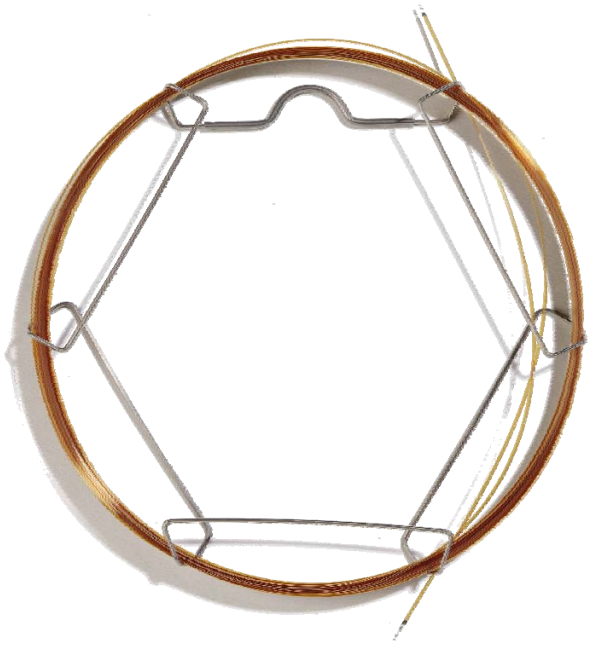
Approaches to Increasing GC Speed, Resolution and Response

Overview of Presentation

Fast GC

Ionic liquids for GC

Chiral GC



GC Innovations

- **Fast GC – Column dimensions & instrument settings**
- Ionic liquids for GC
- Chiral GC

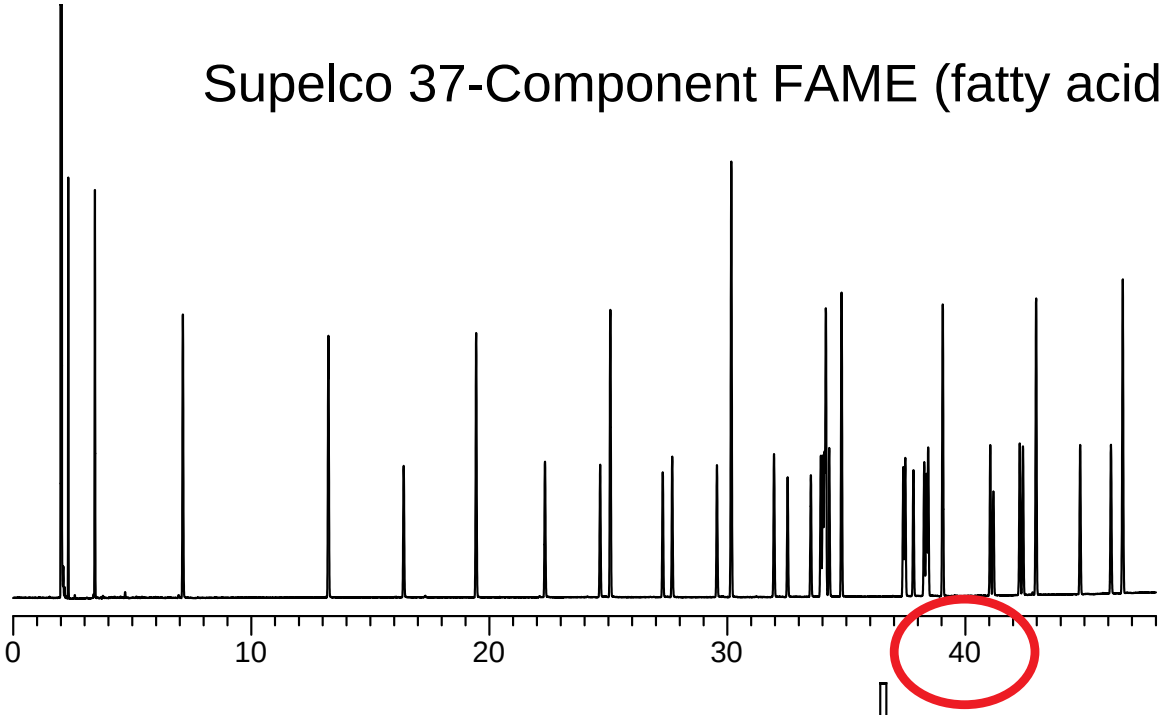
Users are.....
- **GC and GC-MS analysts**

Interested in...
- **Decreasing run time**
- **Maintaining resolution**
- **Using existing GC systems**

Users can expect...
- **High speed, high efficiency, adequate resolution GC separations**

The Possibilities of Fast GC

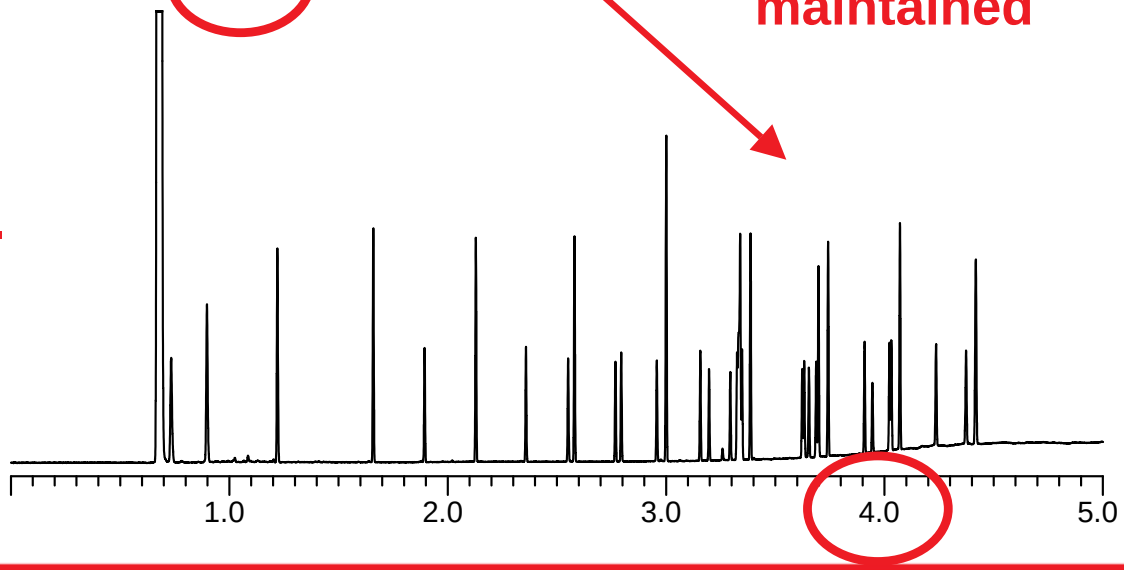
Supelco 37-Component FAME (fatty acid methyl ester) Mix



Conventional GC ~40 mins.

10-fold speed improvement, resolution maintained

Fast GC ~4 mins.



Why Use Fast GC?

Fast GC offers four distinct benefits:

1. Reduced analysis time (typically 3- to 10-times faster analyses)
2. Increased sample throughput
3. Faster GC method development
   - Alter analysis conditions and see results faster
4. Improved precision and accuracy
   - Allows more replicates and standards to be analyzed in a shorter time frame

How do we achieve Fast GC?

Foundations: Factors Affecting GC Retention Time

The goal in Fast GC is to reduce the total analysis time without losing resolution. How can this be accomplished?

The following equation defines GC retention time:

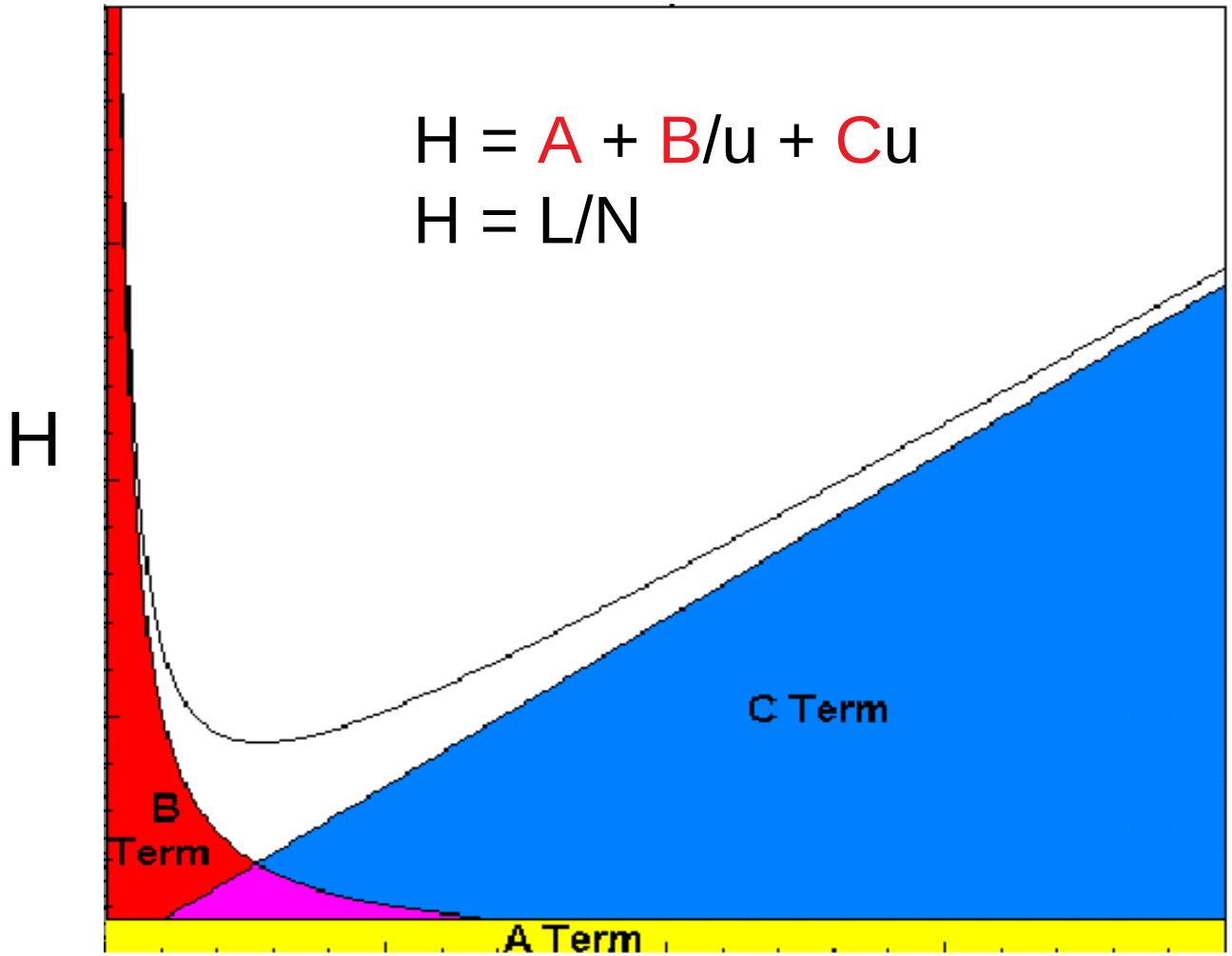
$$t_r = \frac{L\,(k+1)}{u}$$

There are three options to reduce the retention time (t_r) of an analyte:

- Reduce column length (L)
- Reduce retention factor (k) by:
  - Changing the stationary phase
  - Increasing temperature
- Increase carrier gas linear velocity (u)

But these factors can reduce efficiency and resolution.

The van Deemter Relationship Visualized



Foundations: The Golay Equation

The Golay equation is just the classic van Deemter equation minus the A-term, which does not apply to open tubes (H = B/u + Cu).

Low values of H are better.

The Golay equation looks complex, but from it a few simple truths relevant to Fast GC are obvious.

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

1. Smaller column radii give higher efficiency.

2. Thin stationary phase films with high D_s (diffusivity) values give higher efficiency.

3. Carrier gases with high D_m (diffusivity) give higher efficiency. (Use hydrogen.)

How is Fast GC Achieved?

Column and instrument improvements and run conditions that give 3- to 10-times faster analyses, while still giving adequate resolution.

Fast GC column characteristics:

- Short length (< 20 m)
- Narrow I.D. (0.10 mm or 0.18 mm)

Film thickness: any thin film phase can be used

Carrier gas: hydrogen

Programming rates: rapid

What Columns are Used in Fast GC?

Based solely on column internal diameter (I.D.), GC can be grouped into three types:

- Standard GC: Columns with I.D. > 0.25 mm
- Fast GC: Various I.D. Columns (0.10 and 0.18 mm are typical)
- Ultra-Fast GC: Column I.D. < 50 µm

Column lengths are typically < 20 meters

Any thin-film stationary phase can be used

How is Fast GC Achieved?

On standard GC columns (> 0.2 mm I.D.):

- Switch from helium to hydrogen carrier gas.
  - This could reduce runtime by as much as 50%
- Hardware modifications to the GC system that would allow for faster heating and cooling, such as the GC Racer
- Using microwave energy with compatible columns for rapid heating
- Use of resistive heating technology (this requires modified columns and an oven modification as well)

(continued)

How is Fast GC Achieved?

On short columns with narrow I.D. (≤0.2 mm)

- High carrier gas linear velocity
- Fast oven temperature programming rates

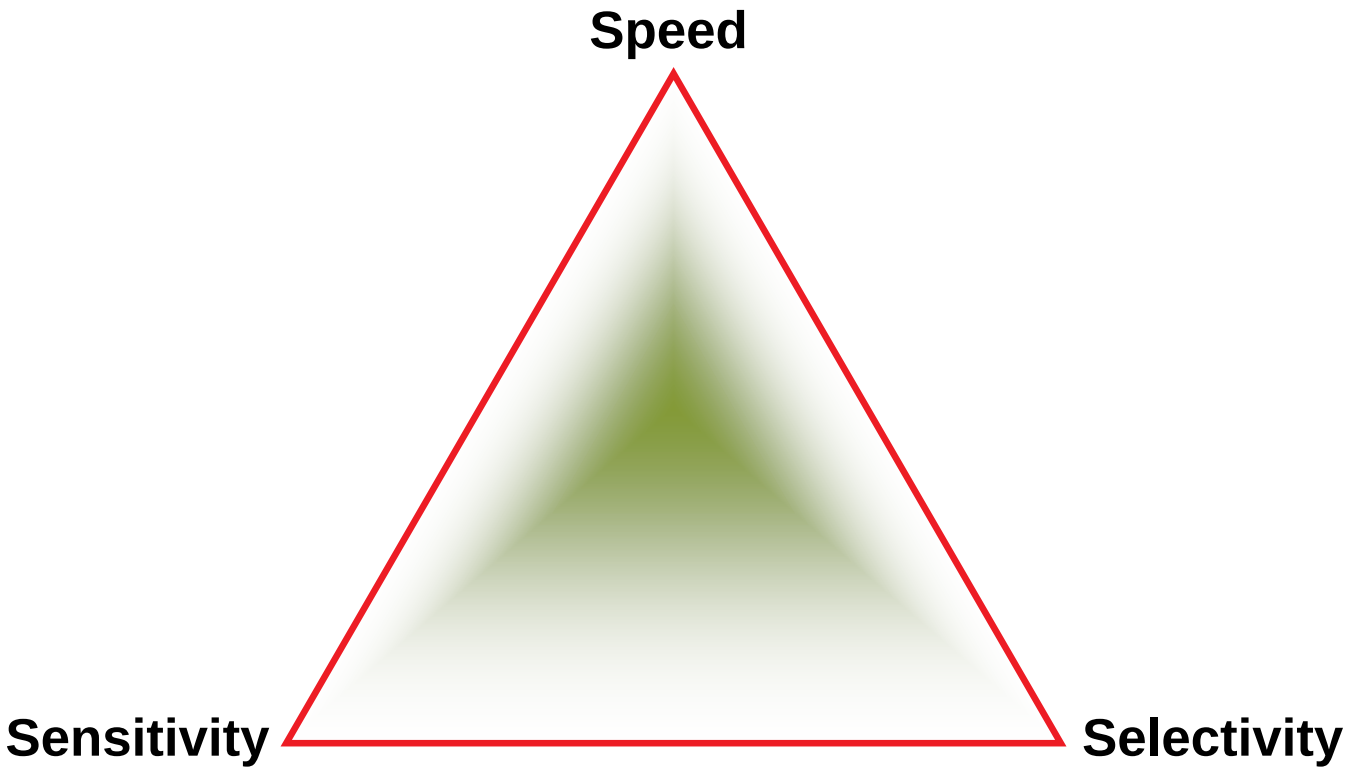
To offset the losses in efficiency of shorter columns:

- Decrease the column I.D. (reduced “C” term of the Golay)
- Use thinner stationary phase films (less resistance to mass transfer, C_s)
- Use hydrogen as the carrier gas (higher u_{opt} than helium or nitrogen)

These parameters must be optimized together! Changing only one may decrease run time, but will likely cause a loss of resolution.

