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GC×MS of Diesel: A Two-Dimensional Separation Approach

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Comprehensive two-dimensional gas chromatography can be viewed as a traditional gas chromatography with a sophisticated "elution-resolved" flame ionization detector (GC/FID) or a detector with separation capability. The concept of multidimensional chromatography can be extended to other detectors that also have separation capability, such as ultraviolet, infrared, and mass spectrometer. Mass spectrometry, combined with gas chromatography, GC/MS, has been a powerful separation/identification device for many years. However, if one applies the multidimensional separation concept to this combination with a nonfragmentation ionization method, GC/MS not only can be used as a separation/identification tool, but also a two (multiple) dimensional separation device, GC×MS. In this study, a two-dimensional separation (GC×MS) study of diesel composition is demonstrated and compared with the GC×GC technique. The major advantage of GC×MS is the compound class separation. The compound groups within a compound class are also well-separated on the basis of their parent masses. Because of the exact mass operation, the specific element containing compound distribution can also be generated through the extraction of specific mass groups. For qualitative analysis, GC×MS is a technique where one experiment can generate a wide range of information. GC×MS may also perform quantitative analysis when appropriate response factors for various compound groups are available. From GC×GC to GC×MS, the power of two (multiple) dimensional separation has just started exposing its advantages for complex mixture analysis. To achieve multiple dimensional separation in different forms, many improvements remain to be made. The challenge now is to combine/accommodate two or more different techniques to solve a specific complex separation problem. The GC×MS experience has pushed this effort one step ahead toward complete application of this new concept in the analysis of complex mixtures.

One way to view the difference between comprehensive two-dimensional gas chromatography (2DGC or GC×GC)[1−4] and traditional gas chromatography (GC) is the detector. The 2DGC or GC×GC can be viewed as a traditional GC and a detector with a separation capability consisting of a sophisticated "elution-resolved" flame ionization detector (GC/FID).

The concept of multidimensional chromatographic separation can be extended to other types of separation techniques. Other separations, such as mass separation by mass spectrometry (MS), wavelength/internal atomic/molecular motion separation by ultraviolet (UV), visible (vis), and infrared (IR) spectrometer, and thermal separation by thermogravimeric analysis (TGA) techniques, all use different mechanisms of separation. When combined with any of the techniques, a two (multiple) dimensional separation can be accomplished.

The term "separation" requires a mechanism that is able to produce a "distinguishable label" of individual components after acting on a mixture. Mass spectra produced by electron ionization (70 eV EI) cannot meet this "distinguishable label" requirement, because EI produces multiple fragments and similar classes of compounds (e.g.. paraffins) have similar fragmentation patterns. However, when applied with a soft ionization technique, such as field ionization (FI), only one type of ion (parent ions) is produced in the mass spectrum for each component, and the approach can achieve a separation of unknown mixtures through measurement of the mass of each component.

Gas chromatography coupled with mass spectrometry, GC/MS, has become a powerful technique for separation/identification of unknown components over many years.[5,6] In this procedure, the GC performs separation and MS masters in separated component identification. For a complex mixture such as petroleum, this technique, similar to traditional GC, still suffers a lot of coelution of components in the GC separation and many mixed mass spectra (caused by coelution) that create difficulty for MS interpretation.

GC/MS not only can be used as a separation/identification tool but also a two (multiple) dimensional separation device, GC×MS. A recent technology breakthrough in coupling GC and "soft" ionization MS made the two-dimensional separation feasible.[7]

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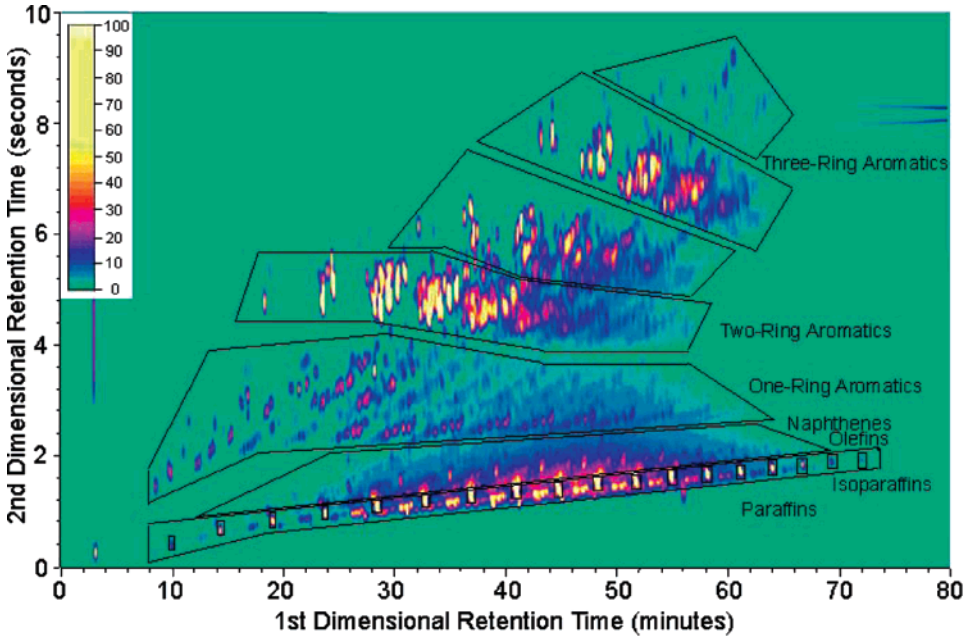

Figure 1. 2DGC or GC×GC chromatogram of a refinery stream boiling at diesel temperature range. The scale indicates the relative signal intensity.

