

GC-C and GC-Pyrolysis IRMS Short Course:

Putting the Gas In Gas Chromatography

Paul Eby



GC-C and GC-Pyrolysis IRMS Short Course:

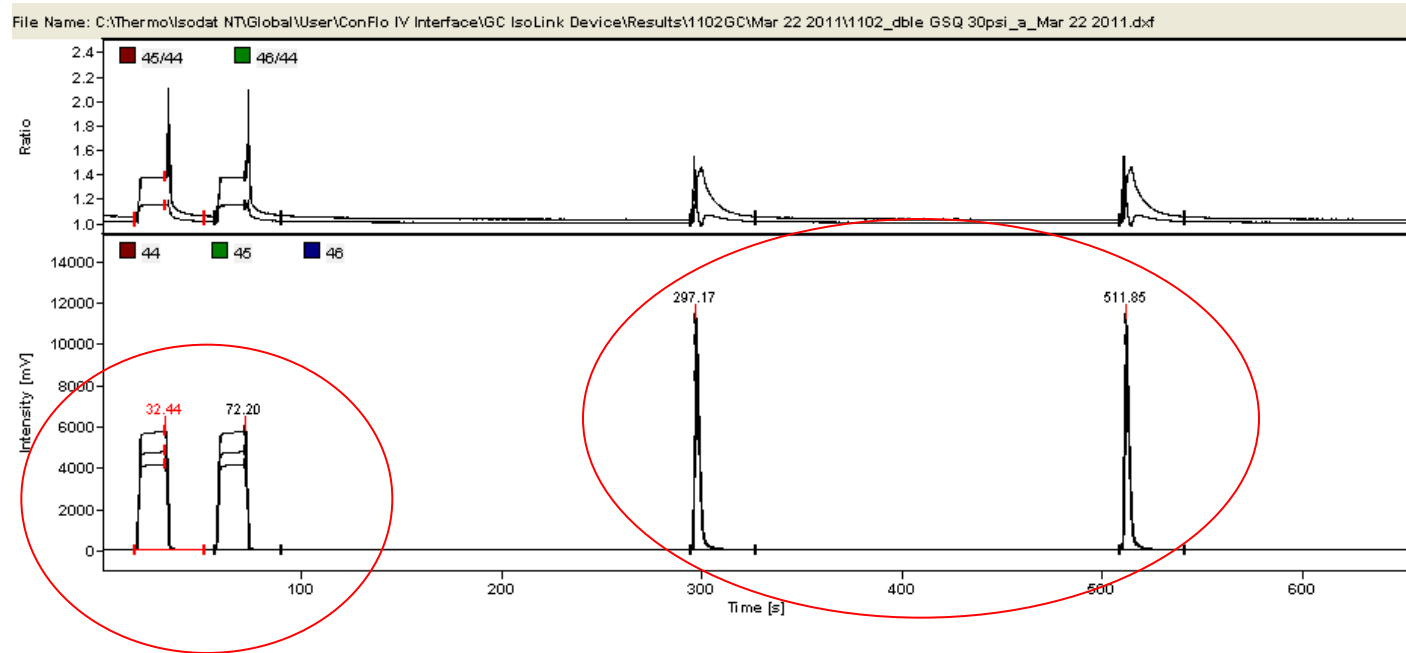
Putting the Gas In Gas Chromatography

Part 1: Standards

Part 2: GC Set Up

Part 3: Combustion & Pyrolysis

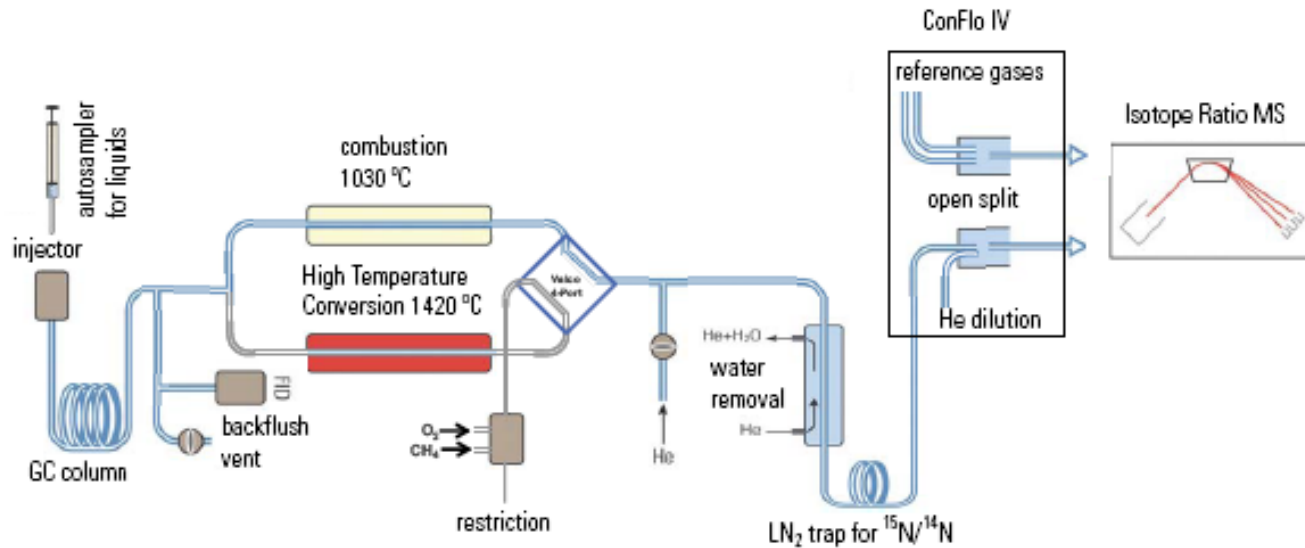
Part 1: Standards



AVOID USING A REFERENCE GAS PULSE AS YOUR STANDARD!!!!!!!

Thermo GC IsoLink

- Thermo Fisher product literature



Potential Sources of Error:

- Sample handling
- Injection
- Interferences
- Column effects
- Reactors
- Poor separation
- Leaks
- Open split
- Integration

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

Where Do You Find Reference Materials?

- 1) NIST / IAEA
- 2) Commercial Products
- 3) Make it yourself
- 4) Beg/borrow/steal

NIST - Light Stable Isotopic Materials (gas, liquid and solid forms)

SRM	Status	Description	Unit Size	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$	$\delta^{18}\text{O}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$	$\delta^2\text{H}$
8529	Now Selling	IAEA S 3 (Sulfur Isotopes in Silver Sulfide)	1 bottle x 0.5g					
8535a	Now Selling	VSMOW2 Vienna Standard Mean, Ocean Water	20 mL				0	0
8536	Now Selling	GISP-Water	20 mL				-24.78	-189.5
8537	Now Selling	SLAP-Water Light Stable Isotopic Standard	20 mL				-55.5	-428
8539	Now Selling	NBS 22-Oil	1 mL	-30.03				-116.9
8540	Now Selling	PEFI-Polyethylene Foil	3.5 g	-32.15				-100.3
8541	Now Selling	USGS24-Graphite	0.8 g	-16.05				
8542	Now Selling	Sucrose ANU-Sucrose	1 g	-10.45				
8543	Now Selling	NBS18-Carbonatite	0.4 g	-5.01		-23.01	+7.20	
8544	Now Selling	NBS19-Limestone	0.4 g	+1.95		-2.2	+28.65	
8545	Now Selling	LSVEC-Lithium Carbonate	0.4 g	-46.6		-26.41	+3.69	
8546	Now Selling	NBS28-Silica Sand	0.4 g				+9.58	
8547	Now Selling	IAEAN1-Ammonium Sulfate	0.4 g		+0.43			
8548	Now Selling	IAEAN2-Ammonium Sulfate	0.4 g		+20.41			
8549	Now Selling	IAEA-NO3 Nitrogen and Oxygen Isotopes in Nitrate	0.4 g		+4.7		+25.6	
8550	Now Selling	USGS25-Ammonium Sulfate	0.5 g		-30.41			
8551	Now Selling	USGS26-Ammonium Sulfate	0.5 g		+53.75			
8552	Now Selling	NSVEC-Gaseous Nitrogen	300 umol		-2.78			
8553	Now Selling	Soufre De Lacq-Elemental Sulfur	0.5 g					
8554	Now Selling	NZ1-Silver Sulfide	0.5 g					
8555	Now Selling	NZ2-Silver Sulfide	0.5 g					
8556	Now Selling	NBS123-Sphalerite	1.5 g					
8557	Now Selling	NBS127-Barium Sulfate	0.5 g				8.59	
8558	Now Selling	USGS32 Nitrogen and Oxygen Isotopes in Nitrate	0.9 g		+180		+25.7	
8559	Out of Stock	Natural Gas, Coal Origin	cyl	-29.0(CH ₄)				-138(CH ₄)
8561	Out of Stock	Natural Gas, Biogenic	cyl	-72.8(CH ₄)				-176(CH ₄)
8562	Now Selling	CO2-Heavy, Paleomarine Origin	set (2)	-3.72		-18.49	+11.86	
8563	Now Selling	CO2-Light, Petrochemical Origin	set (2)	-41.59		-33.52	-3.64	
8564	Now Selling	CO2-Biogenic, Modern Biomass Origin	set (2)	-10.45		-10.09	+20.52	
8568	Now Selling	USGS34 Nitrogen and Oxygen Isotopes in Nitrate	0.9 g		-1.8		-27.9	
8569	Now Selling	USGS35 Nitrogen and Oxygen Isotopes in Nitrate	0.9 g		+2.7		+57.5	
8573	Now Selling	L-glutamic Acid USGS40	1 g	-26.39	-4.52			
8574	Now Selling	L-glutamic Acid USGS41	0.5 g	+37.63	+47.57			

