Analysis of Permanent Gases:

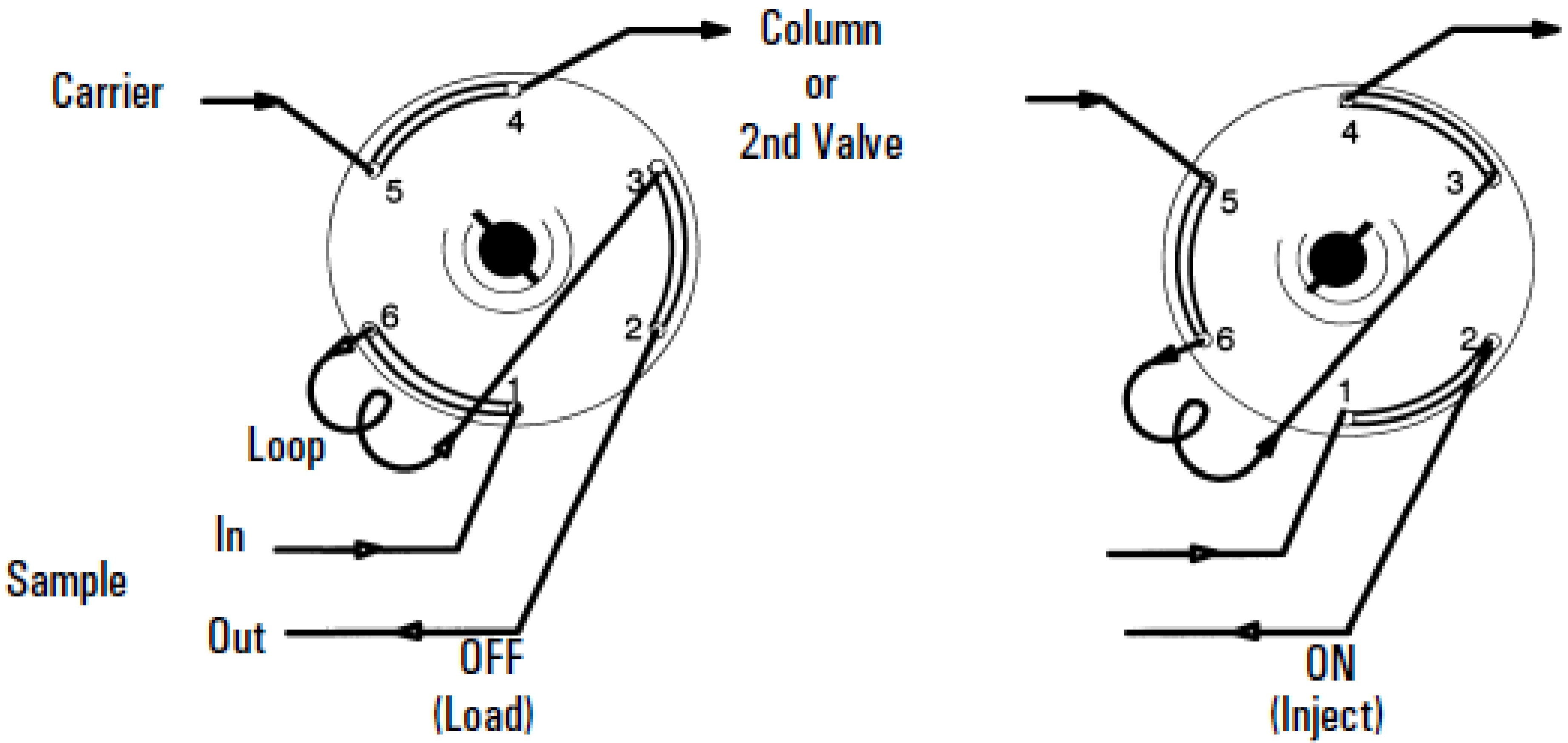
More Challenging Than You Might Think

Mark Sinnott
October 9, 2018

Analysis of Permanent Gases

- 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’s, C_3’s, etc. is also needed
  - Column Isolation
  - Parallel columns
  - Cryogenic separations
  - Unique selectivity packed columns
- Techniques for low level detection of hydrogen

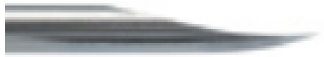
Gas Sampling Valve



Gas sampling valve

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 Tight Syringes

PLOT columns

Column Type	Phase Type	Chromatographic Process	Stationary Phases
WCOT	Liquid	Gas - Liquid partitioning	Polysiloxanes PEG
PLOT	Solid	Gas - Solid adsorbtion	Porous Polymers Al_2O_3, Zeolites, etc

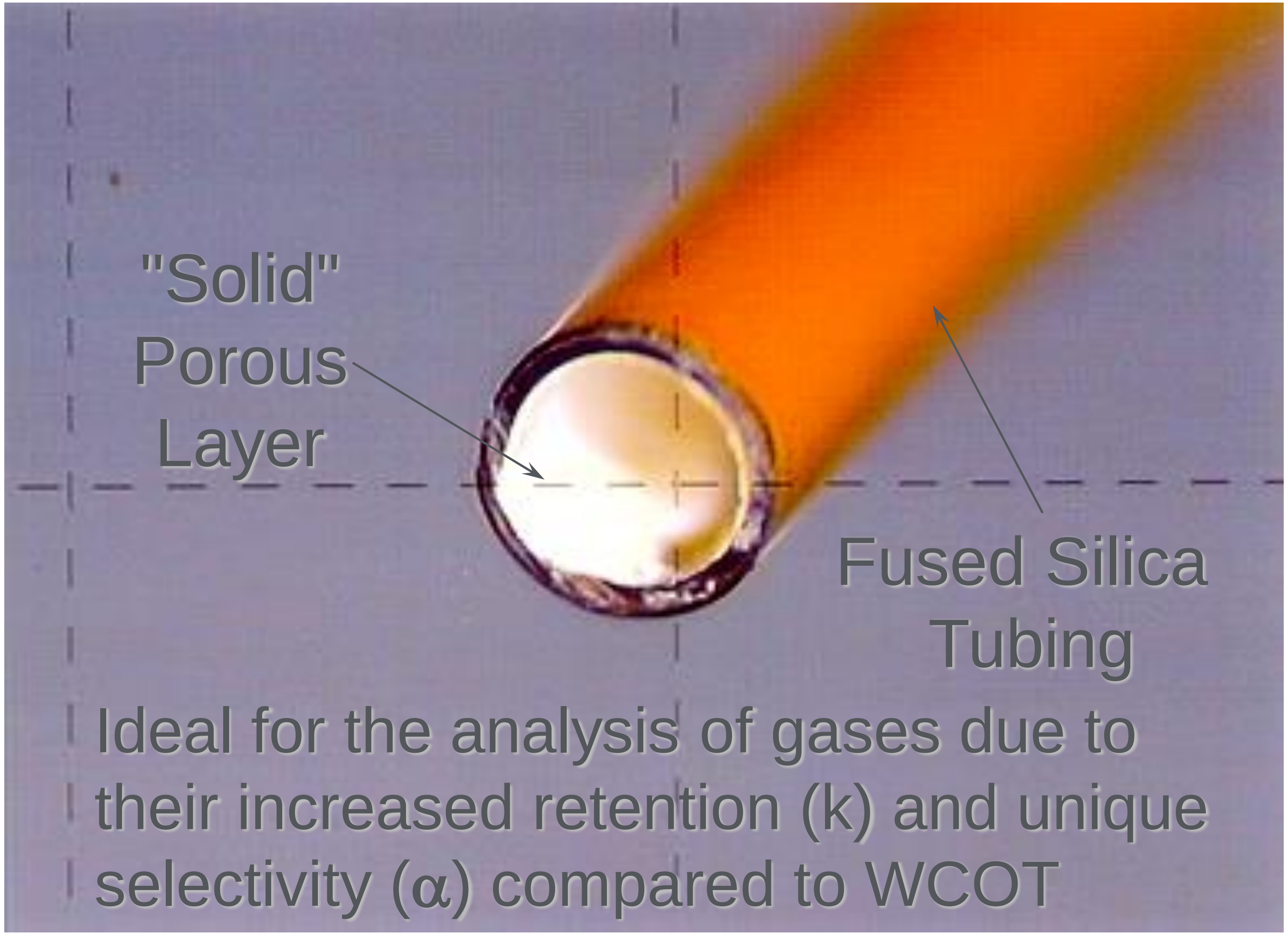
WCOT = **W**all **C**oated **O**pen **T**ubular

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

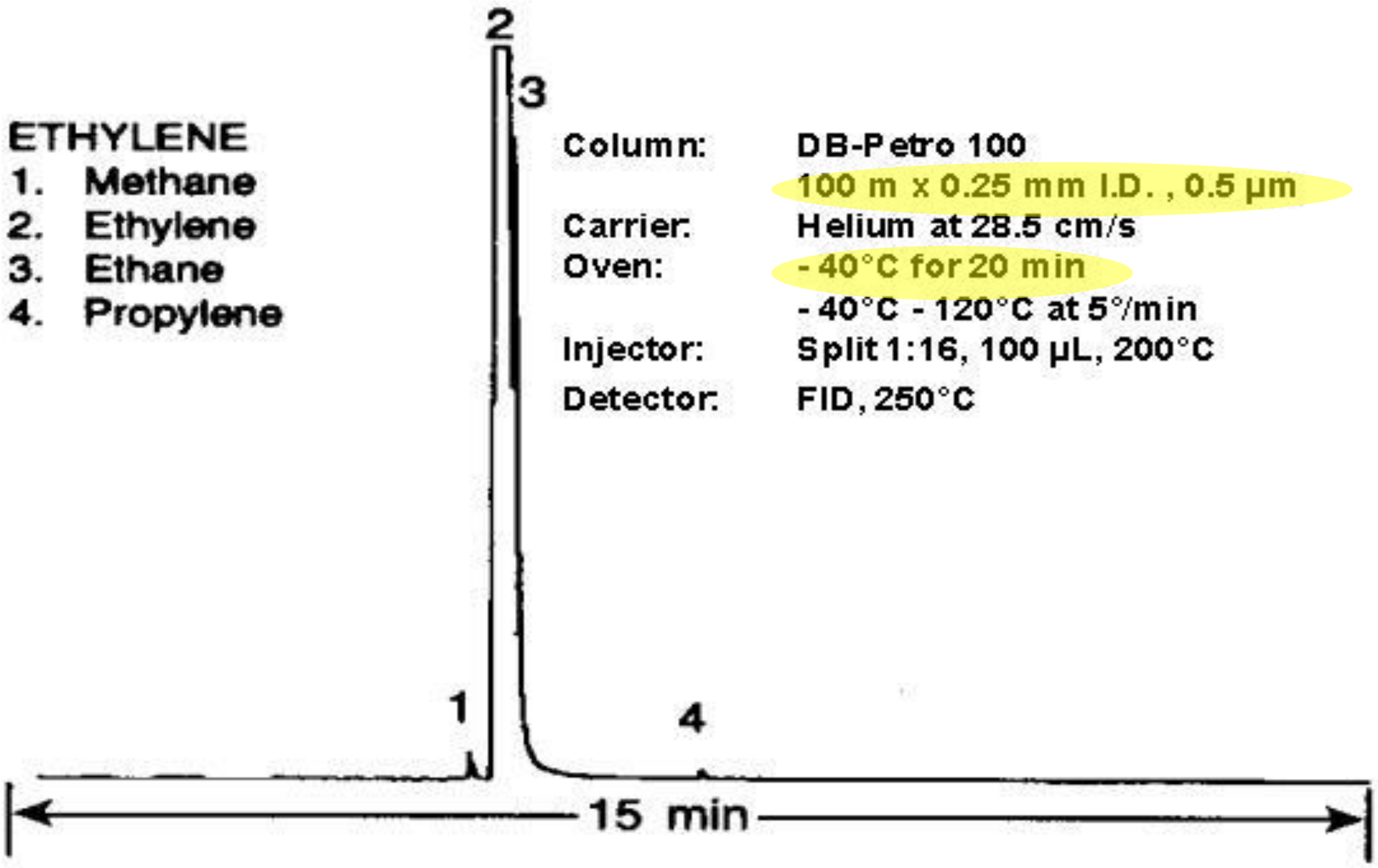
Why use a PLOT column?

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

PLOT Columns



WCOT Ethylene Analysis

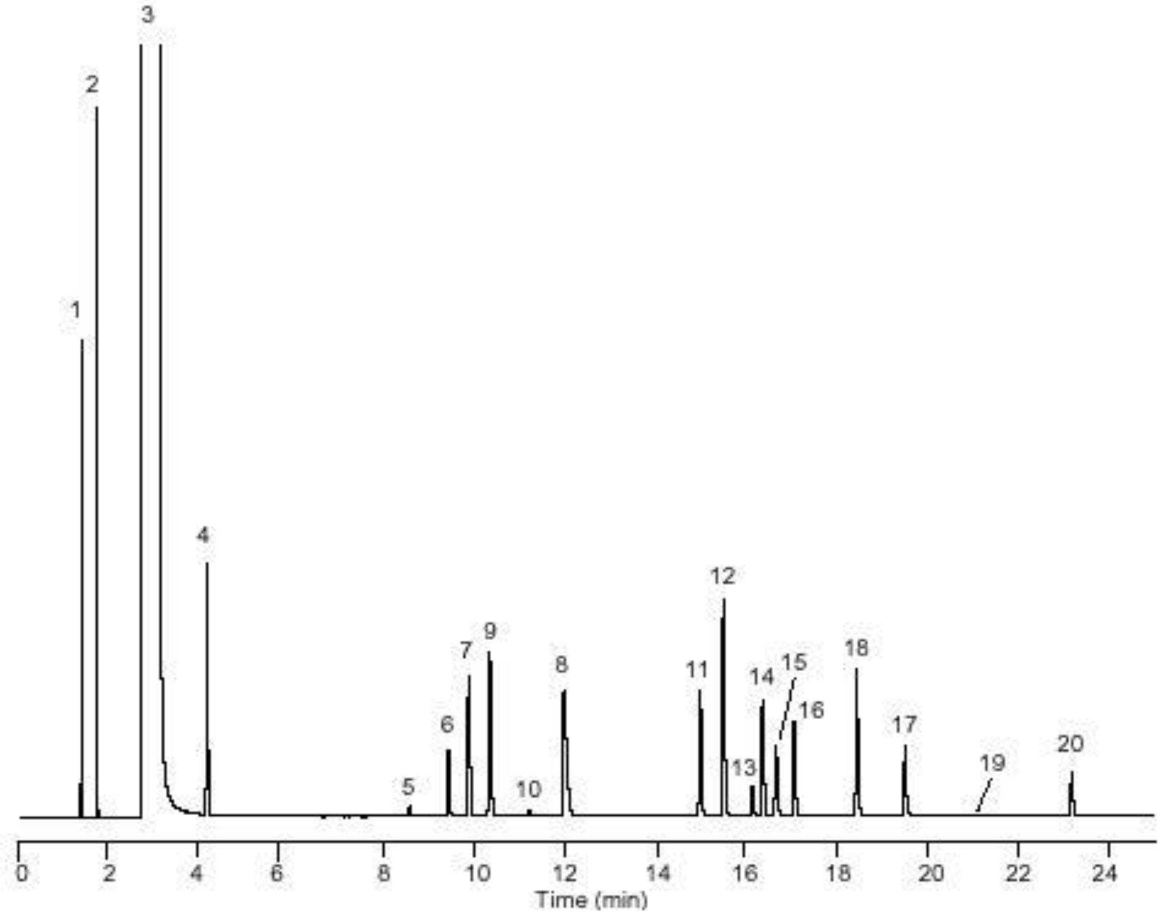


PLOT Ethylene Analysis

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

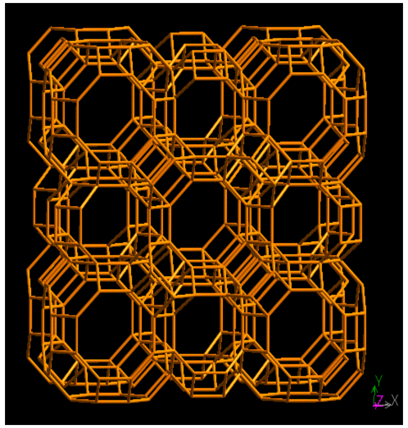
JW Column PLOT column Portfolio- DB, HP, CP

