Comparing Detectability: Thermally Modulated GCxGC vs 1D GC

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NOTE: This document is intended to provide an introduction to LECO's GCxGC systems. Suggestions and recommendations are intended to help new users familiarize themselves with the technique and how the ChromaTOF® software is utilized. Many advanced parameters and options in GCxGC-related Methods are not addressed in this document. It is not designed and is not intended as a substitute for attendance at the LECO GCxGC Training Course. Methodology and Method Content are discussed at a level intended to enable a new user to begin system familiarization at a basic level.

Introduction

One of the most common advantages cited when comparing Comprehensive Two-Dimensional Gas Chromatography (GCxGC) and conventional One-Dimensional Gas Chromatography (1D GC) is the increase in detectability observed when utilizing GCxGC. It would be inaccurate to describe this as an increase in sensitivity because the detector still provides the same response per unit-mass of analyte. Sensitivity is detector dependant. A change in sensitivity would require that there was a change in detector response per unit-mass of analyte from one technique to the other. In this work, both 1D GC and GCxGC utilize the LECO Pegasus® Time-of-Flight Mass Spectrometer (TOFMS) as a detector. In fact, the same instrument, with the same column set, was used for both studies. For the 1D GC work, the thermal modulator was not enabled. In the GCxGC work, the thermal modulator was enabled and operational.

Two-Dimensional Gas Chromatography (GCxGC) Utilizing a Thermal Modulator

GCxGC is a technique that utilizes two columns of different selectivities, connected in series, to increase chromatographic resolution and peak capacity. The columns are joined by a modulator. The purpose of the modulator is to collect segments of effluent from the first column or first dimension, focus it into a narrow plug, and rapidly inject it onto the second column, or second dimension, where a rapid separation is performed every cycle, or modulation period. The technique is "comprehensive" in that the modulator functions in such a fashion that all effluent from the first dimension column is transferred onto the second dimension column.

The modulator serves two basic functions in GCxGC. Its first function is to collect segments of effluent from the first dimension column. Its second function is to act as the injector for the second dimension column. There are two main approaches to collecting segments of effluent from the primary column, Thermal Modulation and Valve-based Modulation. Only Thermal Modulation will be discussed here.

First, it is important to understand how a thermal modulator functions. The basis for Thermal Modulation can best be demonstrated by looking at the Band Migration Equation (Equation 1). In the Band Migration Equation, $u_{i,z}$ is the linear velocity of compound i at position z, u_z is the linear velocity of the carrier gas at position z, and k_i is the retention factor for compound i.

$$u_{i,z} = \frac{u_z}{k_i + 1}$$

Equation 1.

Position z will be defined as the location where modulation occurs. For analytes to be "focused" in the modulator, the goal is to have $u_{i,z}$ be equal to zero. This can be accomplished in one of two ways. The value of u_z can be decreased to zero, or the value of k_i can be increased to near infinity. Thermal modulators focus analytes by decreasing the temperature, in the cold zone of the modulator (CZM), to increase the value of k_i to near infinity. The colder the temperature that can be obtained in the CZM, the more volatile the analytes that can be focused. In the thermal modulator utilizing liquid nitrogen (LN_2), the modulator is capable of focusing n-butane. This means that the temperature on the CZM is not low enough to focus the helium used as the carrier gas. The helium passes through the modulator, but the temperature in CZM is cold enough to cause analytes with volatilities less than or equal to n-butane to be focused in the CZM. The process of a gaussian chromatographic band being modulated is shown in Figure 1. The gaussian chromatographic band is migrating down the column. As the leading edge of the chromatographic band enters the CZM, its temperature is rapidly decreased and its retention factor increases very rapidly. This causes the linear velocity of the band to decrease very rapidly, while at the same time, the center and trailing edge of the chromatographic band continue to migrate along the column. As the middle of the chromatographic band enters the CZM, its temperature is rapidly decreased and its retention factor increases very rapidly. Since the CZM is a finite length at a fixed location, the middle portion of the chromatographic band will be focused in the same portion of the CZM where the leading edge of the band was focused. This process will continue until the entire chromatographic band is focused in the CZM. When the modulation cycle is almost complete, the CZM is heated rapidly to inject the focused band as a narrow injection plug onto the second column.