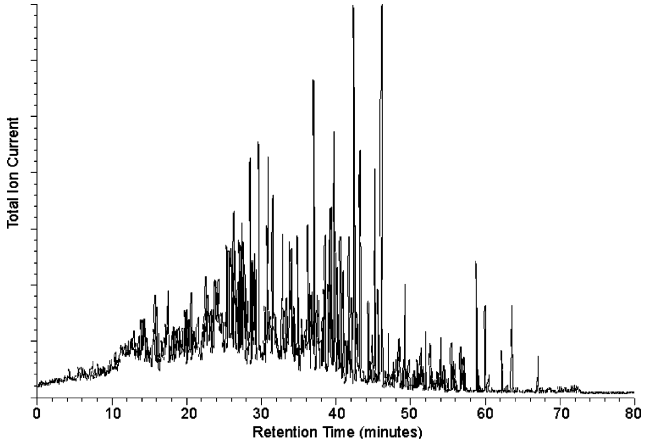

Figure 2. GC/MS chromatogram of a refinery stream boiling at diesel temperature range.

The theoretical separation capability and possible sensitivity variation of GC/MS and GC×MS have been compared;[8] however, there are no real GC×MS data reported to provide real access of two (multiple) dimensional separation advantages. In this study, a two (multiple) dimensional separation, GC×MS, of diesel boiling point range mixtures is presented and compared with the GC×GC technique. The advantages and disadvantages of this alternate technique will also be discussed.

EXPERIMENTAL SECTION

a. Diesels. The diesel fuel boiling point range mixtures used in this study are typical refinery streams boiling between 150 °C (300 °F) and 430 °C (800 °F) with carbon number from approximately C_8 to C_{28}.

b. GC×GC Conditions. The GC×GC system consists of an Agilent 6890 gas chromatograph (Agilent Technology, Wilmington, DE) configured with inlet, columns, and detectors. A split/splitless inlet system with an eight-vial tray autosampler was used. The two-dimensional capillary column system utilizes a weak-polar first column (SPB-5, 30 m, 0.25 mm i.d., 1.0 μm film) (SUPELCO Inc., Bellefonte, PA) and a midpolar second column (BPX-50, 3 m, 0.25 mm i.d., 0.25 μm film) (SGE Inc., Austin, TX). A dual jet thermal modulation assembly[9] based on Zoex technology (Zoex Corp., Lincoln, NE), which is a liquid nitrogen cooled "trap-release" dual jet thermal modulator, is installed between these two columns. A flame ionization detector (FID) was used for this study.

A 0.2 μL sample was injected via a split/splitless (S/S) injector with 75:1 split at 300 °C in constant pressure mode at 45 psi at oven temperature 60 °C. The oven was programmed from 60 °C with 0 min hold and 3 °C per min increment 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 was acquired, it was processed for qualitative analysis. The data were first converted to a two-dimensional image by a commercial program, Transform (Research Systems Inc., Boulder, CO). This two-dimensional image was further treated by "PhotoShop" (Adobe System Inc., San Jose, CA) to generate publication-ready images.

c. GC×MS Conditions. The GC system used is an Agilent 6890 gas chromatograph configured with inlet and column. The detector is a mass spectrometer. The GC column used is a midpolar column (BPX-50, 30 m, 0.25 mm i.d., 0.25 μm film). This column separates petroleum molecules by both boiling point and polarity.

About 1.0 μL of the sample was injected via a S/S injector with a split ratio 50:1 at 300 °C in constant pressure mode at 45 psi at oven temperature 60 °C. The oven was programmed from 60 °C

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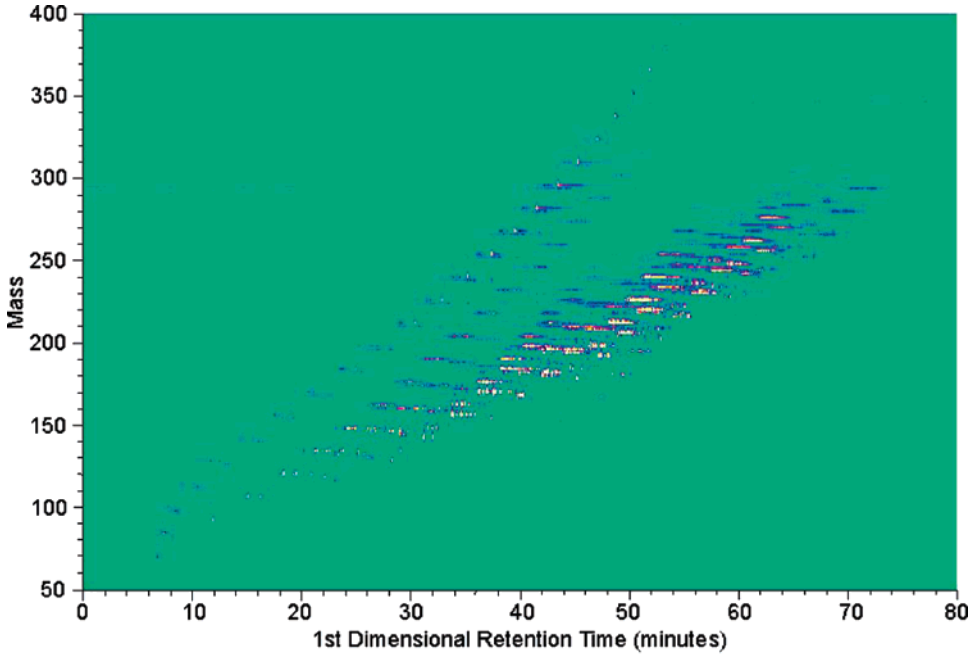

Figure 3. GC/MS chromatogram of a refinery stream boiling at diesel temperature range.