Commercial Products

1) Oztech – Chuck Douthitt

- Lecture bottles of pure Hydrogen, Carbon Dioxide and Nitrogen
- Isogeochem Wiki

CO_2 ($\delta^{13}\text{C}_{\text{PDB}}$, $\delta^{18}\text{O}_{\text{PDB}}$) (-3.6, -16), (-10.5, -10), (-40.7, -30), (-44.5, -31), (-47.6, -37)

H_2 ($\delta\text{D}_{\text{SMOW}}$) (+100), (0), (-60), (-120), (-160), (-225), (-400), (-800)

N_2 ($\delta^{15}\text{N}_{\text{AIR}}$) (0)



Commercial Products

2) Isometric Instruments – Michael Whiticar

- Lecture bottles of Methane mixtures in air
- Isogeochem Wiki
- 250, 2500, and 25000 ppm
- $\delta^{13}\text{C}$ of -66.5, -54.5, -38.3, and -23.9 ‰
- dD in progress



Commercial Products

3) Indiana University – Arndt Schimmelmann

Isogeochem Wiki

Pure compounds and mixtures

dD, d¹³C, d¹⁵N, and d¹⁸O

GC and EA

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

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

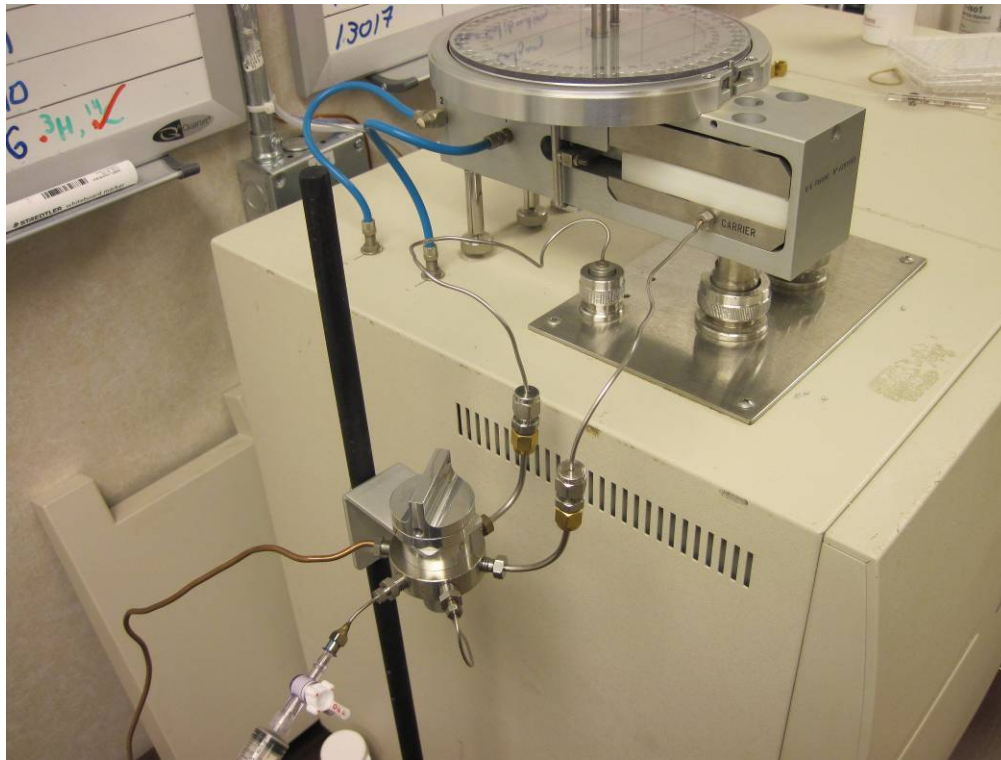
B) Find a way to calibrate vs NIST/IAEA standards

- Dual Inlet
- EA (combustion or pyrolysis)

Make It Yourself

2) Elemental Analyzer Methods

- Even liquids and gases!
- IAEA/NIST standards, Oztech standards
- Combustion ($d^{13}C$) and Pyrolysis (dD)



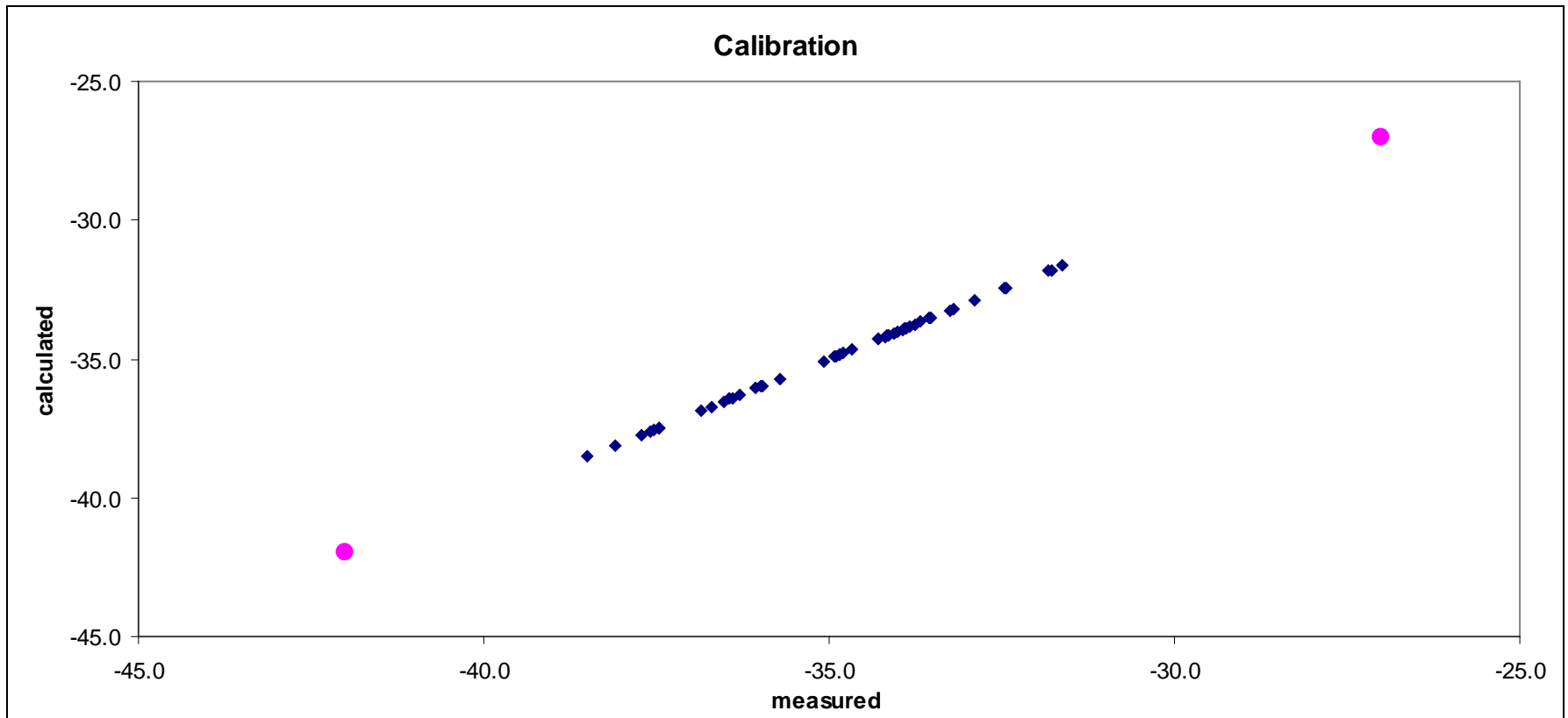
Beg/Borrow/Steal....

