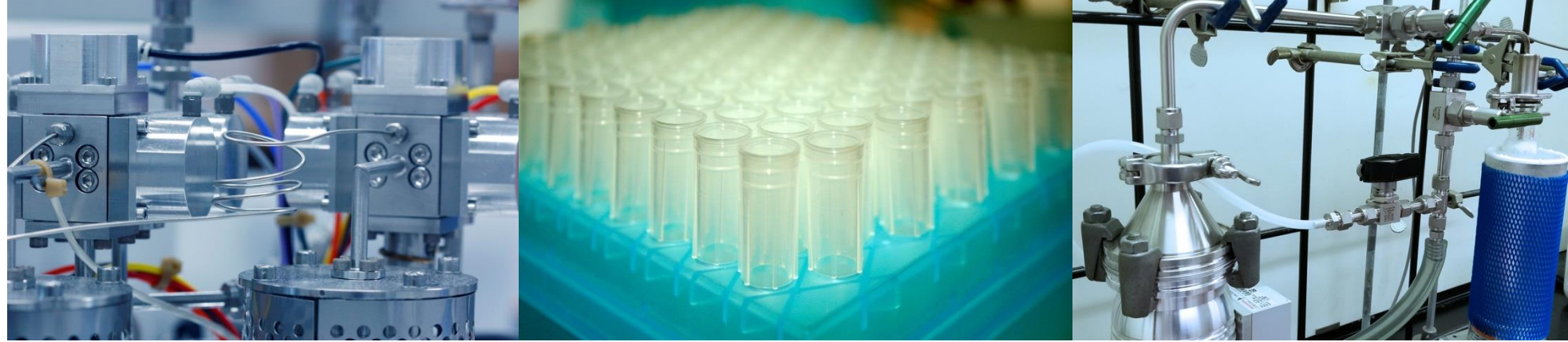


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de la Terre et de l'atmosphère

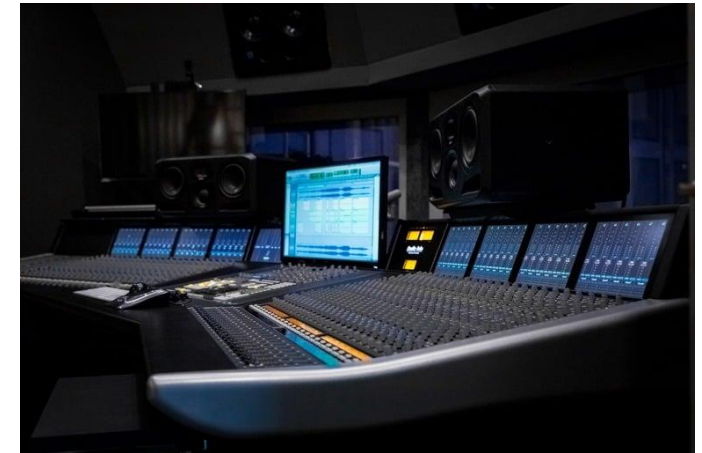
geotop | Centre de Recherche sur la
Dynamique du Système Terre



From Gas Torches to Lasers, Measuring Stable Isotopes

Jean-François Hélie

Geotop – Université du Québec à Montréal
helie.jean-francois@uqam.ca



David Gilmour: The Studio Interview 2025



Rick Beato
5,59 M d'abonnés

S'abonner

133 k



Partager



Enregistrer



Merci



Télécharger



Centre de Recherche sur la
Dynamique du Système Terre



Département des sciences
de la Terre et de l'atmosphère

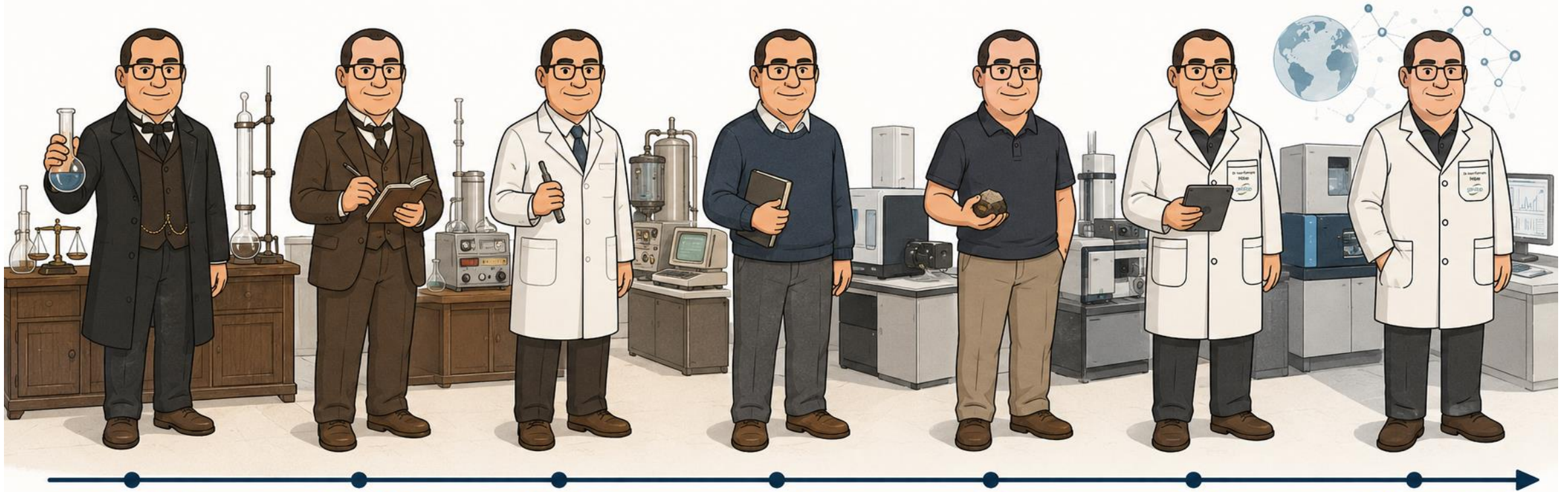


From Gas Torches to Lasers, *Measuring Stable Isotopes*

ChatGPT

The Evolution of Stable Isotope Geochemistry

Through Time and Experience



ChatGPT

Early mass spectrographs

Rays of positive electricity

Joseph John Thomson

Proceedings of the Royal Society A 89, 1-20 (1913) [as excerpted in Henry A. Boorse & Lloyd Motz, *The World of the Atom*, Vol. 1 (New York: Basic Books, 1966)]



Clovis Granger, my great grand father, 1900

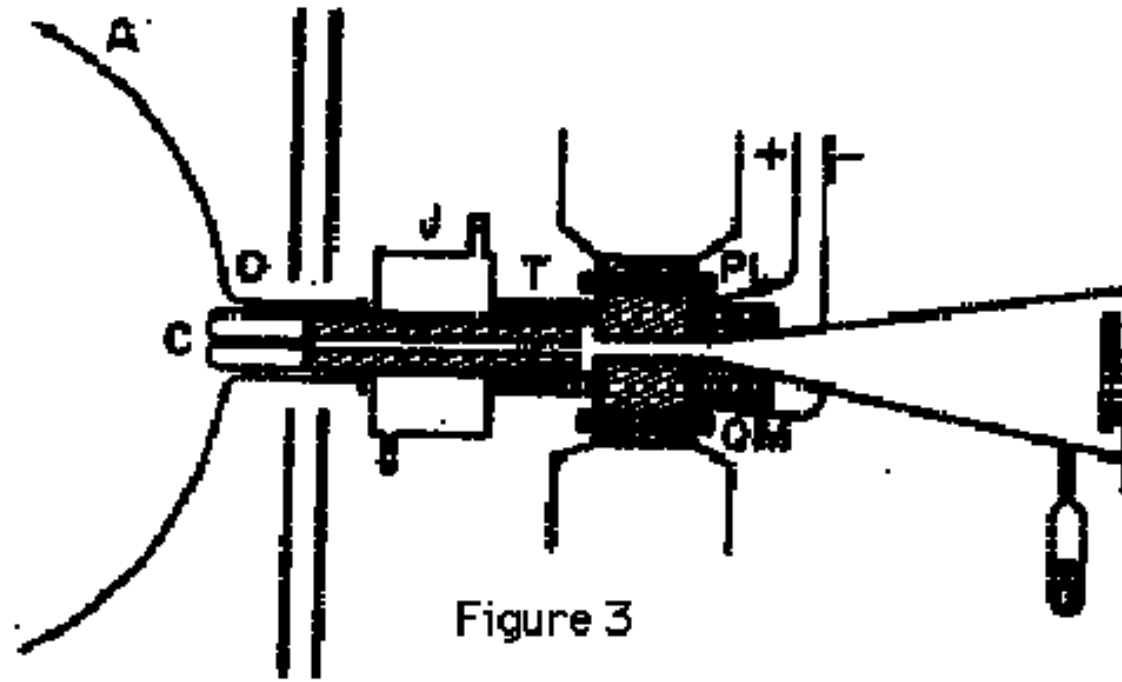


Figure 3

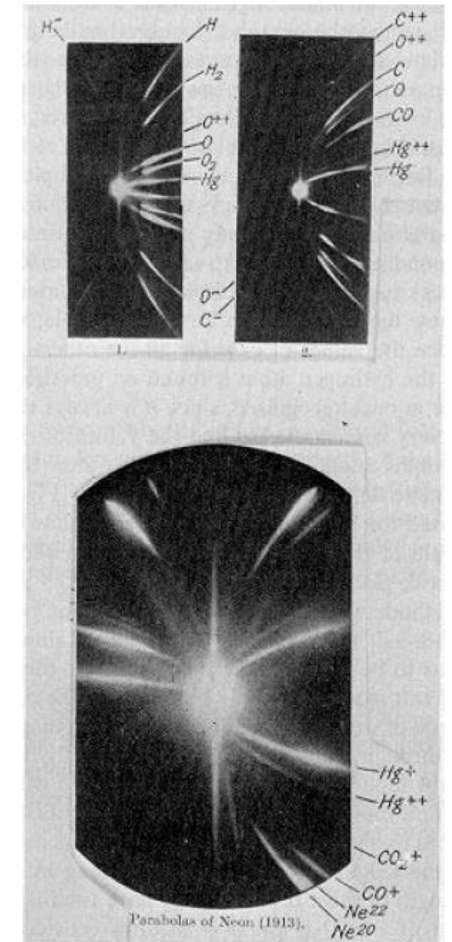


Figure 2

Electron impact source

A NEW METHOD OF POSITIVE RAY ANALYSIS.

By A. J. DEMPSTER.

Dempster, A. J. (1918-04-01). ["A new Method of Positive Ray Analysis"](#). *Physical Review*. 11 (4): 316–325.

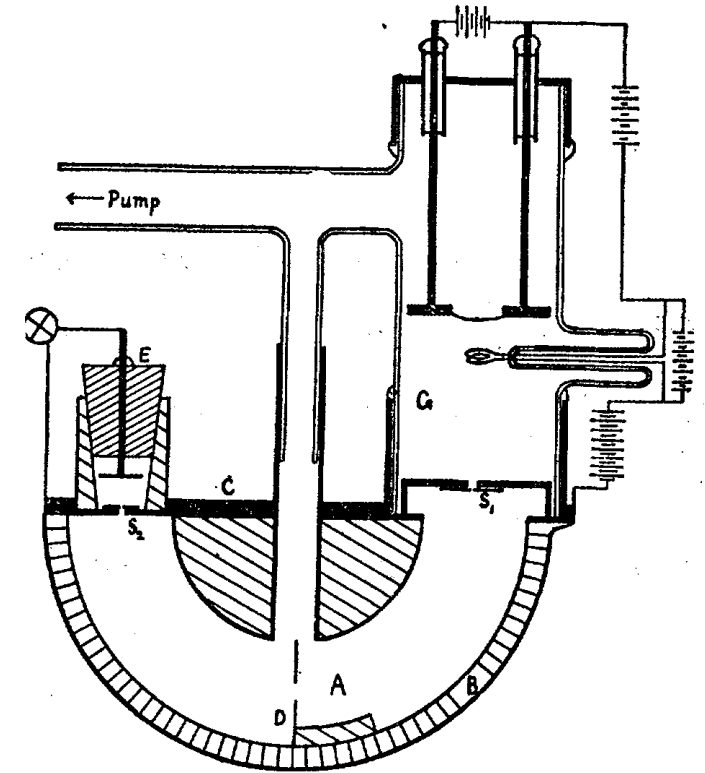


Fig. 1.

LXXIV. A Positive Ray Spectrograph. By F. W. ASTON, M.A., D.Sc., Clerk Maxwell Student of the University of Cambridge*.

* Communicated by the Author.
 † 'Rays of Positive Electricity,' p. 7 *et seq.*
 ‡ Phys. Review, vol. xi. p. 316 (1918).
 § *L. c.* p. 12.



Roger Hélie, my grand father, 1920

Fig. 3.

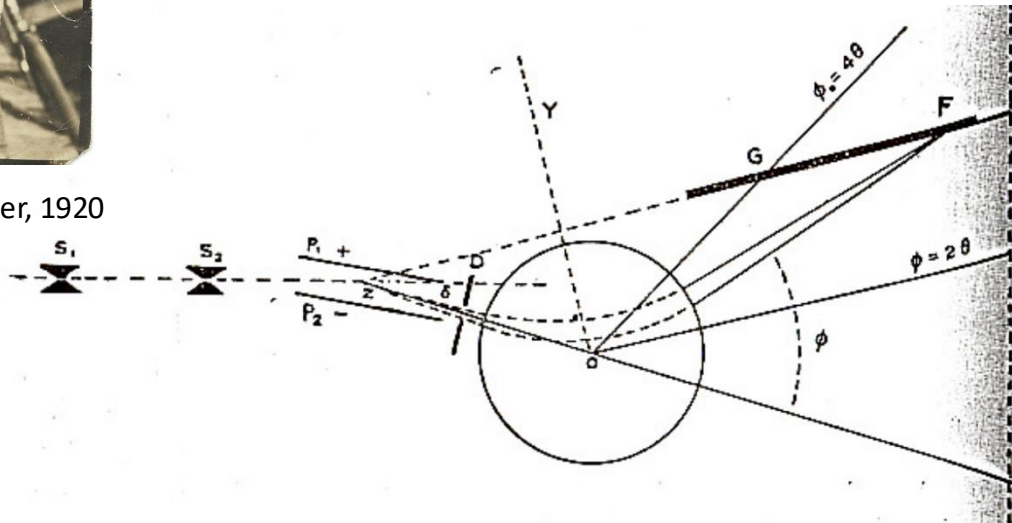
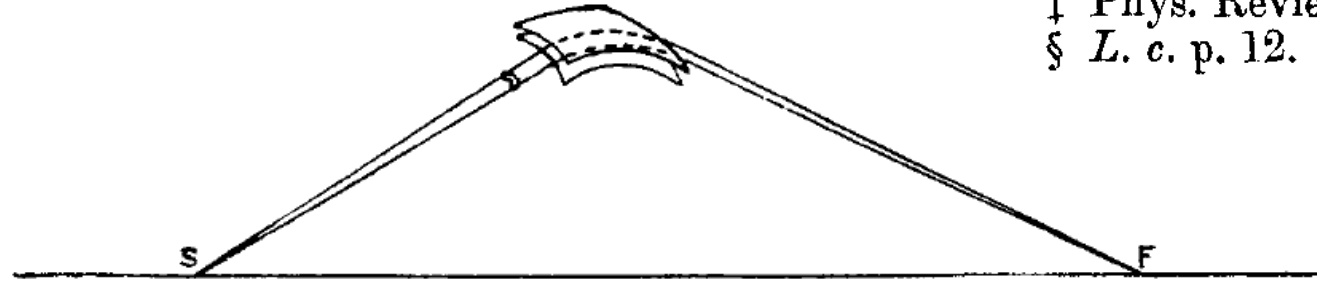


FIG. 1

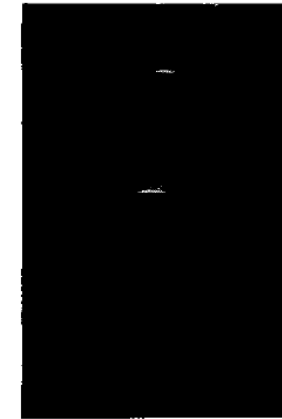
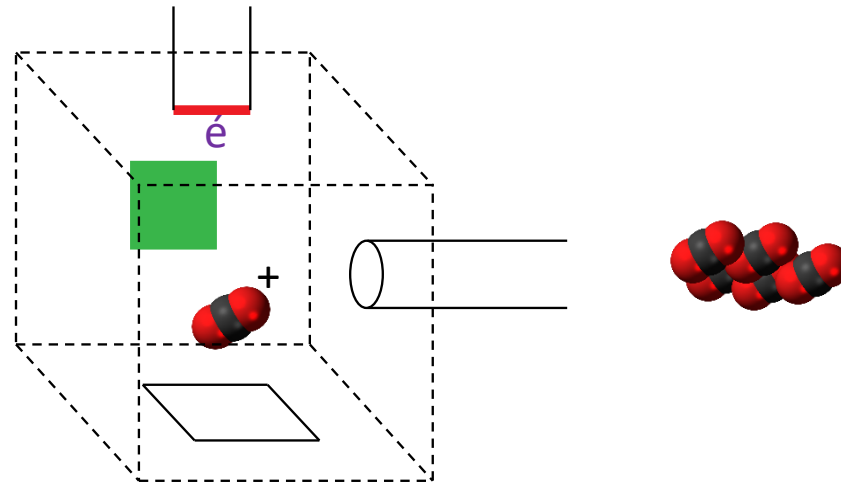


FIG. 2.

