Polyionic Ionic Liquid GC Stationary Phase Evaluations

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May 21, 2014

38th ISCC, Riva del Garda, Italy

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Overview of Presentation

- **Overview of Ionic Liquids**
- **SLB-IL111**
- **SLB-Il60**
- **New GC Applications**
- **Conclusions**

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

Desirable IL Properties for GC Use

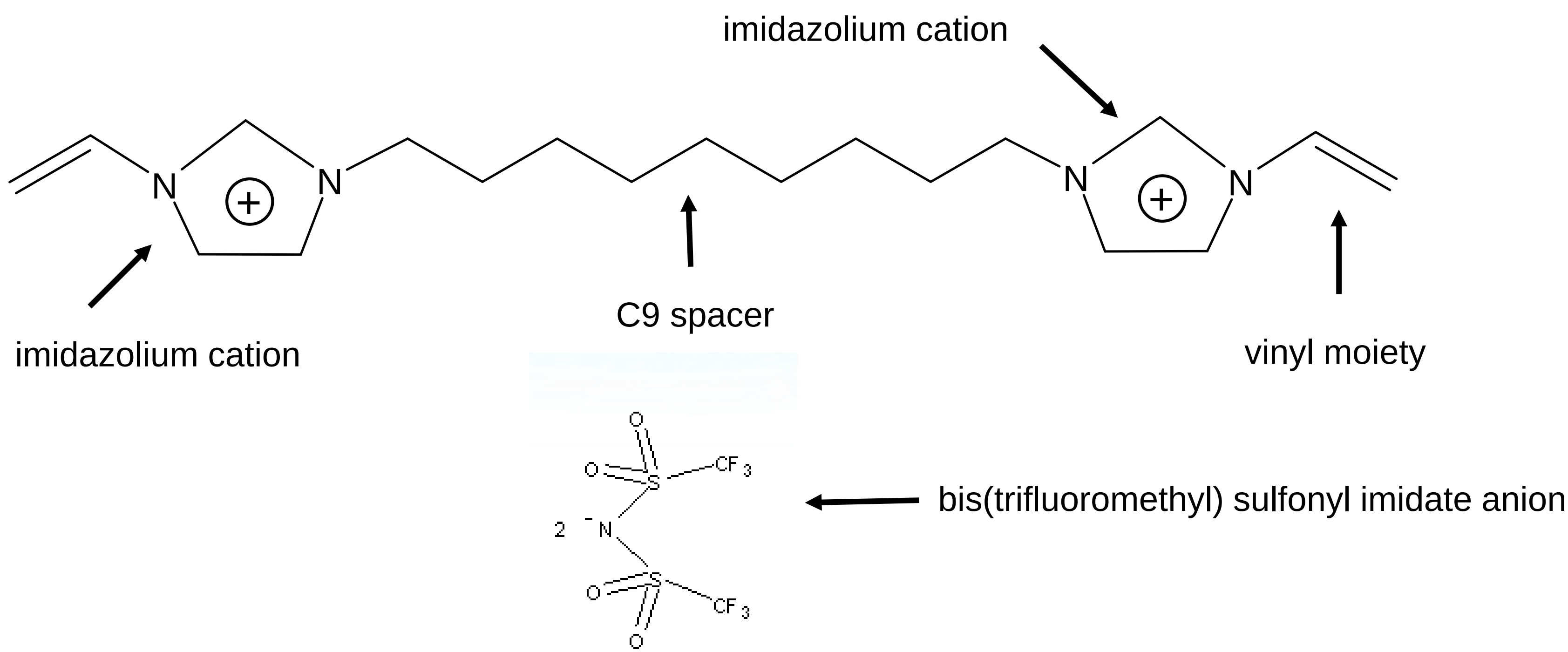
Several properties make ILs desirable as GC stationary phases

- remain liquid over a wide temperature range (Room Temperature→350 $^{o+}$C)
- very low volatility
- highly polar nature
- broadest range of solvation interactions of any known solvent
- good thermal stability
- high viscosity
- easily tailored to provide different polarities/selectivities

Geminal Dicationic Ionic Liquid Stationary Phase

SLB-IL100

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



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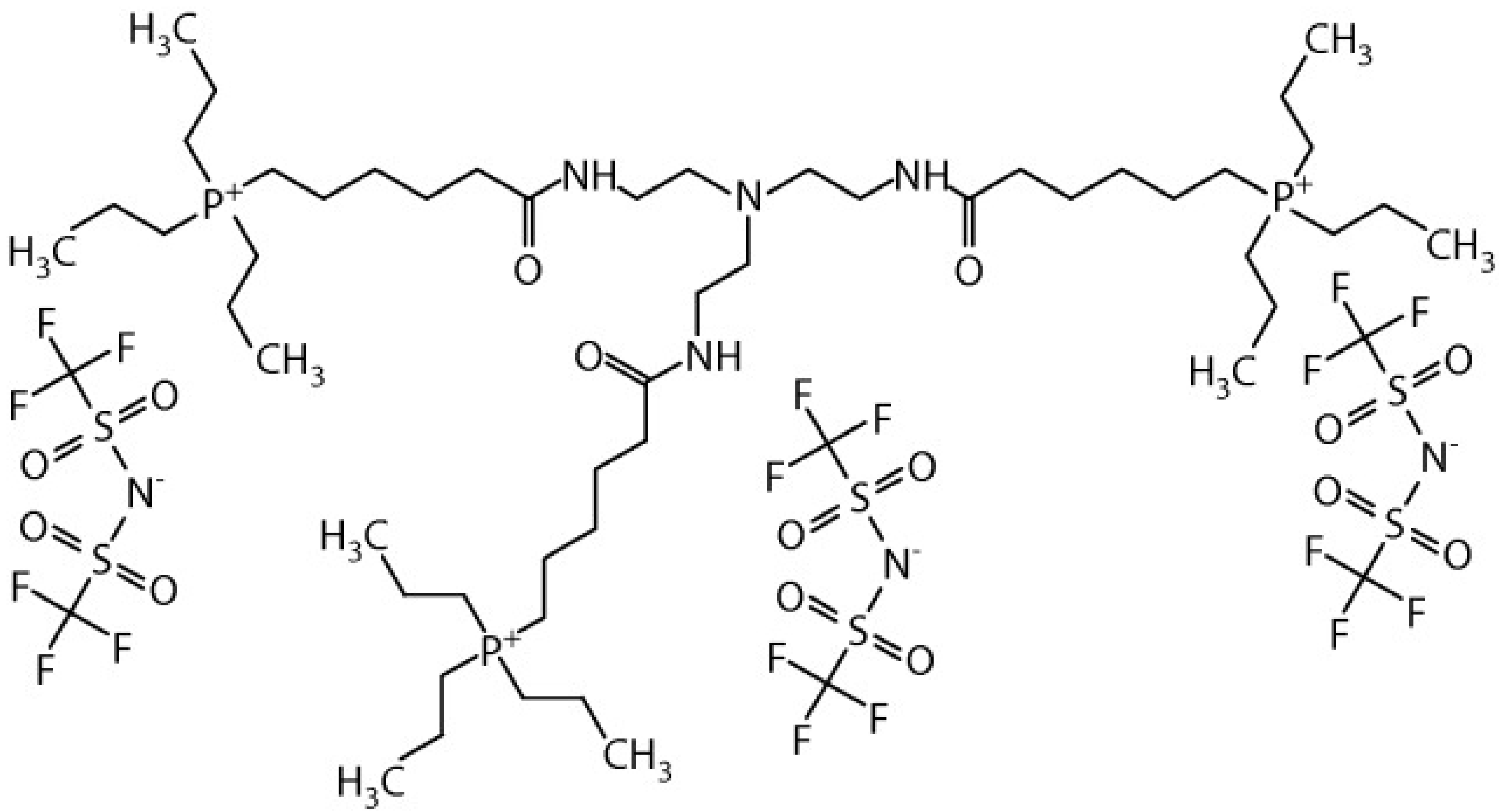
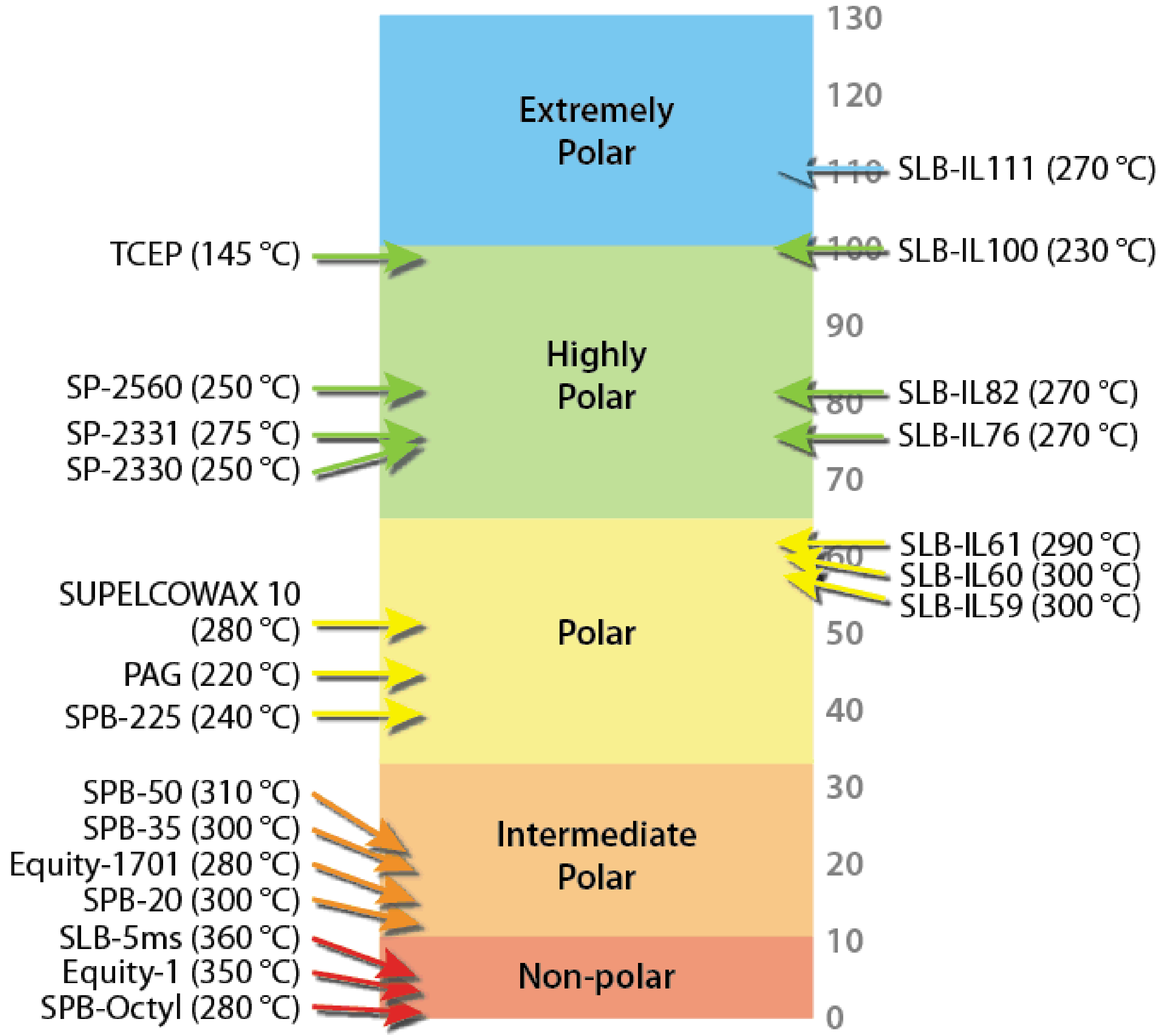
SLB-IL76

Phase Structure

Tri(tripropylphosphoniumhexanamido)triethylamine bis(trifluoromethylsulfonyl)imide



