

Fast GC in Environmental Analysis

Increase Sample Throughput without Sacrificing Quality

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Agenda

Overview

- 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

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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). A detailed section will put it all together, taking a PAH application using conventional GC and observing the chromatographic changes while applying the Principles of Fast GC. Popular applications, such as volatiles, semivolatiles, dioxins, pesticides, PCBs, and PAHs, will also be shown.



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? What is Fast GC?

- Time and money! Fast GC yields faster analysis times than conventional GC (often 3-10x faster), the benefits are:
 - **Decrease costs**: need fewer analysts and/or instruments
 - **Increase revenue**: analyze more samples
 - Can provide faster method development
 - Can be applied to any application with **no sacrifice in quality**
 - Typically, **no additional capital equipment** is required
- Fast GC is manipulating a number of column and instrument parameters to provide **faster analysis times while maintaining resolution**

3

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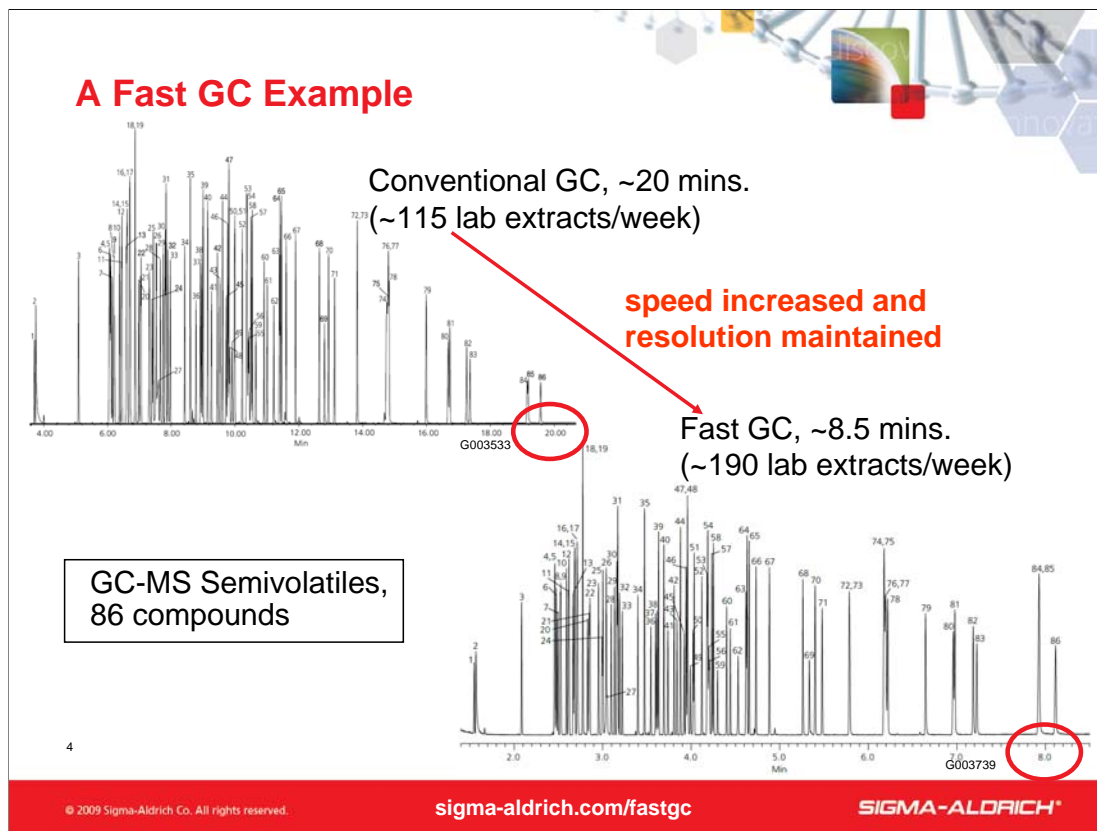
Why should you consider implementing Fast GC into your lab? Time and money!

Fast GC yields faster analysis times than conventional GC, often three to ten times faster. 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.

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



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 μ m (28471-U)
 oven: 40 $^{\circ}$ C (2 min.), 22 $^{\circ}$ C/min. to 240 $^{\circ}$ C, 10 $^{\circ}$ C/min. to 330 $^{\circ}$ C (1 min.)
 inj.: 250 $^{\circ}$ C
 MSD interface: 330 $^{\circ}$ 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 μ L, 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 μ m (28564-U)
 oven: 40 $^{\circ}$ C (0.7 min.), 55 $^{\circ}$ C/min. to 240 $^{\circ}$ C, 28 $^{\circ}$ C/min. to 330 $^{\circ}$ C (2 min.)
 inj.: 250 $^{\circ}$ C
 MSD interface: 330 $^{\circ}$ 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

The Principles of Fast GC

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

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

5

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The six 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!



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):
 - 1. Reduce L (column length)
 - 2. Reduce k (retention factor) by increasing temperature
 - 3. Increase u (carrier gas linear velocity)

But these changes also decrease resolution!

7

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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:

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

- N (efficiency, as plates) and H (plate height) have an inverse relationship

$$N = L/H$$

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

8

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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

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

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

9

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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

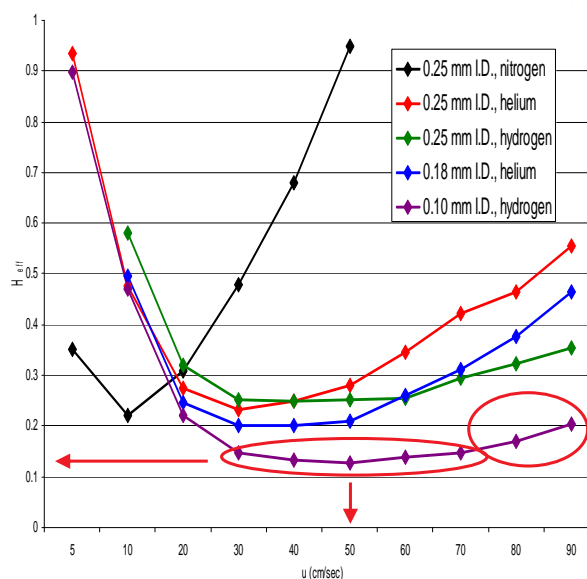
A stationary phase with a higher diffusivity (D_s) results in a lower plate height (H) - tells us to use a column with a thinner film thickness

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

'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}]



10

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Let's consider column I.D. and carrier gas together. Shown are Golay plots of five combinations of column I.D. and carrier gas. 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. 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 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:
 - 1. Shorter column
 - 2. Quicker oven temperature ramp rate
 - 3. Higher carrier gas linear velocity

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

11

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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

12

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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.

Practical Considerations

- **Sample Capacity**
 - Use high split ratios to prevent column overload (sensitivity does not suffer, due to the fact that peaks with much greater signal-to-noise ratios will be generated)
- **Oven Temperature Ramp Rates**
 - Do not set-up an oven temperature program with a rate faster than your instrument can manage
- **Detector Acquisition Rates**
 - Verify the detector can obtain sufficient data points per peak to ensure proper peak quantitation
- **Mass Spec Detectors**
 - Some older MS instrumentation may not work properly with hydrogen as the carrier gas

13

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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.