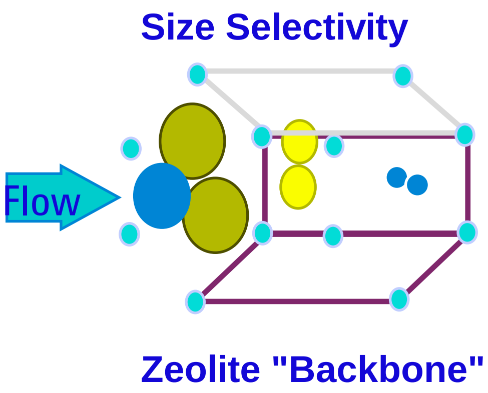
HP-PLOT Al_2O_3
GS-Alumina
GS-Alumina KCl
HP-PLOT Al_2O_3 S
HP-PLOT Al_2O_3 M
CP- Al_2O_3/KCL
CP- Al_2O_3/Na2SO4
CP-SilcaPLOT
CP-CarboBOND
CP-CarboPLOT P7
GS-CarbonPLOT
CP-PoraPLOT Amines
CP-PoraPLOT S

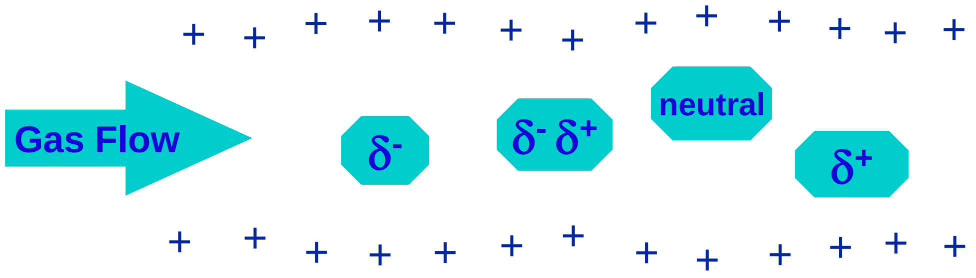
CP-PoraBOND Q
CP-PoraPLOT Q
CP-PoraPLOT Q-HT
HP-PLOT Q
CP-PoraBOND U
HP-PLOT U
GS-Q
CP-PoraPLOT U
HP-PLOT Molesieve
CP-Molsieve 5A
GS-GasPro
ShinCarbon ST
Select Permanent Gas Column

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 web site (www.izo-online.org).

Vapor pressure always plays a leading role in solute interactions

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
  - SF_6
- Limitations…cannot use for…
  - CO_2
  - Water
  - C_2 HC's and larger

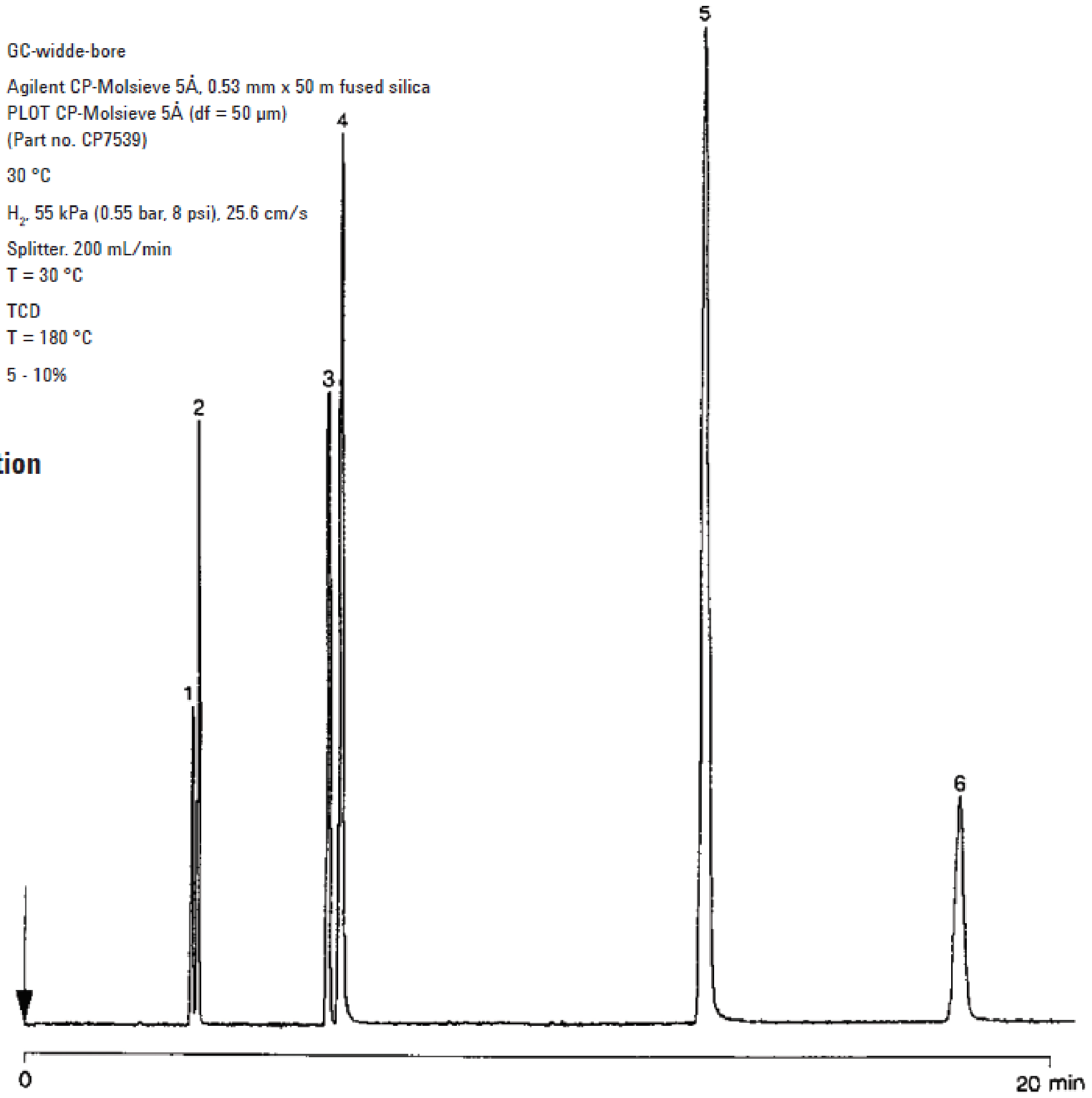
Molesieve Separations

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

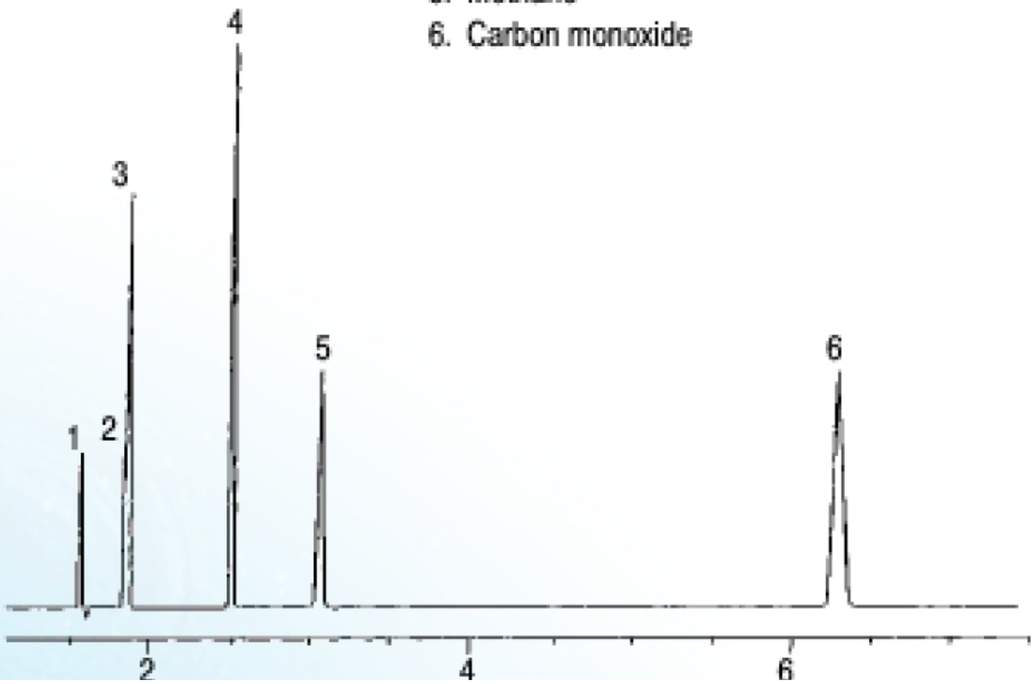


GC:	6890
Sample:	250 ml, split (75:1)
Carrier:	Helium, 2 µl/min
Column:	HP-PLOT/MoleSieve, 30 m x 0.32 mm x 12 µm (Part No. 19091P-MS4)
Oven:	40°C Isothermal
Detector:	TCD

Pub No.: 5964-2129E

Permanent Gases

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



Molesieve Separations

Gases Application 2077 GC

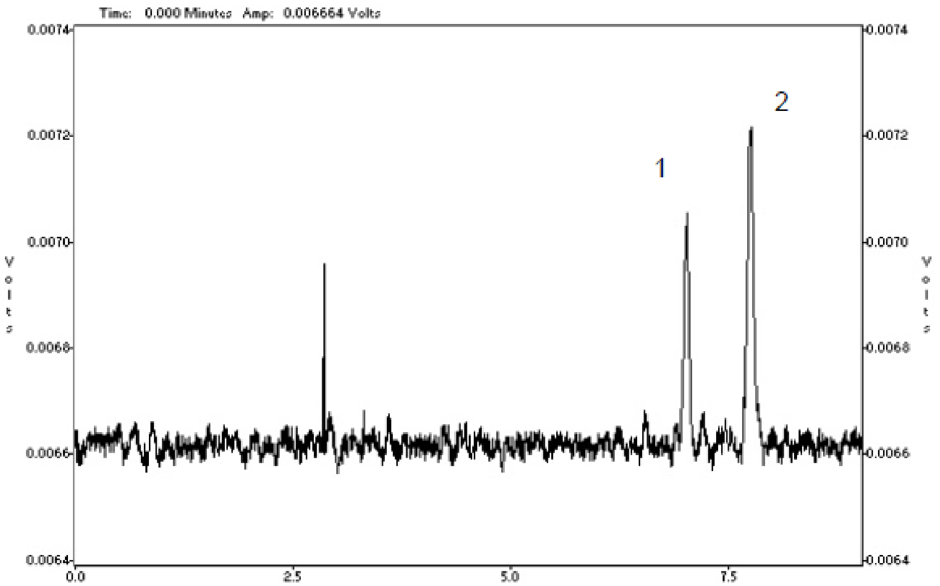
Separation of hydrogen and helium

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

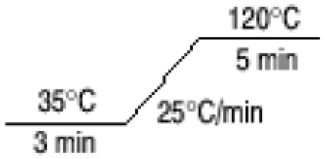
Peak identification

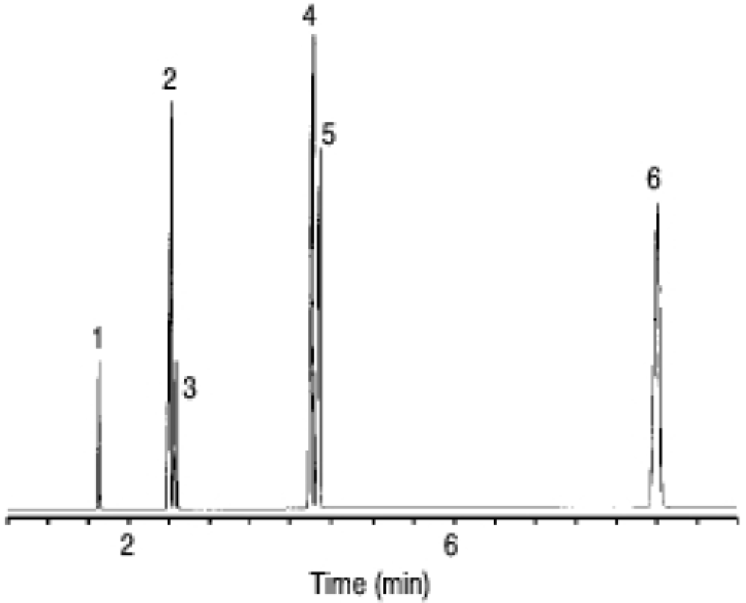
1 Helium
2 Hydrogen



Noble Gases

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



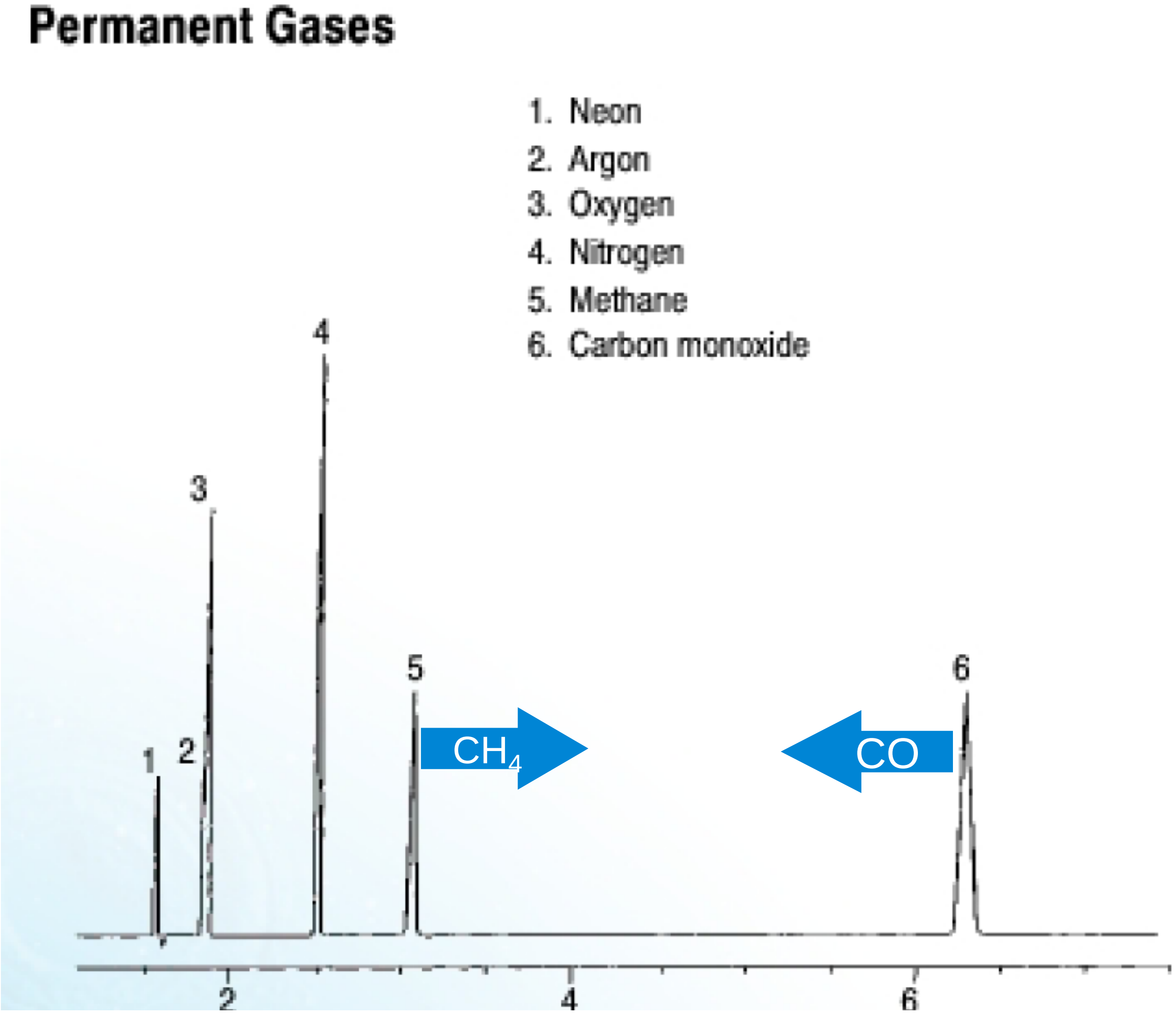


GC:	6890
Sample:	250 µl, split (50:1)
Carrier:	Helium, 4 ml/min
Column:	HP-PLOT/MoleSieve, 30 m x 0.53 mm x 50 µm (Part No. 19095P-MS0)
Oven:	Temperature program listed above
Detector:	TCD