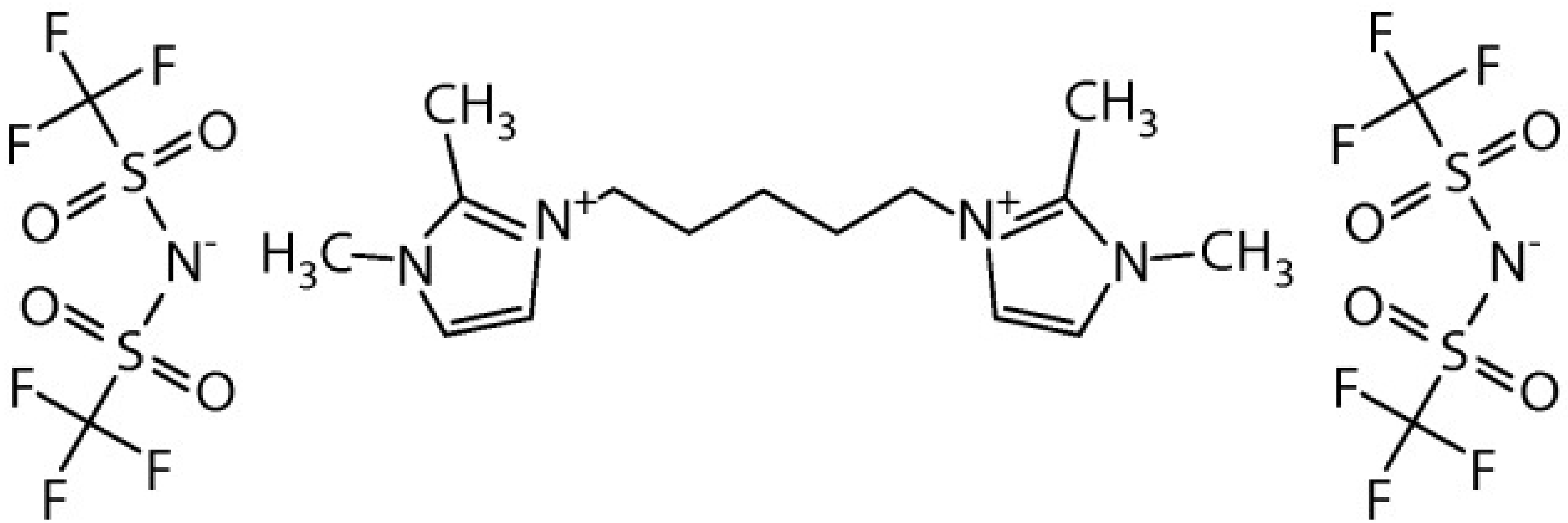
Visual Representation



SLB-IL111

Phase Structure

1,5-Di(2,3-dimethylimidazolium)pentane bis(trifluoromethylsulfonyl)imide



Cis/Trans FAME separations

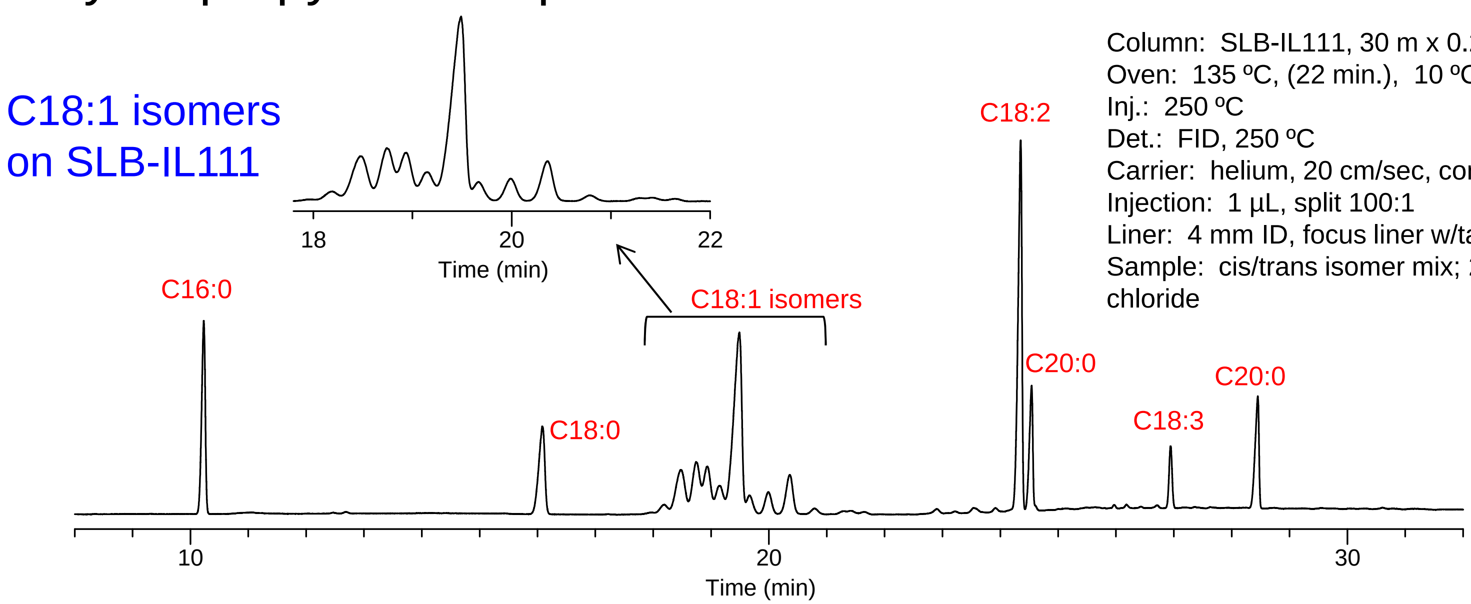
C18:1 cis/trans isomers of specific interest

Need high polarity phases to separate cis and trans geometric positional isomers

Normally use cyanopropylsilicone phases

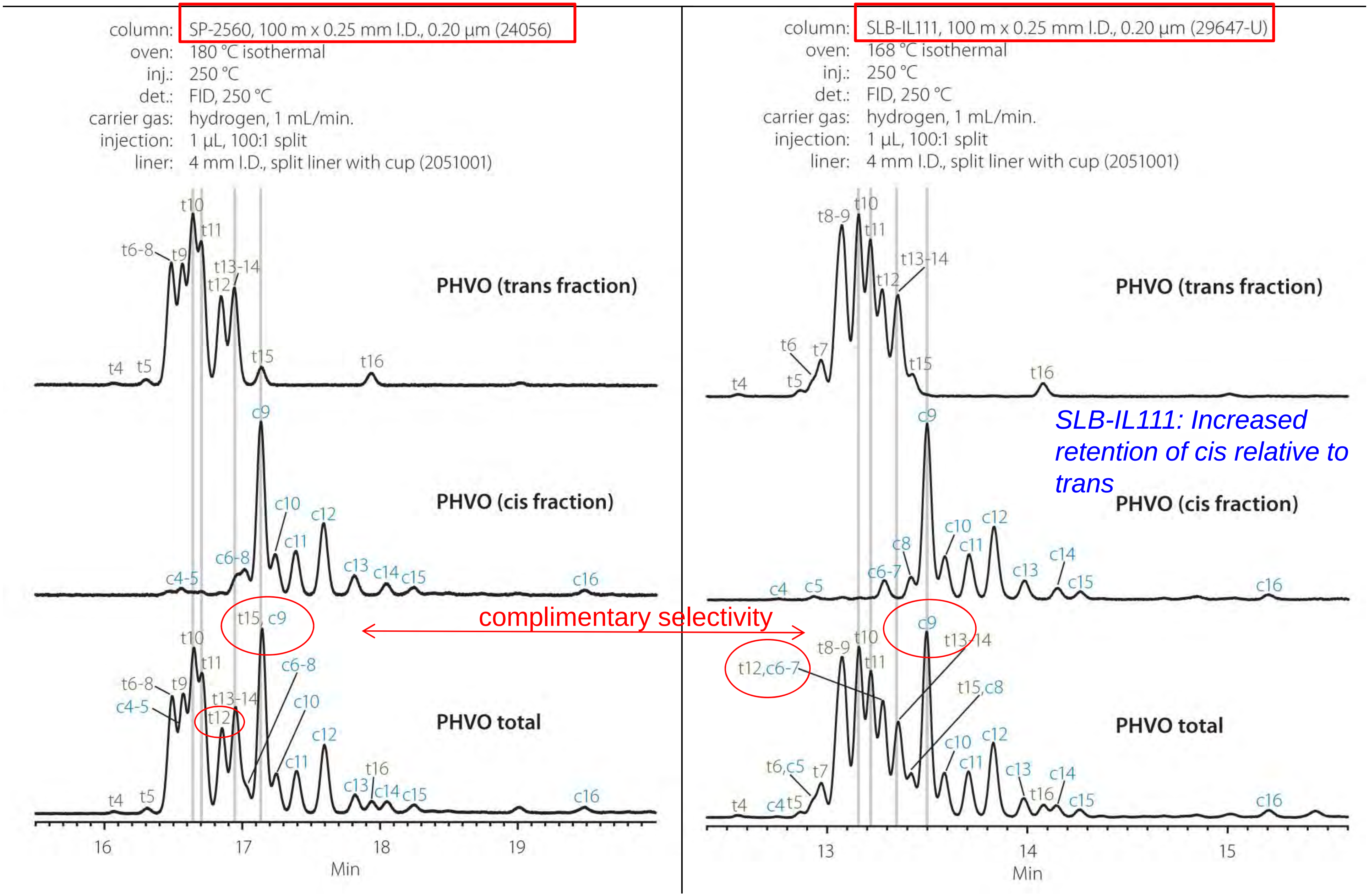
100 m SP-2560 is a mainstay column for this application

Ionic liquid columns SLB-IL100 and SLB-IL111 provide resolution of cis/trans isomers and complimentary selectivity to cyanopropylsilicone phases



Column: SLB-IL111, 30 m x 0.25 mm I.D. x 0.20 µm
Oven: 135 ºC, (22 min.), 10 ºC/min. to 170 ºC
Inj.: 250 ºC
Det.: FID, 250 ºC
Carrier: helium, 20 cm/sec, constant
Injection: 1 µL, split 100:1
Liner: 4 mm ID, focus liner w/taper
Sample: cis/trans isomer mix; 2.5 mg/ml in methylene chloride

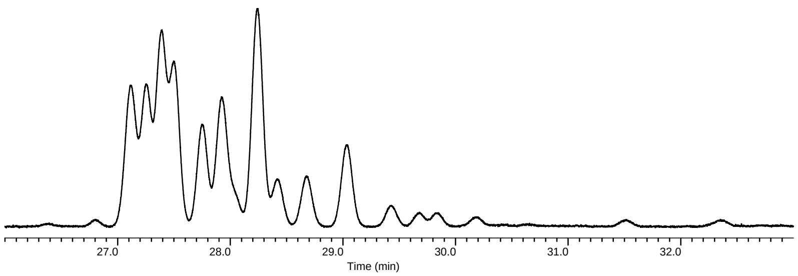
C18:1 cis/trans FAME Isomers in Partially Hydrogenated Vegetable Oil (PHVO) SLB-IL111 vs. SP-2560: 100 m columns



Positional cis/trans FAME Isomers

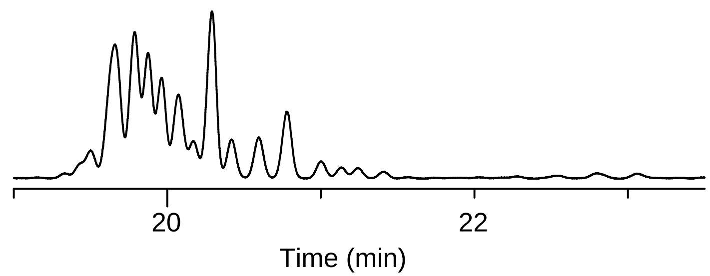
column: SP-2560, 200 m x 0.25 mm I.D., 0.20 µm
oven: 180 °C isothermal
inj.: 250 °C
det.: FID, 250 °C
carrier gas: hydrogen, 1 mL/min.
injection: 1 µL, 100:1 split
liner: 4 mm I.D., split liner with cup (2051001)

PHVO total FAMEs

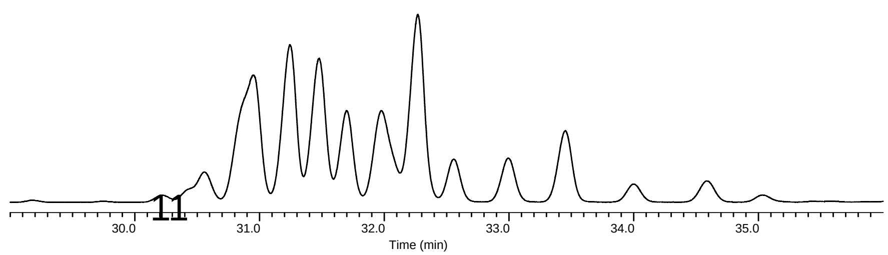


column: SLB-IL111, 200 m x 0.25 mm I.D., 0.20 µm
oven: 168 °C isothermal
inj.: 250 °C
det.: FID, 250 °C
carrier gas: hydrogen, 1 mL/min.
injection: 1 µL, 100:1 split
liner: 4 mm I.D., split liner with cup (2051001)

PHVO total FAMEs



PHVO total FAMEs on SLB-IL111 @ 150 °C isothermal



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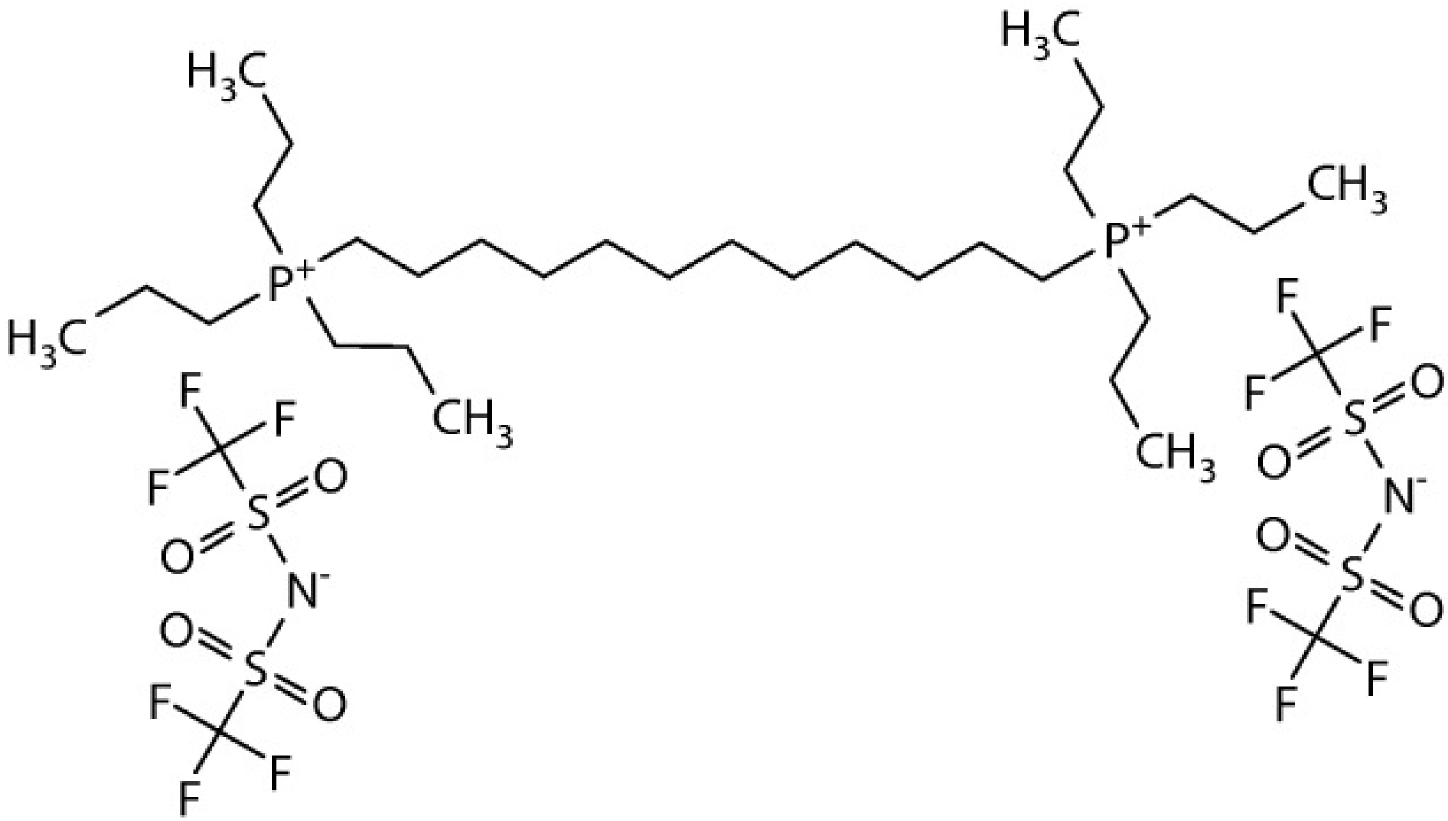
SLB-IL60

Phase Structure

1,12-Di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonyl)imide



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Why SLB-IL60?