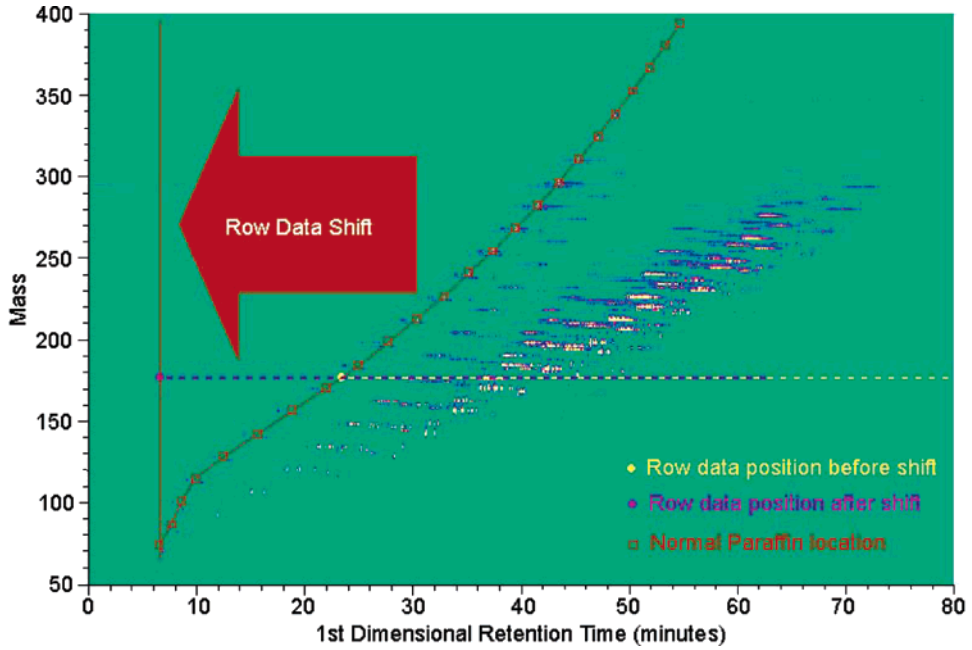

Figure 4. Illustration of data transformation to show the relative polarity of compound classes.

with 0 min hold and 5 °C/min increment to 360 °C with 20 min hold and with total run time 80 min.

After GC, a time-of-flight (TOF) mass spectrometer (Macro-Mass GCT, Waters Inc., Milford, MA) was used to perform the mass spectrometry analysis. The detailed description of FI and TOF has been described in previous work.[7] In brief, the temperature of the GC/TOF interface was maintained at 350 °C. Field Ionization (FI) was used to ionize diesel molecules eluting from the GC. The FI emitter (CarboTech, Gesellschaft für instrumentelle Analytik mbH) consists of a 10 μm tungsten wire onto which carbon microneedles have been grown. The FI emitter is carefully aligned with the end of the GC capillary column so that effluent molecules pass near the tips of the carbon dendrites. The emitter (at ground voltage) is about 1.5 mm away from a pair of extraction rods held at high potential (−12 kV), producing very high electric fields (~10^{-7} to 10^{-8} V/cm) around the tips of the carbon dendrites. It is generally believed that under the influence of these fields, an electron can be removed from a molecule via quantum tunneling effects, generating radical molecular ions with minimal fragmentation. FI emitter current was typically set at 0 mA during the scan. The emitter was flashed by a current of 12 mA during an interscan cycle (0.2 s) to regenerate the emitter.

Ions generated by FI were accelerated and focused into a pusher region of the TOF. A voltage pulse of 960 V is applied, ejecting ions orthogonal to the original ion path. The ion packet drifts through a TOF with an effective path length of 1.2 m. A reflectron reflects ions back to a dual microchannel plate detector. Ion arrivals are recorded using a time to digital