Chromatographer's Triangle

Optimizing chromatographic parameters requires compromise:



Why Column Length Affects Efficiency

Resolution equation:

Selectivity (α)

$$R_S = \{k/(1 + k)\}\{(\alpha - 1)/\alpha\}\{N^{1/2}/4\}$$

Capacity (k)

Efficiency (N)

Relationship between L and N:

$$N = L/H$$

Therefore:

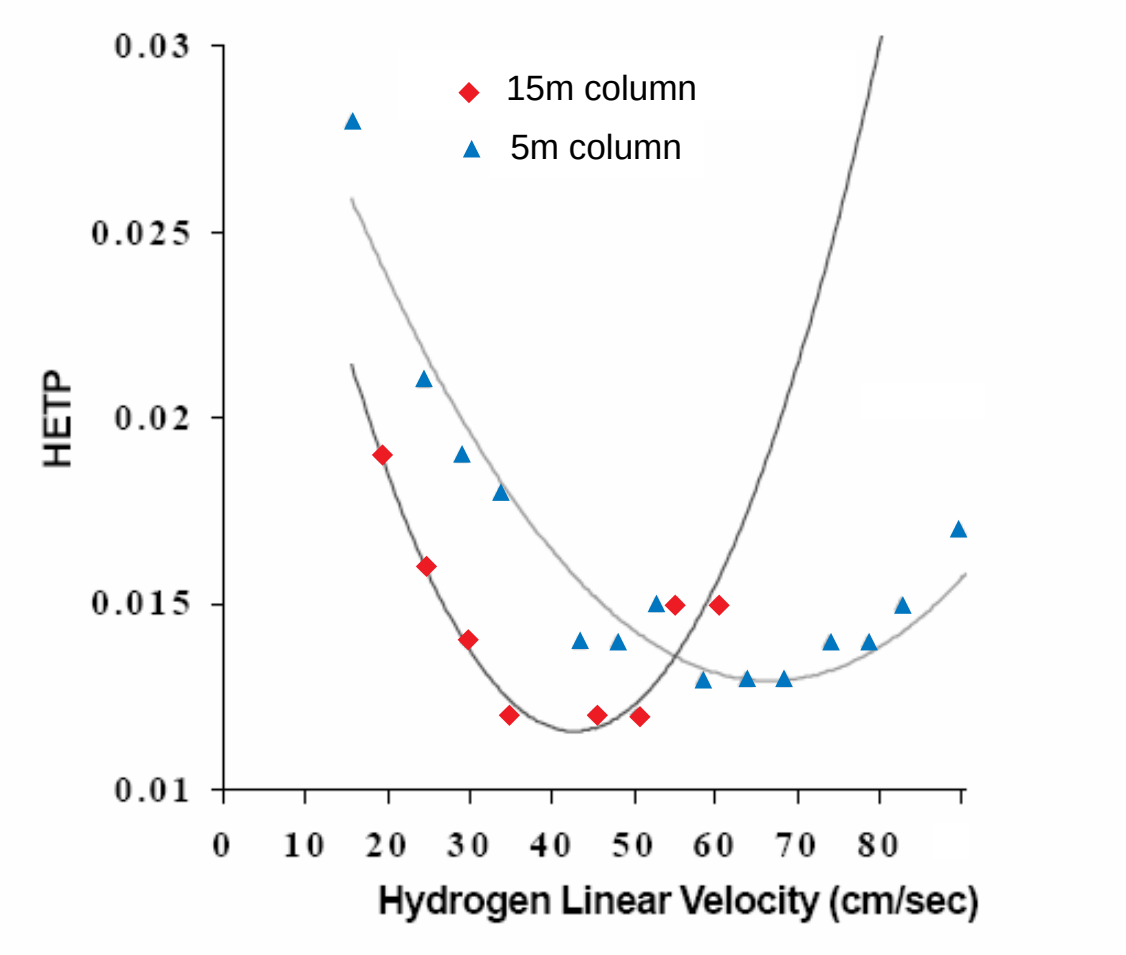
- Reducing L, reduces N

Column Length and Efficiency

Golay plots for long (15 meter) and short (5 meter) capillary columns

- 0.10 mm I.D.
- Hydrogen carrier gas

Short columns give higher efficiency at higher linear velocities



Narrow I.D. Columns: Efficiency Advantages

Typical plate numbers generated by capillary columns of various dimensions.

Also improves s/n ratio.

Column ID (mm)	Plate Number (N_{eff})	Plates/meter (N_{eff}/m)
0.10	219000	7300
0.18	121500	4050
0.20	109500	3650
0.25	87750	2925
0.32	69000	2300

Theoretical values, calculated at a retention factor of 6.00 and 85% coating efficiency.

Other parameters for Fast GC

Stationary phase & film thickness

- Changing the phase can result in a decrease in analysis time.
- Decreasing the film thickness will decrease the analysis time.

Carrier gas

- Hydrogen is the best choice for Fast GC
  - High diffusivity, high u_{opt}

Carrier gas linear velocity

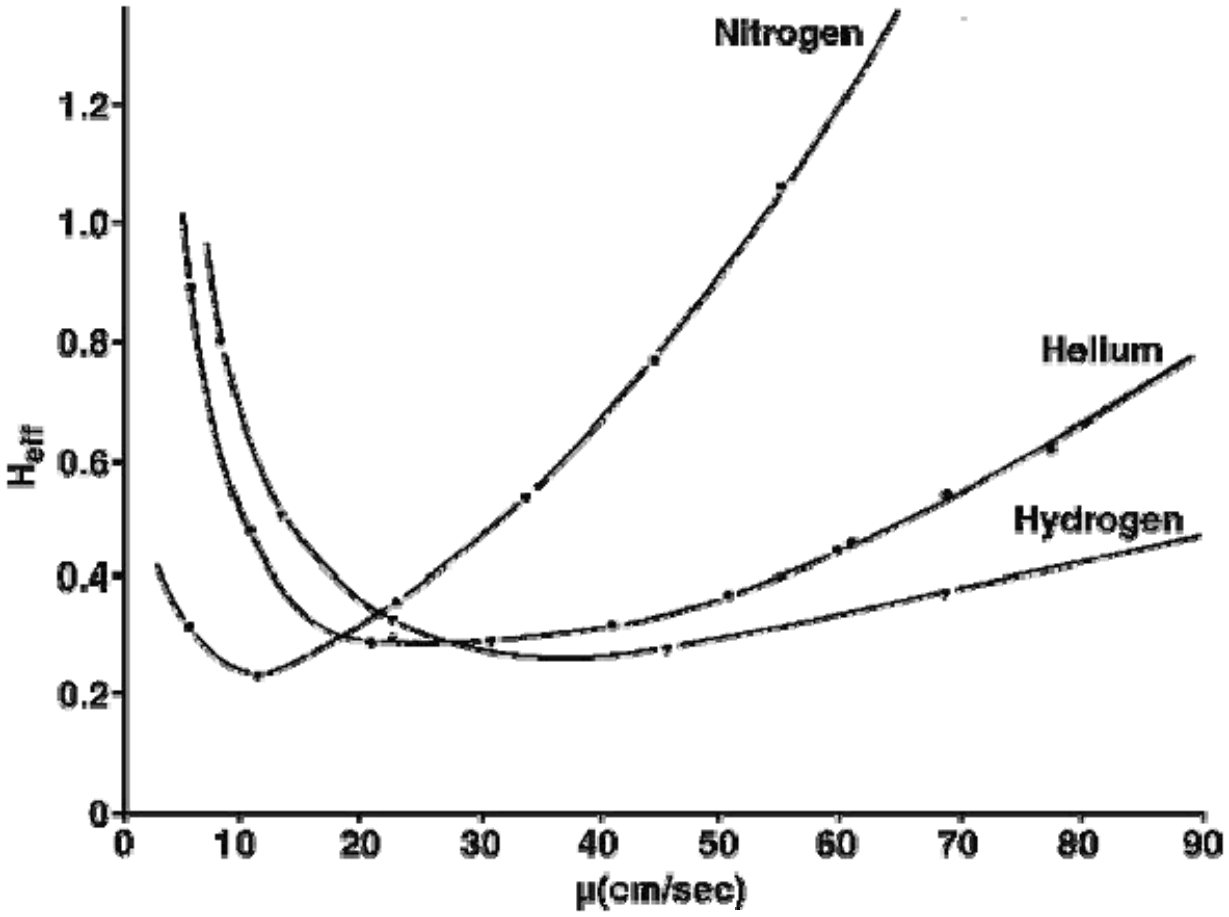
- Increasing the carrier gas linear velocity will increase the speed of analysis.
- Loss of resolution can occur if the speed is increased much higher than the optimal velocity for the carrier gas.

(continued)

Golay Plots: Comparing Carrier Gases

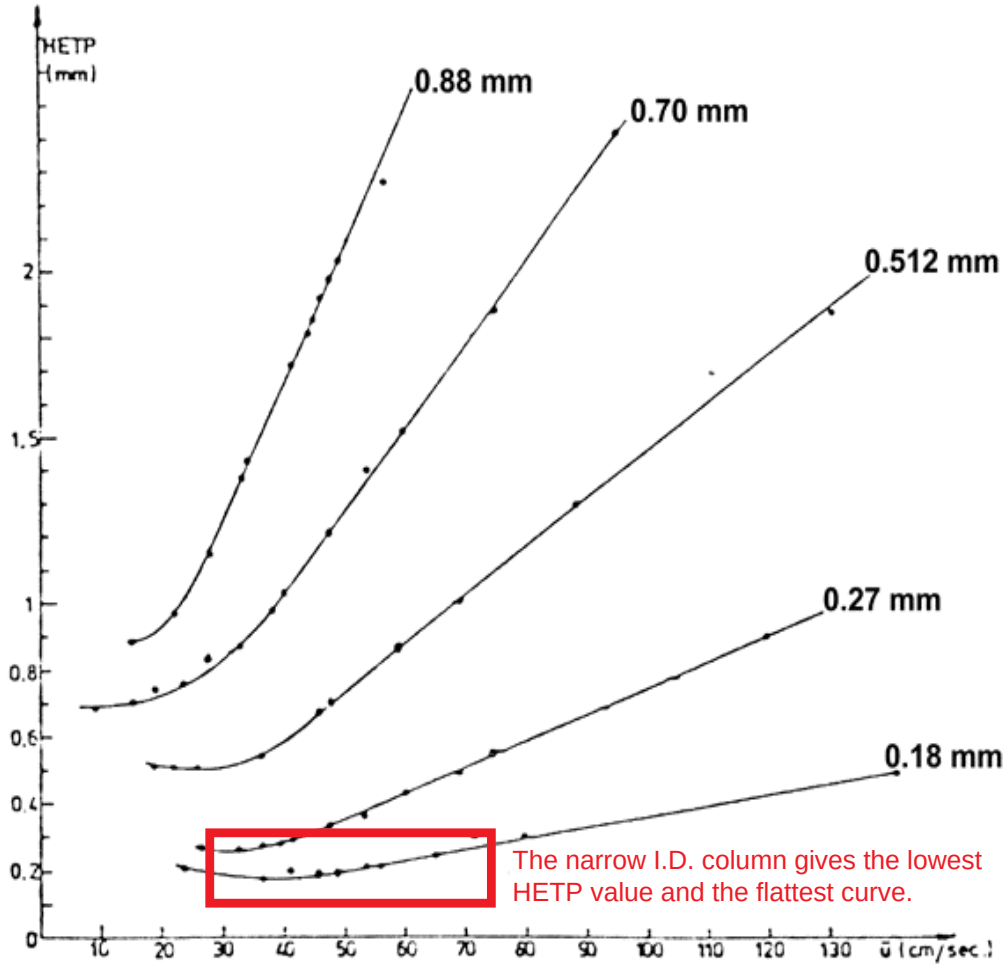
Using hydrogen and higher linear velocity will improve efficiency.

Hydrogen also has a flatter Golay relationship than helium and gives better efficiency at higher linear velocities.



Column I.D. and Optimum Linear Velocity

As this figure shows, columns with narrow I.D. have higher efficiency (lower HETP) and can be operated at higher linear velocities than larger I.D. columns.



From P. Sandra and C. Bicchi, “Capillary Gas Chromatography in Essential Oil Analyses,” Huethig, 1987

Other Parameters for Fast GC (cont'd)

Analysis temperature & temperature program rate:

- Increasing the analysis temperature for an isothermal analysis will decrease analysis time.
- It may result in a loss of resolution if the temperature increase is too high.
- A faster temperature program rate will decrease analysis time, but may result in a loss of resolution.
- 0.10 mm I.D. capillary columns typically require a program rate of 1.5 to 2 times faster than a wider bore column to retain their inherent efficiency.

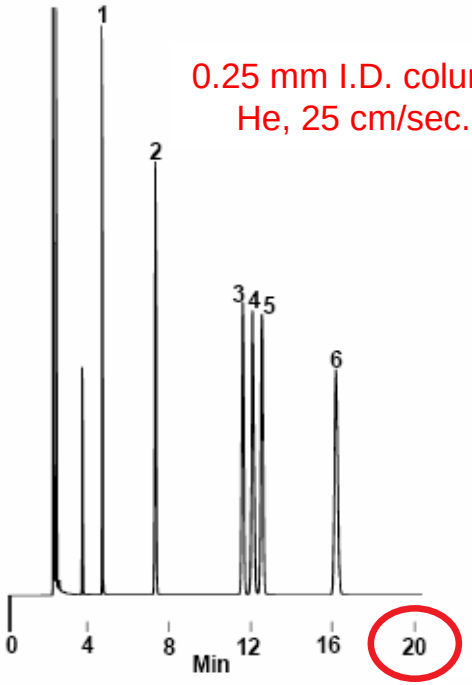
BTEX compounds

0.10 mm I.D. column provides over 10-times faster analysis than the 0.25 mm I.D. column

Columns: Supelcowax 10, 30m x 0.25mm ID, 0.25µm film
or 5m x 0.10mm ID, 0.1µm film
Oven: 60°C
Carrier: 0.25mm ID: helium, 25cm/sec, set at 60°C
0.10mm ID: helium, 50cm/sec, set at 60°C
Det.: FID, 250°C
Inj.: 1µL split, 100:1 (0.25mm ID) or 200:1 (0.10mm ID), 250°C

Narrow column I.D. (0.1 mm) and high linear velocity

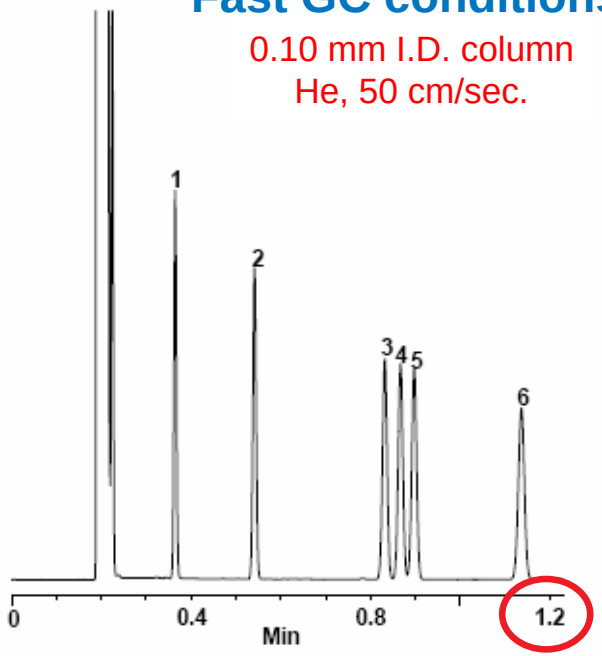
0.25 mm I.D. column
He, 25 cm/sec.



1. Benzene
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. m-Xylene
6. o-Xylene

Fast GC conditions

0.10 mm I.D. column
He, 50 cm/sec.



