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Determination of sulfur-containing compounds in diesel oils by comprehensive two-dimensional gas chromatography with a sulfur chemiluminescence detector

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Abstract

This article reports an analytical method for separating, identifying and quantitating sulfur-containing compounds and their groups in diesel oils (170–400 °C) using comprehensive two-dimensional gas chromatography coupled with a sulfur chemiluminescence detector. The identification of target compounds and their groups was based on standard substances, the group separation feature and tile-effect of comprehensive two-dimensional gas chromatography. The quantitative analysis on major sulfur compounds and total sulfur was carried out based on the linear response of sulfur chemiluminescence detector and the internal standards method. The results of total sulfur determination in the samples were compared with those from ASTM D 4294 standard method, the R.S.D. percentage were <6.02%, correctness of this method can meet the industrial requirement. To the end, the method developed was used to investigate the sulfur-containing compounds in different diesel oils, the result shows that the distribution of sulfur-containing compounds in diesel oils from different process units are apparently different. The sulfur compounds in fluid catalytic cracking (FCC), residuum fluid catalytic cracking (RFCC) diesel oils mainly exist in the form of alkyl-substituted dibenzothiophenes that add up to about 40–50% of the total sulfur, while this number is only 6–8 and 20–28% in visbreaking (VB) and delayed-coking (DC) diesel oils, respectively.

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1. Introduction

The implementation of the revised law of clean air in USA has brought stricter limitation on sulfur

content in petroleum products. The sulfur contents in new formula gasoline and clean diesel oil are required to be no higher than 100 and 500 mg/kg, respectively. Meanwhile, this has exerted a great influence on other areas, and environment protection authorities in many countries are beginning to make strict regulations on sulfur content in gasoline and diesel oil correspondingly. The increasingly stringent limitation

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on SO_x emission is imposing an urgent requirement on refineries to reduce the sulfur content in the fuels they produce. However, a common problem that faces the refineries around the world is that the crude oils are getting worse and heavier with sulfur content getting higher, which results in higher sulfur level in both straight-run and secondary-processed diesel oil. Therefore, deep desulfurization of diesel oil will remain one of the several major problems for the refining industry. Detailed information on the distribution of sulfur containing compounds in different kind of diesel oils can serve as an important basis for improving desulfurization technology. But due to the complexity of sulfur compound isomers, people have to adopt laborious and time-consuming combination technologies [1–3] in the analysis of diesel oil. So there is an urgent need for a method to quickly determine the distribution of sulfur containing compounds in diesel oil.

Comprehensive two-dimensional gas chromatography (GC \times GC) [4–13] is a hyphenated technique in which two different chromatographic separation mechanisms act in series and greatly improve the result of component separation and identification [14–16]. The system contains a jet-cool modulator between the two chromatographic columns with different selectivity, and all the effluents out of the second column enter the detector. GC \times GC has been successfully used to separate or analyze oxygenates, benzene, toluene, ethylbenzene, xylenes (BTEXs) and other heavier aromatics in gasoline [17–21]. It has also been applied to forensic fingerprinting of a marine diesel fuel spill [22] and separation and identification of biomarkers in petroleum samples [23–25].

SCD is a type of detector that responds specially to the sulfur contained in the samples. It has many advantages [26–30] including a linear ($>10^5$) and equimolar response to all sulfur compounds, little quenching effects of hydrocarbons, low picogram detection level, excellent sensitivity (<0.5 pg S/s) and by far the best selectivity ($S/C > 10^7$). In 1997, Beens and Tijssen [2] used a LC-GC-SCD hyphenated system and identified the various groups of sulfur compounds, such as thiols + sulfides + thiophenes, benzothiophenes, dibenzothiophenes and benzonaphthothiophenes in middle petroleum distillation fractions (boiling range, 150–450 °C). Disanzo [31] successfully separated

and quantified sulfur compounds in a new formula gasoline sample with a limit of detection of 0.05 $\mu\text{g/g}$ with SCD.

To develop a new method that can achieve important sulfur compounds and group separation in different kind of diesel oils (170–400 °C) with one direct injection, we planned to take advantage of the coupling technique of GC \times GC and SCD with optimized column system and operation conditions. Based on the linear response of the sulfur chemiluminescence detector, quantification of major sulfur compounds and their groups in diesel oils from different process units, i.e. crude distillation, fluid catalytic cracking (FCC), residuum fluid catalytic cracking (RFCC), visbreaking (VB) and delayed-coking (DC), was achieved by internal standard method. The results of total sulfur obtained in the study were consistent with those from ASTM D-4294 method (standard test method for sulfur in petroleum and petroleum products by energy-dispersive X-ray fluorescence spectrometry) [32]. In the meantime, dibenzothiophene levels in diesel oils from different original crude oils and different units were compared.

