Inorganic analytical chemistry in 5 dimensions: concentration, isotopes, speciation, spatial resolution, time resolution and the way to combine all of them; some developments in LA in proteomics

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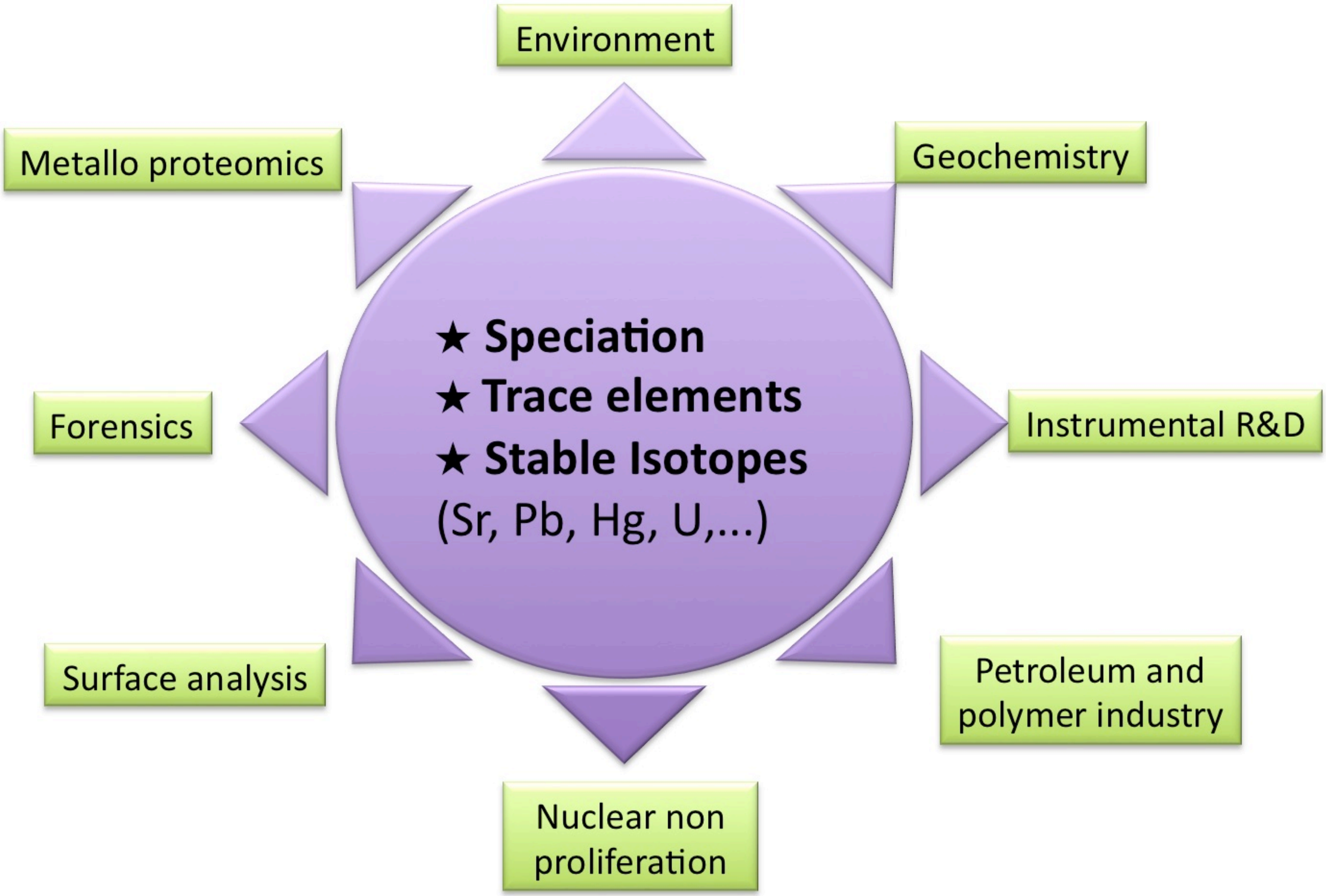
Ultra trace, Isotopes and laser ablation in LCABIE-IPREM



LCABIE-IPREM (University of Pau – CNRS)

- **30** permanent position **scientists**.
- **275** peer reviewed **publications** (last 4 years).
- **22** PhD **thesis** (last 4 years).

