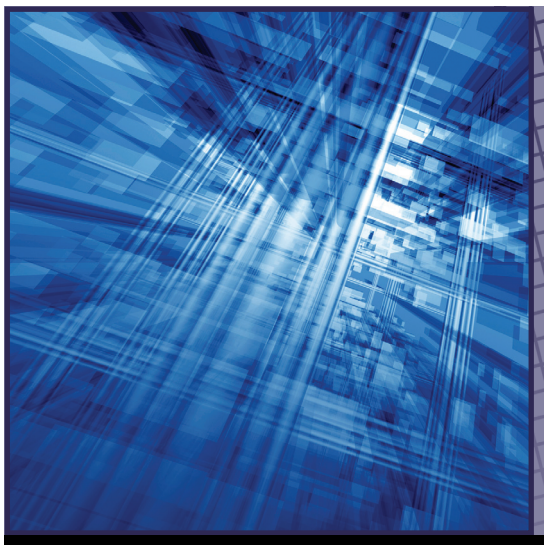

Quantifying FAMEs at ppm Levels in a Petroleum Diesel and Biodiesel Blend Using GCxGC

Jack Cochran, Restek Corporation
110 Benner Circle, Bellefonte, PA, U.S
Tel: 1-814-353-1300 (outside U.S.) or 1-800-356-1688 (inside U.S.) • Email: support@restek.com • Web: www.restek.com

Comprehensive 2D GC, also known as GCxGC, is still an emerging technology in many industries. However, since it separates components from a single injection across 2 chromatographic planes, it offers a great deal of potential for improving the analysis of complex petroleum and petrochemical samples. In general, GCxGC can be used to analyse hydrocarbons ranging in volatility from C4 (butane) to C40 (tetracontane). This work demonstrates the potential application of GCxGC to the analysis of ppm levels of fatty acid methyl esters (FAMEs) in petroleum diesel:biodiesel blends.

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 short (1-2 m) and typically polar. 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 greater separation space, which can be used to increase resolution and improve quantitative accuracy for compounds that coelute in the first dimension.

The analysis of FAMEs in diesel:biodiesel blends is a good example of how greater resolution can be achieved, and also of how column choice in the first dimension ultimately affects the overall separation. While the analysis of FAMEs at higher concentrations in petroleum diesel is relatively straightforward, the quantification of low ppm levels of FAME impurities required for some products, such as the 30 ppm maximum level in aviation fuel established by the U.S. Federal Aviation Administration [1], can be quite challenging. GCxGC offers a powerful way to determine ppm level FAME content in the presence of bulk hydrocarbon material, but the key to using it effectively is to maximise use of the second dimension space. Column choice is an integral part of any GCxGC analysis, and, as noted by Seeley et al. in an upcoming publication about their solvation parameter model, the first dimension column can have a large impact on the second dimension separation [2].

To demonstrate this, a diesel:biodiesel standard diluted in petroleum diesel was analysed by GCxGC-FID using 2 different first dimension columns, each paired with the same second dimension column (Rxi®-17Sil MS, 50% phenyl polysilarylene-siloxane) and used under identical conditions. The first dimension columns, an Rxi®-5ms (5% diphenyl 95% dimethyl polysiloxane) column and an Rtx®-200 (trifluoropropylmethyl-siloxane) column were of the same length and inner diameter. As shown in Figure 1, when using the Rxi®-5ms as the first dimension column, the FAME compounds eluted above the n-alkanes in a region where interferences could occur with the cyclic alkanes and monoaromatics. However, when the Rtx®-200 column was used as the first dimension column, the position of the FAMEs moved slightly below and to the right of the bulk petroleum hydrocarbons.

Perhaps surprisingly, it is the column choice and elution temperature in the first dimension that explains the retention crossover of the alkanes and FAMEs in the second dimension. The hydrocarbons in petroleum diesel are less retained by the Rtx®-200 column than by the Rxi®-5ms column, which means that most of these compounds experience more retention on the Rxi®-17Sil MS column since they're "injected" onto it by the GCxGC modulator while the secondary column is at a lower temperature. This is even more apparent in Figure 2, which shows the full contour plots on exactly the same time scale. Note the broader distribution of compounds across the second dimension space when the Rtx®-200 column is used in the first dimension. Not only do the petroleum hydrocarbons elute earlier on the Rtx®-200 column and show increased retention on the Rxi®-17Sil MS column as a consequence, but the FAMEs also elute proportionately later on the Rxi®-5ms column (Table I). On the Rxi®-5ms column, the alkanes (and other hydrocarbons) elute so late that they have less retention on the Rxi®-17Sil MS column and cross over into the FAMEs region. Ultimately, the influence of the first dimension column results in better calibration curves for FAMEs in a diesel:biodiesel blend at the ppm level when using the Rtx®-200 and Rxi®-17Sil MS column setup (Table II).