2. Experimental

2.1. Instrumentation

The comprehensive two-dimensional gas chromatographic system consists of an HP 6890 GC (Hewlett-Packard, Wilmington, DE) fitted with a jet-cooled thermal modulator assembly (Zoex Corp., Lincoln, NE). Description of the theoretic and operational characteristics of the jet-cooled thermal modulator is available [14,15]. The collected data are detected, analyzed and integrally quantitated by the GC \times GC special software “GC Image” (Zoex Corp.).

Sulfur Chemiluminescence Detector used was Sievers 355B with “flameless burner” at 800 °C (Sievers Inc., Boulder, CO, USA) by using ozone excitation of sulfur oxides and the PMT detection filtered at wavelengths between 260 and 480 nm [26,33]. The data acquisition rate of the SCD is 100 Hz. The peak width in the second dimension of the GC \times GC–SCD is 0.8–1.2 s, which is much wider than that (0.2–0.3 s) in the GC \times GC–FID because of a bigger cell volume in SCD detector.

Table 1
Operation conditions of GC × GC system

Columns	First column 6.0 m × 0.18 mm × 3.5 μm VB-5; second column 2.0 m × 0.1 mm × 0.1 μm 007-17
Injection	0.5 μl, split 100:1; 340 °C
Detector	SCD, 800 °C
Column oven	30–280 °C, 2 °C/min
Carrier gas	He, 99.999% constant flow, 50 cm/s

In the experiment, a non-polar dimethylpolysiloxane stationary phase provides volatility-based selectivity in the first dimension. A 50% phenyl–methylpolysiloxane phase provides polarity-based selectivity in the second dimension. This phase combination is effective for separating sulfur components in petroleum samples. Table 1 gives the GC × GC chromatographic column system and its operational conditions.

2.2. Materials

The standard sulfur compounds were obtained from Sigma (New Jersey, USA), Fluka (Germany), Aldrich (Germany) and Tokyo Kasei Kogyo Co. Ltd. Internal standard was 3-chlorothiophene from ACROS Organics (New Jersey, USA). All 30 standard sulfur compounds were GC-reagent grade (purity ≥ 98%) except 4,6-dimethyl dibenzothiophene (4,6-DMeDBT) 95%, 4-methyl-dibenzothiophene 96%, 2-ethyl thiophene 97% were analytical-reagent grade.

Two type of diesel oils were studied, i.e. diesel oils as feed to hydrofining units (straight-run diesel oil, FCC diesel oil, RFCC diesel oil, VB diesel oil, DC diesel oil) and hydrofined diesel oils. Their boiling ranges were 170–400 °C.

To analyze the sample, 30 μl of solution of internal standard with known concentration is added into 970 μl of petroleum sample, and vortex well. The mixture is analyzed under given conditions. The sulfur compounds and groups are determined based on standard substances and the separation mechanism of sulfur-containing components in the comprehensive two-dimensional gas chromatography. The collected data are detected, analyzed and integral quantitated by the GC × GC special software “GC Image” of Zoex Corp.

3. Results and discussion

3.1. Study on group separation, identification and quantification of sulfur-containing compounds with GC × GC–SCD

In the GC × GC system, columns 1 and 2 are non-polar and polar, respectively. With a linear temperature increase program, cross information between the two dimensions can be zero, which leads to a maximized peak capacity [14,15] (equal to the product of that of the two dimensions). In this paper, five column sets are evaluated (Table 2). After comparing the chromatograms of the five set of column systems, it was found that number 5 was the best one for the analysis of diesel oil. Therefore, the operation conditions for column system number 5 were optimized (see Table 1). Fig. 1 is a comprehensive two-dimensional gas chromatogram of a known mixture of standard substances containing thiols, sulfides, thiophenes, benzothiophenes, dibenzothiophenes and benzonaphthothiophenes given in Table 3. In the graph, we can

Table 2
Capillary column systems evaluated for analysis of diesel oils^a

Number	First column	Second column
1	007-1: 60 m × 0.25 mm × 1.0 μm	DB-17ht: 2.2 m × 0.1 mm × 0.1 μm
2	DB-Petro: 50 m × 0.2 mm × 0.5 μm	OV-17: 1.0 m × 0.1 mm × 0.1 μm
3	007-5MS: 10 m × 0.25 mm × 0.25 μm	DB-17ht: 0.8 m × 0.1 mm × 0.1 μm
4	007-1: 4 m × 0.1 mm × 3.5 μm	DB-17ht: 2 m × 0.1 mm × 0.1 μm
5	VB-5: 6 m × 0.1 mm × 3.5 μm	007-17: 2 m × 0.1 mm × 0.1 μm