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.

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.

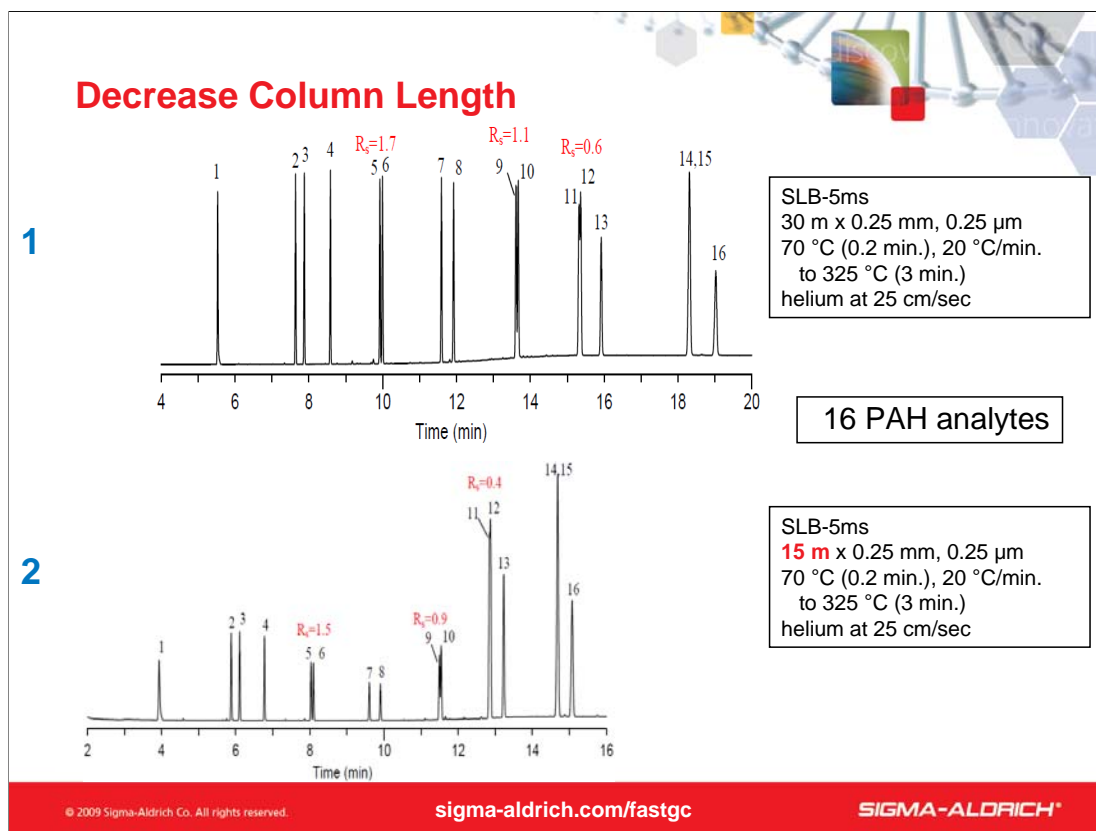


Putting it All Together

14

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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.

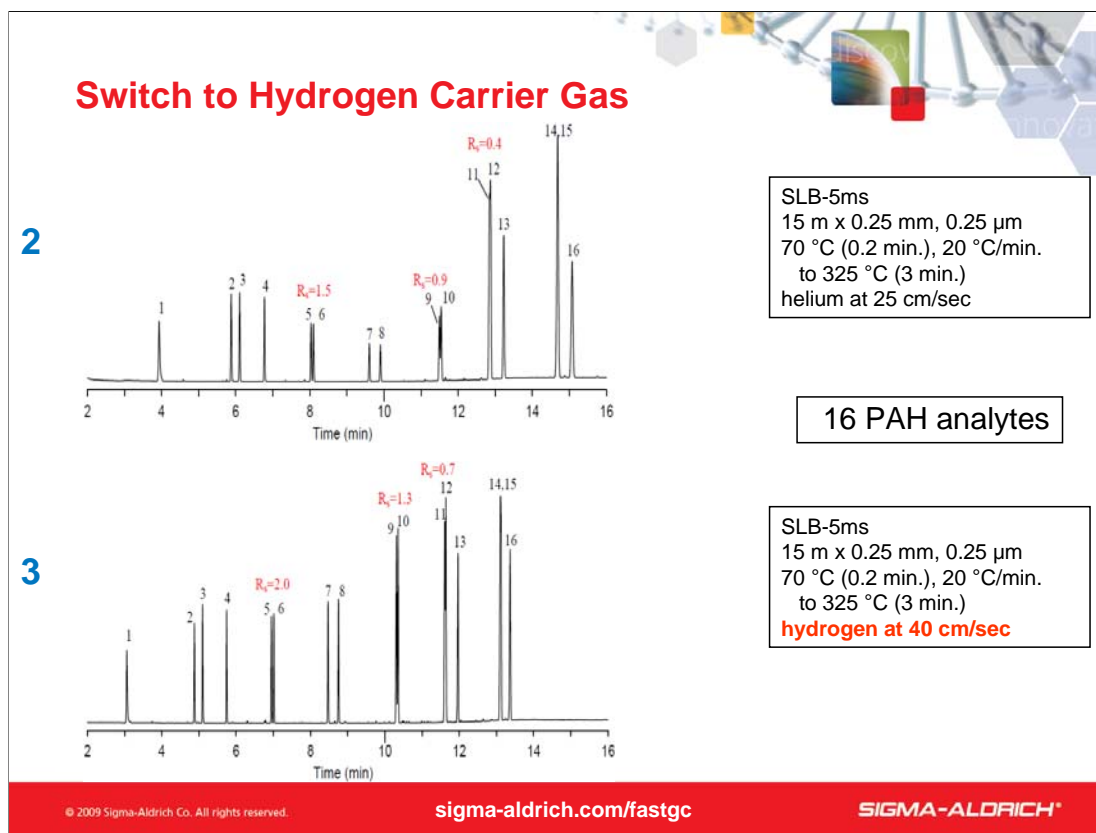
Chromatogram 2 shows the same application with a shorter column (15 m instead of 30 m). As expected, analysis time decreases (~19 minutes to ~15 minutes), and resolution values are lower (1.5, 0.9, and 0.4). This is a shorter run, but the resolution is unacceptable.

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.

