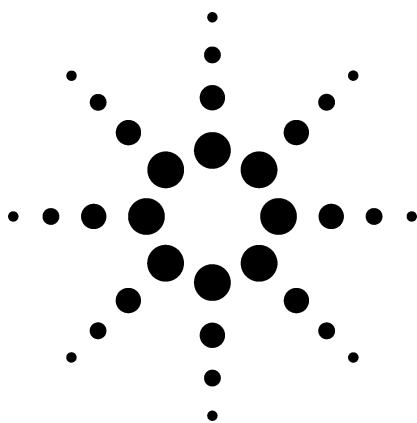


# Predictable Translation of Capillary Gas Chromatography Methods for Fast GC



## 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, reformat gasoline, hydrocarbon emissions, semivolatiles mixtures, and a chemical process intermediate.

## Key Words

Capillary GC, fast GC, gas chromatography, laboratory productivity, method translation, solvent analysis, styrene monomer analysis, reformat gasoline analysis, hydrocarbon emission analysis, semivolatiles 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 labo-

ratory 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



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**Table 1. Benefits and Drawbacks of Changing to Fast GC Methods**

Parameter	Benefit	Detriment
Increase speed of injection process	Faster, more reproducible injections; automation	Cost of purchasing an automatic injector
Decrease column id (50 mm = current practical limit)	Faster optimum carrier gas velocity; shorter columns (higher plates/m); fastest possible separations	Lower column capacity; requires high inlet pressure; requires high split ratios or low injection volume
Increase carrier gas velocity	No new equipment/supplies required	Lower resolution; may degrade detector performance
Shorten column	Standard id columns (capacity); low pressure drops; standard hardware	Low separation power (resolution)
Perform isothermal analysis	No cool down cycle; short time until elution of early peaks of interest	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
Increase oven program rate	Elutes full volatility range in minimum time	Lower resolution; limited by instrument capabilities; peak reversals possible
Change carrier gas (H <sub>2</sub> > He > N <sub>2</sub> )	Same efficiency in shorter time with H <sub>2</sub> ; cost savings	Safety issues with H <sub>2</sub>

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 semivolatiles 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

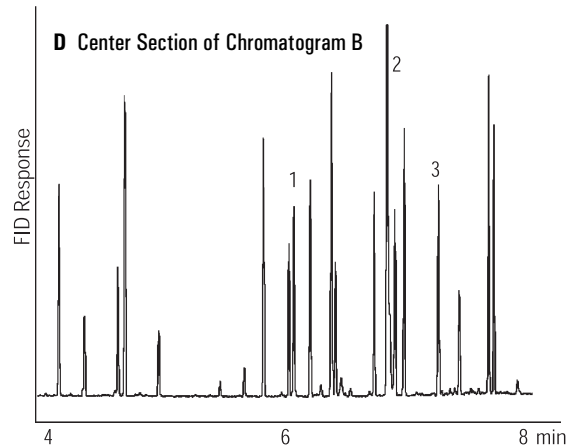
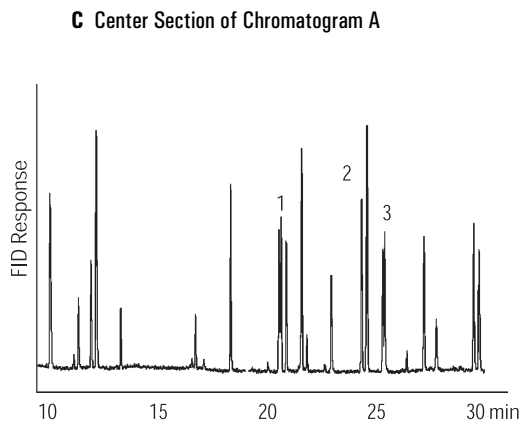
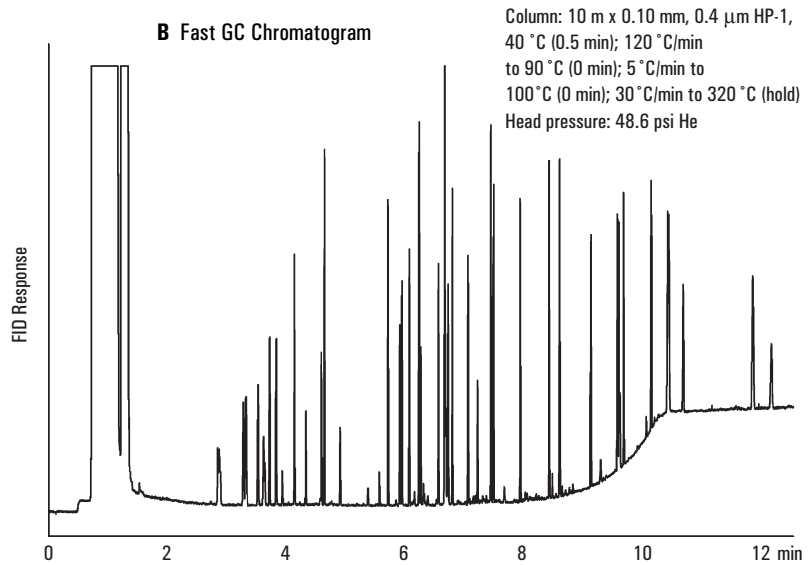
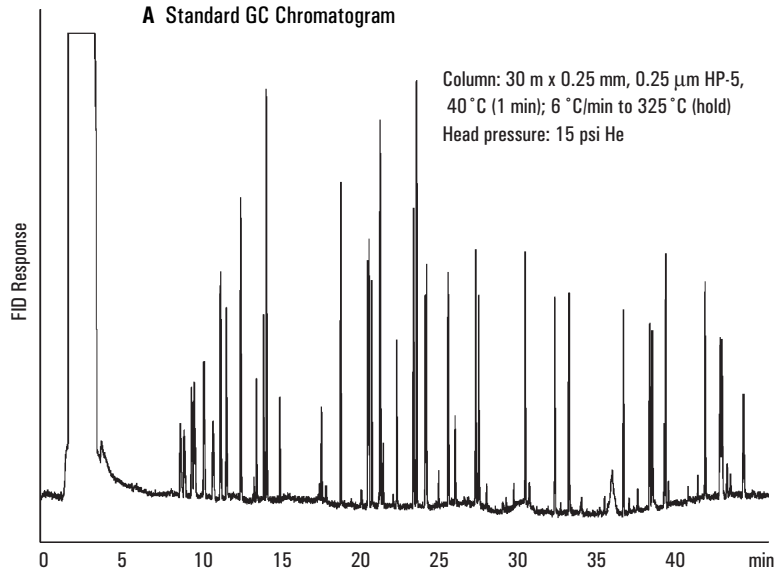
The Agilent GC method translation software, version 2.0, is a freeware program that simplifies fast GC method development. (For the web site address to download the freeware, refer to the last page of this publication.) The main data screen of the software is shown in figure 2.