Focus on Fast GC in Food Labs

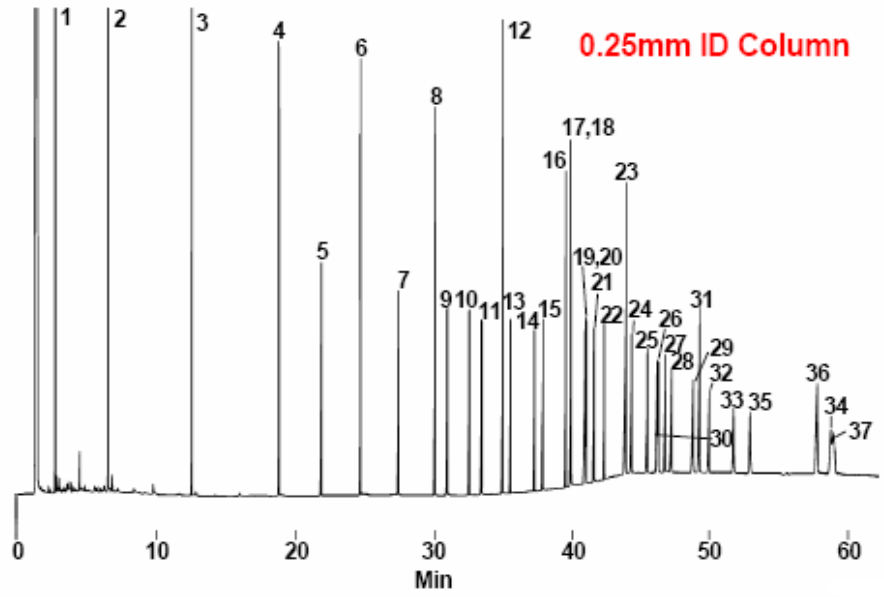
Challenges in food analysis:

- Labeling requirements
- More detailed analysis
- More samples to analyze
- Resolve positional cis/trans isomers
- Trans fats and the Omega 3 and 6 fatty acids (as FAMEs)
  - AOAC Method 996.06
  - 100 meter capillary column
  - Expensive & time-consuming

Fatty Acid Methyl Esters – 0.25 mm I.D. Column (Conventional GC)

Analysis time on the conventional 0.25 mm I.D. column is nearly one hour.

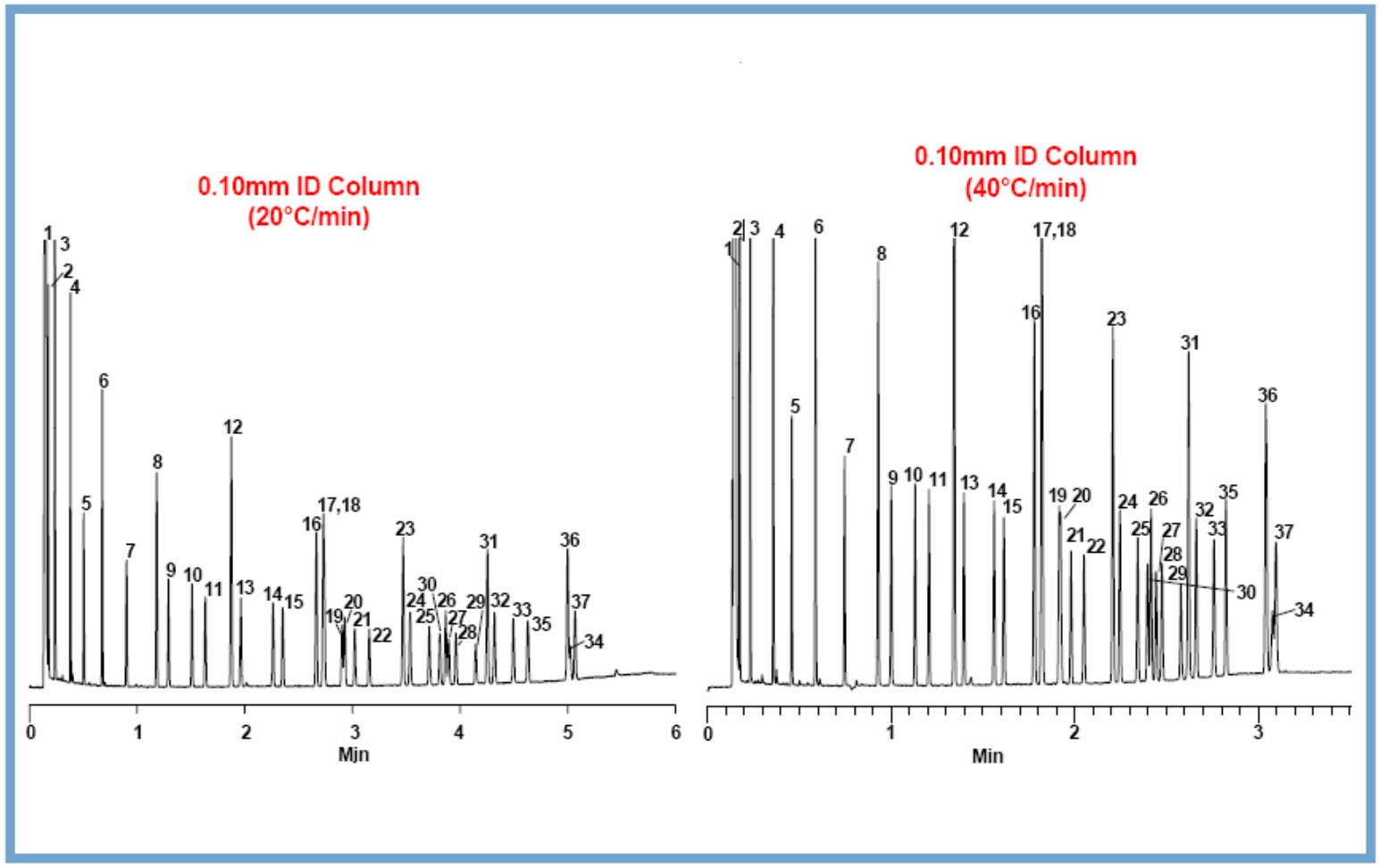
Columns: Supelcowax 10, 30m x 0.25mm ID, 0.25µm film
or 5m x 0.10mm ID, 0.1µm film
Oven: 0.25mm ID: 50°C (2 min) to 220°C at 4°C/min (hold 15 min)
0.10mm ID (center): 140°C to 250°C at 20°C/min (hold 5 min)
0.10mm ID (bottom): 140°C to 250°C at 40°C/min (hold 5 min)
Carrier: 0.25mm ID: helium, 30cm/sec, set at 205°C
0.10mm ID: helium, 50cm/sec, set at 140°C
Det.: FID, 250°C
Inj.: 1µL split, 100:1 (0.25mm ID) or 200:1 (0.10mm ID), 250°C



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

Fatty Acid Methyl Esters – 0.10 mm I.D. Column (Fast GC)

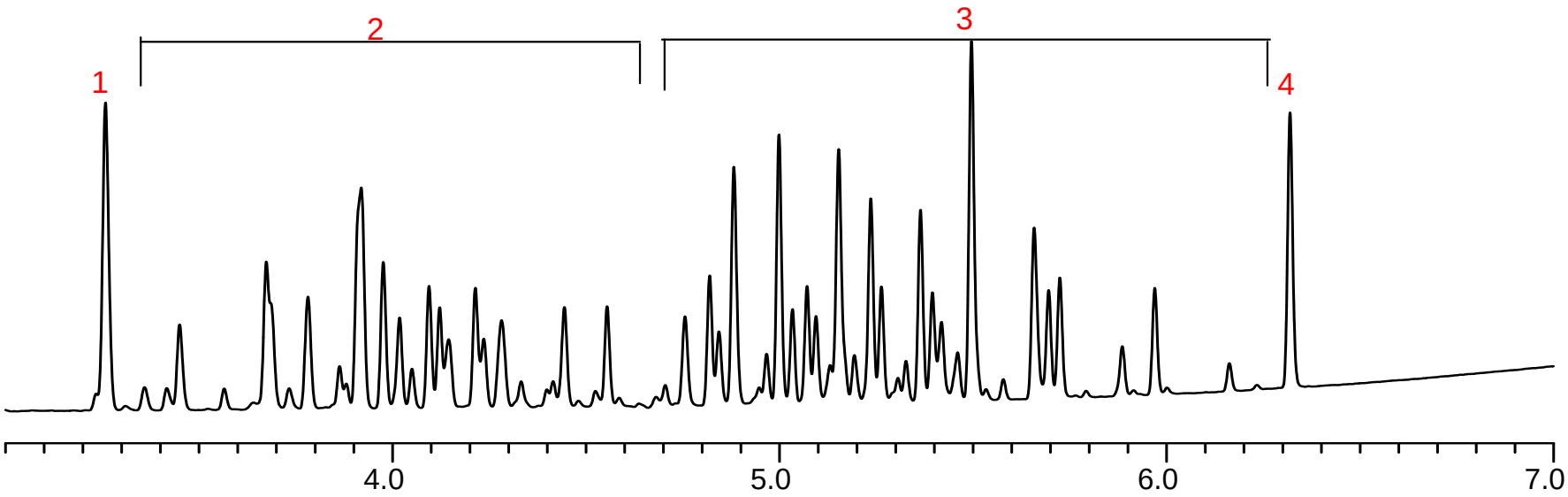
Analysis time on the 0.10 mm I.D. columns, shown here at two different temperature programs, is as much as 20-times faster than the 0.25 mm I.D. column.



SIGMA-ALDRICH®

Aroclors: Fast GC Analysis

6 minutes analysis on 0.10 mm I.D. column.



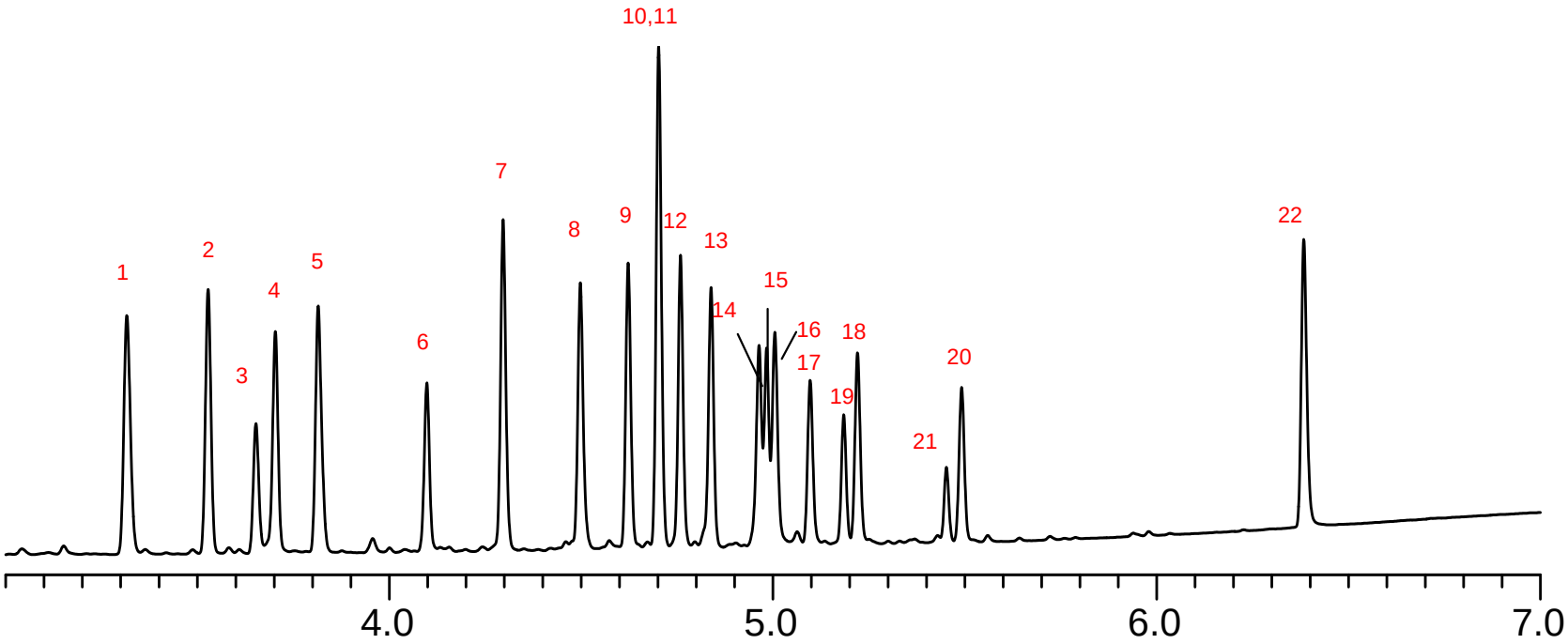
Column:	Equity-5, 15 m x 0.10 mm I.D., 0.10 µm
Oven:	100°C (0 min), 50°C/min. to 200°C (0 min.), 35°C/min. to 360°C (1 min.)
Inj.:	225°C
Det.:	ECD, 360°C
Carrier:	Hydrogen, 30 cm/sec. constant
Injection:	2µL, splitless (0.75 min.)
Liner:	4mm I.D. single taper
Sample:	200ppb of Aroclors® 1016 & 1260 with surrogates at 20ppb

Peak ID:

1. 2,4,5,6-Tetrachloro-m-xylene (surr.)
2. Aroclor 1016
3. Aroclor 1260
4. Decachlorobiphenyl (surr.)

Organochlorine Pesticides: 0.10 mm I.D. Column (Fast GC)

6 minutes analysis on 0.10 mm I.D. column.



Column: Equity-5, 15 m x 0.10 mm I.D. x 0.10 µm
Oven: 100 °C, 50 °C/min. to 200 °C, 35 °C/min. to 360 °C (1 min.)
Inj.: 225 °C
Det.: ECD, 360 °C
Carrier: Hydrogen, 30 cm/sec. constant
Injection: 2µL, splitless (0.75 min.)
Liner: 4 mm I.D., single taper
Sample: 50 ppb of a 22 component chlorinated pesticide standard in n-hexane

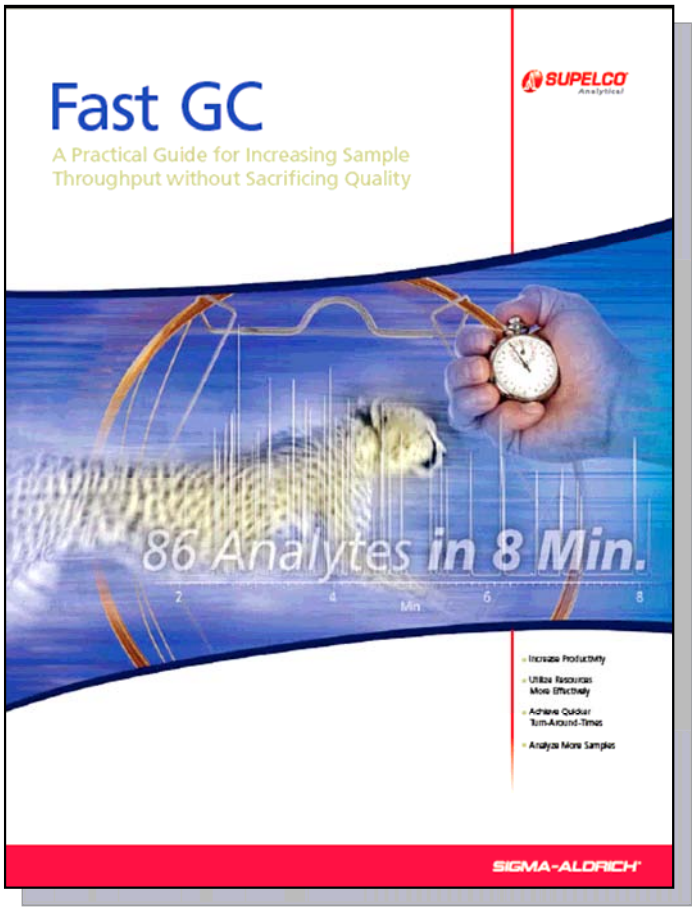
Instrument Requirements for Fast GC

Fast automatic injection
Split/splitless inlets
Fast ramp rate capability
High-speed detectors
Fast data handling
Method translation software

Agilent's 6890 and 6850 systems accommodate fast GC separations. Most GC instrument suppliers have Fast GC models.

Fast GC Dimensions

Phase	I.D. (mm)	Length (m)	df (µm)	Beta Value	Cat. No.
SPB-624	0.18	20	1.0	45	28662-U
VOCOL	0.18	20	1.0	45	28463-U
SLB-5ms	0.10	10	0.10	250	28465-U
		15	0.10	250	28466-U
	0.18	20	0.18	250	28564-U
		12	0.30	150	28566-U
		30	0.30	150	28575-U
		20	0.36	125	28576-U
Equity-1701	0.10	15	0.10	250	28343-U
TCEP	0.10	15	0.18	139	28348-U
Omegawax 100	0.10	15	0.10	250	23399-U
SP-2560	0.18	75	0.14	321	23348-U
SUPELCOWAX 10	0.10	5	0.10	250	25025-U
		10	0.10	250	25026-U
		15	0.10	250	24343
Equity-1	0.10	15	0.10	250	28039-U
SPB-1	0.10	15	0.10	250	24338
Equity-5	0.10	15	0.10	250	28083-U
SPB-5	0.10	15	0.10	250	24341



http://www.sigma-aldrich.com/gc

GC Innovations

- Fast GC – Special column dimensions
- **Ionic liquids for GC – SLB-IL100**
- Chiral GC

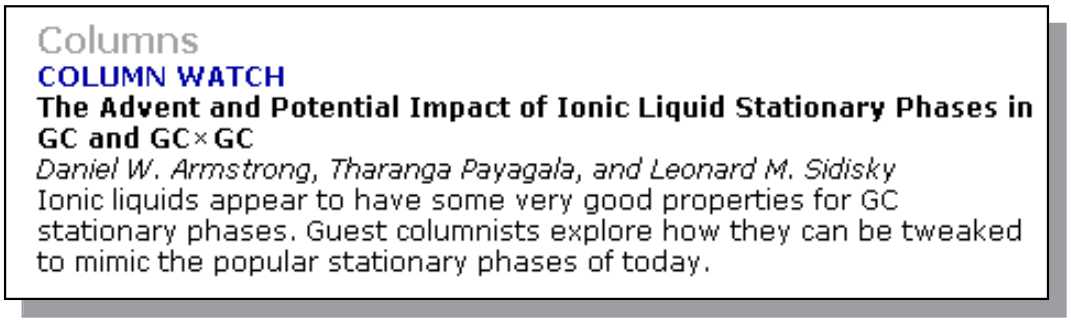
Ionic Liquids

Ionic liquids - a class of ionic solvents with low melting points.

