

Comparison of Comprehensive Two-Dimensional Gas Chromatography Coupled with Sulfur-Chemiluminescence Detector to Standard Methods for Speciation of Sulfur-Containing Compounds in Middle Distillates

Rosario Ruiz-Guerrero¹, Colombe Vendeuvre¹, Didier Thiébaud², Fabrice Bertoncini^{1,*}, and Didier Espinat¹

¹Institut Français du Pétrole, BP3, 69390 Vernaison, France and ²ESPCI, Laboratoire Environnement et Chimie Analytique, 10 rue Vauquelin, 75235 Paris Cedex 05, France

Abstract

The monitoring of total sulfur content and speciation of individual sulfur-containing compounds in middle distillates is required for efficient catalyst selection and for a better understanding of the kinetics of the reactions involved in hydrotreatment processes. Owing to higher resolution power and enhanced sensitivity, comprehensive two-dimensional gas chromatography (GC×GC) hyphenated to sulfur chemiluminescence detection (SCD) has recently evolved as a powerful tool for improving characterization and identification of sulfur compounds. The aim of this paper is to compare quantitatively GC×GC–SCD and various other methods commonly employed in the petroleum industry, such as X-ray fluorescence, conventional GC–SCD, and high-resolution mass spectrometry, for total sulfur content determination and speciation analysis. Different samples of middle distillates have been analyzed to demonstrate the high potential and important advantages of GC×GC–SCD for innovative and quantitative analysis of sulfur-containing compounds. More accurate and detailed results for benzothiophenes and dibenzothiophenes are presented, showing that GC×GC–SCD should become, in the future, an essential tool for sulfur speciation analysis.

Introduction

The total sulfur content for refined products or for commercial fuels has recently been revised in European countries because the total sulfur content of gasoils or diesel oils should be lower than 10 ppm after 2005. Besides, sulfur compounds act as poison for catalysts as they can exhibit strong bonding with them. Thus, the content of sulfur in petroleum products requires careful monitoring of not only total sulfur but also speciation of

individual sulfur components for efficient catalyst selection and for a better understanding of the kinetics of hydrogenation processes. In this perspective, there is an urgent need for more efficient desulfuration technologies and, at the same time, for improved analytical techniques for the characterization of samples, keeping in mind the real interest, which is reducing the time-consuming sample work-up and cost.

Gas chromatography (GC) with a specific detector has been the preferred characterization technique for the detailed analysis of sulfur compounds in petroleum (1–3). Flame photometric detectors (4–6), atomic emission detectors (7,8), or sulfur chemiluminescence detectors (SCD) (9,10) have been widely used. The chemiluminescence detector has been particularly popular because of its linearity and equimolar response to all kind of sulfur compounds, as well as its excellent sensitivity ($< 0.5 \text{ pg S/s}$) and selectivity ($S/C = 10^7$) as the hydrocarbon interference is negligible. However, detailed separation cannot be obtained using conventional GC because of the lack of chromatographic resolution.

In recent papers, the use of comprehensive gas chromatography (GC×GC) has been reported with SCD (GC×GC–SCD) for the identification of various sulfur compounds in middle distillates from petroleum (11–14). The potential of GC×GC–SCD for the identification and distribution of sulfur compounds present in crude oils was evidenced: mercaptans, aliphatic sulfides, cyclic sulfides, and thiophenic compounds could be identified according to their organization by structure in the GC×GC–SCD chromatogram.

The aim of this paper is to determine the analytical features of GC×GC–SCD for performing the specifications of sulfur compounds in diesel samples. These data were compared with those obtained using standard methods for sulfur speciation [conventional GC–SCD, X-ray fluorescence (XRF), and high-resolution (HR) mass spectroscopy (MS)] in terms of total sulfur content and detailed analysis. Agreements and differences between these methods are evaluated and explained.

*Author to whom correspondence should be addressed: email Fabrice.Bertoncini@ifip.fr.

Two types of gasoils were studied: straight run (SR) gasoils, which were directly obtained from the atmospheric distillation of crude oils, and light cycle oils (LCO) produced in the fluid catalytic cracking (FCC) units.

Experimental

Instrumentation

A Sievers 355 (Sievers Inc., Boulder, CO) SCD equipped with a "flameless burner" was coupled to an HP 5890 Series II GC (Agilent Technologies, Massy, France) and was used for conventional GC–SCD analysis.

The GC×GC–SCD System consisted of an HP 6890 GC (Agilent Technologies) hyphenated to a Sievers 355 or Antek 7090S (Antek instruments, Houston, TX) SCD equipped with a ceramic flameless burner. A CO₂ dual jets modulator was built in-house as described by Beens (15) and installed in the GC. The acquisition rate was set at 50 Hz. After acquisition, data were exported as a CSV-file. Data handling, such as contour plotting, GC×GC peaks collection, retention time measurements, peak volume calculation, and integrated area report, were performed using an in-house routine under Matlab (The Mathworks, Natick, MA).

