

# Speciation of Sulfur-Containing Compounds in Diesel by Comprehensive Two-Dimensional Gas Chromatography

Frank Cheng-Yu Wang\*, Winston K. Robbins, Frank P. Di Sanzo, and Frank C. McElroy

Analytical Sciences Laboratory, ExxonMobil Research and Engineering Company, 1545 Route 22 East, Annandale, NJ 08801

## Abstract

Sulfur-containing compounds in diesel have been speciated by comprehensive two-dimensional gas chromatography (GC×GC) with a sulfur chemiluminescence detector (SCD). The advantages of GC×GC technique are higher resolution and greater sensitivity. GC×GC–SCD can achieve the class separation of sulfur-containing compounds with an appropriate separation column combination. The major classes of sulfur-containing compounds in diesel are benzothiophenes and dibenzothiophenes. Relative concentration of each class as well as each carbon number family can be quantitated by the summation of the integrated areas corresponding to the individual group(s) in the GC×GC space. In practical applications, GC×GC–SCD can be used to characterize different diesels and to reflect desulfurization process efficiency. In this study, GC×GC–SCD has demonstrated its value in speciation of sulfur-containing compounds classes, which is difficult to accomplish by any other single technique.

## Introduction

Sulfur speciation in diesel is an important task because sulfur-containing compounds create problems in poisoning of catalysts (1) in refining; corrosion of pipelines, vessels, as well as engines (2,3); and exhaust emission to cause air pollution (4). In order to investigate these problems effectively, a good sulfur speciation technique is required.

There are many different approaches to study sulfur in diesel. Some of them can only be used to determine total sulfur concentration, and others not only measure total sulfur but also further analyze the types of compounds present. X-ray fluorescence (XRF) can measure total sulfur. Spectroscopically, X-ray photoelectron spectroscopy (XPS) can distinguish its

oxidation states. Compound type speciation requires some degree of separation, combined with a specific detection system. Gas chromatography (GC) (6), liquid chromatography (LC) (7), and capillary zone electrophoresis (8) have been combined with mass spectrometry (MS) or a sulfur-selective detection system. However, each technique has different sampling requirements, limitation of detection, and dynamic range of detection.

Sulfur-containing compounds in diesel have been studied by GC with a sulfur chemiluminescence detector (SCD) (6). The SCD has high selectivity and sensitivity to sulfur, making it possible to quantitate the sulfur-containing compounds that coelute with hydrocarbons during chromatographic separation. The sulfur selectivity of the SCD helps to overcome coelution always obtained with a single capillary column. The sulfur sensitivity allows the SCD to be applied where heavy interference of coeluted hydrocarbons limits the detection in GC–MS.

During the last ten years, two-dimensional GC (GC×GC) separation has been shown to be feasible, and multidimensional partition has been achieved in GC×GC. There are two major advantages of GC×GC separation: greater resolution and higher sensitivity. GC×GC with a flame ionization detector to study petroleum streams has been reported in literature (11). The approach has been extended to GC×GC–SCD to study the complex problem of sulfur-containing compounds found in diesel. The GC×GC–SCD arrangement combines the SCD sulfur selectivity with the resolution and sensitivity of GC×GC. This combination largely overcomes the problems of coeluting, unresolved peaks, and relatively poor sulfur selectivity of traditional one-dimensional GC techniques for sulfur compounds in diesel.

In this study, GC×GC–SCD has been applied for the analysis of sulfur-containing compounds in diesel. Sulfur-containing compounds can be categorized as classes by their structures such as benzothiophenes and dibenzothiophenes. The alkyl analogues in each class can be further grouped by their carbon

\* Author to whom correspondence should be addressed.

number. The relative concentration of each class, as well as each carbon number group, can be quantitated by integrating those corresponding peaks. In practical applications, this technique can be used to monitor composition or to measure the efficiency of a specific desulfuration process.

## Experimental

### Diesels

The diesels used in this study are typical refinery streams distilled into diesel temperature range [150°C (300°F) to 430°C (800°F)] containing compounds with a carbon number from approximately C<sub>8</sub> to C<sub>28</sub>.

