IONIC LIQUID GC COLUMNS

Extending the dimensions in Gas Chromatography

Anders Fridström
Technical Marketing Manager, Advanced Analytical

MERCK

Agenda

- Overview of Ionic Liquids
- New Ionic Liquid Column Developments
  - Watercol™ series
  - SLB® IL (i-series)
- Summary/Conclusions

Ionic Liquids

Properties as GC Columns

- A class of ionic solvents with low melting points
- Remain liquid over a wide temperature range (Room Temperature→350 $^{o+}$C)
- Unique combination of cations and anions that can provide different selectivities when used as stationary phases in GC
- Broadest range of solvation interactions of any known solvent

Unique Selectivity

The Importance of Selectivity

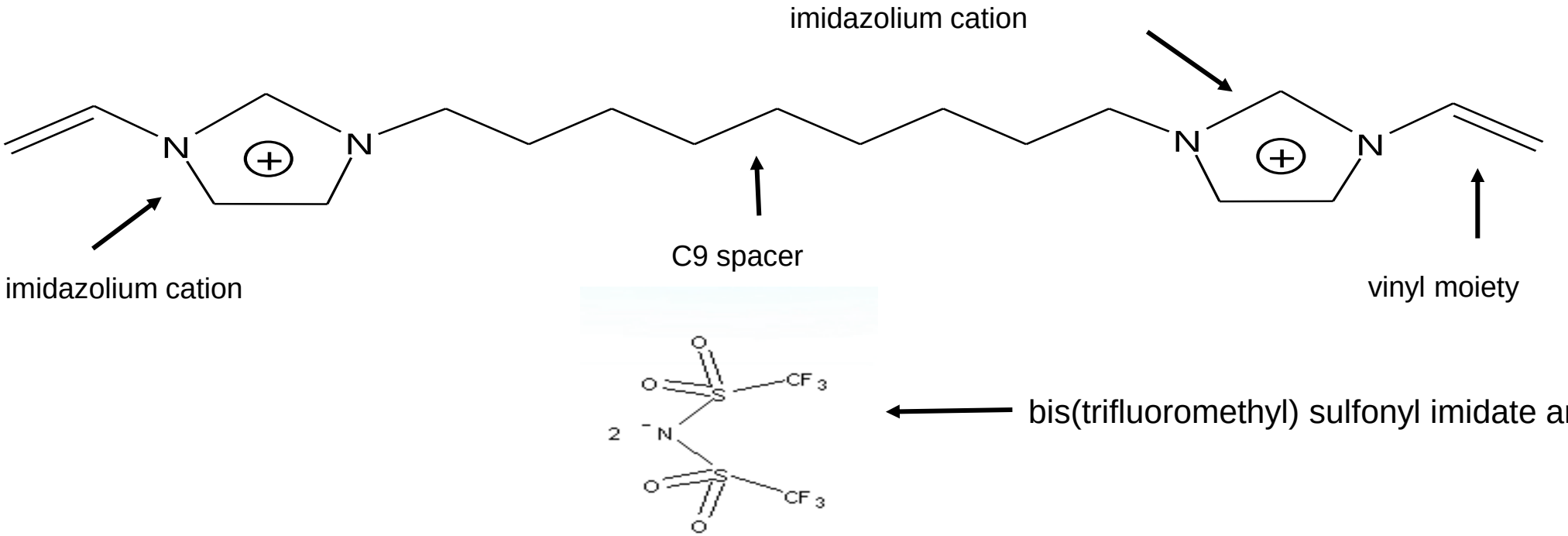
- A column's selectivity has the greatest influence on resolution

- Extensive evaluations of ionic liquid GC columns
  - Main strength is unique selectivity
  - Often resulting in
    - Increased resolution
    - Shorter run times

