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CHEMICAL & ENGINEERING NEWS

Agilent Technologies

Reformulated Fuels and Refinery Gas Analysis using a Large Valve Oven

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Large Valve Oven Analyzers for Refinery Gas Analysis

Fast and High Capacity Analysis including O_2 and H_2S

7890B Large Valve Oven (LVO)

Isothermal Zone for Valves and Columns

- **Temperature control:**
  - Independent control of LVO and GC oven zones
- **Temperature Limit:**
  - Max 330˚C (valve and column dependent)
- **Valve configurations:**
  - Accommodates 4/6/10/14 port valves including Hastelloy valves
- **Column Compatibility:**
  - Large Mandrel: Accommodates 15 feet of 1/8 inch OD metal column
  - Small Mandrel: Accommodates 7 Ft of 1/8” OD metal column

Large Valve Oven
Features/Benefits

- 6 position isothermal valve oven for actuated valves, microgasifiers, needle valves, and columns (including 1/8 in packed columns) with access to valves connections without removing actuators
- Uses only one 7890B heated zone
- Current multi-valve configurations may quickly consume 6 heated zones, LVO uses 5 leaving 1 for future applications
- Dual thermal zones allow for thermal isolation between column oven and LVO
- Ability to configure analyses that require multiple thermal zones. Can run isothermal temperatures in the LVO while temperature ramping the GC oven

7890B with Large Valve Oven

Importance of Refinery Gases and RGA
Process Characterization Quickly and Reliably

- Produced from FCC operations and other refinery processes
- Typically contains saturated and unsaturated HCs (C_1-C_5)
  - H_2, O_2, N_2, CO, and CO_2.
  - C_1 - C_6 or higher hydrocarbons
  - Sulfur contaminants, e.g., H_2S
- Challenging analysis due to variable source and composition
- Engineers require quick accurate analysis to monitor process
  - Typically complex mixtures from a broad range of samples

Importance of Refinery Gas Analysis
Analytes of Interest

Analyzers typically measure:

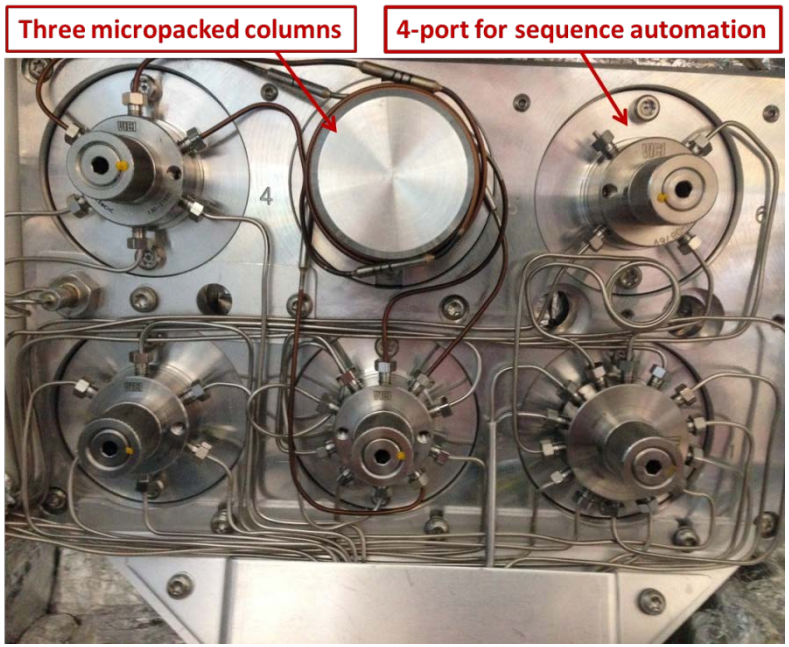
- Permanent gases
- Hydrocarbon content
  (C_1-C_5 with C_{6+} as backflush)
- Extended hydrocarbon analysis
- Sulfur containing hydrocarbons

Two Analyzer Configurations

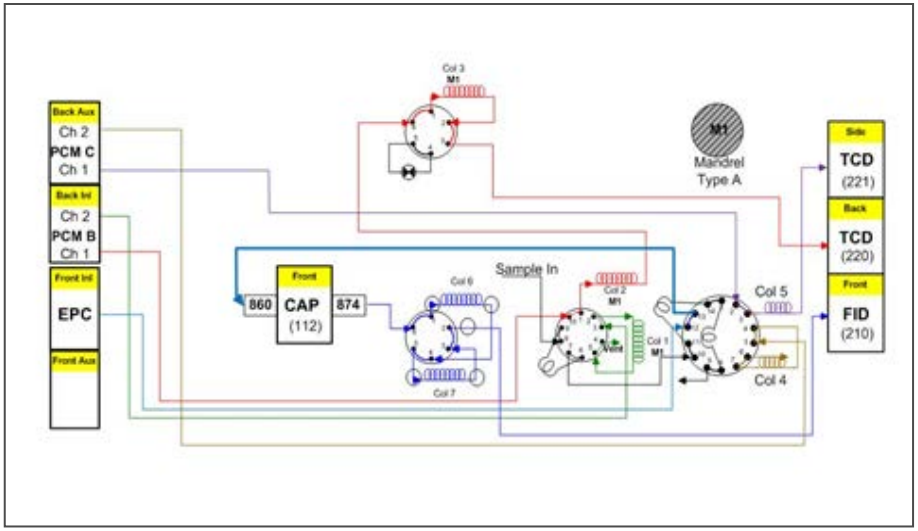
- 1/8 inch Packed Columns
- 1/16 inch Micropacked Columns

LVO Fast RGA with Micropacked Columns

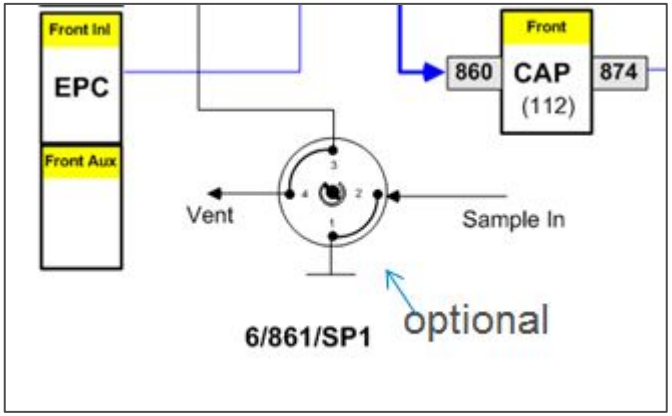
GC/FID/TCD/TCD



Micropacked LVO Plumbing



Micropack System Flow Diagram



4-port for sequence automation

UltiMetal tubing used for sample loops, Columns, and tubing on the Permanent Gas channel

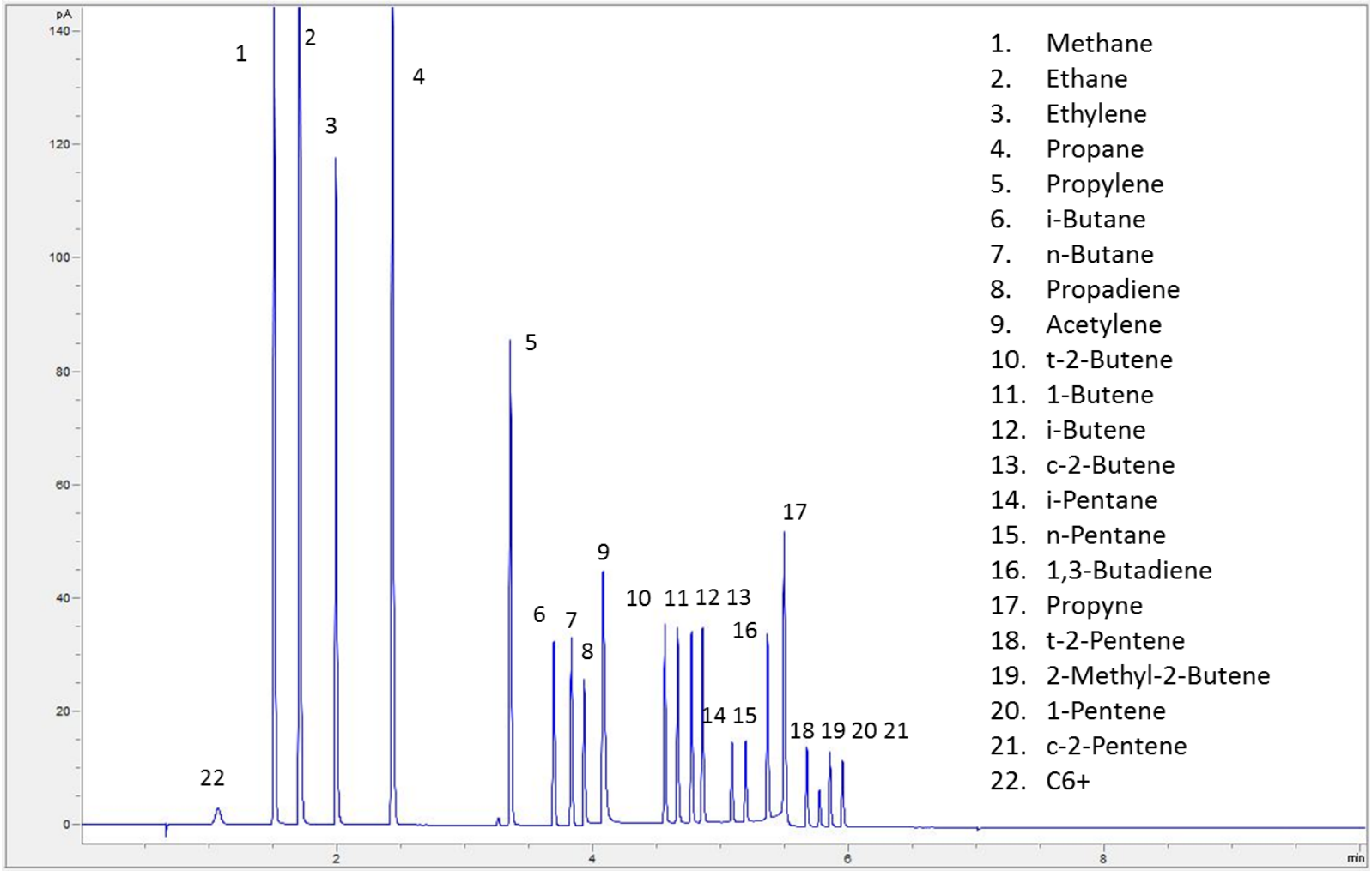
Fast RGA with Micropacked Columns – Helium Carrier

Selected Method Parameters

Split/Splitless inlet:	120 ºC, 100:1 split
FID (front):	250 ºC
TCD (rear):	260 ºC
	He carrier
	Ref. 30 mL/min
	Makeup 2 mL/min
TCD (side):	250 ºC
	N2 carrier
	Ref. 45 mL/min
	Makeup 2 ml/min, neg. polarity
Main Oven Program:	60 ºC (1 min) to 80 ºC @ 20 ºC/min
	to 190 ºC @ 30 ºC/min
Large Valve Oven:	Isothermal, 65 ºC and 70 ºC

