Applications of Comprehensive GCxGCMS Using a Quadrupole Mass Spectrometer With Ultra-high Scan Speed

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Introduction

GCxGC, or comprehensive two dimensional GC employs two columns of dissimilar phase connected in series using a thermal "modulator". Effluent from the first column is intermittently focused in the modulator for a given period of time, and then released into the second column. The chromatogram obtained by repeated trapping and injection is rendered in two dimensions using specialized software; chromatograms in the first and second dimensions are displayed graphically on respective axes. Chromatographic peak widths in the second dimension are very narrow – 0.2 – 0.3 sec., so very fast mass spectral scanning and data acquisition are required.

In the past, comprehensive GCxGCMS was mainly the realm of Time of Flight (TOF) mass spectrometers or other GC detectors due to the relatively slow data acquisition capabilities of quadrupole mass spectrometers.

A new quadrupole GCMS system, capable of scanning 20,000amu/sec and 100Hz has been developed that meets the data acquisition requirements of the comprehensive GCxGCMS technique. In this study, complex naturally-occurring products 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)

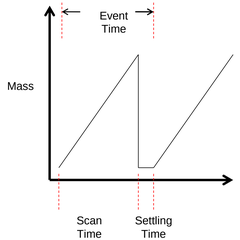
Data Acquisition Equations for qMS

$$\text{Scan speed (amu/s)} = \frac{\text{Mass Scan Range (amu)}}{\text{Scan Interval (Sec)}}$$

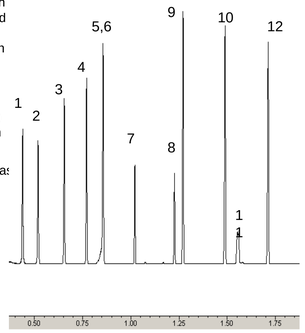
$$\text{Data acquisition rate (Hz)} = \frac{1}{\text{Event Time (sec)}}$$

Where: Event Time (sec) = Scan Time + Settling Time

Quadrupole Mass Spectrometer Scan Cycle



Fast GC - Grob Mix



Column: 0.1mmID X 10 X 0.1uf
INJ: 1ul 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

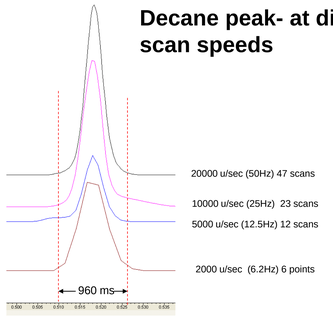
- FAST GC chromatographic peaks are on the order of 500 up to 1000msec. In the case of this chromatogram, the peak widths are about 960msec wide at the base. In this study the sample was run at different scan speeds in order to visually compare the differences in peak shape as a function of the number of data points each contains.
- Below is a table of scan speeds and theoretical number of data points expected for a 960msec peak.

Relationship Between Acquisition Rate and Peak Width of 960msec.

Scan Speed AMU/Sec	Mass Range (45 to 345 AMU)	Hz	Points per peak with 960 msec base	Actual Scans Acquired*
2000	295	6.25	6	6
5000	295	12.5	12	12
10000	295	25	24	23
20000	295	50	48	47

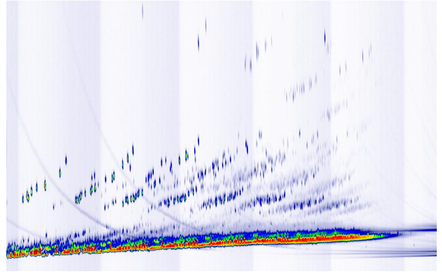
* Difference of calculated vs. actual acquired scans is due to settling time between each scan cycle

Decane peak- at different scan speeds

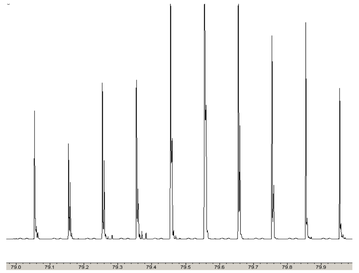


- Comparing the four chromatographic peaks, it's easy to see the effect of low acquisition rate on peak shape. The 2000u/sec peak with only 6 scans has a poorly defined apex making it difficult to judge the actual height and retention time. This peak is also slightly wider than the others. This is caused by the poor definition of the leading and trailing edges.
- The 5000 u/sec peak with 12 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 quantification.
- 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 mass scan range.

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



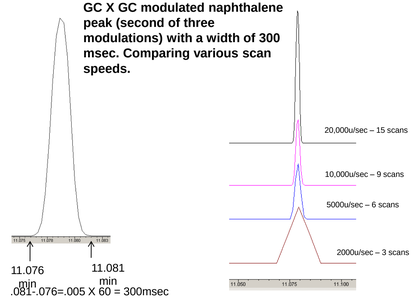
GC X GC Raw Linear Plot Chromatogram: 1 Minute of Run Time Showing 10 Modulation Cycles. Each Peak has a width of approx. 300ms at the base.



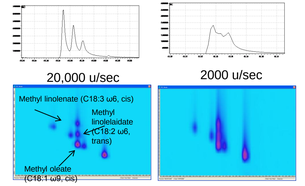
Relationship Between Acquisition Rate and Peak Width of 300msec.

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

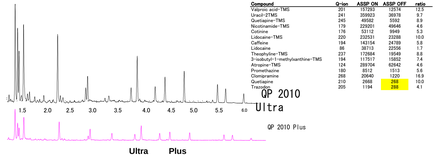
GC X GC modulated naphthalene peak (second of three modulations) with a width of 300 msec. Comparing various scan speeds.



- 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.

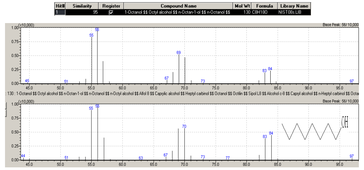


Sensitivity Comparison QP 2010 Ultra vs QP 2010 Plus at 10,000u/second Scan Speed



Spectral Integrity of Fast Scan Data

The spectral integrity was evaluated at 20,000 u/sec by averaging the scans above the n-octanol 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.



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 2000 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%