- Improved inertness over SLB-IL59
- Complimentary selectivity to PEG phases
- Higher maximum temperature than PEG phases
- Lower bleed than PEG phases

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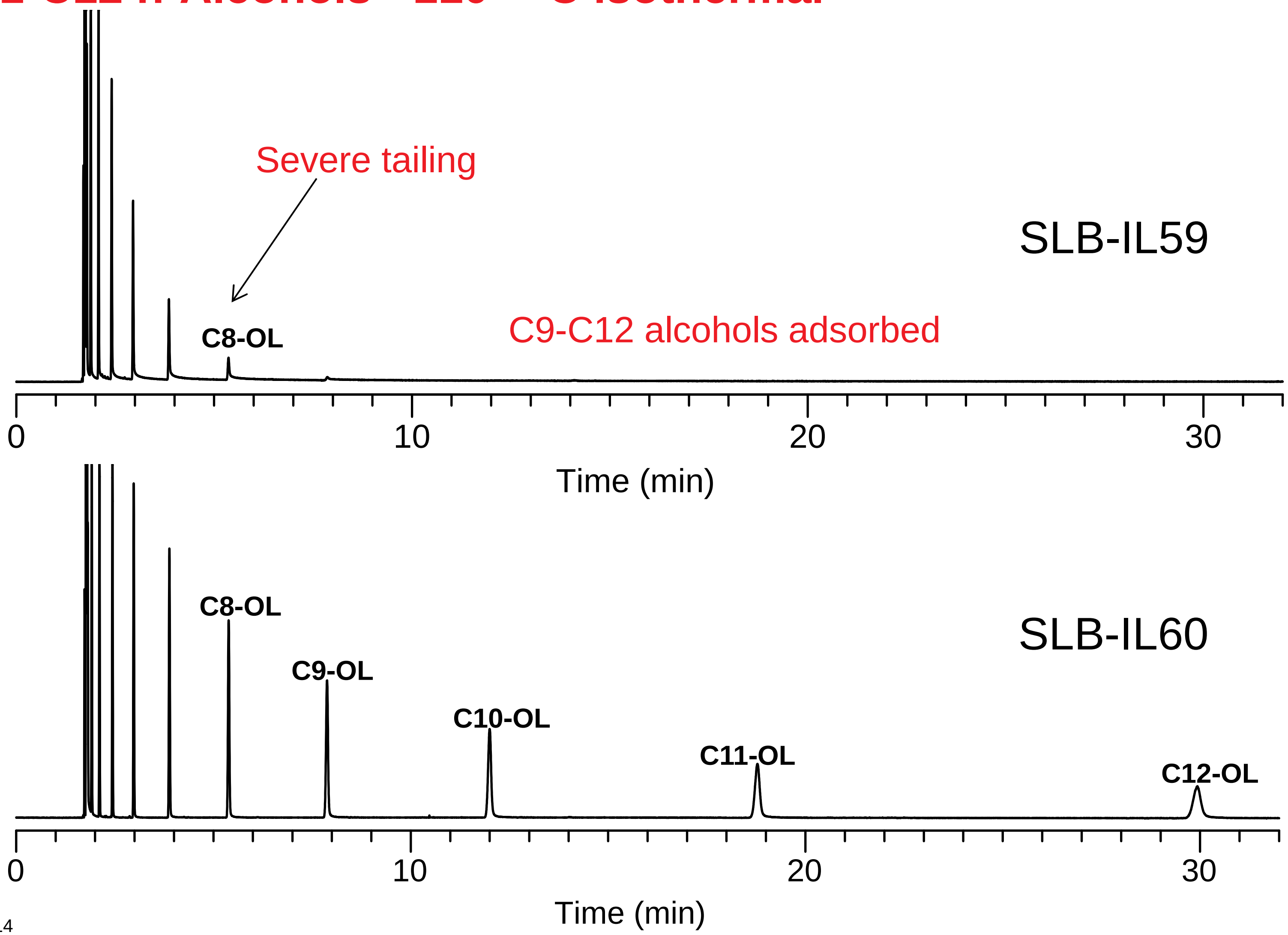
Improved Inertness

C1-C12 n-Alcohols - 110 ° C isothermal



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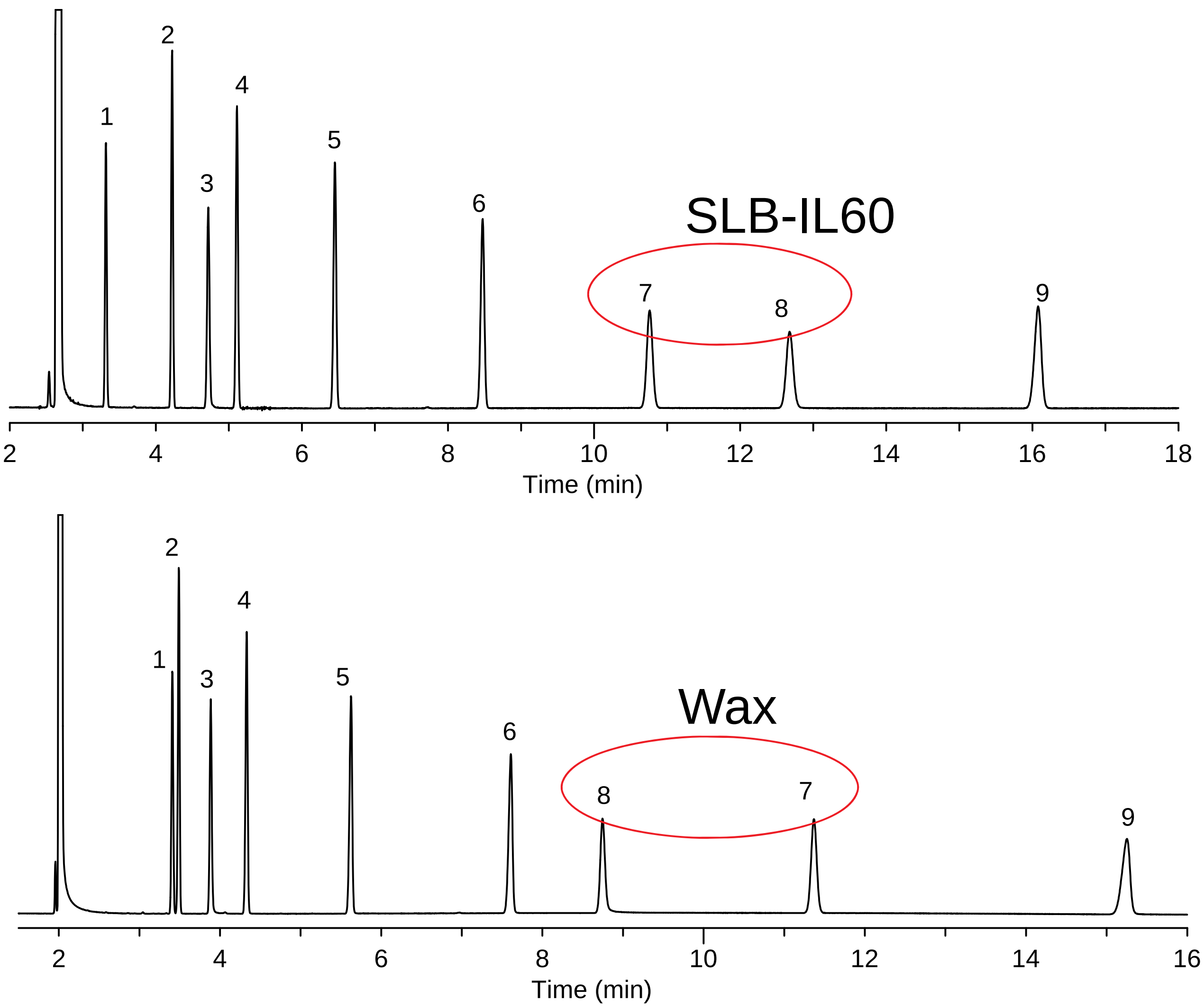
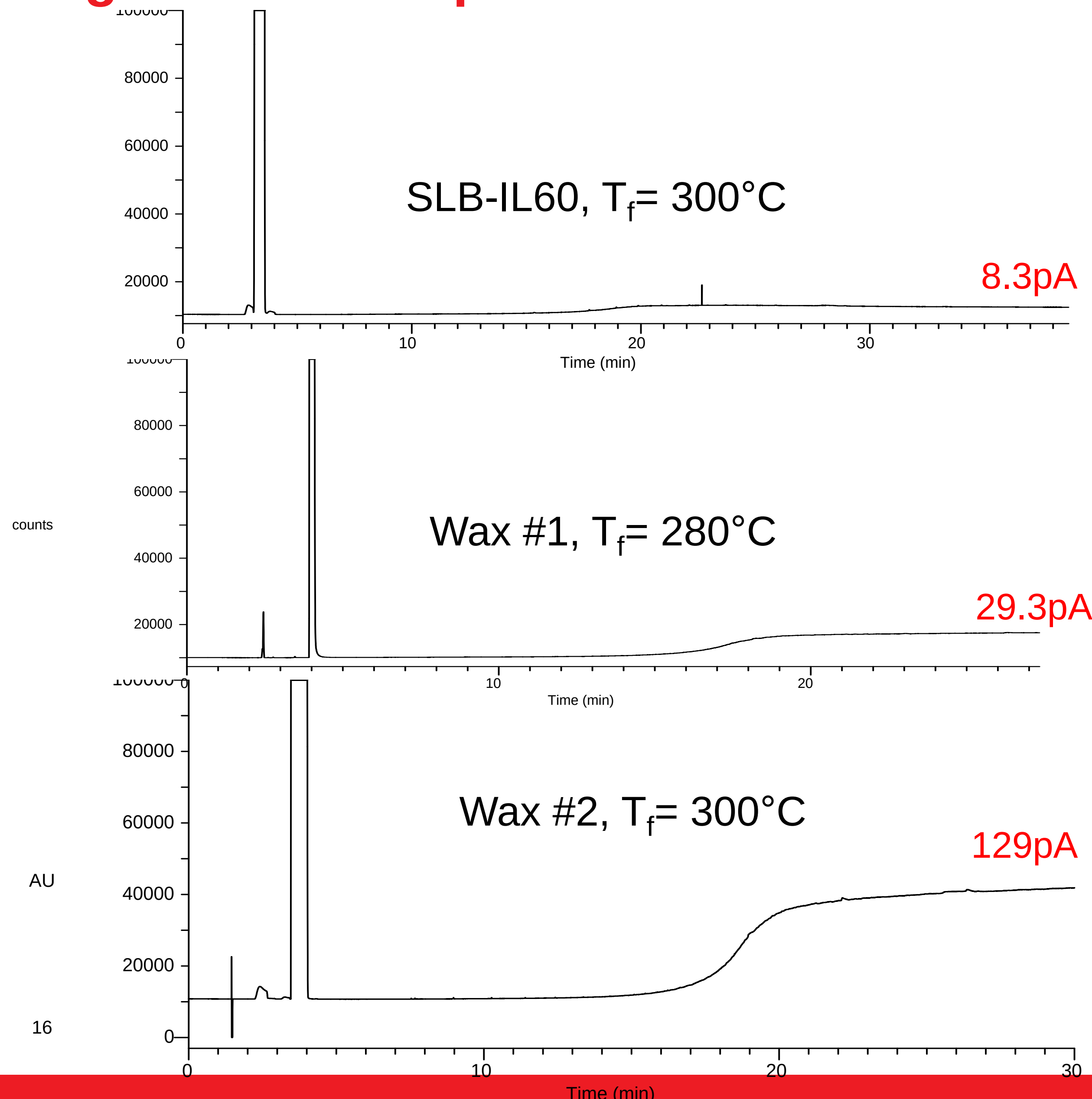
Complimentary Selectivity to Wax



1. 2-Octanone
2. n-C15
3. n-Octanol
4. n-C16
5. n-C17
6. n-C18
7. 2,6-Dimethylphenol
8. 2,6-Dimethylaniline
9. n-C20