How does it work?

IRMS electron impact source



Incomplete ionization

The dual inlet system

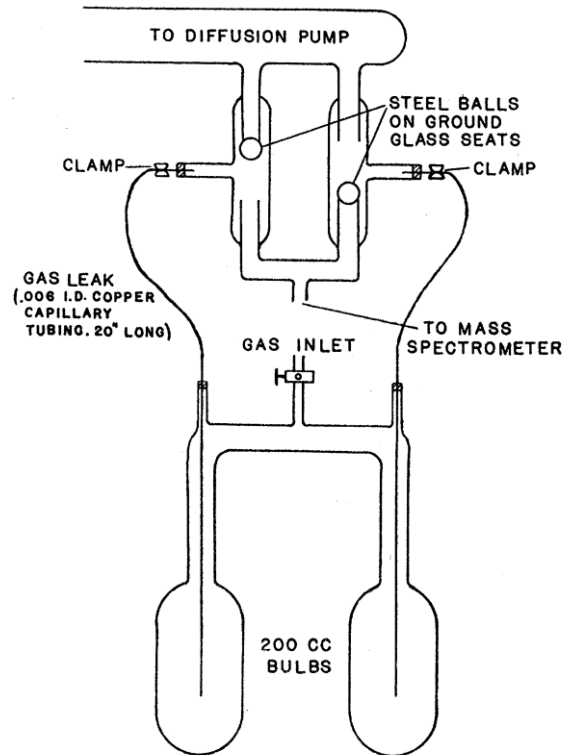
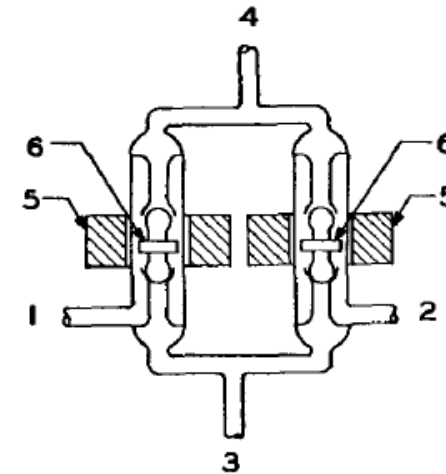


FIG. 1. Twin bulbs and gas leaks. The connecting tubing between the bulbs consisted of 25 cm of tubing of 1.13 cm² average cross section. The steel balls were $\frac{1}{32}$ " in diameter. The pumping speed in the line marked "to diffusion pump" was about $\frac{1}{2}$ liter per second, whereas the pumping speed toward the mass spectrometer was about one percent of that value.

Murphey (1947)

FIG. 6. Valve for reversing samples. 1, inlet for sample 1; 2, inlet for sample 2; 3, outlet to waste vacuum; 4, outlet to mass spectrometer; 5, coil windings; 6, soft iron washer on glass valve.



McKinney et al. (1950)

We normalize to a “known” CO₂

THE REVIEW OF SCIENTIFIC INSTRUMENTS

VOLUME 21, NUMBER 8

AUGUST, 1950

Improvements in Mass Spectrometers for the Measurement of Small Differences in Isotope Abundance Ratios

C. R. MCKINNEY, J. M. MCCREA, S. EPSTEIN, H. A. ALLEN, AND H. C. UREY
Institute for Nuclear Studies, University of Chicago, Chicago, Illinois
(Received March 30, 1950)

A Nier-type mass spectrometer and its associated electronic units have been constructed for the purpose of measuring small variations in the abundances of oxygen of mass 18 and of carbon of mass 13 in carbon dioxide, and of oxygen of mass 18 in oxygen gas, to an accuracy of ± 0.01 percent of the abundance of these isotopes.

The electronic units of the necessary stability for this degree of accuracy are described. A gas feed system is described which permits fast alternate introduction of the sample of gas to be analyzed and a standard gas into the mass spectrometer. All measurements of the variation in the abundance of the oxygen and carbon isotopes are made with reference to a standard.

recorded figures are the differences in permils of the normal ratios between the sample and the standard working gas, i.e.,

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) 1000,$$

where R_{sample} and R_{standard} are the ratios of CO¹⁶O¹⁸ to CO₂¹⁶ for the unknown sample and reference gas respectively. These examples of analysis on carbon dioxide



André Hélie, my father, 1951

So...

- We need an IRMS.

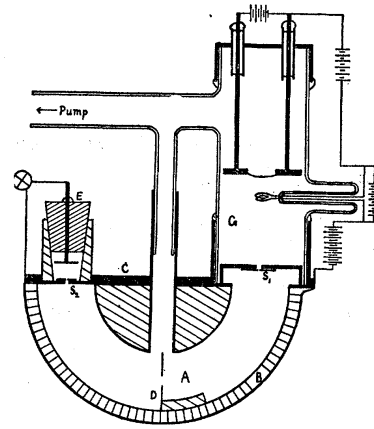
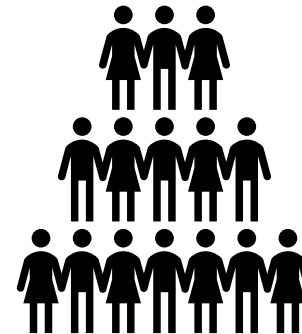


Fig. 1.

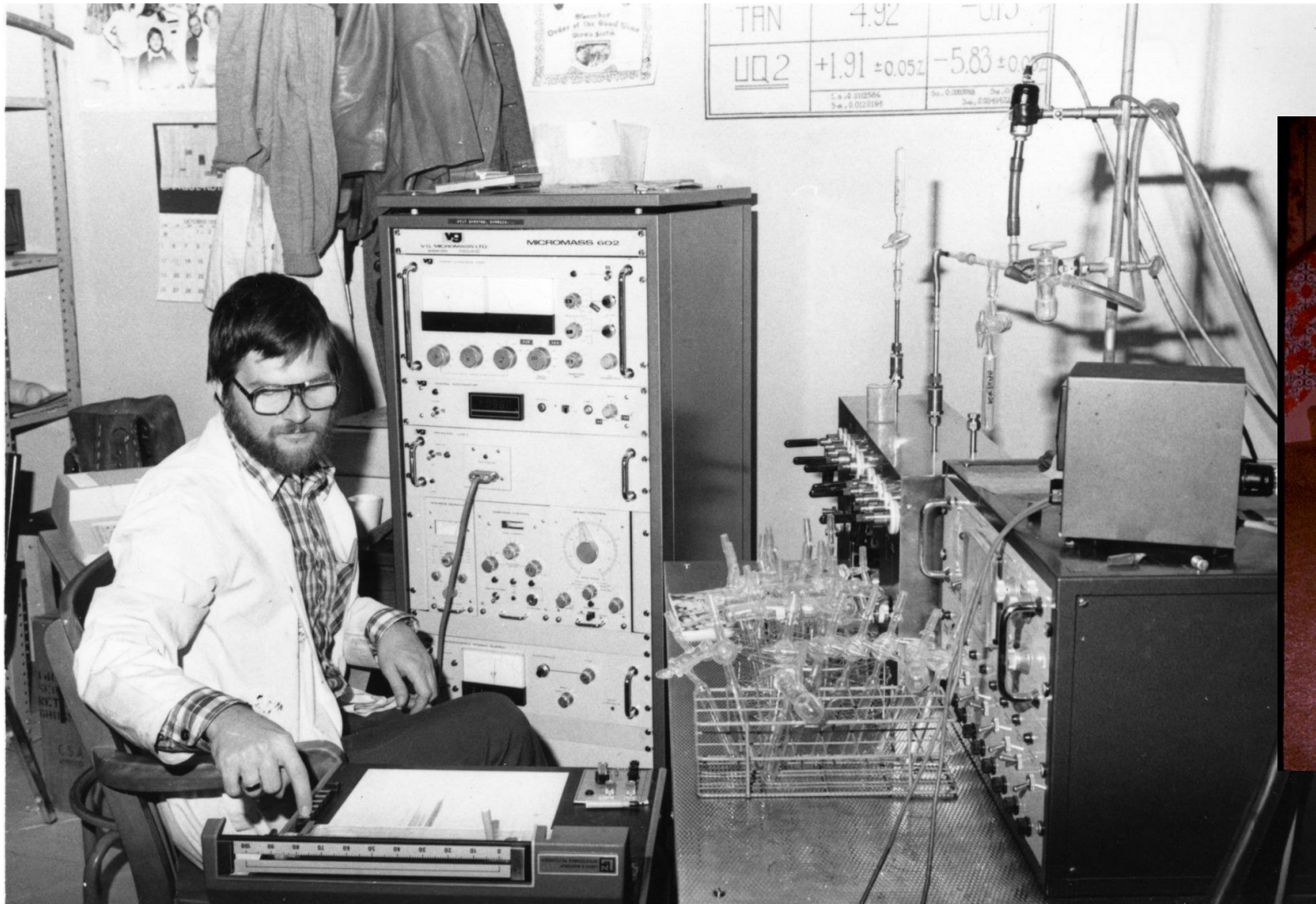
- We need gases... thus vacuumed prep lines



- We need lots of people!



Micromass VG 602 at Geotop 1970's



1978

VG Isogas PRISM II at Geotop early 1990's



1997

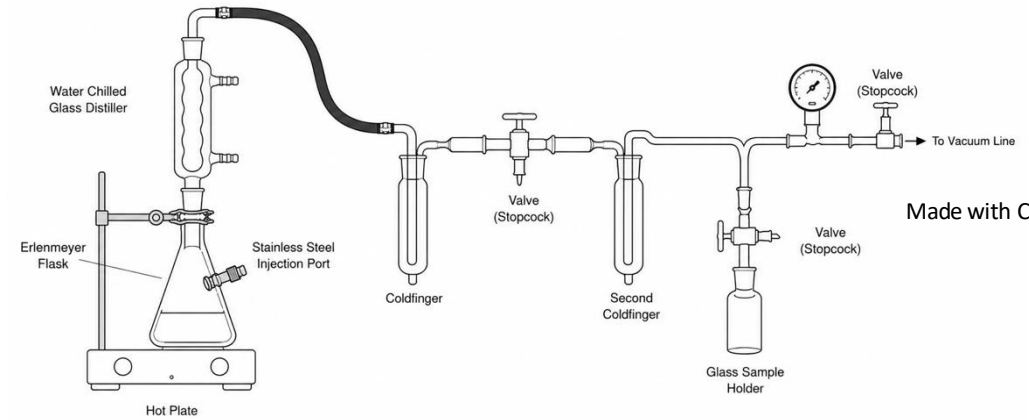
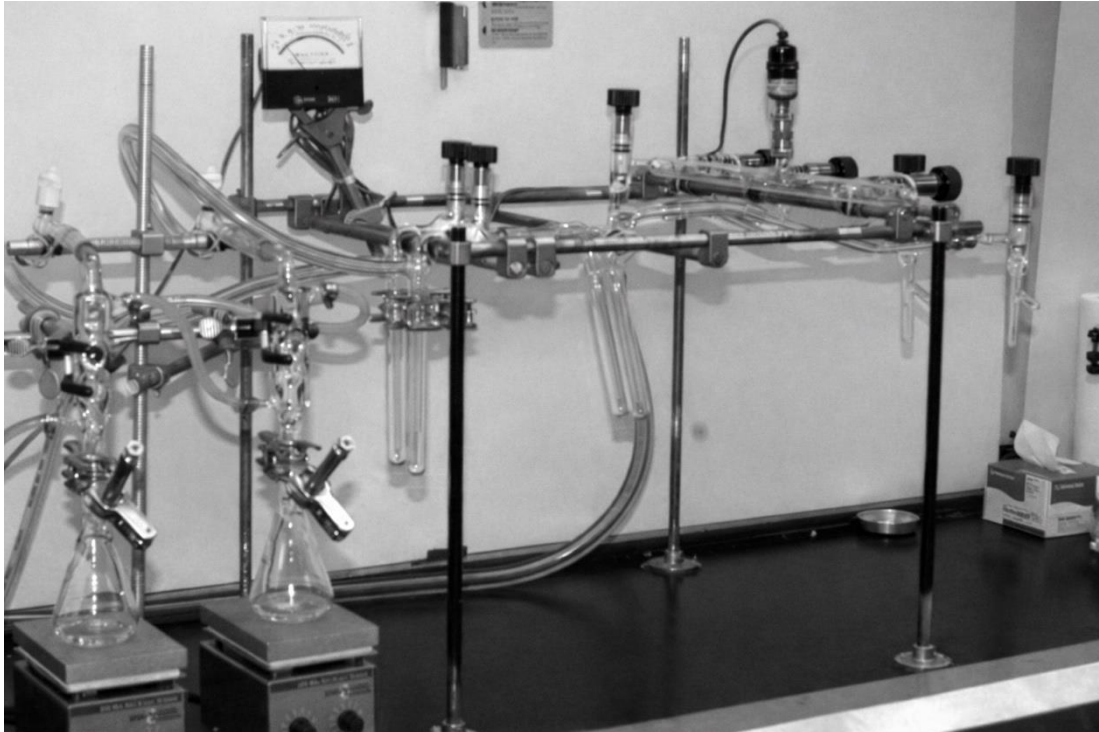
Methods of the classic period

- Offline conversion of sample to a gas
- Measurement of a raw delta value on the IRMS
- Calculations

Let's do 3 examples

- Dissolved Inorganic Carbon
- Organic Matter
- Water

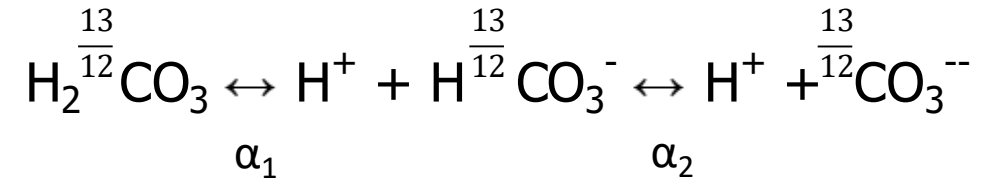
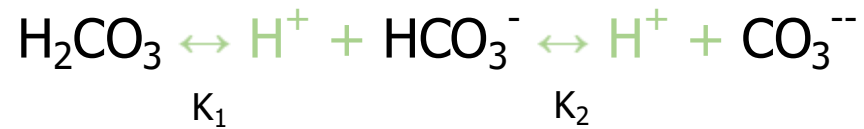
$\delta^{13}\text{C}$ of DIC



Made with ChatGPT



Dissolved inorganic carbon (DIC)



$$\text{DIC} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \quad \text{pK1} = 1.1 \cdot 10^{-4} \cdot T^2 - 0.012 \cdot T + 6.58$$