Pub No.: 5964-2129E

Tips for using a Molesieve column

- Molesive 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 when column should be reconditioned (300 º c 8 hours +)

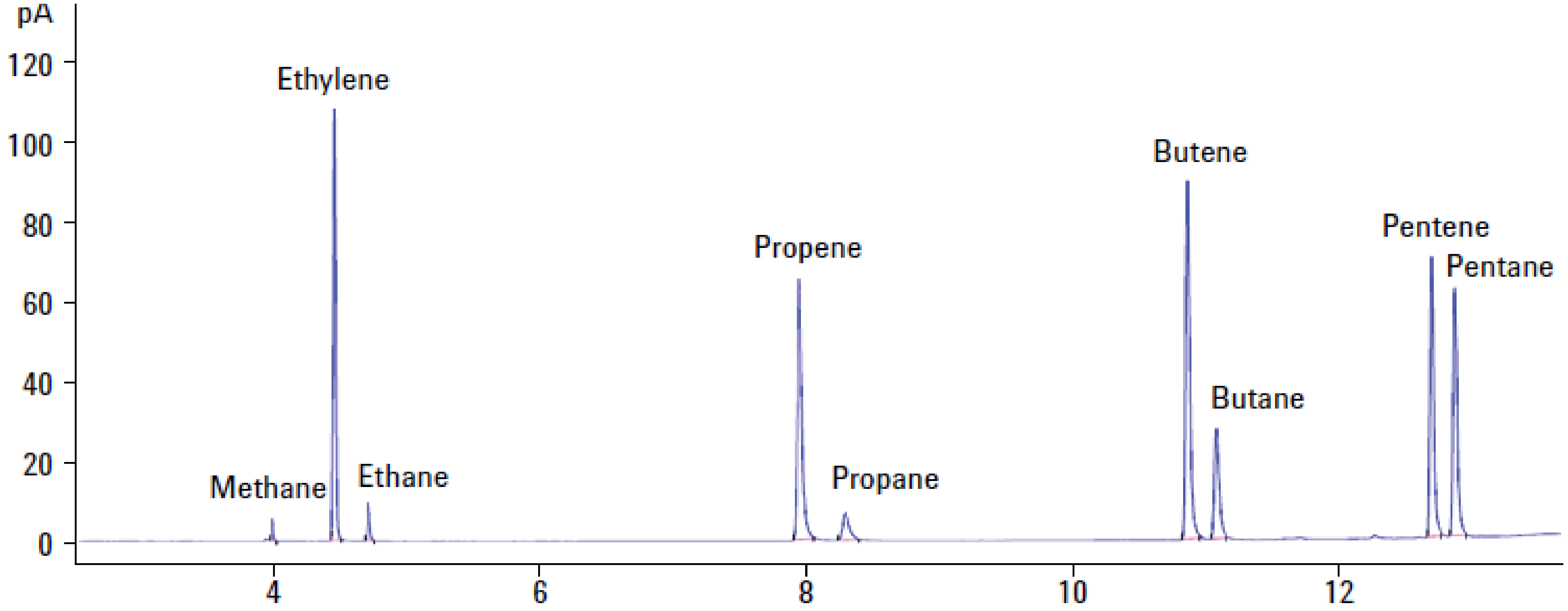


But I also need to analyze for CO2….its getting complicated…

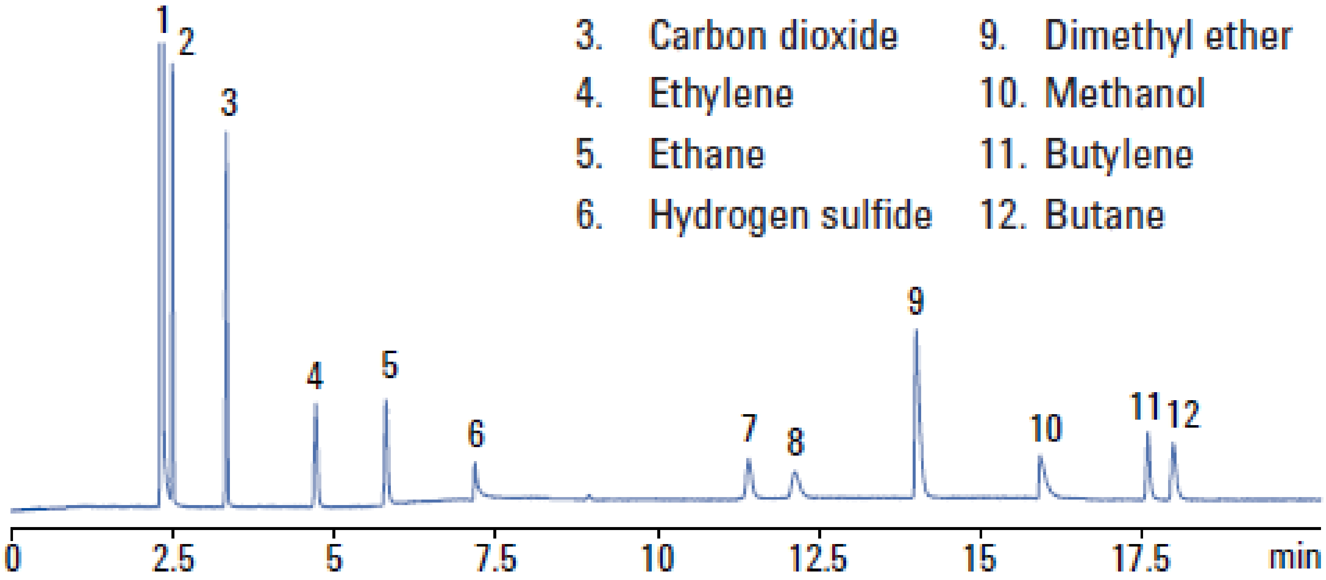
- Recall that CO_2 cannot be done on a molesieve column (absorbed)
- Alternative options:
  - 2 unique injections on 2 columns
    - Molesieve + PLOT-Q
  - 1 injection on 1 column at Cryo temps (-80 ^{o}c!)
    - GasPro
  - 1 Injection on 1 column – ShinCarbon ST (packed column)
  - 1 injection with 2 columns + valve to “direct traffic”
    - Column Isolation - Molesieve + PLOT-Q
  - 1 injection with 2 columns in parallel
    - Select Permanent Gas Column - Molesieve + PLOT-Q

…did I mention this would get complicated?? ☺

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

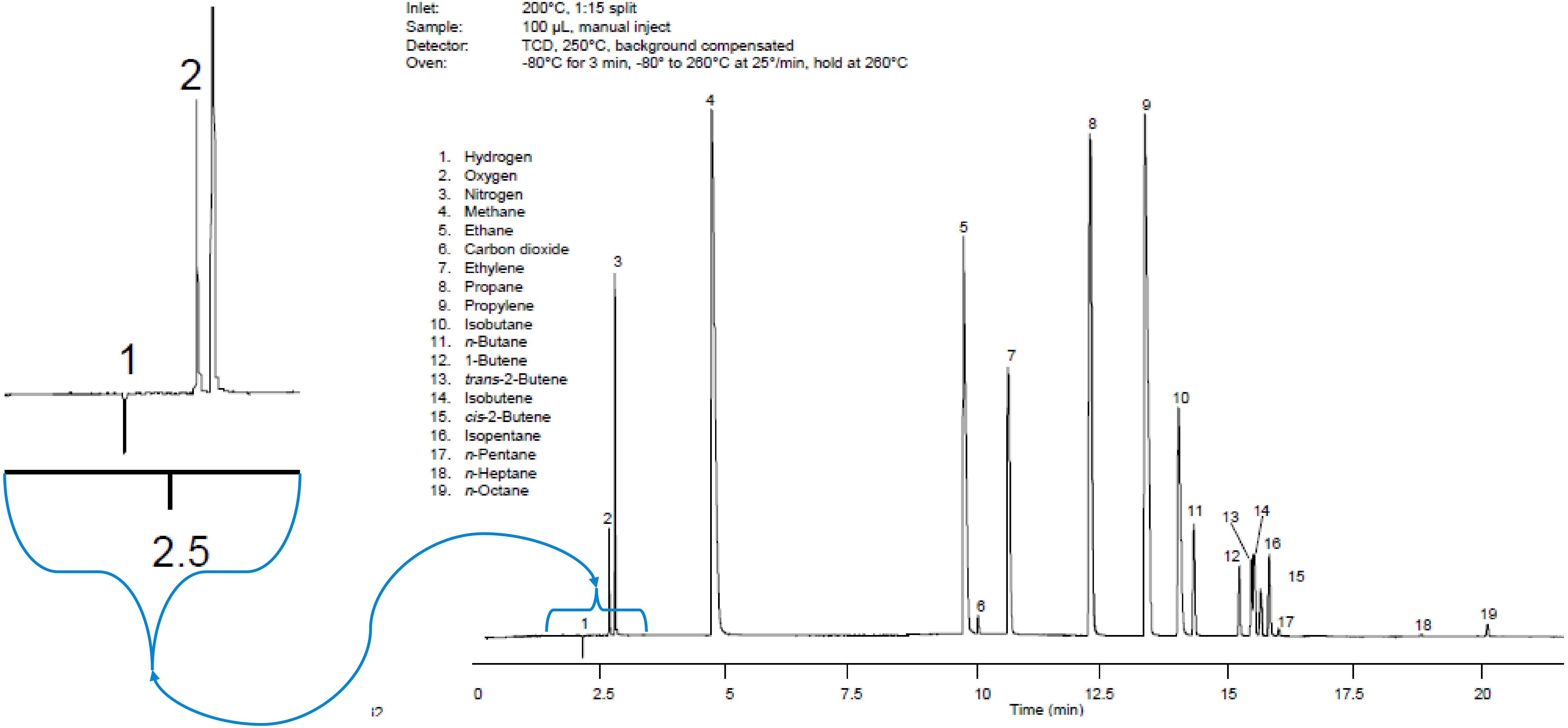


GasPro - Cryo

Permanent Gases in Hydrocarbon Blend

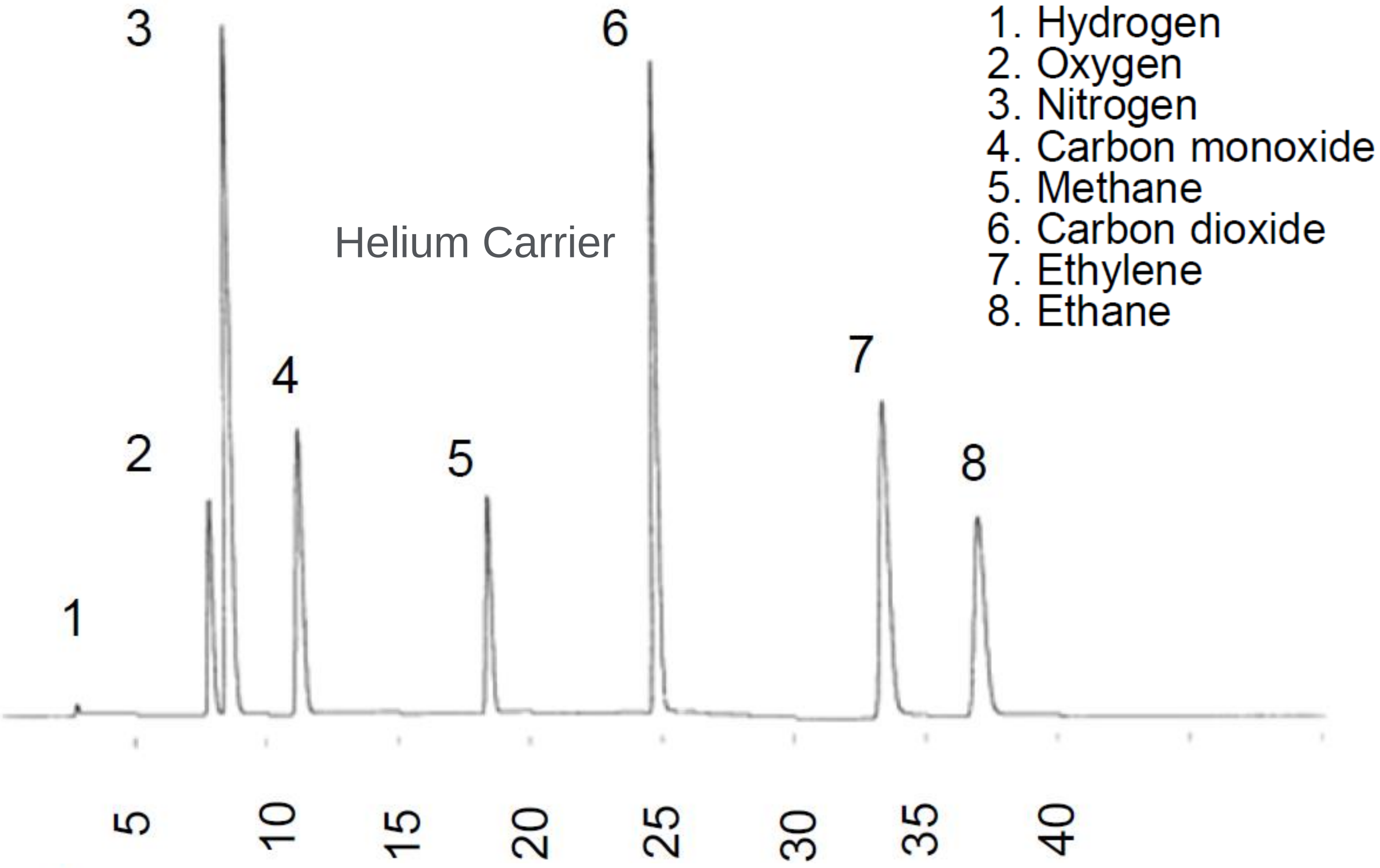
Column: **GS-GasPro, 60 m x 0.32 mm I.D.**
J&W P/N: **113-4362**