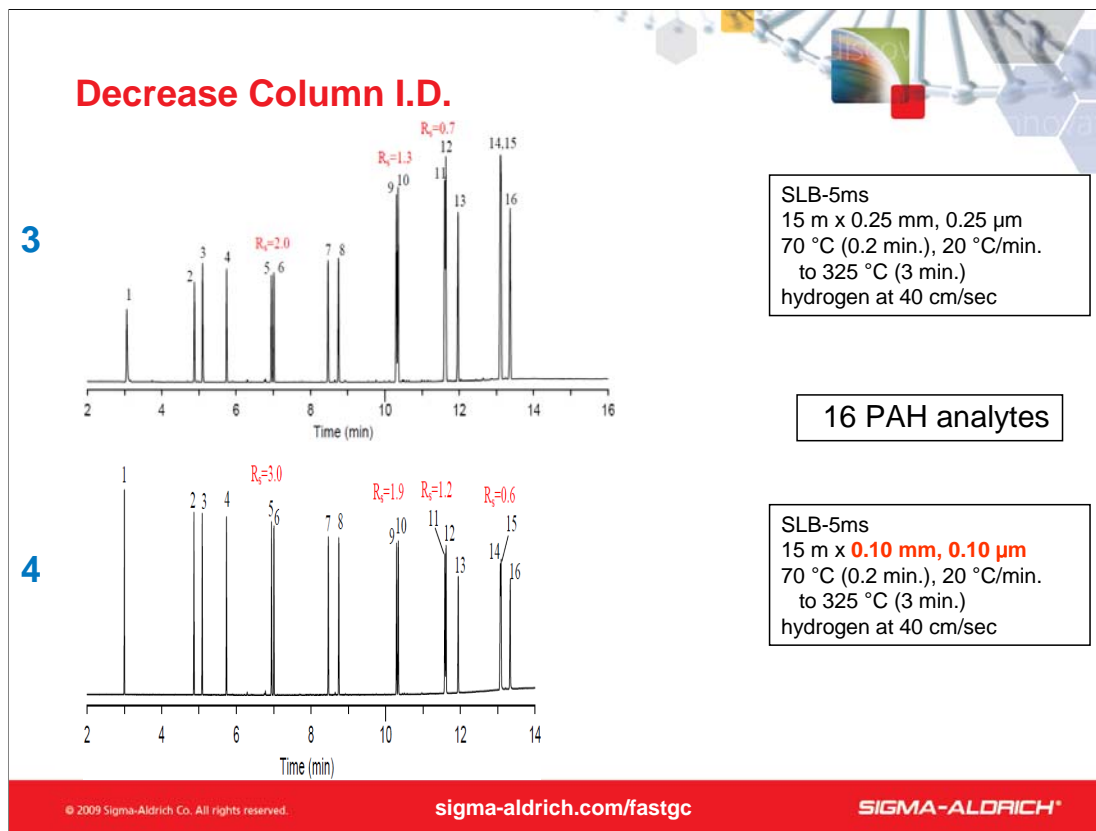
Chromatogram 3 shows what happens when we change the carrier gas (hydrogen at 40 cm/sec instead of helium at 25 cm/sec.. As expected, analysis time is even shorter (~13.5 minutes compared to ~15 minutes). Now look at the resolution values (2.0, 1.3, and 0.7). Why did they get better? Hydrogen at its 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.

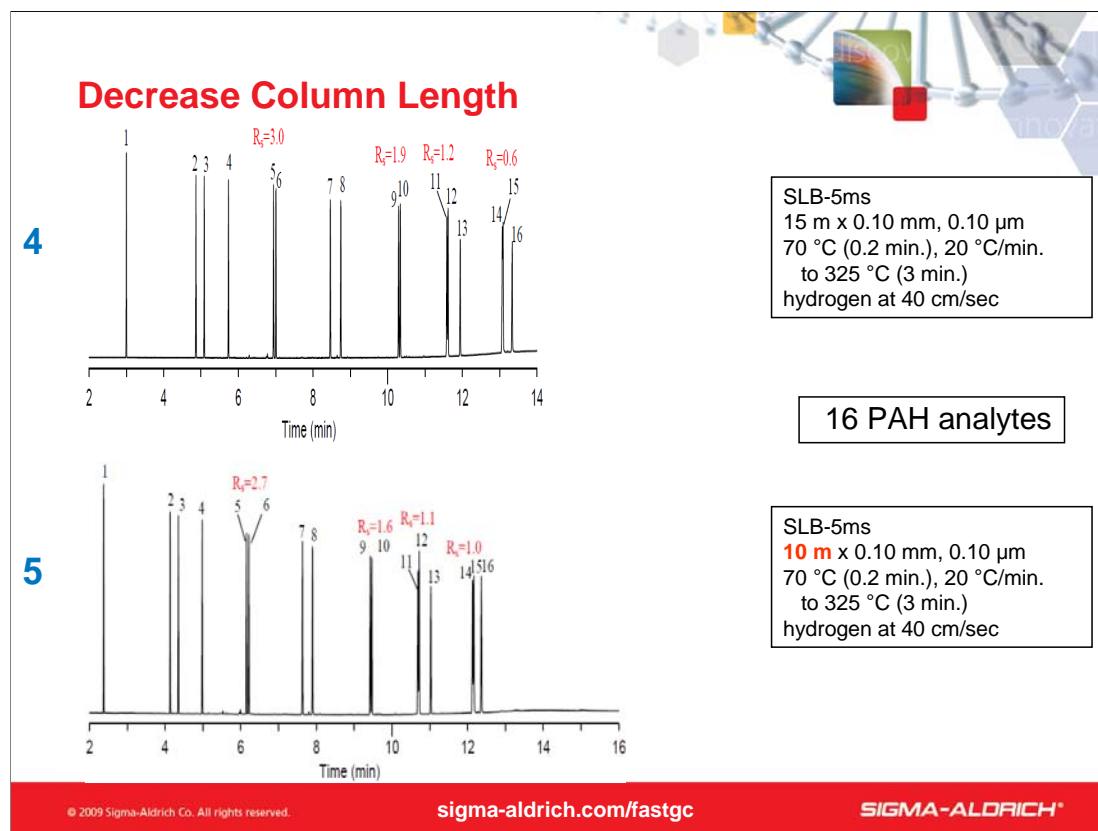
We discussed earlier that decreasing column I.D. was a way to decrease plate height (H), which increases efficiency (N) and subsequently resolution (R_s). We're scientists, so let's experiment and see what happens! Chromatogram 4 shows the same application on smaller I.D. column (0.10 mm I.D. instead 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.