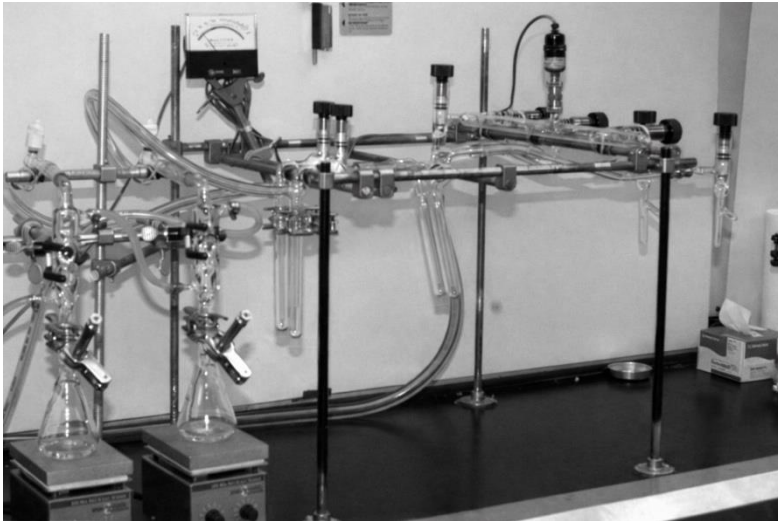
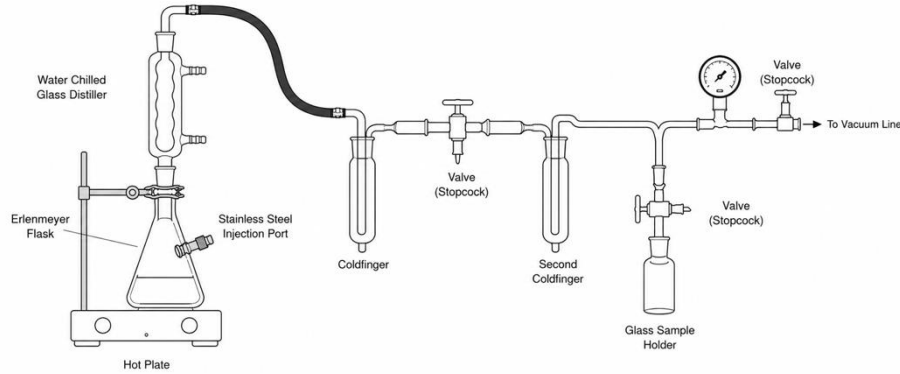
$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad \text{pK2} = 9 \cdot 10^{-5} \cdot T^2 - 0.0137 \cdot T + 10.62$$

$$\frac{\delta^{13}\text{C}_{\text{CO}_2\text{diss.}} + 10^3}{\delta^{13}\text{C}_{\text{HCO}_3^-} + 10^3} = \alpha_1 \quad 10^3 \text{Ln } \alpha_1 = 9,866 \left(\frac{10^3}{T} \right) - 24,12$$

$$\frac{\delta^{13}\text{C}_{\text{CO}_3^{2-}} + 10^3}{\delta^{13}\text{C}_{\text{HCO}_3^-} + 10^3} = \alpha_2 \quad 10^3 \text{Ln } \alpha_2 = -0,867 \left(\frac{10^3}{T} \right) + 2,52$$

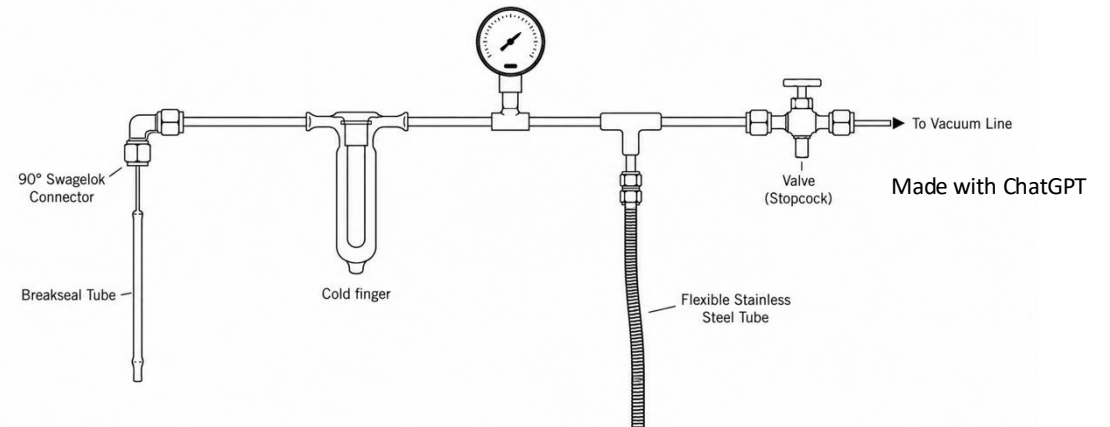
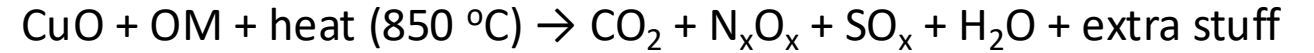
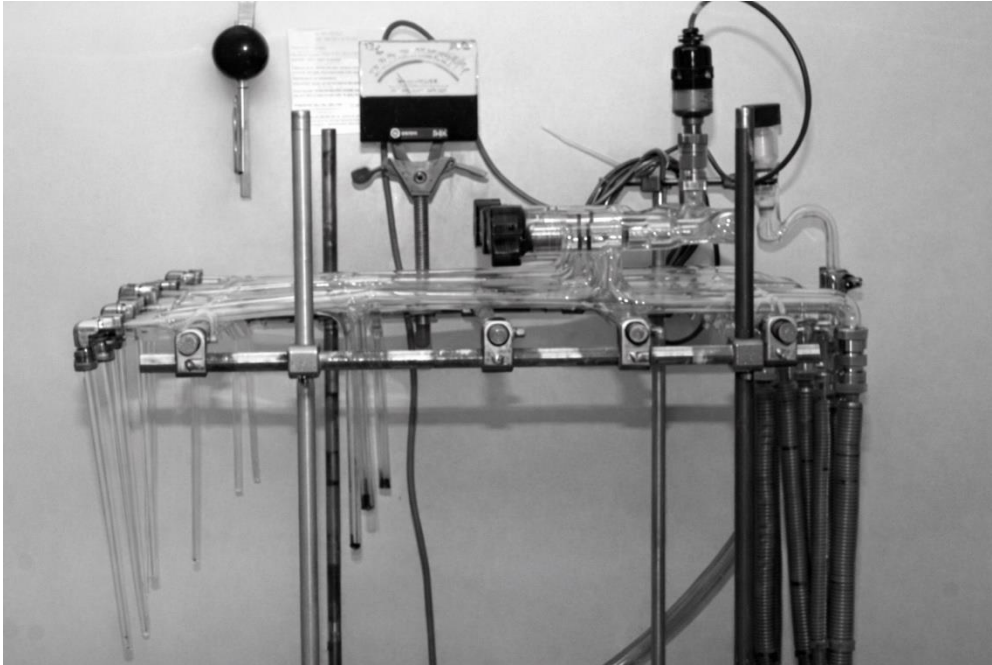
(Mook *et al.*, 1974)

$\delta^{13}\text{C}$ of DIC

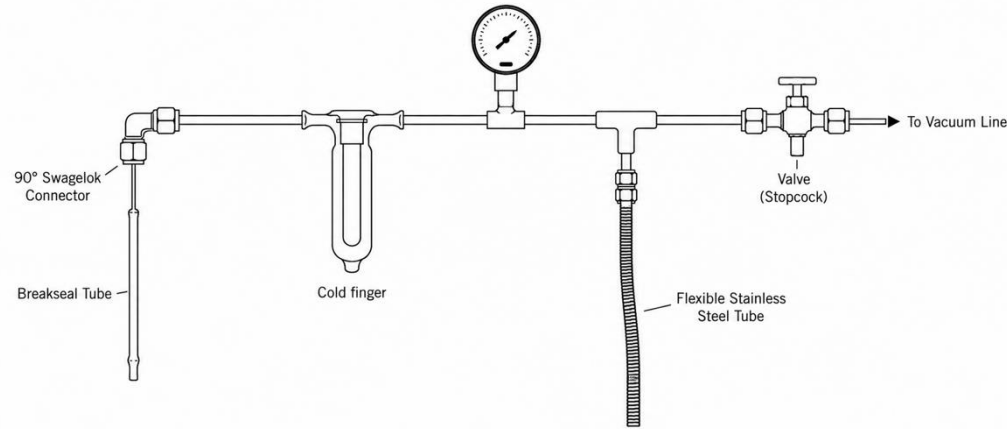


- Inject 60 cc of sample
- 10 to 15 minutes of reaction, trapping and pumping of incondensable gases
- Clean the dishes
- Vacuum the system for about 1 hour (water is sticky)
- Analyze the 2 samples on the DI-IRMS vs CO_2 gas
- About 12 sample in a day

$\delta^{13}\text{C}$ of solid organic matter

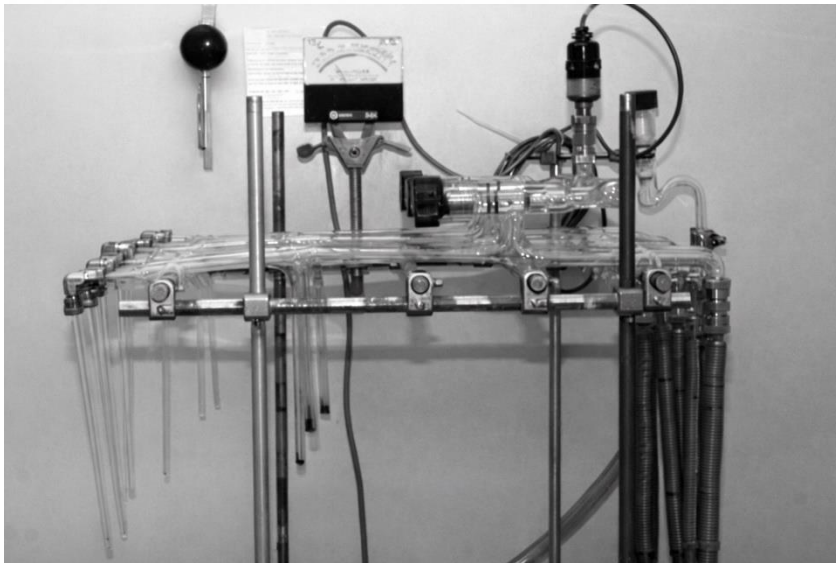


δ^{13} of solid organic matter

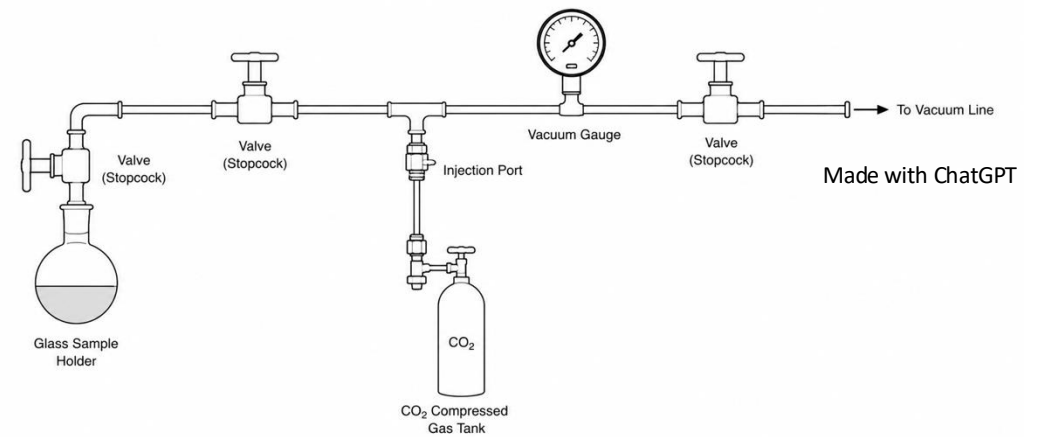
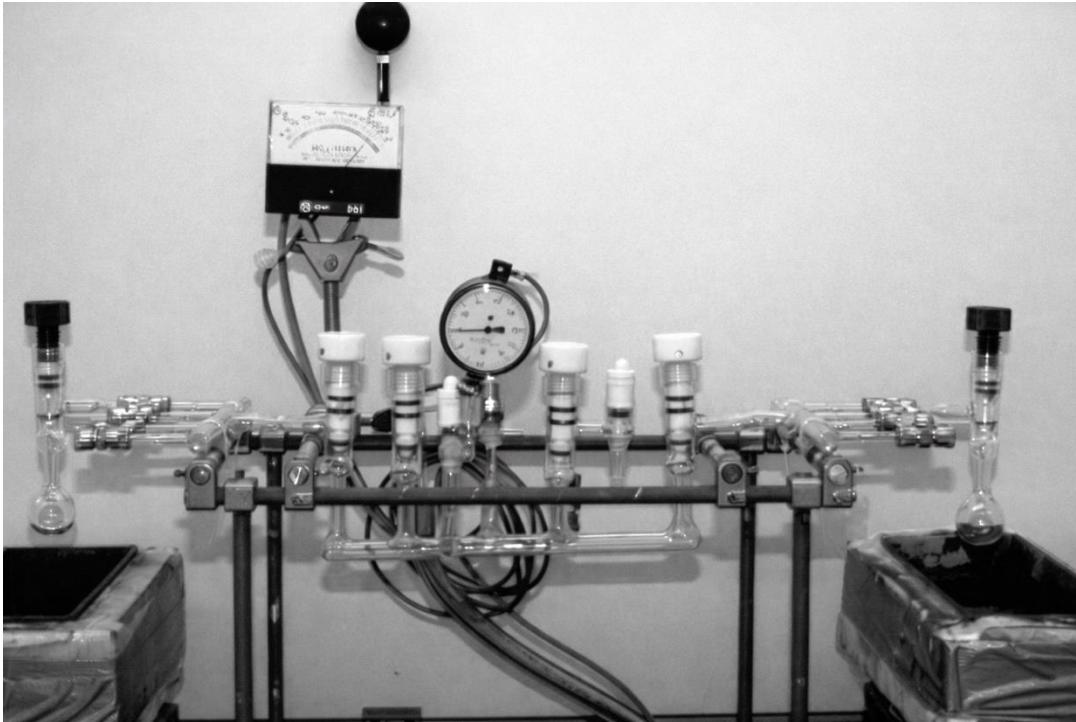


- Insert sample with CuO in a pyrex tube
- Vacuum and seal with a gas torch (n=16)
- Cook overnight in a muffle furnace (800-850 °C)
- Vacuum in flex tube and break
- 10 to 15 minutes of reaction, trapping and pumping of incondensable gases
- Vacuum line for an hour.
- Repeat for the second batch
- Analyze the 16 samples on the DI-IRMS vs CO₂ gas

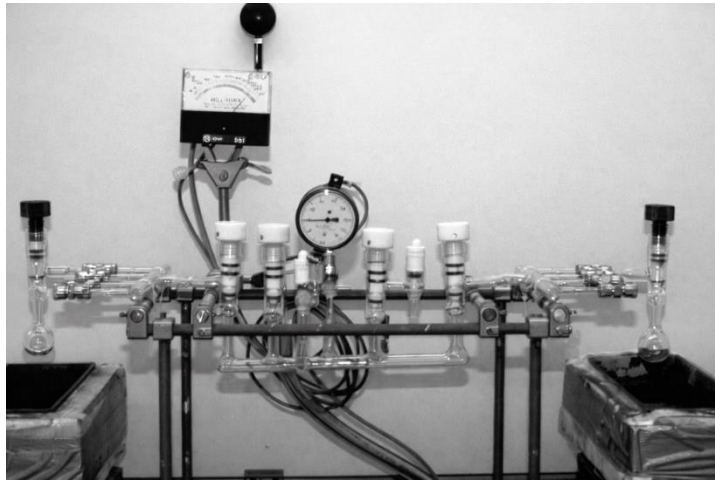
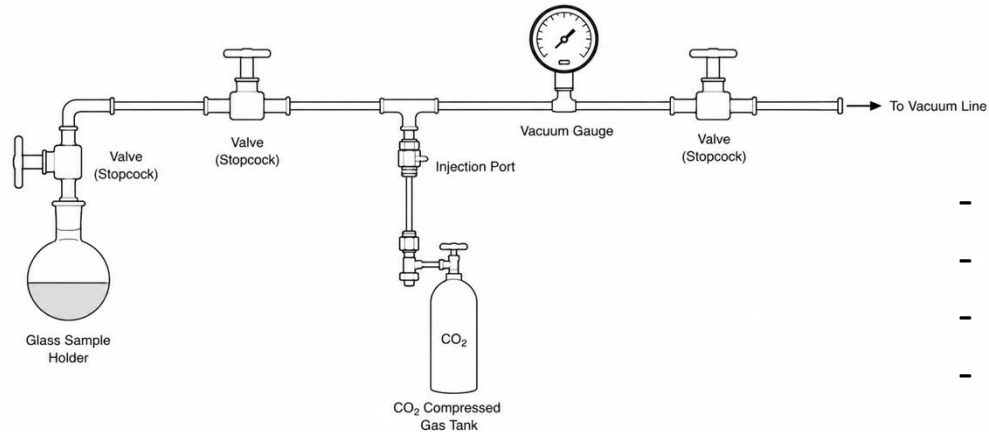
- About 16 samples every 2 days
- If you have 2 students, you can go twice as fast



$\delta^{18}\text{O}$ measurements in H_2O



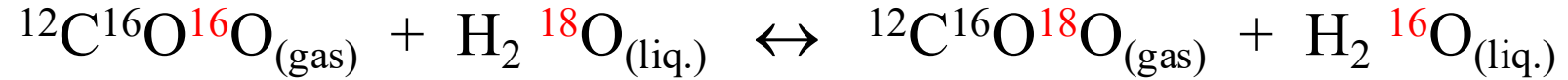
$\delta^{18}\text{O}$ measurements in H_2O