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.



**Figure 1. Comparison of traditional GC and fast GC for a splitless injection of a semivolatle 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.

GC Method Translator										
Criterion: <input checked="" type="radio"/> Translate Only <input type="radio"/> Best Efficiency <input type="radio"/> Fast Analysis <input type="radio"/> None		Speed gain: 4.43545								
		Original Method			Translated Method					
<b>Column</b>										
Length,	m	100.0			<input type="checkbox"/> 40.00					
Internal Diameter,	µm	250.0			<input type="checkbox"/> 100.0					
<b>Film</b>					<input type="radio"/> Unlock					
Thickness,	µm	0.500			<input type="radio"/> 0.200					
Phase Ratio		125.0			<input checked="" type="radio"/> 125.0					
<b>Carrier Gas</b>		Helium			<input type="checkbox"/> Hydrogen					
Enter one Setpoint										
Head Pressure,	psi	40.000			85.242					
Flow Rate,	mL/min	1.7619			0.8810					
Outlet Velocity,	cm/sec	62.33			194.77					
Average Velocity,	cm/sec	23.77			42.17					
Hold-up Time,	min	7.01259			1.58103					
Outlet Pressure (absolute),	psi	14.696			<input type="checkbox"/> 14.696					
Ambient Pressure (absolute),	psi	14.696			<input type="checkbox"/> 14.696					
<b>Oven Temperature</b>		3-ramp Program								
		Initial								
		Ramp 1								
		Ramp 2								
		Ramp 3								
		Ramp Rate	Final Temp.	Final Time	Ramp Rate	Final Temp.	Final Time	Ramp Rate	Final Temp.	Final Time
		°C/min	°C	min	°C/min	°C	min	°C/min	°C	min
		10.000	35.00	13.000	44.354	35.00	2.931	44.354	35.00	3.382
		1.000	60.00	15.000	4.435	60.00	3.382	4.435	60.00	3.382
		2.000	220.00	5.000	8.871	220.00	1.127	8.871	220.00	1.127

Figure 2. The Agilent GC Method Translation Software, Version 2.0a.

