Supelco Ionic Liquid GC Columns

Introduction

GC Column Chemistry

SLB-IL100

The Polarity You Need

The Selectivity You Require

The Stability You Desire

Updated: March 8, 2009

Introduction

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Introduction

- Ionic liquids are:
  - *A class of solvents with low melting points*
  - *Consist of organic cations plus either inorganic or organic anions*
- Several properties make them desirable as GC stationary phases
  - Remain liquid over a wide temperature range
    - *Potential for columns with* ***extended temperature ranges***
  - Very low volatility
    - *Potential for columns with* ***lower bleed***
  - Highly polar nature
    - *Potential for columns with* ***extreme polarity***
  - Broadest range of solvation interactions of any known solvent
    - *Potential for columns with* ***unique selectivity***

Introduction (cont.)

- Prior work focused on monocationic ionic liquids
  - *These did not exhibit the predicted chromatographic benefits*
- Prof. Daniel W. Armstrong (University of Texas at Arlington)
  - *Has successfully used **dicationic** and **polycationic** ionic liquids as viable GC stationary phases*
  - *These exhibit the predicted chromatographic benefits*
- The use of dicationic and polycationic ionic liquids for use in chromatography is **patented by Supelco**
  - *US 2008/0027231 A1*
  - *Other patents pending*

GC Column Chemistry

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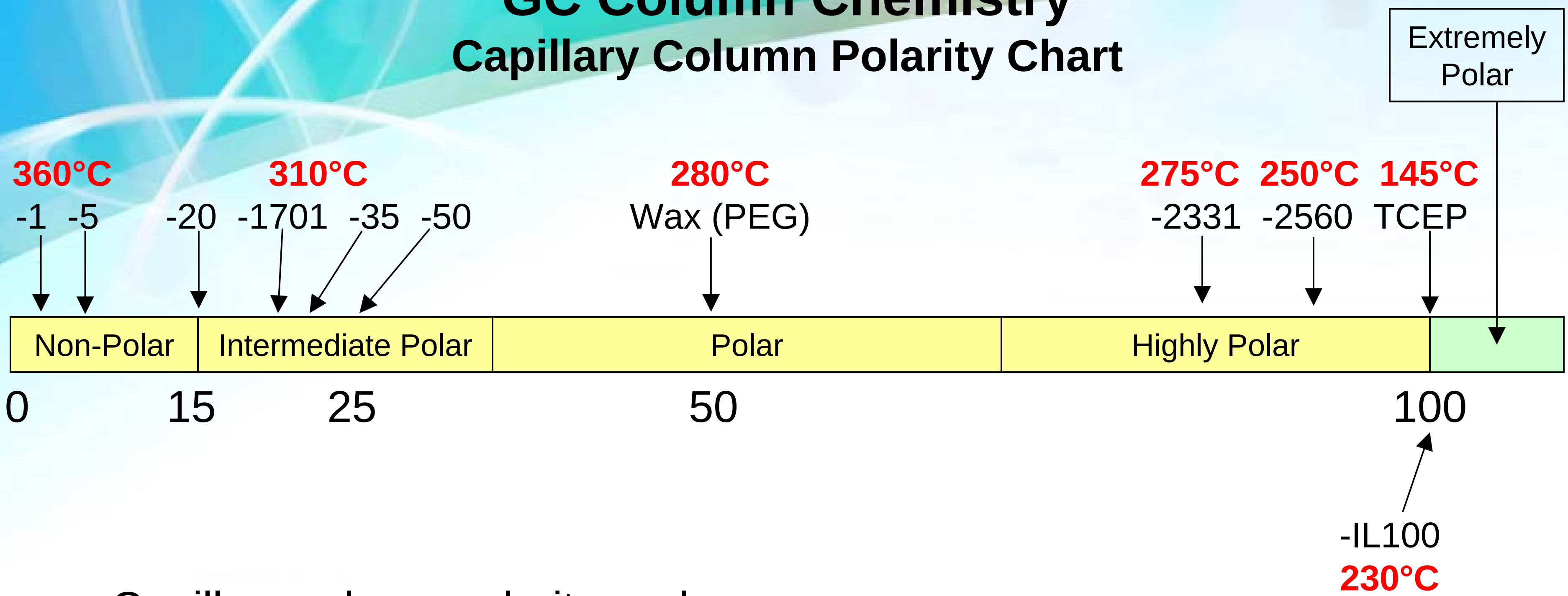
GC Column Chemistry

Capillary Column Polarity Chart



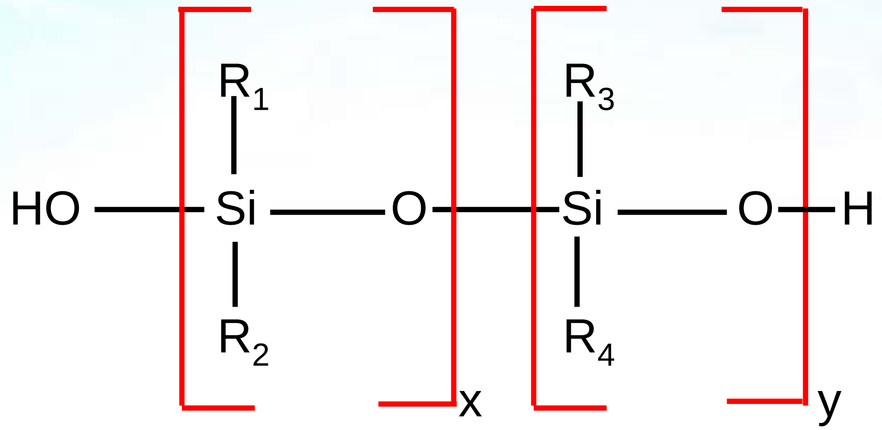
- Capillary column polarity scale
  - *0 = squalane (considered the most non-polar GC stationary phase)*
  - *100 = TCEP (considered the most polar traditional GC stationary phase)*
- Above the scale: locations of **non-ionic liquid** GC columns and their maximum temperatures
- Below the scale: location of the **SLB-IL100 ionic liquid** GC column
  - *Additional ionic liquid columns from Intermediate Polar to Extremely Polar are planned*

GC Column Chemistry
Phase Choices

- Currently, most GC columns are based on two phase chemistries
  - **Polysiloxane Polymers**
    - *Introduced early 1950's, several improvements over the years*
    - *Common columns: -1, -5, -20, -1701, -35, -50, -2331, -2560*
  - **Polyethylene Glycols**
    - *Introduced mid 1950's, few improvements over the years*
    - *Common columns: usually has 'wax' or 'PEG' in name*
- Now, a new phase chemistry is available for GC columns
  - **Ionic Liquids**
    - *Introduced in 2008 (dicationic and polycationic ionic liquids)*
    - *Exclusive to Supelco*