The column features and the operating conditions for conventional GC–SCD and GC×GC–SCD experiments are listed in Table I. A VG 70-SEQ MS (VG Analytical, Manchester, UK) was used for HRMS group-type analysis according to an internal method (16) developed by Castex et al. (17), derived from ASTM D2425. It was based on the representation of a hydrocarbon family by the sum of molecular ions and their fragments and on the calculation of the concentration from coefficient matrices depending on the average number of carbon atoms. The electron ionization source

conditions were set at 220°C, 200 μA, and 70 eV.

The total sulfur content was measured by XRF spectrometry and was carried out on a Philips PW 2510 according to ASTM method D2622.

Experimental samples

A synthetic mixture of standard sulfur compounds (STD1) was prepared using 46 chemical standards obtained from Chiron (Villeurbanne, France), Sigma-Aldrich (Lyon, France), and from Pr. Dr. J. Andersson (University of Munster, Munster, Germany) at concentrations ranging from 30 to 50 ppm (w/w) in toluene. The composition of this mixture is given in Table II.

A mixture of thiophene (TP), benzothiophene (BT), and dibenzothiophene (DBT) (10 ppm of sulfur each in toluene) was used as the external standard (STD2).

Different types of diesel oils were studied: diesel oils as feed for hydrocracking processes, such as LCOs from an FCC unit, SR diesel oils from the Middle East (SR1) and South America areas (SR2), and an SR sample obtained after hydrotreatment (SR-H). All these samples were provided by the IFP Research Center (IFP, Lyon, France). Their boiling point ranges were 170–400°C, and the samples were diluted in toluene so that the total sulfur content was between 100 to 400 ppm.

Results and Discussion

Choice of sulfur-selective detector

Because of the solute focusing/re-injection process involved in GC×GC using the cryogenic modulator, secondary peaks were as sharp as 120 ms at baseline (15). In order to minimize extra column effects to properly define these narrow peaks, the SCD should have a low time constant and a small internal volume. Acquisition should also be performed at a high rate. Flame ionization detection (FID) and time-of-flight MS easily met these criteria (18).

To evaluate the ability of SCD for implementation in GC×GC, the analysis of 2,3,5-trimethylthiophene (100 ppm of sulfur diluted in toluene) was performed using two different types of SCD, each SCD being tuned according to the recommendations of the manufacturers.

Because the burner of SCD operates under reduced pressure where as FID works at atmospheric pressure, the retention times of solutes depend on the detector used for the same chromatographic conditions. As it was not possible to hyphen simultaneously FID and SCD on our system, GC×GC–FID and GC×GC–SCD analyses were achieved independently (according to the conditions in Table I), and the chromatograms were overlaid for comparison.

Figures 1A and 1B show the chromatograms obtained without and with modulation using regular GC conditions, respectively. It is clear in Figure 1A that no difference can be observed according to the detector used for peak monitoring. The baseline peak widths have been measured to be approximately 11 s. Consequently, the detection time constant and internal volume, which are considered to be more important in the case of SCD compared with FID, suit the requirements of conventional GC for monitoring the elution peak. Obviously this is not the case for

Table I. Operating Conditions for GC×GC–SCD and GC–SCD Analysis

GC×GC–SCD	
1st column	PONA*, 10 m × 0.2-mm i.d.; 0.5 μm
2nd column	BPX50†, 0.8 m × 0.1-mm i.d.; 0.1 μm
Column oven	50–280°C; 2°C/min
Carrier gas	He; constant pressure, 200 kPa
Injection	0.5 μL, split ratio 1:50; 280°C
Detector	SCD, 800°C (burner temperature)
Acquisition rate	50 Hz
Modulation period	8 s
GC–SCD	
Column	DB1* 60 m × 0.25-mm i.d.; 0.25 μm
Column oven	65–120°C; 10°C/min, 120–240°C; 1°C/min; 240–280°C (10 min); 10°C/min
Carrier gas	He; constant pressure, 240 kPa
Injection	0.5 μL, split ratio 1:50; 270°C
Detector	SCD, 800°C
Acquisition rate	20 Hz

* Polydimethylsiloxane, J&W Scientific (Folsom, CA).

† (50% Phenyl)polysilphenylene-siloxane, SGE (Courtaboeuf, France).

modulated peaks obtained by GC×GC–SCD (Figure 1B): the FID signal provides the narrowest elution peak (0.29 s of baseline peak width) and the peak widths using SCD were 5.1 and 50.6 times greater for the Sievers and Antek detectors, respectively. Moreover, strong tailing was obtained using SCD, leading to increased peak widths and decreased efficiency. Blomberg et al. (11) recently reported that band broadening using SCD could be caused by the electronics. Modification of operating parameters of Antek SCD (reagent gas, flow-rate, and temperature of ceramic oven) did not improve the peak shape. The ratio of peak width at 10% peak-height, between Antek SCD and Sievers SCD, was still approximately 4.5. The deformation of peak shape could be bound to the electronic device, which should not be compatible with narrow GC×GC elution peaks or to void volume in the detection cell. The tailing of the eluting peak seems to show that the lack of efficiency was bound to void volume. Nevertheless, the Sievers detector seems to be better than the Antek one. Only the Sievers SCD was used for this work, without modification.


