Analysis of Permanent Gases
More Challenging Than You Might Think

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May 17, 2023
Application Engineer

Analysis of Permanent Gases

- Reduce the list to only mission critical solutes
- Sample introduction – syringes and valves
- General discussion on PLOT columns
  - The molesieve column is at the heart of permanent gas separations
- Techniques when CO_2 + C_2, C_3 + is also needed
  - Column isolation
  - Parallel columns
  - Cryogenic separations
  - Unique selectivity packed columns
- Techniques for low level detection of hydrogen
- Micro GC
- Ammonia
- MSD?

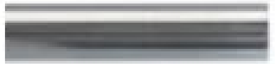
Reduce the List First!

- Reduce your list to only mission critical solutes
  - This is a critical step and can greatly simplify things
  - Eliminating even one solute can help (i.e. do I really need CO_2?)

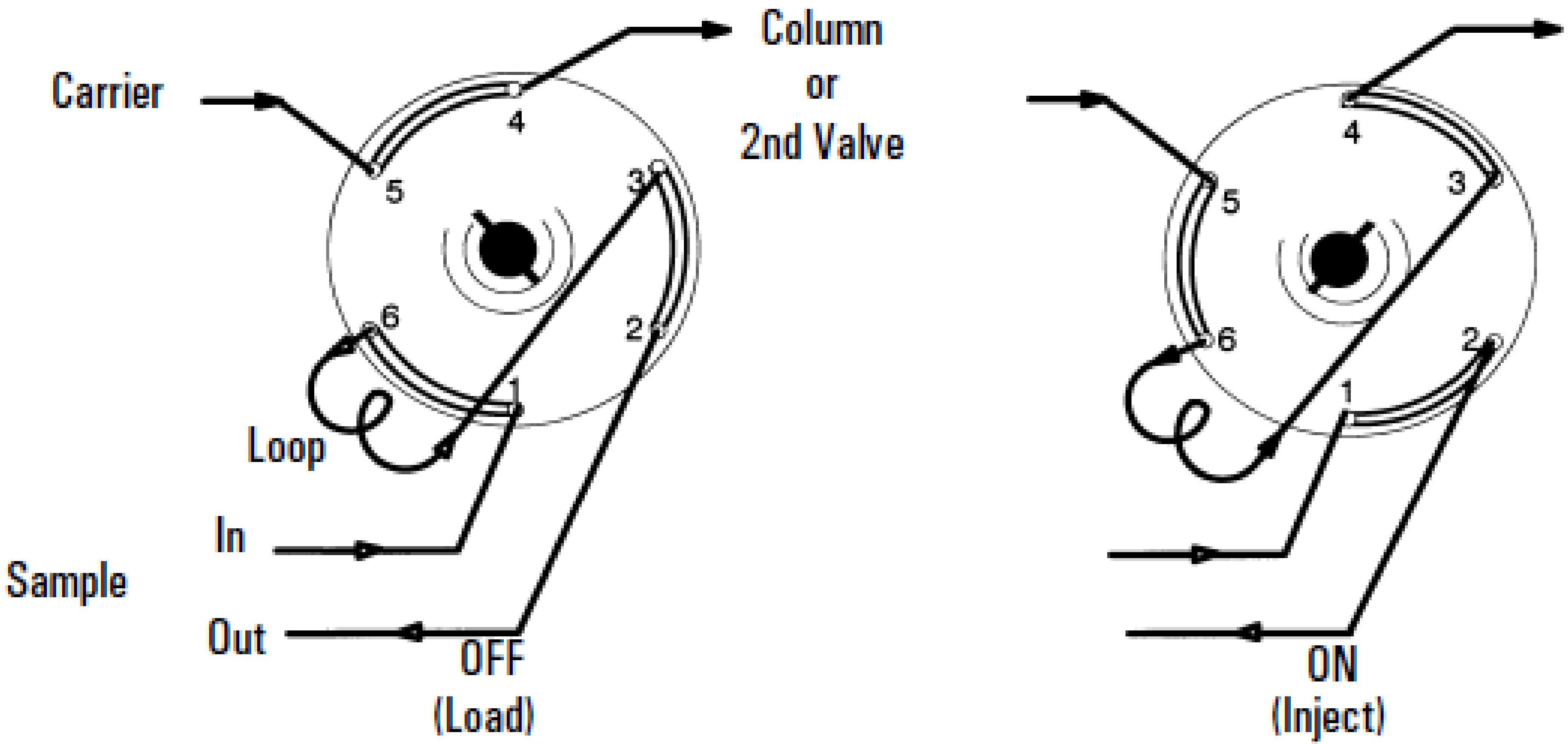
Gas Tight Syringes

Syringes for Gas Injection

http://pconlab.net/Hamilton-Syringes.html

Point Style		Description	Application
2		10–12° sharp, beveled, curved non-coring	Gas chromatography, septum piercing
3		Blunt, electro-polished	High performance liquid chromatography (HPLC) injection, thin layer chromatography (TLC), general liquid handling, controlled animal injections
3T		Blunt, electro-polished, coated with PTFE 19 mm from the tip	Thin layer chromatography (TLC) applications
4		Sharp 10–12° beveled needle	Life science/animal injections
5		Conical with side port for penetration without coring	Headspace, applications prone to needle clogging, causes minimal septum damage
AS		Conical, non-coring designed to withstand multiple injections	Autosampler injection, pre-pierced septa

Gas Sampling Valve



Gas sampling valve

PLOT Columns

Column Type	Phase Type	Chromatographic Process	Stationary Phases
WCOT	Liquid	Gas – Liquid partitioning	Polysiloxanes PEG
PLOT	Solid	Gas – Solid adsorption	Porous polymers Al_2O_3, zeolites

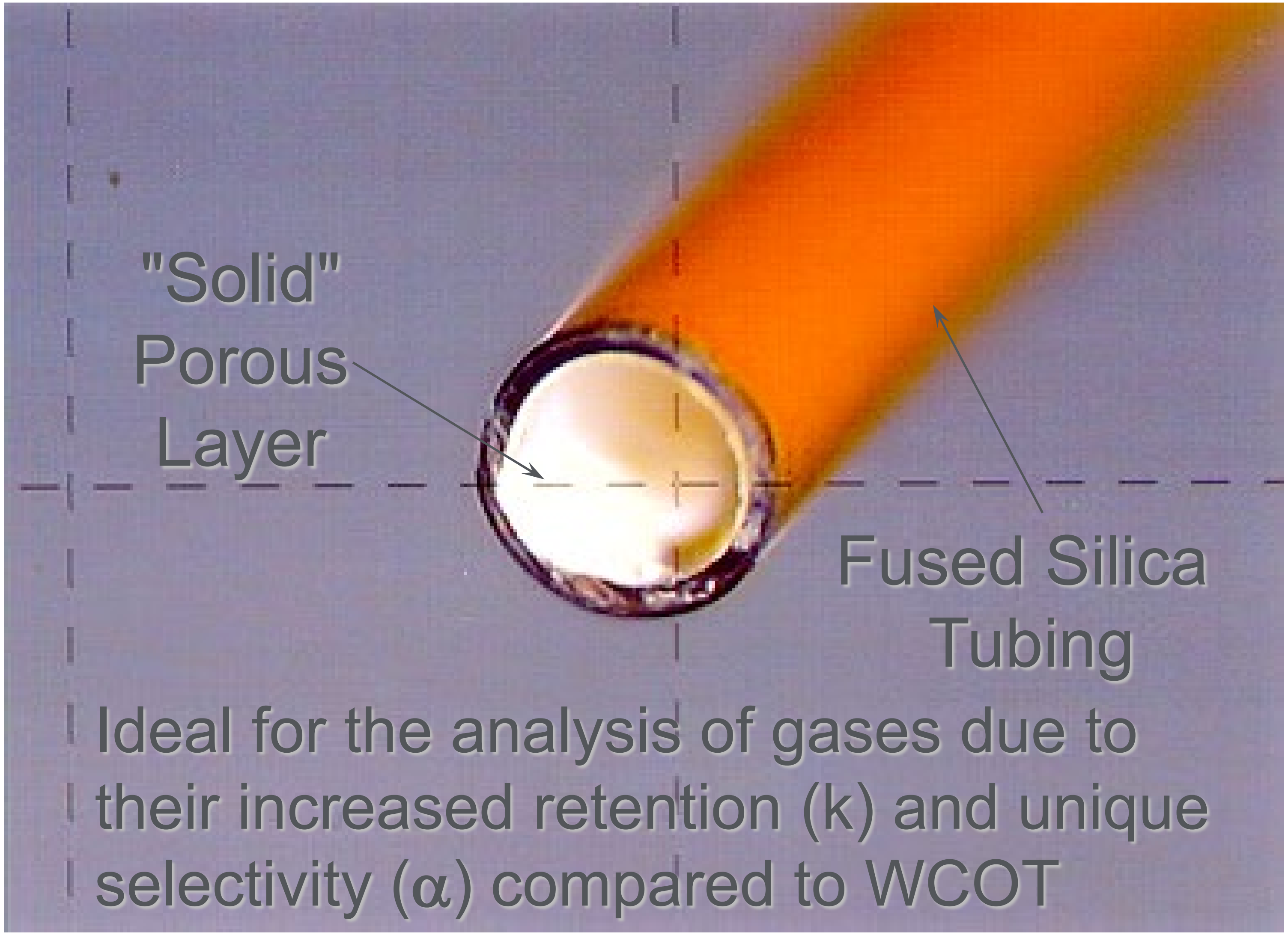
WCOT = **W**all **C**oated **O**pen **T**ubular

PLOT = **P**orous **L**ayer **O**pen **T**ubular

Why Use a PLOT Column?

- Highly retentive
  - Can resolve gases at non-cryo temperatures
- Unique selectivity
- Permits higher initial oven temperatures than WCOT

PLOT Columns



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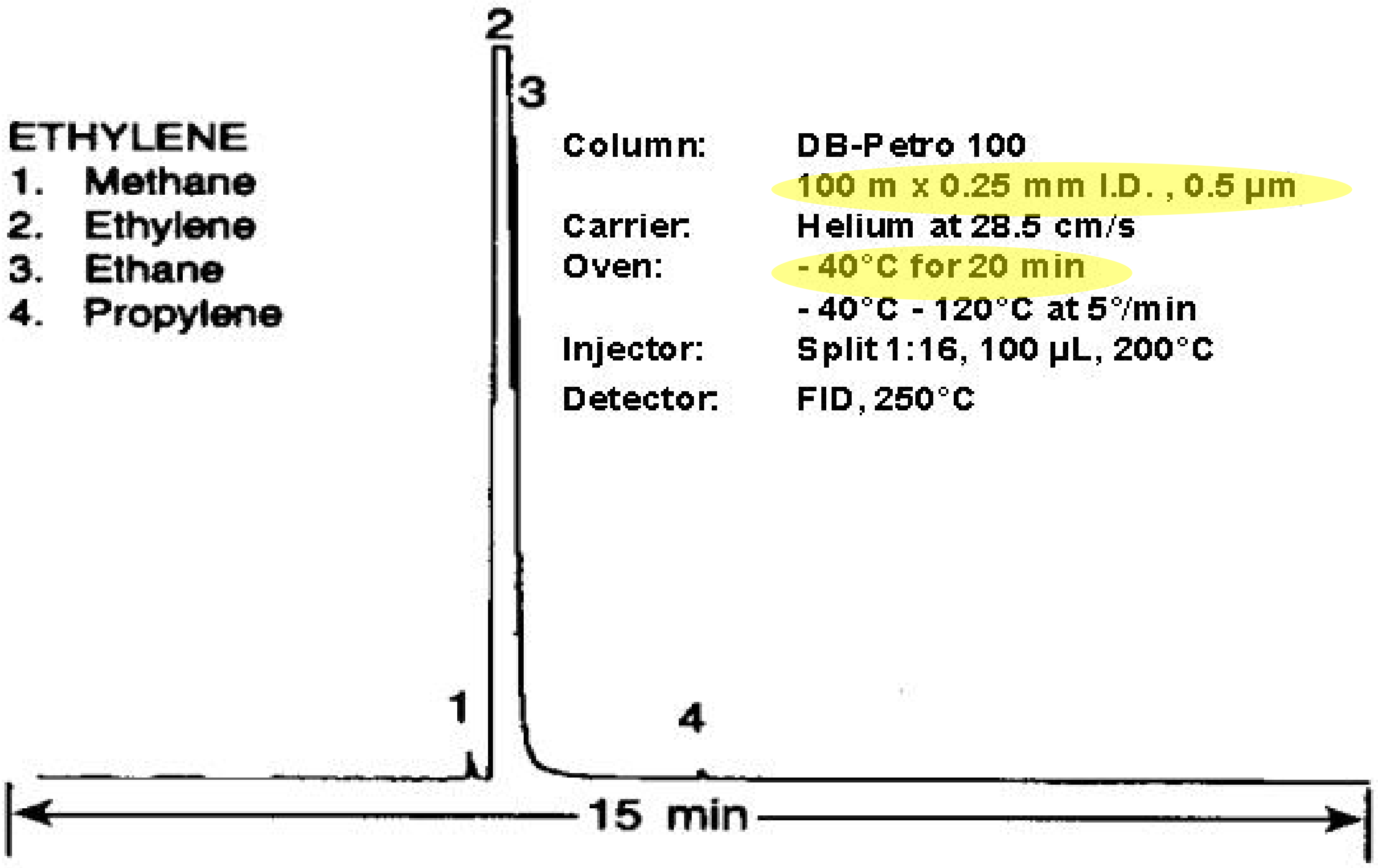
WCOT Ethylene Analysis



ETHYLENE
1. Methane
2. Ethylene
3. Ethane
4. Propylene

Column:	DB-Petro 100
	100 m x 0.25 mm I.D. , 0.5 µm
Carrier:	Helium at 28.5 cm/s
Oven:	- 40°C for 20 min
	- 40°C - 120°C at 5°/min
Injector:	Split 1:16, 100 µL, 200°C
Detector:	FID, 250°C

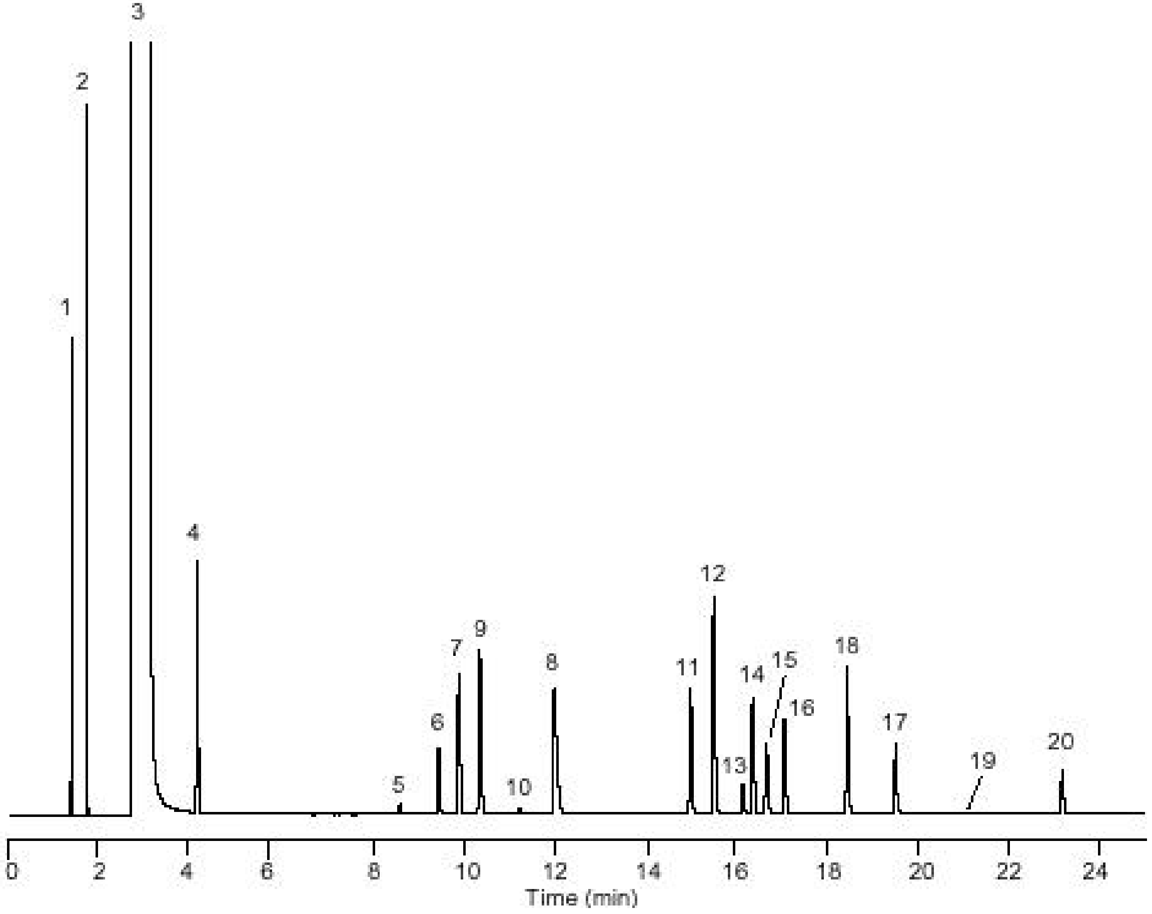
PLOT Ethylene Analysis

Ethylene

Column:	**GS-Alumina**
	50 m x 0.53 mm I.D.
J&W P/N:	**115-3552**
Carrier:	Helium at 11 mL/min, measured at 35°C
Oven:	35°C for 2 min
	35-190°C at 6°/min
	190°C for 3 min
Injector:	Split 1:30, 200°C
	0.2 mL of trace hydrocarbons in ethylene
Detector:	FID, 200°C
	Nitrogen makeup gas at 20 mL/min