Unique combination of cations and anions that can provide different selectivities when used as stationary phases in GC.

Numerous combinations of cations and anions are possible allowing for “tailored” selectivity, application or function.

Featured in August 2009 LC/GC:


Columns

COLUMN WATCH

The Advent and Potential Impact of Ionic Liquid Stationary Phases in GC and GC×GC

Daniel W. Armstrong, Tharanga Payagala, and Leonard M. Sidisky

Ionic liquids appear to have some very good properties for GC stationary phases. Guest columnists explore how they can be tweaked to mimic the popular stationary phases of today.

Desirable Ionic Liquid Properties for GC Use

Several properties make ionic liquids desirable as GC stationary phases:

1. Remain liquid over a wide temperature range (ambient →350^{o}C)
2. Very low volatility
3. Highly polar nature
4. Broadest range of solvation interactions of any known solvent
5. Good thermal stability for an intermediate to high polarity phase
6. High viscosity
7. Easily tailored to provide different polarities/selectivities

Ionic Liquids Characteristics as GC Phases

Compared to conventional GC phases:

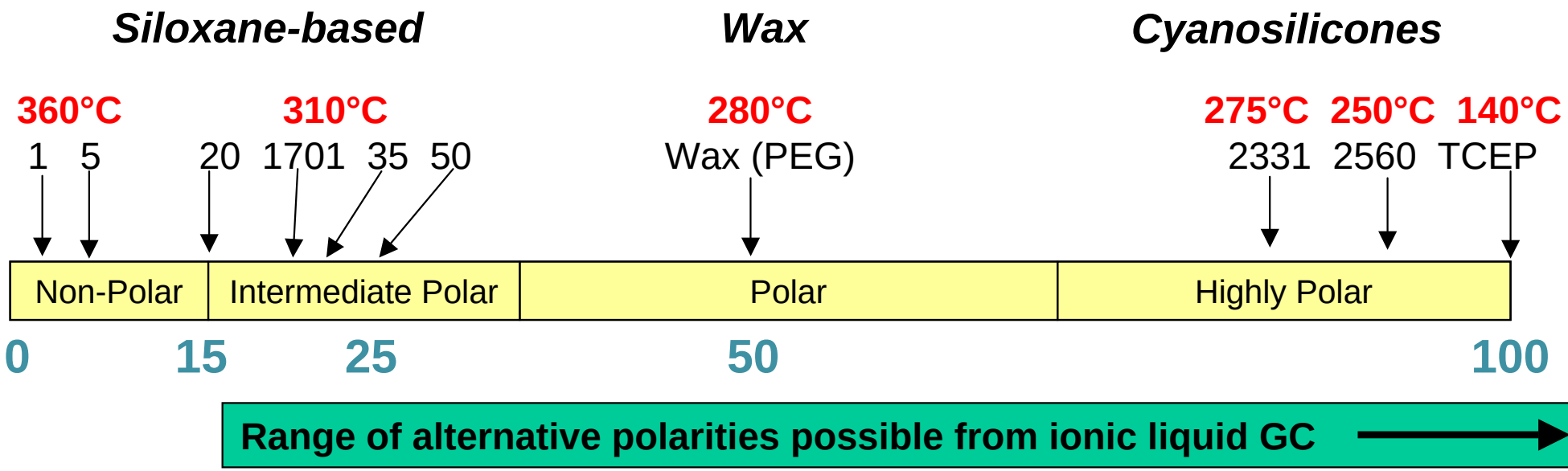
- Selectivity differences:
  - Intermediate to extremely polar
  - Multiple solvation interactions yields unique selectivity
- Stability & operating range:
  - Higher thermal stability than traditional phases of similar polarity
  - Lower column bleed
  - Simple m/z bleed fragmentation patterns (smaller m/z fragments)
  - Stable retention times
  - Long column life
  - Lower minimum operating temperature
  - Resistant to damage from moisture/oxygen in carrier gas/samples
  - Less prone to damage from acidic/basic compounds in samples

GC Column Polarity Scale

GC column polarity scale:

0 = squalane (considered the least polar GC stationary phase)

100 = TCEP (considered the most polar GC stationary phase)



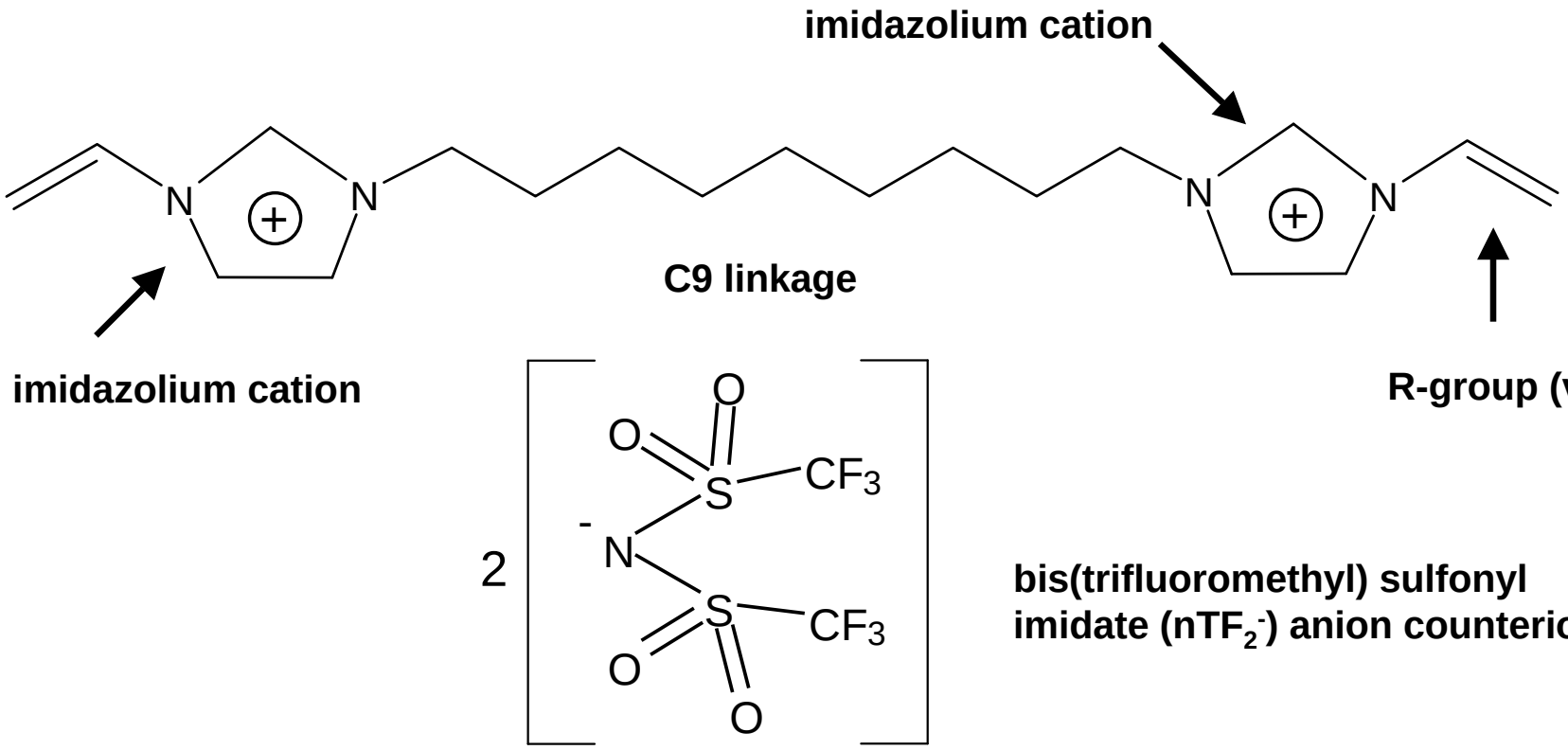
Ionic Liquid Stationary Phases for GC

ILs for GC possess:

- Cation (imidazolium shown)
- Anion (nTF_2^- shown)
- Linker or connecting group
- Functional groups on the cation

SLB-IL100 – Geminal dicationic ionic liquid

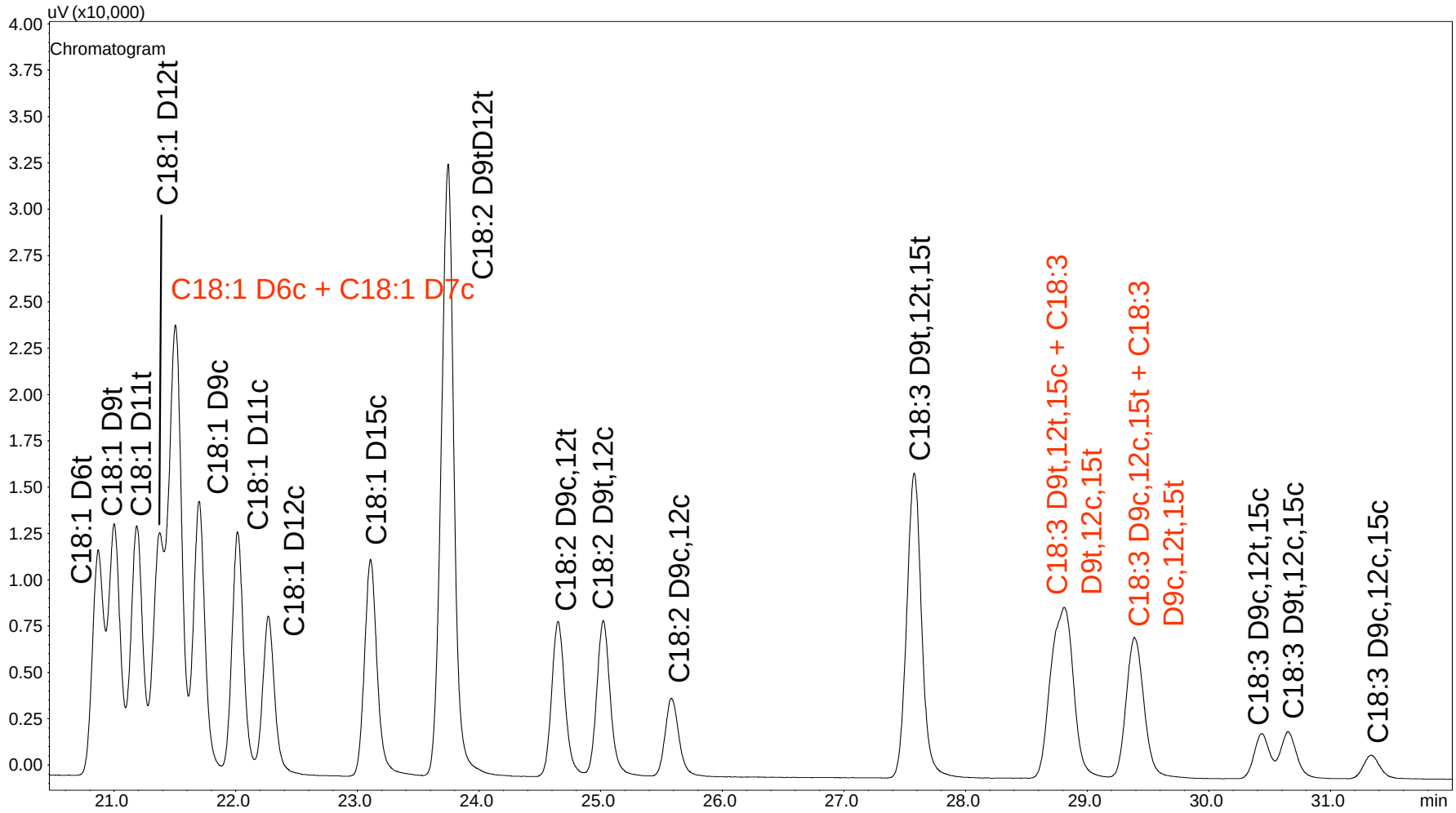
1,9-di(3-vinyl-imidazolium) nonane bis(trifluoromethyl) sulfonyl imidate



bis(trifluoromethyl) sulfonyl imidate (nTF_2^-) anion counterion

SP-2560: 22 Isomers, AOCS Conditions

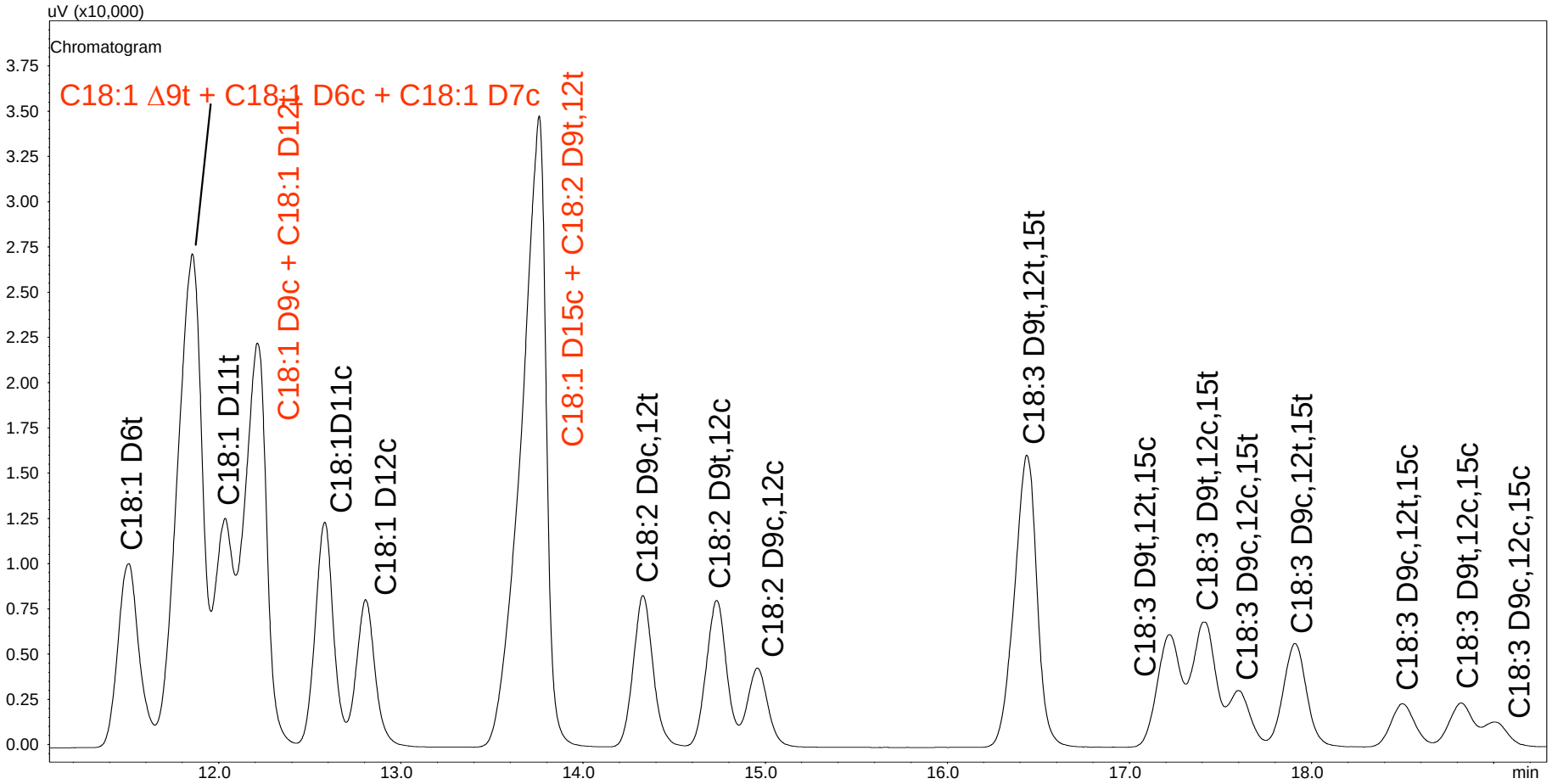
180°C, H_2 at 25 cm/s in ~ 32 min.