### GC×GC–SCD conditions

The GC×GC system consists of an Agilent 6890 GC (Agilent Technologies, Wilmington, DE) configured with an inlet, columns, and detectors. The inlet system contains an eight-vial tray autosampler and a split/splitless inlet. The capillary column system contains a first-dimension column (SPB-5, 30 m, 0.25-mm i.d., 1.0- $\mu$ m film) (Supelco, Bellefonte, PA) and a second-dimension column (BPX-50, 3 m, 0.25-mm i.d., 0.25- $\mu$ m film) (SGE, Austin, TX). Between the first and the second dimension columns is a dual jet thermal modulation assembly (10) (Zoex Corp., Lincoln, NE). The detection system is an SCD (Ionics, Boulder, CO). The set-up and analysis conditions are based on recommendations from the manufacturer.

A 0.2- $\mu$ L diesel sample was injected through the split/splitless injector with 100:1 split. The inlet temperature was 300°C in constant head pressure mode at 45 psi. The oven temperature program started from 60°C with 0 min hold and 3°C/min ramp rate to 300°C with 0 min hold. The total run time was 80 min. The modulation period was 10 s; the sampling rate for the detector was 100 Hz.

After data acquisition, data were further processed for qualitative and quantitative analysis. The qualitative analysis was to convert data to a two-dimensional image that is processed by a program called Transform (Research Systems, Boulder, CO). The two-dimensional image is further treated by PhotoShop (Adobe System, San Jose, CA) to generate publication-ready images. A program developed in house is used to accomplish the quantitative analysis.

## Results and Discussion

Study of sulfur compounds in diesel GC has been performed for many years (6). Figure 1 illustrates a GC–SCD chromatogram of a typical diesel sample with approximately 7000 wt/ppm total sulfur compounds. Major peaks have been identified either by matching retention time with standards or by isolating carefully with other techniques such as LC and identified by MS. Among those identified compounds, two major classes of compounds are present: benzothiophenes and dibenzothiophenes. However, because of unresolved coeluting sulfur-containing compounds, they formed a large “envelope” from a retention time of 30–80 min. This envelope hinders quantitative analysis of peaks and complicated assignment of the major sulfur-containing compound

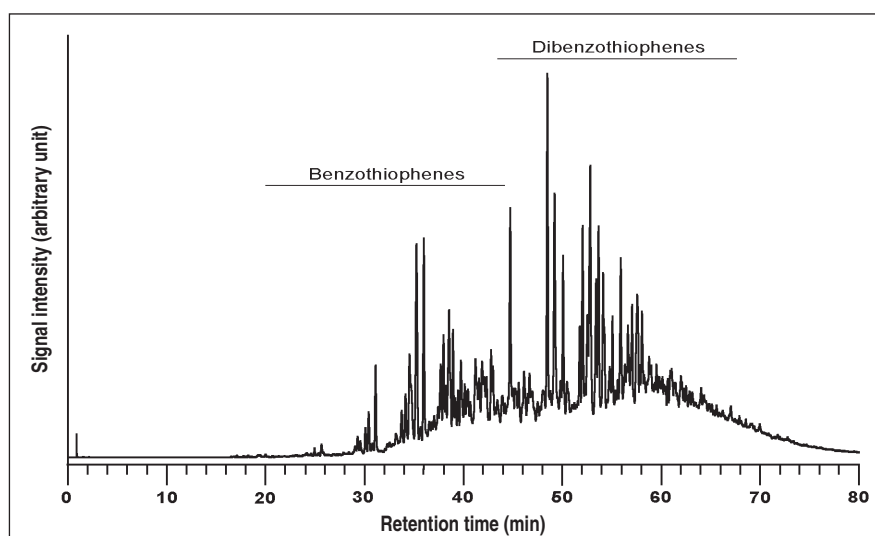


Figure 1. A traditional GC–SCD chromatogram of a typical diesel sample with 7000-ppm (wt% of sulfur) total sulfur compounds.