1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Cyclopropane
6. Propylene
7. Isobutane
8. Acetylene
9. *n*-Butane
10. Propadiene
11. *trans*-2-Butene
12. 1-Butene
13. Isobutylene
14. *cis*-2-Butene
15. Isopentane
16. *n*-Pentane
17. Propyne
18. 1,3-Butadiene
19. 1-Pentene
20. *n*-Hexane

C585



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JW Column PLOT column Portfolio- DB, HP, CP

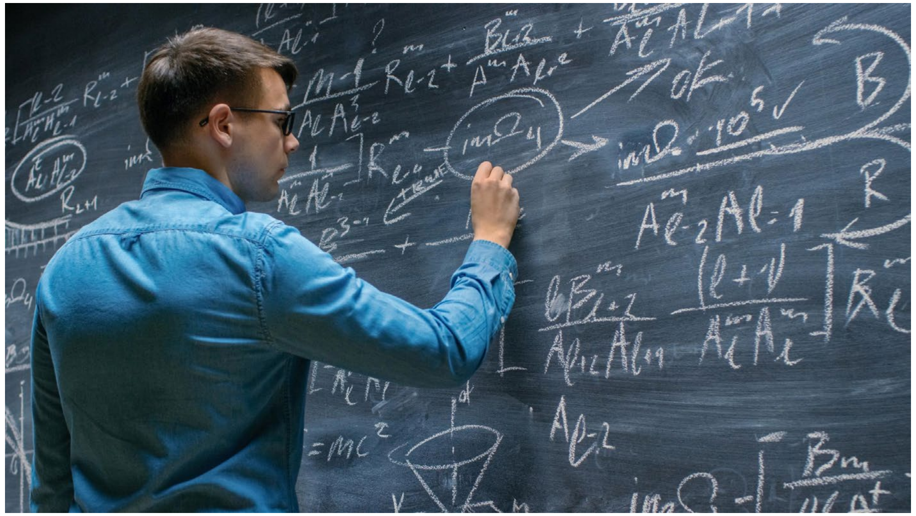
HP-PLOT Al_2O_3
GS-Alumina
GS-Alumina KCl
HP-PLOT Al_2O_3 S
HP-PLOT Al_2O_3 M
CP- Al_2O_3/KCL
CP- Al_2O_3/Na_2SO_4
CP-SilcaPLOT
CP-CarboBOND
CP-CarboPLOT P7
GS-CarbonPLOT
CP-PoraPLOT Amines
CP-PoraPLOT S

CP-PoraBOND Q
CP-PoraPLOT Q
CP-PoraPLOT Q-HT
HP-PLOT Q
CP-PoraBOND U
HP-PLOT U
GS-Q
CP-PoraPLOT U
HP-PLOT molesieve
CP-molesieve 5A
GS-GasPro
ShinCarbon ST
Select Permanent Gas Column

But I Also Need to Analyze for CO_2…It's Getting Complicated

- Recall that CO_2 cannot be done on a molesieve column (absorbed)
- Alternative options:
  - – Two unique injections on two columns
    - Molesieve and PLOT-Q
      - Be aware how retentive the molesieve is!
  - – One injection on one column at Cryo temps (-80 ^{o}C)
    - GasPro
  - – One injection on one column – ShinCarbon ST (packed column)
  - – One injection with two columns and a valve to "direct traffic"
    - Column isolation – molesieve and PLOT-Q
  - – One injection with two columns in parallel
    - Select permanent gas column – molesieve and PLOT-Q

…did I mention this would get complicated?



Molesieve Column

- Separation based mostly on molecular size and shape
- Excellent at what it does but very limited
  - H_2, O_2, N_2, CH_4, CO
  - Noble gases
  - NO_2
- Limitations…cannot use for…
  - CO_2
  - Water
  - C_2 HCs and larger

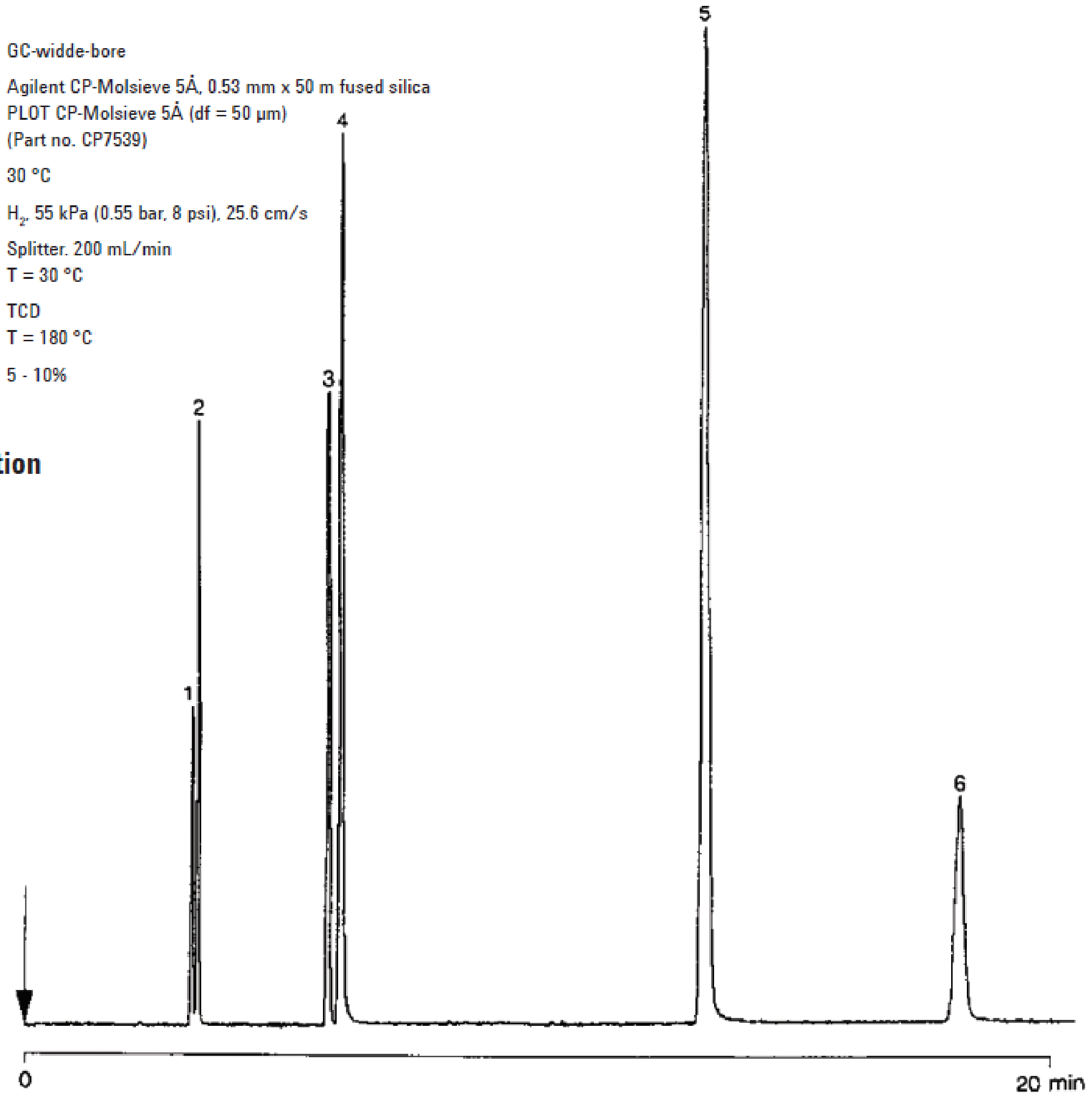
Molesieve Separations

Conditions

Technique	:	GC-widde-bore
Column	:	Agilent CP-Molsieve 5Å, 0.53 mm x 50 m fused silica PLOT CP-Molsieve 5Å (df = 50 µm) (Part no. CP7539)
Temperature	:	30 °C
Carrier Gas	:	H_2, 55 kPa (0.55 bar, 8 psi), 25.6 cm/s
Injector	:	Splitter. 200 mL/min T = 30 °C
Detector	:	TCD T = 180 °C
Concentration Range	:	5 - 10%

Peak identification

1. helium
2. neon
3. argon
4. oxygen
5. nitrogen
6. methane

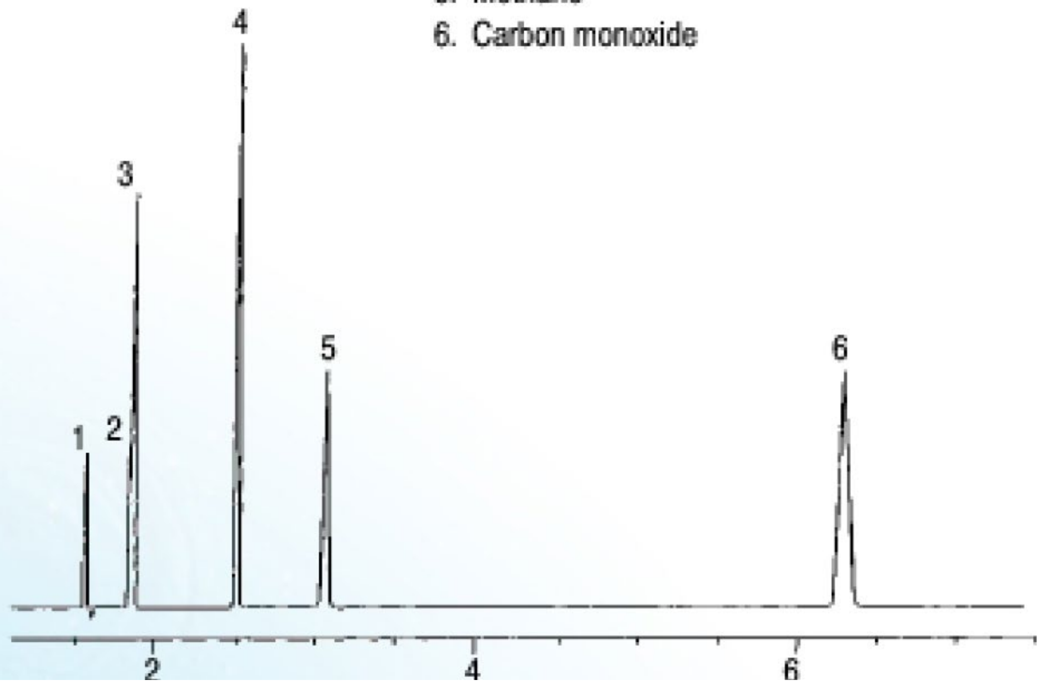


GC:	6890
Sample:	250 ml, split (75:1)
Carrier:	Helium, 2 µl/min
Column:	HP-PLOT/MoleSieve, 30 m x 0.32 mm x 12 µm (Part No. 19091P-MS4)
Oven:	40°C Isothermal
Detector:	TCD

Pub No.: 5964-2129E

Permanent Gases

1. Neon
2. Argon
3. Oxygen
4. Nitrogen
5. Methane
6. Carbon monoxide



Molesieve Separations

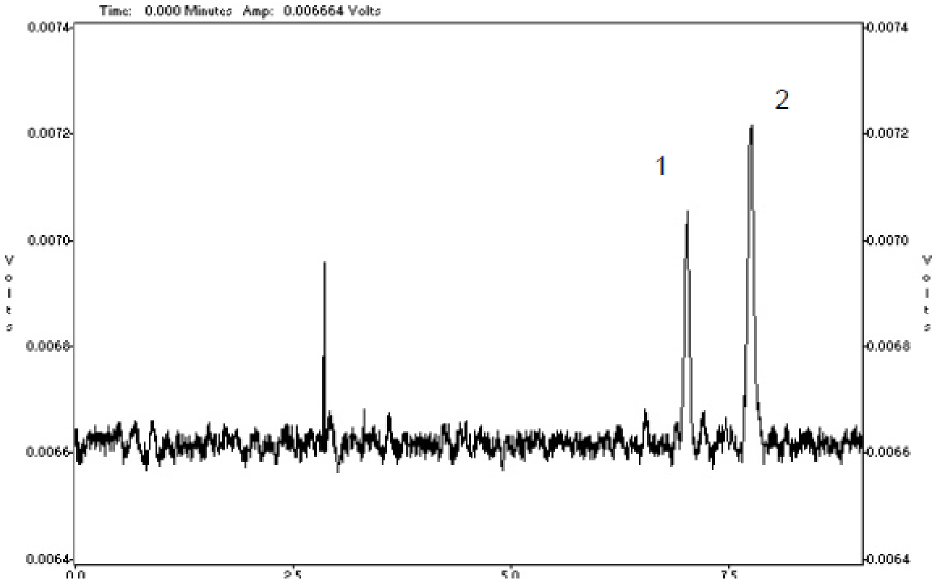
Separation of hydrogen and helium

Technique	: GC
Column	: CP-Molsieve 5A fused silica 50 m x 0.53 mm df = 50 µm, Part nr. CP7539
Temperature	: 40°C
Carrier Gas	: Nitrogen, 50kPa (7.2 psi)
Injector	: Splitter, 40 ml/min
Detector	: µ-TCD, 200°C
Sample Size	: 40 µl
Concentration range	: 1% in nitrogen

Reference : C. Duvekot, Varian R&D laboratories, Middelburg, The Netherlands

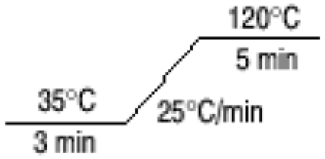
Peak identification

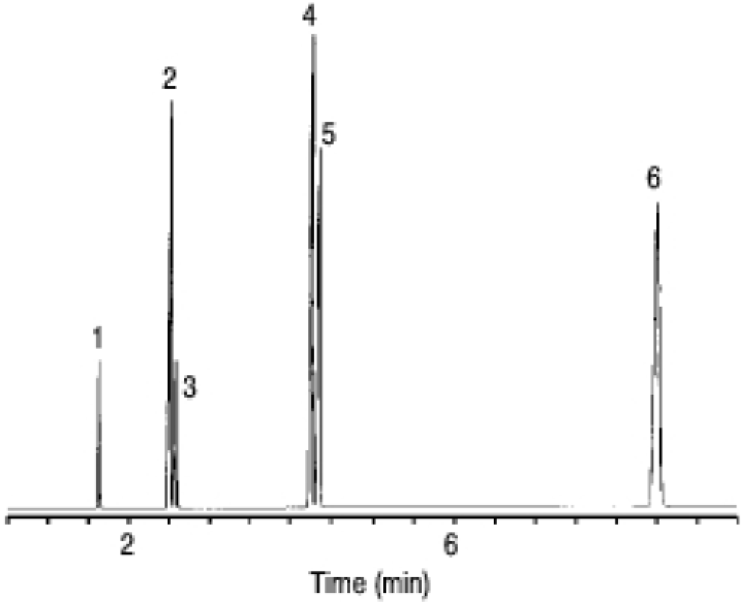
1 Helium
2 Hydrogen



Noble Gases

1. Neon
2. Argon
3. Oxygen
4. Nitrogen
5. Krypton
6. Xenon





GC:	6890
Sample:	250 µl, split (50:1)
Carrier:	Helium, 4 ml/min
Column:	HP-PLOT/MoleSieve, 30 m x 0.53 mm x 50 µm (Part No. 19095P-MS0)
Oven:	Temperature program listed above
Detector:	TCD