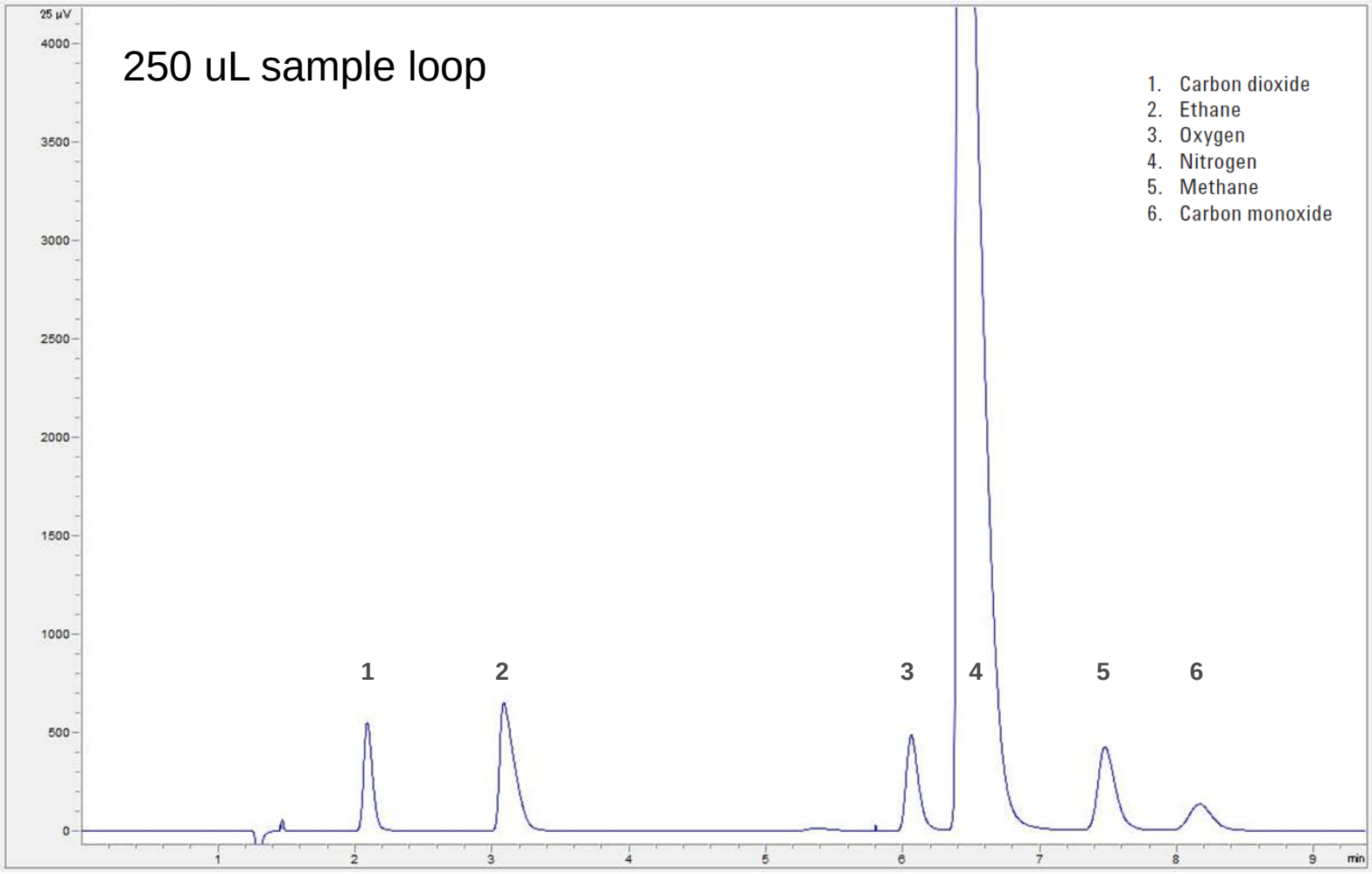
RGA Plot Column Channel

Analytical Performance – Hydrocarbon Channel (FID)
Same for Packed and Micropacked Systems



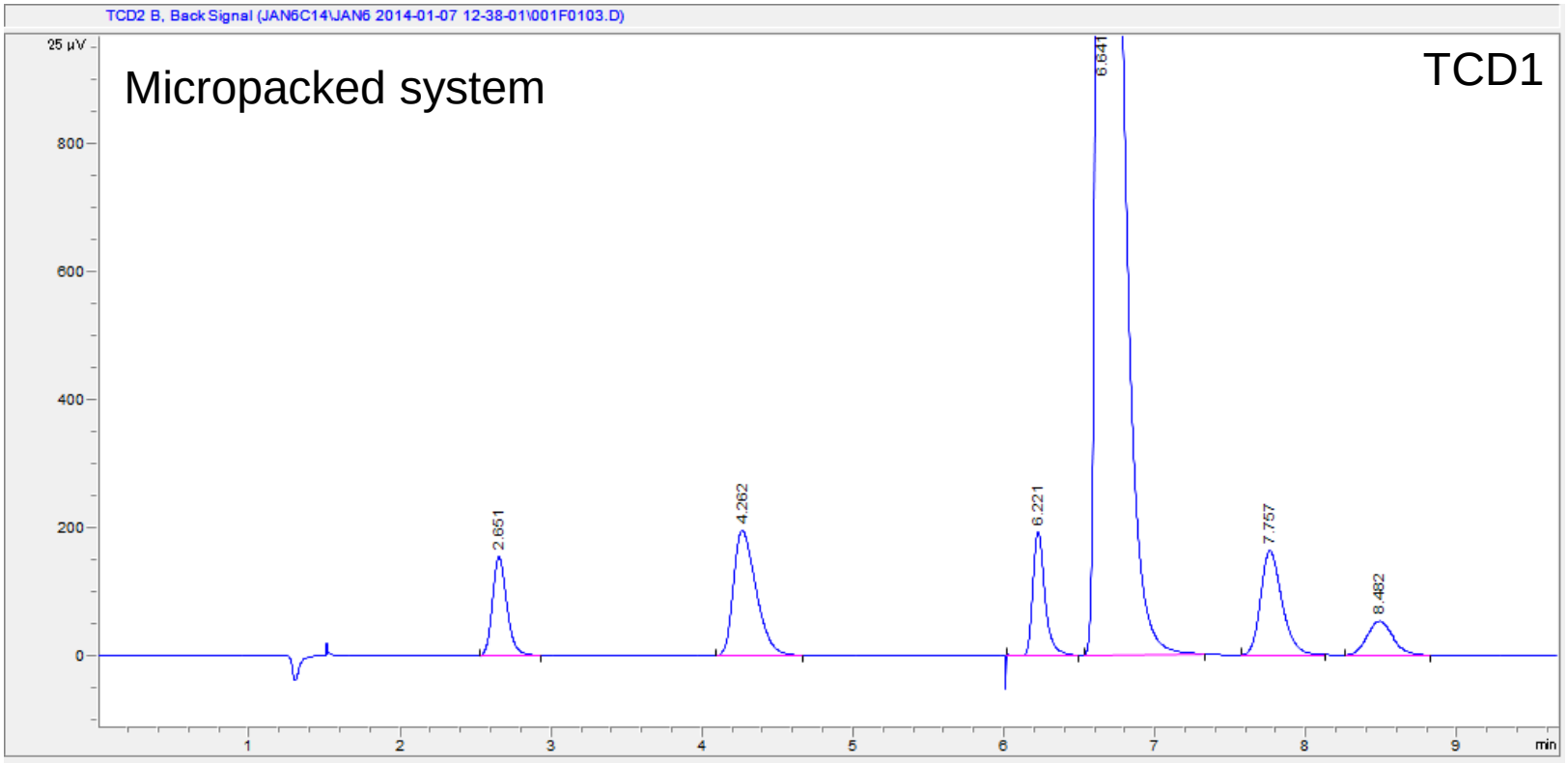
Fast RGA with Micropacked Columns

Analytical Performance – Permanent Gas Channel (TCD), LVO at 70 °C



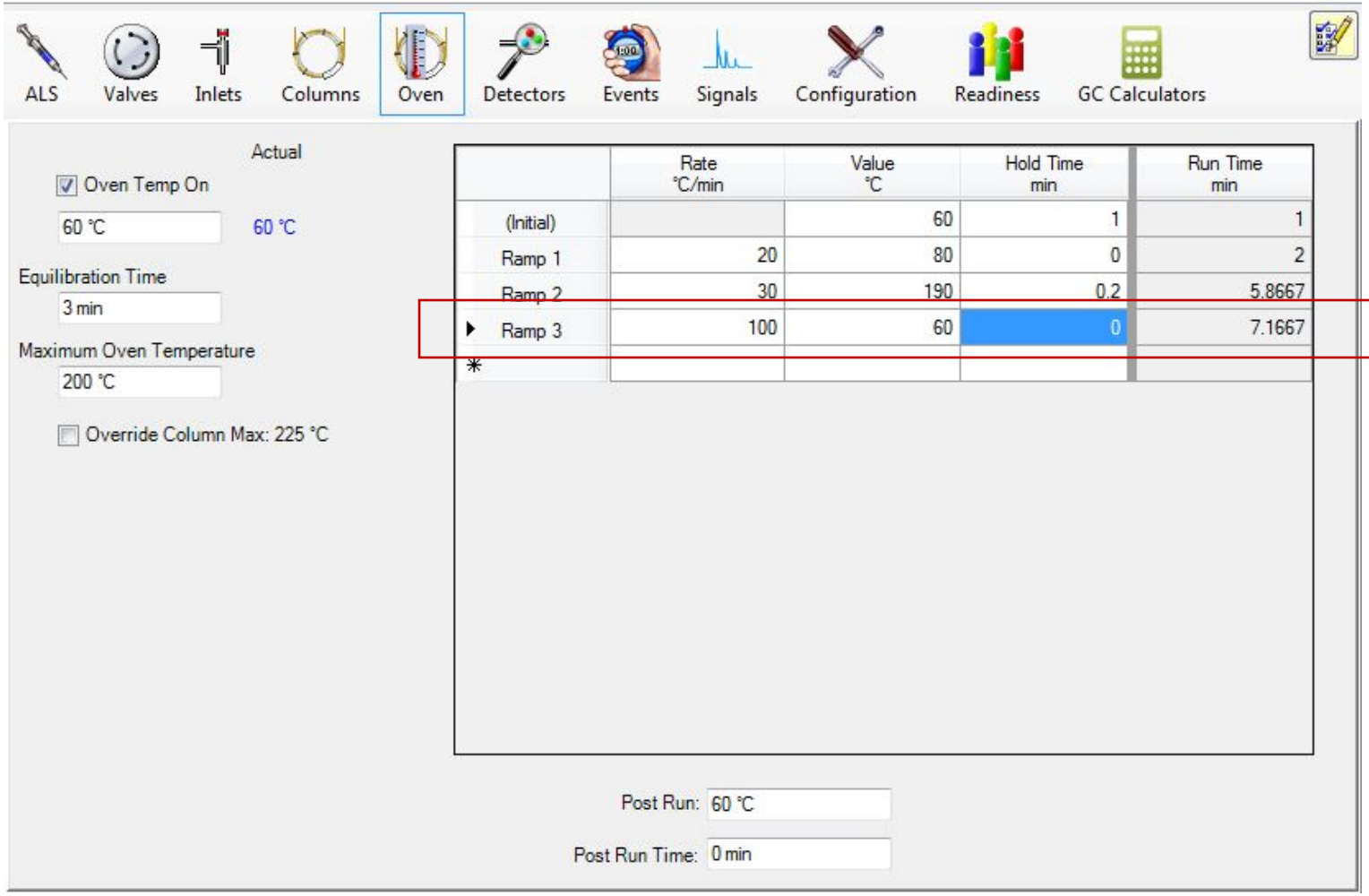
100 uL Sample Loop on Permanent Gas Channel