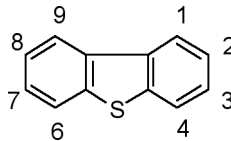
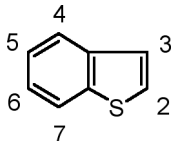
Quantitation of chromatographic data procedure

Before each analytical run of the real samples, the analytical performance of the SCD was checked using the STD2 mixture. Equimolar response and detectability were evaluated by (i) the calculation of the elemental response of sulfur (bias inferior to 10% relative) and (ii) the determination of the limit of detection (inferior to 0.5 pg/s), respectively. If the results were within the limits, GC–SCD or GC×GC–SCD chromatograms were integrated and normalized using external calibration based on the average response of sulfur calculated from the analysis of the STD2 mixture. Finally, the total sulfur content calculated by GC–SCD or GC×GC–SCD was compared with the total-sulfur content measured by XRF.

Identification of standard sulfur-containing compounds by GC×GC–SCD

The separation of the STD1 mixture (Table II) was performed by GC×GC–SCD. As already reported in the literature (11–13),

Table II. Composition and Retention Times of Sulfur-Containing Test Compounds

No.	Compound	¹ t _R (min)*	² t _R (s)	No.	Compound	¹ t _R (min)*	² t _R (s)
Mercaptans							
1	1-Nonanethiol	21.95	1.92	21	7-MeBT [†]	25.68	4.40
2	Isoamyl sulfide	23.15	2.24	22	4-MeBT	26.61	4.52
3	1-Decanethiol	30.08	2.28	23	3-MeBT	27.02	4.60
4	Hexyl sulfide	40.21	2.32	25	2,4-DiMeBT	33.41	4.28
5	1-Dodecanethiol	43.28	2.36	26	2,6-DiMeBT	33.81	4.40
6	1,9-Nonanedithiol	44.75	3.74	27	3,5-DiMeBT	34.35	4.50
7	1-Pentadecanethiol	60.88	2.62	28	2,3-DiMeBT	34.61	4.54
8	Dioctylsulfide	63.28	2.56	29	2,5,7-TriMeBT	39.28	4.14
9	1-Hexadecanethiol	66.21	2.68	30	2,3,4-TriMeBT	41.68	4.36
Thiophene							
				31	2,3,6-TriMeBT	44.35	4.86
10	2- <i>n</i> -PropylT [†]	7.81	1.48	32	2,3,4,7-TriMeBT	50.08	4.66
11	2,3,5-TriMeT	8.88	1.54	Dibenzothiophene			
12	2- <i>n</i> -BuT	12.31	1.92				
13	3- <i>n</i> -BuT	13.15	2.20	33	Dibenzothiophene	53.15	6.44
14	2- <i>n</i> -PhenylT	18.62	2.38	34	4-MeDBT [§]	58.75	6.06
15	3- <i>n</i> -HexylT	26.08	2.62	35	2-MeDBT	59.81	6.08
24	3- <i>n</i> -HeptylT	32.88	2.72	36	4-EtDBT	63.55	5.92
16	3-PhenylT-	33.41	5.26	37	4,6-DiMeDBT	64.08	5.82
17	3- <i>n</i> -OctylT	38.75	2.74	38	2,3-DiMeDBT	65.01	5.80
18	2- <i>n</i> -OctylT	39.55	2.76	39	2-EtDBT	66.08	5.76
19	3- <i>n</i> -OctadecylT	91.81	3.14	40	2,8-DiMeDBT	67.81	6.18
Benzothiophene							
				41	2,4,6-TriMeDBT	69.95	5.54
20	Benzothiophene	19.55	4.34	42,43	2,4,8 and 2,4,7-TriMeDBT	70.88	5.62
				44	2,3,8-TriMeDBT	73.55	5.98
				45	2-BuDBT	75.15	5.56
				46	2-PentylDBT	79.95	5.46