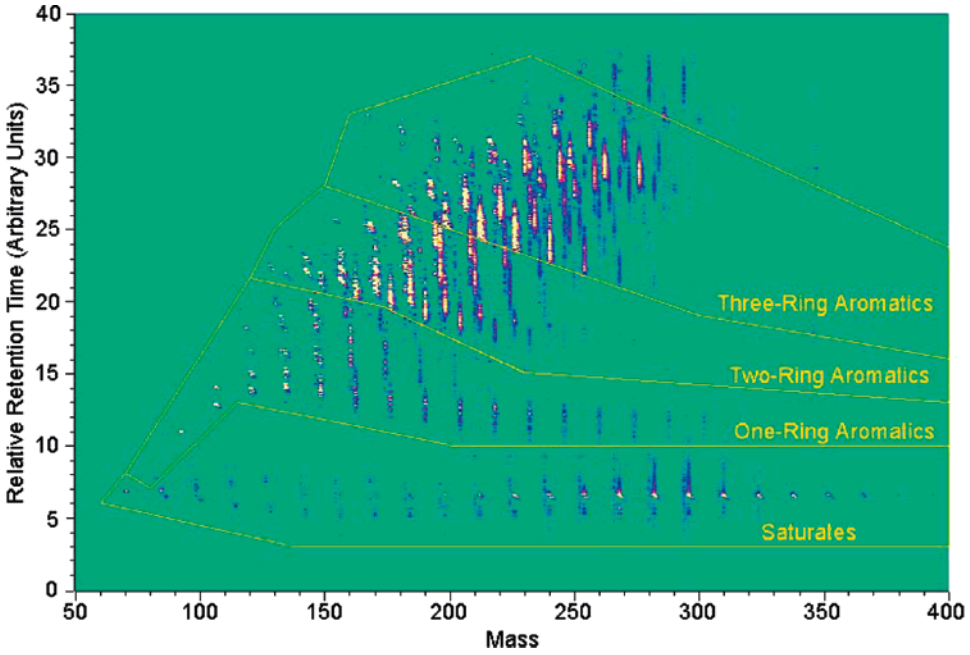

Figure 5. GC×MS chromatogram of a refinery stream boiling at diesel temperature range.

converter (TDC) with a sampling rate of 3.6 GHz. The voltage pulse was applied at a frequency of 30 kHz. A full spectrum was generated every 33 μS. The mass range was normally set at 50−800 Da. The scan duration time or spectrum accumulation time was 1 s (i.e. every "scan" is an accumulation of 30 000 spectrum).

Since FI generates mostly a single molecular ion, a mixture of compounds (normally halogenated hydrocarbons) was used to calibrate a wide mass range from 50 to 800 Da. A typical calibration mixture contains heptacosapentafluorobenzene, hexafluorobenzene, pentafluoroiodobenzene, pentafluorochlorobenzene, perfluorotrimethylcyclohexane, xylene, and acetone. The calibrants were introduced into the ion source via a batch inlet and were pumped out after the calibration. During sample analyses, a single lock compound was introduced as an internal reference for accurate mass measurement. In our experiments, pentafluoroiodobenzene with a monoisotopic mass of 293.896 Da was used as the internal reference.

RESULTS

Figure 1 demonstrates the 2DGC (GC×GC) chromatogram of a typical petroleum stream in the diesel boiling point range. The distribution of different compound classes as well as the different carbon number components within the compound class can be clearly shown and matched with that of a previous report.[1] This two-dimensional plot is a representative chromatogram when hydrocarbon compounds have been separated by their boiling point (*X*-axis) as well as their polarity (*Y*-axis).

Figure 2 is a typical GC/MS chromatogram with FI as the ionization mechanism. The *X*-axis is retention time or a scan number and the *Y*-axis is total ion current (TIC). If a peak in the TIC is of interest, the MS scan corresponding to that peak can be brought up and examined to identify the chemical structure of that specific component. In this situation, the GC is used as a separation device and the MS is used as an identification apparatus. The combination of GC and MS, GC/MS, provides a much more powerful instrument than GC/FID for separated component identification.

Since every data point in Figure 2 is representative of an MS scan, instead of one point (TIC), the *Y*-axis can display the whole mass spectrum, where the *Y*-axis becomes a mass axis and the *Z*-axis is the ion intensity. This way, the GC/MS chromatogram can be turned from a two-dimensional display to a three-dimensional display. Figure 3 shows the GC/MS three-dimensional chromatogram with all mass spectra plotted in the *Y*−*Z* plane and staggered up along the *X*-axis. Figure 3 is the three-dimensional chromatogram of the same sample as Figure 2. Each component in the original mixture has a peak in Figure 3. However, Figure 3 does not provide the same detailed insight as Figure 1, at least the compound class separation is not obvious.

In order for a GC/MS chromatogram to look like the two-dimensional GC×GC and provide similar compound class separation information, one needs to manipulate the display to change the GC/MS to a GC×MS chromatogram. During this conversion, one aspect to consider is the mass axis. It is generally true that the higher the parent mass, the higher the boiling point of the molecule. Therefore, the mass axis can be viewed as approximately equivalent to the boiling point axis in Figure 1. The other aspect is the *Y*-axis. In GC×GC, the *Y*-axis is a relative polarity scale; it represents the polarity separation of each compound class with the same first dimensional retention time. The *Y*-axis in Figure 1 can be viewed as the relative polarity reference to paraffin (or normal-paraffin). In Figure 3, each mass axis slice (or row data slice) can be horizontally shifted to make the normal paraffins line up vertically; that way, the relative retention time (relative polarity) is referenced to the normal paraffins (graphically illustrated in the Figure 4).

After this transformation, the mass axis is rearranged as the *X*-axis and the *Y*-axis is the relative polarity axis and Figure 3 is converted to Figure 5. Figure 5 has the same features as Figure