How much trust do you give these standards?

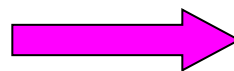
How were they created?

Are they traceable to NIST/IAEA standards?

How Many Standards Do You Need?

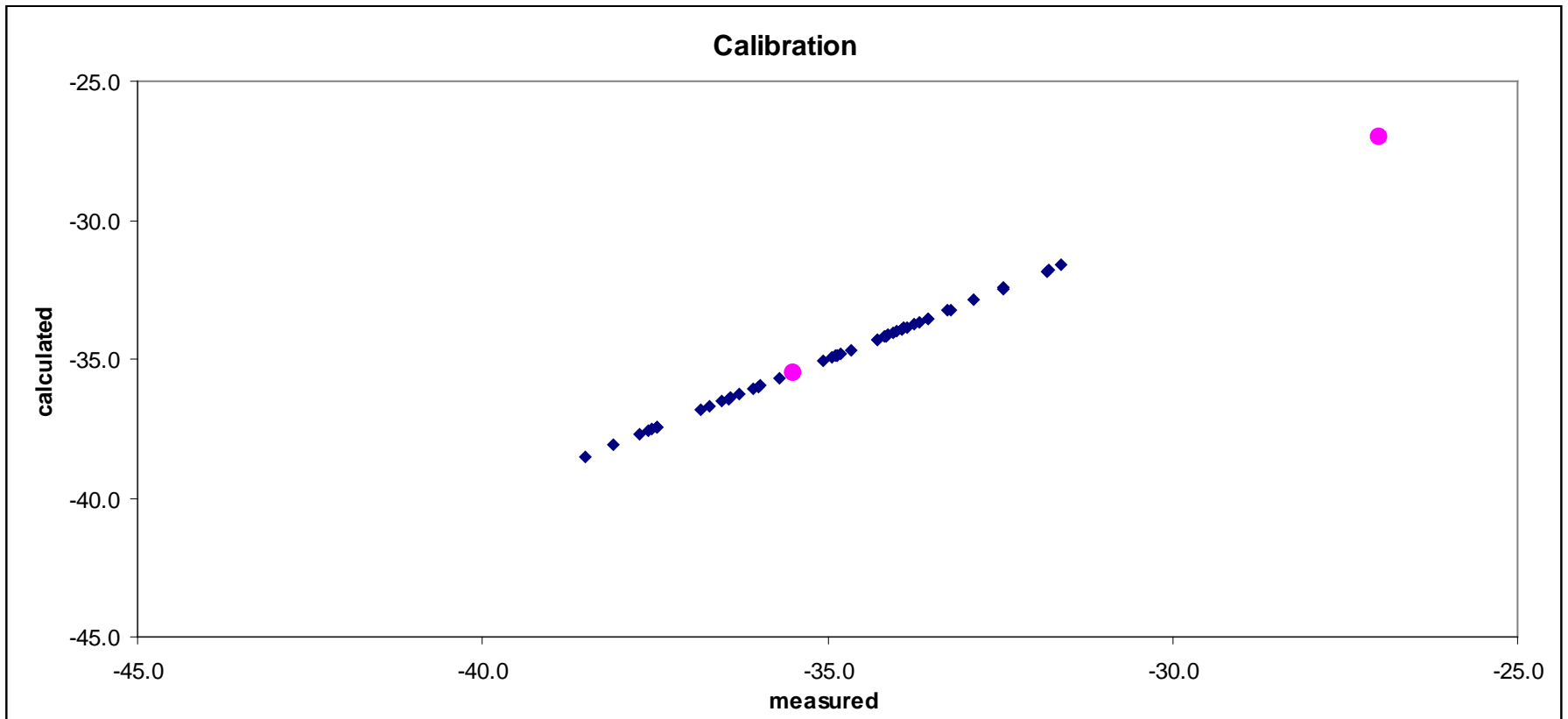


standard	known	measured
#1	-42.1	-42.5
#2	-27.4	-28.0

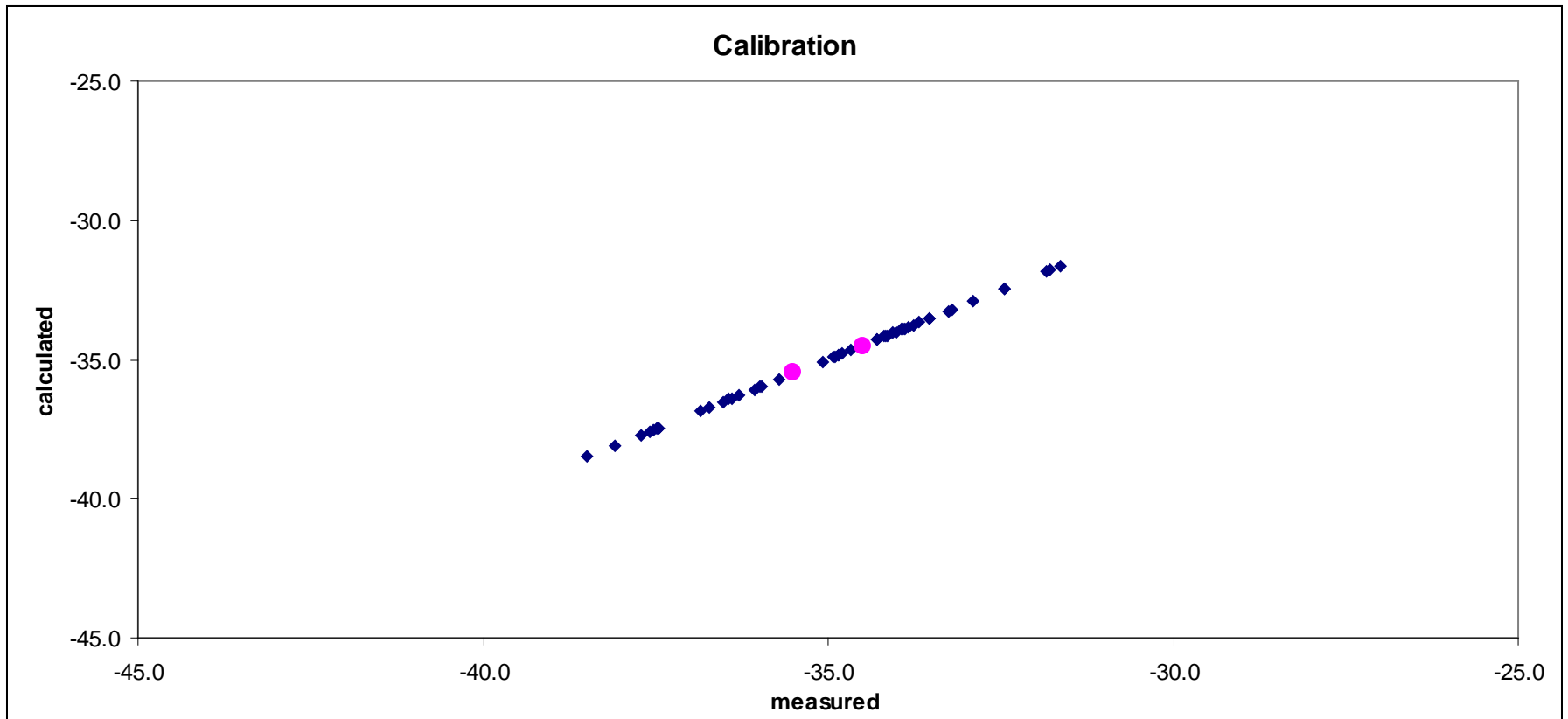


slope = 1.014
