

Introduction of a New Fast Scanning, Highly Sensitive Single Quadrupole GCMS: A Platform for Modern Chromatography Techniques

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Introduction



The modern gas chromatography techniques of Fast-GC and comprehensive GC X GC offer the analyst a variety of desirable advantages over conventional gas chromatography. Fast-GC utilizes extremely narrow bore capillary columns which allow the analyst to drastically shorten analysis times while maintaining resolution. Comprehensive GC x GC offers the user a much greater ability to resolve complex mixtures into individual components. These techniques are powerful but at the same time very demanding in terms of instrument performance. The very narrow peak widths (100 to 600 milliseconds) generated by these techniques require fast data acquisition rates for full characterization. Publications agree that at least 10 data points across a chromatographic peak are necessary for reliable quantification. Due to the relatively slow scan speed limitations of current quadrupole mass spectrometers, the modern techniques mentioned above have been feasible only with GC detectors or by TOFMS.

A quadrupole GCMS system, capable of scanning 20,000amu/sec and 100Hz, has been developed that meets the data acquisition requirements of the comprehensive GCxGCMS and Fast-GC techniques. In this study, complex natural product extracts will be analyzed that demonstrate the utility of this new GCMS.

How many points are needed for quantitation?



Dallüge, J. et al., J. Sep. Sci. 2002, 25, 608-614. → 5/6 points / peak

Poole, C.F., The Essence of Chromatography, Elsevier, Amsterdam, 2003, pp. 66-67. → 10 points / peak

Hinshaw, J.V., LCGC North Am., 2003, Vol 21, no. 3, 268-272. → 10 points / peak
(above half-height)

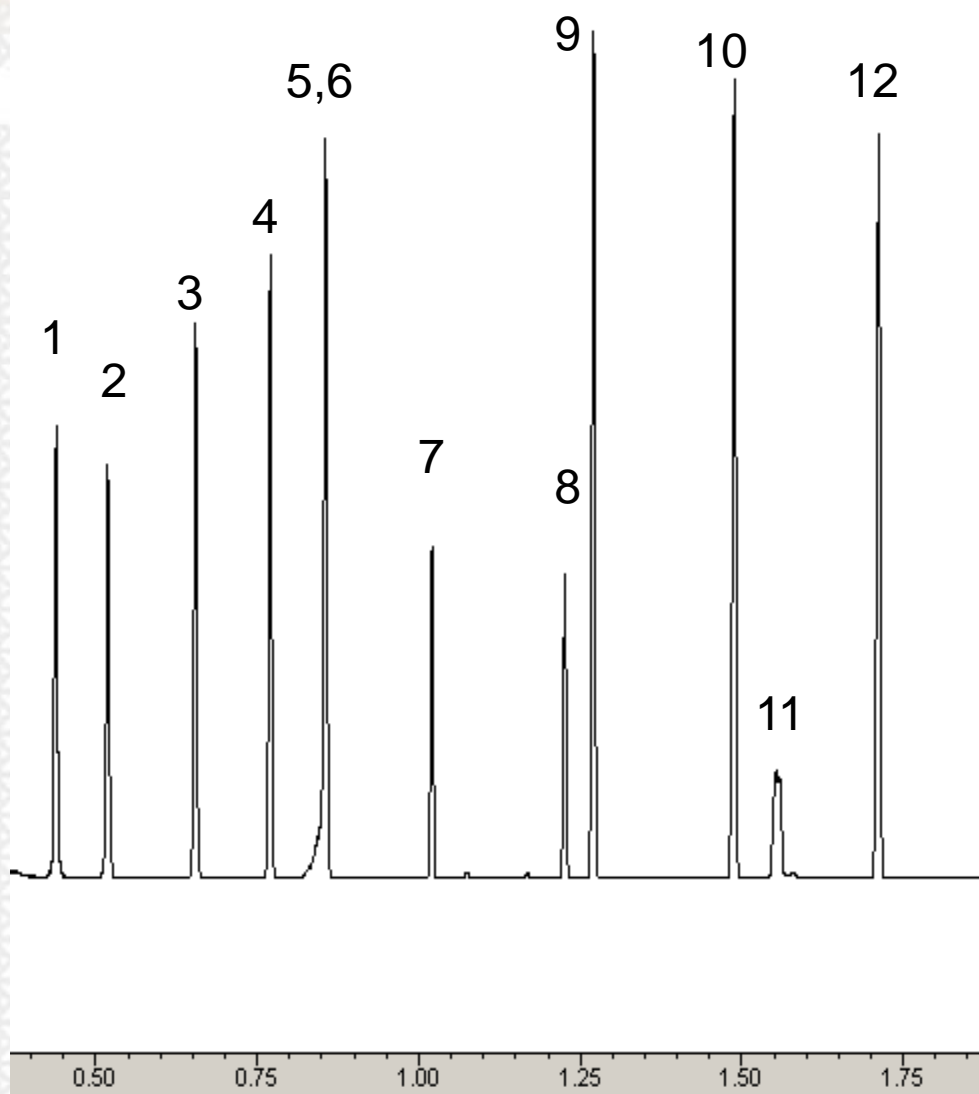
Data Acquisition Equations for qMS



$$\text{Scan speed (amu/s)} = \frac{\text{Mass range scanned (amu)}}{\text{Scan interval (S)}}$$

$$\text{Data acquisition rate (Hz)} = \frac{\text{Scan Speed (amu/s)}}{\text{Mass Range (amu)}}$$

