

Fast GC

Increase Sample Throughput without Sacrificing Quality



sigma-aldrich.com

Agenda

Why do Fast GC?

What is Fast GC?

The Principles of Fast GC

Theoretical Discussion

Practical Considerations

Putting it All Together

Application Examples

Review and Summary

Updated: 21-Jan-2011

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Abstract:

Analytical GC chemists are continually striving to reduce analysis times, because shorter analysis times increase sample throughput, which translates to the completion of more billable samples per shift. However, any decrease in analysis time must not diminish the resolution necessary to adequately resolve peaks of interest, and identify specific elution patterns. Applying the Principles of Fast GC to any application can achieve both of these objectives.

The information presented will provide a background in the basic theory behind Fast GC, and highlight the practical aspects of making it work (often without having to invest a significant amount of money in new equipment). Popular applications, such as PAHs, GC-MS volatiles, GC-MS semivolatiles, FAMES, and BTEX, will be shown.



Why do Fast GC?
What is Fast GC?
The Principles of Fast GC

2

© 2009 Sigma-Aldrich Co. All rights reserved. sigma-aldrich.com/fastgc SIGMA-ALDRICH®

We will begin by answering “Why” Fast GC should be considered, defining “What” it is, and providing a short overview of “How” it works.

Why do Fast GC?

- Fast GC yields faster analysis times than conventional GC (often 3-10x faster), offering higher throughput and allowing more samples to be analyzed per shift
 - **Decrease costs**: need fewer analysts and/or instruments
 - **Increase revenue**: analyze more samples
 - Can provide faster method development
- Can be done with **no sacrifice in quality**
- Typically, **no additional capital equipment** is required

3

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

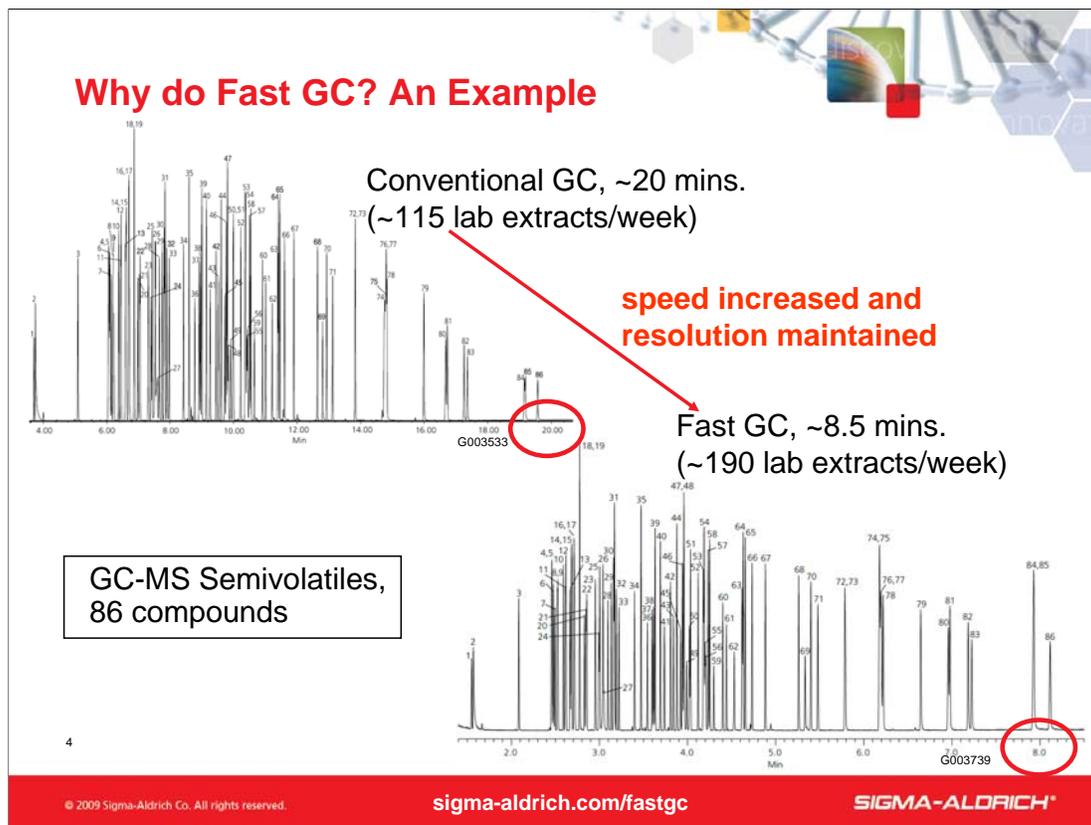
Why should you consider implementing Fast GC into your lab? Time and money!

Fast GC yields faster analysis times than conventional GC, often three to ten times faster, offering higher throughput and allowing more samples to be analyzed per shift. The main benefits to a laboratory are that:

- Costs can be decreased if fewer analysts and/or instruments are needed
- Revenue can be increased if more samples are analyzed
- Method development can occur faster

Fast GC can be applied to any application with no sacrifice in quality!

Lastly, Fast GC typically does not require any additional capital equipment.



Here is an example of why Fast GC should be considered. Both of these chromatograms are the analysis of GC-MS semivolatiles, an application routinely performed in environmental laboratories. This method requires the GC-MS to be 'tuned' and calibrated prior to the analysis of any lab extracts (blanks, QA samples, and billable samples), and that all lab extracts must be injected within 12 hours of when the 'tune' solution was injected. The shorter the run time, the more lab extracts that can be run within the 'tune' window.

The top chromatogram was obtained using conventional GC. Assuming a single 'tune' window is set-up per day, each instrument can analyze ~115 lab extracts per week after taking into account the cool down period between runs.

The bottom chromatogram was obtained after applying the Principles of Fast GC. Assuming a single 'tune' window is set-up per day, each instrument can now analyze ~190 lab extracts per week after taking into account the cool down period between runs. This increase of 75 lab extracts per week does not require any increase in staff or equipment. Additionally, the quality of the analysis is not diminished!

Conditions (top chromatogram):

- column: SLB-5ms, 30 m x 0.25 mm I.D., 0.25 µm (28471-U)
- oven: 40 °C (2 min.), 22 °C/min. to 240 °C, 10 °C/min. to 330 °C (1 min.)
- inj.: 250 °C
- MSD interface: 330 °C
- scan range: m/z 40-450
- carrier gas: helium, 1.0 mL/min (11 min.), 10 mL/min² to 1.5 mL/min. (hold remainder of run)
- injection: 0.5 µL, splitless (0.50 min.)
- liner: 2 mm I.D., straight
- sample: 80 component semivolatile standard at 50 ppm plus 6 internal standards (at 40 ppm) in methylene chloride

Conditions (bottom chromatogram):

- column: SLB-5ms, 20 m x 0.18 mm I.D., 0.18 µm (28564-U)
- oven: 40 °C (0.7 min.), 55 °C/min. to 240 °C, 28 °C/min. to 330 °C (2 min.)
- inj.: 250 °C
- MSD interface: 330 °C
- scan range: m/z 40-450
- carrier gas: helium, 40 cm/sec, constant
- injection: 0.5 µL, 10:1 split
- liner: 2 mm I.D., fast FocusLiner™ inlet liner with taper (2879501-U)
- sample: 80 component semivolatile standard at 50 ppm plus 6 internal standards (at 40 ppm) in methylene chloride

What is Fast GC?

- Fast GC is manipulating a number of parameters to provide **faster analysis times while maintaining resolution**
- These parameters include:
 - **Column dimensions** (inside diameter, length, and film thickness)
 - **Oven temperature ramp rate**
 - **Carrier gas** (type and linear velocity)
 - **Stationary phase**

5

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

So, what exactly is Fast GC? Simply stated, Fast GC is the manipulation of a number of parameters to provide faster analysis times while maintaining resolution. These parameters include:

- Column dimensions, such as the inside diameter (I.D.), length, and film thickness
- Oven temperature ramp rates
- The carrier gas type and/or linear velocity
- The type of stationary phase

The Principles of Fast GC

- Decrease analysis time by using:
 - Shorter column
 - Quicker oven temperature ramp rate
 - Higher carrier gas linear velocity

But these changes also decrease resolution!
- Offset the decrease in resolution by also using:
 - Narrow I.D. column
 - Hydrogen carrier gas
 - Low film thickness

6

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

The underlying Principles of Fast GC are pretty simple.

Analysis times can be decreased by using:

- Short columns
- Fast oven temperature ramp rates
- High carrier gas linear velocities

The loss in resolution caused by the above steps can be offset by using:

- Narrow I.D. columns
- Hydrogen carrier gas
- Low film thickness

The more Principles that are applied, the greater the benefit!



Theoretical Discussion

7

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Before we look at how to perform Fast GC, let's take a step back and look at why it works through a short theoretical discussion.

Retention Time in GC

- The following equation defines GC retention time:

$$t_R = \frac{L(k+1)}{u}$$

- There are three options to reduce t_R (retention time):
 - Reduce L (column length)
 - Reduce k (retention factor) by increasing temperature
 - Increase u (carrier gas linear velocity)

But these changes also decrease resolution!

8

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

How long analytes are retained in a column dictates the overall analysis time. Simply logic tells us that if retention times can be shortened, the result will be a shorter overall analysis time. The retention time (t_R) of an analyte is a function of column length (L), retention factor (k), and carrier gas linear velocity (u). This equation defines those relationships. For this discussion, we do not need to worry about the correct units for each term. Rather, we are interested in the relationships (cause and effect).

There are three options for reducing retention time:

- Use a shorter column
- Increase oven temperature to reduce analyte partitioning into the stationary phase
- Increase the carrier gas linear velocity to move analytes through the column quicker

These three steps comprise the first half of the Principles of Fast GC. They accomplish shortening analysis time, but sacrifice resolution in doing so. The second half of the Principles of Fast GC focus on gaining back the resolution.

How Efficiency Affects Resolution

- The resolution (R_s) equation:

$$R_s = \underbrace{\{k/(1 + k)\}}_{\text{Capacity (k)}} \underbrace{\{(\alpha - 1)/\alpha\}}_{\text{Selectivity } (\alpha)} \underbrace{\{N^{1/2}/4\}}_{\text{Efficiency (N)}}$$

- Relationship between N (efficiency, as plates) and H (plate height):

$$N = L/H$$

- Decreasing H (plate height) will increase N (efficiency, as plates) and also increase R_s (resolution)

9

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Before we look at the second half of the Principles of Fast GC that focus on gaining back the resolution, we need to understand the relationships between resolution and plate height. The resolution equation tells us that resolution (R_s) is the result of capacity times selectivity times efficiency. Focusing on efficiency (expressed as plates), we see that it is inversely related to plate height (H). If we can decrease plate height (H), we will increase efficiency (N), which in turn will increase resolution (R_s). Therefore, the second half of the Principles of Fast GC deal with decreasing plate height (H) as the means to gain back the resolution lost when the first half of the Principles of Fast GC were applied.

How to Decrease H (Plate Height)

- The Golay equation ($H = B/u + Cu$) is the classic van Deemter equation minus the A term, which does not apply to open tubes
- Looks complex, but from it a few simple truths relevant to Fast GC are obvious

$$H = \frac{B/u}{u} + \frac{C_m u + C_s u}{u} = \frac{2 D_m}{u} + \frac{(1 + 6k' + 11k'^2) r^2}{24(1 + k')^2 D_m} u + \frac{k' r^2}{6(1 + k')^2 K^2 D_s} u$$

- 1. A smaller r (radius) results in a lower H**
[use a column with a narrower I.D.]
- 2. A higher D_m (diffusivity, mobile phase) results in a lower H**
[use hydrogen instead of helium as the carrier gas]
- 3. A higher D_s (diffusivity, stationary phase) results in a lower H**
[use a column with a thin film thickness]

10

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

So, how do we decrease plate height (H)? The Golay equation ($H = B/u + Cu$) is the classic van Deemter equation minus the A term, which does not apply to open tubes. The Golay equation is useful for us because it describes plate height (H), and its relationships to several terms. It looks complex, but from it a few simple truths relevant to Fast GC are obvious:

A smaller radius (r) results in a lower plate height (H) – tells us to use a column with a narrower I.D.

A mobile phase with a higher diffusivity (D_m) results in a lower plate height (H) - tells us to use hydrogen instead of helium as the carrier gas

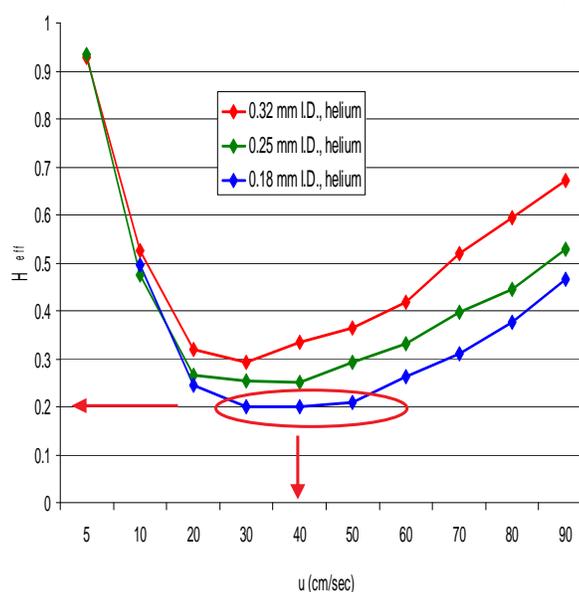
A stationary phase with a higher diffusivity (D_s) results in a lower plate height (H) - tells us to use a column with a thinner film thickness

van Deemter Review:

- The A term concerns eddy (axial) diffusion [not applicable to open tubes]
- The B term concerns longitudinal diffusion
- The C term concerns resistance to mass transfer

Why Use a Narrow Column I.D.?

- Golay plots comparing different I.D. columns
- A narrow I.D. exhibits
 - **Lower H_{eff}** [increases efficiency leading to increased resolution]
 - **Higher u_{opt}** [can use a faster u than with larger I.D. columns]
 - **Flatter Golay relationship** [can be run at $u > u_{opt}$ without a significant increase in H_{eff}]



11

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Let's take a moment and look at some data relating to column I.D. and carrier gas. First up is column I.D.

Shown are Golay plots of three different I.D. columns. The X-axis shows linear velocity (u), and the Y-axis shows effective plate height (H_{eff}). The phrase optimal linear velocity (u_{opt}) is used to define the linear velocity value when the Golay plot is at its lowest. As we have already discussed, lower plate height (H) values result in higher resolution, and that higher linear velocity (u) values result in shorter analysis times. From a Fast GC point of view, we want to choose a column I.D. whose Golay plot reaches low and to the right.

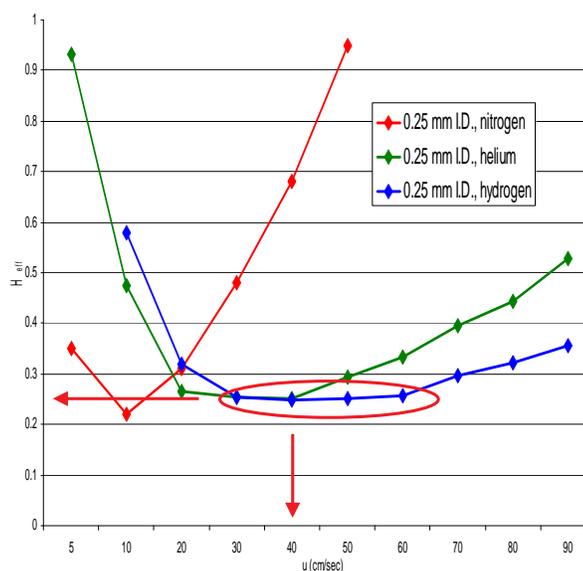
For Fast GC, a narrow I.D. column is the best choice, because:

- It has a lower effective plate height (H_{eff}) than larger I.D. columns, which increases efficiency and leads to increased resolution
- It has a higher optimal linear velocity (u_{opt}) than larger I.D. columns, which allows faster analysis
- It has a flatter Golay relationship than larger I.D. columns, which allows the use of a linear velocity (u) greater than optimal (u_{opt}) without a significant increase in effective plate height (H_{eff})

Note: Data for a 0.10 mm I.D. column with helium carrier gas could not be obtained due to high backpressure.