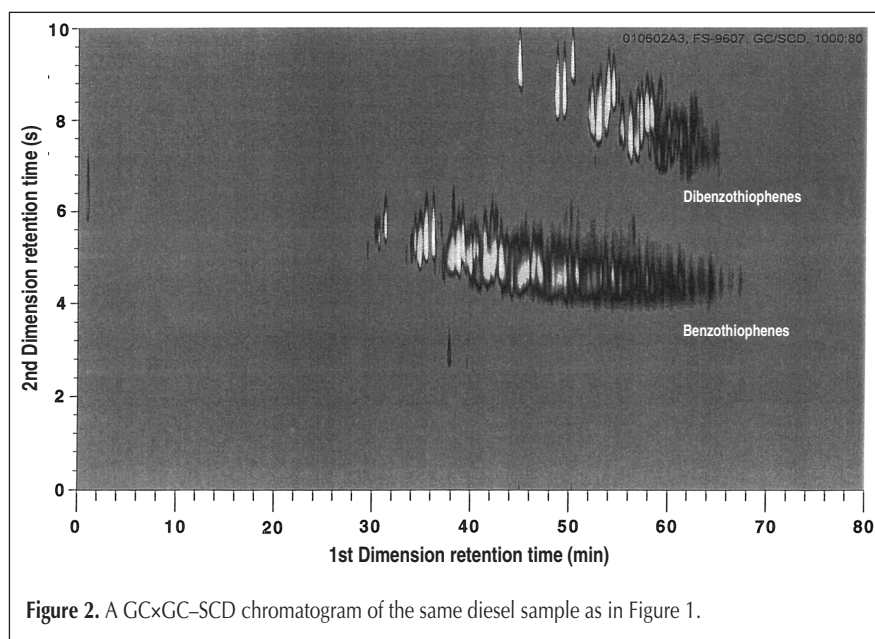


Figure 2. A GC×GC–SCD chromatogram of the same diesel sample as in Figure 1.

to groups such as benzothiophenes and dibenzothiophenes.

Figure 2 demonstrates a GC×GC–SCD chromatogram of the same sample as in Figure 1. The experimental conditions are exactly the same as in Figure 1, except the modulator has been turned on and the data has been processed in a different way in order to represent two-dimensional separation. There are two well-separated major bands shown in the GC×GC–SCD chromatogram. The upper is dibenzothiophenes and the lower is benzothiophenes. Within each band, one can further divide into carbon-number compound groups (e.g., in the class of benzothiophenes there are benzothiophene, methyl benzothiophene, benzothiophene with C<sub>2</sub> branch... and so on). The same grouping can also be found in the class of dibenzothiophenes. Because of this resolution, each group, as well as the whole class, can be integrated independently, and the amount can be quantitatively analyzed.

Comparing Figures 1 and 2, GC×GC–SCD has resolved this envelope in the retention time from 30 to 80 min. In addition, all peaks are baseline resolved for integration. This is a definite advantage of this two-column or two-dimensional separation. Based on the GC×GC–SCD chromatogram, the envelope appears to consist mainly of a large number of isomers of alkyl branched benzothiophenes, dibenzothiophenes, and naphthno analogues.