Geminal Dicationic Ionic Liquid Stationary Phase

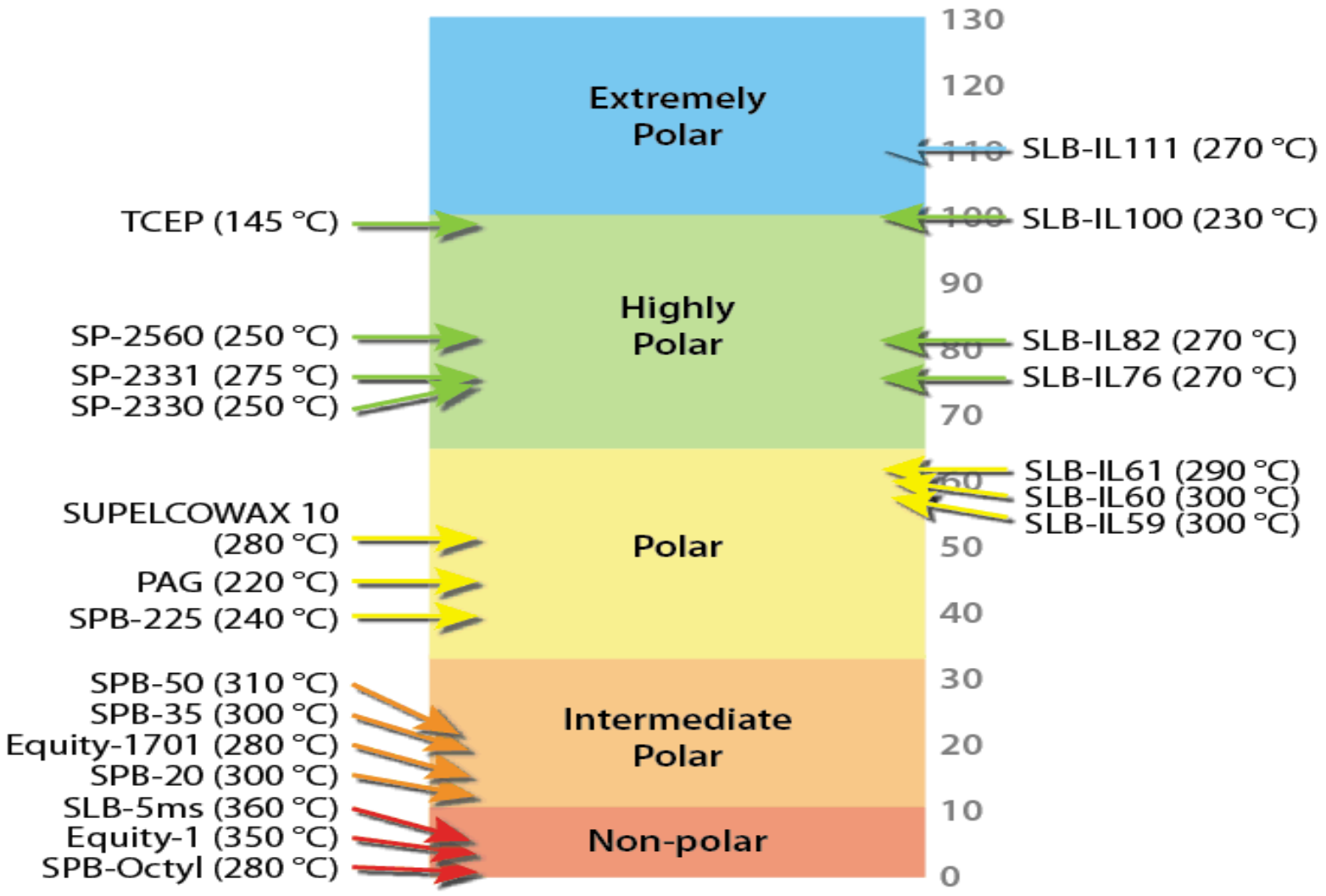
SLB-IL100

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



GC Column Polarity Scale

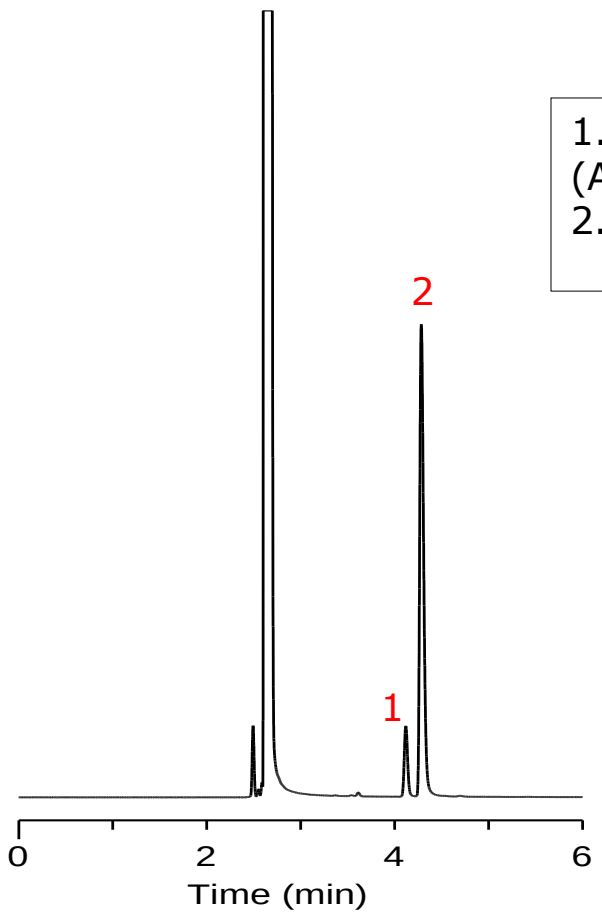
Visual Representation



Unique Selectivity

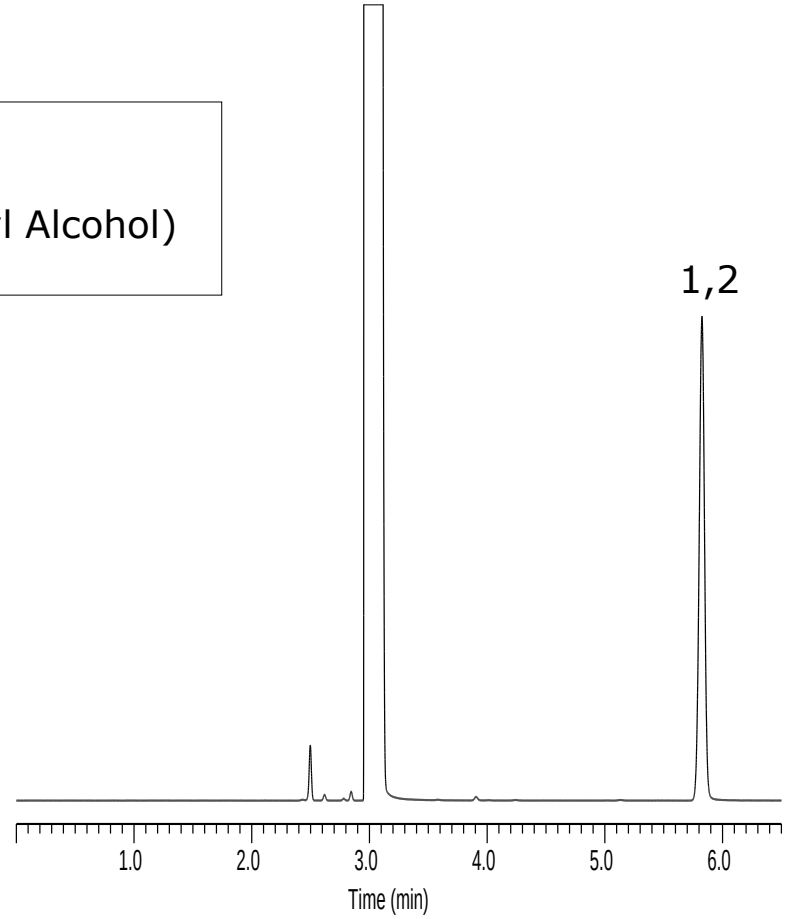
Fuel Alcohols; 90 ºC Isothermal

SLB-IL60
30 m x 0.25 mm I.D., 0.20 µm



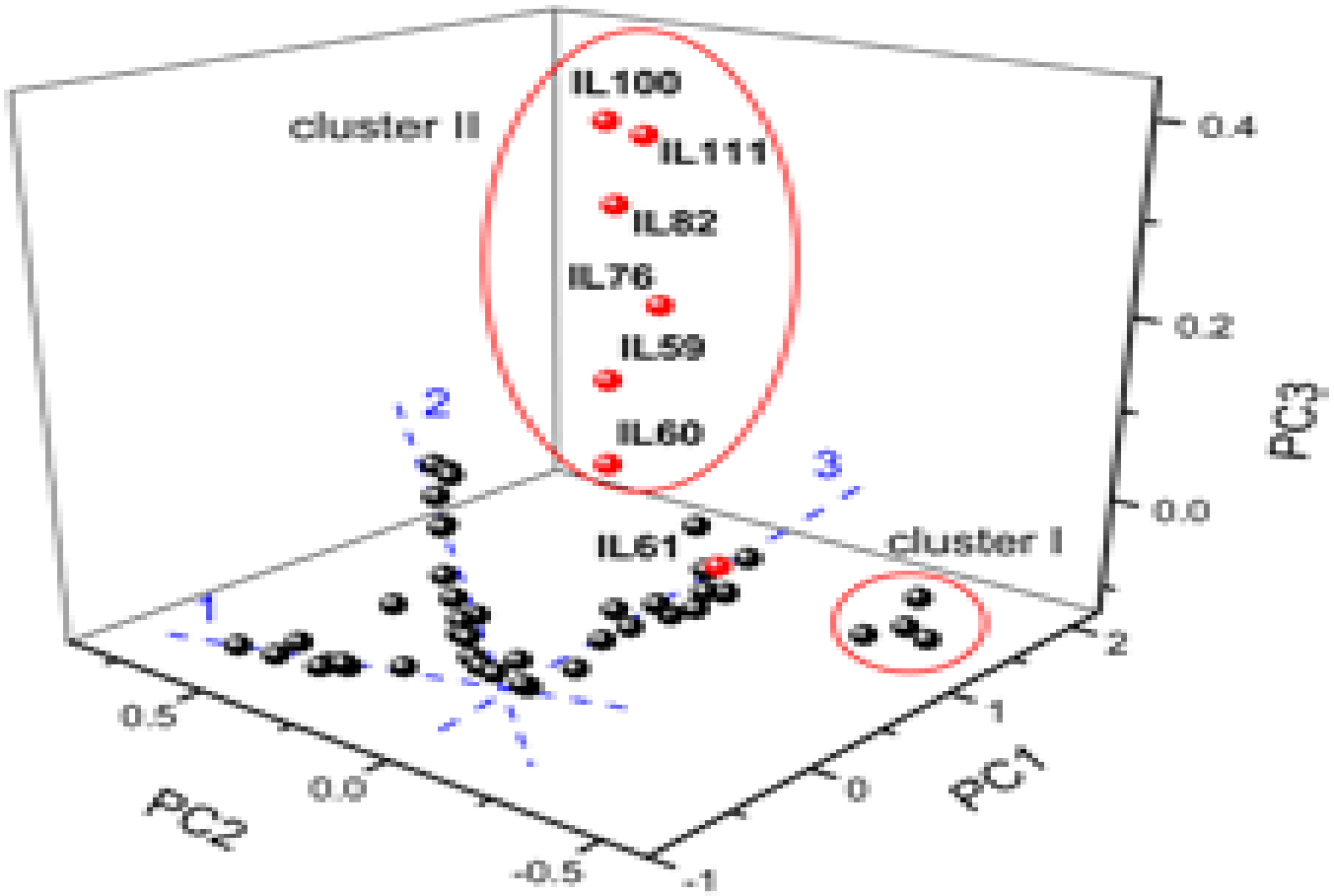
1. 2-Methyl-1-Butanol (Active Amyl Alcohol)
2. 3-Methyl-1-Butanol (Isoamyl Alcohol)

PEG
30 m x 0.25 mm I.D., 0.25 µm



Polarity vs. Selectivity

Principle Component Analysis (PCA) of Solvation Parameter Model (SPM) Data



Ref: Supelco Reporter 33.1 (March 2015), page 3-4.
Courtesy of Rosa Lebrón-Aguilar, CSIS, Madrid, Spain

Only the ionic liquids are capable of simultaneously providing:

- ✓ Intense H-acceptor interactions (*a* constant)
- ✓ Intense H-donor interactions (*b* constant)
- ✓ Dipolar interactions (*s* constant)
- ✓ π-π interactions (*e* constant)
- ✓ Limited dispersive interactions (*l* constant)

95 probes / 52 columns

- Line 1: Poly(trifluoropropyl)siloxane
- Line 2: Poly(phenyl)siloxane
- Line 3: Poly(cyanopropyl)siloxane
- Cluster I: Polyethylene glycol
- Cluster II: Ionic liquid

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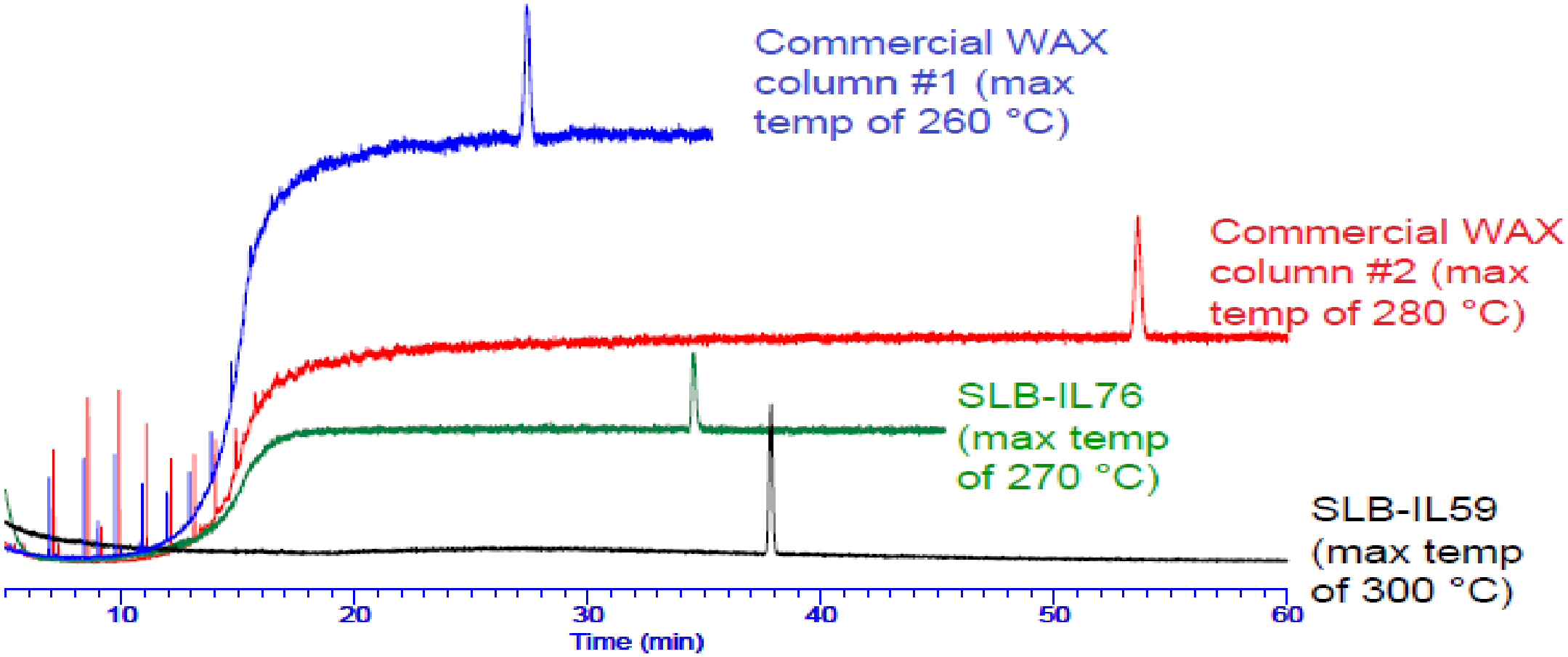
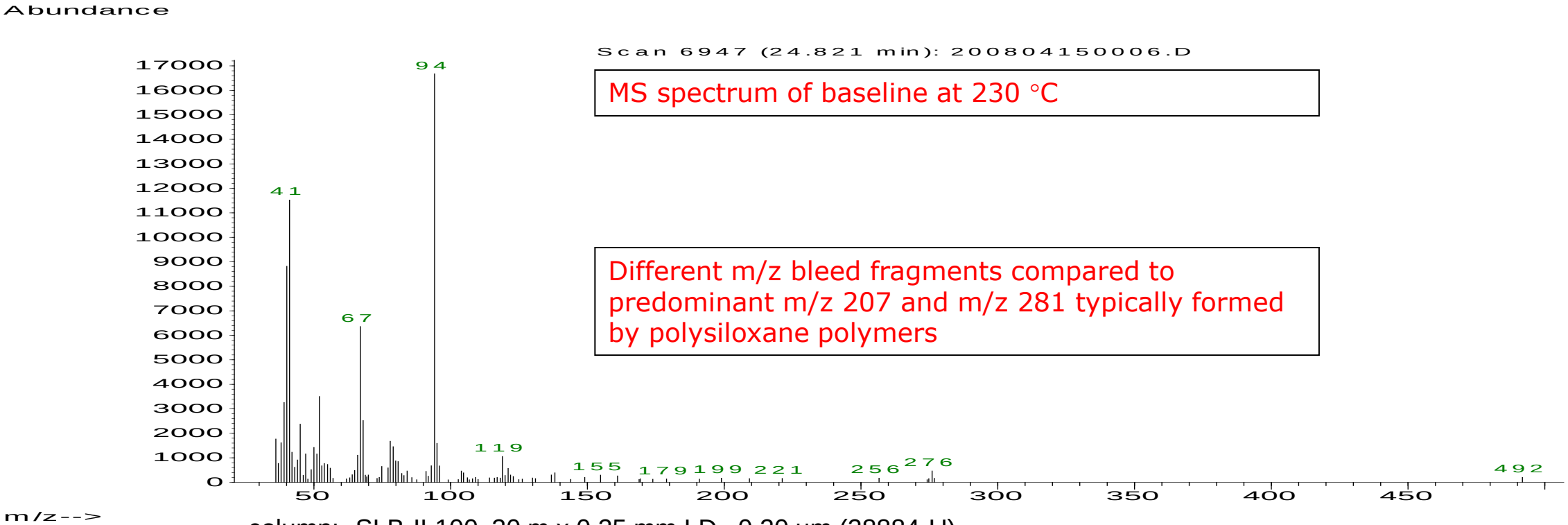
Comparison of GC-MS TIC Bleed



