Predictable Translation of Capillary Gas Chromatography Methods for Fast GC

Application

Gas Chromatography
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Abstract
The time required for capillary gas chromatography (GC) runs is often the major factor in sample turnaround time. Fast GC can significantly improve laboratory productivity by decreasing analysis time. However, converting established capillary GC methods to fast GC can be a daunting task.

The Agilent GC method translation software is a freeware program that logically and predictably translates traditional capillary GC methods. The translation program preserves the elution order for each compound, so that identification of each peak does not have to be repeated. Validation for the new method is made easier. The method translation software will instantly calculate temperature and flow conditions to meet various requirements including retention time locking, best theoretical efficiency, and decreased run time.

This application note discusses considerations involved in choosing fast GC over conventional GC, describes the Agilent GC method translation software, and demonstrates translating methods for faster analysis of solvents, styrene monomers, reformate gasoline, hydrocarbon emissions, semivolatile mixtures, and a chemical process intermediate.

Key Words
Capillary GC, fast GC, gas chromatography, laboratory productivity, method translation, solvent analysis, styrene monomer analysis, reformate gasoline analysis, hydrocarbon emission analysis, semivolatile analysis.

Introduction
A goal of many laboratories is to decrease the turnaround time for each sample. Shorter turnaround times mean quicker analytical results, lower operating costs, increased laboratory productivity, and higher revenues. Fast gas chromatography (GC) promises faster sample analysis, and is thus appealing as a component of increased productivity.

Fast GC is only one possible way to improve productivity. Many of the contributions to the total time required for sample analysis are not affected by the GC run time.

A complete analysis involves sample preparation, sample introduction, the GC cycle time (including run time and oven cool-down), data analysis, report generation, and the time required to document and track each sample. If the GC run time is short compared to the other steps, changing to fast GC may not result in concomitant productivity improvement.

Fast GC is most appropriate when GC run times are a major contribution to total sample turnaround time. The laboratory should streamline as many operations as possible as part of a total productivity improvement program.

Once the GC run time is targeted as an area to improve, there are a
Table 1. Benefits and Drawbacks of Changing to Fast GC Methods

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Benefit</th>
<th>Detriment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase speed of injection process</td>
<td>Faster, more reproducible injections; automation</td>
<td>Cost of purchasing an automatic injector</td>
</tr>
<tr>
<td>Decrease column id (50 mm = current practical limit)</td>
<td>Faster optimum carrier gas velocity; shorter columns (higher plates/m); fastest possible separations</td>
<td>Lower column capacity; requires high inlet pressure; requires high split ratios or low injection volume</td>
</tr>
<tr>
<td>Increase carrier gas velocity</td>
<td>No new equipment/supplies required</td>
<td>Lower resolution; may degrade detector performance</td>
</tr>
<tr>
<td>Shorten column</td>
<td>Standard id columns (capacity); low pressure drops; standard hardware</td>
<td>Low separation power (resolution)</td>
</tr>
<tr>
<td>Perform isothermal analysis</td>
<td>No cool down cycle; short time until elution of early peaks of interest</td>
<td>No focusing possible; no splitless or cool on-column possible; applicable to narrow volatility range of solutes unless using multiple columns; contamination by late eluters</td>
</tr>
<tr>
<td>Increase oven program rate</td>
<td>Elutes full volatility range in minimum time</td>
<td>Lower resolution; limited by instrument capabilities; peak reversals possible</td>
</tr>
<tr>
<td>Change carrier gas (H₂ &gt; He &gt; N₂)</td>
<td>Same efficiency in shorter time with H₂; cost savings</td>
<td>Safety issues with H₂</td>
</tr>
</tbody>
</table>

number of ways to speed up the GC analysis time. However, there are tradeoffs in any attempt to decrease analysis time. A balance between speed, sensitivity, and resolution must be selected for each analysis to meet the laboratory goals. Table 1 lists the major benefits and potential disadvantages of optimizing each run parameter for speed. Adapting methods for fast GC can be complicated because peak reversals are common, and some fast GC methods decrease separation efficiency. This is illustrated in figure 1.

Figure 1, chromatogram A, shows a standard GC chromatogram for a semivolatile mixture using splitless injection. The run time is 45 minutes. Figure 1, chromatogram B, shows the same sample using fast GC. The run time has been decreased from 45 minutes to 12.5 minutes, but the oven temperature program was changed with little regard for possible peak shifting or reversals.

Although the chromatograms are similar and most peaks are adequately separated, a closer examination reveals problems typical of method adaptation. Figure 1, chromatograms C and D, compare the center sections of the two chromatograms A and B, respectively.

The three peaks labeled “1” in chromatogram C are reversed in chromatogram D. The peak pair at “2” is reversed in the fast GC run, and the two peaks at “3” in chromatogram C co-elute in chromatogram D.

