GC-C and GC-Pyrolysis IRMS Short Course

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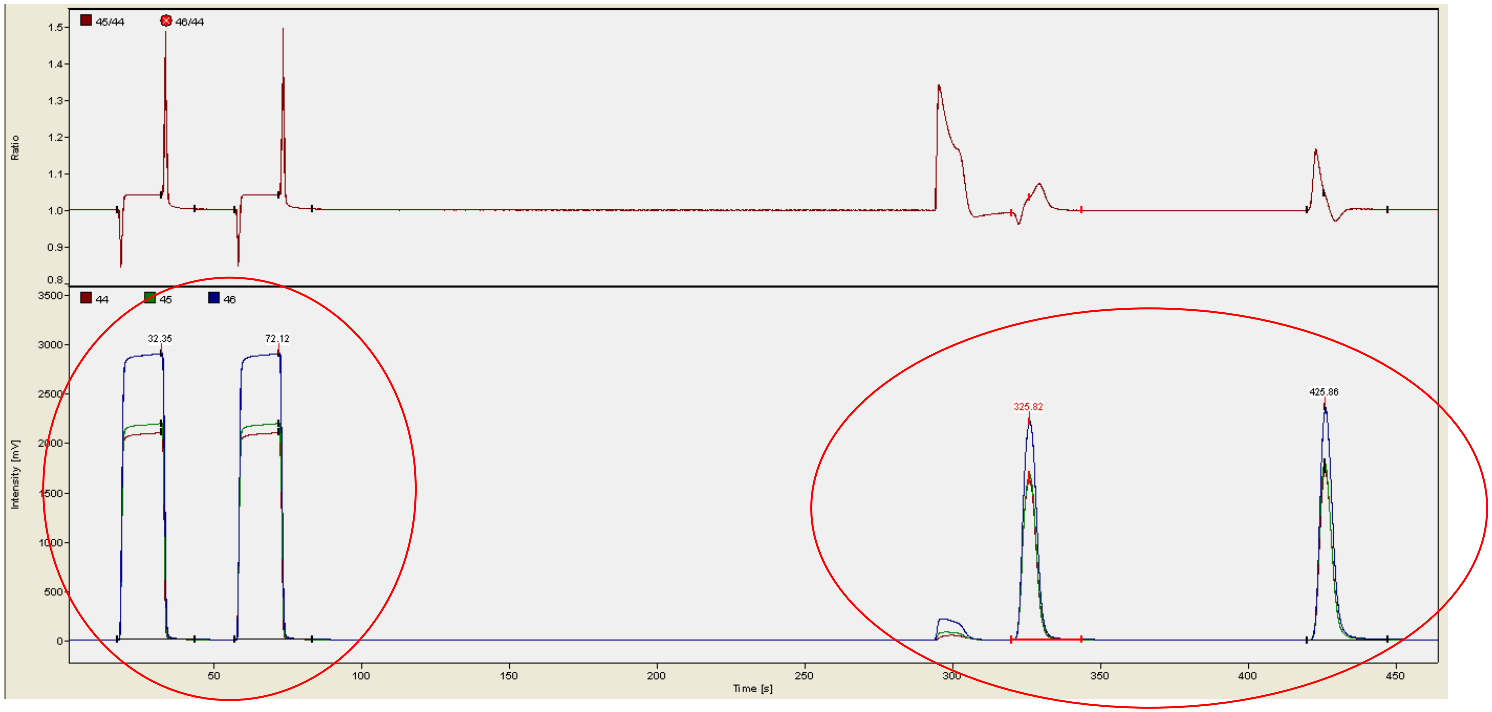
Calibrations and Standards

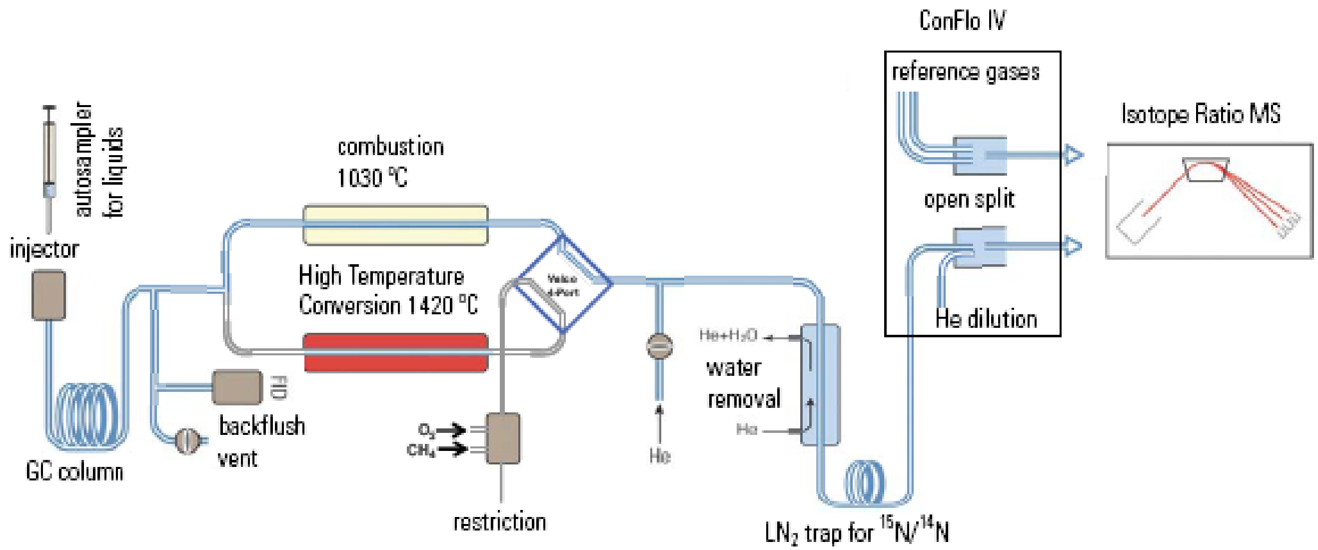
How Not to Calibrate



DON'T USE A REFERENCE GAS PULSE AS YOUR STANDARD!!!!!!!

Thermo GC IsoLink

- Thermo Fisher product literature



Potential Sources of Error:

-Sample handling
-Column (time shift)
-Leaks

- Injection
- Reactors
- Open split

- Interferences
- Poor separation
- Integration

-ZERO ENRICHMENT TEST!

Identical Treatment:

1) The reference and sample should be measured in the same way

2) The reference and sample should be the same compound (or class of compound)

3) The reference and sample should be as similar in composition and concentration as possible

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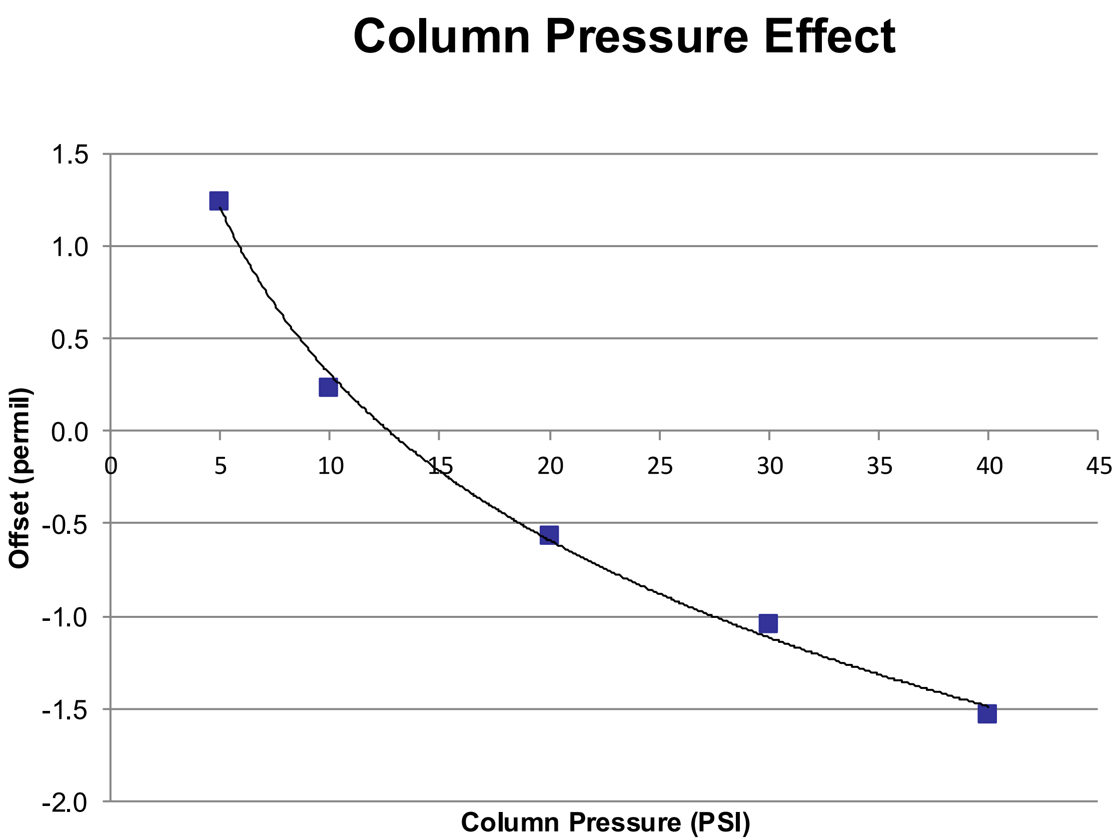
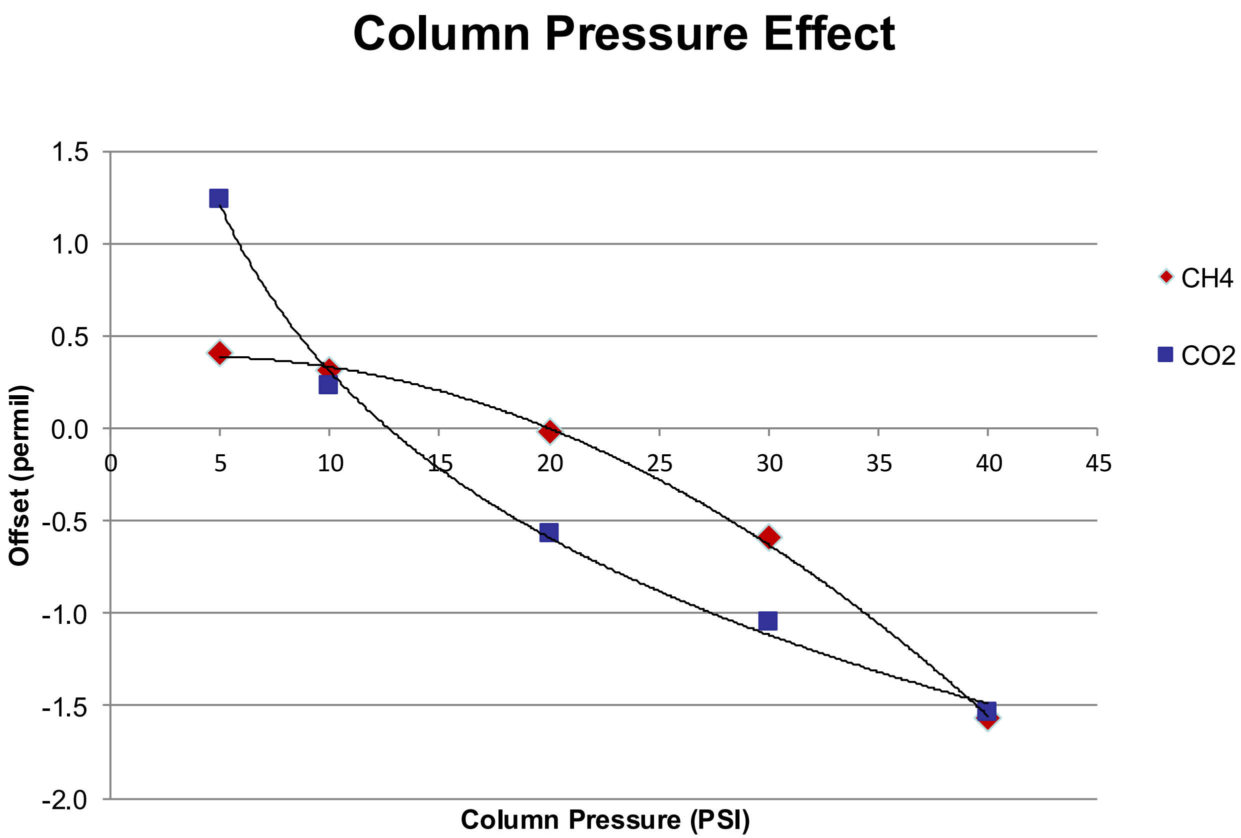
$\delta^{13}C$ on CH_4 and CO_2



GSQ PLOT column

60m, 0.32mm ID, 30C

$\delta^{13}C$ on CH_4 and CO_2



GSQ PLOT column

60m, 0.32mm ID, 30C

Where do you find reference materials?