All TICs are on the same Y-scale

SLB-IL100 GC-MS Bleed Profile



MS spectrum of baseline at 230 °C

Different m/z bleed fragments compared to predominant m/z 207 and m/z 281 typically formed by polysiloxane polymers

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

Watercol™ Series Capillary GC Columns

Convenient Measurement of Water

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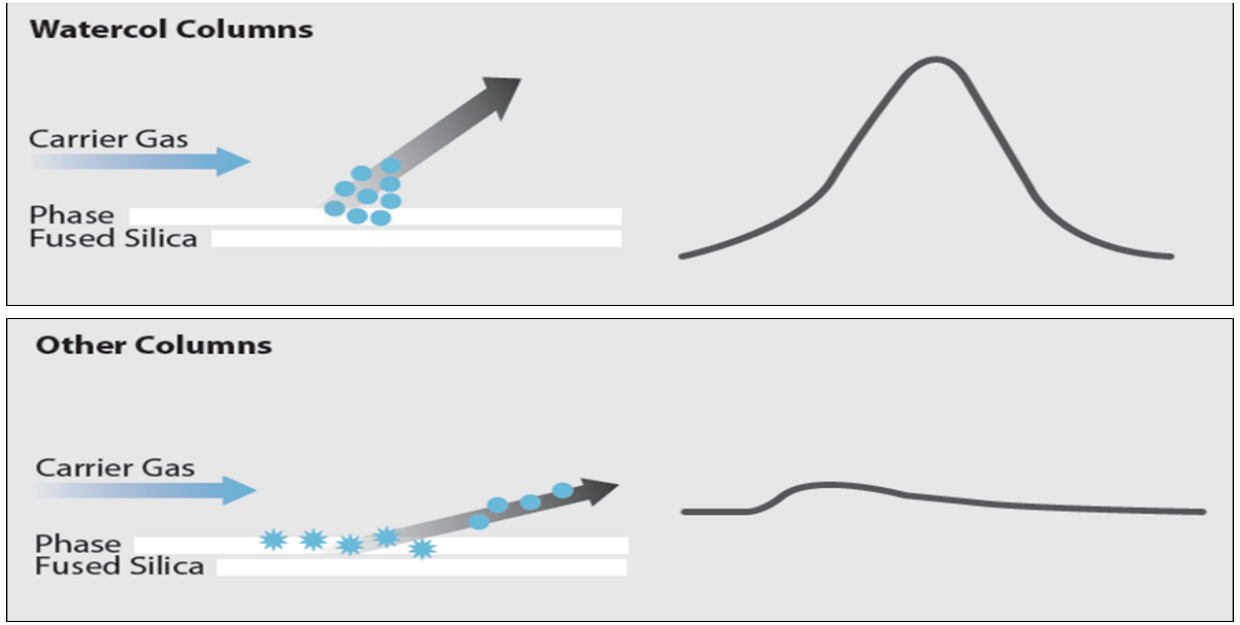
Watercol Series Capillary GC Columns

Overview

- Contain innovative ionic liquid stationary phases
- Produce a sharp peak shape for water



Three chemistries, each with a different selectivity.

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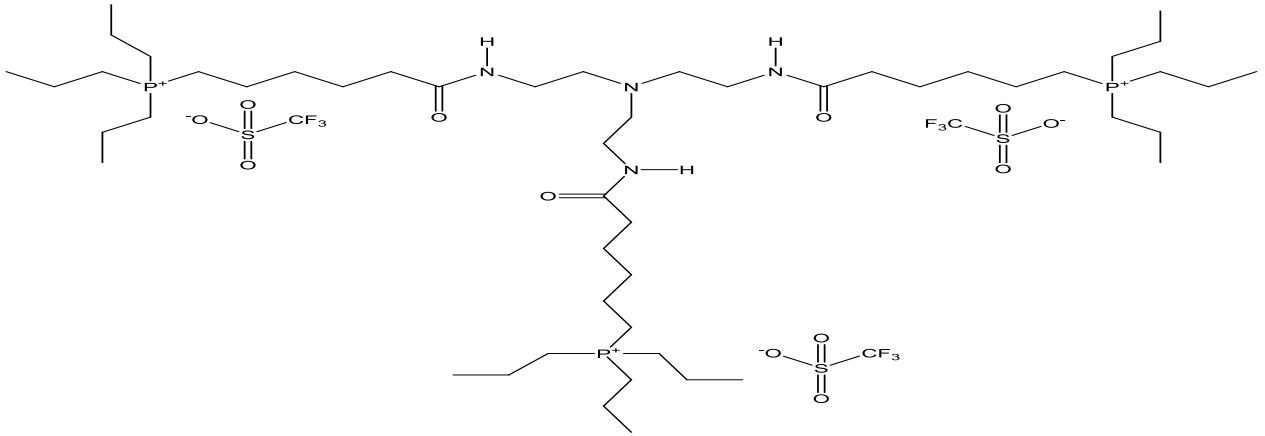
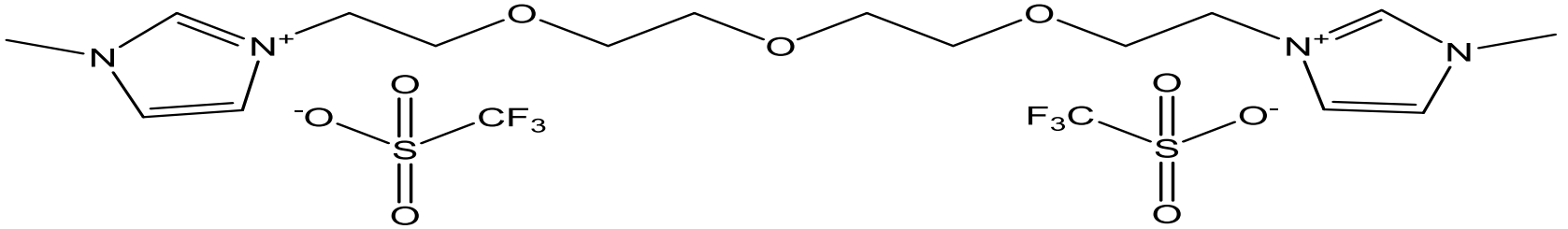
Watercol™ Series

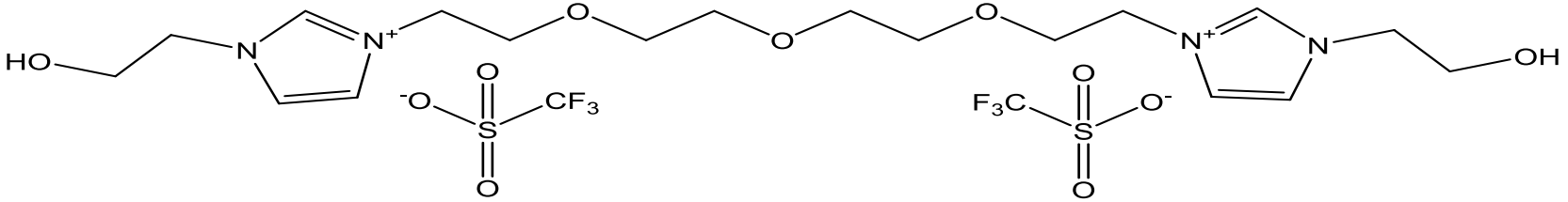
Watercol™1460



Watercol™1900



Watercol™1910



Watercol Series Capillary GC Columns

Key Benefits of a Sharp Water Peak Shape

- Measurement of water (qualitative and quantitative)
- Linear response over a very wide range (0.01% water to 100% water)
- Great sensitivity
  - 100 ppm using a thermal conductivity detector (TCD)
  - Anticipate much better sensitivity with
    - A mass spectrometer (MS) operated in the SIM mode
    - Vacuum ultraviolet (VUV) absorption spectroscopy
    - A barrier discharge ionization detector (BID)
- Reproducibility (virtually no change in column performance over time)

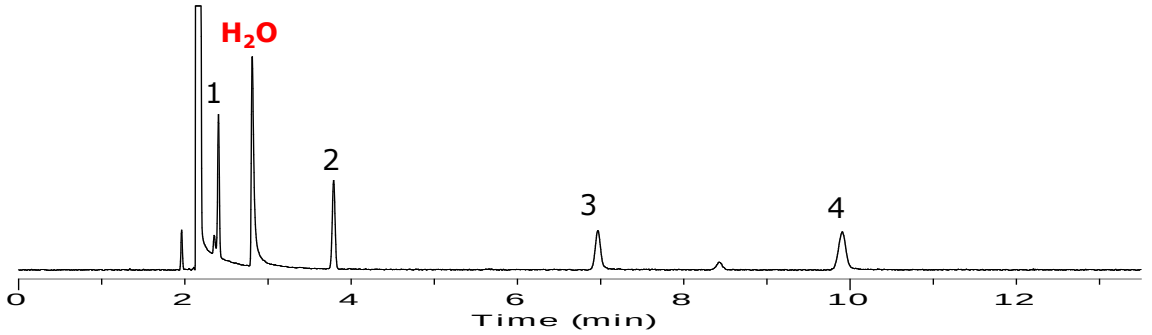
NOTE: The detector being used must be able to detect water.