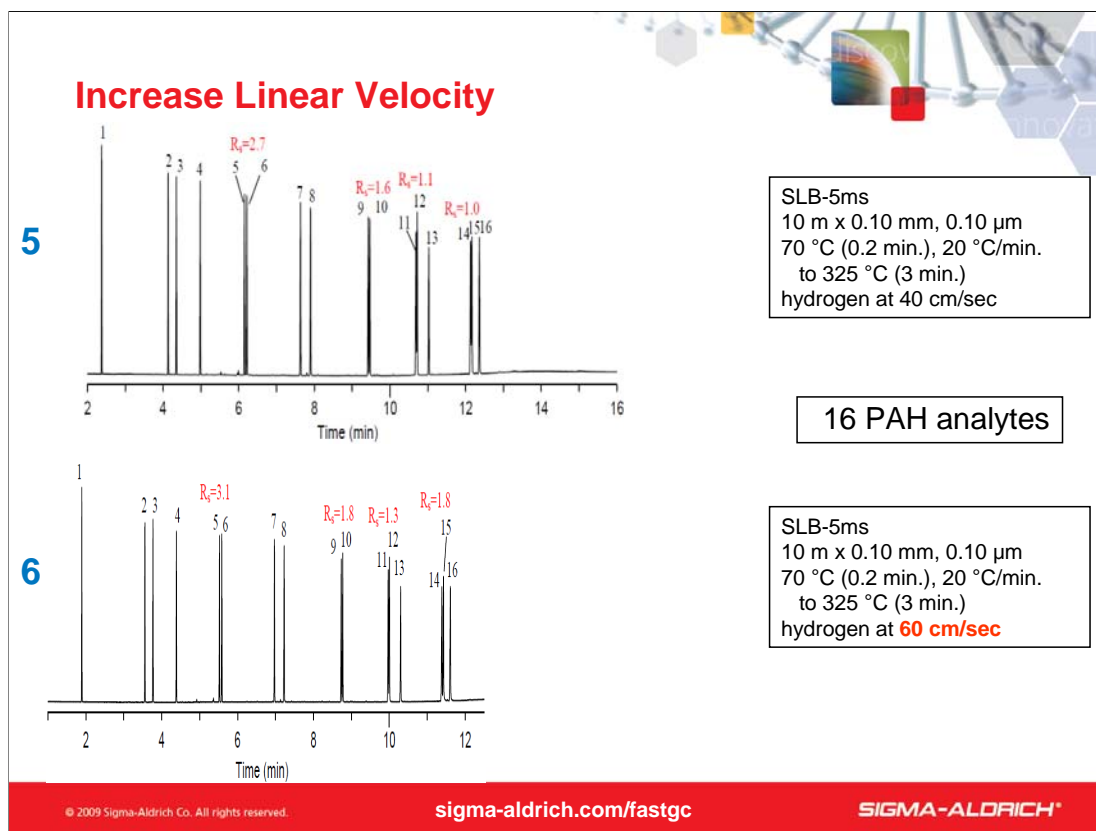
Having excess resolution is great, because it provides the opportunity to manipulate parameters to decrease retention time. We chose to decrease column length again, this time from 15 m to 10 m, resulting in Chromatogram 5. As expected, analysis time decreases (~13.5 minutes to ~12.5 minutes), and resolution 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 °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:

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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.

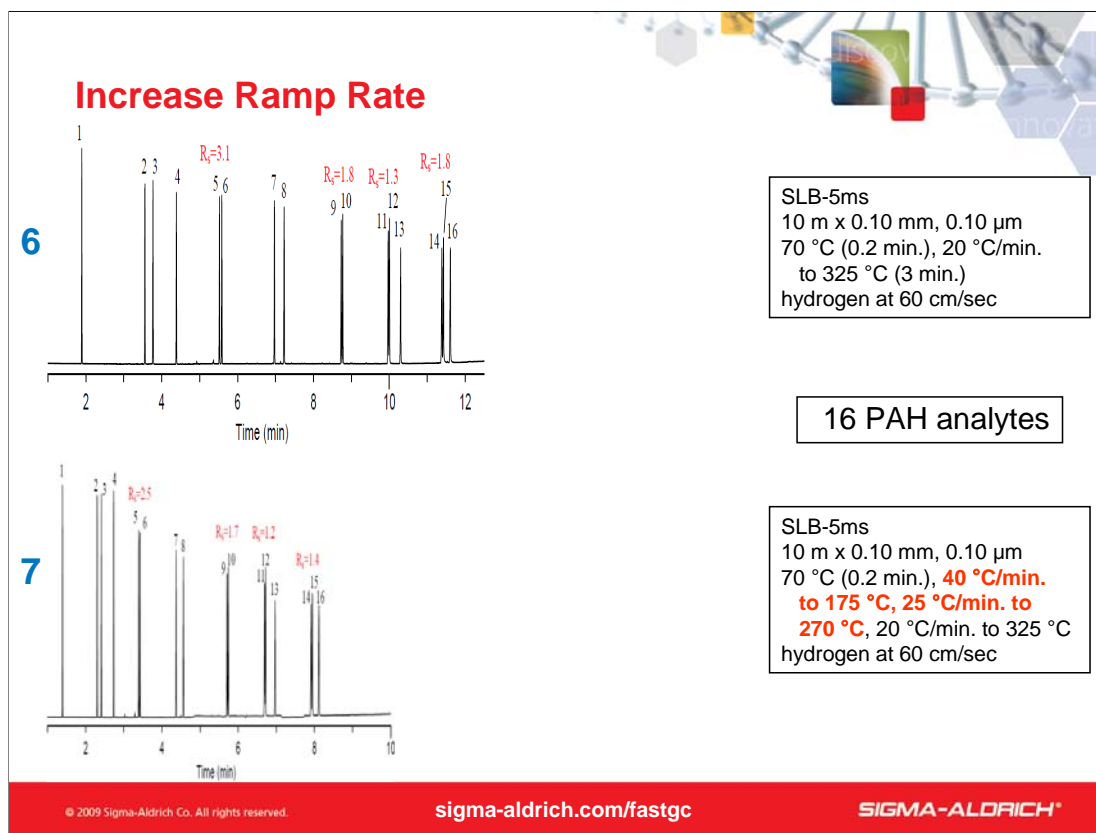
Chromatogram 6 shows the same application with the linear velocity increased from 40 cm/sec to 60 cm/sec. As expected, analysis time did decrease (from ~12.5 min. to ~11.8 min.). But, why did resolution increase (3.1, 1.8, 1.3, and 1.8)? Was this expected? Remember the Golay plots we looked at during 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:

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3. Acenaphthene
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5. Phenanthrene
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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.