Buy it or make it

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Indiana University – Arndt Schimmelmann

https://hcnisotopes.earth.indiana.edu/index.html

- Pure compounds and mixtures
- δ^2H, $\delta^{13}C$, $\delta^{15}N$, and $\delta^{18}O$
- GC and EA

- n-Alkanes (C1 to C50)
- Fatty acid esters
- Aromatics
- Nitrogen containing organics

Natural Gas Standards

- USGS Bob Dias – Mark Dreier (mdreier@usgs.gov)

- Replacing SRM8559, 8560, 8561
- 50 mL steel vessels

- Methane, Ethane, Propane
- Light, Intermediate, Heavy
- $\delta^{13}C$ and $\delta^{2}H$

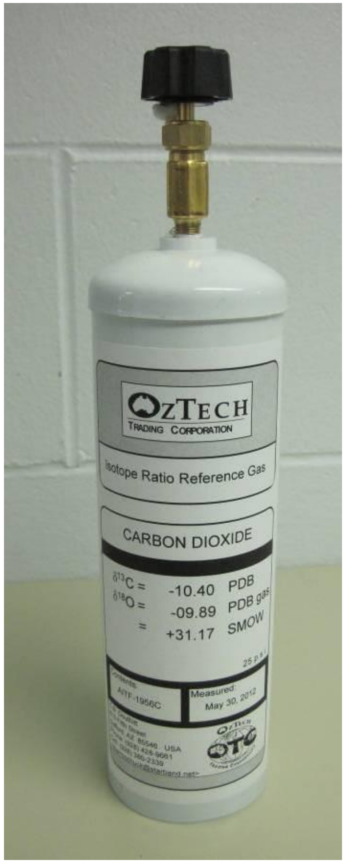
	USGS HCG-1			USGS HCG-2			USGS HCG-3		
	$\delta^{13}C$			$\delta^{13}C$			$\delta^{13}C$		
	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
Avg.	-1.51	-10.22	-15.43	-43.09	-29.80	-19.35	-61.39	-45.31	-36.80
Std. Dev.	0.08	0.03	0.10	0.10	0.04	0.09	0.12	0.06	0.06
n	12	21	21	30	21	21	6	6	6
	$\delta^{2}H$			$\delta^{2}H$			$\delta^{2}H$		
	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
Avg.	-64.0	54.3	74.6	-183.2	-125.6	-171.0	-224.3	-262.2	-245.2
Std. Dev.	3.1	4.6	7.6	5.7	1.9	2.0	3.2	3.0	2.3
n	12	21	18	29	21	20	6	5	6
	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
~mol %	46	43	11	59	33	8	93.5	1.2	0.4

Isomass

Oztech – Chuck Douthitt

Lecture bottles of pure H_2, CO_2 and N_2

Part #	Description	Pack	$\delta^{13}C$ ‰	$\delta^{2}H$ ‰	$\delta^{15}N$ ‰	$\delta^{18}O$ ‰	$\delta^{34}S$ ‰
Gases for Thermo instruments							
BRE0018705	Start-up kit with CO2 gas bottle and gas bottle regulator	Bottle	-25‰				
BRE0018708	Start-up kit with CO2 gas bottle and gas bottle regulator	Bottle	-3‰				
BRE0018710	Start-up kit with N2 gas bottle and gas bottle regulator	Bottle			0‰		
BRE0018712	Start-up kit with H2 gas bottle and gas bottle regulator	Bottle		-250‰			
BRE0018687	CO2 gas bottle	Bottle	-25‰				
BRE0018689	CO2 gas bottle	Bottle	-3‰				
BRE0018691	N2 gas bottle	Bottle			0‰		
BRE0018693	H2 gas bottle	Bottle		-250‰			
Gases for all instruments[4]							
	N2	Bottle			0‰		
	H2	Bottle		0‰			
	H2	Bottle		-60‰			
	H2	Bottle		-125‰			
	H2	Bottle		-360‰			
	H2	Bottle		-750‰			
	CO2	Bottle	-3‰			-16‰	
	CO2	Bottle	-10‰			-10‰	
	CO2	Bottle	-41‰			-30‰	
	CO2	Bottle	-47‰			-37‰	

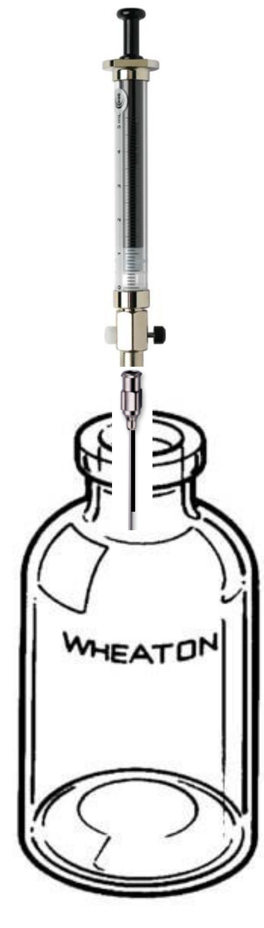


Air Liquide

Airgas
an Air Liquide company

Elements	Delta Ratio of	Range	Gas Selections
C	^{13}d ~‰ VPDB	-70 to +20	Air, CH_4 and mixtures
C	^{13}d ~‰ VPDB	Please inquire	C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, n-C_5-H_{12}, i-C_5H_{12} and mixtures
O	^{18}d ~‰ VSMOW	-30 to +10	CO, CO_2, Air and mixtures
H	^{2}d ~‰ VSMOW	-300 to +100	CH_4 and mixtures
H	^{2}d ~‰ VSMOW	Please inquire	C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, n-C_5-H_{12}, i-C_5H_{12}, and mixtures
N	^{15}d ~‰ AIR	-20 to +20	N_2, N_{20}, NOx, Air and mixtures
S	^{32}d ~‰ VCDT	-20 to +20	SO_2, H_2S and mixtures
S	^{32}d ~‰ VCDT	-25 to +25	SF_6 and mixtures (under development)

Dilution into bottle
(Wheaton bottle with big blue stopper from Bellco Glass)



Make It Yourself

A) Obtain materials as potential in-house standards
- Same as your samples
- Should be pure, and isotopically homogeneous
- Gather from different sources, then cross your fingers
- Spiking, evaporating

B) Find a way to calibrate vs NIST/IAEA/USGS standards
- GC
- Dual Inlet
- **EA (combustion or pyrolysis)**

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Make It Yourself

Elemental Analyzer Methods

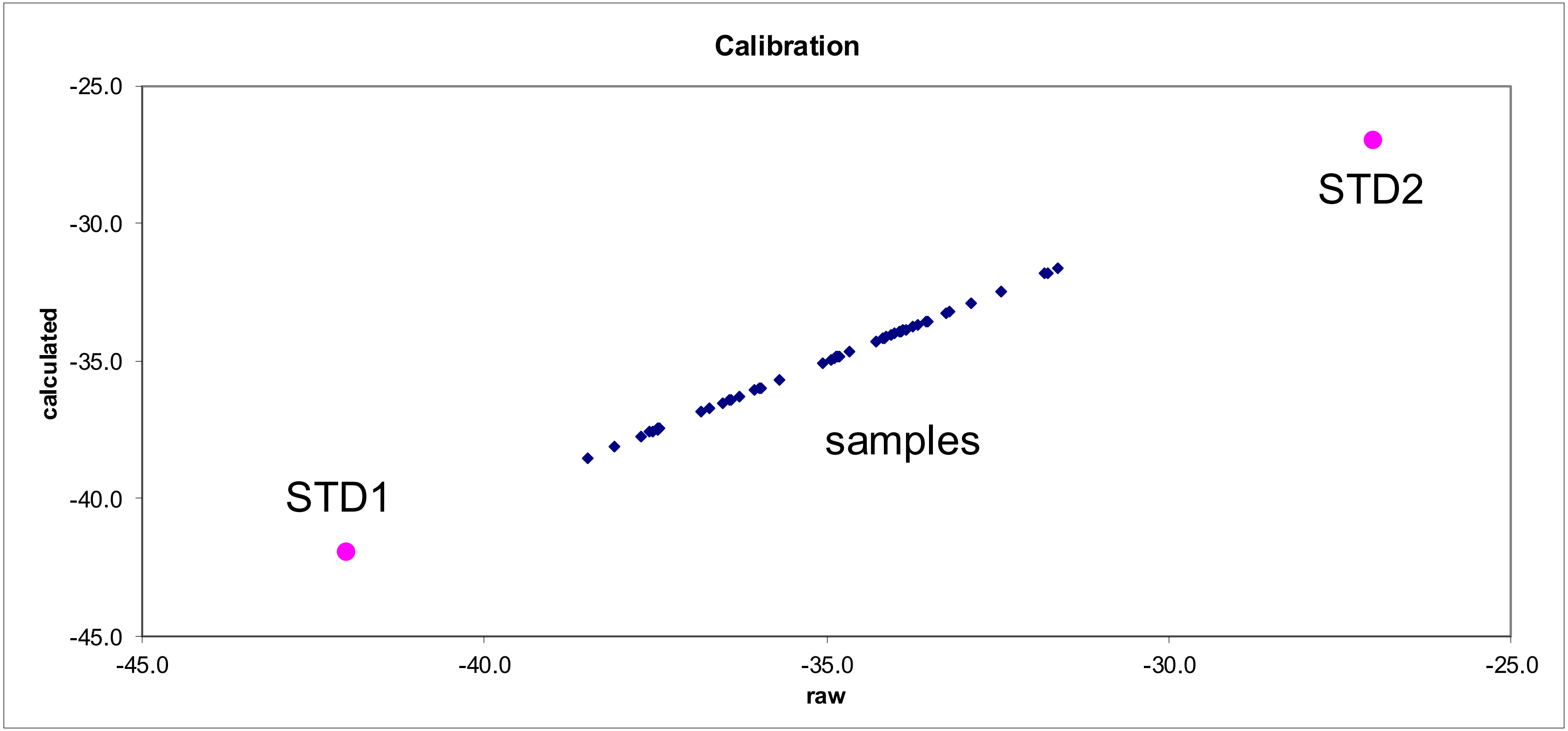
- Even liquids and gases!
- IAEA/NIST standards, Oztech standards
- Combustion ($\delta^{13}C$) and Pyrolysis ($\delta^{2}H$)

Sperlich, P. et. al.

A robust method for direct calibration of isotope ratios in gases against liquid/solid reference materials, including a laboratory comparison for δ^{13} C-CH_4.

Rapid Commun Mass Spectrom. 2021 Jan 15;35(1).

How Many Standards Do You Need?