Watercol Series Capillary GC Columns

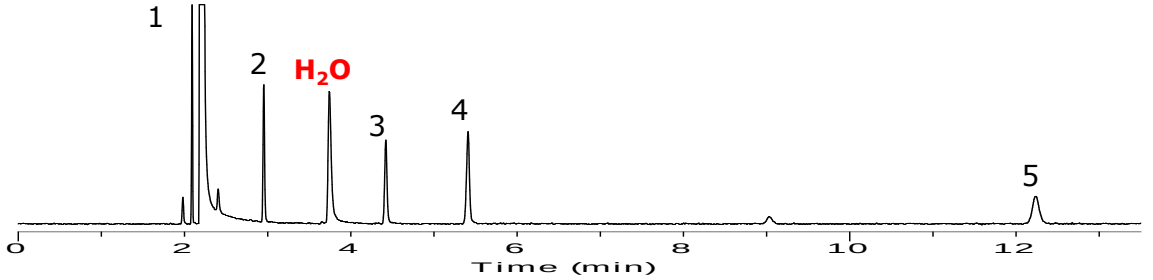
Selectivity Options; 96 ºC, using a GC/TCD

1. n-tridecane
2. 2-octanone
3. 1-heptanol
4. 1-octanol
5. naphthalene

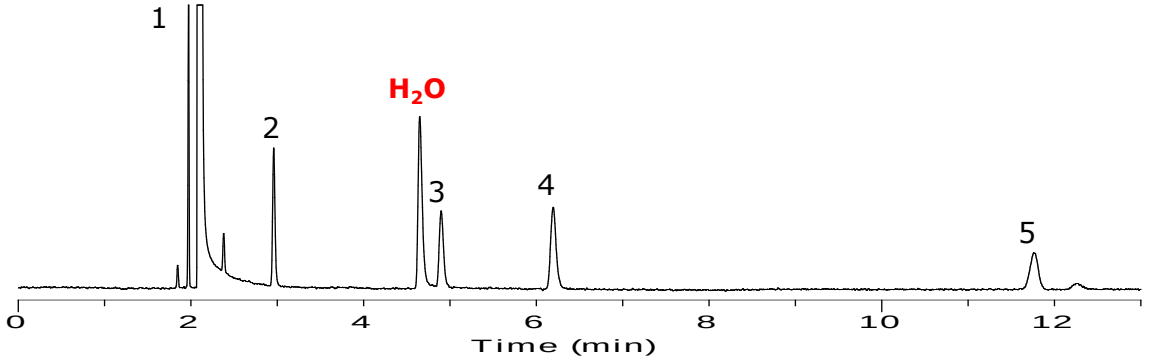
Watercol™1460



Watercol™1900



Watercol™ 1910



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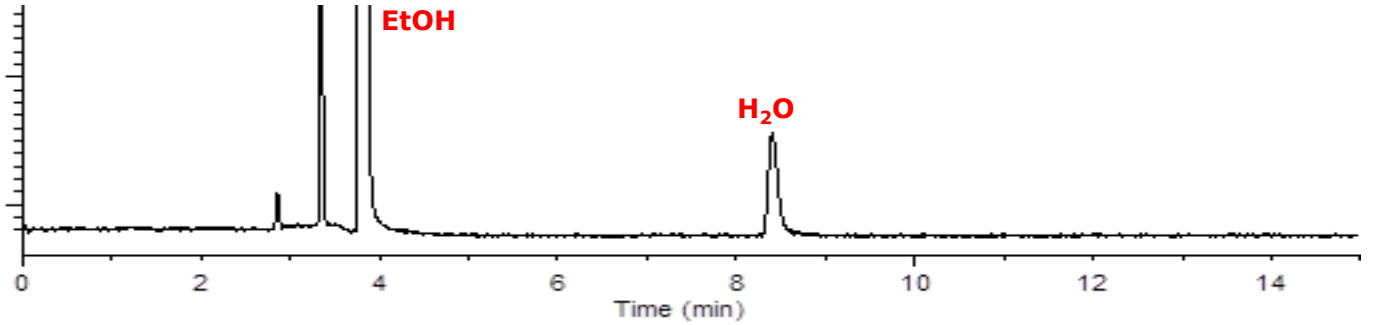
Comparison of water selectivity and peak shape

GC/TCD, Temp. 80 ºC (isothermal)

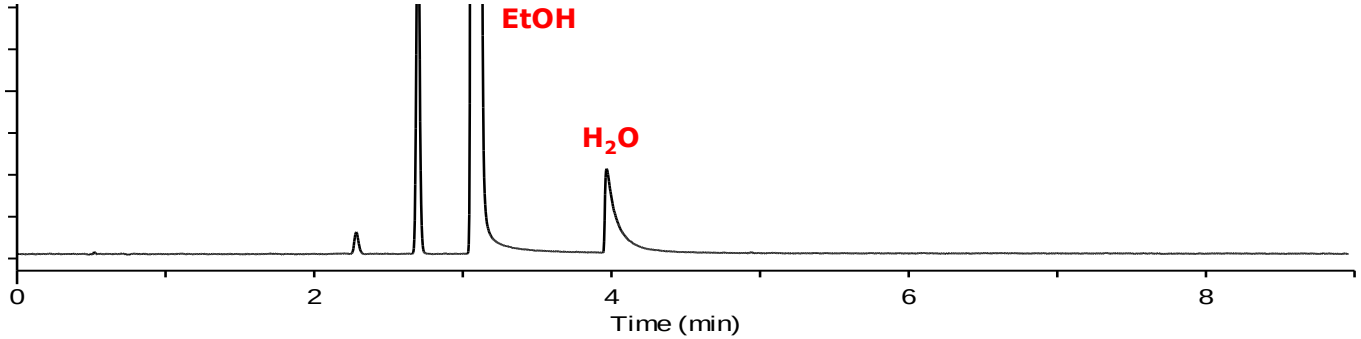
Watercol™ 1910

30-m x 0.25 mm i.d x 0.20 µm df.



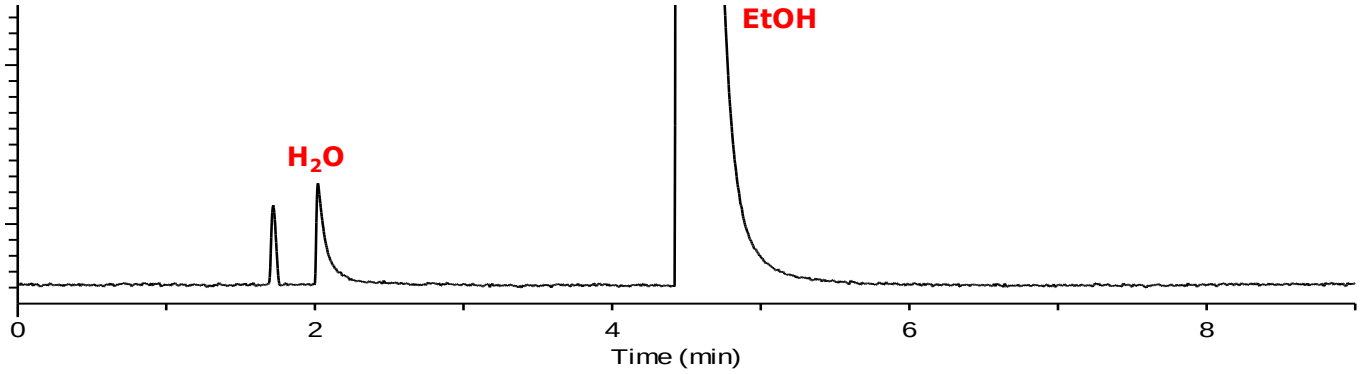
Wax-type column

30-m x 0.25 mm i.d x 0.25 µm df.

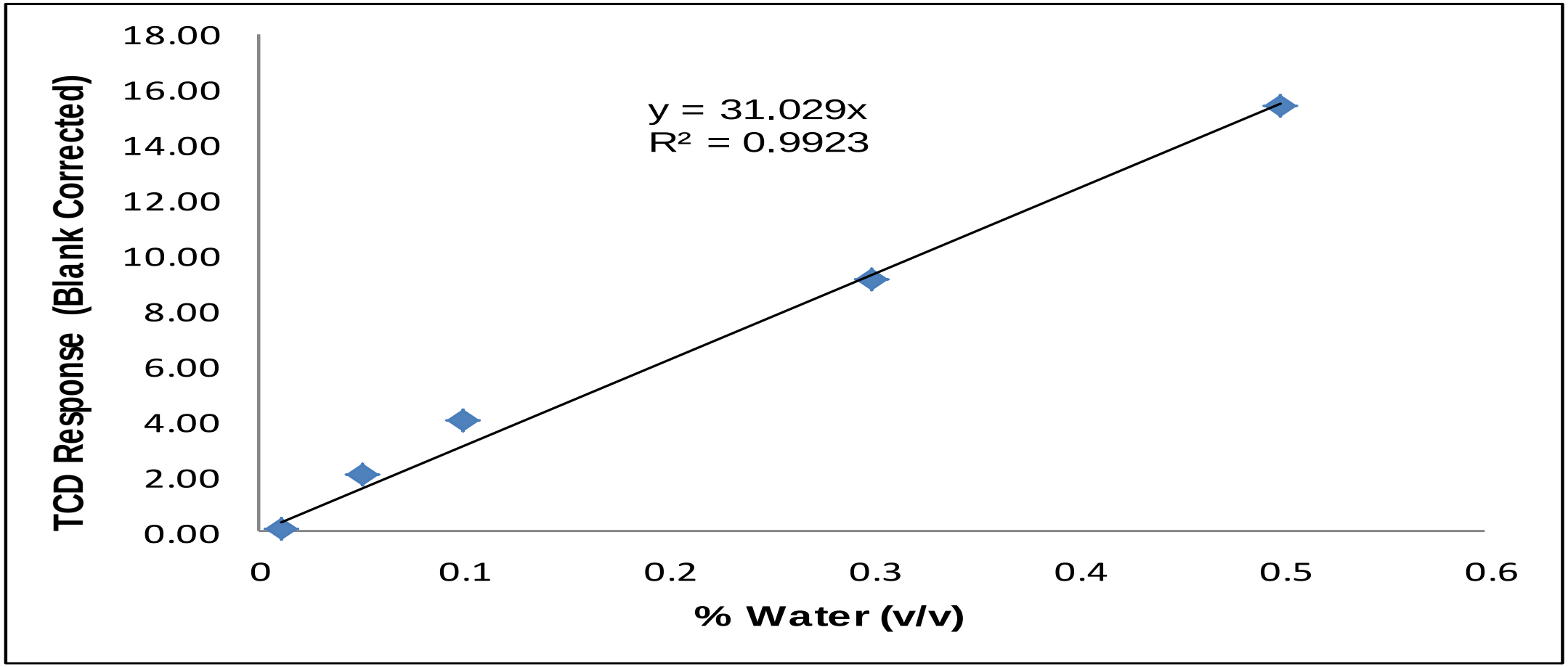


Q-Plot

30-m x 0.32 mm i.d



Water Calibration Curve (0.01-0.5%) on Watercol™1910

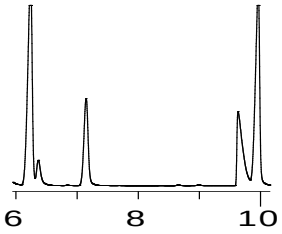


Watercol Series Capillary GC Columns

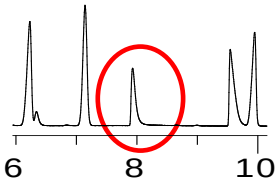
Measure Water in a 60-Component Solvent Mix (Chemical Application)

- Water peak is baseline resolved from a complex matrix that consists of the most common solvents used in chemical/API production
- Good peak symmetry, suitable for water quantification