- Transfer a known amount of sample to the sample holder (3 ml)
- Freeze water sample with dry ice/alcohol bath
- Vacuum line
- Thaw
- Repeat 3 times
- Fill glass line & sample holder (frozen) with know pressure of CO_2
- Close sample holder, thaw sample and let equilibrate at $25.1\text{ }^\circ\text{C}$ overnight
- Freeze water sample, vacuum line, trap CO_2 in a sample holder with LN_2 .
- Analyze the 8 samples on the DI-IRMS vs CO_2 gas

- About 8 samples every 2 days
- If you have 2 students, you can go twice as fast

Equilibration



$$\delta_{\text{eau}} = \left[\frac{(f_{\text{CO}_2} * (\frac{\delta_m}{10^3} + 1)) + (F_{\text{H}_2\text{O}} * \frac{1}{\alpha_{\text{CO}_2-\text{H}_2\text{O}}} * (\frac{\delta_m}{10^3} + 1)) - (f_{\text{CO}_2} * (\frac{\delta_i}{10^3} + 1))}{F_{\text{H}_2\text{O}}} - 1 \right] * 10^3$$

$\alpha_{\text{CO}_2-\text{H}_2\text{O}}$ = Oxygen fractionation factor at equilibrium $\text{CO}_2-\text{H}_2\text{O}$ (thermodependent: 25.1°C; thus $\alpha = 1.0412$)

δ_m = Measured $\delta^{18}\text{O}$ of the CO_2 after equilibration

δ_i = $\delta^{18}\text{O}$ of the original CO_2 before equilibration

δ_{eau} = $\delta^{18}\text{O}$ of the water before equilibration

f_{CO_2} = Molar fraction of oxygen as CO_2 (depends on CO_2 pressure and volume of sample holder)

$F_{\text{H}_2\text{O}}$ = Molar fraction of oxygen as H_2O (depends on water volume)

Equilibration



$$\delta_{\text{eau}} = \left[\frac{f_{\text{CO}_2} * \left(\frac{\delta_m}{10^3} + 1 \right) + F_{\text{H}_2\text{O}} * \frac{1}{\alpha_{\text{CO}_2-\text{H}_2\text{O}}} * \left(\frac{\delta_m}{10^3} + 1 \right) - \left(f_{\text{CO}_2} * \left(\frac{\delta_i}{10^3} + 1 \right) \right)}{F_{\text{H}_2\text{O}}} - 1 \right] * 10^3$$

$\alpha_{\text{CO}_2-\text{H}_2\text{O}}$ = Oxygen fractionation factor at equilibrium $\text{CO}_2-\text{H}_2\text{O}$ (thermodependent: 25.1°C; thus $\alpha = 1.0412$)

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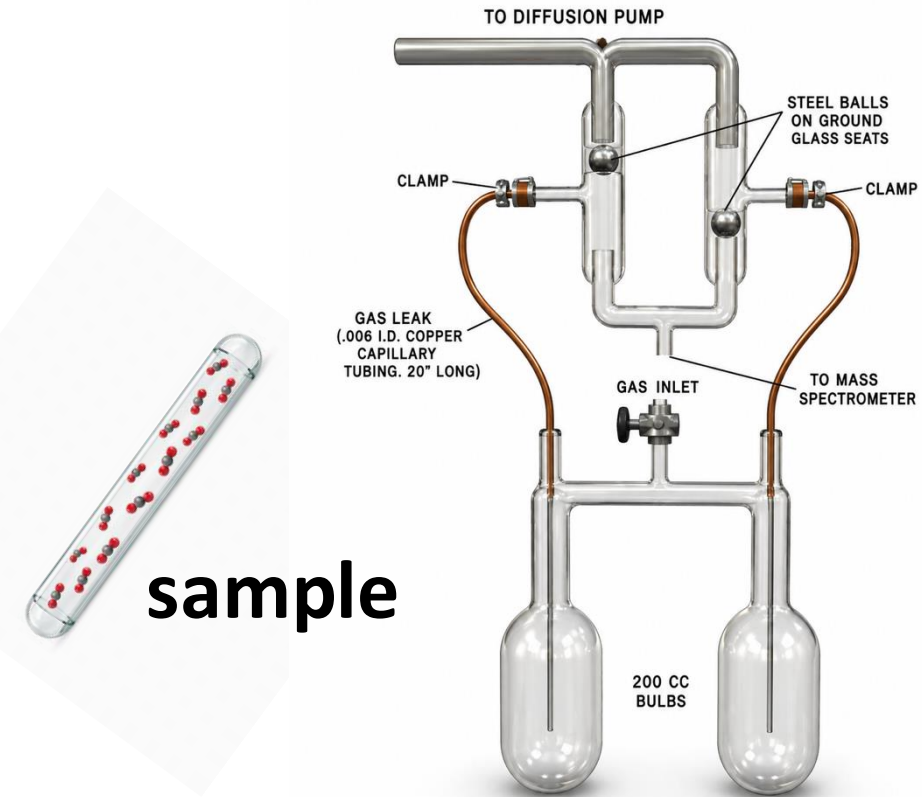
f_{CO_2} = Molar fraction of oxygen as CO_2 (depends on CO_2 pressure and volume of sample holder)

$F_{\text{H}_2\text{O}}$ = Molar fraction of oxygen as H_2O (depends on water volume)

CO₂ measurements on the IRMS

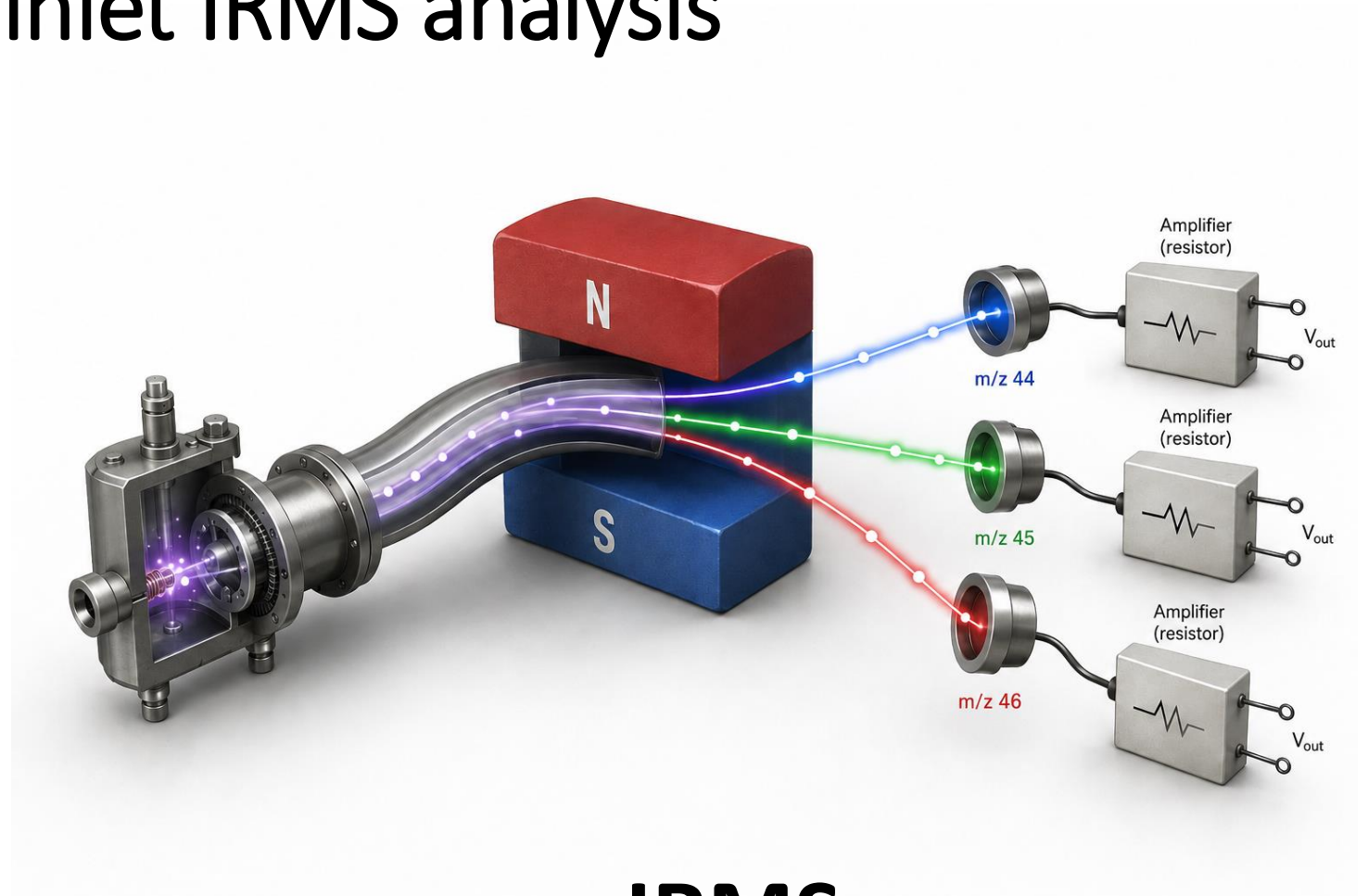


Dual inlet IRMS analysis



sample

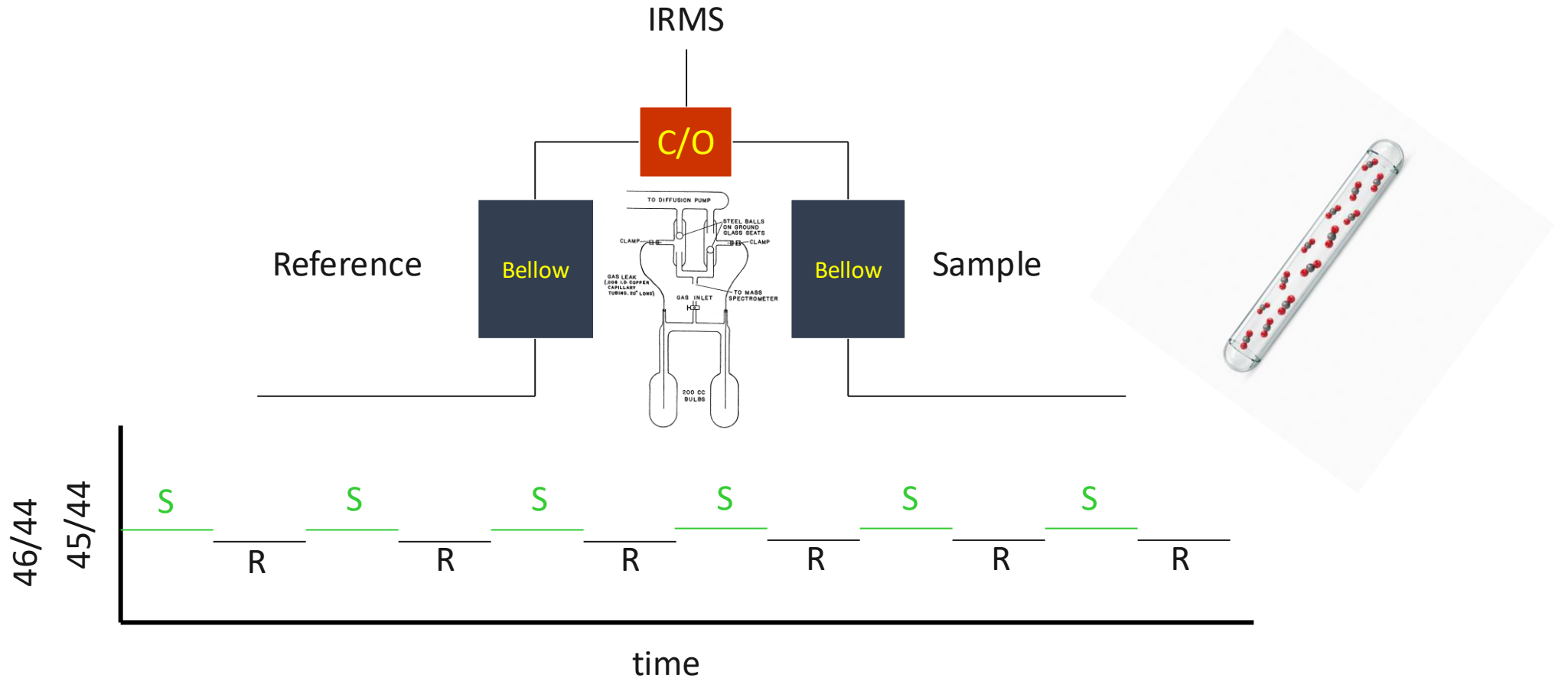
Dual inlet



IRMS

Made with ChatGPT

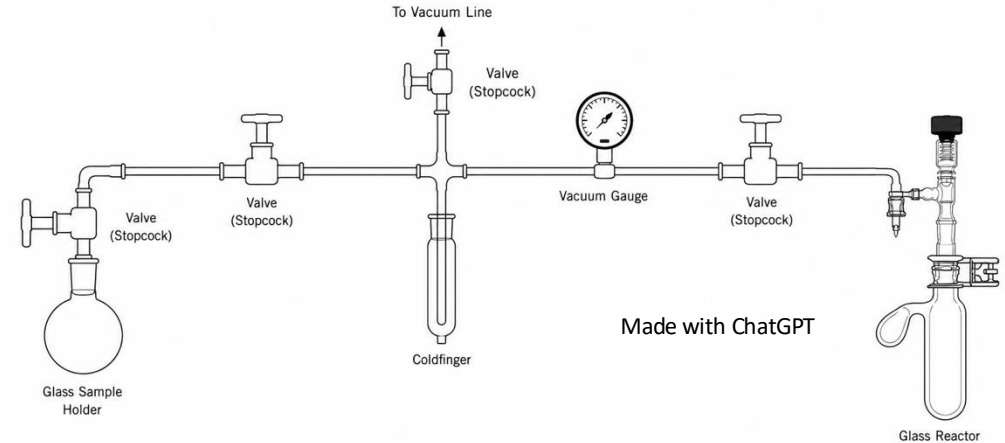
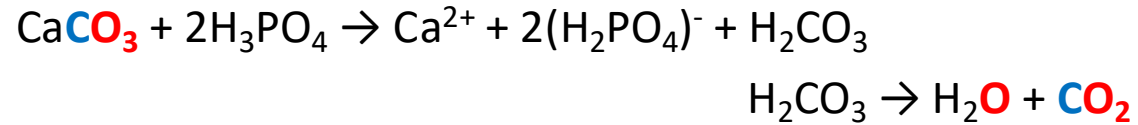
Dual inlet analysis



I need a
reference...



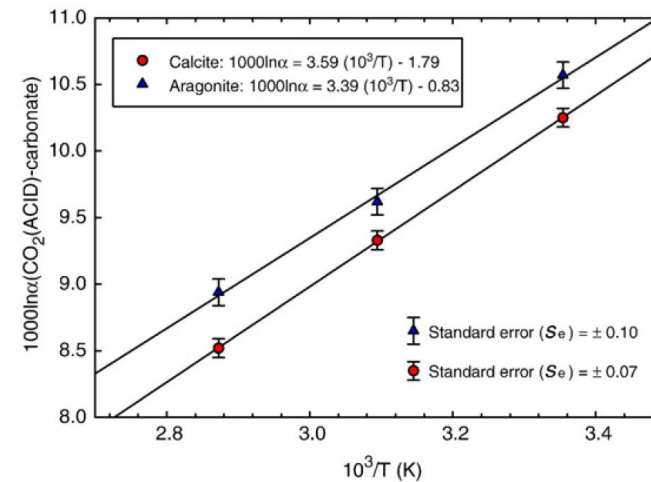
Making a reference CO₂



$$1000 \cdot \ln \alpha_{\text{CO}_2(\text{acid})-\text{Calcite}} = 3.59 \cdot (10^3/T) - 1.79$$

Where $\alpha_{\text{CO}_2(\text{acid})-\text{Calcite}}$ is the phosphoric acid fractionation factor, and T is the temperature in kelvin.