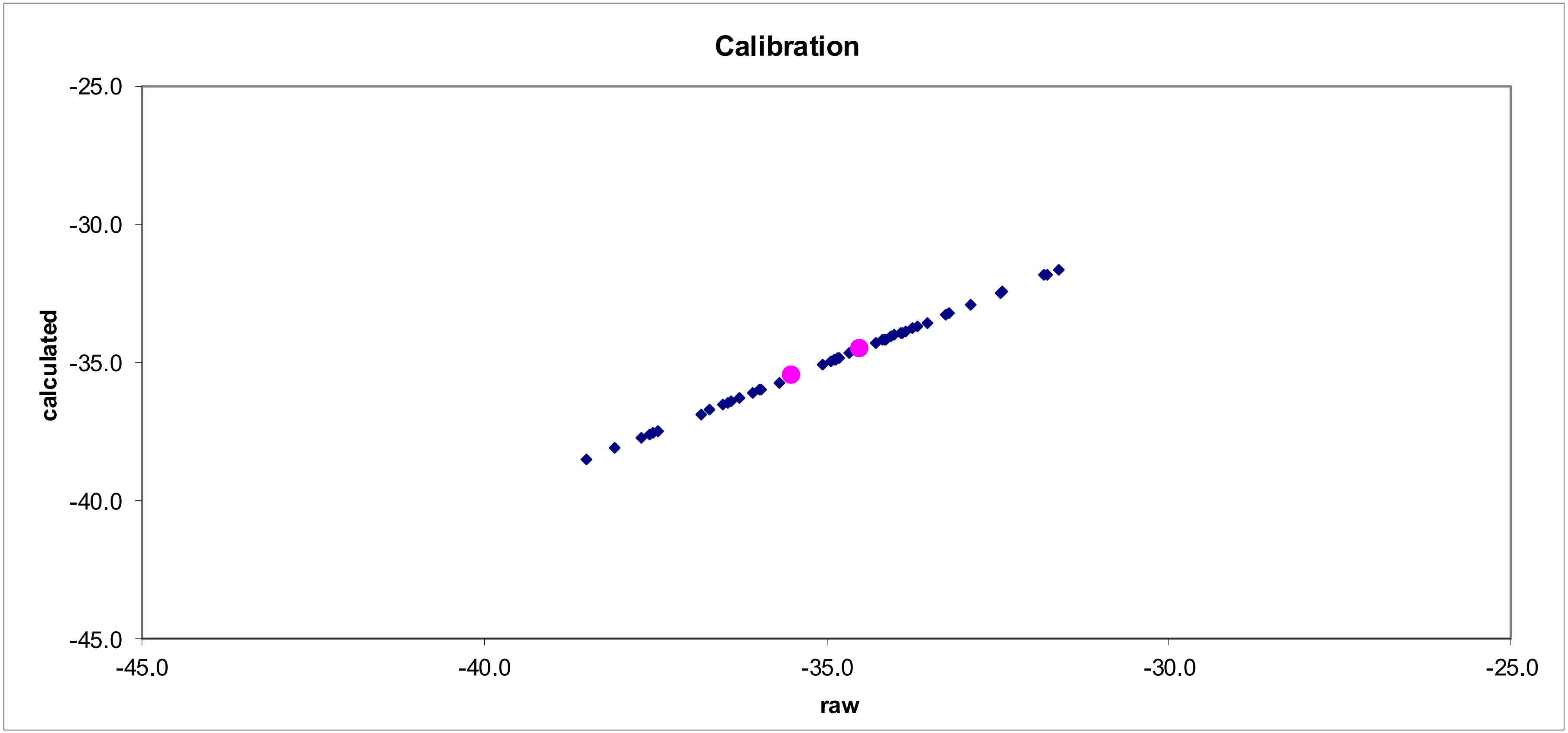


standard	known	raw
#1	-42.1	-42.5
#2	-27.4	-28.0

Linear Regression →

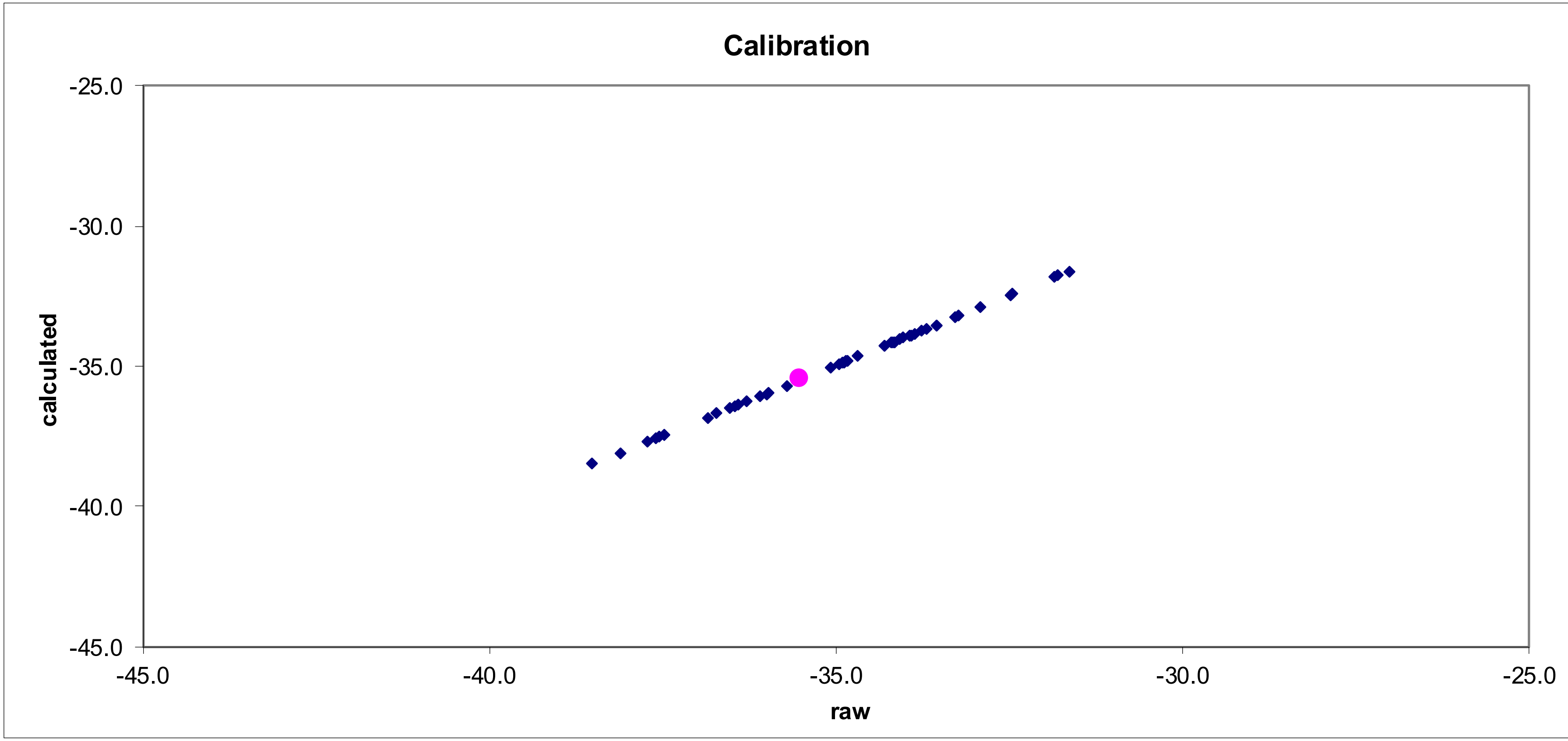
slope = 1.014
intercept = 0.99

How Many Standards Do You Need?



The values of your standards need to be far apart

How Many Standards Do You Need?



standard	known	raw
#1	-42.1	-42.5
#2	---	---

slope = 1

intercept = offset

My Gas Standards – d^2H

Methane standards

- Praxair -54‰
- Air Liquide -285‰ (-288‰)

How did I calibrate them?

- USGS natural gas standards
- Injection on HDevice

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My Gas Standards – d^{13}C

CO_2	Oztech	-3.58 & -47.44‰	
CH_4	Isometric	-23.9 & -66.5‰	
C_1-C_4	Praxair	CO_2	-32.0 ‰
		C_1	-42.4 ‰
		C_2	-30.1 ‰
		C_3	-33.1 ‰
		i-C_4	-30.2 ‰
		n-C_4	-33.5 ‰

Calibration check

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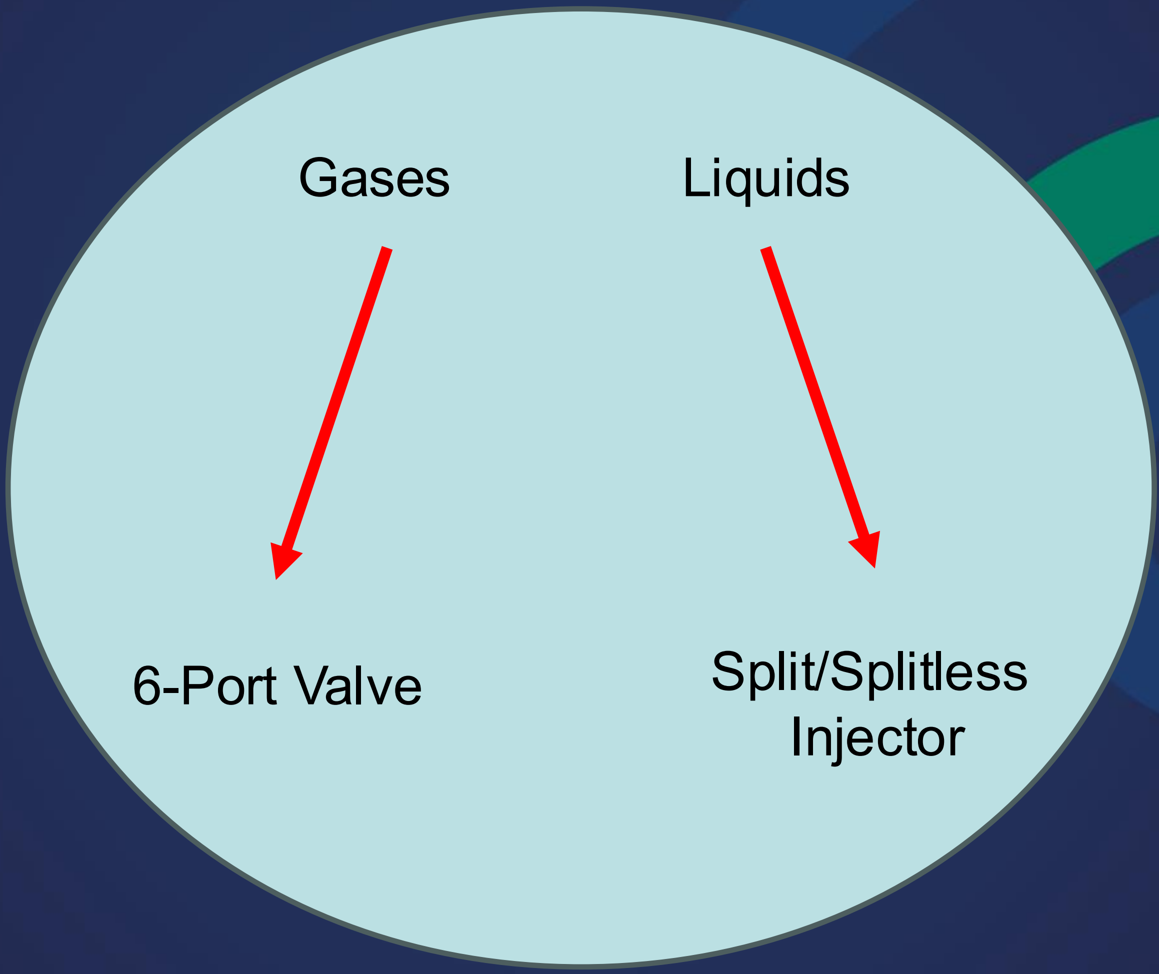
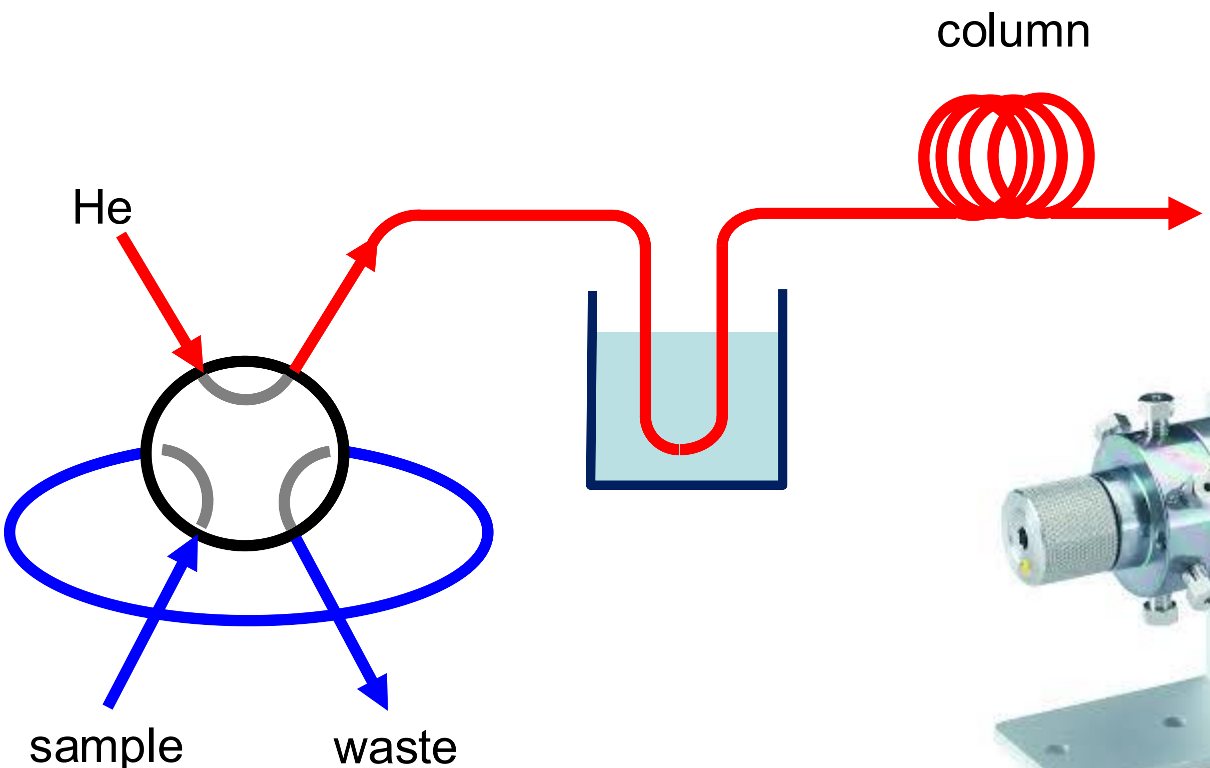
GC Setup