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The area of the focused chromatographic band will be equal to the area of the original chromatographic band. This is because the entire mass of the analyte that comprised the original chromatographic band is still present in the focused band. Detector signal is directly proportional to the mass of analyte striking the detector. In the case of the narrower, focused peak, more analyte strikes the detector per unit time, resulting in a more intense detector signal.

These narrow focused peaks also require adjustments in the sampling rate of the detector. In order to be able to quantify compounds in conventional, single dimensional gas chromatography, a minimum of 10 data points are required across a baseline resolved peak in order to accurately define the peak shape. For a one second wide peak, this translates to a minimum sampling rate of 10 Hz. For 100 millisecond wide peaks, which are regularly generated in the second dimension of GCxGC, a minimum sampling rate of 100 Hz is required in order to obtain the necessary number of data points. LECO recommends a minimum of 18 to 20 data points across a baseline resolved peak for optimal performance of the deconvolution algorithm. This would necessitate 20 Hz for a 1 second wide peak and 200 Hz for a 100 millisecond wide peak.

In the examples that follow, all analyses were performed on the same instrument. The sample in all cases was an identical injection of a mixture of n-C_{14} to n-C_{18}. The only variables were whether the modulator was functioning and the sample acquisition rate. For a direct comparison of the effects of the thermal modulator's operation, a 1D GC and a GCxGC sample collected at the same sampling rate, will be compared. In all cases, the chromatogram will consist of the trace for m/z 57. Figure 2 shows the peaks from n-C_{14} to n-C_{18} for the sample run in 1D GC at 200 Hz. The peaks' height, signal-to-noise (S/N) and Full-Width-at-Half-Height (FWHH) are shown.

Figure 3 shows the peaks from n-C_{14} to n-C_{18} for the sample run in GCxGC at 200 Hz. The base peaks' height, S/N and FWHH are shown.

A direct comparison of the S/N values for each technique shows a marked increase in the S/N for the GCxGC peaks. The percentage increase in S/N from 1D GC to GCxGC, both collected at 200 Hz, is shown in Table 1.

Table 1: A table showing the percentage increase in S/N from 1D GC to GCxGC, both collected at 200 Hz, for n-C_{14} to n-C_{18}.

GC [200 Hz] to GCxGC [200Hz]			
Name	S/N [GC]	S/N [GCxGC]	% Change in S/N
TETRADECANE	276.33	6562.7	2275.0%
PENTADECANE	364.14	7592.7	1985.1%
HEXADECANE	354.51	7540.1	2026.9%
HEPTADECANE	325.92	6994.1	2046.0%
OCTADECANE	138.03	6269.5	4442.1%

Figure 4 is an overlay of the 1D GC (green) and GCxGC (red) chromatograms that were both collected at 200 Hz. Note the difference in signal intensity between the focused and unfocused peaks.