intercept = 0.99

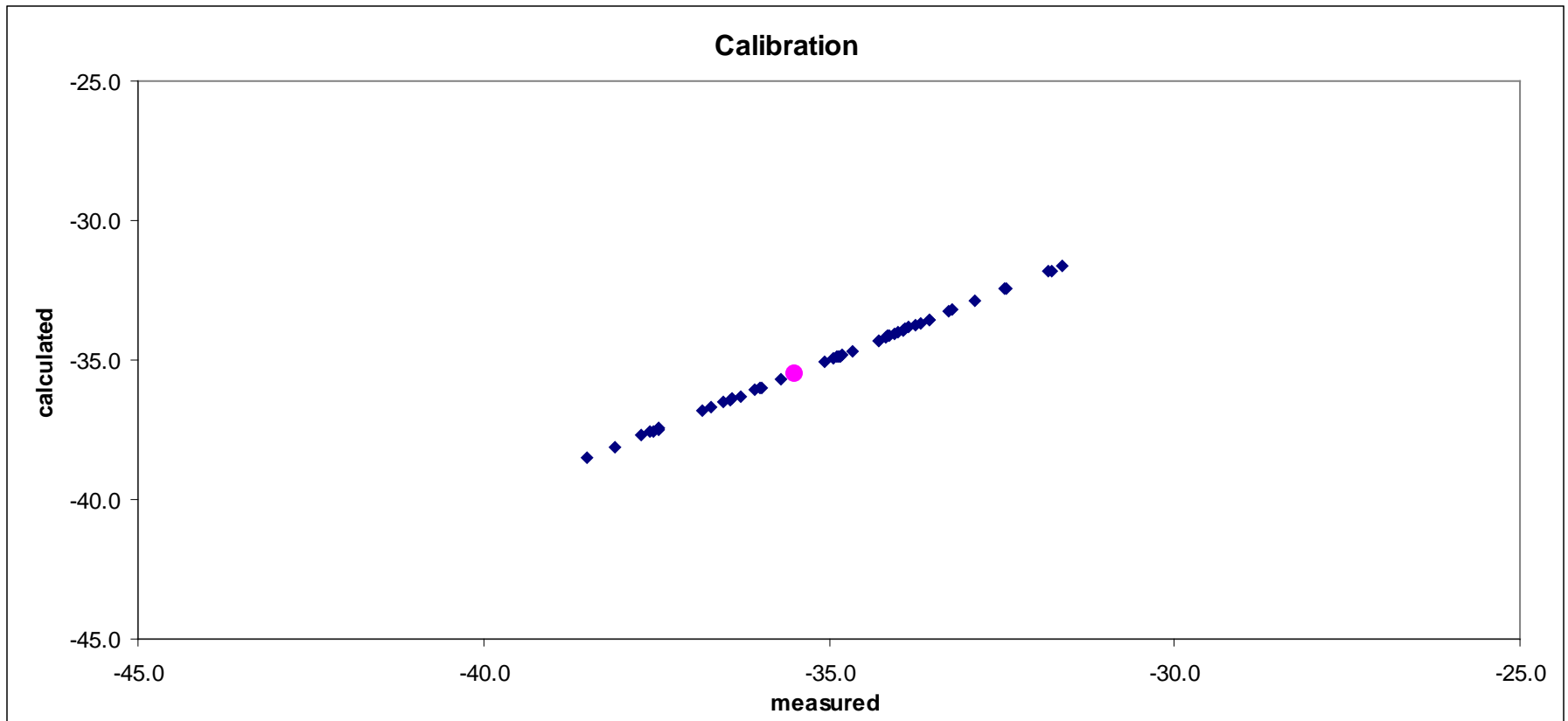
How Many Standards Do You Need?



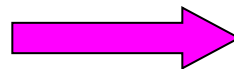
How Many Standards Do You Need?



How Many Standards Do You Need?



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



slope = 1
intercept = offset

Part 2: GC Set Up

How do you inject samples?