How do you inject samples?

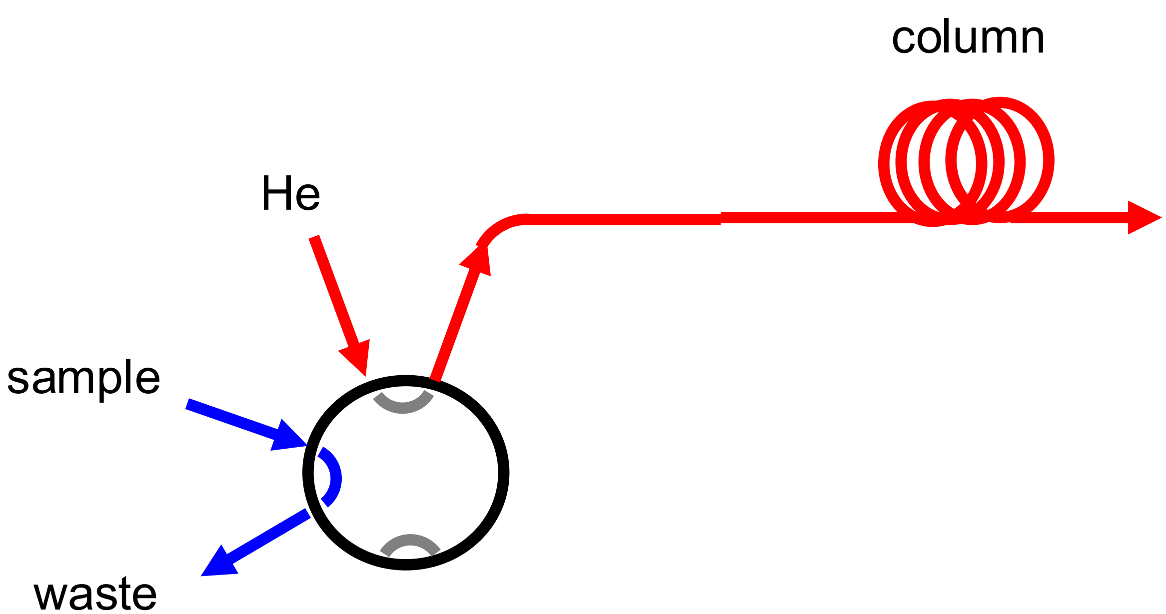


6 Port Valve for Injection of Gas



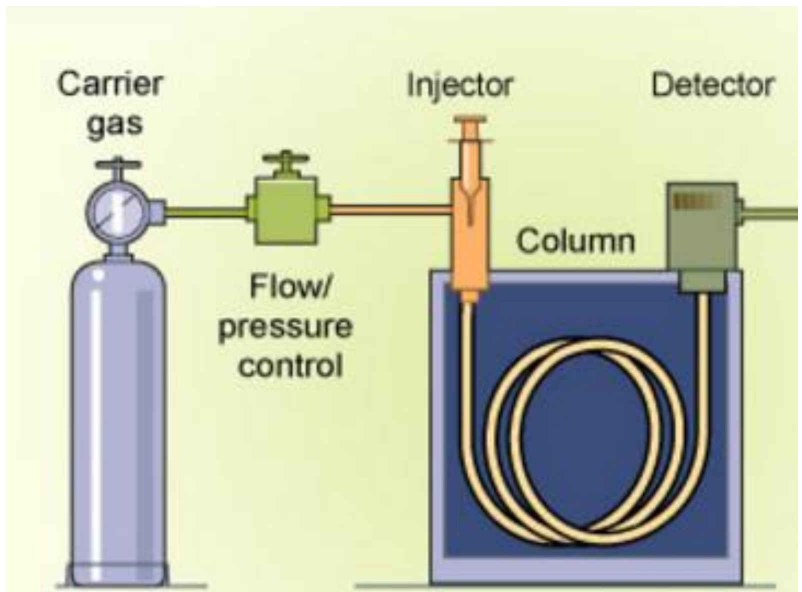
- Max loop size: 1.0mL → 20ppm CH_4
- Max loop size without focusing: 100uL → 200ppm
- Min loop size: 5uL → 5% CH_4

Internal Volume Valve for Injection of Gas

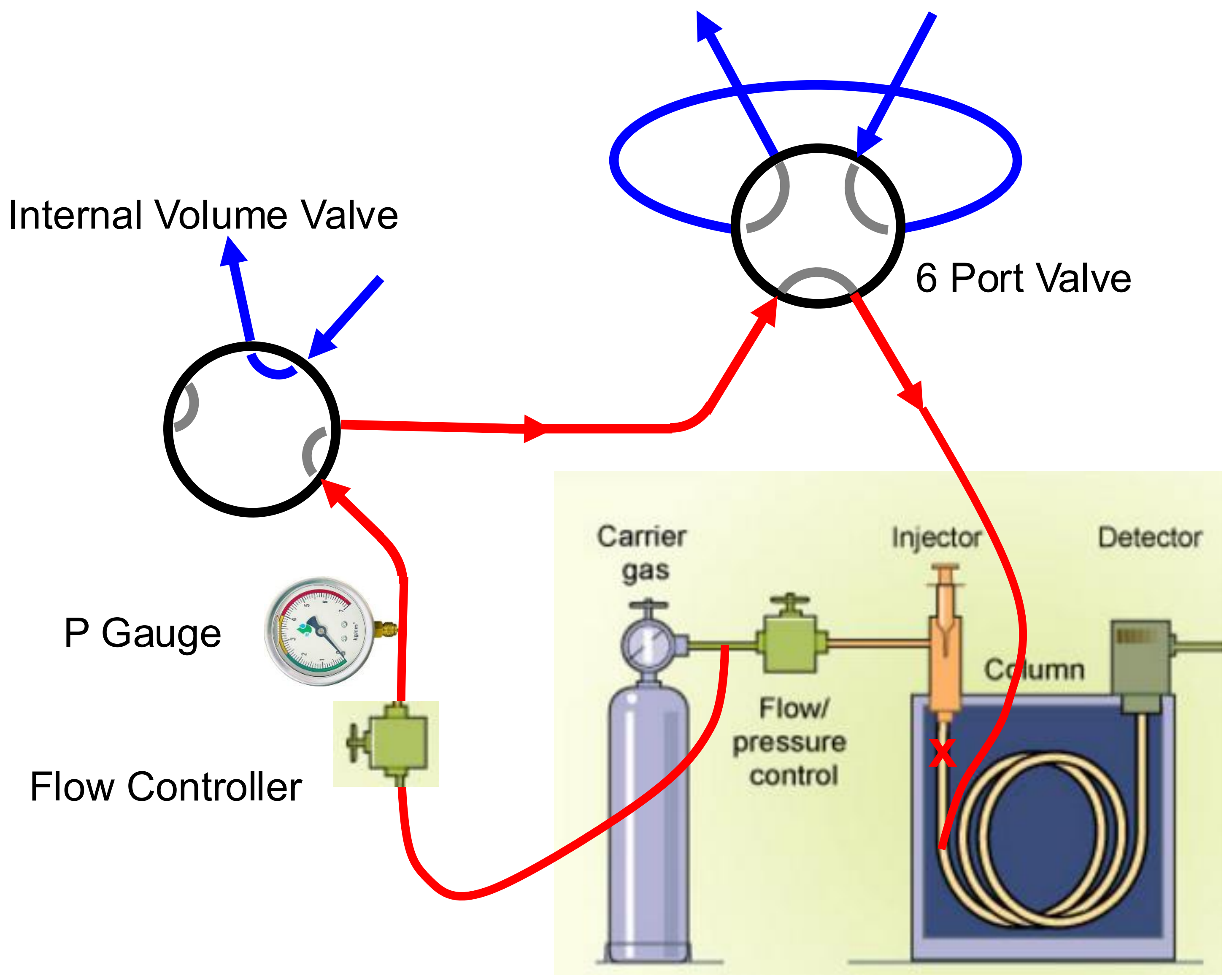


- Sample volume is the path etched on the rotor
- 0.06 uL to 2 uL → 100% CH_4 (0.5uL)