Higher Max Temp and Lower Bleed than Wax



FID bleed at published temp. program max

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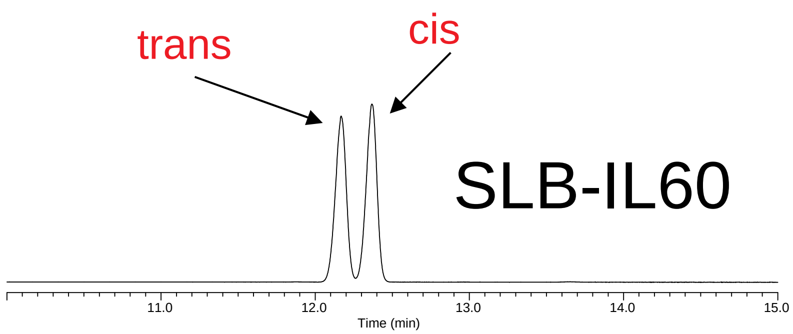
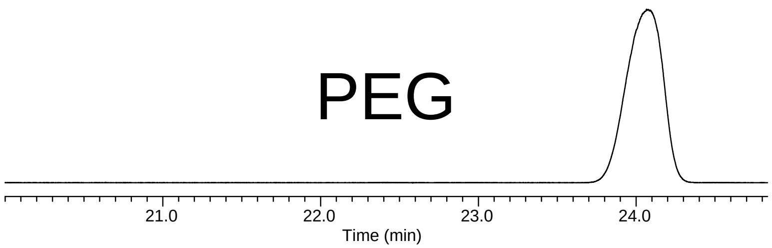
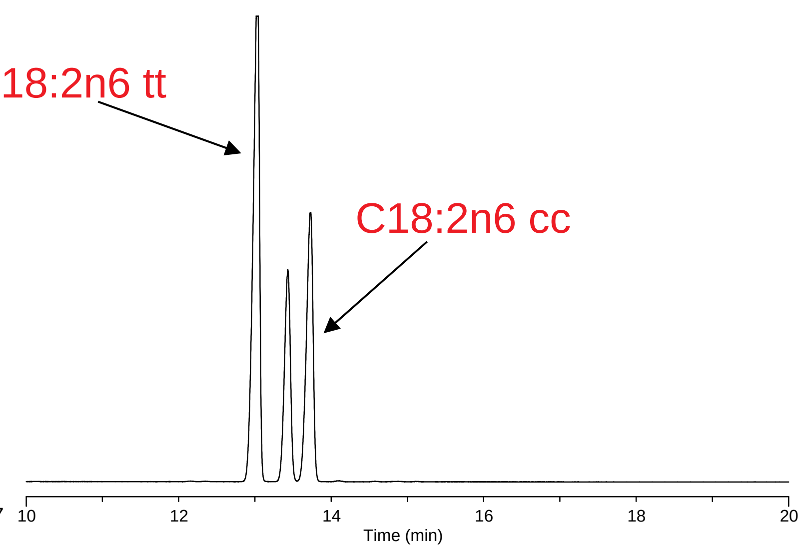
Cis/ trans FAMES on SLB-IL60 vs. PEG Type Phase

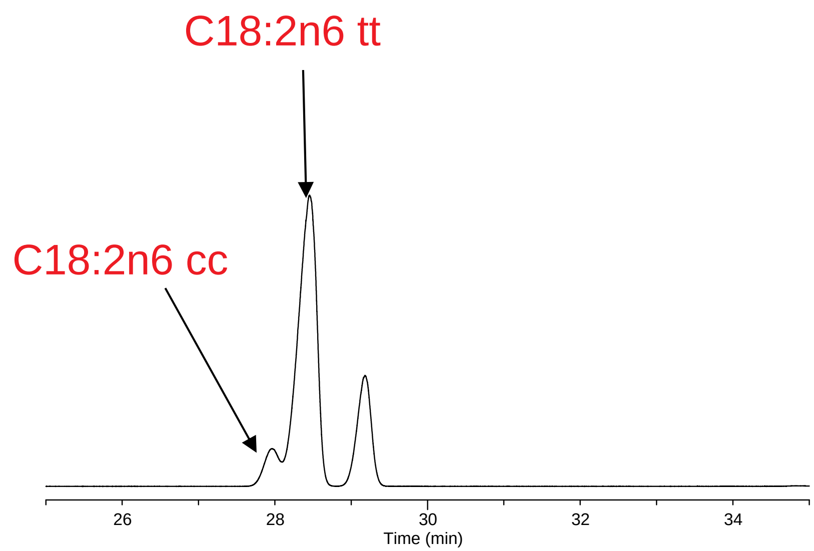
C18:1n9 cis / trans FAMEs @ 180°C





C18:2n6 cis & trans FAME Isomers- 180°C





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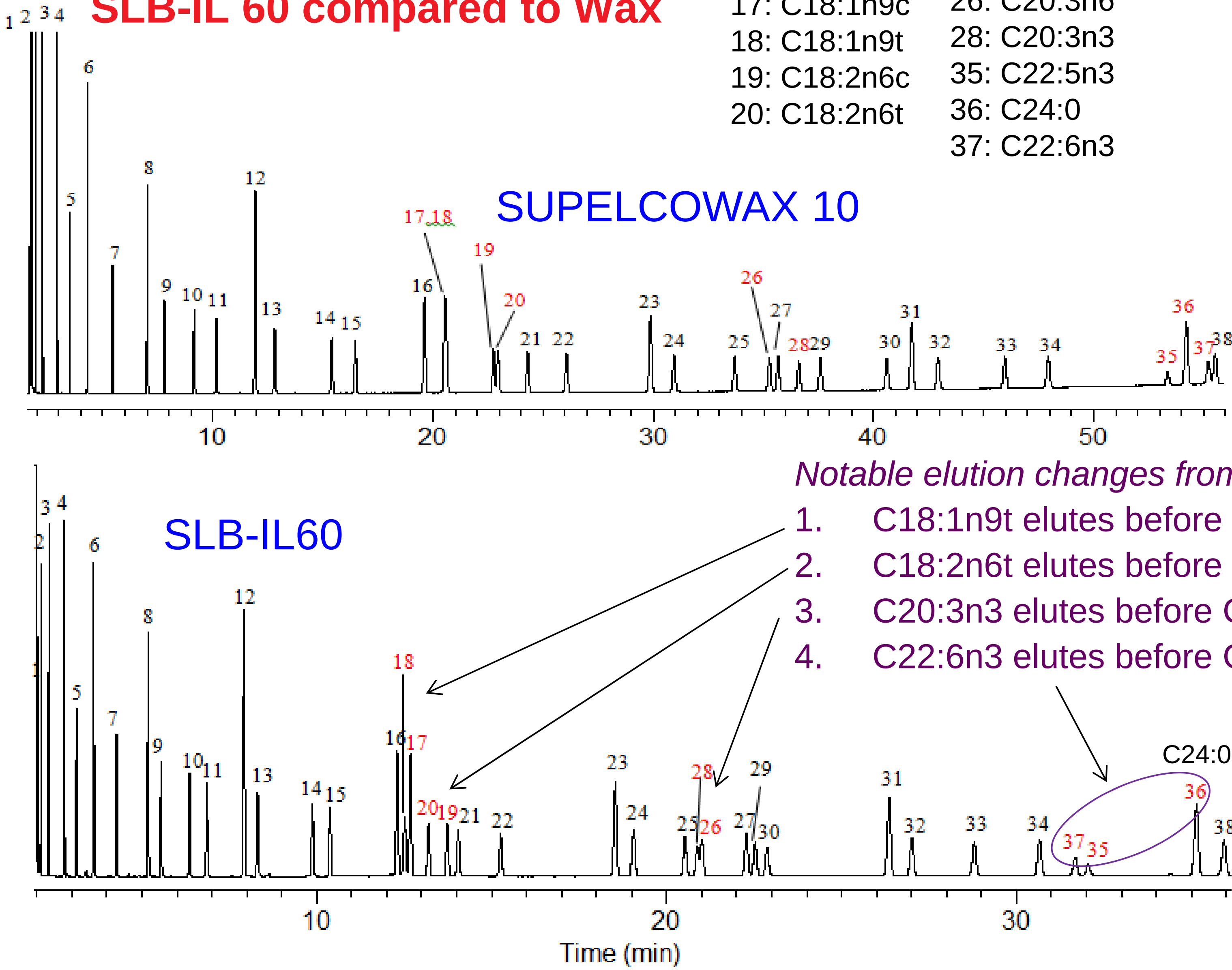
Fame Elution order-
SLB-IL 60 compared to Wax

17: C18:1n9c
18: C18:1n9t
19: C18:2n6c
20: C18:2n6t

26: C20:3n6
28: C20:3n3
35: C22:5n3
36: C24:0
37: C22:6n3



Notable elution changes from wax column:

1. C18:1n9t elutes before C18:1n9c
2. C18:2n6t elutes before C18:2n6c
3. C20:3n3 elutes before C20:3n6
4. C22:6n3 elutes before C22:5n3 and C24:0

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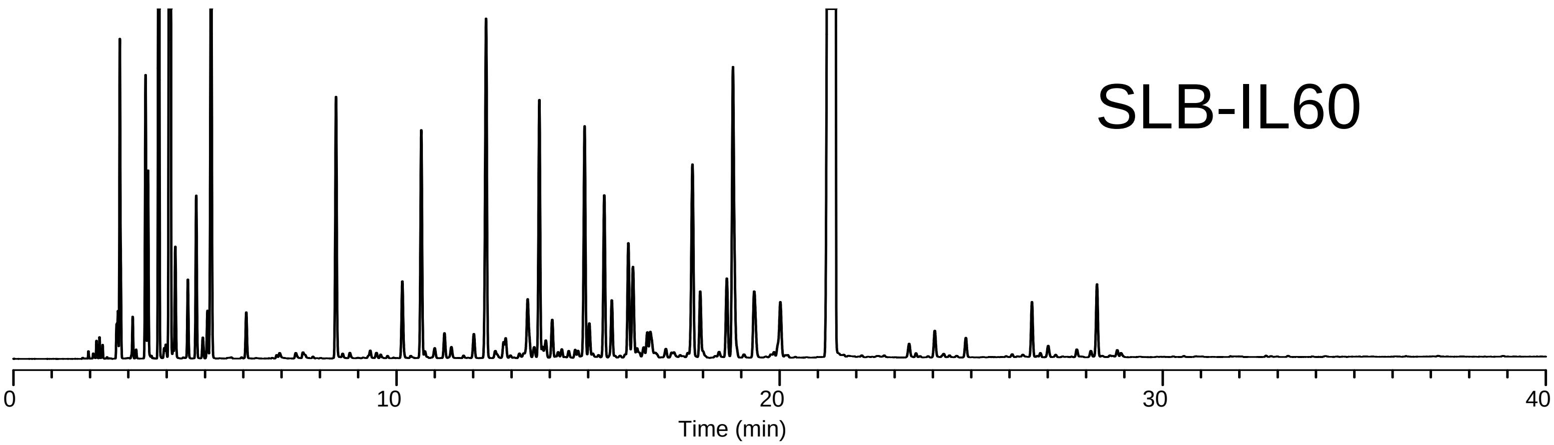
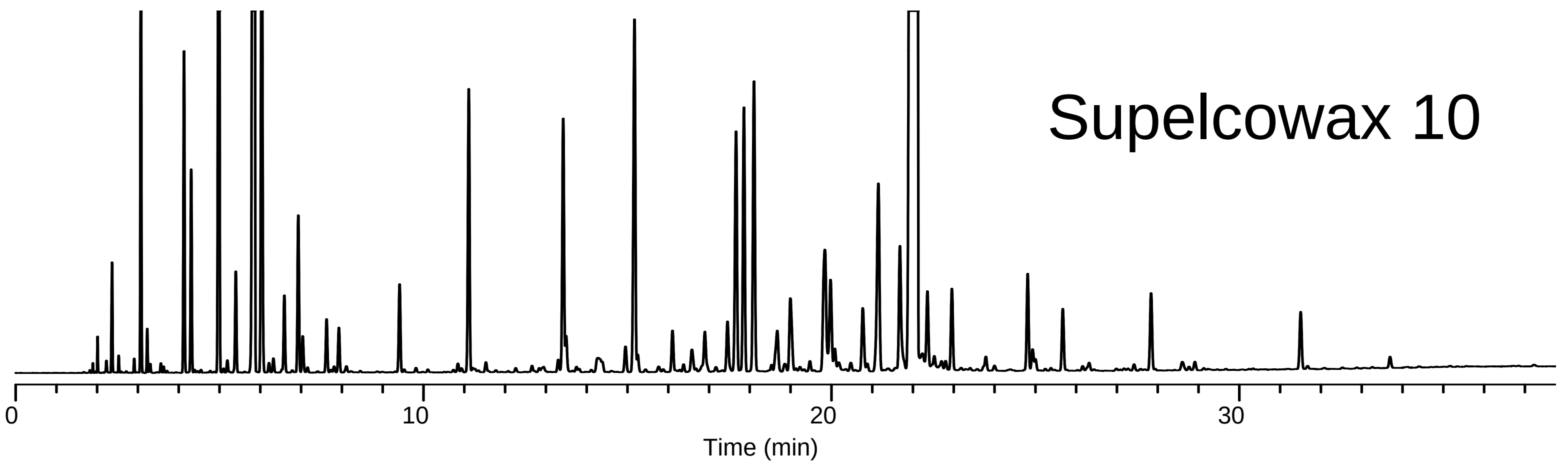
Native Spearmint Oil Analysis