Fast GC- Grob Mix



Column: 0.1mmID X 10 X 0.1 μ f
INJ: 1 μ l split injection 2ng on-column of each
Oven Temp: 65C to 200C @ 70C/min
INJ/DET: 250C
Carrier Gas: Helium
Linear Velocity: 70cm/sec
Split Ratio:200:1

1. 2,3 butanediol
2. Decane
3. Undecane
4. 1-octanol
5. Nonanal
6. 2-ethylhexanoic acid
7. 2,6-dimethylphenol
8. 2,6-dimethylaniline
9. nC10-FAME
10. nC11-FAME
11. Dicyclohexylamine
12. nC12-FAME

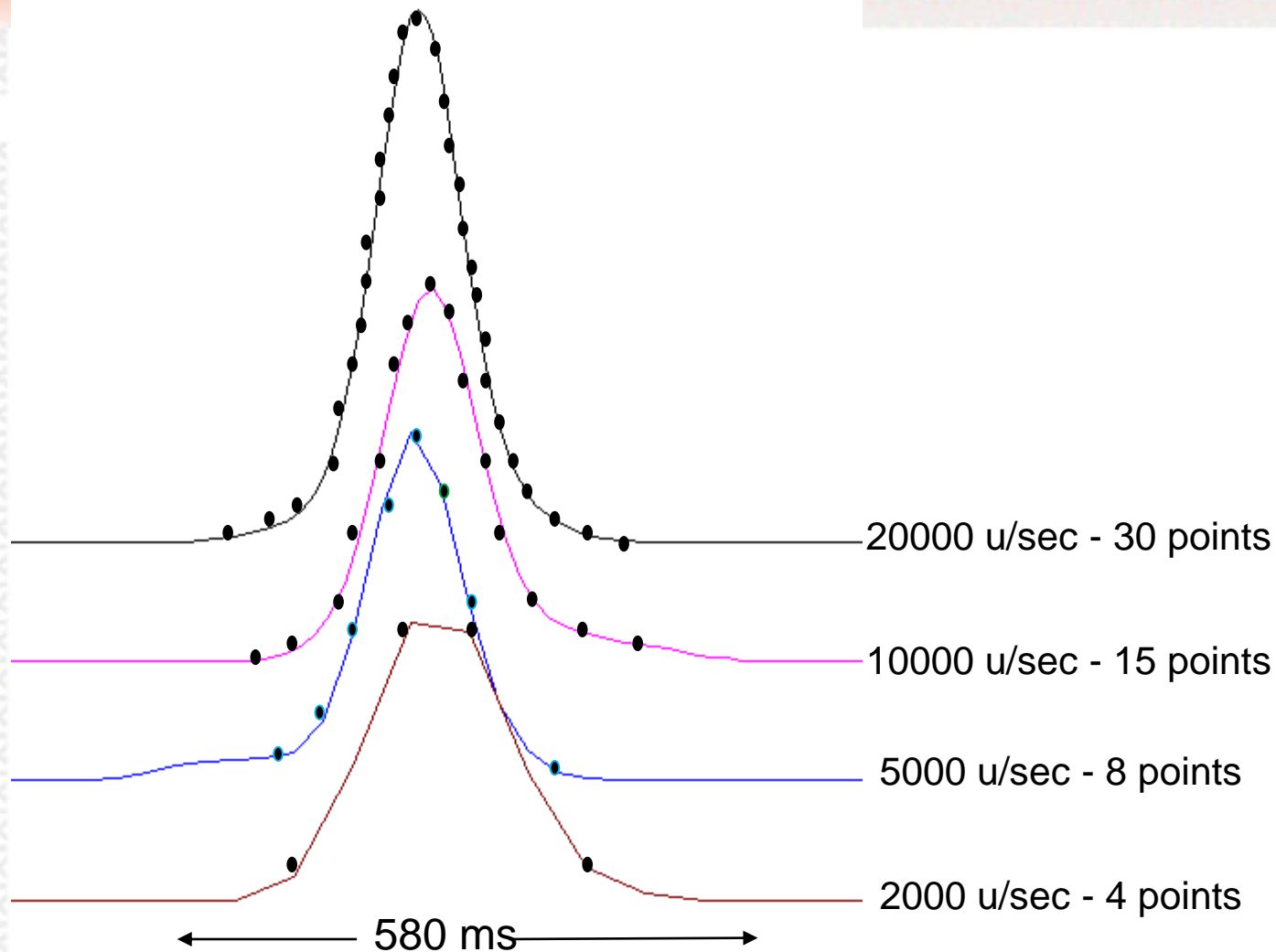
- FAST GC chromatographic peaks are on the order of 500 up to 1000msec. In the case of this chromatogram, the peak widths are about 600msec wide at the base. In this study the sample was run at different scan speeds in order to visually compare the differences in peak shape as a function of the number of data points each contains.
- Below is a table of scan speeds and theoretical number of data points expected for a 580msec peak.