GC Column Chemistry

Polysiloxane Polymers



R = methyl, phenyl, fluoropropyl, or cyanopropyl

(least) ——— polarity ——— (most)

x,y = percentage in the overall polymer composition

- Benefits: *good stability, pendent groups can be changed to cover full GC column polarity range, widely used*
- Drawbacks: *bulky polymers, active hydroxyl (-OH) groups at termini allow back-biting reaction resulting in column bleed, limited chemistry modifications possible*

GC Column Chemistry

Polyethylene Glycols

$$HO-CH_2-CH_2-\left[O-CH_2-CH_2\right]_n-O-CH_2-CH_2-OH$$

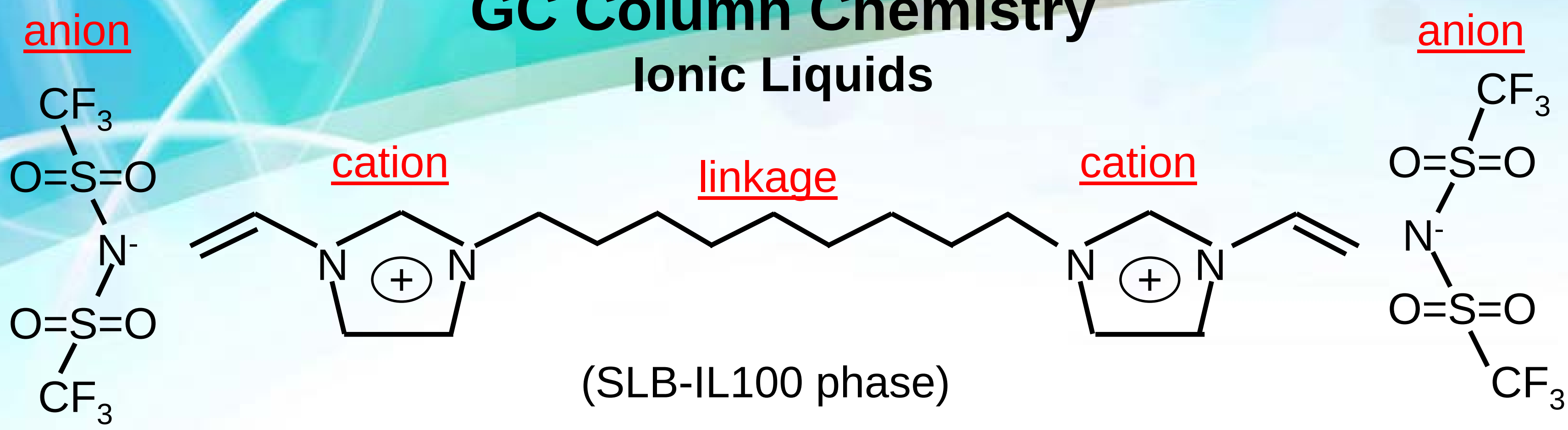
n = number of monomer repetitions to make the overall polymer

In fact, Carbowax 20M (commonly used) has a MW of 20,000

- <u>Benefits</u>: *benchmark polar columns, more stable than other non-ionic liquid columns with similar polarity/selectivity, widely used*
- <u>Drawbacks</u>: *bulky polymers, active hydroxyl (-OH) groups at termini allow phase degradation resulting in column bleed, limited to 280 °C maximum temperature, very limited chemistry modifications possible*

GC Column Chemistry

Ionic Liquids



(SLB-IL100 phase)

- Benefits: *not polymers, greater phase stability compared to non-ionic liquid columns, vast chemistry modifications possible*
  - *Dicationic (shown) or polycationic*
  - *Multiple choices exist for cations, linkages, and anions, including:*
    - *Cations: imidazolium (shown), phosphonium, pyrrolidinium, etc.*
    - *Linkage: alkane (shown), polyethylene glycol, etc. of various lengths*
    - *Anion: nTf2$^-$ (shown), triflate, etc.*
  - *Cation and linkage can be further modified with pendent groups, such as vinyl (shown), alkyl, phenyl, chiral, etc.*
- Drawbacks: *new, not in methods, cannot be made non-polar*

SLB-IL100

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SLB-IL100
Introduction / Applicability

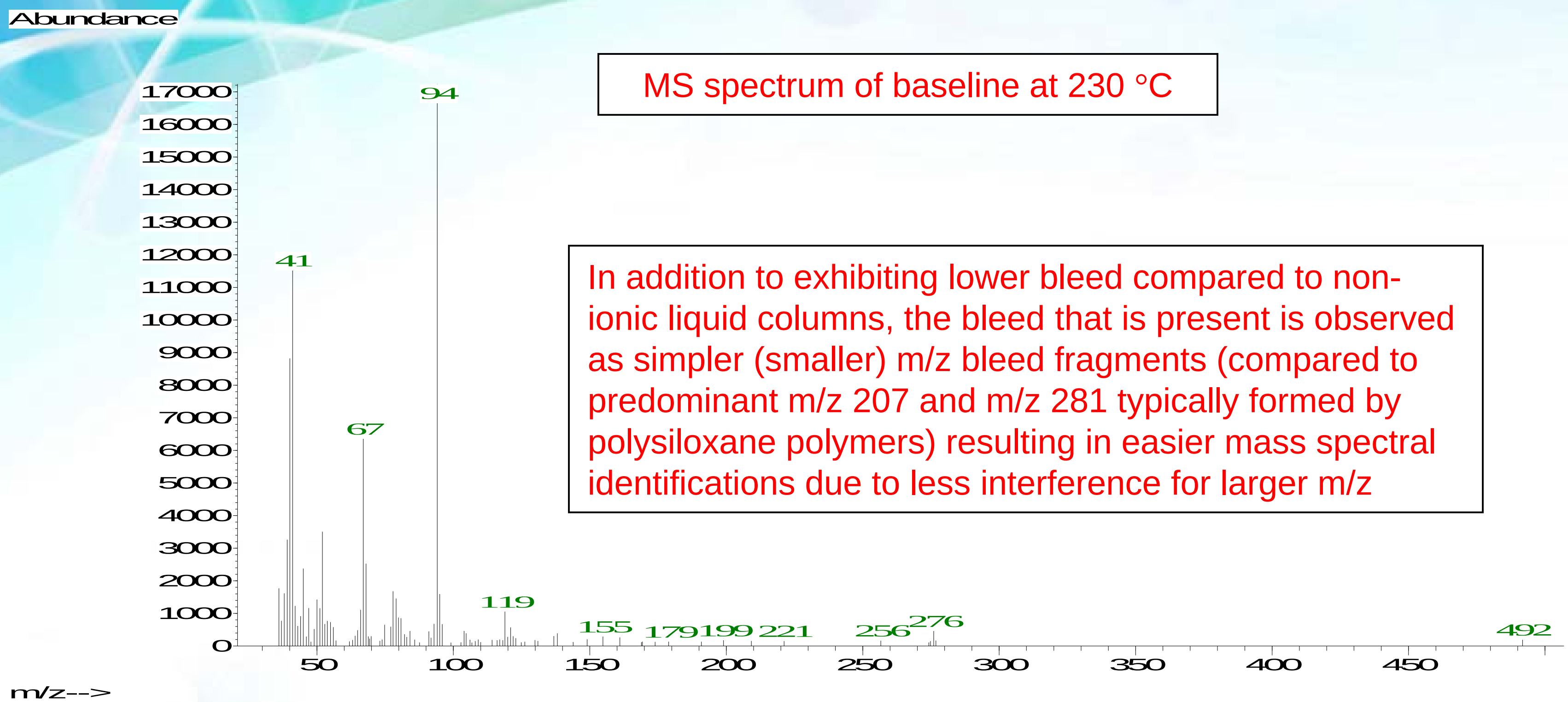
- The **world's first ionic liquid GC column**, the SLB-IL100, was introduced at PittCon 2008
- Based on its polarity/selectivity, it is a **highly polar column**
  - *Located at '100' on the 'Capillary Column Polarity Chart' (Slide 6)*
- Exhibits **greater phase stability** compared to non-ionic liquid columns with equivalent polarity/selectivity
  - *Lower bleed, higher maximum temperature, and greater durability*
- Can be used for any application currently performed with non-ionic liquid highly polar columns
  - *Namely, fatty acid methyl esters (FAMEs) and aromatics*
- Has the same limitations as non-ionic liquid highly polar columns
  - *Peak tailing observed with polar analytes (alcohols, aldehydes, ketones, amines, etc.)*