6 Port Valve for Injection of Gas



6 Port Valve for Injection of Gas



Chromatographic Issues

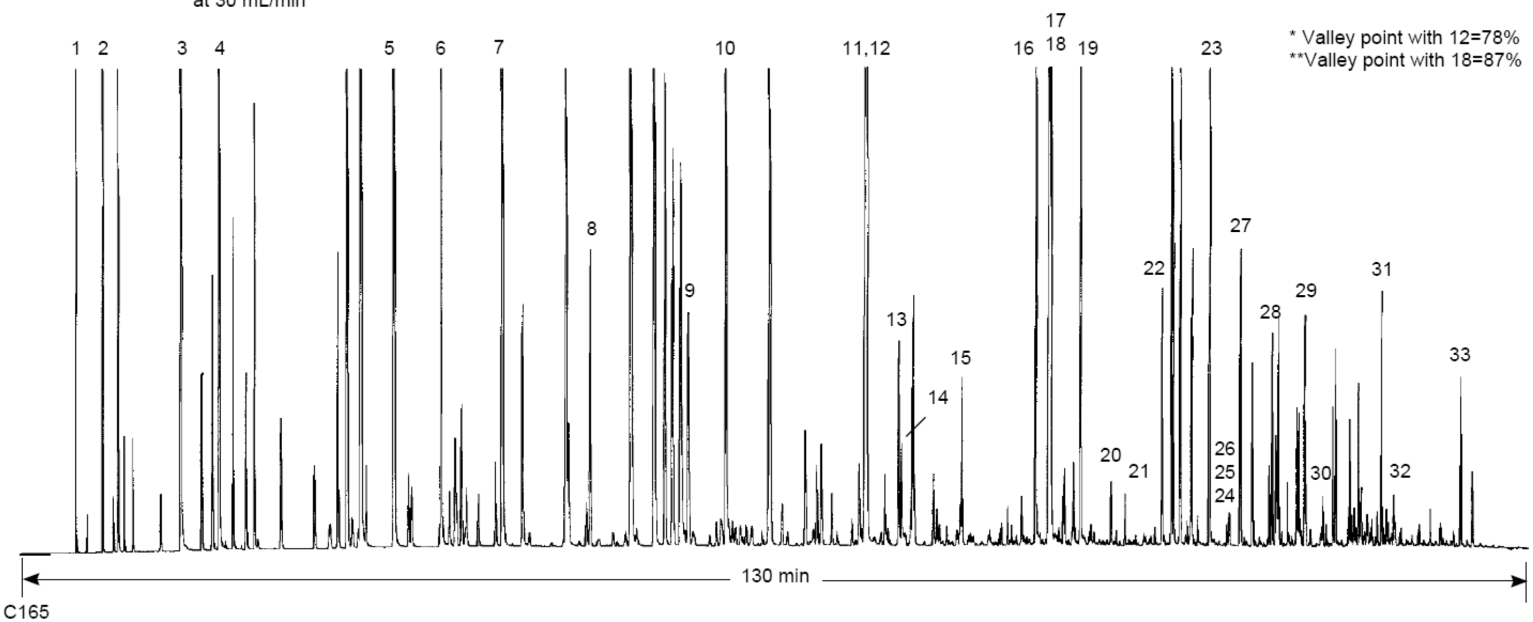
Baseline Separation

Unleaded Gasoline

Column: **DB-Petro100**
100 m x 0.25 mm I.D., 0.5 µm
J&W P/N: **122-10A6**
Carrier: Helium at 25.6 cm/sec
Oven: 0°C for 15 min
0-50°C at 1°/min
50-130°C at 2°/min
130-180°C at 4°/min
180°C for 20 min
Injector: Split 1:300, 200°C
1 µL of neat sample
Detector: FID, 250°C
Nitrogen makeup gas
at 30 mL/min

1. Methane
2. *n*-Butane
3. Isopentane
4. *n-Pentane*
5. *n*-Hexane
6. Methylcyclopentane
7. Benzene
8. Cyclohexane
9. Isooctane
10. *n*-Heptane
*11. Toluene
12. 2,3,3-Trimethylpentane
13. 2-Methylheptane
14. 4-Methylheptane
15. *n*-Octane
16. Ethylbenzene
**17. *m*-Xylene
18. *p*-Xylene
19. o-Xylene
20. *n*-Nonane
21. Isopropylbenzene
22. Propylbenzene
23. 1,2,4-Trimethylbenzene
24. Isobutylbenzene
25. *sec*-Butylbenzene
26. *n*-Decane
27. 1,2,3-Trimethylbenzene
28. Butylbenzene
29. *n*-Undecane
30. 1,2,4,5-Tetramethylbenzene
31. Naphthalene
32. Dodecane
33. Tridecane

* Valley point with 12=78%
**Valley point with 18=87%



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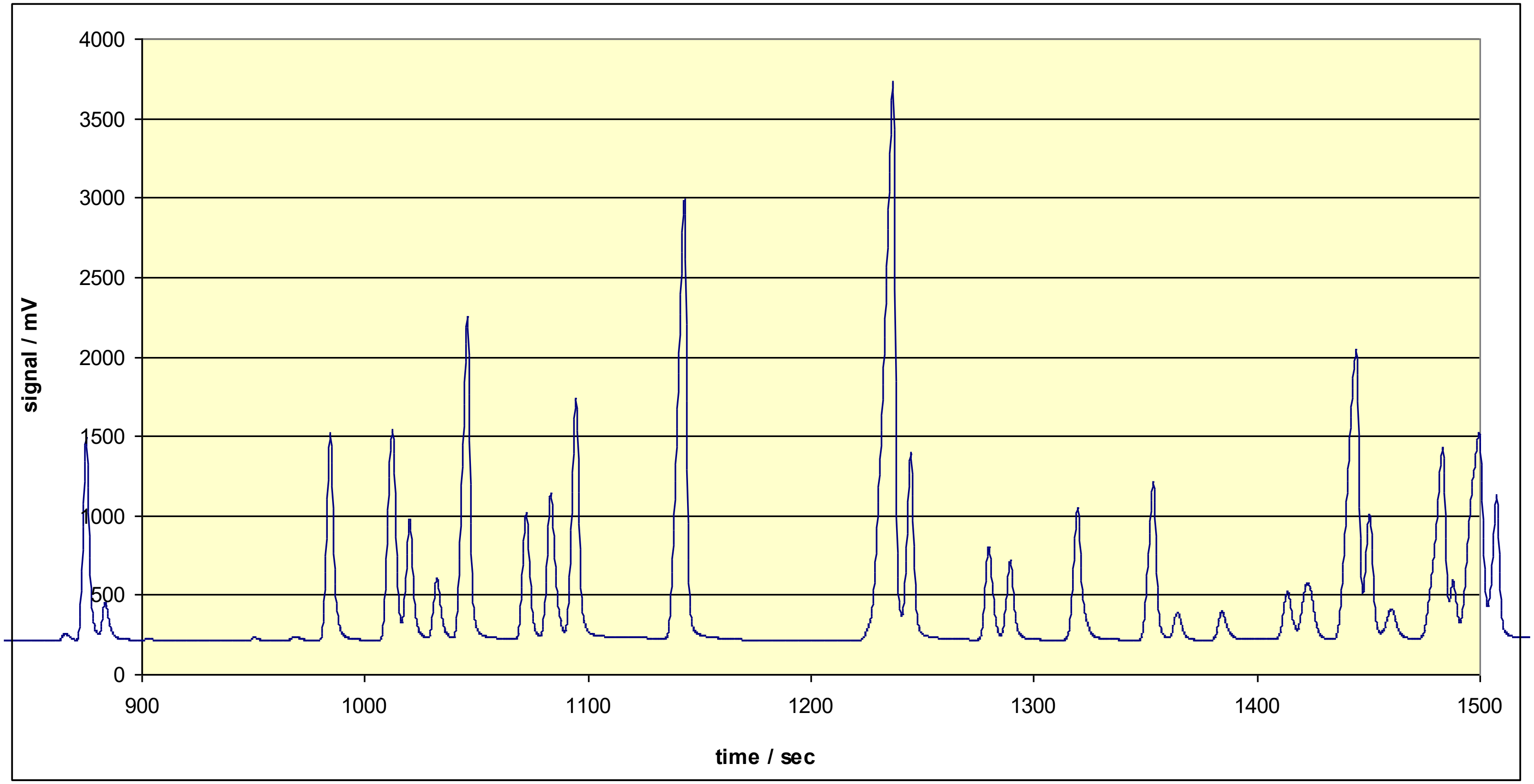
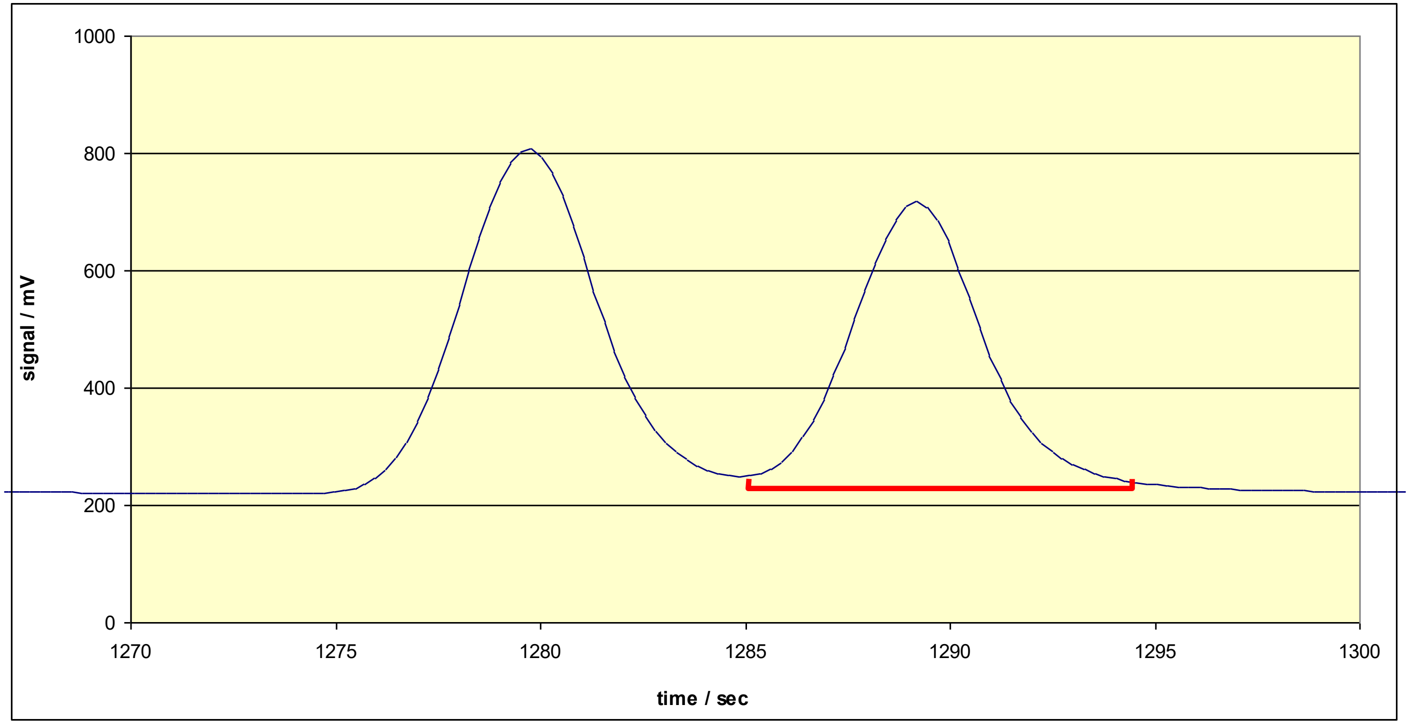
Chromatographic Issues

