GC-C and GC-Pyrolysis IRMS Short Course:

Putting the Gas In Gas Chromatography

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Alberta Innovates Technology Futures

GC-C and GC-Pyrolysis IRMS Short Course:

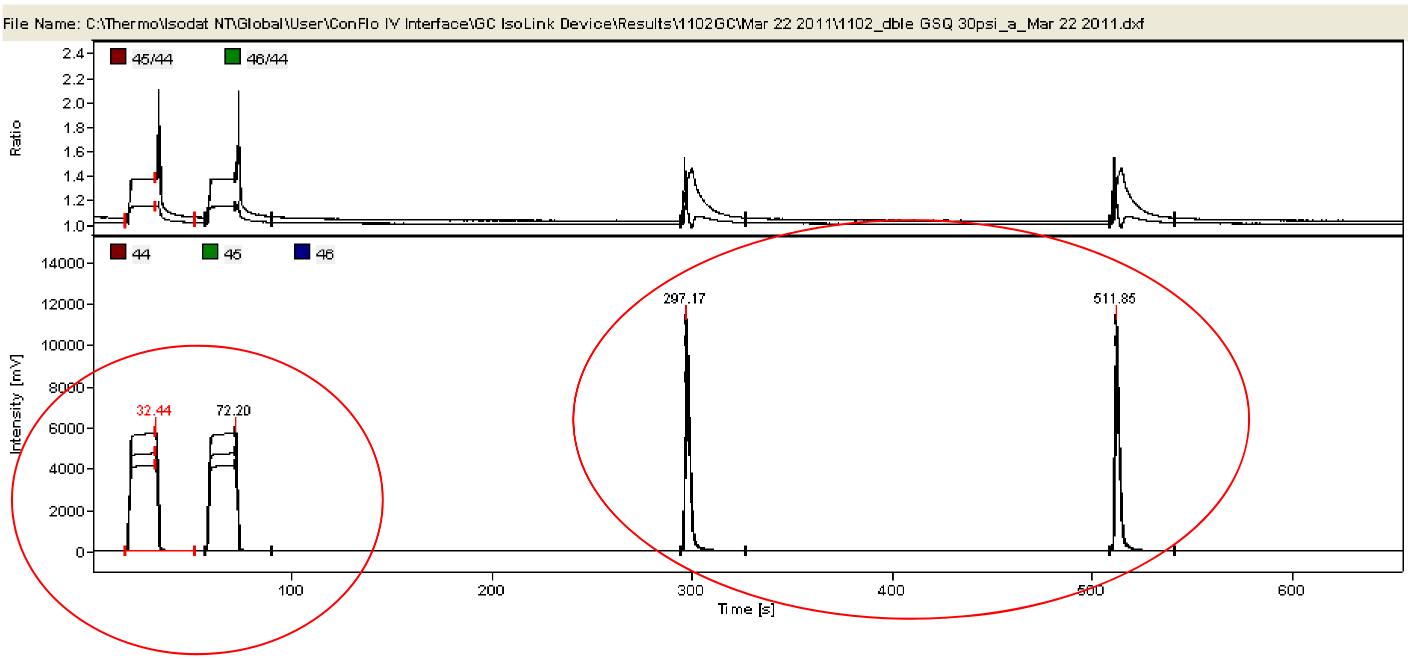
Putting the Gas In Gas Chromatography

Part 1: Standards

Part 2: GC Set Up

Part 3: Combustion & Pyrolysis

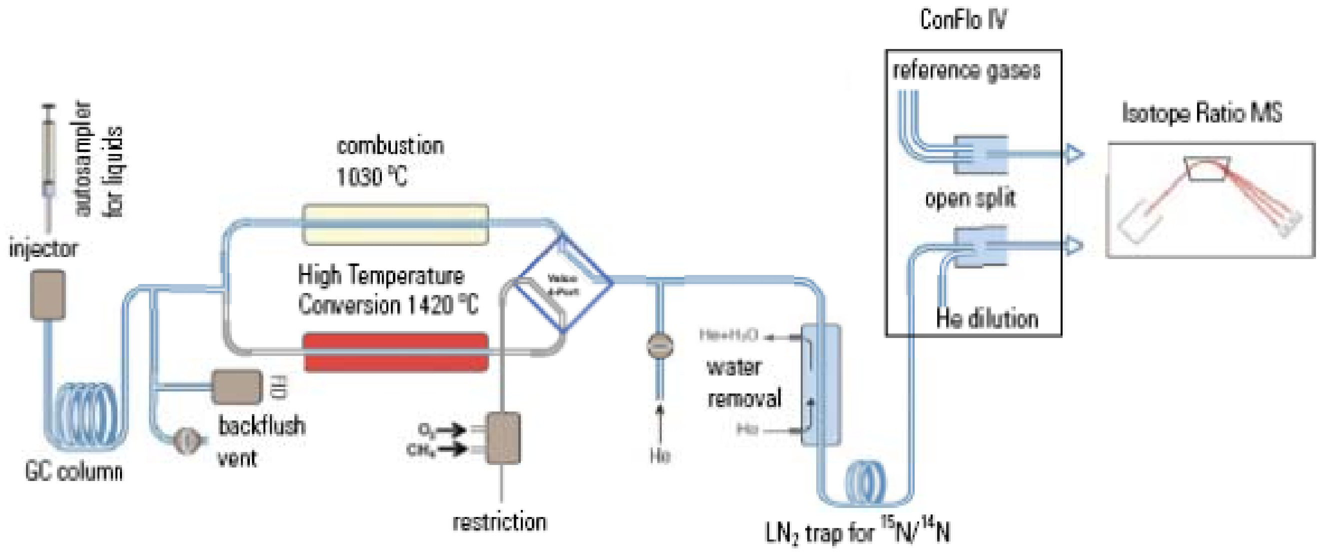
Part 1: Standards



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

Thermo GC IsoLink

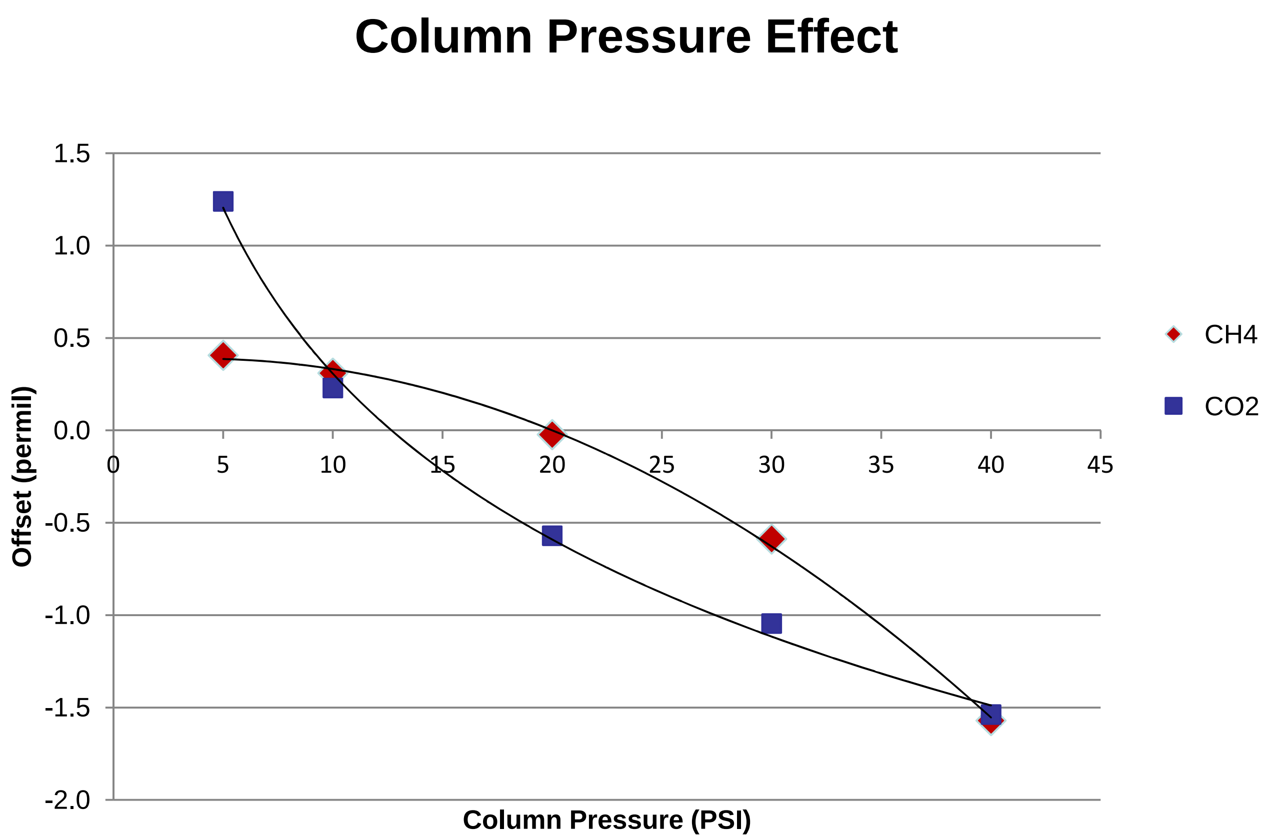
- Thermo Fisher product literature



Potential Sources of Error:

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

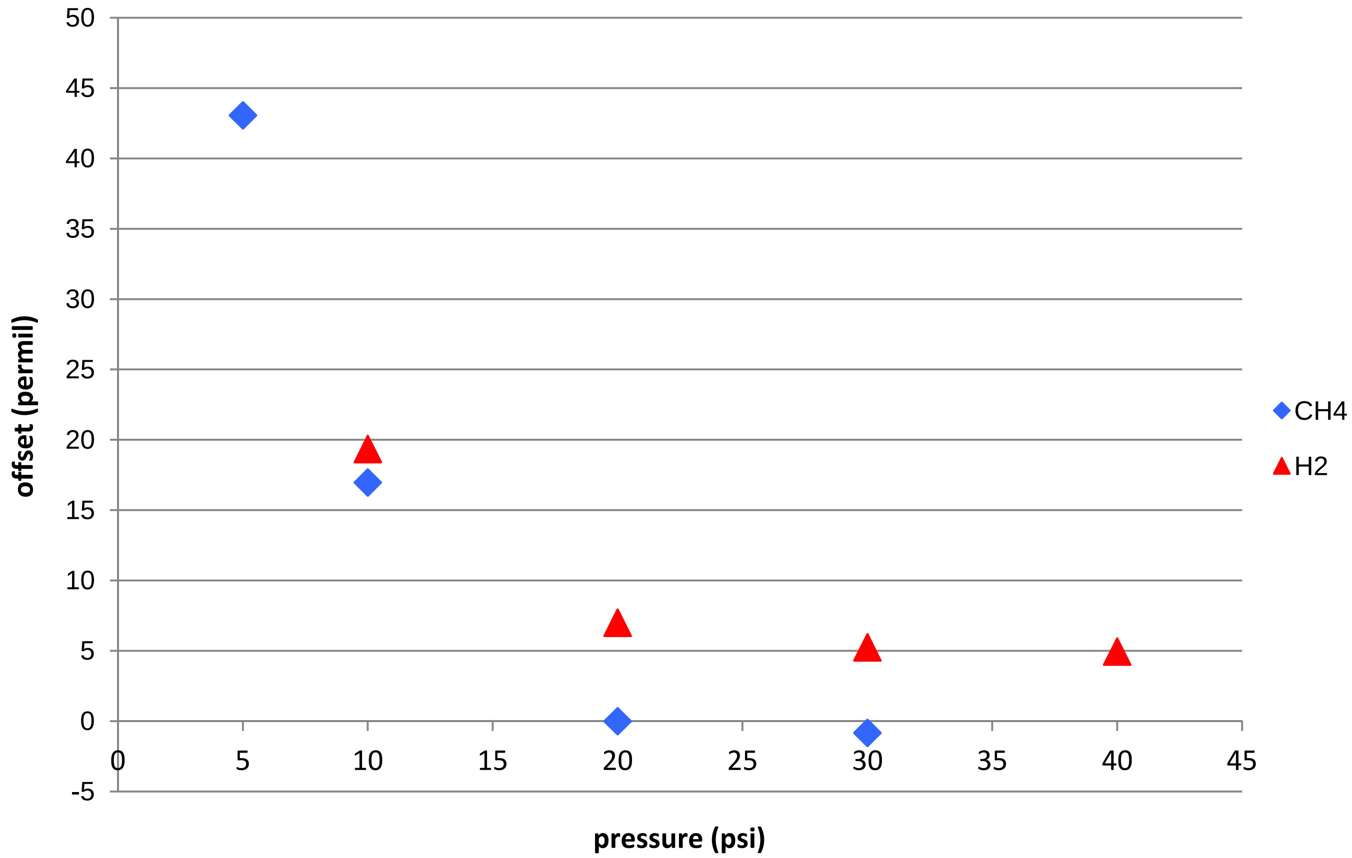
d^{13}C on CH_4 and CO_2



GSQ PLOT column

60m, 0.32mm ID, 30C

dD on CH_4 and H_2



60m GSQ PLOT column

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	$\delta^{13}C$	$\delta^{15}N$	$\delta^{18}O_{VPDB}$	$\delta^{18}O_{VSMOW}$	$\delta^{2}H$
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(CH4)*
8561	Out of Stock	Natural Gas, Biogenic	cyl	*-72.8*(CH_4)				*-176(CH4)*
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

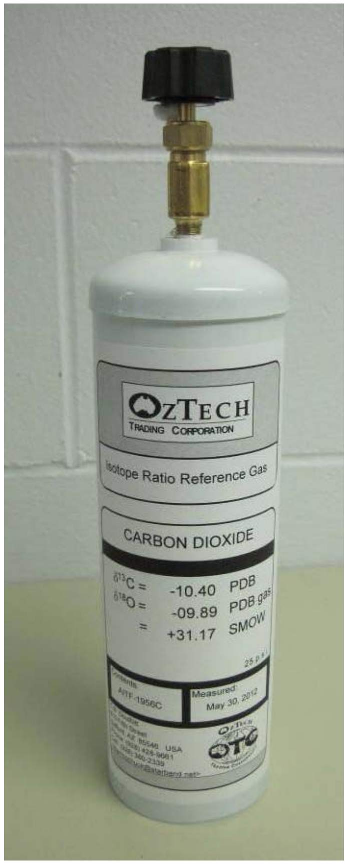
1) New Natural Gas Standards!!!!!

- Replacing SRM8559, 8560, 8561
- Bob Dias USGS
- Ready this summer

Commercial Products

2) Oztech – Chuck Douthitt

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



CO_2 ($d^{13}C_{PBD}$, $d^{18}O_{PDB}$)	(-3.6, -16), (-10.5, -10), (-40.7, -30), (-44.5, -31), (-47.6, -37)
H_2 (dD_{SMOW})	(+100), (0), (-60), (-120), (-160), (-225), (-400), (-800)
N_2 ($d^{15}N_{AIR}$)	(0)

Commercial Products

3) Isometric Instruments – Michael Whiticar

- Lecture bottles of Methane mixtures in air
- Isogeochem Wiki

- 250, 2500, and 25000 ppm
- d^{13}C of -66.5, -54.5, -38.3, and -23.9 ‰
- dD in progress

Commercial Products

4) Indiana University – Arndt Schimmelmann

Isogeochem Wiki

Pure compounds and mixtures

dD, $d^{13}C$, $d^{15}N$, and $d^{18}O$

GC and EA

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

Commercial Products

5) ISOLAB (Max-Planck Institute)

- CH_4 in air

Commercial Products

6) Air Liquide

Stock pure gases and mixtures

Custom mixtures

- Methane dD (-300 to +200‰) and $d^{13}C$ (-70 to +20 ‰)
- C2 to C5 dD (-200 to +100‰) and $d^{13}C$ (-30 to +10 ‰)
- CO_2 $d^{18}O$ (-30 to +10‰) and $d^{13}C$ (-60 to +20 ‰)
- CO $d^{18}O$ (-30 to +10‰) and $d^{13}C$ (-40 to +20 ‰)
- N_2 $d^{15}N$ (-20 to +20‰)
- N_2O $d^{15}N$ (-20 to +20‰)
- H_2S $d^{34}S$ (-20 to +20‰)
- SO_2 $d^{34}S$ (-20 to +20‰)