More symmetric peak shapes

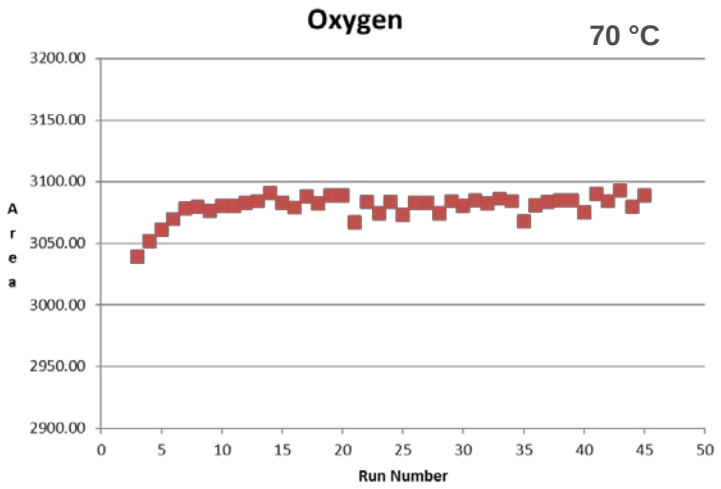


Cool Down Ramp Used During Run for Main Oven

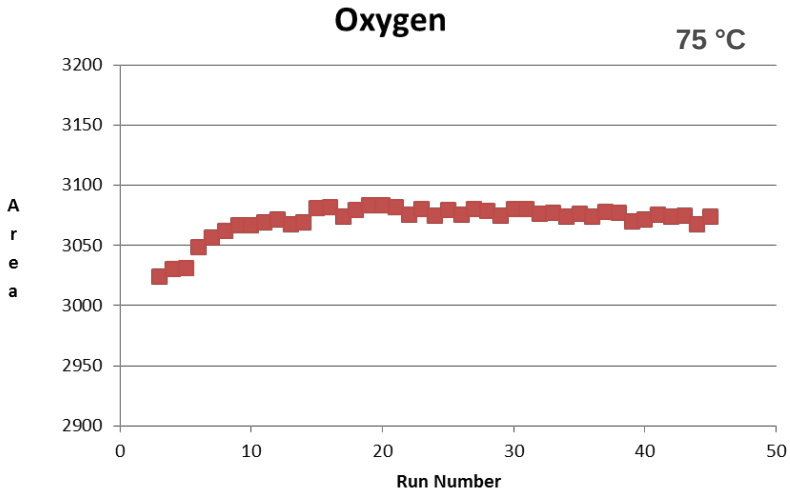
Will shorten overall cycle time



Fast RGA with Micropacked Columns
Analytical Performance – Oxygen Stability



Stability of Oxygen – Isothermal Oven at 70 °C



Stability of Oxygen – Isothermal Oven at 75 °C

Fast RGA with Micropacked Columns – Helium Carrier

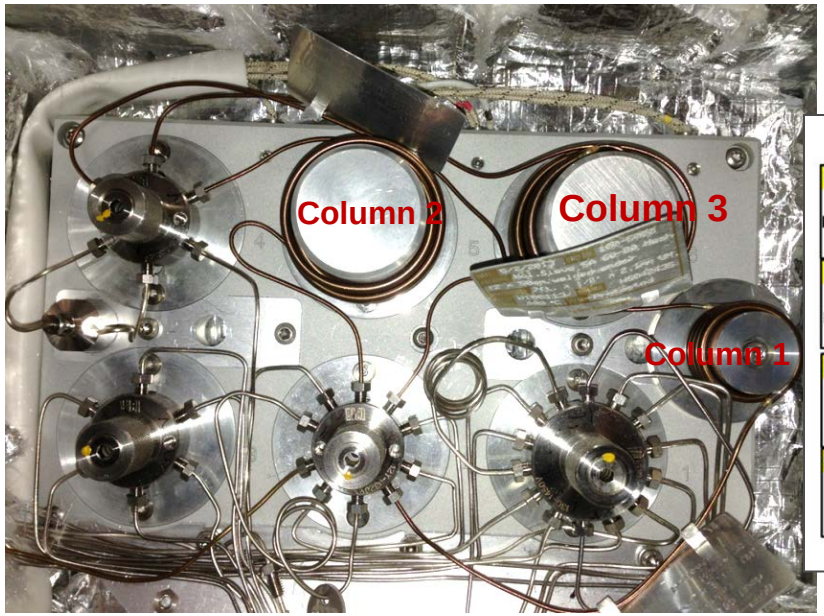
Analytical Performance, % RSD's

Compound	Concentration	RT	Area
C6+	0.06	0.027	0.28
Methane (FID)	4.99	0.006	0.14
Ethane (FID)	4	0.011	0.15
n-butane	0.3	0.045	0.15
t-2-butane	0.3	0.059	0.17
1-butene	0.3	0.059	0.21
n-pentane	0.1	0.038	0.20
Hydrogen	12.1	0.036	0.15
Oxygen	2.98	0.026	0.64
Nitrogen	balance	0.022	0.18
Carbon Monoxide	1.52	0.035	0.15
Carbon Dioxide	2.01	0.086	0.15
Methane (TCD)	4.99	0.031	0.16
Ethane (TCD)	4	0.09	0.16
Hydrogen Sulfide	0.5	0.215	4.80

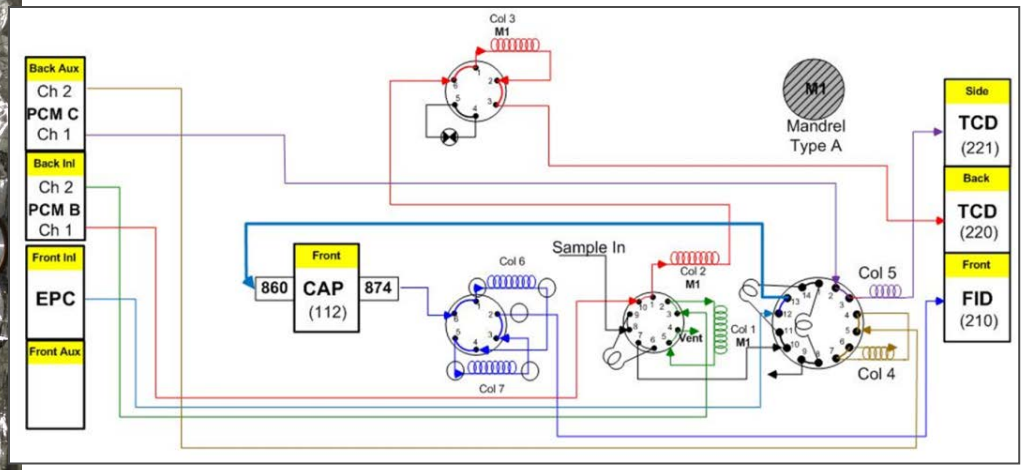
Repeatability of Select Refinery Gas Components

(% RSD's for retention times and areas with the large valve oven at 70 °C)

Refinery Gas Analysis with Packed Columns
GC/FID/TCD/TCD



Standard Column LVO Plumbing



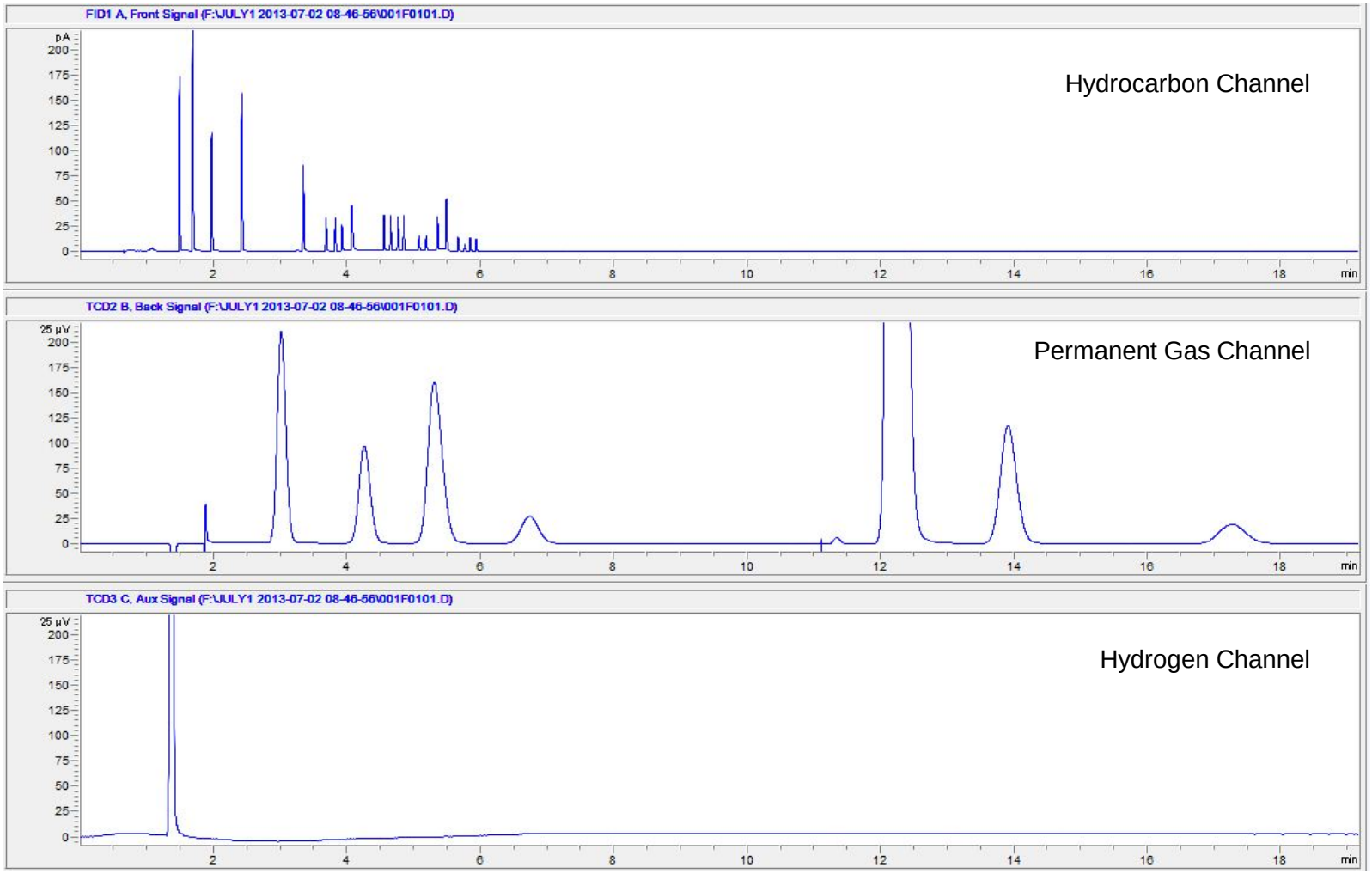
Std Column LVO Flow Diagram

Refinery Gas Analysis – Helium Carrier
Selected Method Parameters

Split/Splitless inlet:	120 ºC, 100:1 split
FID (front):	250 ºC
TCD (rear):	260 ºC
	He carrier
	Ref. 30 mL/min
	Makeup 2 mL/min
TCD (side):	250 ºC
	N2 carrier
	Ref. 45 mL/min
	Makeup 2 ml/min, neg. polarity
Main Oven Program:	60 ºC (1 min) to 80 ºC @ 20 ºC/min
	to 190 ºC @ 30 ºC/min
Large Valve Oven:	Isothermal, 65 ºC and 70 ºC

