Practical Time Savings in Gas Chromatography Method Development

by Chris Linton, Sherry Sponsler, & Jingzhen Xu

The speed of analysis in capillary gas chromatography can be significantly improved by reducing the bore size of the column (<100μm). Researchers have successfully produced chromatograms on the order of milliseconds using this approach. Unfortunately, heavy demands are placed on sample introduction and peak detection which are not within the realm of capabilities of common instrumentation. The following discussion concentrates on practical time reduction in gas chromatographic separations using standard diameter columns and sample introduction with the Hewlett-Packard 5890 GC.

Theory

Selectivity, efficiency and time are interdependent in chromatography. Theoretically we can predict the minimum time required to maximize selectivity and efficiency.

Considering:

Tp = the time to get a solute past 1 plate
Nreq = the number of plates required for resolution
Tr = retention time required for desired resolution
H = height equivalent to a theoretical plate
μ = linear velocity
k' = partition coefficient
α = selectivity ratio
1+k' = the amount of time a solute spends in the stationary phase
R = resolution

$$Tr = Nreq * Tp$$
$$Tp = (1+k'/\mu)H$$

so: $$Tr = Nreq(1+k')(H/\mu)$$

substituting:

$$Nreq = 16R^2(\alpha/\alpha-1)^2(1+k'/k')^2$$ Purnell equation

so: $$Tr = 16R^2(\alpha/\alpha-1)^2[(1+k')^3/(k')^2](H/\mu)$$

solve for the first derivative holding all values constant except k'

$$Tr = C(k'^3+3k'^2+3k'+1)/k'^2)$$
$$dTr/dk' = C - 3Ck'^{-2} - 2Ck'^{-3}$$

in order to find Tr minimum, dTr/dk' must be set to 0

$$k'^3 - 3k' - 2 = 0 \qquad k' = 2 \text{ or } -1$$

Theoretically, the optimum time for a solute to exit a column is at k'=2. At this time, selectivity and efficiency are optimized. Unfortunately, this model breaks down if a multicomponent sample is considered (all analytes cannot have k'=2). In reality, column length, initial starting temperature and temperture programming can be utilized to adjust retention times close to the theoretical optimum k'=2. **The stationary phase must provide adequate retention (film thickness) and selectivity for the resolution requirements of the separation at hand.**

Temperature Programming

Sample mixtures may contain analytes that vary in volatility to the extent where temperature programming becomes essential in the analysis. A temperature program can be selected such that high volatility compounds elute at low column temperature and low volatility compounds elute at higher column temperature ensuring the minimization of k' values. Program rates may be as high as 25 degrees per minute or greater in order to achieve near optimum k values.

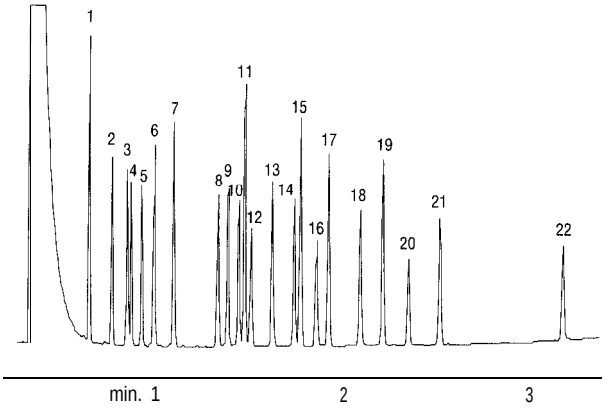
Another important aspect of temperature programming and column selection is the requirement that all analytes elute during the temperature program. This general rule helps to define column length and limits analysis time and band broadening by preventing isothermal elution of low volatility analytes. Since the temperature program was not optimized for the 45-meter column in **Figure 1,** the last five components were forced to elute under isothermal conditions.