Column: SP-2560, 100 m x 0.25 mm I.D. 0.20mm film; Inj. vol.: 1µL; Sample: C18:1 isomer mix + Linolenic acid methyl ester isomer mix (Supelco Cat. No. 47792) + Linoleic acid methyl ester mix, cis/trans (Supelco Cat. No. 47791) in dichloromethane. Split ratio: 1:20 (220 °C); Temp. progr.: Isothermal at 180°C; Press. progr.: 161.6 kPa at linear velocity constant; Carrier gas: H_2; u: 25.0 cm/s; Detector: FID (220 °C) H_2: 50 mL/min., Air: 400 mL/min, Make-up: 50 mL/min kPa (N_2); Sampling rate: 80 msec; Filter Time Constant: 200 msec

SLB-IL100: Ionic Liquid GC Phase

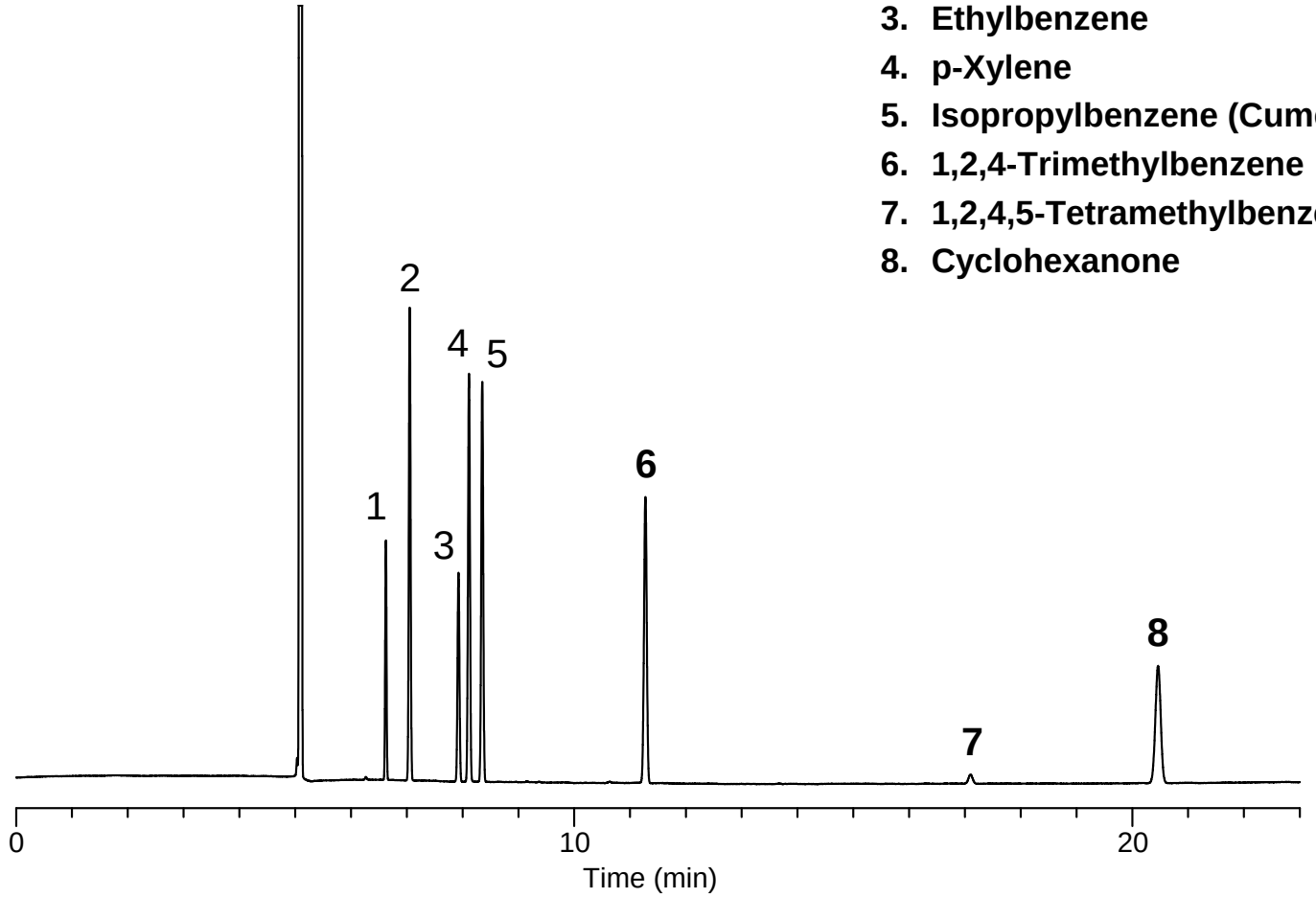
150°C, H_2 at 30 cm/s in ~ 19 min.



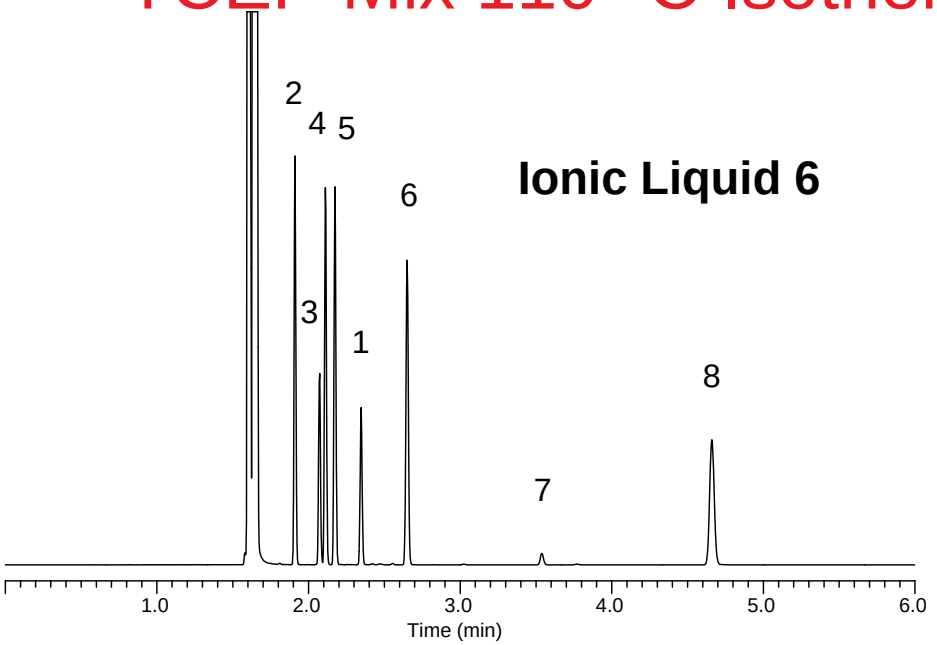
Column: SLB-IL100 30 m x 0.25 mm I.D., 0.20mm film; Inj. vol.: 2 µL; Sample: C18:1 Isomer mix + Linolenic acid methyl ester isomer mix (Supelco Cat. No. 47792) + Linoleic acid methyl ester mix, cis/trans (Supelco Cat. No. 47791) in dichloromethane. Split ratio: 1:20 (240 °C); Temp. progr.: Isothermal at 150°C; Press. progr.: 52.8 kPa at linear velocity constant; Carrier gas: H_2; u: 30.0 cm/s; Detector: FID (240 °C) H_2: 50 mL/min, Air: 400 mL/min, Make-up: 50 mL/min kPa (N_2); Sampling Rate: 80 msec; Filter Time Constant: 200 msec

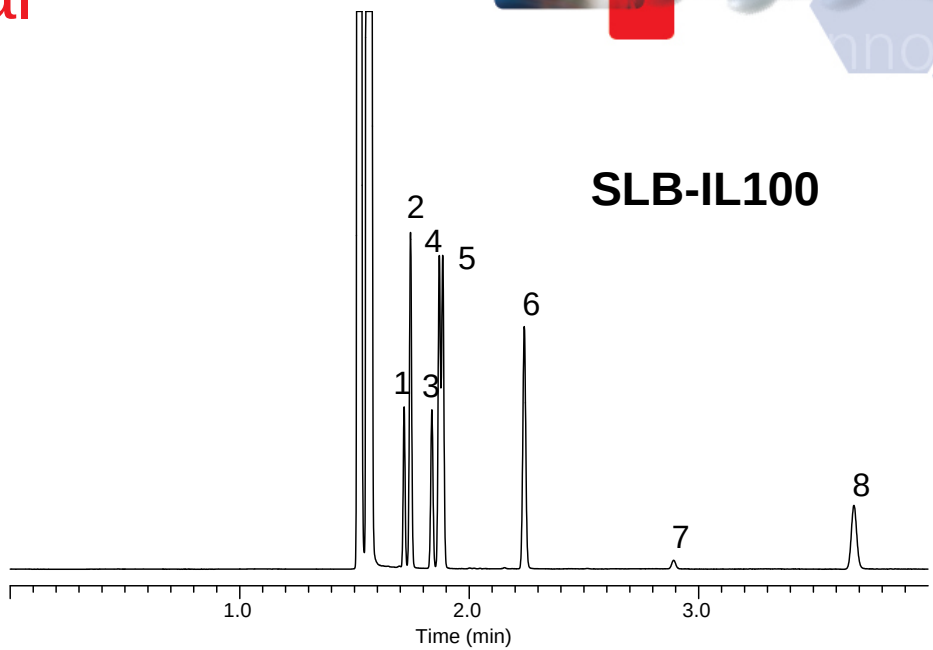
TCEP Mix on TCEP Column 110 °C

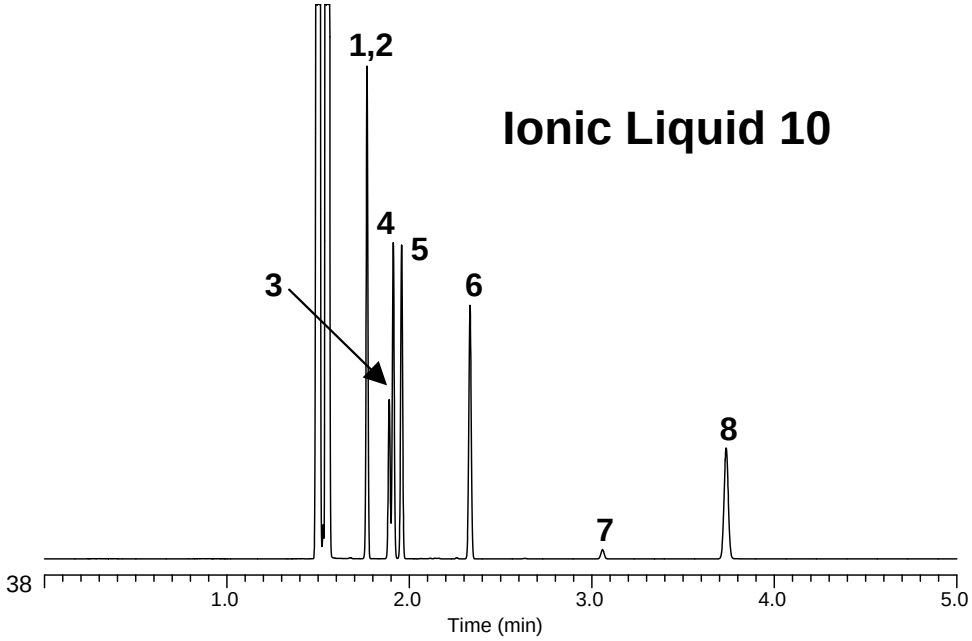
1. n-Tridecane
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. Isopropylbenzene (Cumene)
6. 1,2,4-Trimethylbenzene
7. 1,2,4,5-Tetramethylbenzene (Durene)
8. Cyclohexanone



TCEP Mix 110 °C Isothermal

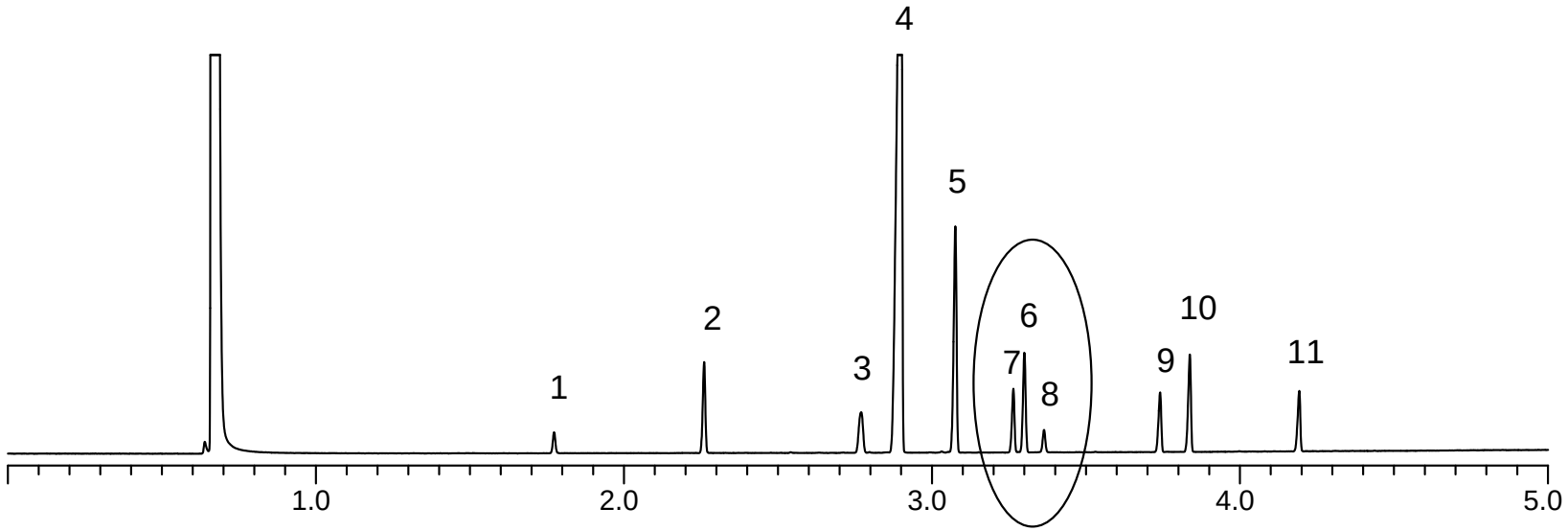






1. n-Tridecane
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. Isopropylbenzene (Cumene)
6. 1,2,4-Trimethylbenzene
7. 1,2,4,5-Tetramethylbenzene (Durene)
8. Cyclohexanone

Rapeseed Oil – SP-2560

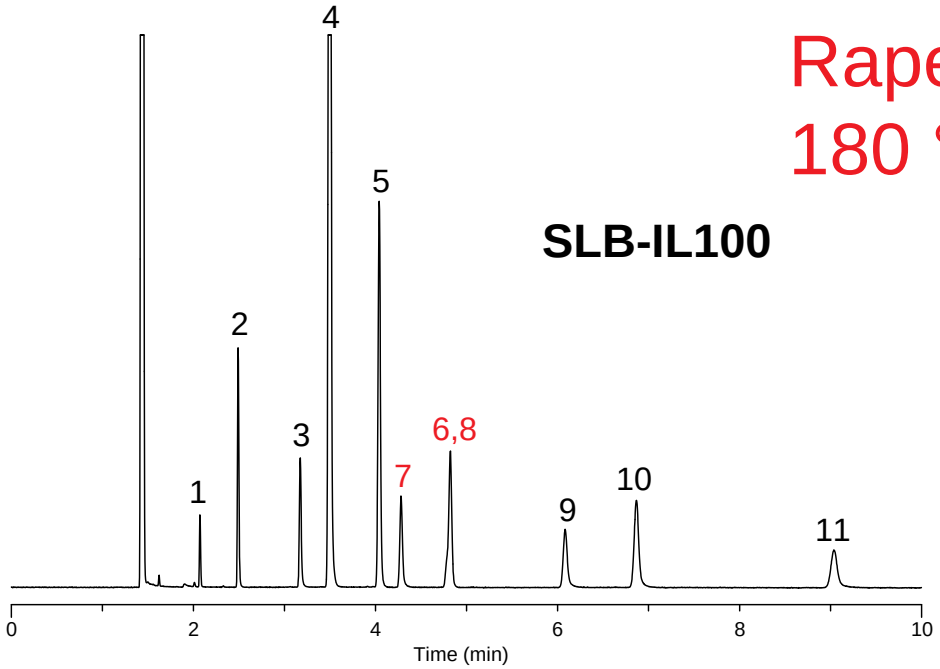


column:	SP-2560, 15 m x 0.10 mm I.D. x 0.08 µm
oven:	125 °C (0 min.), 25 °C/min. to 245 °C (1 min.)
inj.:	220 °C
det.:	260 °C (FID)
carrier:	hydrogen, 45 cm/sec., constant flow
injection:	0.1 µL, split 300:1
liner:	4 mm I.D. cup split
sample:	rapeseed oil reference mix (methylated) (Cat. No. O7756-1AMP), diluted to 10 mg/mL in methylene chloride