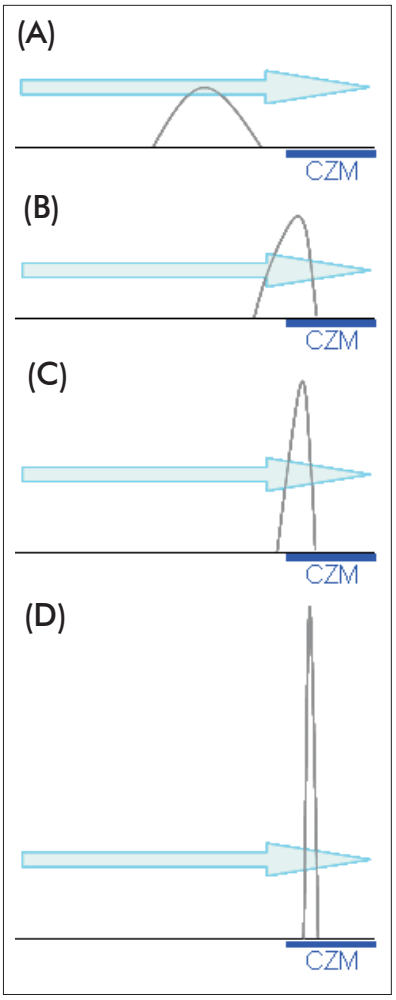

Figure 1: An example of a gaussian chromatographic band migrating down the column (A). As the leading edge of the chromatographic band enters the CZM (B), its temperature is rapidly decreased and its retention factor increases very rapidly. This causes the linear velocity of the band to decrease very rapidly, while at the same time, the center and trailing edge of the chromatographic band continue to migrate along the column. As the middle of the chromatographic band enters the CZM (C), its temperature is rapidly decreased and its retention factor increases very rapidly. Since the CZM is a finite length at a fixed location, the middle portion of the chromatographic band will be focused in the same portion of the CZM where the leading edge of the band was focused. This process will continue until the entire chromatographic band is focused in the CZM (D). The carrier gas flow is represented by the light blue arrow.

While comparing 1D GC and GCxGC collected at the same sampling rate does demonstrate signal enhancement due to modulation, it can also be argued that the 1D GC trace in this example is oversampled and is therefore not a valid comparison of 1D GC vs. GCxGC. According to LECO's recommendation of 18 to 20 data points across a peak, the 1D GC analysis should be performed with a data acquisition rate of 20 Hz for an ~1 second wide peak. The implications of a peak being oversampled are that the intensity of its signal will be decreased and the amount of noise will increase. In a summing detector, such as the TOFMS, slowing the acquisition rate can help increase signal intensity. In the case of LECO's Pegasus TOFMS, the detector is sampled at 5000Hz. Groups of transient signals are summed by the data acquisition system. If the data acquisition rate is set to 200 spectra/second, 25 transient signals are summed and recorded as a data point. If the data acquisition rate is set to 20 spectra/second, 250 transient signals are summed and recorded as a data point. The drawback is that all signal is summed, including noise.

In order to provide a sampling rate-optimized comparison, a GCxGC analysis sampled at 200 Hz will be compared with a 1D GC analysis sampled at 20 Hz. The GCxGC chromatogram was shown previously in Figure 3. Figure 5 shows the peaks from n-C_{14} to n-C_{18} for the sample run in 1D GC at 20 Hz. The base peaks' height, S/N and FWHH are shown.

Figure 6 is an overlay of the 1D GC collected at 20 Hz (green) and GCxGC, collected at 200 Hz (red) chromatograms for m/z 57. Note the difference in signal intensity between the focused and unfocused peaks and that the baseline of the 1D GC at 20 Hz chromatogram is elevated when compared to the chromatograms collected at 200 Hz. The summing of a larger number of transients leads to an increase in signal intensity, not only for the signal due to analytes, but also from background and noise.

The percentage increase in S/N from 1D GC, collected at 20 Hz, to GCxGC, collected at 200 Hz, is shown in Table 2.

Conclusions

One of the advantages that thermally modulated GCxGC has demonstrated over 1D GC is the increase in S/N that is obtained for identical amounts of analyte on-column. This increase in S/N is attributed to compression of the chromatographic band during focusing in the thermal modulator. In a mass dependant detector, such as an MS, FID, ECD, etc., the areas of peaks with a given mass of analyte will be equal. For a given peak area, a narrower peak must have a larger amplitude and therefore a larger signal from the detector.

Table 2: A table showing the percentage increase in S/N from 1D GC, sampled at 20 Hz, to GCxGC, sampled at 200 Hz, for n-C_{14} to n-C_{18}.