Pub No.: 5964-2129E

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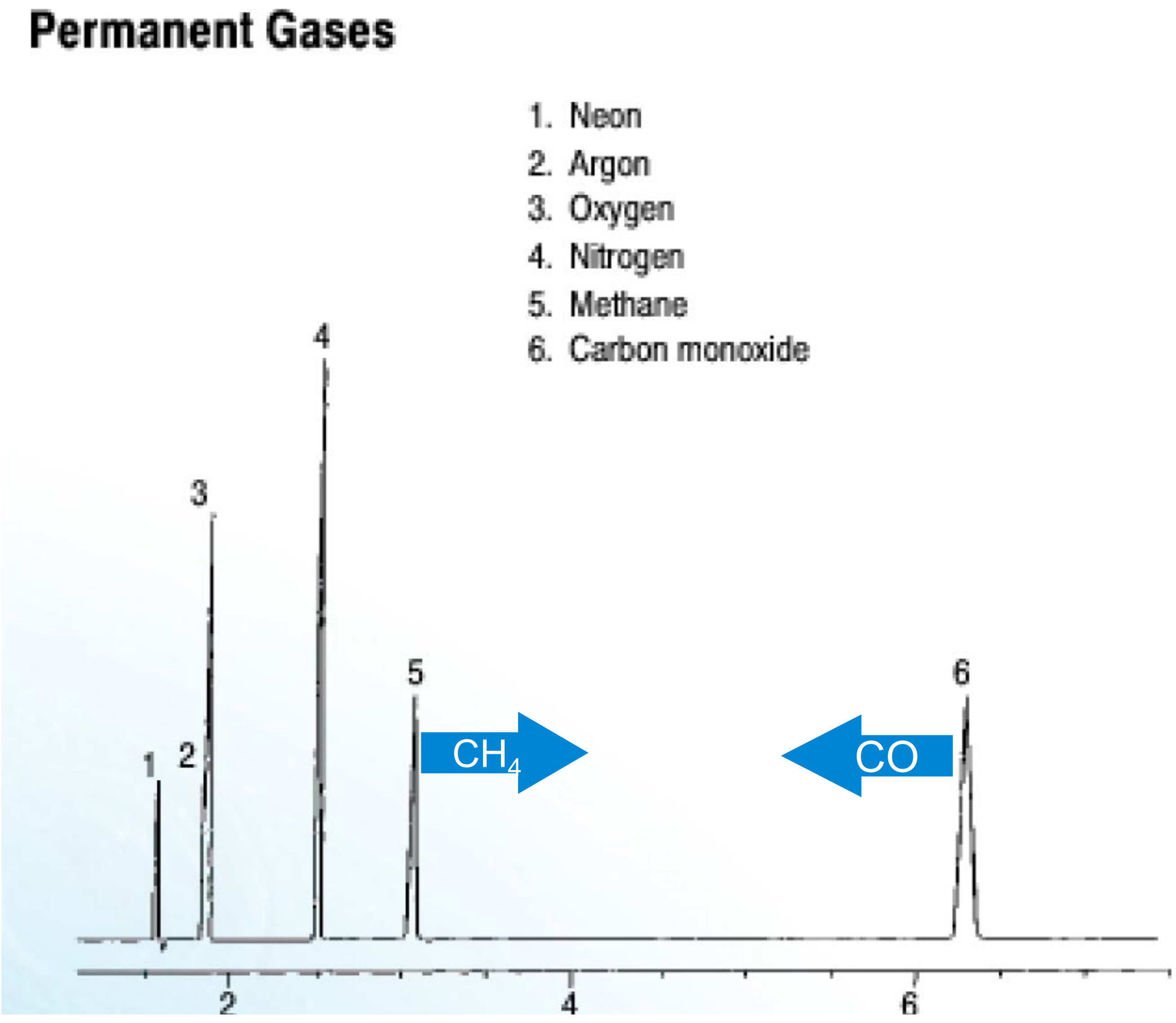
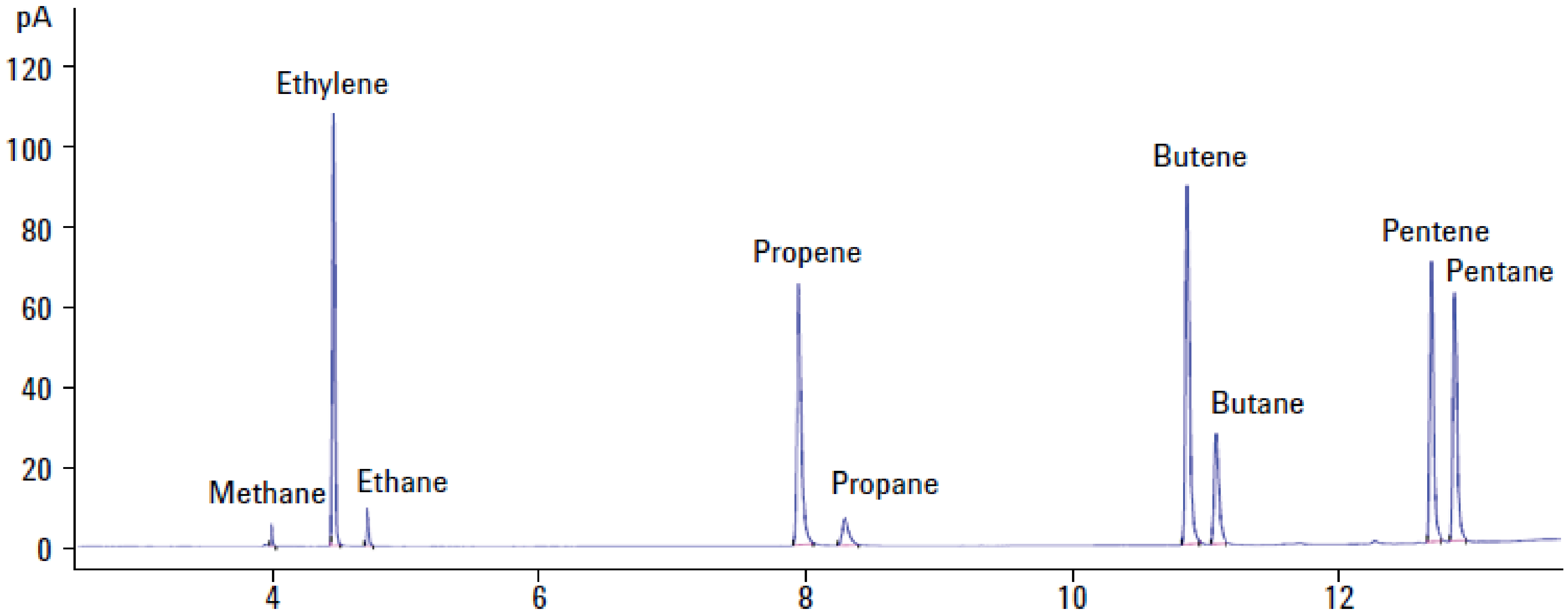
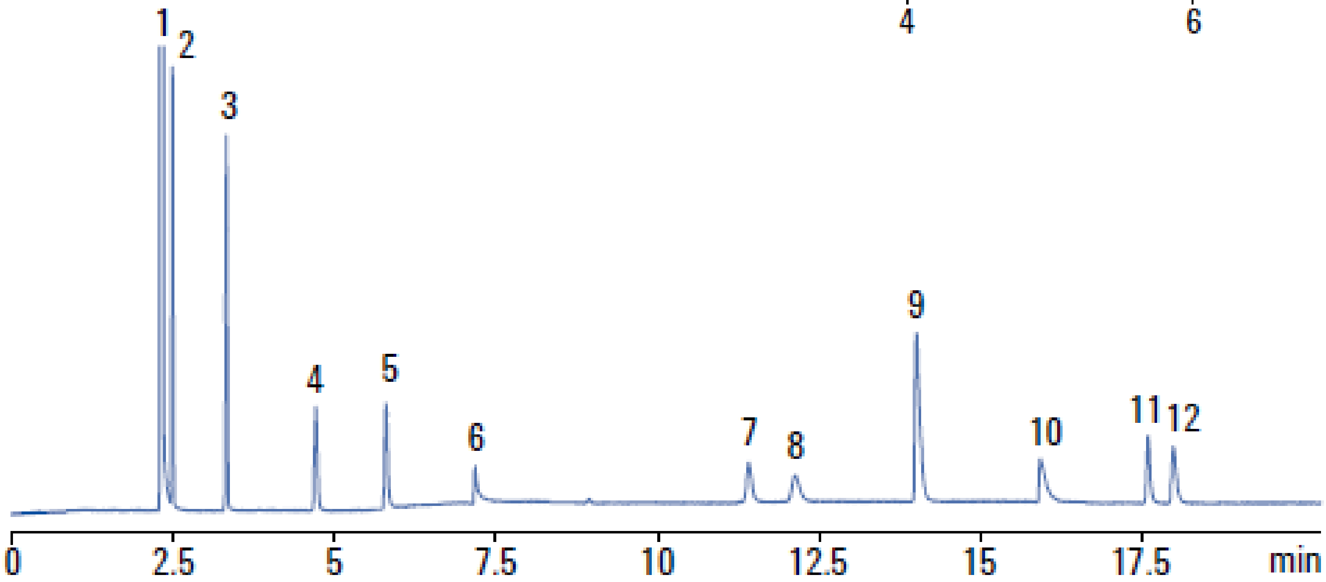
Tips For Using a Molesieve Column

- Molesieve material is commonly used as a moisture trap
- Samples must be reasonably dry
- Separation will change as column absorbs water over time
  - Resolution loss between CH_4 and CO indicates that the column should be reconditioned (300 ^oC 8 hours+)



PLOT-Q





1. CO/air
2. Methane
3. Carbon dioxide
4. Ethylene
5. Ethane
6. Hydrogen sulfide
7. Propylene
8. Propane
9. Dimethyl ether
10. Methanol
11. Butylene
12. Butane

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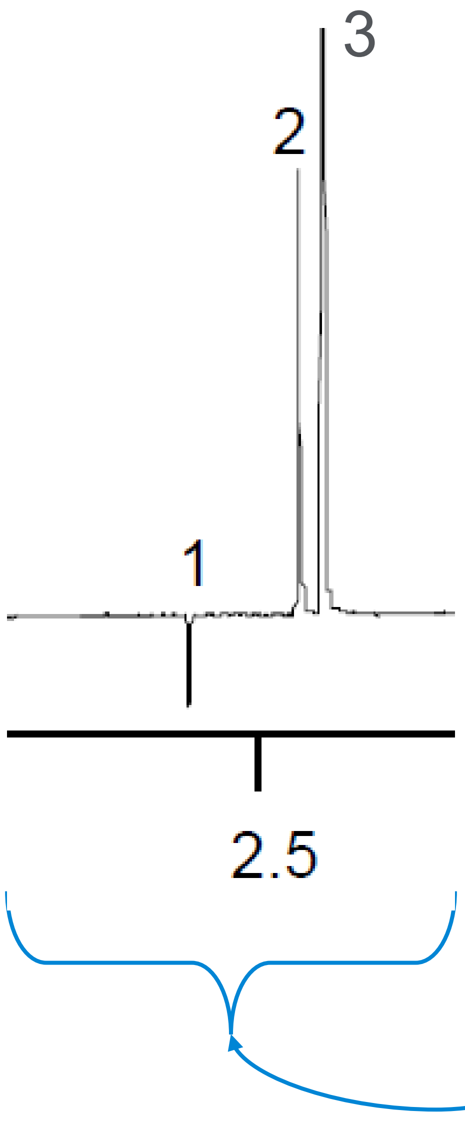
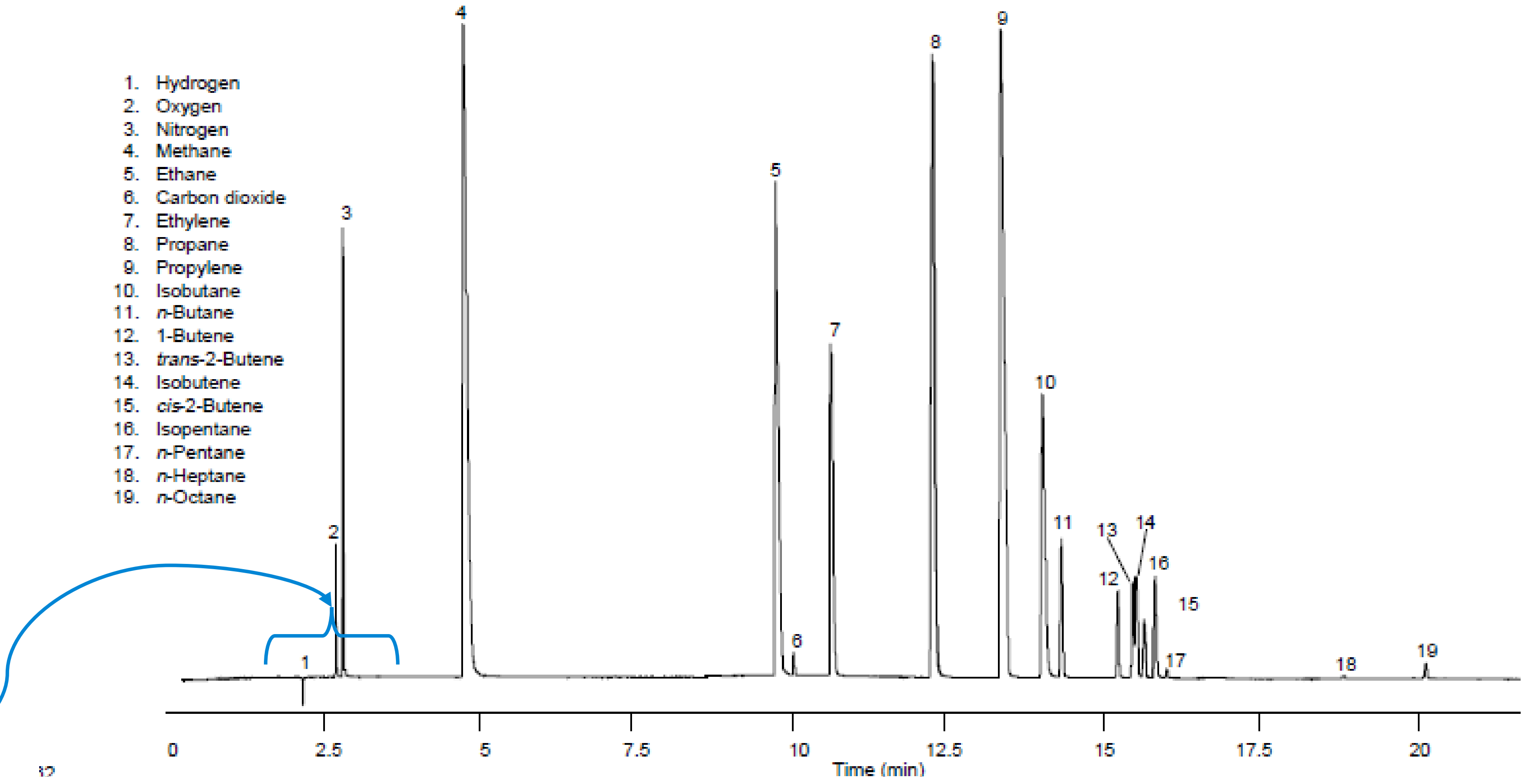
GS-GasPro – Cryo

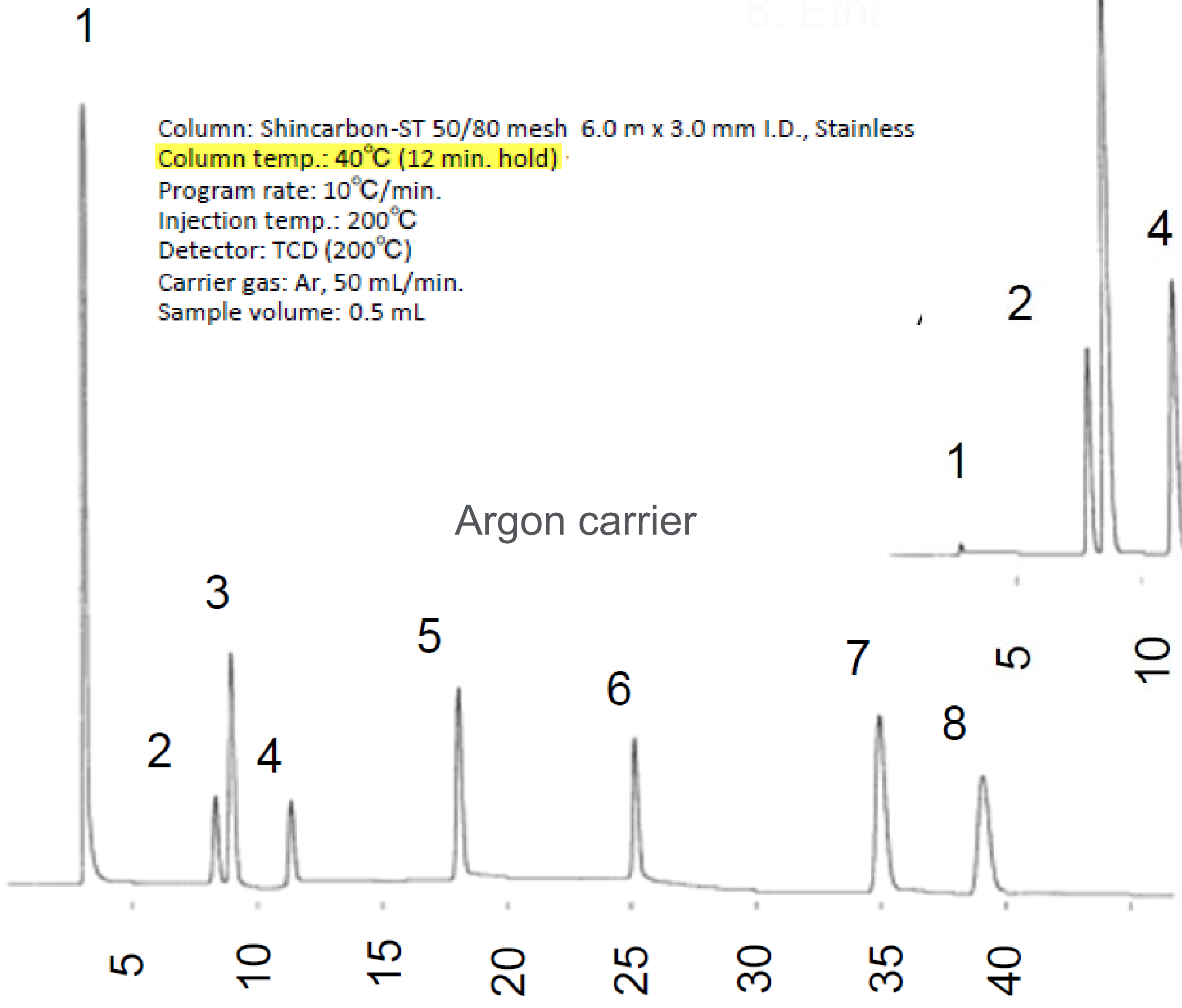


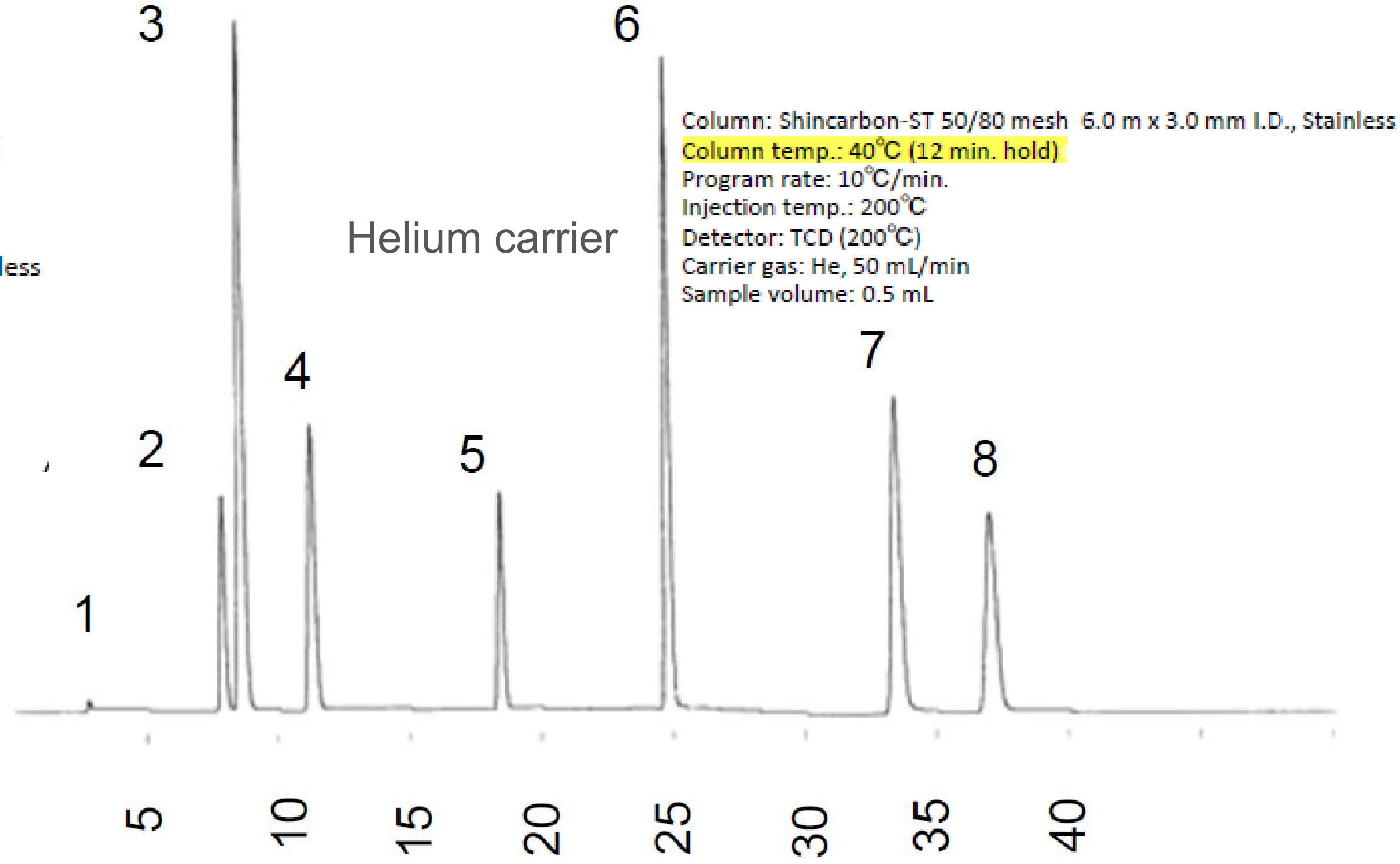
Permanent Gases in Hydrocarbon Blend

Column: **GS-GasPro, 60 m x 0.32 mm I.D.**
J&W P/N: **113-4362**
Carrier: Helium, 20 psig (constant pressure)
Inlet: 200°C, 1:15 split
Sample: 100 µL, manual inject
Detector: TCD, 250°C, background compensated
Oven: -80°C for 3 min, -80° to 260°C at 25°/min, hold at 260°C