Baseline Separation



Chromatographic Issues

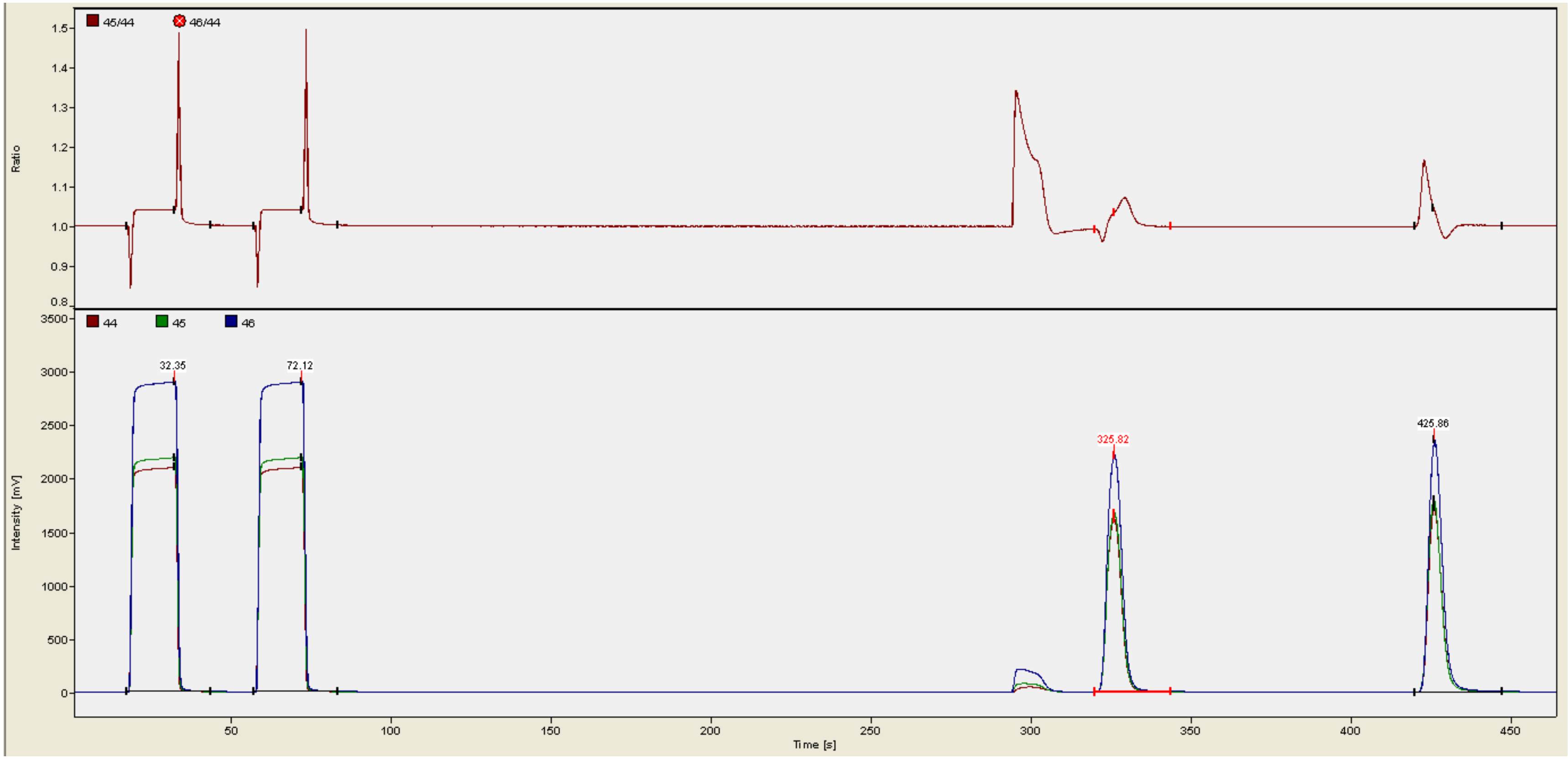
Integration Sensitivity



- Shift the start and stop integration time
- Change the baseline measurement
- Does the value change?

Chromatographic Issues

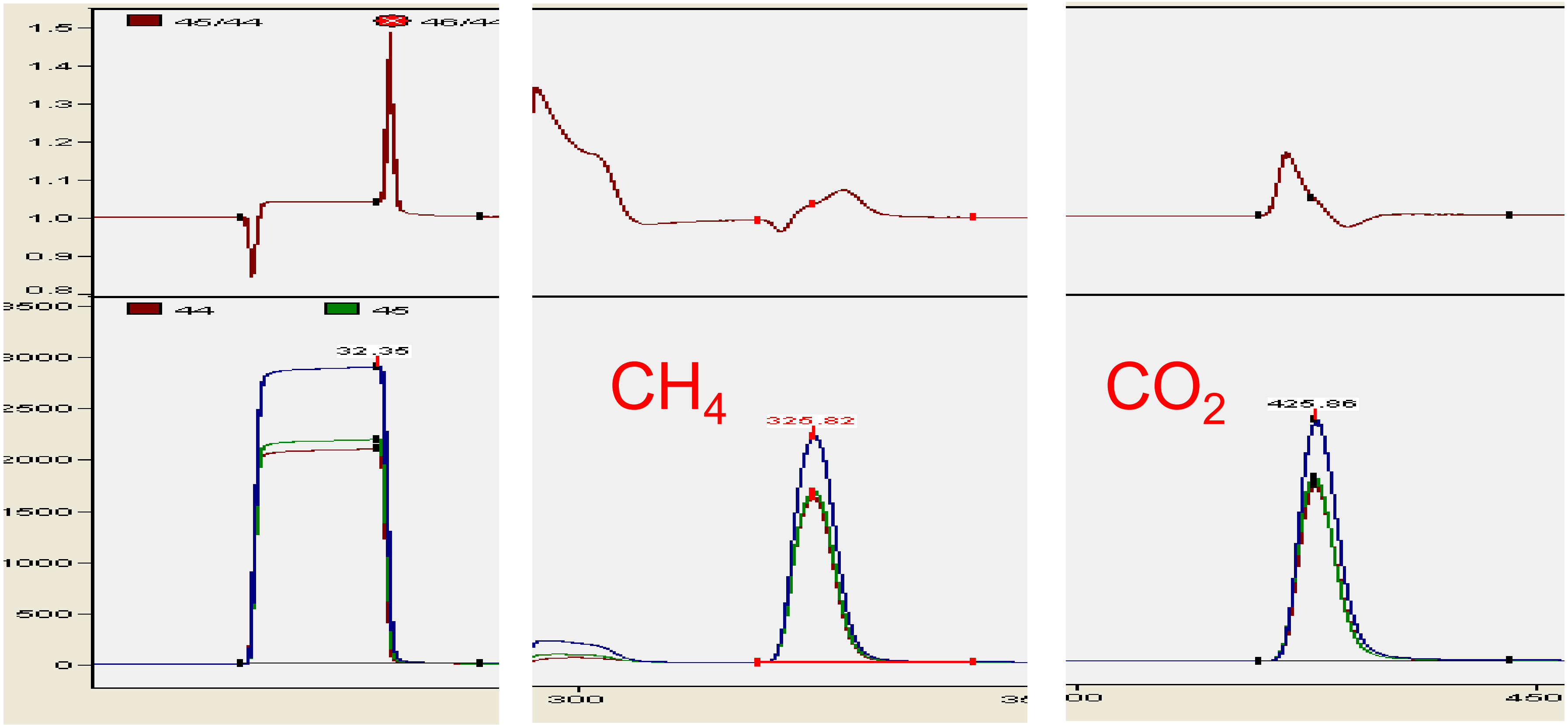
Why is baseline separation so important?



1. 45/44 is NOT homogenous through the peak
2. Tails are important for the integration

Chromatographic Issues

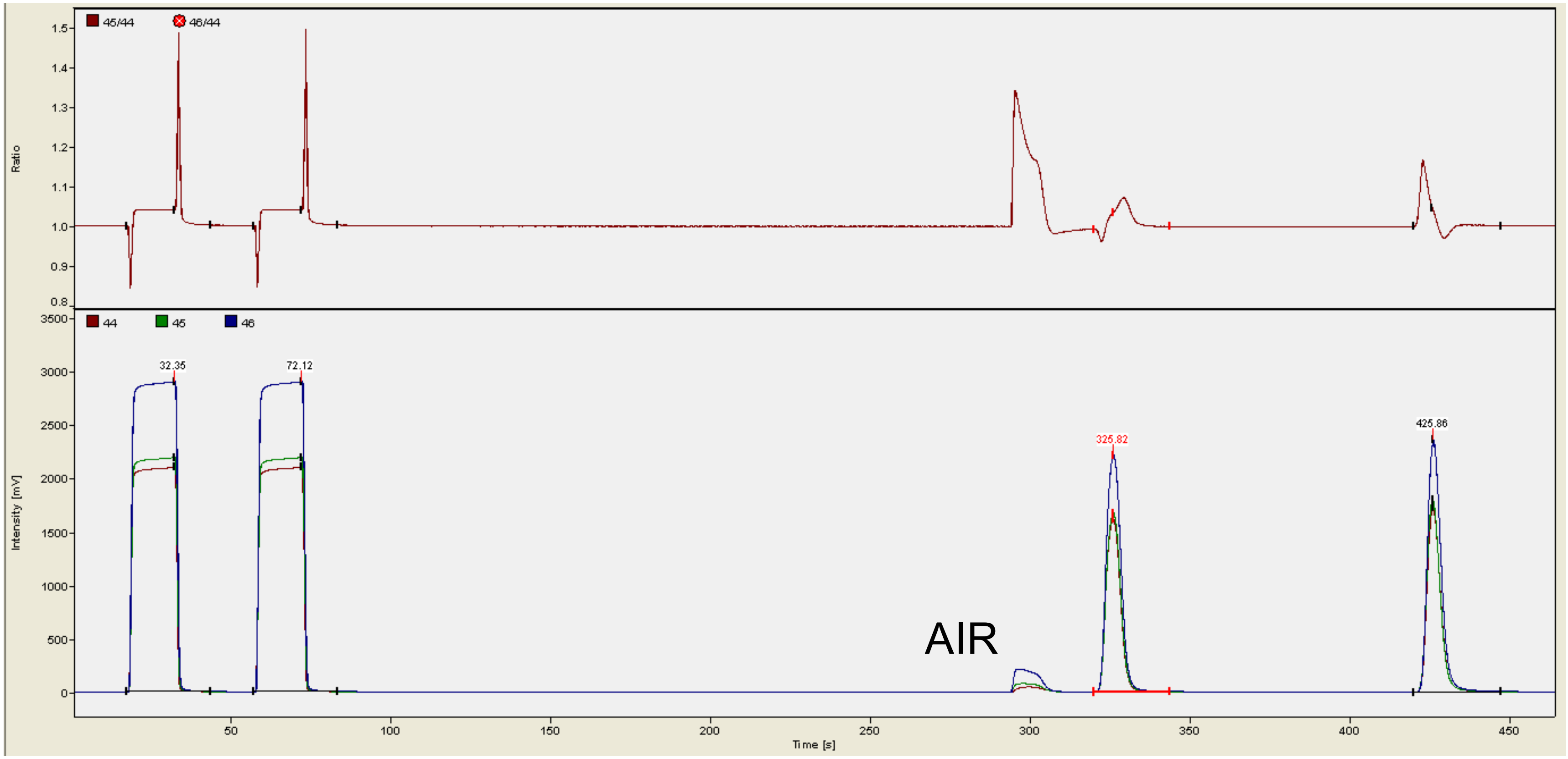
Why is baseline separation so important?



1. 45/44 is NOT homogenous through the peak
2. Tails are important for the integration