^a 007-1 (Quadrex, USA), a 100% dimethylpolysiloxane, 007-5 MS (Quadrex, USA), silphenylene polysiloxane, 007-17 (Quadrex, USA), a 50% phenyl–methylpolysiloxane, DB-Petro (J&W Scientific, Folsom, CA, USA), a 100% dimethylpolysiloxane, DB-17ht (J&W Scientific, Folsom, CA, USA), a 50% phenyl–methylpolysiloxane, OV-17 (J&W Scientific, Folsom, CA, USA), a 50% phenyl–methylpolysiloxane, VB-5 (Valco Instruments Co., USA), a 5% phenyl, 95% dimethylpolysiloxane.

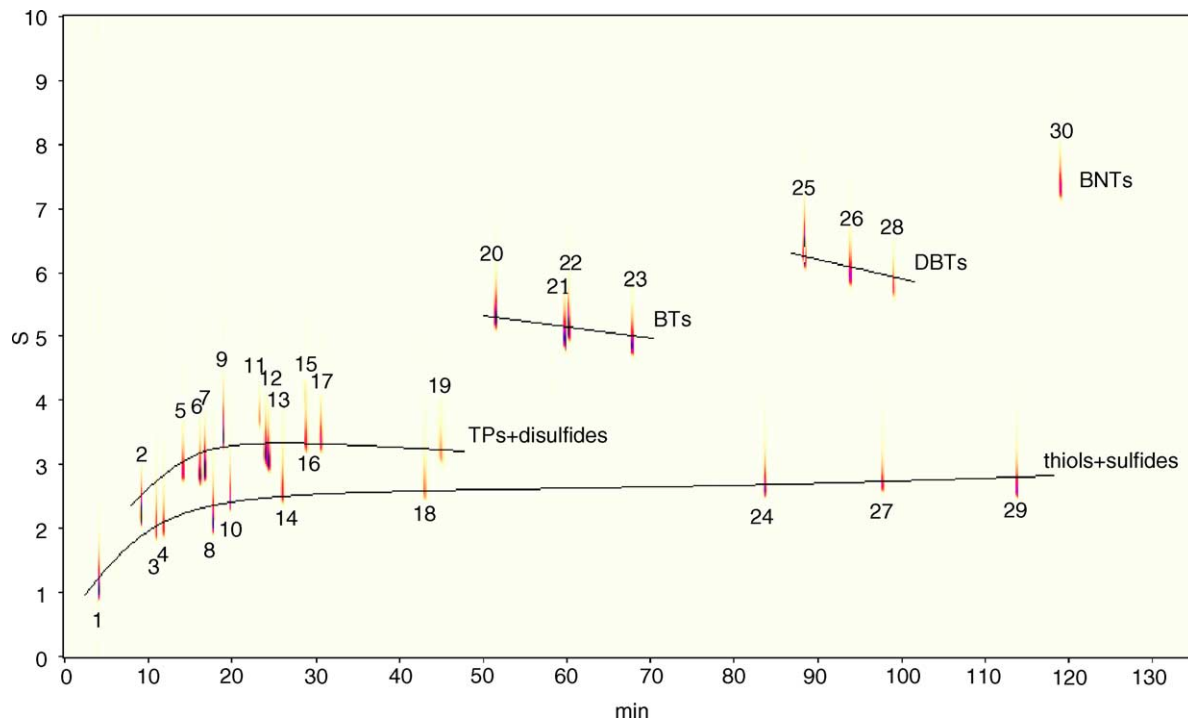


Fig. 1. Chromatogram of standard substances obtained by GC \times GC–SCD. The system works with different separation mechanisms in two dimensions and linear temperature increase programming. Orthogonal separation is achieved. The X-axis of the GC \times GC chromatogram is the volatility-based retention time (min). The Y-axis is the polarity-based retention time (s). The Z-axis is the SCD response. The marked peaks of sulfur compounds are those identified with standard substances listed in Table 3. The operational conditions are given in Table 1. In the figure, TPs: thiophenes, BTs: benzothiophenes, DBTs: dibenzothiophenes, BNTs: benzonaphthothiophenes.

clearly see that thiols and sulfides cluster in an almost straight line, next to which are disulfides + thiophenes (TPs), benzothiophenes (BTs), dibenzothiophenes (DBTs) and benzonaphthothiophenes (BNTs) in order, each group forming a line almost parallel to one another. Therefore, orthogonal separation is achieved in the system and the spaces of the two dimensions are made full use of.