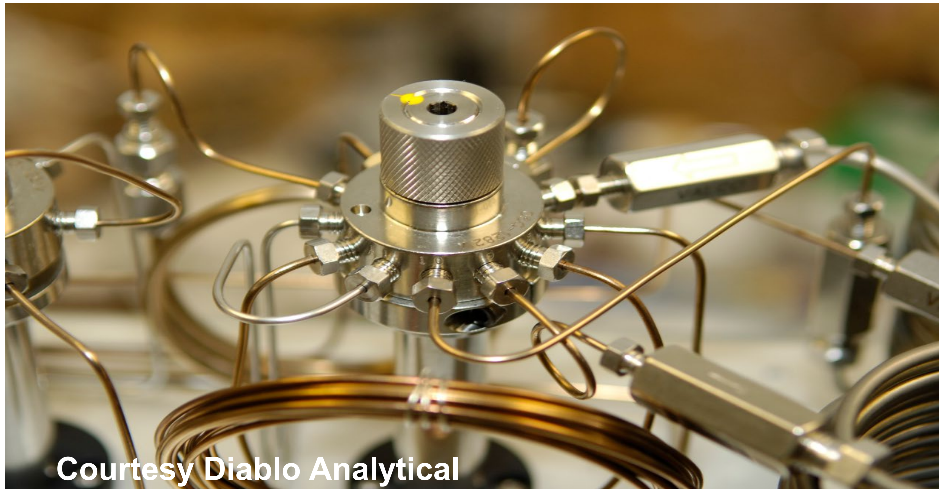
ShinCarbon ST

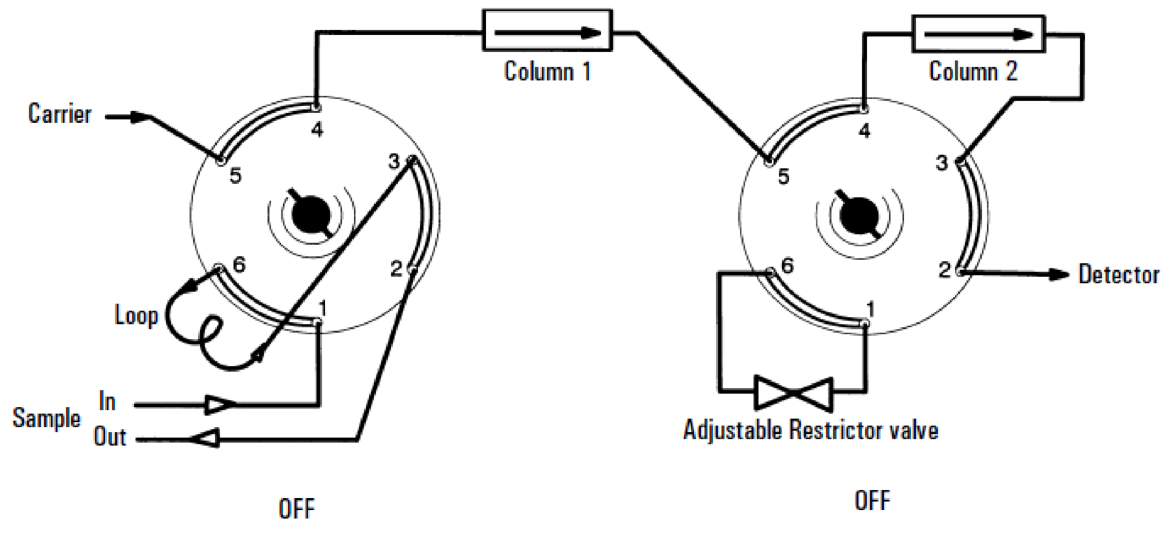




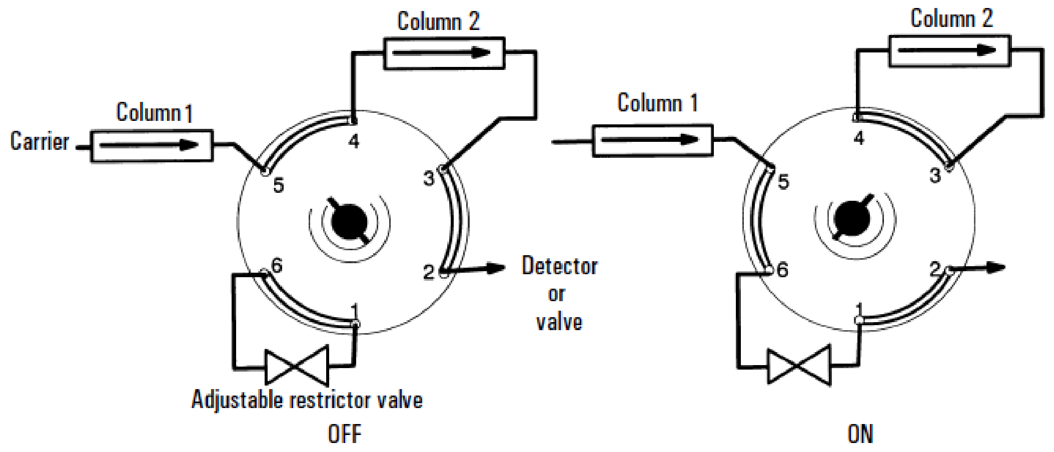
1. Hydrogen
2. Oxygen
3. Nitrogen
4. Carbon monoxide
5. Methane
6. Carbon dioxide
7. Ethylene
8. Ethane