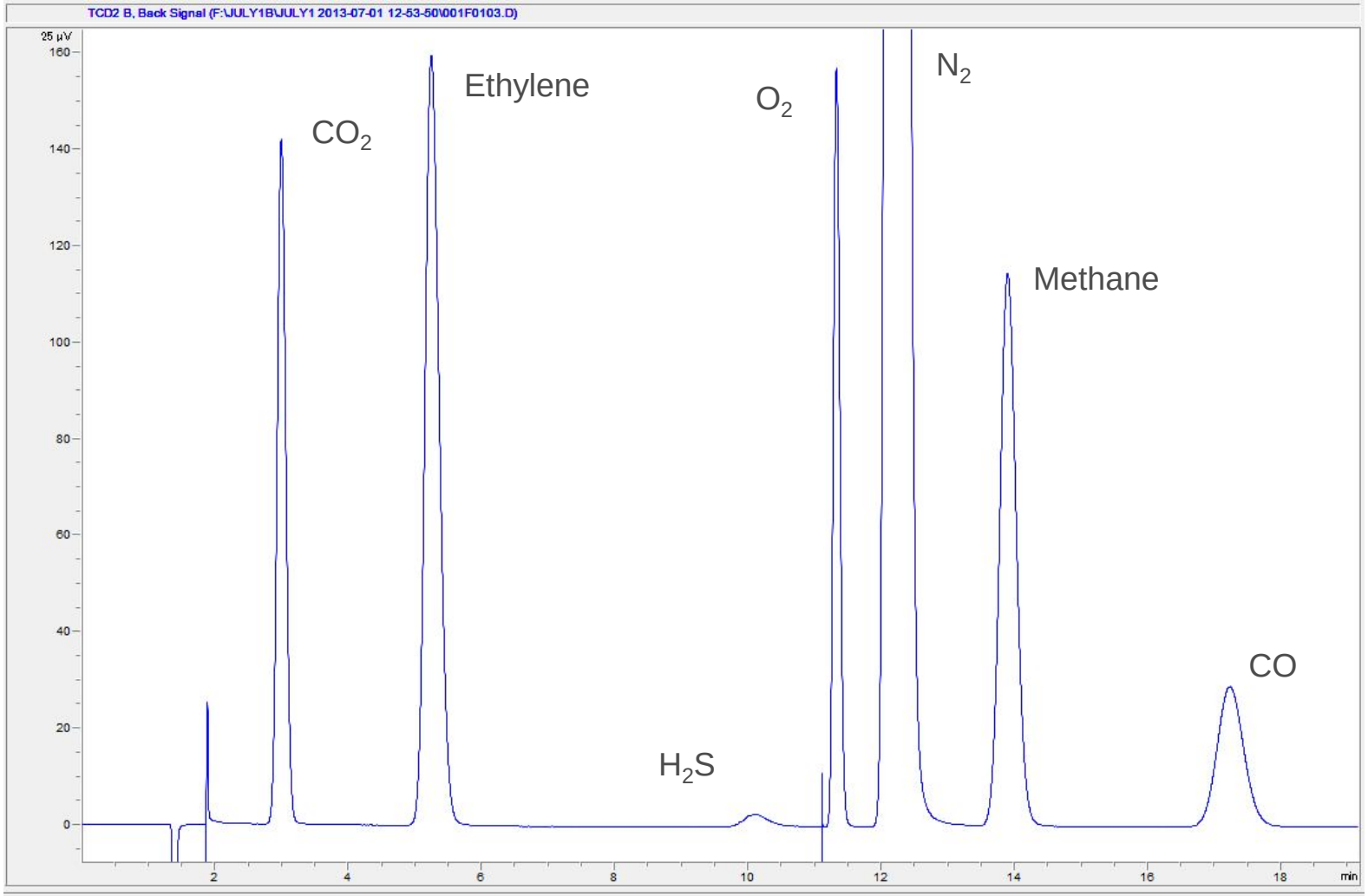
RGA with Packed Columns

Analytical Performance - LVO at 70 °C



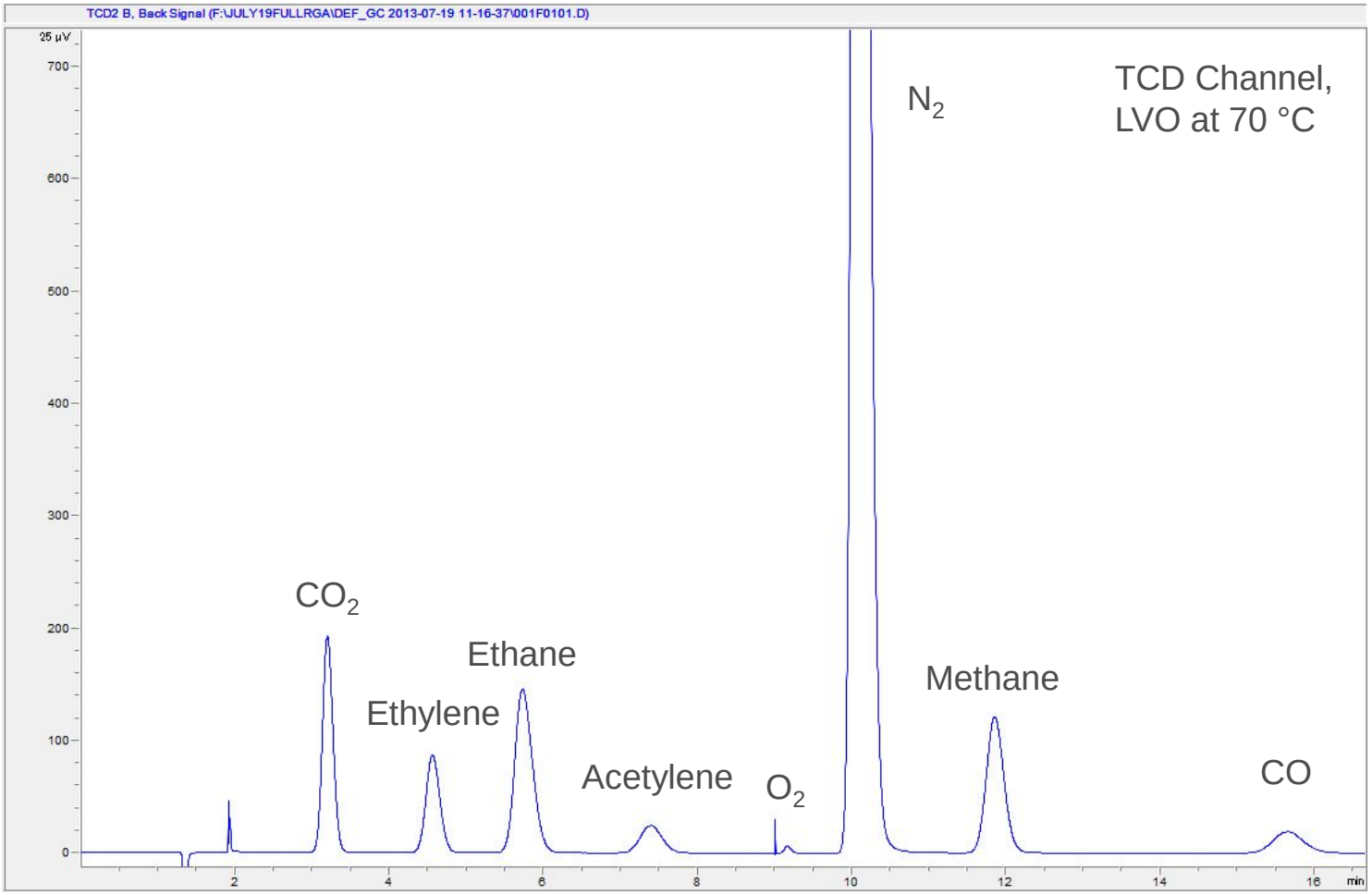
RGA with Packed Columns

Analytical Performance with H_2S – TCD Channel, LVO at 70 °C

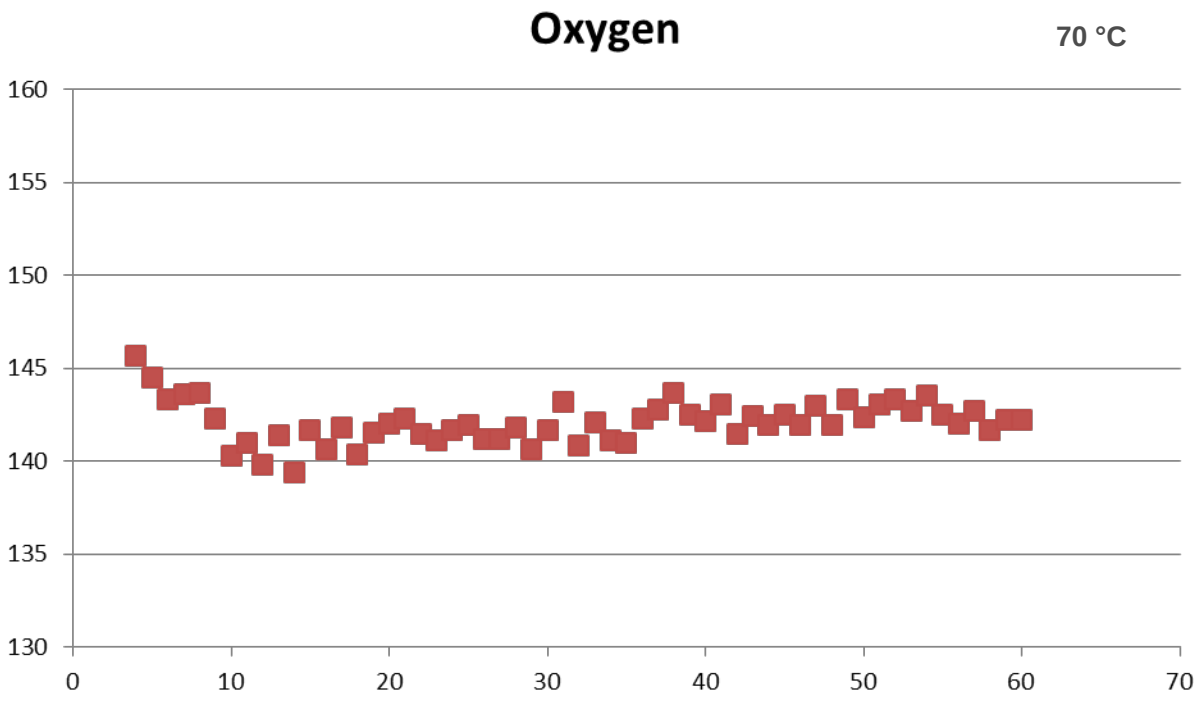


RGA with Packed Columns

Analytical Performance with RGA Checkout Sample, No H_2S



RGA with Packed Columns
Analytical Performance – Oxygen Stability



Stability of Oxygen – Isothermal Oven at 70 °C

RGA with Packed Columns– Helium Carrier
Analytical Performance

Compound	Concentration	RT 65 C	RT 70 C	Area 65 C	Area 70 C
C6+	0.06	0.026	0.022	0.35	0.31
Methane (FID)	4.99	0.009	0.011	0.19	0.12
Ethane (FID)	4	0.02	0.016	0.21	0.15
n-butane	0.3	0.103	0.038	0.23	0.16
t-2-butane	0.3	0.13	0.055	0.22	0.19
1-butene	0.3	0.13	0.056	0.34	0.26
n-pentane	0.1	0.082	0.034	0.29	0.22
Hydrogen	12.1	0.021	0.037	0.13	0.1
Oxygen	2.98	0.015	0.01	1.36	0.7
Nitrogen	balance	0.026	0.017	0.18	0.12
Carbon Monoxide	1.52	0.044	0.023	0.16	0.12
Carbon Dioxide	2.01	0.11	0.048	0.13	0.14
Methane (TCD)	4.99	0.031	0.02	0.25	0.13
Ethane (TCD)	4	0.099	0.055	0.22	0.14

