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# Elemental Analysis for Stable Isotope determinations A quick overview

Asita 2026

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# Disclaimer

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- Eh, just saying this imperfect talk is for people with little EA experience. If you have experience and later realise you just wasted an hour of your life, well ... go figure.



- However if you want more on the topic, YOU can give a talk next year.

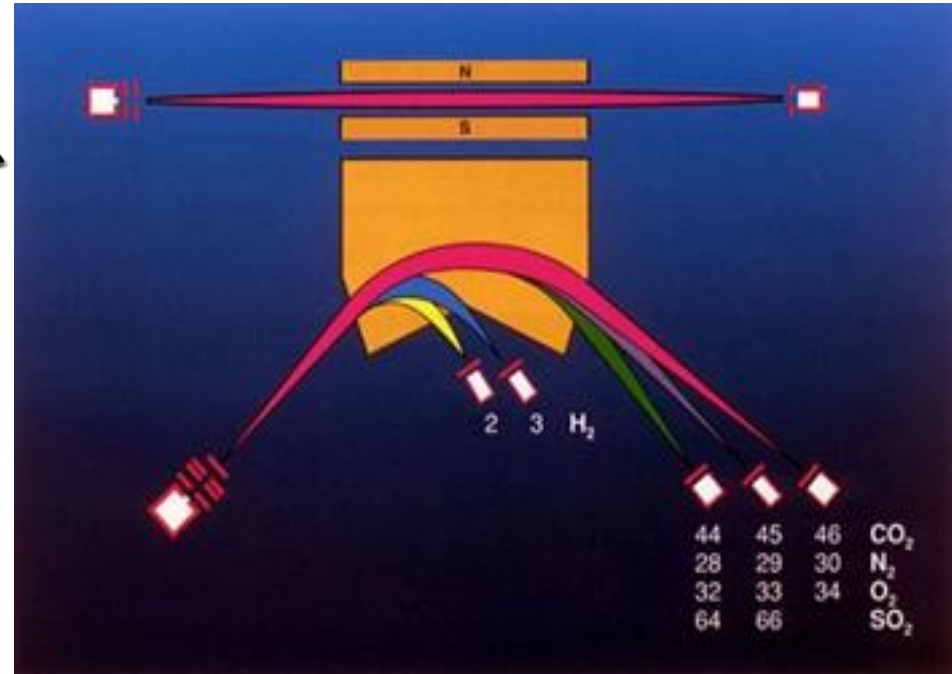


- No endorsement here except my own. But I can be bought for a beer or three.



# Solid to gas

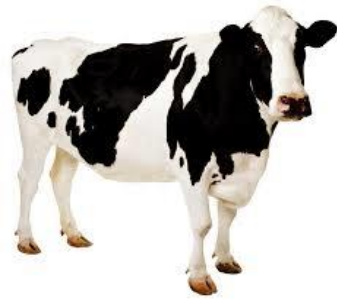
The reason we are here: IRMS



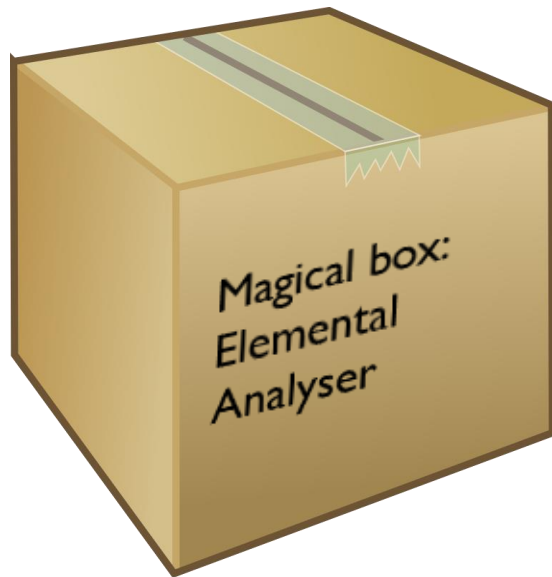
**SAMPLE**



# So why EA?

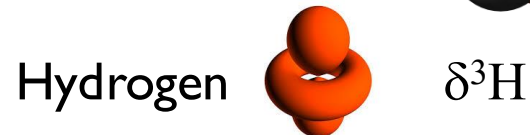
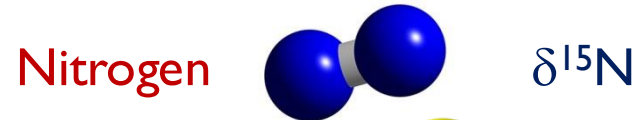


Your Grandma

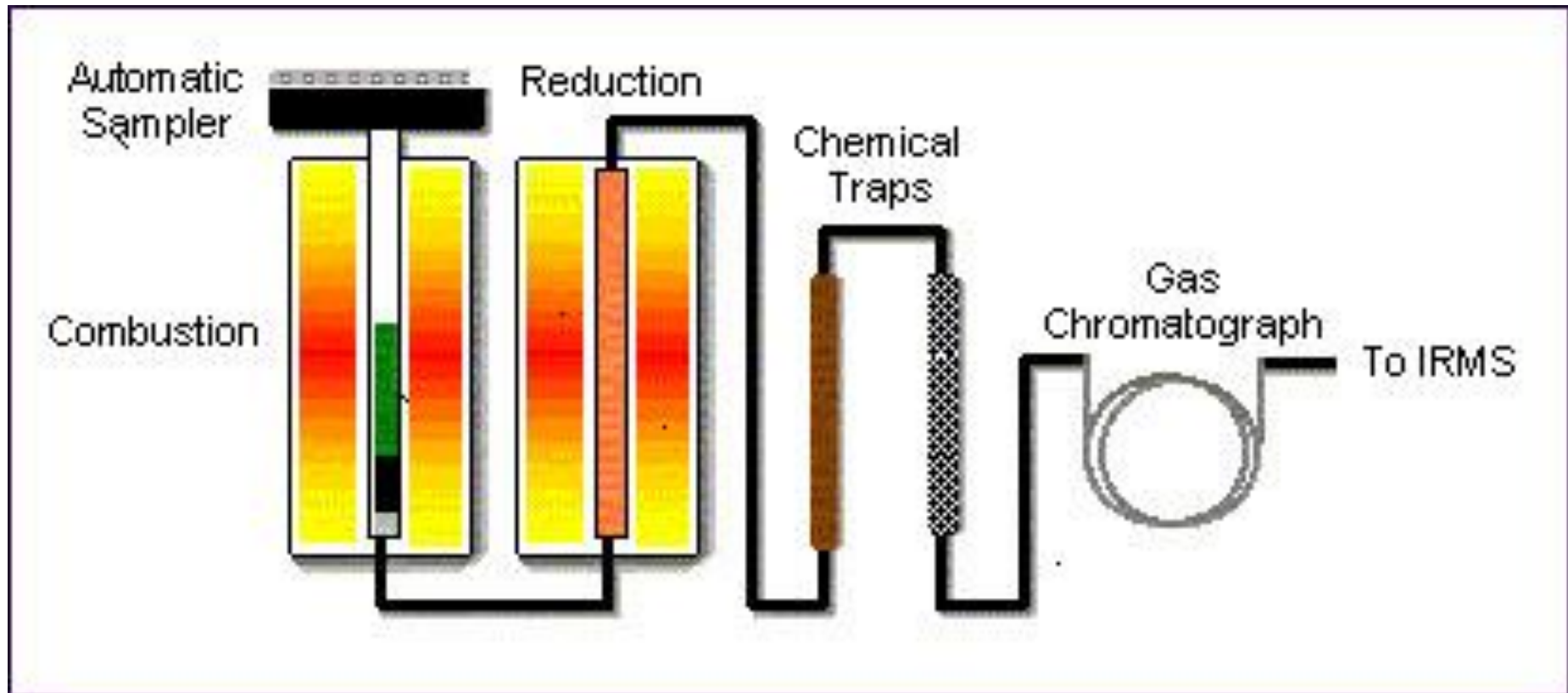


Combustion

Hi-Temperature Conversion



# Elemental analyser, low resolution



# So back to 2024, today's instruments

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# Elemental Analyser processes

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- ▶ Sample Preparation
- ▶ Combustion
- ▶ Reduction
- ▶ Removal of Interferences
- ▶ Separation
- ▶ Concentration Detection
- ▶ Dilution/Reference Gas Injection
- ▶ Measurement of Stable Isotope Ratios stuff
- ▶ Standards

Mainly CN mode



**WHY  
ARE  
YOU  
SO  
LAZY?!!!**



# Sample preparation



How much sample do I need?

Wendy knits a lot.