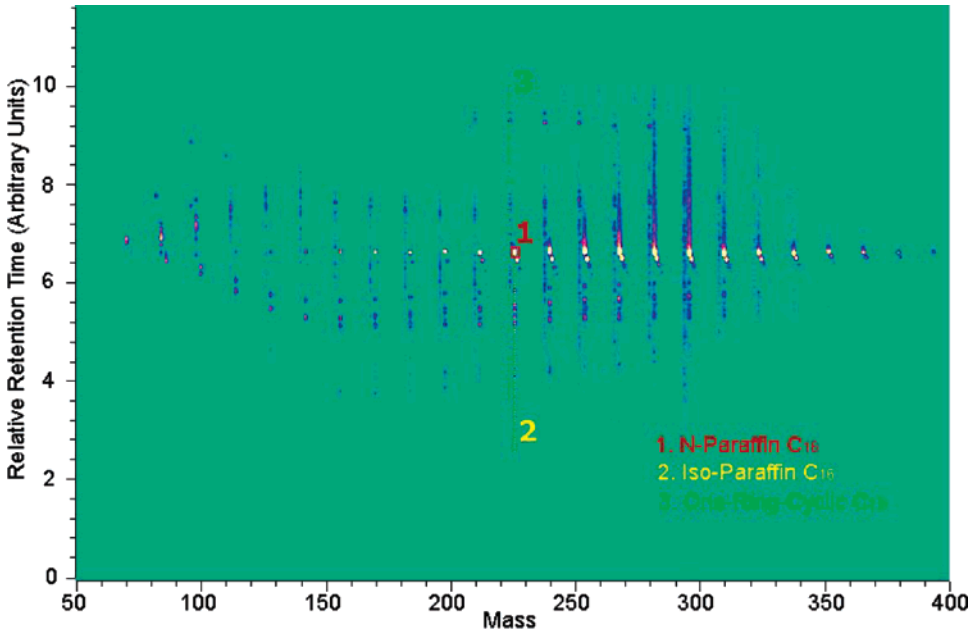

Figure 6. Saturates part of the chromatogram in Figure 5.

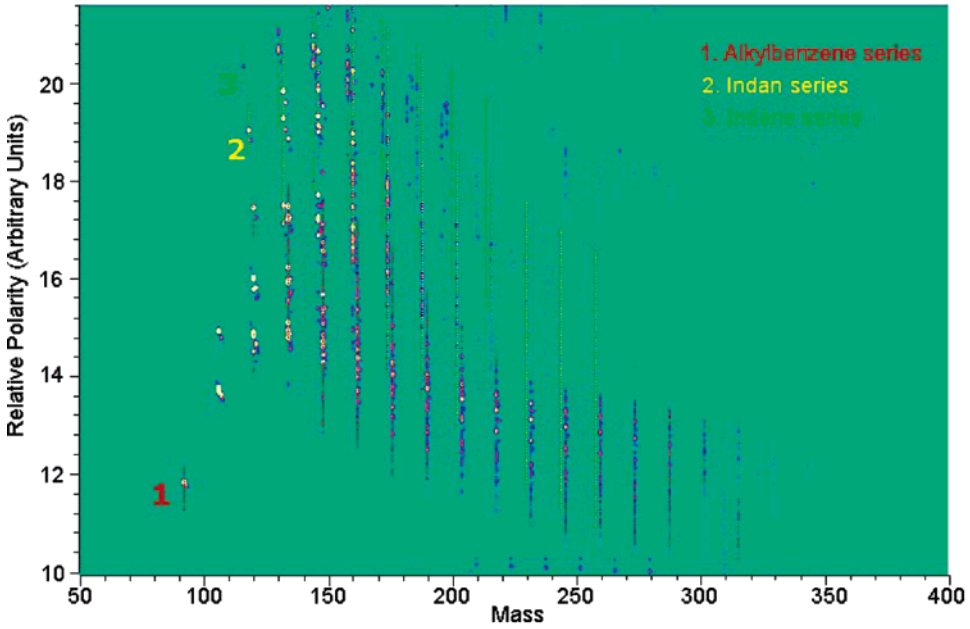

Figure 7. One-ring portion of the chromatogram in Figure 5.

1. The compound classes are identified in both Figures 1 and 5, and they have similar patterns. Thus when operating the GC/MS with MS in a soft ionization mode (FI), the traditional GC/MS separation/identification of a mixture can be appropriately visualized as a two-dimensional separation (GC×MS).

The three-dimensional visualization of GC×MS provides a clear separation of compound classes. However, this new visualization also gives an easy way for compound assignment/identification, because each compound series can be tracked by their parent masses. Figure 6 shows the saturates compound class portion of this diesel mixture with detailed isomer distribution of each compound group in the chromatogram. The paraffins, one-ring saturated cyclic compounds, and two-ring saturated cyclic compounds can be assigned by their masses. There are clear separations based on their parent mass without worry of any interference.

Figure 7 shows the one-ring aromatic portion of this diesel mixture. There are three major compound groups identified in carbon series under this compound class. Figures 8 and 9 show the two- and three-ring aromatic portions of this diesel mixture. The most abundant compound groups in these two portions are also assigned.

DISCUSSION

This new visualization of GC×MS data gives a new way to treat GC/MS results. The most valuable advantage of this visualization