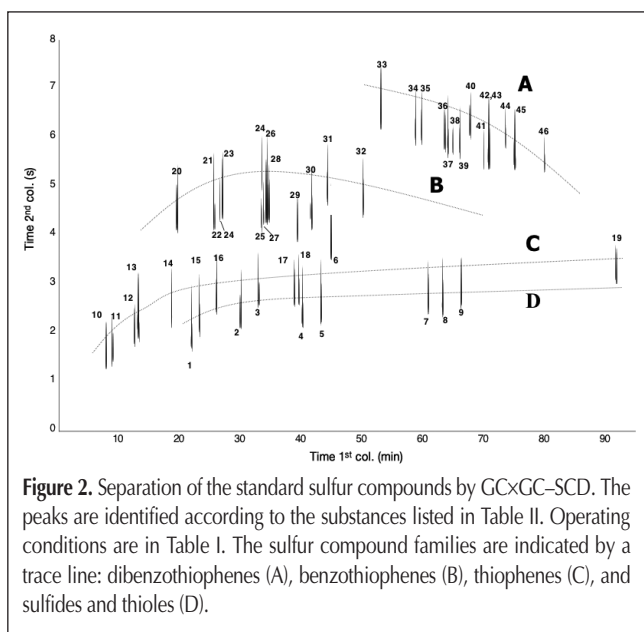
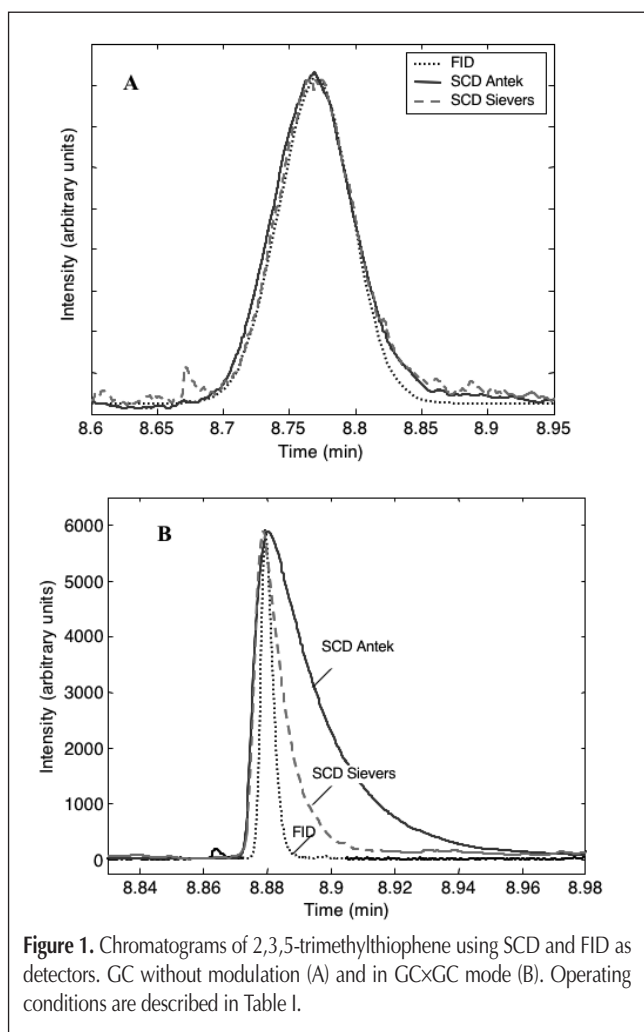
* First dimension retention time is considered for the apex of the most intense modulated peak.

[†] T = Thiophene.

[‡] BT = Benzothiophene.

[§] DBT = Dibenzothiophene.

GC×GC–SCD provides a well-structured two-dimensional chromatogram, as can be seen in Figure 2. Sulfur-containing compounds were separated according to their boiling point [i.e., their increasing number of carbon atoms of alkyl-groups (X-axis)] and



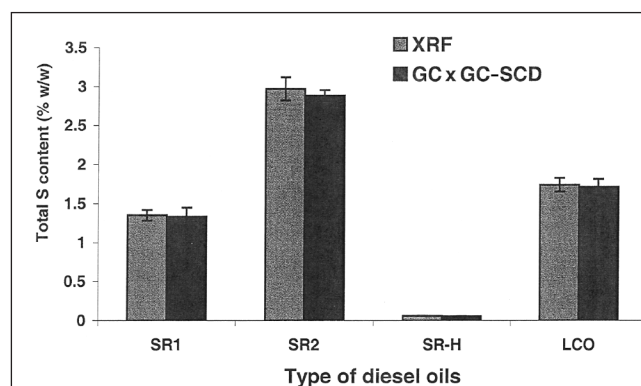
upon their polarity [i.e., their type or the number of aromatic rings (Y-axis)]. Table II reports the retention times (t_R) in the first dimension (1t_R in minutes) and in the second dimension (2t_R in seconds). The general elution profile was close to what has been reported by Hua et al. (13), but it included more standard compounds for BT and DBT families. Of particular importance, it is still possible to elute BTs and DBTs in two well-defined bands, clearly separated from the bands of thiophenes and sulfides or thiols, which have a lower polarity. This was the main advantage of this technique versus conventional GC–SCD, and it was applied to sulfur-specific analysis of diesel oils.

Comparison of GC×GC–SCD analysis with standard methods for sulfur speciation

GC×GC–SCD was used for the quantitative analysis of sulfur compounds: total sulfur content, BT–DBT ratio determinations, and, finally, quantitative detailed analysis of sulfur compounds according to the sulfur family, which is currently called sulfur speciation. This system has been compared with the analytical methods usually employed for this type of analysis: XRF, conventional GC–SCD, and HRMS. To make this comparison, four different diesel oils (LCO, SR1, SR2, and SR-H) were chosen in order to have a good representation of typical chemical compositions in terms of BT, DBT, and nonthiophenic compounds.

Total sulfur content determined by GC×GC–SCD and XRF

The STD2 mixture was used as the external standard to check for the equimolar response of the SCD, regardless of the chemical structure of the sulfur compound. In GC, the concentration of a component was directly proportional to its peak area; however, in GC×GC, the concentration of a compound is directly proportional to the sum of areas of each integrated secondary elution peak. The total sulfur content (% w/w) determined by GC×GC–SCD and by XRF (ASTM D2622) for five replicate injections of different diesel samples is shown on Figure 3. These quantitative results demonstrate an excellent agreement between the reference method (XRF) and GC×GC–SCD because the bias between XRF and GC×GC–SCD results were in-between the standard variation of each method (Figure 3). The average bias has been calculated as 6.8%, which is acceptable for this type of detector used without applying response factors; it demon-



strates that the GC×GC–SCD system provides accurate quantitative data for total sulfur content. To our knowledge, this is the first time such quantitative results are presented.