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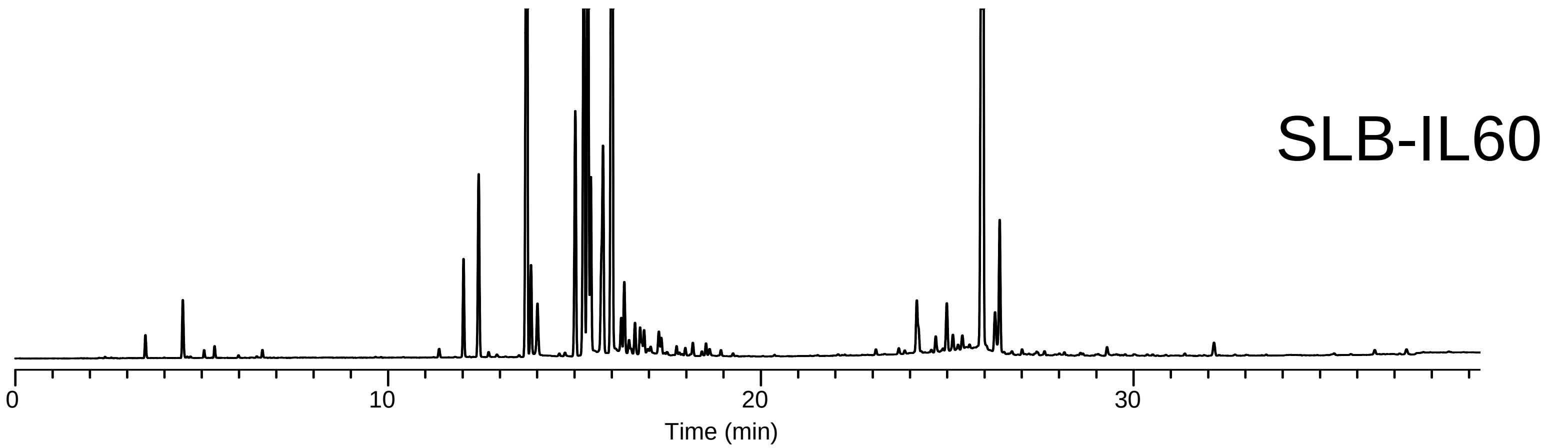
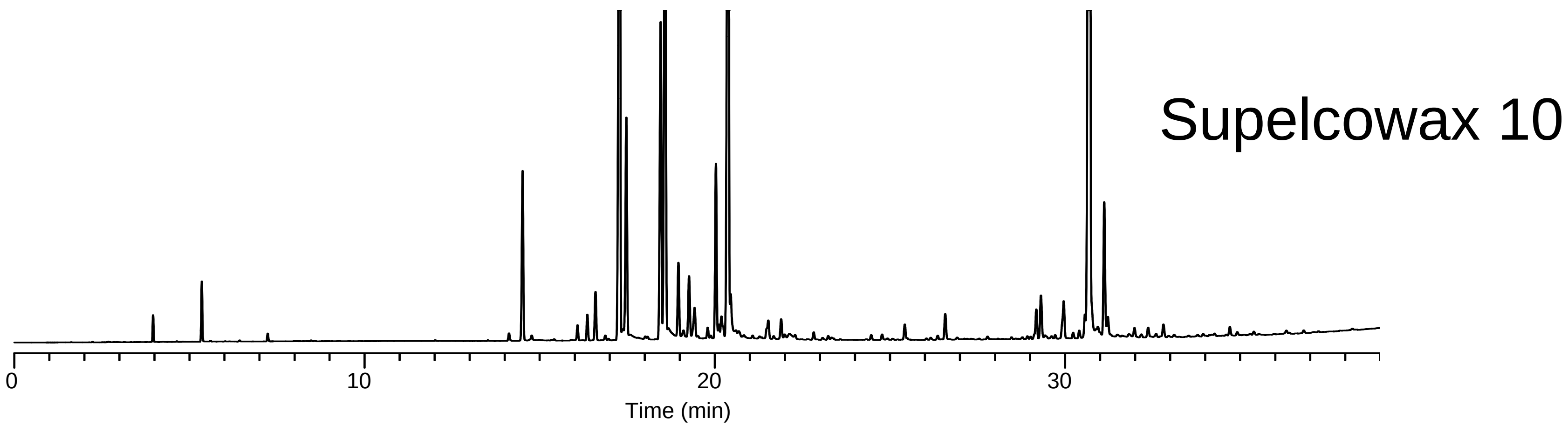
Patchouli Oil Analysis





PAHs on SLB-IL 59 20m x 0.18mm x 0.04umd$_f$

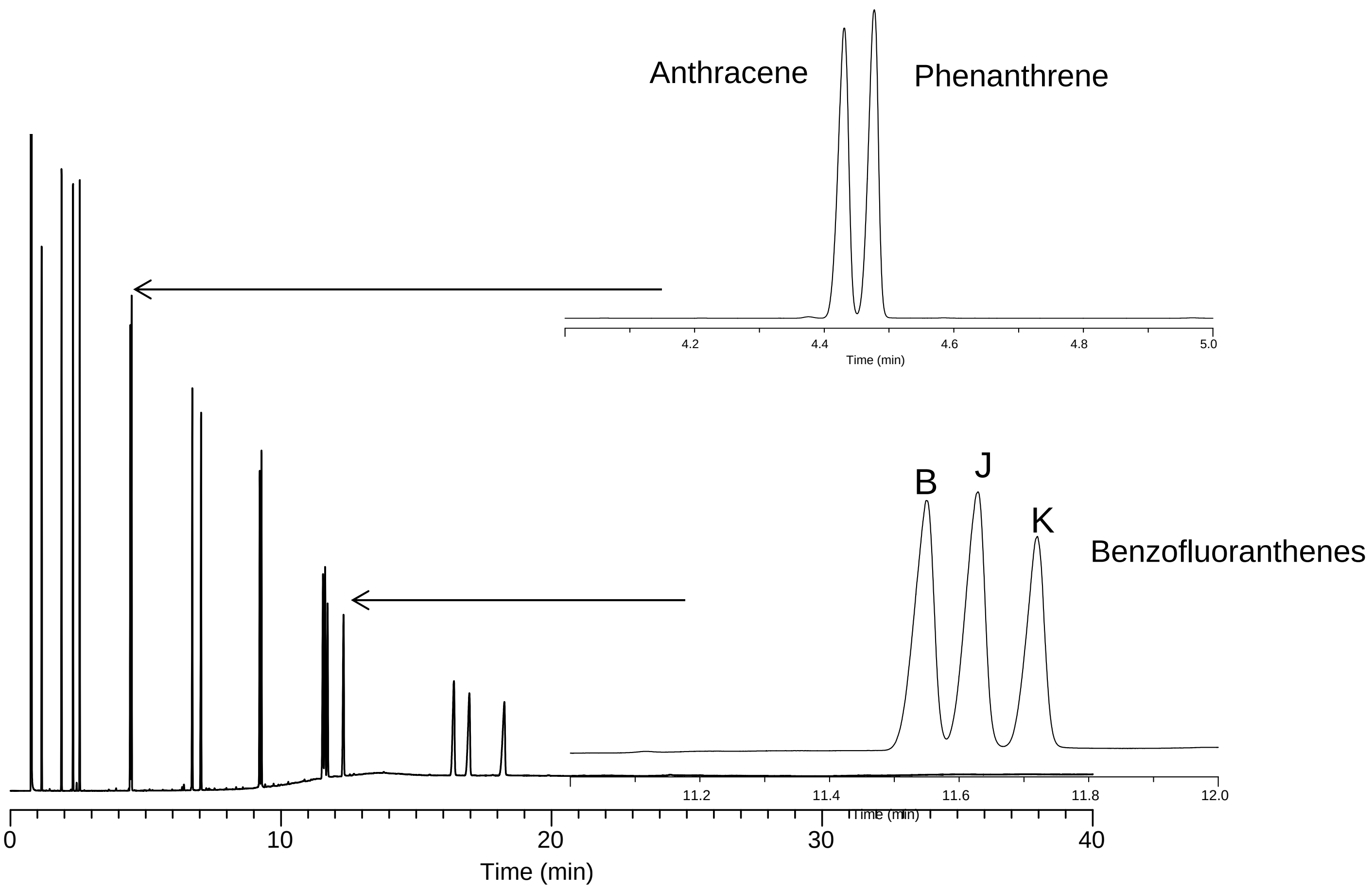


Figure 6. TCL PAHs on SLB-IL 59, 20m x 0.18mm x 0.04umdf, H_2 carrier gas; Expanded views show anthracene/phenanthrene and benzofluoranthene isomers

Ionic Liquid Water Separations

Column: SLB-IL 94, SLB-IL 107, IL 200 30m x 0.25mm x 0.20umd_f

Oven: 35˚C, 4˚C/min to 125˚C, 125˚(2min)

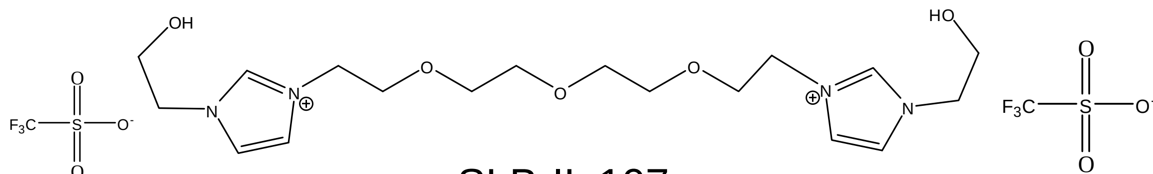
Det: TCD, 300˚C

Flow Rate: 25cm/sec constant pressure He

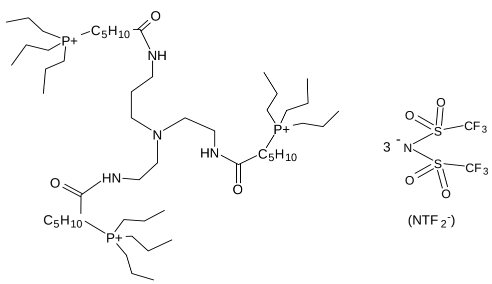
Inj: 250˚C,1uL, split, 100:1

Liner: 4mm ID cup design split liner

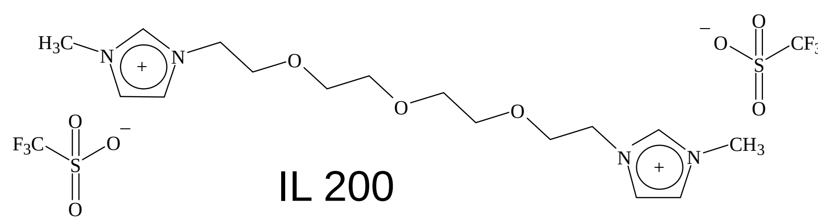
Samples: IL Solvent Test Mix: MeOH, EtOH, Acetone, IPA, n-propanol, 1-butanol, 1,4-Dioxin in water



SLB-IL 107



SLB-IL 94



IL 200

IL Solvent Mix on SLB-IL 94 30m x 0.25mm x 0.20umd$_f$

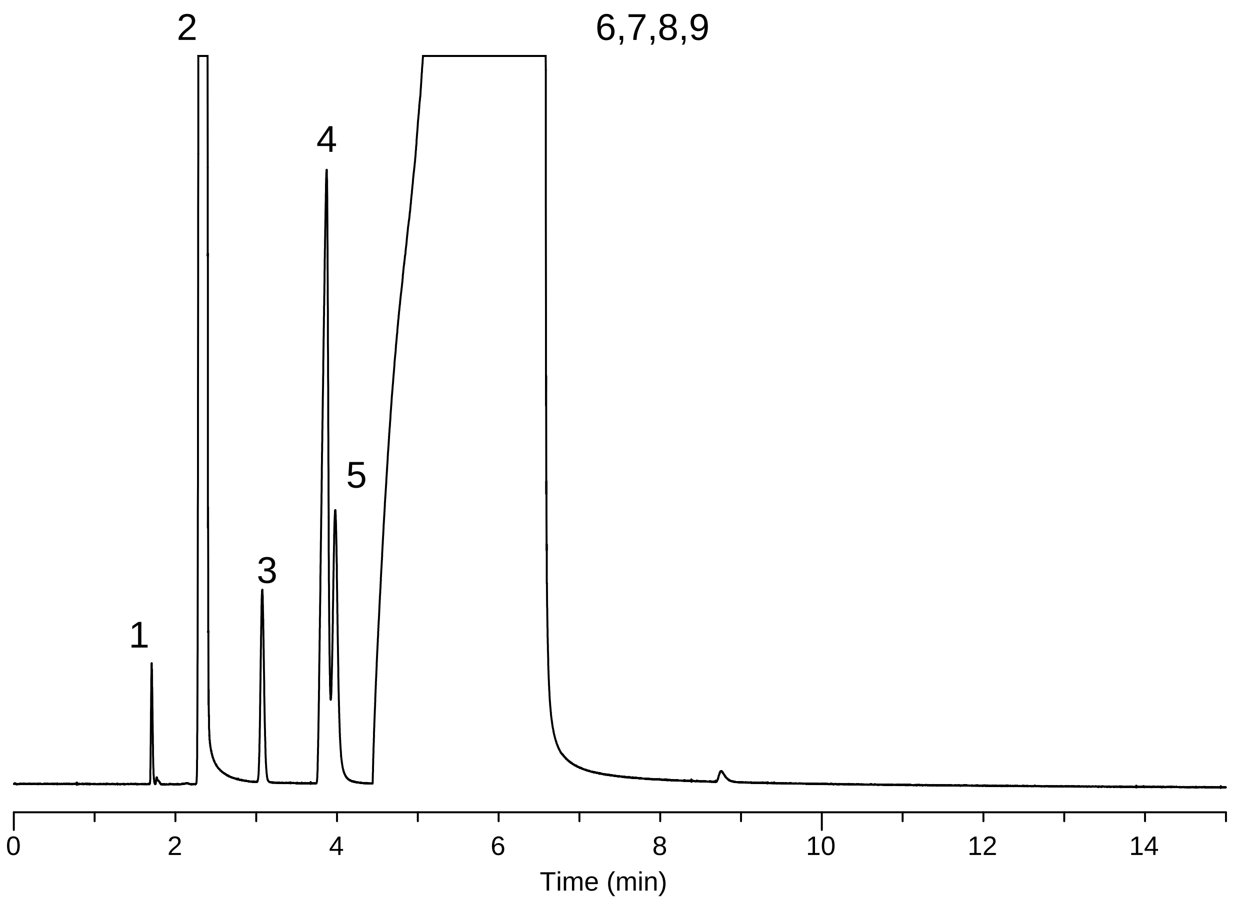


Figure 9. Solvent test standard programmed separation on SLB-IL 94; 1) MeOH, 2) $MeCl_2$ 3) acetone, 4) ethanol, 5) IPA, 6) n-Propanol, 7) 1,4dioxane, 8) butanol 9) water