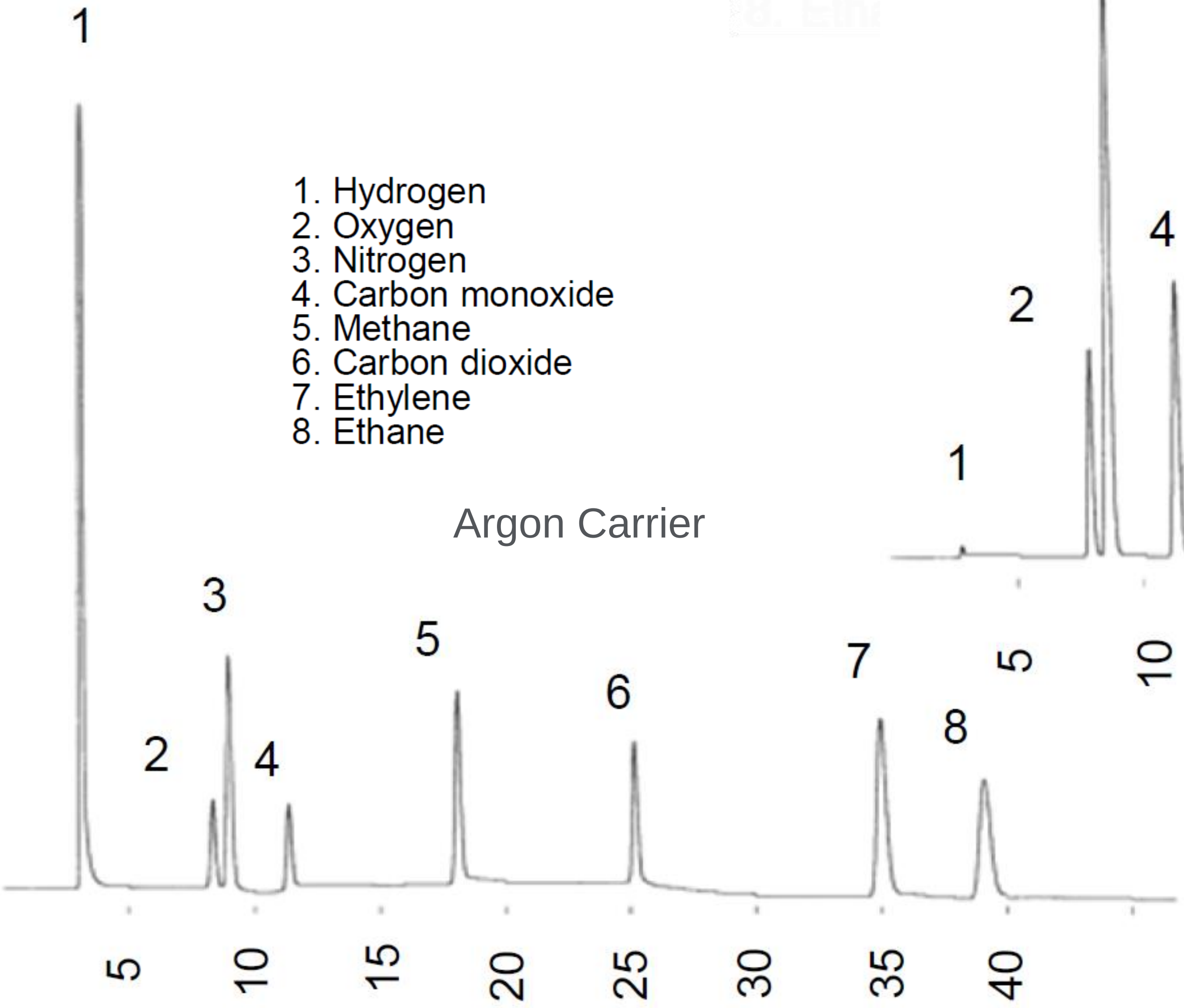
Carrier:	Helium, 20 psig (constant pressure)
Inlet:	200°C, 1:15 split
Sample:	100 µL, manual inject
Detector:	TCD, 250°C, background compensated
Oven:	-80°C for 3 min, -80° to 260°C at 25°/min, hold at 260°C