Mathematical Relationship Between Acquisition Rate and Peak Width of 580msec.



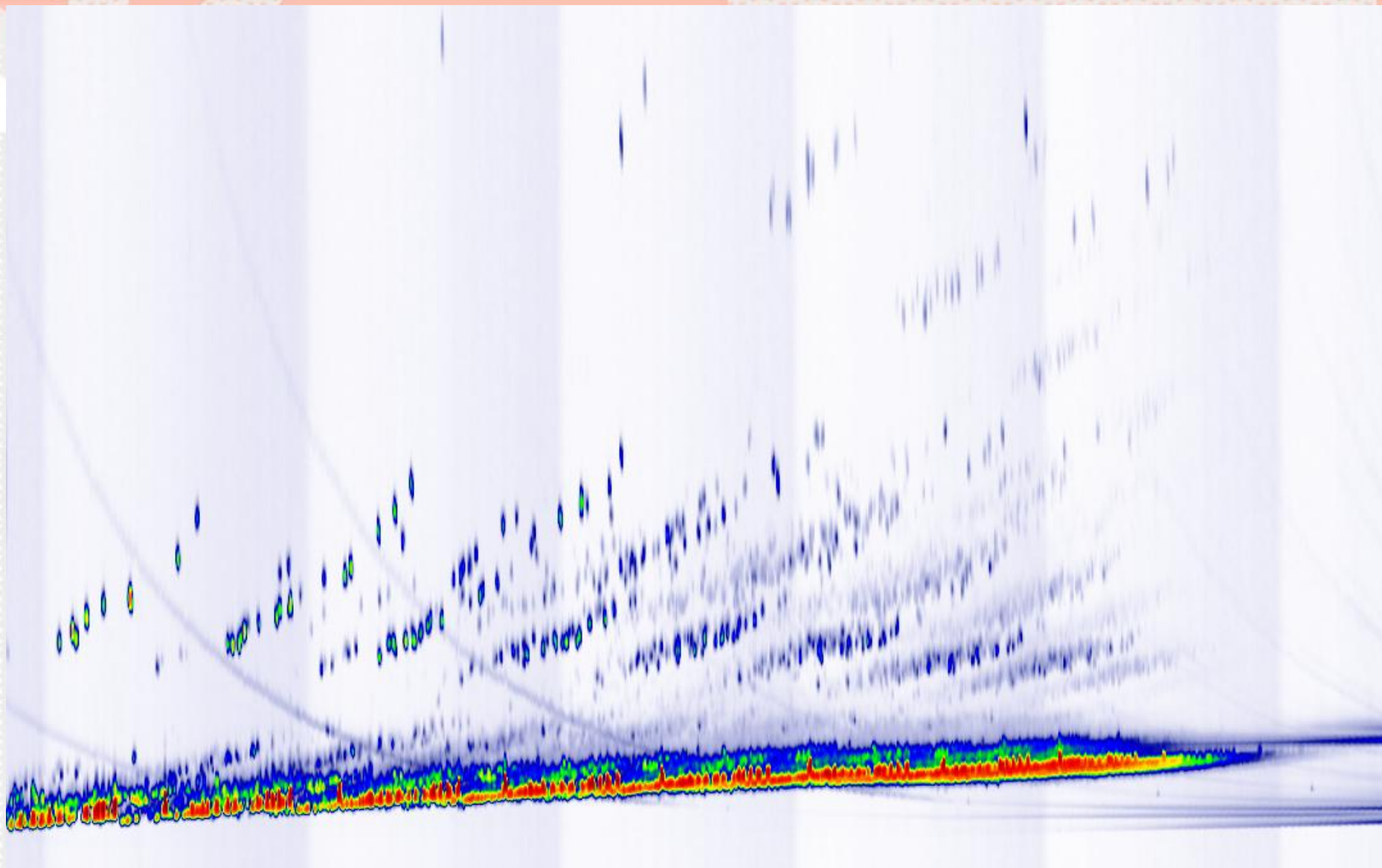
Scan Speed AMU/Sec	Mass Range (45 to 345 AMU)	Hz	Points per peak with 580 msec base
2000	295	6.25	<4
5000	295	12.5	7
10000	295	25	14
20000	295	50	29