- **8** quadripole **ICPMS** (12 including the spinoff UT2A)

(Perkin, Agilent, Thermo, Brucker (loan))

- **2 HR-ICPMS** *(Thermo)*
- **1 MC-ICPMS** *(Nu Instrument)*
- **1 ICPAES** *(JY) + 1 Spectro (spinoff UT2A)*
- **2** High repetition rate **femtosecond lasers**

(Nexeya-Aplitude Systemes)

- GC, HPLC, ULPC, FFF, etc...
- Organic mass spectrometry (**orbitrap**, GCMS, ESIMS)

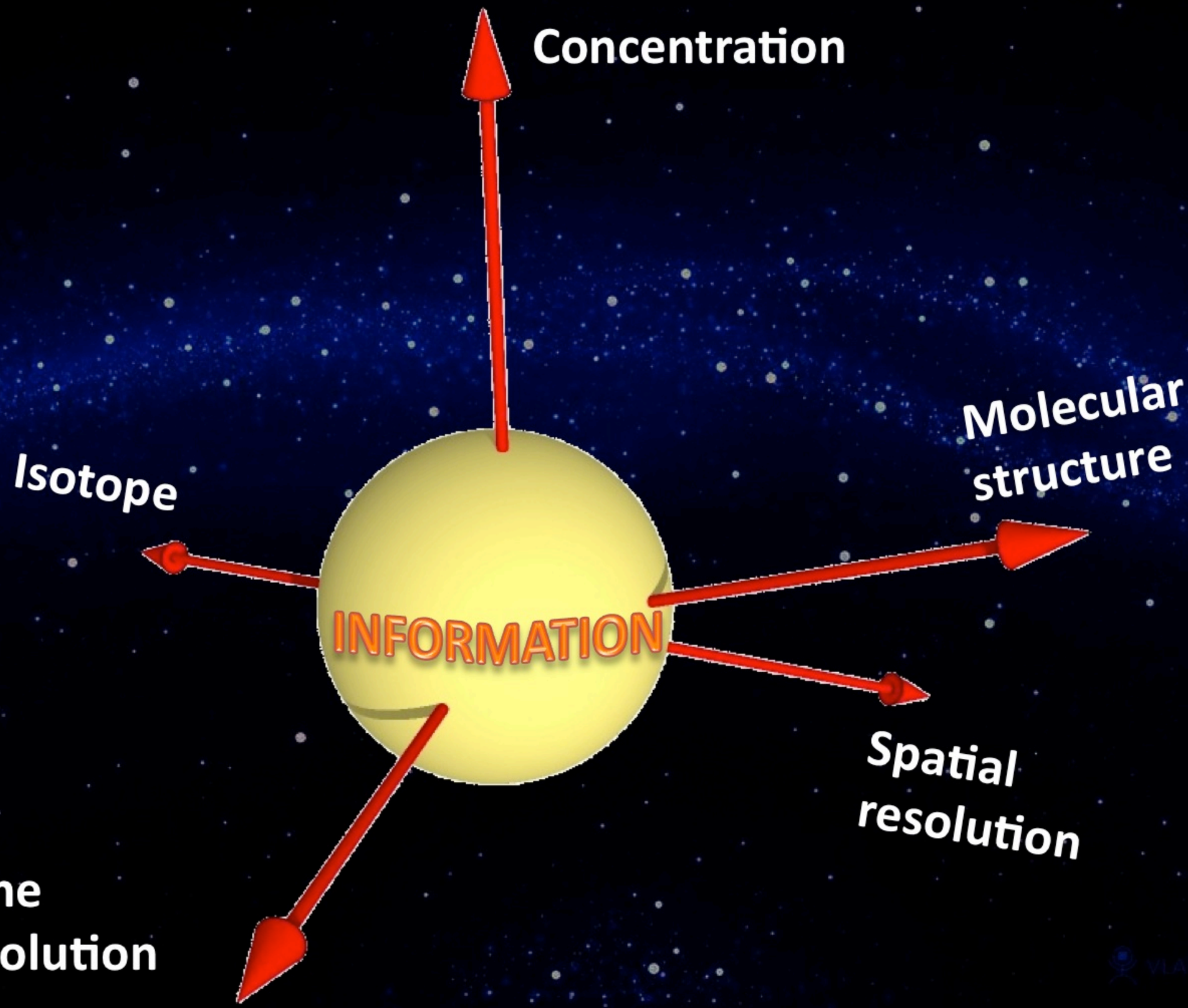
- MARSS (MAss Spectrometry Center for Reactivity and Speciation Sciences)

: (1 **nano SIMS**, 1 **FTICR**, 1 **HR-MCICPMS** to be installed)

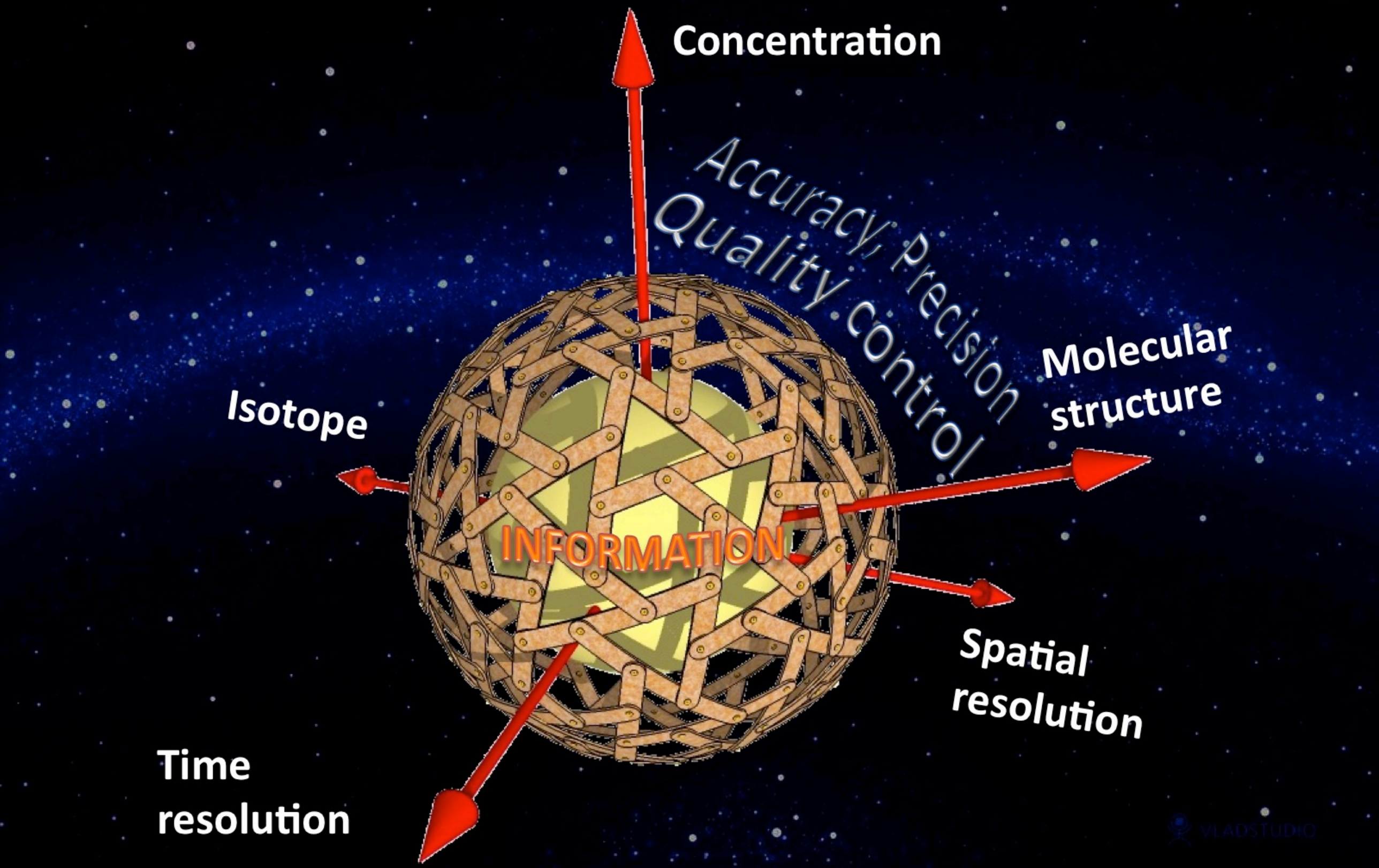
Analytical chemistry in 5 dimensions

INFORMATION

Analytical chemistry in 5 dimensions



Analytical chemistry in 5 dimensions



Hyphenation with the ICPMS family

Speciation &
Laser ablation

=

Short transient signals

Hyphenation with the ICPMS family

- ➔Fastest signal acquisition
- ➔Highest sensitivity
- ➔Best precision (conc.& IR)
- ➔Best accuracy (conc. & IR)
- ➔Robustness

Analytical chemistry in 5 dimensions

Concentration

GC-ICPMS Coupling

Molecular structure

INFORMATION

GC-/ICPMS coupling: General Principles

Aim : ***Speciation*** → distribution of an element among defined chemical species in a system.

Speciation analysis → Identification and/or measurement of the quantities of one or more individual chemical species in a sample.

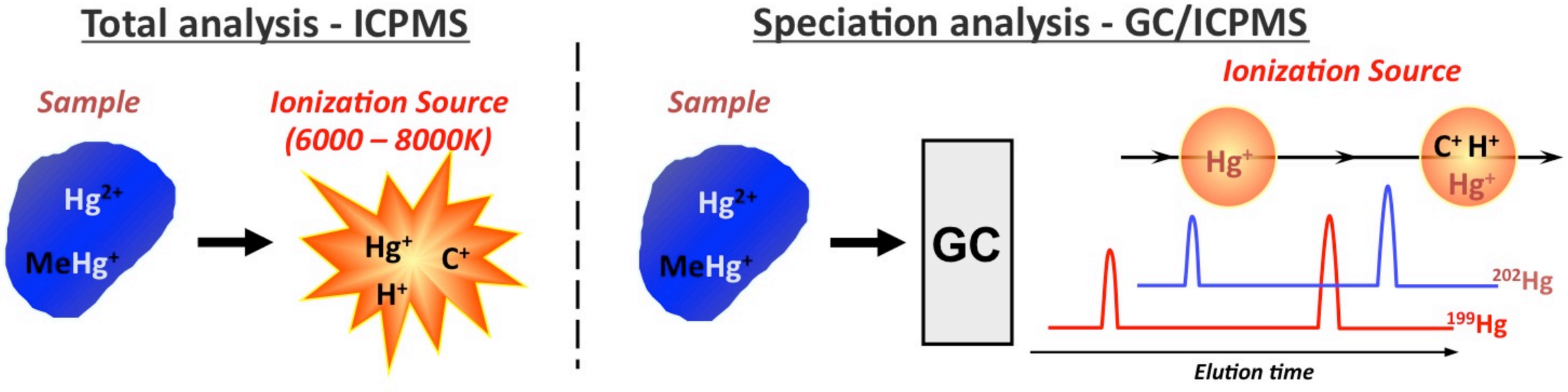
Principle : ***Sequential separation***

ICPMS is suitable for Elemental analysis, but do not allow to differentiate or to identify the various chemical species of an element in a sample (→ simultaneous ionization & detection).