Valves



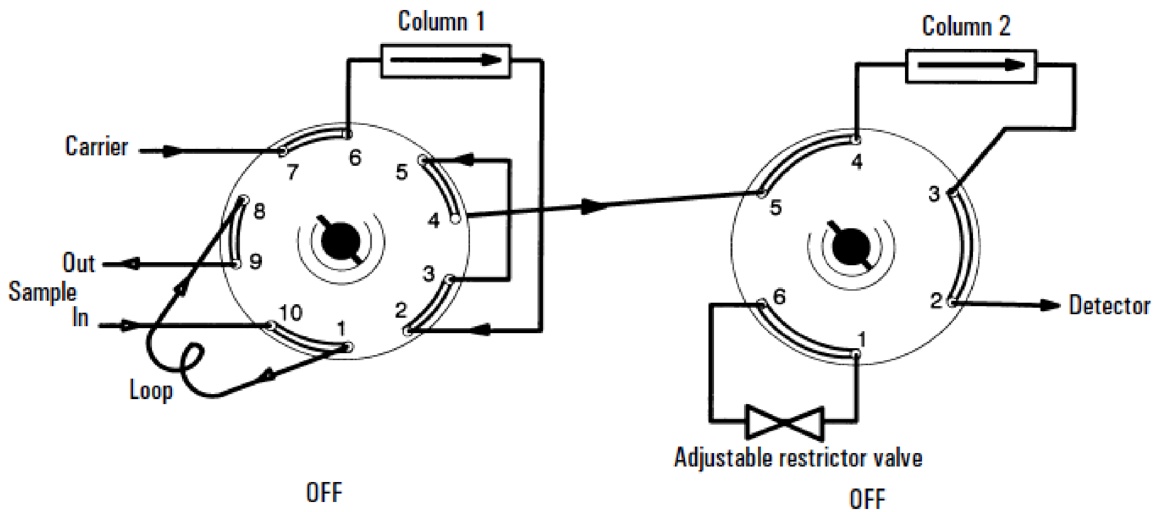


Gas sample and column isolation



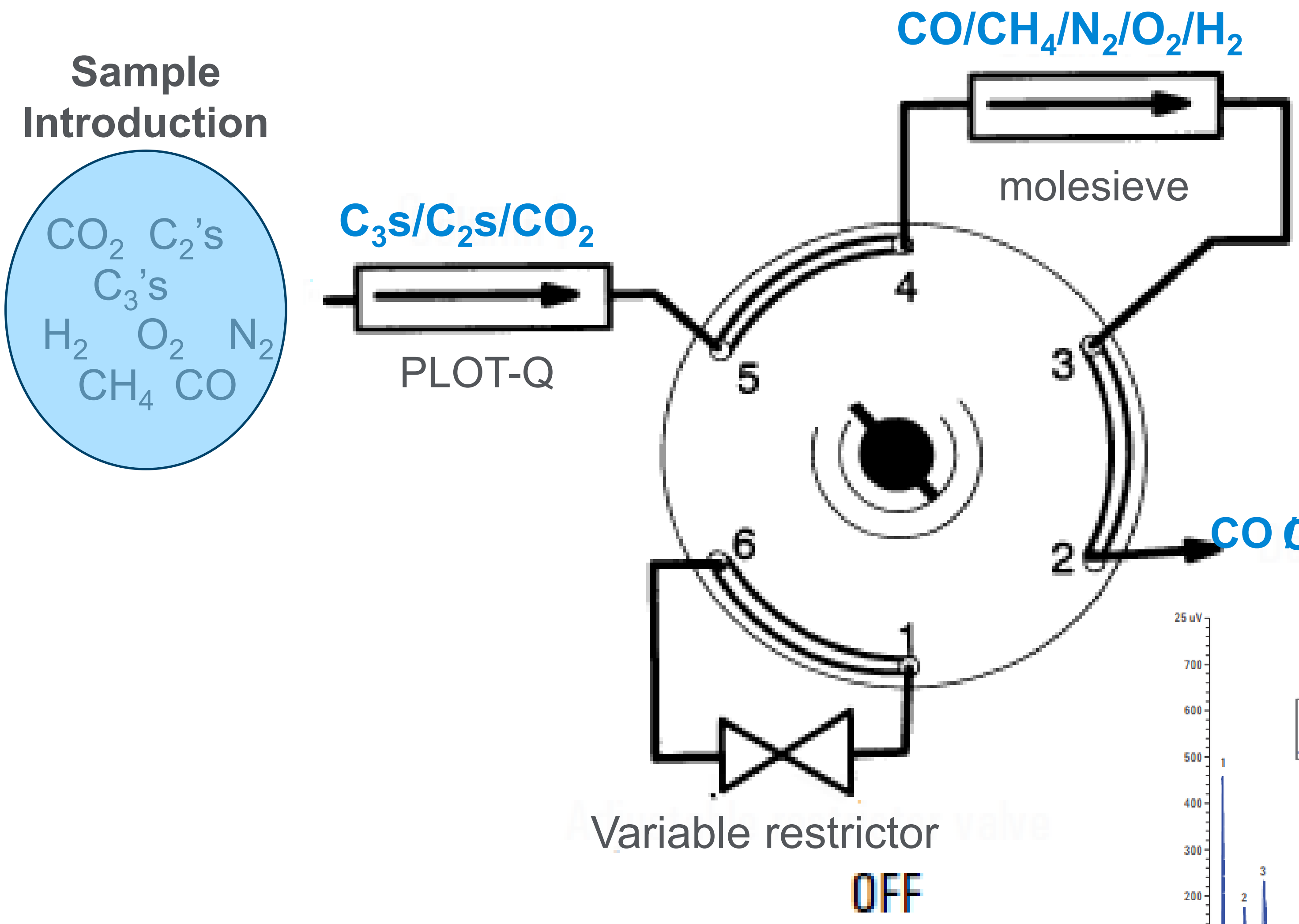
Column isolation*

*Temperature limited to 235°C by micrometering needle valves

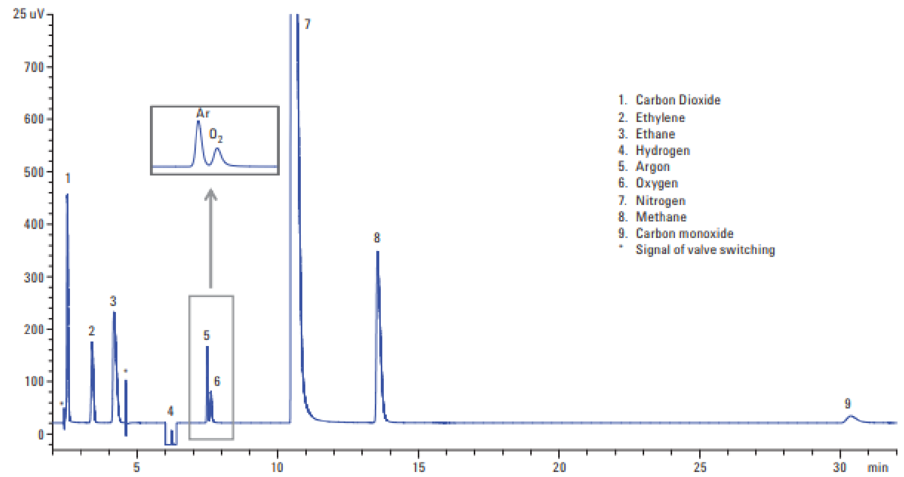


Gas sample/backflush and column isolation

One Injection, Two Columns and Valve…Column Isolation



System must be flow balanced
Use flow meter G6691A



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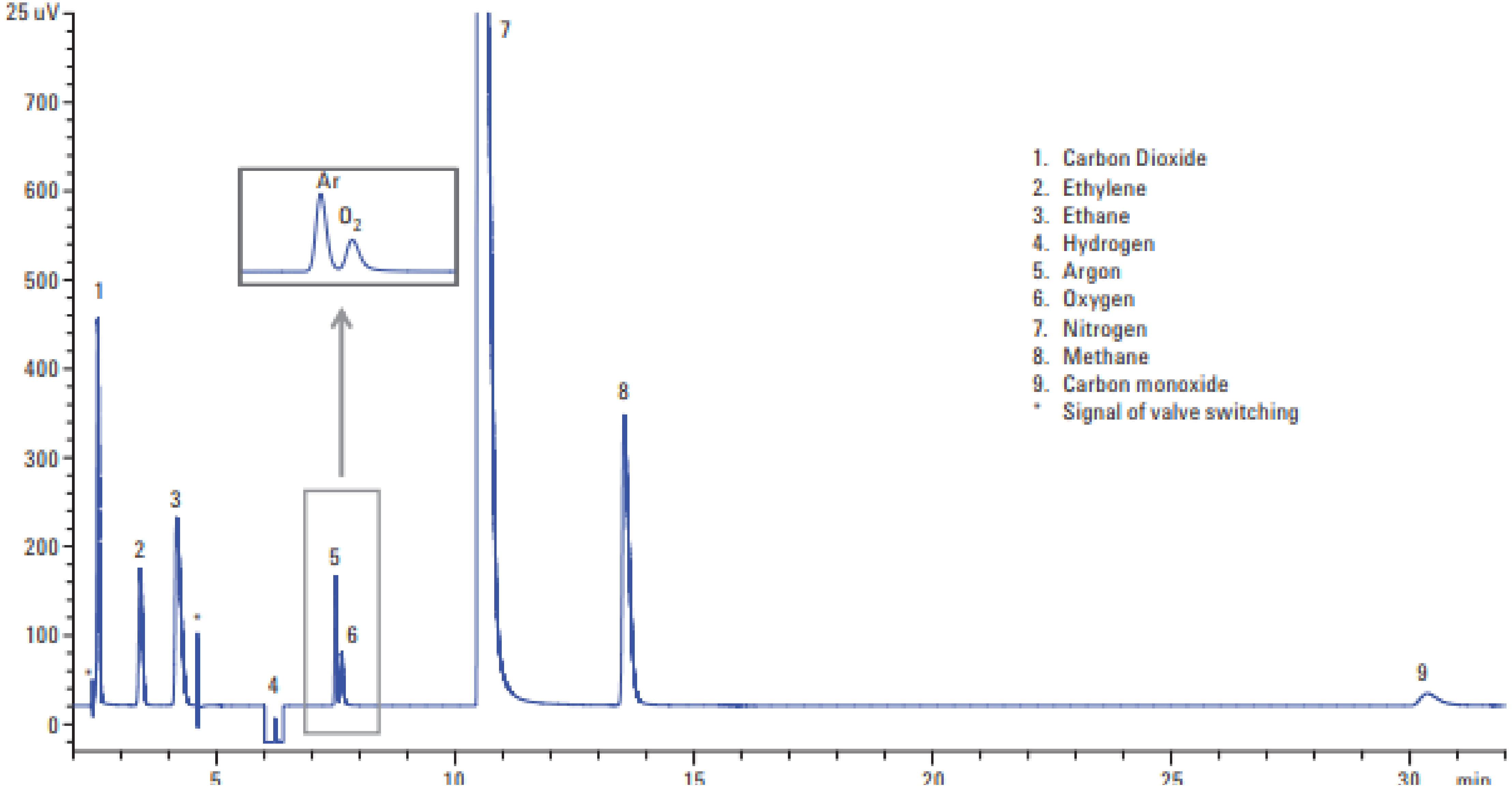
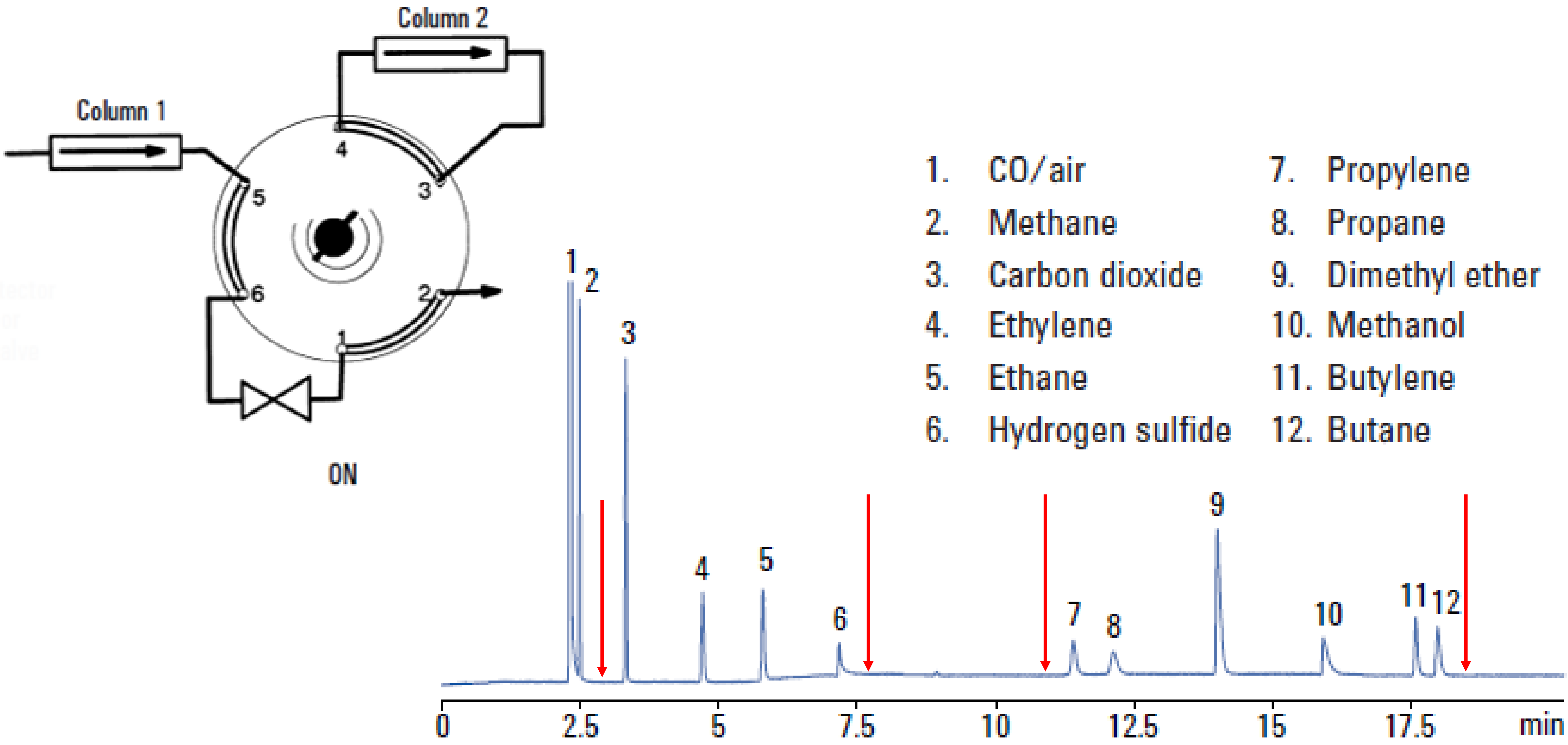
Column Isolation



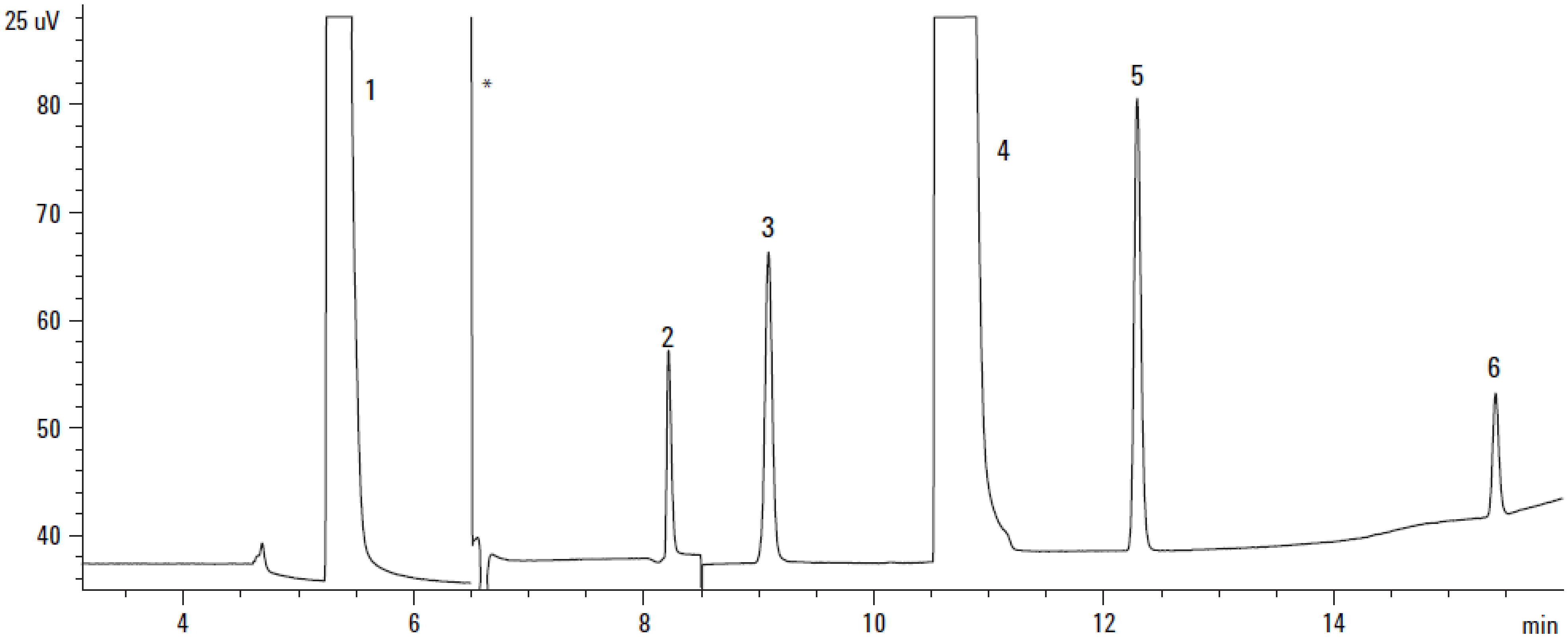
Column Isolation: Setting Up Valve Timing



Column Isolation – Flexibility of Elution Order

Carrier gas:	Helium
Inlet:	Purged packed 55 °C
Sample loop:	0.1 mL
Oven:	50 °C (10 min) with 10 °C/min to 120 °C (5 min)
TCD:	180 °C

1 H_2: 50%
2 CO_2: 10%
3 O_2: 172 ppm
4 N_2: Balance
5 CH_4: 5%
6 CO: 50 ppm
* Signal of valve switching



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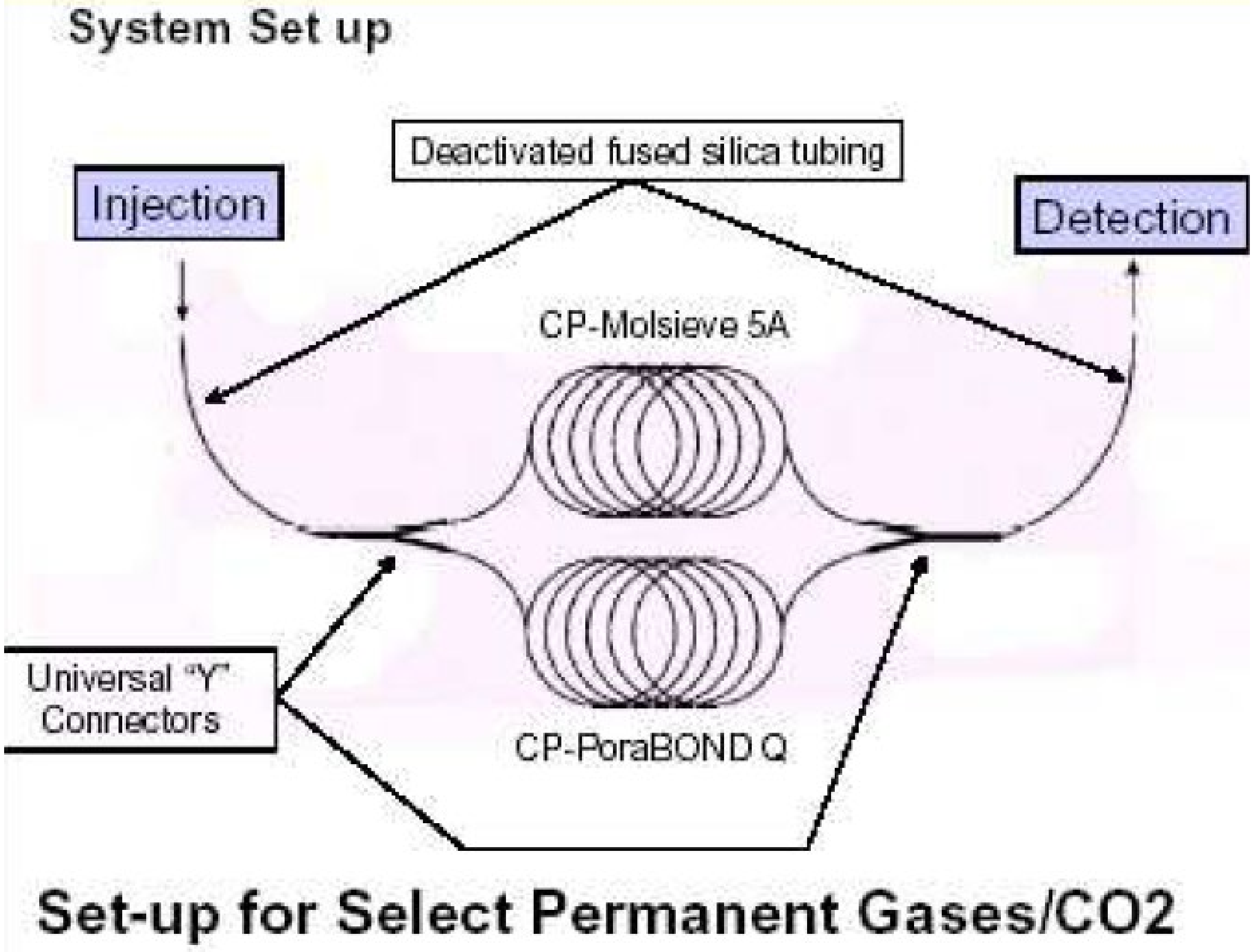
One Injection, Two Columns in Parallel – Select Permanent Gas Column

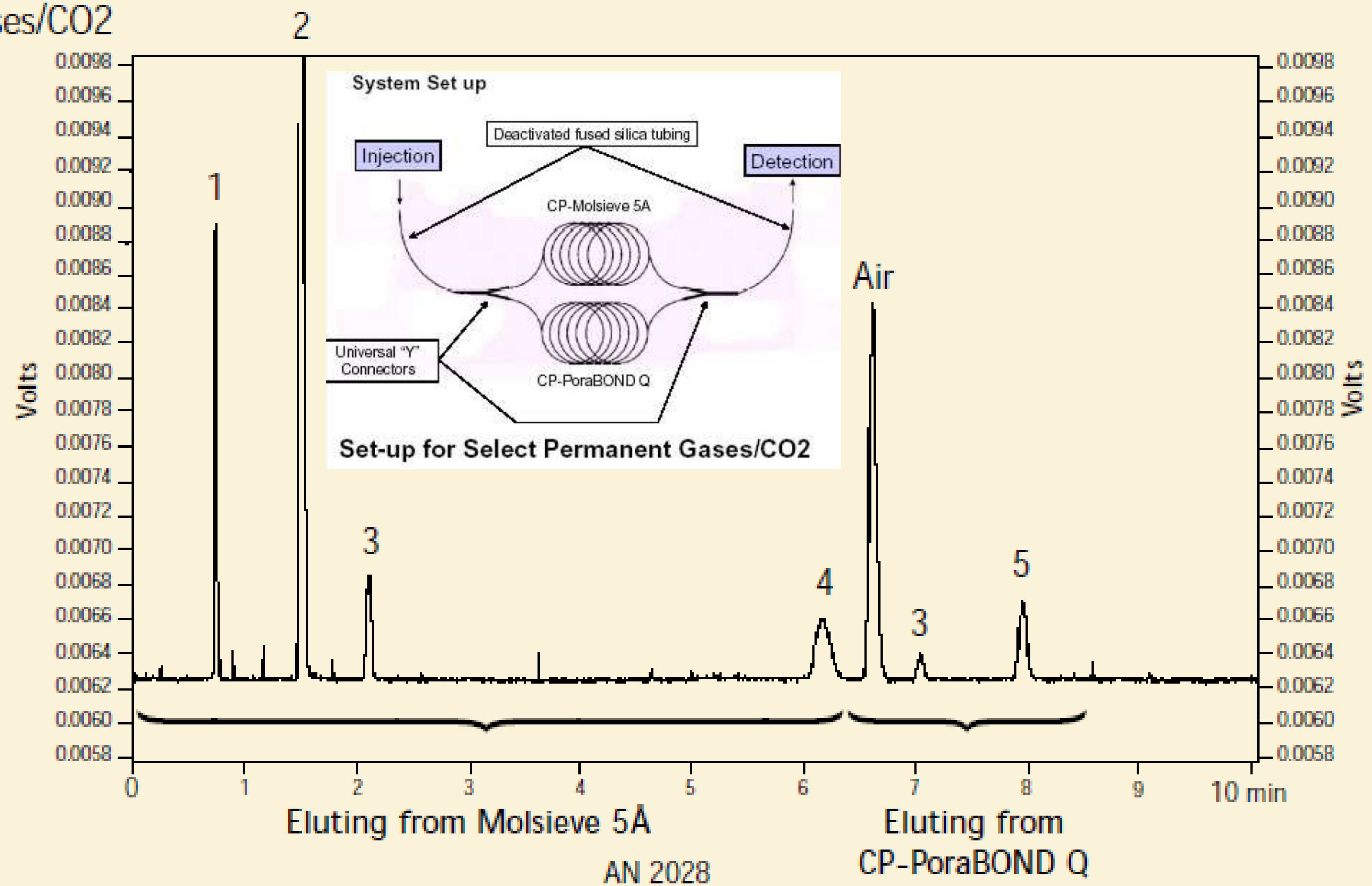


Select Permanent Gas Column

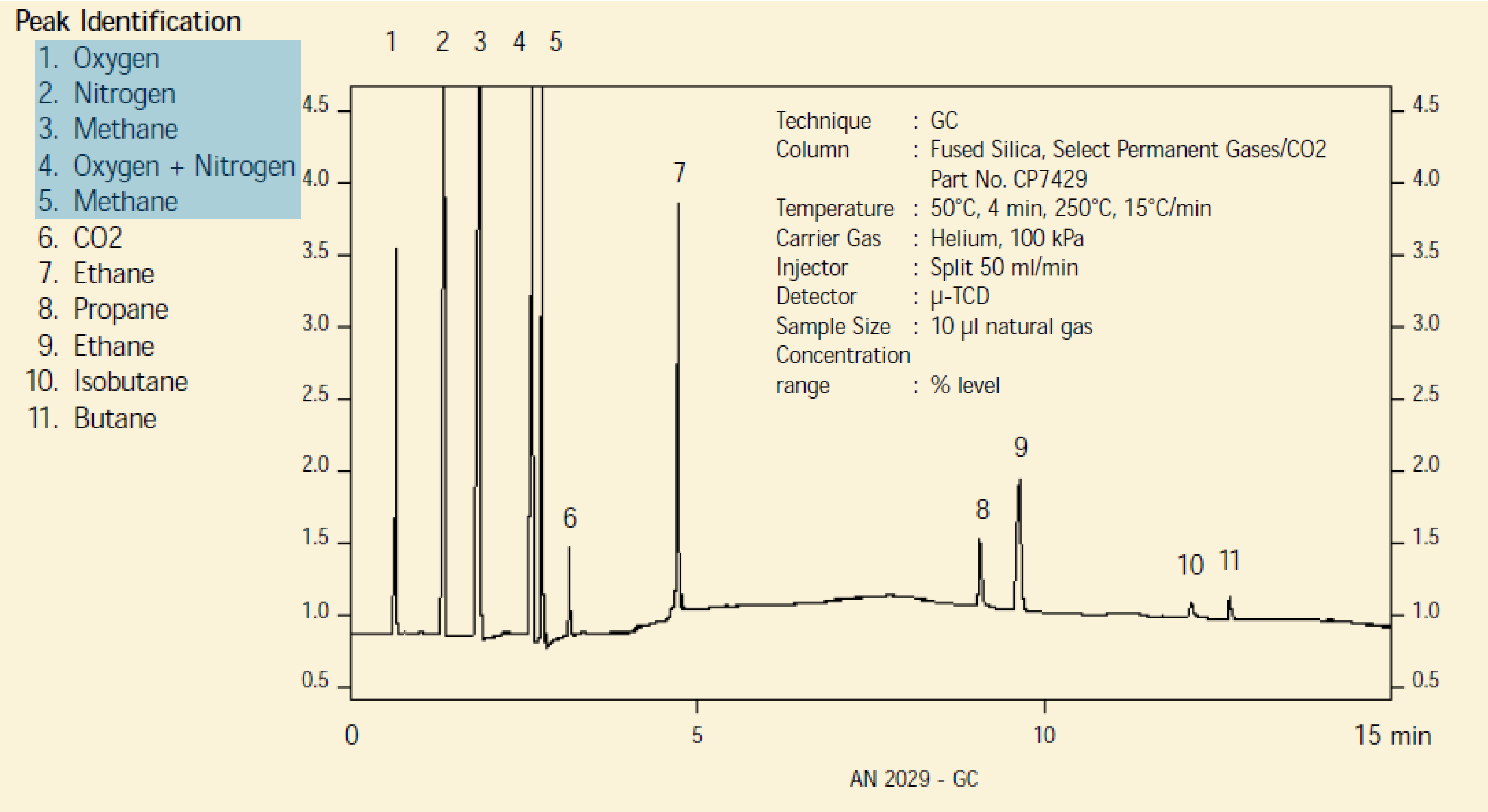
Technique : GC
Column : Select Permanent Gases/CO2
Part No. CP7429
Temperature : 50°C
Carrier Gas : Helium, 100 kPa
Injector : Split 50 ml/min
Detector : TCD
Sample Size : 20 µl
Concentration range : % level