Decane peak- at different scan speeds

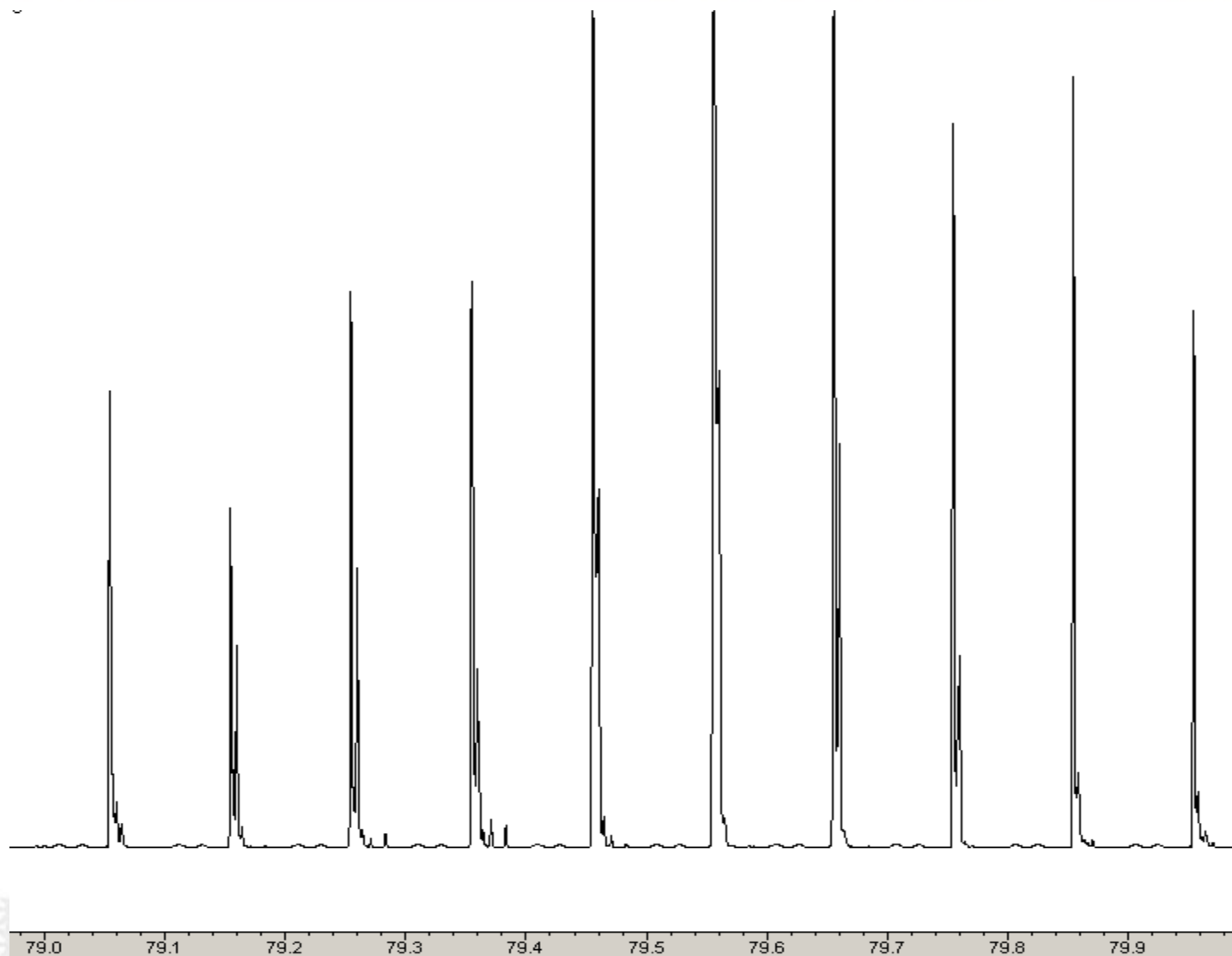


- Comparing the four chromatographic peaks, it's easy to see the effect of low acquisition rate on peak shape. The 2000u/sec peak with only 4 scans has a poorly defined apex making it difficult to judge the actual height and retention time. This peak is also slightly wider than the others. This is caused by the poor definition of the leading and trailing edges.
- The 5000 u/sec peak with 11 points is still not completely defined even though it meets the requirements of Dallüge and Poole. Straight lines are seen at the apex where only three scans are available to define the peak apex. As a result some uncertainty will remain in this peak in terms of retention time and area.
- The 10,000 and 20,000 u/sec peaks each contain 20 or more points and comfortably meet the requirements as outlined by Hinshaw. The 20,000 u/sec peak is well within the range and would lend itself to more complex measurements such as SIM/Scan data collection or expansion of the spectral mass scan range.