As shown here, GCxGC-FID offers an intriguing opportunity to quantify ppm levels of FAMEs in diesel:biodiesel blends, but the first dimension column has a significant influence on the second dimension separation and the overall results. By choosing an Rtx®-200 and Rxi®-17Sil MS column combination, the fatty acid methyl esters are largely placed in the region of least interference, where more accurate quantification is possible.

References

[1] U.S. Federal Aviation Administration, Special Airworthiness Information Bulletin NE-09-25R1, Fuel: Jet Fuel Containing FAME (Fatty Acid Methyl Ester), August 19, 2009.

[2] J.V. Seeley, C.T. Bates, J.D. McCurry, S.K. Seeley, Stationary phase selection and comprehensive two-dimensional gas chromatographic analysis of trace biodiesel in petroleum-based fuel, J. Chromatogr. A in press.

Table I: Retention times of FAMEs and alkanes in a petroleum diesel:biodiesel blend. Note that the petroleum hydrocarbons elute earlier on the Rtx®-200 column than on the Rxi®-5ms column, which results in increased retention and later elution on the Rxi®-17Sil MS column.

FAME and Alkane Compounds	C:DB	Rtx®-200 RT 1 (sec.)	Rxi®-17Sil MS RT 2 (sec.)	Rxi®-5ms RT 1 (sec.)	Rxi®-17Sil MS RT 2 (sec.)
Methyl palmitate	16:0	2125	2.68	2440	1.76
Methyl oleate	18:1	2340	2.85	2685	1.78
Methyl linoleate	18:2	2345	2.95	2680	1.85
Methyl linolenate	18:3	2355	3.07	2690	1.90
Methyl stearate	18:0	2370	2.68	2770	1.70
Methyl arachidate	20:0	2595	2.69	2980	1.65
Methyl behenate	22:0	2805	2.70	3215	1.61
Methyl lignocerate	24:0	3000	2.70	3435	1.58
C20	-	2010	3.05	2550	1.51
C22	-	2255	3.05	2815	1.49
C24	-	2485	3.03	3065	1.45

Experimental

GCxGC-FID analysis of low level FAMEs in diesel:biodiesel was performed using 2 primary columns for comparison: an Rtx®-200 column (30 m x 0.25 mm x 0.25 µm) and an Rxi®-5ms column (30 m x 0.25 mm x 0.25 µm). The secondary GC column in both cases consisted of an Rxi®-17Sil MS column (1 m x 0.15 mm x 0.15 µm). Both column combinations were operated with helium carrier gas at a corrected constant flow of 1.6 mL/min. To prepare a low FAME content diesel sample for injection, an 80:20 diesel:biodiesel standard was diluted in petroleum diesel, resulting in a 99:1 diesel:biodiesel sample for injection. One microliter 20:1 split injections of this sample 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 305°C at 4°C /min. (hold 1.05 min.) The secondary oven program was: 45°C (hold 2.25 min.) to 340°C at 4.50°C /min. (hold 0.49 min.) For GCxGC, the thermal modulator temperature offset was 40°C and a modulation time of 5 seconds was used. The hot pulse time was 1.7 sec. A GCxGC-FID (LECO, St. Joseph, MI, USA) was used for analysis with a detector temperature of 350°C and a data acquisition rate of 200 Hz.

Table II: FAME calibration in a petroleum diesel:biodiesel blend is affected by first dimension column choice. Linear calibrations down to low ppm levels can be achieved using the Rtx®-200 and Rxi®-17Sil MS column combination, due to increased retention and better use of the separation space.

FAMEs	C:DB	Concentration Range (ppm)	Number of Points	Correlation (r) Rtx®-200*	Correlation (r) Rxi®-5ms*
Methyl palmitate	16:0	22-550	5	0.986	0.994
Methyl oleate	18:1	11-460	6	0.993	0.648
Methyl linoleate	18:2	27-540	5	0.981	0.961
Methyl linolenate	18:3	14-690	6	0.998	0.945
Methyl stearate	18:0	8.6-860	7	0.998	0.468
Methyl arachidate	20:0	18-750	6	0.999	0.991
Methyl behenate	22:0	9.2-460	6	0.997	0.992