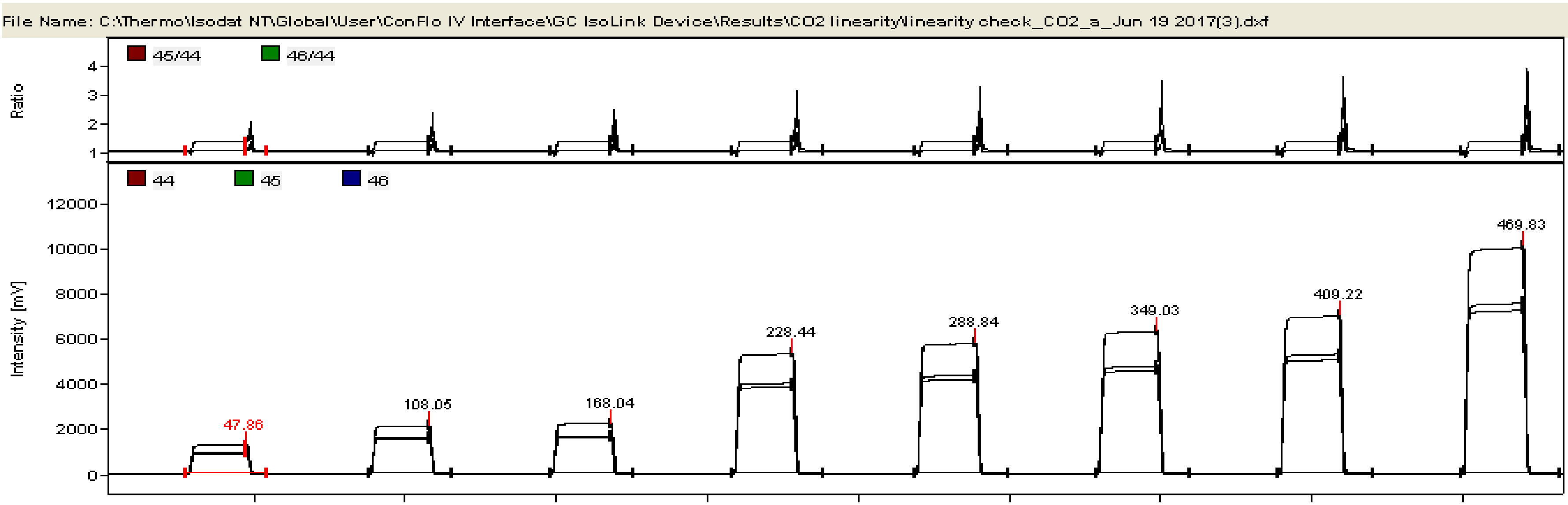
Chromatographic Issues

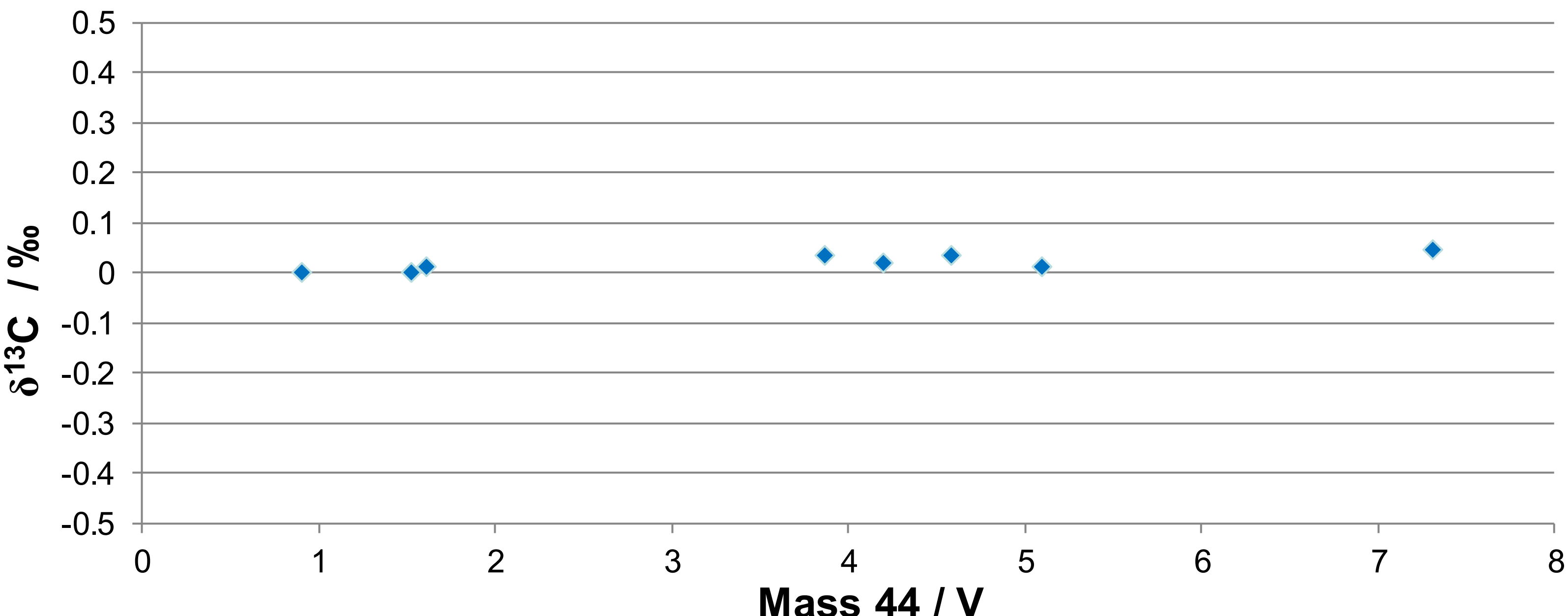
Air Peak



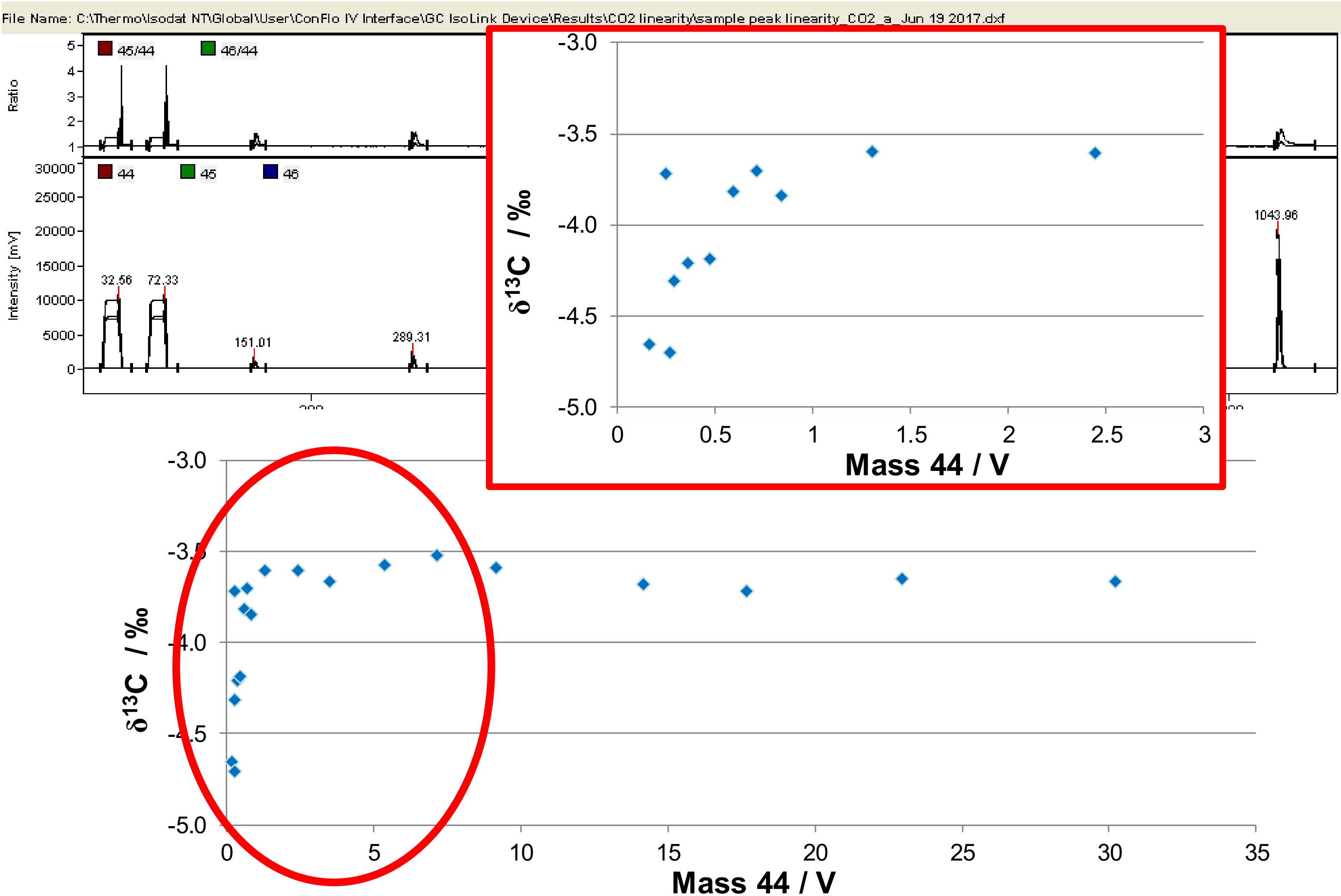
1. Integrates at +500 permil
2. Why does air show up on 44/45/46?

Source Linearity





Whole System Linearity



Combustion and Pyrolysis

Converting your peaks to H_2 and CO_2

Combustion

1. Ceramic Tube
   - 0.5 mm ID
   - Alumina (inert, gas impermeable)
2. Metal wires
   - 0.1mm diameter
   - Copper or nickel
   - Platinum
3. Oxygen
4. Heat

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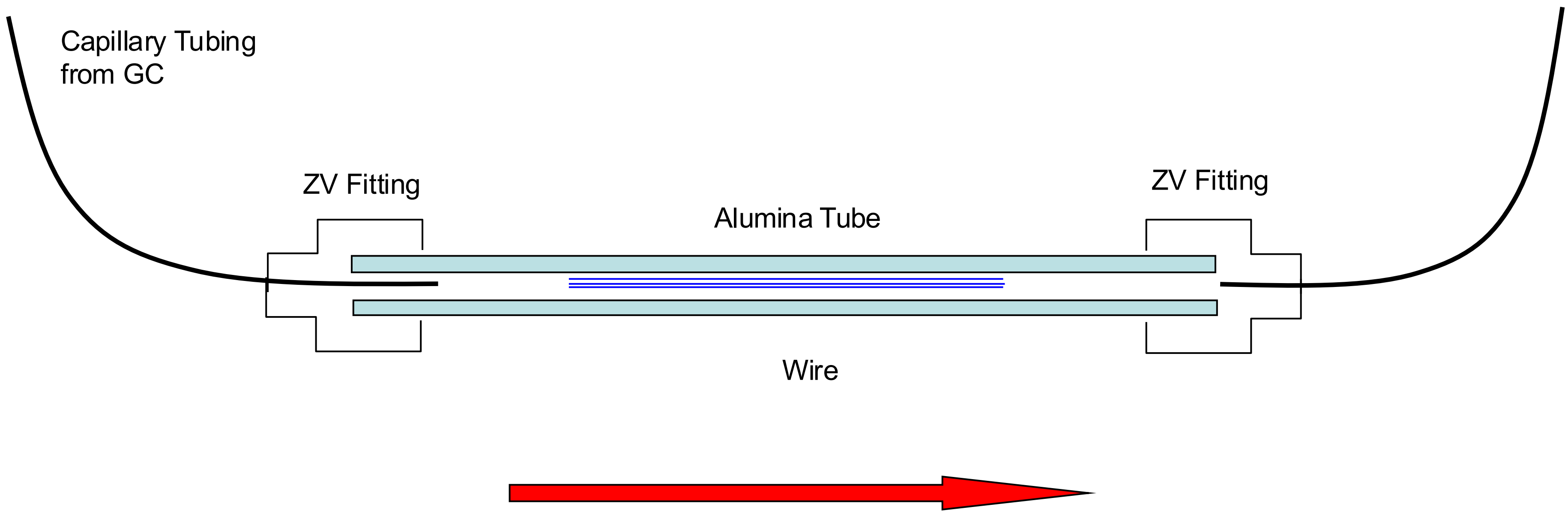
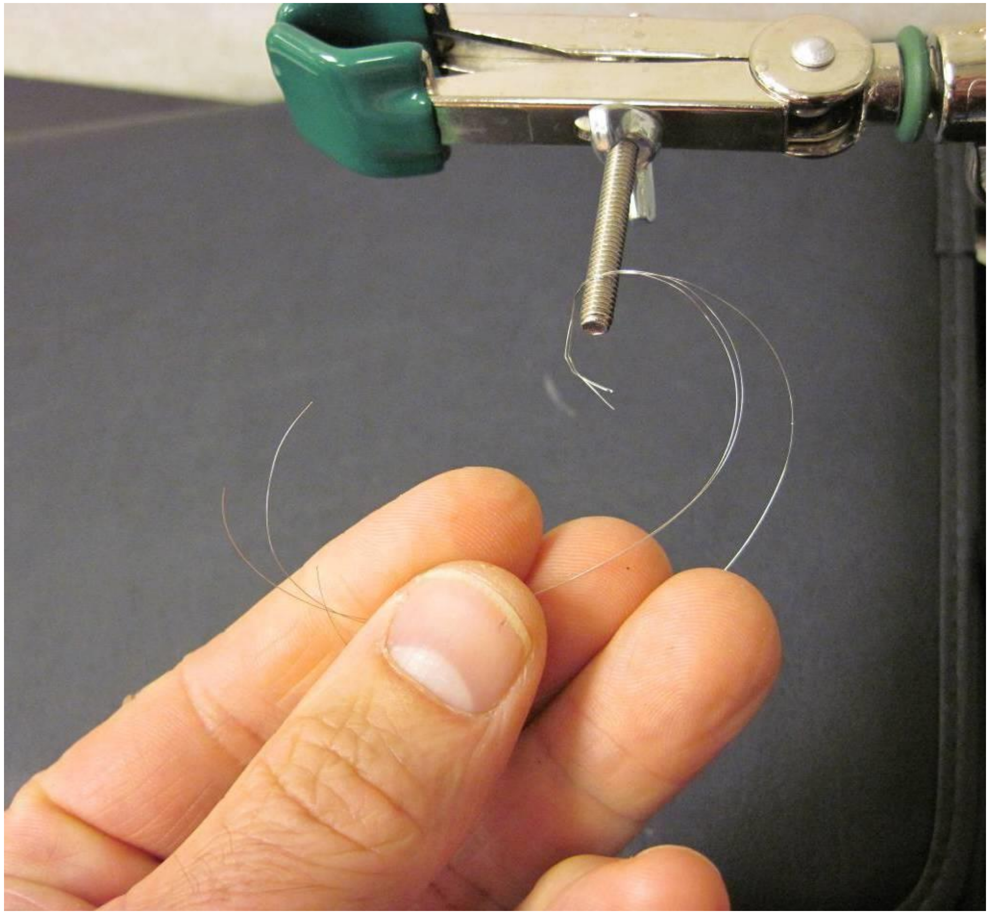
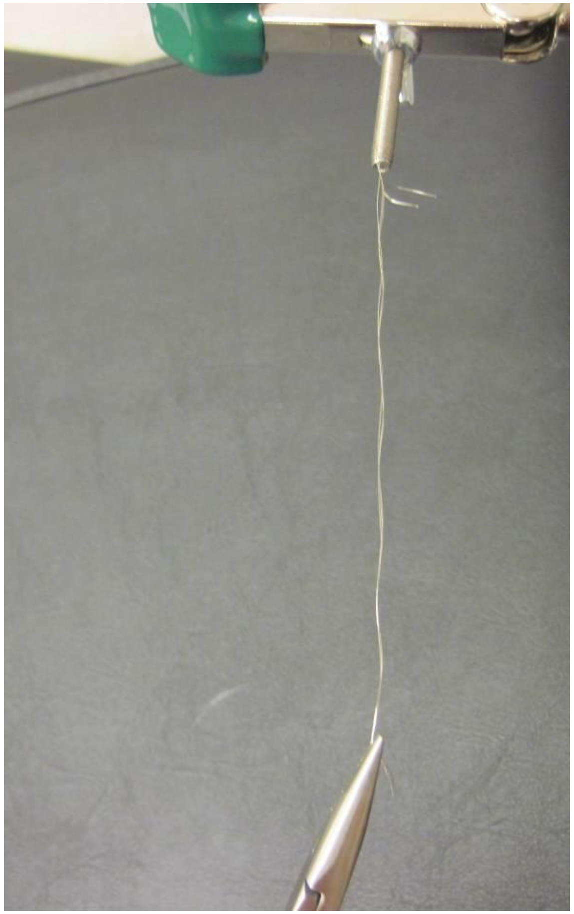
Combustion



