The Use of Extended Temperature Range Liquid Chromatography and Temperature Programming for Petroleum Product Analysis

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Outline

- Introduce use of temperature in liquid chromatography to optimize separations
- Effect of temperature on selectivity of aromatic compounds
- Use temperature programming to improve class separation of aromatics in diesel fuels using LC and RI detection (ASTM D6591)

High Temperature Liquid Chromatography Advantages

- The advantages of using temperature to optimize separations in HPLC are well documented in the literature.
- The major advantages are
  - Increased speed
  - Higher efficiencies and resolution
  - Ability to tune selectivity with temperature

Increased Diffusivity

- Increasing the temperature increases the enthalpy of solute transfer from mobile phase to stationary phase
  - Improves efficiency, particularly for large analytes
  - Allows operation at higher flow rates without penalty

*F.D. Antia and C S. Horvath, *J. Chromatogr*. **435** (1988) 1-15.

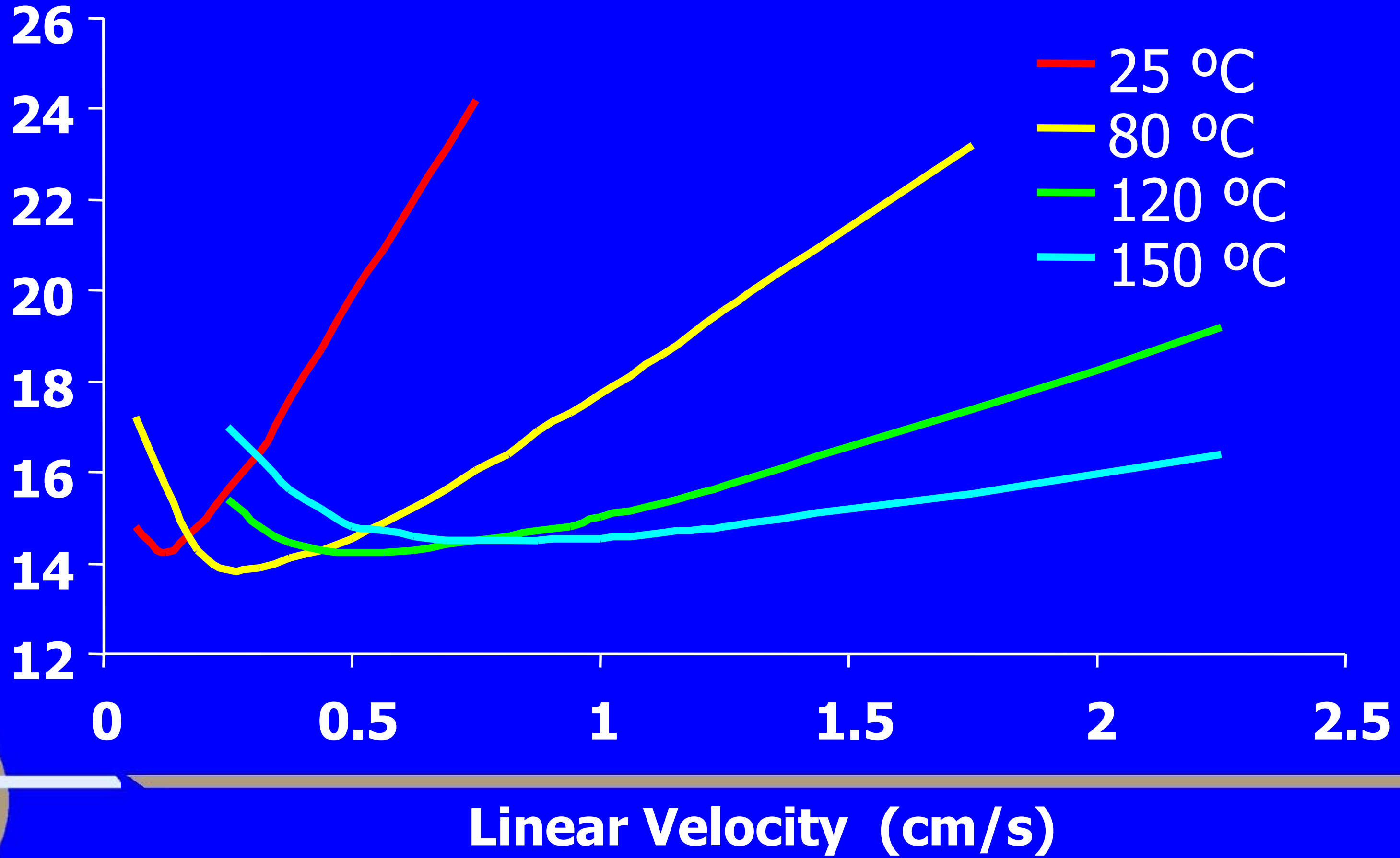
*B. Yan, J. Zhao, J.S. Brown, J. Blackwell, P. W. Carr, *Anal. Chem.* **72** (2000) 1253-1262

Decreased Viscosity

- As the temperature increases the viscosity of the eluent decreases thus lowering the system back pressure
  - Perform analysis at higher flow rates without over-pressurizing the pump
  - Use smaller size packing materials in columns increasing efficiency

Efficiency with High Speed

Temperature effects on plate height



Temperature Programming

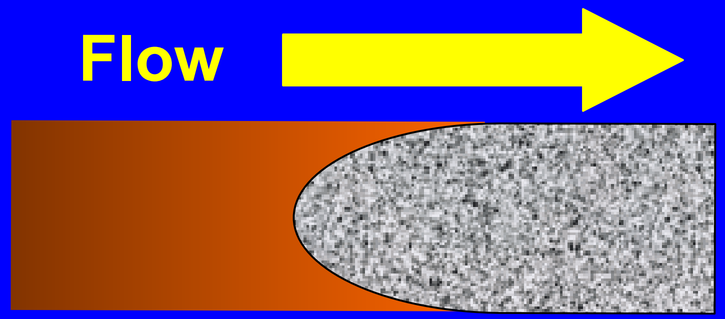
- Temperature Programming in HTLC provides added benefits
  - Elute smaller less polar solutes at low temperatures and ramp the temperature to elute the highly retained solutes
  - Sharpens peaks improving detectability for highly retained solutes*
  - Offers an alternative to gradient elution*

Obstacles in the Pathway of Temperature Programmed Liquid Chromatography

- Column technology especially under reversed phase conditions
- Column heating compartments were not sufficient for temperature programming
- Preheating the mobile phase to overcome band broadening was difficult

Why is Solvent Pre-heating so Important?

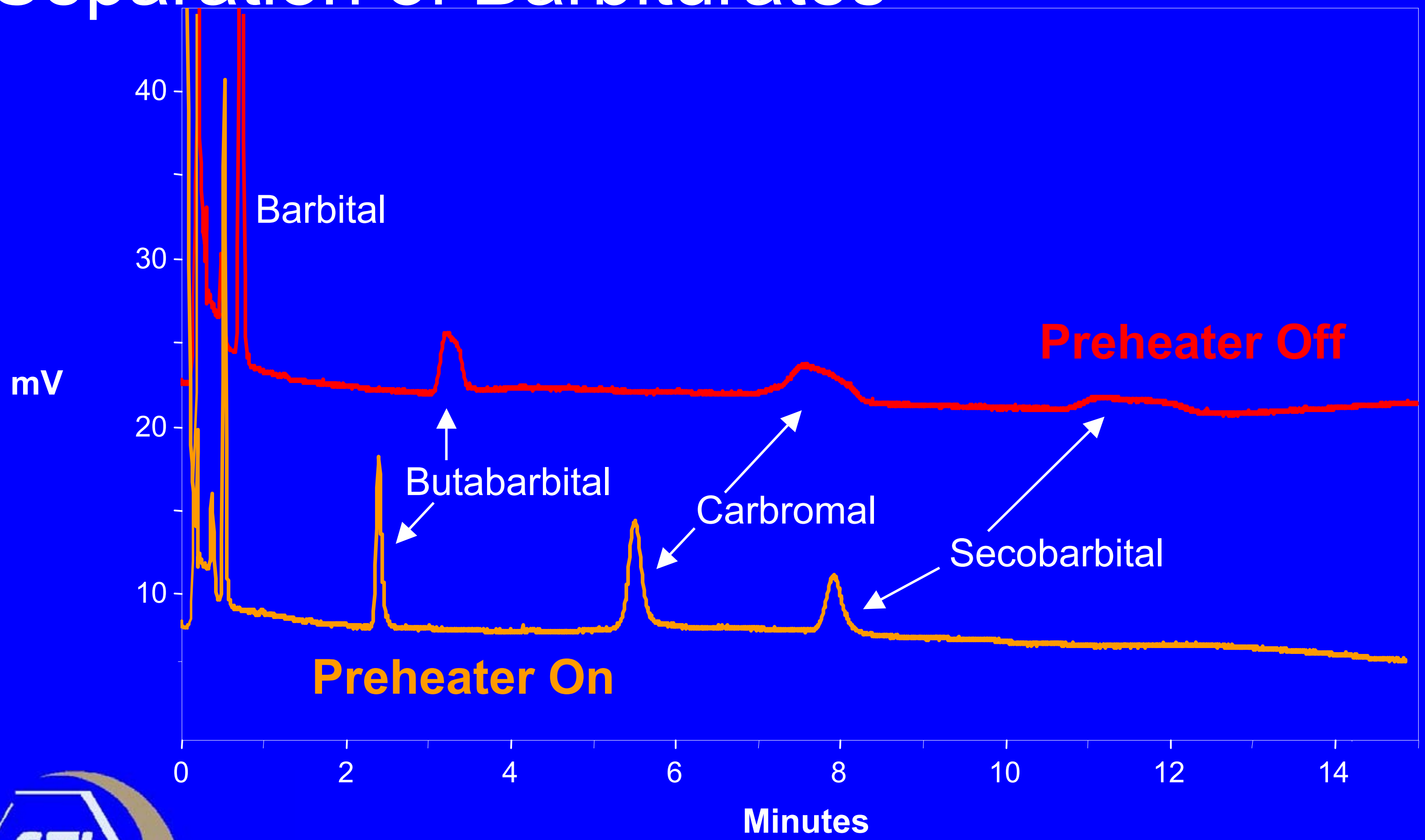
No Pre-heating



With Pre-heating

Mobile Phase Pre-heating

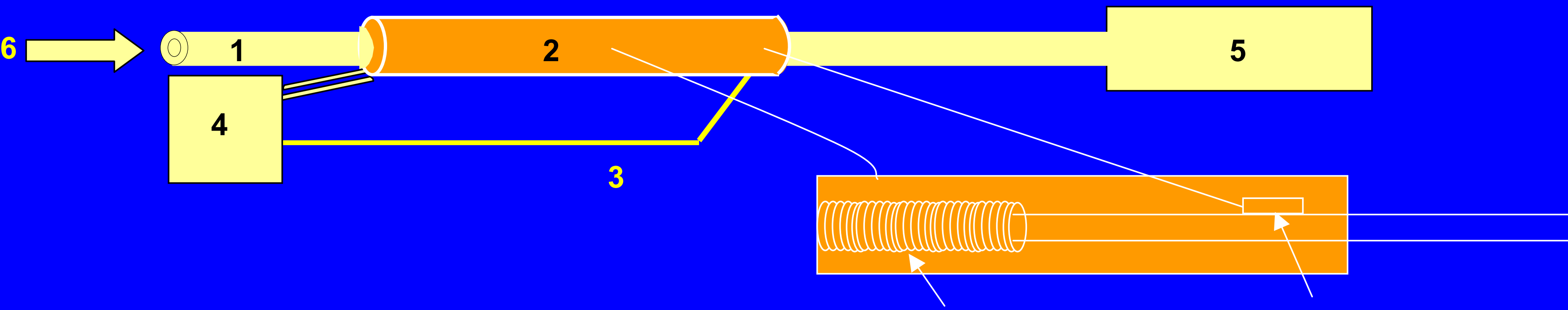
Separation of Barbiturates



The Polaratherm Series 9000 Total Temperature Controller

- Forced air column compartment
- Isothermal and thermal gradient operatior
    - Sub-zero to 200°C
    - Flow rates up to 6.0 mL/min
    - Temperature ramps up to 30°C/min
- Mobile phase pre-heating
- Peltier effluent cooling
- Vapor sensor
- Compatible with any HPLC system
- Knauer pump
- HP RI detector

Integrated Preheater Design



(1) stainless steel tubing, (2) heater, (3) thermocouple sensor, (4) temperature controller, (5) column, (6) from pump

**Patent pending Selerity Technologies, Inc.

ASTM D6591

- Applicable to fuels in diesel boiling range
- Specifies HPLC with RI detection
- Use of a switching valve to obtain a single peak for PAH’s
- Run at room temperature
- Column: amino bonded or polar amino-cyano bonded silica stationary phase
- Typical run time is 25-30 min.

Method Enhancement Goals

- Improve the resolution between saturates and mono-aromatic hydrocarbons (MAH)
- Decrease total analysis time
- Simplify method by eliminating the need to use a switching valve

Experimental Design

- Temperature effects on aromatics
- Isothermal and temperature programmed runs
- Partisil Amino-Cyano (PAC) column- SS
  - 5µm, 250 x 4.6 mm
- Econosphere Silica-SS
  - 3µm, 150 x 4.6 mm
- Hexane mobile phase for all analyses

Preparation of Standards

- Saturates
  - hexadecane, octadecane
- Mono-aromatic hydrocarbons (MAH)
  - toluene, tetralin, thiophene
- Di-aromatic hydrocarbons
  - naphthalene, acenaphthene, benzothiophene, dibenzothiophene
- Polyaromatic Hydrocarbons (PAH)
  - anthracene (3-ring)
  - pyrene (4-ring)

Retention Data for PAC Column Isothermal Conditions

Analyte	Retention Time			
	0°C	30°C	60°C	100°C
toluene	4.56	4.23	3.89	3.54
tetralin	4.59	4.29	4.00	3.69
thiophene	5.02	4.46	4.08	3.69
naphthalene	6.81	5.69	4.99	4.32
acenaphthene	7.49	5.89	4.92	4.47
benzothiophene	7.81	5.82	5.22	4.49
dibenzothiophene	11.25	8.38	6.73	5.47
anthracene	12.14	9.04	7.30	5.86

Selectivity Changes for Di-aromatic Hydrocarbons

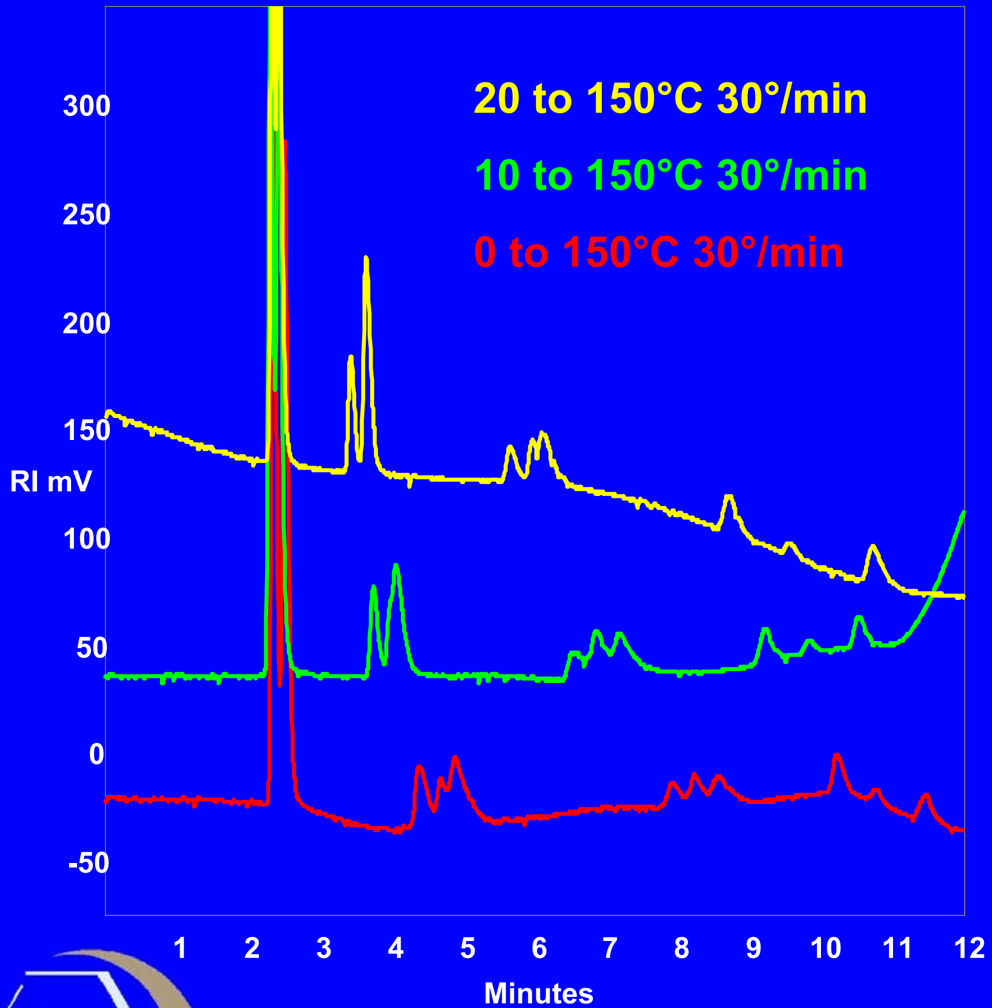
Analyte	Elution Order			
	0°C	30°C	60°C	100°C
naphthalene	1	2	2	1
acenaphthene	2	3	1	2
benzothiophene	3	1	3	3

Retention Data for Standard Temperature Programmed Conditions

	0 to 100°C 20°/min		20 to 100°C 20°/min	
RT	PAC	Silica	PAC	Silica
Saturates	3.43	2.42	3.46	2.10
MAH	5.44	3.49	6.08	2.99
	5.75	4.18	6.32	3.34
DAH	7.76	4.39	8.01	3.60
	8.00	5.01	8.45	4.06
	10.14	5.22	8.83	4.28
3ring	10.73	5.86	9.63	4.66
4ring	12.24	5.96	11.19	4.78

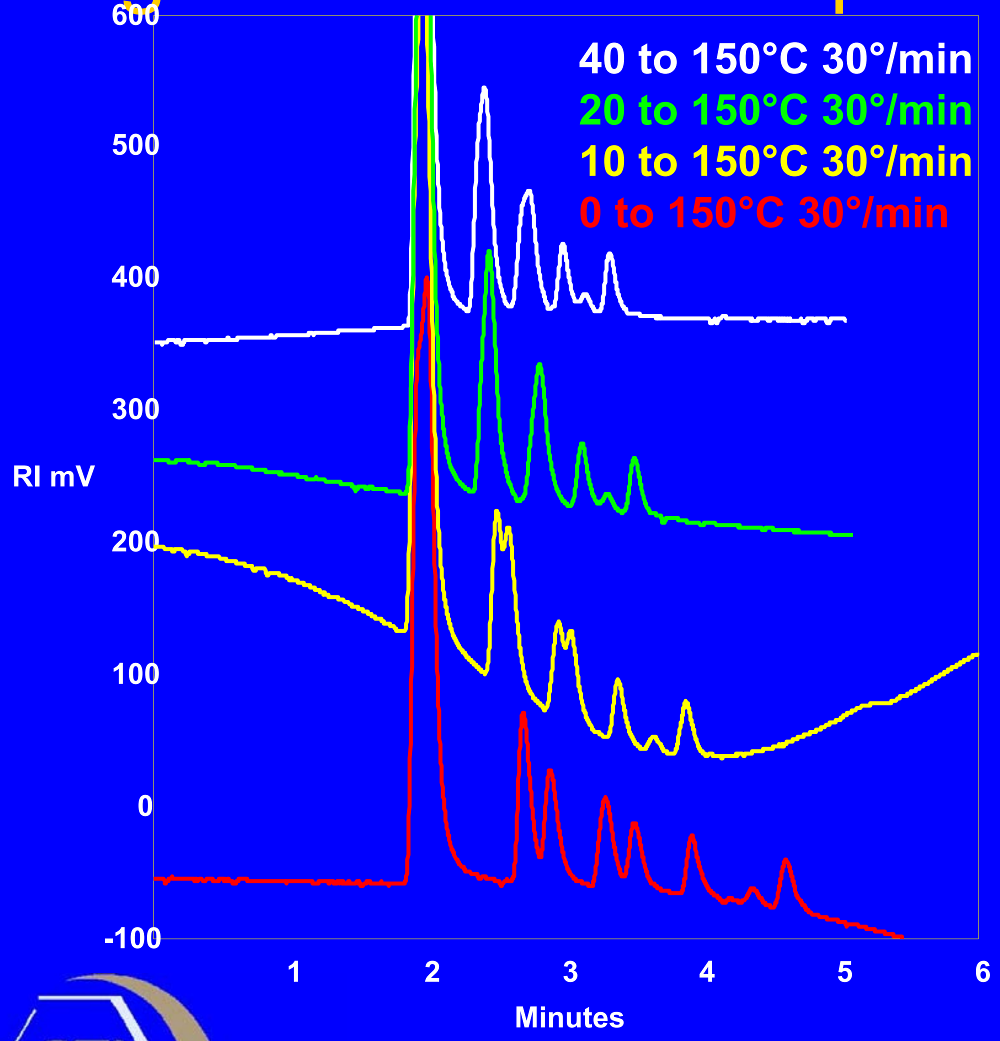
1.0 mL/min

Aromatic Standards Using Three Temperature Programs and PAC Column



Column: Partisil PAC, 5µm, 250 x 4.6 mm
Flow Rate: 1.5 mL/min
Detection: refractive index
Temperature Program: initial temp (hold five minutes), ramp to 150°C at 30°/min, hold five minutes
Elution Order:
saturates
toluene
tetralin
thiophene
naphthalene
acenaphthene
benzothiophene
dibenzothiophene
anthracene
pyrene

Aromatic Standards Using Four Temperature Programs and Econosphere Silica Column



Column: Econosphere Silica, 3µm, 150 x 4.6 mm

Flow Rate: 1.5 mL/min

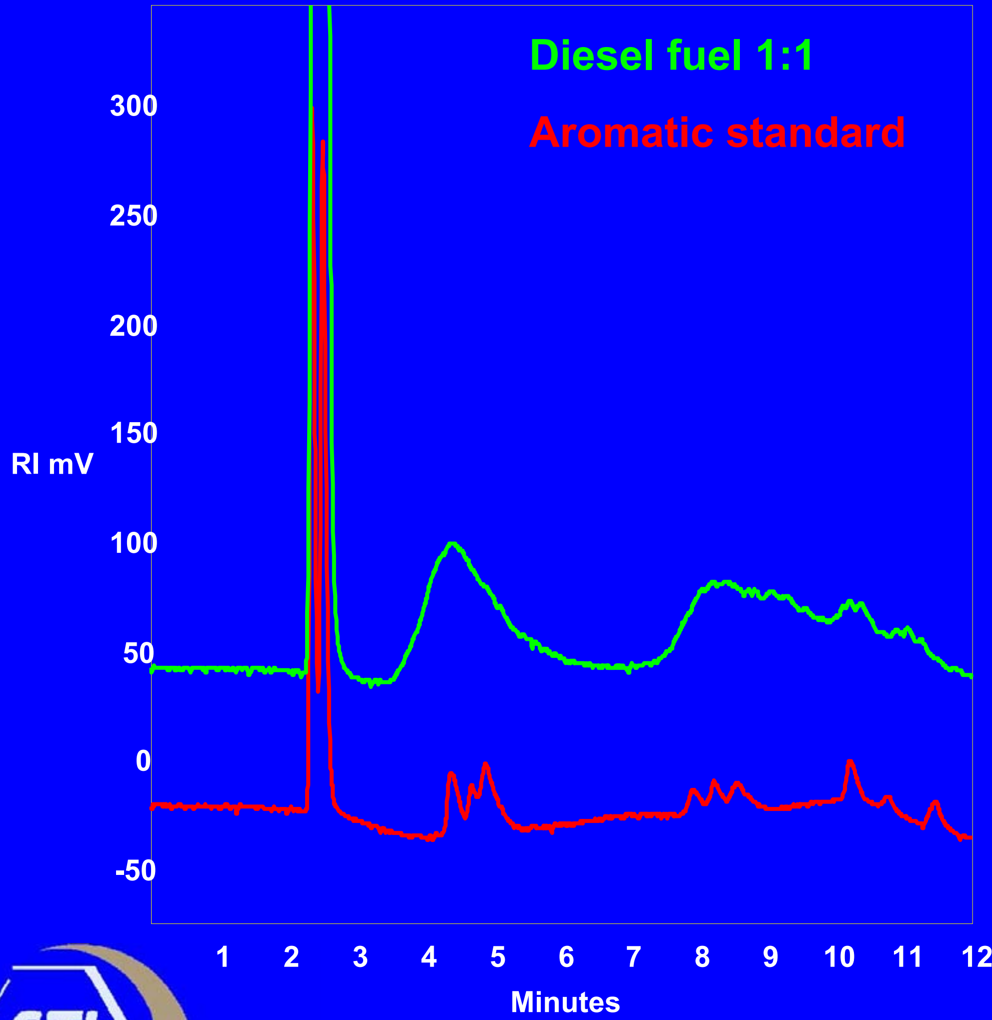
Detection: refractive index

Temperature Program: initial temp (hold five minutes), ramp to 150°C at 30°/min, hold five minutes

Elution Order:

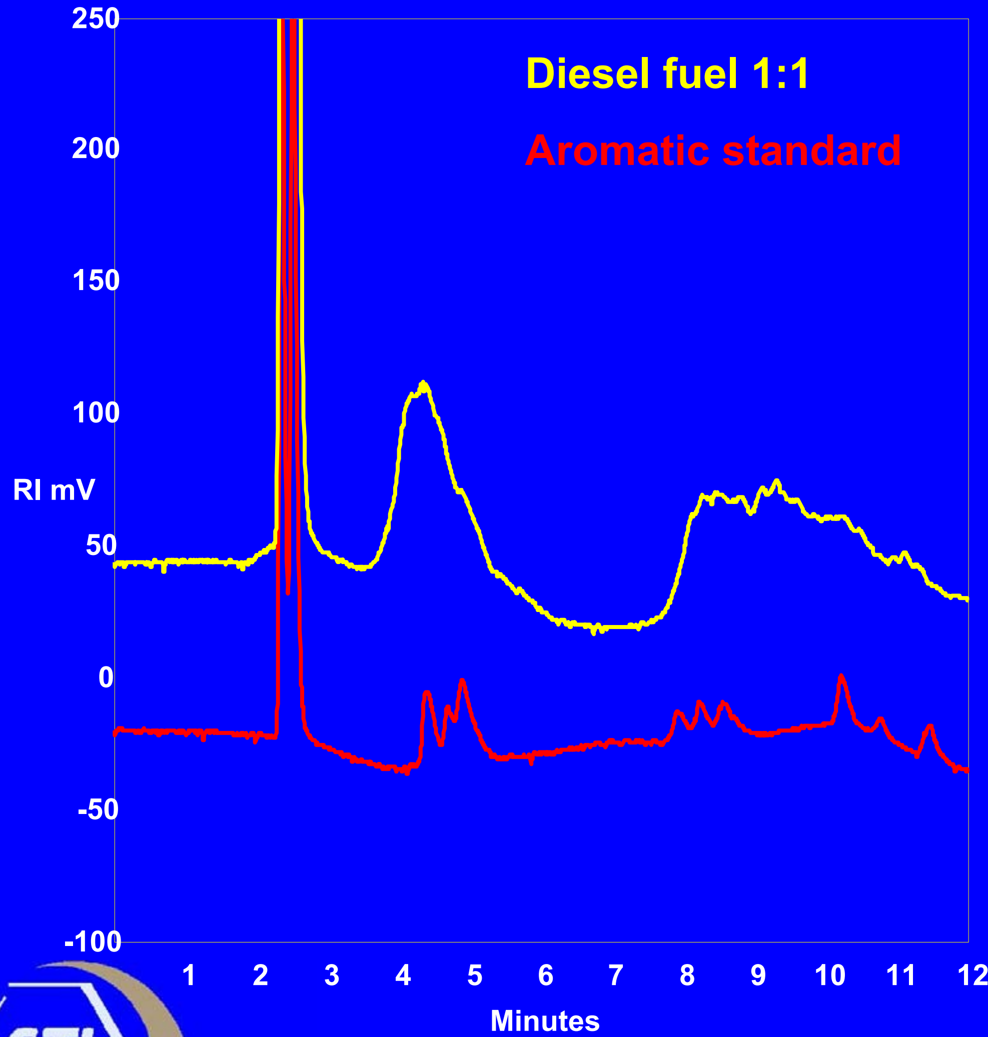
saturates
toluene
tetralin/thiophene
naphthalene
acenaphthene
benzothiophene/dibenzothiophene
anthracene
pyrene

Diesel Sample Using Temperature Program and PAC Column



Column: Partisil PAC, 5μm, 250 x 4.6 mm
Flow Rate: 1.5 mL/min
Detection: refractive index
Temperature Program: 0°C (hold five minutes), ramp to 150°C at 30°/min, hold five minutes
Elution Order:
saturates
toluene
tetralin
thiophene
naphthalene
acenaphthene
benzothiophene
dibenzothiophene
anthracene
pyrene

Diesel Sample Using Temperature Program and PAC Column



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Elution Order:
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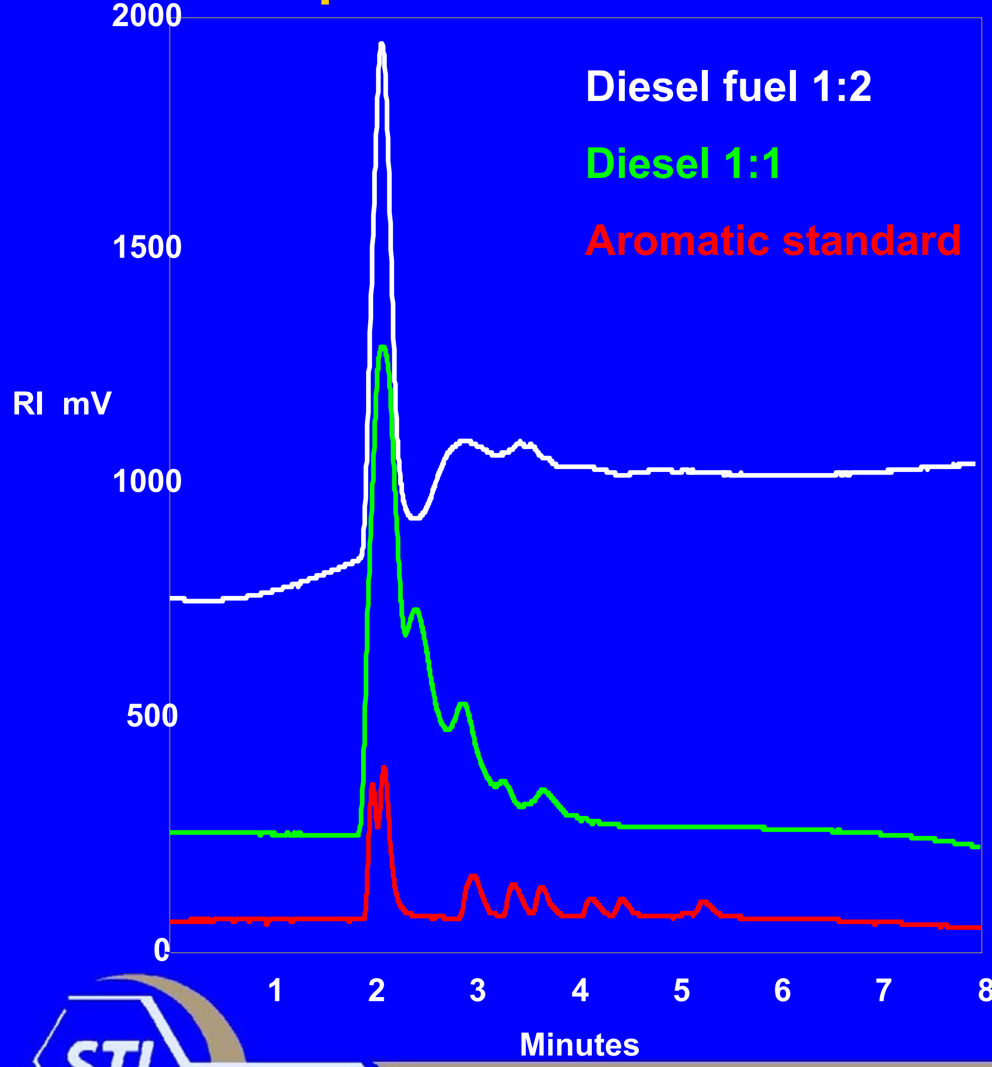
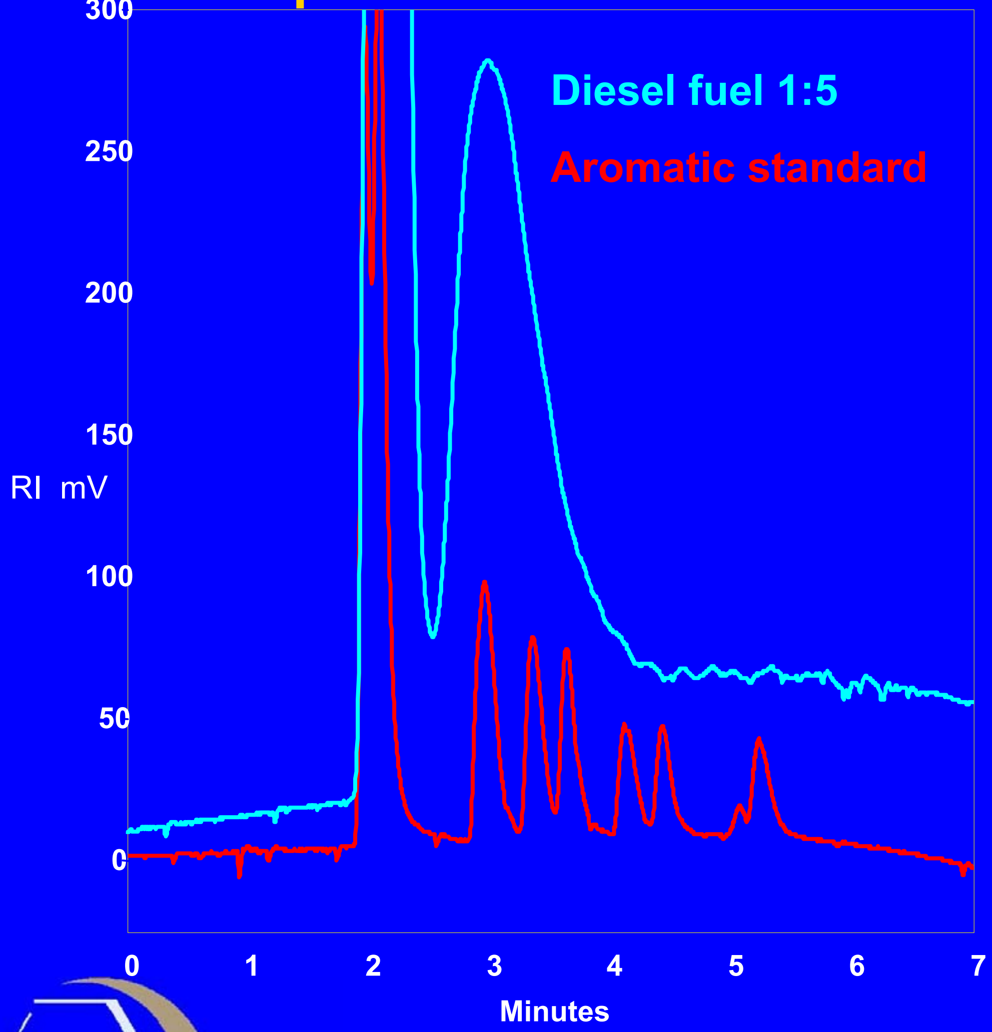
toluene
tetralin
thiophene
naphthalene
acenaphthene
benzothiophene
dibenzothiophene
anthracene
pyrene

Diesel Sample Using Temperature Program and Econosphere Silica Column



Column: Econosphere Silica, 3μm, 150 x 4.6 mm
Flow Rate: 1.0 mL/min
Detection: refractive index
Temperature Program: 20°C (hold five minutes), ramp to 100°C at 30°/min, hold five minutes
Elution Order:
saturates
toluene
tetralin/thiophene
naphthalene
acenaphthene
benzothiophene/dibenzothiophene
anthracene(small peak)
pyrene

Diesel Sample Using Temperature Program and Econosphere Silica Column



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Detection: refractive index
Temperature Program: 20°C (hold five minutes), ramp to 100°C at 30°/min, hold five minutes
Elution Order:
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toluene
tetralin/thiophene
naphthalene
acenaphthene
benzothiophene/dibenzothiophene
anthracene
pyrene

Conclusion

- Improved resolution between saturates and MAH was achieved
- Temperature programmed HPLC employing sub-ambient temperatures can significantly reduce the analysis time for the class separation of aromatics in diesel fuels compared to ASTM D6591 conditions.
- PAC column was a better column choice for diesel fractions than the silica column
- For single sharp peak of the PAH's a switching valve is still needed

Future Work

- Heavier fractions of petroleum products
- Incorporate switching valve for improved quantitation of PAH’s

Acknowledgements

- Dr. Frank Di Sanzo, Exxonmobil
  - For providing the experiment design suggestions, columns and diesel samples for this work
- Dr. Stephanie J. Marin, Selerity Technologies
  - For doing all of the work