GC/FID



GC/TCD



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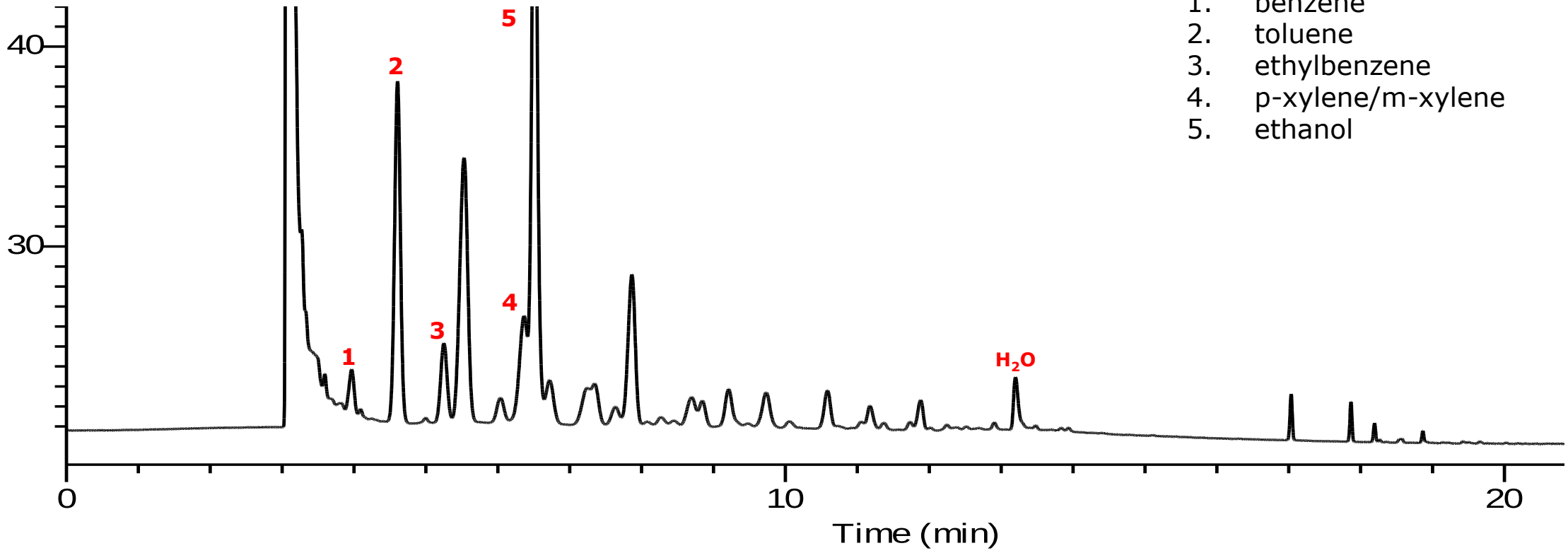
Watercol Series Capillary GC Columns

Measure Water in Gasoline (Petroleum Application)

- Water peak is baseline resolved from other gasoline components
- Analysis of BTEX cmpds, and oxygenates such as Ethanol are also possible. Multiple target analytes can be identified in a single run



1. benzene
2. toluene
3. ethylbenzene
4. p-xylene/m-xylene
5. ethanol

Watercol Series Capillary GC Columns

Comparison to Karl Fischer

- Karl Fischer titration (mostly used)
  - 500 ppm is typical detection limit
  - **Watercol + TCD = 100 ppm**

- Karl Fischer coulometric
  - 5 ppm is typical detection limit
  - Watercol + other detectors =

Watercol columns have several advantages over Karl Fischer

- Reduced costs
  - GC requires less hands-on time
  - Lower volume of chemical waste generated (which must be deposed of)
  - Perform two analysis (water and volatiles/semivolatiles) with a single method
- Reduced amount of sample needed (<0.5 mL for liquids and <0.2 g for solids)
- Eliminate worker exposure to (potentially) harmful chemicals
- No unwanted side reactions
- No solubility issues

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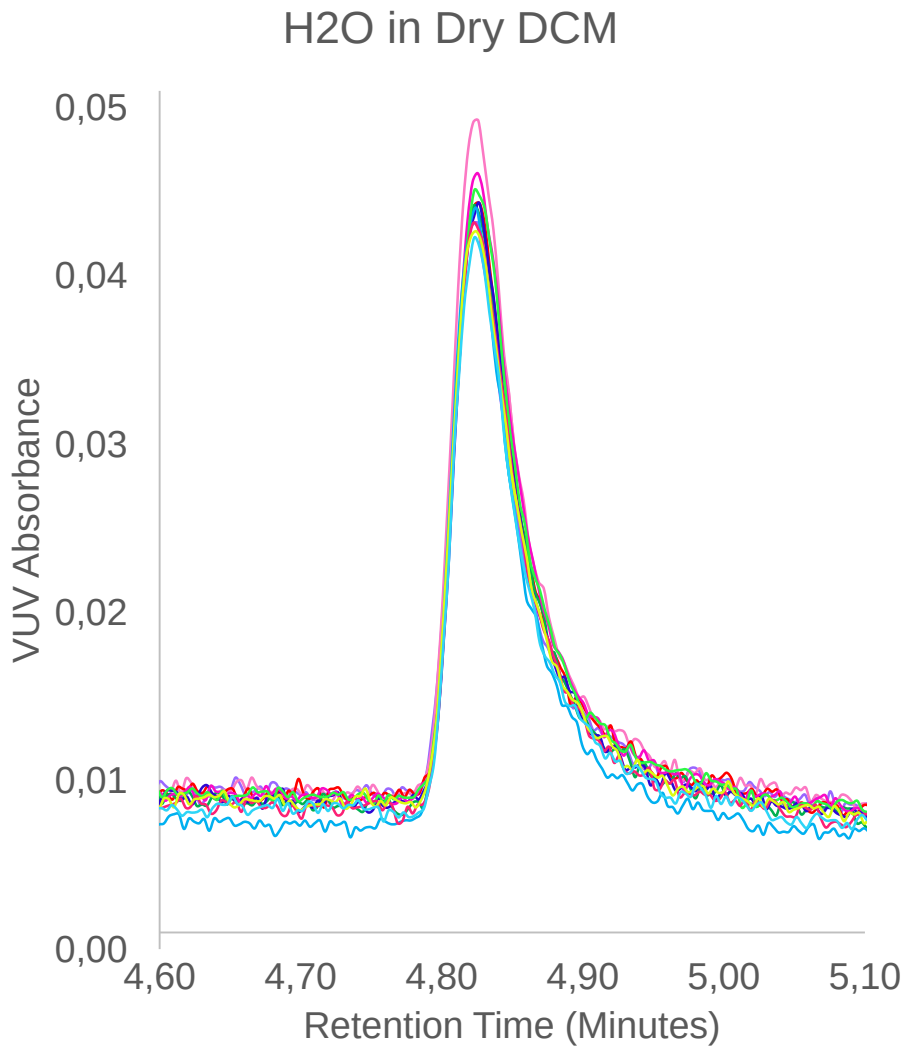
Reproducibility and Detection Limits VUV

A



B

Parameter	Setting	Unit
Average Area	0.00187	AU
% RSD	4.68	-
Conc. Background	100	ppm
MDL	13	ppm
Average Height	0.035	AU
RMS Noise	.00029	AU
S/N	120	-
LOD	2.5	ppm

Shimadzu BID Detector

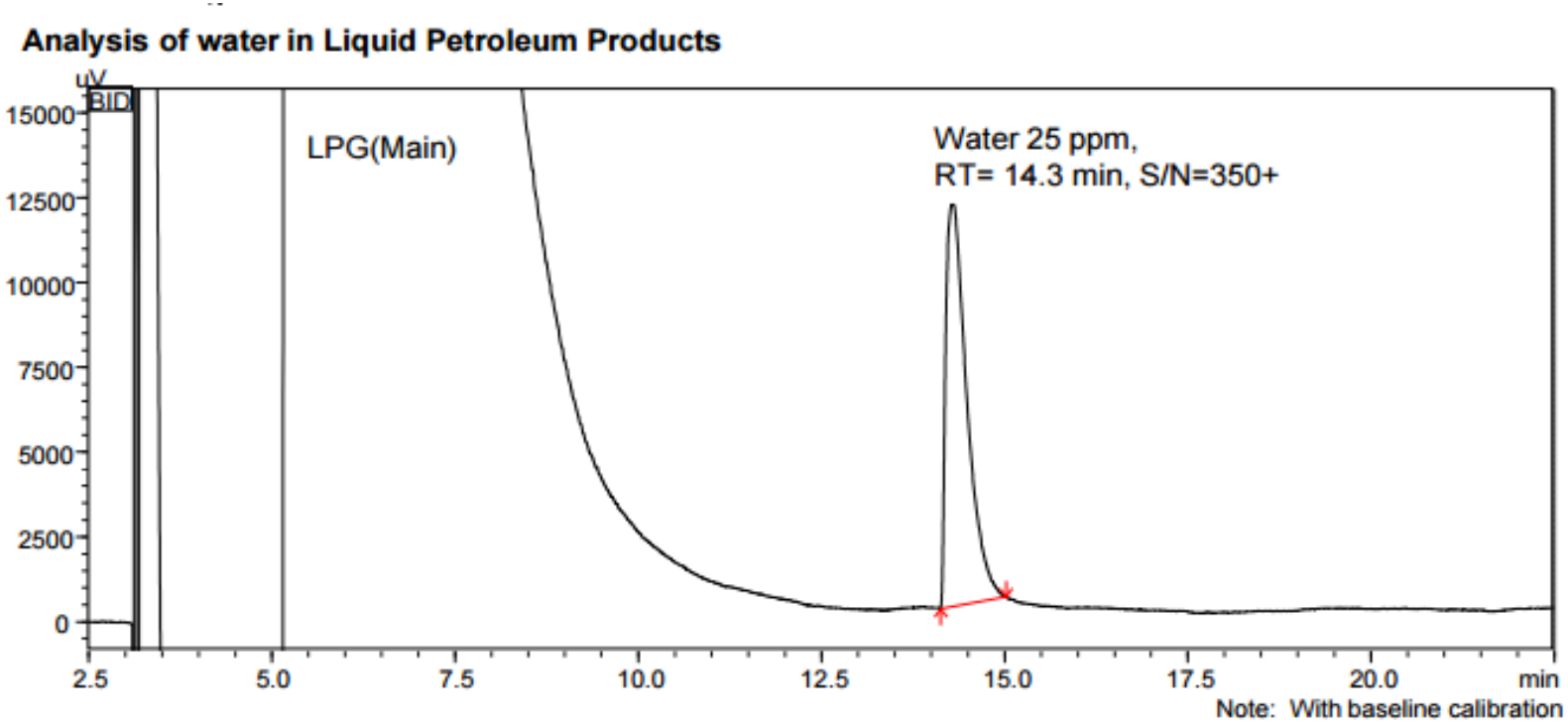


Fig. 1: Chromatogram for water determination (25 ppm) in LPG. Quantification of Limit(S/N=10) and Detection of Limit(S/N=3.3) can be down to 0.66 ppm and 0.22 ppm respectively.