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

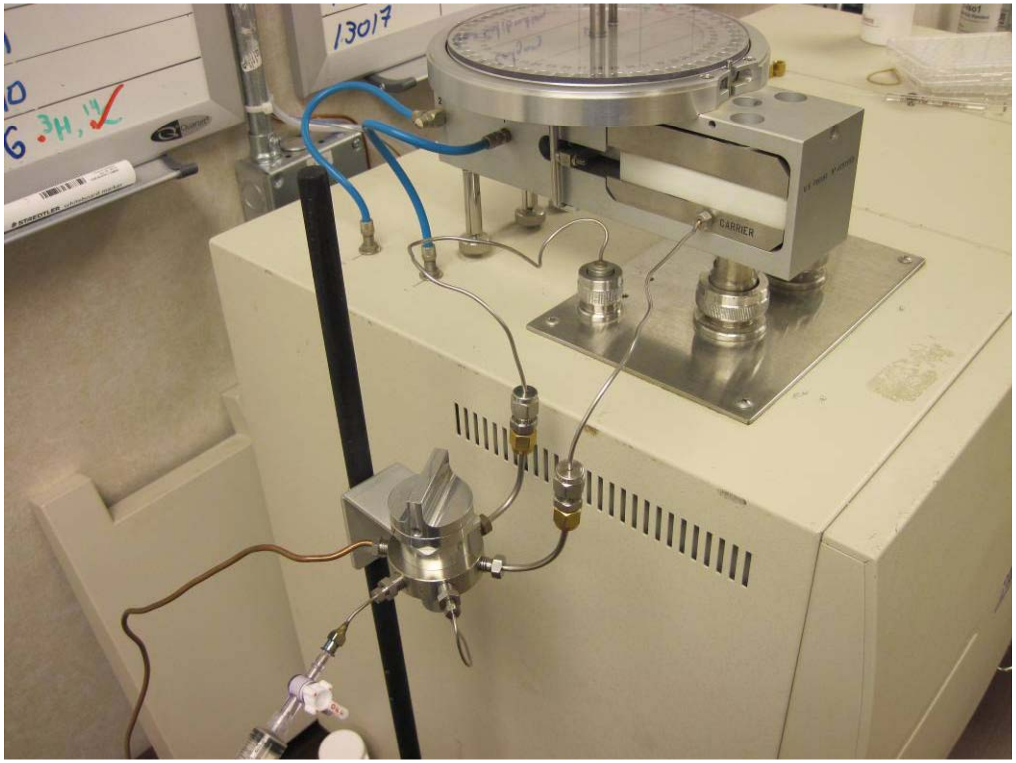
B) Find a way to calibrate vs NIST/IAEA standards

- 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)



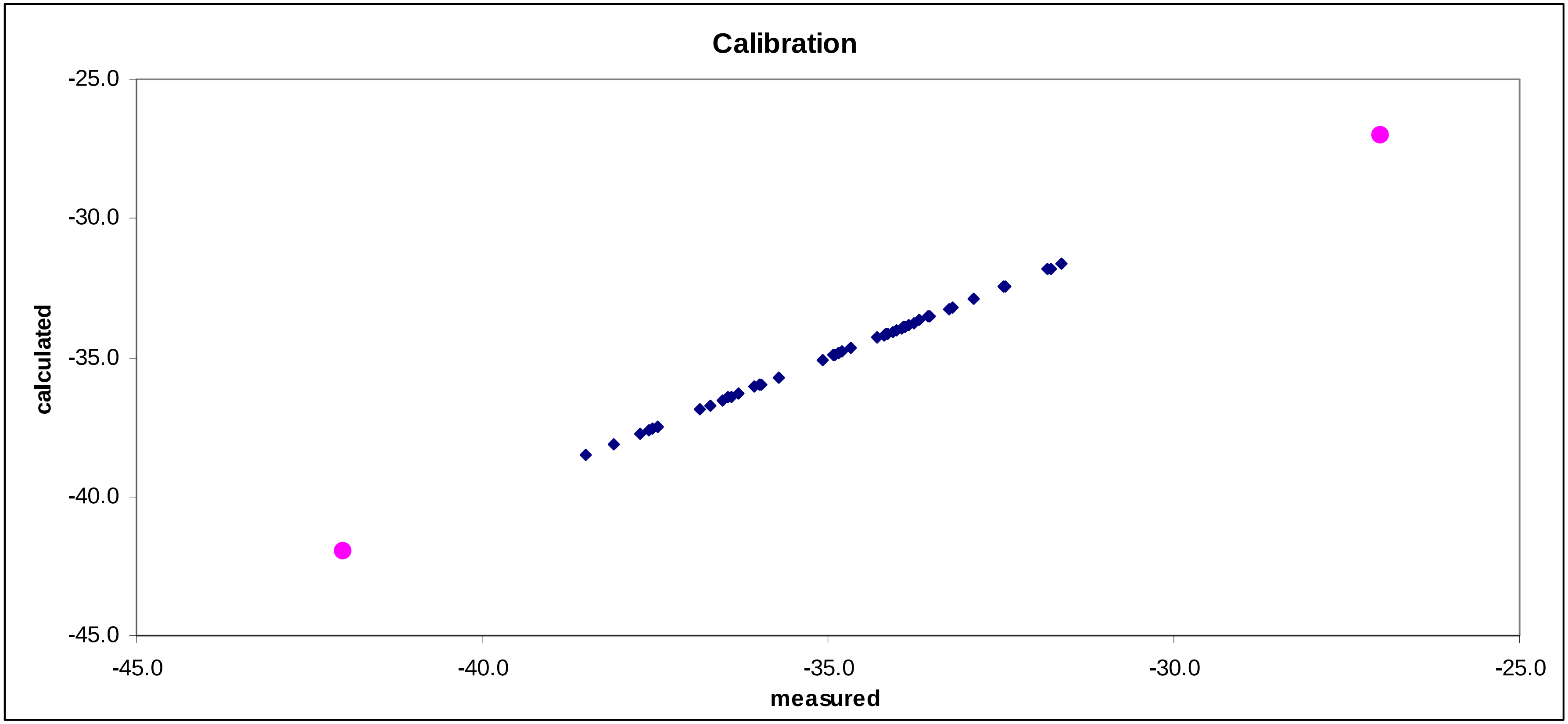
Beg/Borrow/Steal….

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?