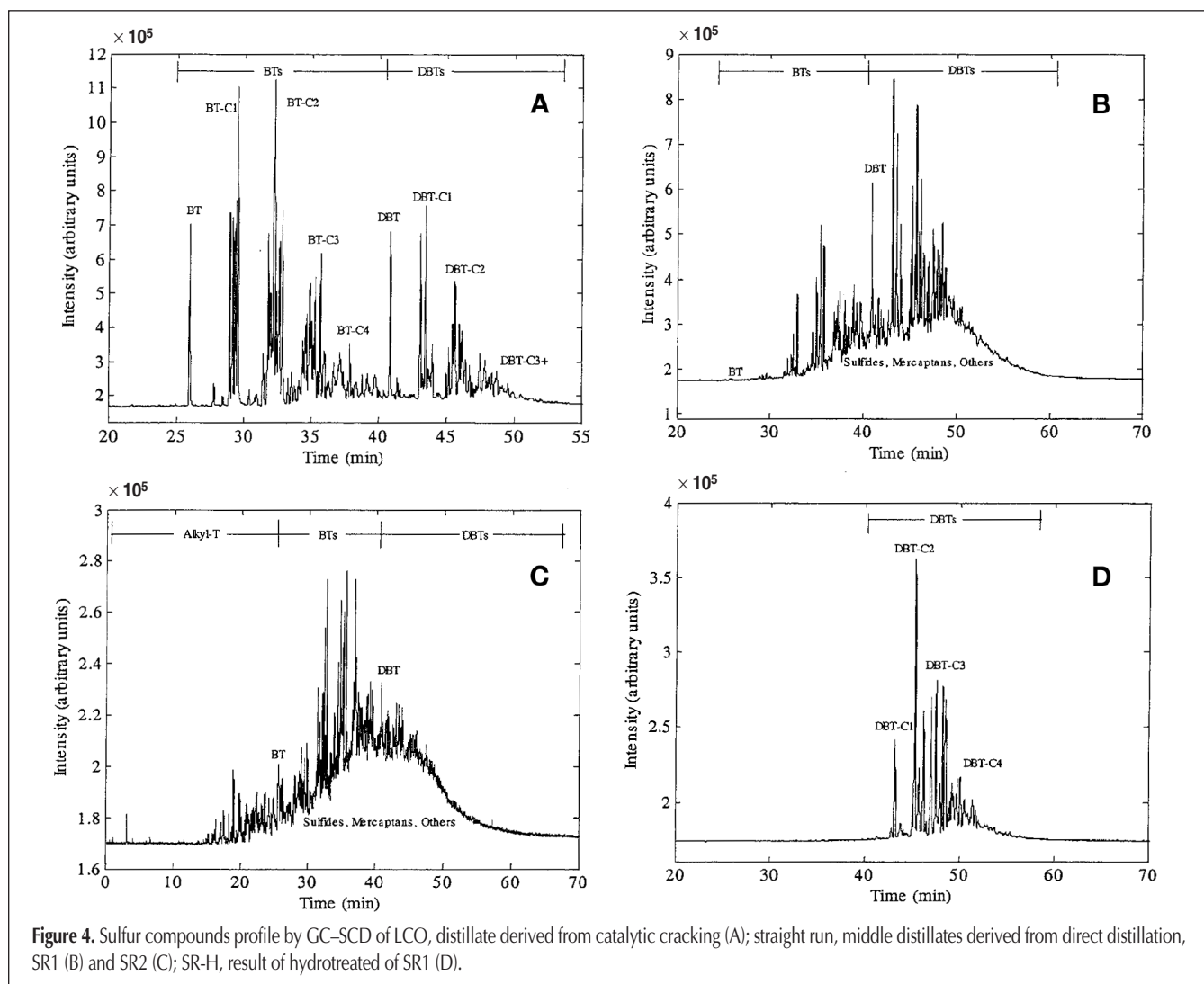
Qualitative detailed sulfur compounds analysis by GC–SCD versus GC×GC–SCD

Figure 4 shows the chromatograms obtained by conventional GC–SCD for the analysis of the diesel oils samples. The complexity of the chromatogram and the efficiency of the separation of sulfur compounds were clearly related to the origin of the sample. Whereas it was possible to identify individual components, such as BTs, DBTs, and several alkylated forms from LCO samples (Figure 4A), the separation of straight-run samples (SR1 and SR2) exhibited an important baseline drift because of overlapping of sulfur component peaks (Figures 4B and 4C). It has been generally assumed that these components should be sulfides and mercaptans (2). This lack of resolution clearly appears as a restriction for quantitative analysis of middle distillates by GC–SCD. Besides, it was also difficult to distinguish the more refractory components because “heavy”-BT and heavy-DBT could be coeluting, leading to inaccurate speciation (2). Therefore, this approach should only be considered for LCO samples or for hydrotreated product samples (Figures 4A and 4D,

respectively), containing mainly BTs and DBTs or only DBTs.