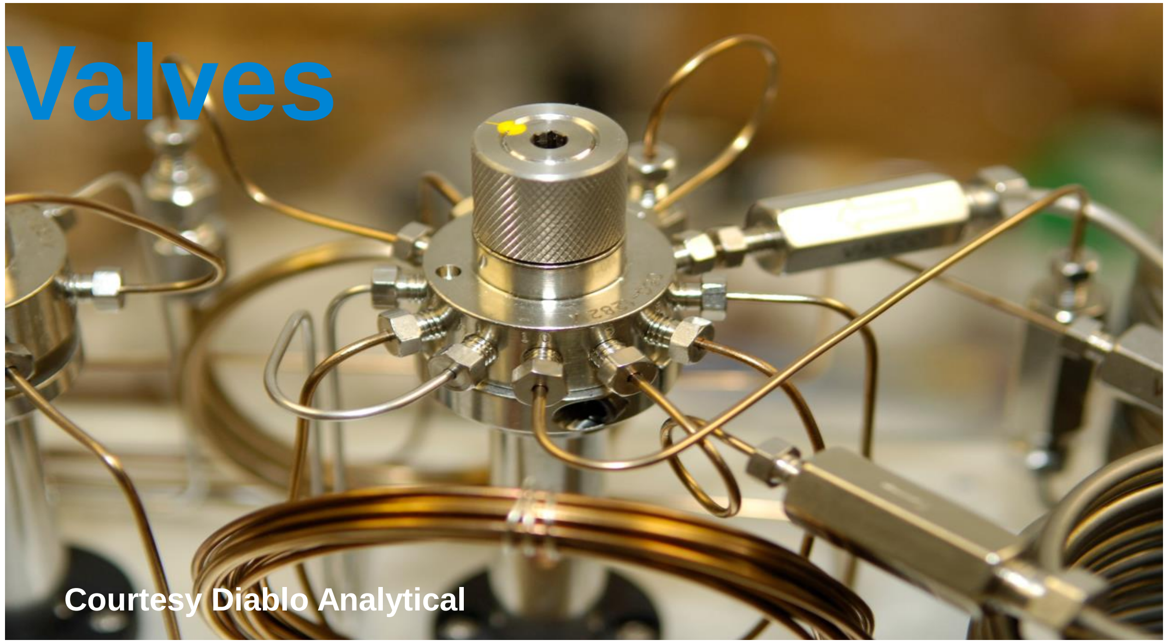
Agilent

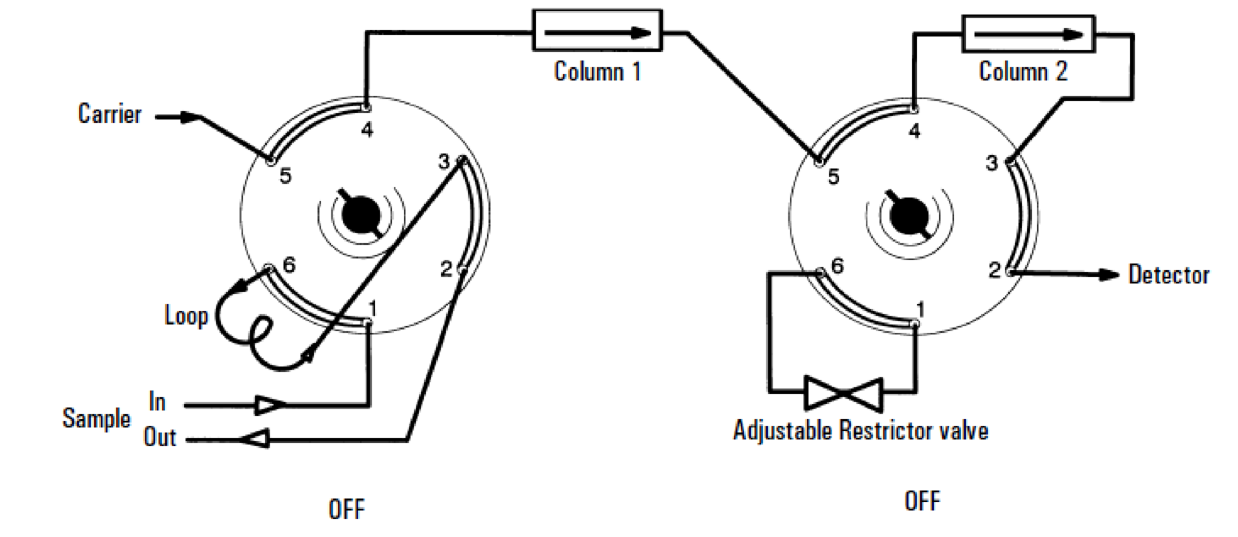
ShinCarbon ST



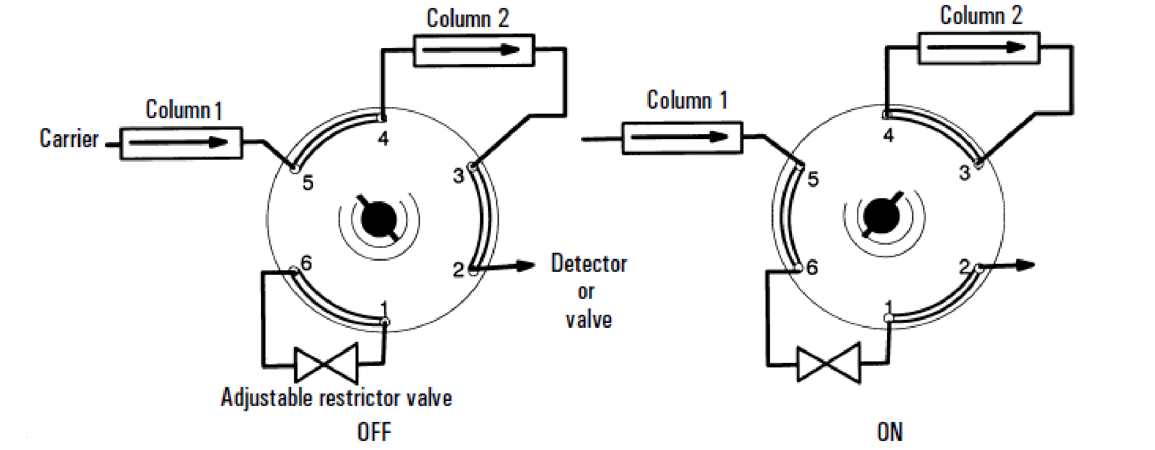


Valves



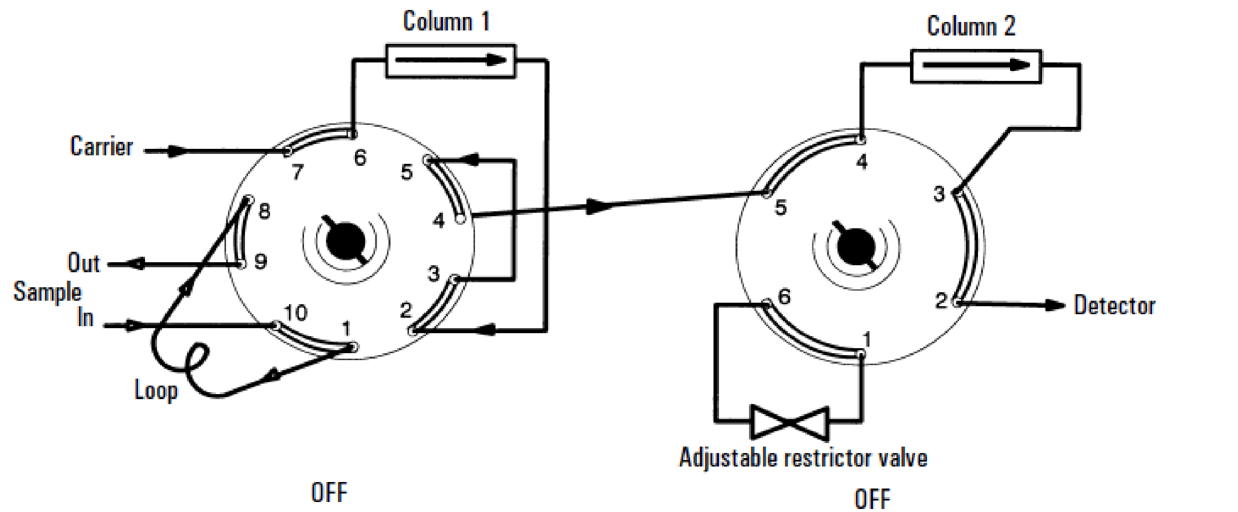


Gas sample and column isolation



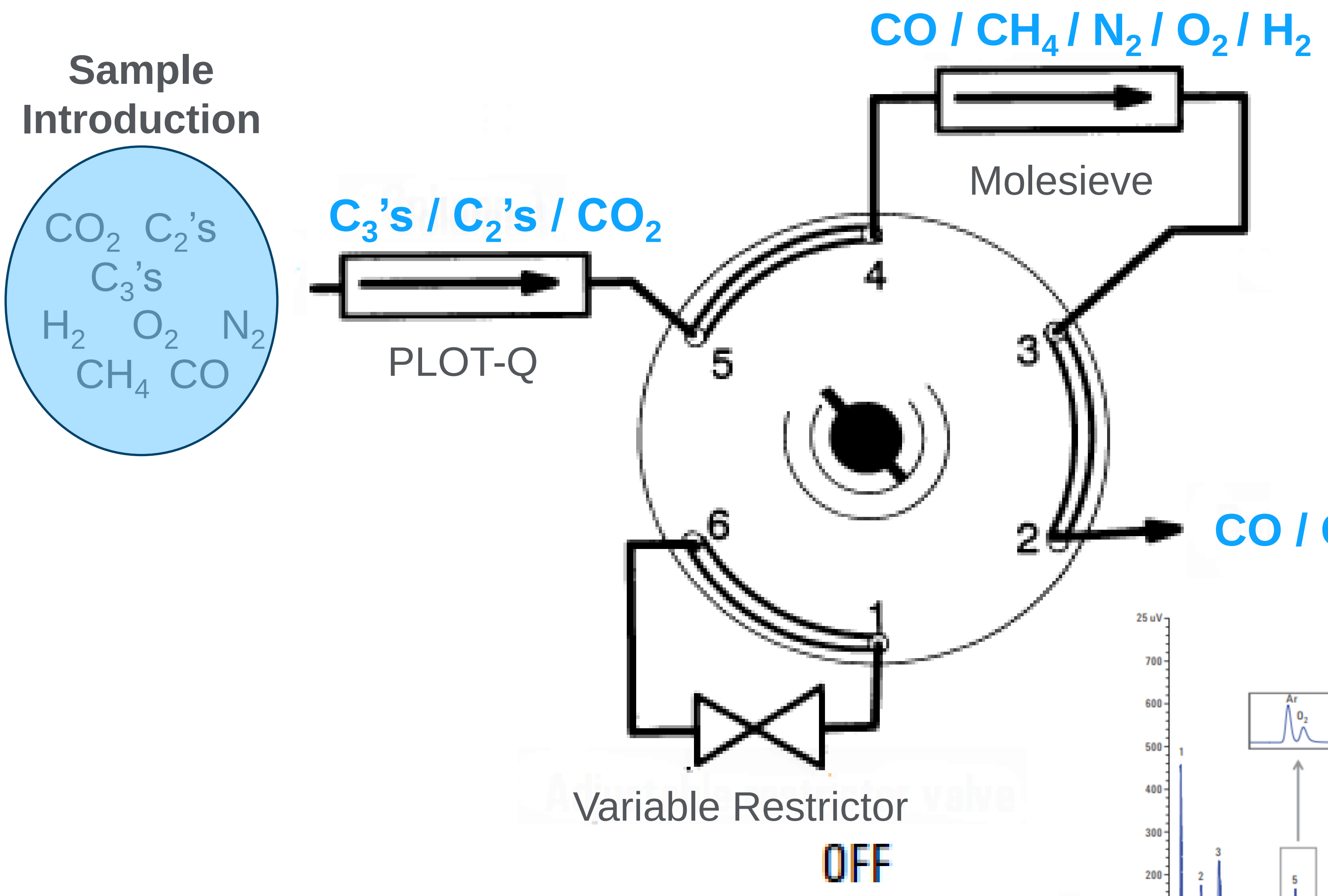
Column isolation*

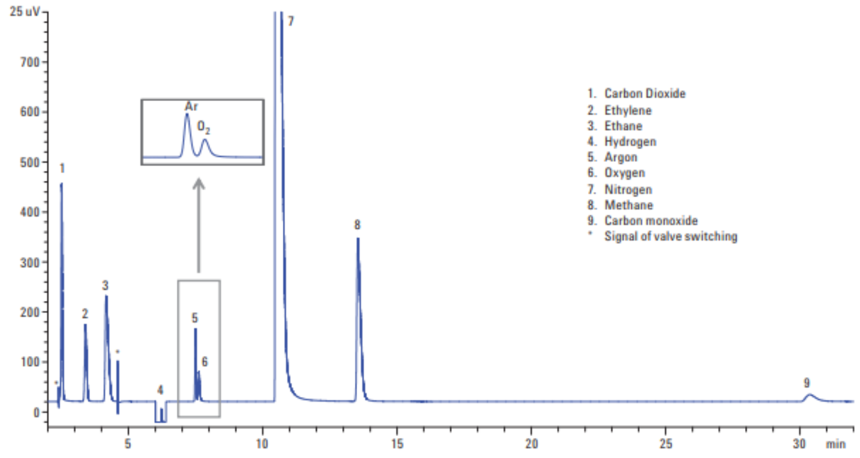
*Temperature limited to 235°C by micrometering needle valves



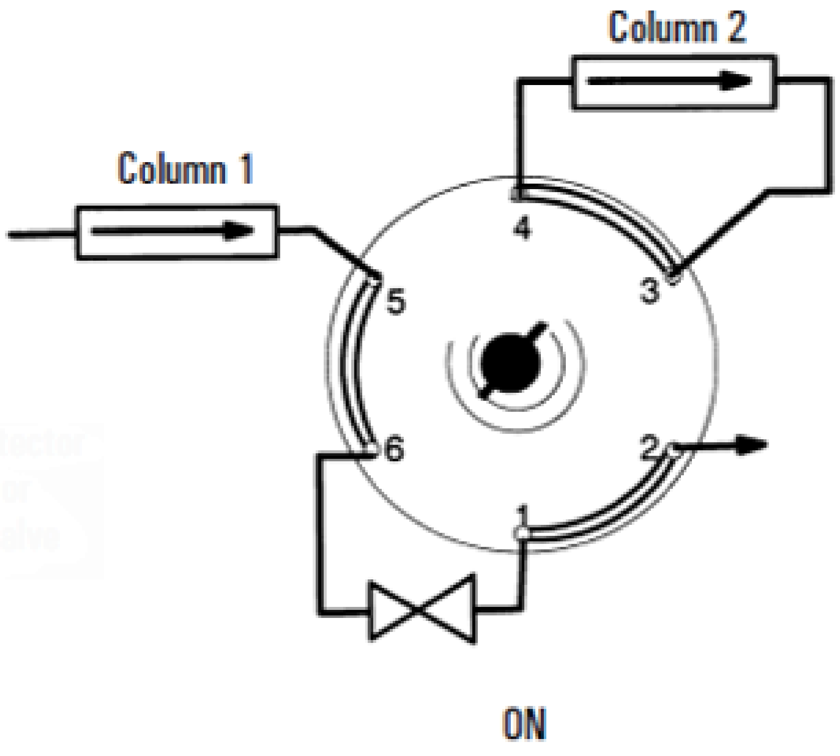
Gas sample/backflush and column isolation

1 Injection 2 Columns + Valve ….Column Isolation

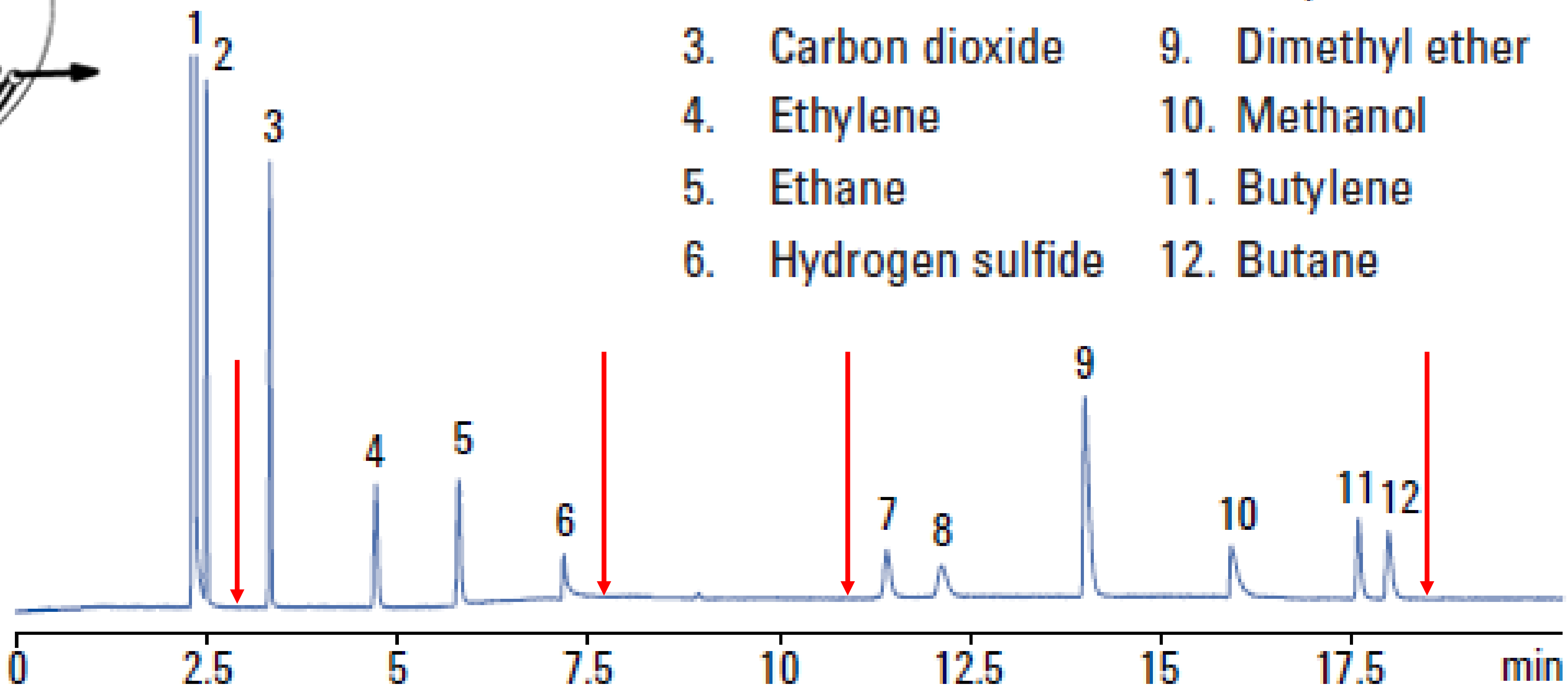




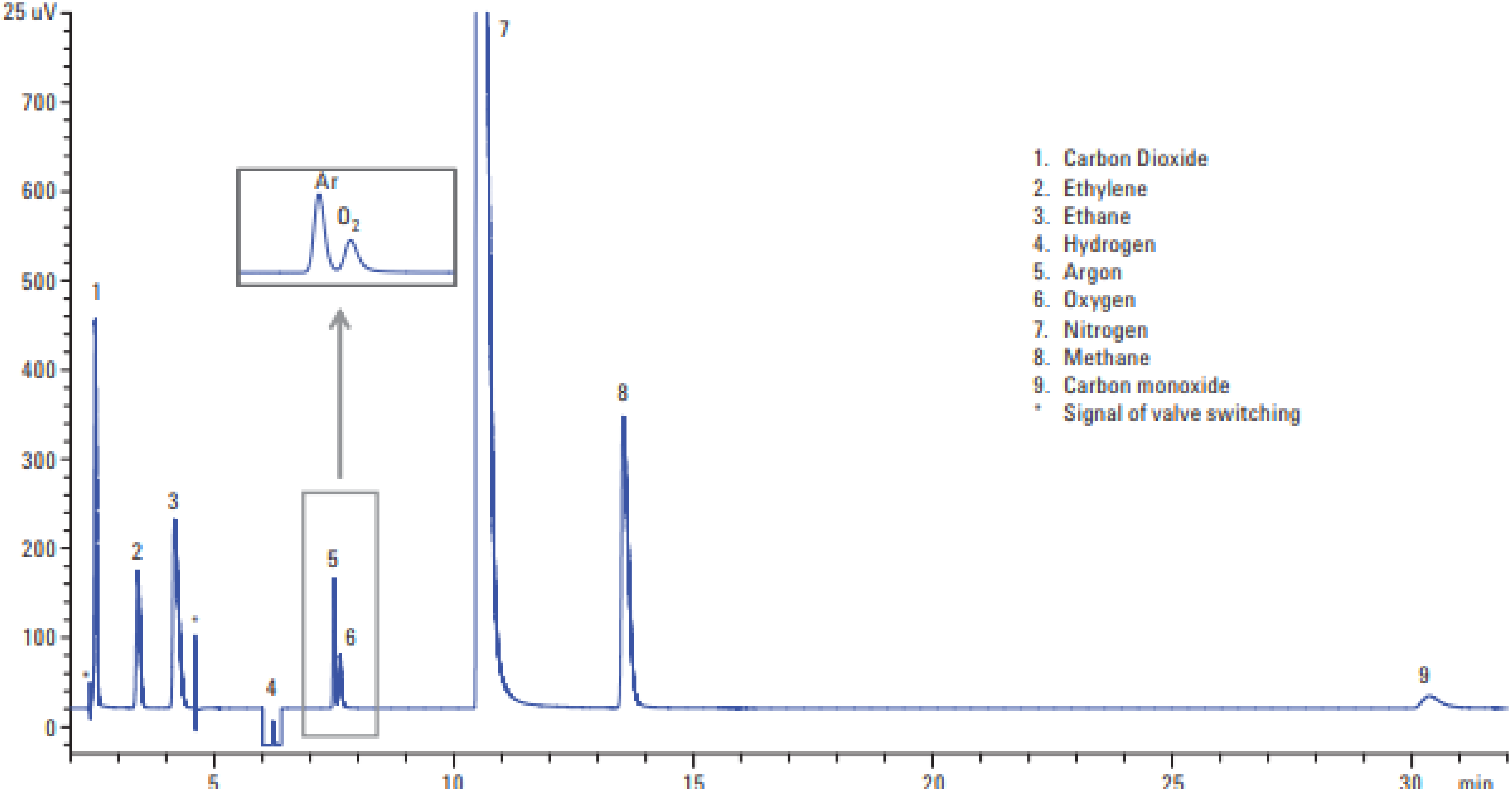
Column isolation: Setting up valve timing