Repeatability of Select Refinery Gas Components
(% RSD for retention times and areas large valve oven temp 65 and 70 °C)

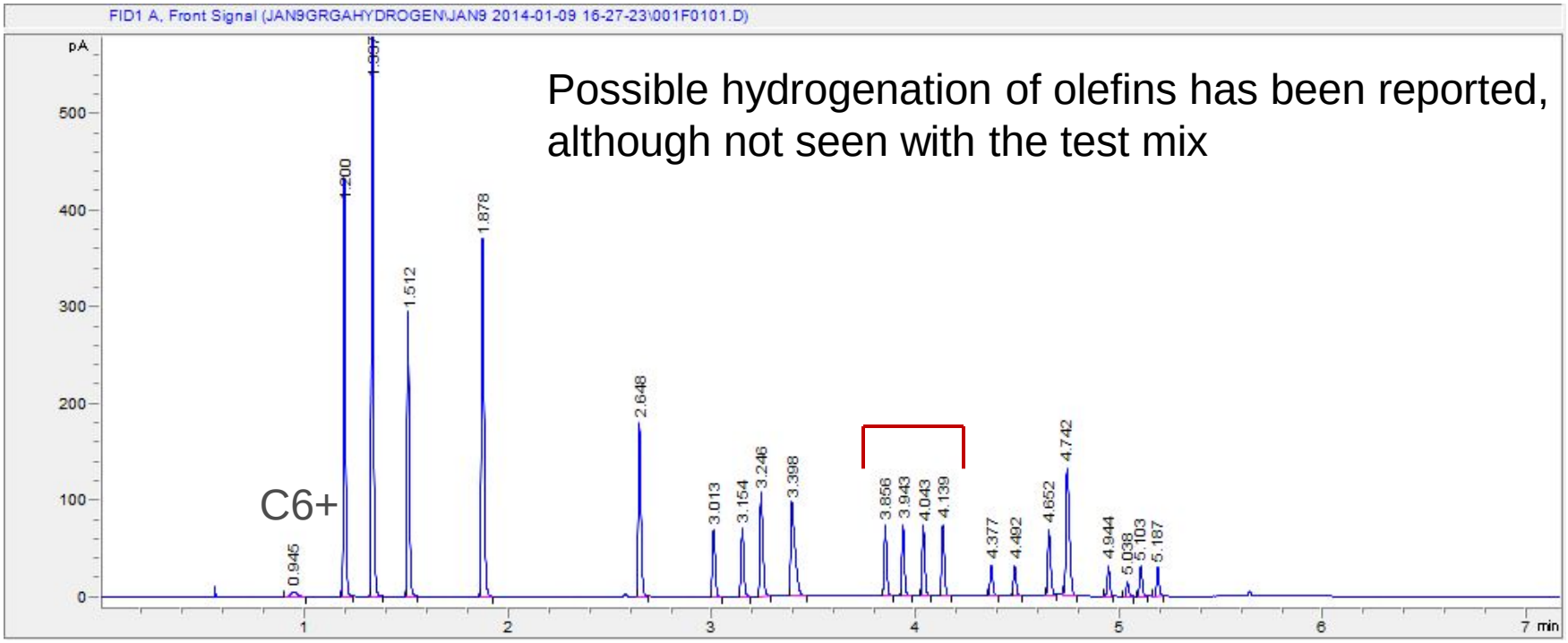
Alternate Carrier Gases for RGA

Thermal Conductivities

GAS	Thermal Conductivity	Diff. He	Diff. N2	Diff H2
Hydrogen	471	95	405	
Helium	376		310	-95
Methane	89	-287	24	-382
Oxygen	68	-308	2	-403
Nitrogen	66	-310		-405
Carbon monoxide	64	-312	-2	-407
Ethane	58	-318	-7	-413
Ethene	55	-321	-11	-416
Propane	48	-328	-17	-423
Carbon Dioxide	44	-332	-22	-427

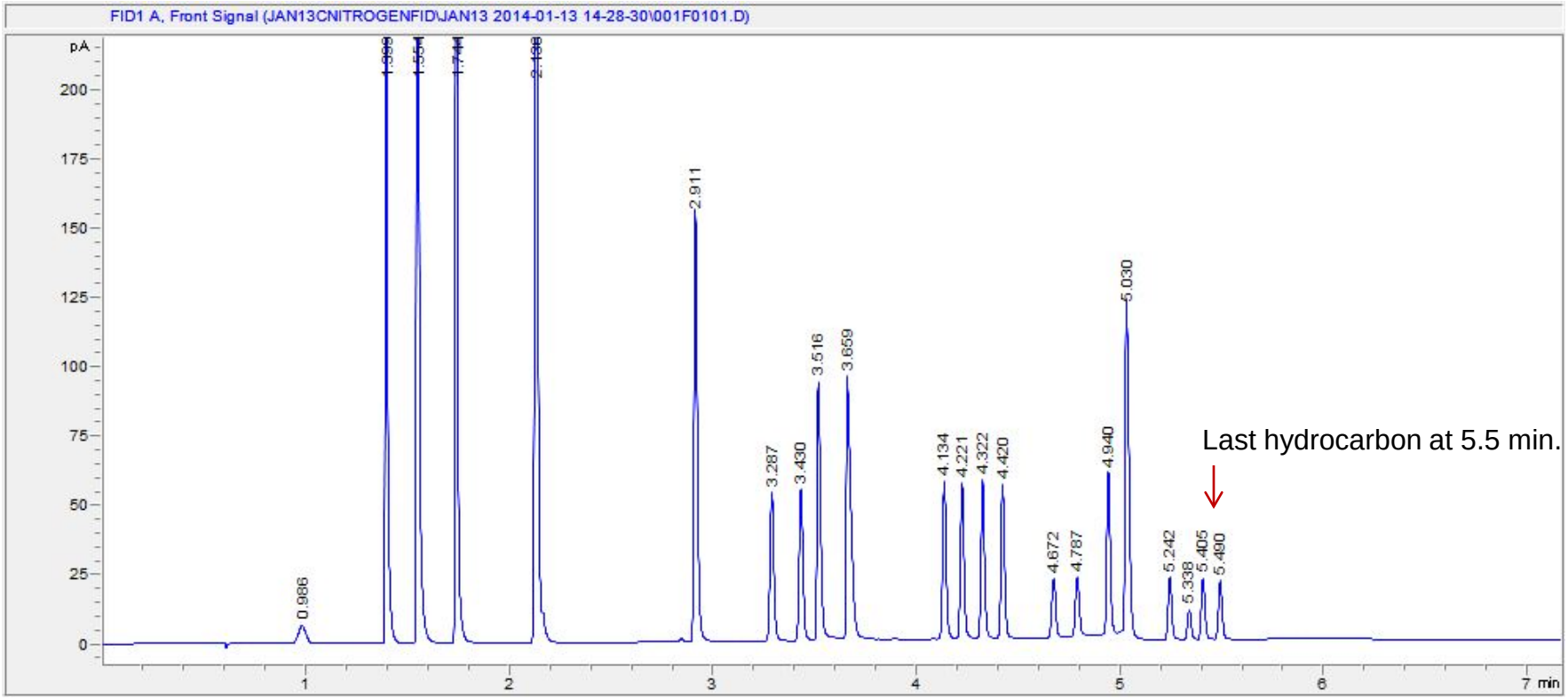
LVO Based RGA with Hydrogen Carrier

FID Channel



LVO Based RGA with Nitrogen Carrier for FID Channel

3.0 mL/min @ constant flow

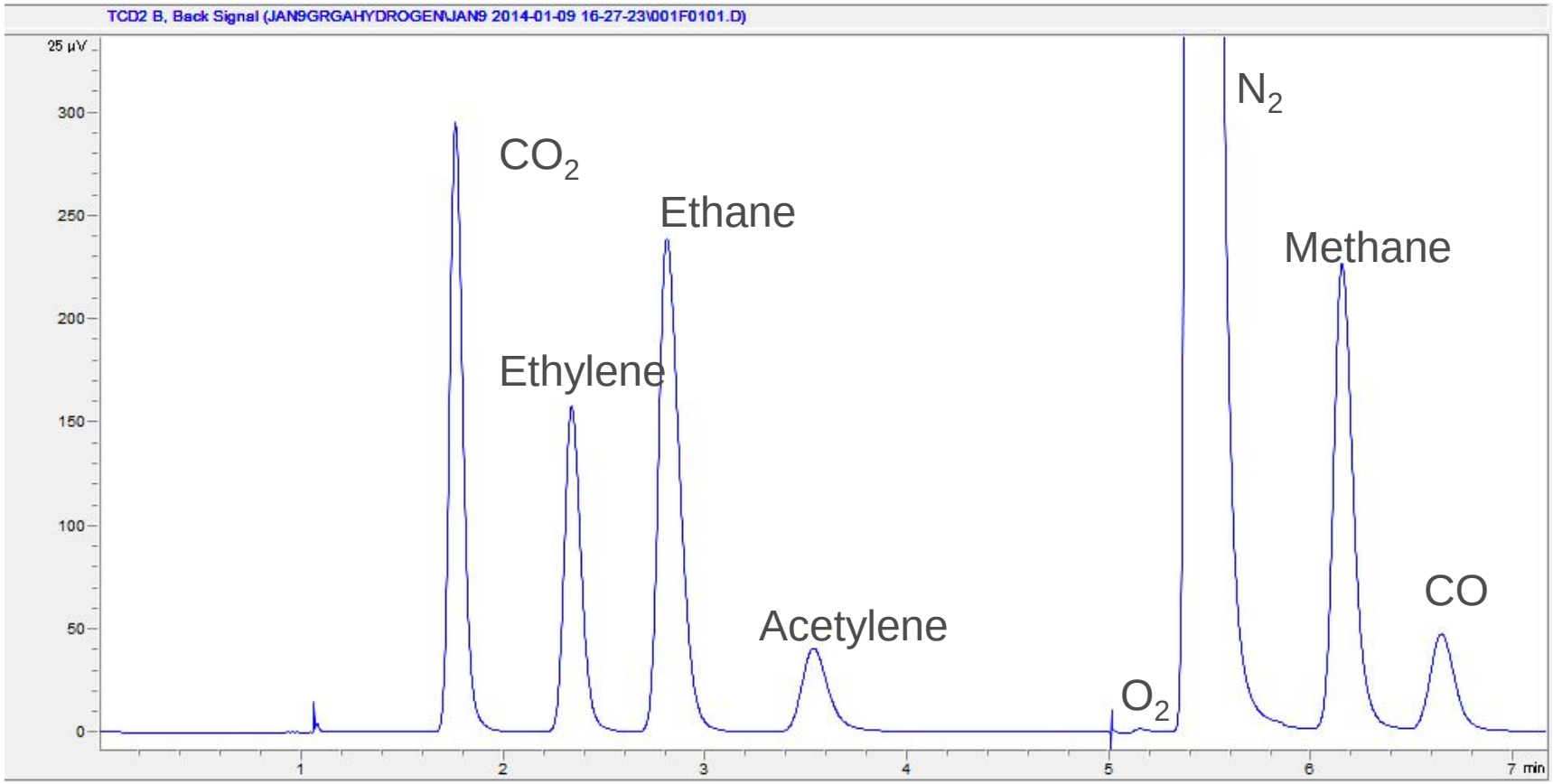


LVO Based Fast RGA with Hydrogen Carrier

Separation with Micropacked columns

TCD1: Permanent Gas Channel

Run Time less than 7 min.