Figure 5 shows the chromatographic profiles obtained by GC×GC–SCD for the same samples. Sulfur components were gathered into large elution bands of spots along the chromatographic plane according to their chemical classes. Moreover, despite the high number of components, (Figures 5B and 5C) BTs and DBTs were easily distinguished according to their number of aromatic rings and were well separated from sulfide and thiol families. Finally, isomers of BTs and DBTs were also identified according to their number of carbon atoms because they have similar retention times on both the *x* and *y* axis of retention. Thus, enhanced chromatographic resolution is provided by GC×GC–SCD.

The analysis of the LCO sample (Figure 5A) enables a clear identification of DBT and BT families, which were used for quantitative comparison of GC–SCD and GC×GC–SCD (see the quantitative detailed sulfur compounds analysis by GC–SCD versus GC×GC–SCD section). The higher separation power was clearly demonstrated for the analysis of SR samples because GC×GC–SCD enables the analysis of sulfur components, which was impossible using a single-column separation (Figures 5B and 5C). There was no baseline drift, and the separation allowed individual identification of BTs and DBTs.



BT-DBT ratio determination by GC×GC-SCD, GC-SCD, and HRMS

Based on the chemical class separation obtained by GC×GC-SCD, it is possible to quantitate the BT and DBT bands in order to calculate the BT-DBT ratio. Figure 5A shows the carbon atom breakdown for BT and DBT elution bands for the LCO sample, which is necessary for the conversion of data from SCD (mass concentration) into molecular concentration for comparison to data obtained by HRMS, expressed as molecular concentration (HRMS results can not be converted into mass concentration). This identification pattern has been applied to the other types of samples for the determination of the total amount of BTs and DBTs.

Figure 6 shows the comparison of GC×GC-SCD results (5 replicate injections) for GC-SCD and HRMS results for the determination of molecular total content of BTs and DBTs in the four diesel oil samples.

GC-SCD and GC×GC-SCD results showed no significant difference (Figure 6A), owing to the accurate quantitation of BTs and DBTs in the LCO sample, as expected from Figures 4 and 5. A higher level of BTs was observed using HRMS, probably because diaromatic compounds interfere (they are highly concentrated in the LCO sample), as discussed later (16,19).

For straight-run samples (SR1 and SR2, Figures 6B and 6C,

respectively), as stressed earlier, GC-SCD suffers from a lack of resolution. Compared with GC×GC-SCD and HRMS, a false identification of sulfur components and dramatic bias for the BT-DBT ratio were obtained. The bias calculated for BT or DBT (or both) may reach 70% of relative standard deviation for BTs (Figure 6B). On the contrary, quite similar results have been obtained for SR1 and SR2 samples using GC×GC-SCD and HRMS: DBT concentration is close for both techniques (bias > 10%), whereas there are some discrepancies for BT determination (bias ranging from 7.5 to 16.5 of relative standard deviation).

In the case of the SR-H (Figure 6D), the agreement between GC-SCD and GC×GC-SCD was excellent because of the correct identification of refractory components (DBTs) and the simple matrix of sulfur-containing solutes. However, because of the low level of total sulfur content (less than 1% w/w) this was beyond the scope of the HRMS standard method

In previous works comparing conventional GC-SCD with HRMS for group-type analysis of petroleum cuts (16,19), some deviations have been measured and attributed to limitations of the quantitation of mass spectral data and bad intensities of the characteristic ions. Indeed, the accuracy of the MS analysis depends on the calibration of the instrument, which can be estimated by (i) the accuracy of average response coefficients of each group and (ii) the correct evaluation of all interferences from one