SLB-IL100
Specifications

- **Application**
  - *This highly polar column exemplifies some of the desired characteristics that ionic liquid columns are predicted to possess, namely, lower bleed and a higher maximum temperature compared to non-ionic liquid columns with similar polarity/selectivity*
  - *This column is applicable for applications such as the analyses of fatty acid methyl esters (FAMEs) and of aromatic hydrocarbons in gasoline*
- **USP Code**
  - *None*
- **Polymer**
  - *Non-bonded*
  - *1,9-di(3-vinyl-imidazolium) nonane bis(trifluoromethyl) sulfonyl imidate*
- **Temperature Limits**
  - *Subambient to 230 °C*

SLB-IL100

Application – GC-MS Bleed Profile

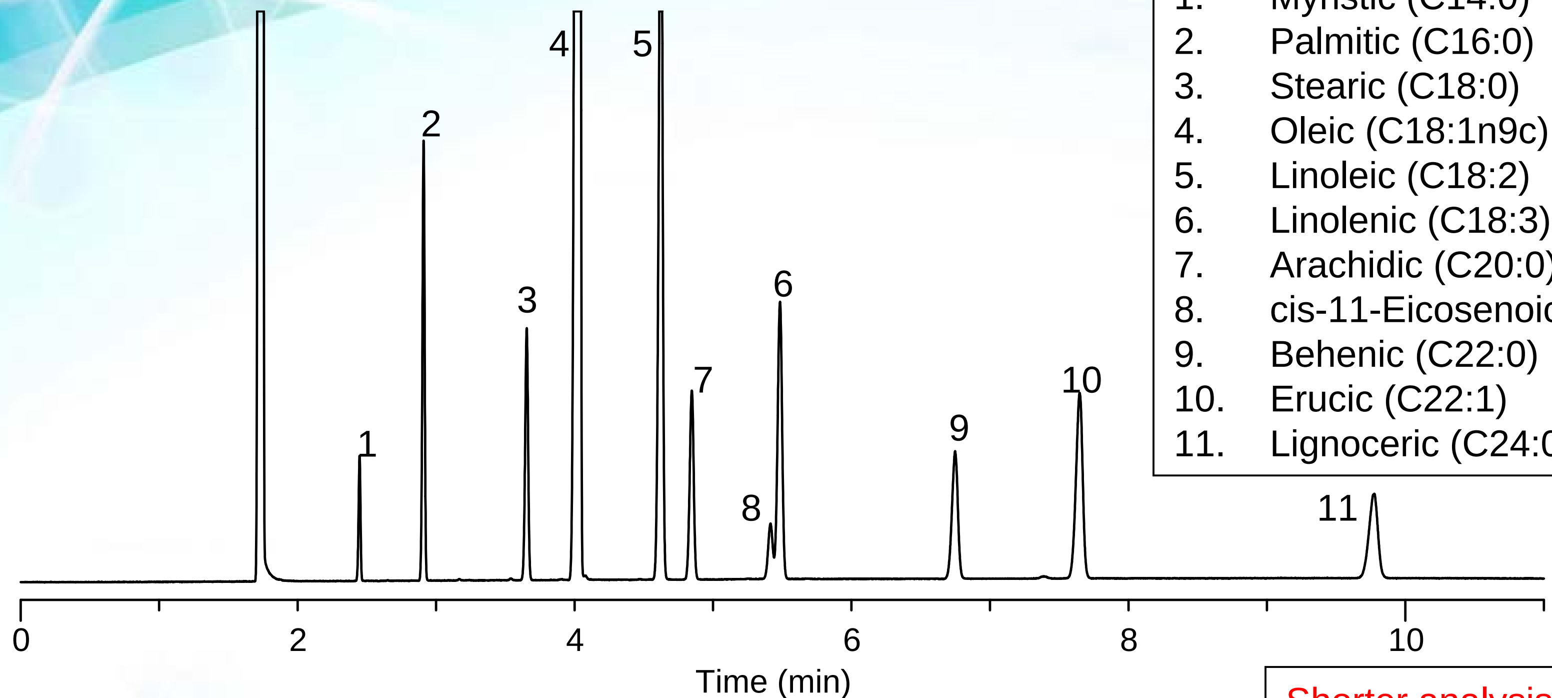


MS spectrum of baseline at 230 °C

In addition to exhibiting lower bleed compared to non-ionic liquid columns, the bleed that is present is observed as simpler (smaller) m/z bleed fragments (compared to predominant m/z 207 and m/z 281 typically formed by polysiloxane polymers) resulting in easier mass spectral identifications due to less interference for larger m/z