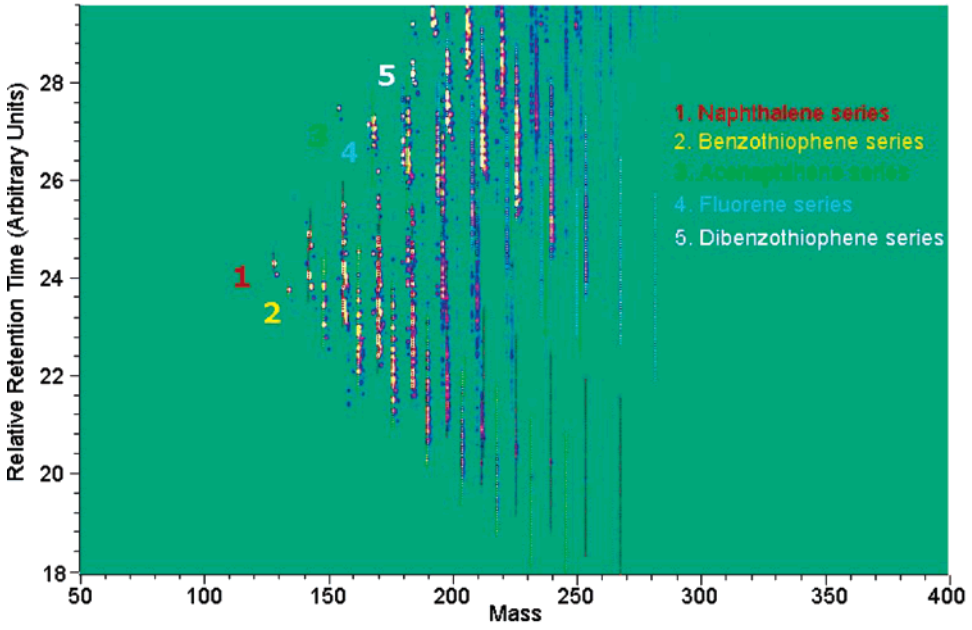

Figure 8. Two-ring portion of the chromatogram in Figure 5.

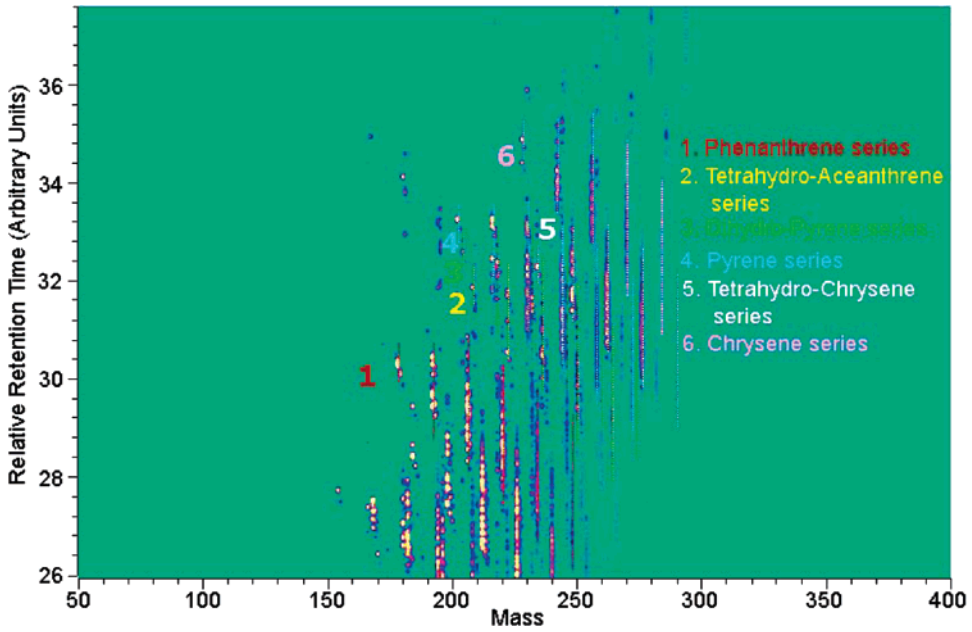

Figure 9. Three-ring portion of the chromatogram in Figure 5.

is the separation of compound classes. From a qualitative analysis point of view, the GC×MS separation is nearly as complete as the GC×GC separation. In addition, the data can be displayed in a more intuitive way, such that either the distribution or the relative intensity is emphasized. Figure 10 is a way to display the three-dimensional chromatogram of the saturates portion in this diesel sample so that the relative intensities are emphasized.

In addition to compound class separation, the separation of compound group within each compound class is another challenging task in petroleum separation. This is difficult by GC×GC, especially in the two and higher ring aromatics. However, the GC×MS does a very good job of providing detailed compositional data. For example, in the saturates class, paraffins can be separated from one-ring saturated cyclic compounds. Another example can be found in two and three aromatic ring portions. The different compound groups can be well-separated on the basis of their parent mass, which is difficult to do in the GC×GC because of the similarity of their relative polarity.

In GC×GC, one needs a sulfur element specific detector, such as a flame photomatric detector (FPD) or a sulfur chemiluminescence detector (SCD), in order to generate a distribution chromatogram of a sulfur-containing compound. However, because the GC/MS runs in the FI mode, the parent masses of all compounds can be obtained in one experiment. The high-resolution mass operation means each mass will represent a unique molecular formula. This particular feature becomes a powerful tool when looking into element specific compound distribution in the complex mixture. In the GC/MS, a specific mass or group of

