As evidenced by recent literature, industrial applications for GCxGC are growing in a number of areas; however, its ability to increase peak capacity and advance separations in complex matrices makes it particularly useful in the petro industries. GCxGC can be used to analyse hydrocarbons ranging in volatility from C4 (butane) to C40 (tetracontane), although with automatic flow programming of the cold jet in the thermal modulator analyses up to C48 have been reported [1].

Other notable recent advances include a full characterisation of middle distillates using supercritical fluid chromatography [2], a high temperature analysis of vacuum gas oils up to nC60 [3], and a partial characterisation of military fog oil [4]. Military fog oil is an extremely complex middle distillate product containing mainly aliphatic compounds. Using GCxGC-TOFMS, Kohl et al. were able to identify a wide range of low concentration aromatics from what would typically be an unresolved complex mixture. Compounds reported included alkanes, cyclohexanes, hexahydroindenanes, decalins, adamantanes, bicyclohexanes, alkylbenzenes, indanes, tetrahydroisopentanes, partially hydrogenated polycyclic aromatic hydrocarbons, biphenyls, dibenzofurans, and dibenzothiophenes. In these and other examples, the analytical power of comprehensive 2D GC is used to achieve a more advanced separation of complex matrices than is possible with 1D GC.

Technical Overview of GCxGC

In comprehensive 2D GC, two independent separations are applied to a single sample injection. A summary of the technique is given here; however, recent review papers provide a more complete description, focusing on recent advances and industrial applications [5,6]. In GCxGC, the first separation is usually based on boiling point and uses a standard nonpolar phase. Next, a thermal or valve modulator is used to focus the effluent from the first column onto the second column, which is a short (1–2 m) column and typically is a polar phase. Inverse polarity column set-ups are also sometimes employed, but with either approach the key to maximising use of the separation space is to choose orthogonal columns that differ significantly in selectivity. Separation results are displayed as a contour plot, which is a three dimensional representation of intensity (z) across the retention times of both column 1 (x) and column 2 (y). The result is a technique with increased peak capacity that can be used to separate compounds which coelute in the first dimension. Ultimately, the increased peak capacity obtainable with GCxGC allows better characterisation of complex petro fractions such as naphtha, gasoline, and diesel.

Sulphur Speciation in Diesel

The analysis of sulphur, such as dibenzothiophenes, in diesel offers a timely example of the benefits of GCxGC for complex hydrocarbon samples. In recent years, new vehicle emissions standards have been adopted across the globe; these requirements have driven the development of ultra low sulphur diesel that is compatible with new emission control technology. In many countries, specifications for total sulphur in diesel have been reduced from 50 ppm to 10–15 ppm, making the analysis of various sulphur components even more crucial for the refinery industry. Using the analysis of dibenzothiophenes as an example, it is clear that 1D GC is insufficient to distinguish sulphur compounds due to coelutions with other components in the diesel matrix (Figure 1). An MS detector was used for this work because it offers the potential to identify a broad range of analytes from a single injection, compared to the limited information that can be obtained using a sulphur-specific detector. However, even with the power of the MS, the diesel sample was too complex to yield usable results. The spectrum taken at the retention time for dibenzothiophene confirms that the separation of components is not sufficient and the sulphur compounds cannot be identified (Figure 2).

In contrast, when GCxGC is used for the analysis of sulphurs in diesel, individual dibenzothiophenes are resolved both from the interferences that obscured them in the one-dimensional analysis and also from each other. The structured chromatogram (contour plot) that
is obtained offers good separation of major groups and even resolves multiple positional isomers within each carbon substituent group (Figures 3-5). Comparison of the sample mass spectrum at the retention time for dibenzothiophene to a reference spectrum reveals a clear match and confirms compound identification (Figure 6). As shown in this example, good use of the separation space is made by optimising parameters for both columns. Often, in order to optimise separations on the second column, the first dimension separation is intentionally slowed in order to produce broader peaks that will accommodate 3-5 modulations per peak. With careful attention to flows, temperatures, and modulator settings, good column efficiencies can be obtained in both dimensions. By employing GCxGC and optimising use of the separation space, peak capacity is significantly increased. This approach, in combination with the use of a powerful MS detector, allows speciation of sulphur compounds in diesel and provides a level of sample characterisation that cannot be obtained using one-dimensional GC.

Analysis of sulphurs in diesel provides a good demonstration of the power of GCxGC for complex matrices. Increased peak capacity allows identification of relevant constituents that cannot be differentiated by GC alone. As this technology is increasingly adopted by the petroleum and petrochemical industries, better materials characterisation and process optimisation can be achieved.

**Experimental**

A Pegasus 4D GCxGC-TOFMS (LECO, St. Joseph, MI, USA) was used with electron ionisation at 70 eV and an MS source temperature of 250°C. The acquired mass range was 45-450 u at 200 spectra/sec. The primary GC column consisted of 2 Rxi®-1ms columns (each 60 m x 0.25 mm x 0.25 µm) press-fitted together. The secondary column, a 1.5 m x 0.25 mm x 0.10 µm Rtx®-FLD column (an experimental phase column), was connected by a press-fit to the end of the primary column. The secondary column was installed in its own oven and terminated in the source of the TOFMS. This column combination was operated with helium carrier at a corrected constant flow of 2.0 mL/min. One microliter 50:1 split injections of a diesel fuel composite were performed into a Sky™ 4.0 mm Precision® inlet liner with wool at 275°C. The primary oven program was: 40°C (hold 1 min.) to 320°C at 1.3°C/min. (hold 1 min.) The secondary oven program was a positive 5°C offset from the primary oven. For GCxGC a quad-jet, dual-stage thermal modulator was used with a temperature offset of 20°C and a modulation time of 3 sec. The hot pulse time was 1 sec. For one-dimensional GC runs, the modulation time was set to zero, and the MS data collection rate was 2 spectra/sec. LECO ChromatTOF software was used for GCxGC-TOFMS data processing and display.

![GCxGC-TOFMS chromatogram (contour plot) of diesel analysed with orthogonal Rxi®-1ms and Rtx®-FLD columns showing structured separation of aliphatics and aromatics.](image1.png)

![GCxGC-TOFMS contour plot (TIC) of the dibenzothiophene elution region for a diesel sample. The dibenzothiophenes are more retained by the Rtx®-FLD column, which means they are higher on the y-axis of the contour plot than most other components.](image2.png)

![GCxGC-TOFMS extracted ion contour plot of the dibenzothiophene elution area for a diesel sample. Plotting m/z ions 184, 198, 212, 226, and 240 enhances visualisation of the separation of the dibenzothiophenes (including the alkyl substituted isomers).](image3.png)

![Mass spectrum of dibenzothiophene for comprehensive two-dimensional GC of diesel. The sample mass spectrum (top) is an excellent match with the NIST library mass spectrum (bottom).](image4.png)

**References**


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