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

SLB-IL100
Application – Rapeseed Oil FAMEs



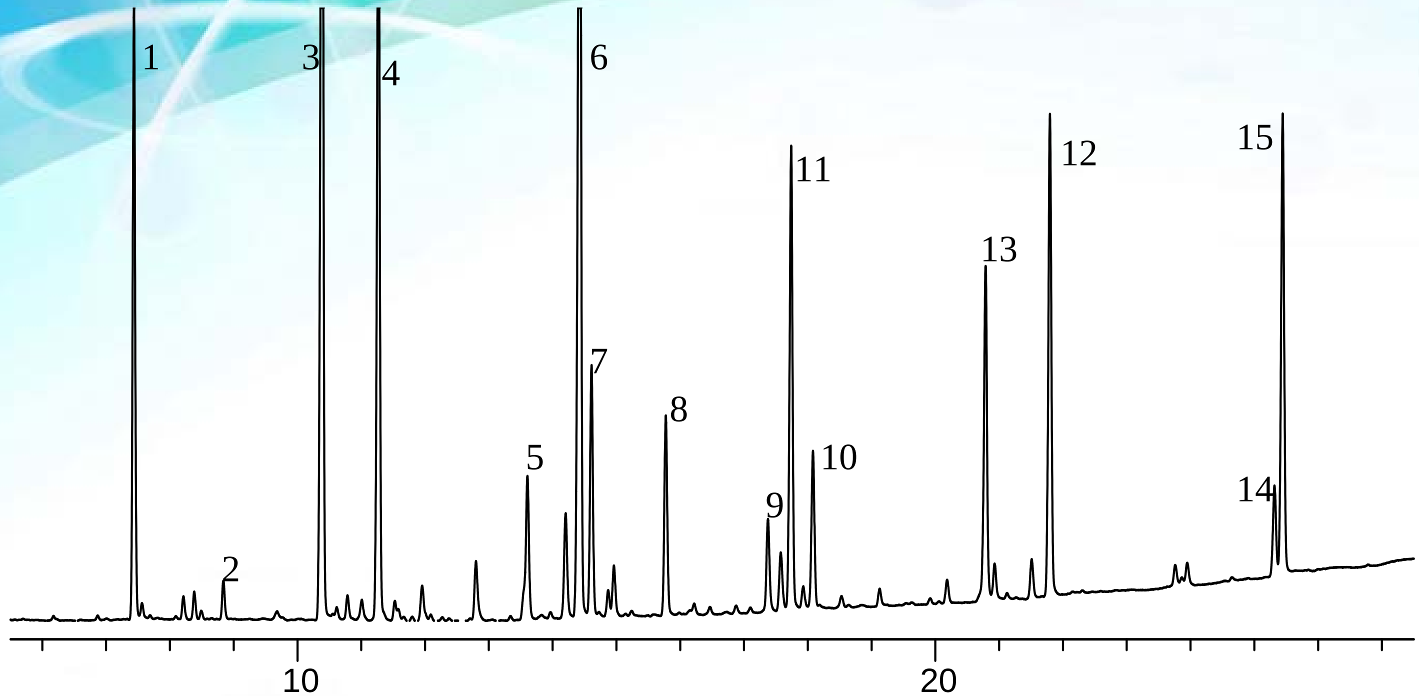
1. Myristic (C14:0)
2. Palmitic (C16:0)
3. Stearic (C18:0)
4. Oleic (C18:1n9c)
5. Linoleic (C18:2)
6. Linolenic (C18:3)
7. Arachidic (C20:0)
8. cis-11-Eicosenoic (C20:1)
9. Behenic (C22:0)
10. Erucic (C22:1)
11. Lignoceric (C24:0)

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: 180 °C
inj.: 250 °C
det.: FID, 250 °C
carrier gas: helium, 30 cm/sec @ 180 °C
injection: 1 µL, 100:1 split
liner: 4 mm I.D., split, cup
sample: rapeseed oil FAME mix, 5 mg/mL total FAMEs in methylene chloride

Elution of C18:3 after both C20:0 and C20:1 highlights the great selectivity for FAMEs by degree of unsaturation

SLB-IL100
Application – Cod Liver Oil FAMEs



1.	C14:0
2.	C15:0
3.	C16:0
4.	C16:1n7
5.	C18:0
6.	C18:1n9
7.	C18:1n7
8.	C18:2n6
9.	C18:3n3
10.	C18:4n3
11.	C20:1n9
12.	C20:5n3
13.	C22:1n9
14.	C22:5n3
15.	C22:6n3

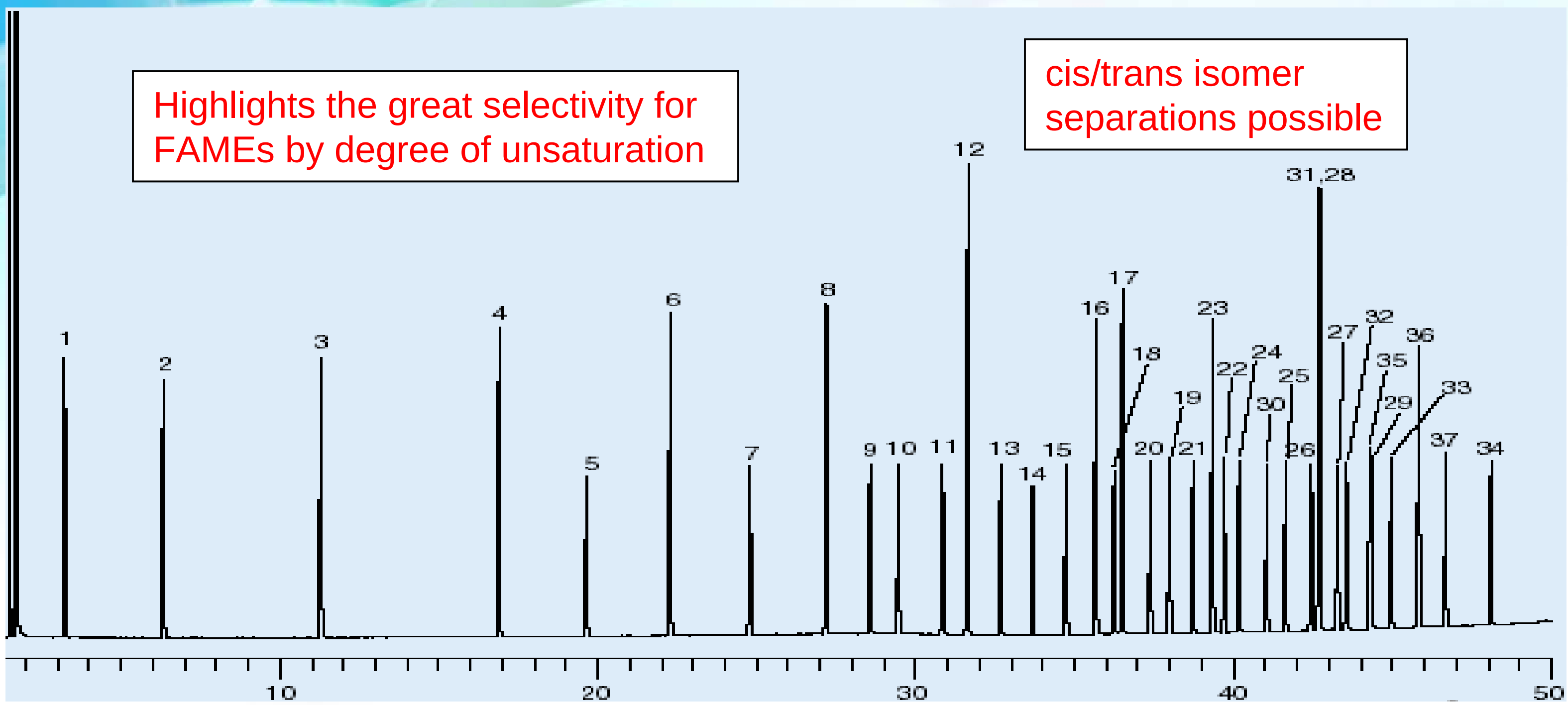
Chromatogram courtesy of Prof. Luigi Mondello (Univ. of Messina, Italy)