Peak List

1. **Myristic (C14:0)**
2. **Palmitic (C16:0)**
3. **Stearic (C18:0)**
4. **Oleic (C18:1n9c)**
5. **Linoleic (C18:2)**
6. **Linolenic (C18:3)**
7. **Arachidic (C20:0)**
8. **cis-11-Eicosenoic (C20:1)**
9. **Behenic (C22:0)**
10. **Erucic (C22:1)**
11. **Lignoceric (C24:0)**

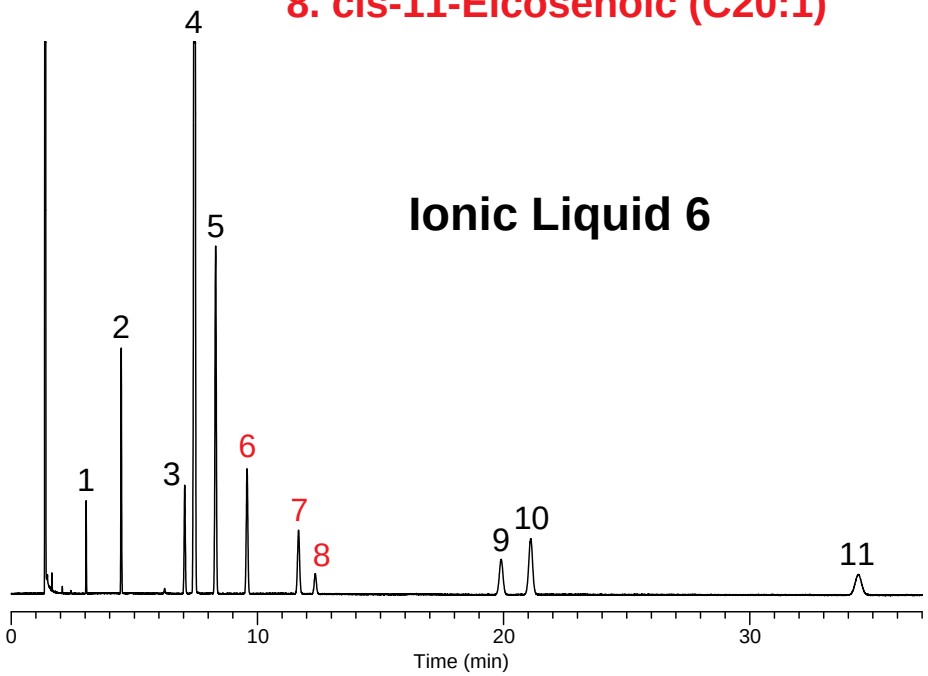
Rapeseed Oil FAMEs
180 °C Isothermal

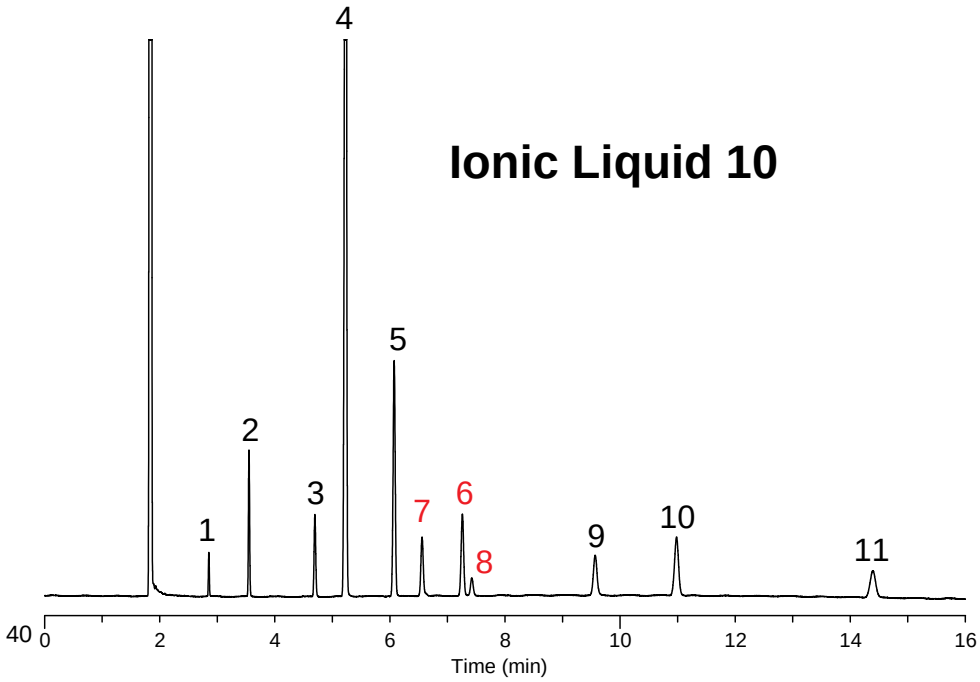


6. Linolenic (C18:3)

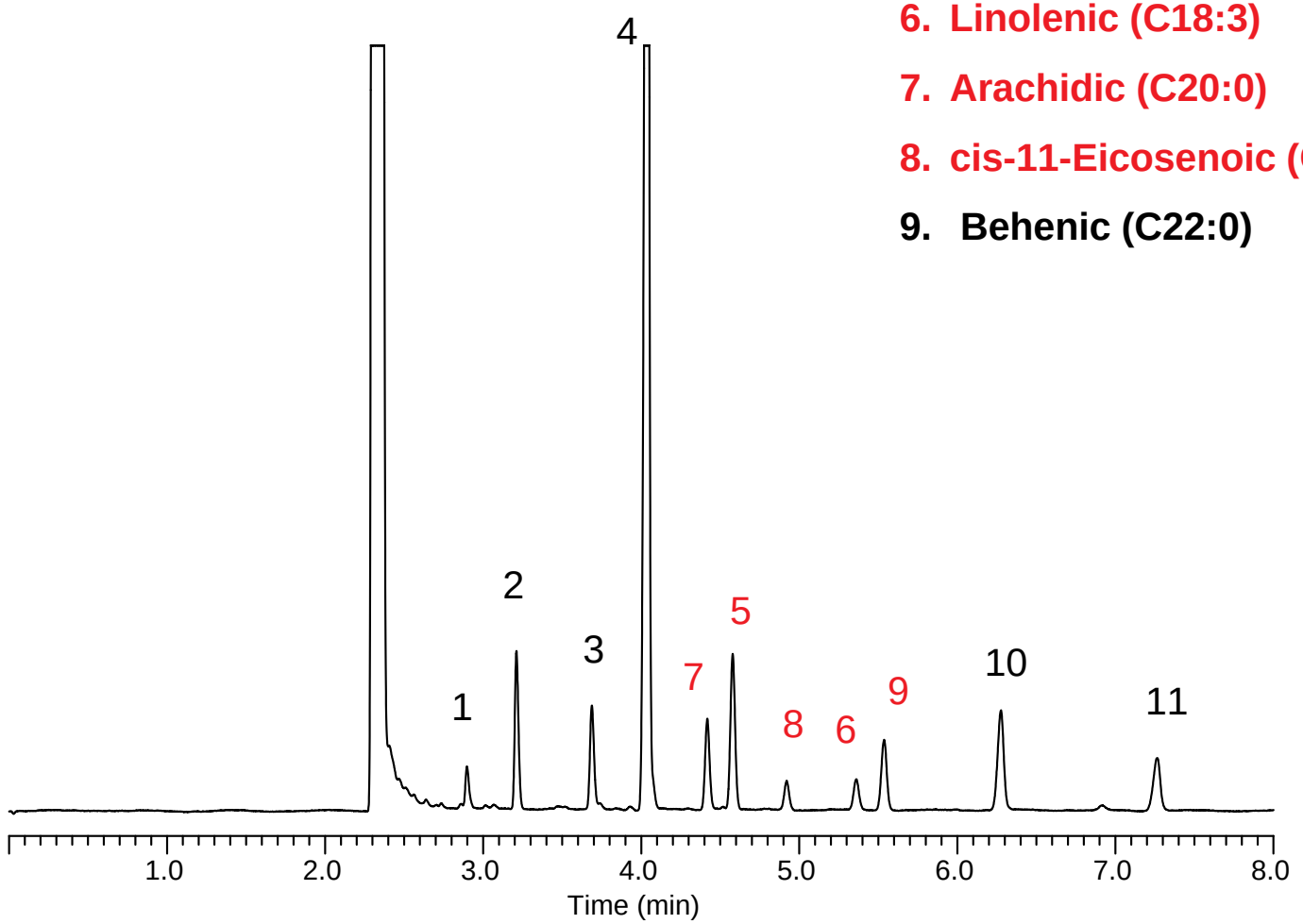
7. Arachidic (C20:0)

8. cis-11-Eicosenoic (C20:1)





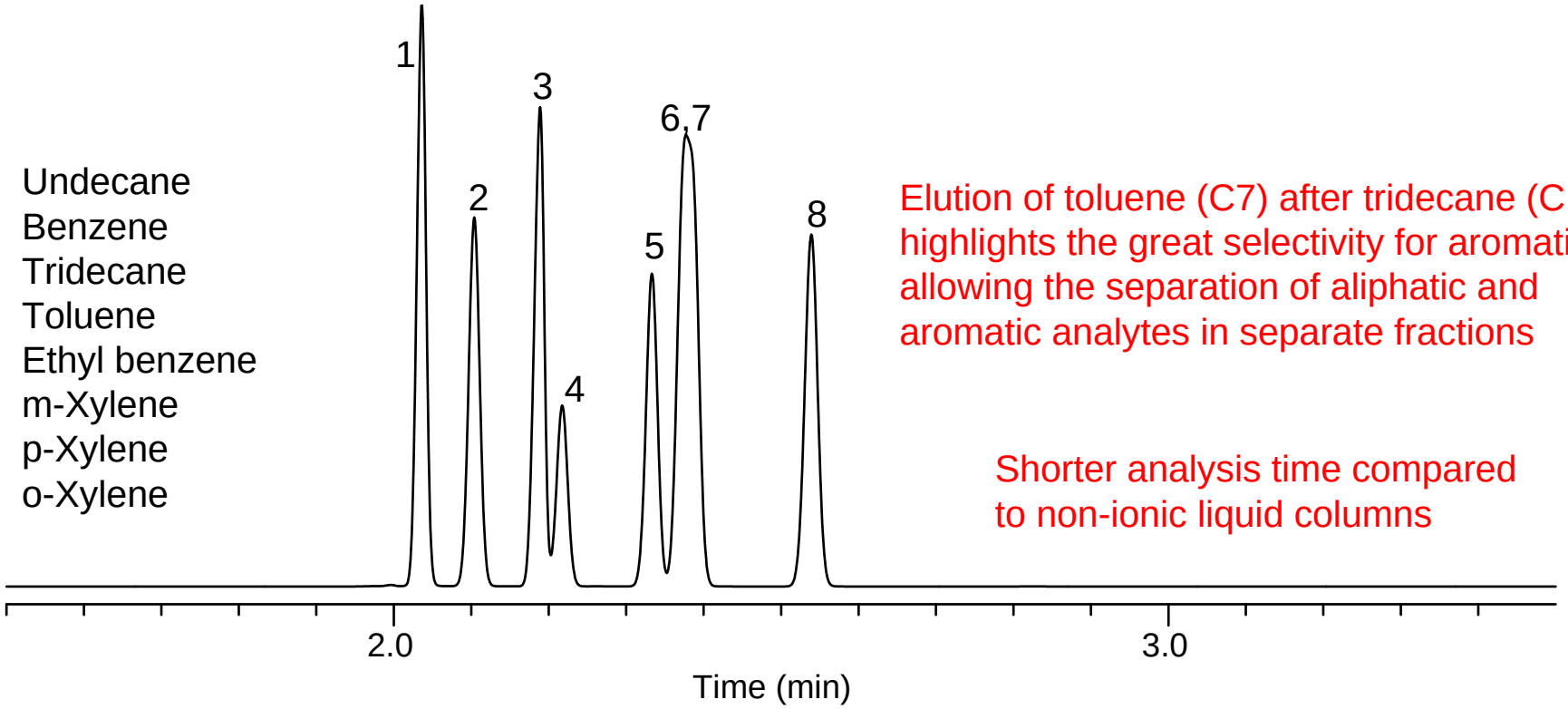
Rapeseed Oil FAMEs on Ionic Liquid 15
180 °C Isothermal



5. **Linoleic (C18:2)**
6. **Linolenic (C18:3)**
7. **Arachidic (C20:0)**
8. **cis-11-Eicosenoic (C20:1)**
9. **Behenic (C22:0)**

SLB-IL100 – BTEX and n-Alkanes

1. Undecane
2. Benzene
3. Tridecane
4. Toluene
5. Ethyl benzene
6. m-Xylene
7. p-Xylene
8. o-Xylene

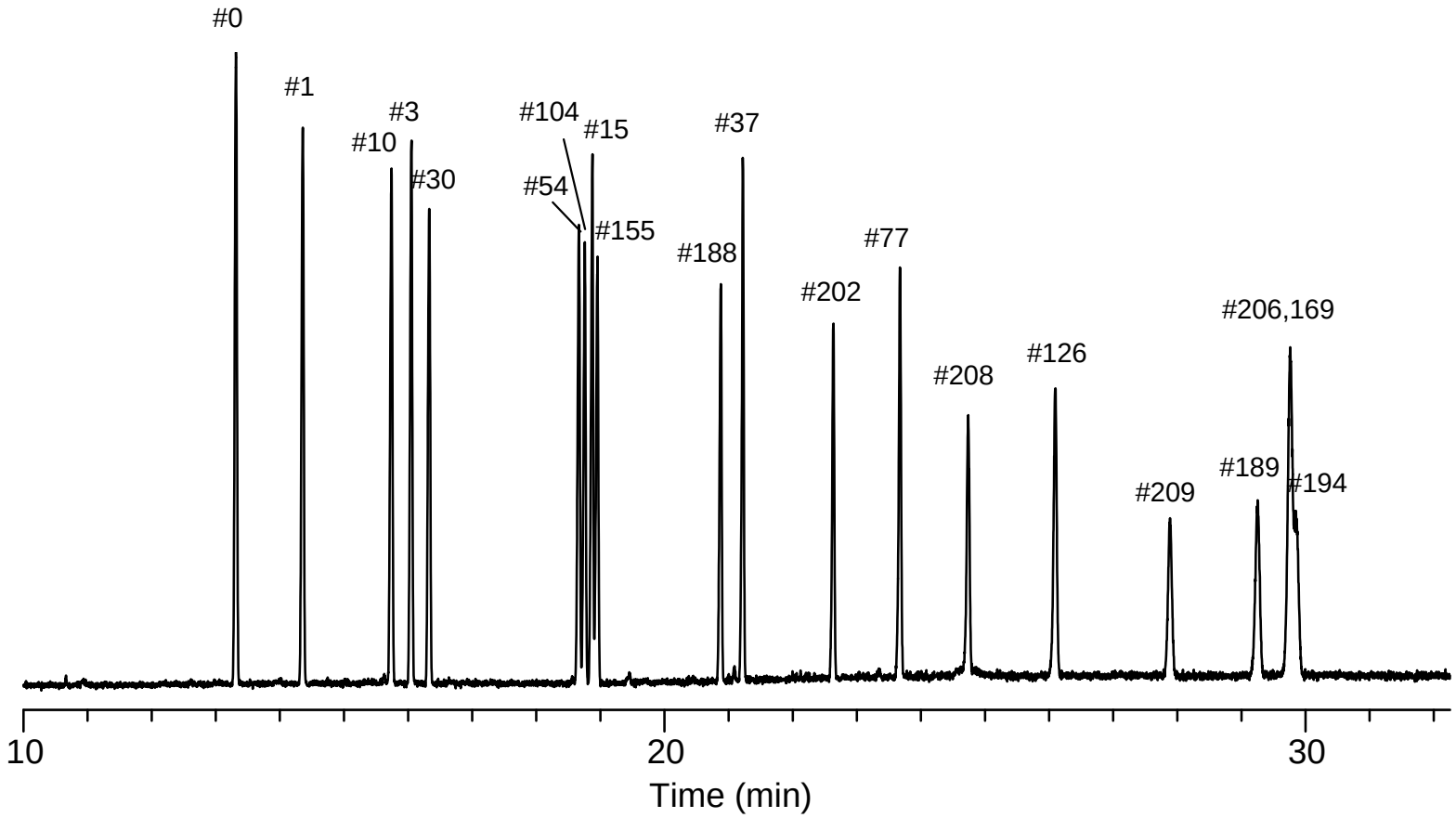


Elution of toluene (C7) after tridecane (C13) highlights the great selectivity for aromatics, allowing the separation of aliphatic and aromatic analytes in separate fractions