**“I knit  
so i don't  
kill  
people”**

Percent % of sample	Amount required for 0,1 mg of element
100%	0,1
10%	1,0
1,0%	10
0,5%	20
0,1%	100

Isotope	formulae
C13 with 70% dil	30 / %C
C13 no dil	5 / %C
N15	10 / %N
O18	10 / %O
D	1,5 / %H
S34	5 / %S



# Sample preparation

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**OK but what about C and N?**

**Did you know?**  
**The Web site of the UC Davis Stable Isotope Facility has a very nice sample calculator for CN.**

<https://stableisotopefacility.ucdavis.edu/sample-weight-calculator>

However the recommended maximum CN ratio is 100 : 1, anything more should be done separately.



# Obvious sample prep issues

Availability

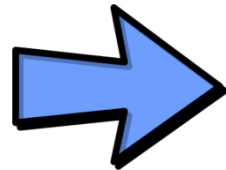


No More Feathers!

Density issues as iron vs fluffy stuff. Encapsulation?



Homogeneity



Dry is good



# ‘Troublesome’ sample prep issues

Flying blind? Go to the literature.

Sample Material	%N	%C
Plant - leaves	2-3%	42-50%
Plant - roots	0.8-1.3%	36-40%
Plant - stems	0.4-0.8%	46-48%
Plant - wood	0.02-0.06%	40-44%
Plant - grain flour (wheat, rye, rice)	1.5-3.5%	43-47%
Plant - grass, alfalfa	2.5-5%	45-47%
Soil - low OM	0.1-0.15%	0.8-1.2%
Soil - medium OM	0.2-0.3%	2.5-3.5%
Soil - high OM	0.3-1.0%	10-14%
Sediment - bulk	0.05-0.15%	0.5-1.5%
Animal, Fish, Invertebrate tissue	10%	40%
Human Hair	14%	47%

Suggest an EA analysis for CN(S) concentration. And make some \$\$\$



# ‘Troublesome’ sample prep issues

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Carbonates, hmmm, no thanks. Please remove. (acid rinse, fumigation, sulfurous acid... not trivial)

Best data possible: run for N on untreated, run for C on acid treated.

Chlorine, hmmm, as little as possible. Please remove. Usually leftover from acid reaction as  $\text{CaCl}_2$ , will readily dissolve in water. Removed by silver in EA.

For large C:N ratio sample,  $\text{CO}_2$  can be removed with NaOH on a support. Don't recommend running for CN with C:N ratio larger than 100.

Add  $\text{WO}_3$  powder (not granular) or  $\text{V}_2\text{O}_5$  as catalyst for difficult samples, sediments and sulfur, from X3 to x10. Test for blanks first. Oh yes.

# Make your life easier with the proper tools

Dilution: _____		Hatch Lab No(s): _____										Weighed by: _____	
ug	1	2	3	4	5	6	7	8	9	10	11	12	ug
<b>A</b>	J-2 (1) (bypass)	J-2 (2) (bypass)	J-2 (3) (bypass)	J-3 (4) (blank)	C-54 (5) 400ug	C-54 (6) 400ug	C-56 (7) 800ug	C-56 (8) 800ug	C-59 (9) 400ug	C-59 (10) 400ug	C-55 (11) 400ug	12	<b>A</b>
<b>B</b>	13	14	15	16	17	18	19	20	21	22	23	24	<b>B</b>
<b>C</b>	C-54 25	26	27	28	29	30	31	32	33	34	35	36	<b>C</b>
<b>D</b>	37	38	39	C-54 40	C-56 41	C-59 42	C-55 43	44	45	46	47	48	<b>D</b>
<b>E</b>	49	50	51	52	53	54	55	56	C-54 57	58	59	60	<b>E</b>
<b>F</b>	61	62	63	64	65	66	67	68	69	70	71	72	<b>F</b>
<b>G</b>	C-54 73	C-56 74	C-59 75	C-55 76	77	78	79	80	81	82	83	84	<b>G</b>
<b>H</b>	85	86	87	88	89	90	91	92	C-54 93	C-56 94	C-59 95	C-55 96	<b>H</b>
ug	1	2	3	4	5	6	7	8	9	10	11	12	ug

# Hammering it out with Thor

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<https://www.pelletpressdiesets.com/collections/low-profile-die-sets>



# Size and shape do matter...



Different carousel sizes are practical

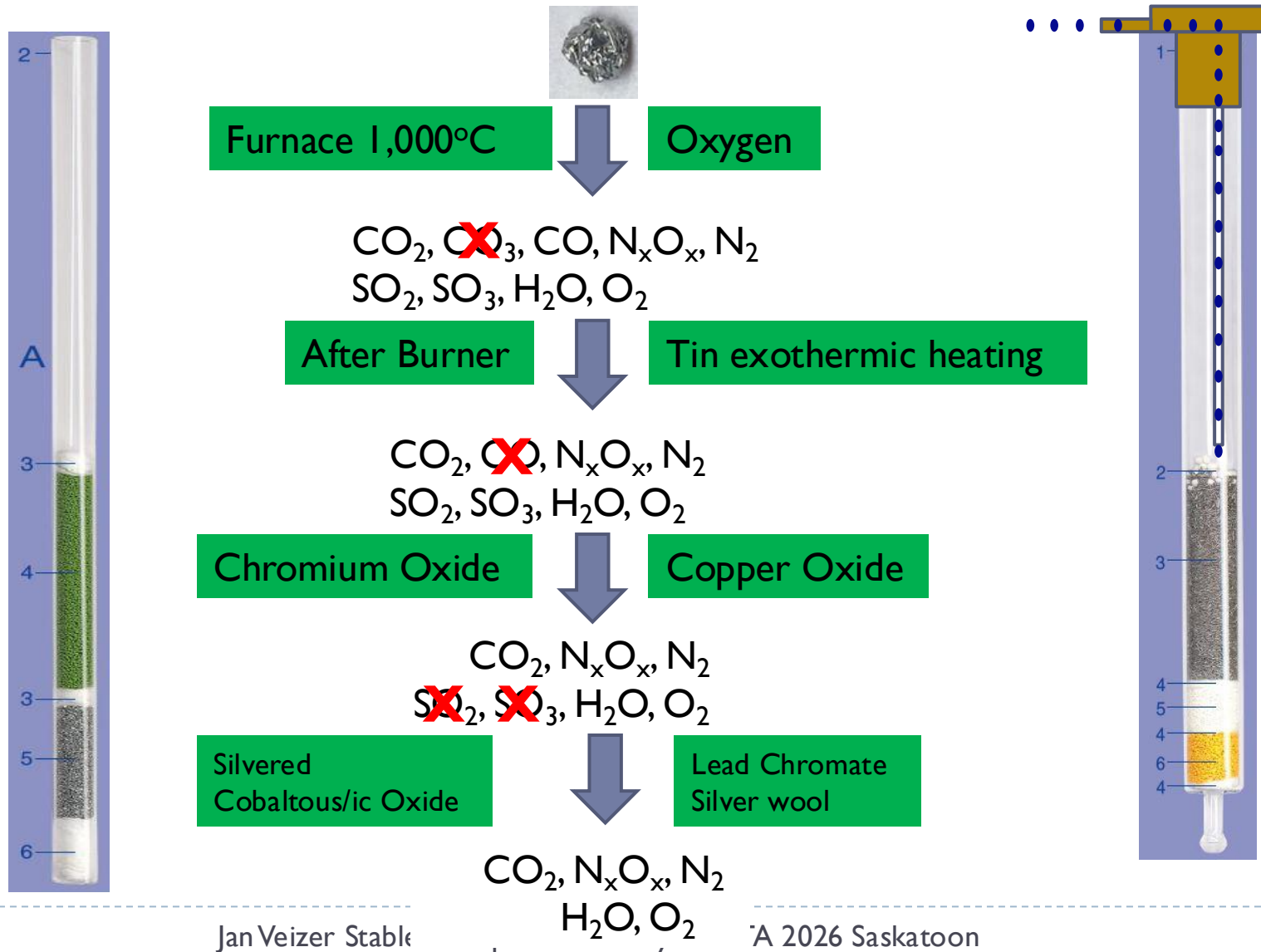


Round or square,  
not flat please



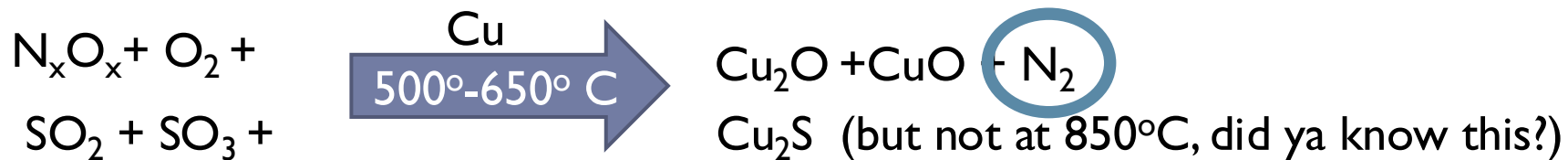


# Hot chemistry



# Reduction

From the combustion:  $\text{CO}_2$ ,  $\text{N}_x\text{O}_x$ ,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$



$\text{CO}_2$

$\text{N}_2$

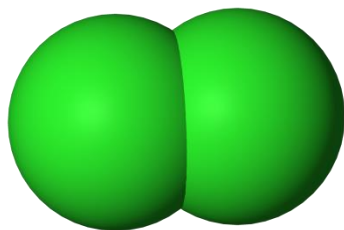
$\text{H}_2\text{O}$



# Interferences



- Magnesium Perchlorate (mix with 33% qtz chips)
- Sicapent ( $P_2O_5$  on support + colorant)

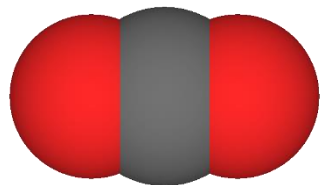


No, not a green butt, but it represents chlorides.  
Can be removed with Silver or Silver compounds.