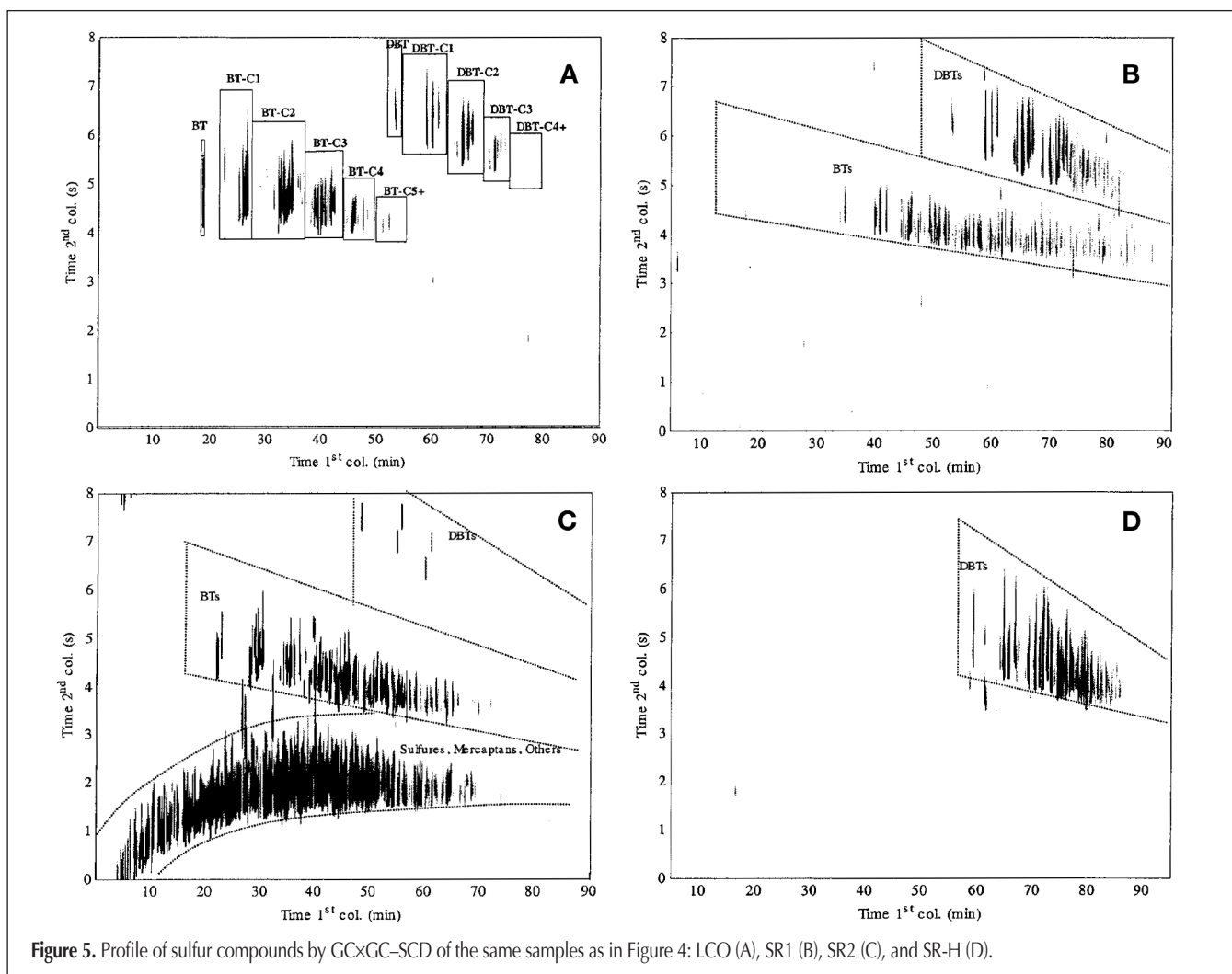


Figure 5. Profile of sulfur compounds by GC×GC-SCD of the same samples as in Figure 4: LCO (A), SR1 (B), SR2 (C), and SR-H (D).

group to the other groups so that the inter-group contribution is taken into account. In particular, it was known that diaromatics can interfere with heavy-BTs, which can explain the bias observed between GC×GC–SCD and HRMS.

Quantitative detailed sulfur compounds analysis by GC–SCD versus GC×GC–SCD

Table III compares the quantitation of sulfur compounds divided in isomer groups obtained by GC–SCD and GC×GC–SCD.

As expected for LCO and SR-H samples, the results obtained by both techniques are in agreement. However, GC×GC–SCD offered a more detailed analysis: heavy BTs (C₅-BT) were better separated though they coelute with DBTs in the case of GC–SCD analysis, and heavy DBTs were separated by carbon atom number (identification of C₄ and C₅DBTs).

For straight-run samples (SR1 and SR2), the enhanced resolution of the GC×GC–SCD compared with GC–SCD allowed a much more detailed quantitation of BTs and DBTs. Indeed, the