column: SLB-IL100, 30 m x 0.25 mm I.D., 0.20 µm (28884-U)
oven: 120 °C, 3.0 °C/min. to 240 °C
inj.: 240 °C
det.: FID, 240 °C
carrier gas: hydrogen, 35 cm/sec constant
injection: 1 µL, 50:1 split
sample: cod liver oil FAMEs

Elution of C18:4n3 after C20:1n9 and of C20:5n3 after C22:1n9 highlights the great selectivity for FAMEs by degree of unsaturation

SLB-IL100

Application – 37-Component FAME Mix



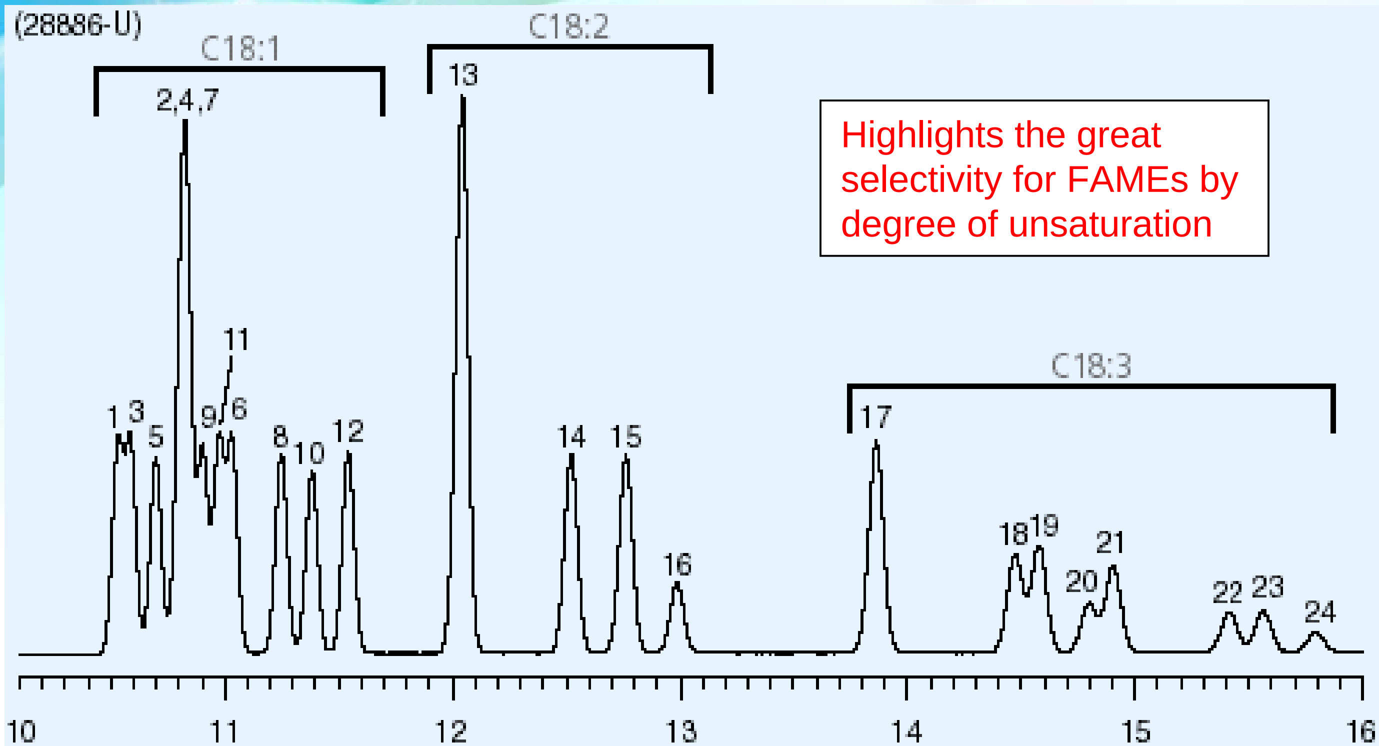
1. C4:0 at 4 wt %
2. C6:0 at 4 wt %
3. C8:0 at 4 wt %
4. C10:0 at 4 wt %
5. C11:0 at 2 wt %
6. C12:0 at 4 wt %
7. C13:0 at 2 wt %
8. C14:0 at 4 wt %
9. C14:1 at 2 wt %
10. C15:0 at 2 wt %
11. C15:1 at 2 wt %
12. C16:0 at 6 wt %
13. C16:1 at 2 wt %
14. C17:0 at 2 wt %
15. C17:1 at 2 wt %
16. C18:0 at 4 wt %
17. C18:1n9c at 4 wt %
18. C18:1n9t at 2 wt %
19. C18:2n6c at 2 wt %
20. C18:2n6t at 2 wt %
21. C18:3n6 at 2 wt %
22. C18:3n3 at 2 wt %
23. C20:0 at 4 wt %
24. C20:1n9 at 2 wt %
25. C20:2 at 2 wt %
26. C20:3n6 at 2 wt %
27. C20:3n3 at 2 wt %
28. C20:4n6 at 2 wt %
29. C20:5n3 at 2 wt %
30. C21:0 at 2 wt %
31. C22:0 at 4 wt %
32. C22:1n9 at 2 wt %
33. C22:2 at 2 wt %
34. C22:6n3 at 2 wt %
35. C23:0 at 2 wt %
36. C24:0 at 4 wt %
37. C24:1n9 at 2 wt %

column:	SLB-IL100, 30 m x 0.25 mm I.D., 0.20 µm (28884-U)
oven:	50 °C, 3.0 °C/min. to 240 °C
inj.:	240 °C
det.:	FID, 240 °C
carrier gas:	helium, 40 cm/sec constant
injection:	1 µL, 50:1 split
sample:	Supelco 37-Component FAME Mix (47885-U), analytes at concentrations indicated in methylene chloride