One-dimensional chromatography is based only on the retention time on the X-axis, which requires a very high column efficiency and stability in retention time of substances to avoid errors of the identification. But in the GC \times GC two-dimensional analysis, a substance is determined by both X- and Y-axis, and this makes it easier and more reliable to be identified. The thirty kinds of known sulfur-containing compounds given in Table 3 were analyzed for six times and their positions in the graph were determined by the retention times on first dimension (min, denoted by 1t_R) and second

dimension (s, denoted by 2t_R). The R.S.D. of 1t_R and 2t_R are given in Table 3, their maximum R.S.D. were 0.93 and 4.25%, respectively.

The GC \times GC chromatogram of a FCC diesel oil is given in Fig. 2. Based on the qualitative results of standard sample in Fig. 1 and the array rule of the groups in order of polarity in the two-dimensional graph, we can easily separate the graph into the four zones representing thiols + sulfides + disulfides + TPs, BTs, DBTs and BNTs, respectively.

In Fig. 2, the sulfur compounds marked with peak number are the same as those listed in Table 3. We can see that isomers with same alkyls come in biases or get together while those with different alkyls are distributed like tiles (domino effect of tiles) [14,15]. Based on this domino effect, we can identify individual isomers from C1-BTs (benzothiophenes with a hydrogen atom substituted by a methyl) to C2-BNTs (benzonaphthothiophenes with a hydrogen atom substituted

Table 3

Thirty peaks identified in Fig. 1 using standard sulfur-containing compounds and retention time reproducibility from six replicative analyses with GC \times GC

Number	Compound	Boiling point (°C)	¹ t _R (min)	R.S.D. ¹ (%)	² t _R (s)	R.S.D. ² (%)
1	2-Propanethiol (iPrSH)	52.6	3.98	0.9	1.08	4.1
2	Thiophene (TP)	84.2	9.00	0.0	2.24	2.5
3	Diethyl sulfide (DES)	92.0	10.80	0.0	1.98	2.3
4	<i>n</i> -Butanethiol (<i>n</i> -BuSH)	98.5	11.72	0.4	1.98	2.3
5	Dimethyl disulfide (DMDS)	109.7	13.98	0.3	2.92	1.5
6	2-Methyl thiophene (2-MeT)	113	16.12	0.7	2.86	1.9
7	3-Methyl thiophene (3-MeT)	–	16.70	0.0	2.94	1.9
8	<i>iso</i> -Propyl sulfide (DiPrS)	–	17.66	0.5	2.14	2.6
9	Tetra-hydro thiophene (THT)	119.0	18.86	0.5	3.48	1.3
10	<i>n</i> -Amyl thiol (<i>n</i> -AmSH)	126	19.70	0.7	2.44	2.2
11	3-Chlorothiophene (3-CIT)	–	23.16	0.4	3.72	1.2
12	2-Ethyl thiophene (2-EtT)	–	23.90	0.0	3.20	2.2
13	2,5-Dimethyl thiophene (2,5-DiMeT)	–	24.32	0.5	3.10	2.3
14	<i>n</i> -Propyl sulfide (DnPrS)	142	25.92	0.2	2.58	4.3
15	2-Bromothiophene (2-BrT)	–	28.74	0.3	3.38	1.3
16	Diethyl disulfide (DEDS)	154.0	28.74	0.3	4.04	1.4
17	Cyclohexane thiol (CheSH)	159	30.48	0.2	3.38	1.3
18	<i>n</i> -Butyl sulfide (DnBuS)	188	42.74	0.4	2.66	2.1
19	Di- <i>n</i> -propyl disulfide (DnPrDS)	195	44.64	0.6	3.22	1.4
20	Benzo[<i>b</i>]thiophene (BT)	221	51.58	0.4	5.28	1.6
21	5-Methyl benzothiophene (5-MeBT)	–	59.72	0.1	5.02	2.2
22	3-Methyl benzothiophene (3-MeBT)	–	60.20	0.1	5.14	1.1
23	3,5-Dimethyl benzothiophene (3,5-DmeBT)	–	67.82	0.1	4.88	1.7
24	C ₇ -Sulfide	–	83.62	0.2	2.68	3.1
25	Dibenzothiophene (DBT)	–	88.36	0.2	6.34	0.9
26	4-Methyl benzothiophene (4-MeDBT)	–	93.80	0.0	6.02	1.4
27	C ₁₆ -Mercaptan	–	97.72	0.2	2.74	3.3
28	4,6-Dimethyl dibenzothiophene (4,6-DMeDBT)	–	99.02	0.1	5.76	1.6
29	C ₁₀ -Sulfide	–	113.84	0.2	2.68	3.1
30	Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]thiophene (B[2,1]NT)	–	118.96	0.1	7.56	2.7