Gases

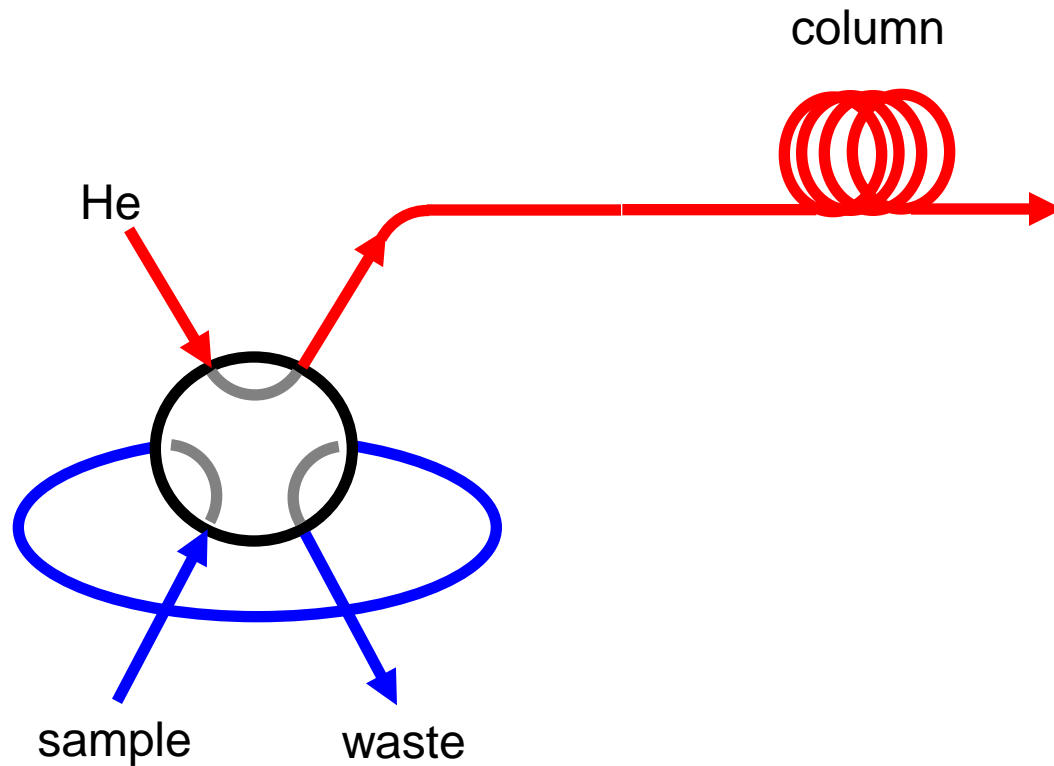
Liquids



6-Port Valve

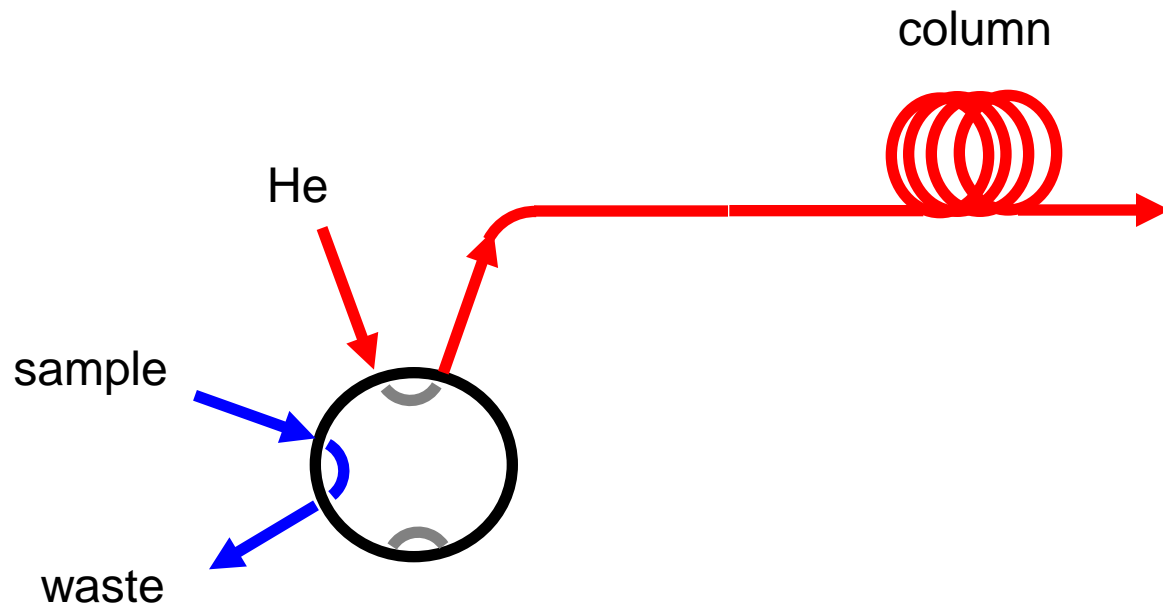
Split/Splitless
Injector

6 Port Valve for Injection of Gas



- Max loop size: 1.0mL → 20ppm CH₄
- Max loop size without focusing: 100uL → 200ppm
- Min loop size: 5uL → 5% CH₄

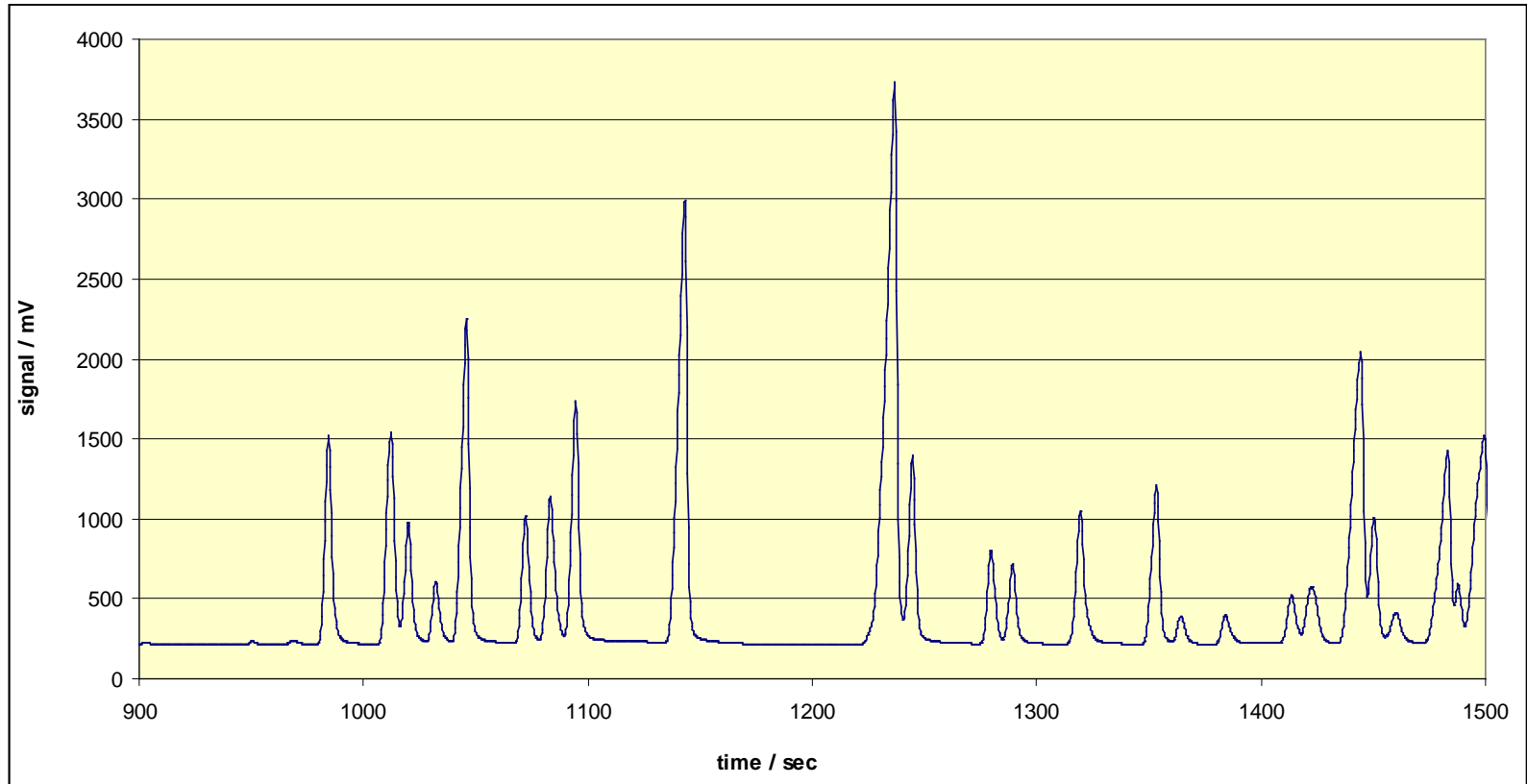
Internal Volume Valve for Injection of Gas



- Sample volume is the path etched on the rotor
- 0.06 μL to 2 μL \rightarrow 100% CH_4 (0.5 μL)