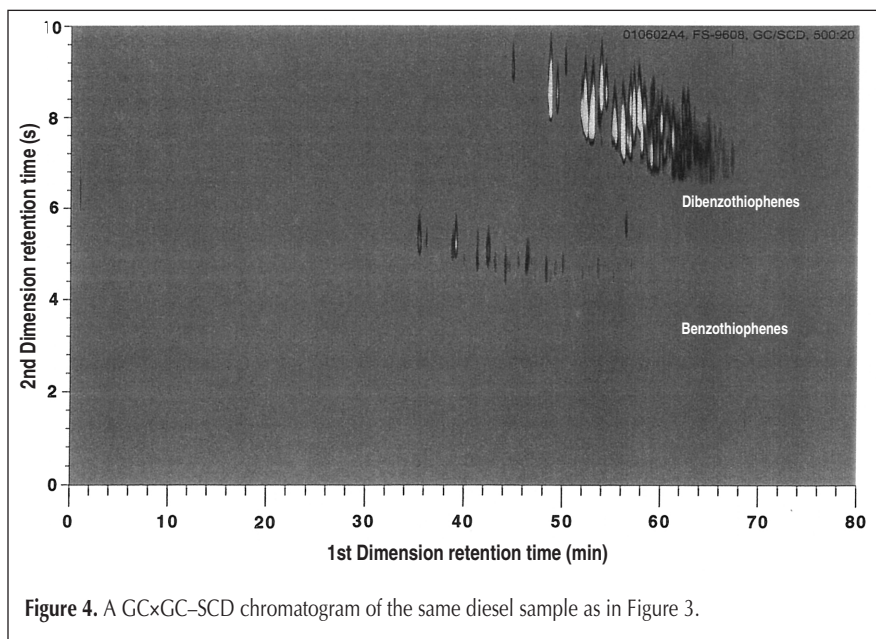
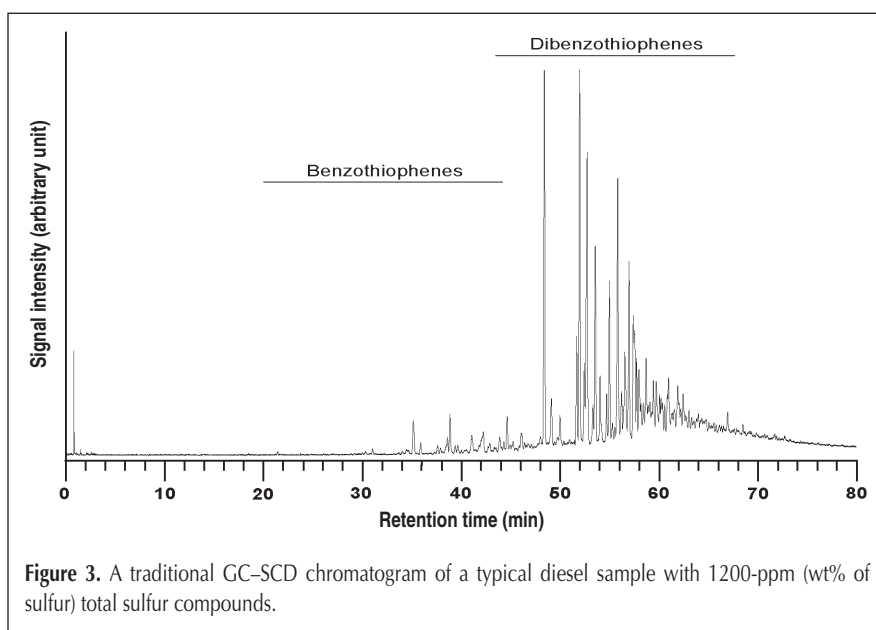
GC×GC–SCD is capable of providing highly detailed fingerprinting of complex mixtures. This capability offers the possibility of examining the changes of sulfur-containing compounds during certain refinery processes. For example, during the refinery desulfurization processes for diesel, the efficiency of catalyst, conditions of the process, and removal mechanism can be studied if one knows the fate of the sulfur compounds.