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

- Fast oven program rates (up to 120 °C/min, depending on the temperature range)

A G1916A automatic liquid sampler (ALS) was used for sample introduction, and an Agilent ChemStation was used for instrument control and data acquisition. Refer to the individual chromatograms for details about columns, temperatures, split ratios, carrier gas, gas flows, and oven ramps.

### Injection Liner

To maximize sensitivity and resolution with split injections, it is important to obtain good peak shape. Using a different column size may require a different size liner to maintain good peak shape. Figure 3 demonstrates the difference in peak shape obtained with a 2-mm liner versus a 4-mm liner with glass wool plugs. The smaller diameter liner improves the peak shape for the 0.05-mm id column in this example.

## Results and Discussion

Examples of fast GC for analysis of hydrocarbons in gasoline and simulated distillation are discussed in other Agilent publications.<sup>1,2</sup> 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

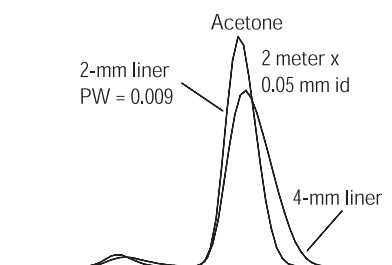


Figure 3. Peak shape vs liner diameter.

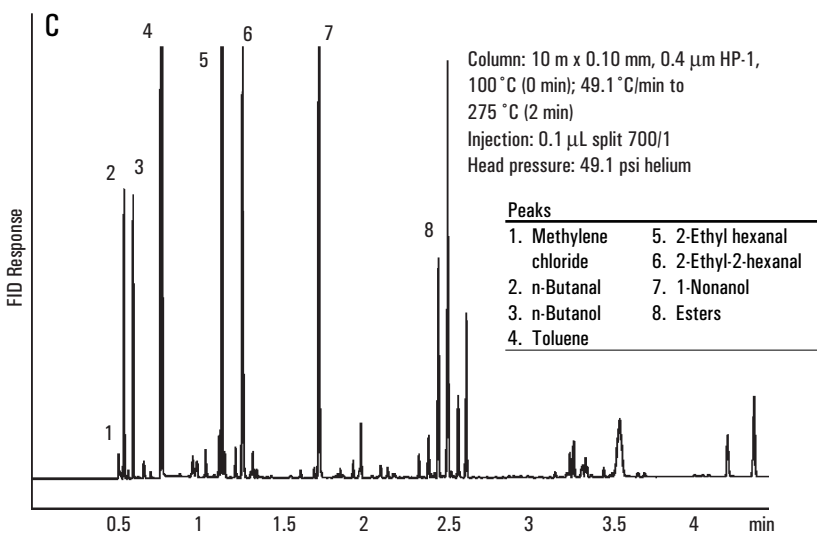
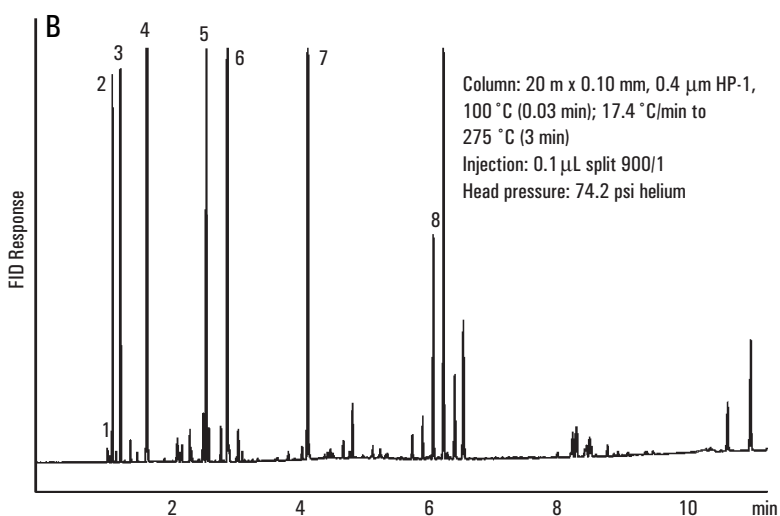
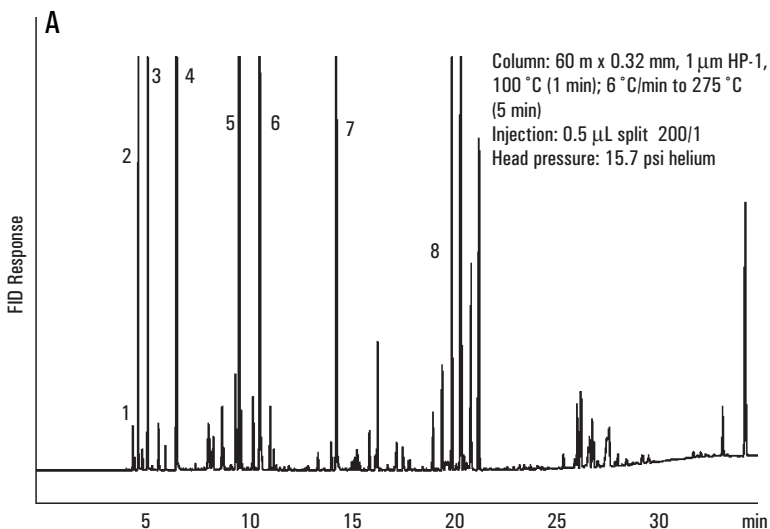