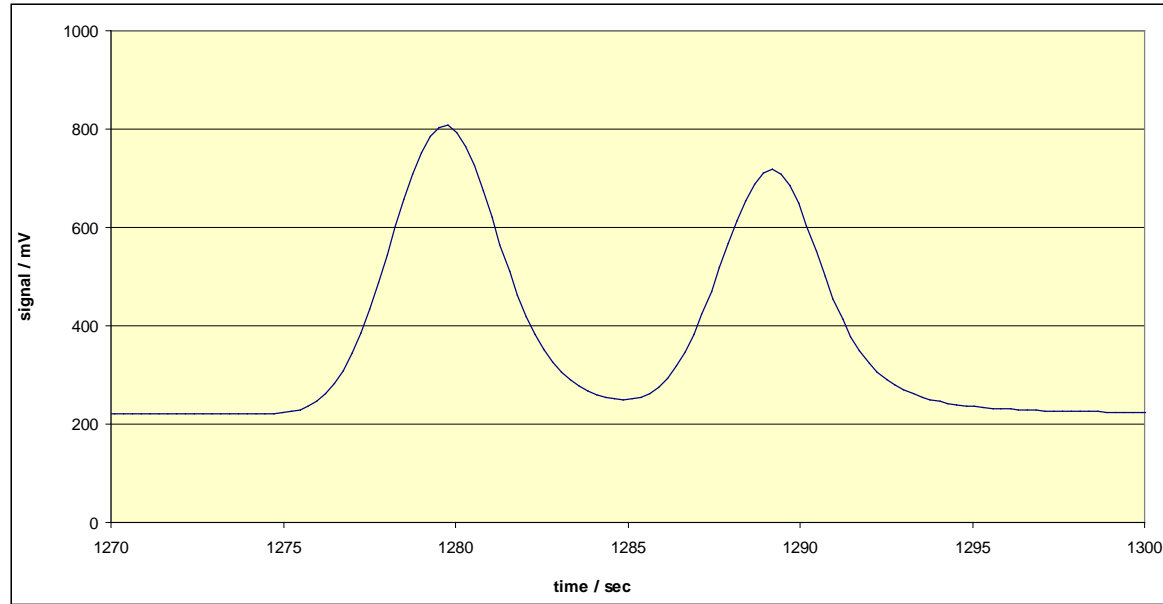
Chromatographic Issues

Baseline Separation



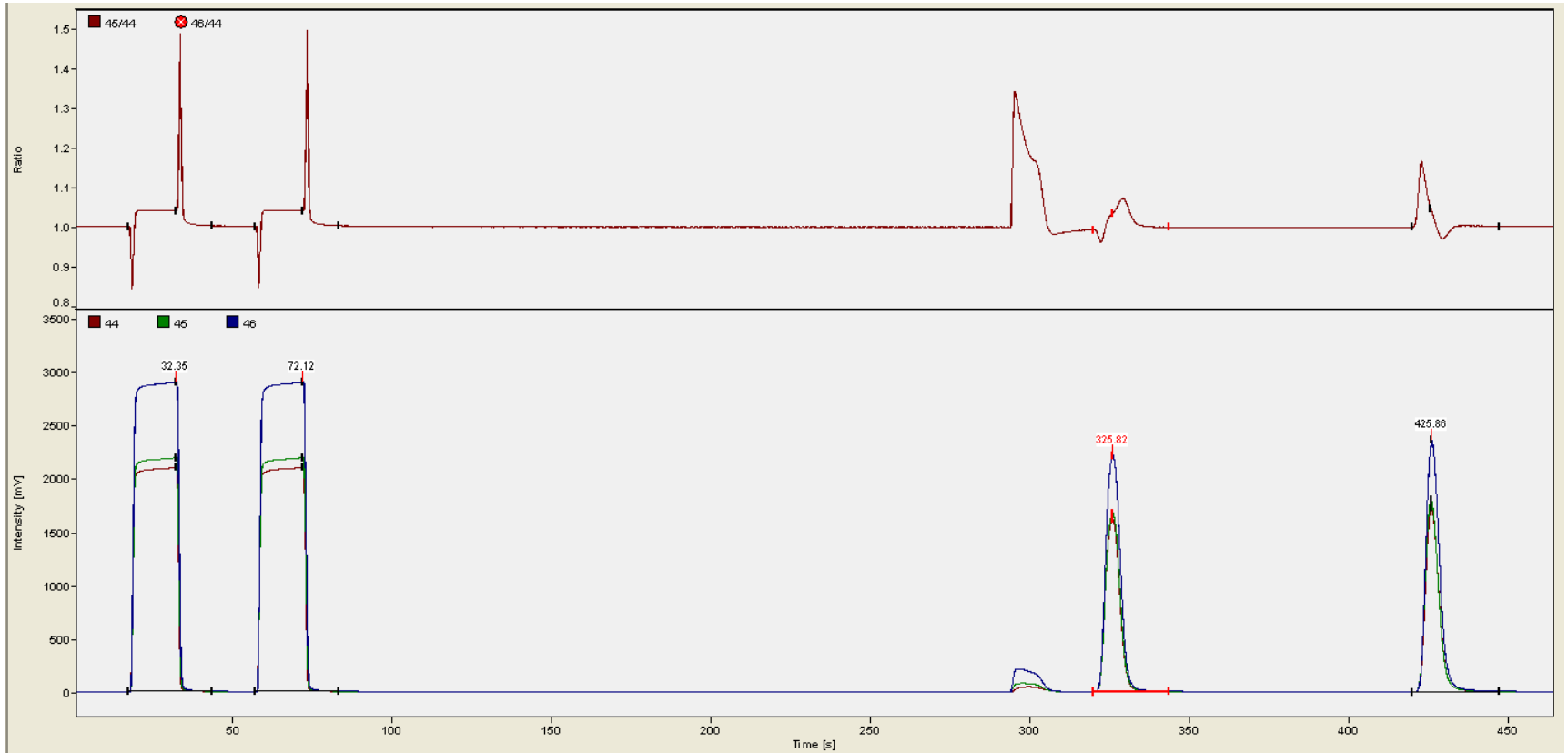
Chromatographic Issues

Integration Sensitivity



Chromatographic Issues

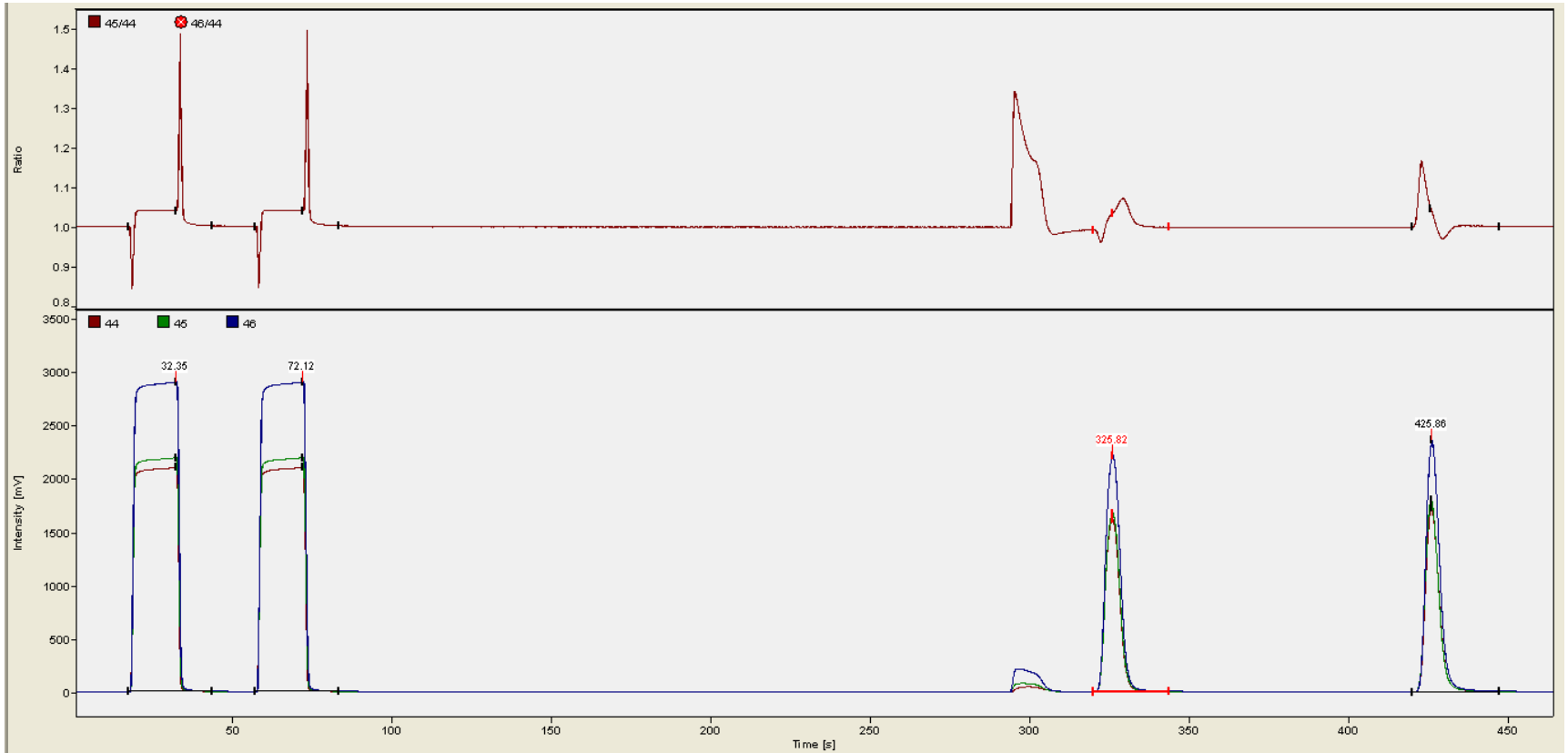
Why is baseline separation so important?



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?