Group  
7B

F <sup>9</sup>
Cl <sup>17</sup>
Br <sup>35</sup>
I <sup>53</sup>
At <sup>85</sup>

Halogens can be removed by adding MgO to the combustion tube, only in CN mode (not as good for NCHS)



**Carbon Dioxide can be removed with NaOH on support (Carbosorb) ... including SO<sub>2</sub>. Used for large c:n ratio.**

# Separation

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- ▶ Most detectors (e.g. TCD) do not speciate.
- ▶ Therefore analyte gasses need to be separated.
- ▶ Avoid ion source interference.



Isothermal Gas Chromatography Column



Purge and Trap Gas column

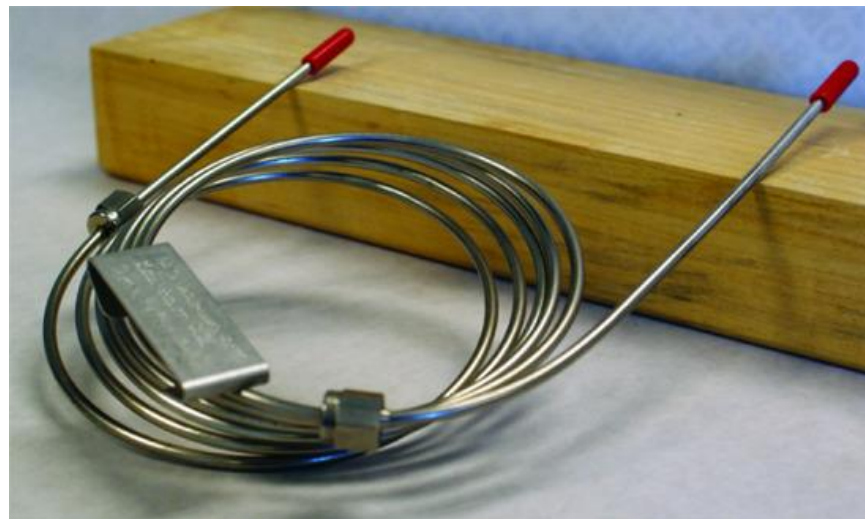


# Separation : GC column

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- Packed GC Column
- Most common
- Inexpensive
- Isothermal or variable
- No valves, simple heaters

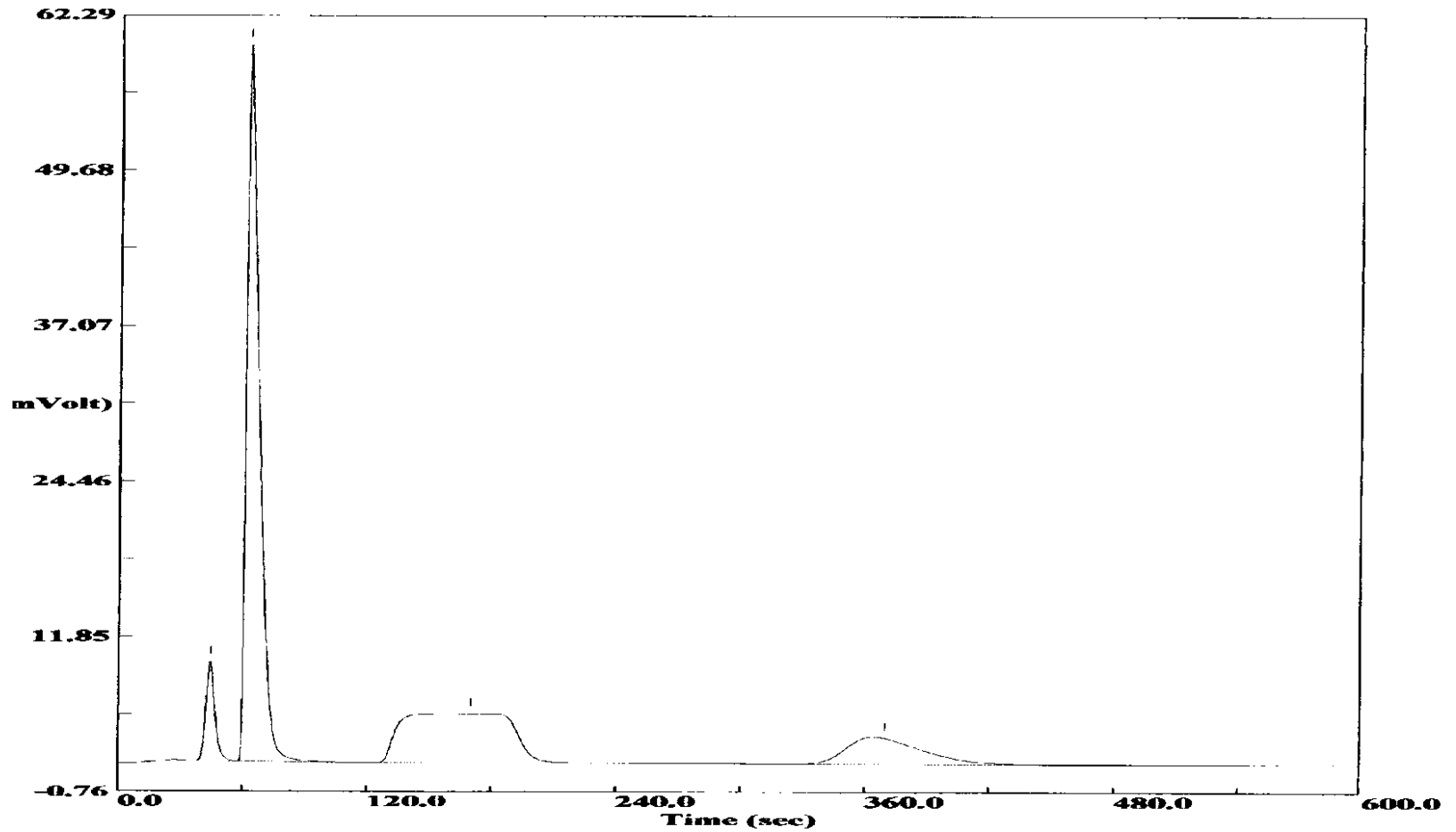


- Smaller dynamic range, can be overloaded easily (shark fin shape)
- Not so good for CNS, compromise.



# Picture perfect

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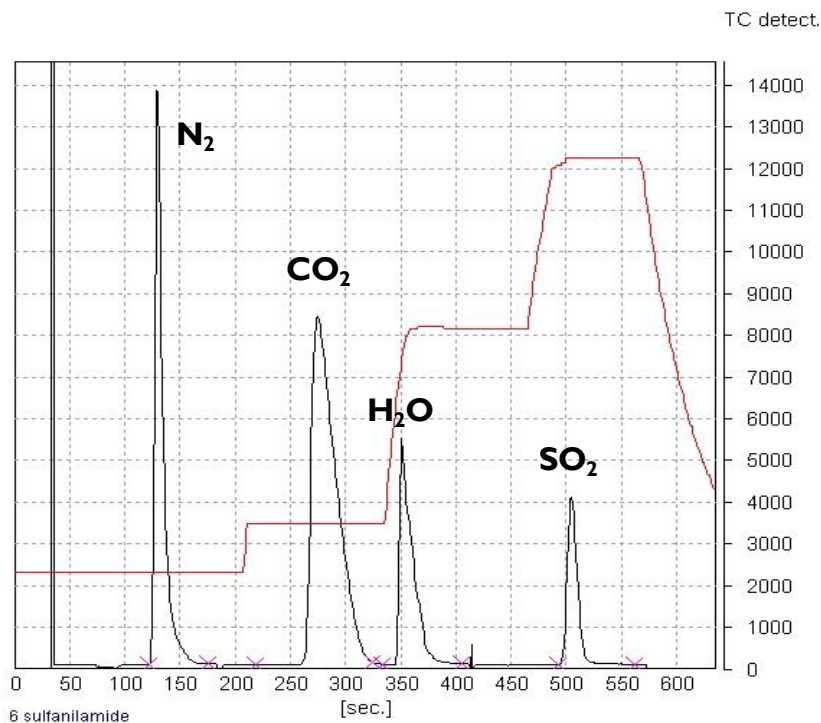
# Separation: Purge and Trap