Example of a GC X GCMSq Chromatogram Jet Fuel N-p Column Set



GC X GC Raw Linear Plot Chromatogram: 1 Minute of Run Time Showing 10 Modulation Cycles

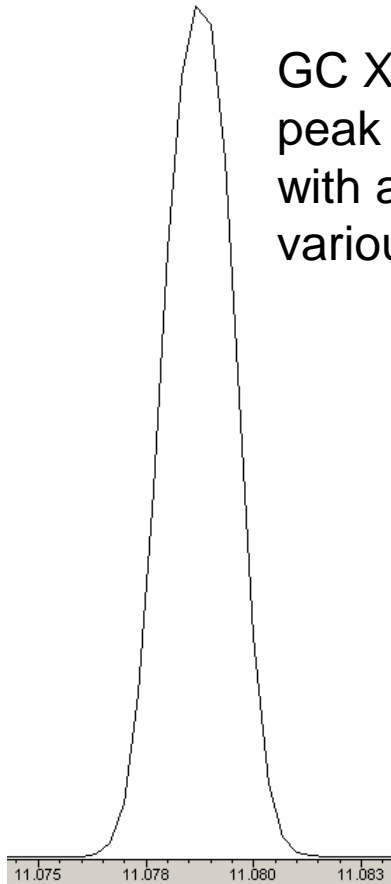


Mathematical Relationship Between Acquisition Rate and Peak Width of 300msec.



Scan Speed AMU/Sec	Mass Range (45 to 345 AMU)	Hz	Points per peak with 300 msec base
2000	295	6.25	<2
5000	295	12.5	4
10000	295	25	7.5
20000	295	50	15

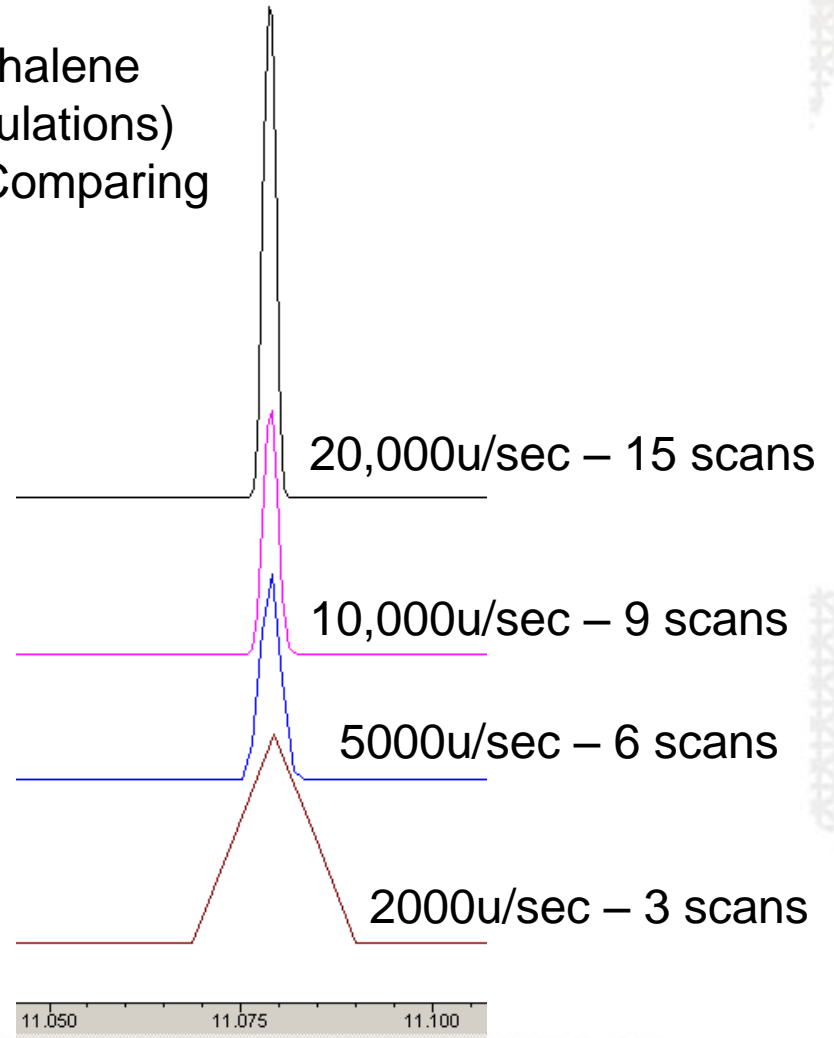
GC X GC modulated naphthalene peak (second of three modulations) with a width of 300 msec. Comparing various scan speeds.