** Second dimension column = Rxi®-17Sil MS column; r = Pearson correlation coefficient.*

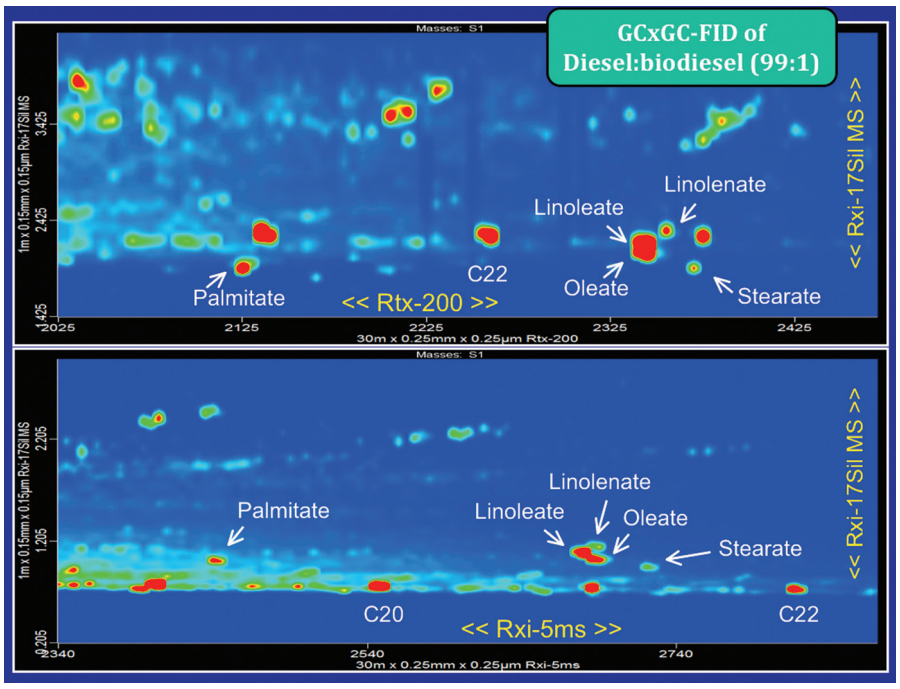

Figure 1: Comparison of the separation of FAMEs in petroleum diesel:biodiesel using different first dimension columns. When the Rtx®-200 column is used as the first dimension column, the FAMEs elute below the majority of the hydrocarbons. In contrast, when an Rxi®-5ms column is used, the FAME compounds elute above the alkanes in a region of greater interference.

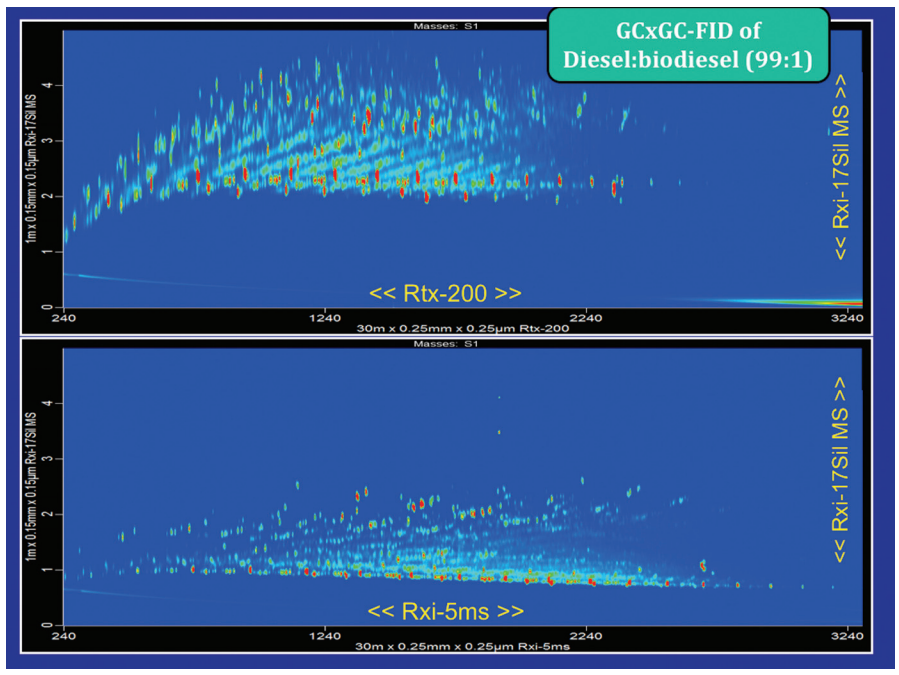

Figure 2: Comparison of the full contour plots on the same scale demonstrates the broader distribution of compounds across the second dimension space that occurs when the Rtx®-200 column is used for the first dimension separation.