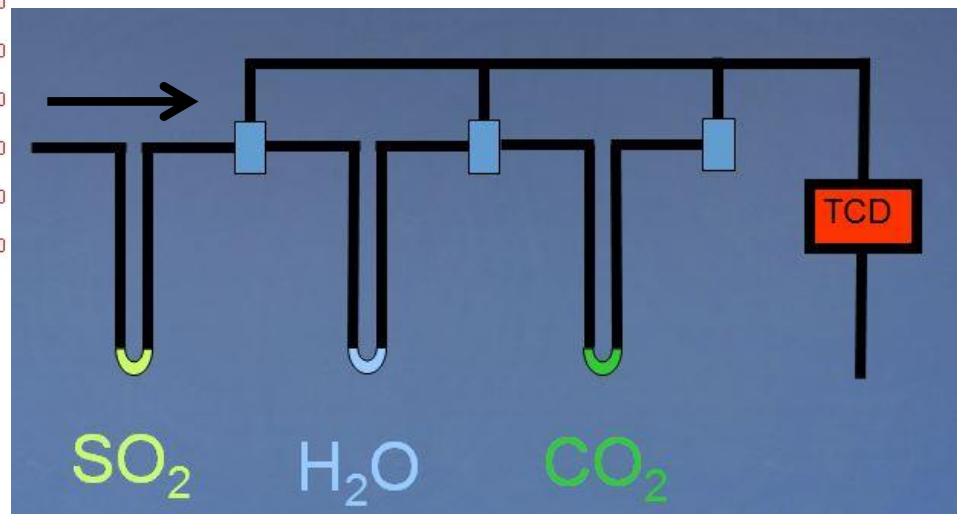
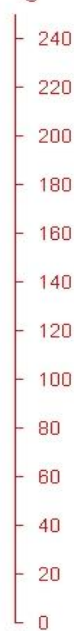
- Large dynamic range
- Baseline separation
- Good for NCS
- Fast



- Expensive
- Needs bakeout
- Valves, Heaters



Ads. column °C



# Moving to Detectors...

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## Thermal Conductivity Detector – TCD

- Non selective detector – one at a time please!
- Non destructive
- Not particularly sensitive, but pretty good with current technology
- Very large dynamic range and reasonably linear
- Robust
- No dilution but possible gain adjustment
- Depending on manufacturer: may or may not require calibration

## Isotope Ratio Mass Spectrometer

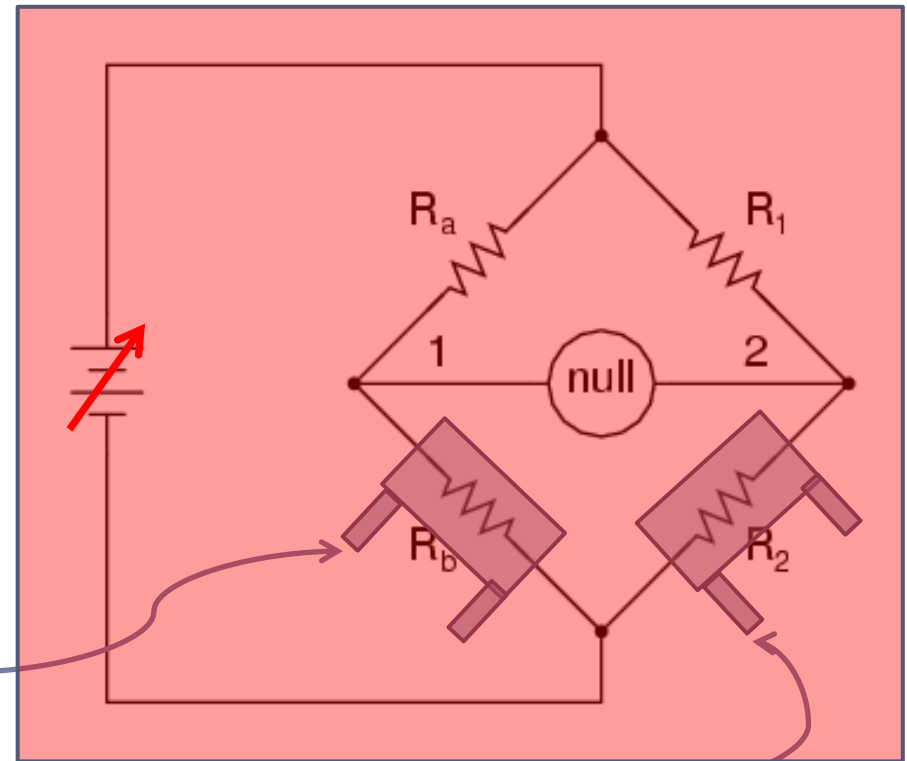
- Sensitive
- Limited range
- Dilution
- Software ... made for isotopes, not concentration



# TCD, how it works

- ▶ Wheatstone Bridge
- ▶ Two of the resistors are “thermistors”
- ▶ Direct flow from combustion to one resistor
- ▶ Direct reference He flow to the other thermistor
- ▶ Put it all in an oven @ 60°C
- ▶ With no sample, just He flow adjust voltage for zero bridge voltage.

From Combustion



Reference Helium

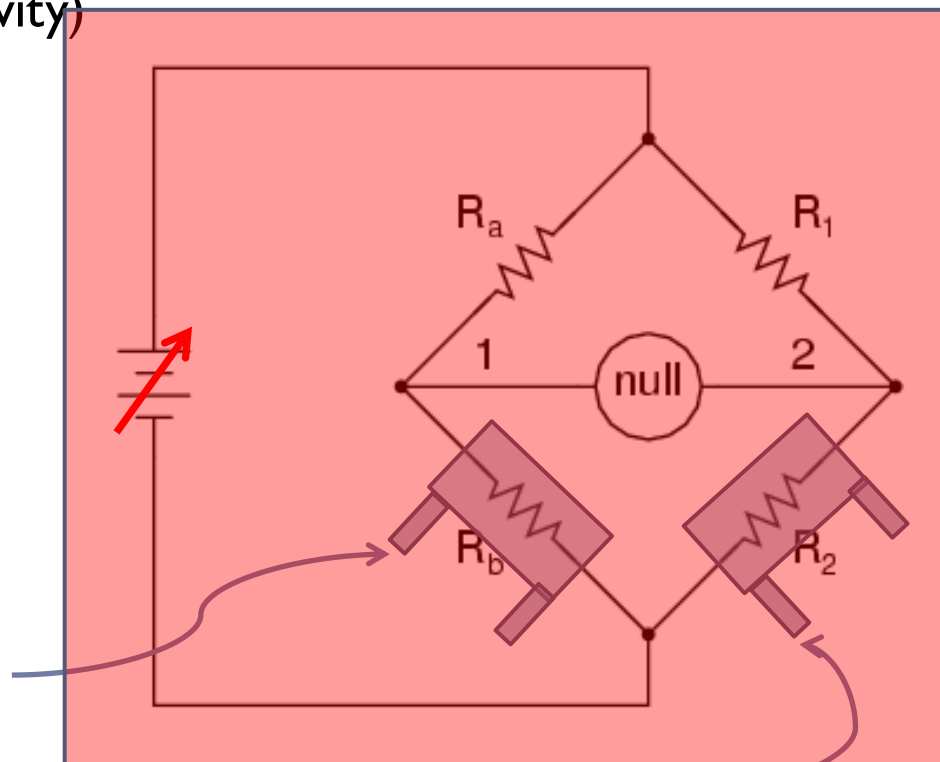


# TCD

- ▶ If the rate of cooling changes on one thermistor, the bridge will go out of balance and there will be a voltage from 1 to 2.
- ▶ A mixture of He and some other gas (analyte) will have a different heat transfer rate (ie thermal conductivity) compared to pure He.

