



Connections

Chromatographers' increasing interest in fast separations raises a number of issues concerning detector and data-handling parameters. Most analysts understand that higher chromatography speeds require faster detector-response times and data-acquisition rates. But what exactly do those requirements involve? In this month's "GC Connections," John Hinshaw examines the effects of system time constants and sampling rates on apparent peak shapes and areas.

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Handling Fast Peaks

Early gas chromatography (GC) separations often relied upon strictly manual peak detection and measurement because suitable recording devices often were unavailable or simply did not exist. Erika Cremer, who experimented with GC in Innsbruck, Austria, from 1946 to 1949, relied upon a team of students to obtain a chromatogram (1). One would operate the chromatographic apparatus, and another would call out the time every second. A third would then read the signal magnitude from the dial of a galvanometer, and the fourth would write down the numbers. They subsequently reconstructed the chromatogram by plotting and connecting the points on a graph to interpret the results. The data-acquisition rate of 1 Hz was just about the maximum that the team could handle.

Today's computerized instruments and data-handling systems have substituted computer hardware and software components for each member of the student team. Computer-based instrument control, a silicon semiconductor clock, a signal-integrating analog-to-digital (A/D) converter, and data-handling software conceptually replace the four team members. Chromatogram interpretation, however, remains an area in which human participation has not yet been supplanted by computer algorithms.

Detector-response time also plays a significant role in achieving the best peak fidelity, as discussed in a previous "GC Connections" column (2). A too-fast response time permits excessive noise in the chromatographic signal, and a too-slow response time distorts peak shapes, poten-

tially reduces peak resolution, and makes peak start- and end-point identification more difficult.

Routine GC speeds now require data-acquisition rates much greater than the 1-Hz rate that the 1940s student team achieved, and data rates will increase even more as chromatographers gradually adopt faster GC methods. Rates that are too slow can affect both qualitative and quantitative results in a manner similar to a detector signal that is too-heavily filtered. Rates that are too high can produce some unexpected side effects and use more storage space than necessary.

Detector-response times and data-system parameters should match peak widths as closely as possible to ensure the most reliable and accurate qualitative and quantitative results. When preparing for higher GC speeds, chromatographers tend to err on the high side by selecting faster rates and more rapid response times than may be necessary for their applications. I'll examine the signal and data realities of GC at higher speeds.

Quick Review — How Fast Is Fast?

In a "GC Connections" column published earlier this year, I defined four GC speeds, somewhat akin to a four-speed transmission in a sports car (3). The first level corresponds to conventional packed or capillary column GC with peak widths at half-height of 1 s or greater, as enumerated in Table I. At this level, a typical chromatogram with 20 or 30 peaks would require approximately 10 min or longer for completion.

The second level drops the peak widths at half-height to as low as 0.5 s. This level

Table I: Gas chromatography speeds and associated parameters

GC Speed	Minimum Peak Width at Half-Height	Maximum Detector Time Constant (s)	Maximum Data-System Sampling Rate (Hz)
Level 1	>1.0	≥200	≤10
Level 2	0.5–1.0	50–100	10–20
Level 3	0.1–0.5	10–50	20–100
Level 4	<0.1	<10	>100

permits an improvement in analysis times from three- to fivefold that of level 1 and retains the same degree of peak resolution. At level 3, the peak widths are as small as 0.5 s, and an analysis can proceed as much as 5- to 10-fold faster than at level 1. The fourth level introduces analysis speeds 10- to 50-fold faster by reducing peak widths to 0.1 s or less.

In practical terms, levels 1 and 2 represent the bulk of routine packed and capillary column GC practiced today. These speeds are achievable on most conventional GC instrumentation and data systems with no hardware modification. Level 3 may require instrumentation that is purposely equipped for so-called high-speed operation with faster oven programming and cooldown rates, higher-pressure pneumatics, and faster detection and data-acquisition rates. Level 4 lies beyond the reach of most commercially available instrumentation and remains in the realm of experimental and academic interest.

As analysis speeds increase, detectors must be capable of responding to a more rapidly changing chemical signal as peaks are eluted from a column. The data system, in turn, must sample the detector signal rapidly enough to ensure that it records acceptable peak shapes and areas in its data files.

Detector Response — Keeping up with the Peaks

A GC detector — whether a flame ionization, thermal-conductivity, or other detector — produces a signal-level shift in response to the changing chemical signal from the column. The response, however, is not instantaneous but instead lags somewhat behind the chemical signal. The simplest representation of this behavior is encapsulated in the overall detector time constant (τ), which represents the time it

takes for the detector output signal to reach a level of $(1 - 1/e) = 63.2\%$ of an instantaneous change in the incoming signal (4).