IL Solvent Mix on SLB-IL 107 30m x 0.25mm x 0.20umd$_f$

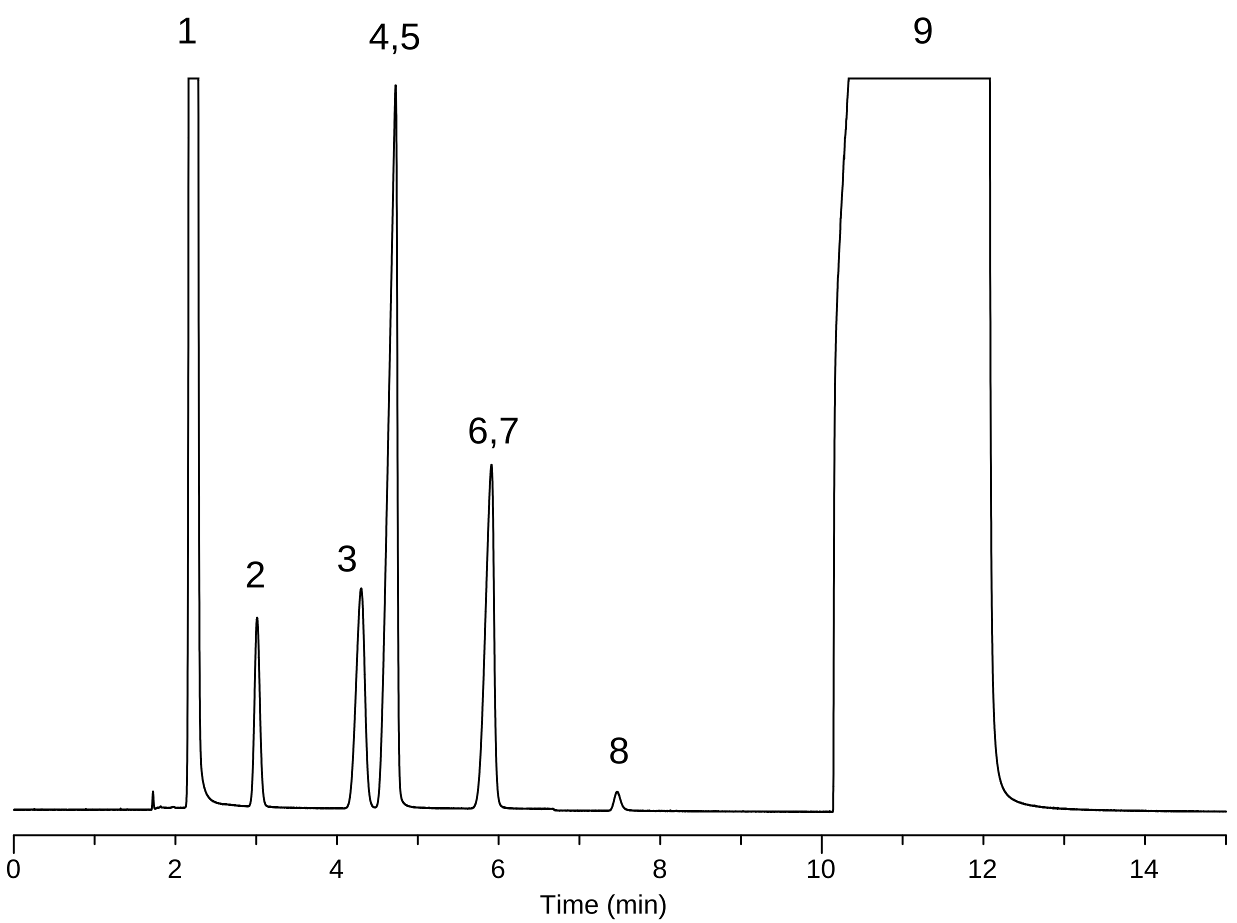


Figure 8. Solvent test standard programmed separation on SLB-IL 107; 1) MeOH/$MeCl_2$, 2) acetone, 3) IPA, 4) ethanol, 5)methanol, 6) n-Propanol, 7) 1,4dioxane 8) butanol, 9) water

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SLB-IL 107 SPME Fiber Test STD

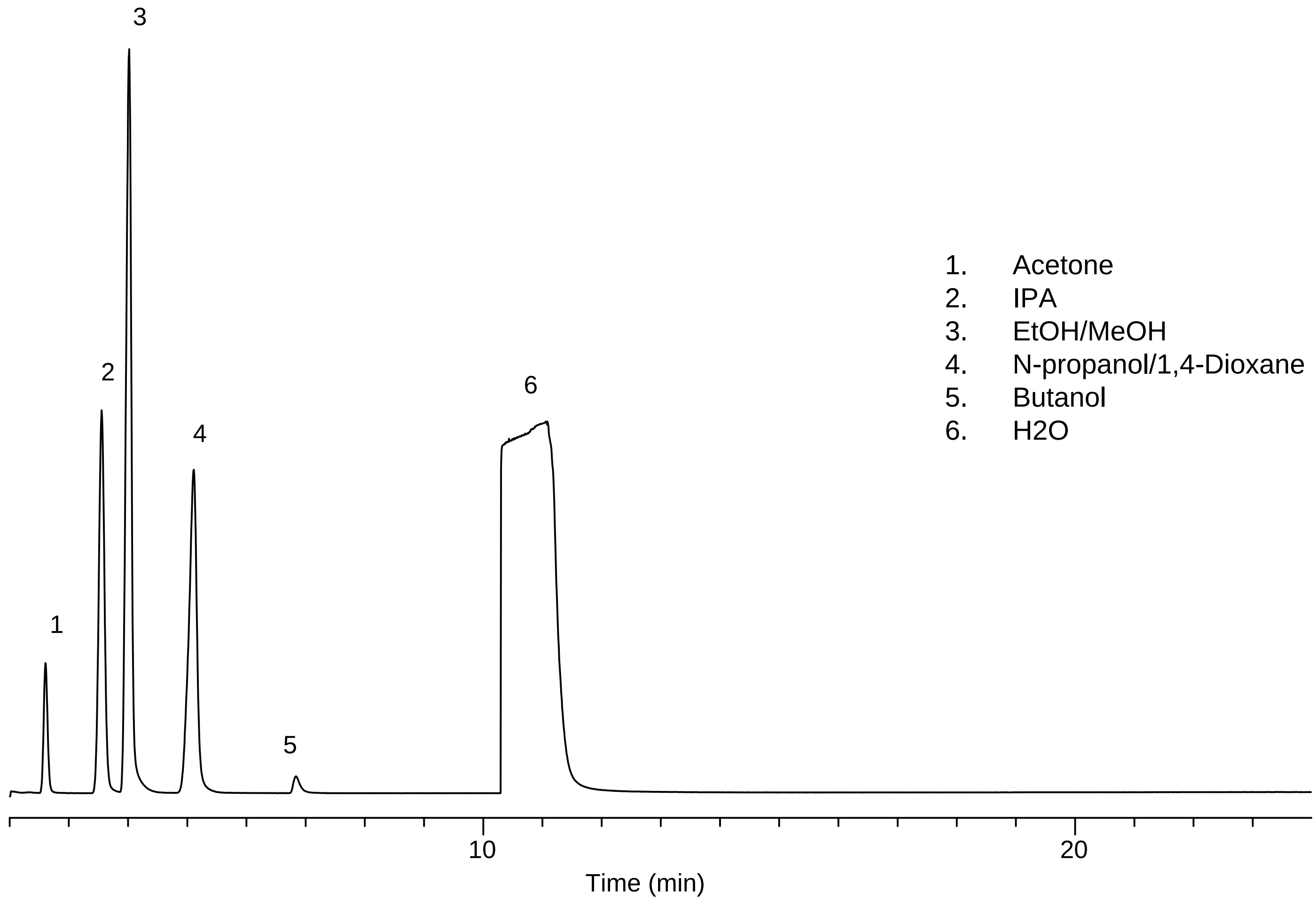

Figure 1. Temperature programmed run for SPME Fiber Test Standard on SLB-IL 107. 1uL injection of standard with varied concentrations (10-200ppm) at 100:1 split. Standard is prepared in water.

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C1-C6 Alcohol Mix

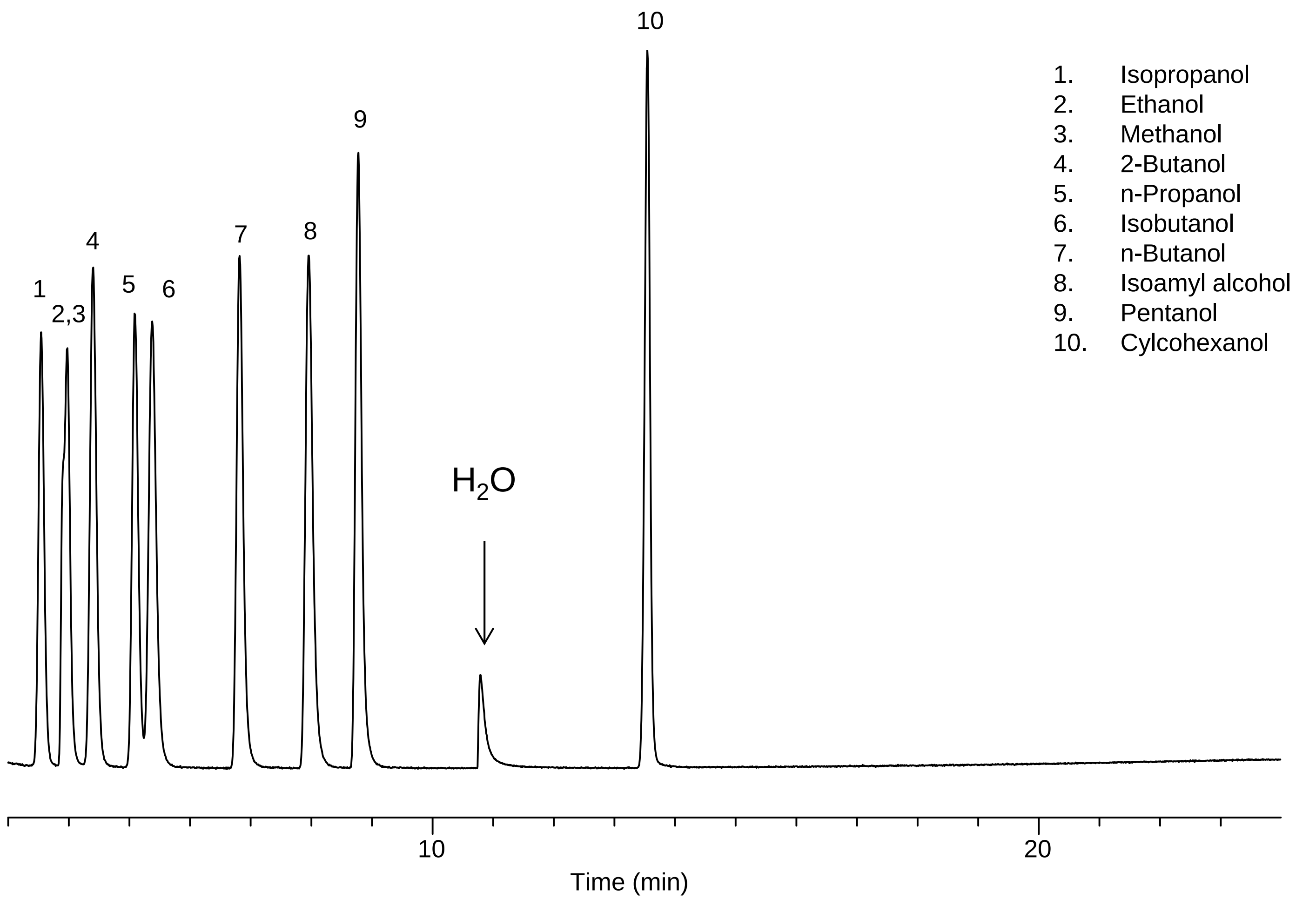

Figure 2. Temperature programmed run for light alcohol mix on SLB-IL 107. 1uL injection of a 500ug/mL sample at 100:1 split. Note the sample has adsorbed some water in storage.

Grappa Bassano

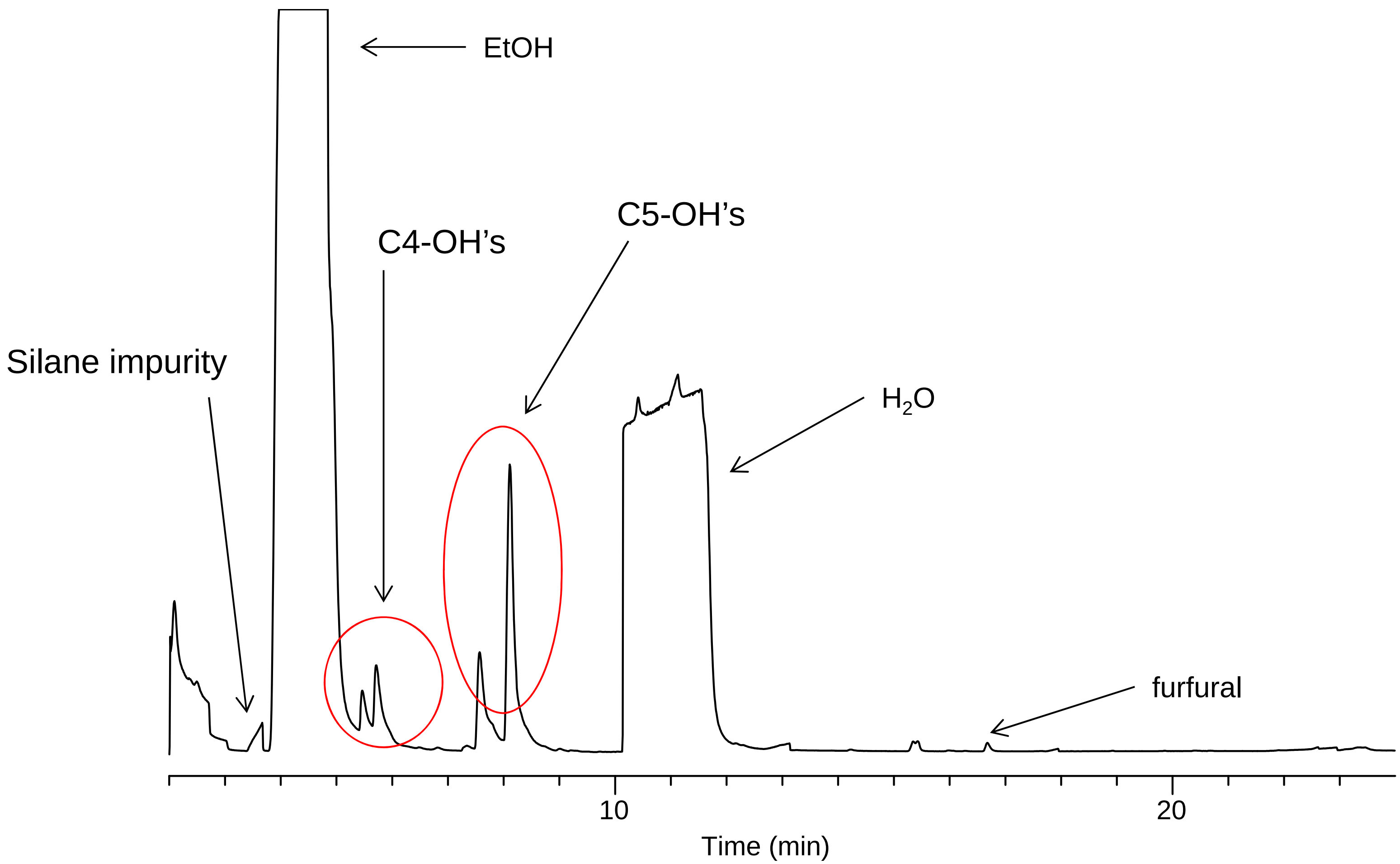

Figure 4. Temperature programmed run for Grappa Bassano on SLB-IL 107. . SPME Carboxen extraction. Selected peaks with high confidence of identification.