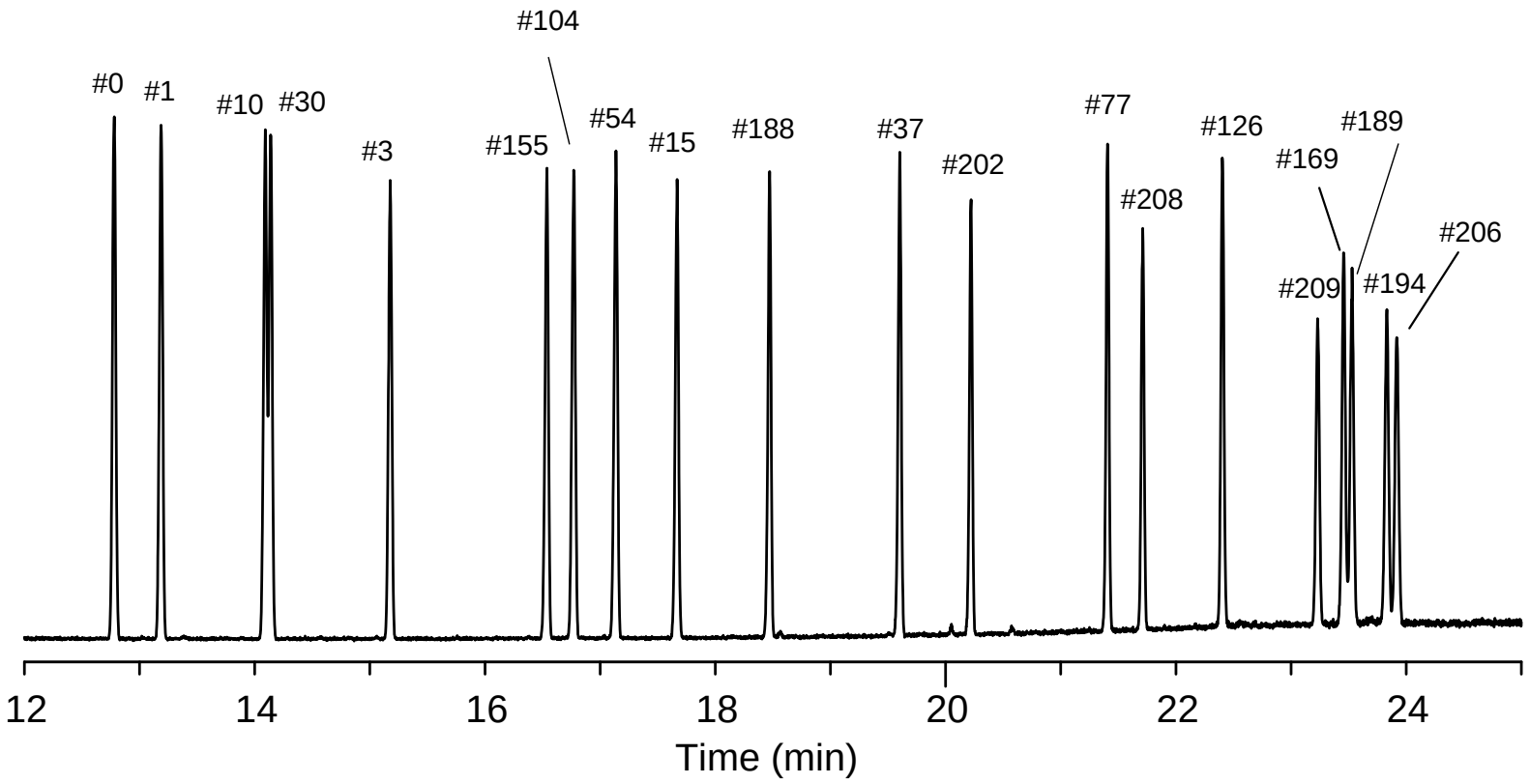
Shorter analysis time compared to non-ionic liquid columns

column:	SLB-IL100, 30 m x 0.25 mm I.D., 0.20 µm (28884-U)
oven:	110 °C
inj.:	250 °C
det.:	FID, 250 °C
carrier gas:	helium, 26 cm/sec @ 110 °C
injection:	0.1 µL, 300:1 split
liner:	4 mm I.D., split, cup
sample:	NEAT mixture containing varying percentages of each component

PCB Congener Standard (Biphenyl through Deca) on SP-2331



PCB Congener Standard (Biphenyl through Deca) on the SLB-IL100



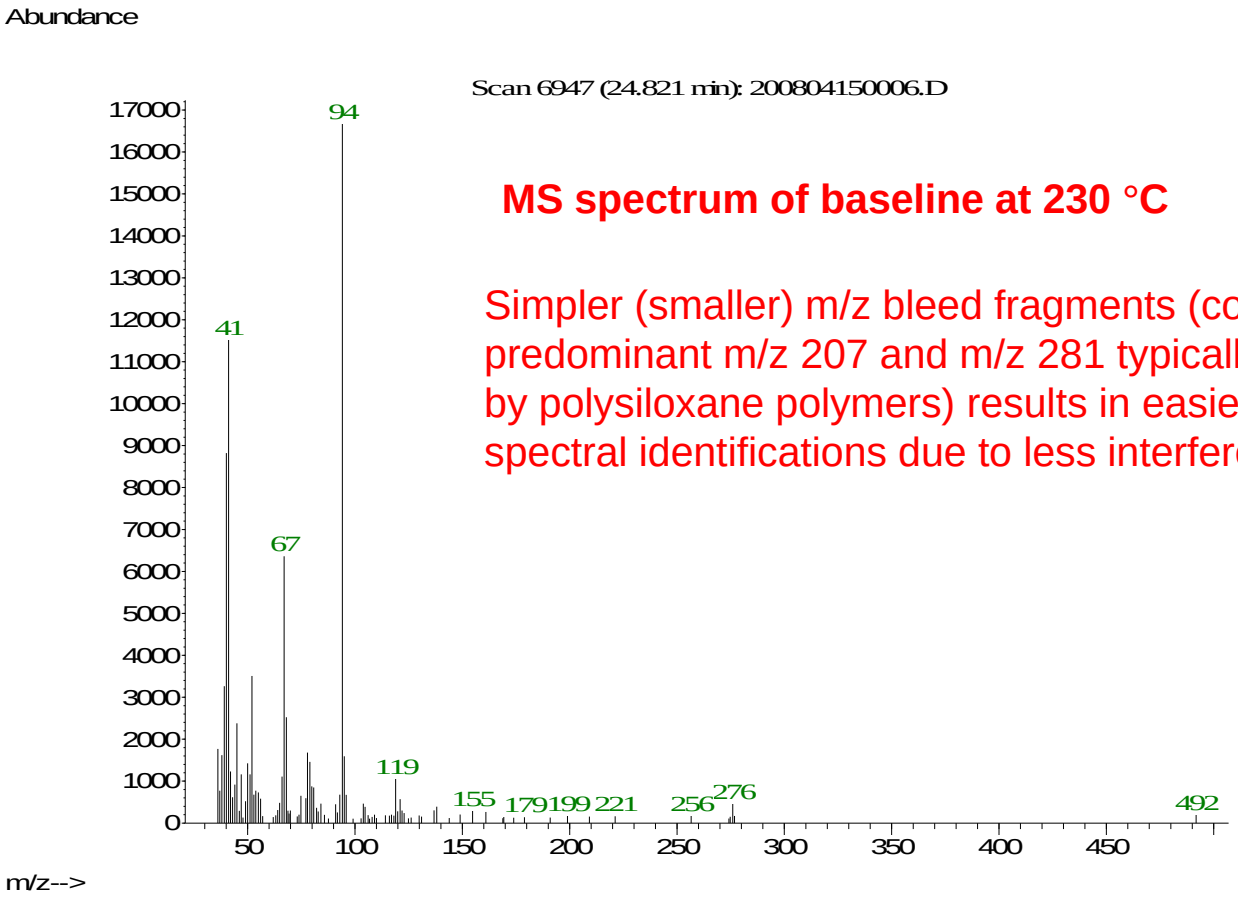
Run Conditions for PCB Congeners

Columns:	SP-2331, 30 m x 0.25 mm I.D., 0.20 µm d_f
	SLB-IL100, 30 m x 0.25 mm I.D., 0.20 µm d_f
Oven:	60 °C (1 min.), 8 °C/min. to 230 °C
Inj.:	250 °C
MSD interface:	220 °C
Carrier Gas:	helium, 1.5 mL/min. constant flow
Injection:	1 µL, splitless (splitter open at 1 min.)
Liner:	4 mm I.D. single taper
Sample:	PCB congener mix, 2.5 ppm each cpd. in n-hexane

PCB Congener ID's

#0: Biphenyl
#1: 2-monochlorobiphenyl
#3: 4-monochlorobiphenyl
#10: 2,6-dichlorobiphenyl
#15: 4,4'-dichlorobiphenyl
#30: 2,4,6-trichlorobiphenyl
#37: 3,4,4'-trichlorobiphenyl
#54: 2,2',6,6'-tetrachlorobiphenyl
#77: 3,3',4,4'-tetrachlorobiphenyl
#104: 2,2',4,6,6'-pentachlorobiphenyl
#126: 3,3',4,4',5-pentachlorobiphenyl
#155: 2,2',4,4',6,6'-hexachlorobiphenyl
#169: 3,3',4,4',5,5'-hexachlorobiphenyl
#188: 2,2',3,4',5,6,6'-heptachlorobiphenyl
#189: 2,3,3',4,4',5,5'-heptachlorobiphenyl
#202: 2,2',3,3',5,5',6,6'-octachlorobiphenyl
#194: 2,2',3,3',4,4',5,5'-octachlorobiphenyl
#208: 2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl
#206: 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
#209: Decachlorobiphenyl

SLB-IL100 – GC-MS Bleed Profile



MS spectrum of baseline at 230 °C

Simpler (smaller) m/z bleed fragments (compared to predominant m/z 207 and m/z 281 typically formed by polysiloxane polymers) results in easier mass spectral identifications due to less interference

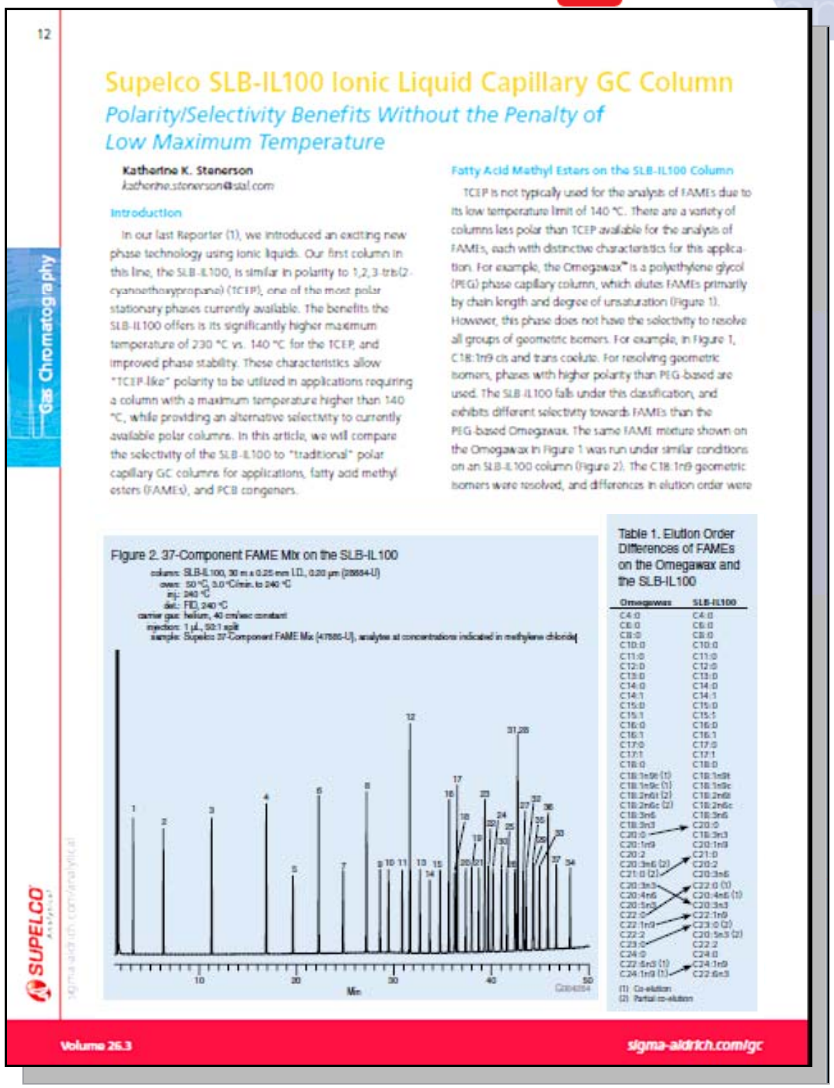
column: SLB-IL100, 30 m x 0.25 mm I.D., 0.20 µm (28884-U)
oven: 60 °C (1 min.), 8 °C/min. to 230 °C (5 min.)
inj.: 250 °C
MSD interface: 220 °C
scan range: m/z = 35-500
carrier gas: helium, 1.5 mL/min. constant
injection: 1 µL, splitless (1.0 min.)
liner: 4 mm I.D., single taper

Ionic Liquid GC Phases

- Higher maximum temperature
- Lower column bleed
- Smaller m/z bleed fragments
- Stable retention times
- Long column life
- Lower minimum temperature
- Resistant to damage from moisture/oxygen in carrier gas/samples
- Less prone to damage from acidic/basic compounds in samples
- Multiple solvation interactions

Supelco SLB-IL100:
15 m x 0.10 mm I.D., 0.08 µm df (28882-U)
20 m x 0.18 mm I.D., 0.14 µm df (28883-U)
30 m x 0.25 mm I.D., 0.20 µm df (28884-U)
60 m x 0.25 mm I.D., 0.20 µm df (28886-U)
30 m x 0.32 mm I.D., 0.26 µm df (28887-U)
60 m x 0.32 mm I.D., 0.26 µm df (28888-U)

IL36:
15 m x 0.10 mm I.D., 0.08 µm df (28880-U)
30 m x 0.25 mm I.D., 0.20 µm df (28891-U)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Supelco SLB-IL100 Ionic Liquid Capillary GC Column

Polarity/Selectivity Benefits Without the Penalty of Low Maximum Temperature

Katherine K. Stenerson
katherine.stenerson@sial.com

Introduction

In our last Reporter (1), we introduced an exciting new phase technology using ionic liquids. Our first column in this line, the SLB-IL100, is similar in polarity to 1,2,3-tris(2-cyanoethoxy)propane) (TCEP), one of the most polar stationary phases currently available. The benefits the SLB-IL100 offers is its significantly higher maximum temperature of 230 °C vs. 140 °C for the TCEP, and improved phase stability. These characteristics allow "TCEP-like" polarity to be utilized in applications requiring a column with a maximum temperature higher than 140 °C, while providing an alternative selectivity to currently available polar columns. In this article, we will compare the selectivity of the SLB-IL100 to "traditional" polar capillary GC columns for applications, fatty acid methyl esters (FAMEs), and PCB congeners.