Kim et al. 2007 doi:10.1016/j.chemgeo.2007.08.005



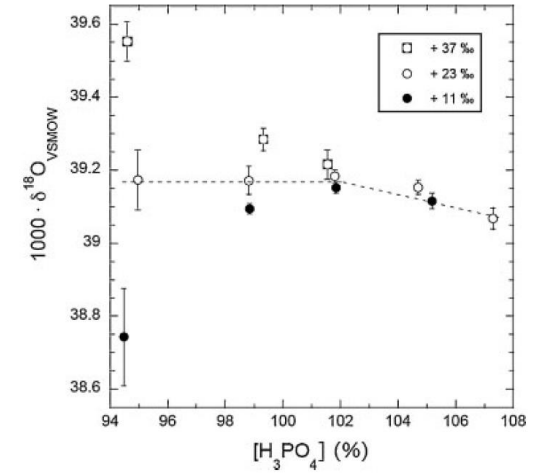
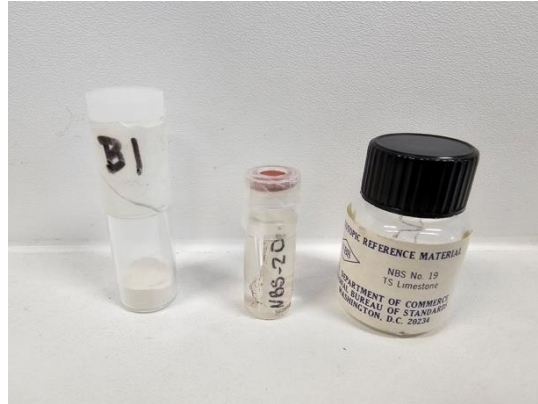
Making a reference CO₂

1950s : PDB

1950s – 1960s: PDB-1 or B1

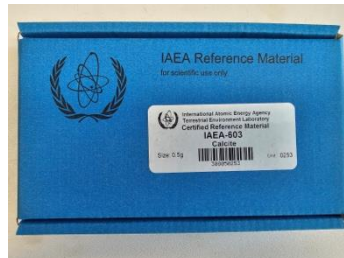
1970s: NBS20

1980s to 2000s: NBS19



Wendeberg et al 2010 DOI: 10.1002/rcm.4933

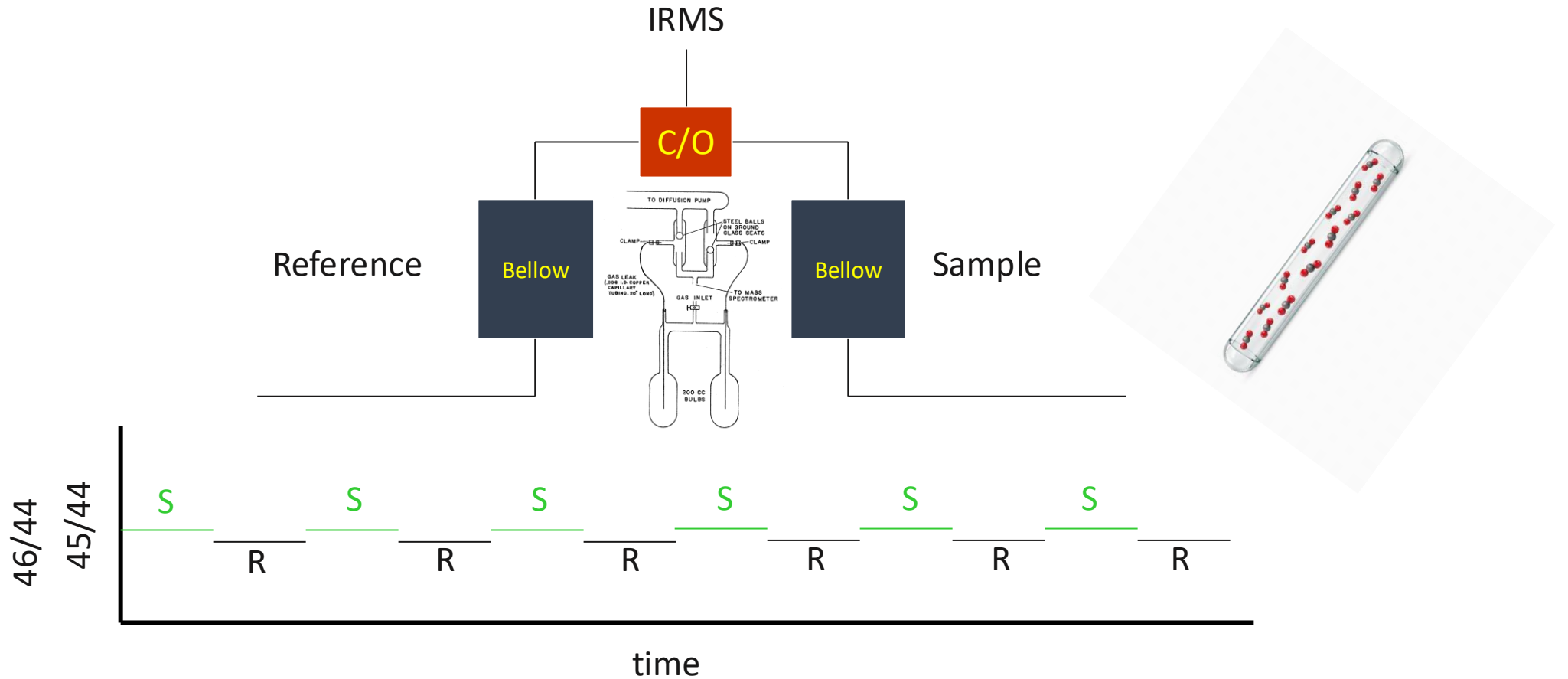
Now: IAEA-603



Making a reference CO₂



Dual inlet analysis



Houston, we have a problem!



ELSEVIER

International Journal of Mass Spectrometry 198 (2000) 45–61



Cross contamination in dual inlet isotope ratio mass spectrometers

H.A.J. Meijer, R.E.M. Neubert*, G.H. Visser

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Received 20 October 1999; accepted 29 November 1999

RAPID COMMUNICATIONS IN MASS SPECTROMETRY

Rapid Commun. Mass Spectrom. 2003; 17: 777–782

Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/rcm.906

RCM

Isotopic metrology of carbon dioxide. II. Effects of ion source materials, conductance, emission, and accelerating voltage on dual-inlet cross contamination^{†,‡,§}

R. Michael Verkouteren^{1*}, Sergey Assonov², Donna B. Klinedinst¹ and Willi A. Brand³

¹Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland, USA

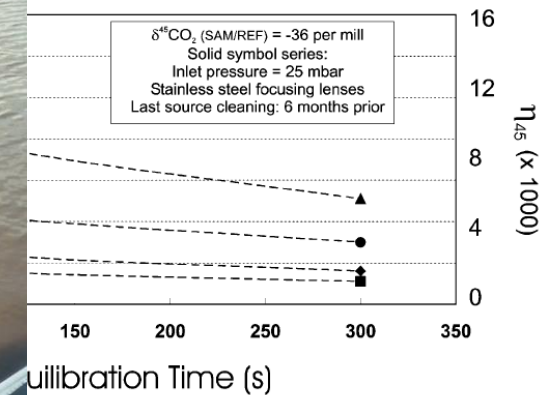
²Max-Planck-Institute for Chemistry, Division of Atmospheric Chemistry, Mainz, Germany

³Max-Planck-Institute for Biogeochemistry, Stable Isotope Laboratory, Jena, Germany (formerly at Finnigan MAT GmbH, Bremen, Germany)

Received 9 September 2002; Revised 25 November 2002; Accepted 25 November 2002

- The further apart the 2 values are, the more the measurement is affected.

- This is due to **cross contamination** in the sample inlet valve of DI-IRMS. Referred to as **scale**



^{17}O correction calculations

$$^{13}\text{R} = ^{45}\text{R} - 2(^{17}\text{R})$$

$$^{17}\text{R} = \text{K} * (^{18}\text{R})^\lambda$$

$$\lambda = 0.528 \quad (\text{Assonov \& Brezina})$$

$$\text{K} = 0.01022461 \quad (\text{Brand et al.})$$

$$\text{R}(^{13}\text{C}/^{12}\text{C}, \text{VPDB}) = 0.011113 \pm 0.000003$$

$$\text{R}(^{17}\text{O}/^{16}\text{O}, \text{VPDB-CO}_2) = 0.0003$$

$$\text{R}(^{18}\text{O}/^{16}\text{O}, \text{VPDB-CO}_2) = 0.0020$$

IUPAC "CIAAW 20 December 2024 News," <https://www.iupac-geochem.org/>



Laboratory Results
Set A

Lab#4	Lab#5	Lab#6	Lab#7	Average(std dev)
-3.79	-3.76	-3.69	-3.65	-3.76(0.04)
-41.52	-41.59	-41.48	-41.30	-41.57(0.09)
-10.45	-10.48	-10.43	-10.33	-10.44(0.03)

Laboratory Results
Set C

Lab#4	Lab#5	Lab#6	Lab#7	Average(std dev)
-3.75	-3.73	-3.66	-3.62	-3.73(0.04)
-41.62	-41.69	-41.58	-41.40	-41.67(0.09)
-10.48	-10.52	-10.46	-10.37	-10.48(0.03)

NIST Special Publication 260-149 2004 Edition Value Assignment and Uncertainty Estimation of Selected Light Stable Isotope Reference Materials: RMs 8543-8545, RMs 8562-8564, and RM 8566 R. Michael Verkouteren Donna B. Klinedinst

How certain are you?

$\delta^{13}\text{C}$ measurement	$\delta^{18}\text{O}$ measurement
ref gas acid reaction	ref gas acid reaction
Stdev of ref gas measurement	Stdev of ref gas measurement
Stdev of sample measurement	Stdev of sample measurement
DI-cross-contamination	DI-cross-contamination
^{17}O correction	^{17}O correction
	Acid "dryness"
	Temperature of acid reaction for ref
	Volume of sample holder
	Volume of water
	Pressure of CO_2 in equilibration line
	Original $\delta^{13}\text{C}$ of CO_2
	Temperature of CO_2 - H_2O equilibration

How certain are you?

$\delta^{13}\text{C}$ measurement	$\delta^{18}\text{O}$ measurement
ref gas acid reaction	ref gas acid reaction
Stdev of ref gas measurement	Stdev of ref gas measurement
Stdev of sample measurement	Stdev of sample measurement
DI-cross-contamination	DI-cross-contamination
^{17}O correction	^{17}O correction
	Acid "dryness"
	Temperature of acid reaction for ref
	Volume of sample holder
	Volume of water
	Pressure of CO_2 in equilibration line
	Original $\delta^{13}\text{C}$ of CO_2
	Temperature of CO_2 - H_2O equilibration