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



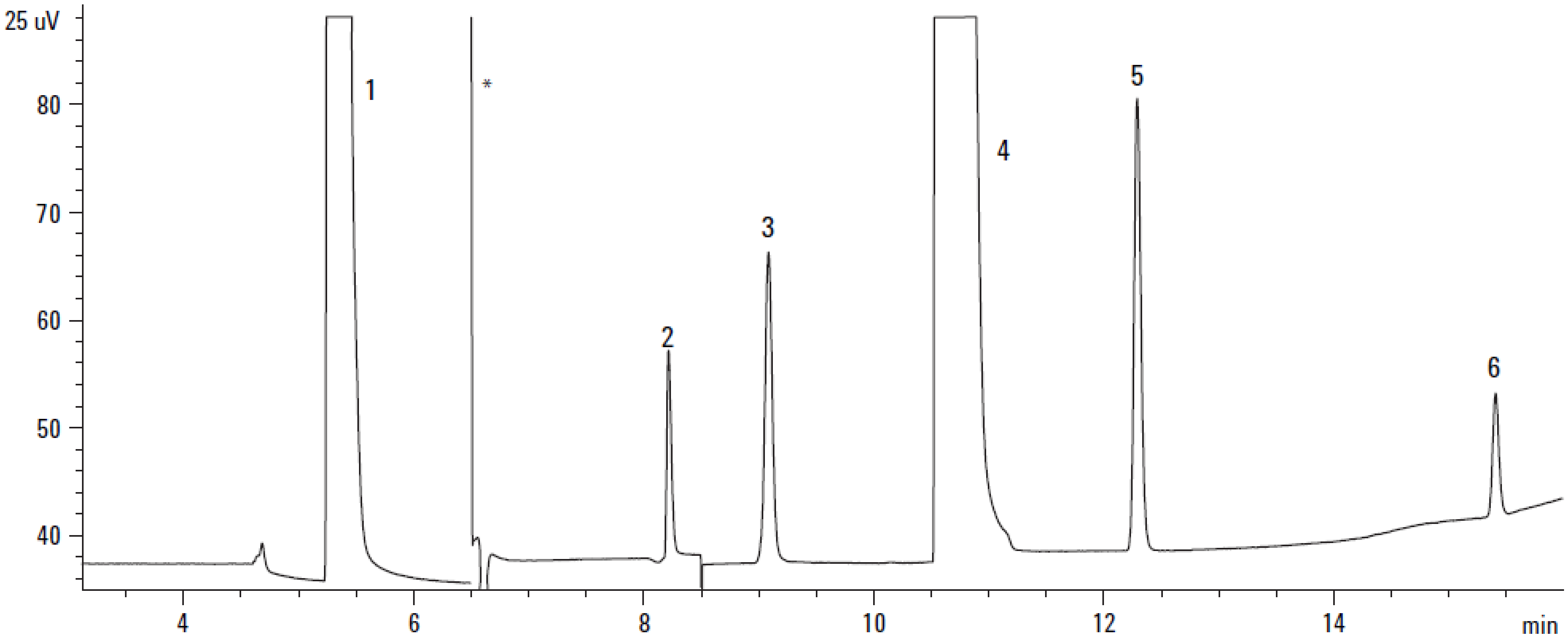
Column isolation



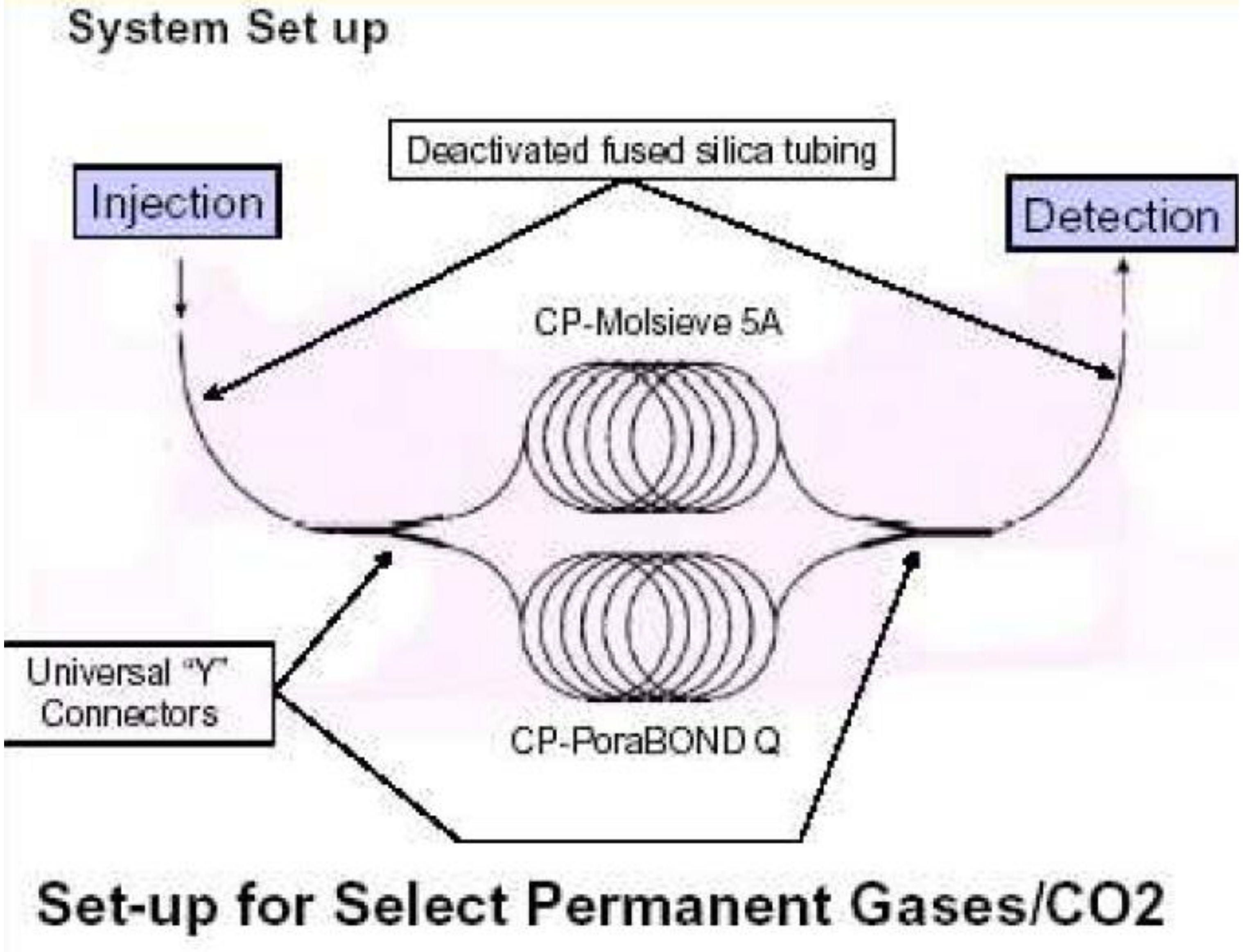
Column Isolation – Flexibility of Elution Order….

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



1 Injection 2 Columns in Parallel…Select Permanent Gas Column

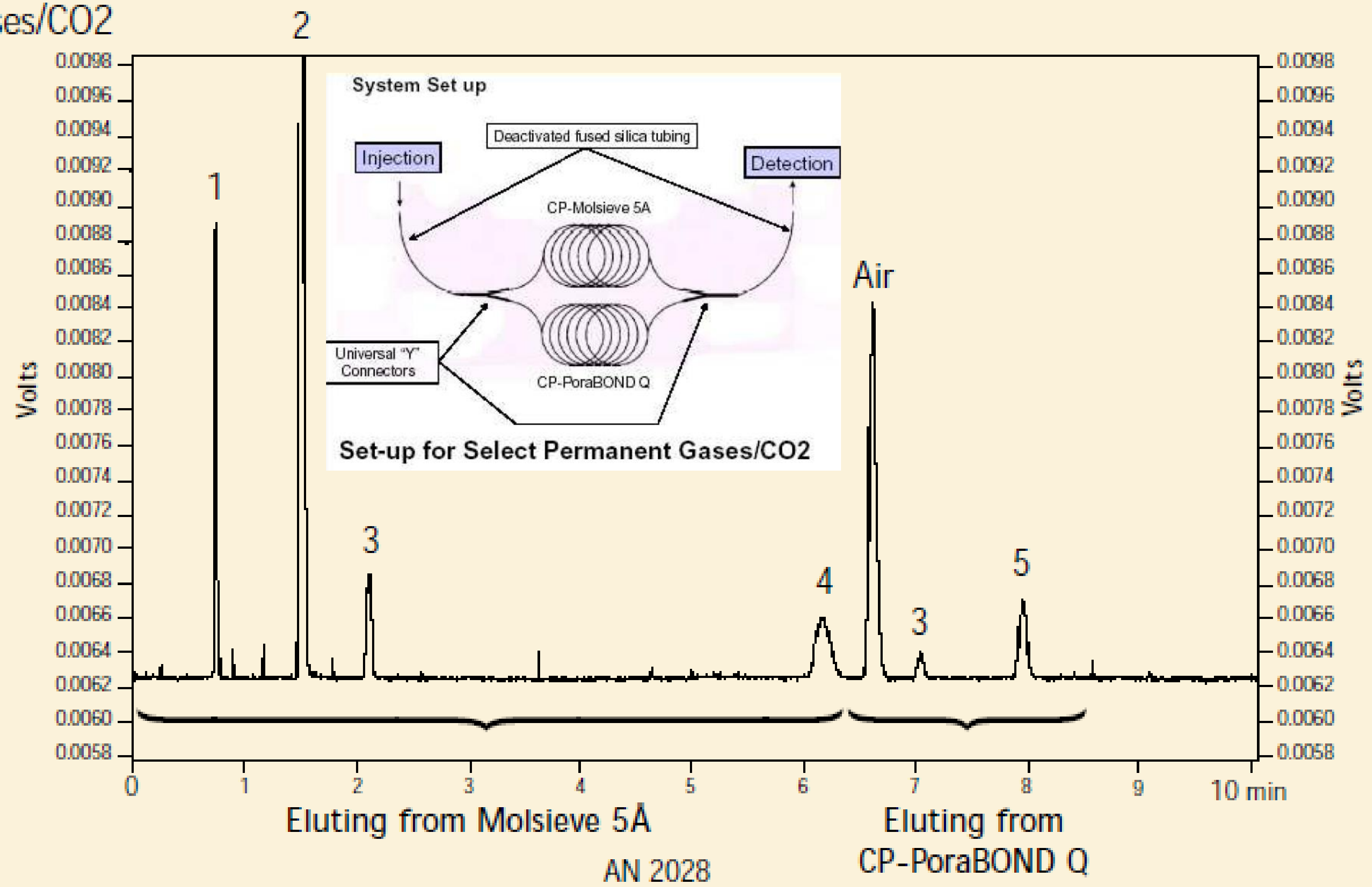


Select Permanent Gas Column

Technique : GC
Column : Select Permanent Gases/CO_2
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:

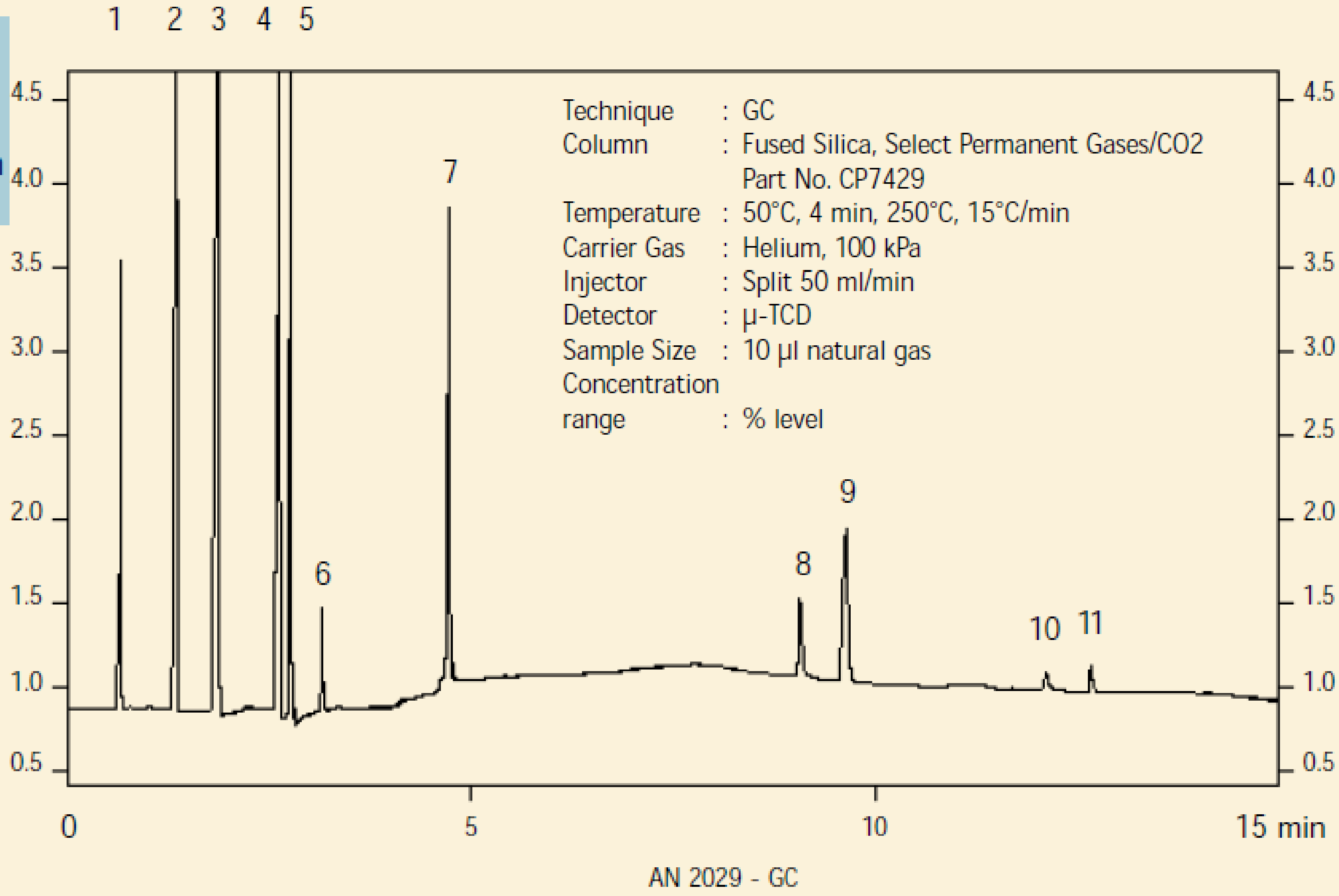
1. Oxygen
2. Nitrogen
3. Methane
4. Carbon monoxide
5. Carbon dioxide



Select Permanent Gas Column

Peak Identification

1. Oxygen
2. Nitrogen
3. Methane
4. Oxygen + Nitrogen
5. Methane
6. CO2
7. Ethane
8. Propane
9. Ethane
10. Isobutane
11. Butane

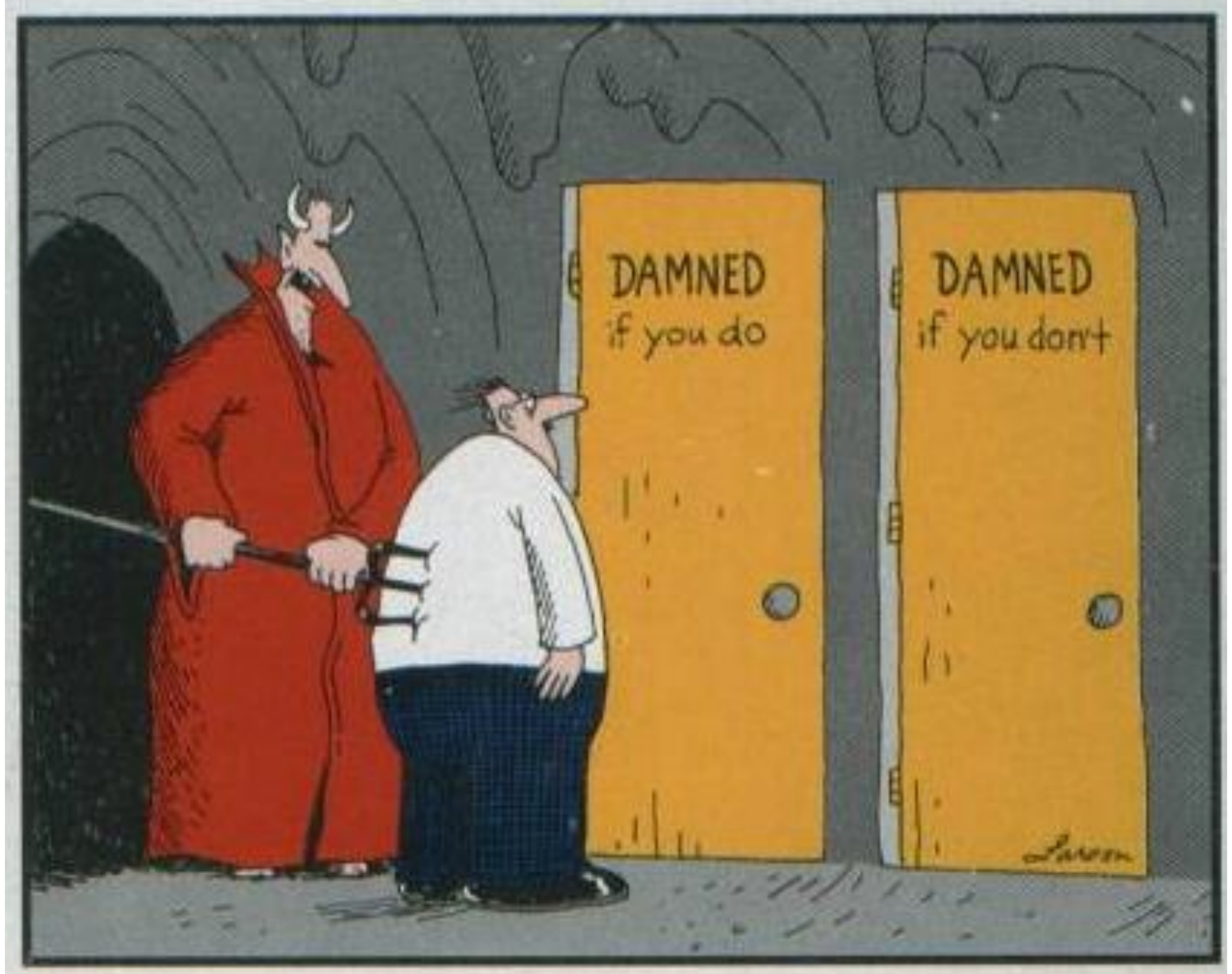


So you think that was complicated… what if I need to analyze for hydrogen too…

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

TCD

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



"C'mon, c'mon — it's either one or the other."