Figure 1 illustrates this effect for time constants from 100 to 800 ms. In this figure, it takes more than 1 s for a full-scale response at the higher time constants. When applied to a chromatographic peak entering the detector with a half-width of 0.5 s, larger time constants cause significant peak broadening and a shift of the peak maximum, as Figure 2 illustrates.

When applied to chromatograms with multiple peaks that are eluted close together, excessively large time constants will create problems with peak resolution. Chromatographers should choose a detector time constant that is approximately 10% of the minimum peak width at half-height in a normal chromatogram. Time constants of approximately 20% will cause slight peak tailing, but they may be desirable when the peaks are small compared with the detector noise. In those situations, the detector-response time acts as a noise filter, as discussed in reference 2.

If analysts are looking only at single peaks, then some degree of peak broadening is not a serious problem. When two adjacent peaks have a resolution of less than roughly 4, however, significant peak tailing can cause the end of one peak to be superimposed over the beginning of the next. Difficulties in determining peak stop and start points as well as mixed spectra with mass spectrometric detectors result from this effect. These problems in turn cause reduced quantitative precision due to less well-defined area counts and poorer mass spectral library matches.

Returning to considerations for fast chromatography, the associated narrow peak widths impose an upper limit on the

detector time constant similar to the values shown in Table I. At level 1, a suitable system should be capable of delivering time constants as small as 200 ms. In many cases, such as for packed columns, a higher setting may be desirable for its noise-reducing effect. For level 2, time constant requirements drop to the 50–100 ms range, where most routine commercial instruments can operate. At levels 3 and 4, however, specialized electronics may be necessary to attain time constants of less than 50 ms.

The overall detector time constant is not merely a function of the electronics. Many older detectors have large internal volumes through which peaks must pass. Significant peak tailing will result when this volume is substantially larger than the volume occupied by the peak. A peak with a half-height of 1 s, for example, spans approximately 2.5 s across its base points. At a column exit flow rate of 2 mL/min, which is typical for a 250- μm column operating close to the optimum flow with helium carrier gas, this peak will occupy approximately 80 μL . With the exception of some micro thermal-conductivity systems, this volume is far smaller than most detectors' internal volumes. The addition of makeup gas to the column effluent increases the flow through the detector and reduces the effective time constant to acceptable levels. Alternatively, some detectors use existing internal gas flows, such as hydrogen in a flame ionization detector, to sweep the column effluent through the detector rapidly.

Data System Sampling

After a detector transduces a chemical signal from a column into an electronic signal that faithfully represents a chromatogram, a recording device makes a permanent record. Older analog chart recorders incorporate a separate response time constant that acts on the chromatogram in the same manner as the detector time constant. The same guidelines for time-constant selection hold for those recorders. Today, however, the vast majority of chromatographers use digital data-handling systems that bring into play a different suite of selectable parameters.

In those systems, the analog chromatographic signal from the detector connects to an A/D converter that transmutes the signal into a digitized version. The digitization process samples the analog signal at regular intervals and expresses it as a number. The resulting pairs of time and signal values then are stored in a data file for sub-

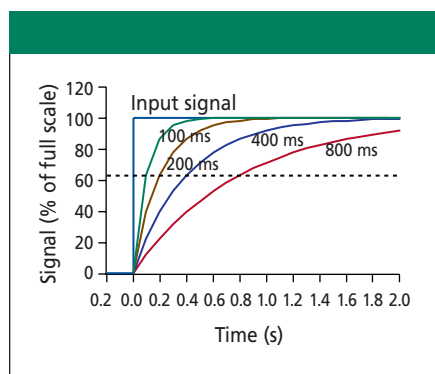


Figure 1: Effect of time constant on the response to an instantaneous input signal.

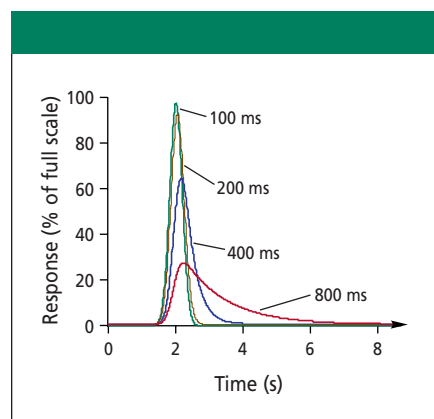


Figure 2: Effect of time constant on peak shapes. The input peak has a 0.5-s width at half-height and was removed for clarity.

sequent measurement and manipulation. The digitization process must proceed without significant distortion of the chromatographic signal.

If peak widths are the determining factor for selecting data-handling conditions, a good guideline is to acquire roughly 10 data points across one peak width at half-height. This acquisition rate produces the figures shown in Table I for the maximum required sampling rates at the four speed levels. Fewer points across a peak mean that a peak shape may be less accurately represented in a data file, and the reproducible determination of the peak start, apex, and stop points could be impaired. In turn, peak-retention time and area repeatability will be compromised, so a data system can add an unwelcome degree of uncertainty to results.