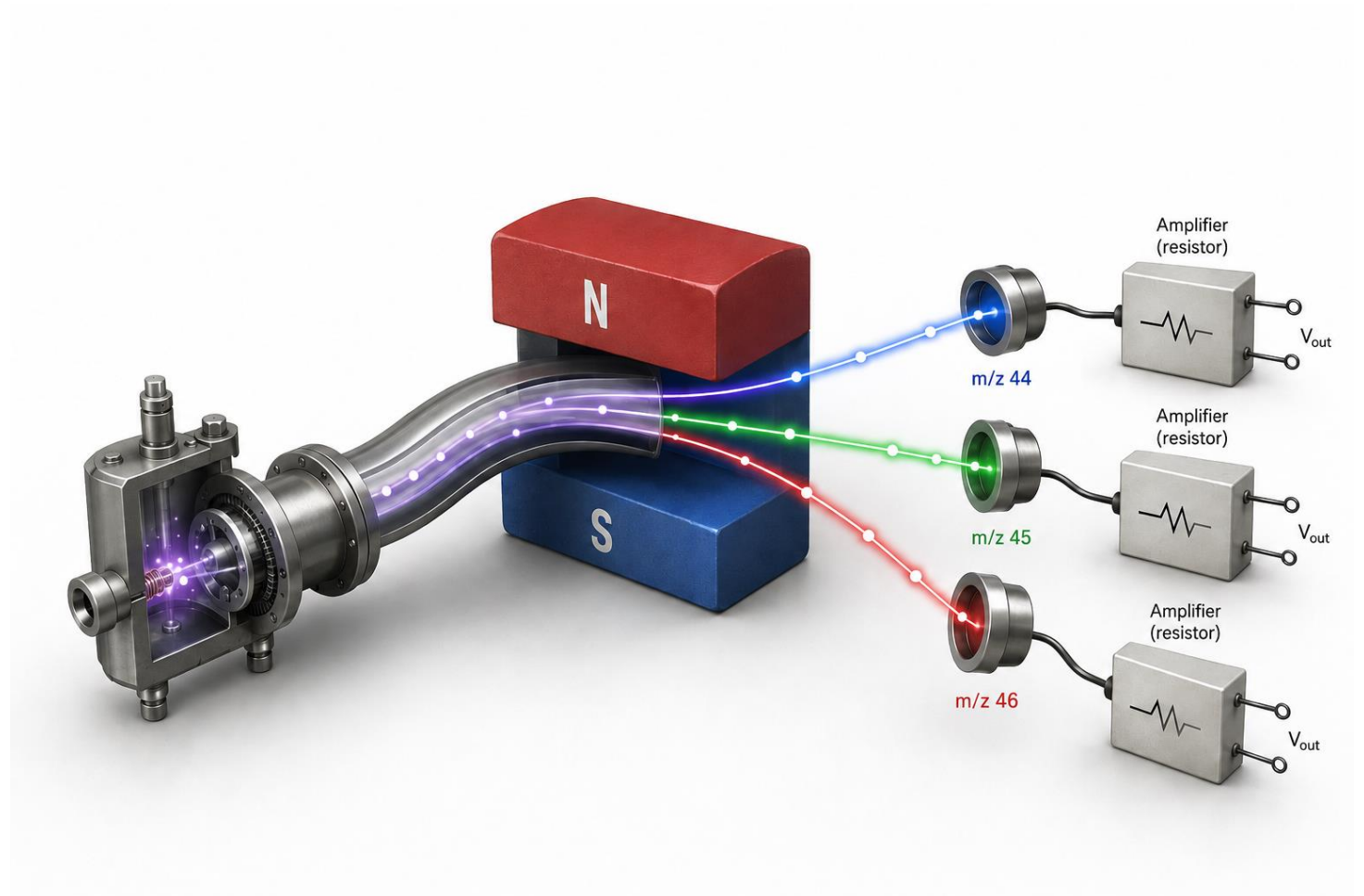
HUMAN ERROR IN MANIPULATION

The “more is better” era

1990's: Continuous Flow IRMS

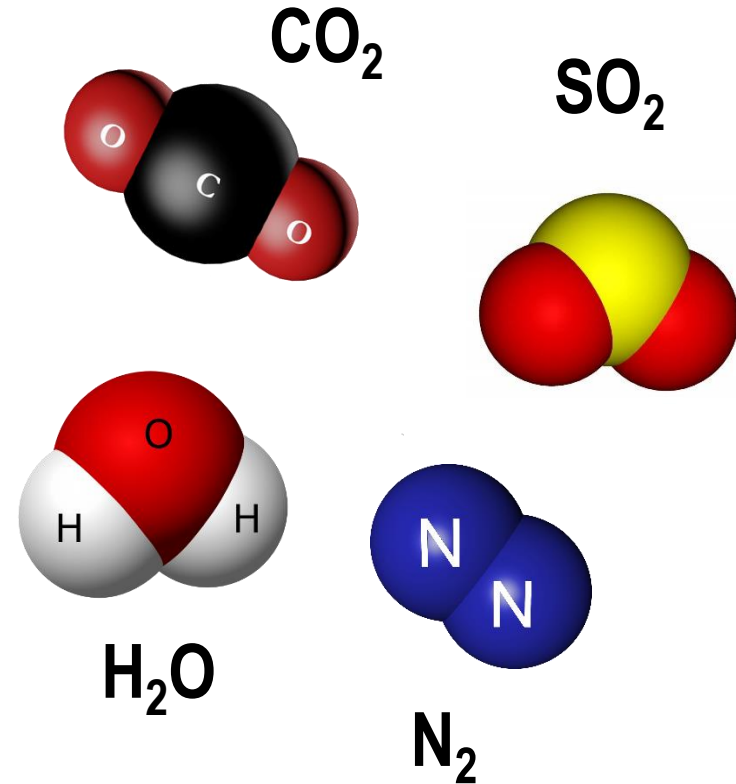
2010's: Laser Absorption Spectroscopy

Continuous Flow IRMS

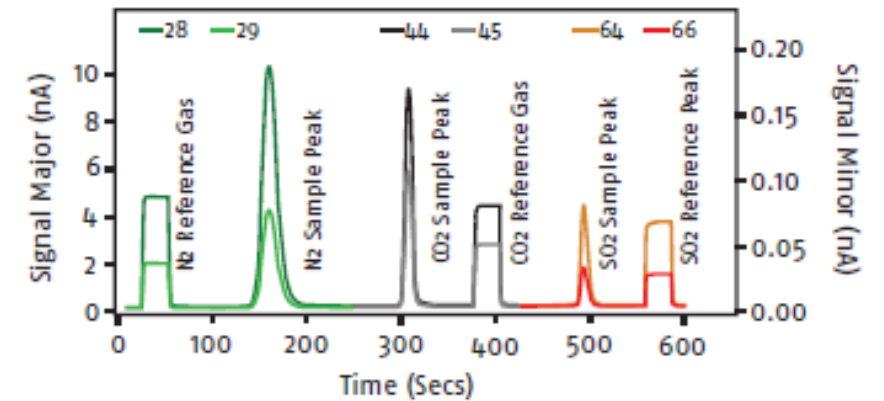
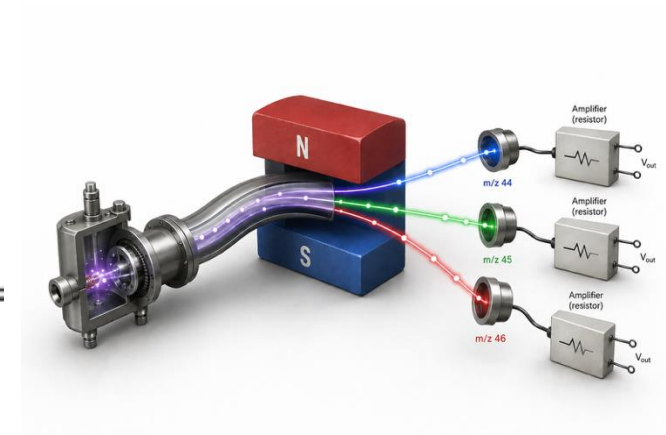
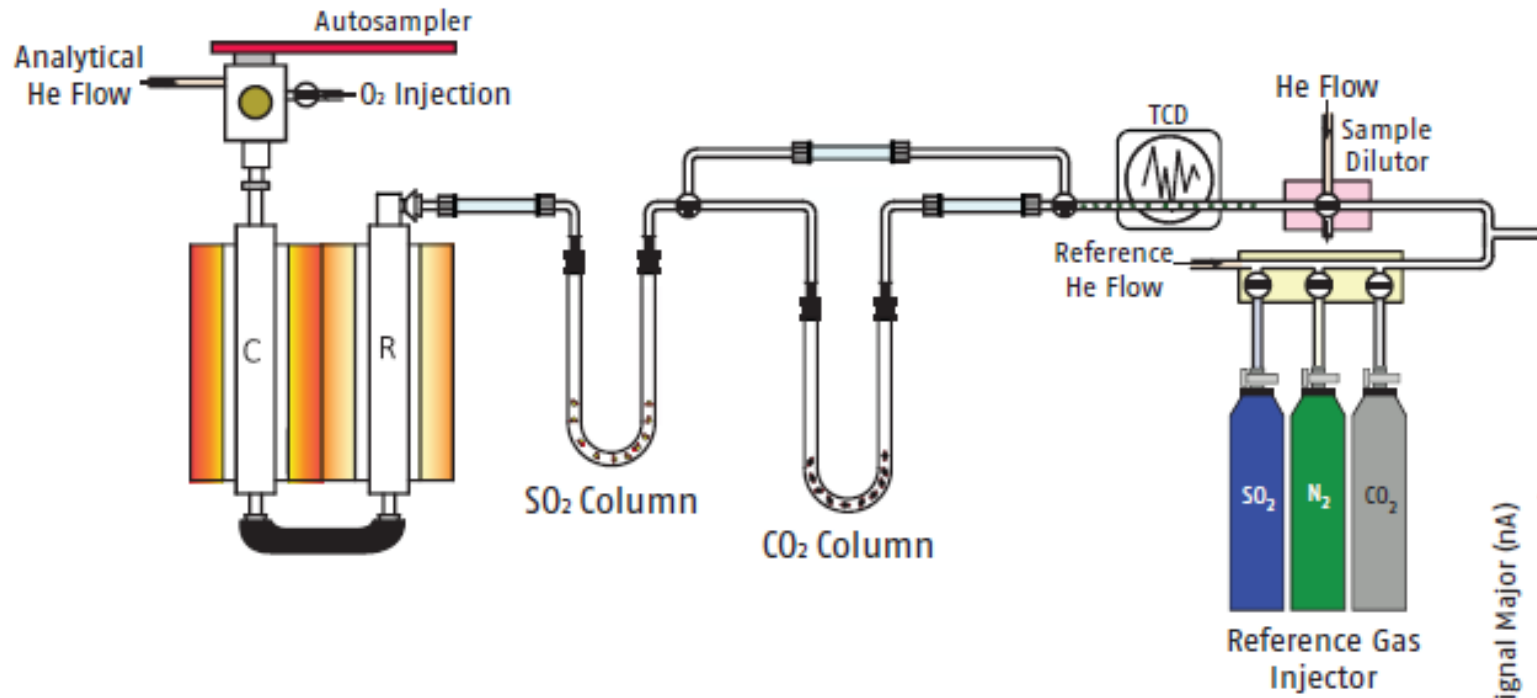


$\delta^{13}\text{C}$, $\delta^{15}\text{N}$ & $\delta^{34}\text{S}$ of OM

CHNOS

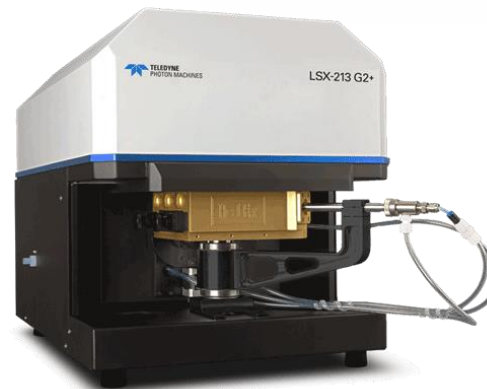
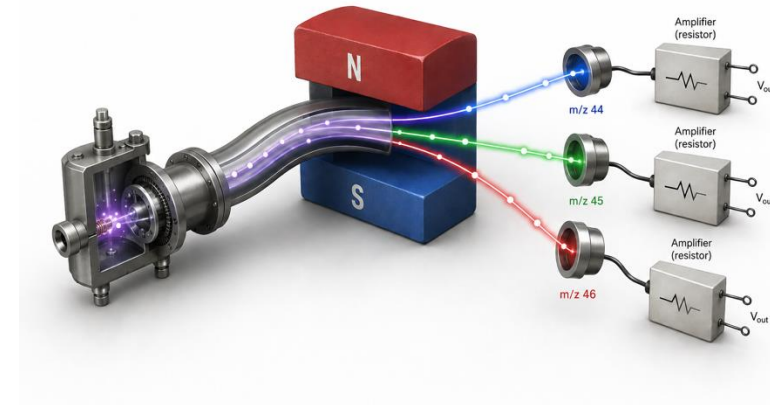


$\delta^{13}\text{C}$, $\delta^{15}\text{N}$ & $\delta^{34}\text{S}$ of SPM



Continuous Flow IRMS

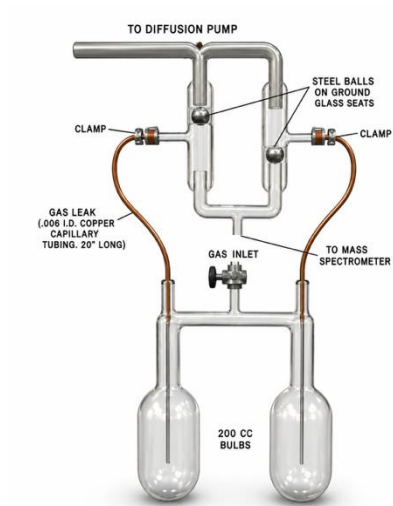
- Elemental analyzer
- Pyrolysis EA
- Gas Chromatograph
- Liquid Chromatograph
- Gas bench/MultiFlow/
- Pre-con/TraceGas/etc
- Laser Ablation



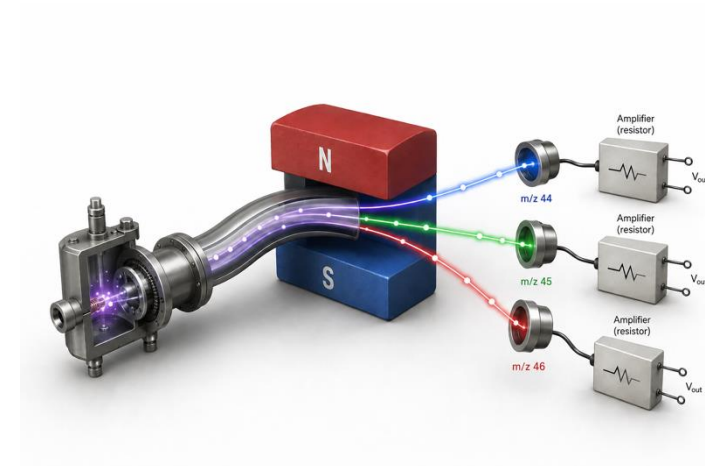
Automated dual inlet IRMS analysis



**Auto-sampler
With prep system**



Dual inlet

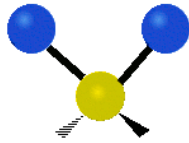


IRMS

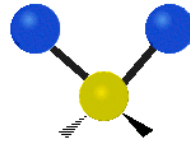
Made with ChatGPT

Laser absorption spectroscopy

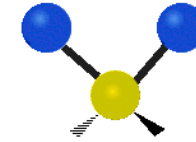
It's all about the good vibrations!



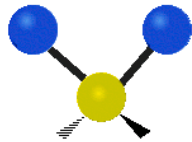
Symmetrical stretching



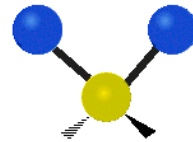
Antisymmetrical stretching



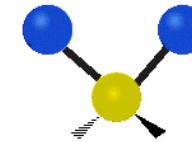
Scissoring



Rocking



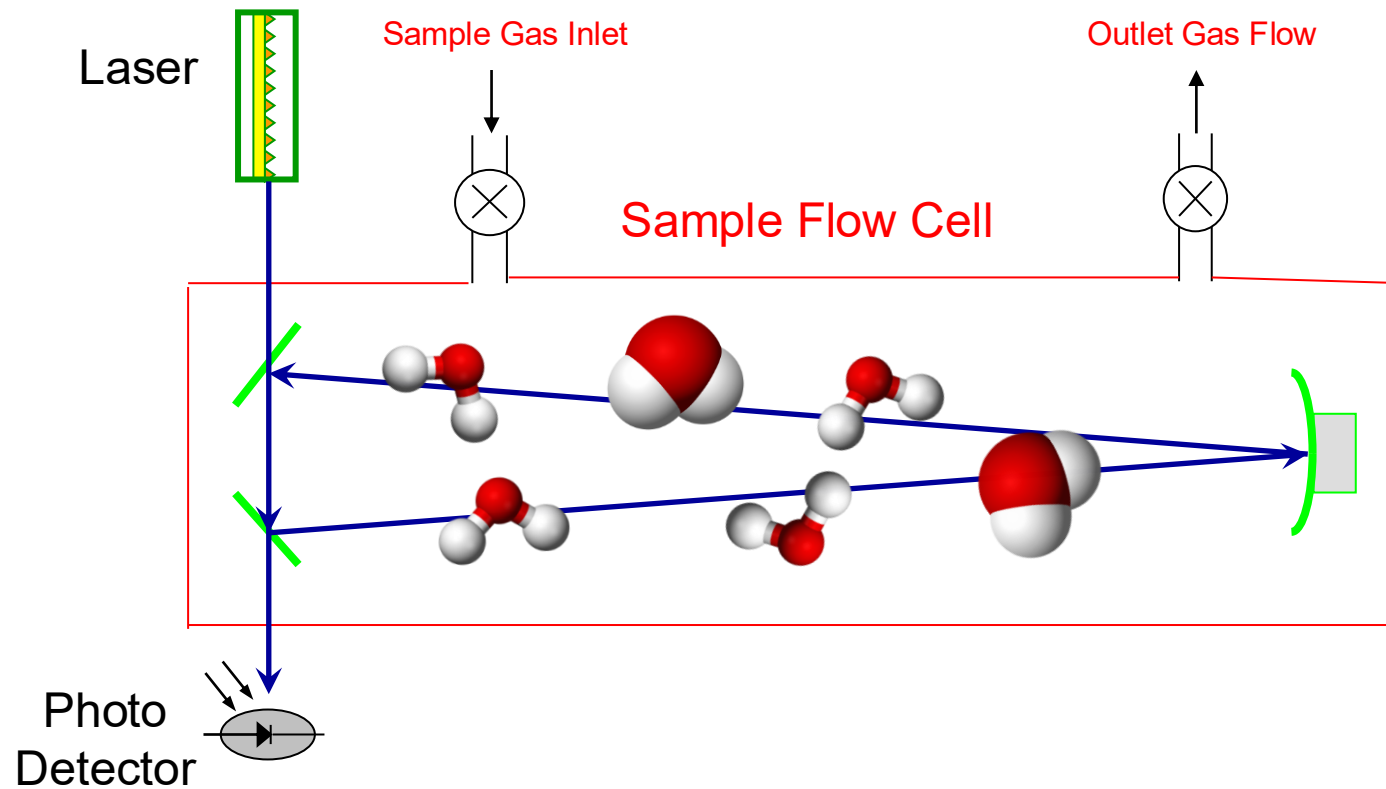
Wagging



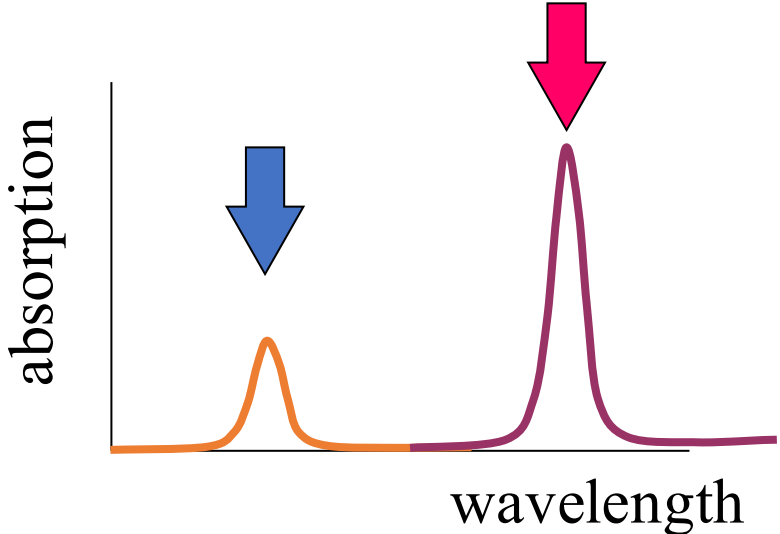
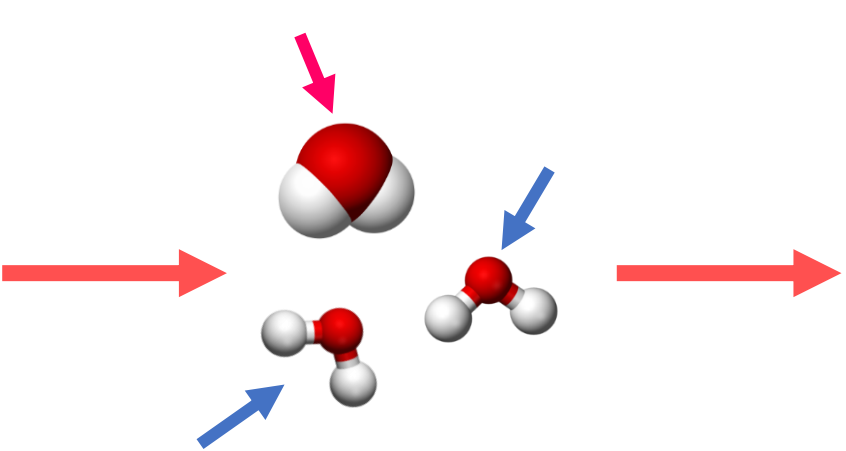
Twisting