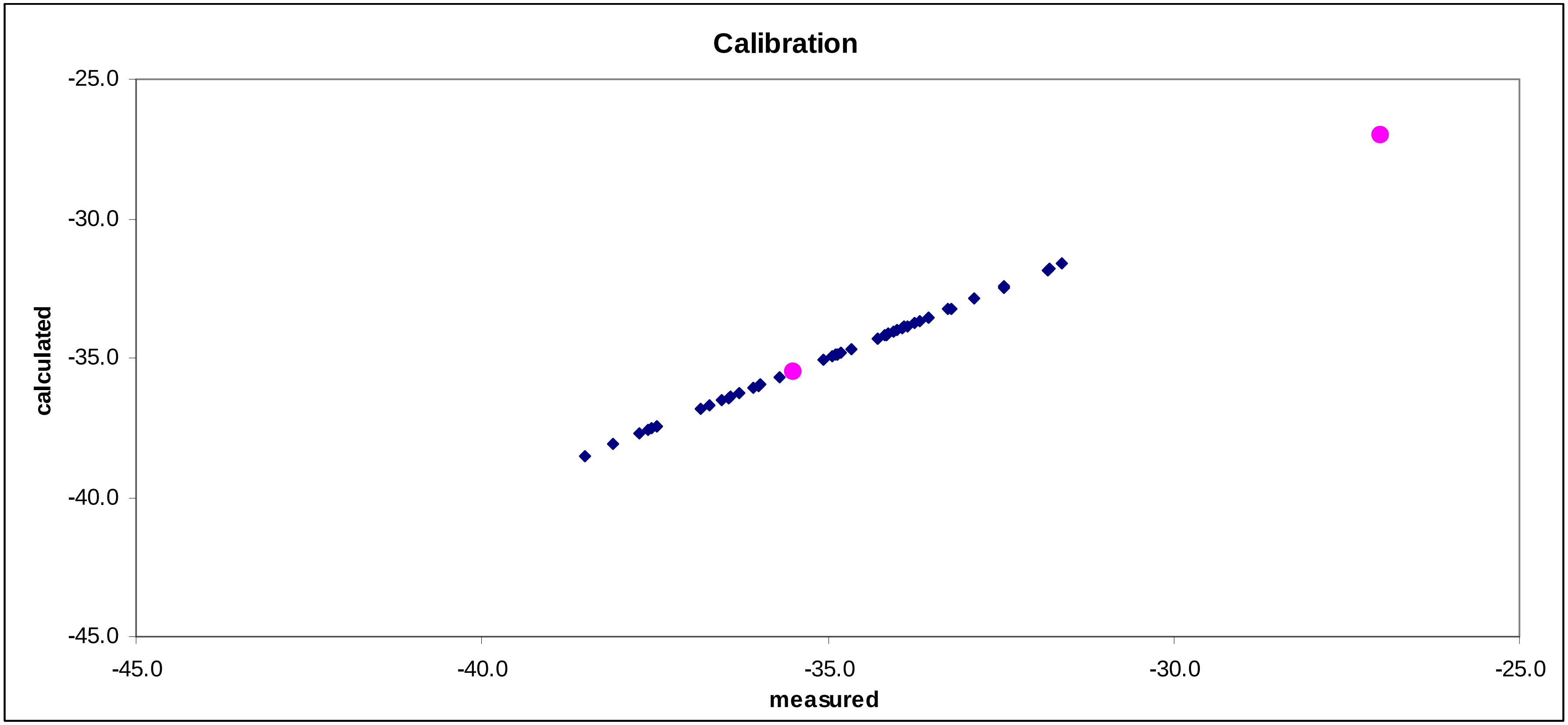


standard	known	measured
#1	-42.1	-42.5
#2	-27.4	-28.0

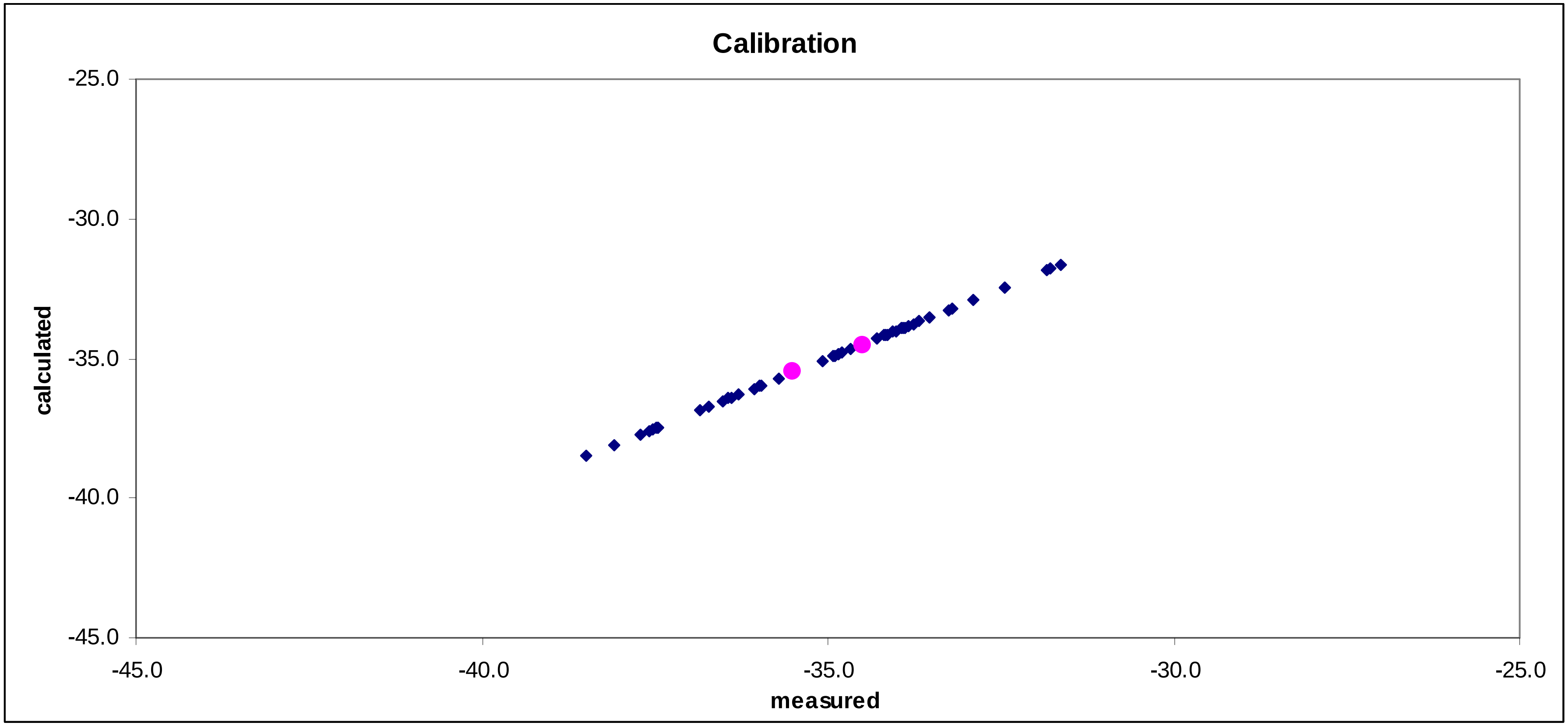
slope = 1.014

intercept = 0.99

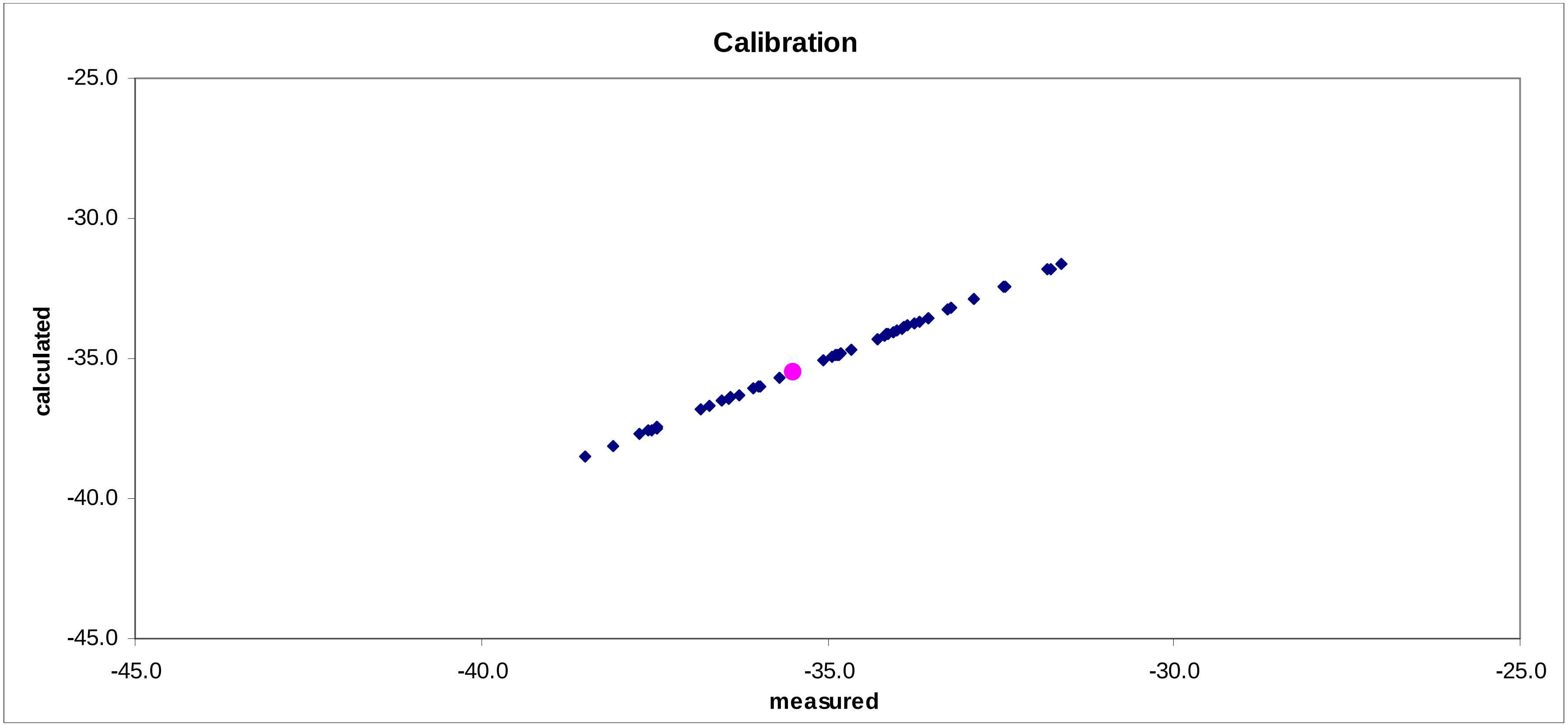
How Many Standards Do You Need?