GC [20 Hz] to GCxGC [200Hz]			
Name	S/N [20 Hz]	S/N [200 Hz]	% Change in S/N
TETRADECANE	454.01	6562.7	1345.5%
PENTADECANE	415.61	7592.7	1726.9%
HEXADECANE	411.14	7540.1	1733.9%
HEPTADECANE	384.34	6994.1	1719.8%
OCTADECANE	347.85	6269.5	1702.4%

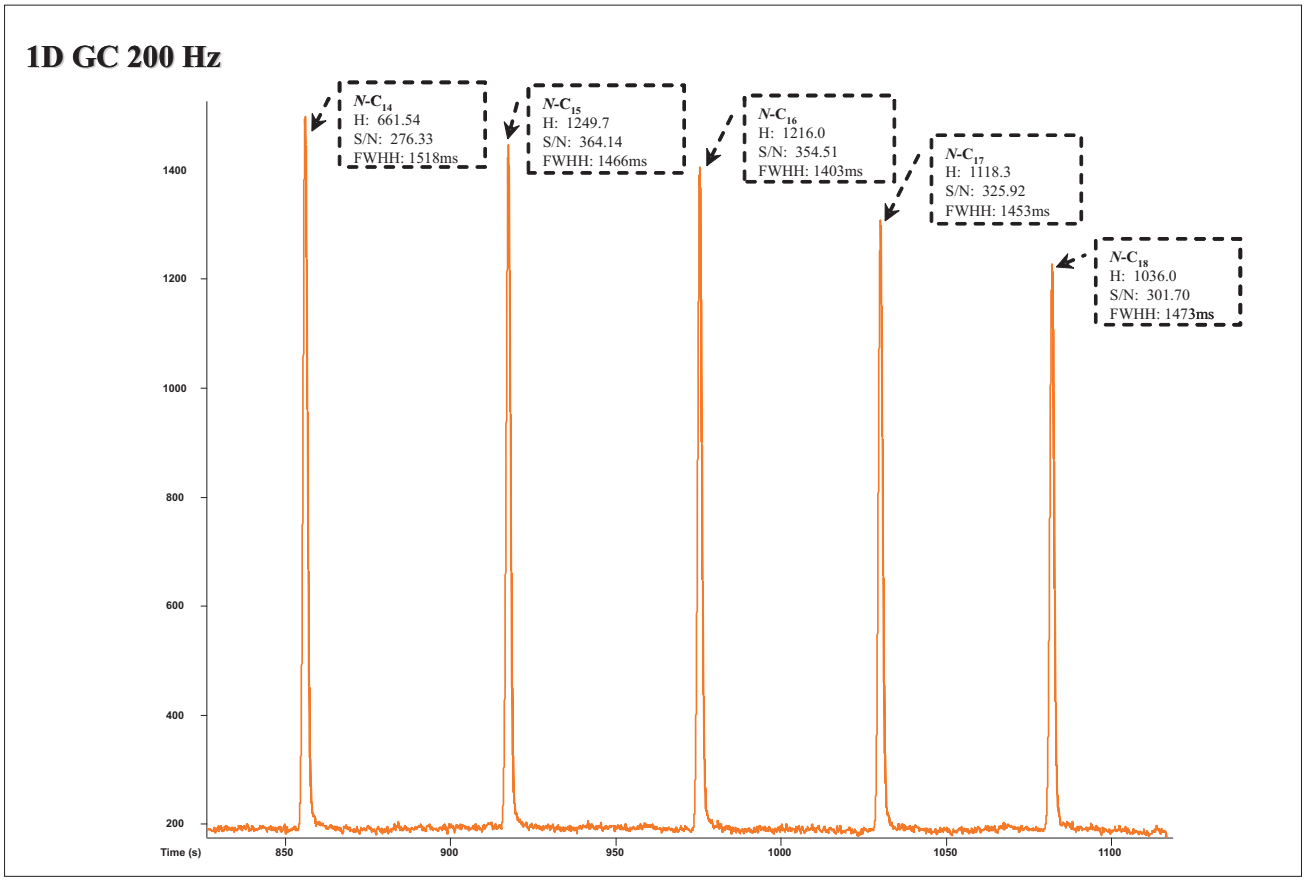

Figure 2: A chromatogram of the peaks from n-C_{14} to n-C_{18} for the sample run in 1D GC at 200 Hz. The peaks' height, S/N and FWHH are shown.