Watercol 1910

Experimental Run Conditions

Instrument:	Shimadzu QP-2010 Plus GC
Column:	Watercol 1910, 30 m x 0.25 mm I.D., x 0.2 µmdf
Oven:	55°C (2min), 4°C/min to 180°C (1 min)
Inj. Temp:	250°C
Carrier Gas:	Helium, (40 cm/sec)
Detector:	BID, 200°C
Liner:	4 mm I.D. split liner with wool
Injection:	0.5 µL, 200:1 split
Sample:	SPME Alcohol Mix in H_2O

Analysis of water in Liquid Petroleum Products

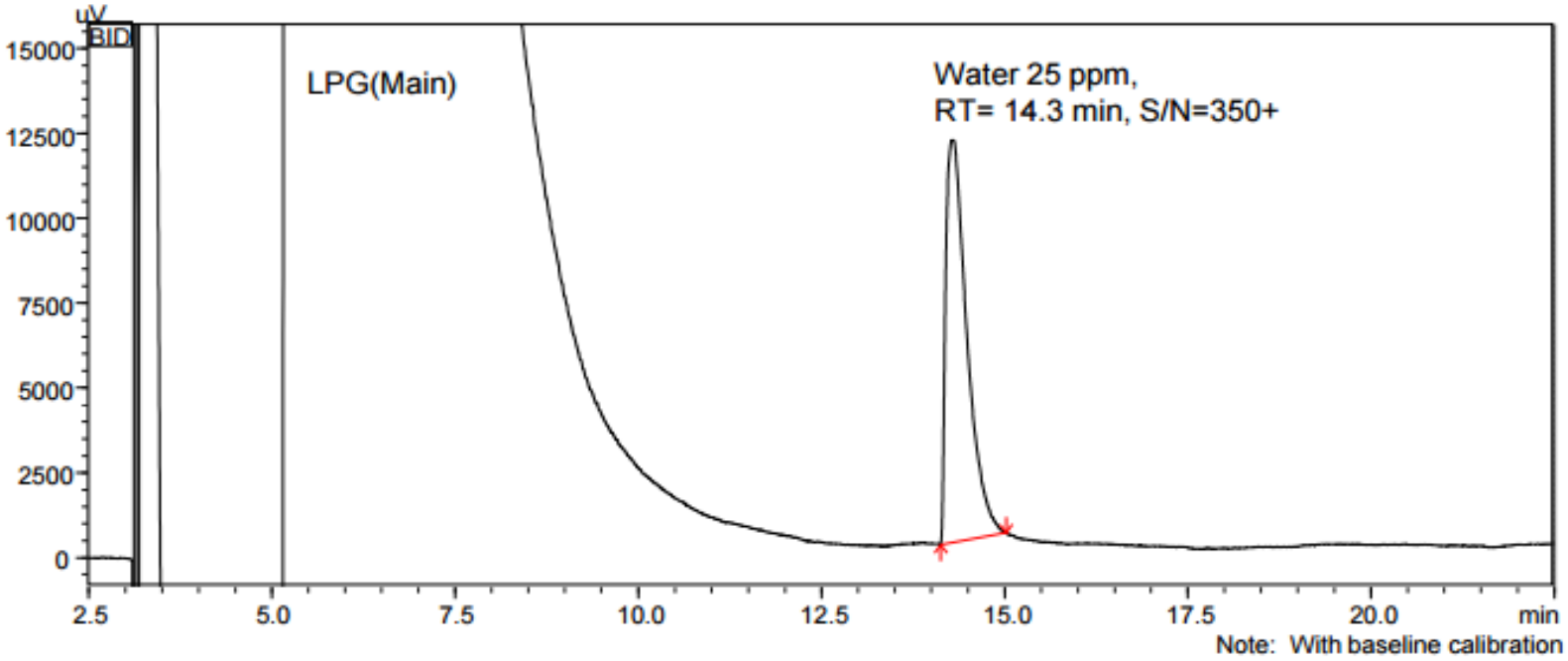
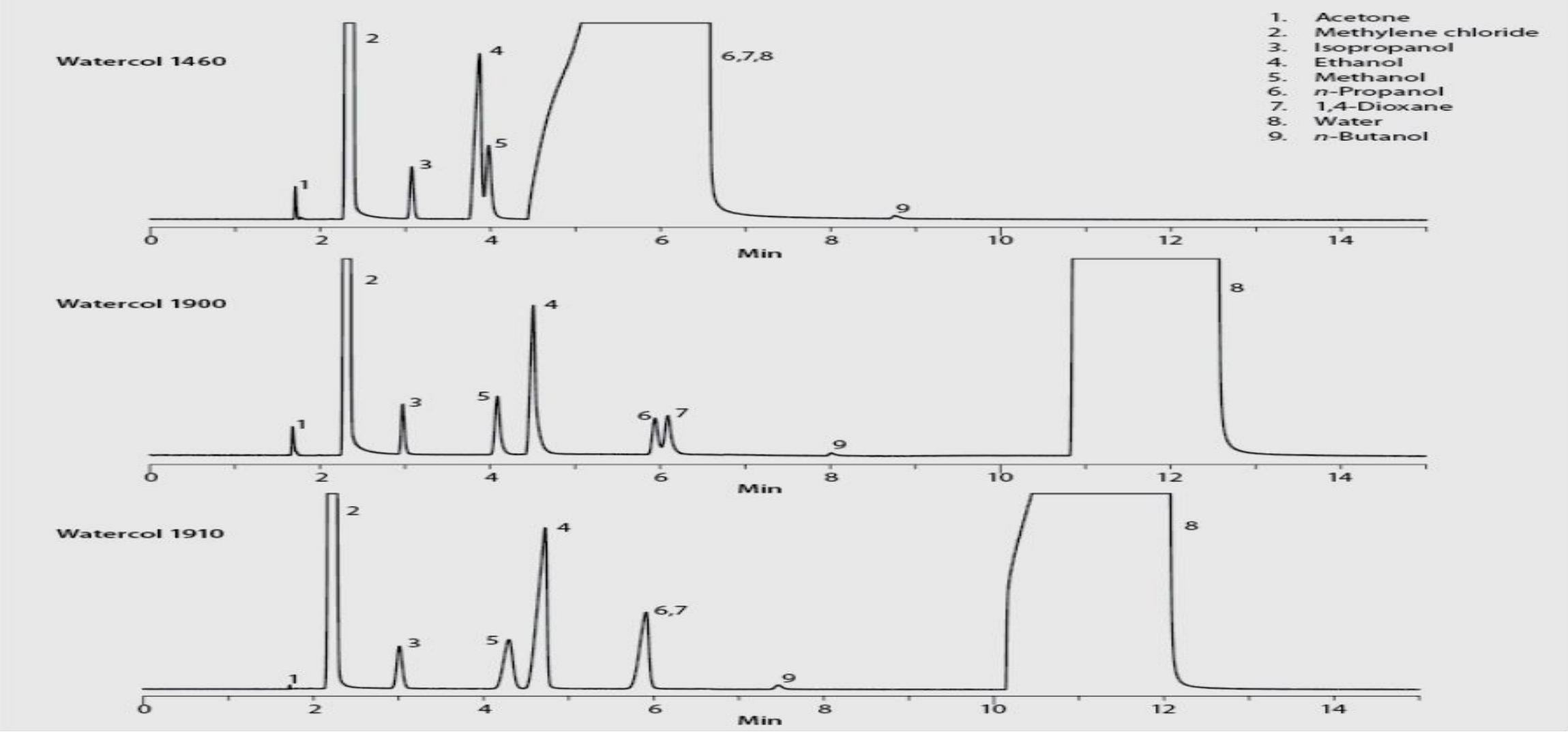


Fig. 1: Chromatogram for water determination (25 ppm) in LPG. Quantification of Limit(S/N=10) and Detection of Limit(S/N=3.3) can be down to 0.66 ppm and 0.22 ppm respectively.

Water as Solvents

Alcohols and other VOC analysis in water; 35 ºC, 4 ºC/min to 125 ºC (2 min)



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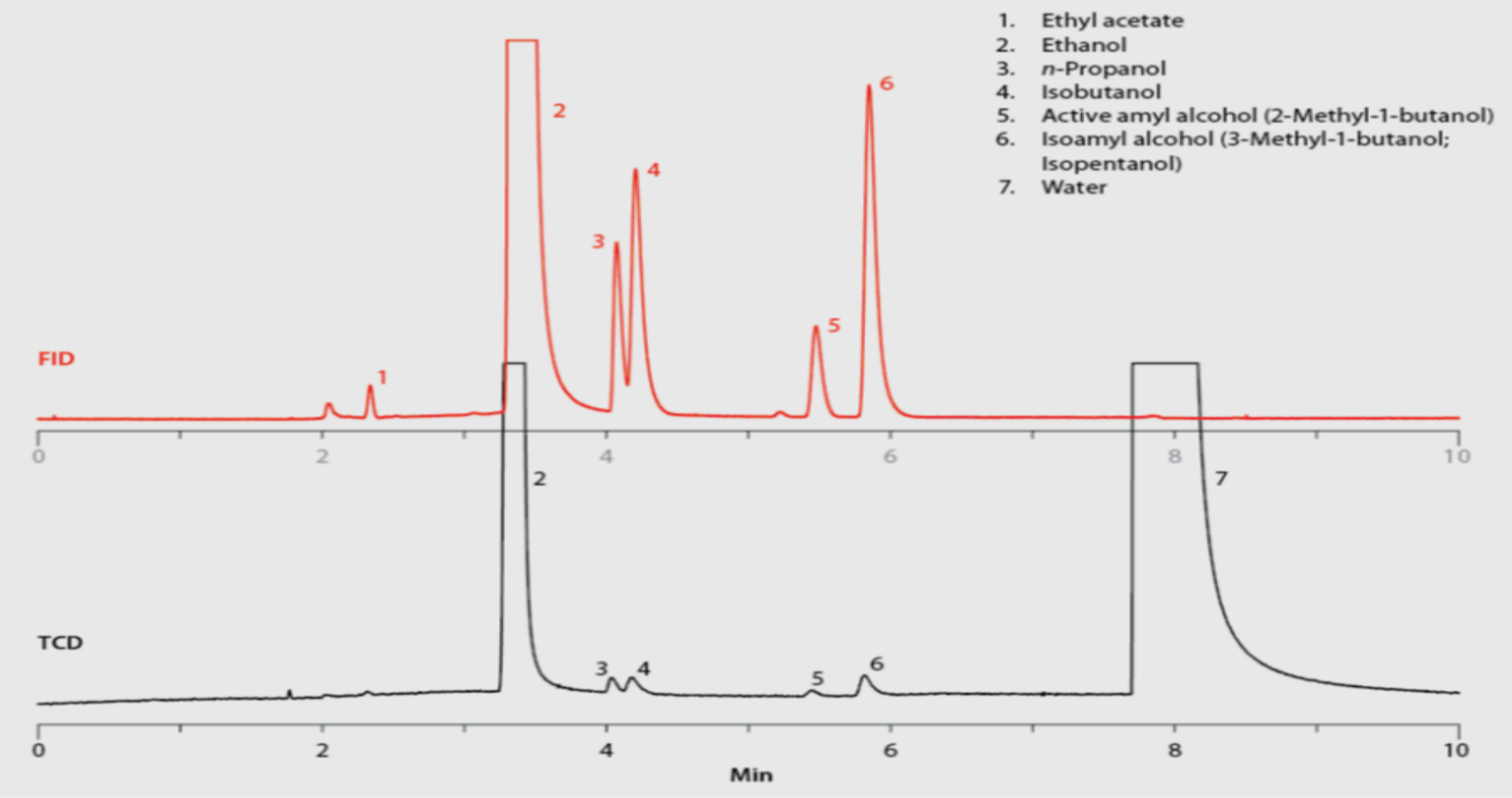
Watercol Series Capillary GC Columns

Measure Aroma Fusel Alcohols in Tequila (Food and Beverage Application)



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Watercol Series Capillary GC Columns

Summary

- Measurement of water with linearity, great sensitivity, and reproducibility
- Less hands-on time compared to other technologies used to measure water
- Less volume of chemical waste
- Possible to obtain results for water + volatiles/semivolatiles in same analysis
- Amendable for water as injection solvent

GC columns made with ionic liquid stationary phases are exclusive to Supelco.