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

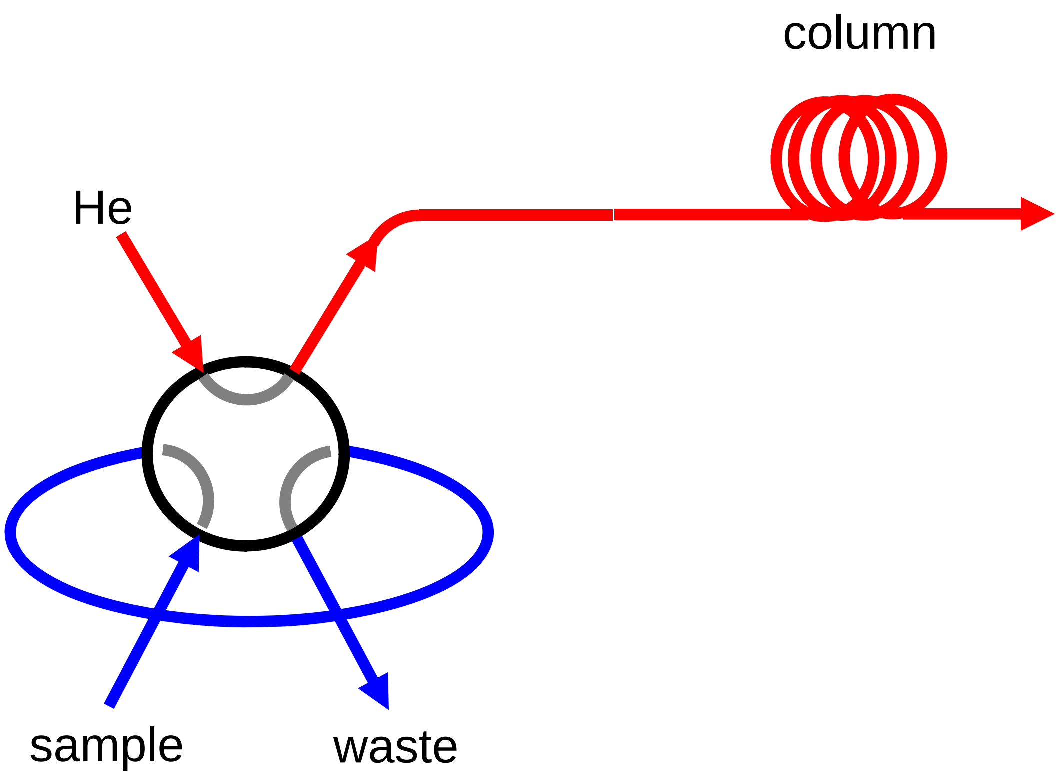
Part 2: GC Set Up

How do you inject samples?

Gases → 6-Port Valve

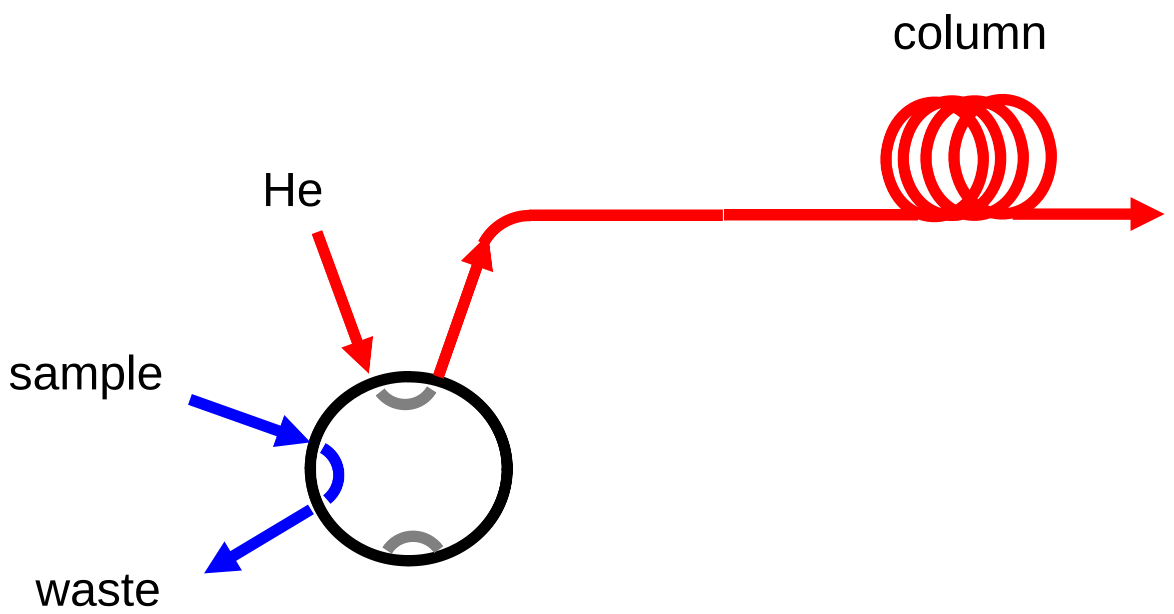
Liquids → Split/Splitless Injector

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

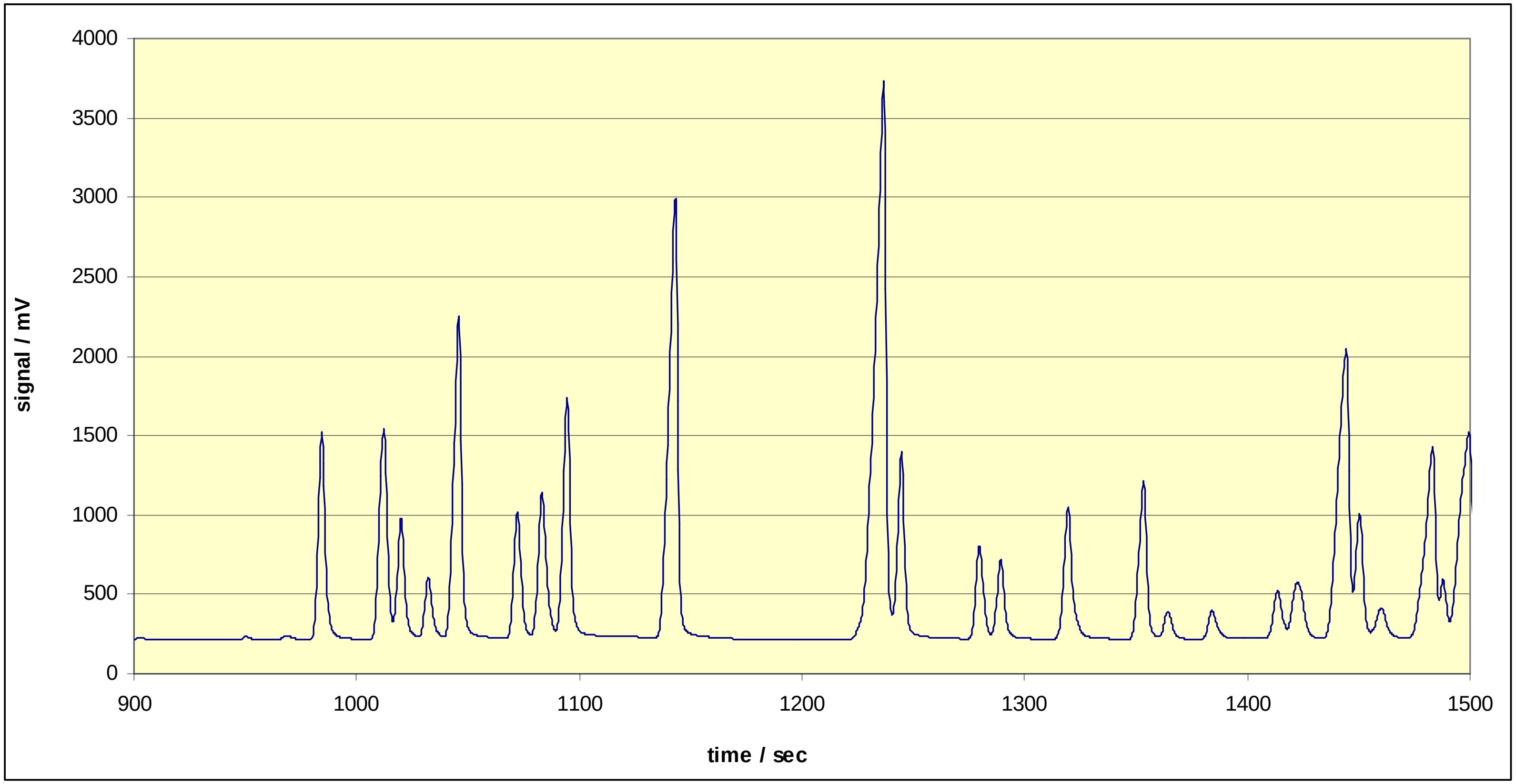
Internal Volume Valve for Injection of Gas