These changes mean that validating the new method will be a time-consuming process. The Agilent GC method translation software avoids these problems by making the change from traditional capillary GC methods to fast GC methods predictable.

It locks the elution order for each compound, so peaks do not have to be painstakingly identified. This decreases the time necessary to validate the new method. The method translation software instantly calculates the correct oven temperature program and column head pressure as a function of the new column dimensions, phase ratio, and carrier gas type.

When using the method translation software to calculate conditions for a different column, the new column should have a stationary phase identical to the original column. Columns of 100 percent methyl and 5 percent phenyl/95 percent methyl can often be used interchangeably from different manufacturers, but more polar columns can vary significantly between manufacturers. Method translation may not preserve the elution order for phases that are chemically different. As a column ages, the stationary phase may decompose or become contaminated. This can also affect peak elution order initially and over time.

Method Translation Software

The Agilent GC method translation software, version 2.0, is a freeware program that simplifies fast GC method development. (For the website address to download the freeware, refer to the last page of this publication.) The main data screen of the software is shown in figure 2.

The tool offers selection of several modes of method translation:
- **Translate Only**. Translates the current method to a new one based on a change of column dimensions, carrier gas type,
outlet pressure, and/or phase ratio. The relative retention times of the peaks are locked, so the order of elution is preserved. In “Translate Only” mode, the relative efficiency of the current method is maintained. This is useful if you need to convert a method from the literature, to convert an established method to use a column with different dimensions or a different phase ratio, or to change to a detector with a different outlet pressure.

- **Best Efficiency.** Calculates new conditions (using your current column) that correspond to the theoretical optimum gas flow rate for the greatest separation efficiency for most compounds. Simply enter your current conditions, and the program adjusts the temperatures and flow rate to match the theoretical optimum. The elution order of the peaks will stay the same, but the retention time will probably change.

- **Fast Analysis.** Calculates the temperature and pressure for your current column and carrier gas for a run that has an outlet carrier gas flow that is twice as fast as the “Best Efficiency” mode. Depending on the pressure drop across the column, run time will decrease 1.5 to 2 times. As always with method translation, the elution order of your current method will hold constant.

![A Standard GC Chromatogram](image1)

![B Fast GC Chromatogram](image2)

![C Center Section of Chromatogram A](image3)

![D Center Section of Chromatogram B](image4)

**Figure 1.** Comparison of traditional GC and fast GC for a splitless injection of a semivolatile mixture. (Concentration: 1 ppm; injection size: 0.5 mL)
• **None.** Allows you to change any run parameter of interest. You can decrease method development time by examining the effects of various parameters on the speed, head pressure, and oven temperature ramp of your method before you do any chromatography. This mode is also useful to try out changes to your current method. For instance, if your current method is already at maximum efficiency and you need to maintain separation power, you can enter a smaller column id to see the exact impact on run time. If you have excess separation power, you can calculate conditions for a shorter column or faster gas flow rate. The method translation software allows you to rapidly develop a feel for the effects of each parameter on speed of analysis, pressure, and oven temperature program rate.

Separation power (resolution) is a function of column dimensions, flow, and oven temperature. When a new column is selected to maintain separation efficiency, the GC method translation software will make sure that the flow and oven temperature ramp rates are scaled appropriately.

### Experimental

All experiments were performed using an Agilent 6890 Series gas chromatograph (GC) with the 240-volt option. The 6890 Series GC has many features specifically designed for the successful migration to faster GC methods. These include:

- 100- and 150-psi EPC split/splitless inlet
- Automated split ratios to 7500:1
- Fast detector sampling rates (0.1–200 Hz) for flame ionization detection (FID) and nitrogen-phosphorus detection (NPD) with a ChemStation

### Results and Discussion

Examples of fast GC for analysis of hydrocarbons in gasoline and simulated distillation are discussed in other Agilent publications.¹, ² This application note demonstrates the time savings achieved for various other analyses.

**Chemical Process Intermediate**

Figure 4 shows the development of a fast GC analysis for a chemical process intermediate. Figure 4, chromatogram A, shows the original method; figure 4, chromatogram B, shows the translated method with the column dimensions decreased by a factor of three and the relative retention times of the peaks constant. For even faster analysis, the column was shortened, as shown in figure 4, chromatogram C.

The relative retention times are still correct, and the run is almost eight...
times as fast. In figure 4, chromatogram C, some resolution is lost due to the shorter column. Scaling the column to 10 m × 0.05 mm (0.2 mm) would have provided the identical resolution because of the higher efficiency per unit length of the smaller id column.