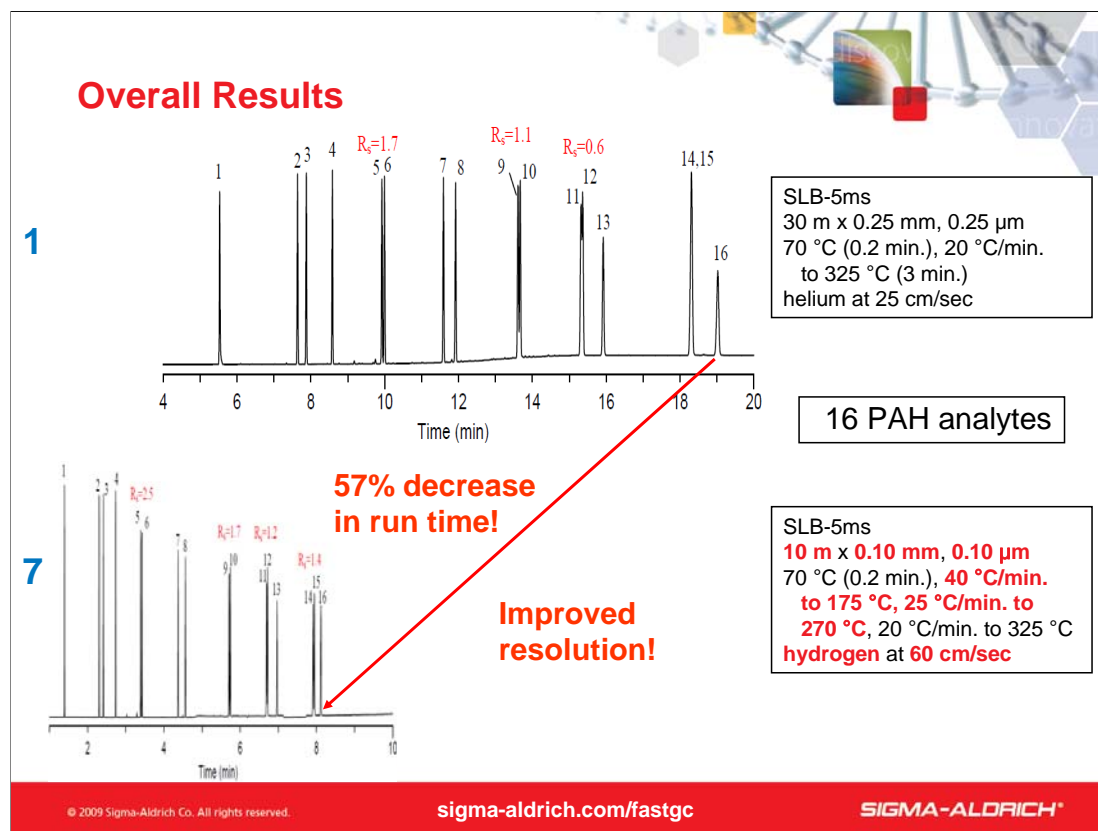
We haven't looked at oven temperature ramp rate yet. What if we pushed the oven to the highest ramp rate possible over each temperature range? After consulting our instrument manual and setting our ramp rates accordingly, we achieved Chromatogram 7. Note that 40 °C/min., 25 °C/min. and 20 °C/min. are 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

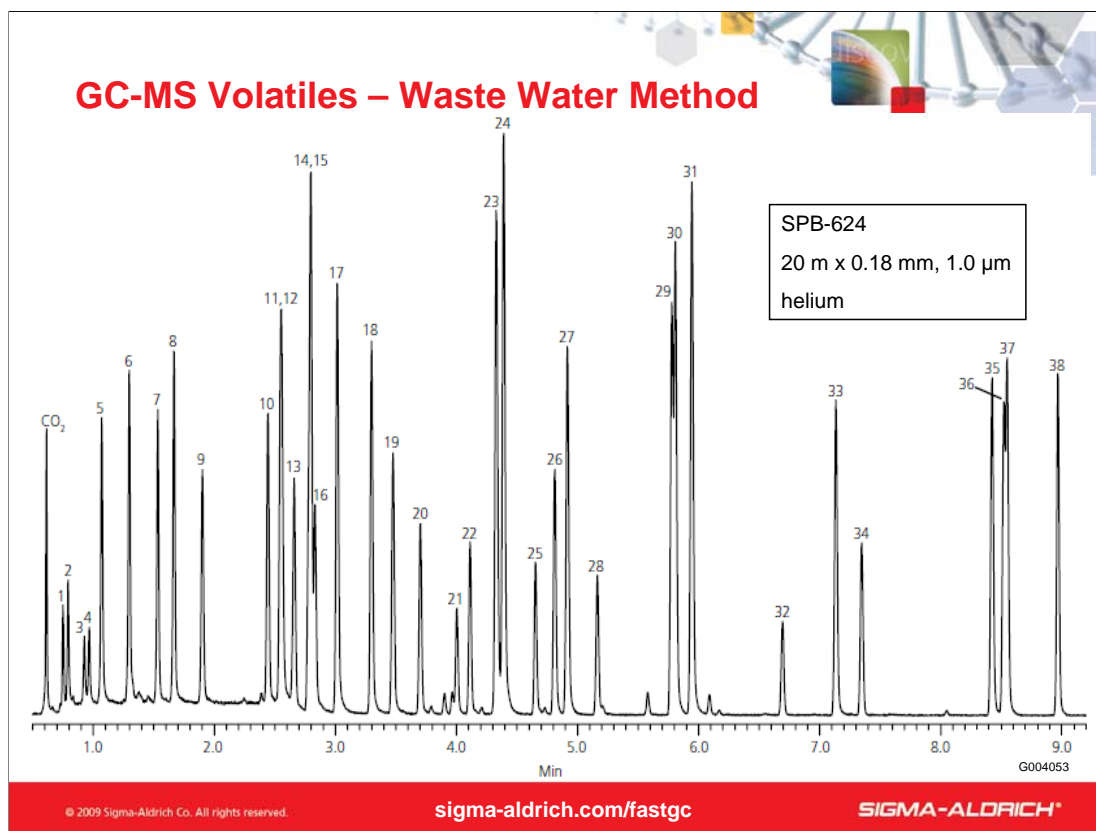
22

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This section contains a handful of environmental applications. 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.



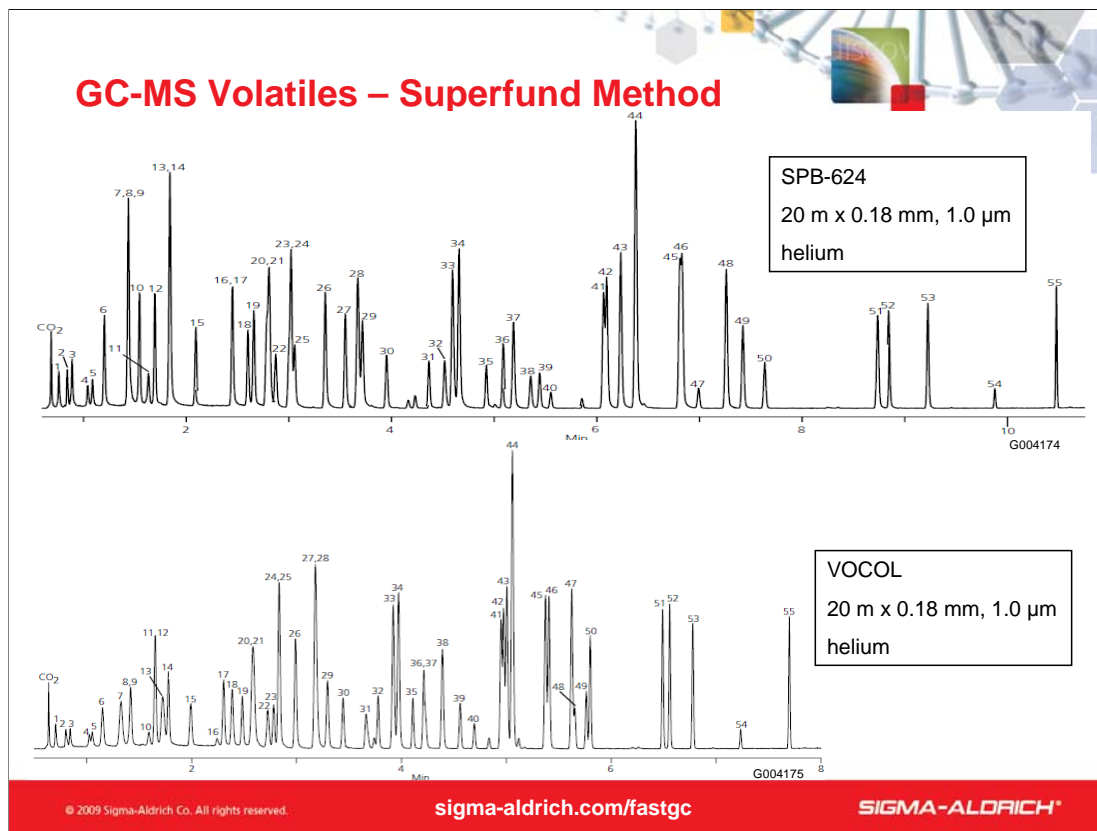
In the environmental industry, the GC-MS analysis of volatiles from drinking water, waste water, ground water, solid waste, and air samples is widely performed. The analyte lists is pretty varied; the 'light' analytes being very volatile gases and the 'heavy' analytes being dichlorobenzenes. This analysis 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