¹t_R and ²t_R are retention times on first and second dimensions, respectively. R.S.D.¹ and R.S.D.² are their relative standard deviations, respectively.

by an ethyl or two hydrogen atoms substituted by two methyls), etc. in Fig. 2. With the professional software GC Image of Zoex Ltd., 1364 peaks were detected consisting of 192 peaks of thiols/sulfides, 280 peaks of disulfides/one-ring thiophenes, 132 peaks of 4-H-thiophenes, 473 peaks of benzothiophenes, 245 peaks of dibenzothiophenes and 42 peaks of benzonothiophenes, from bottom to top. It is impossible to obtain so many peaks from the traditional one-dimensional chromatography.

The concentration of a component is in direct ratio to the volume of its peak in comprehensive two-dimensional gas chromatography. Based on linear and equimolar response of SCD and 3-CIT as internal standard, the target sulfur compounds and groups

in diesel oils from crude distillation unit, FCC unit, RFCC unit, DC unit and VB unit are quantitated with one injection each under the above-stated conditions. The results obtained are listed in Tables 4–6 separately. Compared with those determined by ASTM D-4294 method (XRF), the R.S.D.% of total sulfur determination does not exceed 6.02%.

Based on this study, it can be known that different sulfur compound groups and important target sulfur compounds in a diesel oil sample can be separated and quantitated by using GC \times GC–SCD in one direct injection. It only takes 135 min to separate various sulfur compound groups contained in a diesel oil fraction (170–400 °C). In reverse, 2–3 days were required if LC–GC–SCD method was used [1].