Why Use Hydrogen?

- Golay plots comparing common GC carrier gases
- Hydrogen exhibits
 - **Low H_{eff}** [good efficiency and resolution]
 - **Higher u_{opt}** [can use a faster u than with other carrier gas choices]
 - **Flatter Golay relationship** [can be run at $u > u_{opt}$ without a significant increase in H_{eff}]



12

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

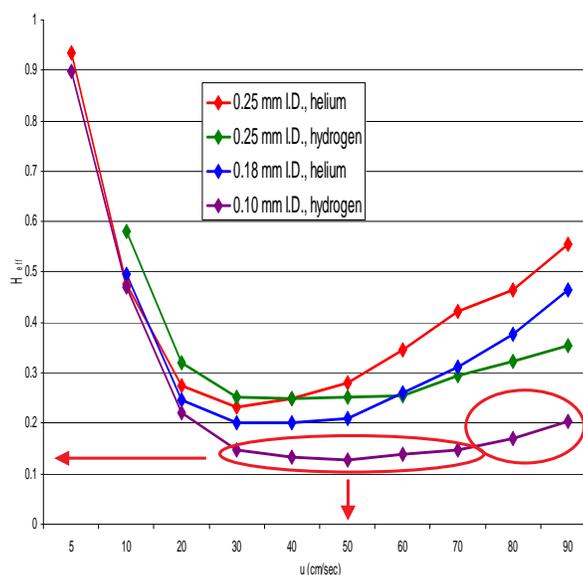
Now let's look at carrier gas. Shown are Golay plots of the common GC carrier gases nitrogen, helium, and hydrogen on the same I.D. column. As stated on the previous Slide, a Golay plot that reaches low and to the right is desirable from a Fast GC point of view.

For Fast GC, hydrogen is the best choice, because:

- It has a low effective plate height (H_{eff}), resulting in good efficiency and resolution
- It has a higher optimal linear velocity (u_{opt}) than other carrier gases, which allows faster analysis
- It has a flatter Golay relationship than other carrier gases, which allows the use of a linear velocity (u) greater than optimal (u_{opt}) without a significant increase in effective plate height (H_{eff})

'Best' Choice: Narrow I.D. and Hydrogen

- Golay plots comparing different I.D. columns and carrier gases
- A narrow I.D. when used with hydrogen
 - Has a **very low H_{eff}** [increases efficiency leading to increased resolution]
 - Has a **very high u_{opt}** [can use a faster u than with other combinations]
 - Has a **very flat Golay relationship** [can be run at $u > u_{opt}$ without a significant increase in H_{eff}]



13

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Let's consider column I.D. and carrier gas together. Shown are Golay plots of four combinations of column I.D. and carrier gas. Remember that from a Fast GC point of view, we want a Golay plot that reaches low and to the right.

For Fast GC, a narrow I.D. column used with hydrogen is the best choice, because:

- It has a **very** low effective plate height (H_{eff}) compared to other combinations, which increases efficiency and leads to increased resolution
 - It has a **very** high optimal linear velocity (u_{opt}) compared to other combinations, which allows faster analysis
 - It has a **very** flat Golay relationship compared to other combinations, which allows the use of a linear velocity (u) greater than optimal (u_{opt}) without a significant increase in effective plate height (H_{eff})
- * Most impressively is that this combinations can be used with a linear velocity of 80-90 cm/sec, and still exhibits a H_{eff} lower than other combinations run at their u_{opt} values

Note: Data for a 0.10 mm I.D. column with helium carrier gas could not be obtained due to high backpressure.

Review: The Principles of Fast GC

- Decrease analysis time by using:
 - Shorter column
 - Quicker oven temperature ramp rate
 - Higher carrier gas linear velocity

But these changes also decrease resolution!
- Offset the decrease in resolution by also using:
 - Narrow I.D. column
 - Hydrogen carrier gas
 - Low film thickness

14

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Review:

The underlying Principles of Fast GC are pretty simple.

Analysis times can be decreased by using:

- Short columns
- Fast oven temperature ramp rates
- High carrier gas linear velocities

The loss in resolution caused by the above steps can be offset by using:

- Narrow I.D. columns
- Hydrogen carrier gas
- Low film thickness

The more Principles that are applied, the greater the benefit!

Note:

Many of these parameters being manipulated are related to each other. Changing just one may produce a shorter analysis, but may result in a loss in quality. Therefore, all parameters must be evaluated to make sure they are set correctly.



Practical Considerations

15

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Before we get into a walk-through of applying Fast GC to an application, there are a few practical considerations we need to be aware of.

Sample Capacity

- Fast GC column dimensions (narrow I.D. and thin film) have lower sample capacities compared to conventional column dimensions
- That is, a smaller amount of sample can be introduced onto the column before peak shapes become distorted
- Therefore, high split ratios may be required to prevent column overload

16

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Fast GC column dimensions (narrow I.D. and thin film) have lower sample capacities compared to conventional column dimensions. That is, a smaller amount of sample can be introduced onto the column before peak shapes become distorted. Therefore, high split ratios may be required to prevent column overload.

Oven Temperature Ramp Rates

- Fast oven temperature ramp rates are essential to decreasing analysis time
- It is important to know the ramp rate abilities of your GC for the temperature ranges in which you will be operating
- Programming a ramp rate that is faster than your GC can handle may result in variations in retention time
- Many newer GC instruments have faster ramp rate abilities due to decreased oven volume or 240V power connections
- On older GCs, decreasing the internal oven volume through the use of an insert is an inexpensive and simple way to increase ramping ability

17

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

As we have already discussed, fast oven temperature ramp rates are essential to decreasing analysis time. However, it is important to know the ramp rate abilities of your GC for the temperature ranges in which you will be operating. Programming a ramp rate that is faster than your GC can handle may result in variations in retention time. Make sure to check your instrument manual or manufacturer's web site for a listing of maximum ramp rates over the temperature ranges you plan to operate in.

Many newer GC instruments have faster ramp rate abilities due to decreased oven volume or 240V power connections. On older GCs, decreasing the internal oven volume through the use of an insert is an inexpensive and simple way to increase ramping ability.

Detection

- Acquisition rates
 - Fast GC applications typically produce rapid and narrow peaks
 - Verify the detector can obtain sufficient data points per peak to ensure proper peak quantitation
 - Most new detectors are able to work with Fast GC
- MS carrier gas requirements
 - Some older MS instrumentation may not work properly with hydrogen as the carrier gas
 - Consult your instrument manual or manufacturer's literature

18

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Because Fast GC produces rapid and narrow peaks, the detector must be able to obtain sufficient data points per peak to ensure proper peak quantitation. Most new detectors are able to work with Fast GC.

We already discussed that the more Principles that are applied, the greater the benefit. However, the instrumentation being used may prohibit applying all of the Principles. An example of this is when working with GC-MS. Some older MS instrumentation may not work properly with hydrogen as a carrier gas. To find out whether your MS is compatible with hydrogen carrier gas, check your instrument manual or manufacturer's web site. If it is not, you will not be able to apply this Principle.

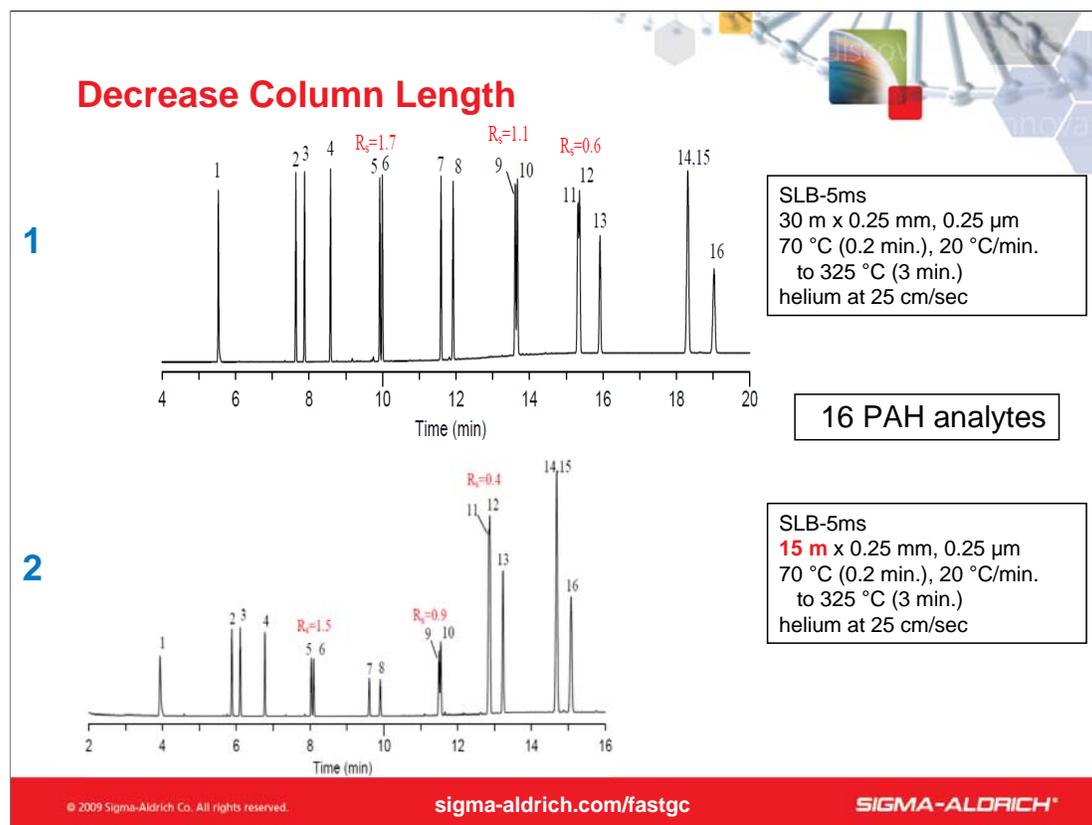


Putting it All Together

19

© 2009 Sigma-Aldrich Co. All rights reserved. sigma-aldrich.com/fastgc SIGMA-ALDRICH®

Now for the fun stuff! In this section we will put it all together, taking an application using conventional GC and observing the chromatographic changes while applying the Principles of Fast GC.



We start with Chromatogram 1, a conventional GC analysis of 16 PAH analytes on a 30 m x 0.25 mm I.D. column. The oven temperature ramp rate of 20 °C/min. was used because this is the maximum single rate that can be used over the 70 – 325 °C temperature range. The difficult separations are phenanthrene/anthracene (peaks 5/6), benzo(a)anthracene/chrysene (peaks 9/10), the isomers benzo(b)fluoranthene/benzo(k)fluoranthene (peaks 11/12), and indeno(1,2,3-cd)pyrene/dibenzo(a,h)anthracene (peaks 14/15). Resolution values for the first two pairs are 1.7 and 1.1, which is borderline acceptable. These should be baseline resolved (value of 1.2 or greater). Resolution for the isomer pair is 0.6, which is generally acceptable. Peaks 14/15 show no separation. Analysis of these analytes is usually by GC-MS where they can be resolved by mass. To achieve better resolutions, a lower initial oven temperature is required, extending the analysis time even longer than the ~19 minutes shown.

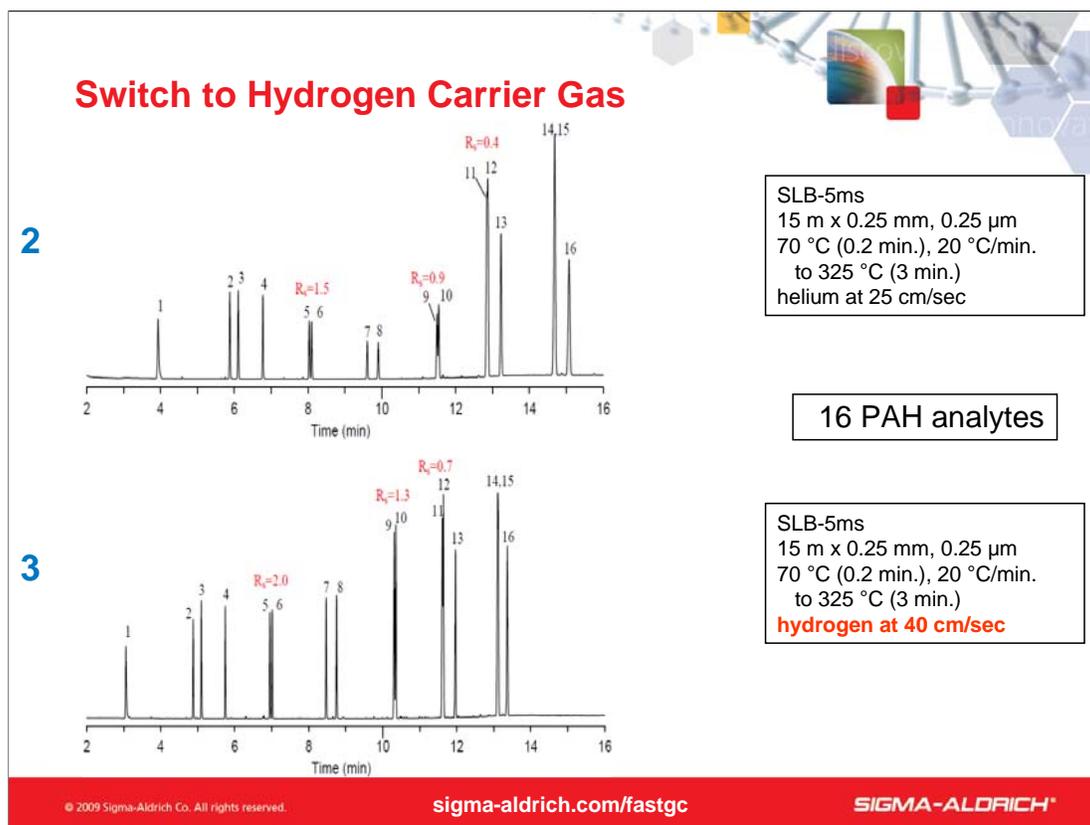
Chromatogram 2 shows the same application with a shorter column (15 m instead of 30 m). As expected, analysis time decreases (~19 minutes to ~15 minutes), and resolution values are lower (1.5, 0.9, and 0.4). This is a shorter run, but the resolution is unacceptable.

Conditions (other than those on the slide):

inj.: 250 °C
det.: FID, 325 °C
injection (0.25 mm I.D. columns): 0.5 μ L, splitless
injection (0.10 mm I.D. columns): 0.5 μ L, 100:1 split
liner: 2 mm I.D. FocusLiner with taper
sample (0.25 mm I.D. columns): 16 PAHs, each at 10 μ g/mL in methylene chloride
sample (0.10 mm I.D. columns): 16 PAHs, each at 100 μ g/mL in methylene chloride

Peak IDs:

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene
10. Chrysene
11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthene
13. Benzo(a)pyrene
14. Indeno(1,2,3-cd)pyrene
15. Dibenzo(a,h)anthracene
16. Benzo(g,h,i)perylene



Chromatogram 2 is where we ended on the previous slide, a short run with unacceptable resolution.

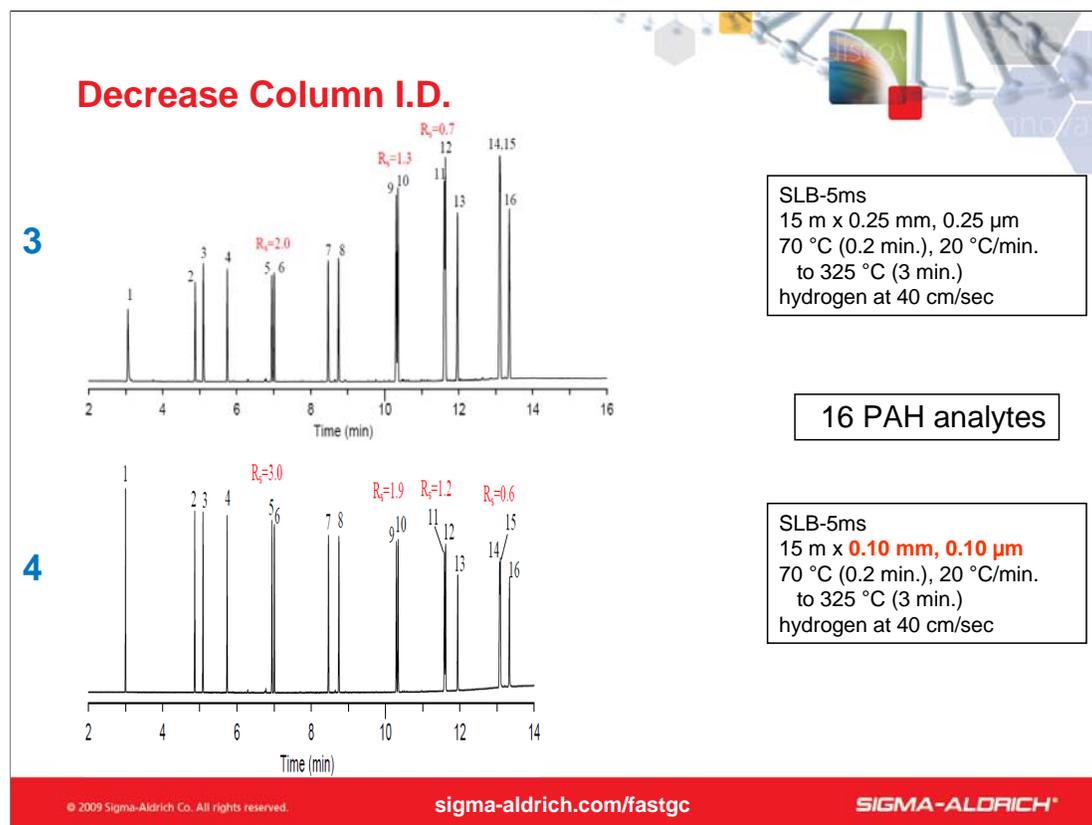
Chromatogram 3 shows what happens when we change the carrier gas (hydrogen at 40 cm/sec instead of helium at 25 cm/sec.. As expected, analysis time is even shorter (~13.5 minutes compared to ~15 minutes). Now look at the resolution values (2.0, 1.3, and 0.7). Why did they get better? Hydrogen at its optimal linear velocity for a 0.25 mm I.D. column ($u_{opt} = 40$ cm/sec) has a lower effective plate height (H_{eff}) than helium at its optimal linear velocity for a 0.25 mm I.D. column ($u_{opt} = 25$ cm/sec). We now have a shorter run with acceptable resolution. Can we do even better?

Conditions (other than those on the slide):

inj.: 250 °C
det.: FID, 325 °C
injection (0.25 mm I.D. columns): 0.5 μ L, splitless
injection (0.10 mm I.D. columns): 0.5 μ L, 100:1 split
liner: 2 mm I.D. FocusLiner with taper
sample (0.25 mm I.D. columns): 16 PAHs, each at 10 μ g/mL in methylene chloride
sample (0.10 mm I.D. columns): 16 PAHs, each at 100 μ g/mL in methylene chloride

Peak IDs:

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene
10. Chrysene
11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthene
13. Benzo(a)pyrene
14. Indeno(1,2,3-cd)pyrene
15. Dibenzo(a,h)anthracene
16. Benzo(g,h,i)perylene



Chromatogram 3 is where we ended on the previous slide, a short run with acceptable resolution.

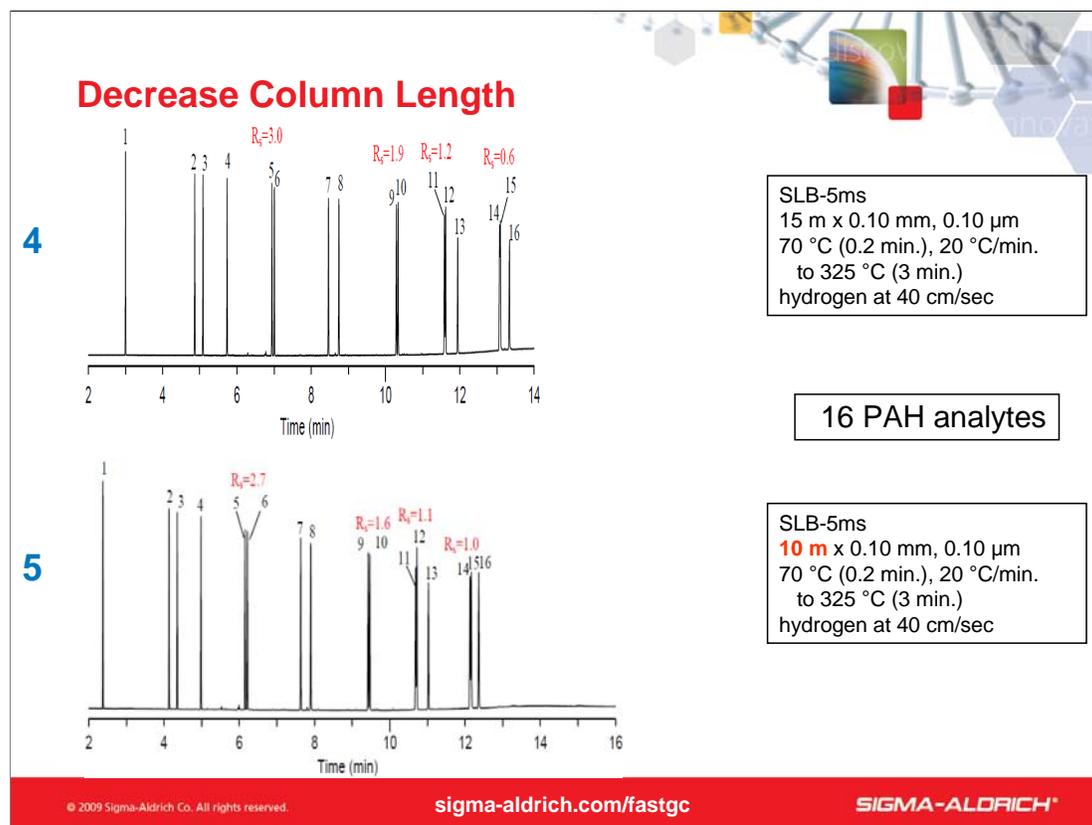
We discussed earlier that decreasing column I.D. was a way to decrease plate height (H), which increases efficiency (N) and subsequently resolution (R_s). We're scientists, so let's experiment and see what happens! Chromatogram 4 shows the same application on smaller I.D. column (0.10 mm I.D. instead of 0.25 mm I.D.). The film thickness was also lowered from 0.25 μ m to 0.10 μ m to keep the same ratio of stationary phase film to column cross-sectional area. To minimize the risk of column overload, we changed from a splitless injection to an injection with a 100:1 split. Observe that resolution increased as we theorized (3.0, 1.9, and 1.2 for the first three pairs). We even see some separation of the fourth pair (resolution of 0.6). We now have a short run with excess resolution. What should we do with it?

Conditions (other than those on the slide):

inj.: 250 °C
det.: FID, 325 °C
injection (0.25 mm I.D. columns): 0.5 μ L, splitless
injection (0.10 mm I.D. columns): 0.5 μ L, 100:1 split
liner: 2 mm I.D. FocusLiner with taper
sample (0.25 mm I.D. columns): 16 PAHs, each at 10 μ g/mL in methylene chloride
sample (0.10 mm I.D. columns): 16 PAHs, each at 100 μ g/mL in methylene chloride

Peak IDs:

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene
10. Chrysene
11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthene
13. Benzo(a)pyrene
14. Indeno(1,2,3-cd)pyrene
15. Dibenzo(a,h)anthracene
16. Benzo(g,h,i)perylene



Chromatogram 4 is where we ended on the previous slide, a short run with excess resolution.

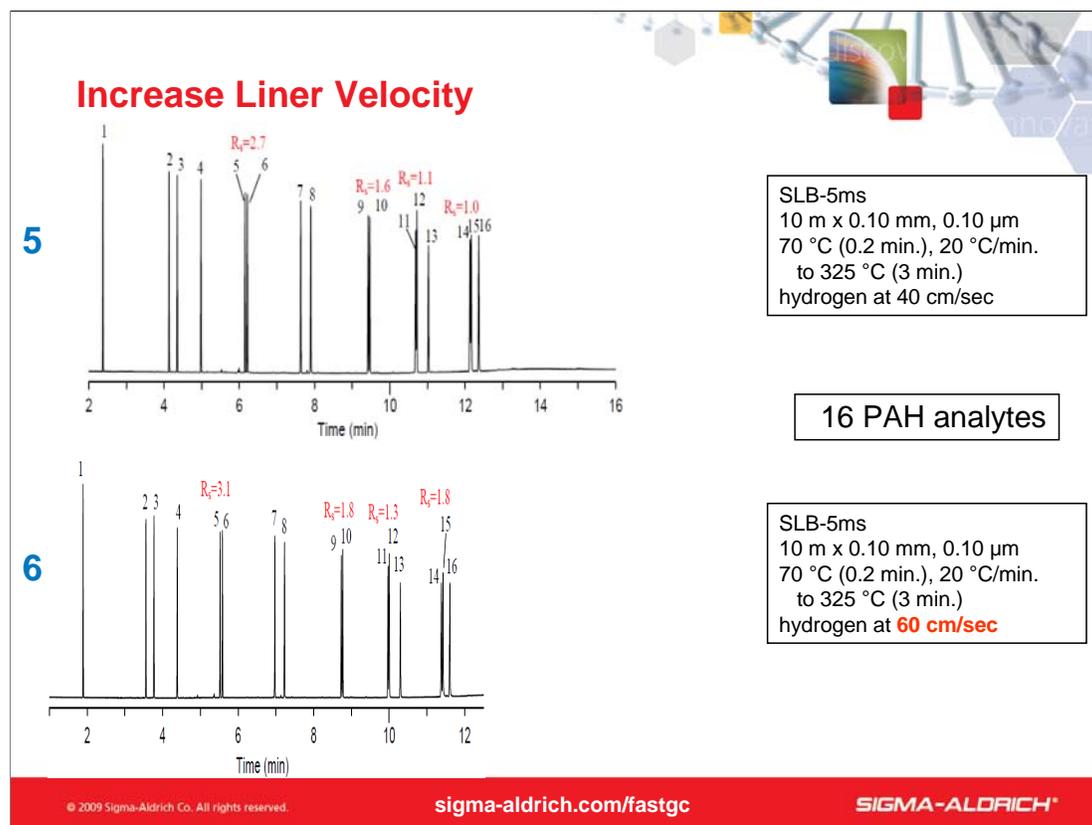
Having excess resolution is great, because it provides the opportunity to manipulate parameters to decrease retention time. We chose to decrease column length again, this time from 15 m to 10 m, resulting in Chromatogram 5. As expected, analysis time decreases (~13.5 minutes to ~12.5 minutes), and resolution values are lower (2.7, 1.6, and 1.1). Note that resolution of the fourth pair actually increased (0.6 to 1.0). How is this possible? Because this pair now elutes on the temperature ramp and not the isothermal portion of the run, resulting in sharper peak shapes. Sharper peak shapes is another way to increase resolution. We now have a shorter run, but still with excess resolution. Can we again trade some of the excess resolution for a shorter run?

Conditions (other than those on the slide):

inj.: 250 $^{\circ}$ C
 det.: FID, 325 $^{\circ}$ C
 injection (0.25 mm I.D. columns): 0.5 μ L, splitless
 injection (0.10 mm I.D. columns): 0.5 μ L, 100:1 split
 liner: 2 mm I.D. FocusLiner with taper
 sample (0.25 mm I.D. columns): 16 PAHs, each at 10 μ g/mL in methylene chloride
 sample (0.10 mm I.D. columns): 16 PAHs, each at 100 μ g/mL in methylene chloride

Peak IDs:

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene
10. Chrysene
11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthene
13. Benzo(a)pyrene
14. Indeno(1,2,3-cd)pyrene
15. Dibenzo(a,h)anthracene
16. Benzo(g,h,i)perylene



Chromatogram 5 is where we ended on the previous slide, a short run with excess resolution.

Let's look at increasing our carrier gas linear velocity as a way to trade excess resolution for a shorter run.

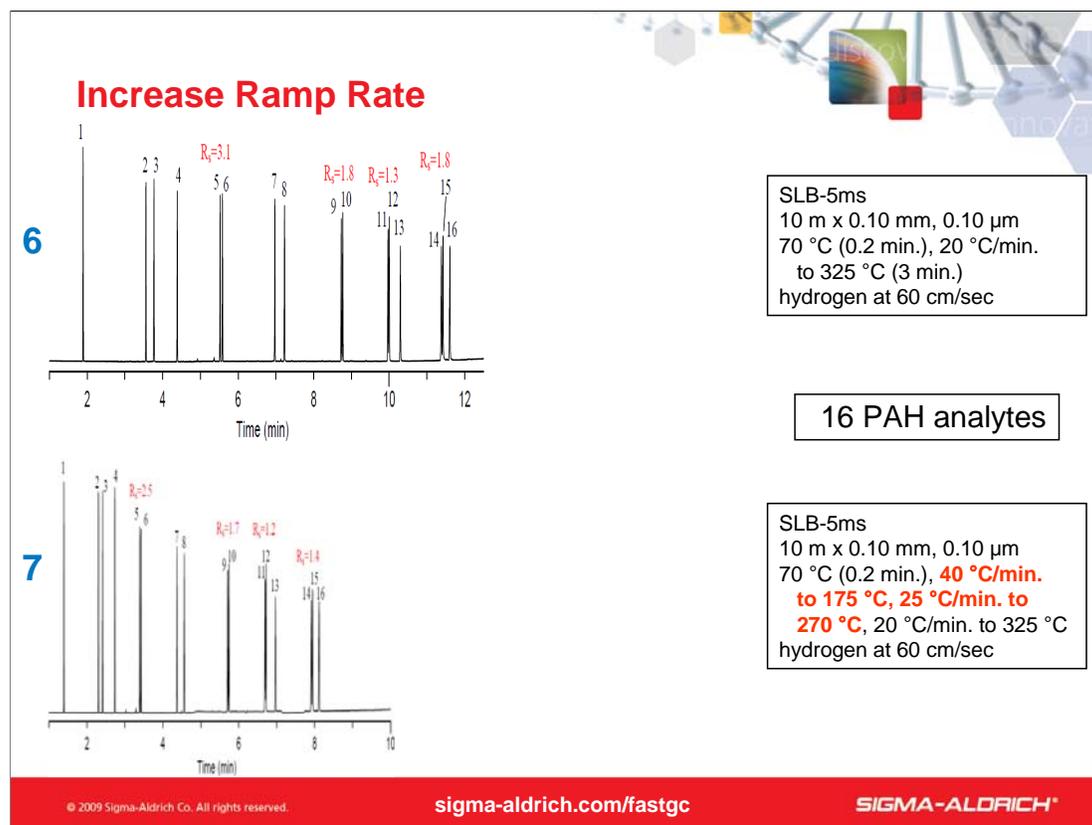
Chromatogram 6 shows the same application with the linear velocity increased from 40 cm/sec to 60 cm/sec. As expected, analysis time did decrease (from ~12.5 min. to ~11.8 min.). But, why did resolution increase (3.1, 1.8, 1.3, and 1.8)? Was this expected? Remember the Golay plots we looked at during the theoretical discussion about optimal linear velocity? We stated that as column I.D. decreases, the plots tend to move more to the right, and that while hydrogen has an optimal linear velocity (u_{opt}) of 40 cm/sec on a 0.25 mm I.D. column, it has an optimal linear velocity (u_{opt}) of 65 cm/sec on a 0.10 mm I.D. column. We now have a shorter run with tons of excess resolution. This is great! What other parameter be manipulated to take advantage of all this excess resolution?

Conditions (other than those on the slide):

inj.: 250 °C
det.: FID, 325 °C
injection (0.25 mm I.D. columns): 0.5 μ L, splitless
injection (0.10 mm I.D. columns): 0.5 μ L, 100:1 split
liner: 2 mm I.D. FocusLiner with taper
sample (0.25 mm I.D. columns): 16 PAHs, each at 10 μ g/mL in methylene chloride
sample (0.10 mm I.D. columns): 16 PAHs, each at 100 μ g/mL in methylene chloride

Peak IDs:

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene
10. Chrysene
11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthene
13. Benzo(a)pyrene
14. Indeno(1,2,3-cd)pyrene
15. Dibenzo(a,h)anthracene
16. Benzo(g,h,i)perylene



Chromatogram 6 is where we ended on the previous slide, a short run with excess resolution that we are eager to trade for an even shorter run.

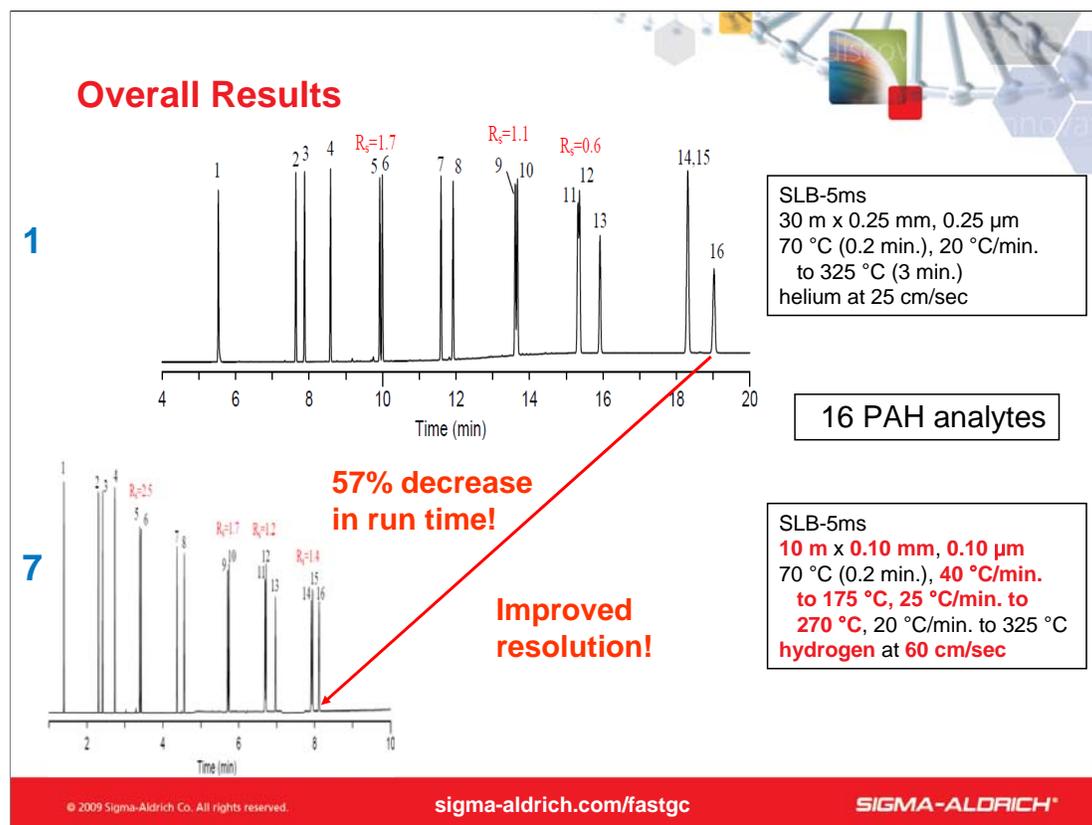
We haven't looked at oven temperature ramp rate yet. What if we pushed the oven to the highest ramp rate possible over each temperature range? After consulting our instrument manual and setting our ramp rates accordingly, we achieved Chromatogram 7. Note that 40 °C/min., 25 °C/min. and 20 °C/min. are used over different temperature ranges throughout the run. These are the maximum rates over these ranges, as found in our instrument manual. Look at the decrease in run time (from ~11.8 min. to ~8.2 min.). While resolution did decrease (2.5, 1.7, 1.2, and 1.4), all values are still acceptable. Who expected the decrease in resolution to be greater? We discussed a few slides ago that sharper peak shapes and better resolution occur if a pair elutes on the temperature ramp and not the isothermal portion of the run. Another way to obtain sharper peak shapes is with a steeper temperature ramp. So, even though the faster temperature ramp will create a decrease in resolution, its effect is minimized due to the sharper peak shapes that are produced. We now have a shorter run that still provided acceptable resolution.

Conditions (other than those on the slide):

inj.: 250 °C
det.: FID, 325 °C
injection (0.25 mm I.D. columns): 0.5 μ L, splitless
injection (0.10 mm I.D. columns): 0.5 μ L, 100:1 split
liner: 2 mm I.D. FocusLiner with taper
sample (0.25 mm I.D. columns): 16 PAHs, each at 10 μ g/mL in methylene chloride
sample (0.10 mm I.D. columns): 16 PAHs, each at 100 μ g/mL in methylene chloride

Peak IDs:

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene
10. Chrysene
11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthene
13. Benzo(a)pyrene
14. Indeno(1,2,3-cd)pyrene
15. Dibenzo(a,h)anthracene
16. Benzo(g,h,i)perylene



Let's stop and have a look at the overall results. Chromatogram 1 is where we started, a conventional GC analysis that may be considered acceptable in many laboratories. Resolution of the first two pairs are borderline acceptable (values of 1.7 and 1.1). Resolution of the isomer pair is generally considered good if the valley is half the height of the taller peak (here we have a value of 0.6). The last pair is typically measured by GC-MS because the MS can resolve by mass.

Chromatogram 7 is where we ended on the previous slide. Compared to Chromatogram 1, it is a very short run (57% decrease in run time) with improved resolution (2.5, 1.7, 1.2, and 1.4). Resolution is still in excess, so additional manipulation could be used to decrease analysis time even further. I would probably look at increasing the linear velocity again. Why?

- The optimal linear velocity for hydrogen on a 0.10 mm I.D. column is 65 cm/sec
- Hydrogen has a flat Golay plot, meaning that it can be run higher than optimal without a significant decrease in resolution

Conditions (other than those on the slide):

inj.: 250 °C
det.: FID, 325 °C
injection (0.25 mm I.D. columns): 0.5 μ L, splitless
injection (0.10 mm I.D. columns): 0.5 μ L, 100:1 split
liner: 2 mm I.D. FocusLiner with taper
sample (0.25 mm I.D. columns): 16 PAHs, each at 10 μ g/mL in methylene chloride
sample (0.10 mm I.D. columns): 16 PAHs, each at 100 μ g/mL in methylene chloride

Peak IDs:

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene
10. Chrysene
11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthene
13. Benzo(a)pyrene
14. Indeno(1,2,3-cd)pyrene
15. Dibenzo(a,h)anthracene
16. Benzo(g,h,i)perylene



Application Examples

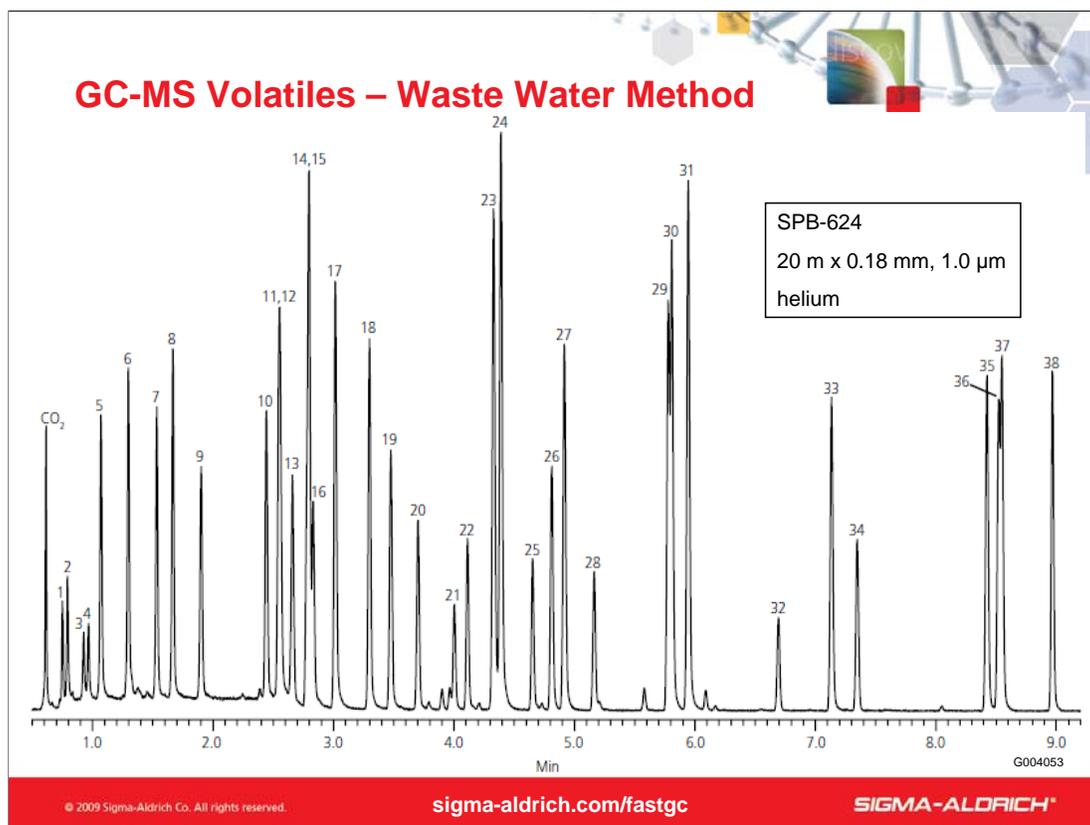
27

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

This section contains a handful of example applications across several industries. Remember, the more of the Principles of Fast GC that are applied, the greater the benefit. Due to instrumentation limitations (such as older GC-MS units), some of these chromatograms use helium and not hydrogen as the carrier gas. In these instances, the slide will contain this information.



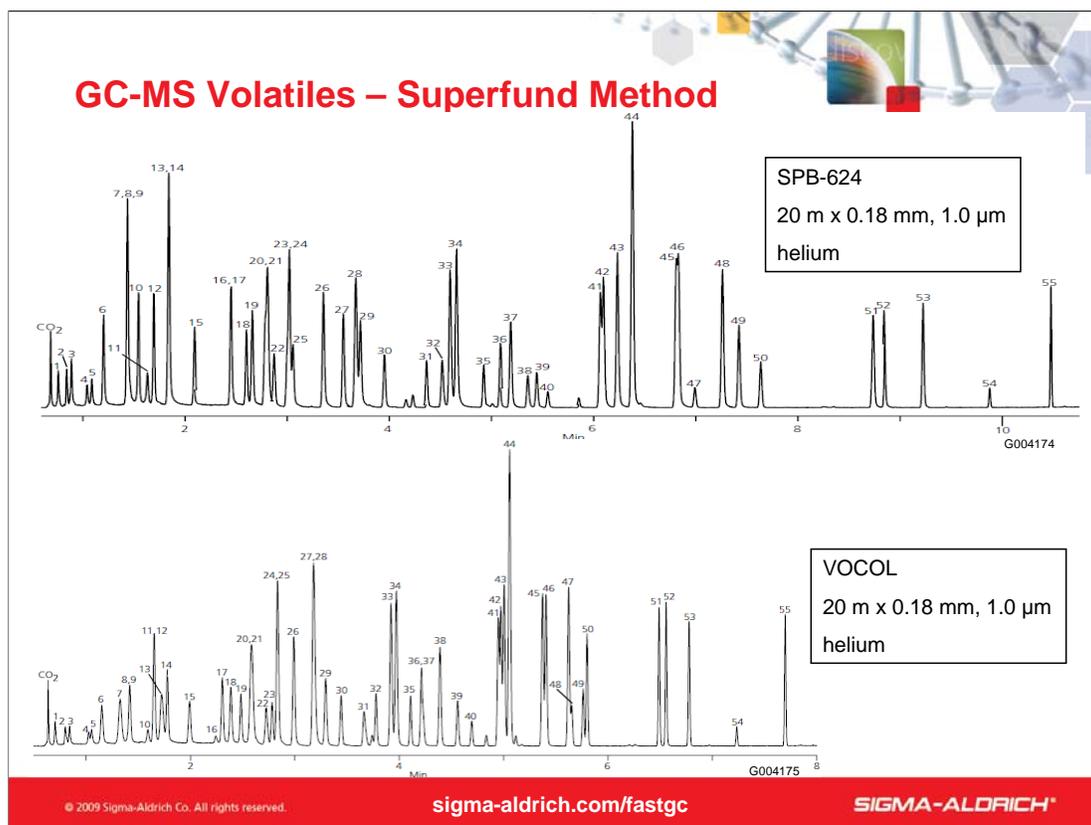
In the environmental industry, the GC-MS analysis of volatiles from drinking water, waste water, ground water, solid waste, and air samples is widely performed. The analyte lists is pretty varied; the 'light' analytes being very volatile gases and the 'heavy' analytes being dichlorobenzenes. This analysis uses helium as the carrier gas, and was used to analyze 38 analytes in ~ 9 min. Note the great peak shapes of the gases (peaks 1-5). The film thickness of 1.0 μm is necessary to retain the volatile gases. Where analytes are not resolved, the MS is used to resolve by mass.

Note:

The raised baseline at the beginning of the run is caused by water. This water is transferred to the GC column during the purge and trap step. When it elutes from the column, it reaches the MS.

Conditions:

sample/matrix: each analyte at 50 ppb in 5 mL water
 purge trap: VOCARB 3000 "K" (24940-U)
 purge: 40 mL/min. at 25 °C for 11 min.
 dry purge: 2 min.
 desorption pre-heat: 205 °C
 desorption: 150 mL/min. at 210 °C for 2 min.
 bake: 260 °C for 10 min.
 transfer line/valve temp.: 110 °C
 column: SPB-624, 20 m x 0.18 mm I.D., 1.0 μm (28662-U)
 oven: 40 °C (1 min.), 11 °C/min. to 125 °C, 35 °C/min. to 230 °C (2 min.)
 inj.: 150 °C
 MSD interface: 200 °C
 scan range: m/z = 35-400
 carrier gas: helium, 1.5 mL/min.
 injection: 100:1 split
 liner: 0.75 mm I.D. SPME



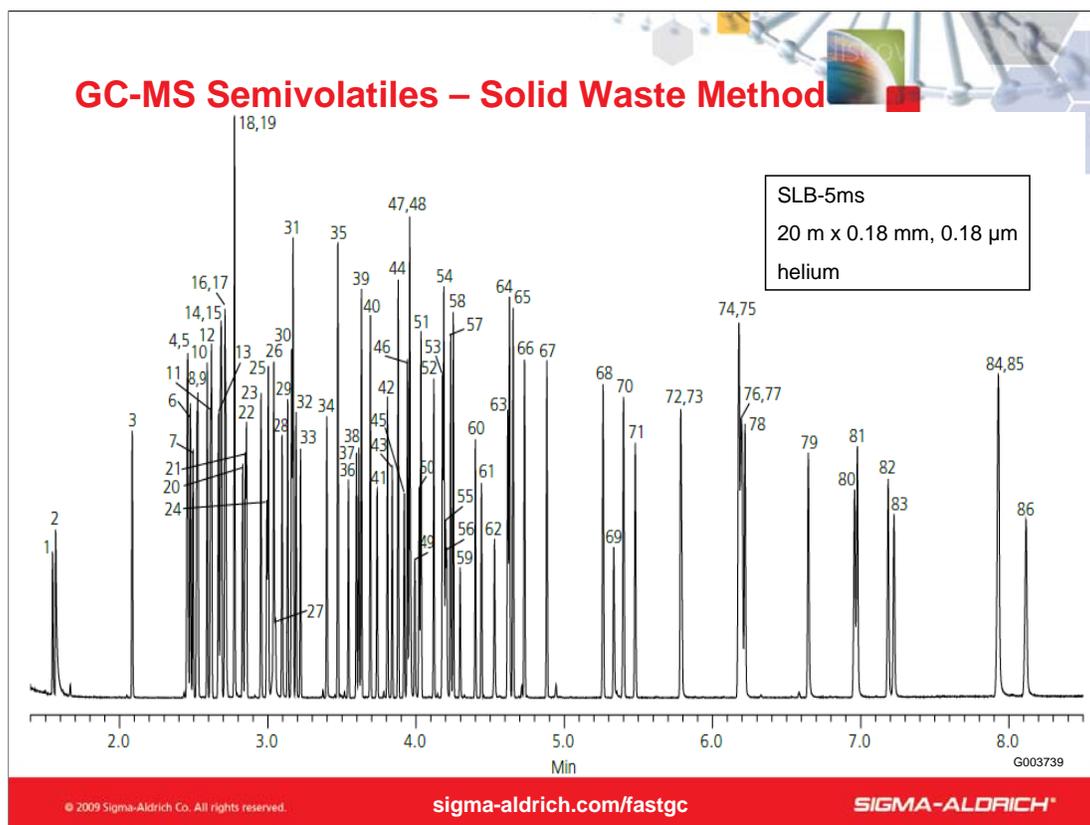
Another environmental GC-MS volatile application is for samples that originate from Superfund hazardous waste sites. This application requires a different, longer analyte list. Here, two columns with different selectivity are shown. In addition to the Principles of Fast GC, changing column selection may allow a shorter analysis time. The SPB-624 was used to analyze 55 analytes in ~10.8 min., whereas the VOCOL was able to analyze the same 55 analytes in ~7.8 min.

Conditions (top chromatogram):

sample/matrix: each analyte at 50 ppb in 5 mL water
 purge trap: VOCARB 3000 "K" (24940-U)
 purge: 40 mL/min. at 25 °C for 11 min.
 dry purge: 2 min.
 desorption pre-heat: 205 °C
 desorption: 124 mL/min. at 210 °C for 2 min.
 bake: 260 °C for 10 min.
 transfer line/valve temp.: 110 °C
 column: SPB-624, 20 m x 0.18 mm I.D., 1.0 μ m (28662-U)
 oven: 40 °C (1 min.), 11 °C/min. to 125 °C, 35 °C/min. to 230 °C (2 min.)
 inj.: 150 °C
 MSD interface: 200 °C
 scan range: m/z = 35-400
 carrier gas: helium, 1.2 mL/min.
 injection: 100:1 split
 liner: 0.75 mm I.D. SPME

Conditions (bottom chromatogram):

sample/matrix: each analyte at 50 ppb in 5 mL water
 purge trap: VOCARB 3000 "K" (24940-U)
 purge: 40 mL/min. at 25 °C for 11 min.
 dry purge: 2 min.
 desorption pre-heat: 205 °C
 desorption: 150 mL/min. at 210 °C for 2 min.
 bake: 260 °C for 10 min.
 transfer line/valve temp.: 110 °C
 column: VOCOL, 20 m x 0.18 mm I.D., 1.0 μ m (28463-U)
 oven: 40 °C (0.8 min.), 19 °C/min. to 125 °C, 32 °C/min. to 220 °C (1 min.)
 inj.: 150 °C
 MSD interface: 200 °C
 scan range: m/z = 35-400
 carrier gas: helium, 1.4 mL/min.
 injection: 100:1 split
 liner: 0.75 mm I.D. SPME



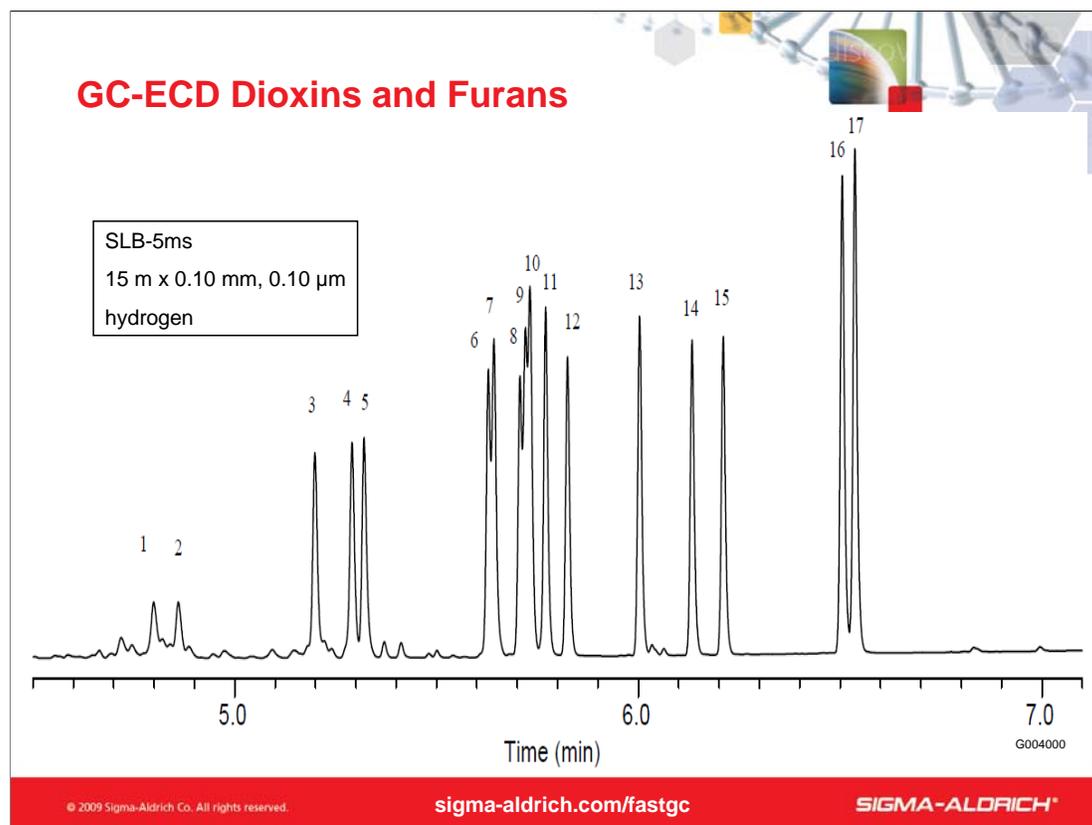
Another common GC-MS application in the environmental industry is the analysis of semivolatile analytes, ranging from N-nitrosodimethylamine and pyridine to the multi-ringed PAHs, such as benzo(g,h,i)perylene. Even with helium as the carrier gas, the other Principles of Fast GC were used to produce a chromatogram with 86 analytes in ~8.2 min. Very impressive!

Note:

The decreasing baseline at the beginning of the chromatogram is the tail end of the methylene chloride solvent peak.

Conditions:

- column: SLB-5ms, 20 m x 0.18 mm I.D., 0.18 μ m (28564-U)
- oven: 40 °C (0.7 min.), 55 °C/min. to 240 °C, 28 °C/min. to 330 °C (2 min.)
- inj.: 250 °C
- MSD interface: 330 °C
- scan range: m/z 40-450
- carrier gas: helium, 40 cm/sec, constant
- injection: 0.5 μ L, 10:1 split
- liner: 2 mm I.D., fast FocusLiner™ inlet liner with taper (2879501-U)
- sample: 80 component semivolatile standard at 50 ppm plus 6 internal standards (at 40 ppm) in methylene chloride



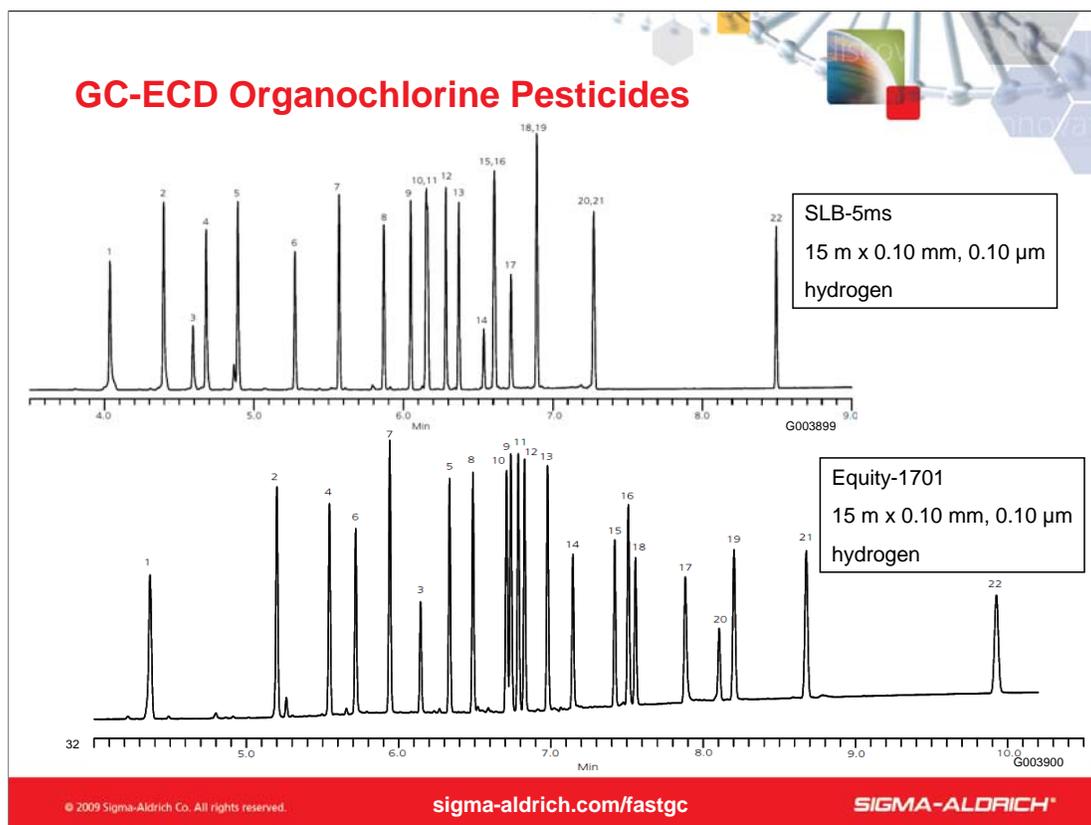
GC-ECD is often used in the environmental industry to screen for the presence of dioxins and furans that have chlorine substitution in the 2, 3, 7, and 8 positions. If detected, the sample extract is then analyzed using high resolution mass spectrometry to verify identifications and perform quantitative measurements. Here, Fast GC was used to shorten the time required for the screening portion of the application to ~6.5 min.

Conditions:

column: SLB-5ms, 15 m x 0.10 mm I.D., 0.10 μ m (28466-U)
oven: 150 °C (1 min.), 35 °C/min. to 340 °C (1 min.)
inj.: 250 °C
det.: ECD, 340 °C
carrier gas: hydrogen, 45 cm/sec, constant
injection: 1 μ L, splitless (1 min.)
liner: 4 mm I.D., single taper
sample: 17 component 2,3,7,8-substituted dioxin standard, 100-500 ppb in n-nonane

Peak IDs:

1. 2,3,7,8-TCDF, 100 ppb
2. 2,3,7,8-TCDD, 100 ppb
3. 1,2,3,7,8-PCDF, 250 ppb
4. 2,3,4,7,8-PCDF, 250 ppb
5. 1,2,3,7,8-PCDD, 250 ppb
6. 1,2,3,4,7,8-HxCDF, 500 ppb
7. 1,2,3,6,7,8-HxCDF, 500 ppb
8. 2,3,4,6,7,8-HxCDF, 250 ppb
9. 1,2,3,4,7,8-HxCDD, 500 ppb
10. 1,2,3,6,7,8-HxCDD, 500 ppb
11. 1,2,3,7,8,9-HxCDD, 250 ppb
12. 1,2,3,7,8,9-HxCDF, 250 ppb
13. 1,2,3,4,6,7,8-HpCDF, 250 ppb
14. 1,2,3,4,6,7,8-HpCDD, 250 ppb
15. 1,2,3,4,7,8,9-HpCDF, 250 ppb
16. OCDD, 500 ppb
17. OCDF, 500 ppb



The analysis of 20 chlorinated pesticides and 2 surrogate compounds by GC-ECD is another application routinely performed in the environmental industry. It is common to analyze each sample extract on two columns with differing selectivity for confirmation of identifications. Here are Fast GC chromatograms showing this application on two different columns, an SLB-5ms and an Equity-1701. Run times of ~8.5 min. and 10 min. were achieved.

Conditions (top chromatogram):

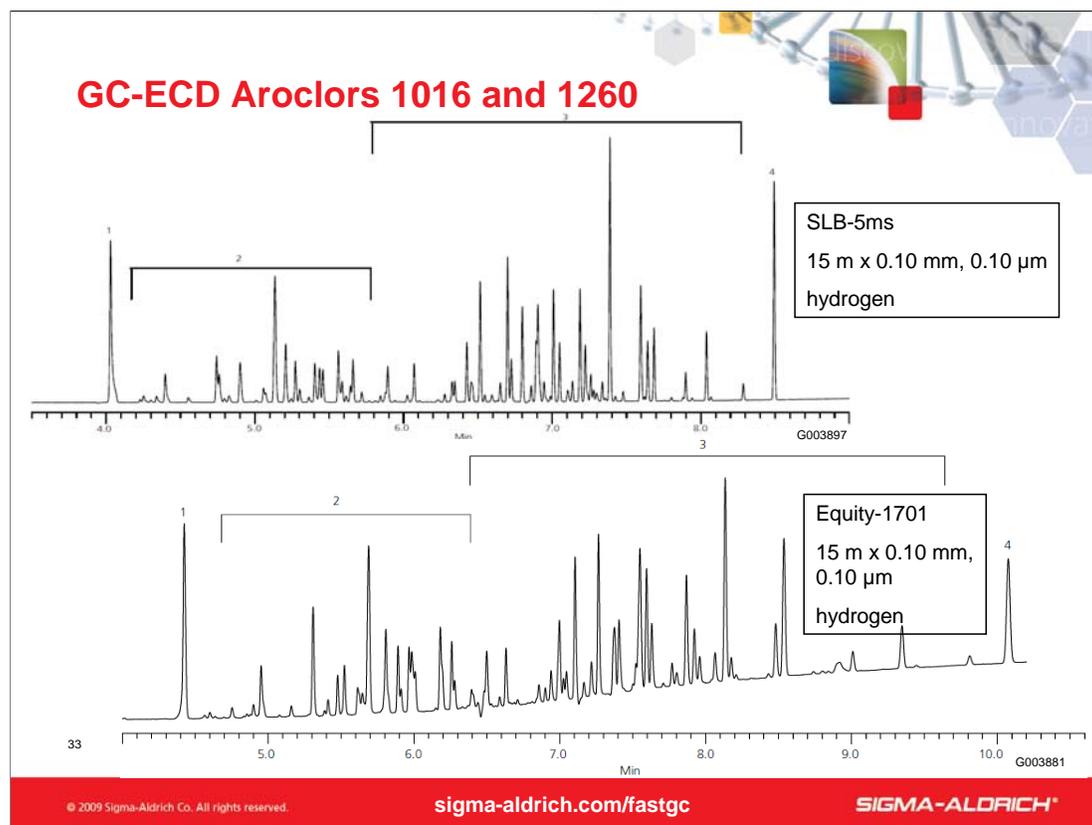
column: SLB-5ms, 15 m x 0.10 mm I.D., 0.10 µm (28466-U)
 oven: 100 °C, 25 °C/min. to 325 °C
 inj.: 225 °C
 det.: ECD, 300 °C
 carrier gas: hydrogen, 40 cm/sec constant
 injection: 2 µL, splitless (0.75 min.)
 liner: 4 mm I.D., single taper
 sample: 50 ppb of a 22 component chlorinated pesticide standard in n-hexane

Conditions (bottom chromatogram):

column: Equity-1701, 15 m x 0.10 mm I.D., 0.10 µm (28343-U)
 oven: 100 °C, 25 °C/min. to 280 °C
 inj.: 225 °C
 det.: ECD, 300 °C
 carrier gas: hydrogen, 40 cm/sec constant
 injection: 2 µL, splitless (0.75 min.)
 liner: 4 mm I.D., single taper
 sample: 50 ppb of a 22 component chlorinated pesticide standard in n-hexane

Peak IDs:

1. Tetrachloro-m-xylene (surr.)
2. α-BHC
3. β-BHC
4. γ-BHC
5. δ-BHC
6. Heptachlor
7. Aldrin
8. Heptachlor epoxide
9. γ-Chlordane
10. Endosulfan I
11. α-Chlordane
12. 4,4'-DDE
13. Dieldrin
14. Endrin
15. 4,4'-DDD
16. Endosulfan II
17. Endrin aldehyde
18. 4,4'-DDT
19. Endosulfan sulfate
20. Methoxychlor
21. Endrin ketone
22. Decachlorobiphenyl (surr.)



Polychlorinated biphenyls (PCBs) are typically analyzed in the environmental industry using pattern recognition to Aroclor mix standards. Similar to the organochlorine pesticide application, each sample extract is typically analyzed on two columns with differing selectivity for confirmation of identification. Analysis times of ~8.5 min. and ~10.2 min. were achieved on an SLB-5ms and an Equity-1701 column by applying the Principles of Fast GC.

Conditions (top chromatogram):

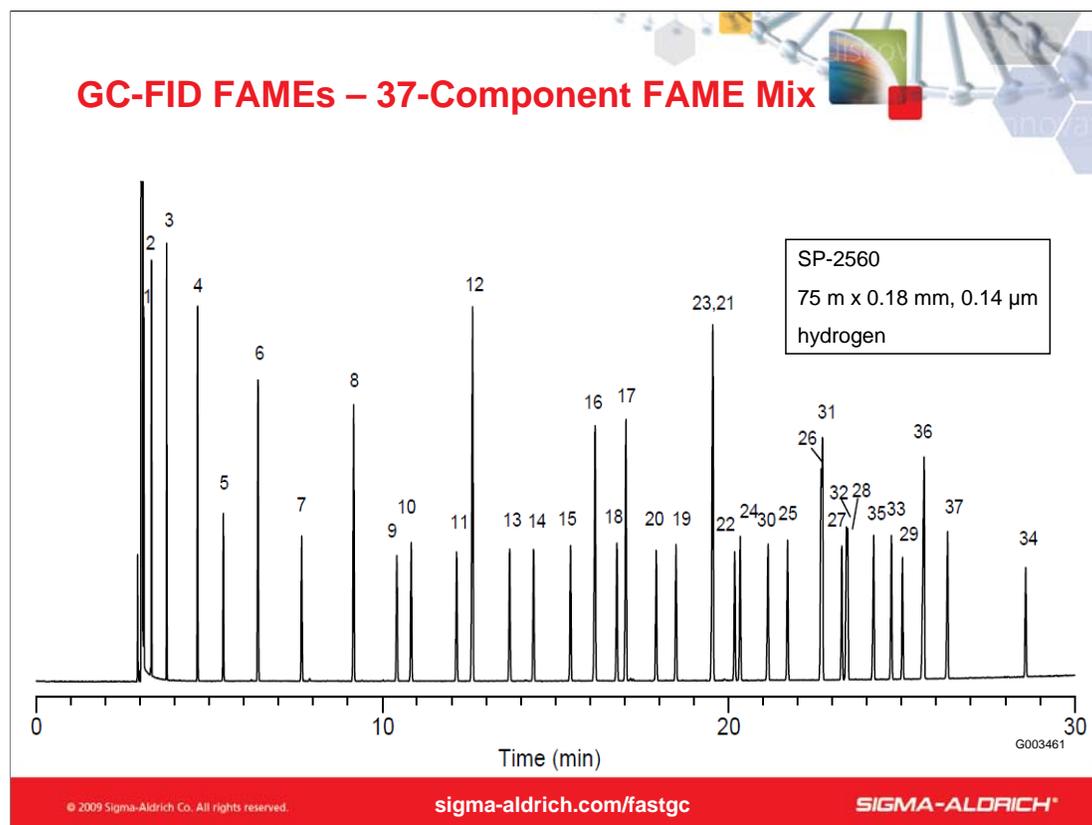
column: SLB-5ms, 15 m x 0.10 mm I.D., 0.10 μ m (28466-U)
oven: 80 °C (0.5 min.), 50 °C/min. to 200 °C, 35 °C/min. to 360 °C (2 min.)
inj.: 225 °C
det.: ECD, 360 °C
carrier gas: hydrogen, 40 cm/sec constant
injection: 2 μ L, splitless (0.75 min.)
liner: 4 mm I.D., single taper
sample: Aroclor standard mix 1 (46846-U) diluted to 500 ppb / 50 ppb (Aroclors / surrogates) in n-hexane

Conditions (bottom chromatogram):

column: Equity-1701, 15 m x 0.10 mm I.D., 0.10 μ m (28343-U)
oven: 90 °C, 35 °C/min. to 280 °C (3 min.)
inj.: 250 °C
det.: ECD, 280 °C
carrier gas: hydrogen, 50 cm/sec constant
injection: 2 μ L, splitless (0.75 min.)
liner: 4 mm I.D., single taper
sample: Aroclor standard mix 1 (46846-U) diluted to 200 ppb / 20 ppb (Aroclors / surrogates) in n-hexane

Peak IDs:

1. Tetrachloro-m-xylene (surr.)
2. Aroclor 1016
3. Aroclor 1260
4. Decachlorobiphenyl (surr.)



Most people would not consider a 75 m long column to be short. It is in the food & beverage industry for analysts performing fatty acid methyl ester (FAME) applications. The conventional GC column required to perform these separations has a 100 m x 0.25 mm I.D. dimension, and requires over 40 min. to elute the last peak. Here, a 75 m x 0.18 mm I.D. SP-2560 column plus other Fast GC Principles were applied to reduce the analysis time to ~29 min., without any sacrifice in resolution.

Conditions:

column: SP-2560, 75 m x 0.18 mm I.D., 0.14 μ m (23348-U)

oven: 140 °C (5 min.), 4 °C/min. to 240 °C (2 min.)

inj.: 250 °C

det.: FID, 250 °C

carrier gas: hydrogen, 40 cm/sec @ 175 °C

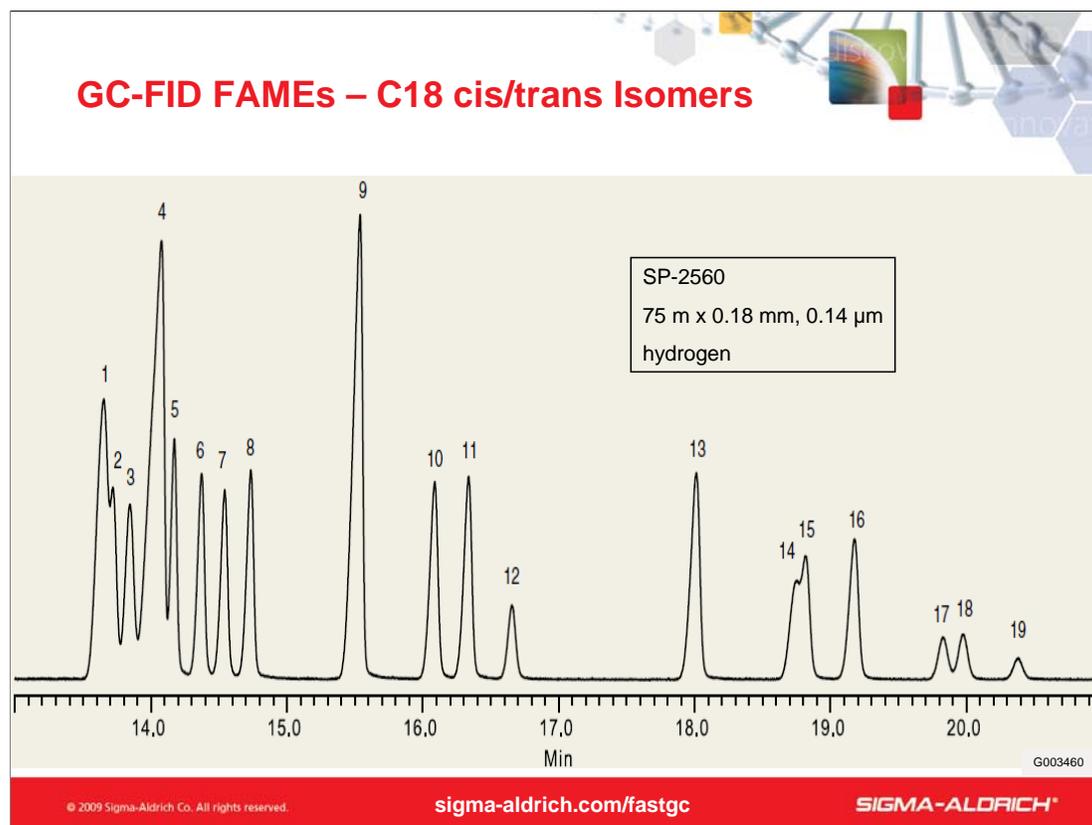
injection: 1 μ L, 100:1 split

liner: 4 mm I.D. split, cup design

sample: Supelco 37-Component FAME Mix (47885-U), analytes at concentrations indicated in methylene chloride

Peak IDs:

1. Butyric Acid Methyl Ester (C4:0) at 4 wt %
2. Caproic Acid Methyl Ester (C6:0) at 4 wt %
3. Caprylic Acid Methyl Ester (C8:0) at 4 wt %
4. Capric Acid Methyl Ester (C10:0) at 4 wt %
5. Undecanoic Acid Methyl Ester (C11:0) at 2 wt %
6. Lauric Acid Methyl Ester (C12:0) at 4 wt %
7. Tridecanoic Acid Methyl Ester (C13:0) at 2 wt %
8. Myristic Acid Methyl Ester (C14:0) at 4 wt %
9. Myristoleic Acid Methyl Ester (C14:1) at 2 wt %
10. Pentadecanoic Acid Methyl Ester (C15:0) at 2 wt %
11. cis-10-Pentadecenoic Acid Methyl Ester (C15:1) at 2 wt %
12. Palmitic Acid Methyl Ester (C16:0) at 6 wt %
13. Palmitoleic Acid Methyl Ester (C16:1) at 2 wt %
14. Heptadecanoic Acid Methyl Ester (C17:0) at 2 wt %
15. cis-10-Heptadecenoic Acid Methyl Ester (C17:1) at 2 wt %
16. Stearic Acid Methyl Ester (C18:0) at 4 wt %
17. Oleic Acid Methyl Ester (C18:1n9c) at 4 wt %
18. Elaidic Acid Methyl Ester (C18:1n9t) at 2 wt %
19. Linoleic Acid Methyl Ester (C18:2n6c) at 2 wt %
20. Linolelaidic Acid Methyl Ester (C18:2n6t) at 2 wt %
21. γ -Linolenic Acid Methyl Ester (C18:3n6) at 2 wt %
22. α -Linolenic Acid Methyl Ester (C18:3n3) at 2 wt %
23. Arachidic Acid Methyl Ester (C20:0) at 4 wt %
24. cis-11-Eicosenoic Acid Methyl Ester (C20:1n9) at 2 wt %
25. cis-11,14-Eicosadienoic Acid Methyl Ester (C20:2) at 2 wt %
26. cis-8,11,14-Eicosatrienoic Acid Methyl Ester (C20:3n6) at 2 wt %
27. cis-11,14,17-Eicosatrienoic Acid Methyl Ester (C20:3n3) at 2 wt %
28. Arachidonic Acid Methyl Ester (C20:4n6) at 2 wt %
29. cis-5,8,11,14,17-Eicosapentaenoic Acid Methyl Ester (C20:5n3) at 2 wt %
30. Heneicosanoic Acid Methyl Ester (C21:0) at 2 wt %
31. Behenic Acid Methyl Ester (C22:0) at 4 wt %
32. Erucic Acid Methyl Ester (C22:1n9) at 2 wt %
33. cis-13,16-Docosadienoic Acid Methyl Ester (C22:2) at 2 wt %
34. cis-4,7,10,13,16,19-Docosahexaenoic Acid Methyl Ester (C22:6n3) at 2 wt %
35. Tricosanoic Acid Methyl Ester (C23:0) at 2 wt %
36. Lignoceric Acid Methyl Ester (C24:0) at 4 wt %
37. Nervonic Acid Methyl Ester (C24:1n9) at 2 wt %



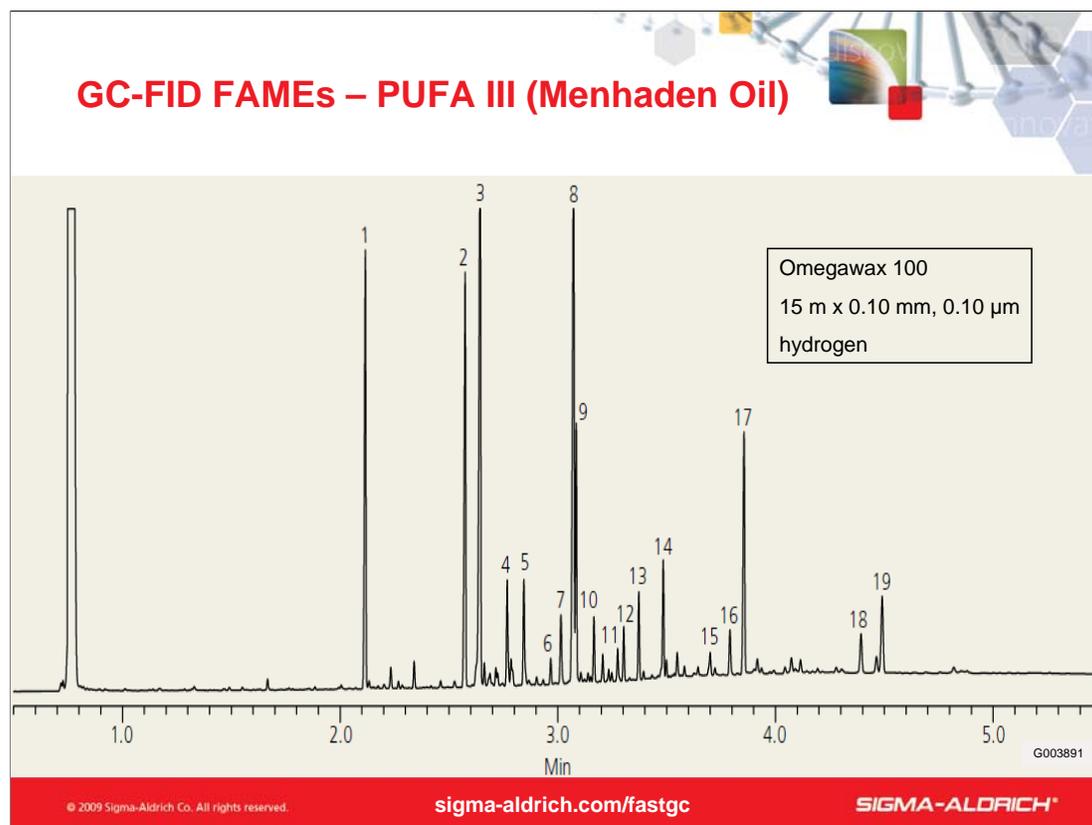
The cis/trans FAME isomers are difficult to separate because they are chemically alike, requiring long columns with highly polar stationary phases, such as the SP-2560. For nutritional purposes, the food & beverage industry needs to identify the type and amount of trans fats. Recent laws governing the information on food labels has increased the number of samples that must be processed. Here, the detailed analysis of the C18 cis/trans FAME isomers was accomplished in ~20.5 min. by applying the Principles of Fast GC.

Conditions:

column: SP-2560, 75 m x 0.18 mm I.D., 0.14 μm (23348-U)
 oven: 180 °C
 inj.: 220 °C
 det.: FID, 220 °C
 carrier gas: hydrogen, 25 cm/sec @ 180 °C
 injection: 0.5 μL , 100:1 split
 liner: 4 mm I.D., split, cup design
 sample: Mixture of C18:1, C18:2, and C18:3 FAMES in methylene chloride

Peak IDs:

1. C18:1 Δ 7t and C18:1 Δ 6t
2. C18:1 Δ 9t
3. C18:1 Δ 11t
4. C18:1 Δ 12t, C18:1 Δ 6c, C18:1 Δ 7c and C18:1 Δ 13t
5. C18:1 Δ 9c
6. C18:1 Δ 11c
7. C18:1 Δ 12c
8. C18:1 Δ 13c
9. C18:2 Δ 9t, 12t
10. C18:2 Δ 9c, 12t
11. C18:2 Δ 9t, 12c
12. C18:2 Δ 9c, 12c
13. C18:3 Δ 9t, 12t, 15t
14. C18:3 Δ 9t, 12t, 15c
15. C18:3 Δ 9t, 12c, 15t
16. C18:3 Δ 9c, 12t, 15t and C18:3 Δ 9c, 12c, 15t
17. C18:3 Δ 9c, 12t, 15c
18. C18:3 Δ 9t, 12c, 15c
19. C18:3 Δ 9c, 12c, 15c



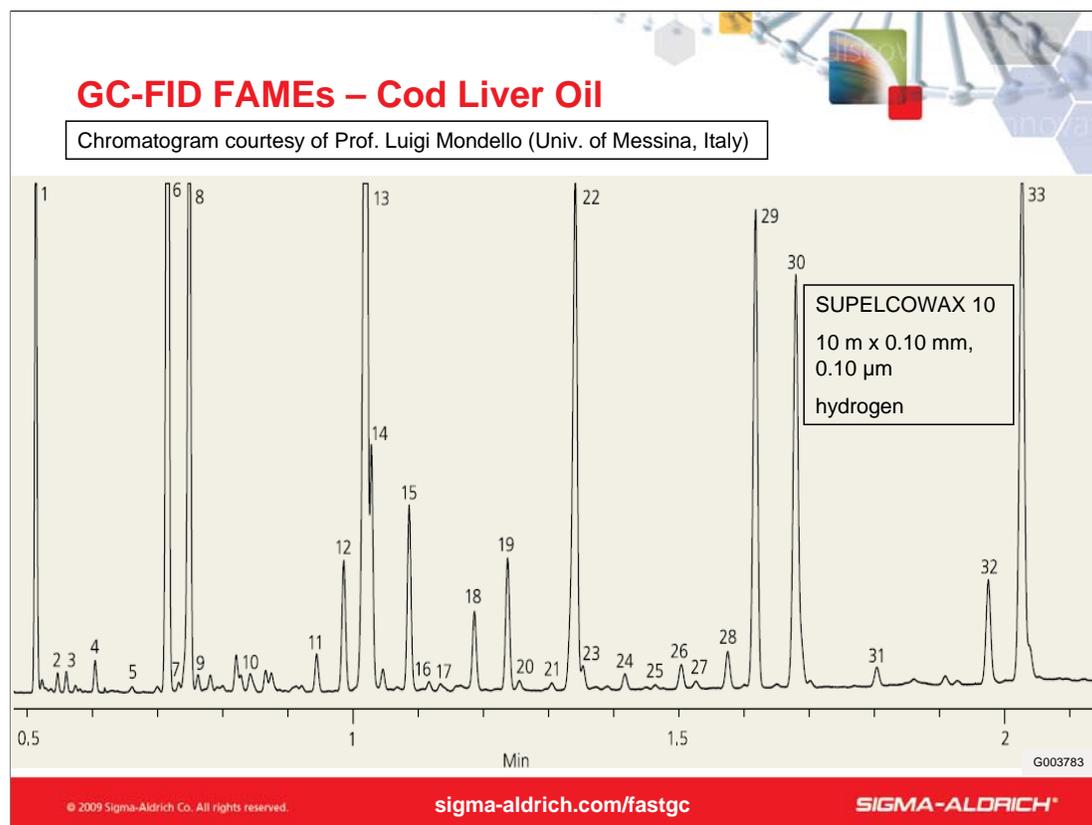
The food & beverage industry must also be concerned with measuring saturated fat content versus monounsaturated and polyunsaturated fat content for nutritional purposes. Here, the short analysis (~4.5 min.) of a polyunsaturated fatty acid (PUFA) mix was accomplished using Fast GC and an Omegawax 100 column.

Conditions:

column: Omegawax 100, 15 m x 0.10 mm I.D., 0.10 µm (23399-U)
 oven: 140 °C, 40 °C/min. to 280 °C (2 min.)
 inj.: 250 °C
 det.: FID, 280 °C
 carrier gas: hydrogen, 50 cm/sec constant
 injection: 0.2 µL, 200:1 split
 liner: 4 mm I.D., split, cup design
 sample: PUFA No. III – Menhaden Oil (47085-U), diluted to 50 mg/mL in methylene chloride

Peak IDs:

1. C14:0
2. C16:0
3. C16:1n7
4. C16:2n4
5. C16:3n4
6. C16:4n1
7. C18:0
8. C18:1n9
9. C18:1n7
10. C18:2n6
11. C18:3n4
12. C18:3n3
13. C18:4n3
14. C20:1n9
15. C20:4n6
16. C20:4n3
17. C20:5n3
18. C22:5n3
19. C22:6n3



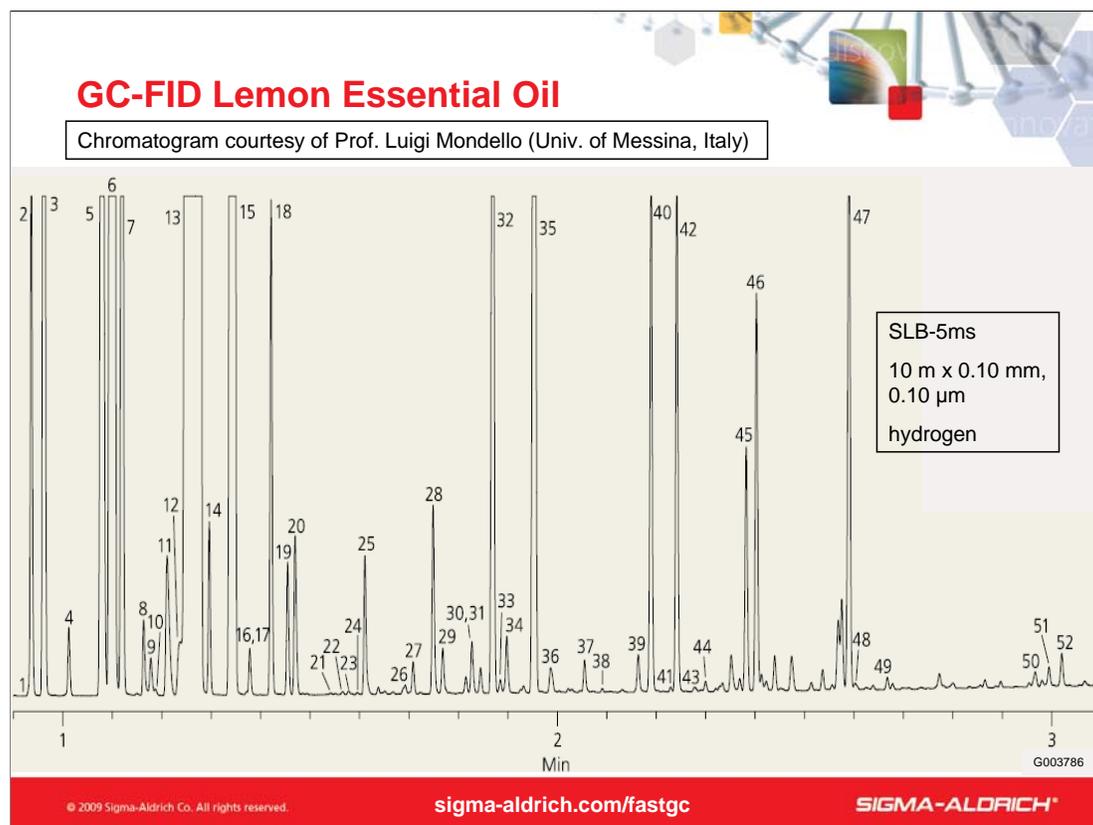
The health benefits of omega 3 and omega 6 fats are well-publicized. Because the human body cannot produce these, they must be obtained through our diet. Data suggests that the omega 3 group provides the greater health benefit. Fish oils tend to be high in omega 3 fat content. The monitoring of the omega 3 and omega 6 amounts and ratios in many foods is routinely performed in the food & beverage industry. This application, provided courtesy of Prof. Luigi Mondello at the University of Messina, Italy, shows the Fast GC analysis of the FAMES in a cod liver oil sample. A short 10 m x 0.10 mm I.D. SUPELCOWAX 10 column, rapid oven heating, and a high hydrogen linear velocity was used to complete the analysis in ~2.1 in.

Conditions:

column: SUPELCOWAX 10, 10 m x 0.10 mm I.D., 0.10 µm (25026-U)
 oven: 180 °C , 40 °C/min. to 270 °C (0.5 min.)
 inj.: 280 °C
 det.: FID, 280 °C
 carrier gas: hydrogen, 100 cm/sec constant
 injection: 0.2 µL, 200:1 split
 sample: cod liver oil FAMES in hexane

Peak IDs:

1. C14:0
2. C15:0 anteiso
3. C15:0 iso
4. C15:0
5. C16:0 iso
6. C16:0
7. C16:1ω9
8. C16:1ω7
9. C16:1ω5
10. C16:3ω4
11. C16:4ω4
12. C18:0
13. C18:1ω9
14. C18:1ω7
15. C18:2ω6
16. C18:2ω4
17. C18:3ω6
18. C18:3ω3
19. C18:4ω3
20. C18:4ω1
21. C20:0
22. C20:1ω9
23. C20:1ω7
24. C20:2ω6
25. C20:3ω6
26. C20:4ω6
27. C20:3ω3
28. C20:4ω3
29. C20:5ω3
30. C22:1ω9
31. C21:5ω3
32. C22:5ω3
33. C22:6ω3



The flavor & fragrance industry needs to test raw materials to ensure purity, and to monitor finished goods to detect any adulteration with less expensive products. Here, the Fast GC analysis of a lemon essential oil sample was accomplished in ~3 min. on an SLB-5ms column.

Conditions:

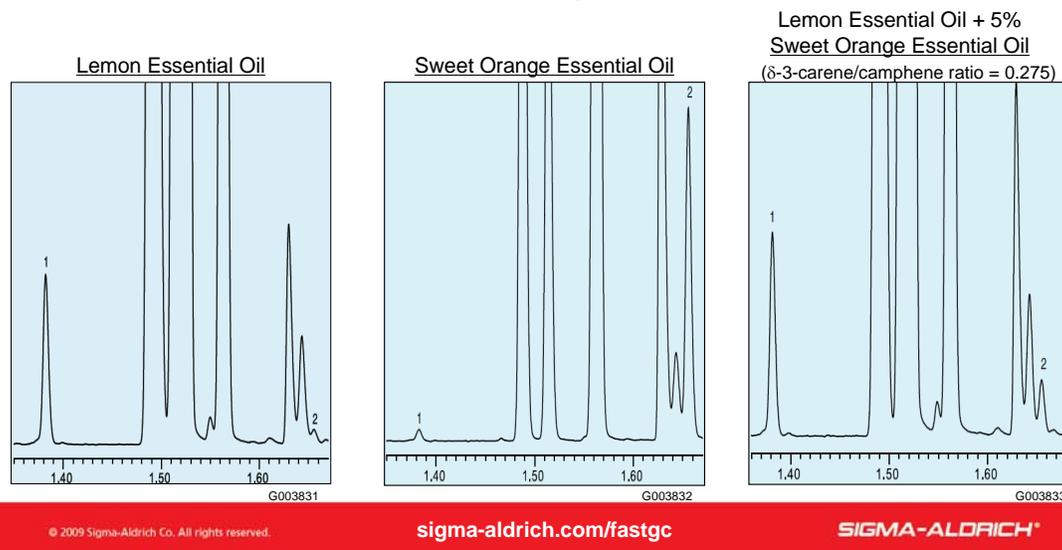
column: SLB-5ms, 10 m x 0.10 mm I.D., 0.10 µm (28465-U)
oven: 40 °C, 50 °C/min. to 320 °C
inj.: 320 °C
det.: FID, 320 °C
carrier gas: hydrogen, 81.5 cm/sec constant
injection: 0.4 µL, 300:1 split
sample: lemon essential oil in hexane

GC-FID Adulterated Lemon Essential Oil

Chromatograms courtesy of Prof. Luigi Mondello (Univ. of Messina, Italy)

The ratio of δ -3-carene/camphene cannot exceed 0.140 for a lemon essential oil to be considered pure

SLB-5ms
10 m x 0.10 mm,
0.10 μ m
hydrogen



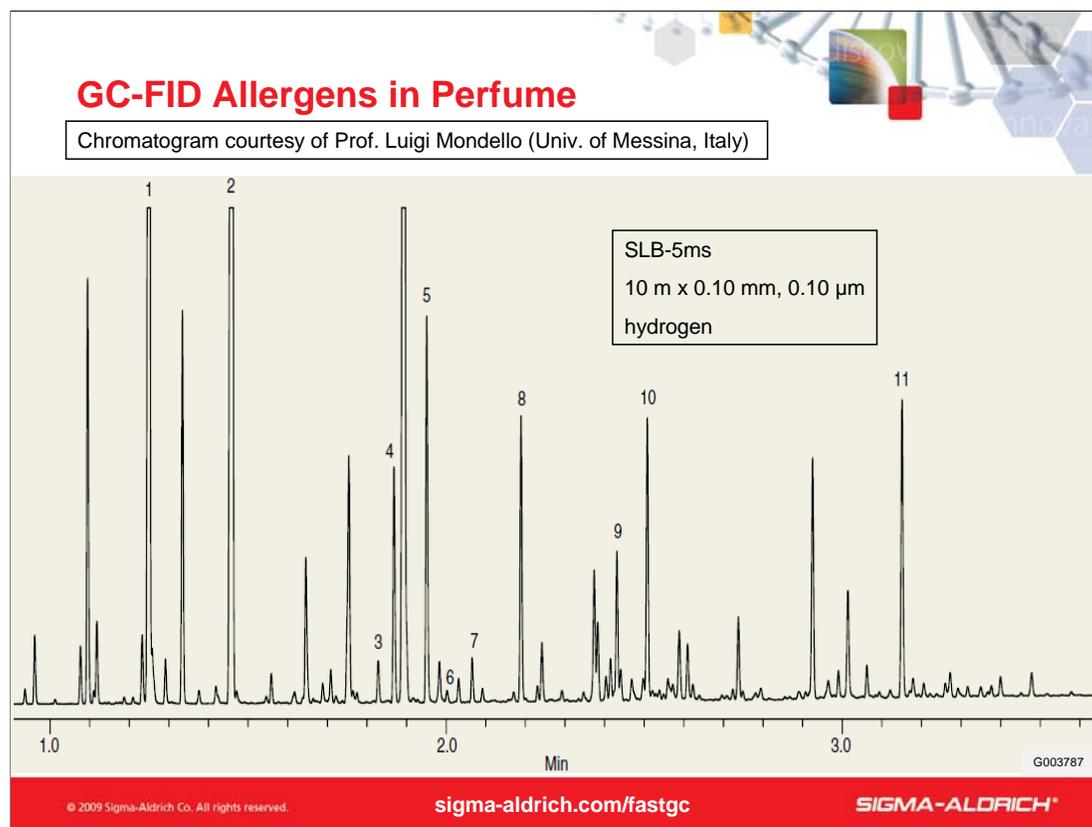
Here is an example of a product adulteration that the flavor & fragrance industry looks for. A less expensive citrus essential oil (such as sweet orange essential oil) is mixed with a more expensive citrus essential oil (such as lemon essential oil) to increase the perceived volume of the more expensive citrus essential oil. Smell and taste alone may not be adequate to detect this adulteration. GC can be used by determining the ratios of two compounds, δ -3-carene/camphene. The ratio of δ -3-carene/camphene cannot exceed 0.140 for a lemon essential oil to be considered pure. In these chromatograms provided by Prof. Mondello, the Fast GC analyses of pure and adulterated products are shown on an SLB-5ms column.

Conditions:

column: SLB-5ms, 10 m x 0.10 mm I.D., 0.10 μ m (28465-U)
oven: 40 °C, 30 °C/min. to 85 °C, 80 °C/min. to 320 °C
inj.: 320 °C
det.: FID, 320 °C
carrier gas: hydrogen, 70 cm/sec constant
injection: 0.4 μ L, 300:1 split
sample 1: lemon essential oil in hexane
sample 2: sweet orange essential oil in hexane
sample 3: lemon essential oil + 5% sweet orange essential oil in hexane

Peak IDs:

1. Camphene
2. δ -3-Carene



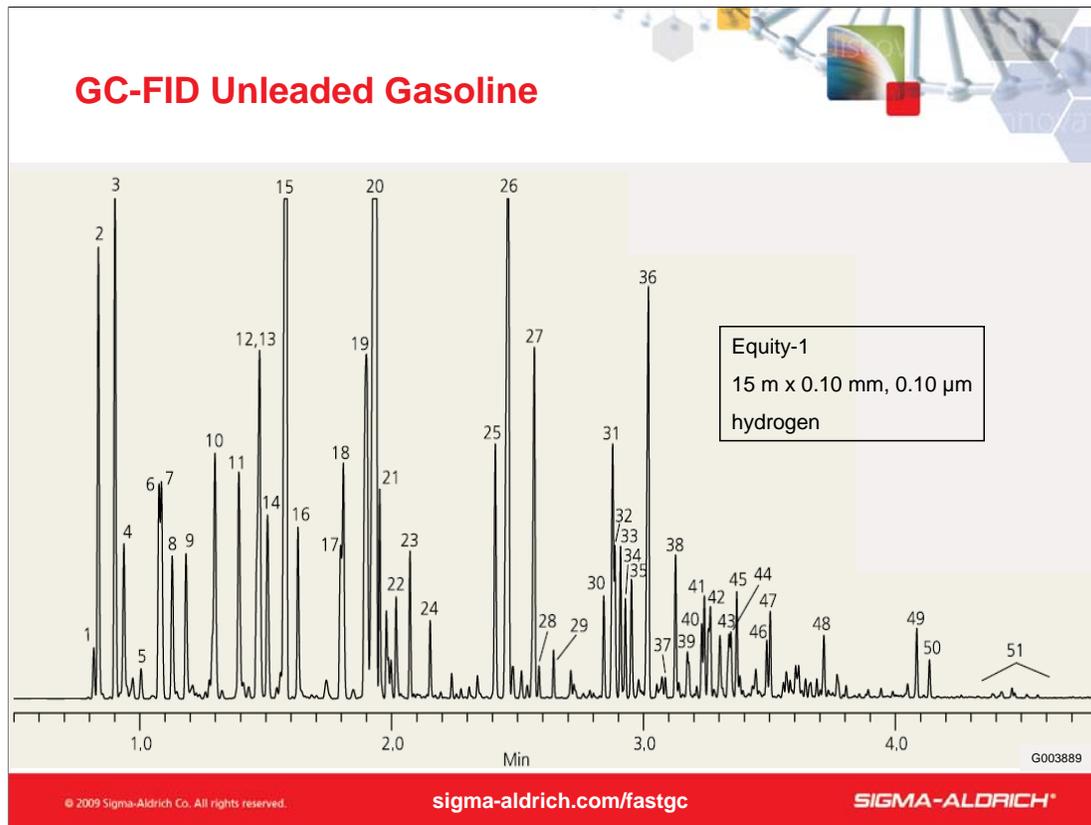
The personal care product industry is interested in determining the type and levels of allergens in many of their commercial items. In this chromatogram provided by Prof. Mondello, the allergens eugenol (peak 8) and coumarin (peak 9) are identified along with some of the major fragrance components in a commercially available perfume. Using Fast GC, the analysis was completed in ~3.5 min. using an SLB-5ms column.

Conditions:

column: SLB-5ms, 10 m x 0.10 mm I.D., 0.10 μ m (28465-U)
oven: 40 °C, 50 °C/min. to 320 °C
inj.: 320 °C
det.: FID, 320 °C
carrier gas: hydrogen, 81.5 cm/sec constant
injection: 0.2 μ L, 500:1 split
sample: Neat perfume

Peak IDs:

1. Limonene
2. Linalool
3. Citronellol
4. Neral
5. Geranial
6. Hydroxycitronellal
7. Cinnamyl alcohol
8. Eugenol
9. Coumarin
10. α -Isomethylionone
11. Hexyl cinnamylaldehyde

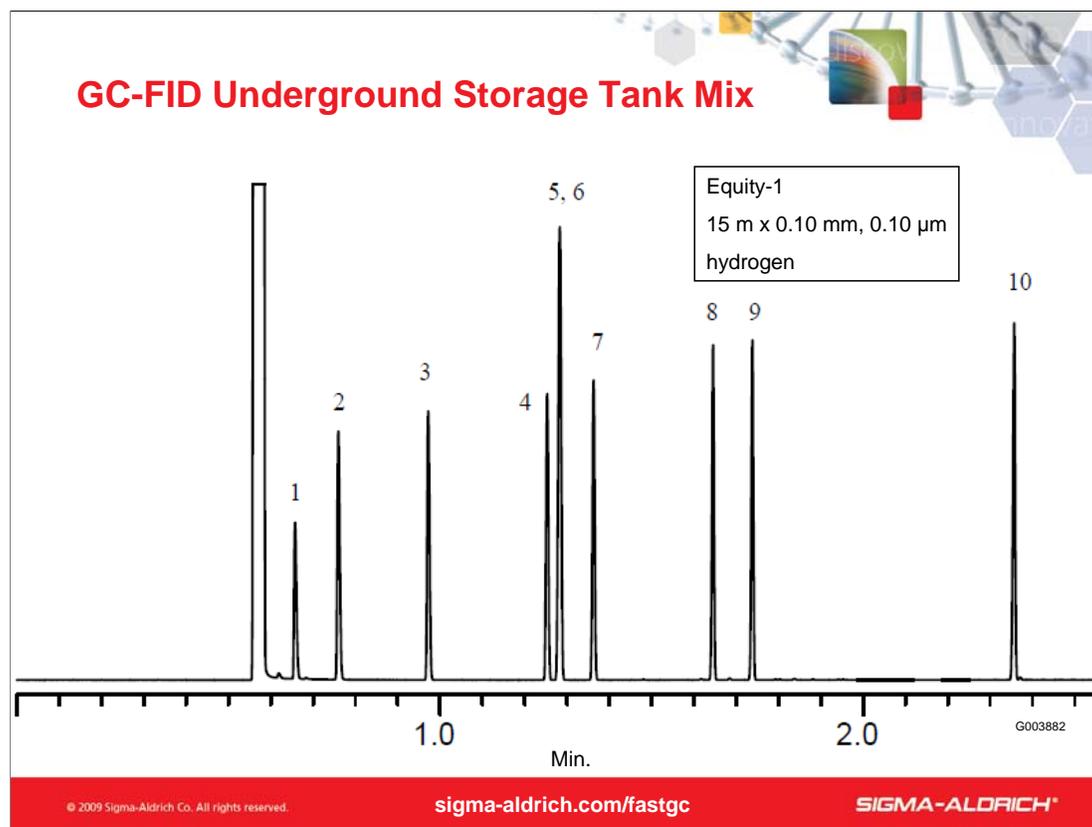


The petroleum industry must deal with very complex fuel samples, that may contain hundreds of individual compounds. Here is the Fast GC analysis of an unleaded gasoline sample with the major peaks identified. An Equity-1 column was used to obtain an analysis time of ~5 min.

Conditions:
 column: Equity-1, 15 m x 0.10 mm I.D., 0.10 µm (28039-U)
 oven: 40 °C (1 min.), 45 °C/min. to 150 °C (2 min.)
 inj.: 175 °C
 det.: FID, 175 °C
 carrier gas: hydrogen, 45 cm/sec constant
 injection: 0.1 µL, 300:1 split
 liner: 2 mm I.D., straight
 sample: Unleaded gasoline (refinery standard), neat

Peak IDs:

1. Isobutane
2. Butane
3. Isopentane
4. Pentane
5. 2,2-Dimethylbutane
6. 2,3-Dimethylbutane
7. 2-Methylpentane
8. 3-Methylpentane
9. Hexane
10. 2,4-Dimethylpentane
11. Benzene
12. 2-Methylhexane
13. 2,3-Dimethylpentane
14. 3-Methylhexane
15. Isooctane
16. Heptane
17. 2,5-Dimethylhexane
18. 2,4-Dimethylhexane
19. 2,3,4-Trimethylpentane
20. Toluene
21. 2,3-Dimethylhexane
22. 2-Methylheptane
23. 3-Methylheptane
24. Octane
25. Ethylbenzene
26. m-o-Xylene
27. o-Xylene
28. Nonane
29. iso-Propylbenzene
30. Propylbenzene
31. 1-Methyl-3-ethylbenzene
32. 1-Methyl-4-ethylbenzene
33. 1,3-Dimethylbenzene
34. 1,3,2-Trimethylheptane
35. 1-Methyl-2-ethylbenzene
36. 1,2,4-Trimethylbenzene
37. iso-Butylbenzene
38. sec-Butylbenzene
39. 1,2,3-Trimethylbenzene
40. Indane
41. 1,3-Diethylbenzene
42. N-Butylbenzene
43. 1,4-Dimethyl-2-ethylbenzene
44. 1,3-Dimethyl-4-ethylbenzene
45. 1,2-Dimethyl-4-ethylbenzene
46. 1,2,4,5-Tetramethylbenzene
47. 1,2,3,5-Tetramethylbenzene
48. Naphthalene
49. 2-Methylnaphthalene
50. 1-Methylnaphthalene
51. Dimethylnaphthalenes



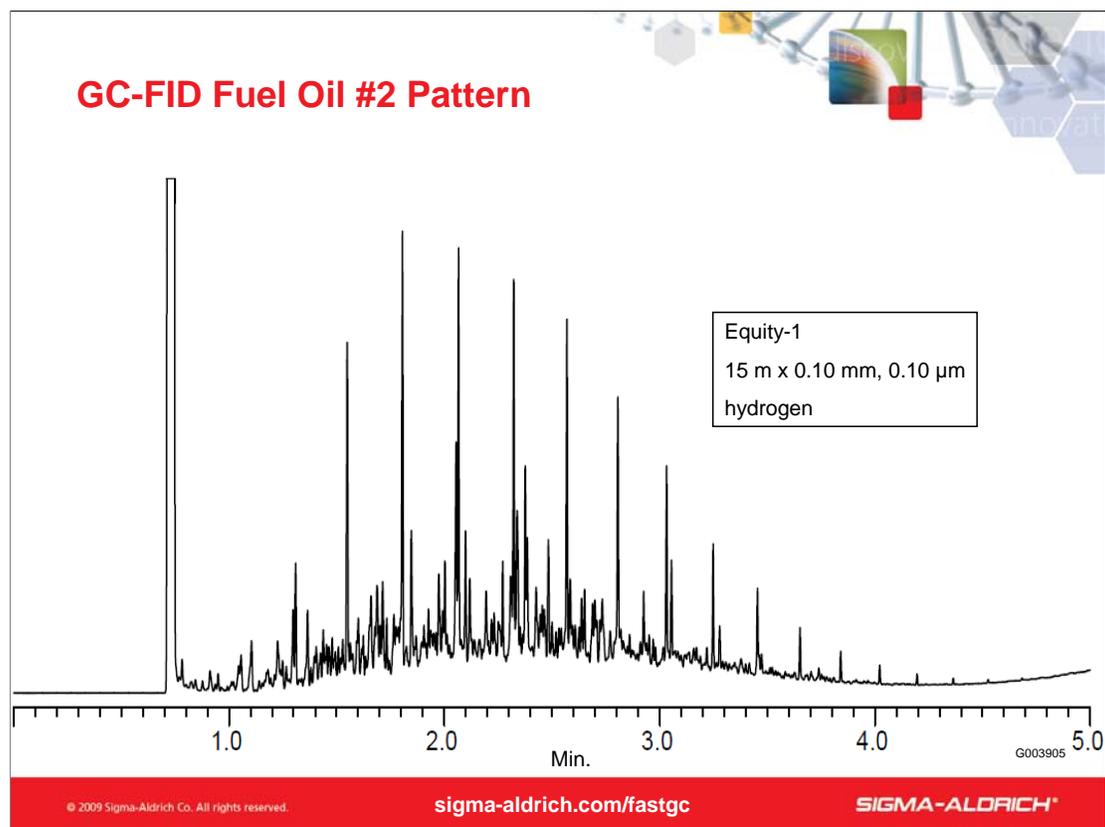
This chromatogram shows an application performed by both the petroleum and environmental industries. Purity of product in an underground storage tank is of interest to the petroleum industry. These analytes may serve as indicator analytes. When an underground storage tank leaks, the contaminated soil is tracked by the environmental industry by looking for these same indicator analytes. The soil that is deemed to be contaminated is remediated. This application was accomplished in ~2.5 min. using an Equity-1 column and the Principles of Fast GC.

Conditions:

column: Equity-1, 15 m x 0.10 mm I.D., 0.10 μm (28039-U)
 oven: 75 $^{\circ}\text{C}$, 40 $^{\circ}\text{C}/\text{min.}$ to 110 $^{\circ}\text{C}$, 7.5 $^{\circ}\text{C}/\text{min.}$ to 190 $^{\circ}\text{C}$
 inj.: 200 $^{\circ}\text{C}$
 det.: FID, 250 $^{\circ}\text{C}$
 carrier gas: hydrogen, 57 cm/sec @ 75 $^{\circ}\text{C}$
 injection: 0.5 μL , 200:1 split
 liner: 4 mm I.D., split, cup design
 sample: UST Modified GRO Mix, each analyte at 1000 ppm in methanol (48167)

Peak IDs:

1. MTBE
2. Benzene
3. Toluene
4. Ethyl benzene
5. m-Xylene
6. p-Xylene
7. o-Xylene
8. 1,3,5-Trimethylbenzene
9. 1,2,4-Trimethylbenzene
10. Naphthalene



Because fuel samples are so complex, especially the more unrefined they are, the petroleum industry may evaluate product based on pattern recognition rather than the identification and quantitation of individual analytes. Here, the Principles of Fast GC were applied to the analysis of a fuel oil #2 sample, with analysis completed in ~4.5 min. on an Equity-1 column.

Conditions:

column: Equity-1, 15 m x 0.10 mm I.D., 0.10 µm (28039-U)
oven: 80 °C, 50 °C/min. to 325 °C
inj.: 250 °C
det.: FID, 350 °C
carrier gas: hydrogen, 45 cm/sec constant
injection: 0.3 µL, 100:1 split, 0.02 min. pre-injection dwell time
liner: 2 mm I.D., straight
sample: No.2 Fuel Oil standard, 20 mg/mL in methanol (47515-U)



Review and Summary

44

© 2009 Sigma-Aldrich Co. All rights reserved. sigma-aldrich.com/fastgc SIGMA-ALDRICH®

Let's do a quick review and summary of Fast GC.

Review: The Principles of Fast GC

- Decrease analysis time by using:
 - Shorter column
 - Quicker oven temperature ramp rate
 - Higher carrier gas linear velocity

But these changes also decrease resolution!
- Offset the decrease in resolution by also using:
 - Narrow I.D. column
 - Hydrogen carrier gas
 - Low film thickness

45

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Review:

The underlying Principles of Fast GC are pretty simple.

Analysis times can be decreased by using:

- Short columns
- Fast oven temperature ramp rates
- High carrier gas linear velocities

The loss in resolution caused by the above steps can be offset by using:

- Narrow I.D. columns
- Hydrogen carrier gas
- Low film thickness

The more Principles that are applied, the greater the benefit!

Note:

Many of these parameters being manipulated are related to each other. Changing just one may produce a shorter analysis, but may result in a loss in quality. Therefore, all parameters must be evaluated to make sure they are set correctly.

Summary

- Fast GC can be applied to **any application in any industry**, and may not require a major investment in new equipment
- By applying the techniques of Fast GC such as using shorter, narrower bore columns, faster oven temperature ramp rates, and hydrogen carrier gas, **analyses times can be significantly reduced while still producing quality data**
- These reduced times can result in **increased productivity**, as sample throughput increases
- Any excess capacity can also be used to analyze additional samples, resulting in **increased revenue**

46

© 2009 Sigma-Aldrich Co. All rights reserved.

sigma-aldrich.com/fastgc

SIGMA-ALDRICH®

Fast GC can be applied to any application in any industry, any may not require a major investment in new equipment. By applying the techniques of Fast GC such as using shorter, narrower bore columns, faster oven temperature ramp rates, and hydrogen carrier gas, analyses times can be significantly reduced while still producing quality data. These reduced times can result in increased productivity, as sample throughput increases. Any excess capacity can also be used to analyze additional samples, resulting in increased revenue.

Thank You



Thank you for your time today.