Low bleed and a stable baseline

SLB-IL100

Application – C18:1, C18:2, and C18:3 FAME Isomers



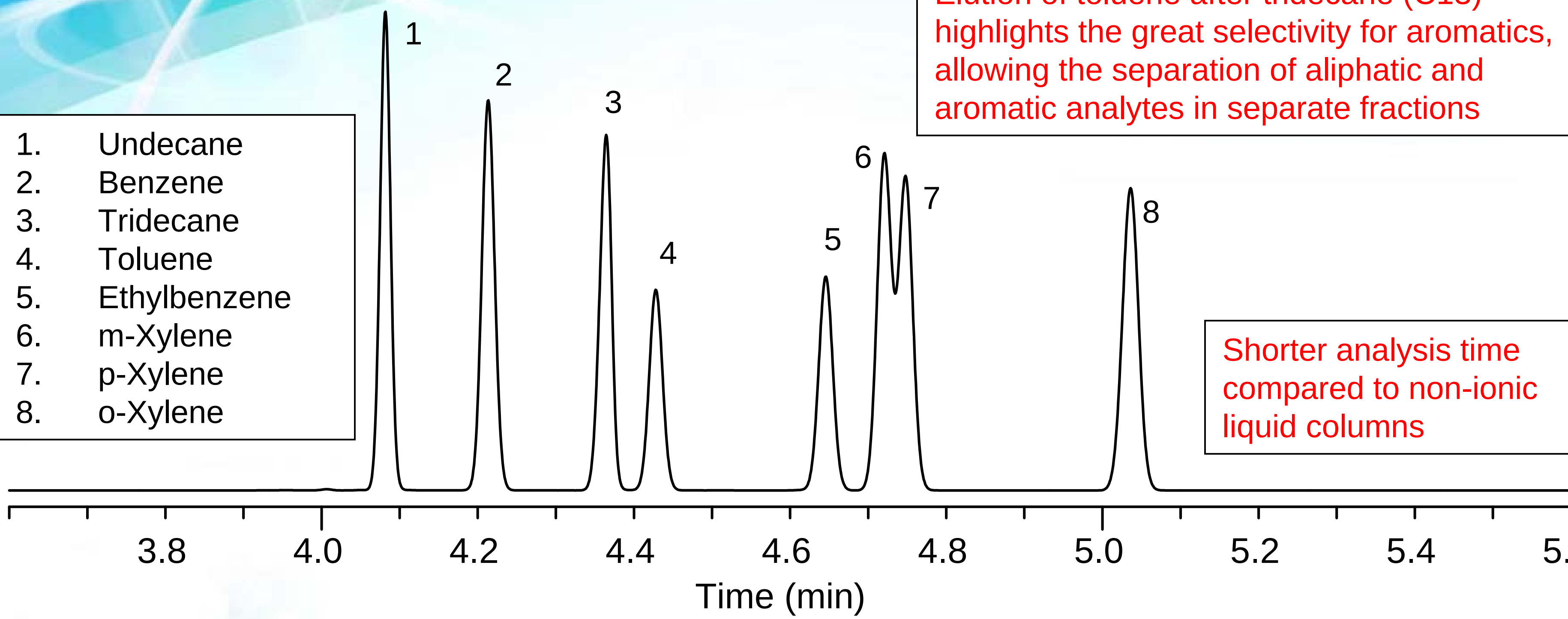
Highlights the great selectivity for FAMEs by degree of unsaturation

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

column: SLB-IL100, 60 m x 0.25 mm I.D., 0.20 µm (28886-U)
oven: 170 °C
inj.: 250 °C
det.: FID, 250 °C
carrier gas: helium, 30 cm/sec
injection: 1 µL, 50:1 split
liner: 4 mm I.D., split, cup design
sample: mixture of C18:1, C18:2, and C18:3 FAMEs in methylene chloride

No other column can be used to identify as many C18 cis/trans FAME isomers

SLB-IL100
Application – BTEX and n-Alkanes



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

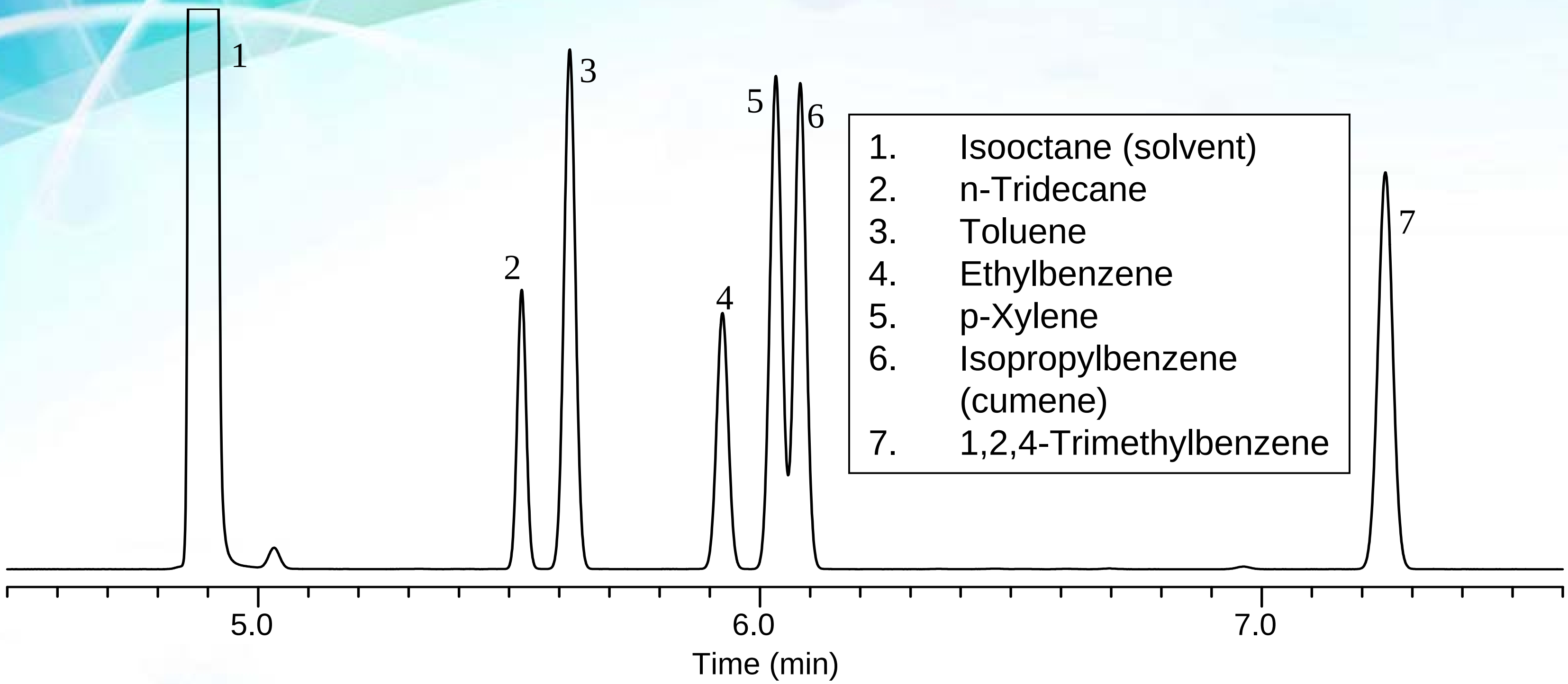
Elution of toluene after tridecane (C13) highlights the great selectivity for aromatics, allowing the separation of aliphatic and aromatic analytes in separate fractions