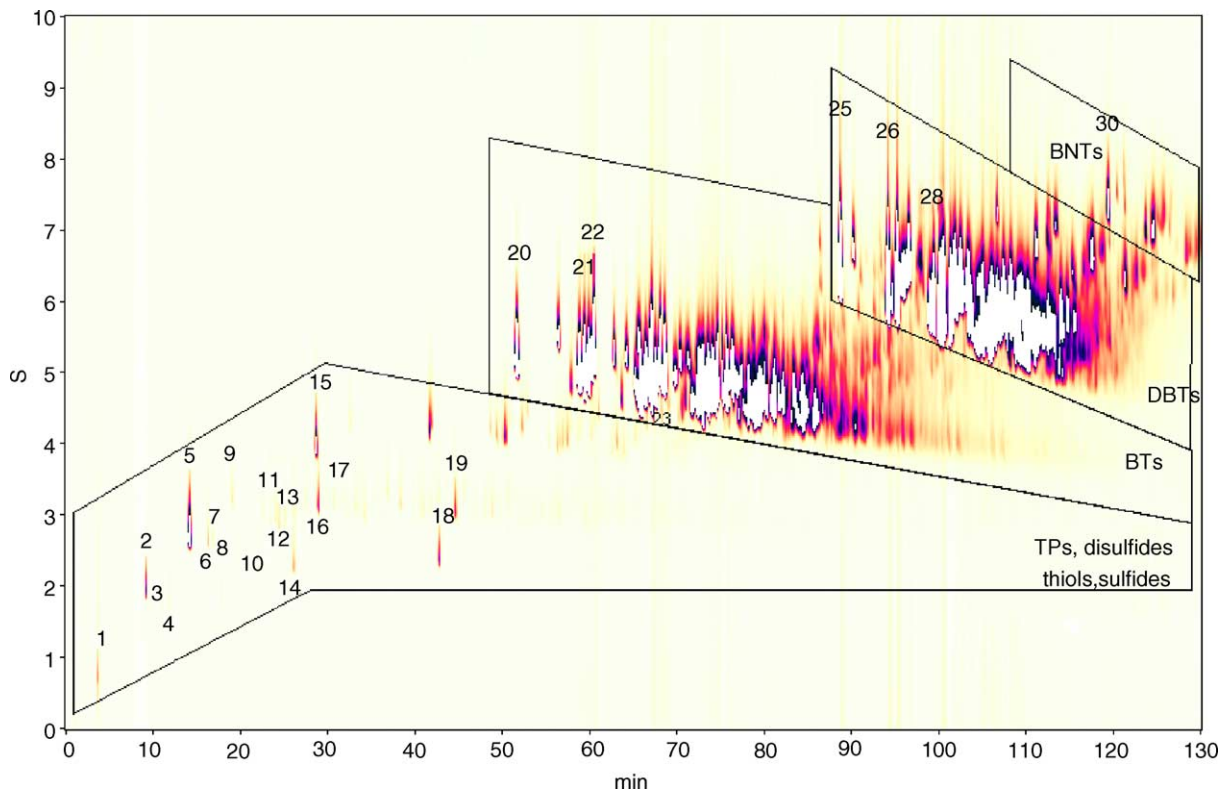


Fig. 2. Chromatogram of a FCC diesel oil sample obtained by GC \times GC–SCD. The peak zones from bottom to top on the Y-axis are thiols + sulfides, disulfides and one-ring thiophenes sulfurs (alkyl S + TPs), and two- (BTs), three- (DBTs), and four-ring (BNTs) aromatics sulfur heterocycles (PASHs), respectively. Others are the same as in Fig. 1.

3.2. Distribution of sulfur compounds in different kind of diesel oils

With the increasingly stringent emission standard for environmental protection, the hydrodesulfurization technology to remove the sulfur-containing compounds in oils is becoming more and more important. Dibenzothiophenes are a type of sulfur compounds that are very stable and difficult to remove through hydrodesulfurization process. In the study, distribution of sulfur compounds in different kind of diesel oils was analyzed by GC \times GC–SCD. It can be seen from Fig. 3 that there are significant differences in the distribution profiles of straight-run diesel oil, FCC diesel oil, RFCC diesel oil, delayed coker diesel oil, visbreaker diesel oil and hydrofined diesel oil. Table 4 lists the quantitative results of these samples. The proportion of dibenzothiophenes concentration

to total sulfur is 51.4, 54.0 and 28.5%, respectively, for straight-run diesel oils from three kind of crude oils (3A1-Cabinda, 3B1-Masila and 3A2-Banama), which indicates significant sulfur content differences in various crude oils.

As shown in Table 4, the dibenzothiophenes/total sulfur proportion in diesel oils from different secondary-process units varies largely. The proportion of diesel oil from FCC, RFCC, DC and VB is 52.8, 41.8, 20.5 and 6.5%, respectively, from which we can infer an order of proportion of dibenzothiophene/total sulfur: FCC diesel oil > RFCC diesel oil > DC diesel oil > VB diesel oil.

The proportion of dibenzothiophene to total sulfur in hydrofined diesel oil (HFU in Table 4) reaches as high as 84.2%, which indicates that dibenzothiophenes are the sulfur compounds most difficult to remove during the hydrofining process. In the FCC and RFCC

Table 4
Sulfur compound distribution in different diesel oils (all concentrations in mg/kg unless otherwise indicated)

Sulfur compound group	Stright run 3A1	Stright run 3B1	Stright run 3A2	FCC	RFCC	VB	DC	HFU
Crude oil origin	Cabinda	Masila	Banama	Masila Zafiro	Oman Kole	Duri	Duri	Diesel feed
DBTs	18.8	37.3	25.4	214.9	261.8	8.8	16.8	4.7
4-MeDBTs	60.6	71.9	78.3	199.6	291.7	19.0	24.9	43.3
2-MeDBTs	48.1	50.8	58.8	354.3	362.9	14.7	23.4	6.8
3-MeDBTs	1.5	1.2	0.9	56.3	97.9	9.3	21.2	0.2
1-MeDBTs	38.1	38.9	53.9	97.1	114.8	9.3	13.7	9.4
4-EtDBTs	21.1	15.4	28.6	49.7	51.2	10.7	9.7	8.9
4,6-DMeDBTs	52.5	38.0	83.0	116.5	133.2	23.8	17.4	35.1
Alkyl S + TPs	420	550	1000	220	210	2900	1000	28
Group BTs	1500	1900	2100	3500	6700	1900	1600	71
Group DBTs	2000	2900	1300	4400	5000	330	700	540
Group BNTs	44	20	130	140	7	–	61	4
Total S value	3900	5400	4500	8300	12000	5100	3400	650
Sulfur (XRF)	4200	5400	4600	8400	11300	5400	3700	600
R.S.D. (%)	4.4	0.3	1.8	0.8	3.8	3.8	6.0	5.3
DBTs/total S (%)	51.4	54.0	28.5	52.8	41.8	6.5	20.5	84.2