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Grappino

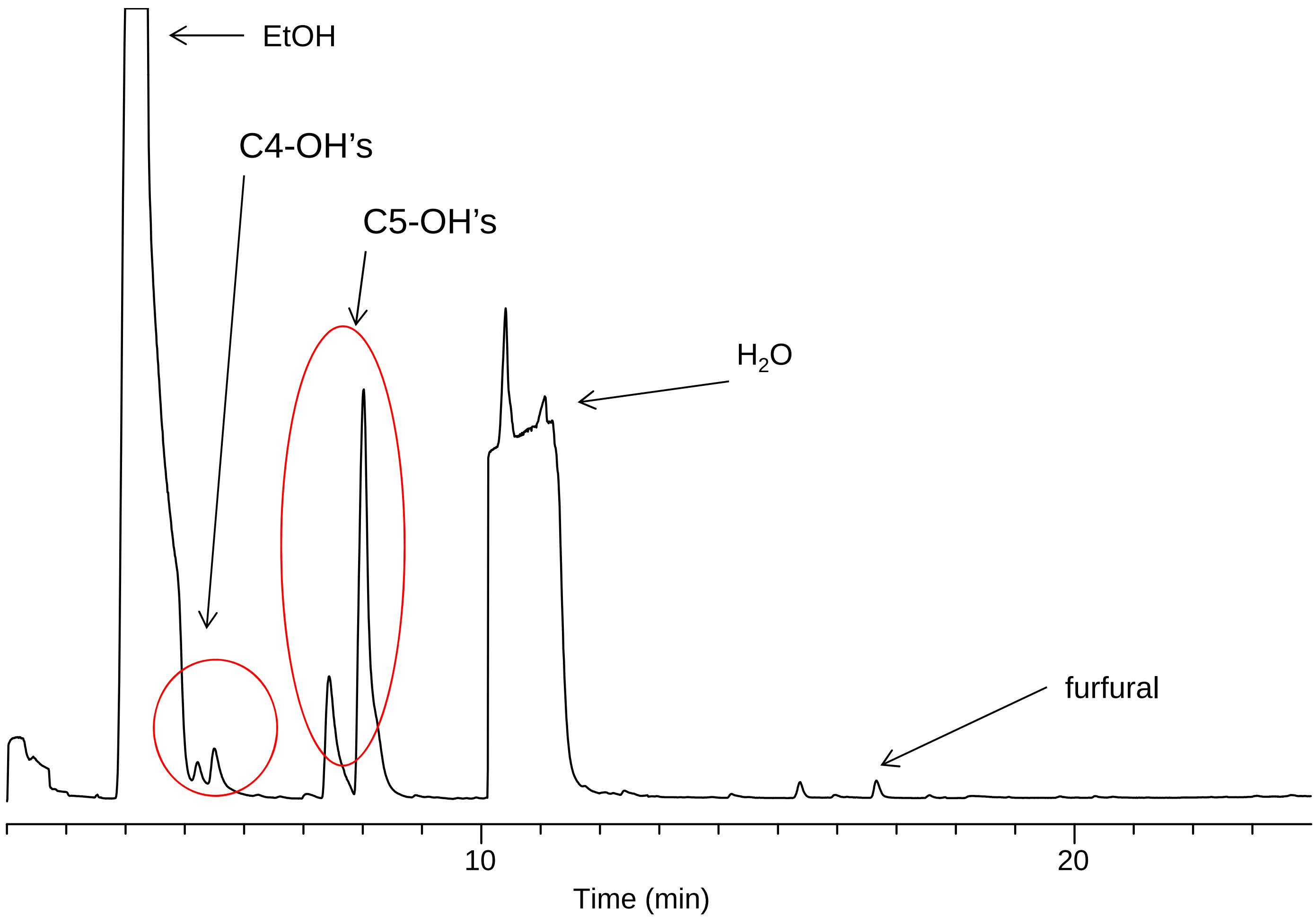

Figure5. Temperature programmed run for Grappino on SLB-IL 107. . SPME Carboxen extraction. Selected peaks with high confidence of identification.

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Tito’s Vodka

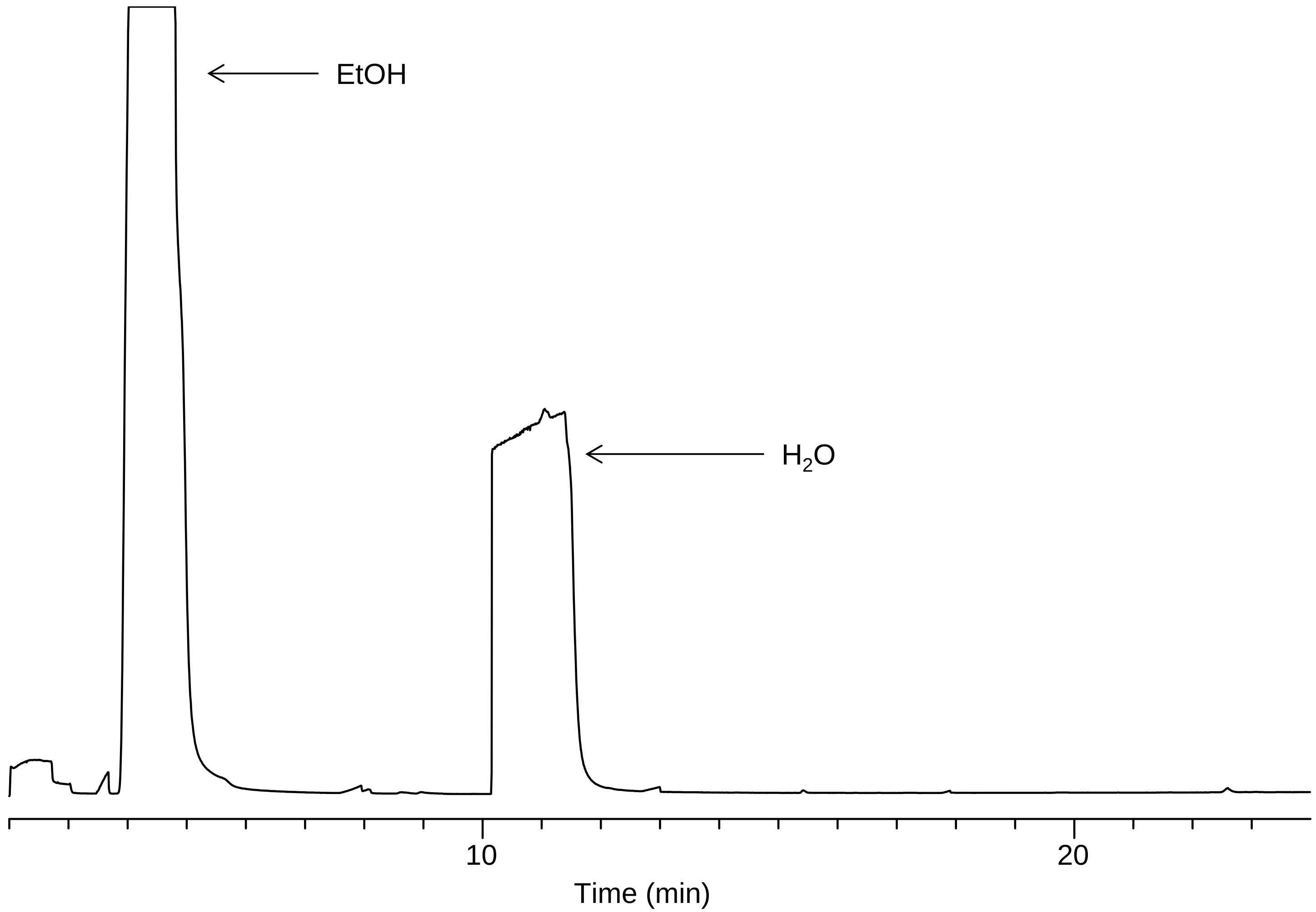


Figure6. Temperature programmed run for Tito’s Vodka on SLB-IL 107. . SPME Carboxen extraction. Selected peaks with high confidence of identification.

Ouzo

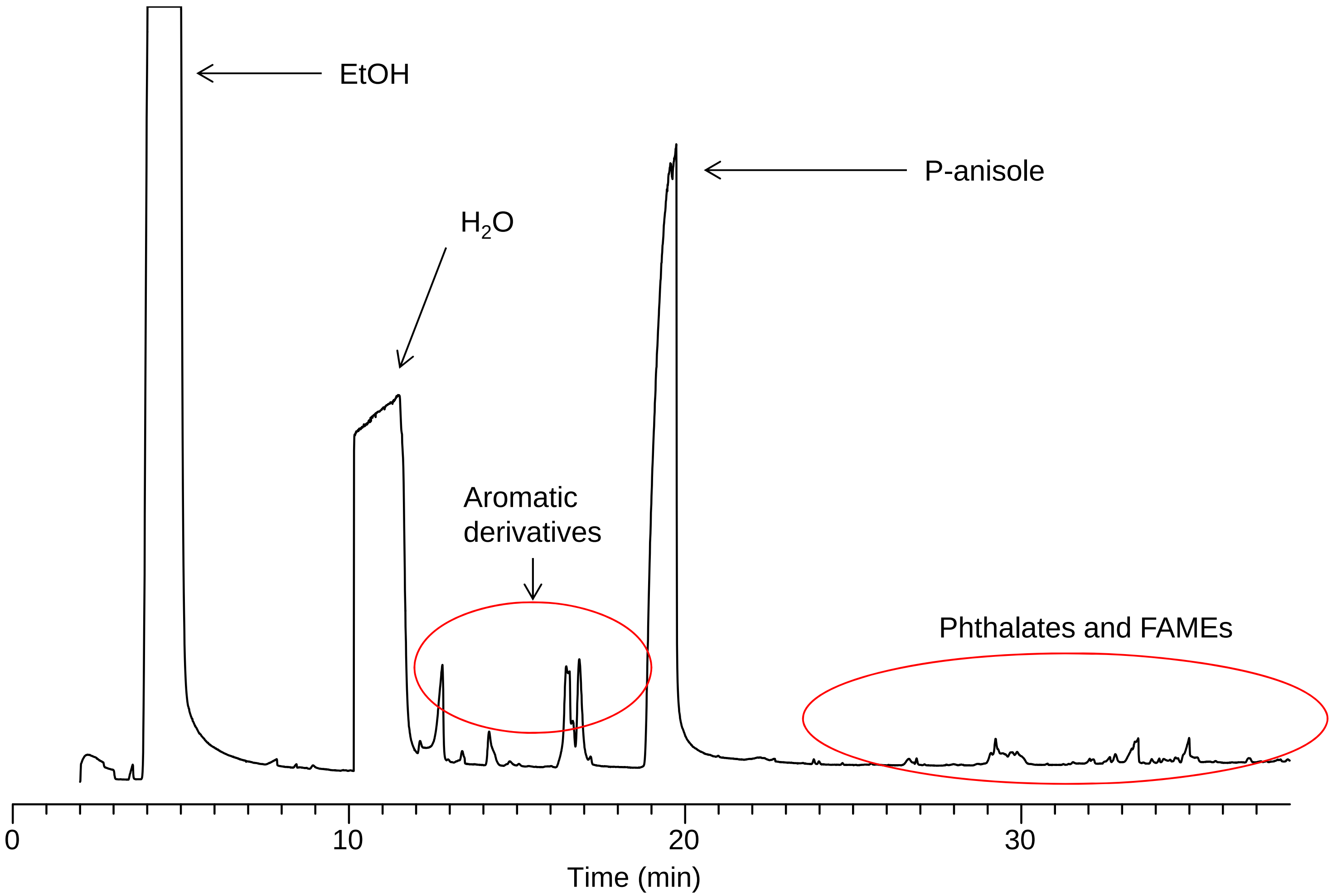
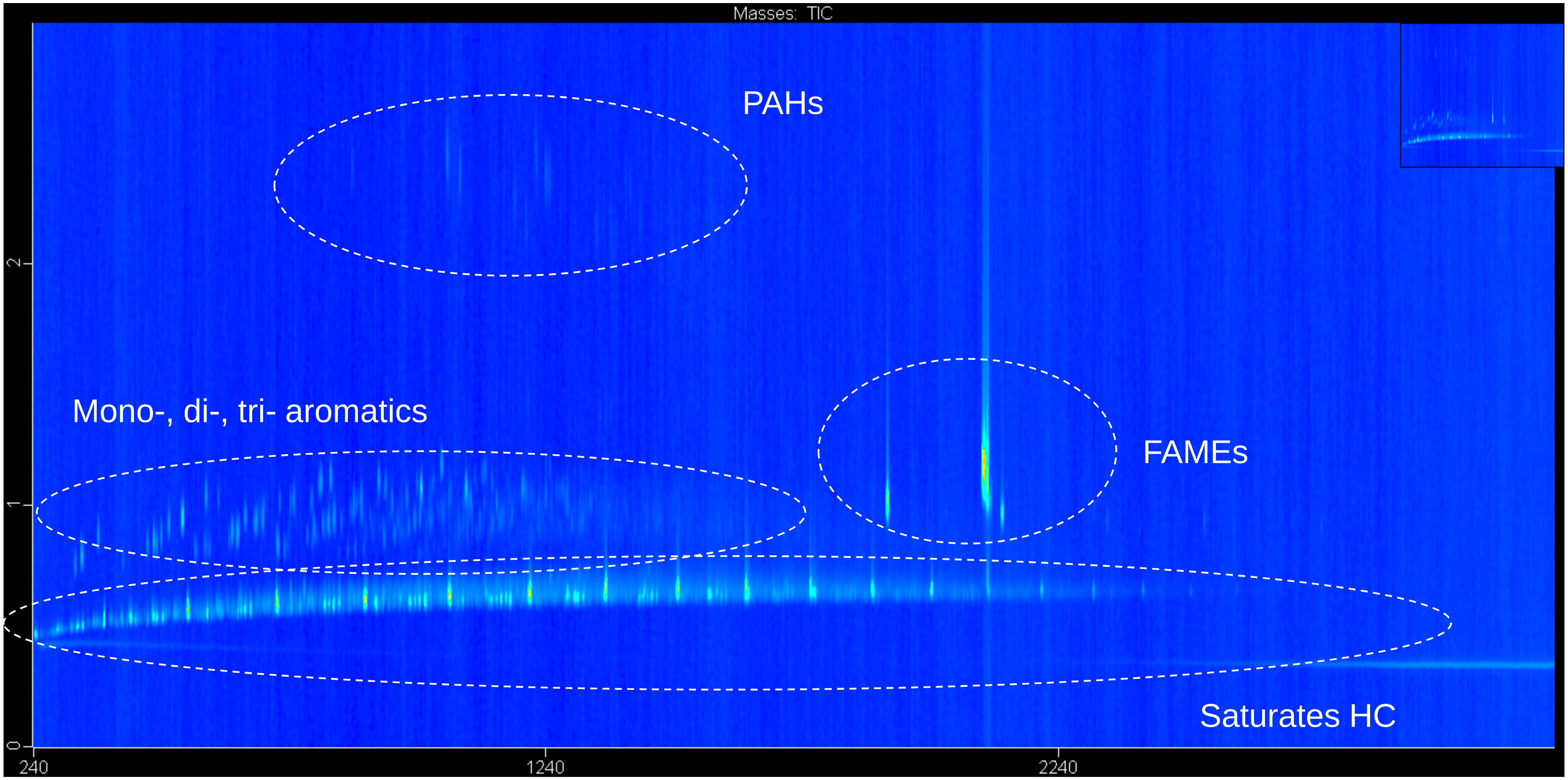