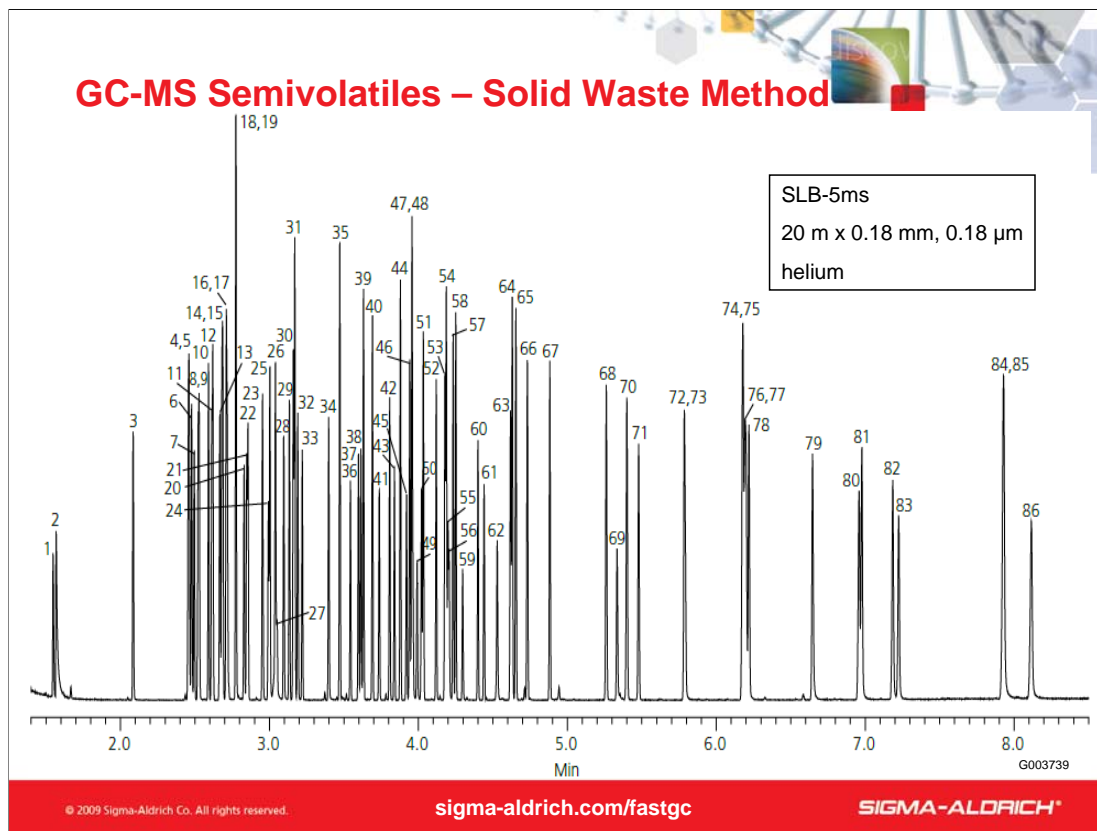
Another environmental GC-MS volatile application is for samples that originate from Superfund hazardous waste sites. This application requires a different, longer analyte list. Here, two columns with different selectivity are shown. In addition to the Principles of Fast GC, changing column selection 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



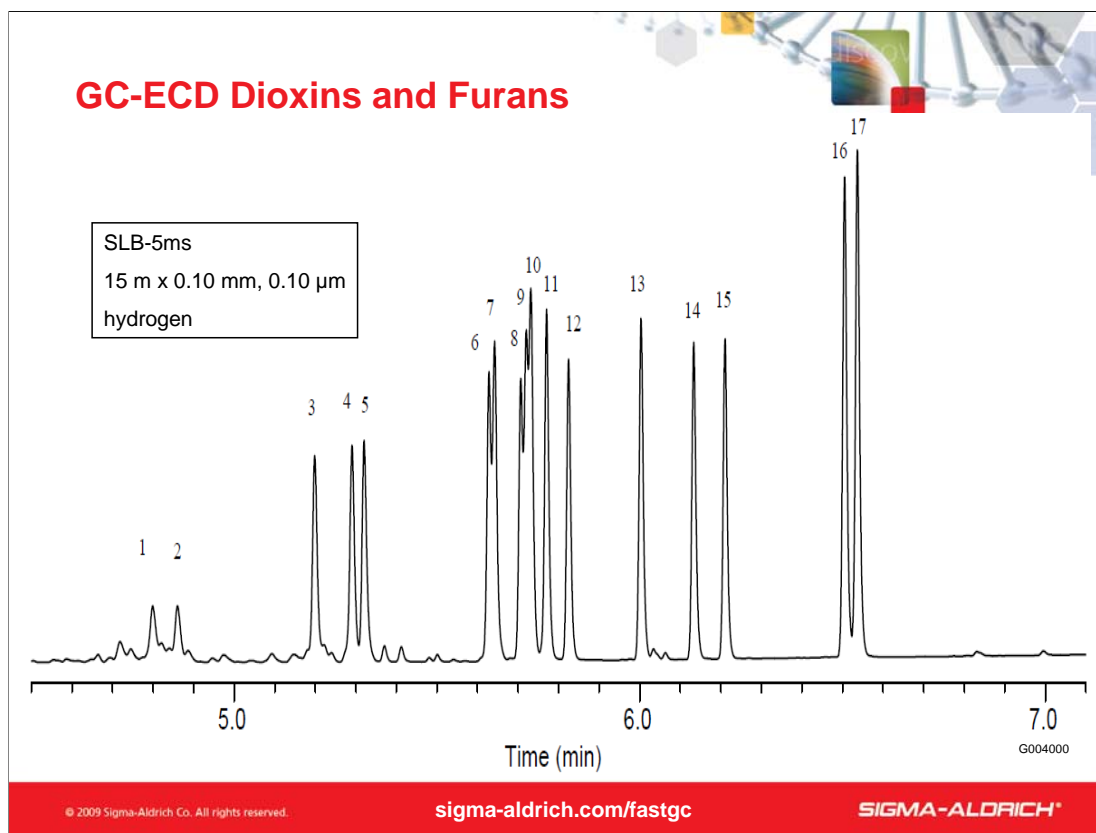
Another common GC-MS application in the environmental industry is the analysis of semivolatile analytes, ranging from N-nitrosodimethylamine and pyridine to the multi-ringed PAHs, such as benzo(g,h,i)perylene. Even with helium as the carrier gas, the other Principles of Fast GC were used to produce a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