Part 3: Combustion and Pyrolysis

Converting your peaks to H₂ and CO₂

Combustion

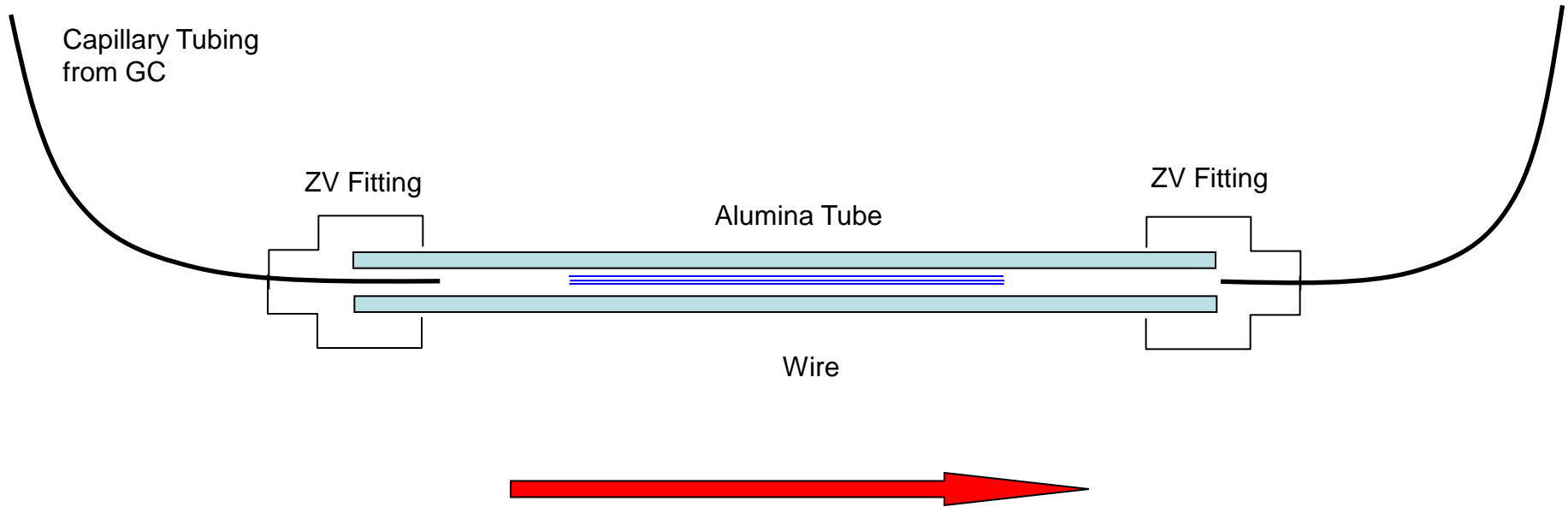
- 1) Ceramic Tube
 - 0.5 mm ID
 - Alumina (inert, gas impermeable)

- 2) Metal wires
 - 0.1mm diameter
 - Copper or nickel
 - Platinum

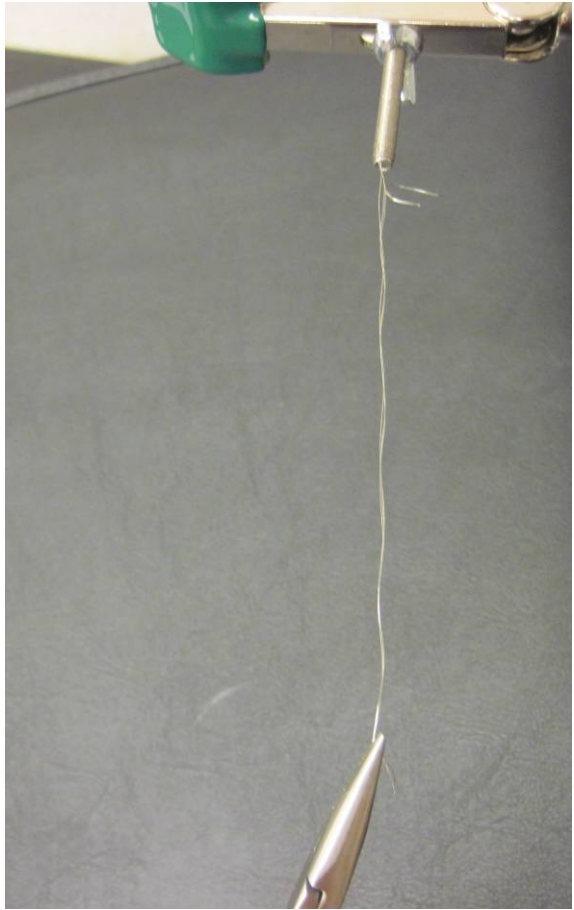
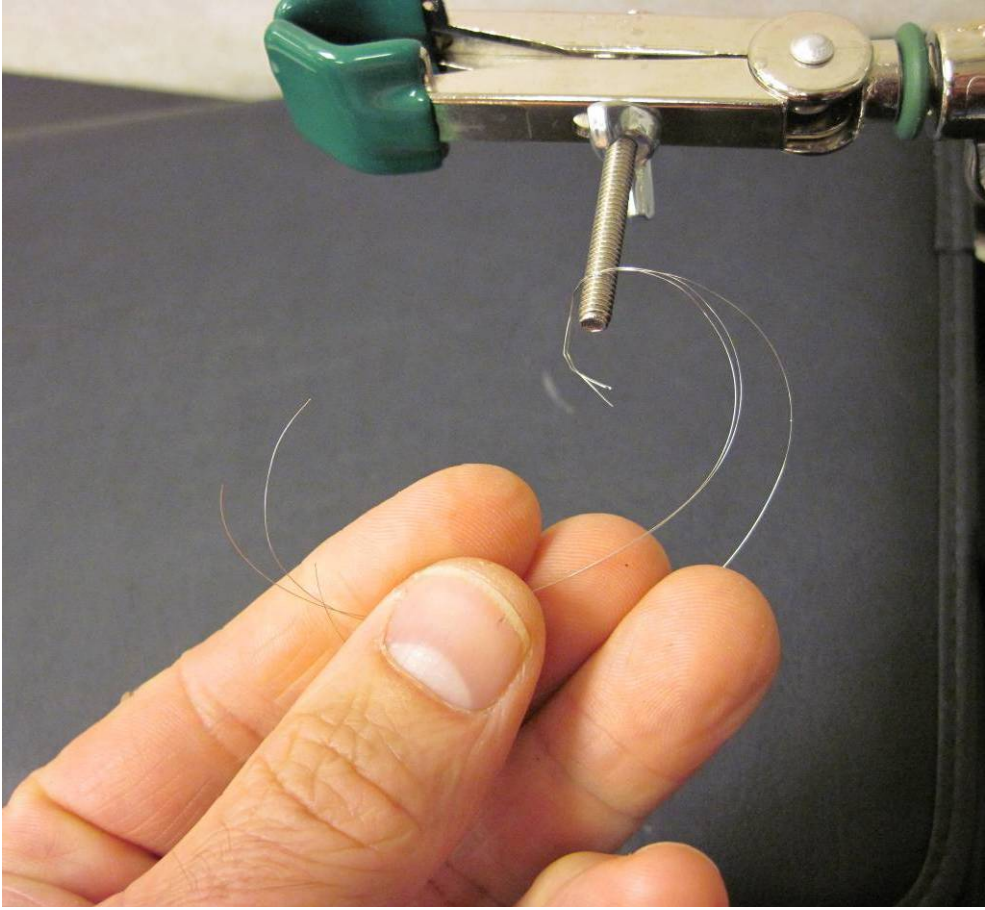
- 3) Oxygen

