

Detection of Siloxanes in Silicone Oils by GCxGC-TOFMS

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Key Words: TOFMS, GCxGC, Deconvolution, Classification

1. Introduction

Two silicone oils, a 5 cStoke oil and a 20 cStoke oil are examined. In the one-dimensional GC-MSD examination of silicone oils for siloxanes approximately 22 peaks were observed in the 5 cS oil, and 35 peaks were observed in the 20 cS oil. The results obtained from a GCxGC-TOFMS examination of the same oils follow.

2. Instruments and Methods

In this study, measurements were made with a LECO Pegasus® 4D GCxGC-TOFMS system. This system consists of an Agilent 6890 gas chromatograph equipped with a LECO dual-jet thermal modulator between the primary and secondary columns, and a LECO Pegasus IV Time-of-Flight Mass Spectrometer (TOFMS) as a detector. For this study, the primary analytical column was a 30.0 m x 0.25 mm ID x 0.25 μ m df RTX-5. The secondary column was a 1.40 m x 0.10 mm ID x 0.10 μ m df DB-17ms. Helium was used as the carrier gas at a constant flow of 1.5 mL/min. The transfer line to the TOFMS consisted of the last 20 cm of the analytical column. The detector was optimized to have a S/N ratio of ≥ 100 for a 20.0 μ g/L injection of hexachlorobenzene with a detector voltage of 1700 volts.

For these non-quantitative analyses, samples of each Silicone Oil were diluted 1:50 in HPLC-grade n-pentane. Injections were 1 μ L using the splitless mode of the split/splitless inlet.

3. Results

The data processing of the 5 cStoke oil yielded 119 relevant peaks with S/N ratios of ≥ 500 . The assignment of peak identifications by the ChromaTOF® software required a spectral match of ≥ 600 . A contour plot of the 5 cS oil with peak markers is shown in Figure 1. Classifications were used to prevent processing of peaks in the band of column bleed along the bottom of the plot. The NIST-MS library used for peak identification has difficulty differentiating between larger linear siloxanes. In Figure 2, sample spectra for peaks identified as hexadecamethyl-heptasiloxane are shown along with the library spectrum for hexadecamethyl-heptasiloxane. The differences in spectra show that they are in fact different compounds that have all been identified as the same compound. The use of a user library generated from standards of siloxanes would aid in proper identification of peaks. The contour plot (in many cases) does show linear, branched, and cyclic siloxanes that were not separated on the first column, but were separated enough on the second column to be identified as a separate peak.

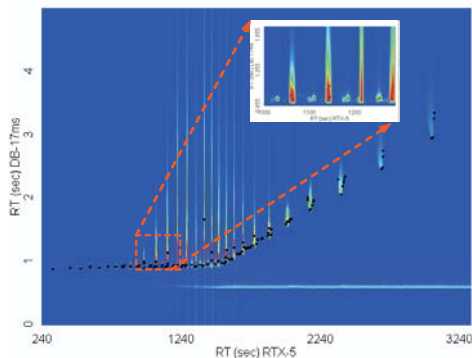


Figure 1: Contour plot of a 1 μ L splitless injection of the diluted (1:50 in n-pentane) 5 cS oil.

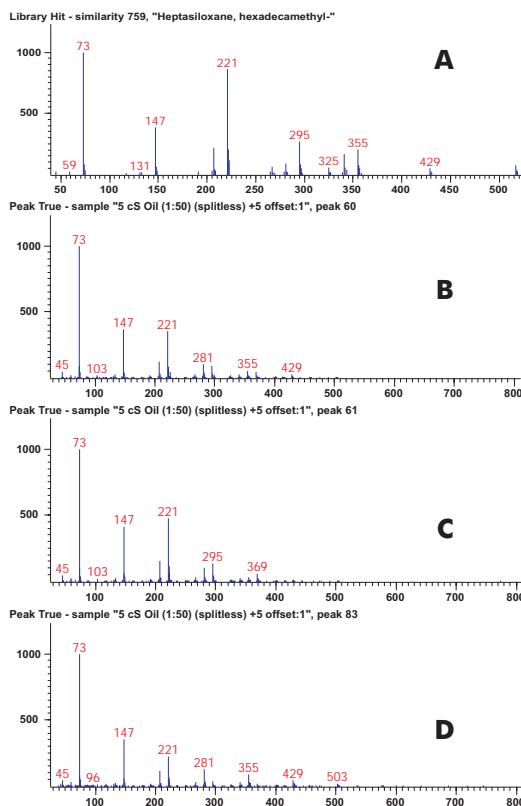


Figure 2: Library Spectrum (A) and Peak True Spectra for 3 different peaks (B, C, D) identified as hexadecamethyl-heptasiloxane by the NIST-MS Library.

The data processing of the 20 cStoke oil yielded 118 relevant peaks with S/N ratios of ≥ 500 . The assignment of peak identifications by ChromaTOF required a spectral match of ≥ 600 . A contour plot of the 5 cS oil with peak markers is shown in Figure 3. Classifications were used to prevent processing of peaks in the band of column bleed along the bottom of the plot.

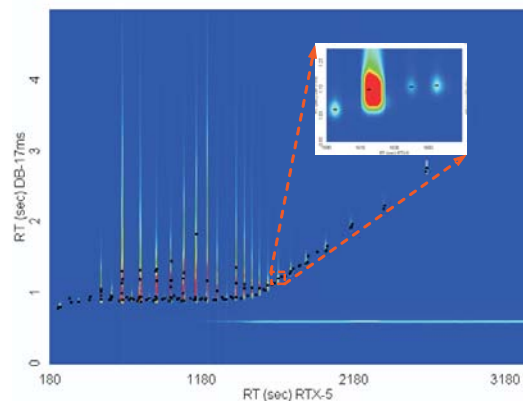


Figure 3: Contour Plot of a 1 μ L splitless injection of the diluted (1:50 in n-pentane) 20 cS oil.