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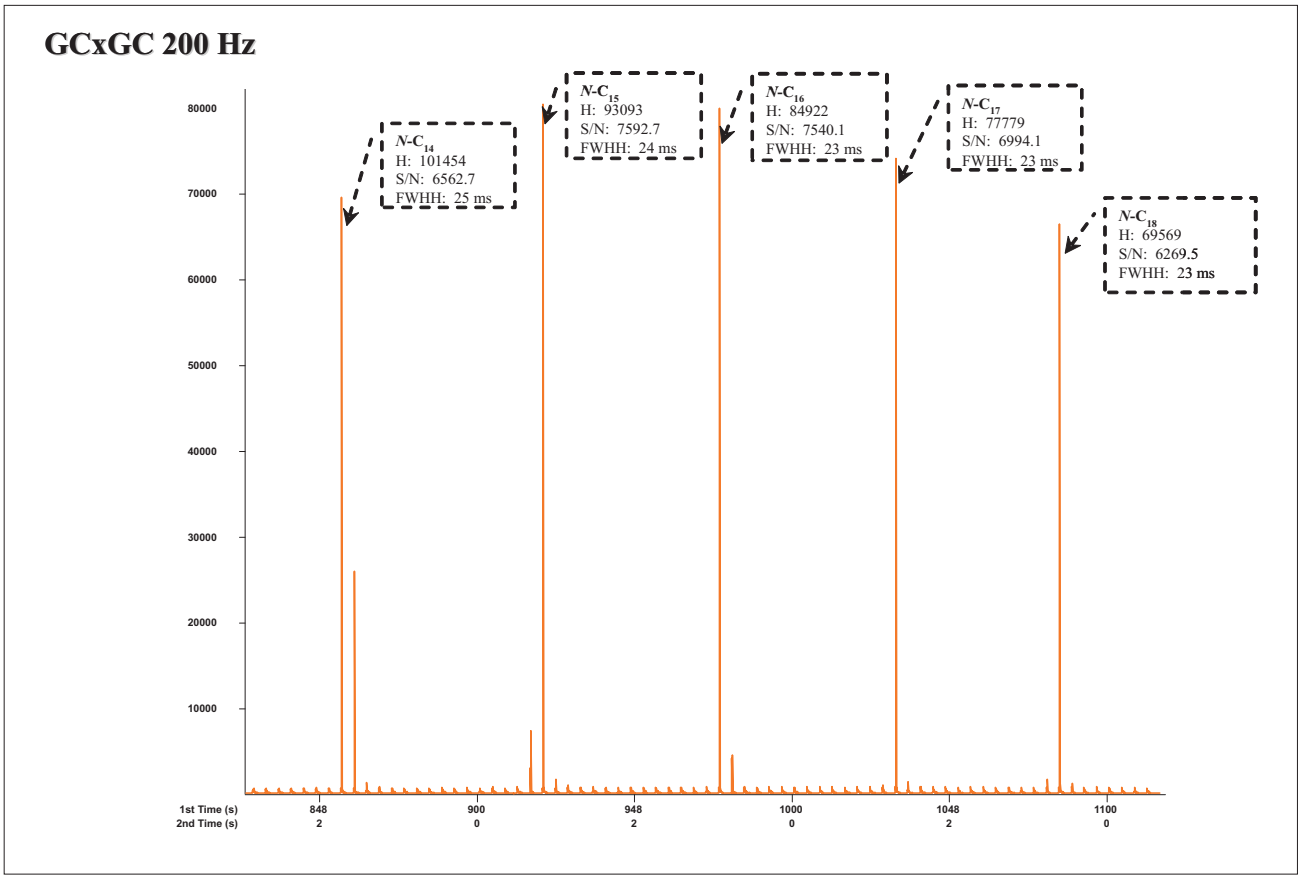

Figure 3: A chromatogram of the peaks from n-C_{14} to n-C_{18} for the sample run in GCxGC at 200 Hz. The base peaks' height, S/N and FWHH are shown.

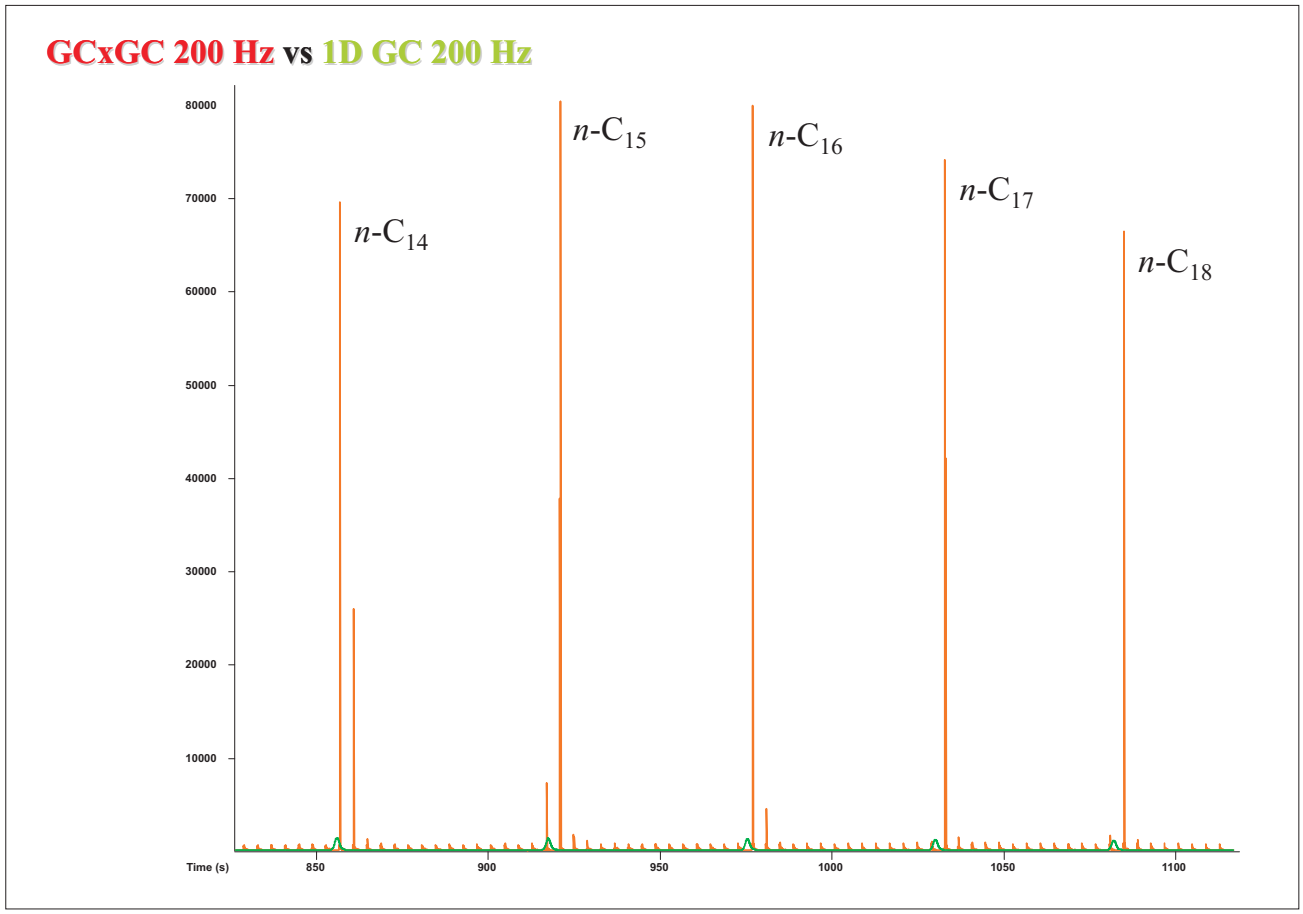

Figure 4: An overlay of the 1D GC (green) and GCxGC (red) chromatograms that were both collected at 200 Hz. Note the difference in signal intensity between the focused and unfocused peaks.

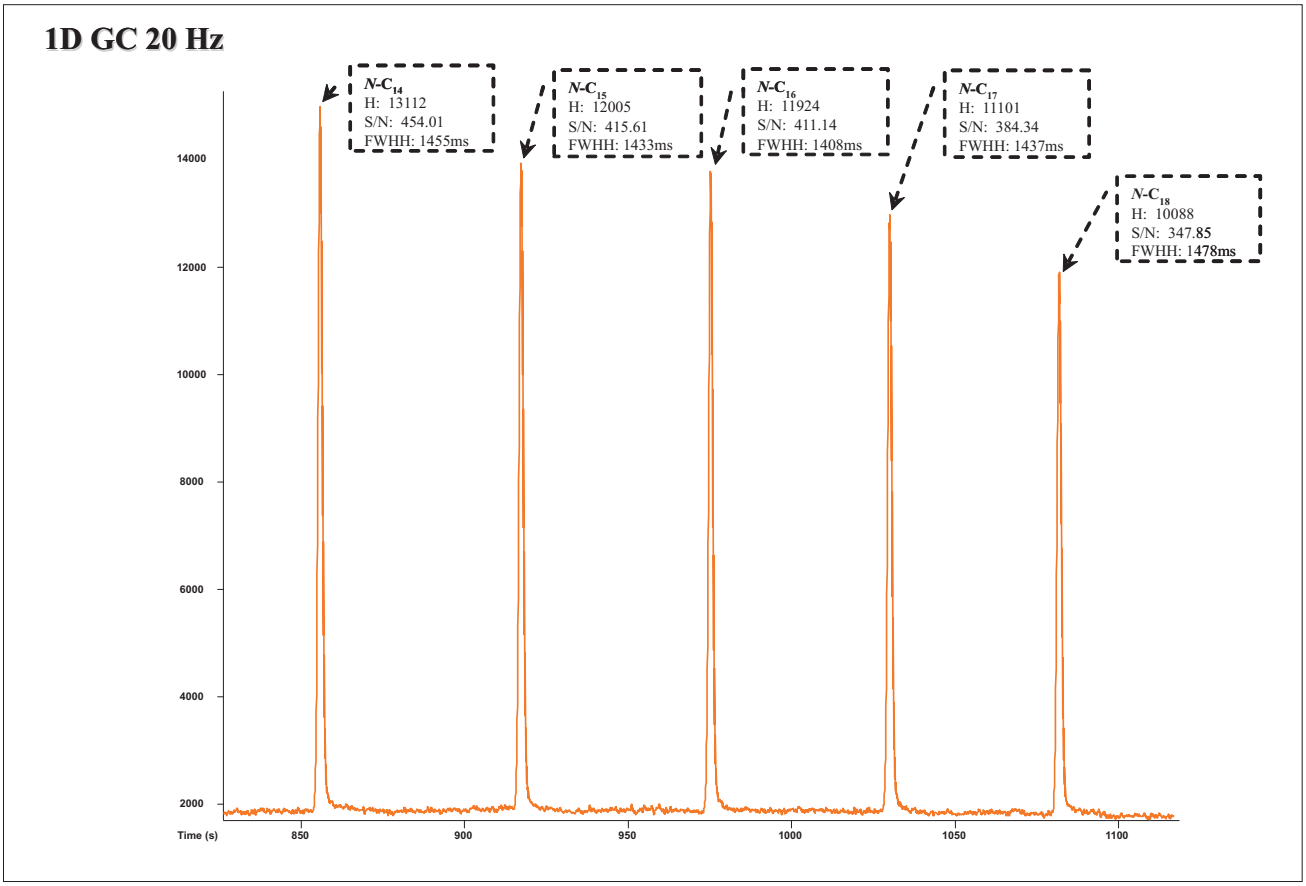

Figure 5: A chromatogram of the peaks from n-C_{14} to n-C_{18} for the sample run in 1D GC at 20 Hz. The peaks' height, S/N and FWHH are shown.

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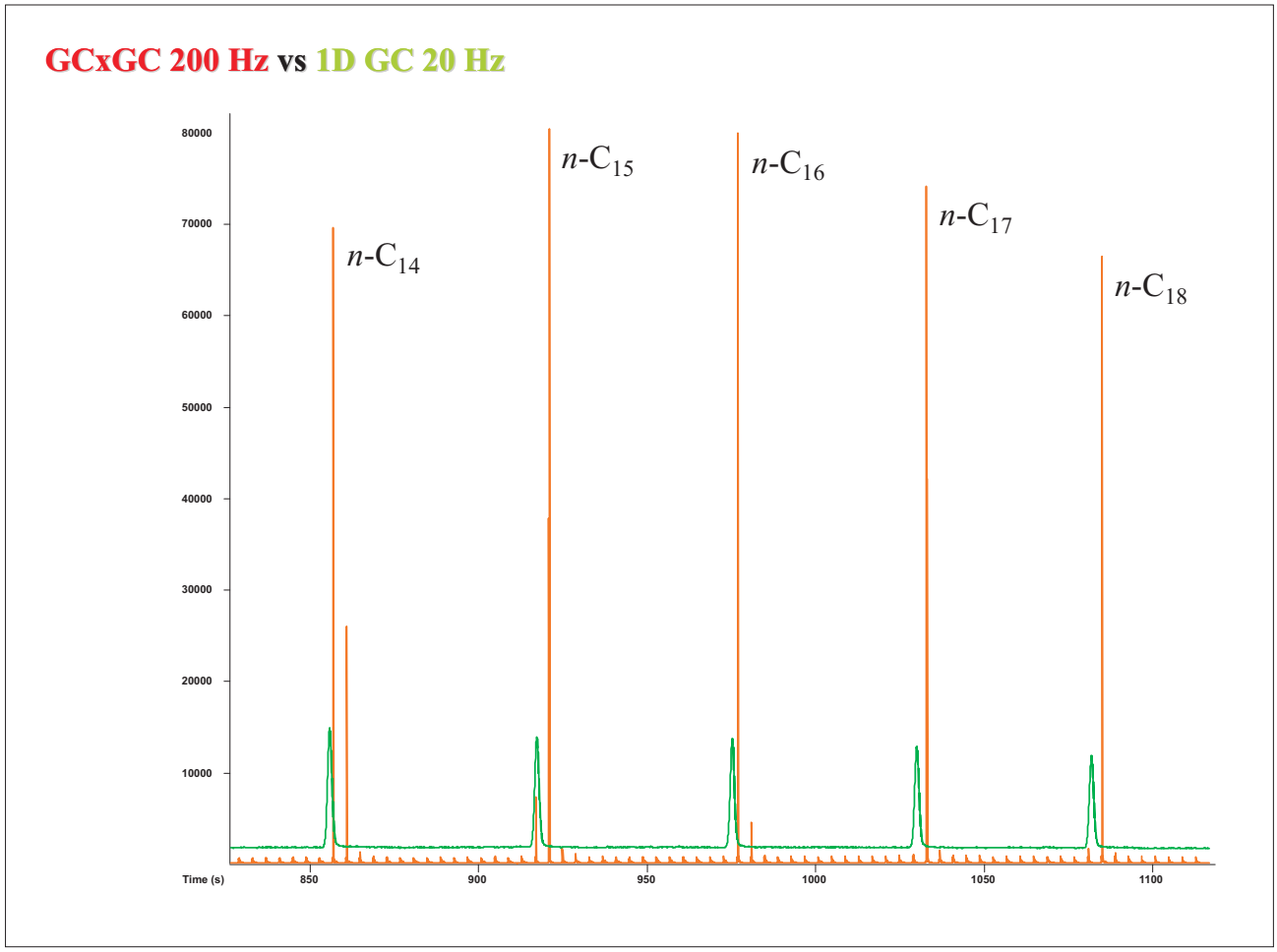

Figure 6: An overlay of the 1D GC collected at 20 Hz (green) and GCxGC, collected at 200 Hz (red) chromatograms for m/z 57. Note the difference in signal intensity between the focused and unfocused peaks.

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Form No. 209-066-012 12/09-REV0