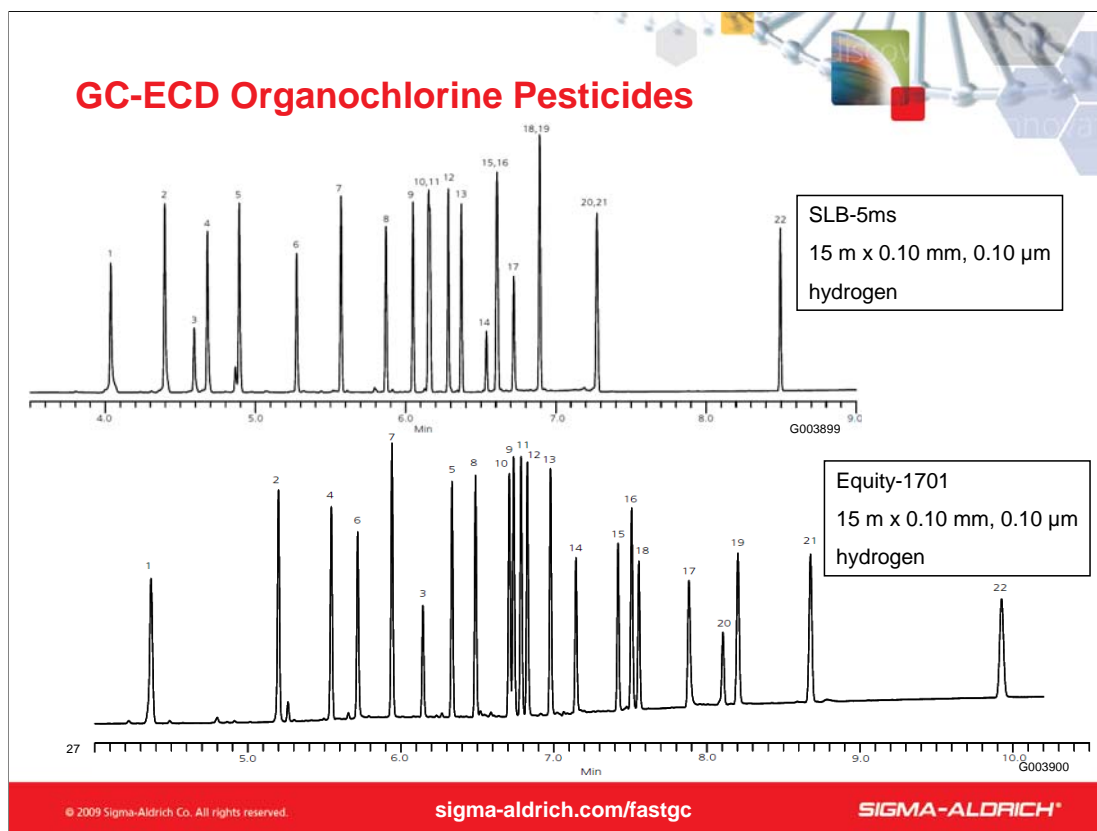
GC-ECD is often used in the environmental industry to screen for the presence of dioxins and furans that have chlorine substitution in the 2, 3, 7, and 8 positions. If detected, the sample extract is then analyzed using high resolution mass spectrometry to verify identifications and perform quantitative 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):

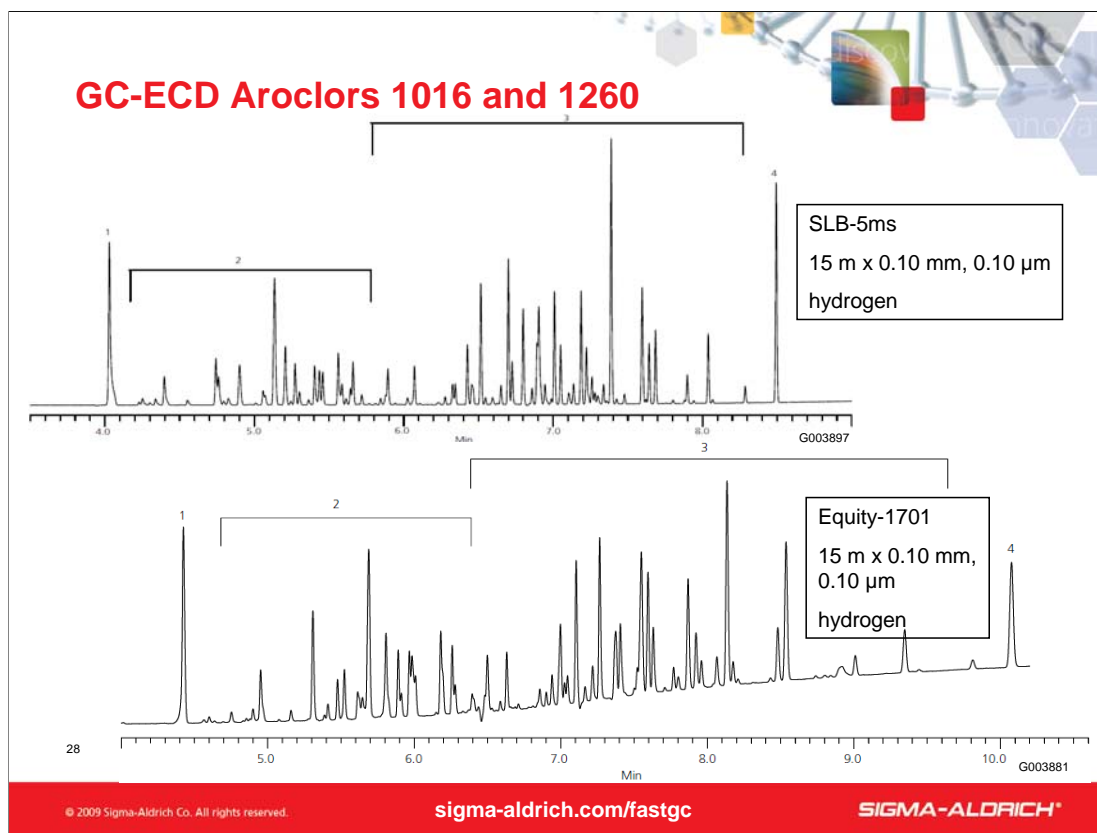
column: SLB-5ms, 15 m x 0.10 mm I.D., 0.10 µm (28466-U)
 oven: 100 °C, 25 °C/min. to 325 °C
 inj.: 225 °C
 det.: ECD, 300 °C
 carrier gas: hydrogen, 40 cm/sec constant
 injection: 2 µL, splitless (0.75 min.)
 liner: 4 mm I.D., single taper
 sample: 50 ppb of a 22 component chlorinated pesticide standard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