Thermal Conductivity Detector - TCD

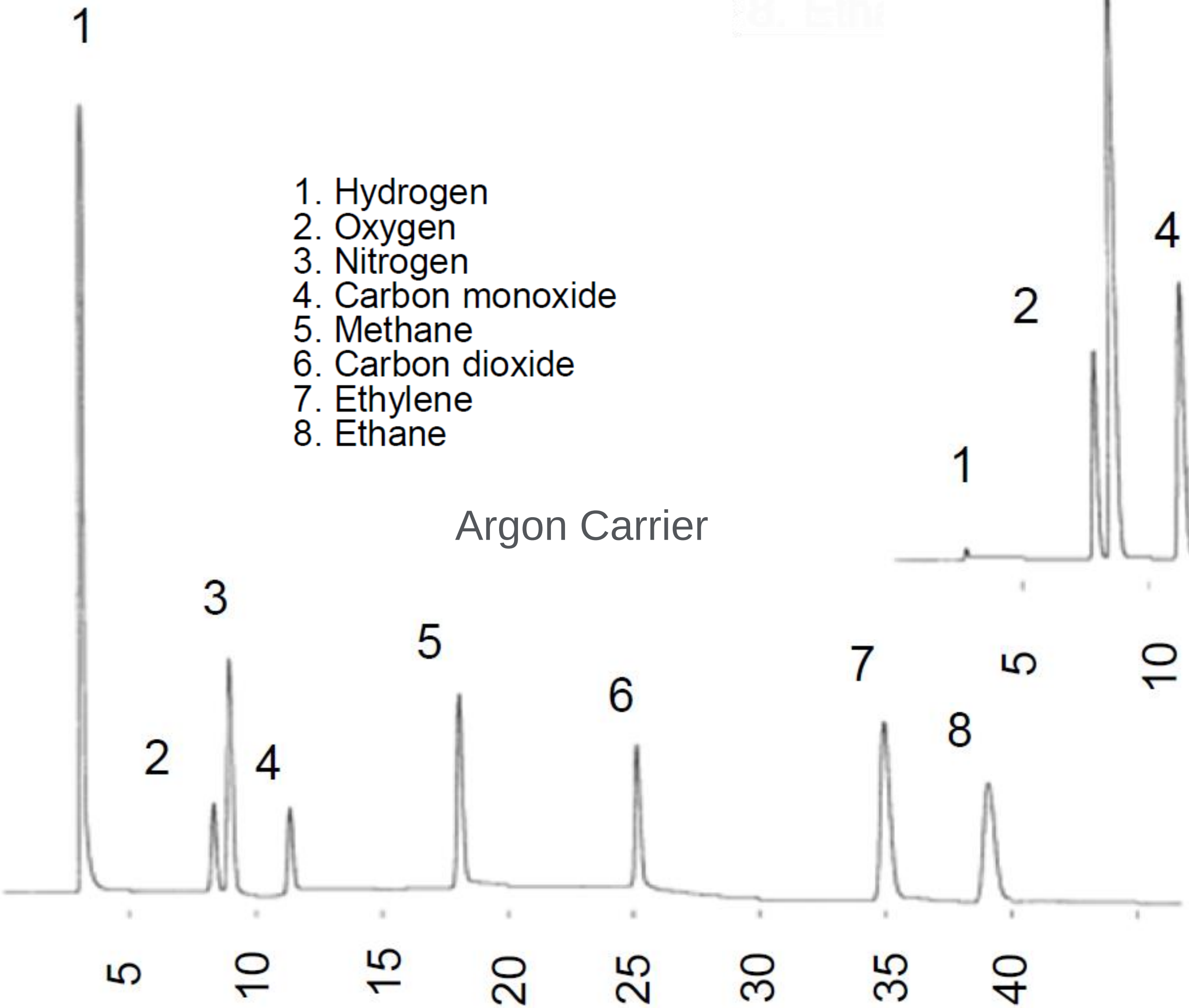
Name	Thermal Conductivity @ 400 K (mW m^{-1} K^{-1})
Argon	22.4
Hydrogen	230.9
Helium	189.6
Nitrogen	32.8
Carbon Monoxide	32.3
Carbon Dioxide	25.2
Acetylene	33.3
Ethylene	34.7
Ethane	36.0
Propane	31.0
Butane	28.3
Pentane	24.9
Hexane	23.4

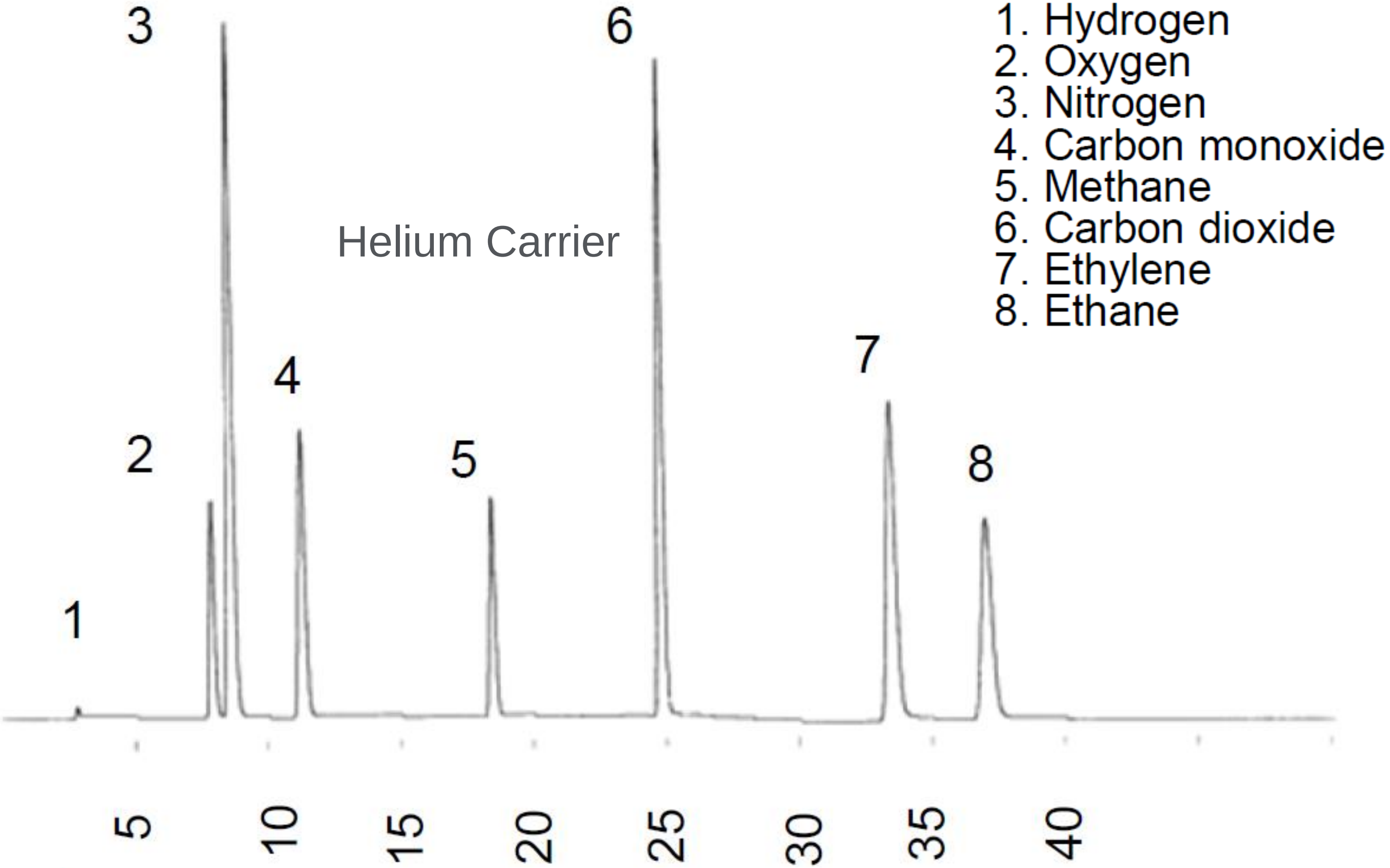
		Thermal conductivity in mW m^{-1} K^{-1}						
		100 K	200 K	300 K	400 K	500 K	600 K	Ref.
	Air	9.5	18.5	26.4	33.5	39.9	46.0	1
Ar	Argon ($P = 0$)	6.3	12.4	17.7	22.4	26.5	30.3	2, 3*
BF_3	Boron trifluoride			19.0	24.6			4
ClH	Hydrogen chloride		9.2	14.5	19.5	24.0	28.1	4
F_6S	Sulfur hexafluoride ($P = 0$)			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





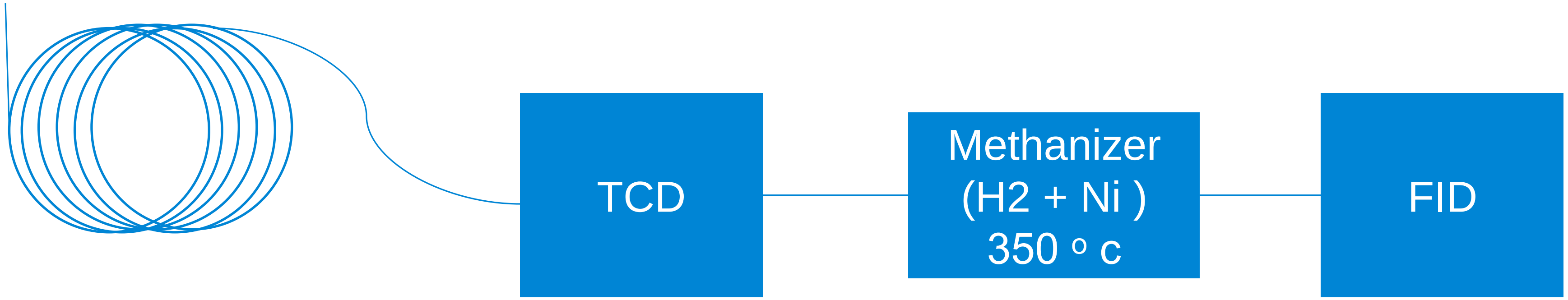
Workarounds for low level hydrogen detection

- 2 unique injections:
  - 1 for hydrogen using Argon or N2 carrier 2nd injection for all other gases using helium carrier
- 1 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): $CO_2 + 4\,H_2 \xrightarrow[\text{Ni}]{400\ ^{o}c} CH_4 + 2H_2O$
- Transformer Oil Gas Analyzer (TOGA)

Conversion of CO/CO2 to methane

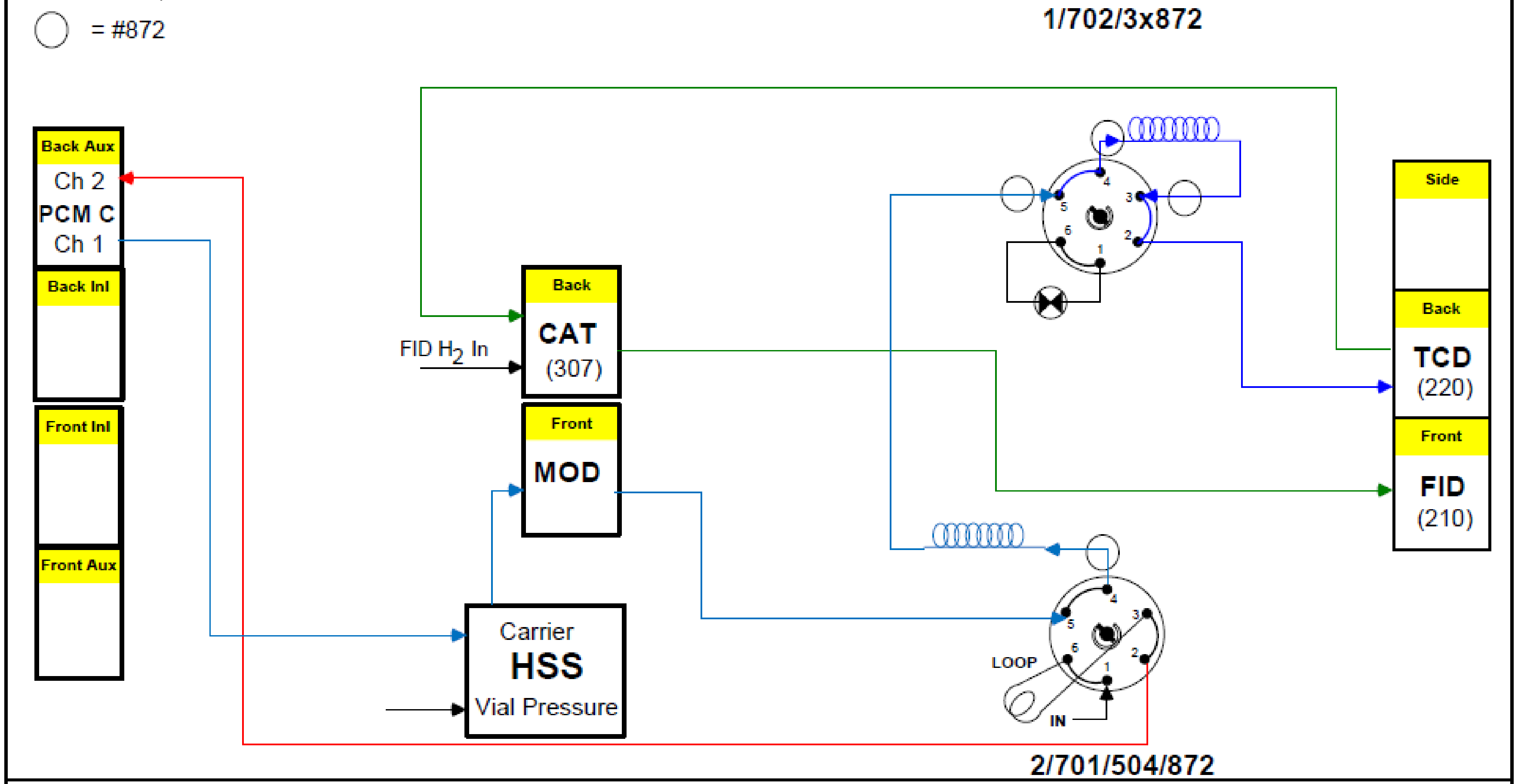
➢ Discovered by French chemist Paul Sabatier in 1897 (Sabatier Reaction)