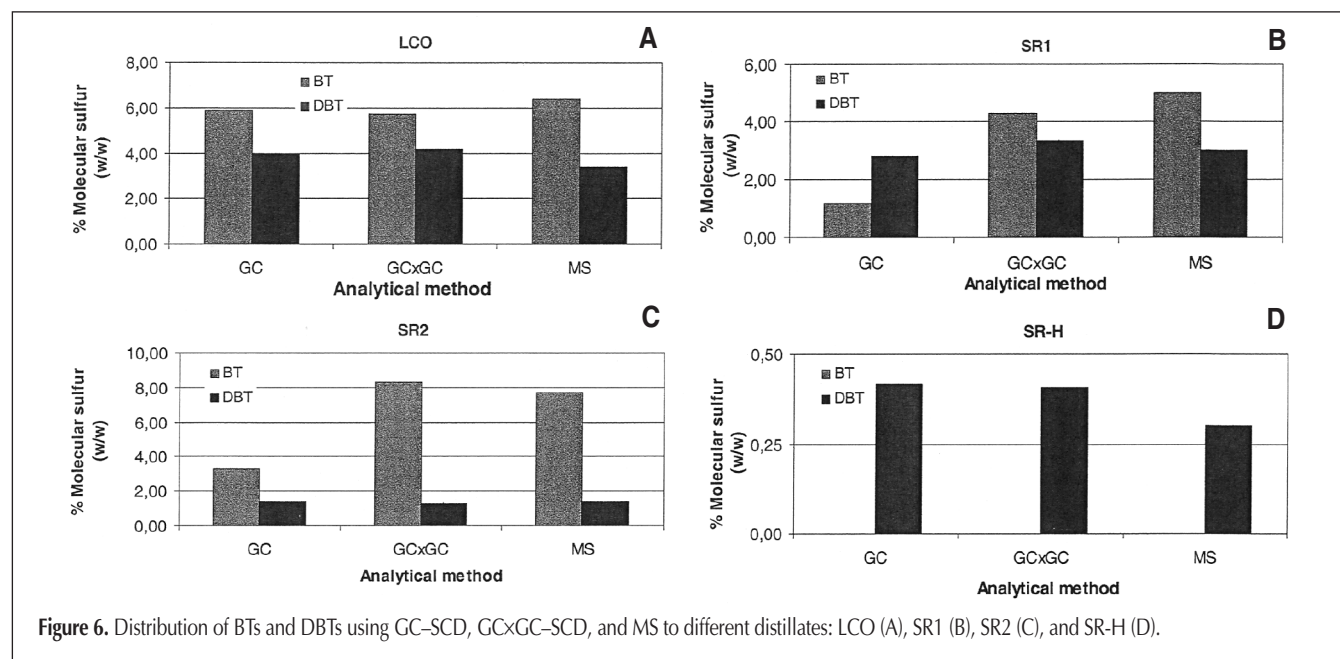


Figure 6. Distribution of BTs and DBTs using GC–SCD, GC×GC–SCD, and MS to different distillates: LCO (A), SR1 (B), SR2 (C), and SR-H (D).

Table III. Quantitation of S Containing Species by GC–SCD and GC×GC–SCD for Different Distillates

	LCO			SR1			SR2			SR-H		
	GC	GC×GC	RSD*	GC	GC×GC	RSD	GC	GC×GC	RSD	GC	GC×GC	RSD
Alkyl-thiophenes + sulfides	0.3	1.0	0.1	– [†]	8.3	0.5	6.6	50.9	0.9	3.7	0.0	0.0
BT	2.3	2.8	0.2	–	0.1	0.0	0.3	0.0	0.0	–	–	–
C1-BT	13.6	14.8	0.5	0.2	0.8	0.0	3.2	0.6	0.0	–	–	–
C2-BT	21.6	17.8	0.9	2.0	1.9	0.1	5.7	2.5	0.0	–	–	–
C3-BT	15.6	13.6	0.9	4.6	2.9	0.4	5.4	5.1	0.3	–	–	–
C4-BT	11.8	8.3	0.4	8.5	4.6	1.1	6.1	8.5	0.2	–	–	–
C5-BT	–	5.8	0.7	–	7.4	0.4	–	7.6	0.2	–	–	–
C6-BT	–	–	–	–	9.2	0.5	–	5.2	0.2	–	–	–
C7-BT	–	–	–	–	6.1	0.1	–	5.3	0.5	–	–	–
C8-BT	–	–	–	–	7.9	0.2	–	4.6	0.1	–	–	–
C9-BT	–	–	–	–	4.4	0.4	–	3.5	0.3	–	–	–
DBT	2.7	2.0	0.1	1.4	0.8	0.0	0.5	0.1	0.0	6.9	6.9	0.1
C1-DBT	11.4	12.3	0.5	8.9	4.6	0.0	2.9	0.6	0.0	20.7	24.8	1.2
C2-DBT	9.8	10.8	0.4	8.9	7.4	0.1	1.2	0.9	0.1	32.4	32.0	0.7
C3-DBT	11.0	7.3	0.8	11.9	7.9	0.4	2.6	1.6	0.2	36.3	36.3	1.9
C4-DBT	–	3.4	0.4	–	8.3	0.0	–	2.9	0.4	–	–	–
C5-DBT	–	–	–	–	4.8	0.1	–	–	–	–	–	–
Others	–	–	–	53.5	12.6	0.7	65.7	0.0	0.0	–	–	–

* RSD = relative standard deviation for GC×GC–SCD
[†] Not present

comparison of the two methods for the analysis of SR1 indicated that more than 60% (w/w) of sulfur components were not identified in GC–SCD, whereas GC×GC–SCD provided a distribution of these coeluted components into heavy isomers of BTs (C₄-BT to C₉-BT), DBTs (C₃-DBT to C₅-DBT), and others sulfur components (alkyl thiophenes and sulfides). This is of major interest for monitoring the effect of desulfurization processes applied to gasoil samples.

GC×GC–SCD provided a better knowledge of the components of these samples and should greatly increase the understanding of hydrotreatment processes and the kinetics of sulfur removal.

Conclusion

This study demonstrates the effectiveness of GC×GC–SCD for the analysis of sulfur-containing compounds: (i) GC×GC–SCD results are similar to XRF determination for total sulfur content and (ii) they are also in line with HRMS results for BT–DBT ratio determination compared with conventional GC–SCD. From a qualitative point of view, GC×GC–SCD has achieved clean separations of chemical classes of sulfur-containing compounds for various diesel oil samples compared with conventional GC, which suffered from an important baseline drift because of coeluting compounds. Thus, GC×GC–SCD also seems to be an unsurpassed tool for quantitative analyses of individual components because of a better separation. New types of distribution of heavy BTs and DBTs, which are the most important refractory compounds for sulfur removal processes, could be obtained by this technique, which should be a key result for a better understanding of hydrotreatment processes.

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