Figure 4. A chemical process intermediate on an HP-1 column at three different column sizes and phase ratios.

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

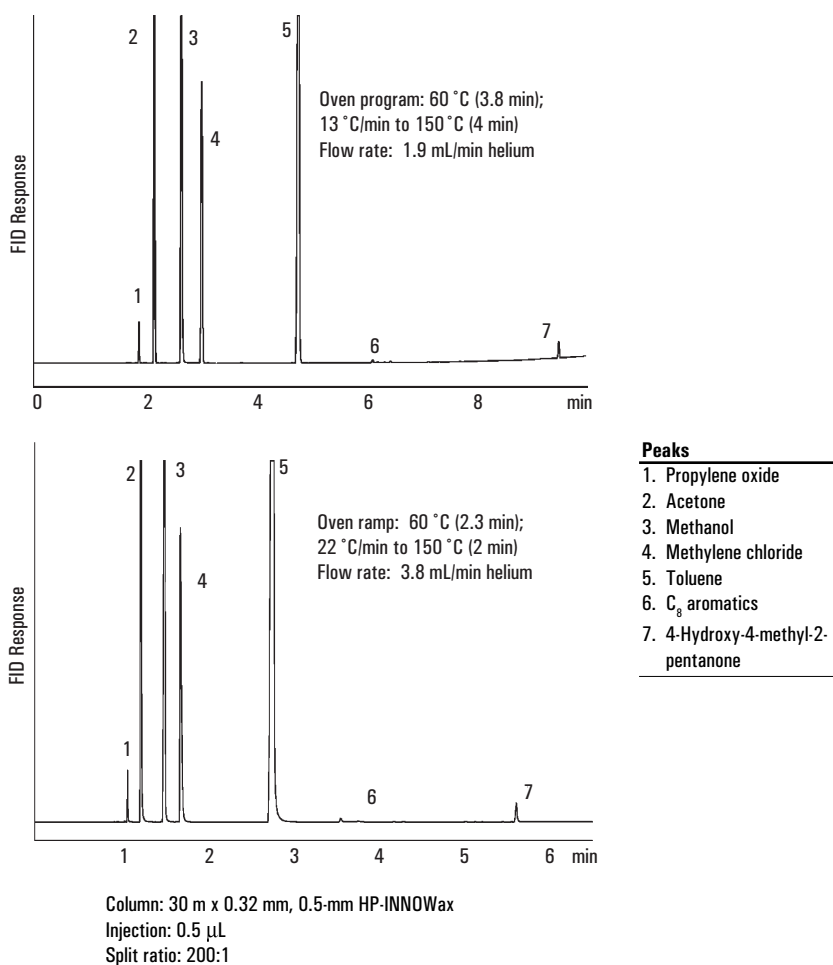


Figure 5. Comparison of solvent analysis from a commercial paint remover at two flow rates

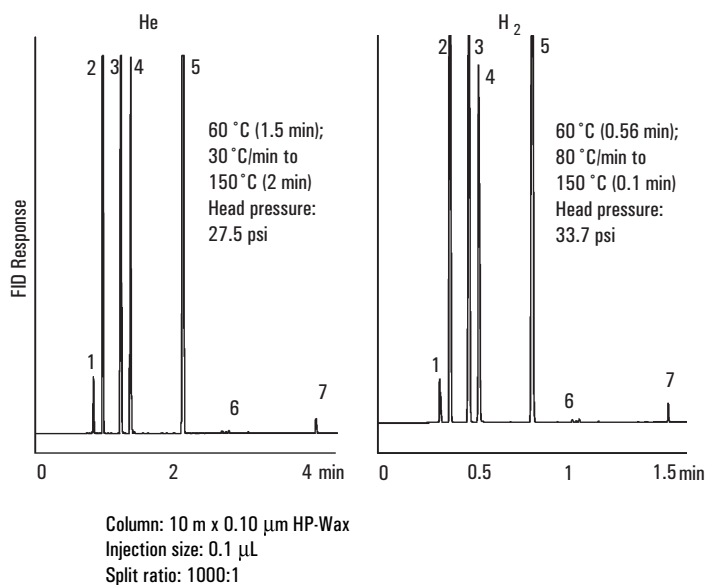


Figure 6. Comparison of using helium and hydrogen carrier gas for analysis of a commercial paint remover