Figure 3 illustrates this effect. The A/D converter systems for chromatography use an integrating converter that accumulates the area under a peak throughout the sampling interval, records the total area for the interval, and then starts over again for the next interval. It effectively chops up the chromatogram into a series of area slices. In Figure 3, the peak represents the incoming analog signal, and the vertical gridlines represent the boundaries between data slices. The straight lines drawn from slice

to slice connect points that represent the area counts measured during individual slices (the area values are scaled down for clarity). The peak is sampled with only approximately two data slices across its width at half-height, which is far fewer than the recommended 10.

In Figure 3a, the true retention time is 5.1 s from the start of the plot, and the apparent retention time after digitization is located at the slice ending at 5.5 s. In Figure 3b, the peak is eluted 150 ms earlier at 4.95 s, yet the apparent retention time is now 5.0 s, 500 ms earlier at the previous area slice. This situation creates an apparently much larger 500-ms deviation in the peak-retention time than the real value of 150 ms.

This situation doesn't affect area counts very much because the total peak area is determined by the integrating A/D converter system. As long as no adjacent peaks are present, the data system can simply extend the start and stop area slices to ensure that the entire peak is contained. When two peaks are eluted close to each other, however, it becomes necessary to determine how to divide the areas between the two peaks.

A common method involves drawing a vertical line from the baseline to the valley point between the two peaks, as Figure 4 shows. If the data-sampling rate is too slow, however, valley-point determination becomes difficult, if not impossible. In Figure 4, the sampling rate is so low that the existence of a valley is cast in doubt by the area count slice values as shown. The data-handling system will have a hard time determining if one or two peaks are present, and it may find one peak some of the time and two peaks at other times.

Chromatographers should choose sufficiently high data-sampling rates to avoid

these situations. Bear in mind, however, that excessively high data rates waste storage space and slow post-run computational processes.

Conclusion

Correct detector time constants and data-system sampling rates are essential for obtaining accurate and reproducible chromatographic results. Choosing too-slow time constants and sampling rates can lead to peak-shape distortion, retention-time irreproducibility, area count errors, and peak misidentification.

Those effects can be avoided easily when performing routine GC using conventional instrumentation. Chromatography at elevated speeds, however, can suffer from those problems unless analysts select suitable equipment and operational parameters. As chromatographers move toward applying higher speeds to their routine analyses, they must be aware of the increased requirements imposed by faster analysis.

References

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For an ongoing discussion of GC issues with John Hinshaw and other chromatographers, visit the Chromatography Forum discussion group at <http://www.chromforum.com>.

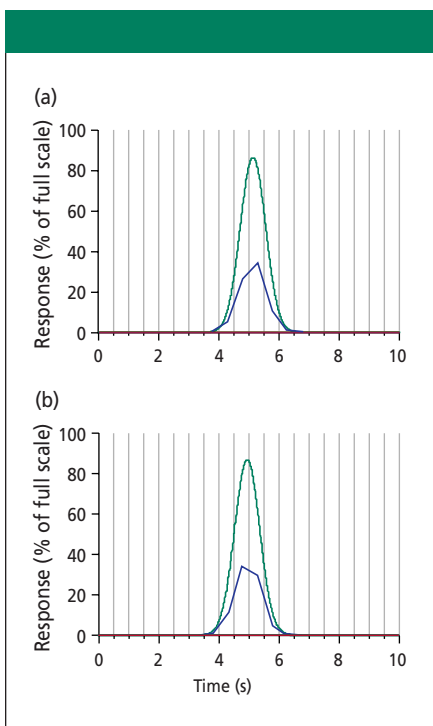


Figure 3: Effect of a slow data-acquisition rate on peak shape and apparent retention time. Peak width at half-height: 1 s; data-acquisition rate: 2 Hz; retention time: (a) 5.1 s, (b) 4.95 s.

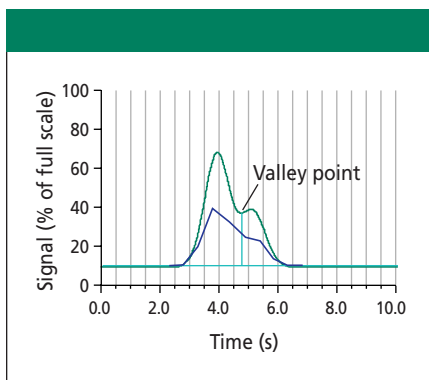


Figure 4: Effect of a slow data-acquisition rate on the detection and quantitation of closely eluted peaks. Conditions same as Figure 3.