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

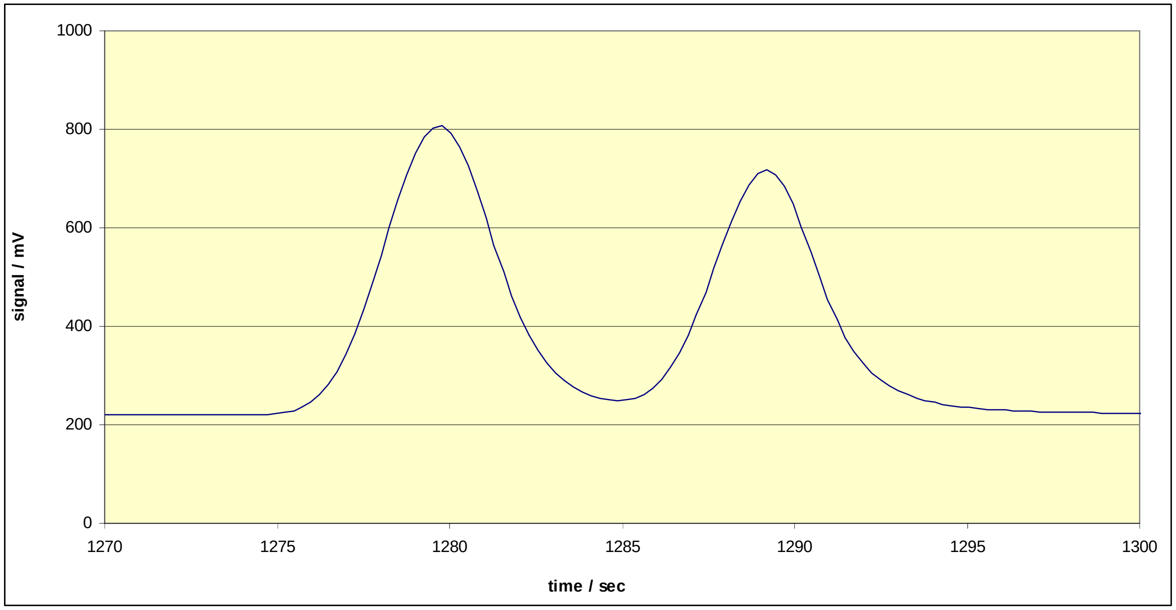
Chromatographic Issues

Baseline Separation



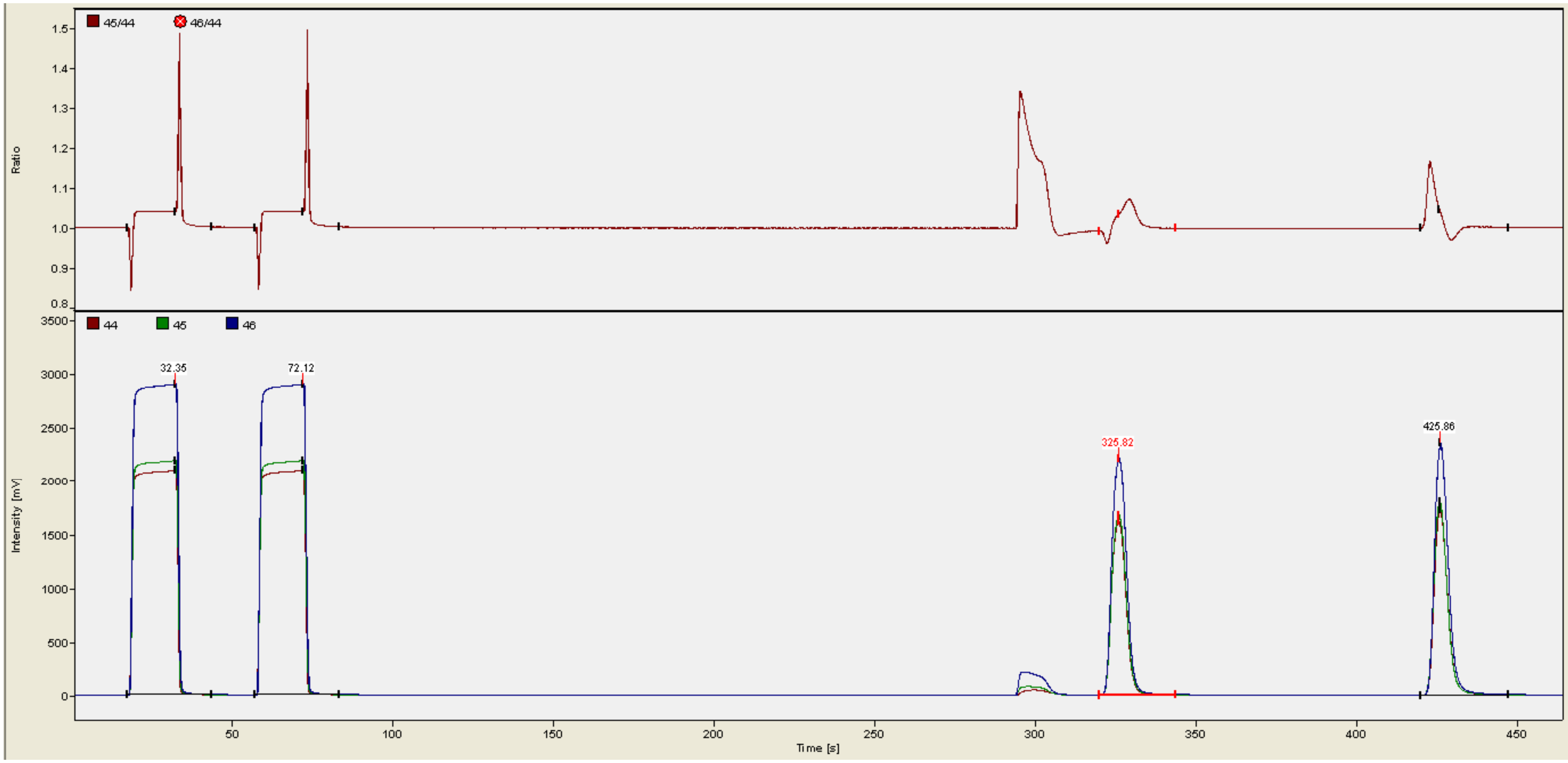
Chromatographic Issues

Integration Sensitivity



Chromatographic Issues

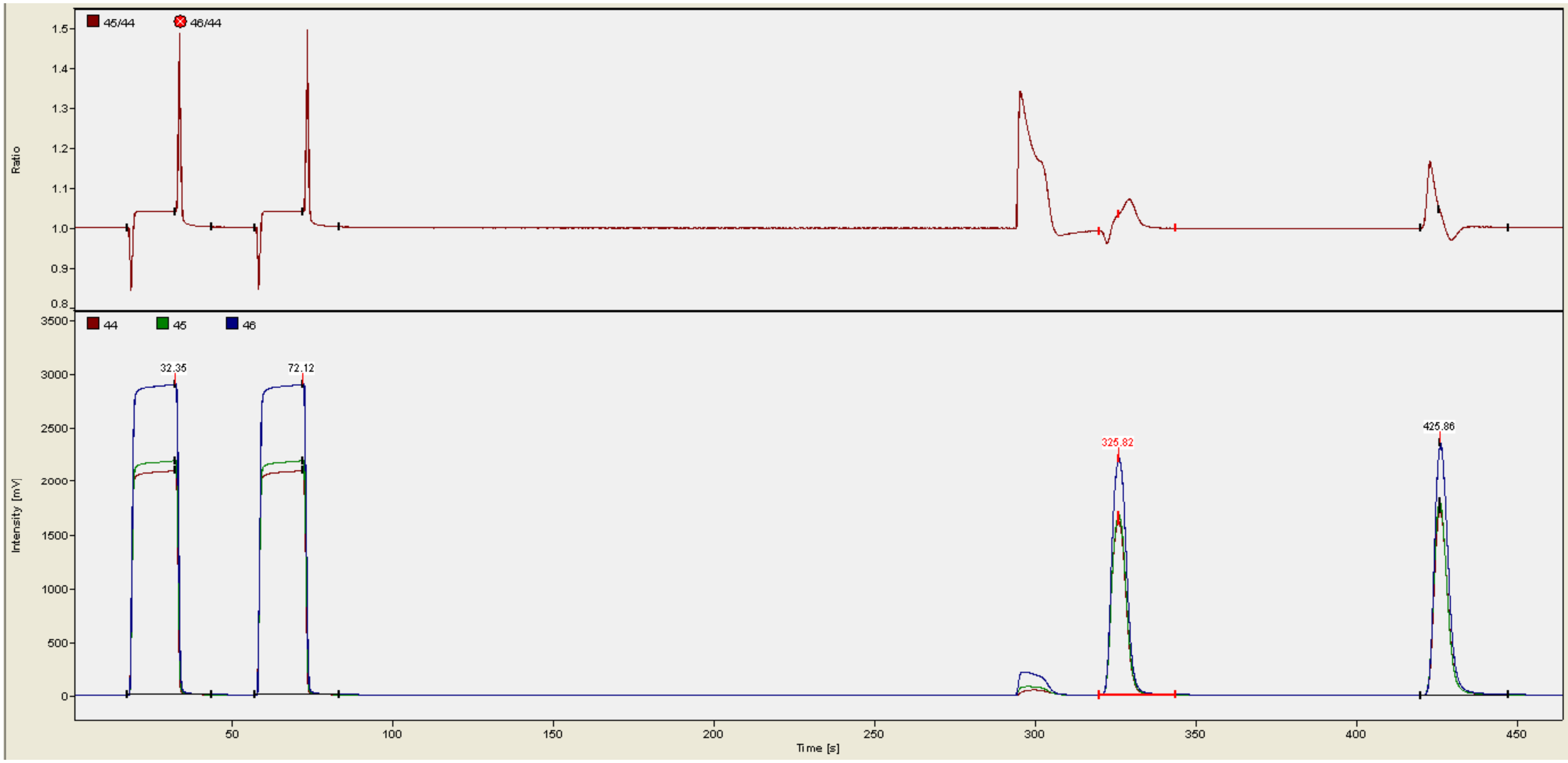
Why is baseline separation so important?