FCC was a mixture of vacuum gas oil (VGO) from Masila and Zafiro, RFCC was a mixture of vacuum distillation residuum from Oman and Kole, VB and DC feeds were vacuum distillation residuum from Duri crude oil. HFU was a hydrofined diesel oil. Alkyl S: thiols + sulfides + disulfides, TPs: thiophenes, BTs: benzothiophenes, DBTs: dibenzothiophenes, BNTs: benzonaphthothiophenes.

diesel oils, the content of 4-MeDBT and 4,6-DMeDBT with great concern exceeds 300 mg/kg in total. So, severe hydrofining conditions and excellent catalysts are needed at present to lower the sulfur content in FCC and RFCC diesel oils to meet the requirement for clean fuel.

Table 5 gives the quantitative results of sulfur-containing compounds in VB diesel oils and DC diesel oils of different crude oils (Djeno, Masila, Zafiro and

Duri). From this table, we can see that the sulfur compounds in VB diesel oils mainly exist in the form of thiols, sulfides, disulfides and one-ring thiophenes that account for about 50% of total sulfur, secondly in the form of two-ring benzothiophenes which amount to about 40%, while dibenzothiophenes only make up 6–8% of total sulfur.

In the DC diesel oils, the sulfur-containing compounds mainly exist as two-ring benzothiophenes

Table 5
Sulfur compound distribution in different VB and DC diesel oils (all concentrations in mg/kg unless otherwise indicated)

Sulfur compound group	VB1	VB2	VB3	VB4	DC1	DC2	DC3	DC4
Crude oil origin	Djeno	Masila	Zafiro	Duri	Djeno	Masila	Zafiro	Duri
Alkyl S ^a + TPs	2400	3700	2700	2900	890	1200	1000	1000
BTs	2100	3900	2900	1900	2100	3500	2000	1600
DBTs	300	680	480	330	1000	1900	1000	700
BNTs	–	–	–	–	160	390	220	61
Total S value	4800	8300	5900	5100	4200	7100	4300	3400
Alkyl S and TPs/total S (%)	50.0	44.7	46.3	56.5	21.5	17.5	23.4	29.8
BTs/total S (%)	43.6	47.1	45.5	36.9	49.9	49.9	47.4	47.9
DBTs/total S (%)	6.4	8.1	8.2	6.5	24.7	27.1	24.0	20.5
BNTs/total S (%)	–	–	–	–	3.9	5.5	5.2	1.8

^a VB1, VB2, VB3 and VB4 are the VB diesel oil, DC1, DC2, DC3 and DC4 are the DC diesel oil. Others are the same as in Table 4.

Table 6
Sulfur compound distribution in different FCC and RFCC diesel oils (all concentrations in mg/kg unless otherwise indicated)

Sulfur compounds group	FCC1	FCC2	FCC3	FCC4	RFCC1	RFCC2	RFCC3	RFCC4
Crude oil origin	Djeno	Masila	Zafiro	Duri	Djeno	Masila	Zafiro	Duri
Alkyl S ^a + TPs	220	180	130	160	210	210	180	130
BTs	3500	3500	2500	2900	6700	5500	5300	4500
DBTs	4400	2900	2400	2500	5000	3200	3700	3000
BNTs	140	490	500	450	7	570	240	330
Total S value	8300	7000	5500	6000	12000	9500	9400	8000
Alkyl S and TPs/total S	2.7	2.6	2.3	2.7	1.7	2.3	2.0	1.7
BTs/total S (%)	47.9	49.3	45.9	48.1	56.4	58.0	56.1	56.4
DBTs/total S (%)	42.8	41.2	42.8	41.6	40.8	38.7	39.4	37.8
BNTs/total S (%)	6.6	7.0	9.0	7.6	1.1	1.0	2.5	4.2

^a FCC1, FCC2, FCC3 and FCC4 are the FCC diesel oil, RFCC1, RFCC2, RFCC3 and RFCC4 are RFCC diesel oil. Others are the same as in Table 4.