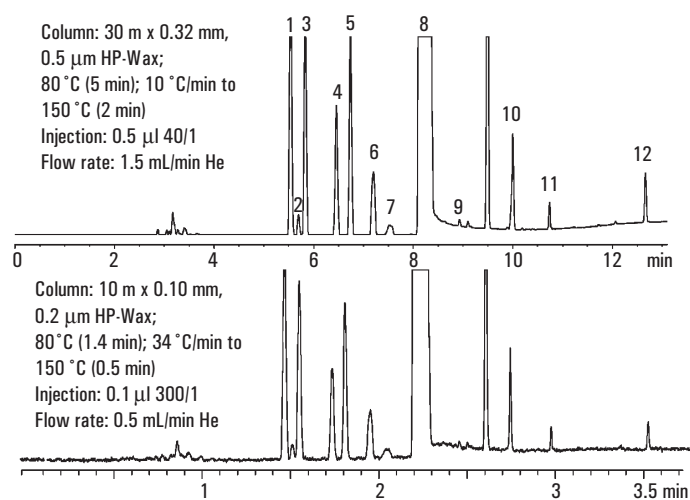
pressure or oven temperature program rate) that would be associated with translating a current method for use on a smaller id column.

### To Obtain Agilent Method Translation Freeware

The Agilent method translation software can be downloaded from the Chemical Analysis Group (CAG) section of the Agilent home page on the World Wide Web at <http://www.chem.agilent.com/cag/servsup/usersoft/main.html>.

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

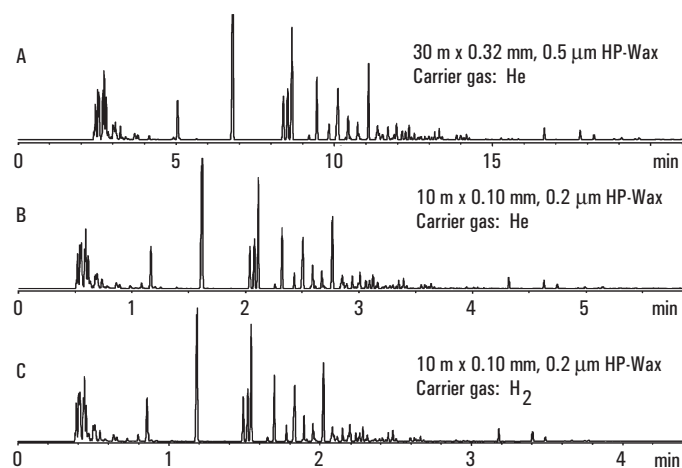
	A	B	C
Column	30 m x 0.32 mm	10 m x 0.32 mm	10 m x 0.10 mm
df	0.5 $\mu$ m	0.2 $\mu$ m	0.2 $\mu$ m
Phase	HP-Wax	HP-Wax	HP-Wax
Carrier	Helium	Helium	Hydrogen
Pressure	6.4 psi	37.3 psi	21.9 psi
Flow	1.2 mL/min	0.37 mL/min	0.33 mL/min
Temperature	60 °C (hold 4 min)	60 °C (hold 1 min)	60 °C (hold 0.7 min)
Rate 1	10 °C/min	36.7 °C/min	55.1 °C/min
Final Temp	140 °C	140 °C	140 °C
Rate 2	15 °C/min	55.1 °C/min	70 °C/min
Final Temp	200 °C (hold 4 min)	200 °C (hold 2 min)	200 °C (hold 1 min)
Injection Volume	0.5 $\mu$ L; split 200:1	0.1 $\mu$ L; split 800:1	0.1 $\mu$ L; split 800:1



#### Peaks

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

1. B. Quimby, V. Giarrocco, and M. Klee. "Speed Improvements in Detailed Hydrocarbon Analysis of Gasoline Using 100- $\mu$ m Capillary Columns," Agilent Technologies, Inc., Application Note 228-294, Publication Number (23) 5963-5190E, February 1995.
2. V. Giarrocco. "Two-Minute Simulated Distillation Analysis of Gasoline-Range Materials—A Preliminary Investigation," Agilent Technologies, Inc., Application Note 228-370, Publication Number (23) 5965-6461E, January 1997.

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