**Solvent Analysis**

A traditional capillary GC method for analysis of solvent from a commercial paint thinner is shown in figure 5, chromatogram A. Using the method translation software with the criterion of “fast analysis” selected, the carrier gas outlet flow rate was doubled. The tool calculated the oven temperature ramp that would maintain relative peak retention times at the faster flow rate. The resulting chromatogram is shown in figure 5, chromatogram B. The run time has decreased from 9 minutes to 6 minutes, and the peaks are still well separated.

Figure 6 shows the effect of changing carrier gas from helium to hydrogen in a similar analysis using smaller id columns. Because the theoretical optimum flow rate is faster for hydrogen than for helium, changing to hydrogen can significantly decrease the run time while not requiring high head pressures.

In figure 6, the flow rate of hydrogen was increased beyond that used for helium to reduce analysis time even

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**Figure 3.** Peak shape vs liner diameter.

**Figure 4.** A chemical process intermediate on an HP-1 column at three different column sizes and phase ratios.
more. The conditions were not “translated.” In the analyses shown in figures 5 and 6 (less than 10 highly resolved peaks), the use of method translation is optional. This is not the case with more complex samples.

**Styrene Monomer Impurities**

A standard GC analysis for impurities in styrene monomer takes about 12 minutes, as shown in figure 7. Using a smaller column with a faster oven program rate and slower carrier gas flow rate, an equivalent analysis was obtained in 3.6 minutes.

**Reformate Gasoline Analysis**

The development of a fast GC method for reformate gasoline analysis is shown in figure 8, chromatogram A, which shows a standard GC analysis that takes about 20 minutes. In figure 8, chromatogram B, a smaller column decreased the run time to 6 minutes. In figure 8, chromatogram C, the carrier gas was changed from helium to hydrogen, and the run time decreased to less than 4 minutes. The peaks are still well resolved and the order of elution is maintained. Table 2 shows the conditions used for the chromatograms in figure 8.

**Conclusions**

Despite the improvements in instrumentation, fast chromatography will always involve tradeoffs among speed, sensitivity, and resolution. The discussion here details considerations involved in choosing fast chromatography, discusses Agilent method translation software, and gives specific examples of some types of mixtures that are amenable to fast GC.

Use of Agilent method translation software eases the migration to faster methods by providing the conditions that will maintain the current order of elution. It can also highlight the potential instrument limitations (head...
pressure or oven temperature program rate) that would be associated with translating a current method for use on a smaller id column.

**To Obtain Agilent Method Translation Freeware**


### Table 2. Conditions for Fast GC of Reformate Gasoline

<table>
<thead>
<tr>
<th></th>
<th>Column</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>df</td>
<td>30 m x 0.32 mm</td>
<td>10 m x 0.32 mm</td>
<td>10 m x 0.10 mm</td>
<td></td>
</tr>
<tr>
<td>Phase</td>
<td>HP-Wax</td>
<td>HP-Wax</td>
<td>HP-Wax</td>
<td></td>
</tr>
<tr>
<td>Carrier</td>
<td>Helium</td>
<td>Helium</td>
<td>Hydrogen</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>6.4 psi</td>
<td>37.3 psi</td>
<td>21.9 psi</td>
<td></td>
</tr>
<tr>
<td>Flow</td>
<td>1.2 mL/min</td>
<td>0.37 mL/min</td>
<td>0.33 mL/min</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>60 °C (hold 4 min)</td>
<td>60 °C (hold 1 min)</td>
<td>60 °C (hold 0.7 min)</td>
<td></td>
</tr>
<tr>
<td>Rate 1</td>
<td>10 °C/min</td>
<td>36.7 °C/min</td>
<td>55.1 °C/min</td>
<td></td>
</tr>
<tr>
<td>Final Temp</td>
<td>140 °C</td>
<td>140 °C</td>
<td>140 °C</td>
<td></td>
</tr>
<tr>
<td>Rate 2</td>
<td>15 °C/min</td>
<td>55.1 °C/min</td>
<td>70 °C/min</td>
<td></td>
</tr>
<tr>
<td>Final Temp 2</td>
<td>200 °C (hold 4 min)</td>
<td>200 °C (hold 2 min)</td>
<td>200 °C (hold 1 min)</td>
<td></td>
</tr>
<tr>
<td>Injection Volume</td>
<td>0.5 μL; split 200:1</td>
<td>0.1 μL; split 800:1</td>
<td>0.1 μL; split 800:1</td>
<td></td>
</tr>
</tbody>
</table>

**Peaks**

1. Ethylbenzene
2. p-Xylene
3. m-Xylene
4. Isopropyl benzene
5. o-Xylene
6. n-Propylbenxene
7. p/m-Ethyl toluene
8. Styrene
9. a-Methylstyrene
10. Phenylacetylene
11. b-Methylstyrene
12. Benzaldehyde

### Figure 7. Comparison of traditional capillary GC and fast GC for the analysis of impurities in styrene monomer.

### Figure 8. Development of fast GC for reformate gasoline.

**References**