The presence of other peaks can be seen by the streaking of the peaks in the second dimension. A single, non-overloaded peak should appear as a dot in the contour plot. In Figure 4, a 3-D view of a single modulation shows the secondary peak in the "tail" of the primary peak. The peak in the "tail" of the primary peak would coelute in a 1-D separation. Deconvolution of the mass spectral information can also separate coeluting peaks. An example of deconvolution is shown in Figure 5. The TIC trace shows a single peak, where deconvolution of the spectra yields 4 peaks. A feature of ChromaTOF that takes advantage of the structured nature of a GCxGC chromatogram is Classifications. Classifications can also be used to speed up data processing. Classifications allow the user to define areas of the contour plot to include or exclude from data processing. Figure 5 shows the Classification area used for the 20cS oil sample. Peaks falling outside of the defined area are not processed. This feature allows for the exclusion of the column bleed—the horizontal streak along the bottom right of the contour plot—from the data processing.

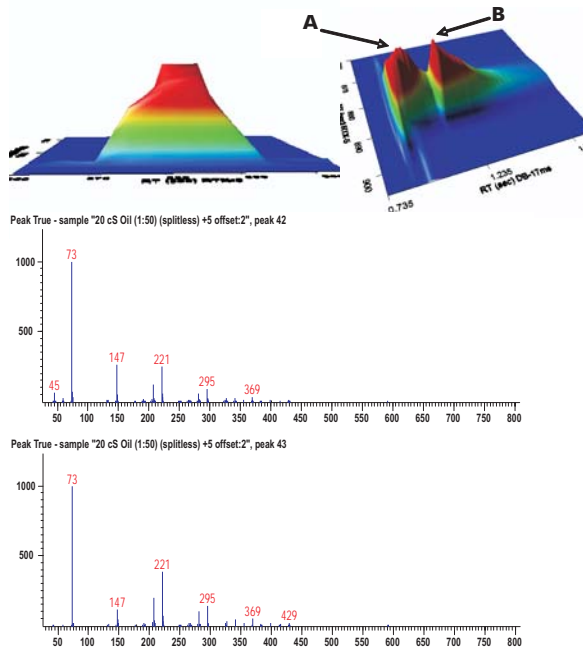


Figure 4: 3-D view of a peak "hidden" in the first dimension, but visible in the second dimension of the rotated view. Spectra for each peak are also shown. Note the same ions are present, but the relative abundances of m/z 147 and 221 differ. This suggests that the two peaks are very similar, perhaps different branching of the same siloxanes.

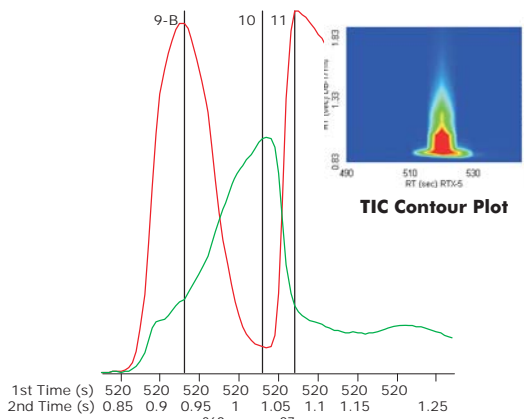


Figure 5: A Deconvoluted and Modulated 1-D Chromatogram of the 20 cS oil showing 4 peaks where the TIC shows only 1 peak.

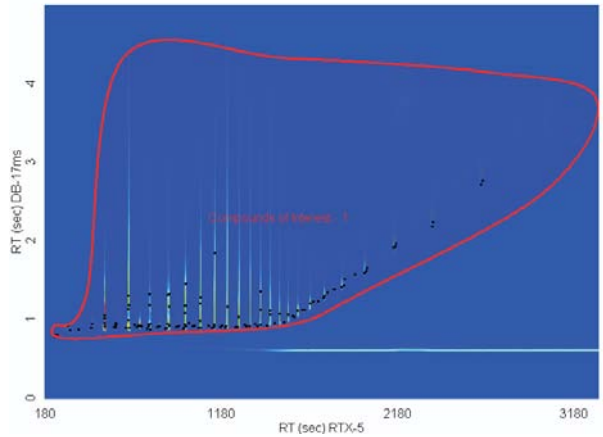


Figure 6: A contour plot of the 20 cS oil sample with the Classifications area's boundary visible.

4. Conclusions

In the GCxGC-TOFMS analysis of the 5 cS oil, 119 peaks were detected inside of the Classification area with S/N ratios >500. In the analysis of the 20 cS oil, 117 peaks were detected inside of the Classification area with S/N ratios >500. Many of the peaks were identified incorrectly by existing mass spectral library. Through the use of a user-defined mass spectral library, the identification of component peaks in these types of samples would be more accurate. The high spectral acquisition rate of the TOFMS allows for the deconvolution of similar compounds that are difficult to separate chromatographically. The resolving power of GCxGC enables the separation of very similar siloxanes that coeluted in the one-dimensional GC-MSD separation, and also allows later eluting compounds to be separated from the column bleed that occurs at high temperatures.

The use of the Classifications feature in ChromaTOF also allows for selective data processing, which results in faster processing and less complex data handling. The increased peak capacity and separating power combined with the spectral information obtained from the TOFMS lead to the conclusion that GCxGC analysis utilizing the LECO Pegasus 4D GCxGC-TOFMS and ChromaTOF software is an excellent choice for the determination of components in silicone oils.