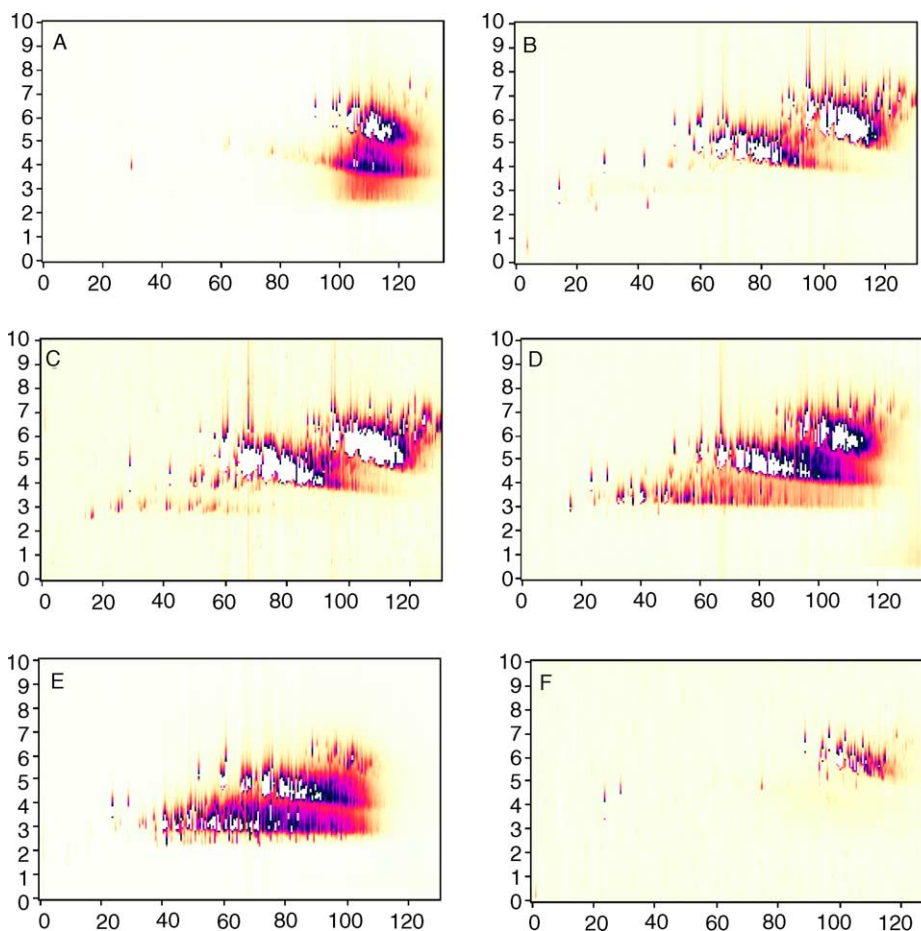


Fig. 3. Chromatograms of six different diesel oil samples obtained by GC × GC–SCD. Sample: (A) straight-run diesel oil; (B) FCC diesel oil; (C) RFCC diesel oil; (D) delayed coker diesel oil; (E) visbreaker diesel oil; (F) hydrofined diesel oil.

(~48%), followed by thiols, sulfides, disulfides and one-ring thiophenes that amount to 18–30% of total sulfur. DBTs make up 20–27% and BNTs about 2–5.5%, respectively.

The distribution results of sulfur-containing compounds in FCC and RFCC diesel oils of different crude oils (Djeno, Masila, Zafiro and Duri) are listed in Table 6. As we can see, the sulfur compounds in FCC and RFCC diesel oils largely exist in the form of BTs and DBTs, which account for 90% of the total sulfur in FCC diesel oil and 95% in RFCC diesel oil separately, while thiols, sulfides, disulfides, one-ring thiophenes and BNTs only make up 5–10% in total.

From Tables 5 and 6, we can draw the conclusion that there are significant differences in distribution of sulfur-containing compounds in diesel oils from different secondary-processed units, while the type (or origin) of crude oils essentially makes a few difference.

4. Conclusions

The coupling technique of comprehensive two-dimensional gas chromatography (GC × GC) and sulfur chemiluminescence detector (SCD) has noticeable advantages such as being easy in operation, quick and reliable when applied to group separation, identification and quantification of sulfur-containing compounds in diesel oil fractions. It only takes a direct injection to obtain all the desired information on important target sulfur compounds and their groups. The results obtained through the GC × GC–SCD analysis method can serve as basis for improving technology of diesel oil desulfurization, equipment selection and production optimization.

The result of this study shows that the distribution of sulfur compounds in diesel oil from different type of crude oils vary largely. Secondary-processed diesel oils have different sulfur distribution profiles depending on different process units, while the influence of the different type of crude oils upon the sulfur distribution is very small. Dibenzothiophenes are one of sulfur compounds most difficult to remove from diesel oil, in some cases catalysts and operation parameters should be selected based on the concentration of dibenzothiophenes instead of total sulfur for the desulfurization process evaluation.

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