -BT	Tetramethyl	2,5,6,7-Tetramethylbenzothiophene	
100.67	C ₀ -DBT	None	Dibenzothiophene	422
102.09	C ₀ -NT	None	Naphtho[2,1- <i>b</i>]thiophene	59
103.81	C ₀ -NT	None	Naphtho[2,3- <i>b</i>]thiophene	<10
107.54	C ₁ -DBT	Methyl	4-Methyldibenzothiophene	440
108.1	C ₁ -NT	Methyl		}81
108.4	C ₁ -NT	Methyl		
108.86	C ₁ -DBT	Methyl	3-Methyldibenzothiophene	}511
108.86	C ₁ -DBT	Methyl	2-Methyldibenzothiophene	
109.3	C ₁ -NT	Methyl		50
109.6	C ₁ -NT	Methyl		31
109.9	C ₁ -NT	Methyl		33
110.3	C ₁ -DBT	Methyl	1-Methyldibenzothiophene	}140
110.45	C ₁ -NT	Methyl		
111.6	C ₁ -NT	Methyl		
113.98	C ₂ -DBT	Ethyl	4-Ethyldibenzothiophene	81
114.76	C ₂ -DBT	Dimethyl	4,6-Dimethyldibenzothiophene	153
115.3	C ₂ -DBT	Ethyl	2-Ethyldibenzothiophene	29
115.85	C ₂ -DBT	Dimethyl	2,4-Dimethyldibenzothiophene	188
116.20	C ₂ -DBT	Dimethyl		}420
116.32	C ₂ -DBT	Dimethyl		
116.4	C ₂ -DBT	Ethyl	1-Ethyldibenzothiophene	
116.6	C ₂ -NT			
117.55	C ₂ -DBT	Dimethyl	2,7-Dimethyldibenzothiophene	}327
117.55	C ₂ -DBT	Dimethyl	2,8-Dimethyldibenzothiophene	
117.55	C ₂ -DBT	Dimethyl	3,7-Dimethyldibenzothiophene	

Table 7 (continued)

t_R (min)	Subfamily	Type of substituent	Component	Sulphur (ppm, w/w)
117.9	C ₂ -DBT	Dimethyl	1,4-Dimethyldibenzothiophene	}64
118.0	C ₂ -DBT	Dimethyl	1,6-Dimethyldibenzothiophene	
118.15	C ₂ -DBT	Dimethyl		
118.5	C ₂ -NT			}207
118.6	C ₂ -NT			
118.85	C ₂ -DBT	Dimethyl	1,3-Dimethyldibenzothiophene	
119.0	C ₂ -DBT	Dimethyl	3,4-Dimethyldibenzothiophene	
119.2	C ₂ -DBT	Dimethyl	1,7-Dimethyldibenzothiophene	
120.25	C ₂ -DBT	Dimethyl	2,3-Dimethyldibenzothiophene	64
120.65	C ₃ -DBT	Propyl	4-Propyldibenzothiophene	29
121.00	C ₂ -DBT	Dimethyl	1,2-Dimethyldibenzothiophene	<10
121.32	C ₃ -DBT	Ethylmethyl	4-Ethyl-6-Methyldibenzothiophene	69
122.10	C ₃ -DBT	Ethylmethyl		32
122.68	C ₃ -DBT	Ethylmethyl		}87
123.04	C ₃ -DBT	Propyl		
123.05	C ₃ -DBT	Ethylmethyl		
123.11	C ₃ -DBT	Ethylmethyl		
123.38	C ₃ -DBT	Trimethyl	2,4,6-Trimethyldibenzothiophene	}139
123.56	C ₃ -DBT	Ethylmethyl		
123.82	C ₃ -DBT	Propyl		
124.22	C ₃ -DBT	Ethylmethyl		}35
124.45	C ₀ -FT	None	Phenanthro[4,5- <i>bcd</i>]thiophene	
124.76	C ₃ -DBT	Trimethyl		}153
124.94	C ₃ -DBT	Trimethyl		
125.38	C ₃ -DBT	Ethylmethyl		}99
125.50	C ₃ -DBT	Ethylmethyl		
125.76	C ₃ -DBT	Trimethyl	1,4,6-Trimethyldibenzothiophene	
125.94	C ₃ -DBT	Trimethyl		
126.15	C ₃ -DBT	Trimethyl		<10
126.33	C ₃ -DBT	Trimethyl		}66
126.72	C ₃ -DBT	Trimethyl	3,4,6-Trimethyldibenzothiophene	
126.85	C ₃ -DBT	Trimethyl		24
127.13	C ₃ -DBT	Trimethyl		36
127.86	C ₃ -DBT	Trimethyl		}112
128.19	C ₃ -DBT	Trimethyl		
128.48	C ₃ -DBT	Trimethyl		<10
129.36	C ₃ -DBT	Trimethyl		59

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