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 H_2 and CO_2

Combustion

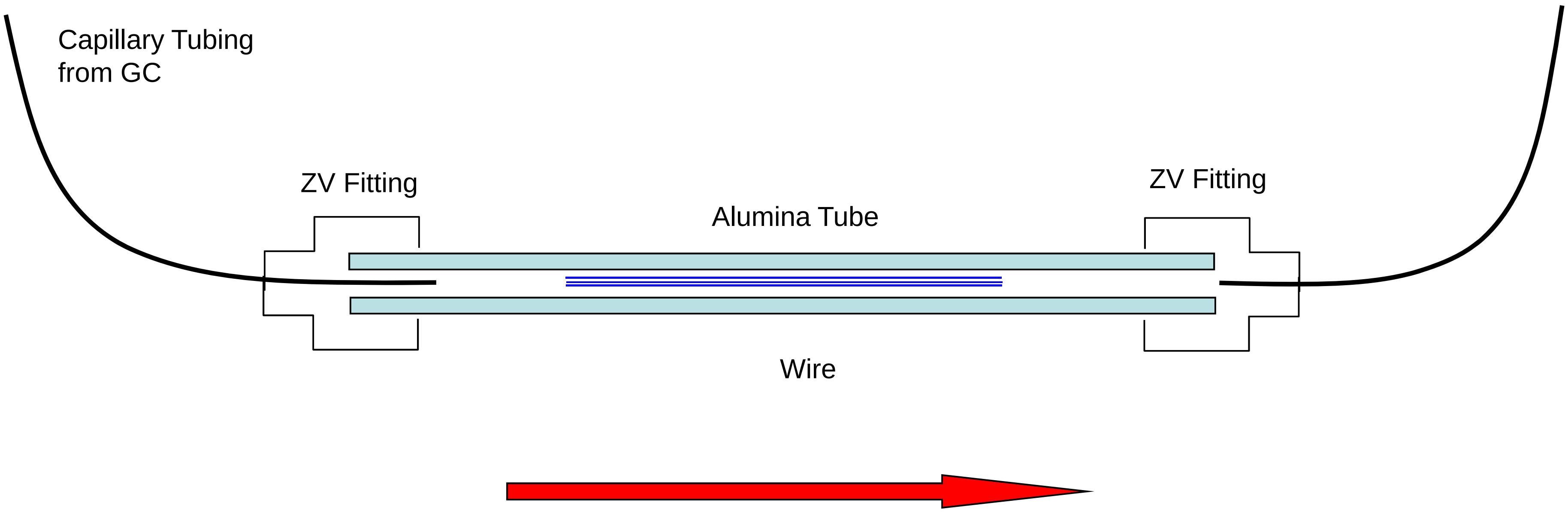
1) Ceramic Tube
   - 0.5 mm ID
   - Alumina (inert, gas impermeable)

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

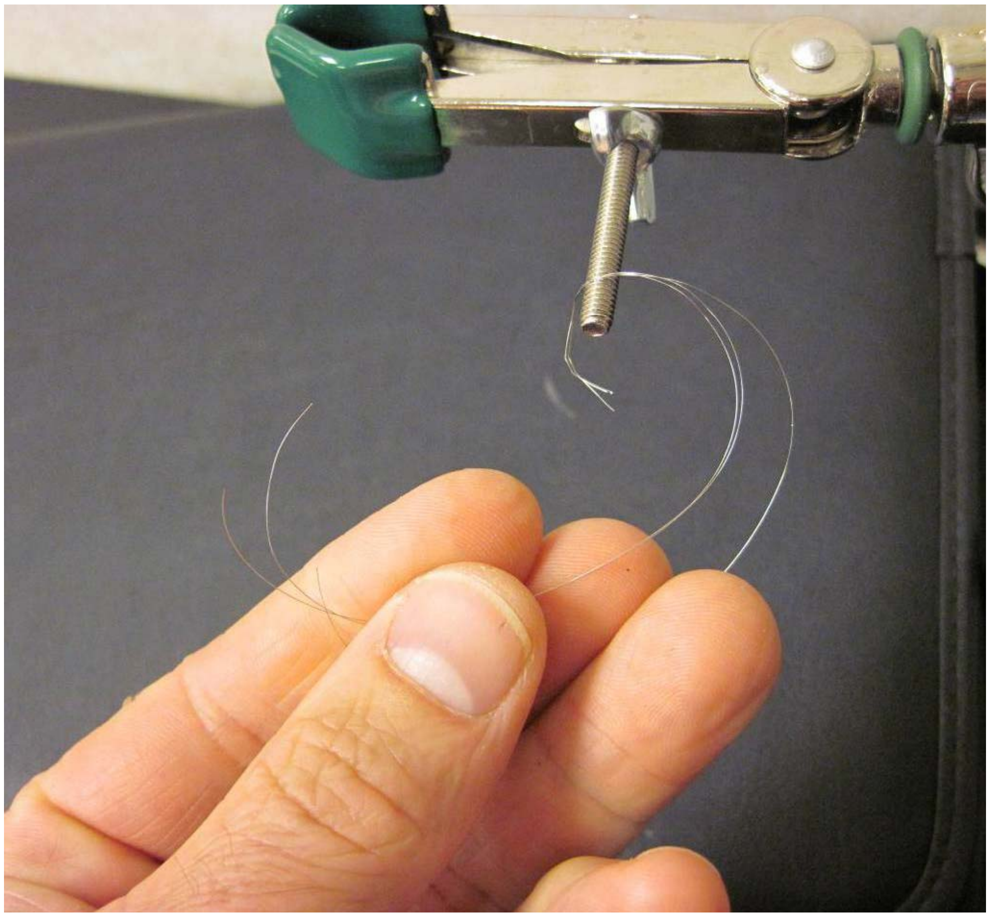
3) Oxygen

4) Heat

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
   - 1050°C

Higher Temperature

Holds on to oxygen longer

Longer life

3) Copper/Nickel/Platinum
   - 950°C

Hybrid

Oxidation

1) Periodic Reoxidation
   - 100% O_2
   - Backflush

Can run out of O_2
Can't use for a while

2) Oxygen Bleed
   - Trickle in 1% O_2 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