LVO Based Micropacked 60 °C %RSD's

TCD1 Permanent gas channel: Hydrogen Carrier
FID Hydrocarbon channel: Nitrogen carrier
TCD2 Hydrogen channel: Nitrogen carrier

Compound	RT	Area
C6+	0.028	0.34
Methane (FID)	0.012	0.133
Ethane (FID)	0.014	0.13
n-butane	0.044	0.15
t-2-butane	0.052	0.13
1-butene	0.052	0.14
n-pentane	0.033	0.30
Hydrogen	0.681	0.64
Oxygen	0.014	2.4
Nitrogen	0.022	0.18
Carbon Monoxide	0.025	0.15
Carbon Dioxide	0.068	0.12
Methane (TCD)	0.020	0.17
Ethane (TCD)	0.071	0.17

Typical Detection Limits
LVO Based RGA's

High Capacity RGA Analyzer

- Total run time is **16- 18 minutes**.
- Hydrocarbons to C_5 (C_{6+} backflush)
- Permanent Gases
- O_2 and H_2S

Fast RGA Analyzer

- Total run time is **8 minutes**
  LVO at 70 °C
- Hydrocarbons to C_5 (C_{6+} backflush)
- Permanent Gases
- O_2 and H_2S

Compounds	Limit
Hydrocarbons	0.01 Mol%
Hydrogen Sulfide	500 ppm
Carbonyl Sulfide	300 ppm
Hydrogen	0.01 Mol%
O2, N2, CO, CO2	0.01 Mol%

Summary

Two configurations available

- Packed Columns: *16 to 18 minute run time*
- 1/16” Micropacked: *7 to 9 minute run time*

Both systems can measure hydrogen sulfide and carbonyl sulfide

The Large Valve Oven allows the permanent gas channel to be isothermal

- Thermally decoupled from the main GC oven
- Better stability of oxygen measurement over time
- Improved separation with greater flexibility
- Better RSD’s

Alternate carrier gases possible

- Hydrogen and Nitrogen give good results

Configuration of ASTM Methods D5580, D3606, and D4815 on a Single GC

Jim McCurry

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Analysis of Oxygenates and Aromatics in Gasoline

ASTM D3606 – Benzene and Toluene in Gasoline

- official EPA method for benzene (0.1 - 5.0 vol%) and toluene (2 to 20 vol%) in gasoline

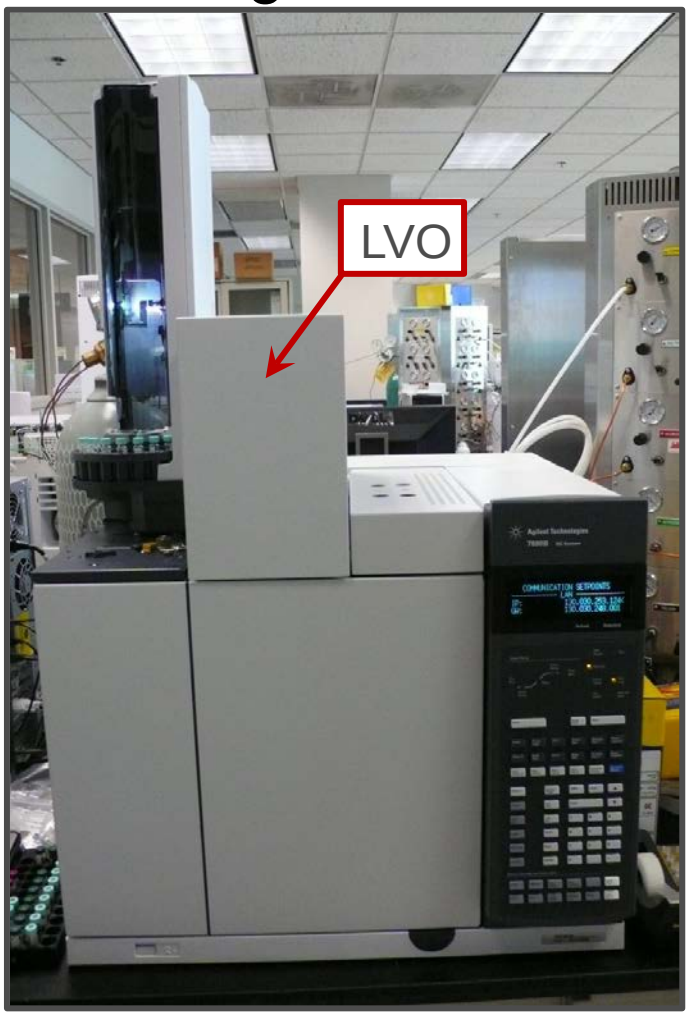
ASTM Method D4815 – Oxygenated Additives

- 14 different ethers and alcohols from 0.1 to 15 wt%
- usually only one or two oxygenates found in a sample

ASTM Method D5580 –Aromatics in Gasoline

- measures benzene (0.1 to 5%), toluene (1 to 15%), C_8 aromatics (0.5 to 10%) C_9 plus aromatics (5 to 30%), and total aromatics (10 to 80%)
- requires two injections per sample for complete analysis

3-in-1 Gasoline Solution using the New 7890B GC with Large Valve Oven (LVO)



- Larger capacity for valves, packed columns and micro-packed columns
- Flexibility for method using complex valve/column configurations
- Enables multiple methods to reside on a single GC
  - reduce instrument costs
  - run more samples in less lab space
  - 3-in-1 Gasoline Solution
    - D3606
    - D4815
    - D5580

LVO Specifications

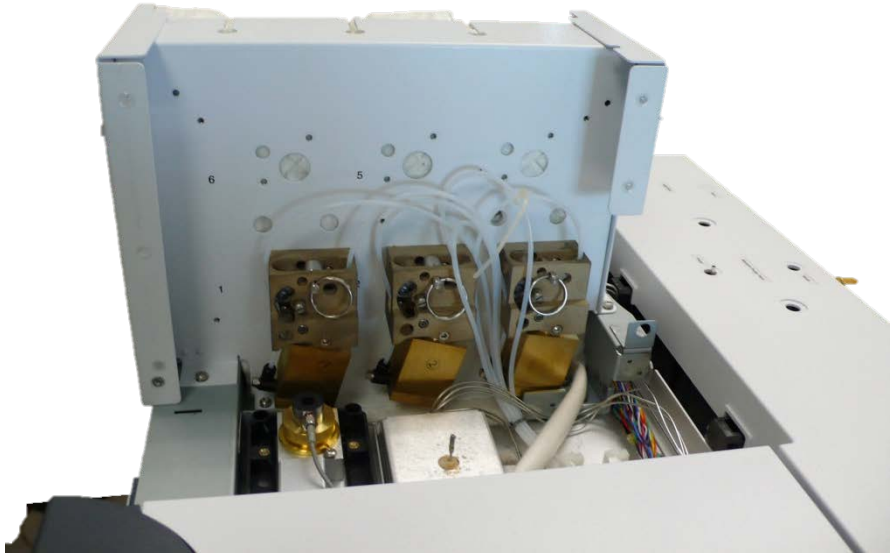
- Temperature Limit: 330˚C (high temperature valve dependent)
- Valves: 6 heated valve positions, 4 needle valve positions
- Temperature control: Independent control of Large Valve Oven and GC oven
- Valve configurations: 4/6/10/14 port valves including Hastelloy valves
- Large column mandrels (each uses 1 valve position) accept up to 15 feet of 1/8inch OD metal column
- Small column mandrel (one allowed, does not use a valve position) accepts up to 7 feet of 1/8 inch OD metal column

3-in-1 Gasoline Solution – LVO Configuration

Cover Off - Front View

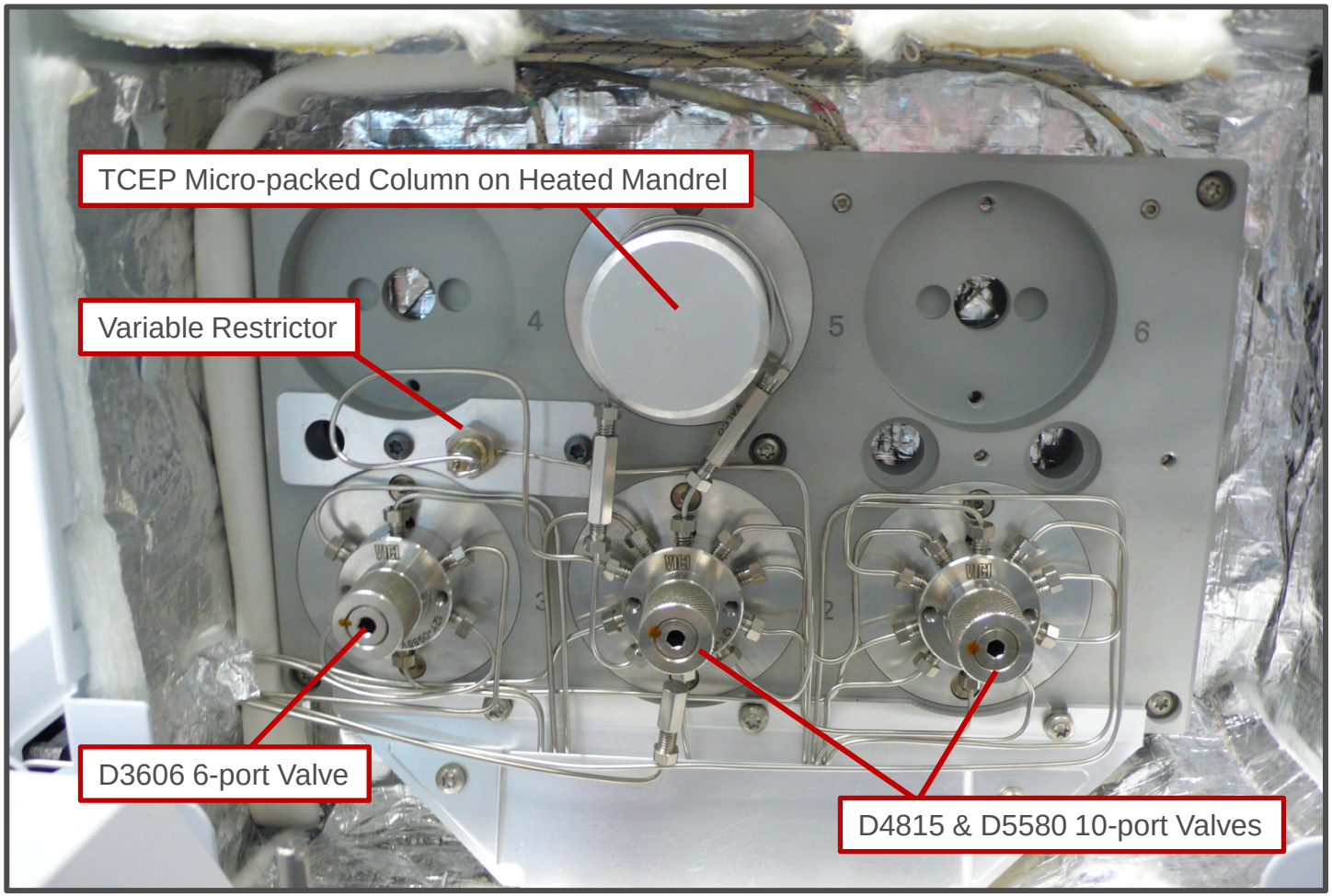
- Valves
- Variable Restrictor
- TCEP Pre-column
- Heated Column Mandrel

Cover Off - Rear View



- Pneumatic Valve Actuators
- Variable Restrictor Control

3-in-1 Gasoline Solution – Detailed LVO Configuration



GC Configuration for D4815 and D5580

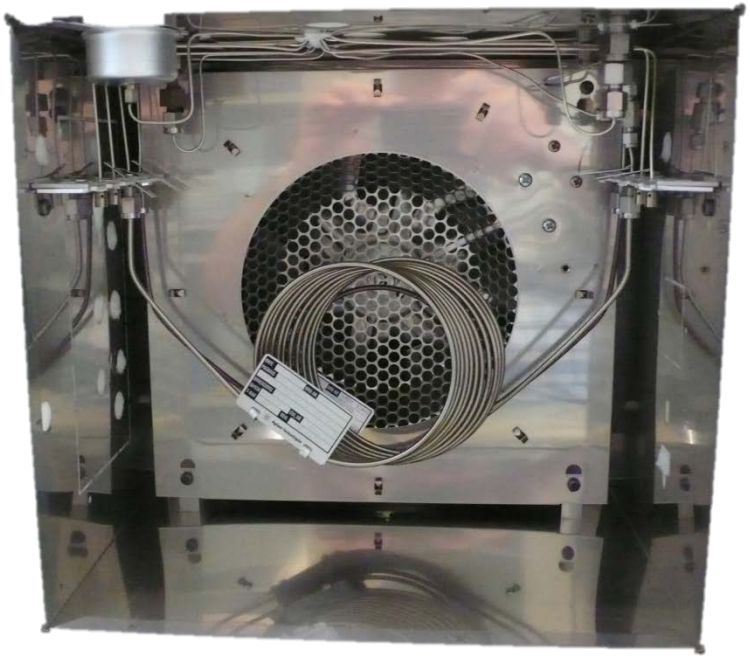
Similarities between each method

- same GC hardware requirements
  - Inlets, detectors, plumbing and valve configuration
- same separation scheme
  - 2-D separation using polar TCEP micro-packed primary column
  - 20% TCEP on 80/100 Chromosorb PAW, 22“ x 1/16“ stainless

- Only one difference in instrument requirements – non-polar capillary column
  - D4815 – 2.65 μm methyl silicone, 30m x 0.53mm
  - D5580 – 5 μm methyl silicone, 30m x 0.53mm

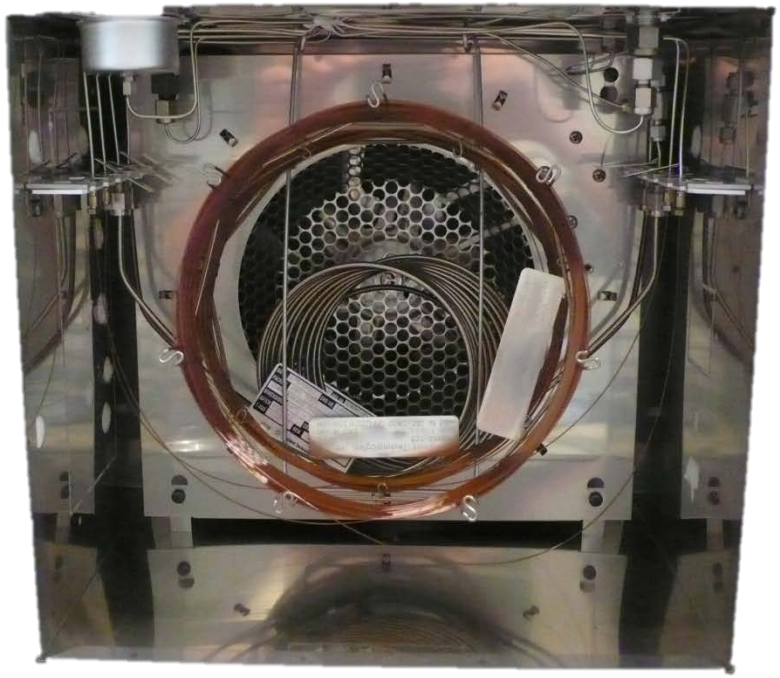
3-in-1 Gasoline Solution – Main Column Oven

D3606 Packed Columns



- PDMS packed pre-column
- Polar packed analytical column

D4815 and D5580
Capillary Columns



- D4815 HP-1
  (30 m x 0.53 mm x 2.65 μm)
- D5580 HP-1
  (30 m x 0.53 mm x 5.0 μm

7890 Instrument Conditions for D3606

carrier gas	helium
Inlet	Purge Packed @ 59.4 psi
Inlet temperature	200 Deg C
Inlet total flow	23 mL/min
Septum purge flow	3 mL/min
Column flow	20 mL/min
Aux pressure	35.5 psi
TCD temperature	250 deg C
LVO Temperature	60 deg C
Main oven temperature	135 deg C isothermal
Backflush time	2.5 min

LVO temperature remains stable with high main oven temperature

D3606 – Comparison of Manual and WorkBench Sample Prep

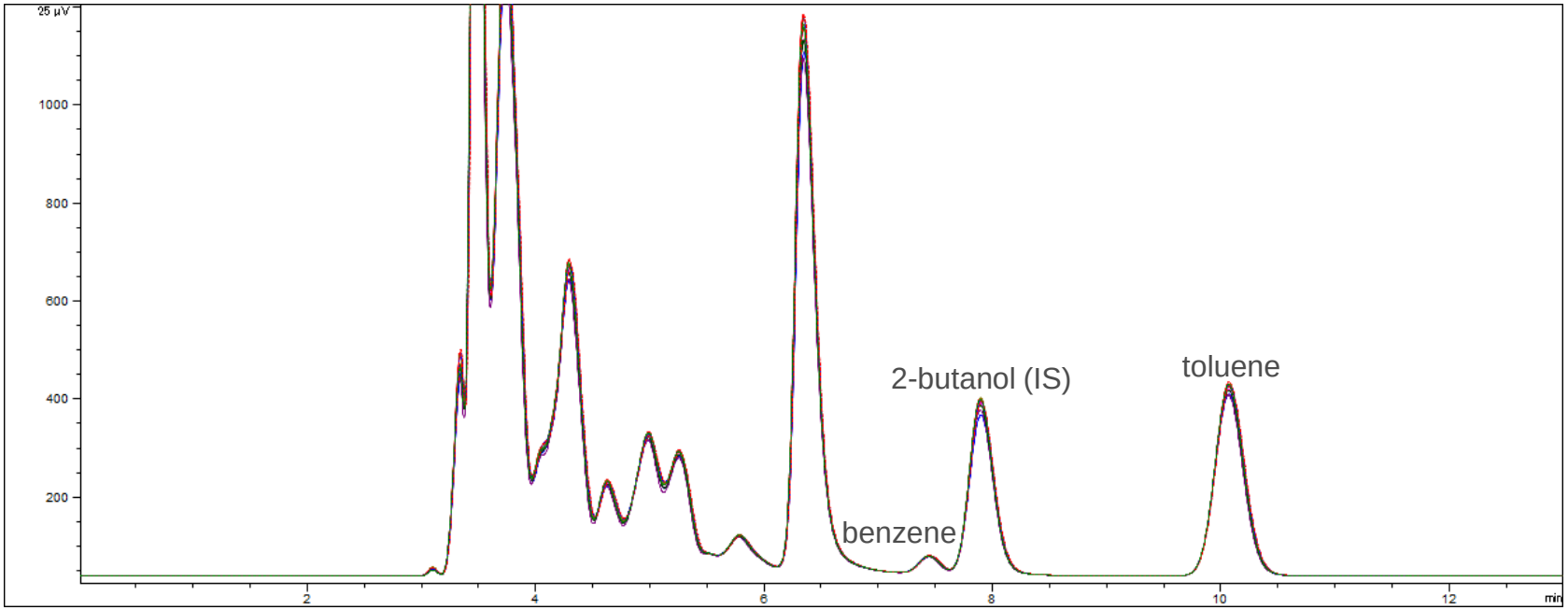
Manual Sample Prep

- Add 1.0 mL 2-butanol to 25 mL volumetric flask
- Add sample to 25 mL mark

Work Bench Sample Prep

- Add 0.04 mL 2-butanol to 2 mL vial
- Add 0.96 mL sample to 2 mL vial

Overlay of 10 Work Bench prepared gasoline samples



D3606 – Precision and Accuracy for Work Bench Prepared Samples

Commercial Gasoline Sample

	Volume %	
run	benzene	toluene
1	0.337	5.527
2	0.344	5.523
3	0.344	5.519
4	0.348	5.524
5	0.347	5.475
6	0.346	5.483
7	0.344	5.545
8	0.346	5.506
9	0.348	5.556
10	0.343	5.604
avg	0.345	5.526
stddev	0.00323	0.03690
RSD	0.938%	0.668%
r (exp)	0.005	0.129
r (ASTM Spec)	0.020	0.186

Meets ASTM repeatability specifications

D3606 Check Sample

	vol%*	
Run	Benzene	Toluene
1	0.98	5.00
2	0.98	4.98
3	0.97	4.98
4	0.98	5.00

*benzene = 1.00 vol% (+/- 0.02)

*toluene = 5.00 vol% (+/- 0.08)