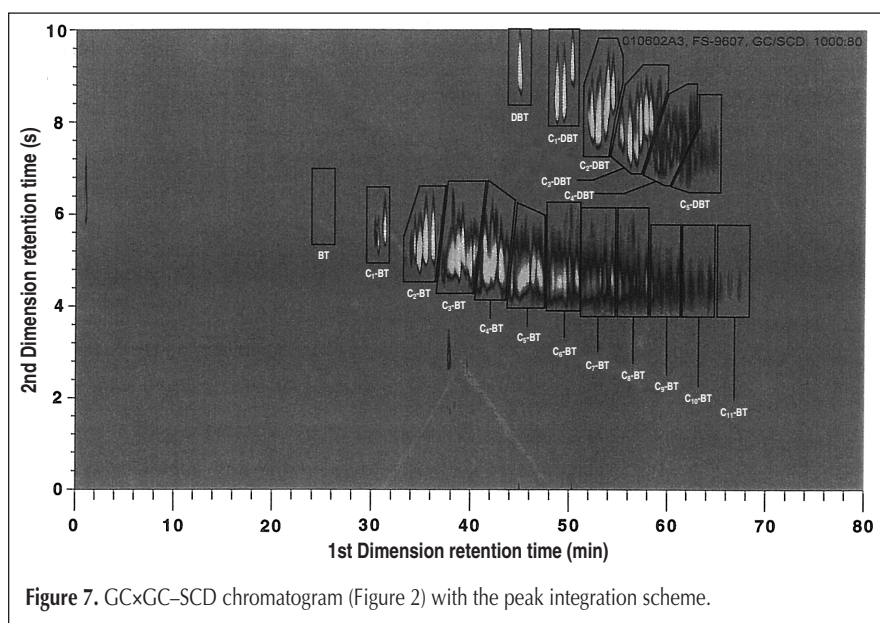
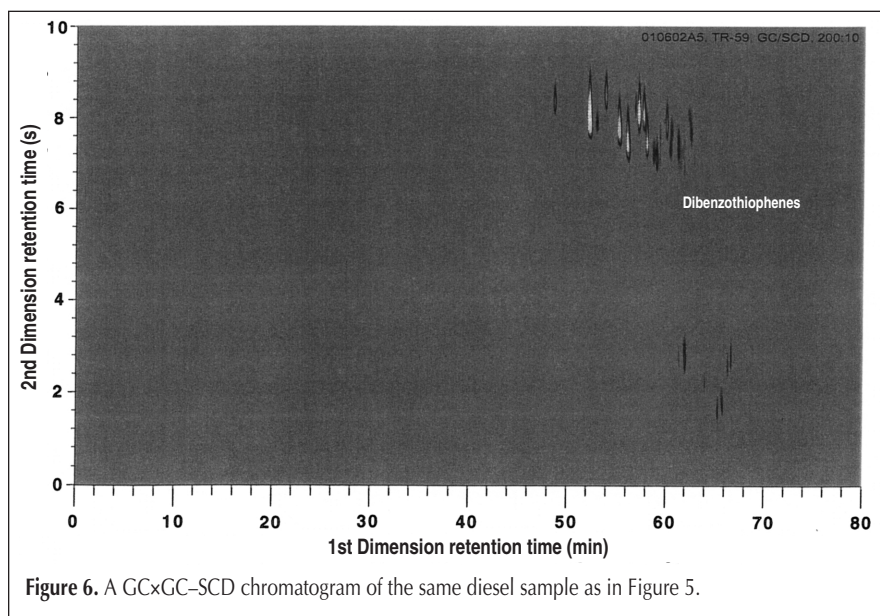
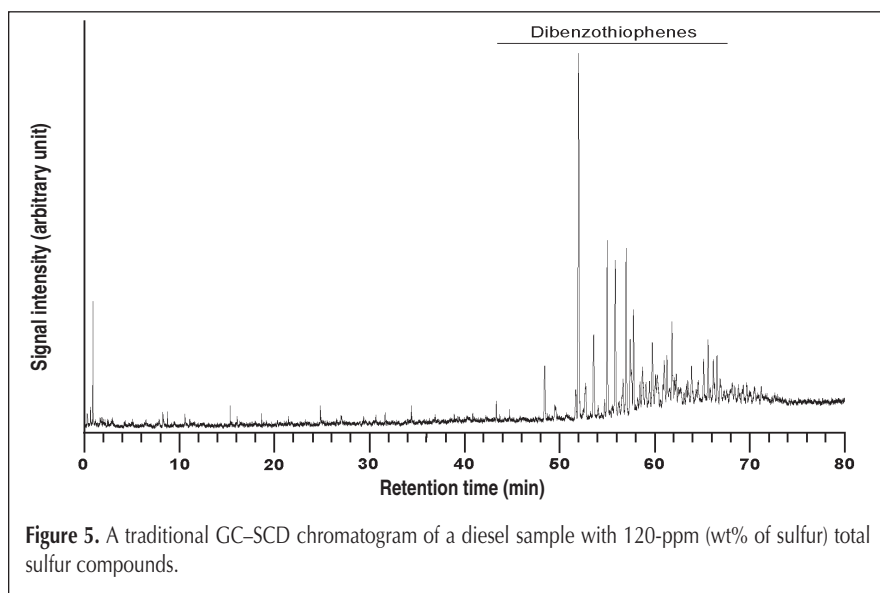
Figure 3 illustrates a treated diesel sample with approximately 1200 wt/ppm total sulfur compounds. This sample is the sulfur-reduced product from the 7000-ppm diesel sample (Figure 1). In the GC–SCD chromatogram, the envelope from retention time 30–80 min has been greatly reduced. Some peak intensities have also decreased or disappeared. However, just based on the chromatogram, it is difficult to distinguish whether benzothiophenes or dibenzothiophenes have been affected.