Gas	TC
Helium	156.7
Nitrogen	26.0
Carbon Dioxide	16.8
Water	18.7
Sulfur Dioxide	9.6
Carbon monoxide	25
Argon	17.9

From Combustion

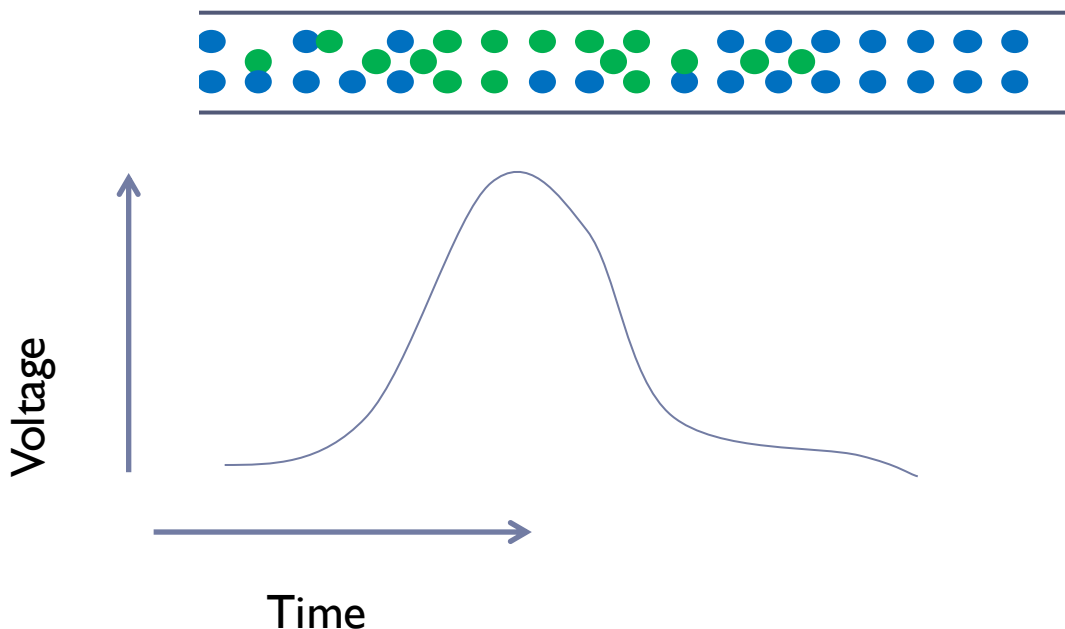


Reference Helium



# TCD

- Graphing the bridge voltage versus time will trace a peak as a plug of helium & analyte passed the sample thermistor.
- The area under the peak will be proportional to the amount of “other gas” which passes through
- System has to be calibrated for each type of gas (analyte).



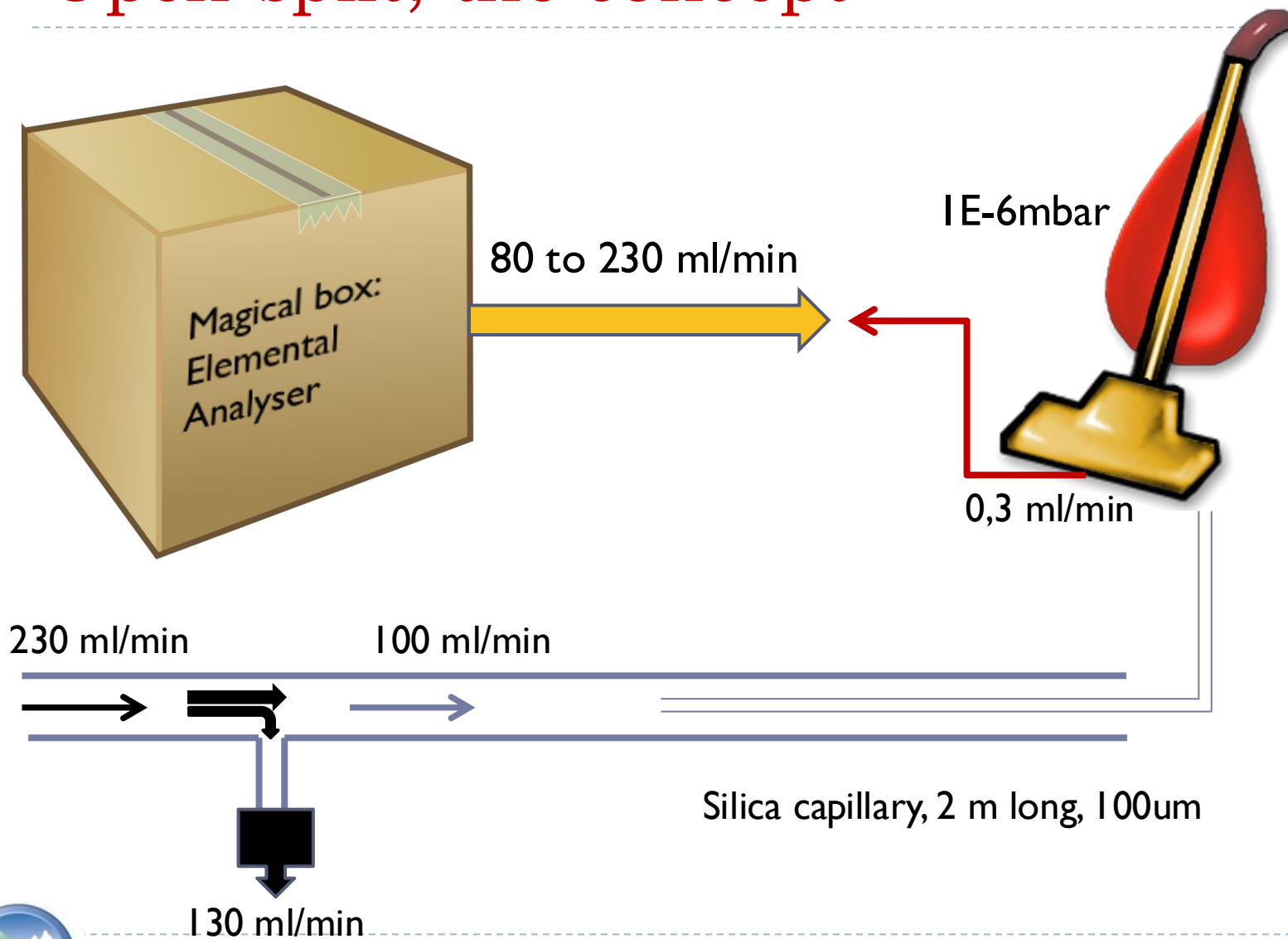
# Geez, is he done yet?

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- ▶ Sample Preparation ✓
- ▶ Combustion ✓
- ▶ Reduction ✓
- ▶ Removal of Interferences ✓
- ▶ Separation ✓
- ▶ Concentration Detection ✓
- ▶ Dilution/Reference Gas Injection
- ▶ Measurement of Stable Isotope Ratios stuff