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SLB®-IL (i-series) Capillary GC Columns

Polar Selectivity *and* Inertness

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SLB-IL (i-series) Capillary GC Columns

Overview

- More inert versions of popular ionic liquid chemistries
- Provide selectivity and inertness for polar analytes
- Polar selectivity and inertness allows
  - Better accuracy (identification and amount)
  - Better sensitivity

SLB-IL (i-series) Capillary GC Columns

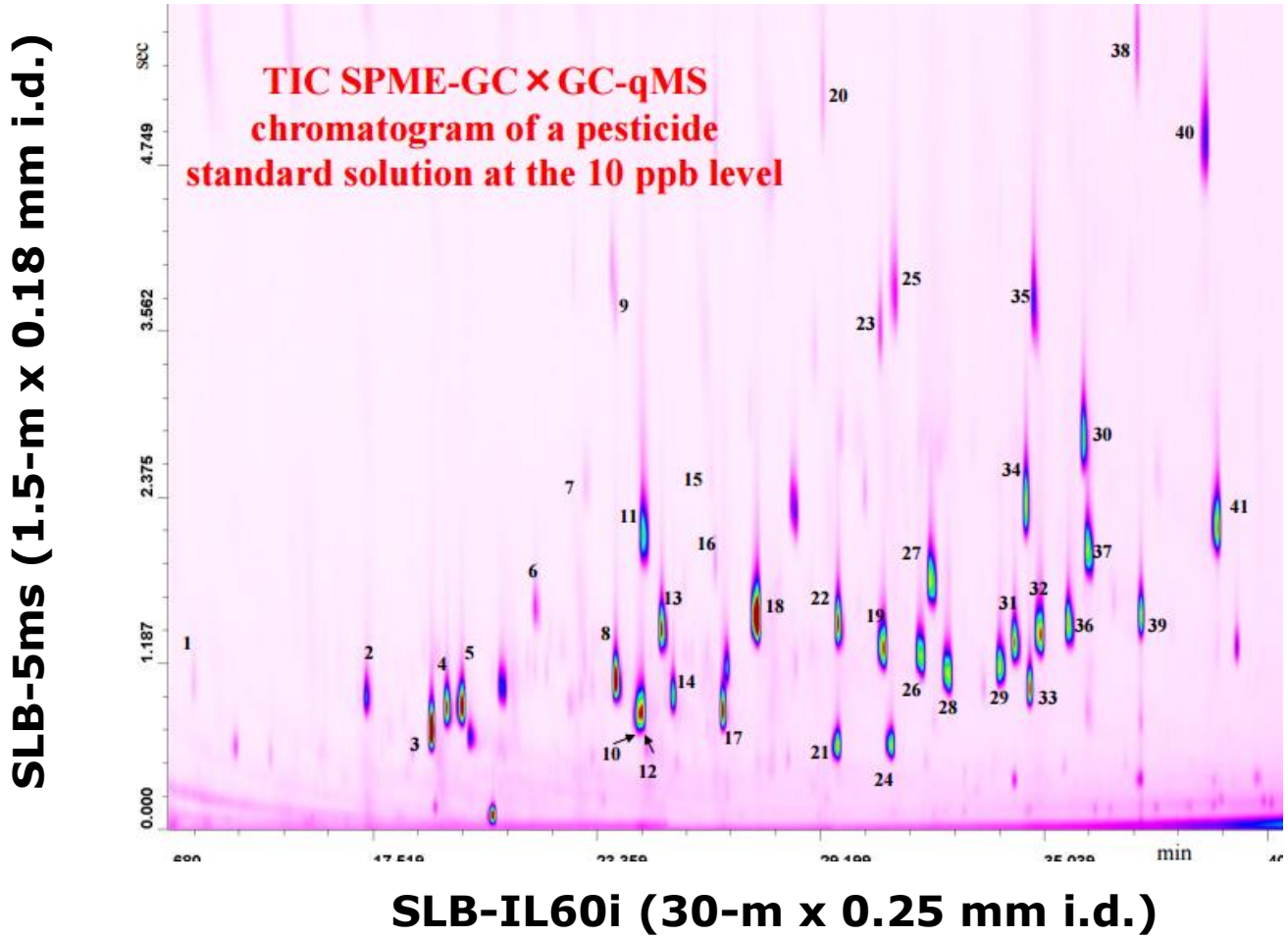
Selectivity Options

- A range of i-series columns were developed and classified as
  - Polar (SLB-IL60i)
  - Highly polar (SLB-IL76i)
  - Extremely polar (SLB-IL111i)
  - **Great choices for 2D GC**

sigma-aldrich.com/il-gc-inert

Ionic Liquids GC columns are great columns for GC×GC

Increase orthogonality when paired with a non-polar stationary phase (e.g. SLB-5ms)

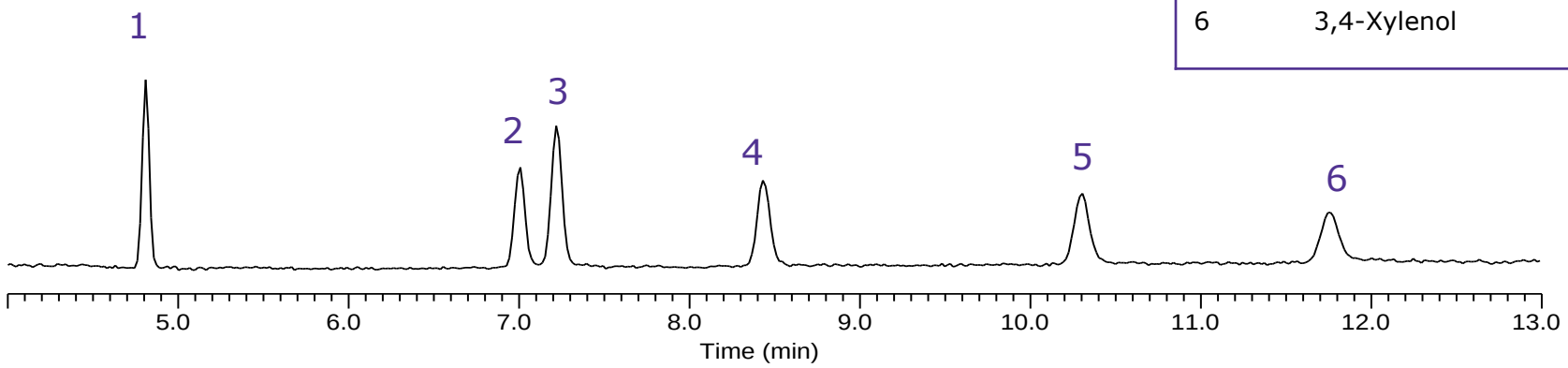


Courtesy of Prof. L. Mondello

SLB-IL 60i

Results-Xylenols Mix 130°C Isothermal

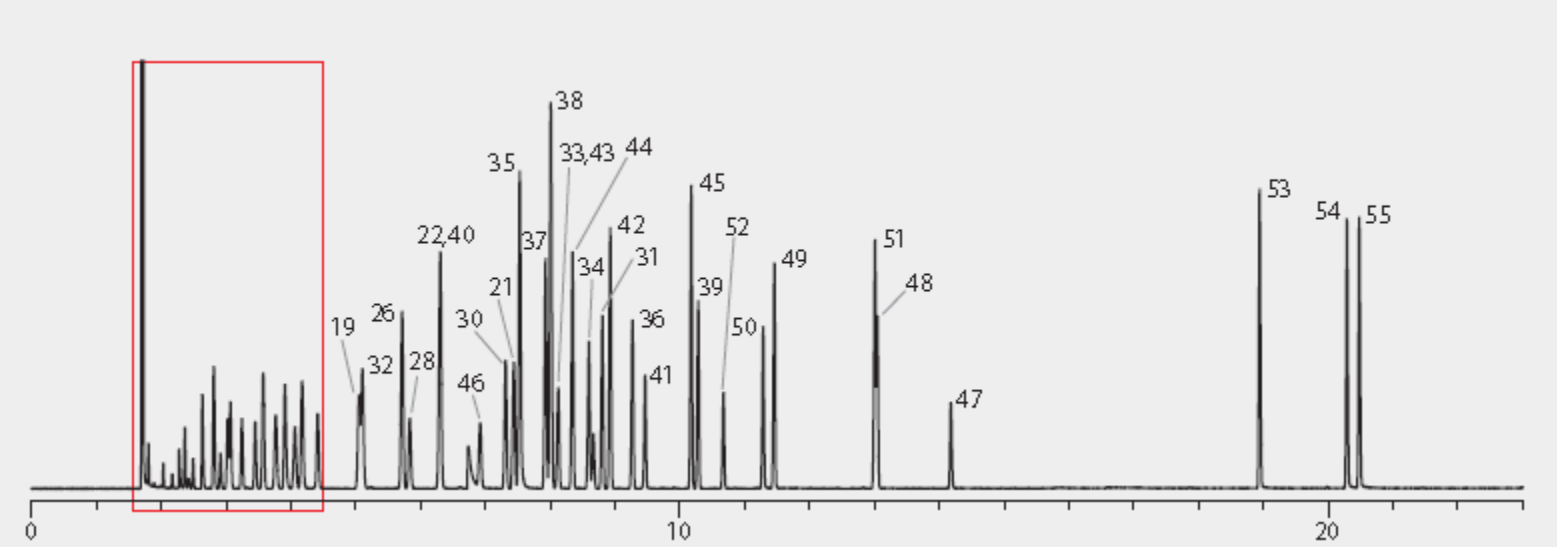
Peak	Compound	t_R
1	2,6-xylenol	4.825
2	2,4-xylenol	7.019
3	2,5-Xylenol	7.236
4	2,3-Xylenol	8.447
5	3,5-Xylenol	10.317
6	3,4-Xylenol	11.769



Industrial Solvents

Figure 2. Industrial Solvents on SLB-IL60i

column:	SLB-IL60i, 30 m × 0.25 mm I.D., 0.20 µm (29832-U)
oven:	40 °C (4 min), 8 °C/min to 200 °C (5 min)
inj. temp.:	250 °C
detector:	FID, 250 °C
carrier gas:	helium, 30 cm/sec
injection:	1 µL, 100:1 split
liner:	4 mm I.D., split type, cup design
sample:	industrial solvents, each at 0.2 % (v/v) in pentane



1. Hexane
2. 1,1-Dichloroethylene
3. Methyl formate
4. Acetone
5. Ethyl formate
6. Methyl acetate
7. trans-1,2-Dichloroethylene
8. Tetrahydrofuran
9. Carbon tetrachloride
10. 1,1-Dichloroethane
11. Ethyl acetate
12. Methanol
13. Isopropyl acetate
14. 2-Butanone
15. 2-Propanol
16. Methylene chloride
17. Ethanol
18. Benzene
19. *n*-Propyl acetate
20. Trichloroethylene
21. 4-Methyl-2-pentanone
22. Isobutyl acetate
23. Tetrachloroethene
24. Chloroform
25. sec-Butanol
26. Toluene
27. *n*-Propanol
28. 1,4-Dioxane
29. 1,2-Dichloroethane
30. *n*-Butyl acetate
31. 2-Hexanone
32. Isobutanol
33. Nitropropane
34. Isoamyl acetate
35. Ethylbenzene
36. Mesityl oxide
37. *p*-Xylene
38. *m*-Xylene
39. 5-Methyl-2-hexanone
40. *n*-Butanol
41. *n*-Amyl acetate
42. *o*-Xylene
43. Isoamyl alcohol
44. Chlorobenzene
45. Styrene
46. 1,1,1,2-Tetrachloroethane
47. Dimethylformamide
48. Diacetone alcohol
49. Cyclohexanol
50. 2-Butoxyethanol (Butyl cellosolve)
51. 1,4-Dichlorobenzene
52. 1,1,2,2-Tetrachloroethane
53. 2-Methylphenol
54. 3-Methylphenol
55. 4-Methylphenol

Industrial Solvents
Selectivity Difference 111i and 60i

column: SLB-IL111i, 30 m x 0.25 mm I.D., 0.20 µm (29883-U)
oven: 40 °C (8 min), 8 °C/min to 200 °C (1 min)
All other conditions and peak IDs are the same as Figure 2.