Peak identification:

1. Oxygen
2. Nitrogen
3. Methane
4. Carbon monoxide
5. Carbon dioxide



Select Permanent Gas Column



So, You Think That Was Complicated, What if I Need to Analyze for Hydrogen Too…

- The trouble with hydrogen
  - Must use TCD**
    - Sensitivity is carrier gas dependent
    - Creates unique issues related sensitivity
    - Recall the negative hydrogen peak from earlier

***Can also use HID/DID, but we will not be covering this here*

Thermal Conductivity Detector (TCD)

- When using He carrier sensitivity for hydrogen is on the order of only ~10%
- No problem, I'll use argon or nitrogen carrier and get down to ppm levels for hydrogen…
- This is true; however, the sensitivity for all the other compounds is now very poor…a real "catch 22"…
- Let's see why this is the case…

Thermal Conductivity Detector – TCD

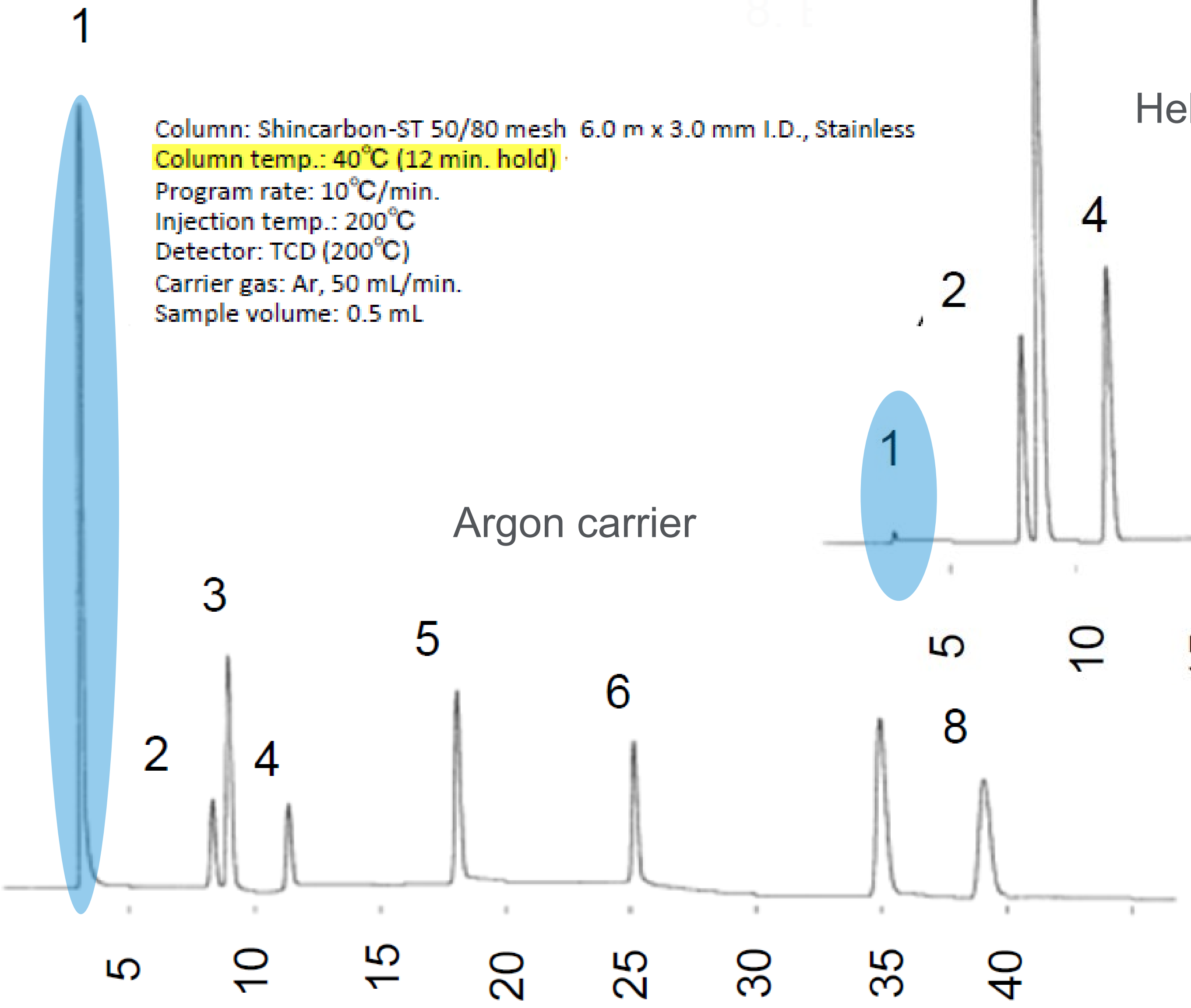
Name	Thermal Conductivity at 400 K ($mW\ m^{-1}\ K^{-1}$)
Argon	22.4
Hydrogen	230.9
Helium	189.6
Nitrogen	32.8
Carbon monoxide	32.3
Carbon dioxide	25.2
Acetylene	33.3
Ethylene	34.7
Ethane	36.0
Propane	31.0
Butane	28.3
Pentane	24.9
Hexane	23.4

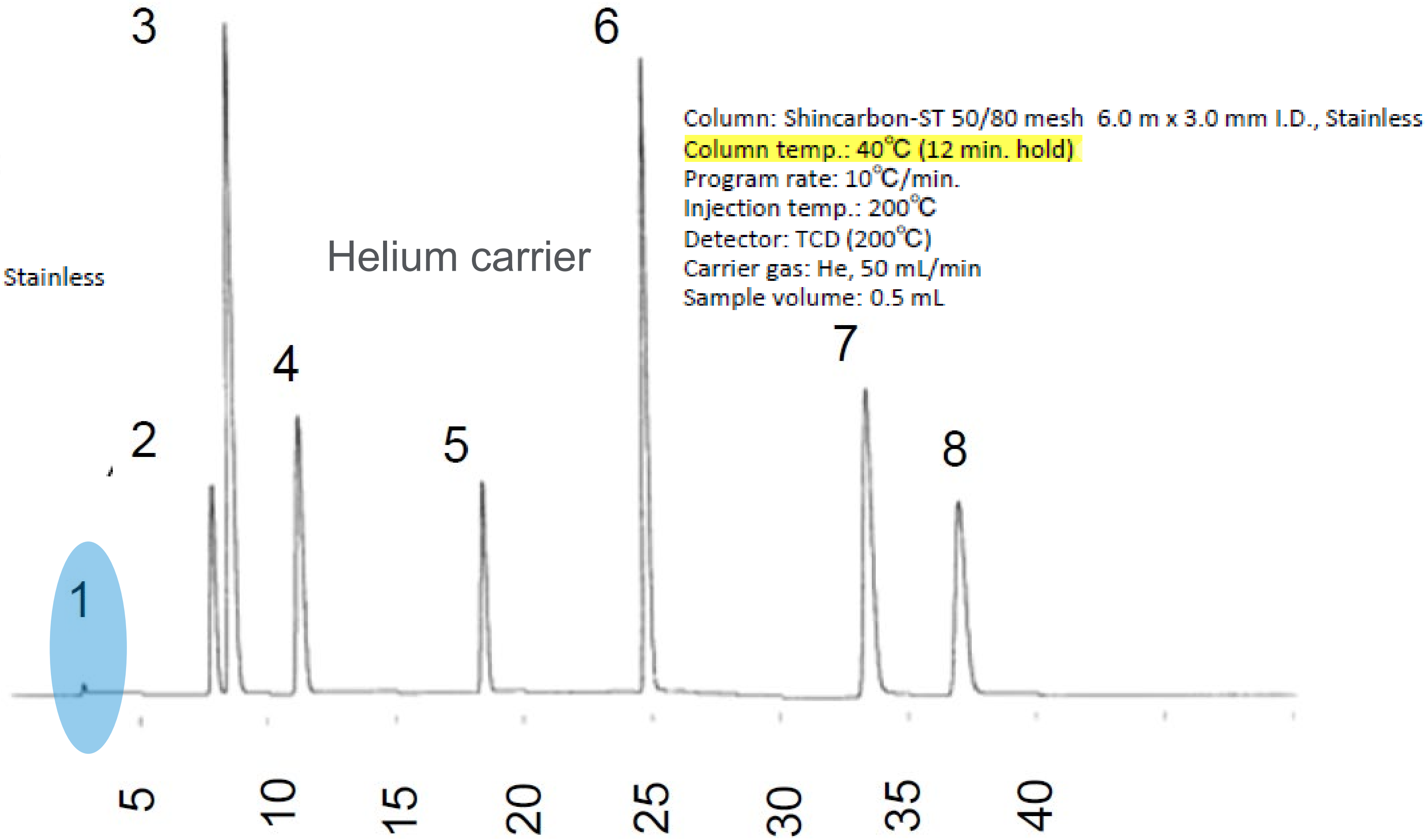
		Thermal conductivity in $mW\ m^{-1}\ K^{-1}$						
		100 K	200 K	300 K	400 K	500 K	600 K	Ref.
	Air	9.5	18.5	26.4	33.5	39.9	46.0	1
Ar	Argon ($P = 0$)	6.3	12.4	17.7	22.4	26.5	30.3	2, 3*
BF_3	Boron trifluoride			19.0	24.6			4
ClH	Hydrogen chloride		9.2	14.5	19.5	24.0	28.1	4
F_6S	Sulfur hexafluoride ($P = 0$)			13.0	20.6	27.5	33.8	5
H_2	Normal hydrogen ($P = 0$)	68.2	132.8	186.6	230.9	270.9	309.1	6
H_2O	Water ($P = 0$)			18.6	26.1	35.6	46.2	7
D_2O	Deuterium oxide ($P = 0$)			18.2	26.6	36.3	47.6	8
H_2S	Hydrogen sulfide			14.6	20.5	26.4	32.4	4
H_3N	Ammonia			25.1	37.2	53.1	68.6	9
He	Helium ($P = 0$)	74.7	118.3	155.7	189.6	221.4	251.6	10
Kr	Krypton ($P = 0$)		6.5	9.5	12.3	14.8	17.1	11
NO	Nitric oxide		17.8	25.9	33.1	39.6	46.2	4
N_2	Nitrogen	9.4	18.3	26.0	32.8	39.0	44.8	1
N_2O	Nitrous oxide		9.8	17.4	26.0	34.1	41.8	4
Ne	Neon ($P = 0$)	22.3	37.4	49.4	59.9	69.5	78.5	12
O_2	Oxygen	9.1	18.2	26.5	34.0	41.0	47.7	1
O_2S	Sulfur dioxide			9.6	14.3	20.0	25.6	4
Xe	Xenon ($P = 0$)		3.7	5.5	7.2	8.8	10.3	3*, 11
CCl_2F_2	Dichlorodifluoromethane			9.9	15.0	20.1	25.2	13
CF_4	Tetrafluoromethane ($P = 0$)			16.0	24.1	32.2	39.9	5
CO	Carbon monoxide ($P = 0$)			25.0	32.3	39.2	45.7	14
CO_2	Carbon dioxide		9.6	16.8	25.2	33.5	41.6	15
$CHCl_3$	Trichloromethane			7.5	11.1	15.1		4
CH_4	Methane ($P = 0$)	10.4	21.8	34.4	50.0	68.4	88.6	16
CH_4O	Methanol				26.2	38.6	53.0	4
$C_2Cl_2F_4$	1,2-Dichloro-1,1,2,2-tetrafluoroethane			10.3	15.7	21.1		13
$C_2Cl_3F_3$	1,1,2-Trichloro-1,2,2-trifluoroethane			9.0	13.6	18.3		13
C_2H_2	Acetylene			21.4	33.3	45.4	56.8	4
C_2H_4	Ethylene		11.3	20.6	34.7	49.9	68.6	17
C_2H_6	Ethane		10.7	21.2	36.0	53.8	73.3	18
C_2H_6O	Ethanol			14.4	25.8	38.4	53.2	4
C_3H_6O	Acetone			11.5	20.2	30.6	42.7	4
C_3H_8	Propane			18.5	31.0	46.4	64.6	19
C_4F_8	Perfluorocyclobutane			12.5	19.5			13
C_4H_{10}	Butane			16.7	28.3	43.0	60.9	20
C_4H_{10}	Isobutane			17.1	28.9	43.2	60.2	21
$C_4H_{10}O$	Diethyl ether			15.1	25.0	37.1		4
C_5H_{12}	Pentane				24.9	37.8	52.7	4
C_6H_{14}	Hexane				23.4	35.4	48.7	4

* More accurate data covering a restricted temperature range.

https://ws680.nist.gov/publication/get_pdf.cfm?pub_id=907540

ShinCarbon ST





1. Hydrogen
2. Oxygen
3. Nitrogen
4. Carbon monoxide
5. Methane
6. Carbon dioxide
7. Ethylene
8. Ethane

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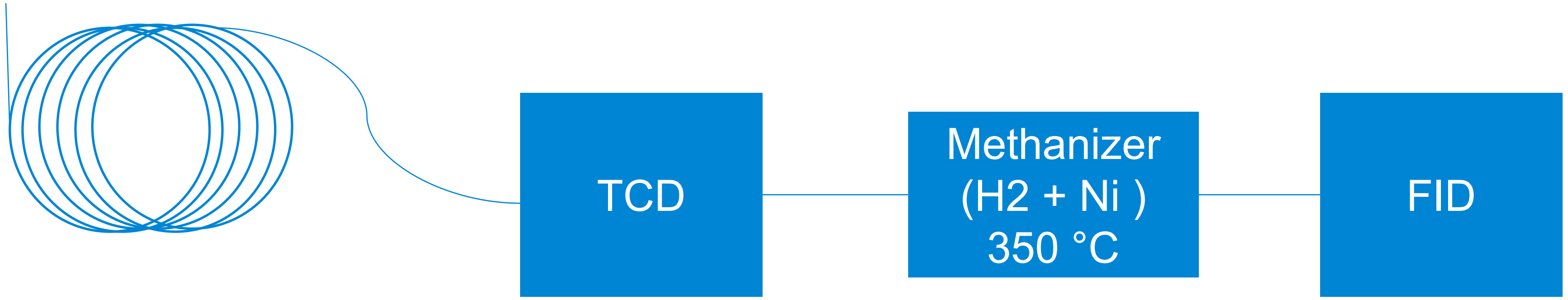
Workarounds for Low Level Hydrogen Detection

- Two unique injections:
  - One for hydrogen using Argon or N_2 carrier second injection for all other gases using helium carrier
- One injection using column isolation and argon carrier + methanizer
  - TCD coupled to FID
    - Methanizer placed after TCD but before FID to convert CO/CO_2 to methane for enhanced detection of these gases by FID
- Sabatier Reaction (1897): $CO_2 + 4\ H_2 \xrightarrow[Ni]{400\ ^oC} CH_4 + 2H_2O$
- Transformer Oil Gas Analyzer (TOGA)