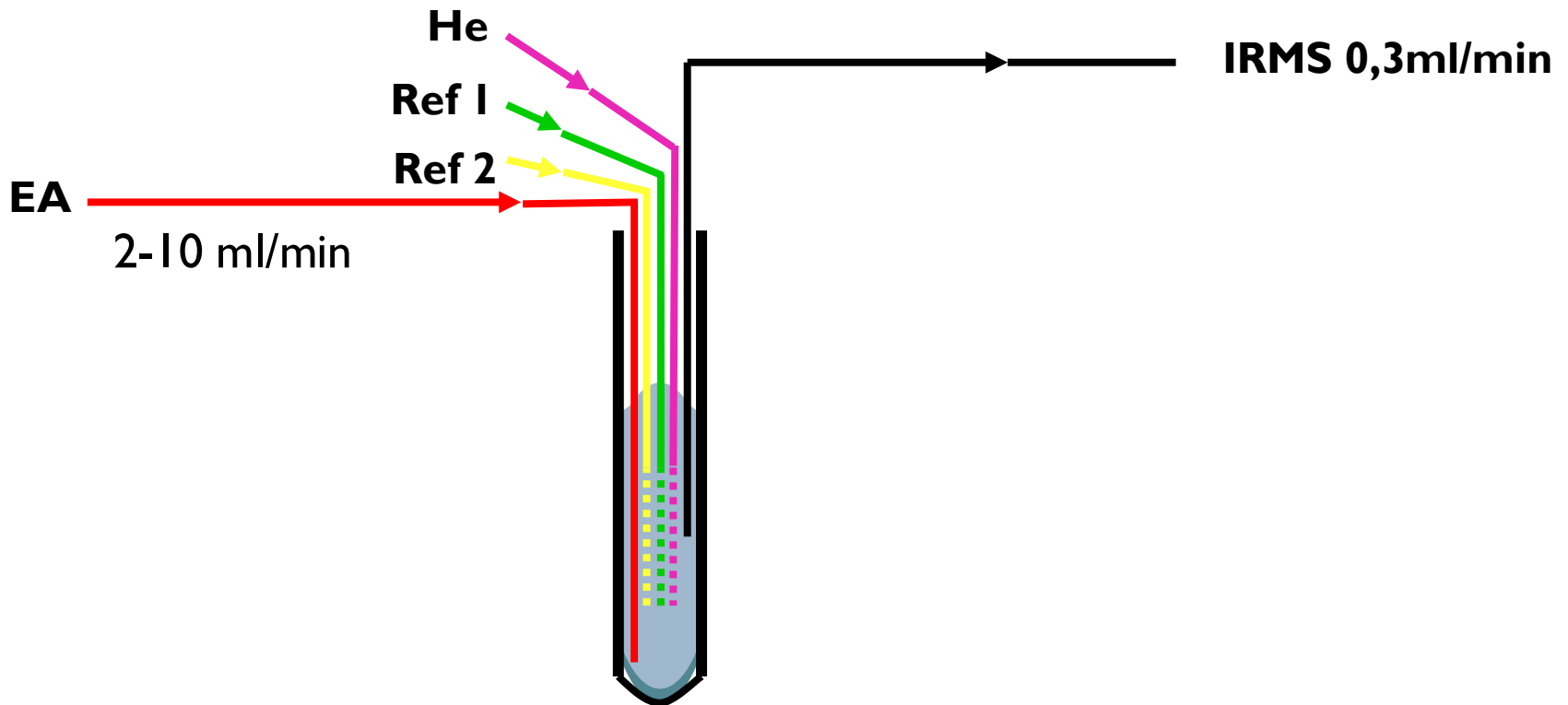


# Open split, the concept

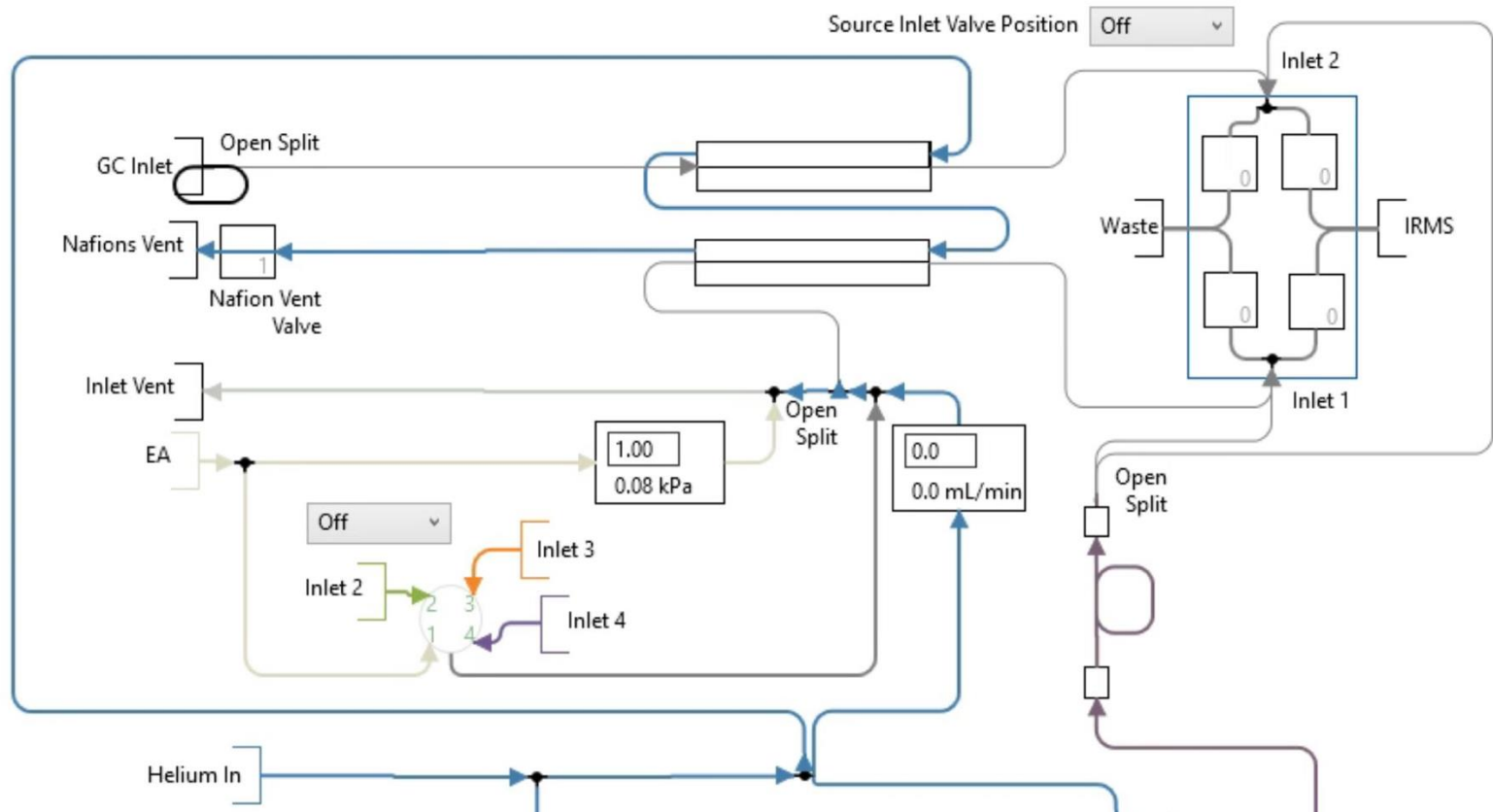


# Conflo principle + dilution

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# CentrION diluter



# Ok so what's next?

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Measurement of Stable Isotope Ratios with an Elemental Analyser...

Hmm ... realistically we are talking about:



# Step #1

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Write down working conditions :

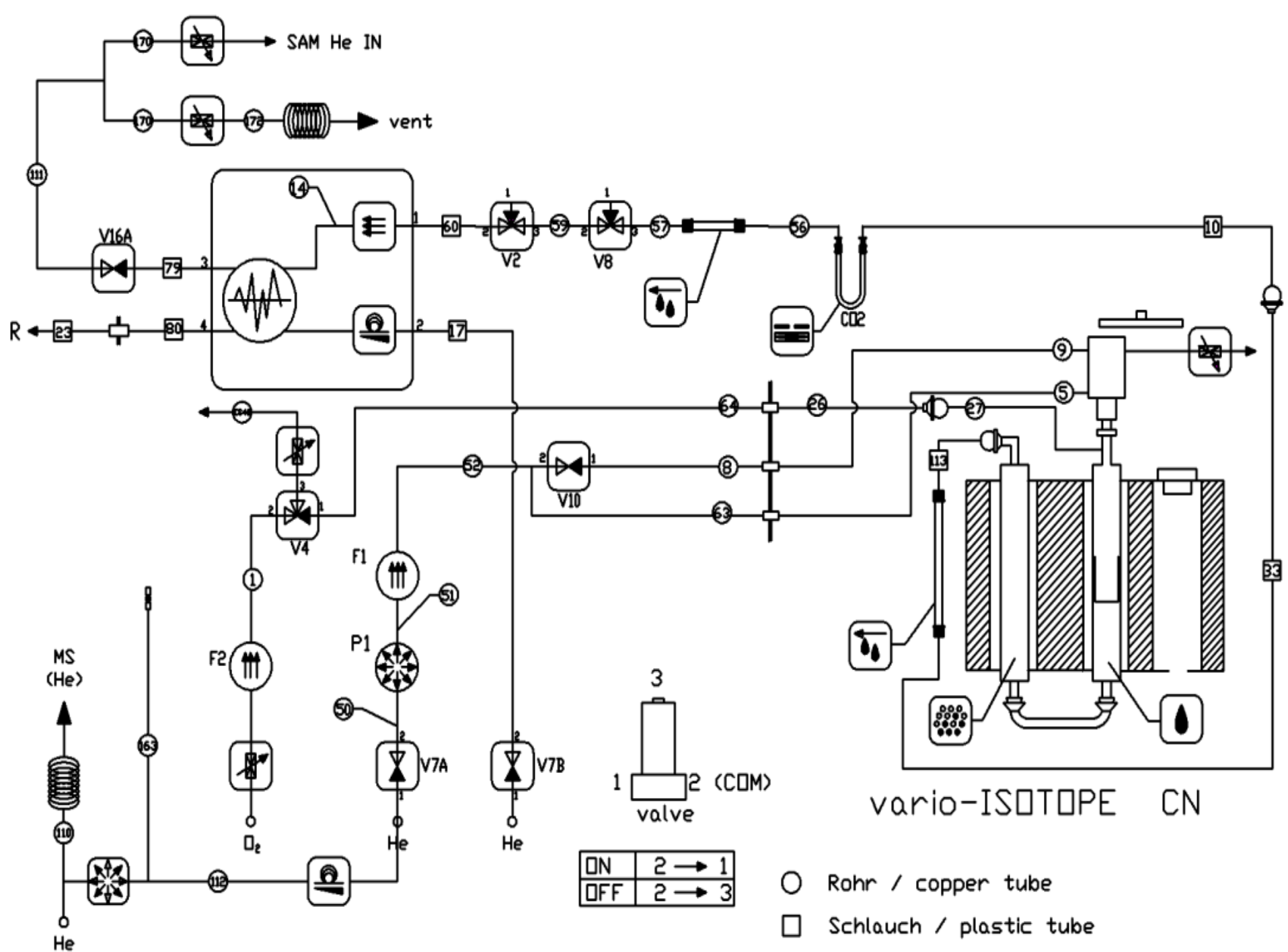
EA: flows, pressures, times (flash, oxygen, retentions),  
expected areas of specific weights of stds.