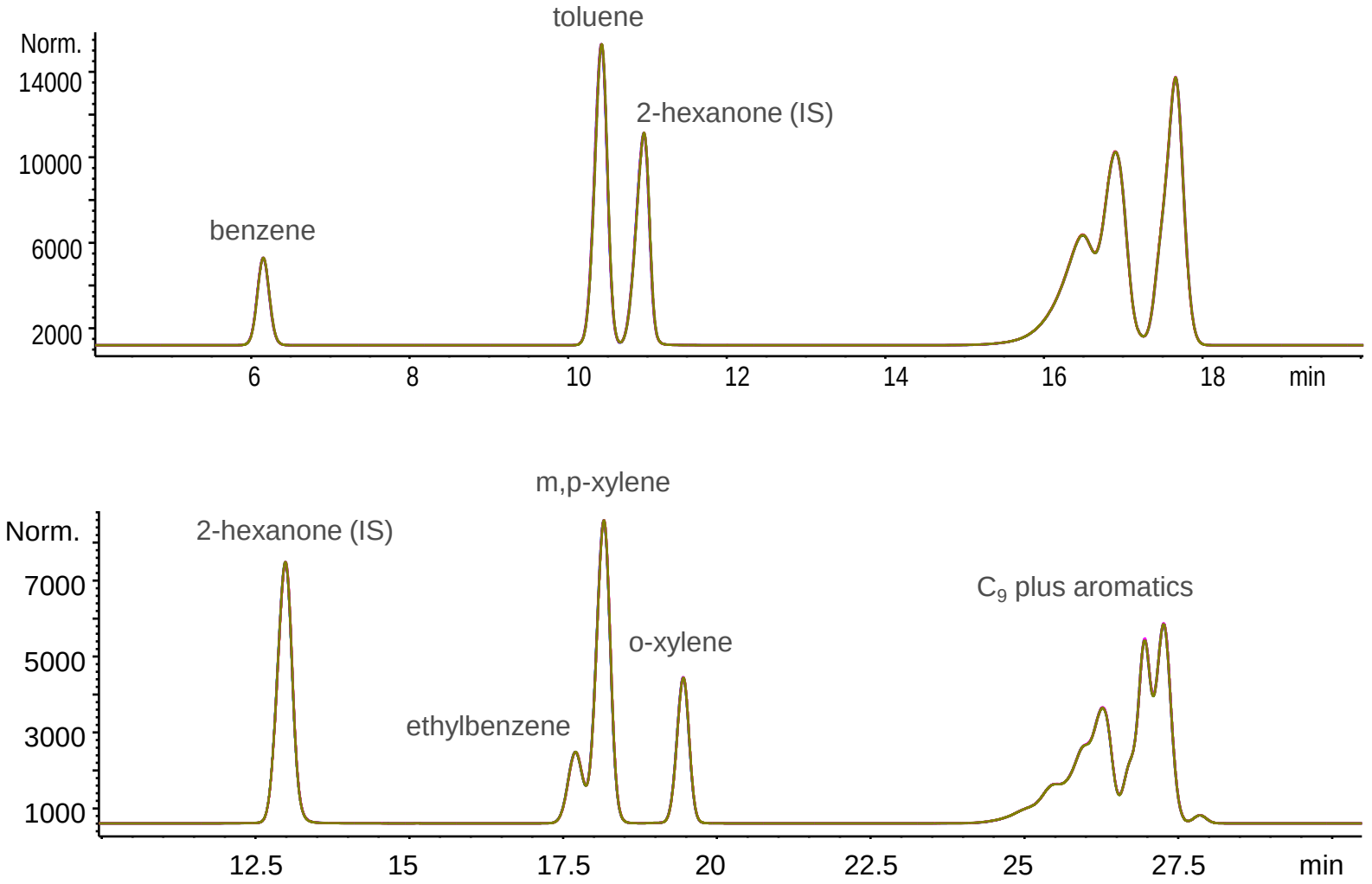
Analysis results match known quantities in sample

7890 Instrument Conditions for D4815 and D5580

	D4815 Method	D5580 Method
carrier gas	helium or N2	helium or N2
Inlet	Split/Splitless	Split/Splitless
inlet temperature	200 Deg C	200 Deg C
inlet presuure	9 psi (constant P)	25 psi (constant P)
TCEP column flow	5 mL/min	10 mL/min
split vent flow	70 mL/min	100 mL/min
split ratio	15:1	100:1
PCM pressure program	13 psi for 14 min	23 psi for 12.1 min
	99 psi/min to 40 psi	99 psi/min to 40 psi
HP-1 column flow	3 mL/min	10 mL/min
FID temperature	250 deg C	250 deg C
LVO temperature	60 deg C	60 deg C
Main oven temperature	60 deg C isothermal	60 C for 6 min
		2 C/min to 115 C
		115 C for 1.5 min

D5580 – Work Bench Prepared Gasoline Sample

Overlay of 5 replicates run on LVO Configuration



D5580 - Precision for WorkBench Samples

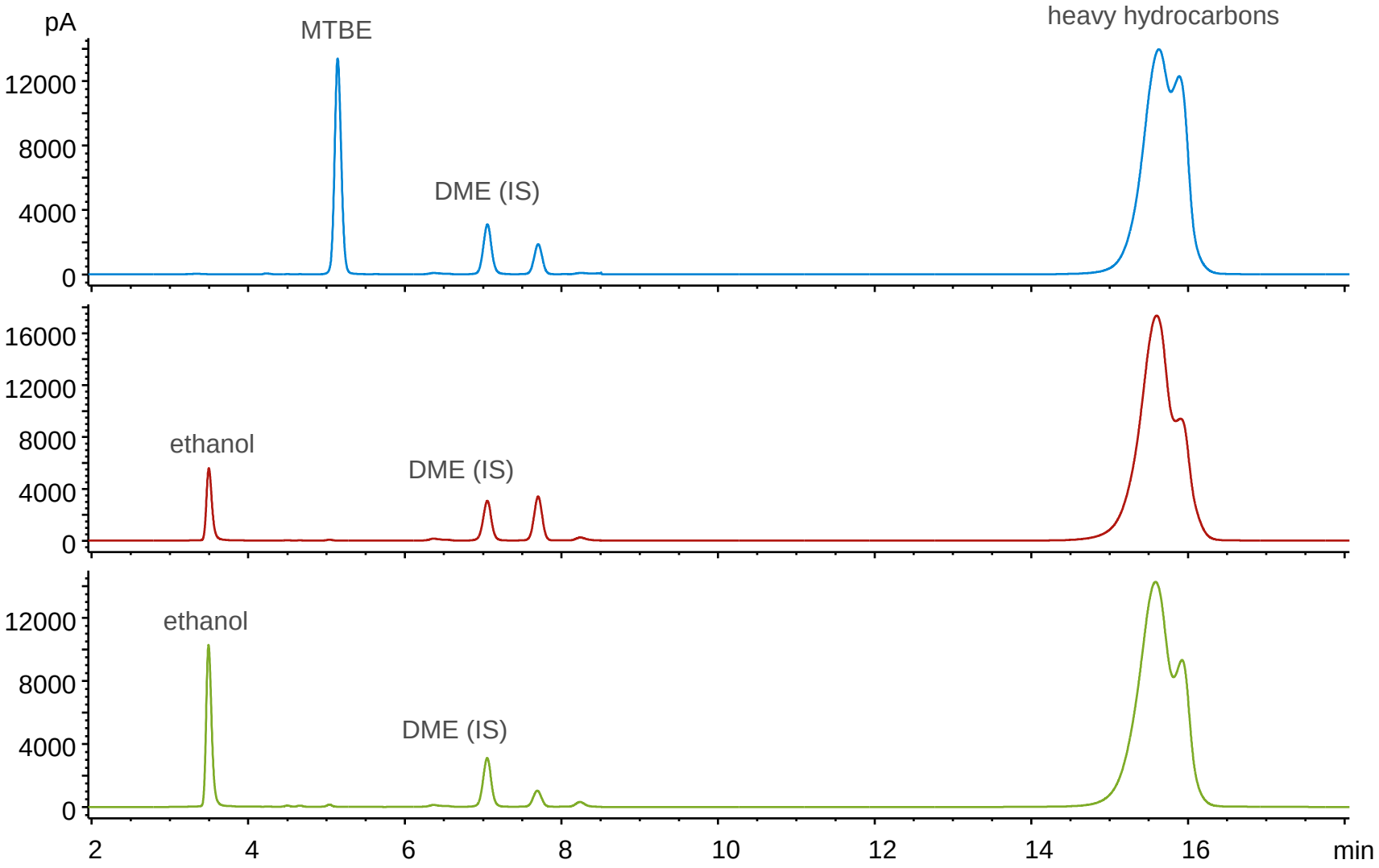
Meets ASTM Repeatability (r) Specifications

	wt% Found in Gasoline Sample 1						
	benzene	toluene	ethylbenzene	m,p-xylene	o-xylene	C9 plus	Total
Run 1	0.96	8.93	2.97	3.00	3.00	6.12	24.98
Run 2	0.96	8.91	2.96	3.00	3.00	6.11	24.94
r (calc)	0.00	0.02	0.01	0.00	0.00	0.01	0.04
r (ASTM spec)	0.03	0.09	0.03	0.07	0.05	0.16	0.45

	wt% Found in Gasoline Sample 2						
	benzene	toluene	ethylbenzene	m,p-xylene	o-xylene	C9 plus	Total
Run 1	1.08	9.56	2.67	6.57	2.35	13.39	35.61
Run 2	1.08	9.49	2.66	6.55	2.33	13.30	35.40
r (calc)	0.01	0.07	0.02	0.02	0.02	0.09	0.22
r (ASTM spec)	0.03	0.09	0.03	0.07	0.05	0.27	0.54

	wt% Found in Gasoline Sample 3						
	benzene	toluene	ethylbenzene	m,p-xylene	o-xylene	C9 plus	Total
Run 1	0.43	5.99	1.27	4.71	1.90	13.79	28.08
Run 2	0.43	6.00	1.27	4.71	1.90	13.81	28.12
r (calc)	0.00	0.01	0.00	0.01	0.00	0.02	0.04
r (ASTM spec)	0.02	0.07	0.03	0.07	0.04	0.27	0.48

D4815 –Work Bench Prepared Gasoline Samples



D4815 – Comparison of Manual and WorkBench Sample Prep

Manual Sample Prep

- Add 0.5 mL DME to 10 mL volumetric flask
- Record DME weight to 0.1 mg
- Add sample to 10 mL mark
- Record sample weight to 0.1 mg
- Mix

Work Bench Sample Prep

- Add 0.95 mL sample to an empty 2 mL vial
- Record sample weight to 0.01 mg
- Add 0.05 mL DME to sample in the 2 mL vial
- Record DME weight to 0.01 mg
- Mix

	Gas1 wt% MTBE		Gas2 wt% Ethanol		Gas3 wt% Ethanol	
	Manual Prep	WorkBench	Manual Prep	WorkBench	Manual Prep	WorkBench
run1	13.15	13.18	6.01	6.08	10.47	10.55
run2	13.13	13.12	5.98	6.13	10.58	10.66
Avg	13.14	13.15	6.00	6.10	10.52	10.61
r (calc)	0.02	0.07	0.02	0.05	0.11	0.11
r (spec)	0.21	0.21	0.18	0.18	0.25	0.25

Summary

- New Large Valve Oven for the 7890B GC

  - greater capacity and flexibility for GC methods using complex valve configurations

  - allows multiple ASTM gasoline methods to be configured on a single GC
    - methods can be run sequentially

  - higher main oven temperature (135 deg C) has no effect on lower LVO temperature (60 deg C)
    - eliminates waiting for valve oven equilibration when switching from D3606 to D4815/D5580

  - reduces costs and saves lab space

Q & A Session