11.076 min

11.081 min

$$.081 - .076 = .005 \times 60 = 300 \text{ msec}$$



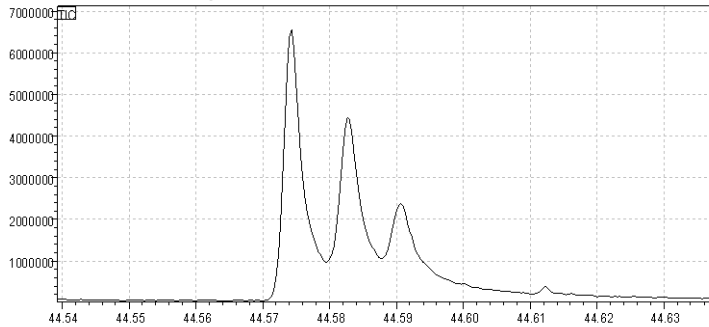
20,000u/sec – 15 scans

10,000u/sec – 9 scans

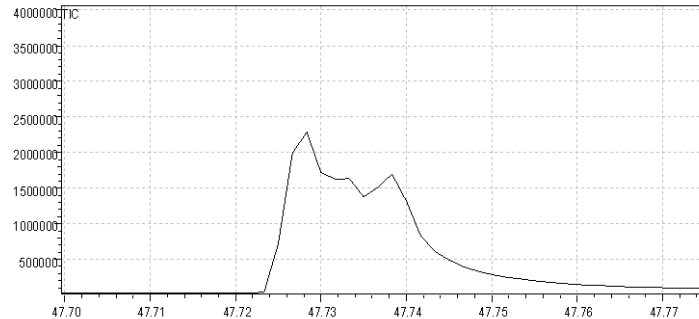
5000u/sec – 6 scans

2000u/sec – 3 scans

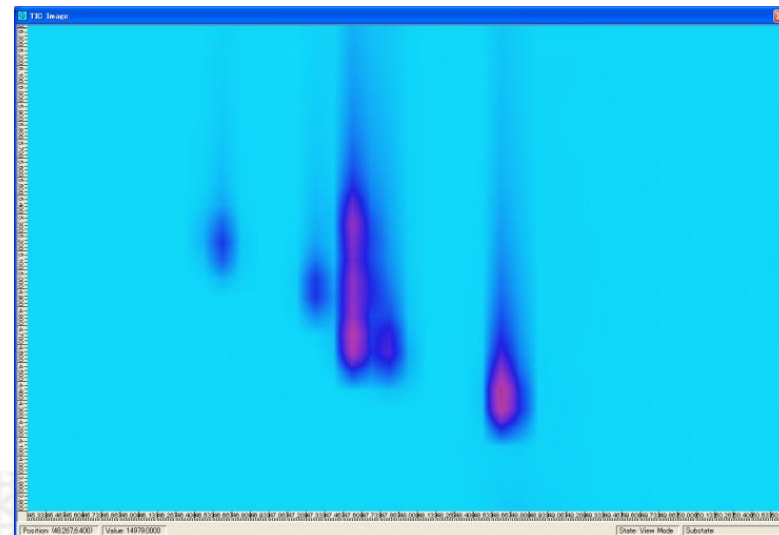
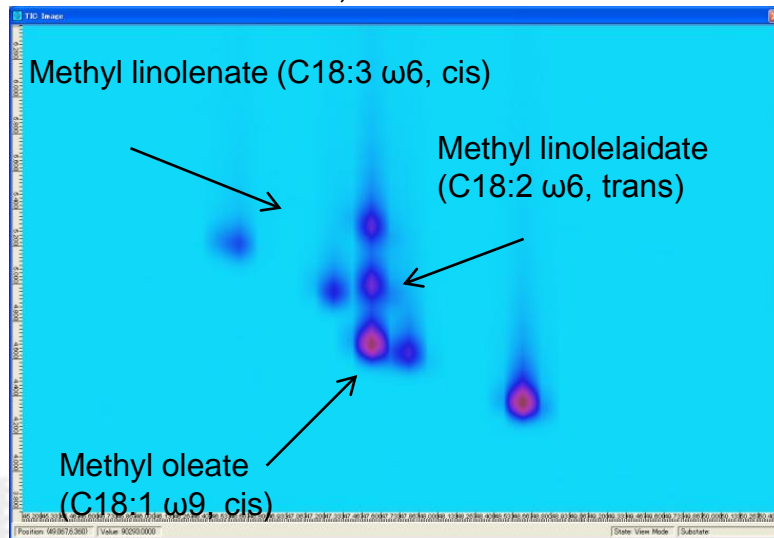
- Data acquisition of 300msec peaks is very demanding. As shown in the above figure, only the 20,000 u/sec scan rate resulted in enough scans to fully characterize the modulated peak as defined by Hinshaw. In contrast, the peaks that resulted from slower acquisition speeds are shorter and wider. This is particularly evident in the 2000 u/sec trace where the peak appears to be about twice as wide and much shorter than the others. Below is a section of a FAMES GC X GC plot that shows the difference in resolution due to data point density.