IRMS: backgrounds (28, 44, 40, 18), sensitivity (ref gas vs  
sample),



Know when your patient is healthy





# So obvious but...

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Flow	Pressure	Think.....
Normal	Normal	Going to have a good day
High	Low	Go back to Bed! - Leak
Low	High	Blockage



# Leak time

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## LARGE LEAKS

- Can't reach expected flow
- May be able to hear it
- Likely from the place you just opened
- Missing O-ring
- Loose connection
- Cracked combustion tube

## small leaks

- Tired-dried O-ring
- O-ring not sitting right
- Dust on O-ring
- Crack in combustion tube
- Autosampler



# Leak testing

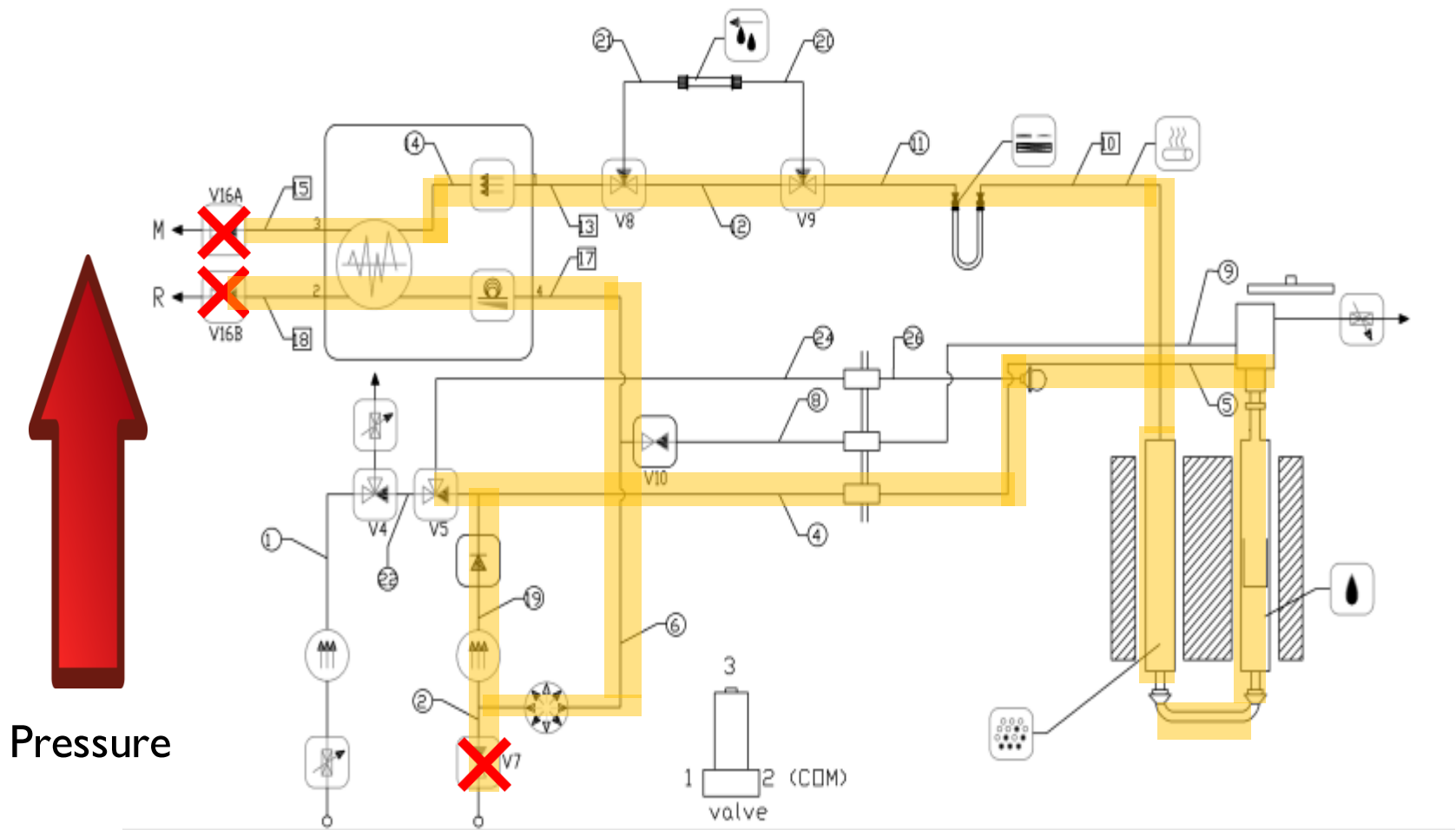
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Most Elemental Analysers have semi-automated leak detection programs...

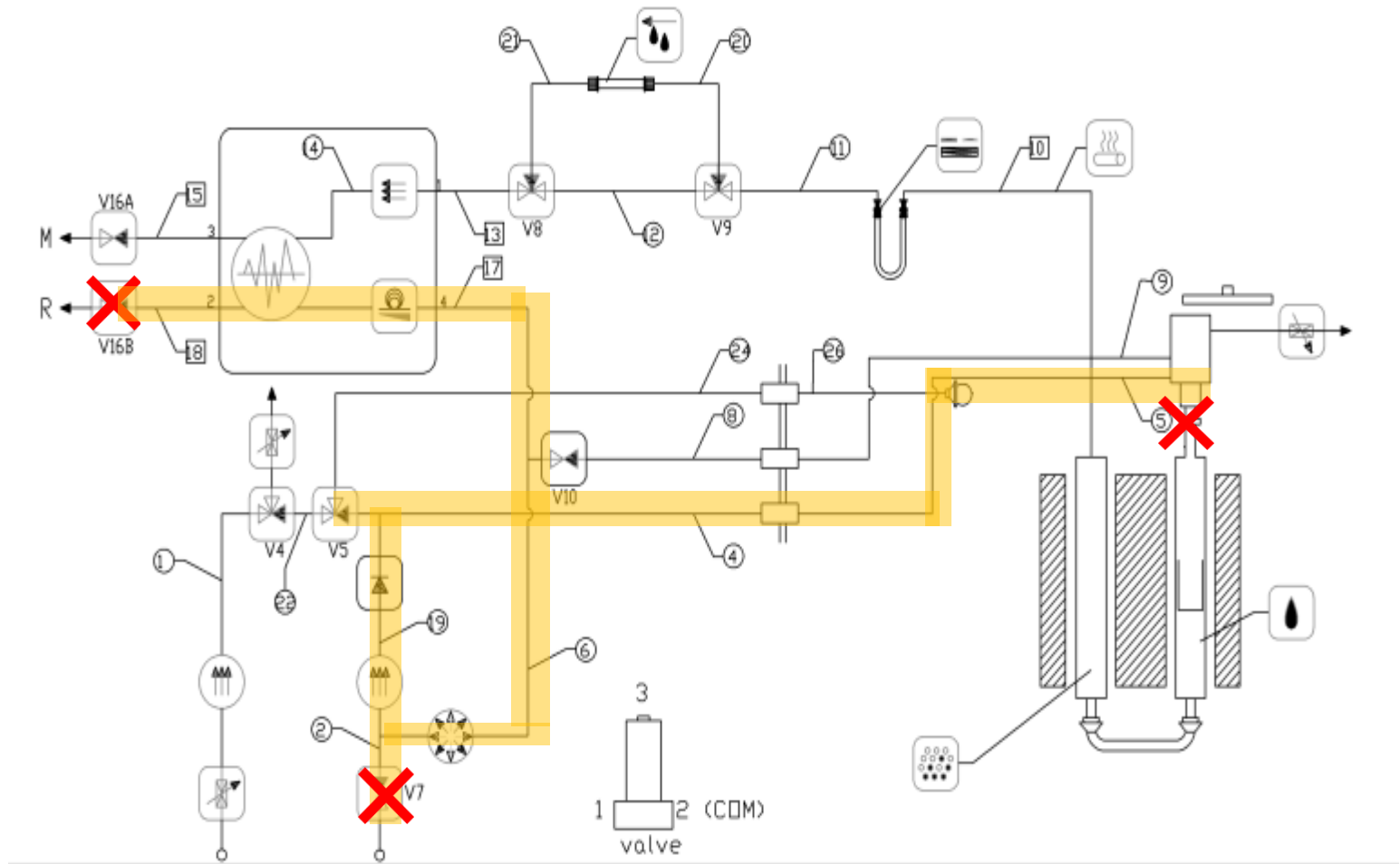
- Perform a leak check every time you open the instrument
- Understand what is being tested exactly
- Don't forget to turn the IRMS dilution ON while testing
- Start testing complete system then reduce tested volume