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



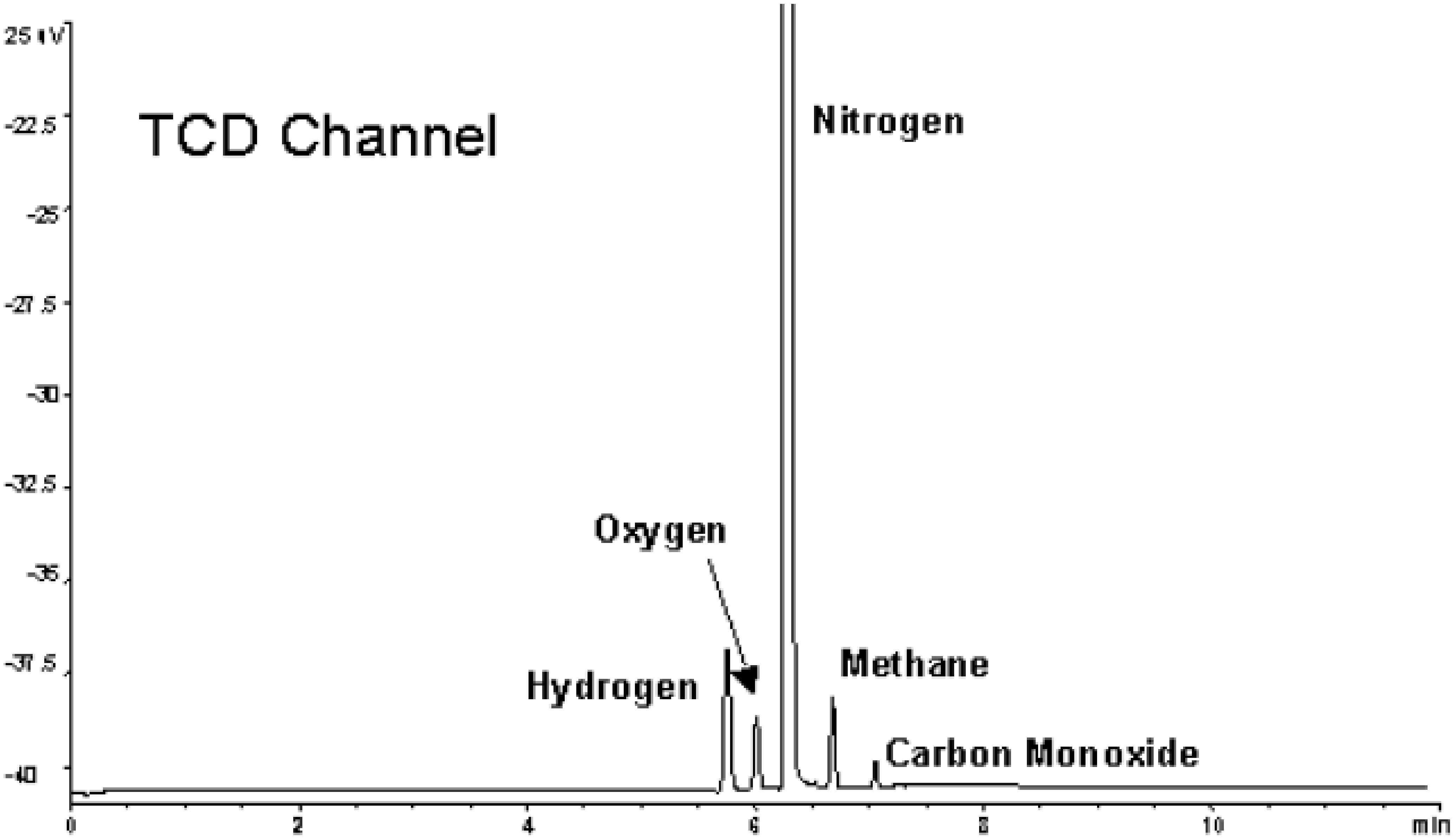
Agilent Technologies	Valve System	Date :	S/N :
		Order No :	Item :

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

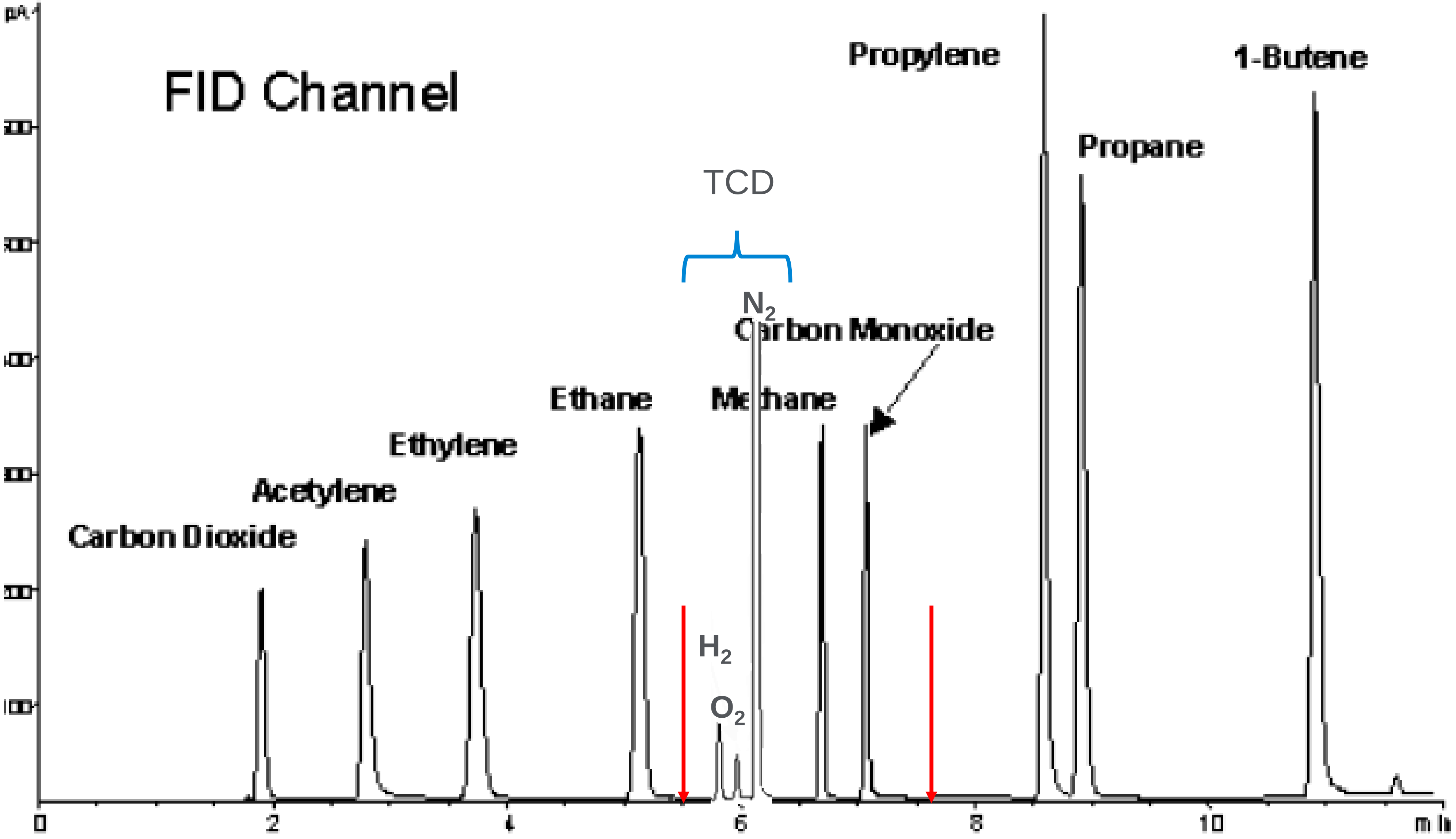


Options	SP1 options	Remarks
210,220,307,309,504,701,702,752,4x872	7890-0261	

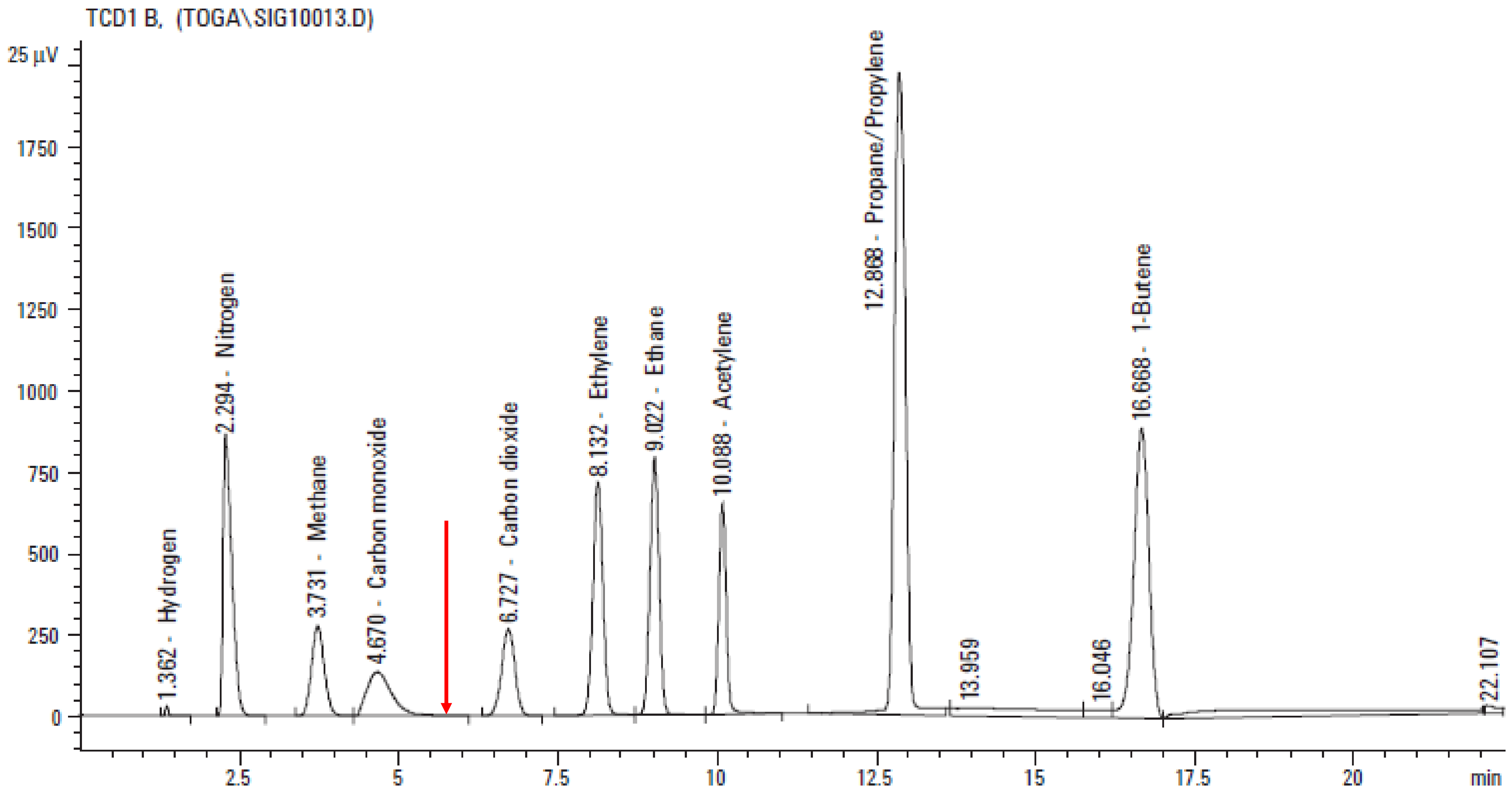
Transformer Oil Gas Analyzer (TOGA) Chromatograms



Transformer Oil Gas Analyzer (TOGA) Chromatograms



Transformer Oil Gas Analyzer (TOGA) Chromatograms



Summary

Analytes	Column	Technique
$H_2/O_2/N_2/CH_4/CO$	Molesieve	• 1 Injection 1 Column
$H_2/O_2/N_2/CH_4/CO$ + Ar	Molesieve (thick film)	• 1 Injection 1 Column
$H_2/O_2/N_2/CH_4/CO$ + CO_2 + C2's etc	Molesieve + PLOT-Q	• 2 Injections 2 Columns • 1 Injection + Valve (Column Isolation) • 1 Injection Parallel Columns (Select Perm Gas Column)
$H_2/O_2/N_2/CH_4/CO$ + CO_2 + C2's etc	GasPro	• Cryo (-80 ^{o} c)
$H_2/O_2/N_2/CH_4/CO$ + CO_2 + C2's etc	ShinCarbon	• Packed only
$H_2/O_2/N_2/CH_4/CO$ + CO_2 + C2's etc + Low level Hydrogen	Molesieve + PLOT-Q	• Single injection onto molesieve for H2 detection only • Argon carrier + Methanizer (TOGA)

Agilent

Contact Agilent Chemistries and Supplies Technical Support

We are always here to help!

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

Option 1 for GC/GCMS Columns and Supplies

Option 2 for LC/LCMS Columns and Supplies

Option 3 for Sample Preparation, Filtration and QuEChERS

Option 4 for Spectroscopy Supplies

Available in the USA 8-5 all time zones

gc-column-support@Agilent.com

lc-column-support@agilent.com

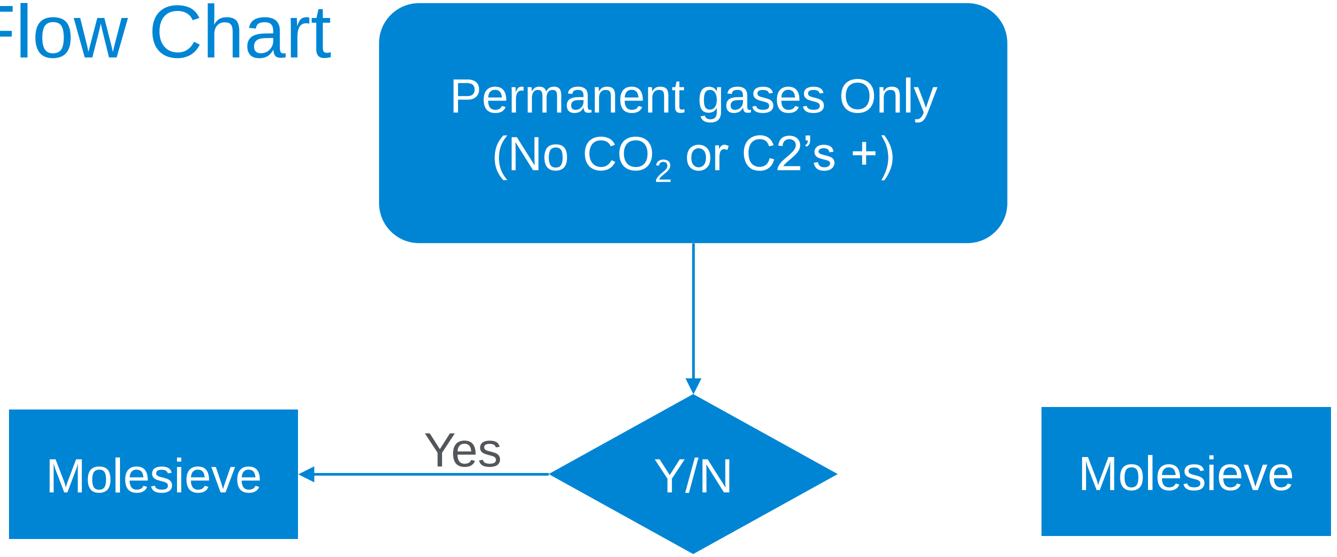
spp-support@agilent.com

spectro-supplies-support@agilent.com

Outline

- Plot columns – General discussion PLOT vs WCOT
- Molesieve
  - Very narrow functionality
  - Great for resolving O_2/N_2 at non-cryo temps
  - Traps CO_2 and water
- The Problem with CO_2 and HC larger than C1
  - Option 1: Make 2 unique injections
  - Option 2: Cryo + GasPro
  - Option 3: Column isolation
  - Option 4: ShinCarbon
- Detection issues when there is a need for H_2
  - Explanation of TCD (catch 22)
  - Work arounds:
    - 2 unique injections
    - Argon carrier + Methanizer (TCD + FID in series)

Flow Chart


Permanent gases Only
(No CO_2 or C2's +)
Y/N
Yes
Molesieve
Molesieve