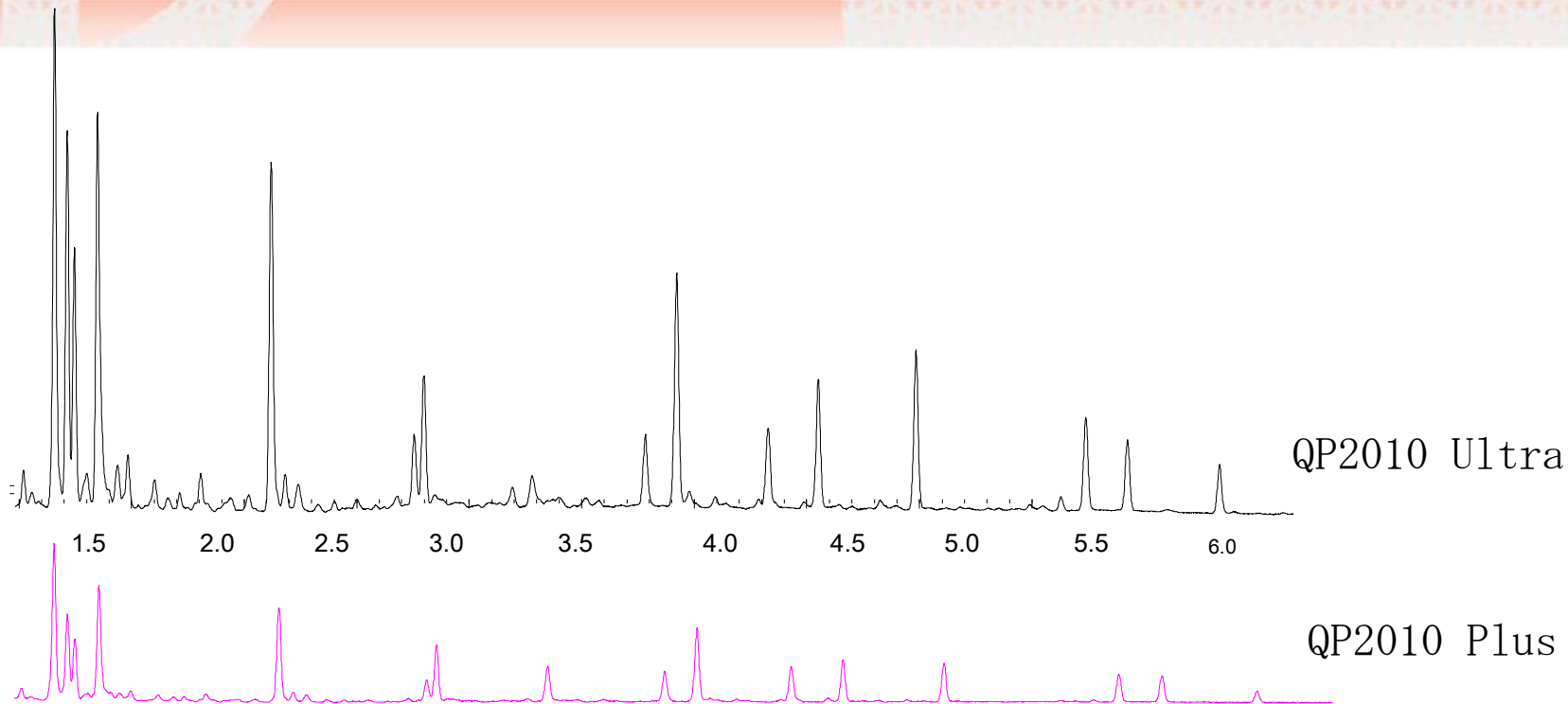
20,000 u/sec



10,000 u/sec



Sensitivity Comparison QP2010 Ultra vs QP2010 Plus at 10,000u/second Scan Speed



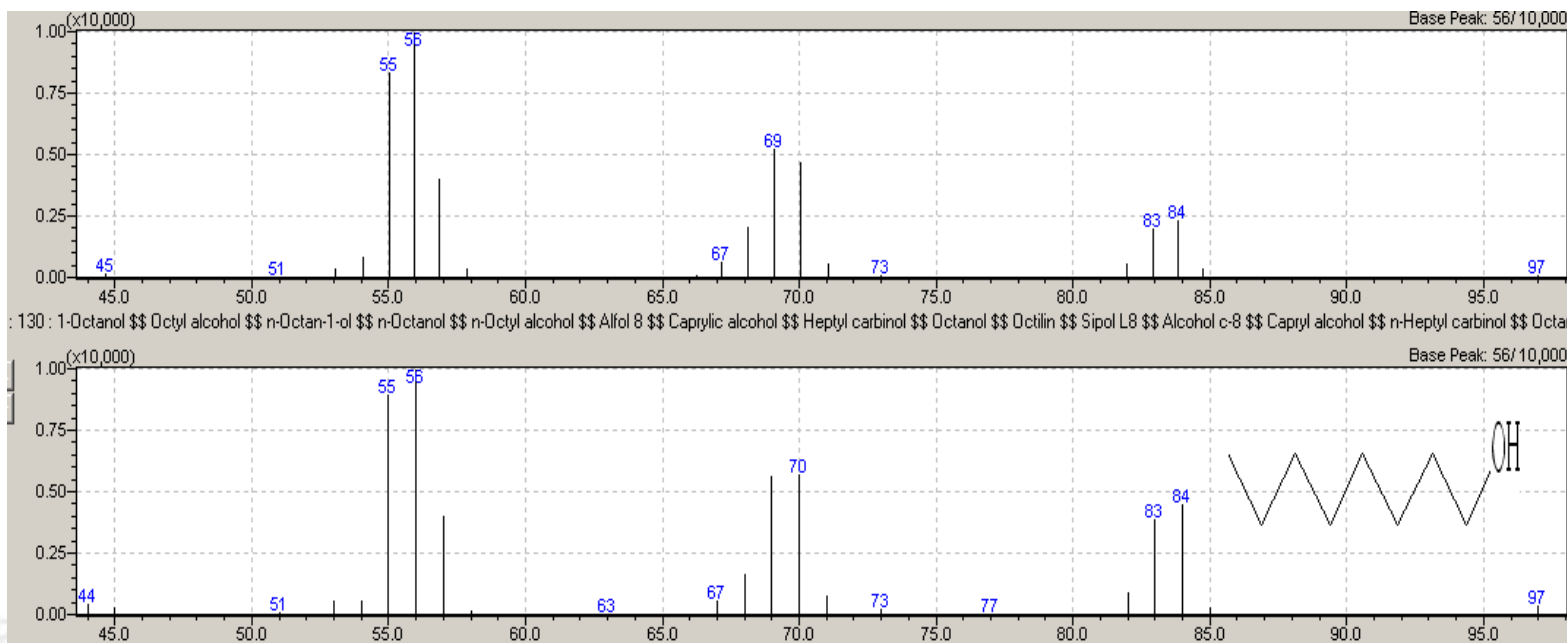
Compound	Q-ion	ASSP ON	ASSP OFF	ratio
Vaproic acid-TMS	201	157293	12574	12.5
Uracil-2TMS	241	359923	36978	9.7
Quetiapine-TMS	245	49582	5592	8.9
Nicotinamide-TMS	179	229201	49646	4.6
Cotinine	176	53112	9949	5.3
Lidocaine-TMS	220	232531	23288	10.0
Caffeine	194	143154	24789	5.8
Lidocaine	86	38713	22556	1.7
Theophylline-TMS	237	172684	19549	8.8
3-isobutyl-1-methylxanthine-TMS	194	117517	15852	7.4
Atropine-TMS	124	289704	62642	4.6
Promethazine	180	8512	1513	5.6
Clonidine	268	20640	1220	16.9
Quetiapine	210	2668	268	10.0
Trazodon	205	1194	288	4.1

Spectral Integrity of Fast Scan Data



The spectral integrity was evaluated at 20,000 u/sec by averaging the scans above the peak half-height and searching against the NIST 08 spectral library. A 95% similarity index match was observed between the NIST spectra and the fast scan data, illustrating that the spectral quality is maintained at the fast scan speed.

Hit#	Similarity	Register	Compound Name	Mol Wt	Formula	Library Name
1	95	<input checked="" type="checkbox"/>	1-Octanol \$\$ Octyl alcohol \$\$ n-Octan-1-ol \$\$ n-Octanol \$\$	130	C ₈ H ₁₈ O	NIST08s.LIB



Conclusion



- Quadrupole GCMS has been shown to have fast enough acquisition rates to be applicable to quantitative Fast GC and GC X GCMSq
 - Slower data rates affect not only peak detection and quantitative precision but also apparent resolution, as described above. The poor resolution seen in the 10,000 u/sec TIC chromatogram leads us to suspect chromatographic problems which the 20,000 u/sec data rate show to be wholly illusory.
- Sensitivity is improved over previous GCMS models.
 - Significant increase in real-world sensitivity over all other previous models.
- Spectral integrity and library matches are not compromised while scanning at 20,000 u/second.
 - Fast Scan data was compared to the NIST 08 library with a similarity index match of 95%