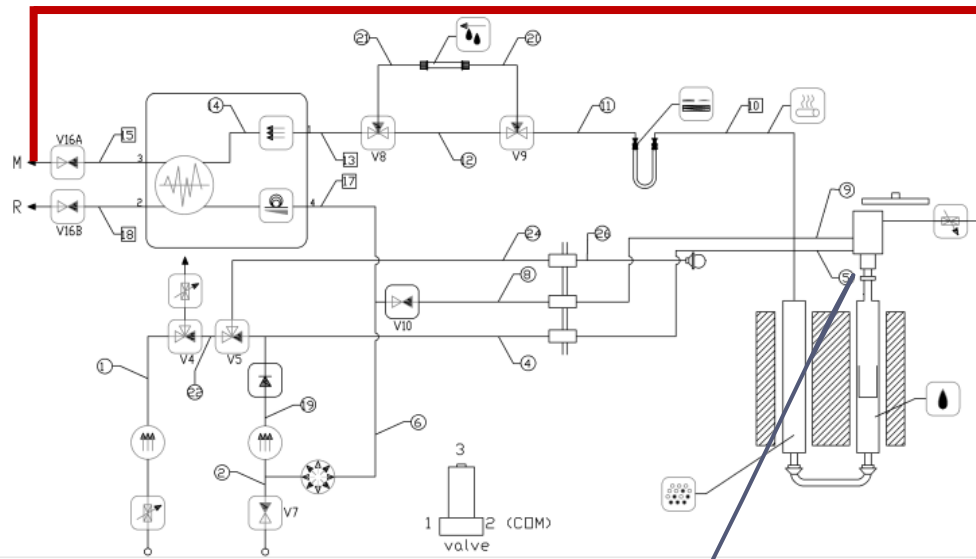
# Pressurize, Stabilize, Wait...



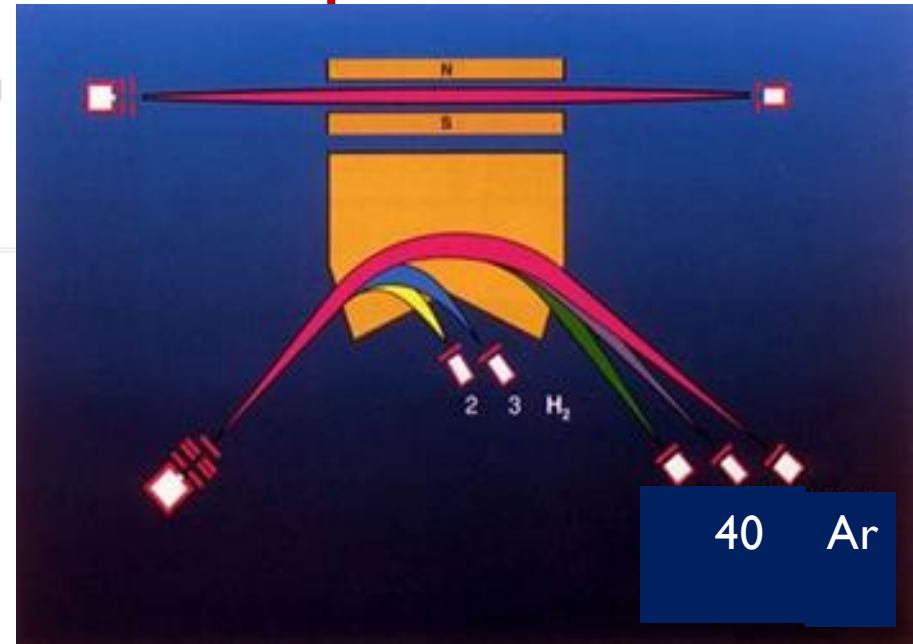
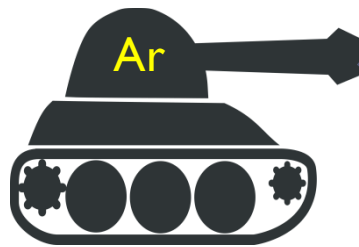
# Back to step #1



# Argon, atmospheric leak



Of course,  
better with Ar  
background



# Standards literacy

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## Primary reference material or calibration material

- From IAEA, they can defined the scale such as VSMOW or VCDT or VPDB.
- For EA, C13 or N15 can be easily directly measured with these stds.
- Calibration material are used when Primary are exhausted or not applicable.
- Such as S-1 for VCDT scale or NBS-19 for VPDB.

## Reference material

- From IAEA, USGS, Microanalysis, other private source.
- Carefully calibrated against Primary or calibration material.
- Such as Glutamic acid from USGS reference and calibration material list

<b>USGS41a</b>	L-glutamic acid enriched in $^{13}\text{C}$ & $^{15}\text{N}$	0.5 g	\$165	$\delta^{15}\text{N} = +47.55 \text{ ‰}$ $\delta^{13}\text{C} = +36.55 \text{ ‰}$
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## Working Standard

- Large amount of material calibrated with above, used every day.



# IAEA Standards (also at NIST)

The screenshot shows the IAEA Reference Products website. The page title is "REFERENCE PRODUCTS FOR ENVIRONMENT AND TRADE". The navigation menu includes Home, Reference Materials, Analytical Methods, Publications, Interlaboratory Studies, Nuclear Instrumentation, Events, and ALMERA. The breadcrumb trail is: Home > Reference Products > Reference Material Online Catalog > Stable Isotopes > Materials with known  $^2\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^{18}\text{O}$  isotopic composition.

The main content area displays a table of reference materials. The table has four columns: Title, Category, Description, and Release Date. The entry for USGS41 (L-glutamic acid) is circled in red.

Title	Category	Description	Release Date
NBS 22		Oil	1995-09-01
NBS 28		Quarz Sand	-
NBS 30		Biotite, <b>!Out of stock!</b>	-
USGS24		Graphite	-
USGS40		L-glutamic acid	-
USGS41		L-glutamic acid	-
USGS41		Caffeine	-
IAEA-600		Benzoic Acid	-
IAEA-601		Benzoic Acid	2004-03-01
IAEA-602		Cellulose	2004-04-01
IAEA-CH-3		Sucrose	1995-09-01
IAEA-CH-6		Polyethylene	1995-09-01
IAEA-CH-7		$^{13}\text{C}$ Labelled Sodium-Bicarbonate	-

On the right side of the page, there are three sections: "My Shopping Cart" (Total: €0, Go to Shopping Cart button), "Your Account" (Edit My Profile, View My Orders), and "Help and Service" (Terms of Service, Contact Us).



# Useful reference and calibration info

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## USGS

<https://www.usgs.gov/labs/reston-stable-isotope-laboratory/reference-materials-and-calibration-services>

## IAEA

<https://analytical-reference-materials.iaea.org/stable-isotopes>

## Indiana University / Arnt Schimmelmann

<https://hcnisotopes.earth.indiana.edu/reference-materials/index.html>

## Microanalysis

[https://www.elementalmicroanalysis.com/product\\_list.php?sub=Isotope-Reference-Materials&category=124&menu=6](https://www.elementalmicroanalysis.com/product_list.php?sub=Isotope-Reference-Materials&category=124&menu=6)



# Working Standards

## Isotope Reference Materials



Isotope Reference Materials from Elemental Microanalysis are traceable to primary standards issued by IAEA Vienna. These materials are supplied with Certificates of Analysis. Values shown are indicative and may vary slightly from batch to batch. Actual values shown on certificate.

### Reference Materials (RM)

Cat no	Standard	Pack	%C	$\delta C^{13}$	%N	$\delta N^{15}$	%S	$\delta S^{34}$
B2151	Sediment	5g	6.5	-26	0.5	+4	0.9	+4
B2153	Soil	5g	1.5	-27	0.15	+7	0.03	+5
B2155	Protein (Casein)	5g	47	-27	14	+6	0.9	+6
B2157	Wheat Flour	5g	40	-27	1.5	+3	0.1	-1
B2159	Sorghum Flour	5g	42	-14	1.5	+2	0.1	+10

### Uncertified Working Reference Materials

Cat no	Standard	Pack	$\delta C^{13}$	$\delta N^{15}$
B2172	Olive Oil	5g	-28.5	-
B2174	Urea	5g	-45	-0.8



# Attention please!

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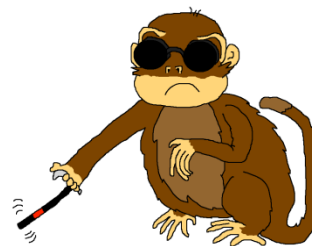


- Always run International Standards vs Internal standards
- You want to be able to link your Internal Standards to the International ones.
- Other good Internal Standards candidates for CN are caffeine, L-glutamic acid, polymers, EA standards.

My favorite of course



Don't forget to include a blind standard !



# Thank You

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Thanks to the Jan Veizer crew, Erin, Wendy, Anic, Elim you're the best

And finally to Scott Hughes for letting me cannibalize his talk