Fatty Acid Methyl Esters on the SLB-IL100 Column

TCEP is not typically used for the analysis of FAMEs due to its low temperature limit of 140 °C. There are a variety of columns less polar than TCEP available for the analysis of FAMEs, each with distinctive characteristics for this application. For example, the Omegawax™ is a polyethylene glycol (PEG) phase capillary column, which elutes FAMEs primarily by chain length and degree of unsaturation (Figure 1). However, this phase does not have the selectivity to resolve all groups of geometric isomers. For example, in Figure 1, C18:1n9 cis and trans coelute. For resolving geometric isomers, phases with higher polarity than PEG-based are used. The SLB-IL100 falls under this classification, and exhibits different selectivity towards FAMEs than the PEG-based Omegawax. The same FAME mixture shown on the Omegawax in Figure 1 was run under similar conditions on an SLB-IL100 column (Figure 2). The C18:1n9 geometric isomers were resolved, and differences in elution order were

Figure 2. 37-Component FAME Mix on the SLB-IL100

Table 1. Elution Order Differences of FAMEs on the Omegawax and the SLB-IL100

Gas Chromatography

Volume 26.3

sigma-aldrich.com/gc

http://www.sigma-aldrich.com/gc

SIGMA-ALDRICH®

Ionic Liquid GC Phases

Currently the project is aimed at identifying research partners to develop novel uses for ionic liquid GC phases

More information and training will follow in the upcoming months

GC Innovations

- Fast GC – Special column dimensions
- Ionic liquids for GC – SLB IL100
- **Chiral GC – CHIRALDEX and Supelco DEX**

Users are...
- **GC and GC-MS analysts**
- **Performing chiral GC separations**

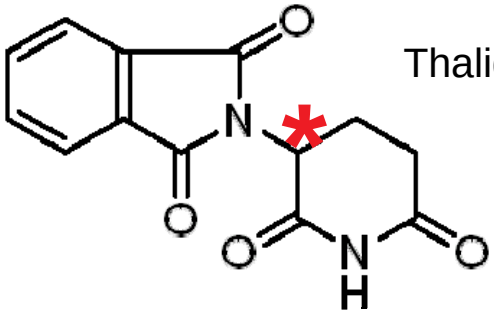
Interested in...
- **High enantioselectivity**
- **Using existing GC systems**

Users can expect...
- **High enantioresolution**
- **Choices in selectivities**

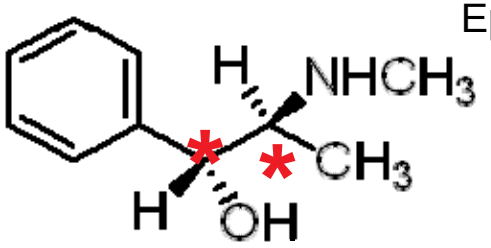
GC Innovations: Chiral GC

Enantiomers

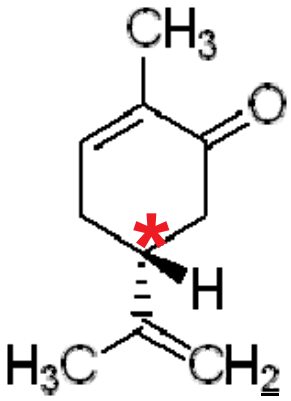
- Stereoisomers that differ in the direction they rotate a plane of polarized light are called optically active, or chiral, and their isomers are called enantiomers
- Non-superimposable mirror images
- Biological systems recognize chirality → **analysis**



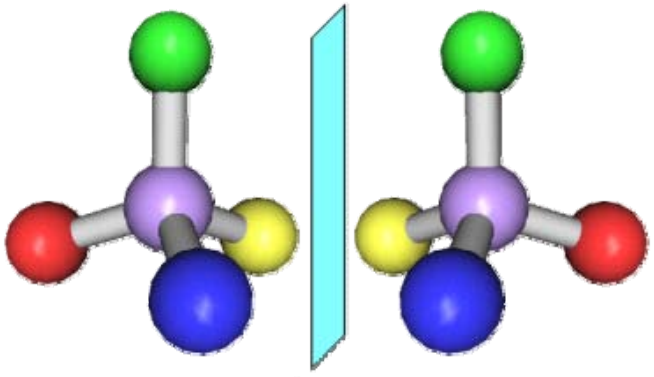
Thalidomide



Ephedrine

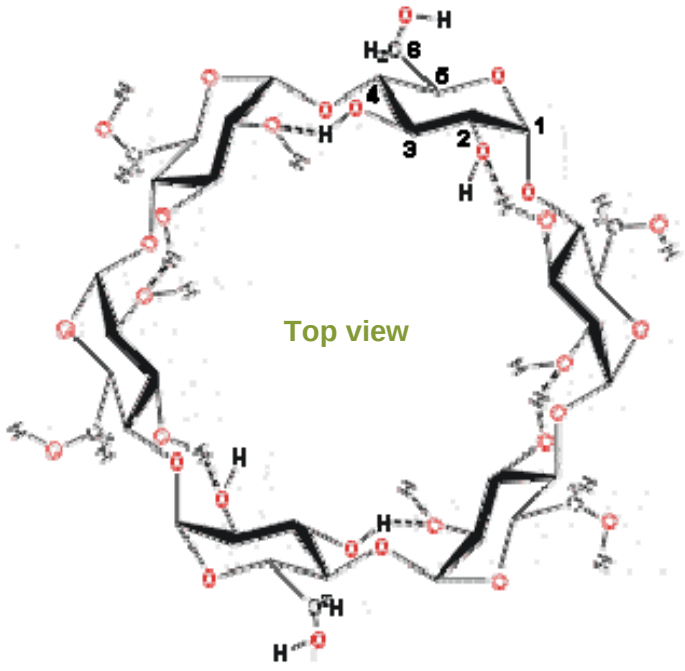


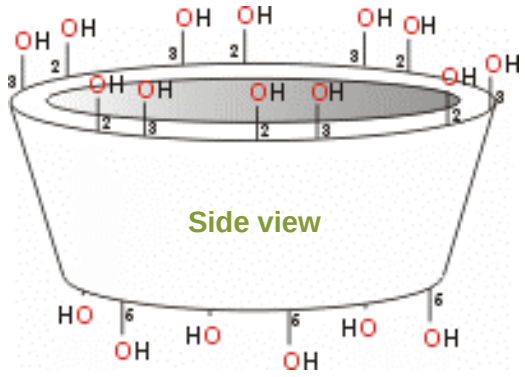
Carvone



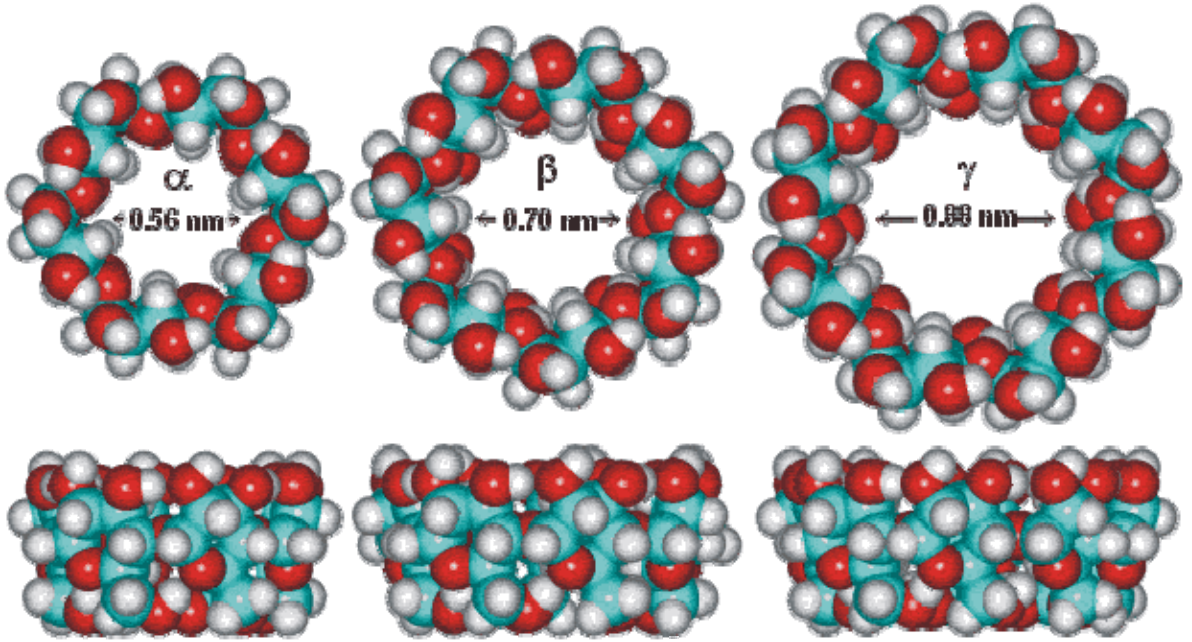
Two chiral molecules (enantiomers). The asymmetric carbon is the purple atom in the middle.

The Cyclodextrin Molecule





http://www.lsbu.ac.uk/water/images/cyclodex.gif



Chiral GC Product offering: CD Derivatives

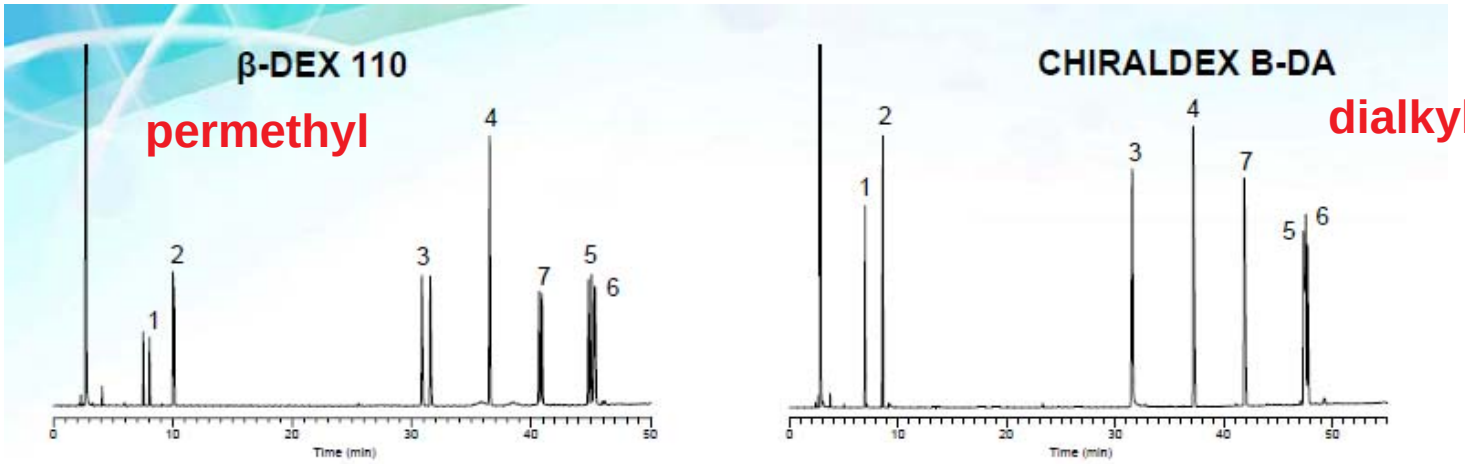
Non-polar chiral GC columns

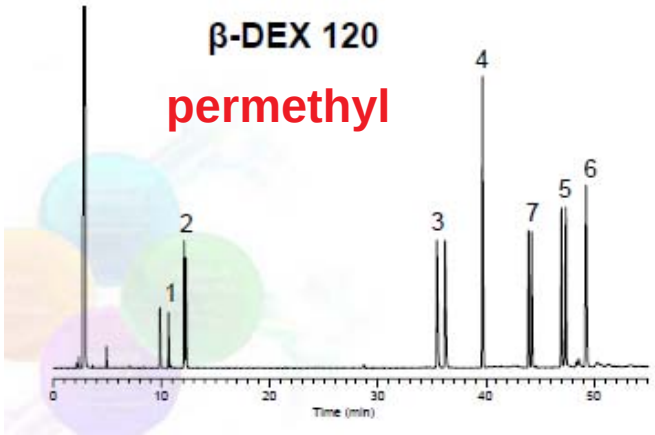
Column	Type of CD	Derivative type
CHIRALDEX B-PM	ß	Permethyl
α, ß, γ-DEX 110/120	α, ß or γ	Permethyl
CHIRALDEX B-, G-DM	ß or γ	Dimethyl
α, ß, γ-DEX 325	α, ß or γ	Dimethyl
CHIRALDEX A-, B-, G-DA	α, ß or γ	Dialkyl

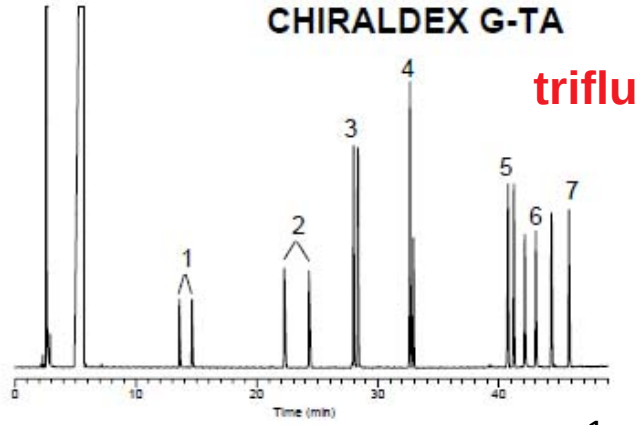
Polar chiral GC columns

Column	Type of CD	Derivative type
CHIRALDEX A-, B-, G-TA	α, ß or γ	Trifluoroacetyl
α, ß, γ-DEX 225	α, ß or γ	Diacetyl
CHIRALDEX B-, G-DP	ß or γ	Dipropionyl
CHIRALDEX G-PN	γ	Propionyl
CHIRALDEX G-BP	γ	Butyryl
CHIRALDEX B-PH	ß	S-Hydroxypropyl

Orthogonality of Chiral GC Phases





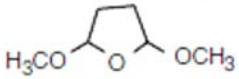


oven:60 °C (0 min. hold) program @ 2 °C/min. to 160 °C (hold 20 min.)
inj.: 250 °C
det.: FID, 250 °C
carrier gas:helium, 25 to 30 cm/sec. set @ 75 °C
injection:1 µL, split 100:1

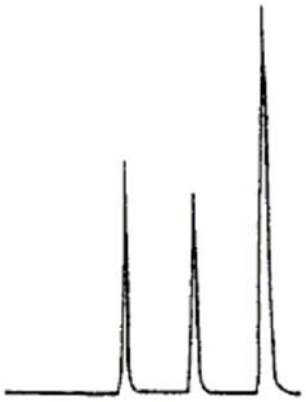
1. methyl lactate
2. β-butyrolactone
3. 1-phenylethanol δ(+)
4. l(-)- carvone
5. α-ionone
6. S(+), R(-) methyl mandelate
7. 1-octanolactone

Examples of Chiral GC Separations

Separation of 2,5-Dimethoxytetrahydrofuran

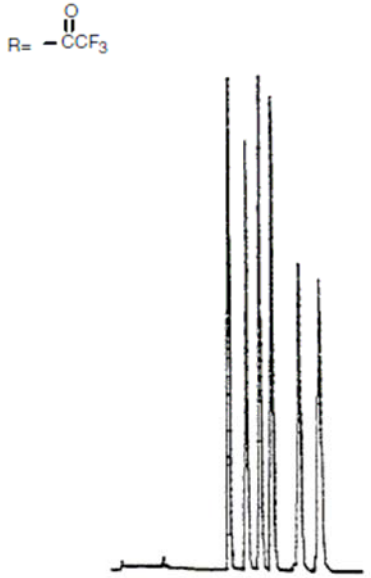


t1 - 5.98
t2 - 7.33
t3 - 8.85 (meso)



CHIRALDEX G-BP (20m)
60°C, Isothermal
Nitrogen @ 6 psi
Split Ratio 100/1

Separation of Chiral Amines



CHIRALDEX G-PN (30m)
130°C
Helium @ 35 psi
Split Ratio - 100/1

Rt	Area	
10.12	765562	R-Amphetamine
10.86	766171	S-Amphetamine
11.41	900479	S-Methamphetamine
11.92	902574	R-Methamphetamine
13.08	668337	d-Pseudoephedrine
13.93	736383	l-Pseudoephedrine

The CHIRALDEX powerhouse trio

These three CHIRALDEX columns will accomplish most Chiral GC separations

- **CHIRALDEX G-TA**
  - γ cyclodextrin derivatized with trifluoroacetate functional groups
  - Separates the greatest number and widest variety of compounds
- **CHIRALDEX B-DM**
  - ß cyclodextrin derivatized with methyl functional groups
  - A second generation dimethylated column, ideal for underivatized acids and bases
- **CHIRALDEX B-DA**
  - ß cyclodextrin derivatized with dialkyl functional groups
  - Size selective, so it can separate analytes based on structural differences

http://www.sigma-aldrich.com/chiral

Supelco Chiral Services

Chiral column screening (HPLC & GC)

Method optimization

Small-scale purification (<10 grams of each enantiomer)

Larger scale through our SAFC partners

http://www.sigma-aldrich.com/chiral

Summary

Fast GC – Dimensions and phases

Ionic liquids for GC – SLB-IL100 and IL36

Chiral GC – CHIRALDEX and Supelco-DEX

Acknowledgements/Collaborators

Prof. Daniel Armstrong, U. Texas Arlington

Prof. Luigi Mondello, U. Messina, Messina, Italy

Supelco and Fluka R&D Teams

For more information on the subjects presented here, please contact techservice@sial.com or your regional sales team.