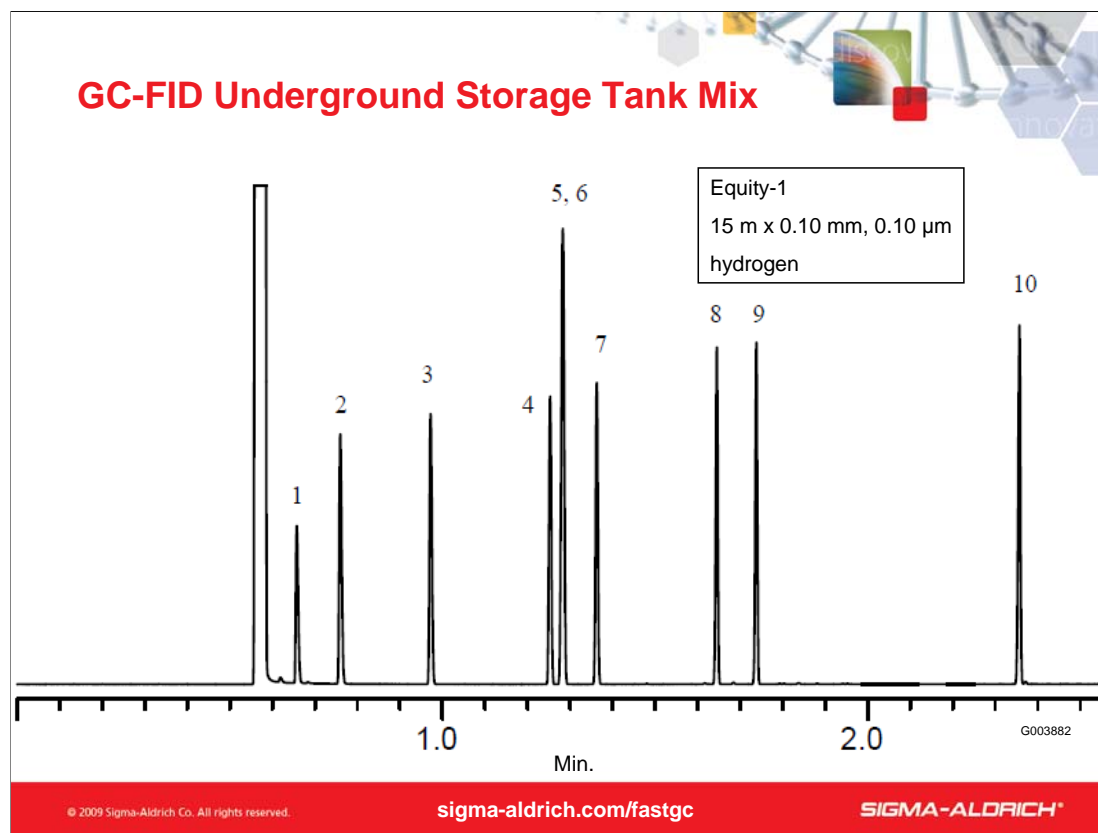
column: SLB-5ms, 15 m x 0.10 mm I.D., 0.10 μm (28466-U)
oven: 80 °C (0.5 min.), 50 °C/min. to 200 °C, 35 °C/min. to 360 °C (2 min.)
inj.: 225 °C
det.: ECD, 360 °C
carrier gas: hydrogen, 40 cm/sec constant
injection: 2 μL, splitless (0.75 min.)
liner: 4 mm I.D., single taper
sample: Aroclor standard mix 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 μm (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 μL, 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.)



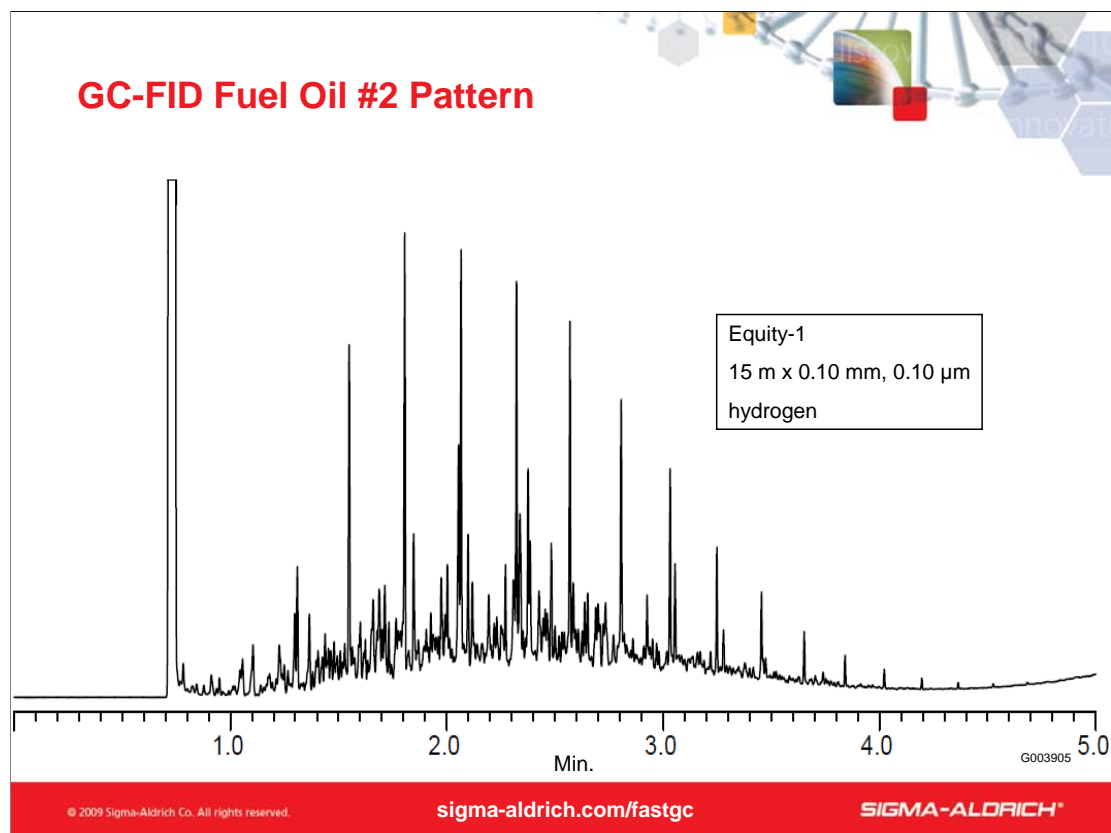
This chromatogram shows an application performed by both the petroleum and environmental industries. Purity of product in an underground storage tank is of interest to the petroleum industry. These analytes may serve as indicator analytes. When an underground storage tank leaks, the contaminated soil 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 °C, 40 °C/min. to 110 °C, 7.5 °C/min. to 190 °C
 inj.: 200 °C
 det.: FID, 250 °C
 carrier gas: hydrogen, 57 cm/sec @ 75 °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 μ m (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 μ L, 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

31

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

Review: The Principles of Fast GC

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

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

32

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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**

33

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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. I also wish to thank the FSEA organizers for allowing me this opportunity to speak today. Lastly, I would like to thank my co-authors (Kathy, Len, and Greg).