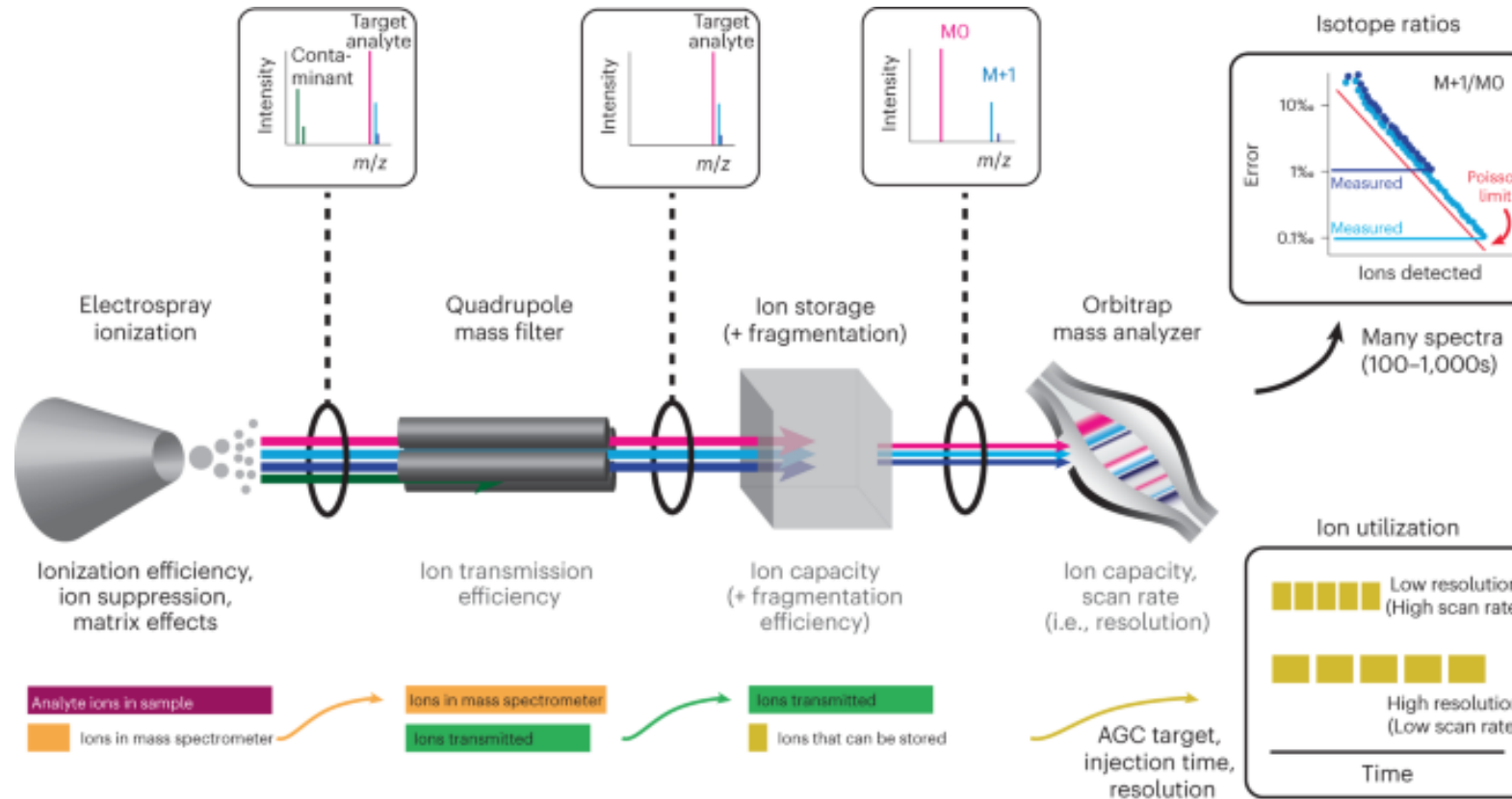
absorption spectroscopy



Laser absorption spectroscopy



Orbitrap



Kantnerová *et al.* (2024). <https://doi.org/10.1038/s41596-024-00981-5>

Identical treatment principle

RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. 2001; **15**: 501–519

RCM

REVIEW

Referencing strategies and techniques in stable isotope ratio analysis

Roland A. Werner and Willi A. Brand*

Max-Planck-Institute for Biogeochemistry, P.O. Box 100164, 07701 Jena, Germany

Received 5 December 2000; Revised 6 December 2000; Accepted 23 December 2000

SPONSOR REFEREE: T. B. Coplen, US Geological Survey, 431 National Center, Reston, VA 20192, USA

Stable isotope ratios are reported in the literature in terms of a deviation from an international standard (δ -values). The referencing procedures, however, differ from instrument to instrument and are not consistent between measurement facilities. This paper reviews an attempt to unify the strategy for referencing isotopic measurements. In particular, emphasis is given to the importance of **identical treatment of sample and reference material ('IT principle')**, which should guide all isotope ratio determinations and evaluations. The implementation of the principle in our laboratory, the monitoring of our measurement quality, the status of the international scales and reference materials and necessary correction procedures are discussed. Copyright © 2001 John Wiley & Sons, Ltd.

CF-IRMS & Auto-DI-IRMS

- Proper standards or RMs
- Proper isotope delta scale
- Identical treatment

$\delta^{13}\text{C}$ measurement	$\delta^{18}\text{O}$ measurement
ref gas acid reaction	ref gas acid reaction
Stdev of ref gas measurement	Stdev of ref gas measurement
Stdev of sample measurement	Stdev of sample measurement
DI-cross-contamination	DI-cross-contamination
^{17}O correction	^{17}O correction
	reaction for ref
	holder
	equilibration line
	O_2
	$\text{O}_2\text{-H}_2\text{O}$ equilibration



Uncertainty components

- Stated uncertainty of your standards or RMs
- Replicate measurement of everything



Everything was better in
the good old days!



Everything is so much
better now!



The Journey from Physical Matrix to Pure Data

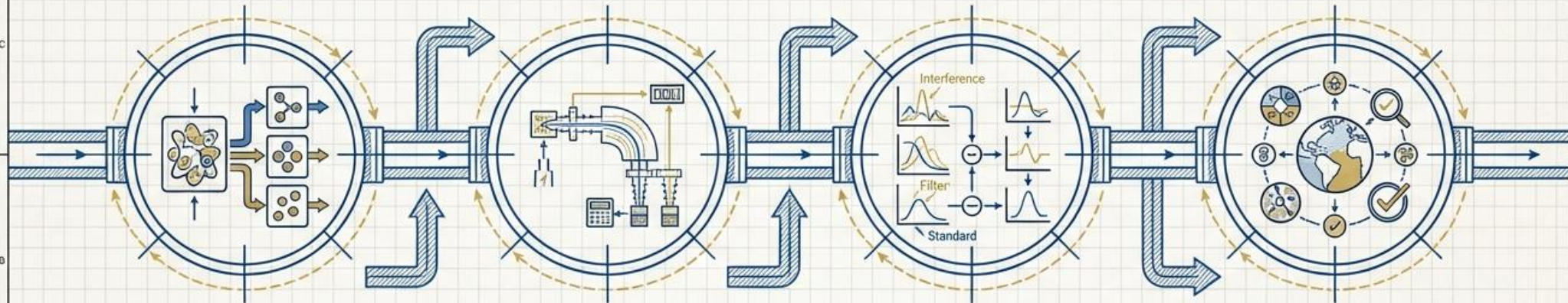
"Isotope analysis is not a single act of measurement. It is a sequence of highly calibrated transformations."

**Node 1:
Matrix Deconstruction**

**Node 2:
Physical Measurement**

**Node 3:
Metrological Anchoring
& Correction**

**Node 4:
Geochemical Insight**



**Node 1:
Matrix
Deconstruction**
(Isolating the target gas)

**Node 2:
Physical
Measurement**
(Counting the isotopic ratios)

**Node 3:
Metrological
Anchoring & Correction**
(Subtracting interference)

**Node 4:
Geochemical
Insight**
(Authenticating reality)

			NAME	REV.
			TITLE	SCALE
				1:1
REVIS.	SCALE	DESIGN		

My publications in NotebookLM

Comparing the Modern Measurement Arsenal

Technology	Dual-Inlet IRMS	Continuous-Flow IRMS	Cavity Ring-Down Spectroscopy (CRDS)
Principle of Operation	Alternating viscous flow of sample and reference gas into the source	Sample carried by a continuous flow of inert helium gas	Laser absorption measured by the decay time of a light pulse in a mirrored cavity
Precision	Highest precision, theoretical limits achieved	High precision, slightly lower than dual-inlet	Excellent precision, rapidly approaching traditional IRMS
Throughput	Low, highly time-intensive	High, automated batch processing	Very high, continuous field deployment possible
Ideal Use-Case	Ultimate reference material calibration and ultra-trace analysis	High-volume geological and ecological sample batches	Real-time atmospheric monitoring and liquid water analysis

NotebookLM



Centre de Recherche sur la
Dynamique du Système Terre

UQAM

Département des sciences
de la Terre et de l'atmosphère

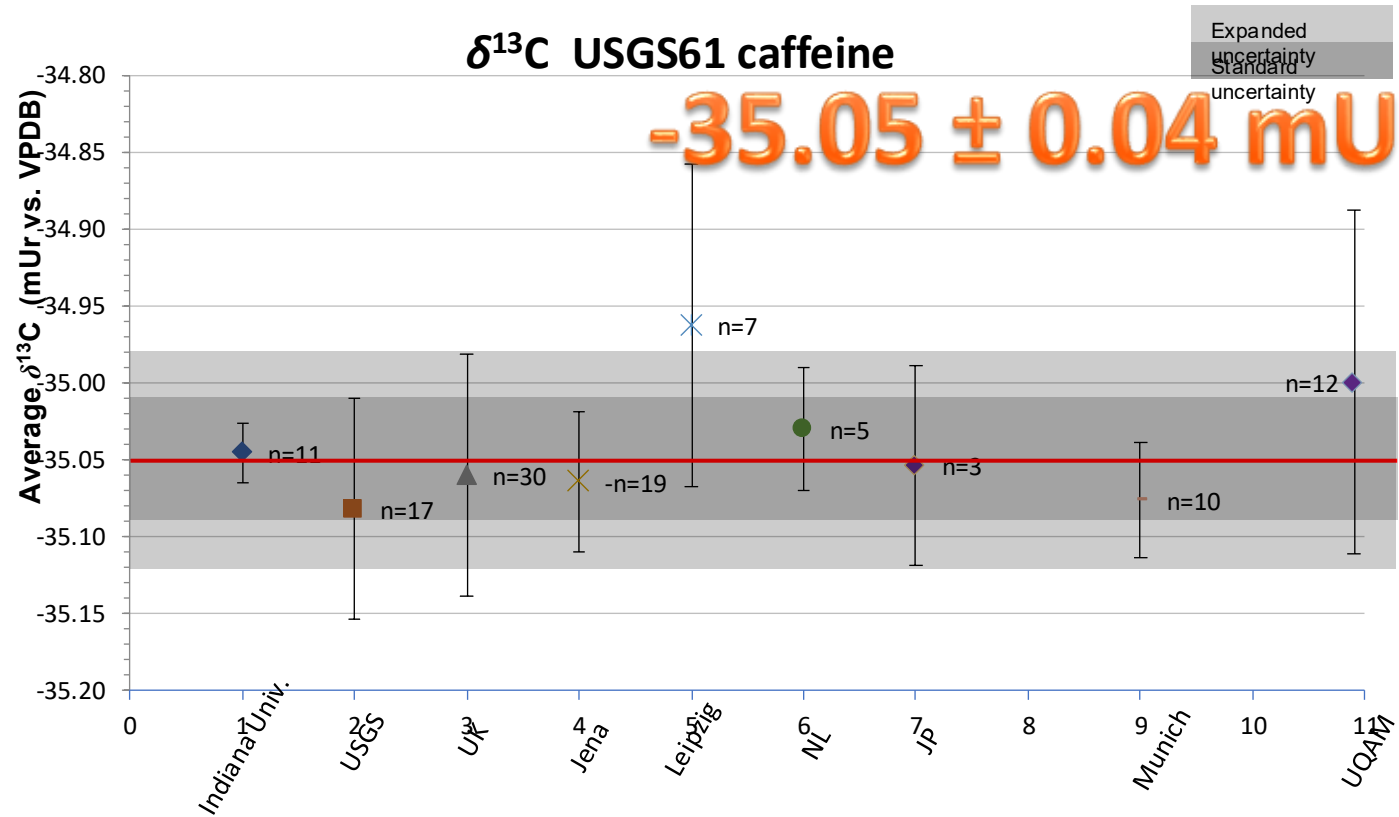
$\delta^{18}\text{O}$ of water

	Method	Typical uncertainty
A	Off-line equilibration	??? But certainly higher than 0.3 ‰
B	Pyrolysis	0.3 ‰
C	Automated DI-equilibration	0.05 to 0.1 ‰
D	LAS	0.1 to 0.2 ‰

$\delta^2\text{H}$ of water

	Method	Typical uncertainty
A	Off-line reduction on U	???
B	Pyrolysis	0.3 to 0.5 ‰
C	Automated DI-equilibration	1.5 to 2 ‰
D	LAS	0.2 to 0.5 ‰

DI vs CF



analytical
chemistry

Article
pubs.acs.org/ac

Organic Reference Materials for Hydrogen, Carbon, and Nitrogen Stable Isotope-Ratio Measurements: Caffeines, *n*-Alkanes, Fatty Acid Methyl Esters, Glycines, L-Valines, Polyethylenes, and Oils

Arndt Schimmelmann,^{*,†} Haiping Qi,[‡] Tyler B. Coplen,[‡] Willi A. Brand,[§] Jon Fong,[†] Wolfram Meier-Augenstein,^{||} Helen F. Kemp,^{||} Blaza Toman,[⊥] Annika Ackermann,[#] Sergey Assonov,[⊗] Anita T. Aerts-Bijma,[○] Ramona Brejcha,[△] Yoshito Chikaraishi,[×] Tamim Darwish,⁺ Martin Elsner,[△] Matthias Gehre,[⊞] Heike Geilmann,[§] Manfred Gröning,[⊗] Jean-François Hélie,[§] Sara Herrero-Martín,[⊞] Harro A. J. Meijer,[○] Peter E. Sauer,[†] Alex L. Sessions,[▽] and Roland A. Werner[#]

DOI: 10.1021/acs.analchem.5b04392



Centre de Recherche sur la
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Département des sciences
de la Terre et de l'atmosphère

REFERENCE SHEET

CERTIFIED REFERENCE MATERIAL

IAEA-603 (calcite)

Stable Isotope Reference Material for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$

Assigned $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for the stable isotopic composition of IAEA-603
expressed in per mille (‰) on the respective VPDB scales [1]

	Assigned value ⁽¹⁾	Combined standard uncertainty ⁽²⁾ at 1 σ -level
$\delta^{13}\text{C}$, ‰ on the VPDB $\delta^{13}\text{C}$ scale	+2.46	± 0.01
$\delta^{18}\text{O}$, ‰ on the VPDB $\delta^{18}\text{O}$ scale	-2.37	± 0.04

⁽¹⁾ The values and combined uncertainties were calculated from the raw data obtained by stable isotope mass spectrometry directly vs remaining NBS19 material, including the necessary ¹⁷O isotopic correction [1, 2], and the weighing uncertainties following [1, 3, 4]. Value and uncertainty for $\delta^{13}\text{C}$ provided here are rounded to two digits, values with the full three digit resolution are given in Table 2.

⁽²⁾ The uncertainty is expressed as a combined standard uncertainty (1 σ -level) using a coverage factor $k = 1$, and estimated in accordance with the JCGM 100:2008 'Evaluation of measurement data – Guide to the expression of uncertainty in measurement' [3] and ISO Guide 35 'Reference materials – General and statistical principles for certification' [4].

All DI-IRMS

Table 3. Results obtained on the IAEA-603 material at all involved laboratories, given are 95%-confidence intervals.

Laboratory/ material:	$\delta^{13}\text{C}$ of IAEA-603, ‰ on VPDB scale ⁽¹⁾	N_1 / N_2 - number of measurements on IAEA-603 and on NBS19	$\delta^{18}\text{O}$ of IAEA-603, ‰ on VPDB scale ⁽¹⁾	N_1 / N_2 - number of measurements on IAEA-603 and on NBS19
GEOTOP, unseparated material sampled before the final material re-mixing and ampouling	2.462 \pm 0.008	$N_1=31$ (120 μg)	-2.392 \pm 0.015	$N_1=31$ (120 μg)
USGS, material sampled before final re-mixing and ampouling	2.464 \pm 0.018	$N_1=8 / N_2=5$	-2.381 \pm 0.030	$N_1=3 / N_2=4$
MPI-BGC, material of 5 ampoules selected from the final product	2.458 \pm 0.006	$N_1=13 / N_2=15$ (40 mg)	-2.364 \pm 0.037	$N_1=13 / N_2=15$ (40 mg)
IAEA, the characterization study on 5 ampoules selected from the final product (Table 2, 1 st row) supported by the homogeneity study on 52 ampoules	2.460 \pm 0.005	$N_1=38$ (10-12 mg) $N_2=38$ (10-12 mg)	-2.373 \pm 0.017	$N_1=38$ (10-12 mg) $N_2=38$ (10-12 mg)

⁽¹⁾ The values and 95%-confidence intervals were calculated from the assessment of isotopic data provided by participating laboratories, as obtained by the stable isotope mass spectrometry including necessary ¹⁷O isotopic correction [1, 2] and combining uncertainties following [1, 3, 4].