The Limitation of Length

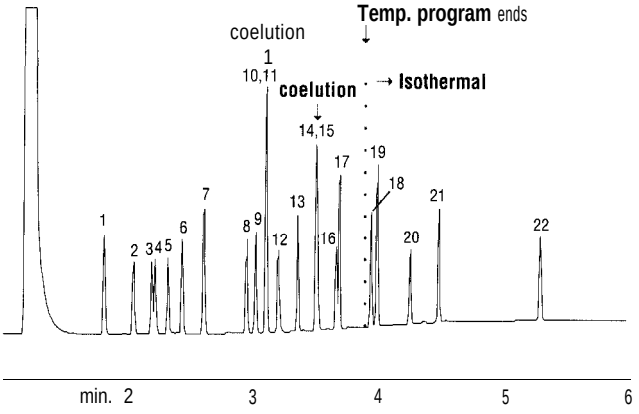
Longer columns generally provide greater challenge for the generation of time savings in gas chromatography. Stationary phases have inherent maximum operating temperatures which in turn limits the the extent of a temperature program. **Therefore, a minimum length of column should be chosen to provide not only the minimum required plates but the shortest retention times around the optimum k' value of 2. The stationary phase must provide adequate retention(film thickness) and selectivity for the resolution requirements of the separation at hand.** The following set of chlorinated pesticide chromatograms illustrates the differences between a near optimized separation on a 15-meter column and the same chromatographic conditions using a 45-meter column. Notice that the retention times are nearly half on the 15-meter column and all components are fully resolved.

Figure 1:

Under optimized conditions, a shorter column can provide improved resolution and decreased analysis time compared to a longer column.



15m, 0.25mm ID, 0.25µm Rtx-CLPesticides column.
Oven temp.: 200°C to 300°C @ 25°C/min. Carrier gas: hydrogen



45m, 0.25mm ID, 0.25µm Rtx-CLPesticides column.
Oven temp.: 200°C to 300°C @ 25°C/min. Carrier gas: hydrogen.

Initial Starting Temperature

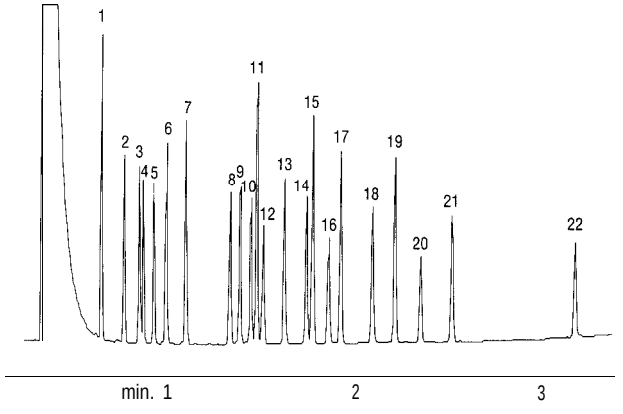
In temperature programming and isothermal gas chromatography, a time savings may be generated by chosing an initial starting temperature which allows for the elution of the first analyte near the solvent front. Starting at initial temperatures which are too low creates an empty gap in time which does not make sense theoretically due to k' elevation. The chromatograms in **Figure 2** illustrate the retention time differences generated by starting temperatures of **40°C** and 200°C in the chlorinated pesticide analysis.

Peak List for Figures 1 & 2

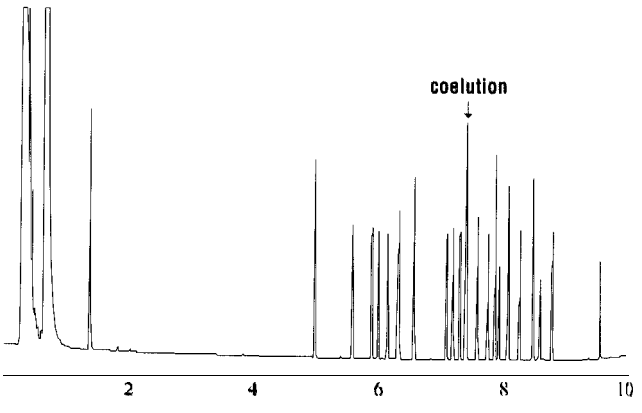
1. 2,4,5,6-tetrachloro-m-xylene
2. a-BHC
3. y-BHC
4. β-BHC
5. S-BHC
6. heptachlor
7. aidrin
8. heptachlor epoxide
9. γ-chlordane
10. a-chlordane
11. 4,4'-DDE
12. endosulfan I
13. dieldrin
14. endrin
15. 4,4'-DDD
16. endoisulfan II
17. 4,4'-DDT
18. endrin aldehyde
19. methoxychlor
20. endosulfan sulfate
21. endrin ketone
22. decachlorobiphenyl

Figure 2:

At higher initial temperatures, analysis times can be decreased without sacrificing resolution.