Figure9. Temperature programmed run for Ouzo on SLB-IL 107. . SPME Carboxen extraction. Selected peaks with high confidence of identification.

NON-POLAR – POLAR STRATEGY

Biodiesel 20



^{2}D (sec) – **SLB IL60** (1 m x 0.10 mm x 0.08 µm df)

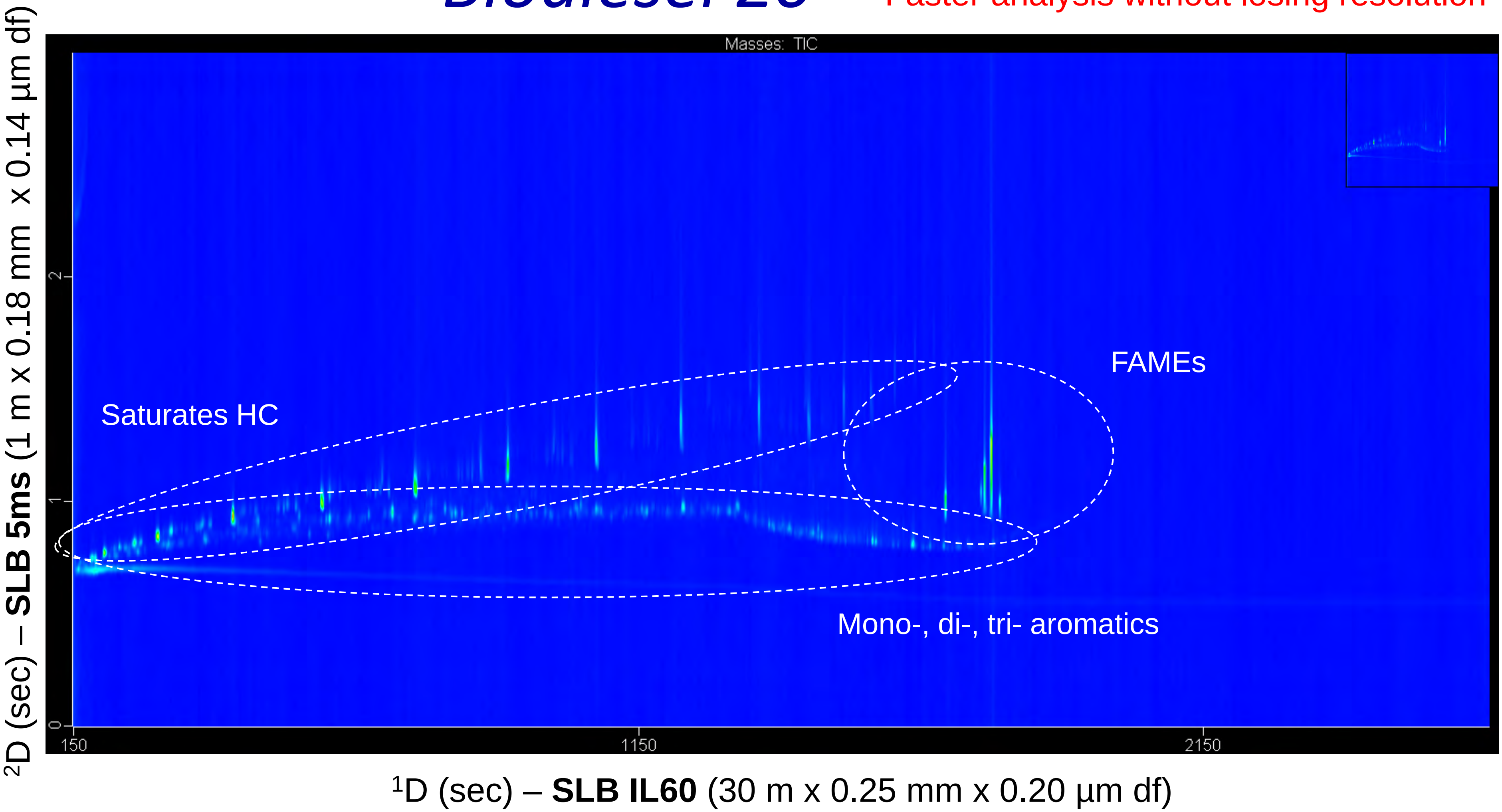
^{1}D (sec) – **SLB 5ms** (30 m x 0.25 mm ID x 0.25 µm df)

Equipment: LECO PEGASUS GC × GC/TOFMS. Carrier gas: Helium set @ 1.0 mL/min. Sample: 1 µL, split ratio 50:1, inlet temp. 250 ºC. GCxGC method temp. program: Primary column: 40 ºC (2 min), ramped @ 4 ºC/min to 270 ºC (20min). Secondary column: 55 ºC (2 min), ramped @ 4 ºC/min to 280 ºC (20min). Modulator temp. offset: 30 ºC. Modulation Period: 3 s. TOFMS method parameters: mass range 35–450 m/z., acquisition rate 200 spectra/s, ion source temp. 250 ºC.

POLAR – NON-POLAR STRATEGY

Biodiesel 20

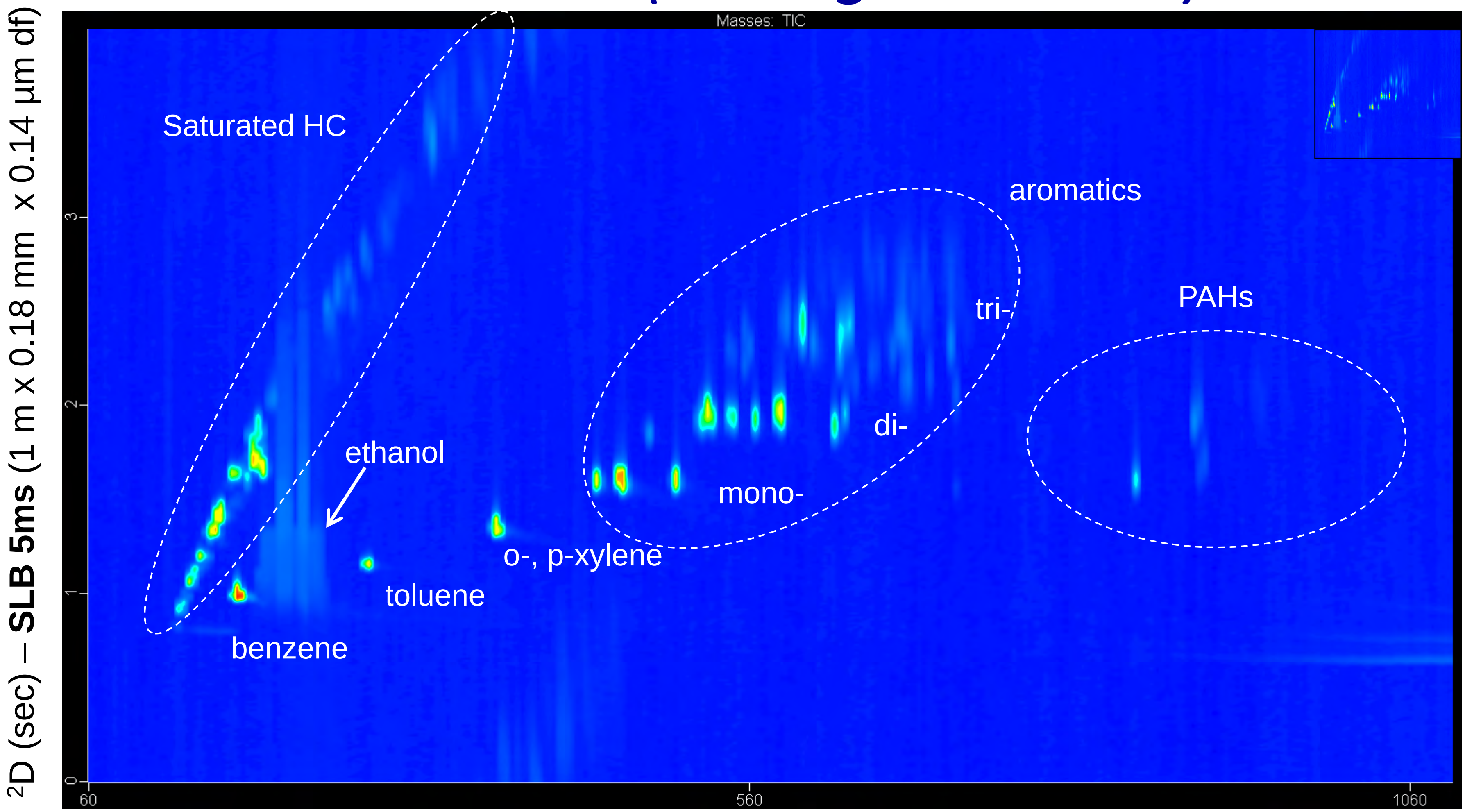
Faster analysis without losing resolution



Equipment: LECO PEGASUS GC × GC/TOFMS. Carrier gas: Helium set @ 1.2 mL/min. Sample: 1 µL, split ratio 50:1, inlet temp. 250 ºC. GCxGC method temp. program: Primary column: 60 ºC, ramped @ 10 ºC/min to 225 ºC (5 min). Secondary column: 75 ºC, ramped @ 10 ºC/min to 240 ºC (5 min). Modulator temp. offset: 30 ºC. Modulation Period: 3 s. TOFMS method parameters: mass range 35–450 m/z., acquisition rate 200 spectra/s, ion source temp. 250 ºC.

POLAR – NON-POLAR STRATEGY

Gasoline (local gas station)



^{1}D (sec) – **SLB IL60** (30 m x 0.25 mm x 0.20 µm df)

Equipment: LECO PEGASUS GC × GC/TOFMS. Carrier gas: Helium set @ 1.2 mL/min. Sample: 1 µL, split ratio 300:1, inlet temp. 250 ºC. GCxGC method temp. program: Primary column: 60 ºC, ramped @ 10 ºC/min to 225 ºC (5 min). Secondary column: 75 ºC, ramped @ 10 ºC/min to 240 ºC (5 min). Modulator temp. offset: 30 ºC. Modulation Period: 4 s. TOFMS method parameters: mass range 35–450 m/z., acquisition rate 200 spectra/s, ion source temp. 250 ºC.

Summary

A series of polar and highly polar Ionic Liquid stationary phases have been evaluated.

Changing the functionality of the cation or anion group will change the selectivity of the IL phase.

The GC column polarity scale demonstrates that the Ionic Liquid stationary phases are typically polar to highly polar. A new phase SLB-IL111 is the most polar phase commercially available.

The new polar SLB-IL60 offers unique cis/ trans FAME separations compared to PEG phases along with unique separation of other FAME isomers.

Highly Polar SLB-IL111 Ionic Liquid capillary columns provide a complimentary separation of positional geometric FAME isomers compared to the SP-2560 columns.

200 meter versions of the SP-2560 and SLB-IL111 provide the best resolution of the positional geometric FAME isomers while providing complimentary selectivity.

Summary

Ionic liquid columns offer potential for the analysis of PAHs.

Highly polar ionic liquid phases can be used for analyzing water.

Initial work has demonstrated the ionic liquid column can be used for the analysis of the alcohols contained in various alcoholic beverages.

The ionic liquid phases offer orthogonal selectivity for use in GC x GC applications as either the primary or secondary column.

Acknowledgements

Prof. Daniel Armstrong, U. Texas Arlington
Prof. Luigi Mondello, U. Messina, Messina, Italy
Dr. Pierluigi Delmonte, US FDA
Supelco R&D Team
Our customers worldwide

Thank You