NBS19



International Atomic Energy Agency

Analyses of NBS #19 by two laboratories that at one time had a sample of the original PDB standard gave the following:

	Laboratory	
	A	B
$\delta^{13}\text{C}$	+2.12	+2.00
$\delta^{18}\text{O}$	-2.26	-2.14

Considering the large differences between the results of the two laboratories, we suggest the following rounded values for NBS 19 relative to PDB: $\delta^{13}\text{C} = +2.00$, $\delta^{18}\text{O} = -2.20$.

Two New Carbonate Stable-Isotope Standards

Irving FRIEDMAN, James O'NEIL¹ and Gerald CEBULA

Geostandards Newsletter, Vol. 6, N° 1, Avril 1982, p. 11 à 12

ADVISORY GROUP MEETING ON STABLE ISOTOPE
REFERENCE SAMPLES FOR GEOCHEMICAL AND HYDROLOGICAL INVESTIGATIONS

IAEA, Vienna, 19 - 21 September 1983

Report to the Director General
by
R. Gonfiantini
Scientific Secretary of the Meeting

March 1984

Inst. Code	Person(s) Responsible	NBS-19	
		$\delta^{18}\text{O}$ vs PDB	$\delta^{13}\text{C}$ vs PDB
BR-1	E. Matsui	-2.01	1.89
CDN-3	F.C. Tan, P.M. Strain, J.H. Abriel	-2.17	1.85
CDN-4	R. Drimmie, D. Palmer	(-2.36)	(-0.51)
RCH-1	A. Pollastri J.	-1.94*	1.90*
CHI-1	Sheng-jin Jin	-2.20	
CS-1	J. Hladikova	-2.17	2.01
F-2	R. Hageman	-2.27	2.01
F-4	A. Filly	-2.20	2.06
F-6	J. Baradat, C. Sourisse	-1.53	2.33
D-3	I. Dumke, U. Rinow	-2.16	1.96
IAEA	R. Gonfiantini M. Koizumi	-2.01	2.08
IND-5	B. Kumar	-2.28	2.04
J-1	O. Matsubaya	(-2.32*)	
J-2	Y. Matsuhisa Y. Morishita	-2.24	1.89



From Gas Torches to Lasers, *Measuring Stable Isotopes*

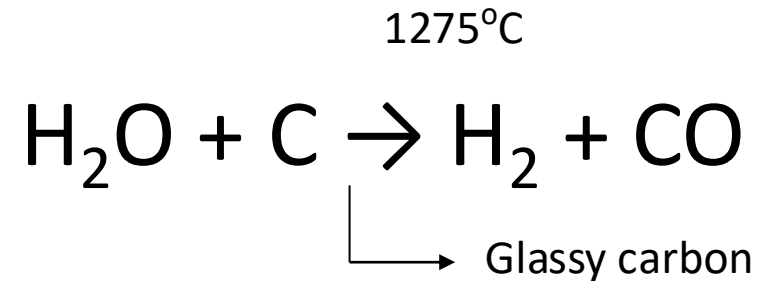
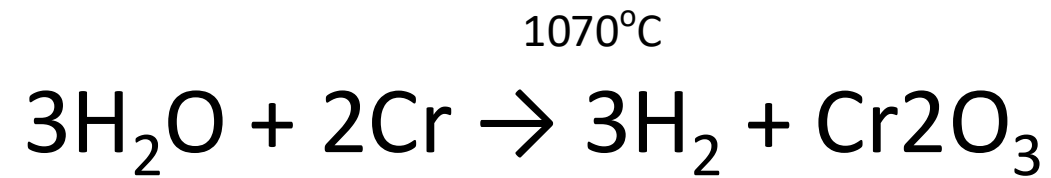
How far away are we from this?



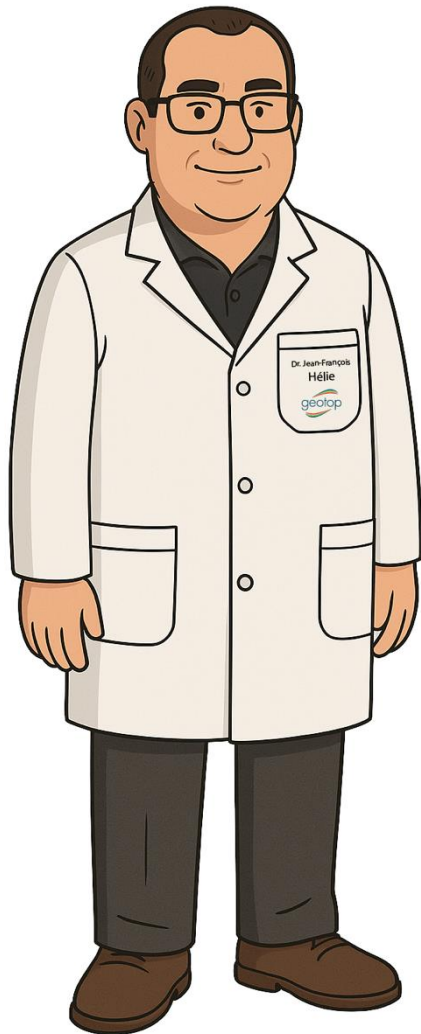
That's it patate frite!



Pyrolysis of water



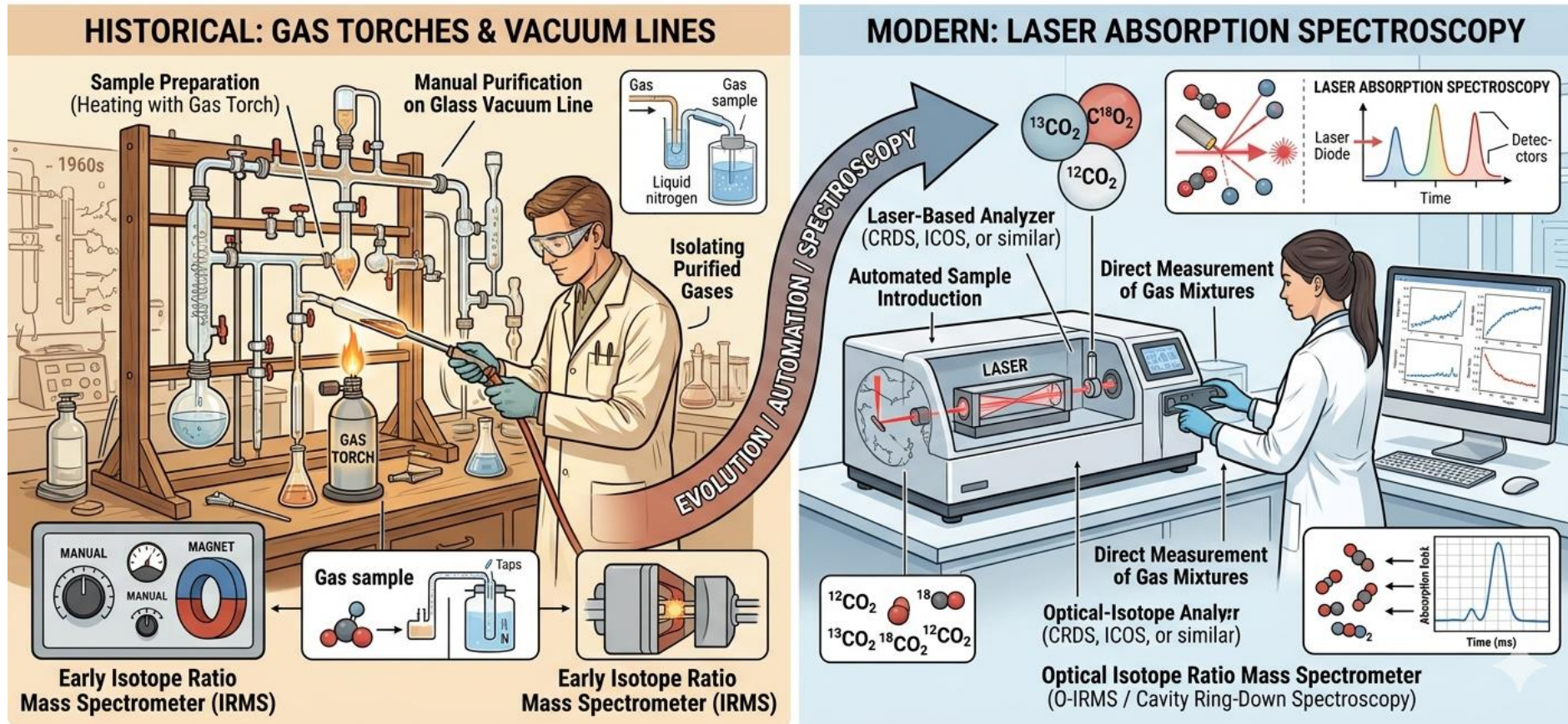
0,3 µl d'eau



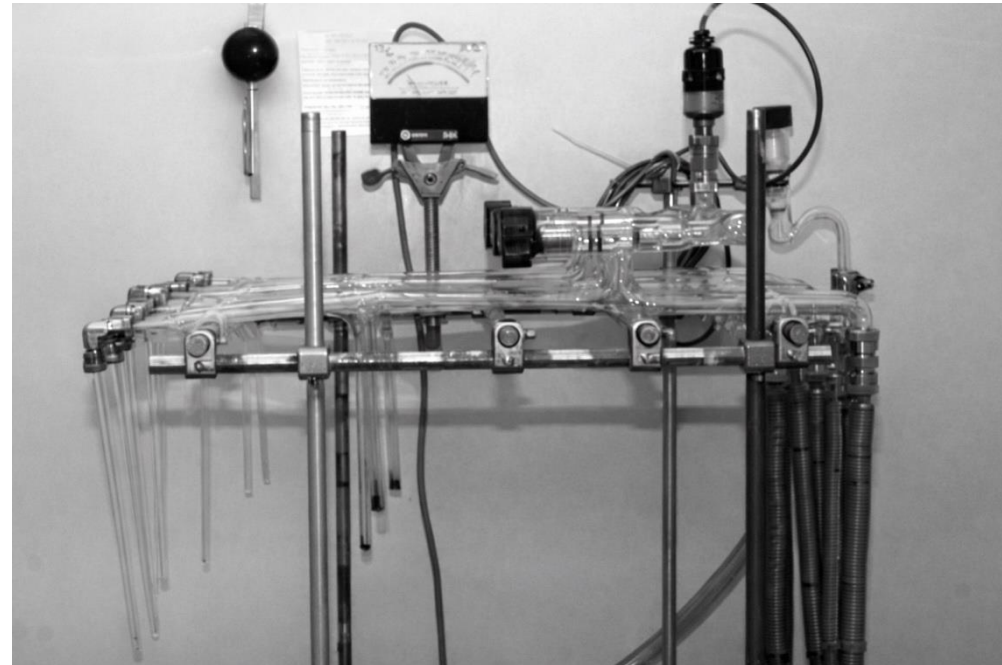
Gemini

EVOLUTION OF STABLE ISOTOPES MEASUREMENT

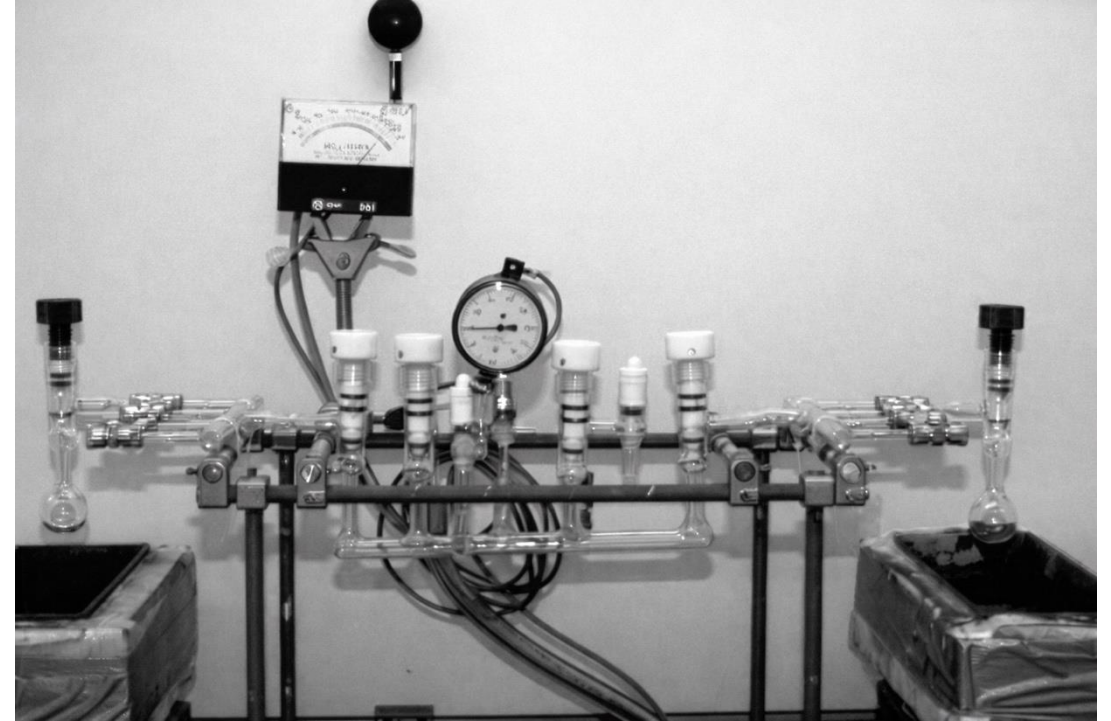
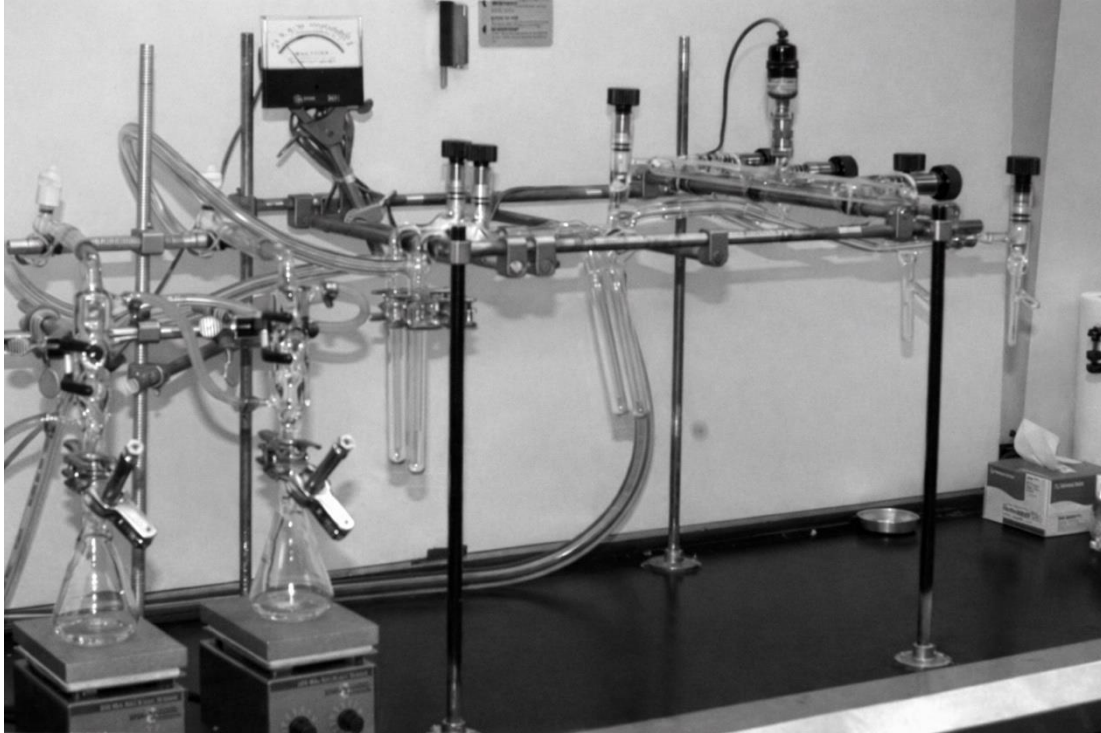
From Gas Torches to Lasers



Titre



Titre



Titre

$$f_{CO_2} = \frac{[O_2]_{CO_2}}{[O_2]_{CO_2} + [O_2]_{H_2O}}$$

$$F_{H_2O} = \frac{[O_2]_{H_2O}}{[O_2]_{CO_2} + [O_2]_{H_2O}}$$

$$[O_2]_{CO_2} = \frac{(V_{bulle} - V_{eau}) * p_{CO_2}}{(22.4 * 10^3 * p_{atmosphérique})}$$

$$[O_2]_{H_2O} = \frac{1}{2} * \frac{V_{eau}}{18}$$