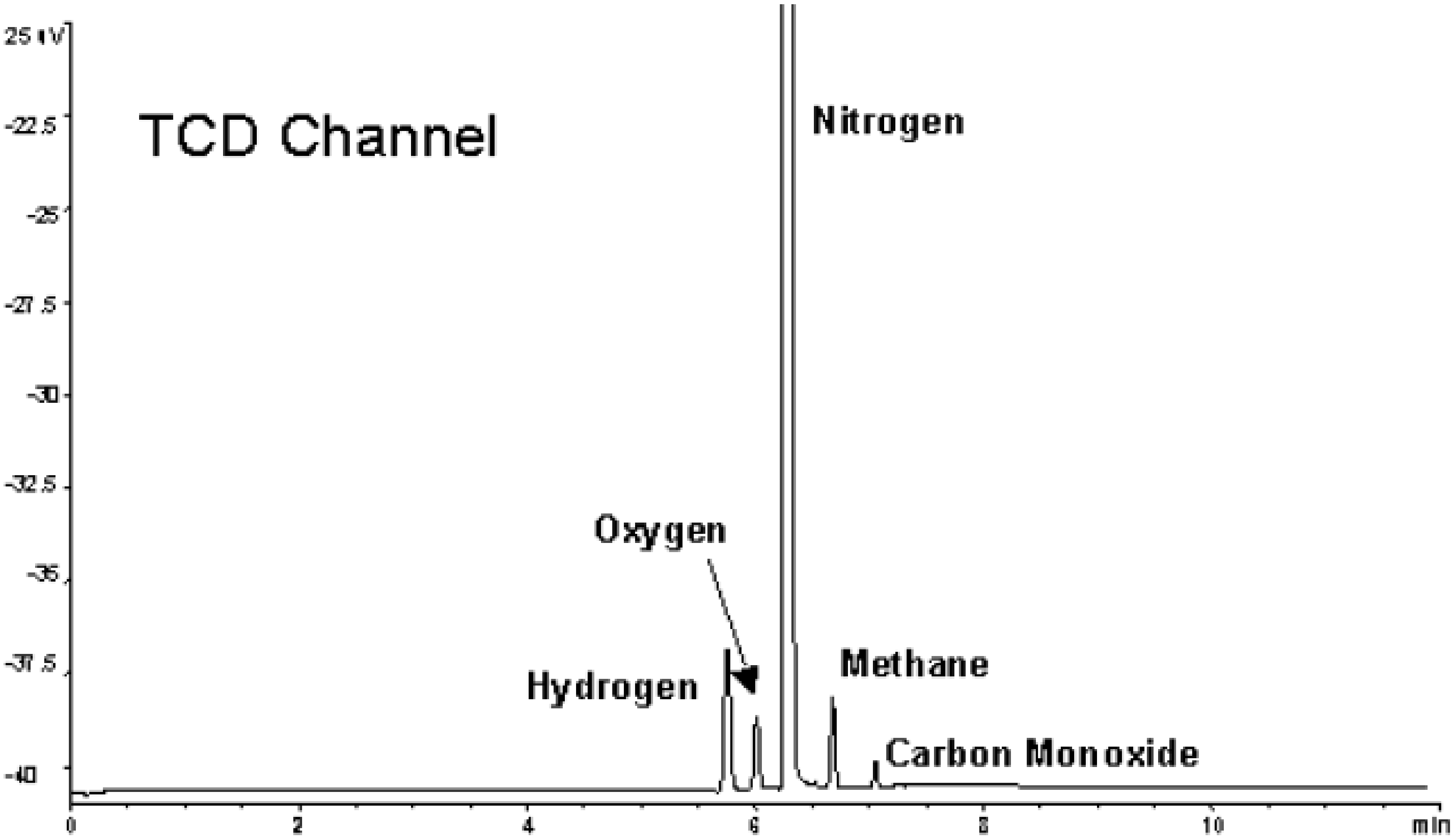
Conversion of CO/CO2 to Methane

➢ Discovered by French chemist Paul Sabatier in 1897 (Sabatier Reaction)

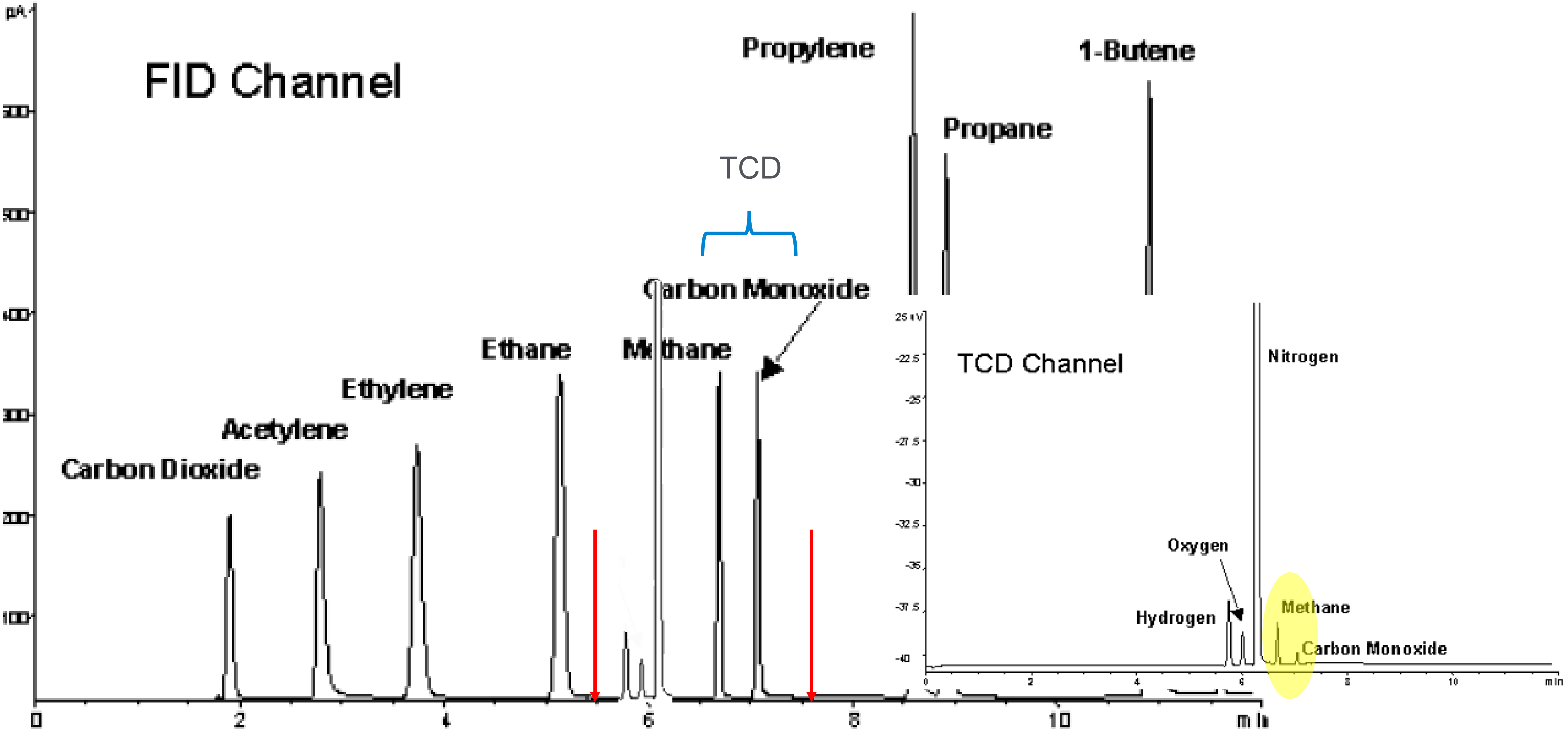
$$CO_2 + 4\,H_2 \xrightarrow[Ni]{400\,^\circ C} CH_4 + 2H_2O$$



Transformer Oil Gas Analyzer (TOGA) Chromatograms



Transformer Oil Gas Analyzer (TOGA) Chromatograms



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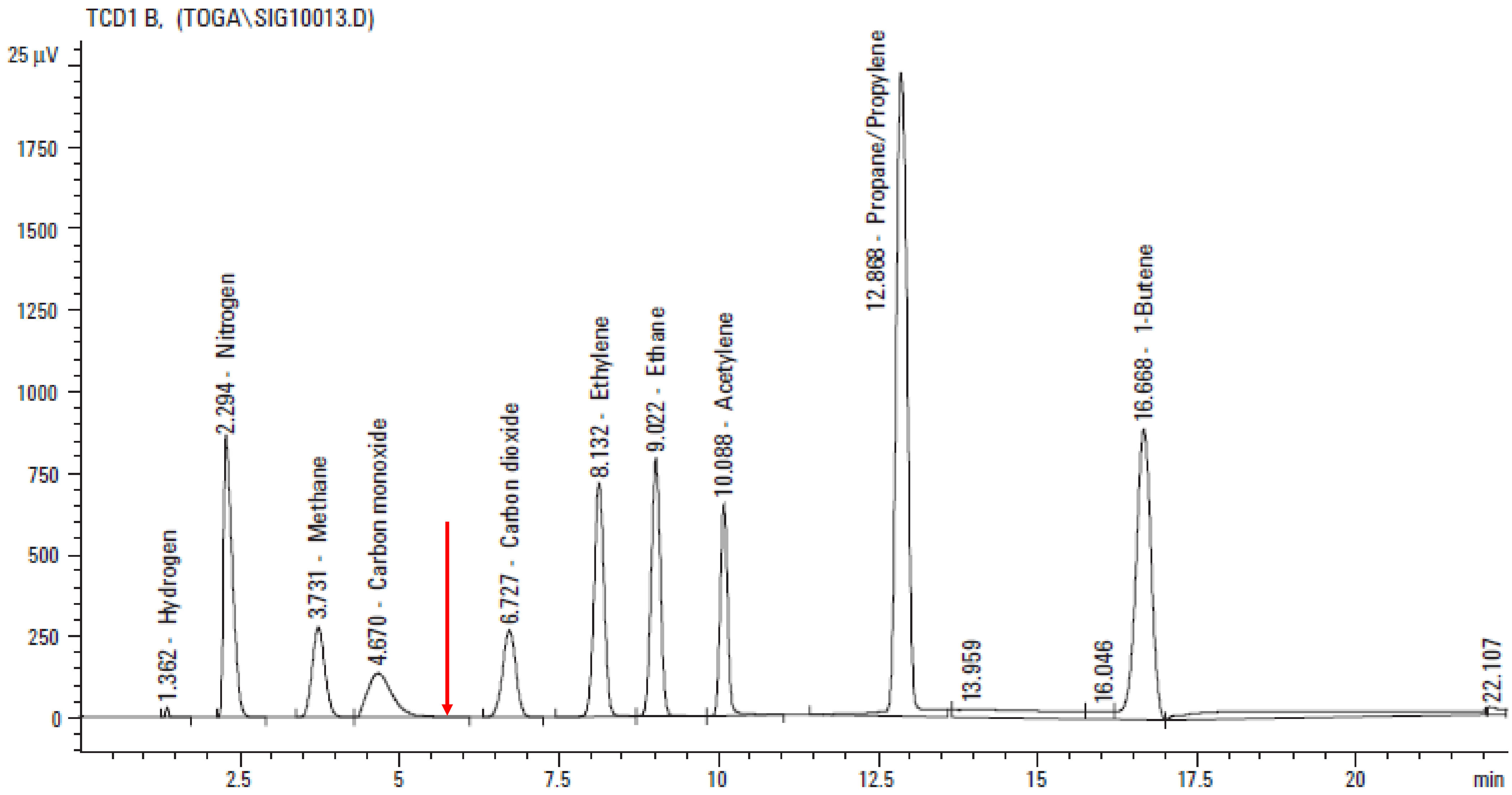
Transformer Oil Gas Analyzer (TOGA) Chromatograms



Micro GC

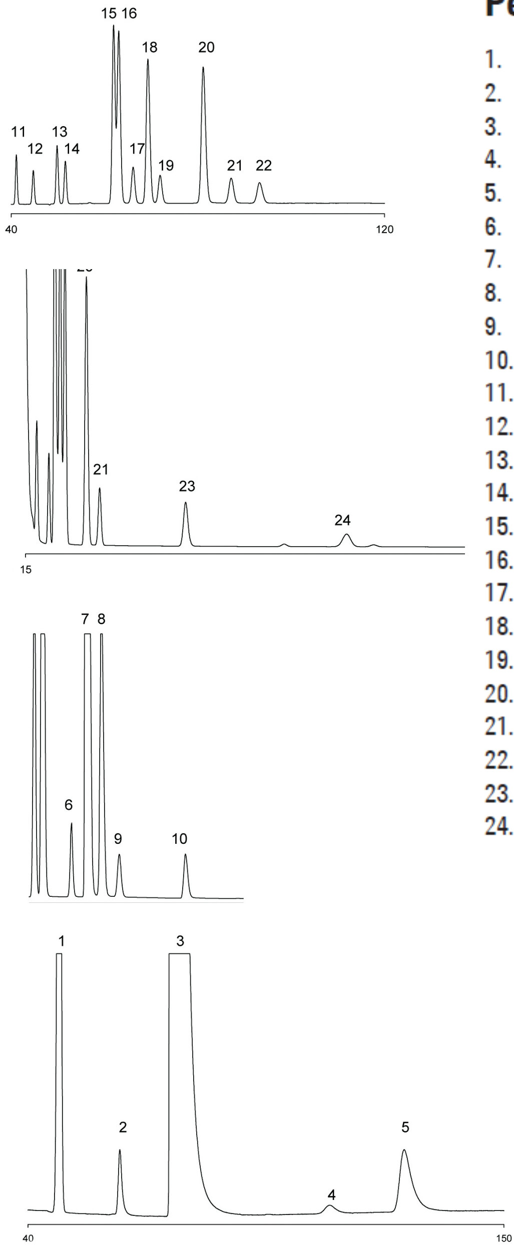
- Up to four separate channels
- 14 column chemistries available
- Gas only injections
- Single injection simultaneously distributed to each channel
- TCD detection (helium carrier)**
  - 0.5 ppm WCOT
  - 2 ppm PLOT
  - 10 ppm micropacked
  - 10^5 dynamic range
- Field portable option

***Best case scenario, some solutes will not meet these. All TCD detection levels are carrier gas dependent*

Micro GC

Single injection

4 signals



Peak identification

1. hydrogen
2. oxygen
3. nitrogen
4. methane
5. carbon monoxide
6. carbon dioxide
7. ethylene
8. ethane
9. acetylene
10. hydrogen sulfide
11. propane
12. propylene
13. iso-butane
14. normal-butane
15. trans-2-butene
16. 1-butene
17. iso-butene
18. cis-2-butene
19. neo-pentane
20. iso-pentane
21. normal-pentane
22. 1,3-butadiene
23. hexane
24. iso-octane

Micro GC

Single injection

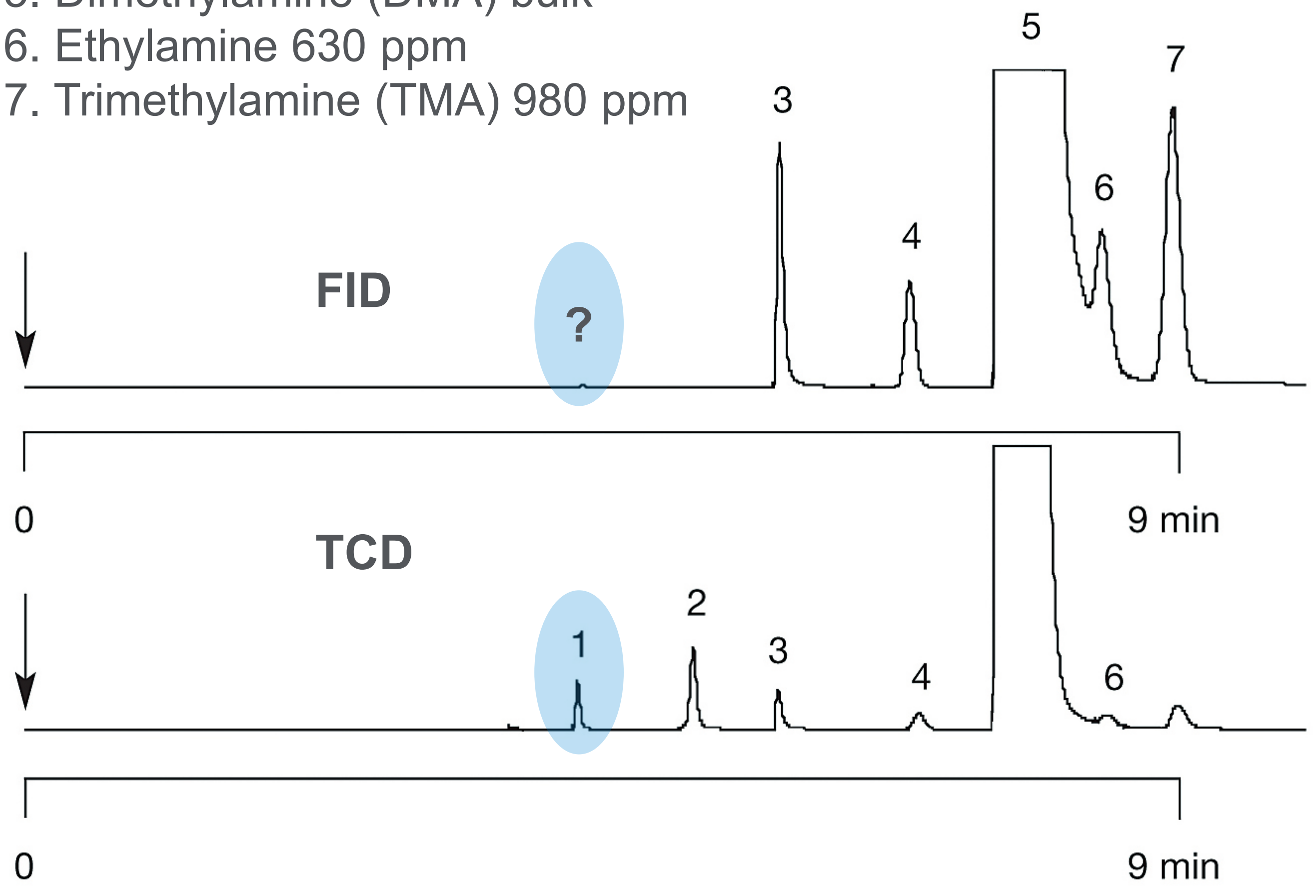
4 signals

4 channels
molesieve – Helium Carrier Low sensitivity H2 (+10%) High sensitivity all others (~ppm)
molesieve – Argon or N_2 Carrier High sensitivity H2 (~ppm) Low sensitivity all others (~1-5%)
Plot-Q – Helium Carrier CO2 + C2+ HC's (~ppm)
CP-Sil 5 – Helium Carrier ~C5+ HC's (~ppm)