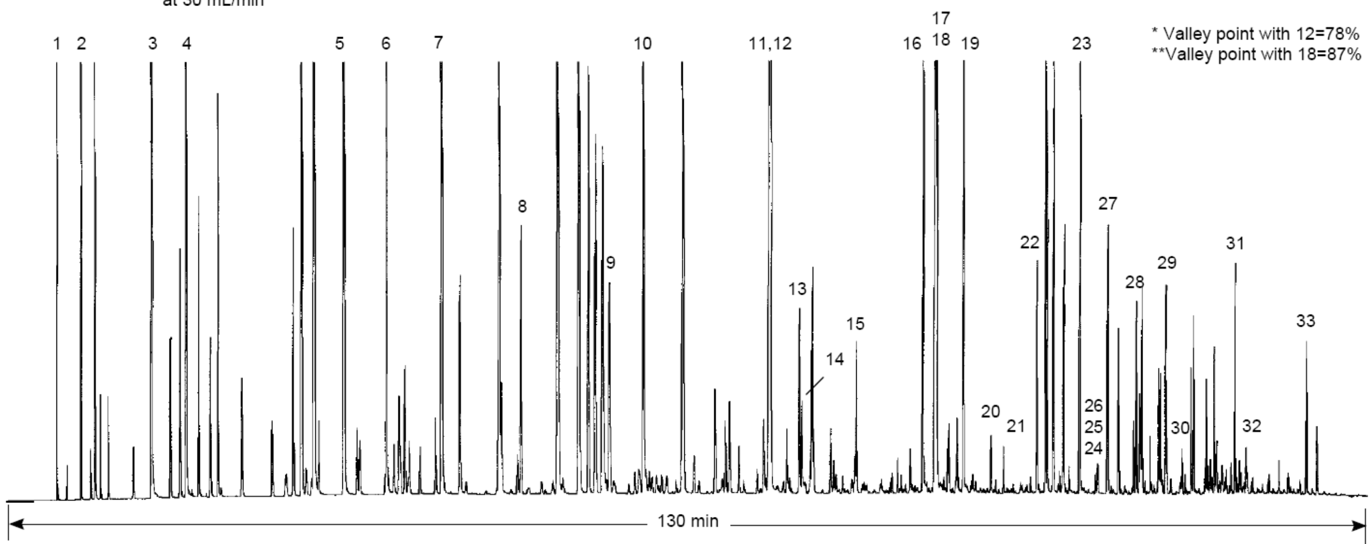
Detector: FID, 250°C
Nitrogen makeup gas
at 30 mL/min

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

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



C165

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?

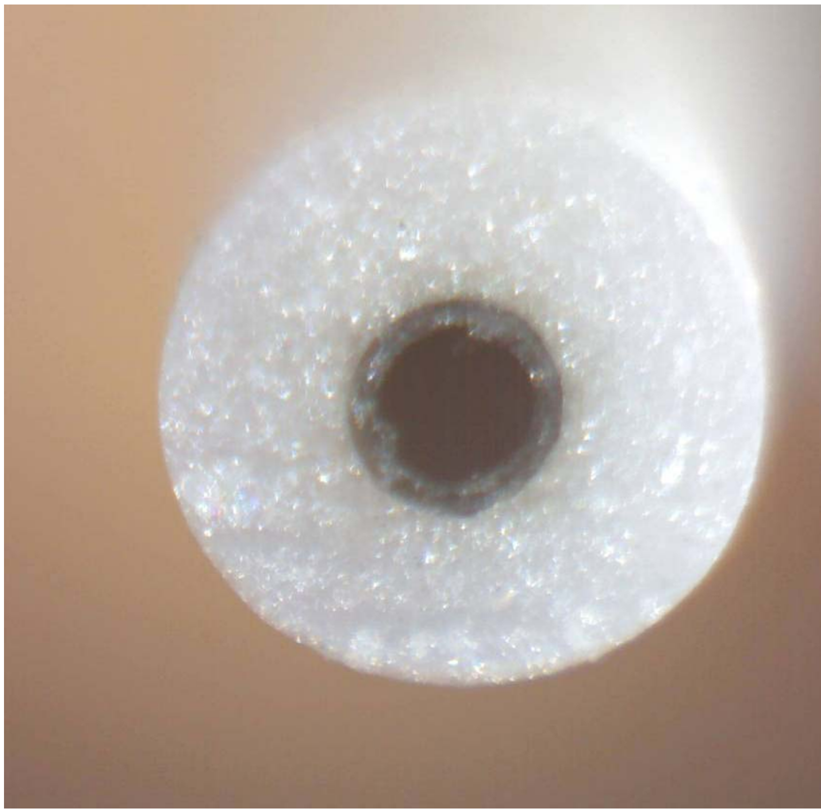
-Conditioning is necessary to deactivate the interior surface

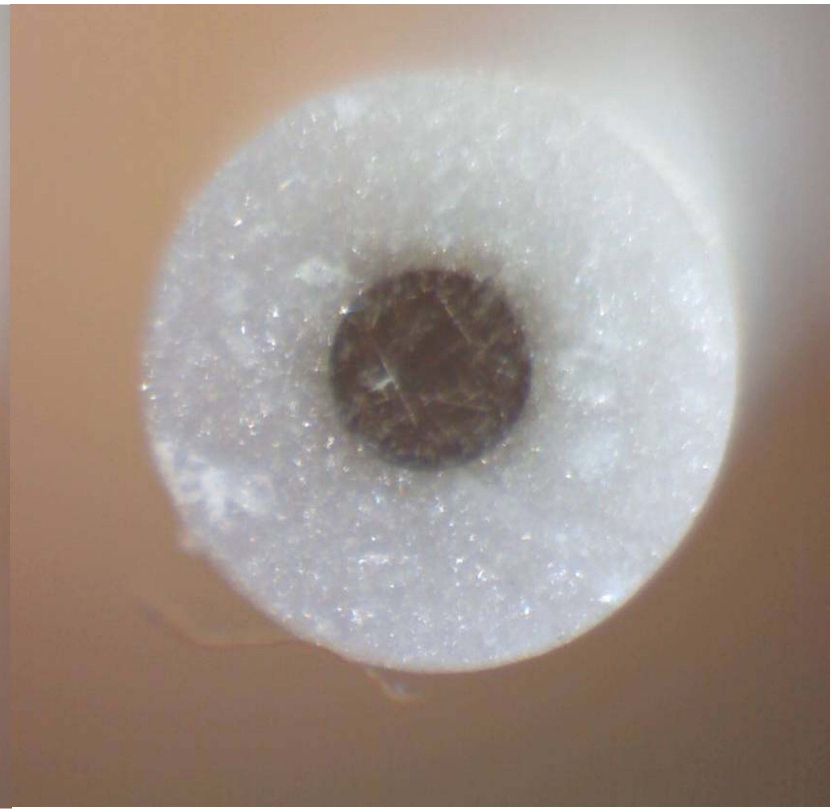
-Large quantity of a hydrocarbon will deposit carbon

-If you do too much you can block the tube:

Pyrolysis:

Shouldn't this be easy?

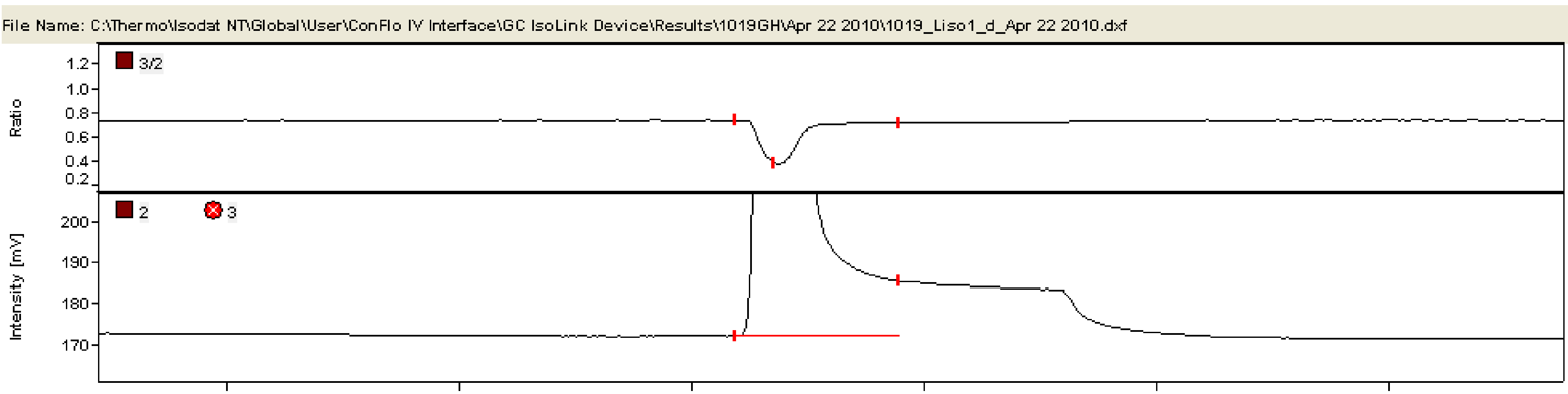




Pyrolysis:

Shouldn't this be easy?

-If you don't do enough:



- 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: