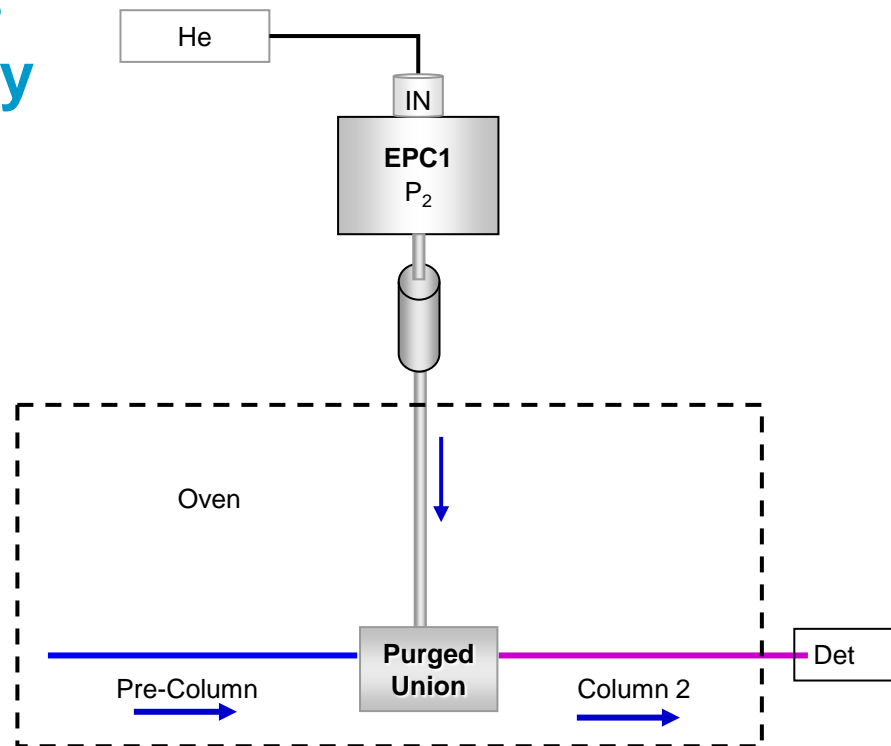# Reliable Analysis of the Light Ends of Petroleum Fractions and Crude Oil Using Capillary Flow Backflush Technology

Roger L. Firor
Agilent Technologies
Chemical Analysis Group
Wilmington, DE   USA

He

IN

EPC1
P_2

Oven

Pre-Column

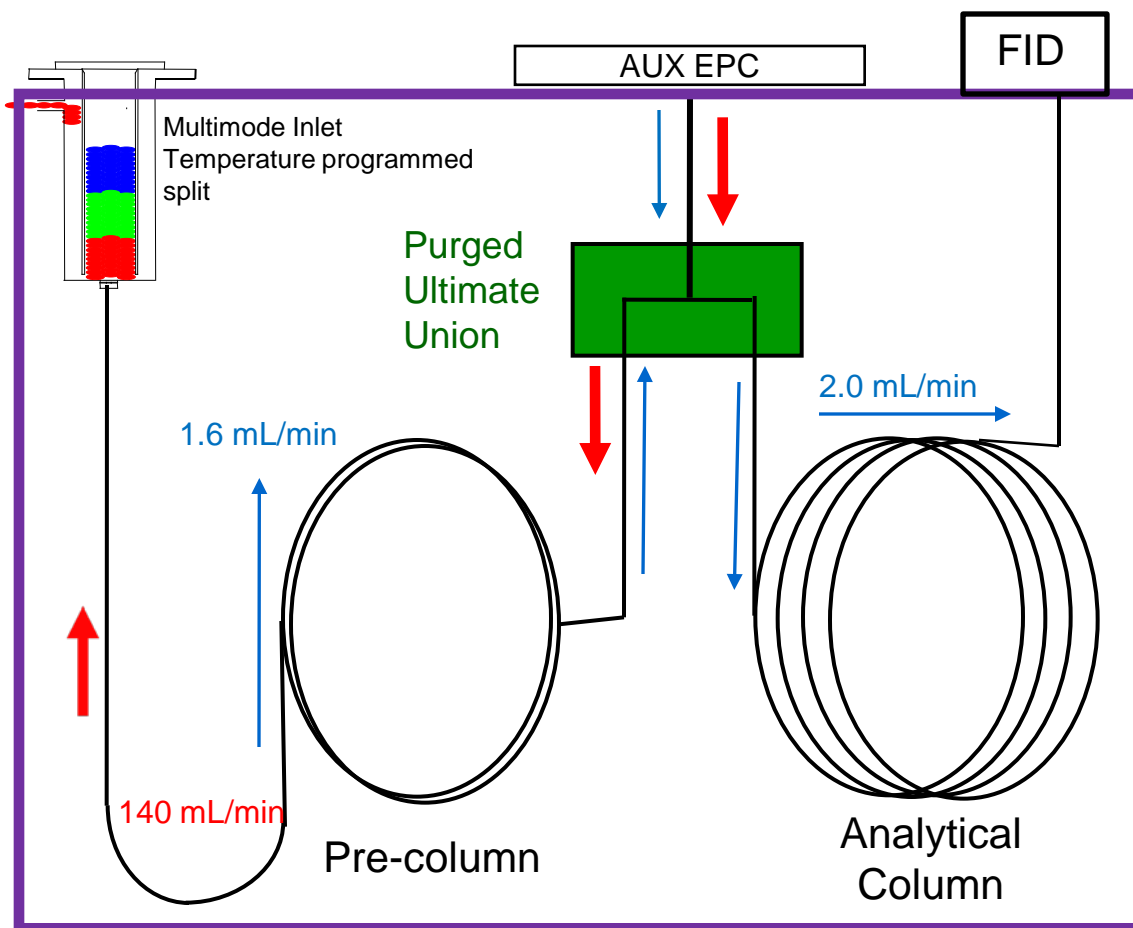Purged Union

Column 2

Det

Agilent Technologies

Outline

- Why pre-column backflush

- System configuration with CFT (Capillary Flow Technology)

- Typical method setup

- Performance

- Application examples
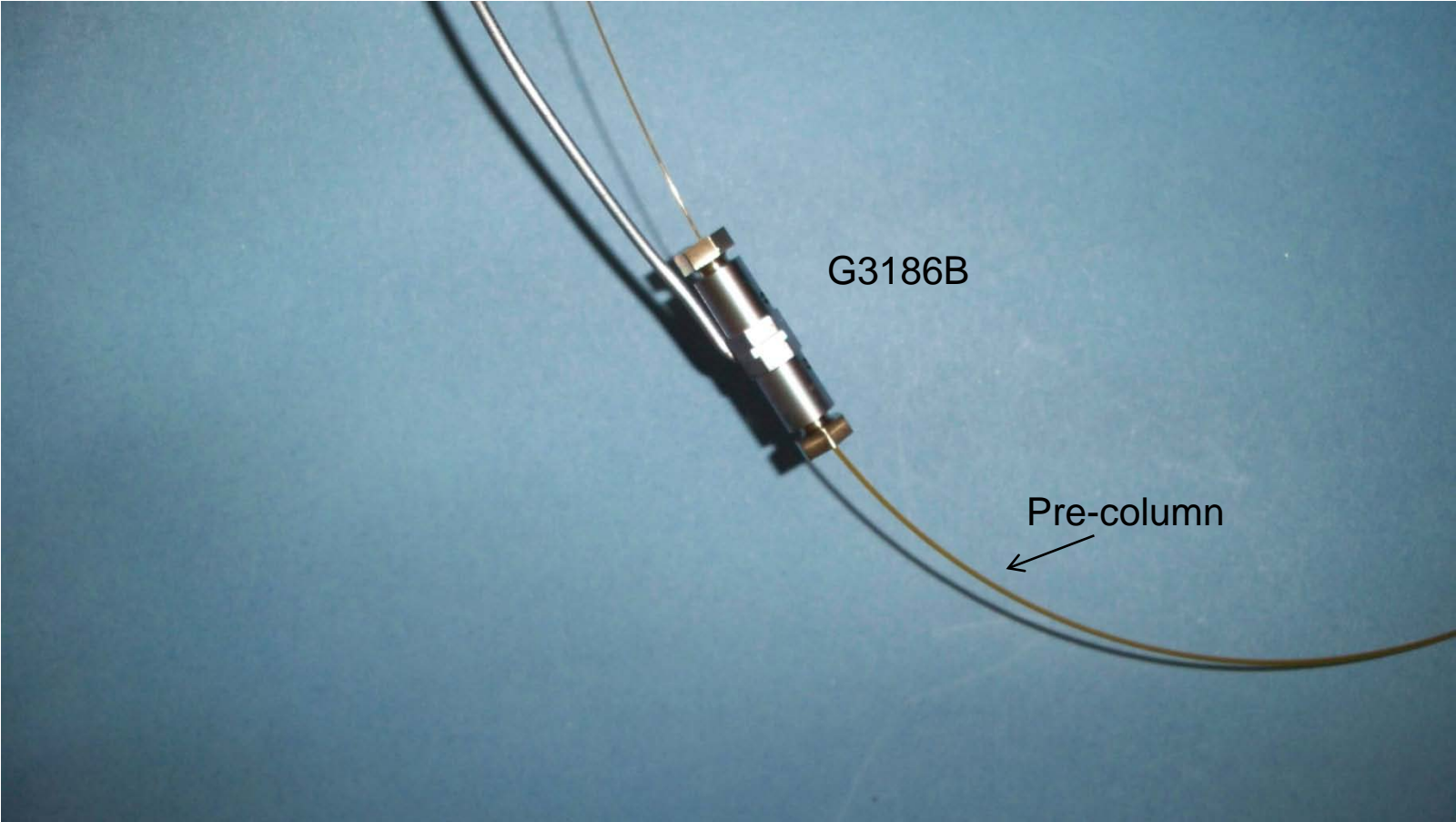
Agilent Technologies

Pre-column Backflush

- Eliminate bake out times at end of runs

- Dirty samples

- Late eluting compounds of no analytical interest

- Need to protect column from high boilers

- Interest in maximizing lab throughput and minimizing cost of operations

- Compatible with GC and GC/MSD systems

Agilent Technologies

Basic System Configuration

Multimode Inlet
Temperature programmed split

AUX EPC

FID

Purged Ultimate Union

1.6 mL/min

2.0 mL/min

140 mL/min

Pre-column

Analytical Column

Purged Union with Columns Installed

G3186B

Pre-column

Agilent Technologies

Advantages of Pre-column Backflush

▪ Backflush is carried out while analysis is occurring on the analytical column

▪ Midpoint pressure control allows analytical column to run at desired flow while pre-column is backflushed

▪ Use of an uncoated pre-column allows transfer of components (in this application up to C12 – C13) at a relatively low temperature (i.e. 35 C) and faster backflushing of the heavier components

▪ Sample matrix has little influence

▪ Wide choice of pre-column and analytical column dimensions and phase ratios possible to meet specific application needs

Agilent Technologies

System Setup and Operation

• A pre-column, typically a deactivated retention gap of 2 meter length is used.

• The inlet of the pre-column is defined as the MMI (multimode inlet) and the outlet as a Aux module channel

• The analytical column (*100*m x 0.20mm x 0.5um HP1 for crude oil analysis) uses an Aux channel (no restrictor) as inlet and FID as outlet

• At the specified runtime the inlet pressure is dropped to reverse flow in the pre-column while the Aux maintains forward flow in the analytical column

• At backflush runtime, the MMI's temperature is ramped to 425 C to clear out the inlet. It is held at this temp to end of run

• Single taper liner with glass wool is used

• Pressure zeros should be set on the GC for the inlet and Aux channel before use

Agilent Technologies

Backflush: Column Settings for Polywax Carbon Number Specific Backflushing

PW 500

Agilent Technologies

Backflush with Purged Tee: Polywax 500

Sample: C5-C18 plus PW500

Agilent Technologies
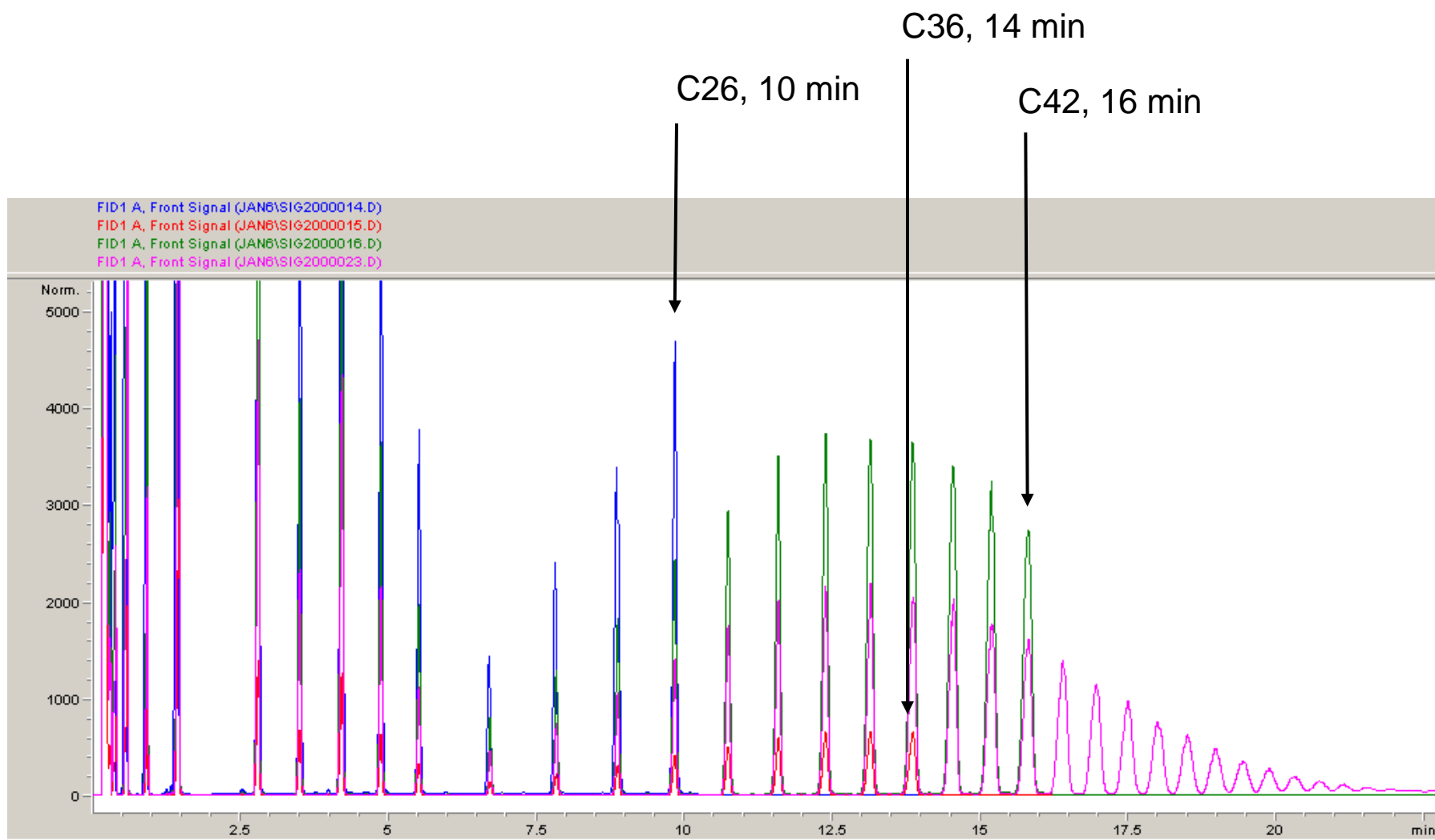
Peak Shapes on Retention Gaps: C12 Only

Agilent Technologies
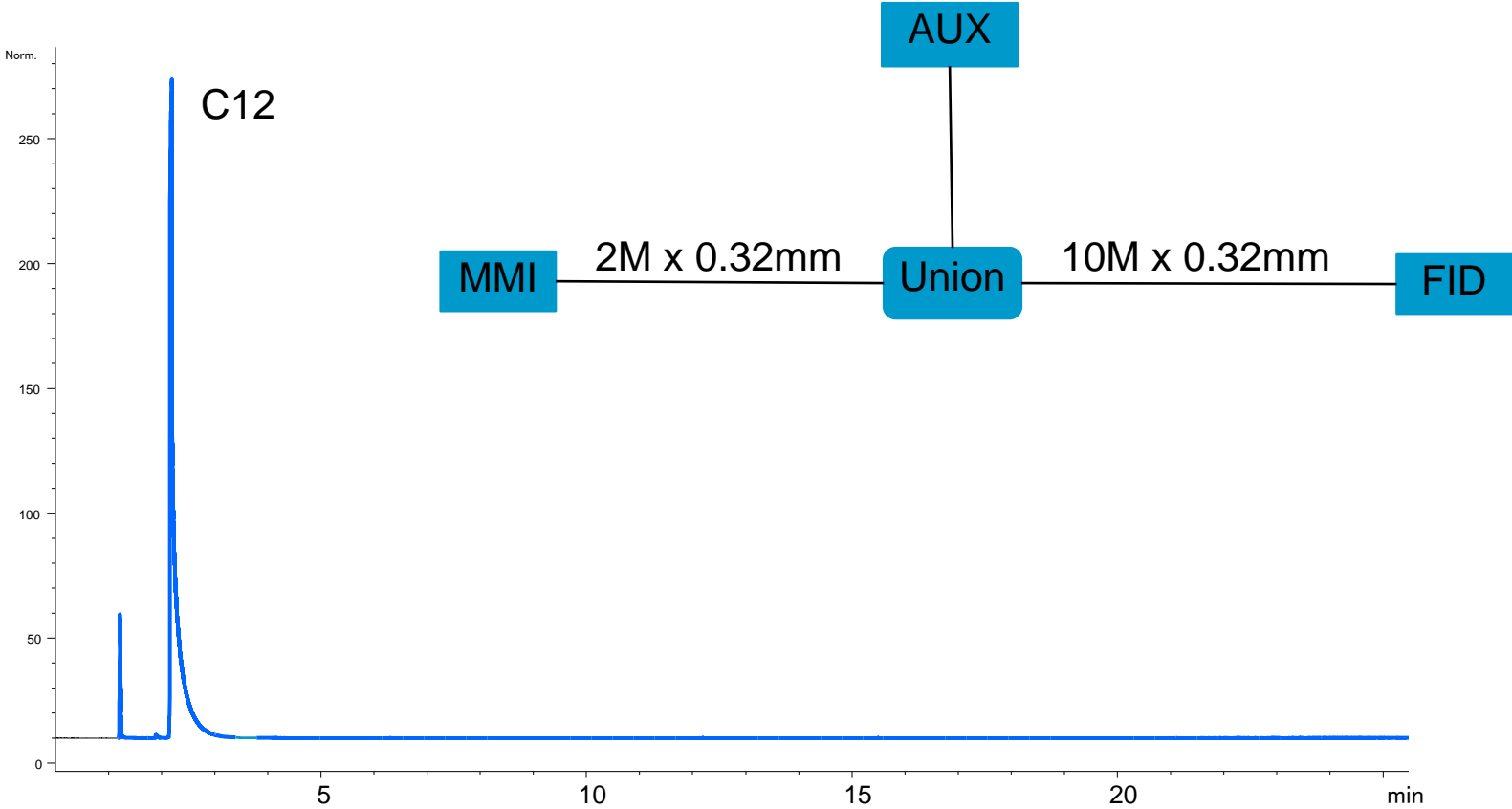
Setup for Pre-column and Analytical Column
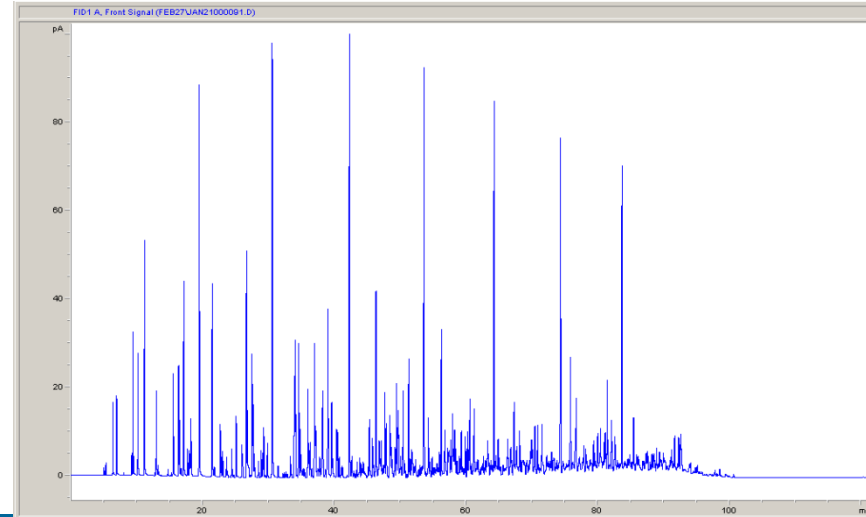
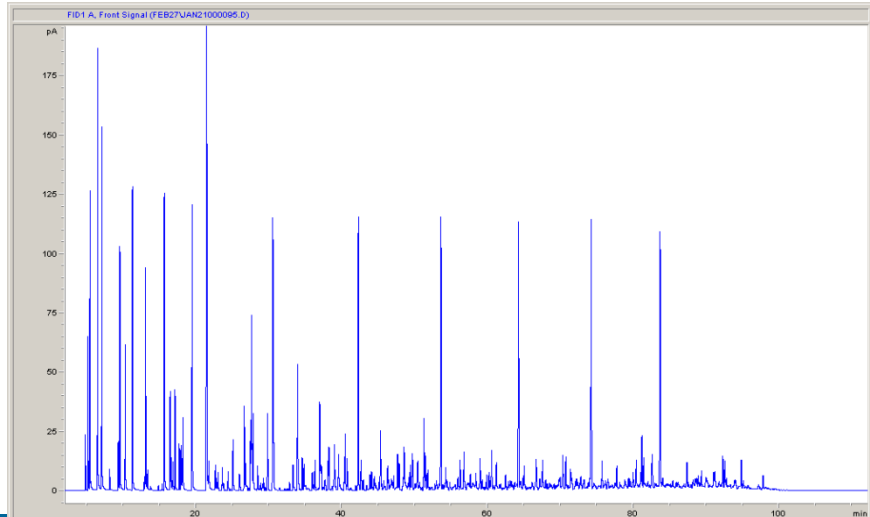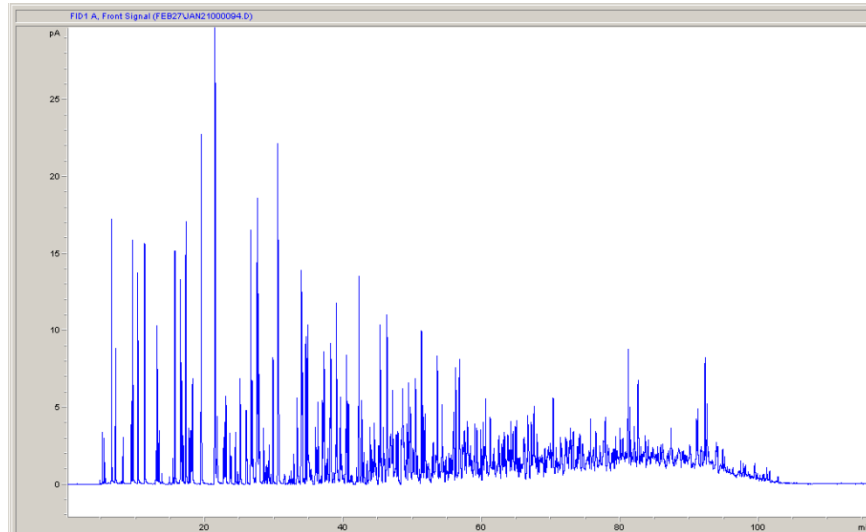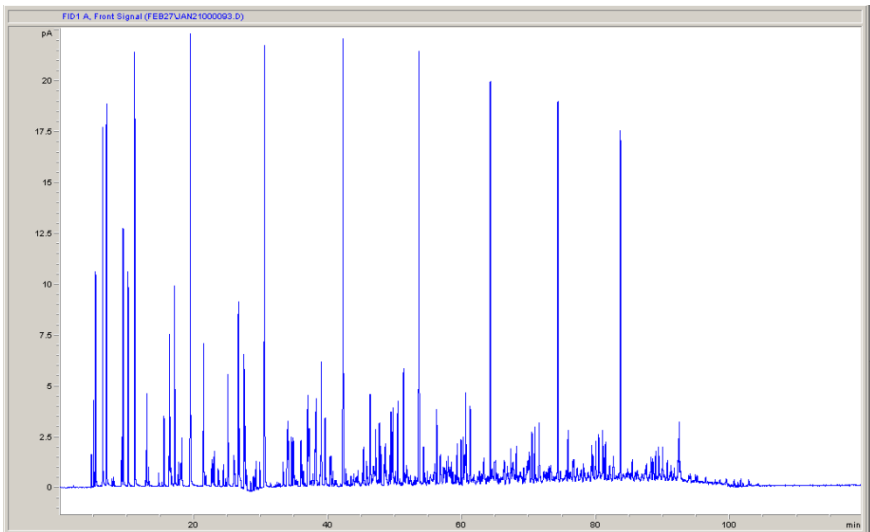Pre-column →
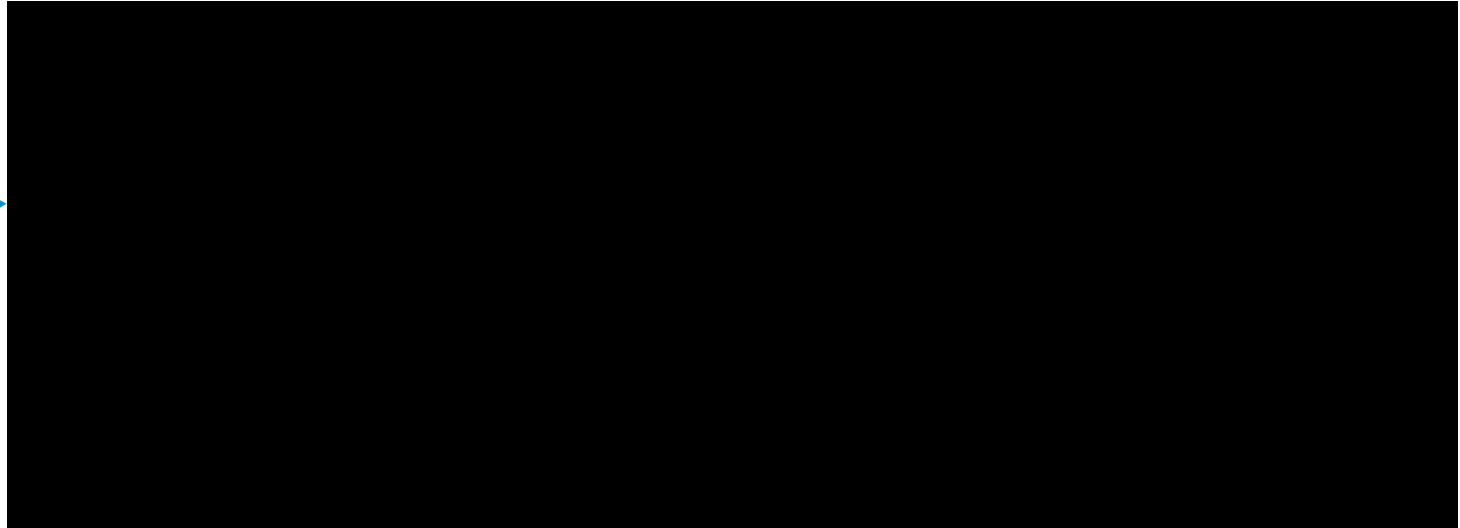
Analytical →

Agilent Technologies

Pre-column Backflush of C5-C18 Mix After C14

1 m x 0.32 mm retention gap, 100 m x 0.25 mm x 0.50 um DB-PETRO
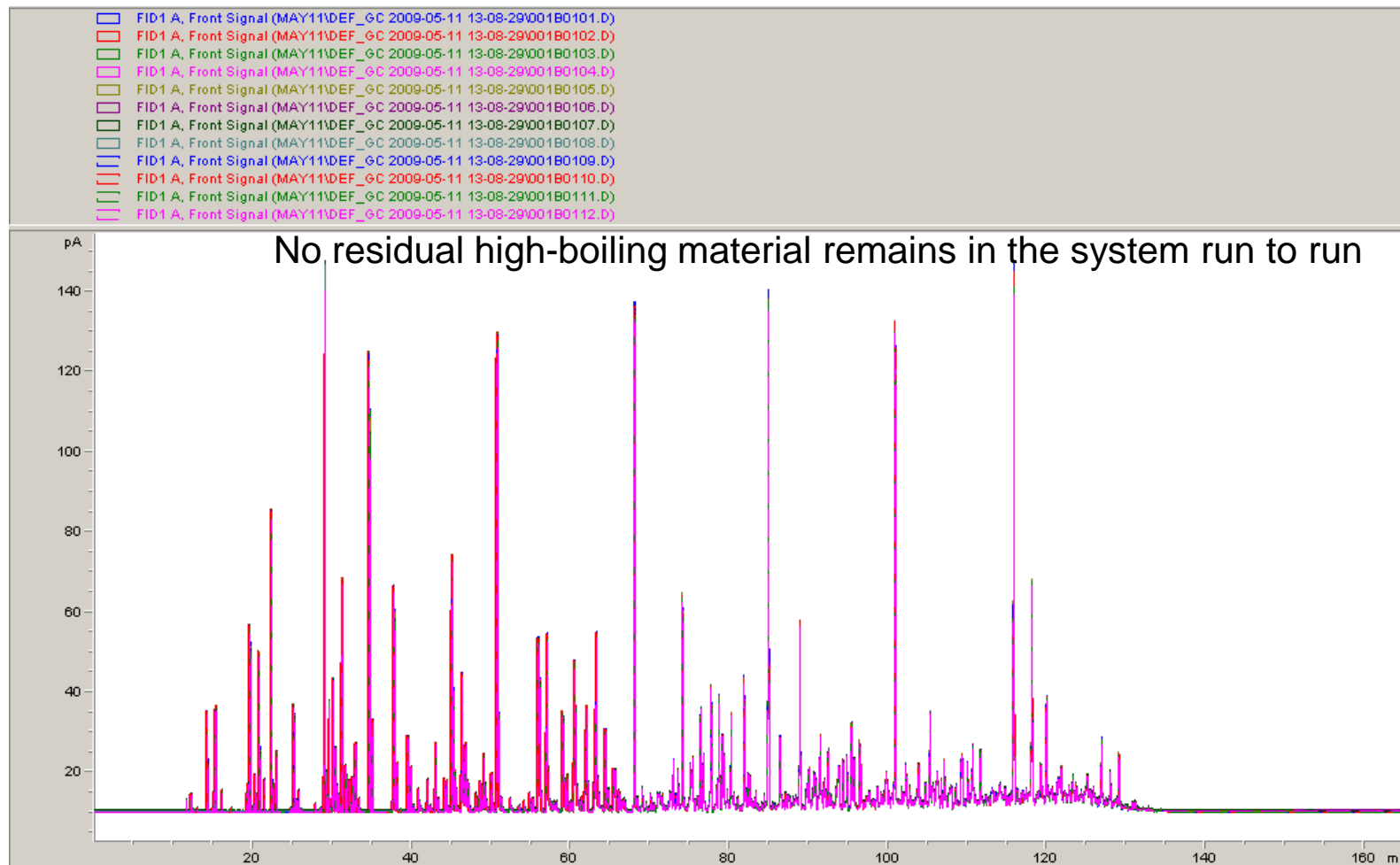
Agilent Technologies
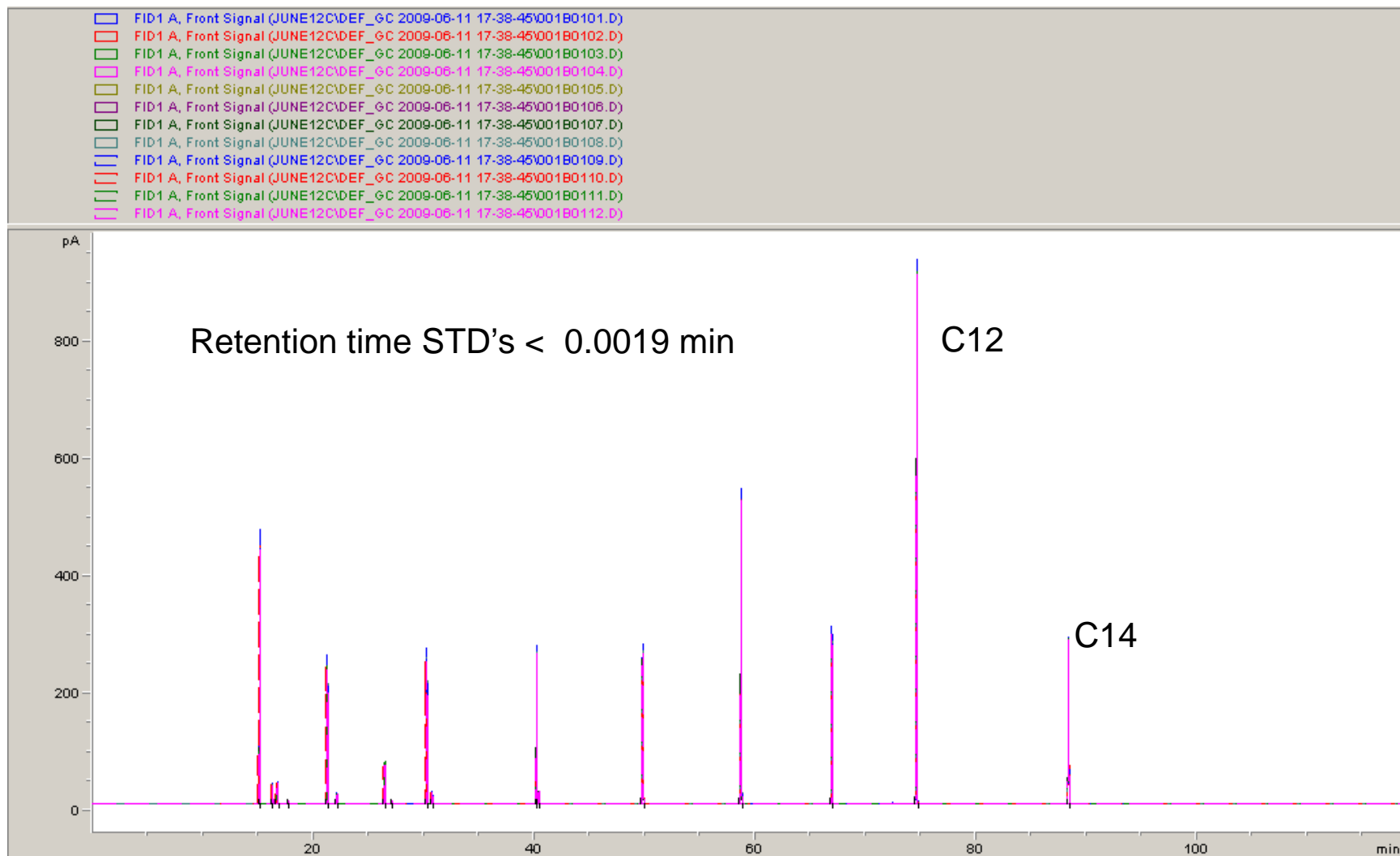
Four Crudes From Different Regions: Backflush after C12

Pre-column: 1.5 m x 0.32 mm deactivated RG, Analytical column: 100 m x 0.25 mm x 0.50u DB-PETRO

Agilent Technologies

12 runs of Crude Oil Overlay: Pre-column Backflush After C12

2 m x 0.32 mm RG

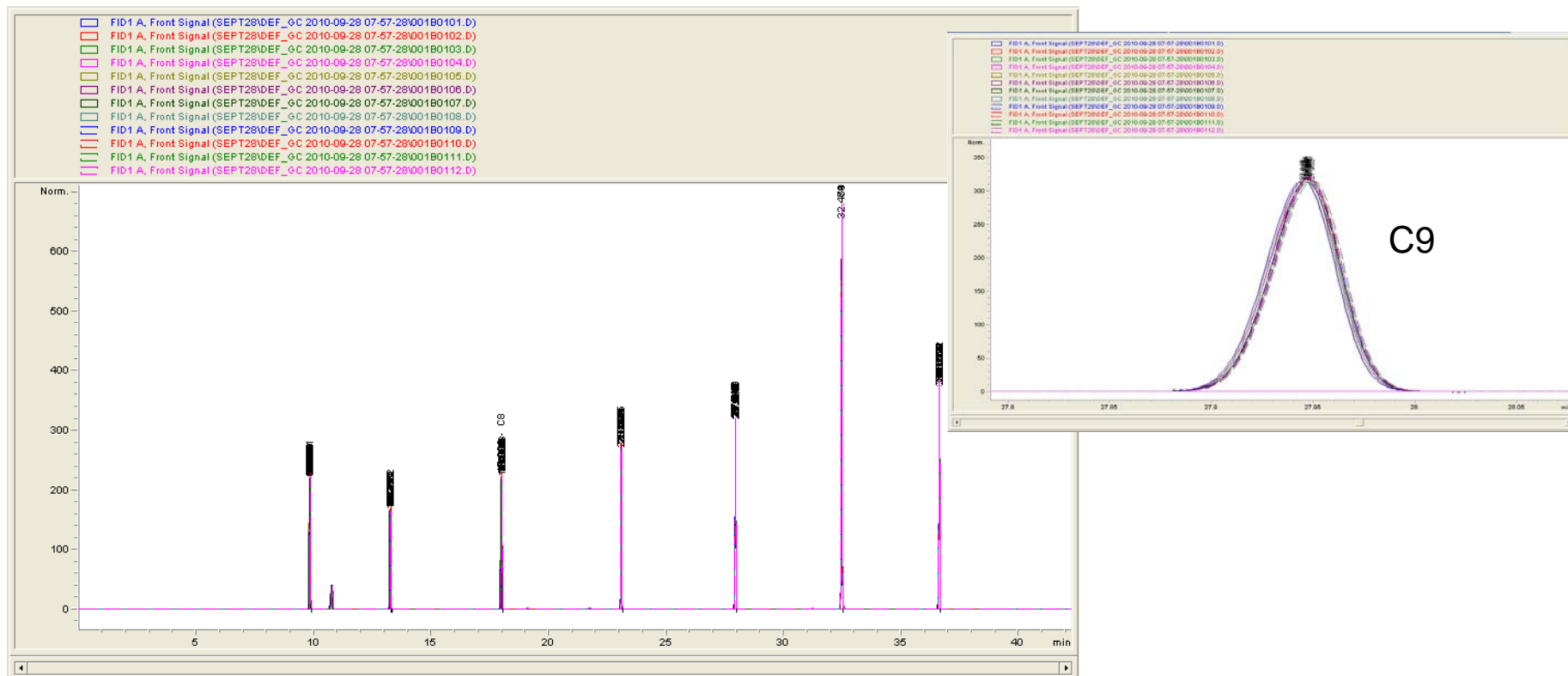No residual high-boiling material remains in the system run to run

Agilent Technologies

Backflush with Coated Pre-columns

- Pre-columns with thin coating (i.e. 0.10 um films) can be used

- Provides finer control of compounds that are backflushed

- Backflush times will be much longer typically

- Backflush of heavy compounds remaining on the pre-column will take longer

- Better inertness

Agilent Technologies

Backflush of C5-C40 Mix After C11

Overlay of 12 runs, 2 m x 0.32 mm x 0.10 um pre-column

Agilent Technologies

Gulf Coast Conference, 2010

Overlay of Souide Crude Oil

C10 Retention time STDEV = 0.0010, % STDEV = 0.315
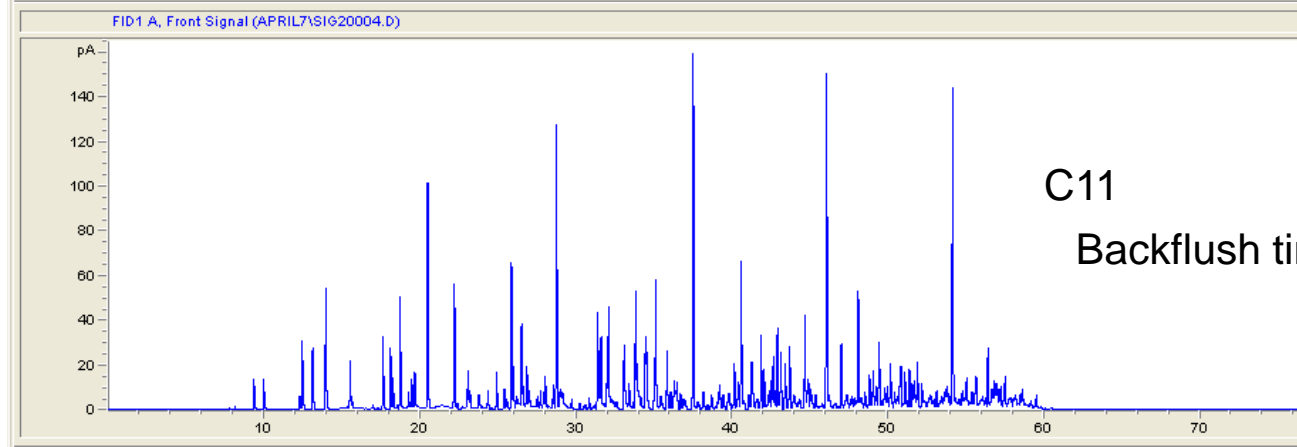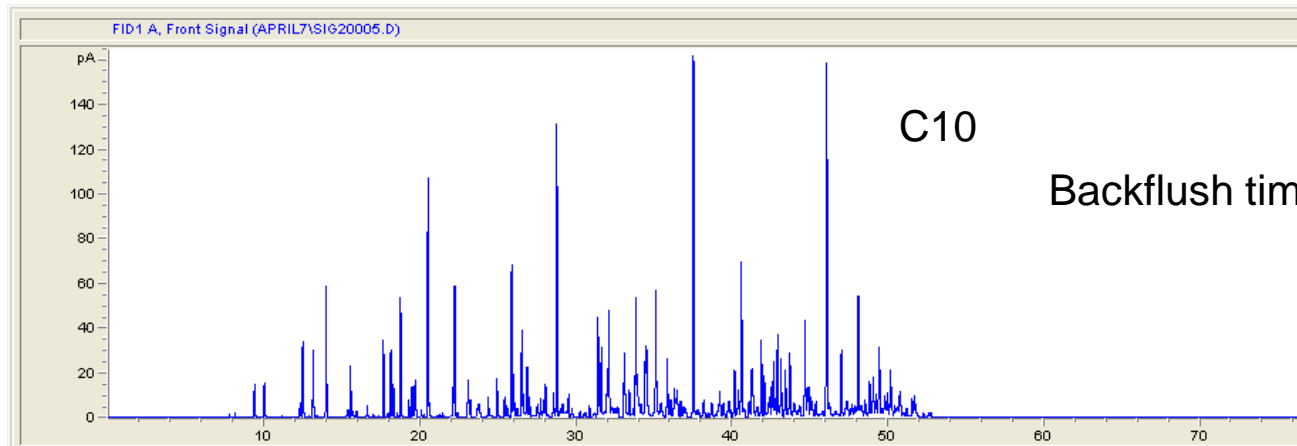
Agilent Technologies

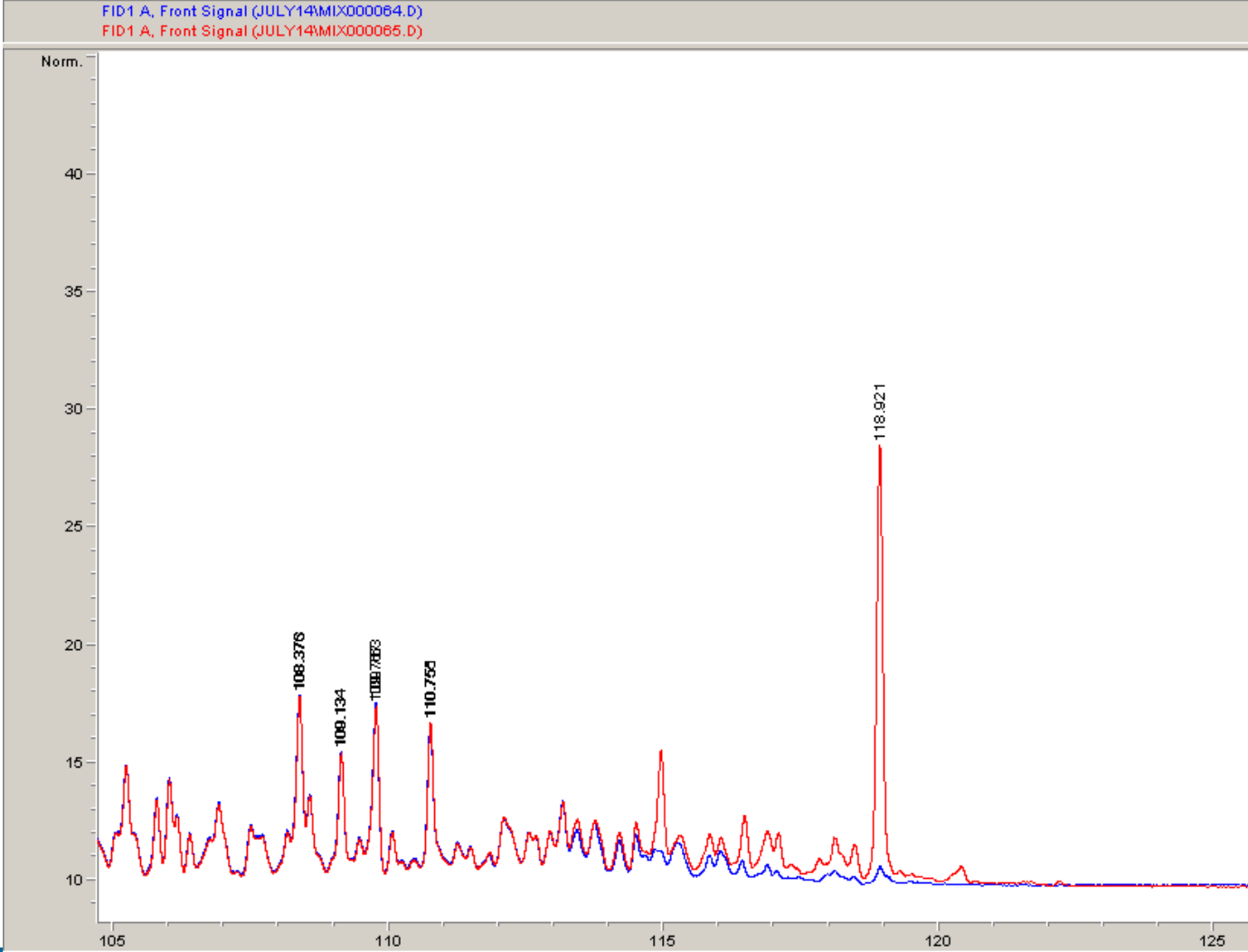# Crude Oil Backflush with Coated 2 m x 0.32 mm x 0.10 um DB-1 Pre-column

Conditions: Pre-column flow 1.6 ml/min, Analytical column flow 2.0 ml/min

MMI: 250 C(0.5 min) to 425 C @ 200 C/min
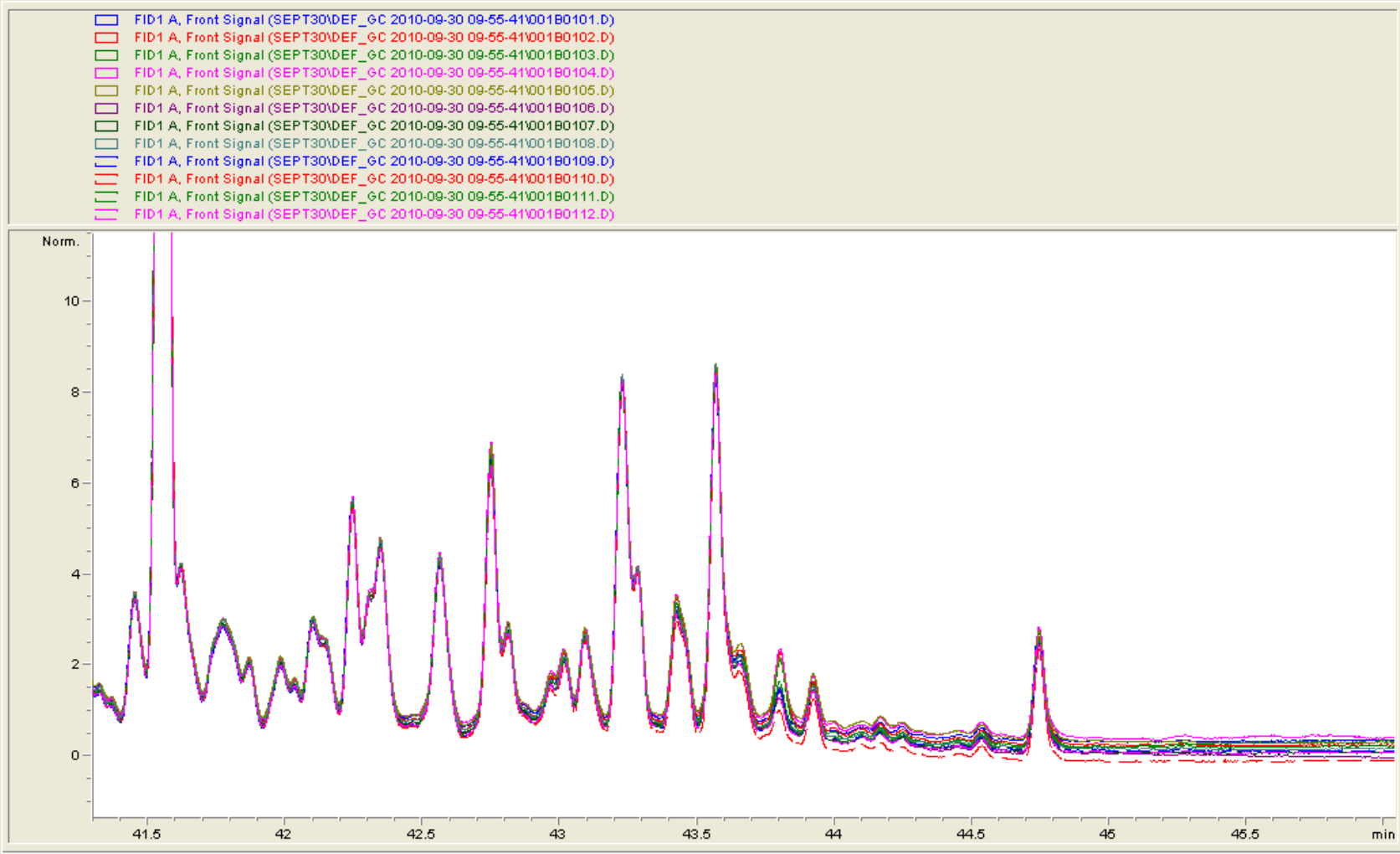Oven Program: 35 C (4 min) to 200 C (1 min) @ 2.0 C/min

C10

Backflush time: 4 min

C11

Backflush time: 8 min

Agilent Technologies

2 m x 0.32 mm x 0.10 um Pre-column: Blue Backflush at 14 min, Red – Backflush at 16 min

Agilent Technologies

Zoom on C11 Plus Hydrocarbons

Stable baseline shows that column is clean after each run

Agilent Technologies
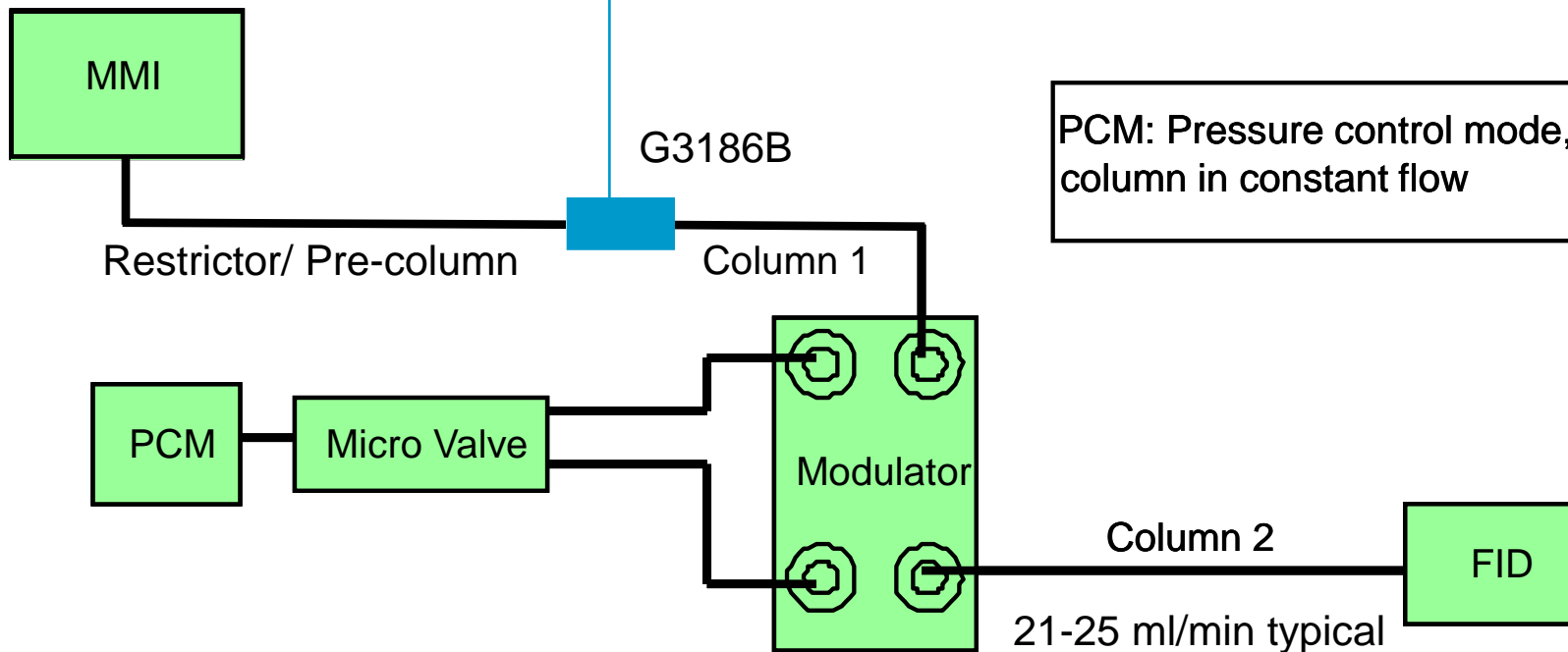
Combining Pre-column Backflush with GCxGC

• Investigate possibility of analyzing heavy crudes with comprehensive gas chromatography

• Apply chemometrics to identify source or contamination

• Process 50 Hz raw data files

• Analyze four different crudes

• Column set

  • First Dimension: 30 m x 0.25 mm x 0.10 um DB-5HT
  • Second Dimension : 5 m x 0.25 mm x 0.15 um DB-17HT

Agilent Technologies

Flow Modulator Diagram: Backflush

MMI: ramped flow,
negative ramp at backflush time

AUX

Aux: Controls Column 1 in
constant flow

MMI

G3186B

PCM: Pressure control mode,
column in constant flow

Restrictor/ Pre-column

Column 1

PCM

Micro Valve

Modulator

Column 2

FID

21-25 ml/min typical

Agilent Technologies

RT Stability and Effect on Modulated Area: C13

Analysis of modulated C13

Single pulse

Gulf Coast Conference, 2010

Agilent Technologies
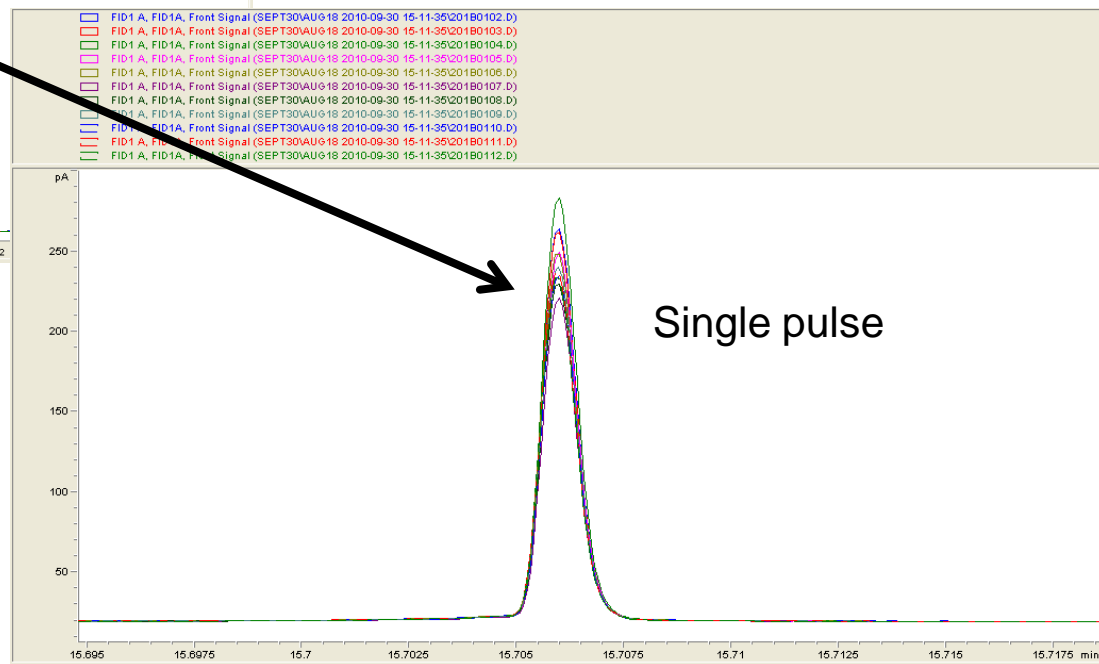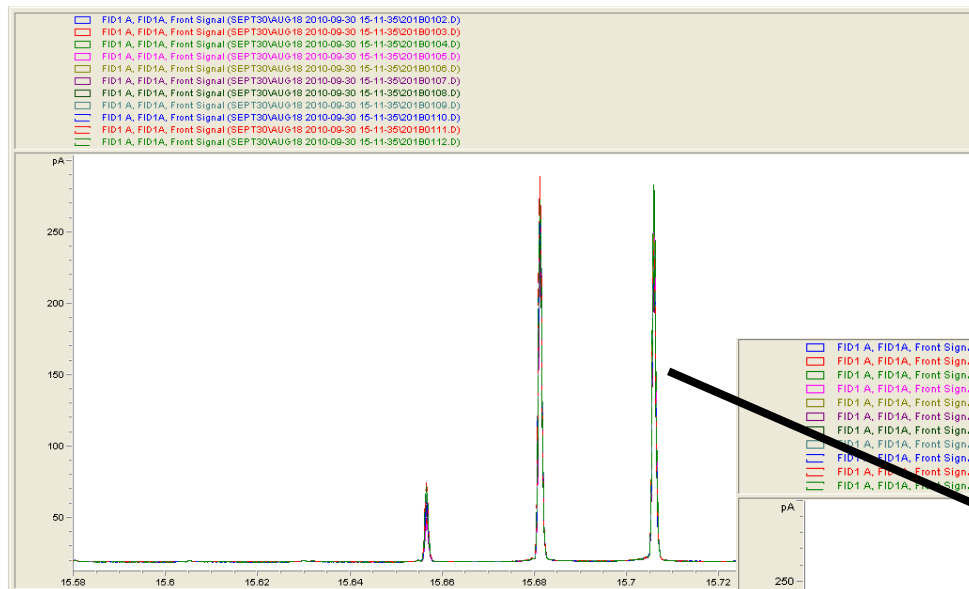
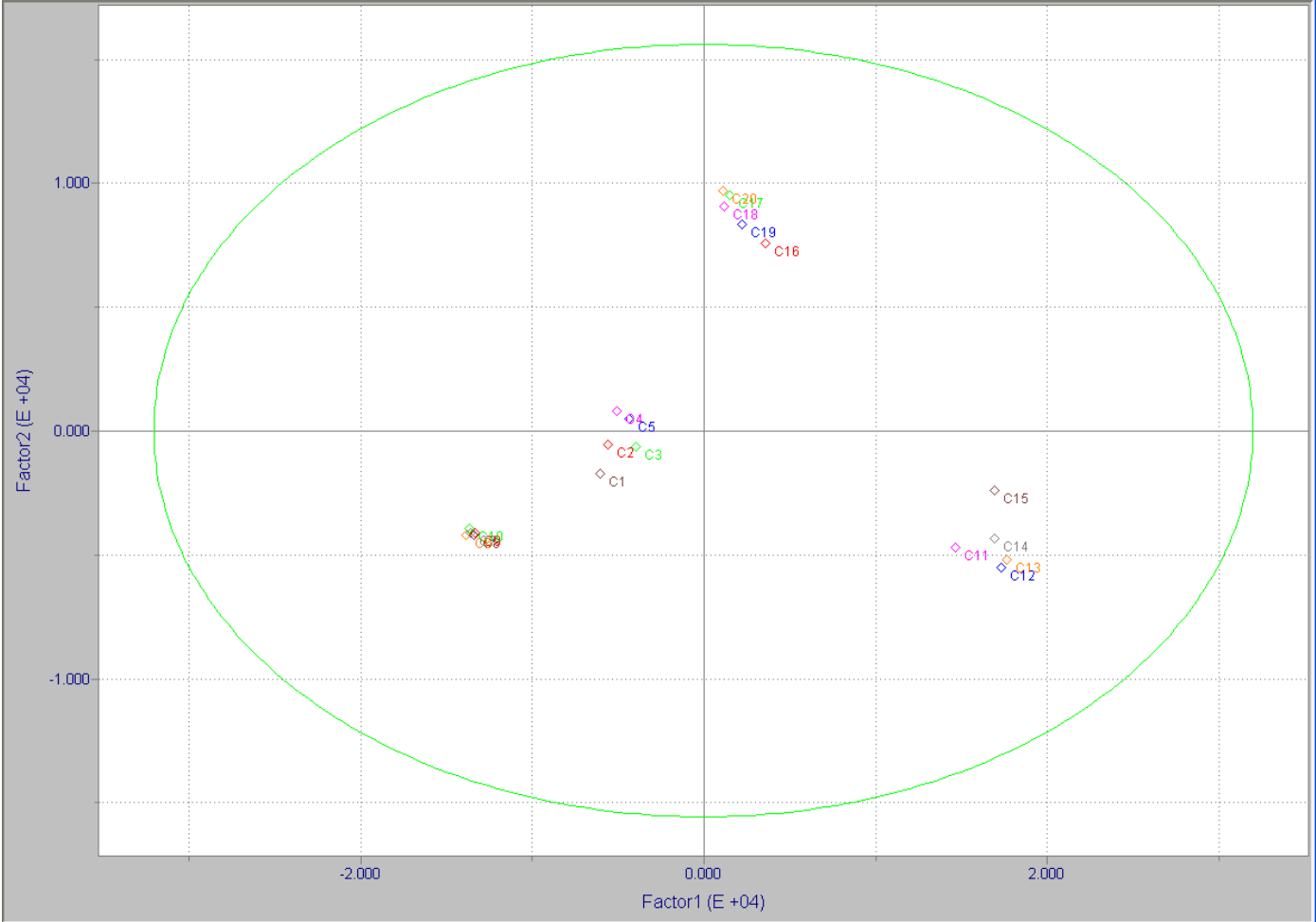# Crude Oil GCxGC: Pre- column Backflush
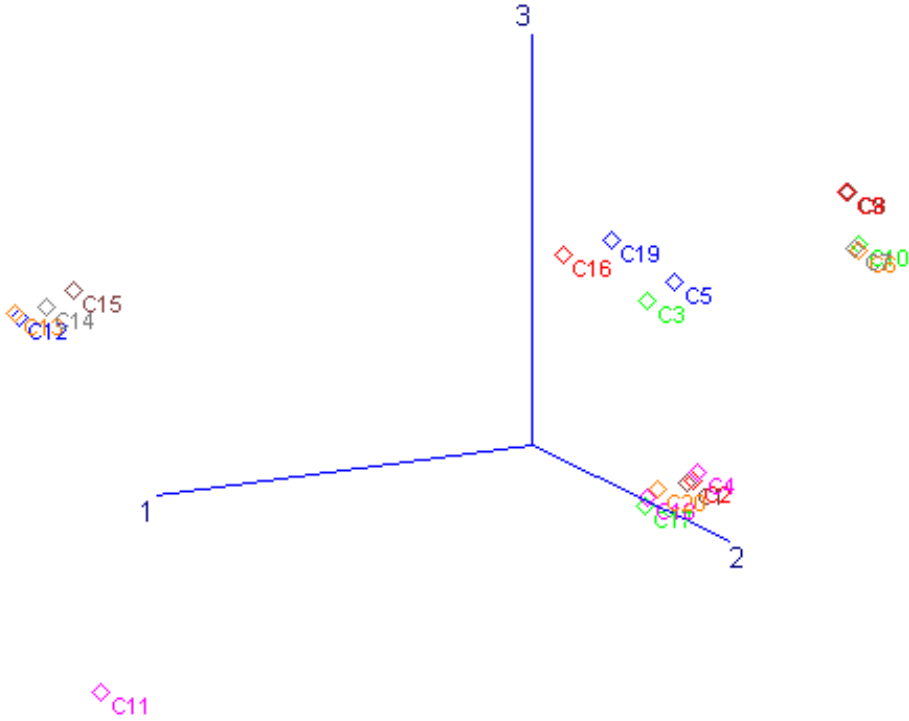
BF at 30 min, Oven programmed to 390 C
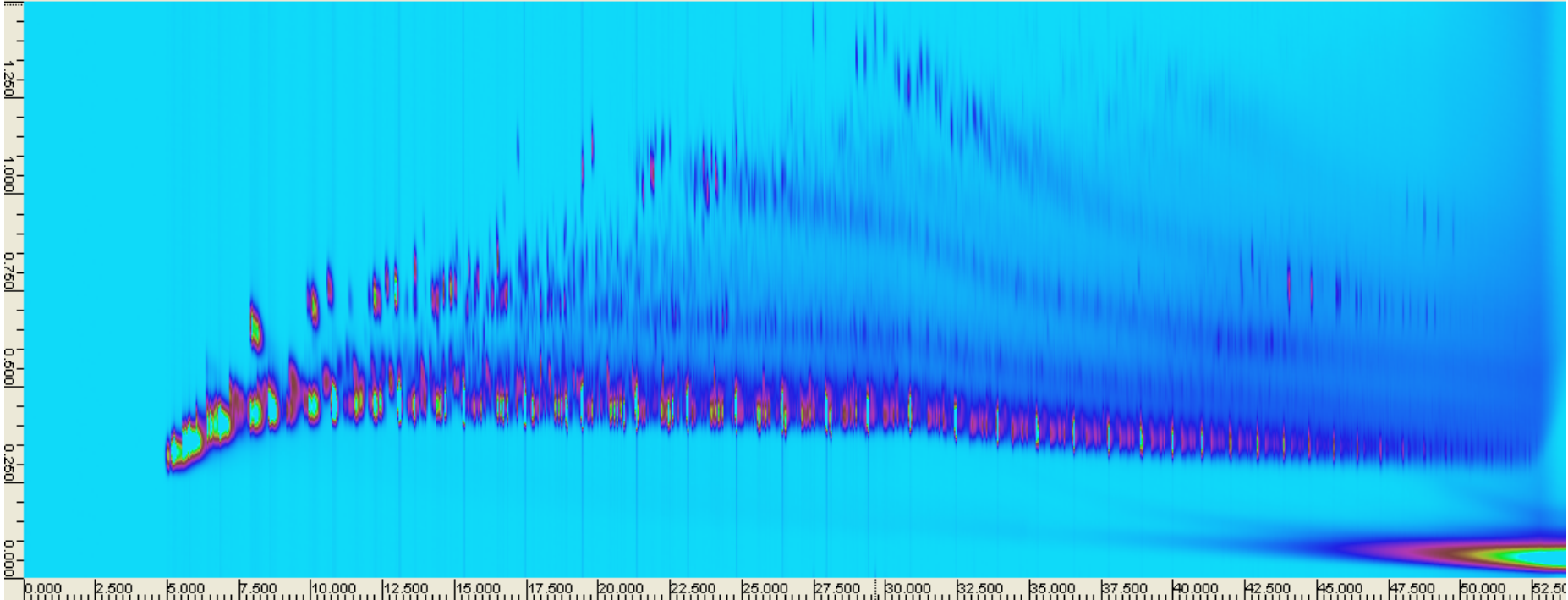
Principal Component Analysis: 2D view

Four crudes

Agilent Technologies

Principal Component Analysis: 3D view

Summary

• The CFT purged union offers a high performance alternative to traditional valved pre-column backflush systems

• Relies on precise EPC midpoint pressure control

• Backflush is concurrent while analytical column runs at constant flow

• Excellent thermal control since all parts are in the oven

• Heavy petroleum including crude oils can be routinely analyzed with complete protection of the high resolution capillary column

• The specific carbon number where backflush beginning can be easily controlled and fine tuned

• Pre-column backflush is compatible with GCxGC

• Coated pre-columns can be used for fine tuning

• Chemometrics can be applied to identify oils

Agilent Technologies

Acknowledgement

Pirouette® Chemometric Software provided by Infometrix, Inc.

Agilent Technologies

Capillary Flow Technology (CFT) Based Pre-fractionator: Pre-column Backflush System

• In oven CFT device is used in a relatively simple hardware configuration

• CFT "purged union"

• The multimode inlet is used to assist with backflushing heavy material from the inlet. Inlet is programmed to 425 C after backflush is started

• Run time backflush is easily programmed from the ChemStation

• Analytical column flow controlled from an Aux module

❑ Key Application: Front-end detailed analysis (DHA) of crude oils

Flow Calculator Parameters

100M Column

2.0M RG

1.5M RG

Agilent Technologies

2 m x 0.32 mm x 0.10 um Pre-column: 12 Run Overlay of Crude Oil

Gulf Coast Conference, 2010

Agilent Technologies