Ammonia

Technique	GC capillary
Column	Agilent CP-Volamine, 0.32 mm x 60 m fused silica
Temperature	WCOT (p/n CP7448)
Carrier Gas	40 °C (1 0 min) → 250 °C, 20 °C/min : He, 100 kPa (1 bar, 14 psi)
Injector	Split, 1:15 T = 180 °C
Detector	FID/TCD
Sample Size	T = 250 °C
Solvent Sample	1 μL, liquid Bulk DMA
Courtesy	Dr. F. de Boever, UCB research center Drogenbos,
	Dr. G. Baele, UCB Gent
	Belgium

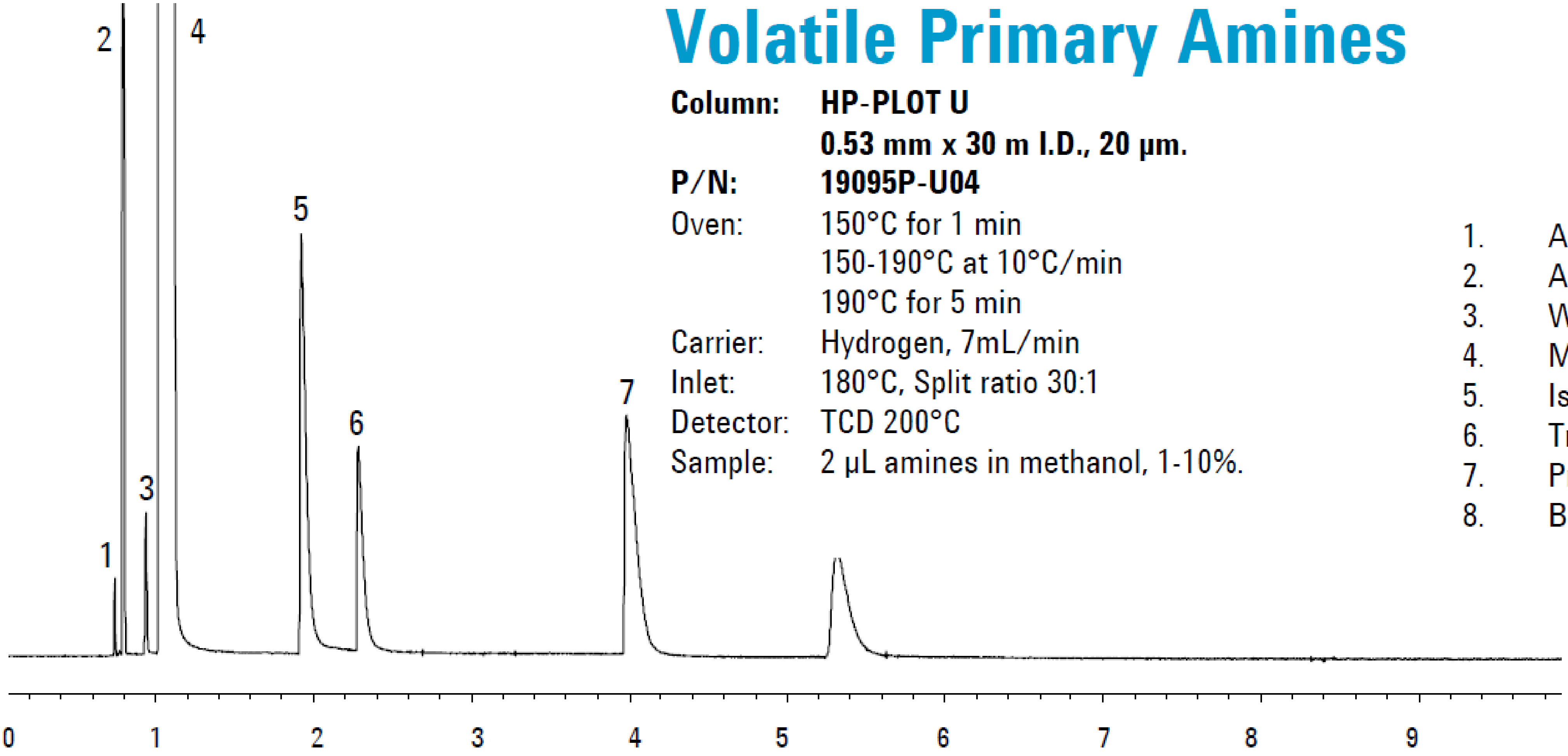
1. Ammonia (NH^3) 700 ppm
2. Water 2000 ppm
3. Methylamine (MMA) 585 ppm
4. Methanol 575 ppm
5. Dimethylamine (DMA) bulk
6. Ethylamine 630 ppm
7. Trimethylamine (TMA) 980 ppm



Ammonia is very reactive!
Lowest practical DL ~100 ppm (TCD)
Will depend on sample handling

Ammonia – HP-PLOT U

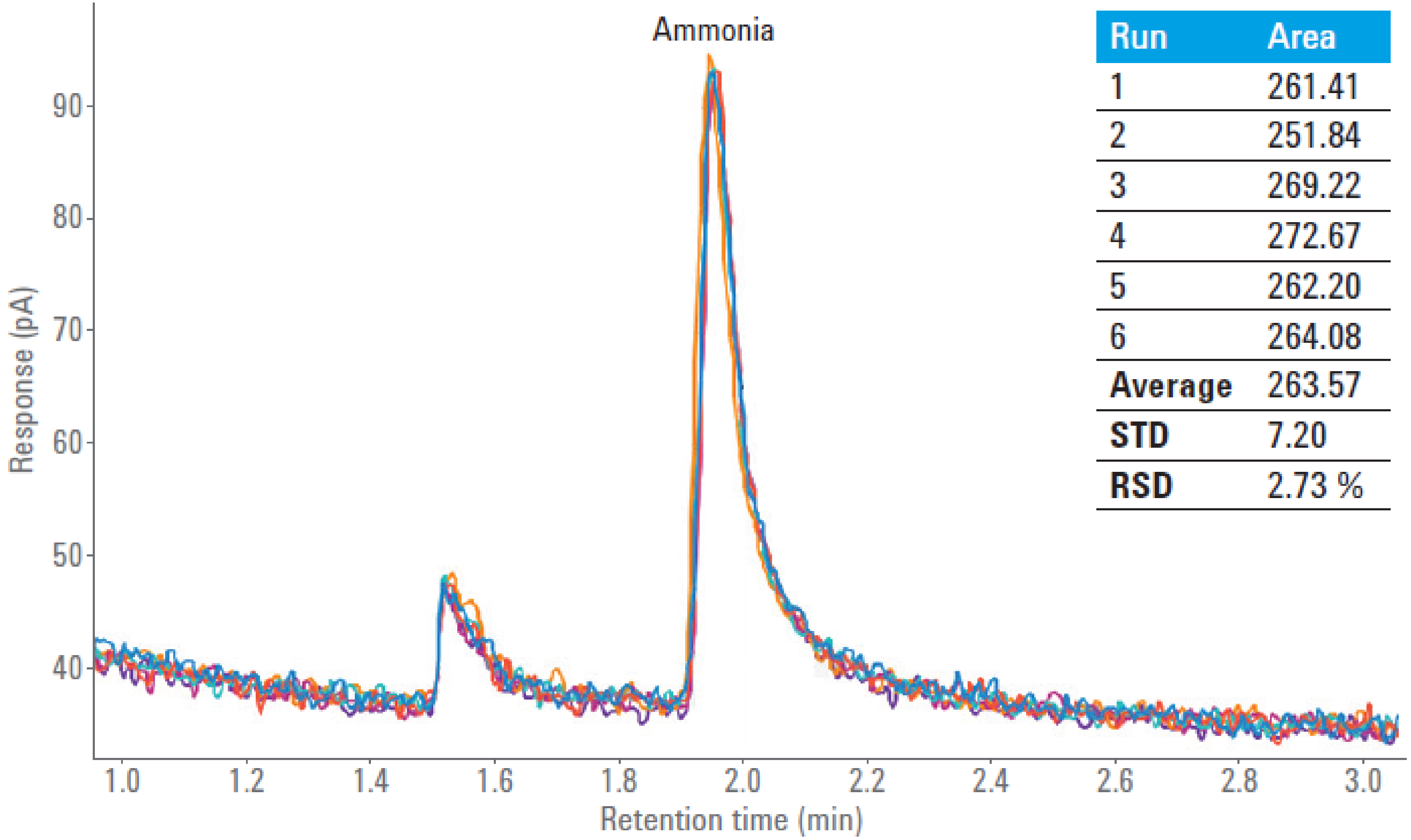
Volatile Primary Amines



Column: **HP-PLOT U**
0.53 mm x 30 m I.D., 20 µm.
P/N: **19095P-U04**
Oven: 150°C for 1 min
150-190°C at 10°C/min
190°C for 5 min
Carrier: Hydrogen, 7mL/min
Inlet: 180°C, Split ratio 30:1
Detector: TCD 200°C
Sample: 2 µL amines in methanol, 1-10%.

1. Air
2. Ammonia
3. Water
4. Methanol
5. Isopropylamine
6. Triethylamine
7. Propylamine
8. Butylamine

Ammonia – Select Low Ammonia NCD



Run	Area
1	261.41
2	251.84
3	269.22
4	272.67
5	262.20
6	264.08
Average	263.57
STD	7.20
RSD	2.73 %

Precision: ammonia 50 ppbv.

NCD=Nitrogen Chemiluminescence detector

Very short column results in…

Very short column residence time and therefore…

Less reactivity and an improved response

Permanent gases on MSD – Generally, not suitable

- Molecules are simply too small for suitable sensitivity (poor signal-to-noise)
- MSD can be modified for smaller mass range, but requires extensive hardware changes
- Most PLOT columns common to permanent gases generate particles which should be avoided

Summary

Analytes	Column	Technique
$H_2/O_2/N_2/CH_4/CO$	molesieve	• One injection one column • Micro GC
$H_2/O_2/N_2/CH_4/CO$ + Ar	molesieve (thick film)	• One injection one column • Micro GC
$H_2/O_2/N_2/CH_4/CO$ + CO_2 + C2s	molesieve + PLOT-Q	• Two injections two columns • One injection and valve (column isolation) • One injection parallel columns (Select perm gas column) • Micro GC
$H_2/O_2/N_2/CH_4/CO$ + CO_2 + C2s	GasPro	• Cryo (–80 °C)
$H_2/O_2/N_2/CH_4/CO$ + CO_2 + C2s	ShinCarbon	• Packed only
$H_2/O_2/N_2/CH_4/CO$ + CO_2 + C2s + Low level hydrogen	molesieve + PLOT-Q	• Single injection onto molesieve for H_2 detection only • Argon carrier + methanizer (TOGA) • Micro GC

Contact Agilent Chemistries and Supplies Technical Support

1-800-227-9770 Option 3, Option 3:

Option 1 for GC and GC/MS columns and supplies

Option 2 for LC and LC/MS columns and supplies

Option 3 for sample preparation, filtration, and QuEChERS

Option 4 for spectroscopy supplies

Option 5 for chemical standards

Available in the USA and Canada 8–5, all time zones

gc-column-support@agilent.com

lc-column-support@agilent.com

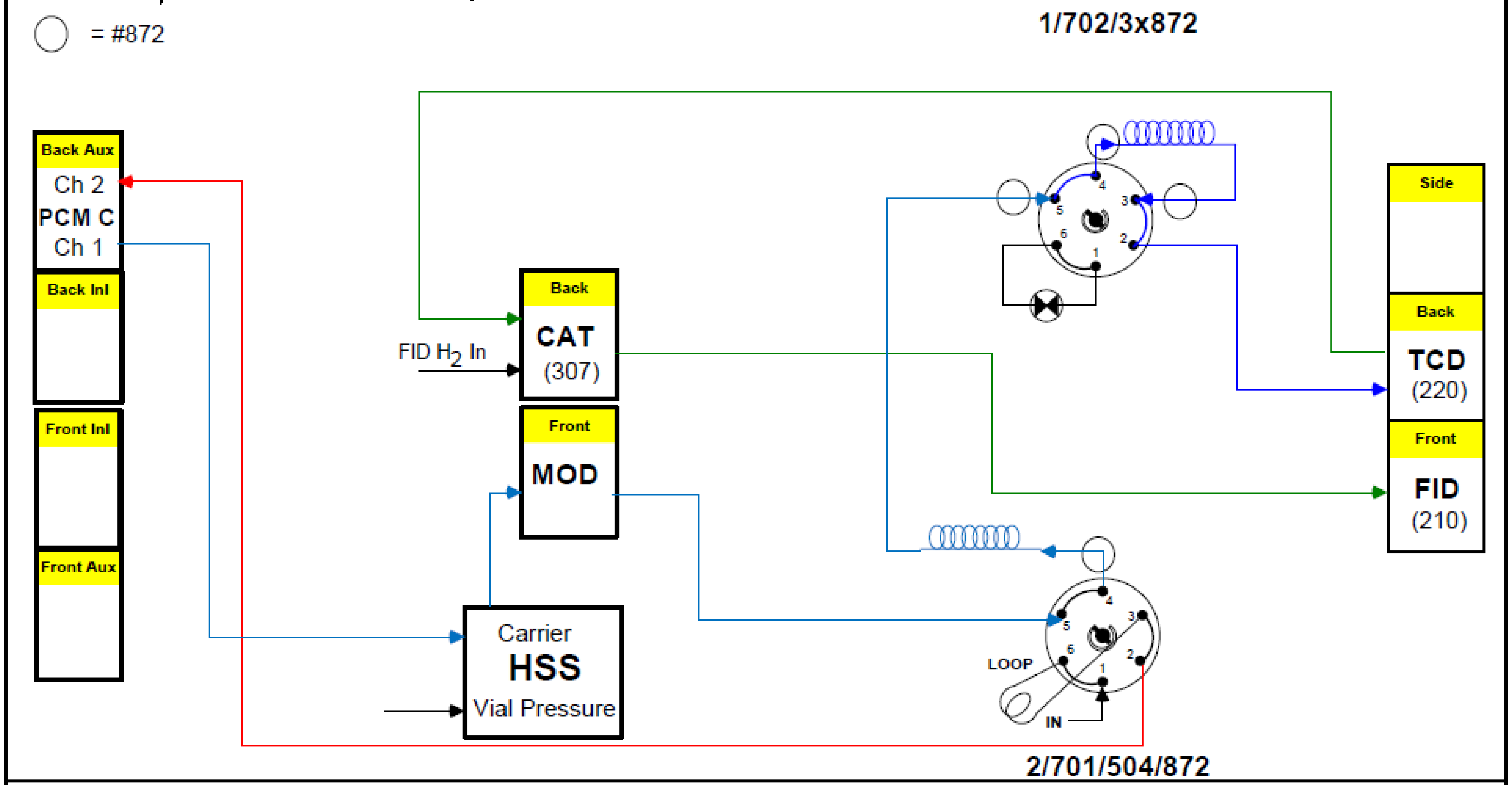
spp-support@agilent.com

spectro-supplies-support@agilent.com

chem-standards-support@agilent.com

Agilent Technologies	Valve System	Date :	S/N :
		Order No :	Item :

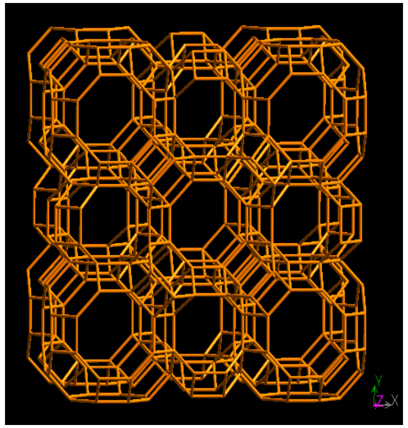
FLOW SOURCE	OVEN LEFT SIDE	INJECTION PORT	VALVE COMPARTMENT BLOCK 2	BLOCK 1	DETECTOR

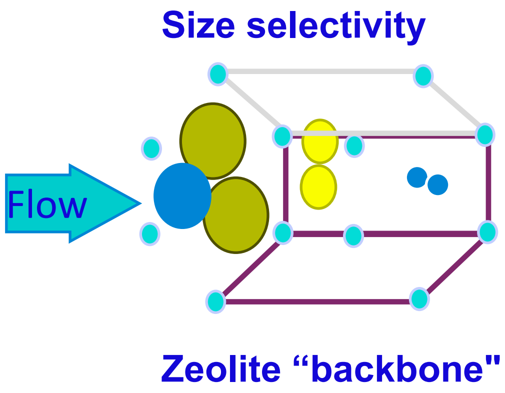


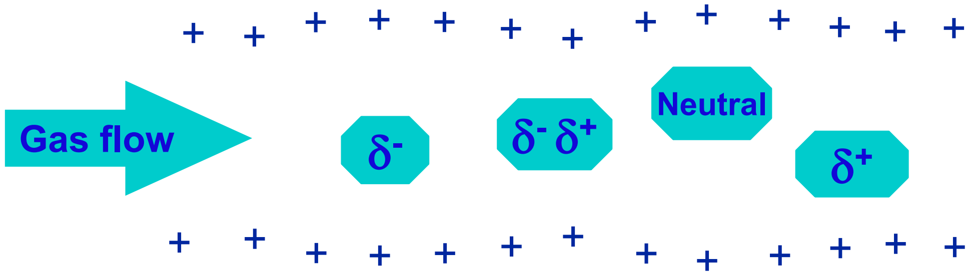
Options	SP1 options	Remarks
210,220,307,309,504,701,702,752,4x872	7890-0261	

Selectivity Interactions in PLOT Phases

Shape/Size	⟵	⟶		Surface
Zeolites	Bonded Carbon/ Molecular Sieves	Porous Polymers	Bonded Silica	Al_2O_3
molesieve	molesieve CarbonPLOT	PLOT-Q/U	GasPro SilicaPLOT	Alumina







Graphic of type KFI molecular sieve obtained from the International Zeolite Association website (www.izo-online.org).

Vapor pressure always plays a leading role in solute interactions.