15m, 0.25mm ID, 0.25µm Rtx-CLPesticides column.
Oven temp.: 200°C to 300°C @ 25°C/min. Carrier gas: hydrogen.



15m, 0.25mm ID, 0.25µm Rtx-CLPesticides column.
Oven temp.: 40°C to 300°C @ 25°C/min. Carrier gas: hydrogen

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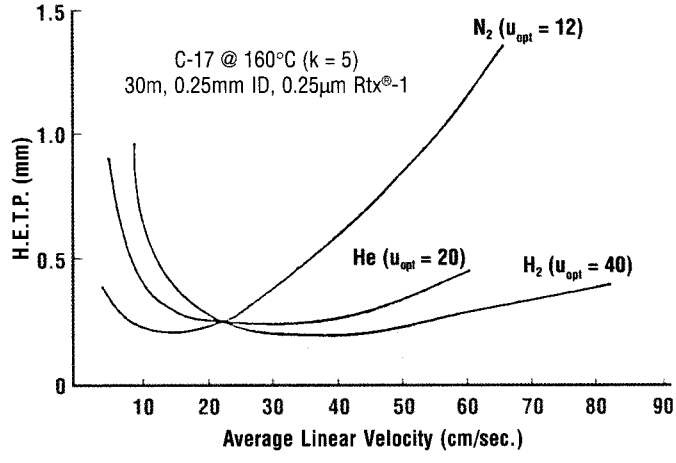
Choosing a Carrier Gas

Figure 3 illustrates the importance of using hydrogen carrier gas to create time savings in gas chromatography. Notice the slopes of the van Deemter plot curves for each of the represented gases. Hydrogen can be used at much higher speeds without significant increases in HETP. Therefore, hydrogen carrier can generate more plates per time than nitrogen or helium making it the time saving carrier gas of choice. As an example, the chromatogram to the left in Figure 1 was generated at approximately 80cm\sec., which is twice the theoretical optimum for hydrogen carrier.

Figure 3:

The van Deemter plots demonstrate the benefits of using hydrogen carrier gas at increased speeds and low HETP values.



Conclusion

The preceeding discussion was presented in order to provide some practical guidelines in gas chromatography method development in a fashion that may help the analyst save time—our most precious resource. The relationship of selectivity, efficiency and time must be realized by the analyst allowing one to choose the appropriate column dimensions, stationary phase, and carrier gas.

In theory, it is fairly easy to derive optimum retention in gas chromatography. Unfortunately, real world samples provide many challenges resulting in deviation from theoretical calculations. The separation of multicomponent mixtures will always require a selective stationary phase and thoughtful selection of chromatographic parameters such as initial starting temperature and temperature programming. The culmination of these ideas should be useful to the analyst concerning practical time reduction in capillary gas chromatography.

Chromatography Reference Books

Modern Practice of Gas Chromatography, 3rd Edition
(Edited by Robert L. Grob, Villanova University)

A book for both beginners and specialists, this work covers principles, instrumentation techniques, and applications of GC.

John Wiley & Sons, Inc., 1995 • 800pp.
cat.# 20464, ea.

Sampling and Analysis of Airborne Pollutants
(Eric D. Winegar and Lawrence H. Keith)

This book provides you with the tools, techniques, and procedures you need to understand and conduct successful sampling and analysis projects. From electro-optical remote sensing to new directions in sampling techniques, this is your guide!

1993 • 384 pp.
cat.# 20468, ea.

Split and Splitless Injection in Capillary GC, 3rd Edition
(Konrad Grob)

Represents one of the most comprehensive, single-volume treatment of all aspects of split and splitless injection. The book is divided into four sections: split injection, splitless injection, problems arising from the heated syringe needle in vaporizing injection, and Programmed Temperature Vaporizing (PTV) injection.

Huethig Publishing, Ltd., 1993 • 547pp.
cat.# 20451, ea.