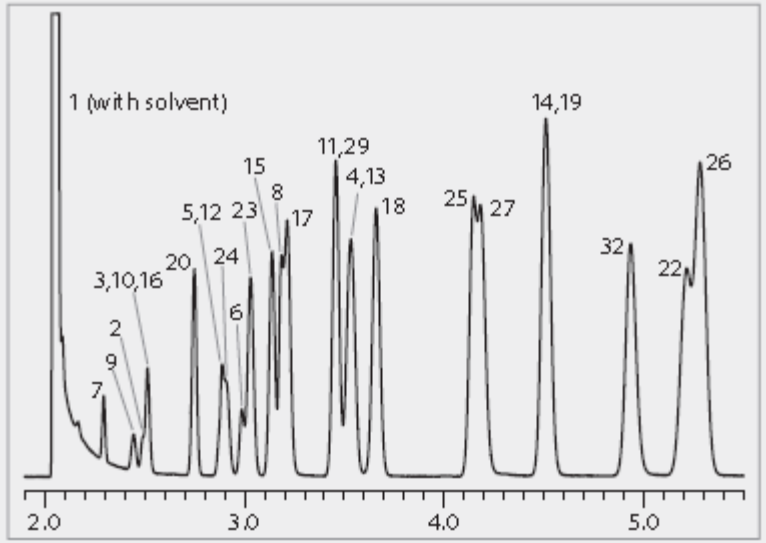
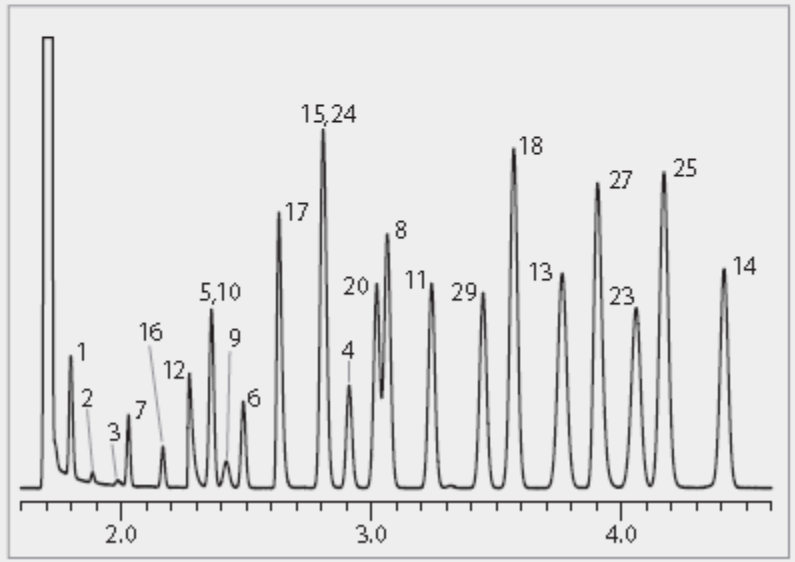


Figure 2. Industrial Solvents on SLB-IL60i

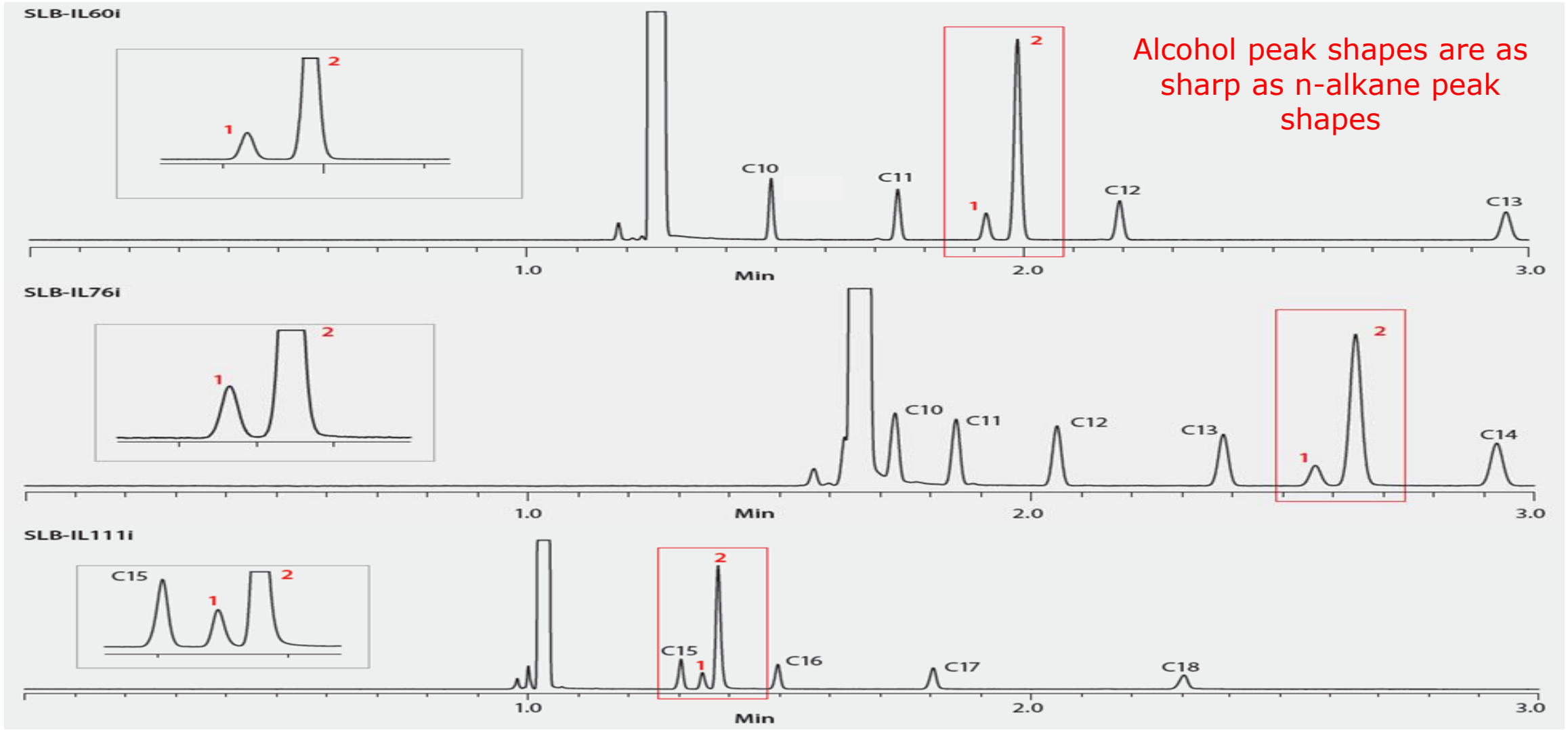
column: SLB-IL60i, 30 m x 0.25 mm I.D., 0.20 µm (29832-U)
oven: 40 °C (4 min), 8 °C/min to 200 °C (5 min)
inj. temp.: 250 °C
detector: FID, 250 °C
carrier gas: helium, 30 cm/sec
injection: 1 µL, 100:1 split
liner: 4 mm I.D., split type, cup design
sample: industrial solvents, each at 0.2 % (v/v) in pentane



1. Hexane
2. 1,1-Dichloroethylene
3. Methyl formate
4. Acetone
5. Ethyl formate
6. Methyl acetate
7. trans-1,2-Dichloroethylene
8. Tetrahydrofuran
9. Carbon tetrachloride
10. 1,1-Dichloroethane
11. Ethyl acetate
12. Methanol
13. Isopropyl acetate
14. 2-Butanone
15. 2-Propanol
16. Methylene chloride
17. Ethanol
18. Benzene
19. *n*-Propyl acetate
20. Trichloroethylene
21. 4-Methyl-2-pentanone
22. Isobutyl acetate
23. Tetrachloroethene
24. Chloroform
25. sec-Butanol
26. Toluene
27. *n*-Propanol
28. 1,4-Dioxane
29. 1,2-Dichloroethane
30. *n*-Butyl acetate
31. 2-Hexanone
32. Isobutanol
33. Nitropropane
34. Isoamyl acetate
35. Ethylbenzene
36. Mesityl oxide
37. *p*-Xylene
38. *m*-Xylene
39. 5-Methyl-2-hexanone
40. *n*-Butanol
41. *n*-Amyl acetate
42. *o*-Xylene
43. Isoamyl alcohol
44. Chlorobenzene
45. Styrene
46. 1,1,1,2-Tetrachloroethane
47. Dimethylformamide
48. Diacetone alcohol
49. Cyclohexanol
50. 2-Butoxyethanol (Butyl cellosolve)
51. 1,4-Dichlorobenzene
52. 1,1,2,2-Tetrachloroethane
53. 2-Methylphenol
54. 3-Methylphenol
55. 4-Methylphenol

SLB-IL (i-series) Capillary GC Columns

Active Amyl Alcohol and Isoamyl Alcohol with n-Alkanes; 90 ºC



sigma-aldrich.com/il-gc-inert

MERCK

Applications

- Critical isobaric PAHs
- TCDD
- Allergens
- Industrial Solvents
- FAMEs
- BTEX
- and Much more..

CONCLUSIONS

- **Something totally new and completely different in the world of GC phases**
- **Have the opportunity to impact current GC and GC-MS practices along several paths**

Watercol™ Series

Watercol 1460

Watercol 1900

Watercol 1910

Three unique different selectivity ionic liquid phases for the GC analysis of H_20

“I” Series column provide unique selectivity with improved inertness

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Web Site (*sigma-aldrich.com/gc*)