- Input capillary should be inserted 1cm
- Wires need to be centered in the hot zone
- Approx 15cm in a 30cm tube





What Metal?

1) Copper/Platinum
   - 3 Cu and 1 Pt wire
   - 850°C

Trouble with methane

2) Nickel/Platinum
   - 3 Ni and 1 Pt wire
   - 1020°C

Higher Temperature

Holds on to oxygen longer

Longer life

3) Copper/Nickel/Platinum
   - 950°C

Hybrid

Oxidation Time

Pyrolysis

Shouldn’t this be easy?

Pyrolysis vs thermal conversion vs thermolysis vs reduction

Just an empty ceramic tube (alumina)

- Conditioning required
- 1400°C to 1450°C

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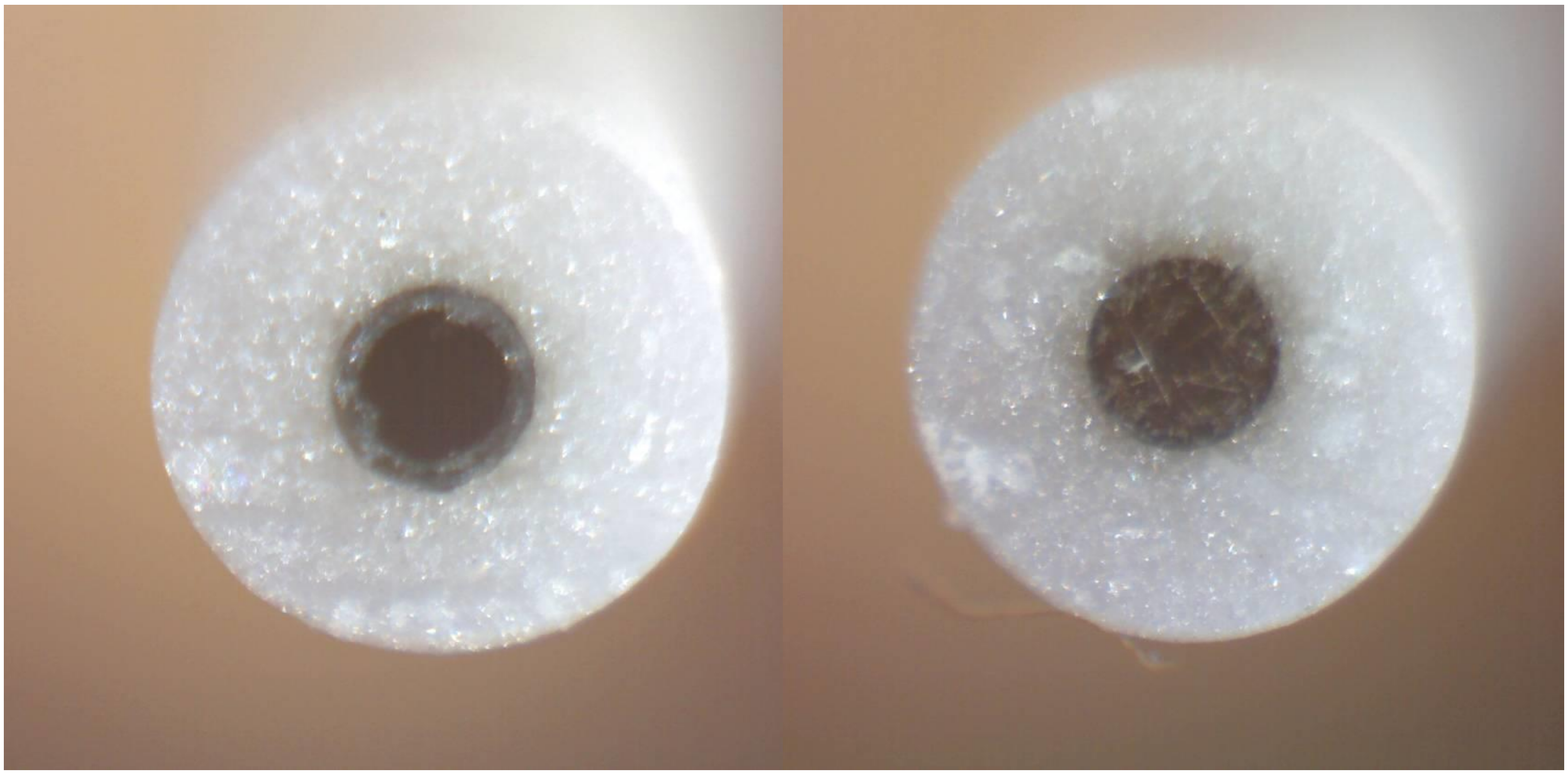
Pyrolysis:

Shouldn't this be easy?

-Conditioning is necessary to deactivate the interior surface
-Large quantity of a hydrocarbon will deposit carbon
-If you do too much you can block the tube:

Pyrolysis:

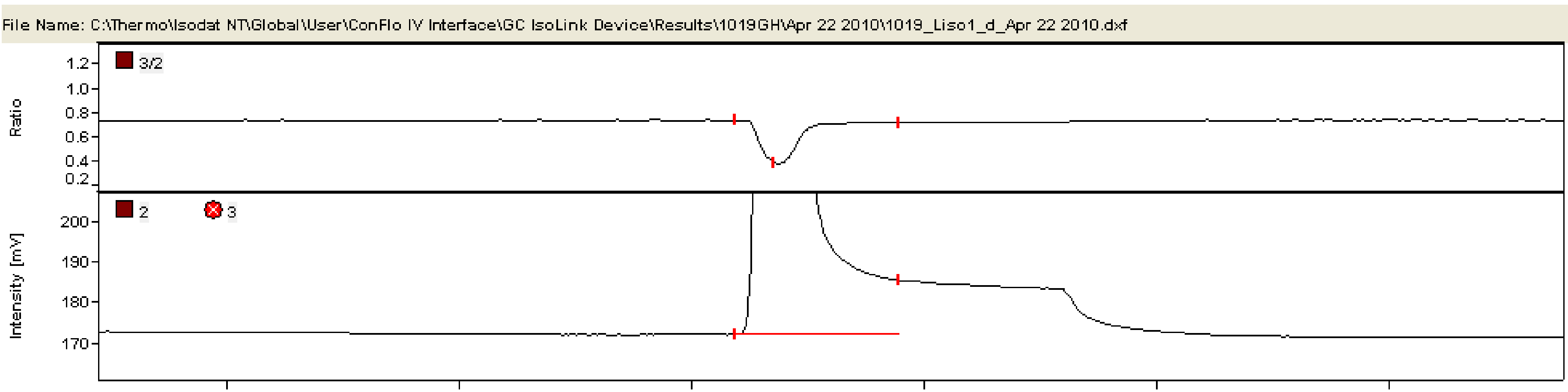
Shouldn’t this be easy?



Pyrolysis:

Shouldn't this be easy?

-If you don't do enough:



- Alumina is actually a poor choice of materials
- Produced H_2 can then combust

Pyrolysis:

Shouldn’t this be easy?

Air samples - Injected oxygen will:

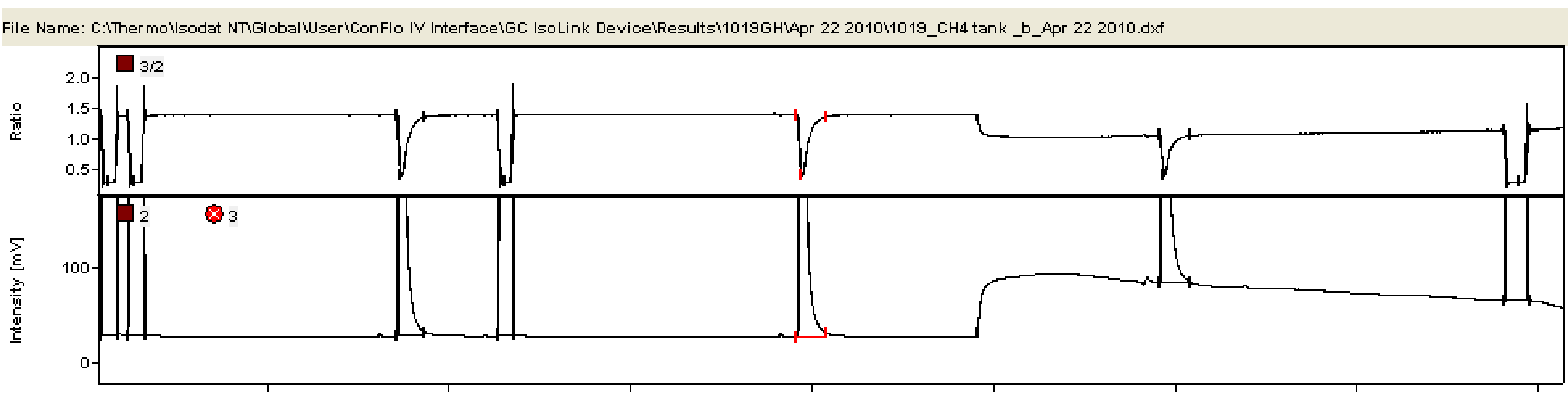
- allow oxidation of your current sample (methane)
- strip off the deactivating layer of carbon

Pyrolysis:

Water Trouble

-No Nafion trap required

-Water contamination injected with the sample:



Contact me

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