Shorter analysis time compared to non-ionic liquid columns

column:	SLB-IL100, 60 m x 0.25 mm I.D., 0.20 µm (28886-U)
oven:	110 °C
inj.:	250 °C
det.:	FID, 250 °C
carrier gas:	helium, 26 cm/sec
injection:	0.1 µL, 300:1 split
liner:	4 mm I.D., split, cup design
sample:	NEAT mixture containing varying percentages of each component

SLB-IL100

Application – QA Column Test

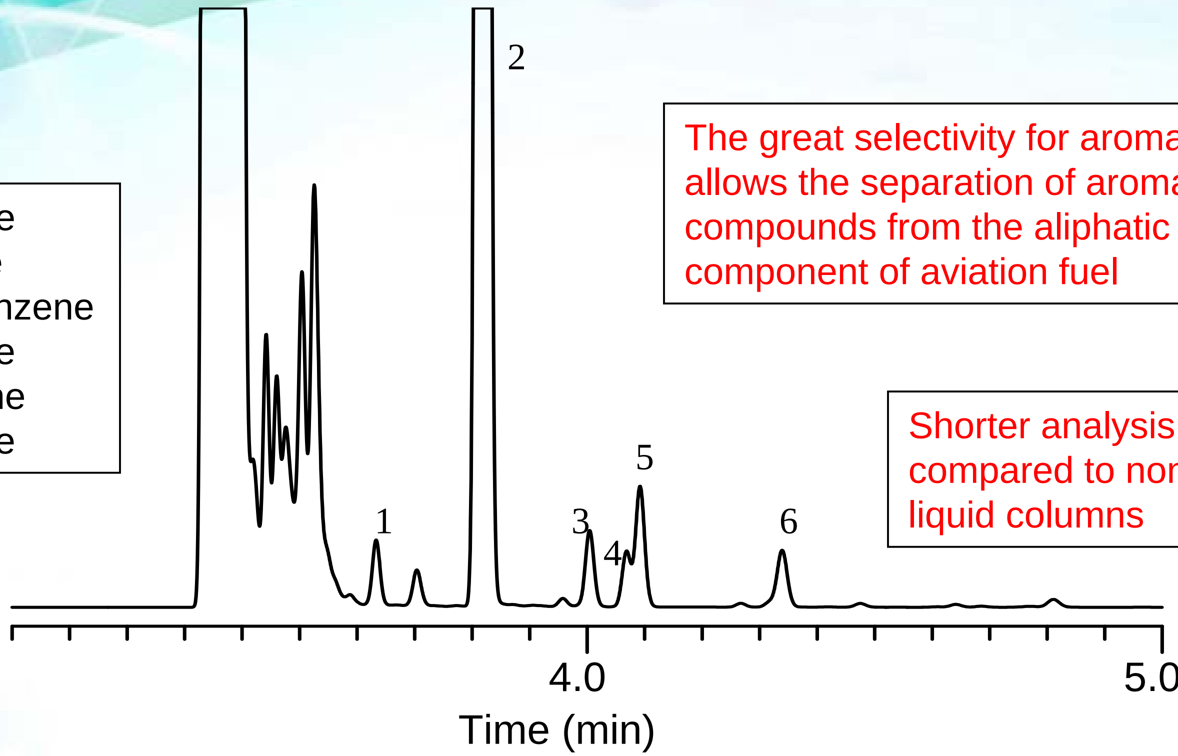


column:	SLB-IL100, 60 m x 0.25 mm I.D., 0.20 µm (28886-U)
oven:	110 °C
inj.:	250 °C
det.:	FID, 250 °C
carrier gas:	helium, 21 cm/sec
injection:	1.0 µL, 100:1 split
sample:	Ionic Liquid Test Mix #1, each analyte at various concentrations in isooctane

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

SLB-IL100

Application – ASTM D3606 (Aviation Fuel)



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

The great selectivity for aromatics allows the separation of aromatic compounds from the aliphatic component of aviation fuel

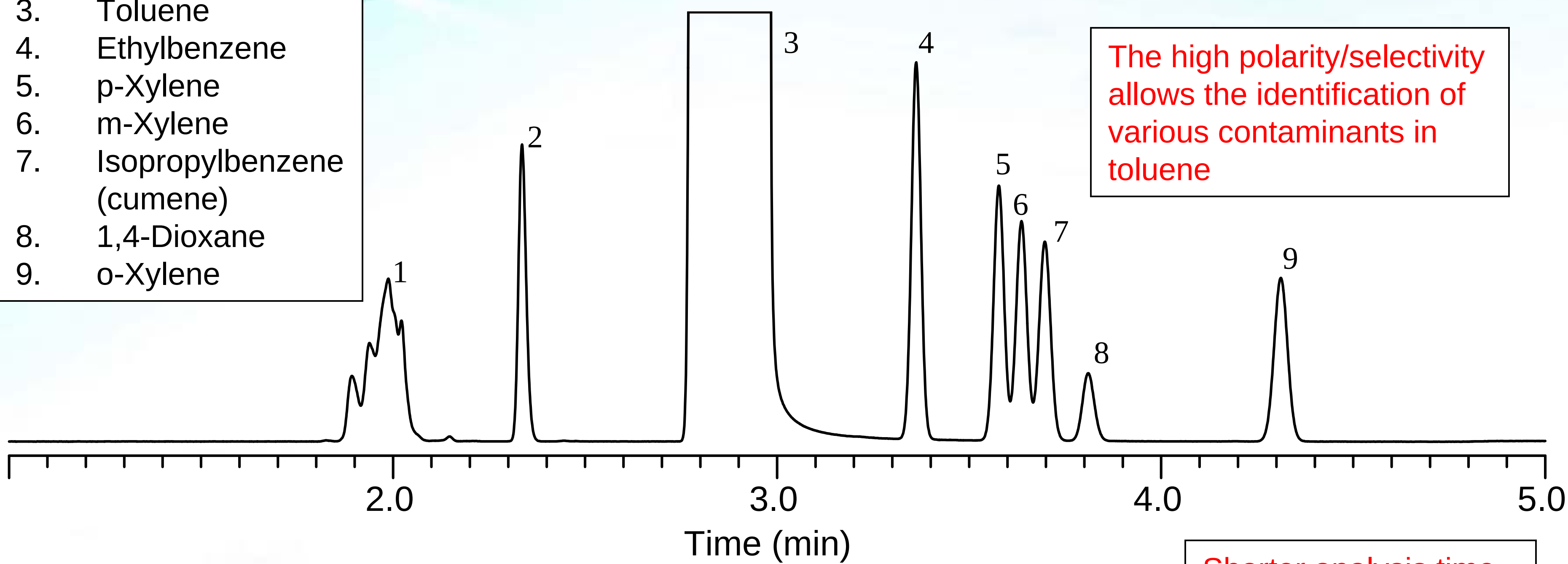
Shorter analysis time compared to non-ionic liquid columns

column:	SLB-IL100, 60 m x 0.25 mm I.D. , 0.20 µm (28886-U)
oven:	110 °C
inj.:	250 °C
det.:	FID, 250 °C
carrier gas:	helium, 30 cm/sec @ 110 °C
injection:	1 µL, 100:1 split
liner:	4 mm I.D., split, cup design
sample:	aviation fuel