Figure 4 shows the GC×GC–SCD chromatogram of the same treated diesel sample as analyzed in Figure 3.

Again, it is exactly the same experimental conditions as in Figure 3, except for the modulation. Similar to Figure 2, GC×GC–SCD provides the detailed component retention and distribution information. Comparing the chromatograms in Figures 2 and 4 permits the disappearance of each sulfur-containing compound to be clearly monitored. This is the first time that the changes of sulfur components can be visualized in such a detailed manner and monitored closely, demonstrating the unique capability of GC×GC–SCD for sulfur-containing-compound fingerprinting.

Figure 5 illustrates a treated diesel sample with approximately 120 wt/ppm total sulfur compounds. This sample is a further sulfur-reduced product from the 1200-ppm diesel sample. In the GC–SCD chromatogram, there are sharp peaks shown. However, there is always some question on the iden-





tivity of the compounds because of insufficient separation/resolution of compounds.

Figure 6 shows the GCxGC-SCD chromatogram of the treated diesel sample as analyzed in Figure 5. Again, the same experiment conditions were employed as in Figure 5, except there is no modulation. Figure 6 clearly indicates that those peaks remaining are mainly dibenzothiophenes. In the envelope area, only alkyl branched dibenzothiophene isomers were detected. With the class separation of GCxGC-SCD, it is clear that the desulfurization process removes all of the benzothiophenes and the majority of dibenzothiophenes. There are certain types of dibenzothiophenes that survived the removal process, and their structures can now be or have been identified by matching their retention times (one-dimensional) or retention positions (two-dimensional) with standards.

Figure 7 shows a GCxGC-SCD chromatogram (Figure 2) with the peak integration scheme. The peak(s) of interest are integrated through a summation of the individual peak chromatograms by drawing a boundary box around the individual or group of peak(s). Table I demonstrates the quantitative analysis results for these three diesel samples with components divided by classes as well as carbon number groups. The difference in total sulfur content as well as sulfur-containing compound distribution can be easily quantitated.

## Conclusion

The detailed fingerprinting capability opens the opportunity to monitor processes that traditional analytical techniques have not been able to address because of a lack of resolution. GCxGC-SCD is well-suited to deal with these process samples. The technique offers resolution, sensitivity, and speciation capabilities that make it a potential tool for general-purpose sulfur in diesel speciation, as well as for tracking the transformation of every component in a mixture during a complex reaction system such as a refinery process.

**Table I. Quantitative Analysis of Sulfur-Containing Compounds of Diesel Samples**

Name	7000 ppm	1200 ppm	120 ppm
MST	1099	19	0
BT	0	0	0
C1BT	9	0	0
C2BT	88	3	0
C3BT	391	17	0
C4BT	477	24	0
C5BT	468	29	0
C6BT	457	35	0
C7BT	470	41	0
C8BT	457	44	0
C9BT	364	43	0
C10BT	328	41	0
C11BT	247	33	0
C11+BT	152	25	0
C0DBT	83	7	1
C1DBT	306	91	3
C2DBT	503	234	23
C3DBT	484	250	34
C4DBT	315	156	23
C5DBT	222	103	16
C6+DBT	164	81	12
Total	7085	1277	111

\* Abbreviations: MST, mercaptan, sulfide, and thiophene; BT, benzothiophene; and DBT, dibenzothiophene.

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