Waters
Lab Highlights
An Internal Communication
of Applications and Techniques
LAH 0323 3/86
AN/System Performance

POOR EFFICIENCY? DON'T ALWAYS BLAME THE COLUMN:

DETECTOR TIME CONSTANTS

In a previous Lab Highlight (LAH 0129) the insidious effect on efficiency due to improper plumbing of LC systems was explained (1).

Another insidious cause of apparent loss of column efficiency - Detector Time Constant - has been examined by Haddad and co-workeers (2,3). Most chromatographers like to see nice, "clean" baselines and smooth curves with a minimum of "noise."

Manufacturers often add an electrical buffer or filter circuit to increase the "time constant" of the circuit to filter out this noise. In many detectors, this time constant is selectable by the operator. These time constants can vary greatly according to the detector design, e. g. the Models 440/441 UV detectors have an extremely low time constant of 25 milliseconds while the models 480/481 UV detectors have time constants selectable from 0.2 to 2.0 seconds.

These time constants can have a significant effect on the apparent efficiency of the column, particularly with fast-eluting peaks. An example of the effect is shown in Figure 1 where the dark peaks are a chromatogram obtained using a time constant of 100 milliseconds and the light peaks were obtained with a time constant of 1.1 seconds. The number of theoretical plates obtained by a standard plate count (5 Sigma) method on a µBondapak™ C_{18} column dropped from 3800 plates at a time constant of 100 milliseconds to 2200 plates at a time constant of 1.1 seconds -- an apparent loss of 58% of its theoretical plates!

Figure 1

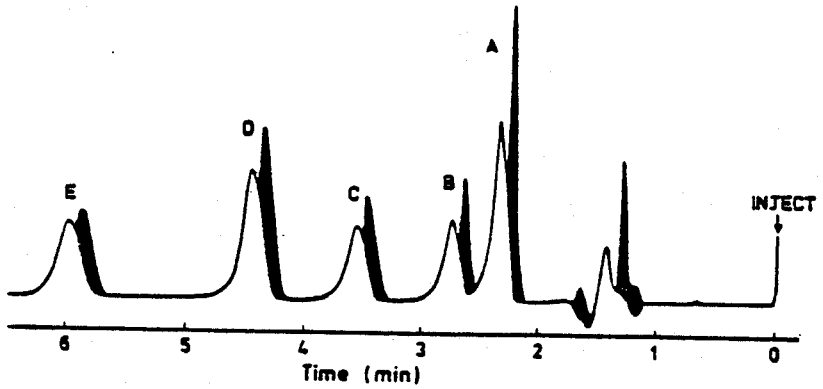

Fig. 1. Chromatogram of test mixture recorded at two different values of time constant. Dark peaks: τ = 0.1; light peaks: τ = 1.1. A = phenol; B = paracresol; C = 2,5-xylenol; D = anisole; E = phenetole.

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This does affect the chromatography as shown more clearly by the separations in Figures 2a, 2b and 2c. Figure 2c certainly does look worse than Figure 2a, but the only difference was a change in the time constant, τ.

Figure 2

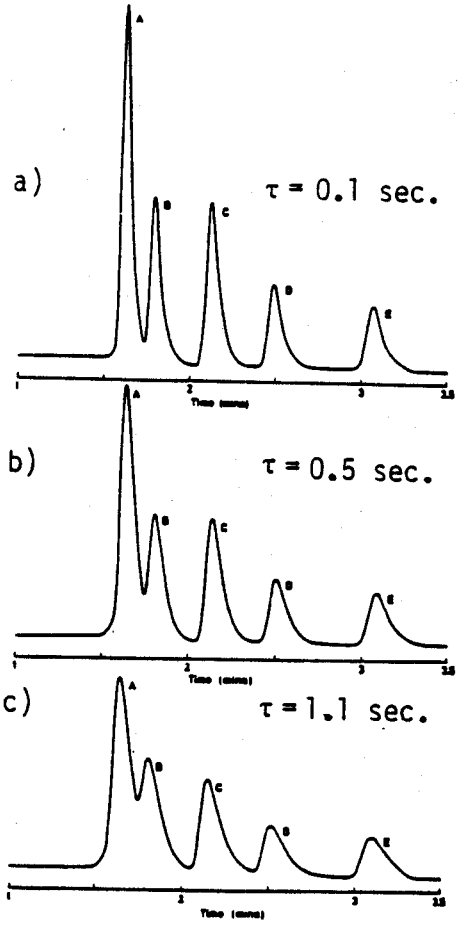
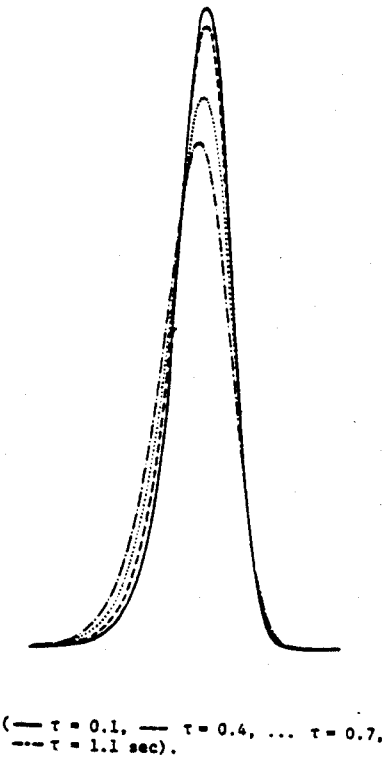


Figure 3. Effect of detector time constant on peak shape without column.



If the column is taken out of the system which is then tested for band broadening, the same phenomenon is readily seen (Figure 3).

Detector time constants affect peak height, peak asymmetry and retention times. Why then is this seldom recognized as a cause of problems? The reason is that analysts seldom change the detector time constant during a series of analyses. If the time constant is not changed during an analysis the results may be precise but if the time constant is changed, the system should be recalibrated. This is particularly important if peak height, rather than peak area, is being used for quantitation.

As a general rule, for the best results, use the lowest time constant possible and recalibrate the instrument each time the time constant is changed.

1. Ekmanis, J. L., *LC Magazine*, 2, (6), (1984) 434.
2. Low, G. K. C. and Haddad, P. R. , *J. of Chromatogr.* 198 , (1980) 235.
3. Haddad, P. R., Keating, R. W. and Low, G. K. C., *J. of Liq. Chromatogr.*, 5 (5), (1982) 835.