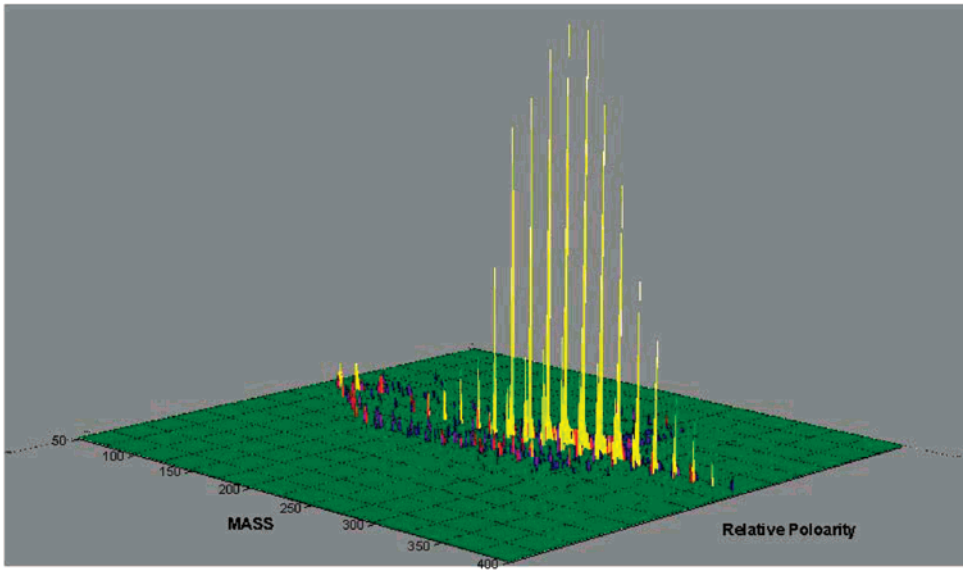

Figure 10. Contour display of the saturates part of the chromatogram in Figure 5.

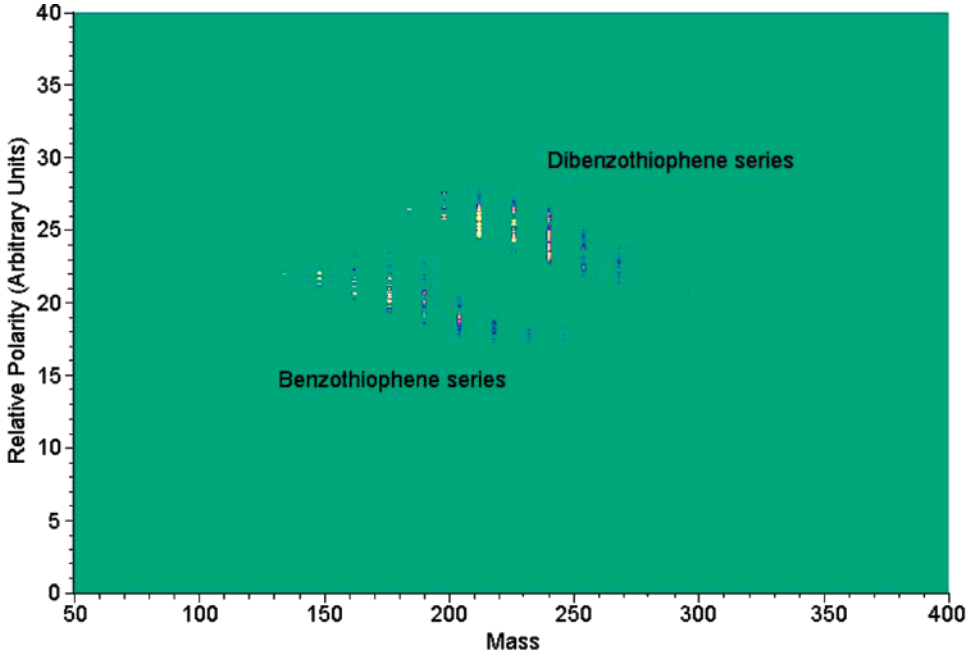

Figure 11. GC×MS chromatogram of the sulfur-containing compounds.

masses can be extracted from data to form a separate chromatogram. This operation is similar to but more advanced than signal ion monitoring in the traditional GC/MS data analysis. Chromatograms of sulfur-containing (e.g., benzothiophenes and dibenzothiophenes) and nitrogen-containing compounds (indoles and carbazoles) can be extracted out from original GC×MS chromatograms to form separate chromatograms.

Figures 11 and 12 illustrate the chromatograms of sulfur-containing (benzothiophenes and dibenzothiophenes) and nitrogen-containing compounds (indoles and carbazoles). During this exact mass extraction process, there is interference that was caused by similar mass of hydrocarbon analogues. However, most of the interference can be easily eliminated after carefully examining their compound class, relative polarity, and appropriate isotopes.

The quantitative analysis of GC×MS faces the same challenge as GC/MS. Because of the nonuniversal response of parent ion production, it is not practical to use the parent ion intensity directly to perform the quantitative analysis. The relative response factor generation has to rely on pure compound calibration or comparison with another detector that has more universal response, such as FID.

The purpose of this GC×MS visualization is to demonstrate the power of two (multiple) dimensional separation. GC×GC for petroleum analysis typically uses a combination of nonpolar and polar columns. This type of combination is intended to achieve a boiling point and a relative polarity separation. In the GC/MS experiment, a nonpolar column is put in the GC to achieve the boiling point separation. This is a typical mode when utilizing the

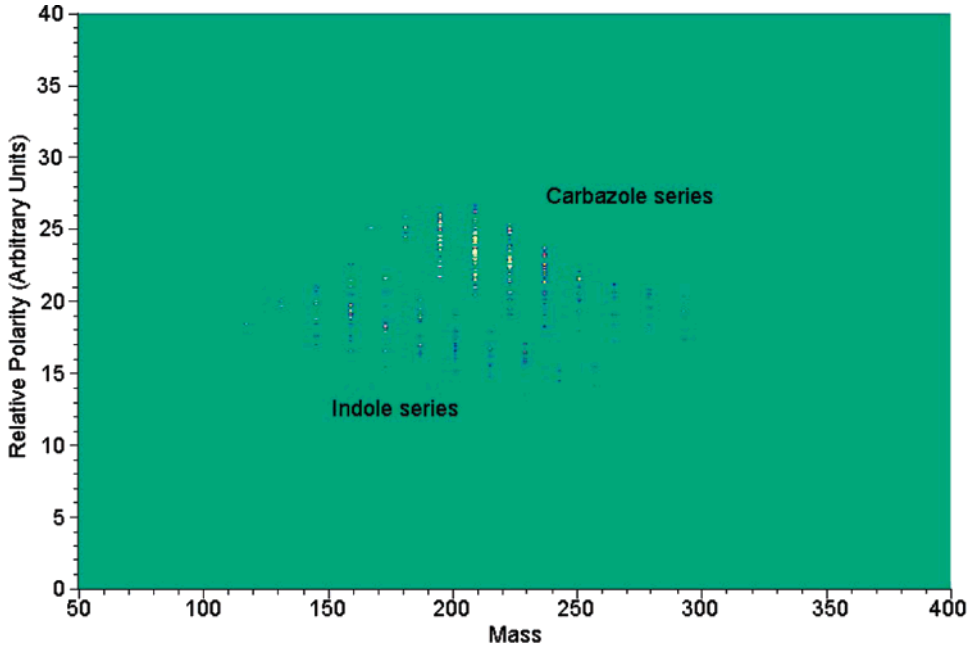

Figure 12. GC×MS chromatogram of the nitrogen-containing compounds.

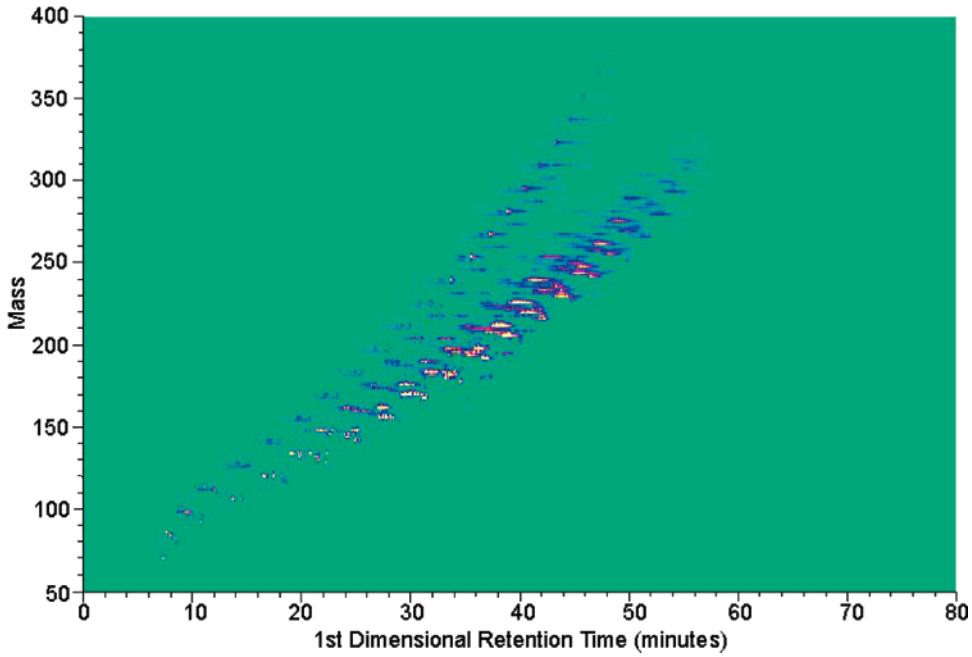

Figure 13. Chromatogram of nonpolar capillary separation column in the GC.

GC to perform the separation and MS to carry out the identification. As discussed earlier, the mass scale can be viewed as a pseudo-boiling-point scale. To accomplish the maximum polarity separation, a polar column will be more appropriate in the GC to achieve the boiling point and relative polarity (two-dimensional) separation. Figure 13 shows a nonpolar column in the GC with similar experimental conditions as in Figure 3. The relative polarity separation in not good enough to claim any advantages of the two (multiple) dimensional separation.

CONCLUSION

GC/MS with an appropriate soft ionization mechanism, such as FI, can be turned into a two-dimensional separation technique, GC×MS. The major advantage of GC×MS is the compound class separation. The compound groups within a compound class are also well-separated on the basis of their parent masses. Because of the high-resolution mass operation, the specific elemental containing compound distribution can also be generated through the extraction of specific mass groups. For qualitative analysis, GC×MS is a one-for-all technique where one experiment can generate most of the information.

GC×GC and GC×MS are both two-dimensional separation techniques. If focused on the boiling point and relative polarity separation, these two techniques are complementary to each other, especially in the compound group separation within a compound

class and quantitative analysis. However, the GC×MS analysis does not require a sophisticated modulation device as GC×GC, as this can be accomplished in the data analysis.

From GC×GC to GC×MS, the power of two (multiple) dimensional separation has just started exposing its advantages for complex mixture analysis. To achieve multiple dimensional separation in different forms, many improvements remain to be made. The biggest challenge now is to combine/accommodate two or more different techniques together to make a reasonable combination to solve a specific complex separation problem. The GC×MS experience has pushed this effort one step ahead toward the complete application of this new concept to the complex mixture separation.

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