- 4) Heat

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

- 2 Cu and 1 Pt wire
- 850°C

Trouble with methane

2) Nickel/Platinum

- 2 Ni and 1 Pt wire
- 1050°C

Higher Temperature

Holds on to oxygen longer

Longer life

3) Copper/Nickel/Platinum

- 950°C

Hybrid

Oxidation

1) Periodic Reoxidation

- 100% O₂
- Backflush

Can run out of O₂

Can't use for a while

2) Oxygen Bleed

- Trickle in 1% O₂ in He
- Always On

Constantly regenerating

Never run out

Difficult to balance

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

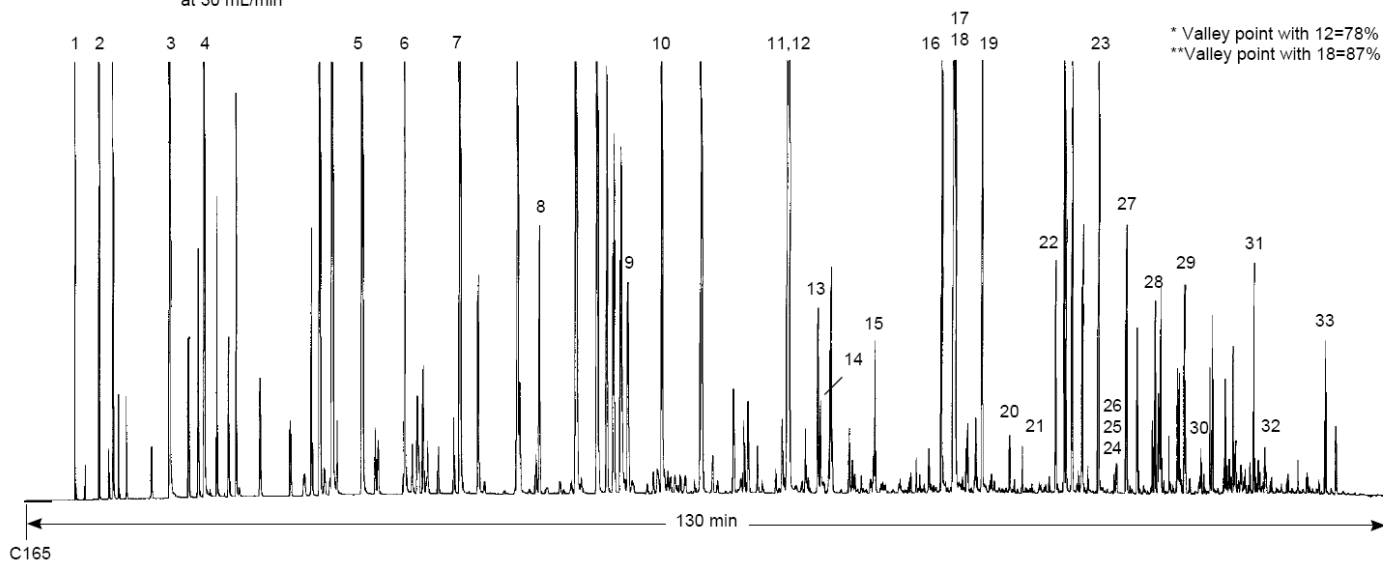
Nitrogen makeup gas

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



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

Pyrolysis:

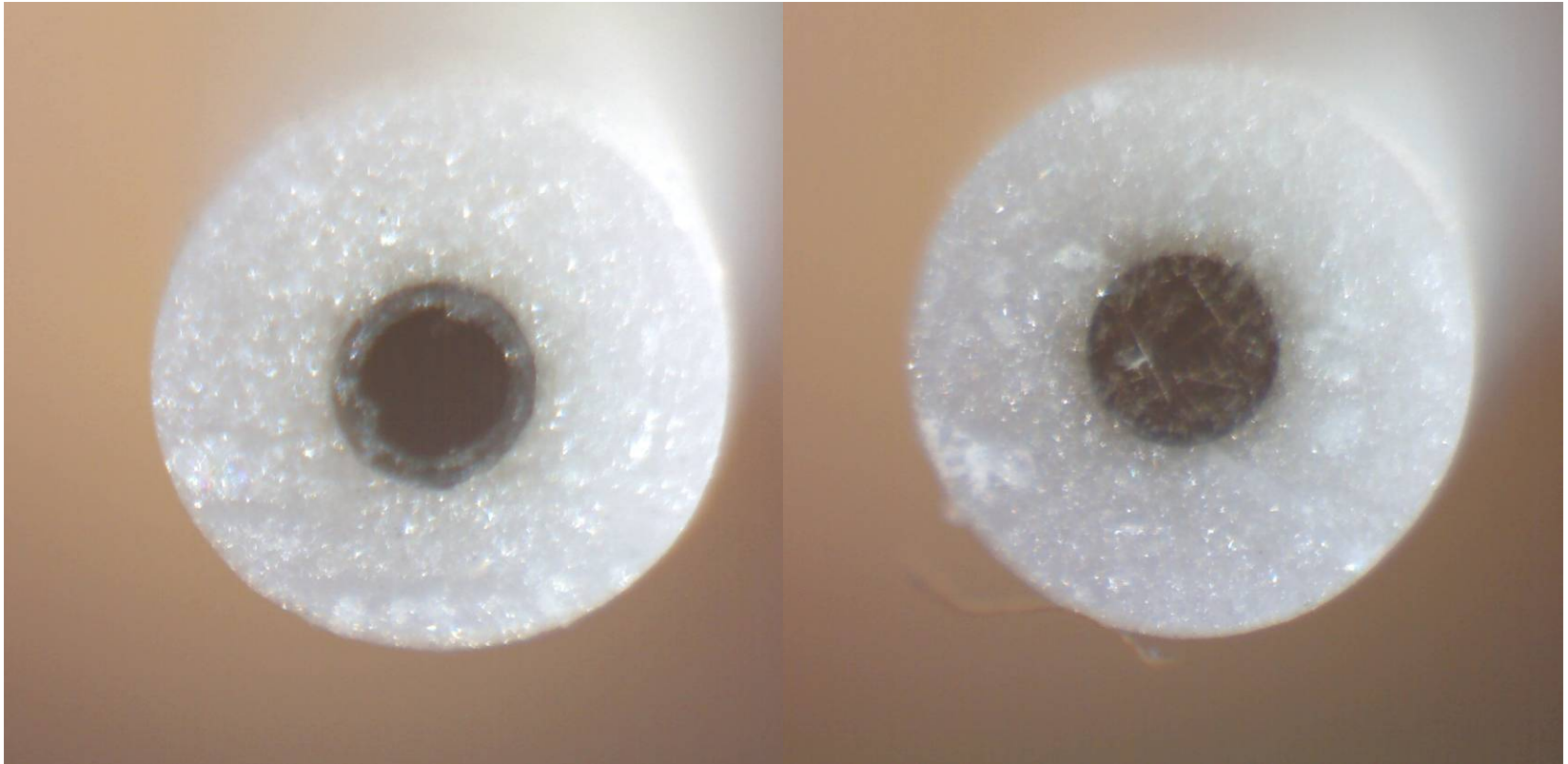
Shouldn't this be easy?

- 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?

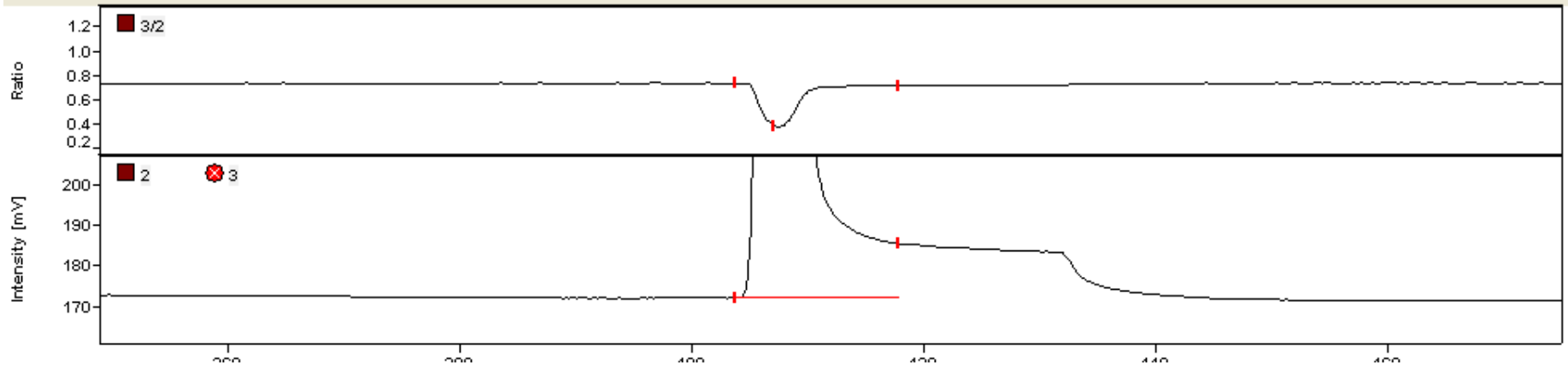


Pyrolysis:

Shouldn't this be easy?

-If you don't do enough:

File Name: C:\Thermo\Isodat NT\Global\User\ConFlo IV Interface\GC IsoLink Device\Results\1019GH\Apr 22 2010\1019_Liso1_d_Apr 22 2010.dxf



- 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:

