

FID /SFC with Agilent 1260 Infinity



sim 
Scientific Instruments Manufacturer GmbH www.sim-gmbh.de

 **Agilent Technologies**

SIM

- SIM, Scientific Instruments Manufacturer
- Formed in 1997, SIM GmbH is a state of the art company focused on activities in the field of chromatography and channel partner of Agilent Technologies. Key areas are custom-made chromatography solutions based on Agilent instruments, development of functional chromatography accessories as well as qualified consulting and support service.
- Oberhausen, Germany

Outline

- SFC-FID, instrumentation coupling Agilent SFC with their FID
- ASTM D-5186
- ASTM-D-6550

ASTM D-5186

- ASTM D-5186: test method to determine the aromatic content of diesel fuels by supercritical fluid chromatography (SFC) with flame ionization detection (FID)
- Separation of test mix:
 - 20% toluene (T)
 - 3 % tetrahydronaphthaline (THN)
 - 2 % naphthaline (N)

Performance-Mix

Substance	Weight in[g]	w [%]
n-Hexadecan (C16)	5,738	73,9
Toluol (T)	1,605	20,7
Tetrahydronaphthalin (THN)	0,259	3,3
Naphthalin (N)	0,162	2,1

Requirements:

Resolution:

C16/T : 4 THN/N : 2

tR-reproducibility

< 0.5 % for C16 and T

Response factor relative to C16

< 10 % of theoretical value

Linearity of detector

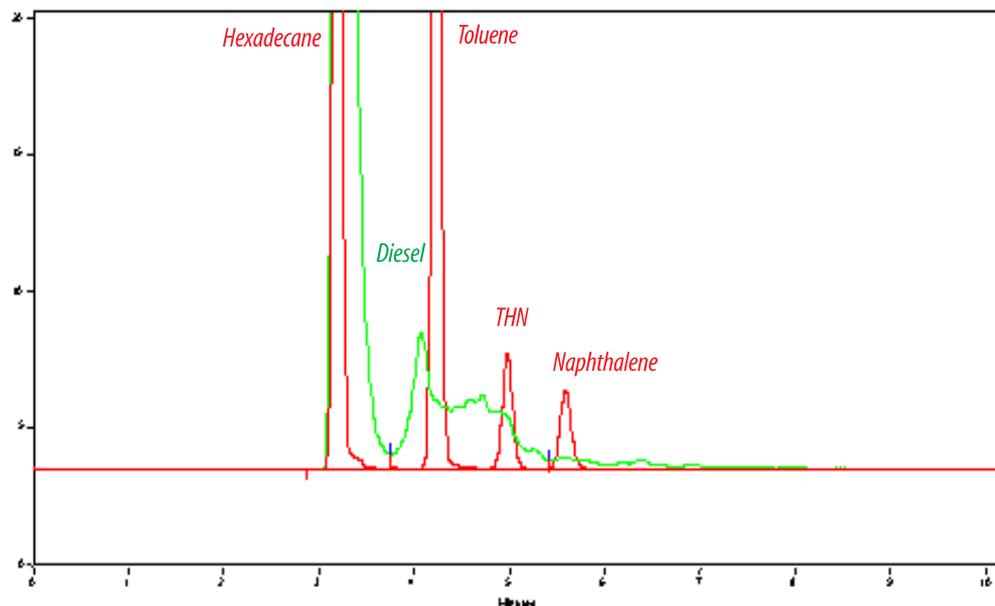
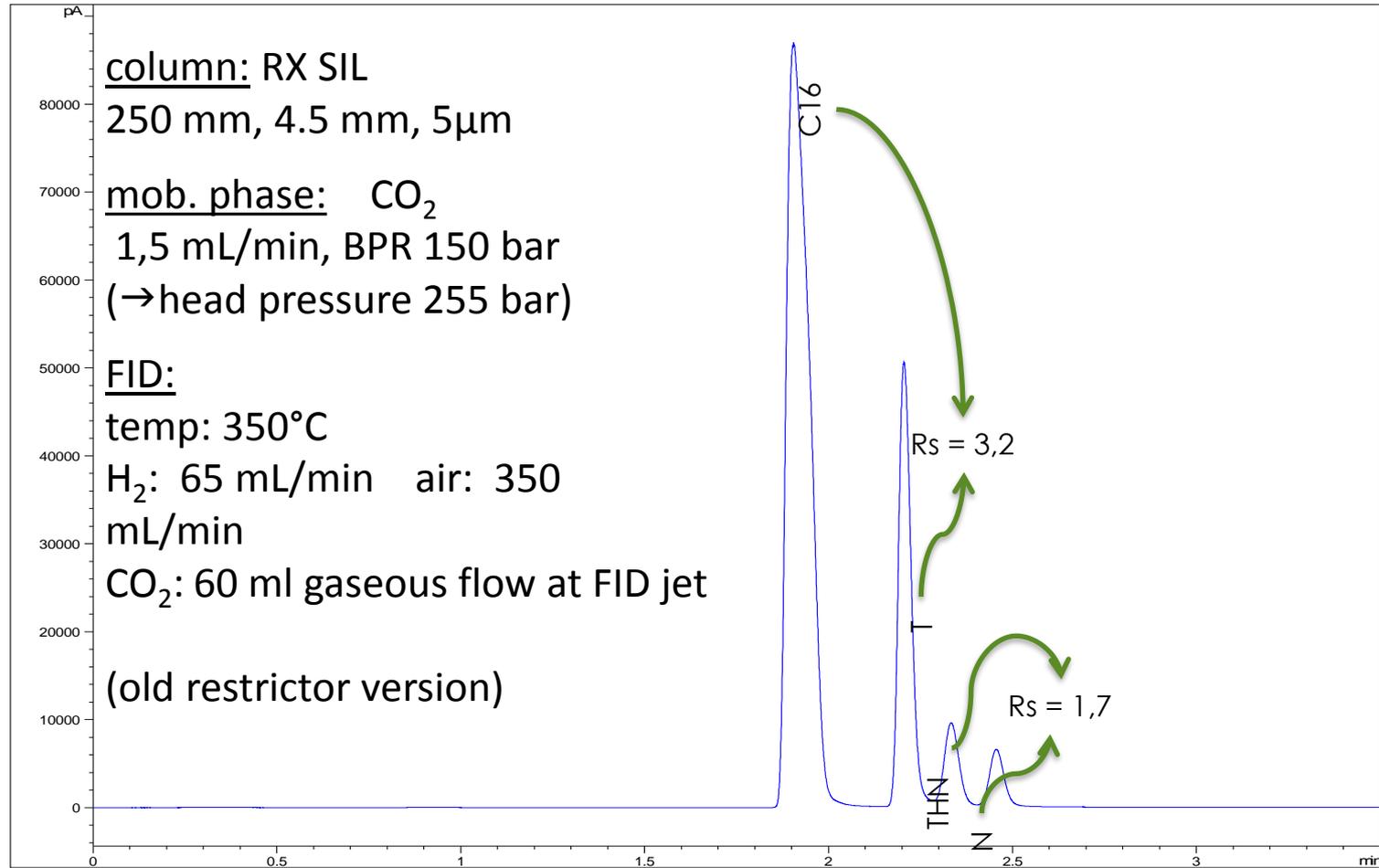


figure from Selerity Techn. Inc. – Application Note 302

Performance-Mix with 5 μ L Sample Loop

Print of window 38: Current Chromatogram(s)

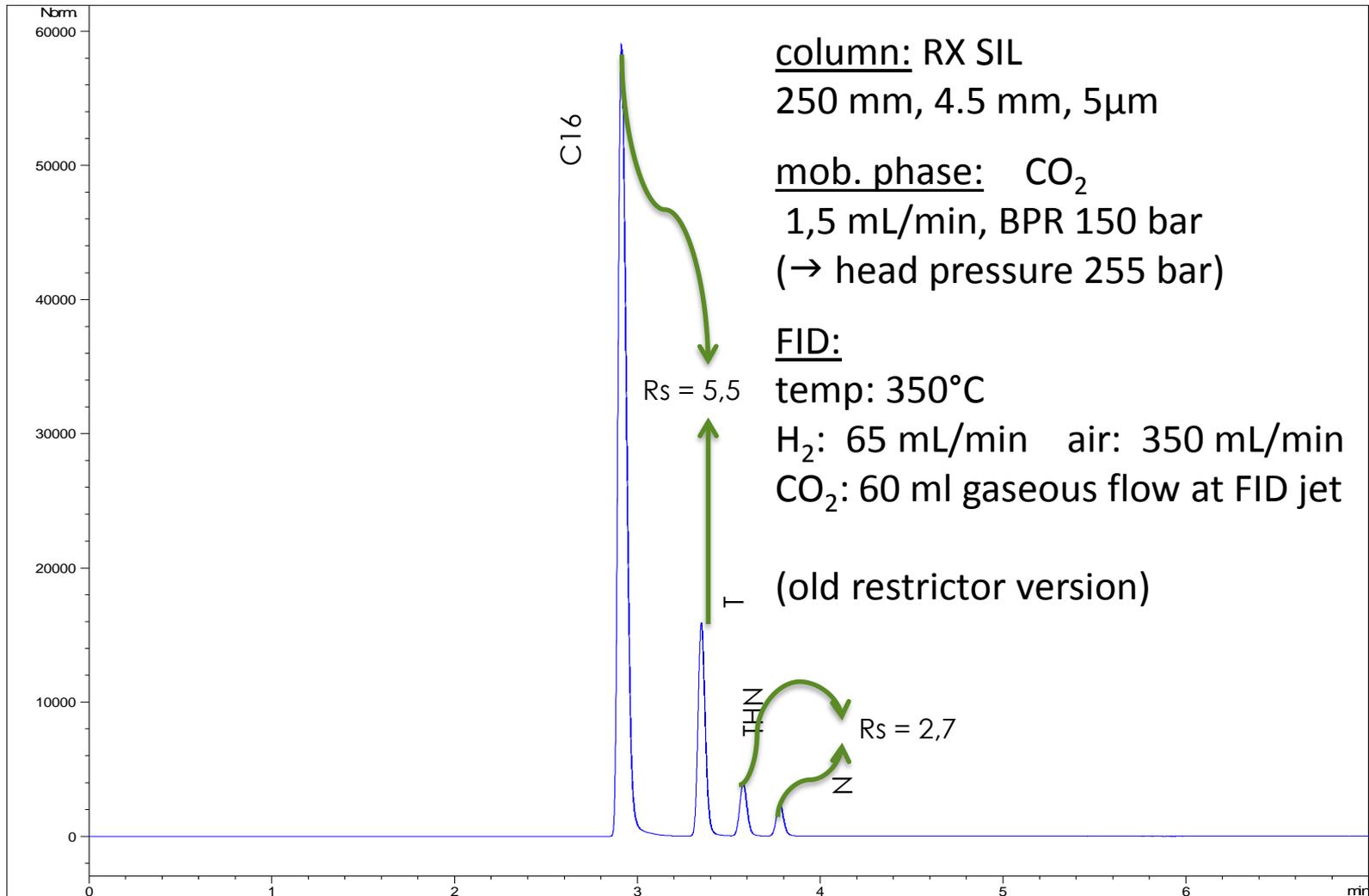
Current Chromatogram(s)



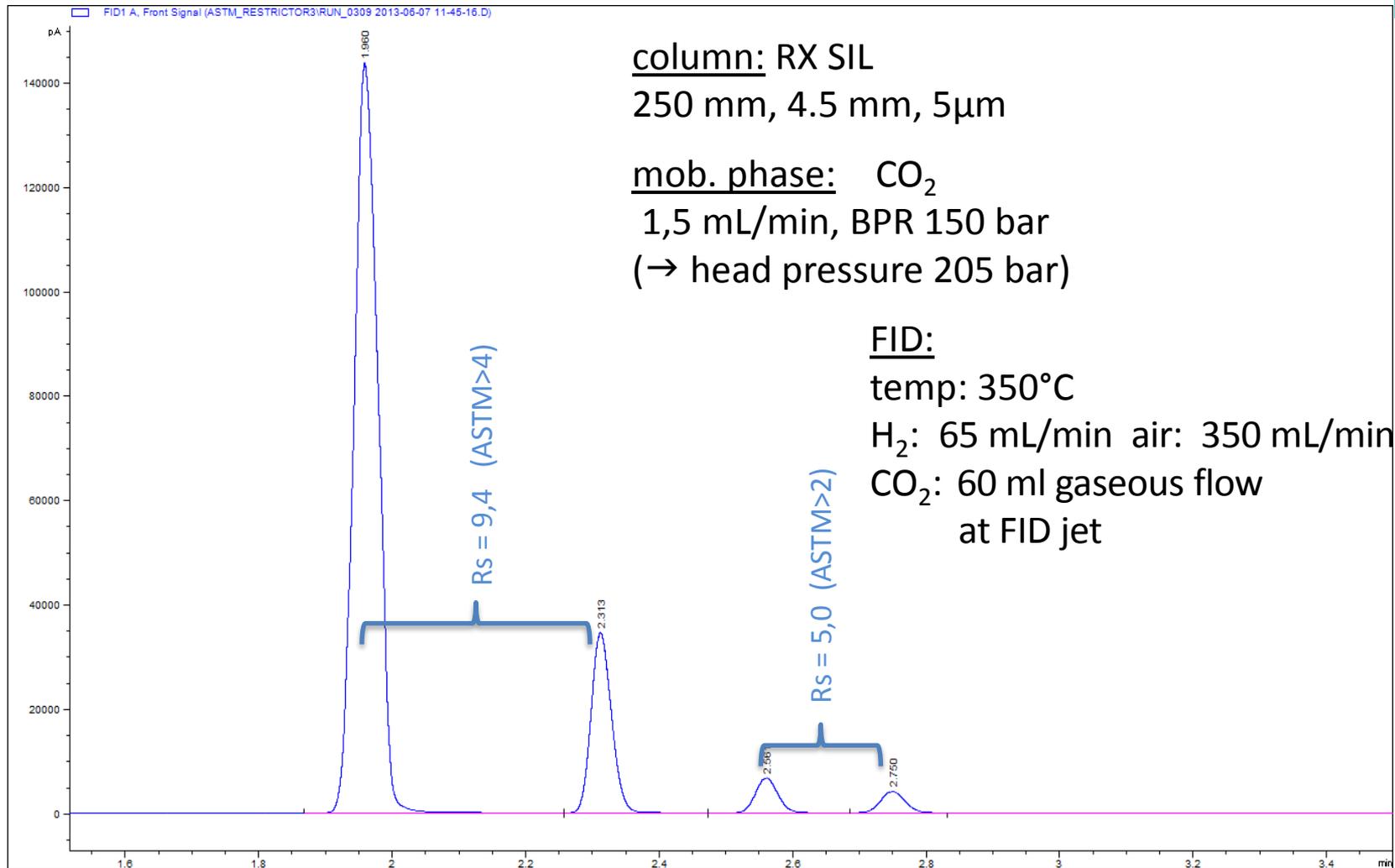
SFC-GC 12/3/2012 12:40:53 PM SYSTEM

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Performance-Mix with 1 μL Sample Loop



Performance-Mix with actual restrictor



ASTM –reproducibility of RT

Requirements:

- Reproducibility RT: $< 0.5 \%$, $n = 10$
- Obtained values:
 - C16 0.07 %
 - T 0.22 %
 - THN 0.17 %
 - N 0.15 %

ASTM - Resolution

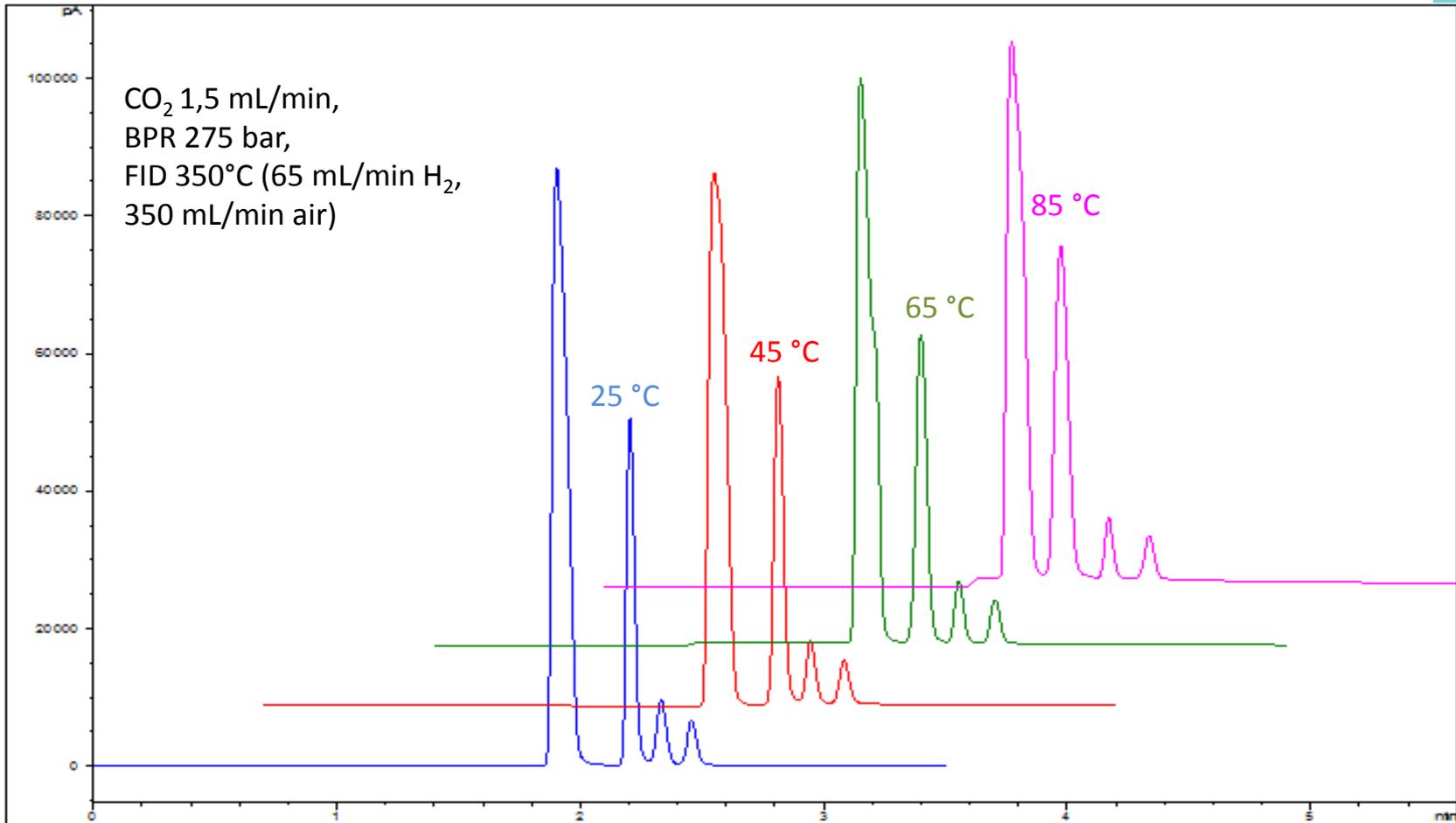
Requirements for $n = 10$:

- Resolution : C16 / T > 4
- Resolution : THN / N > 2

- Measured resolution C16 / T: 9.4 ± 0.14
- Measured resolution THN / N: 5.0 ± 0.05

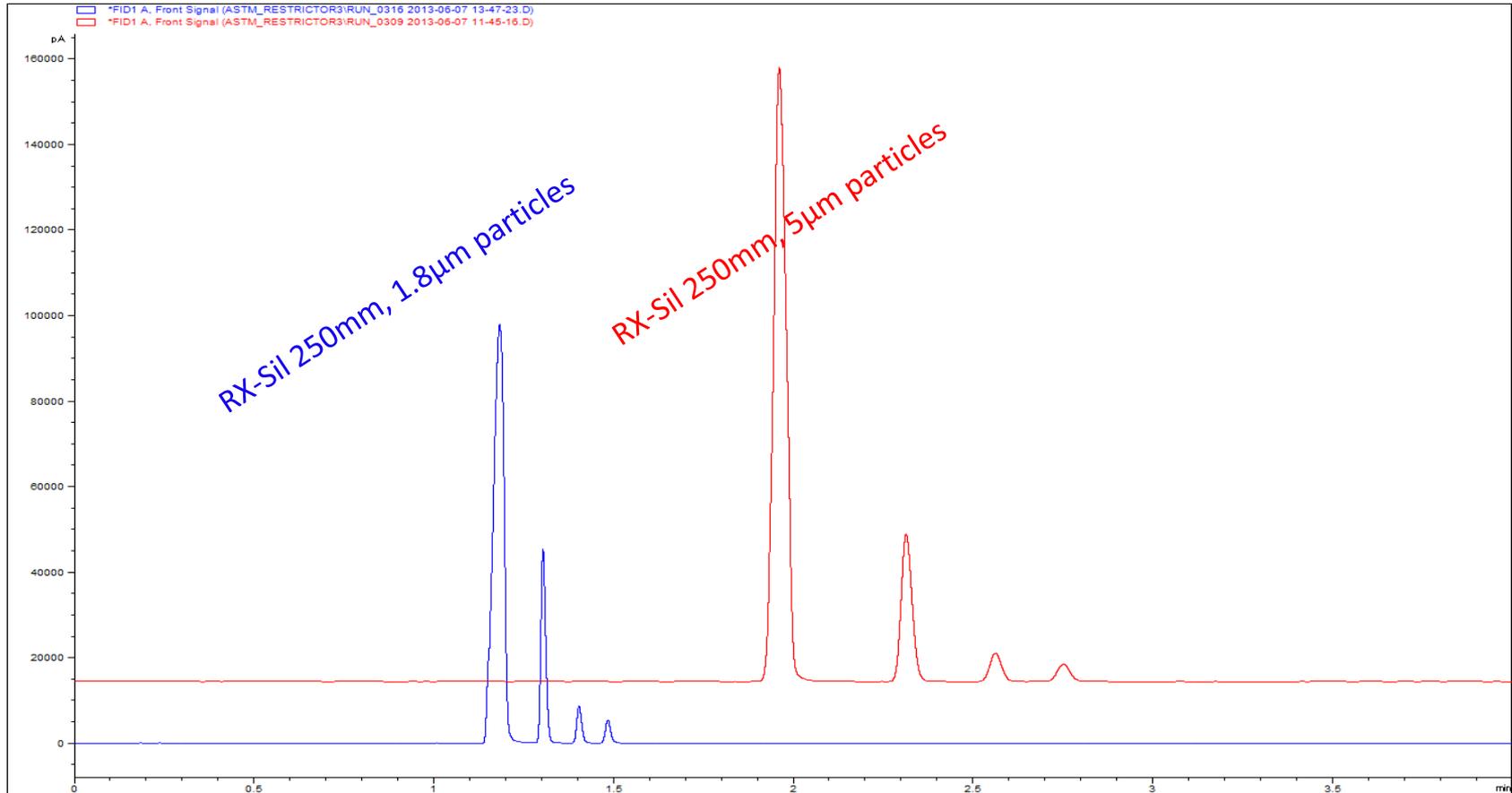
ASTM Performance-Mix

Separation at different column temperatures



→ higher column temperature, decrease of resolution

RX-Sil Column: 5 μ m vs 1.8 μ m Particles



→ reduction of analysis time with 1.8 μ m particles
(head pressure: 300 bar)

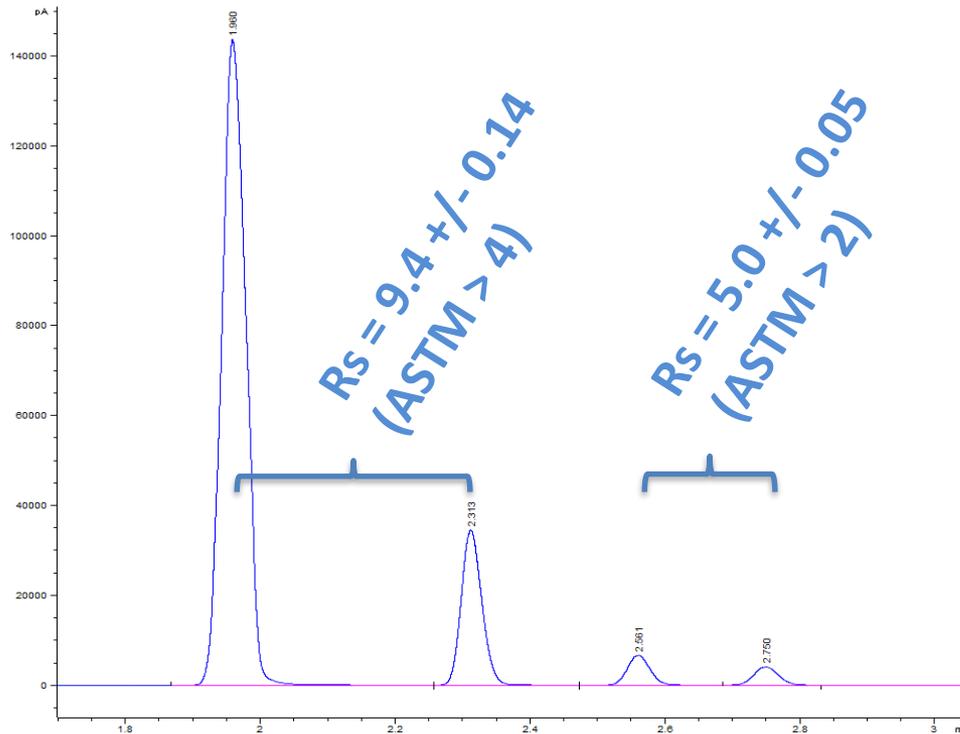
ASTM Performance – Hydrocarbon Mix

Substance	Weight in[g]	w [%]
n-Hexadecane (C16)	5,738	73,9
Toluene (T)	1,605	20,7
Tetrahydronaphthalene (THN)	0,259	3,3
Naphthalene (N)	0,162	2,1

Column: RX-Sil, 250x4.6 mm, 5µm

Mob. phase: CO₂ @ 1.5 mL/min
BPR 150 bar
→ head pressure 205 bar

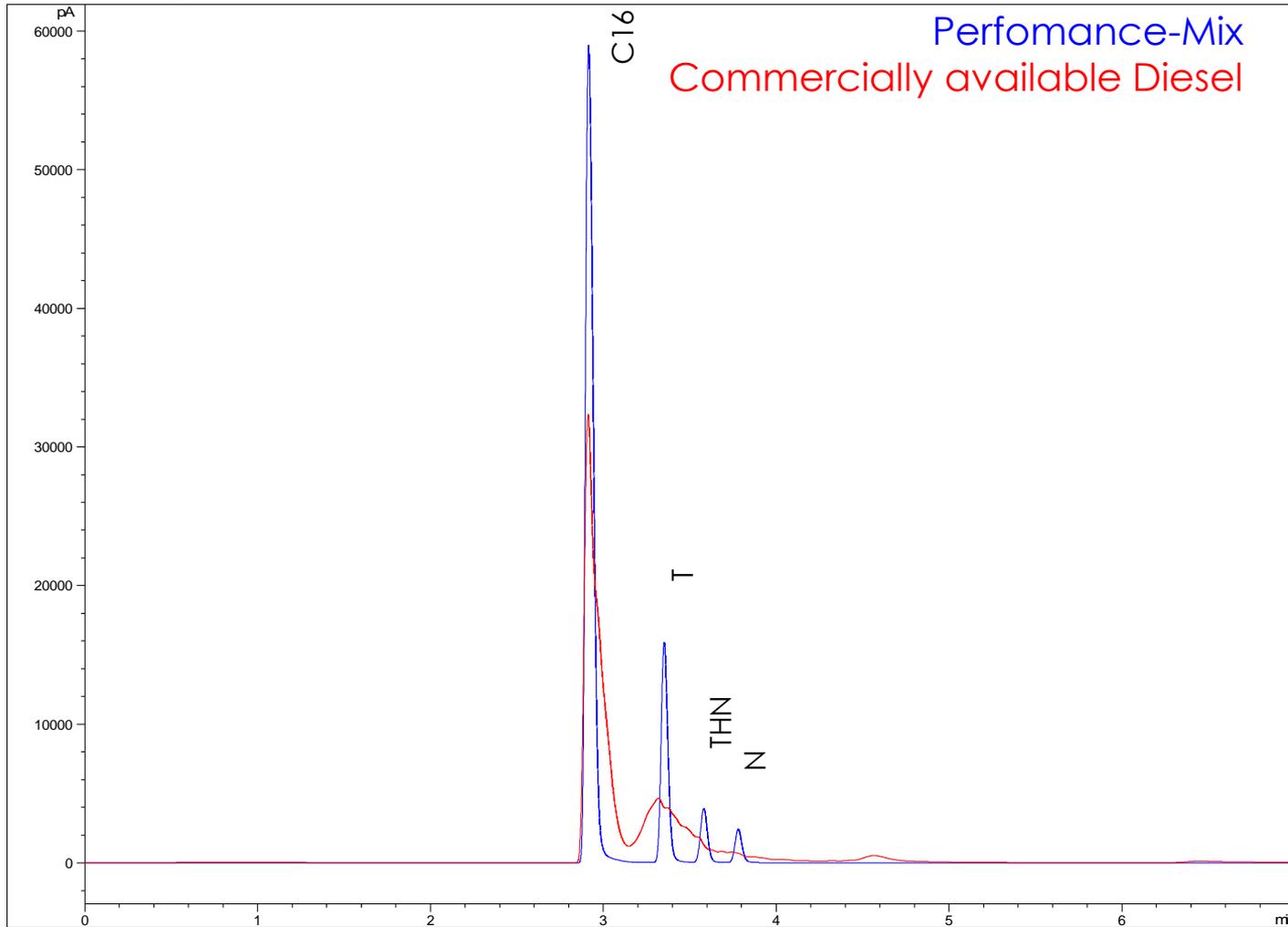
FID: Temp: 350°C
H₂: 65 mL/min
Air: 350 mL/min
CO₂: 60 mL/min*
*gas flow @ FID



ASTM Requirements:

- Reproducibility RT: <0.5 %, n=10
- Obtained values:
- C16 0.07 %
- T 0.22 %
- THN 0.17 %
- N 0.15 %

ASTM 5186-03 – Comparison with Diesel



Supported ASTM methods

- ASTM D-6550: SFC-FID Determination of Olefins in Gasoline

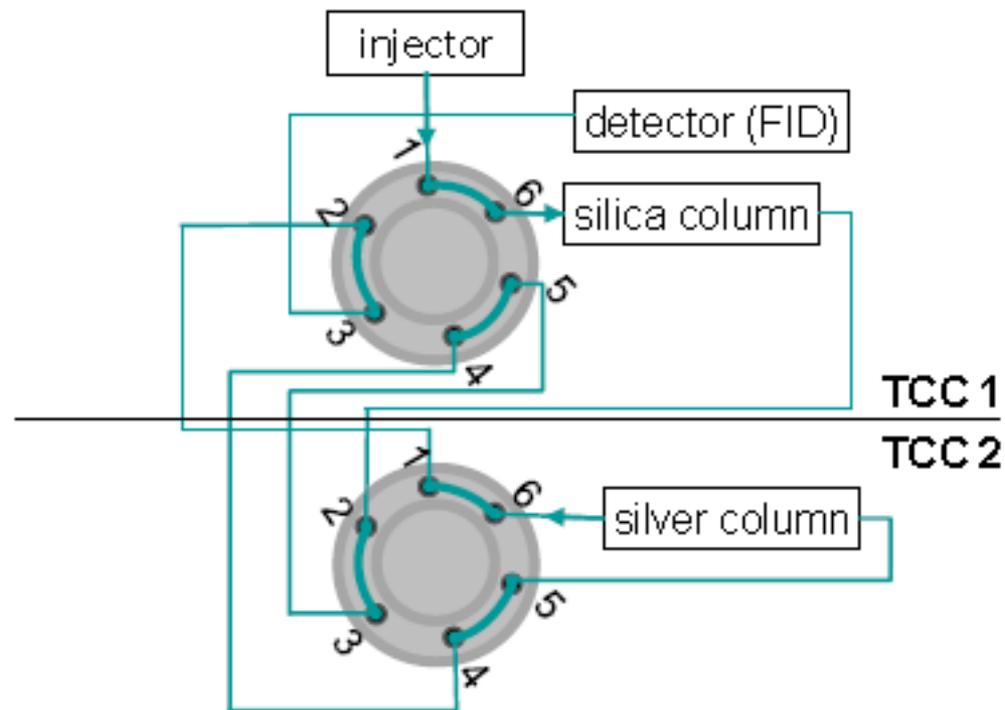
Introduction

- Integration of FID with specially designed splitter into SFC sample path by maintaining constant backpressure combined with binary pump for additional purging (channel A: CO₂, channel B: purge line, hexane)
- Switching solution with four valve positions A, forward-flush mode for silica and silver column in series. B. backflush mode for silica column only C, backflush mode for silver column only D, forward-flush mode for silica column only (this position equals the one for ASTM D5186)

ASTM-6550

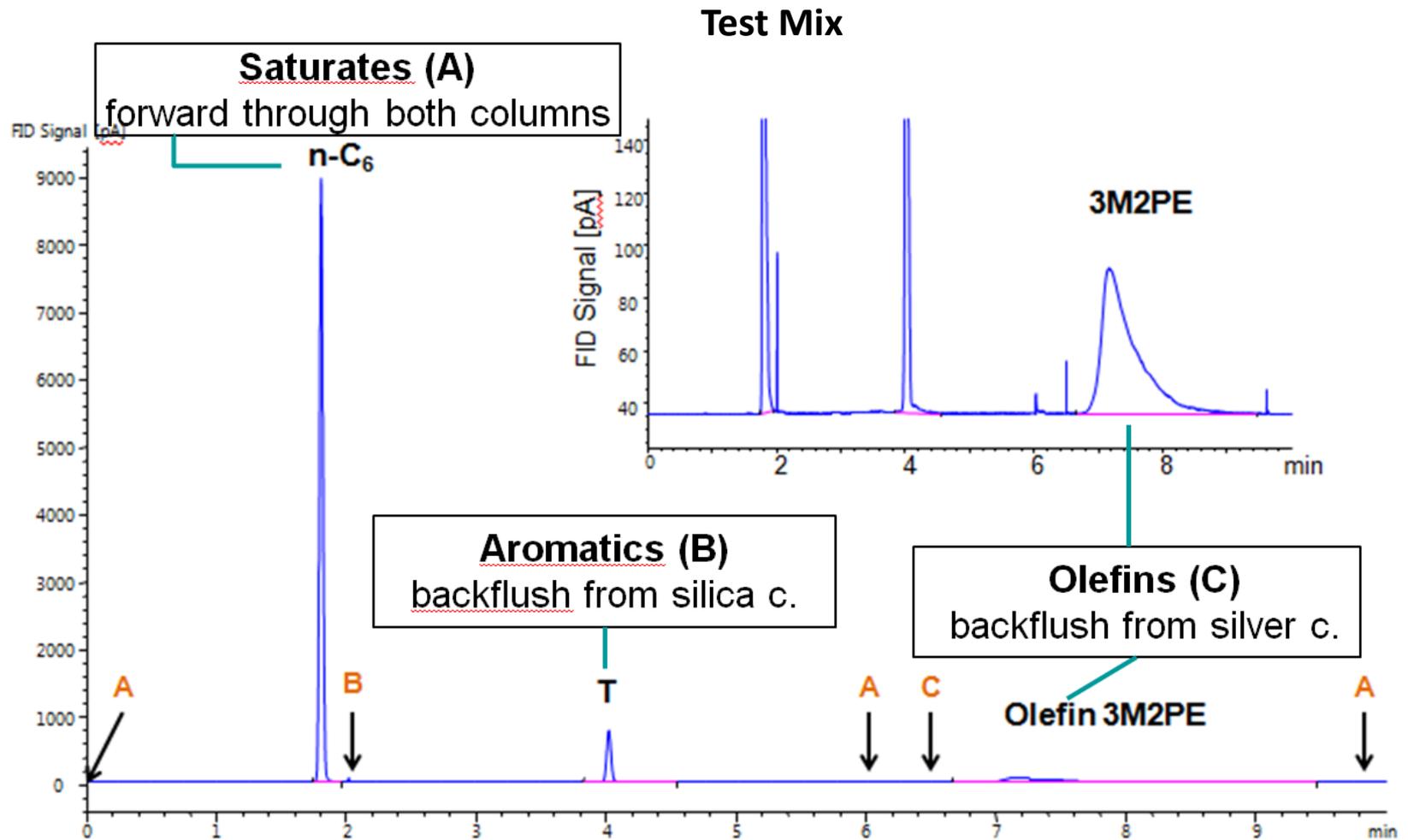
- ASTM D-6550: test method to determine the total amount of olefins in gasolines by supercritical fluid chromatography (SFC) with flame ionization detection (FID) for an application range from 1 – 25 mass % total olefins
- Agilent 1260 Infinity Analytical SFC system with FID developed by SIM for ASTM D5186 should be upgraded for the olefin determination according to ASTM D6550
- two columns with valve switching solution had to be integrated in the flow path
- complete SFC-FID system had to maintain a constant backpressure over the complete flow path to ensure highest precision of retention time and

Switching Valve



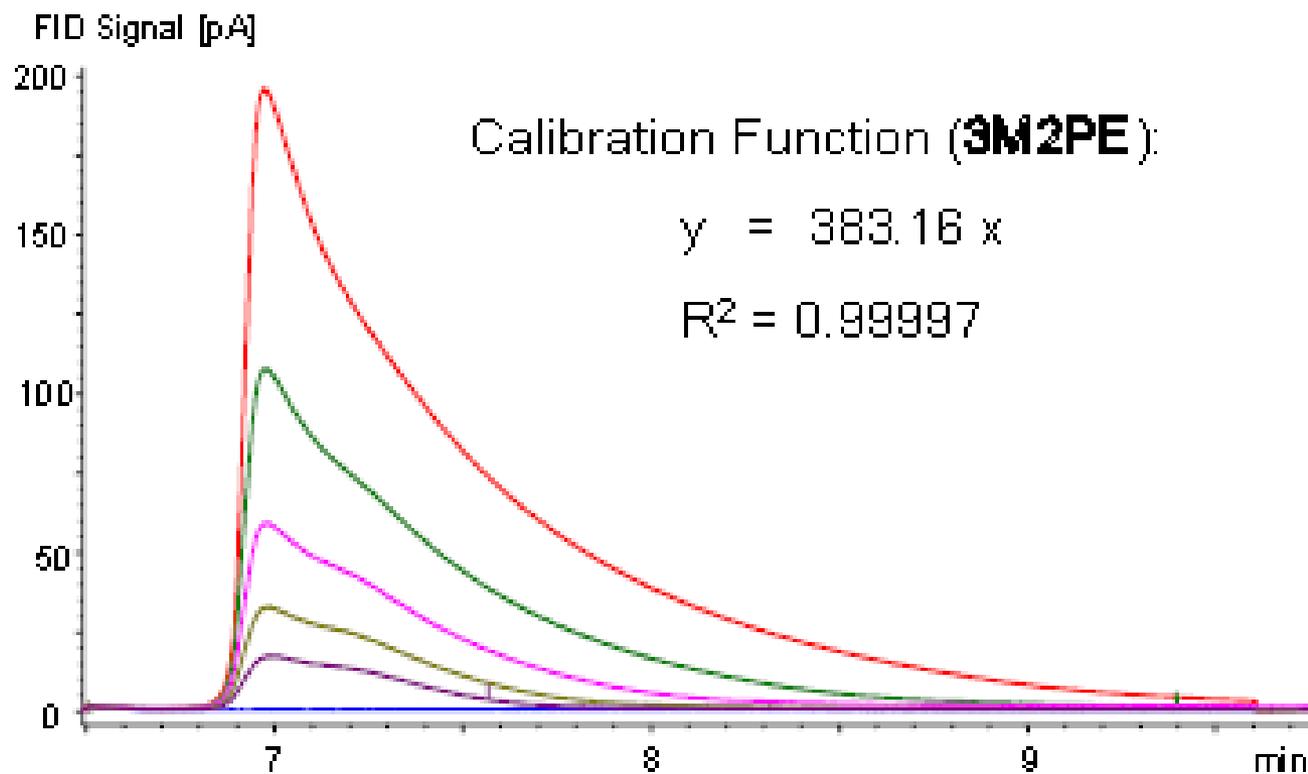
Valve switching position A (consists of two 2-position/6-port Quick-Change Valves)

Determination of Olefins in Gasolines



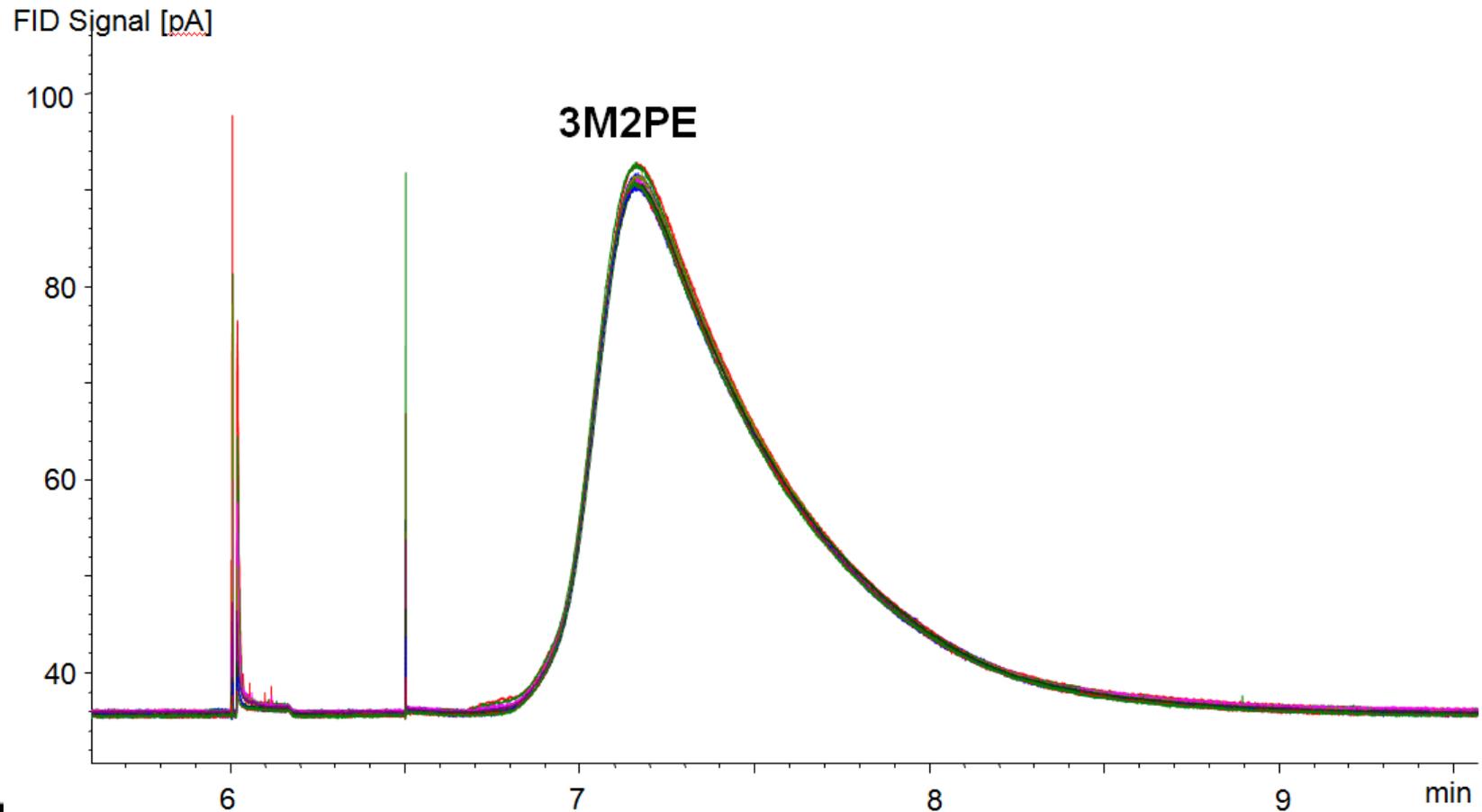
PTM with the valve positions A, B and C

Olefin Calibration

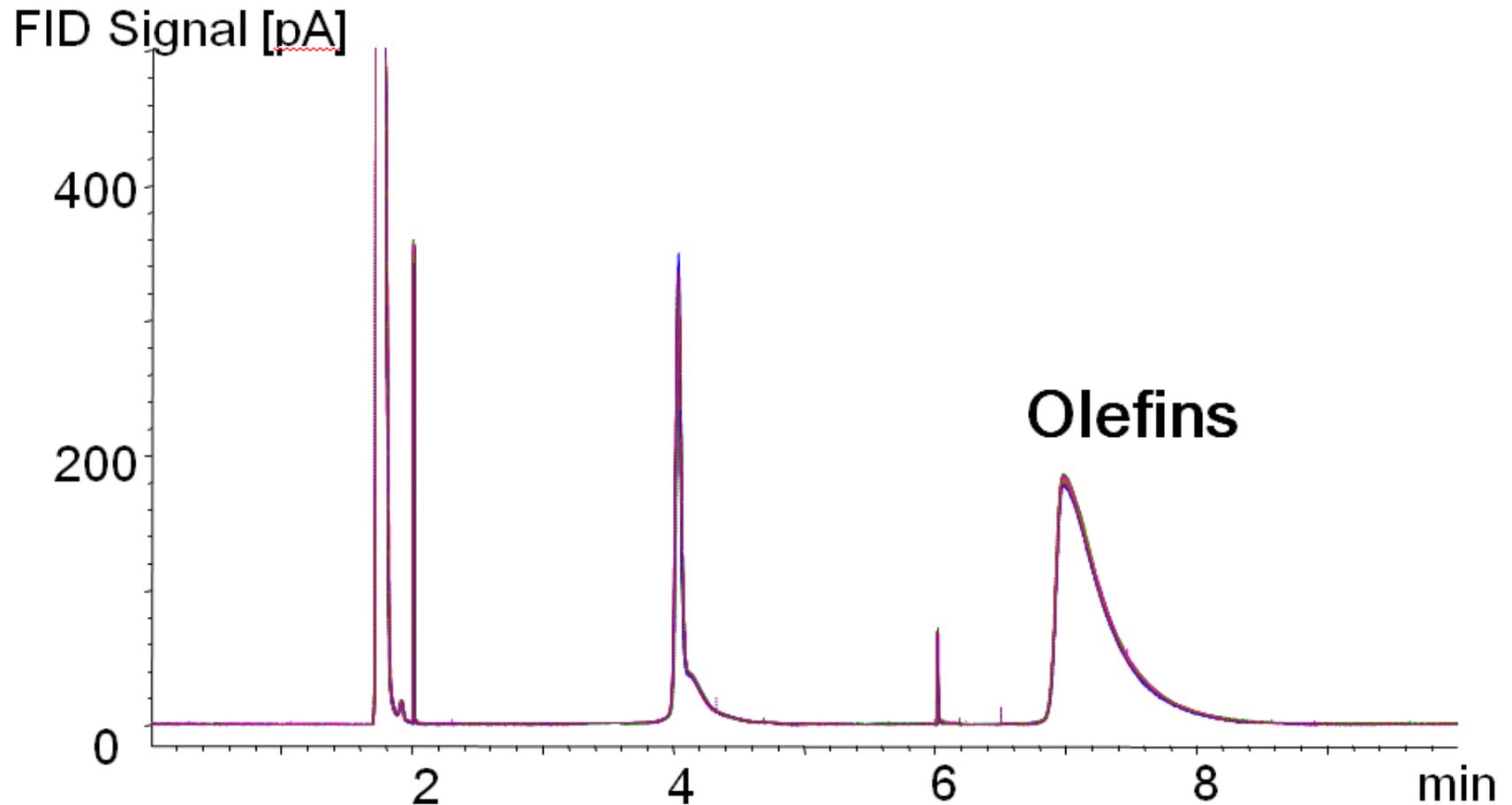


Retention time and area precision

Retention time and area precision of separated olefin
3M2PE (overlay of 10 injections)



Olefin Content of Gasoline Sample



Conclusion

- Agilent 1260 Infinity Analytical SFC system with SIM FID meets the requirements of ASTM D5186
- Detector accuracy and linearity tests show suitability of the FID to determine the aromatic substances in diesel fuels
- Specially designed splitter with connector to FID for high reproducibility
- System is equipped with continuous purging of SFC backpressure regulator
- Trouble-free and reliable operation of the entire SFC-FID system
- Combined system (2 in 1) for ASTM D5186 and ASTM D6550 (olefins in gasoline) soon available

SFC-FID

Instrumentation

1260 SFC/FID



- ✓ Addresses **ASTM 5186** and other standard methods for determining unsaturation in oil, diesel and biofuels
- ✓ Added FID detector to SFC



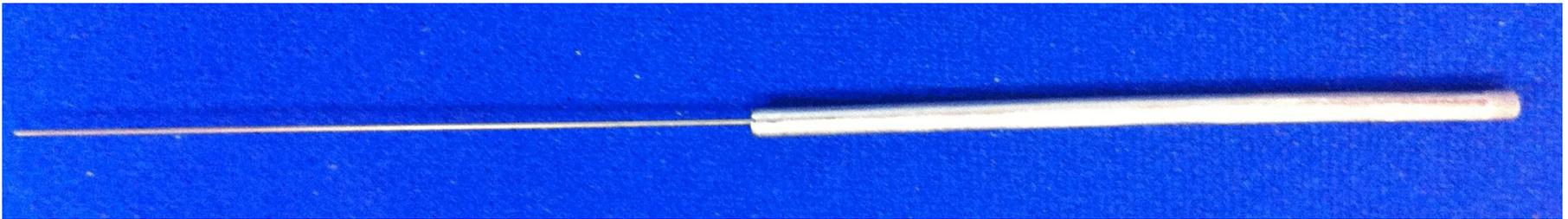
The System

FID mounted to SFC Module:



The System

- pressed stainless steel capillary as restrictor
- optimized dead volume:
T-piece directly at FID , the end of the restriction capillary is directly attached to the FID nozzle



SFC Control Module with FID-detector



SFC-FID coupling with restrictor



Bridging adapter with inbuilt restrictor

Column exit to BPR of the SFC control unit

Eluent stream from detector or column

Integration in OpenLAB ChemStation

The screenshot displays the OpenLAB ChemStation software interface for SFC (Supercritical Fluid Chromatography) control. The main window is titled "SFC (online): Method and Run Control". The interface is divided into several sections:

- Method and Run Control:** A tree view on the left shows the method hierarchy, including "DEF_L.C.M" and various "DEF_SFC-FID" methods.
- Instrument Control:** The top right section shows the status of the Sampler, Binary Pump, Column Comp., and DAD. The Binary Pump is set to 1.000 mL/min and 107.37 bar. The Column Comp. is set to 25.00 °C. The DAD is also set to 25.00 °C.
- Instrument Actuals:** The bottom left section shows the SFC status, including the SFC module status (Run), Booster Pressure (100.0 bar), and BPR Pressure (100.0 bar). The SFC temperature is 60 °C.
- Online Plot:** The bottom right section shows a chromatogram plot with several peaks. The plot is titled "Status of SIM GmbH FID Detector" and shows the Channel 1 Absorbance (1019).
- Run Progress:** The top center shows the run progress, including the elapsed time (0.3) and the current run time (Run 0.28 / 1.00 min).

The interface also includes a "Data Analysis" section on the right and a "Verification (OQ/PV)" section at the bottom left. The system status bar at the bottom indicates "SYSTEM (localhost) SFC" and "Ready".

Conclusions

- Solutions for both D-5186 and D-6550
- Application notes and PDFs of poster presentation are available

Thank you for your attention!