SLB-IL100

Application – ASTM D6526 (Toluene)

1. Alkanes
2. Benzene
3. Toluene
4. Ethylbenzene
5. p-Xylene
6. m-Xylene
7. Isopropylbenzene (cumene)
8. 1,4-Dioxane
9. o-Xylene



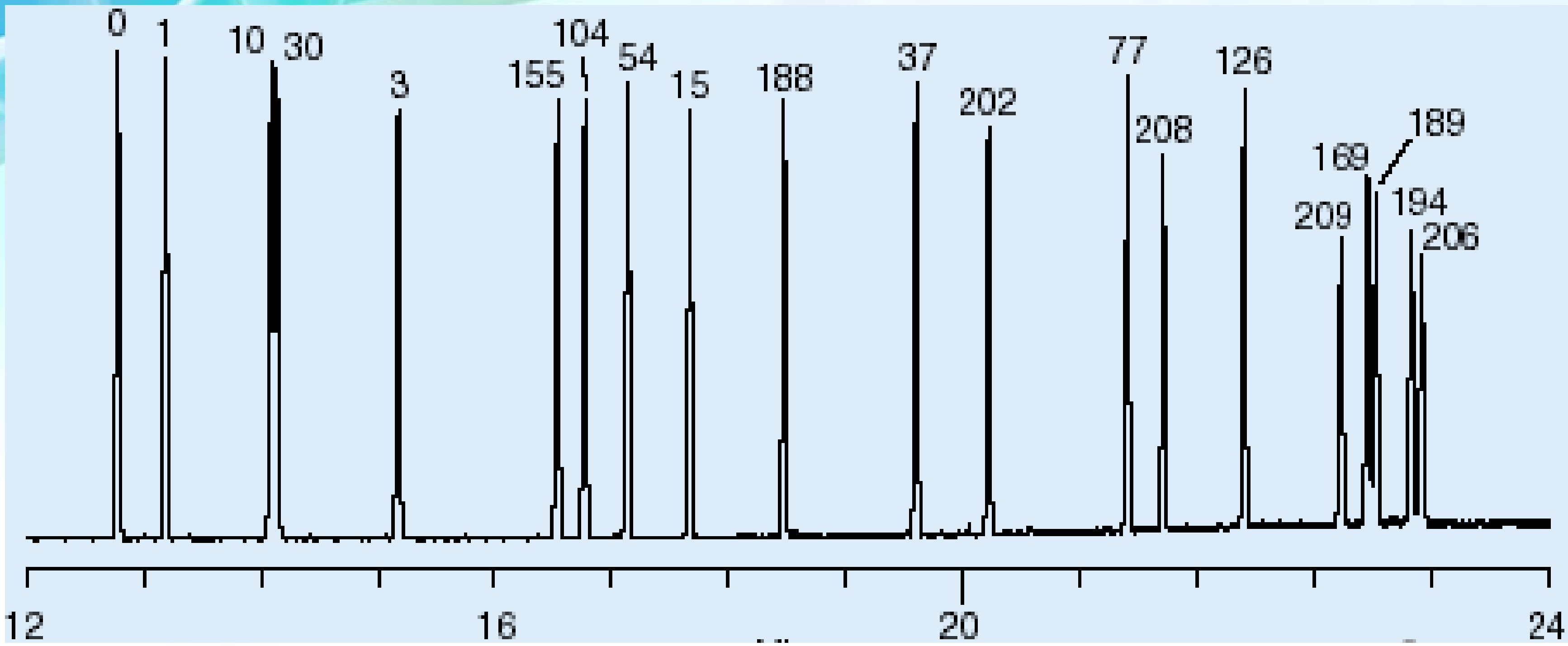
The high polarity/selectivity allows the identification of various contaminants in toluene

Shorter analysis time compared to non-ionic liquid columns

Identification of of all three xylene isomers possible at an oven temperature of 70 °C

column:	SLB-IL100, 30 m x 0.25 mm I.D., 0.20 µm (28884-U)
oven:	70 °C
inj.:	200 °C
det.:	FID, 200 °C
carrier gas:	helium, 28 cm/sec
injection:	1 µL, 40:1 split
liner:	4 mm I.D., split, cup
sample:	toluene spiked with 0.01% (w/w) of benzene, ethylbenzene, p-xylene, m-xylene, cumene, 1,4-dioxane, and o-xylene

SLB-IL100
Application – PCB Congeners



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
inj.:	250 °C
MSD interface:	220 °C
scan range:	m/z = 95-500
carrier gas:	helium, 1.5 mL/min. constant
injection:	1 µL, splitless (1.0 min.)
liner:	4 mm I.D., single taper
sample:	PCB congener mix, each analyte at 2.5 ppm in n-hexane

Low bleed and a stable baseline

Existing non-ionic liquid columns with equivalent polarity/selectivity are unable to perform this application due to their low maximum temperature

SLB-IL100
Available Dimensions

- Stock dimensions and catalog numbers
  - SLB-IL100, 15 m x 0.10 mm I.D., 0.08 µm, Beta = 313 (28882-U)
  - SLB-IL100, 20 m x 0.18 mm I.D., 0.14 µm, Beta = 313 (28883-U)
  - SLB-IL100, 30 m x 0.25 mm I.D., 0.20 µm, Beta = 313 (28884-U)
  - SLB-IL100, 60 m x 0.25 mm I.D., 0.20 µm, Beta = 313 (28886-U)
  - SLB-IL100, 30 m x 0.32 mm I.D., 0.26 µm, Beta = 313 (28887-U)
  - SLB-IL100, 60 m x 0.32 mm I.D., 0.26 µm, Beta = 313 (28888-U)
- Other dimensions (length, I.D., or film) may be available through our Custom Program
- Note: Beta (β) value is the ratio of phase to I.D., calculated as:

$$\beta = \frac{\text{column radius (in µm)}}{2 * \text{film thickness (in µm)}}$$

Thank You

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TUBING
SYRINGES
FocusLiner™