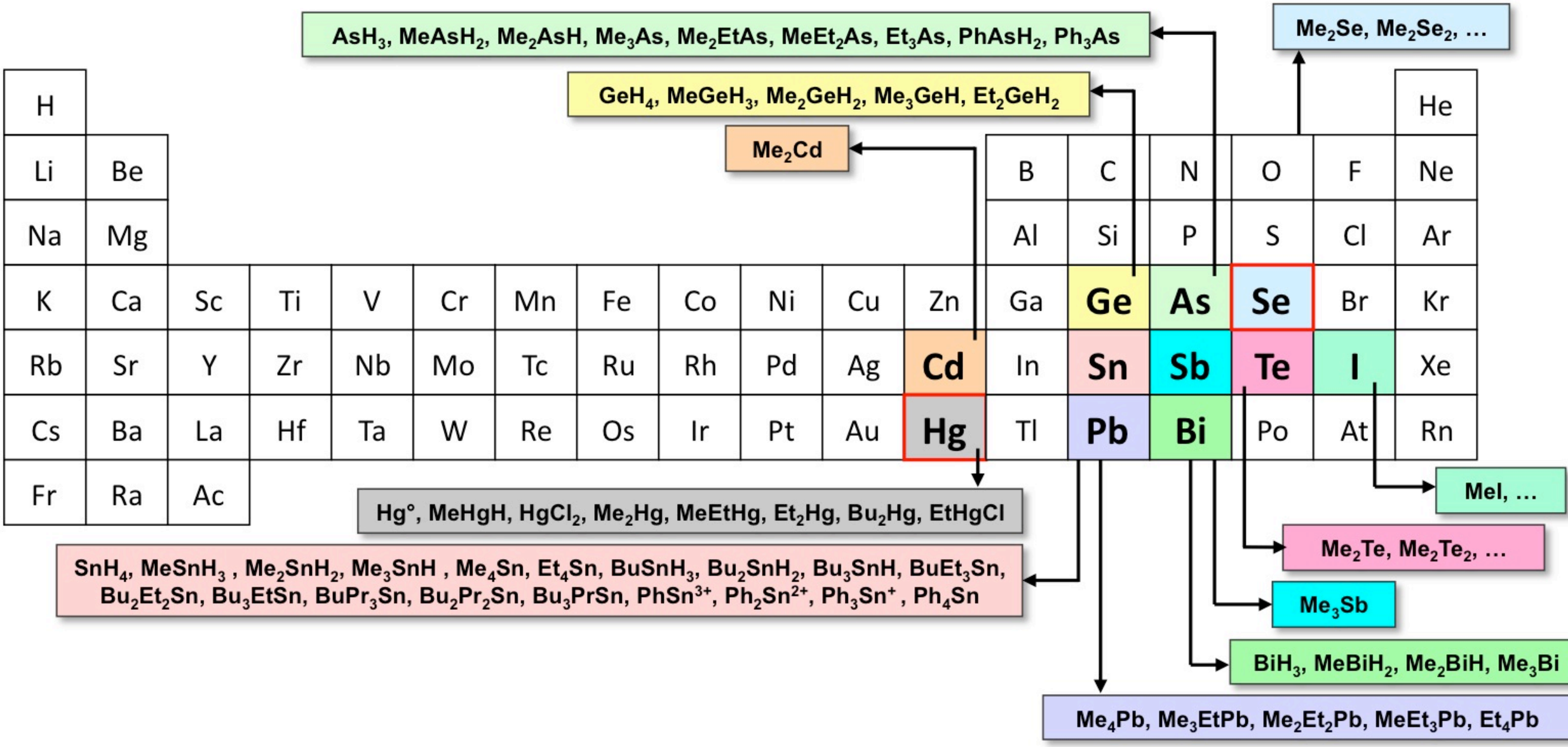
⇒ The **sequential introduction** of the analytes in the spectrometer is able to solve that problem and to discriminate the chemical species and their proper isotopic signature.

⇒ This separation is achieved prior to the ionization and must be well characterized in term of **elution order** and **time**.

⇒ A **transient signal** is obtained : peak intensity proportional to concentration.

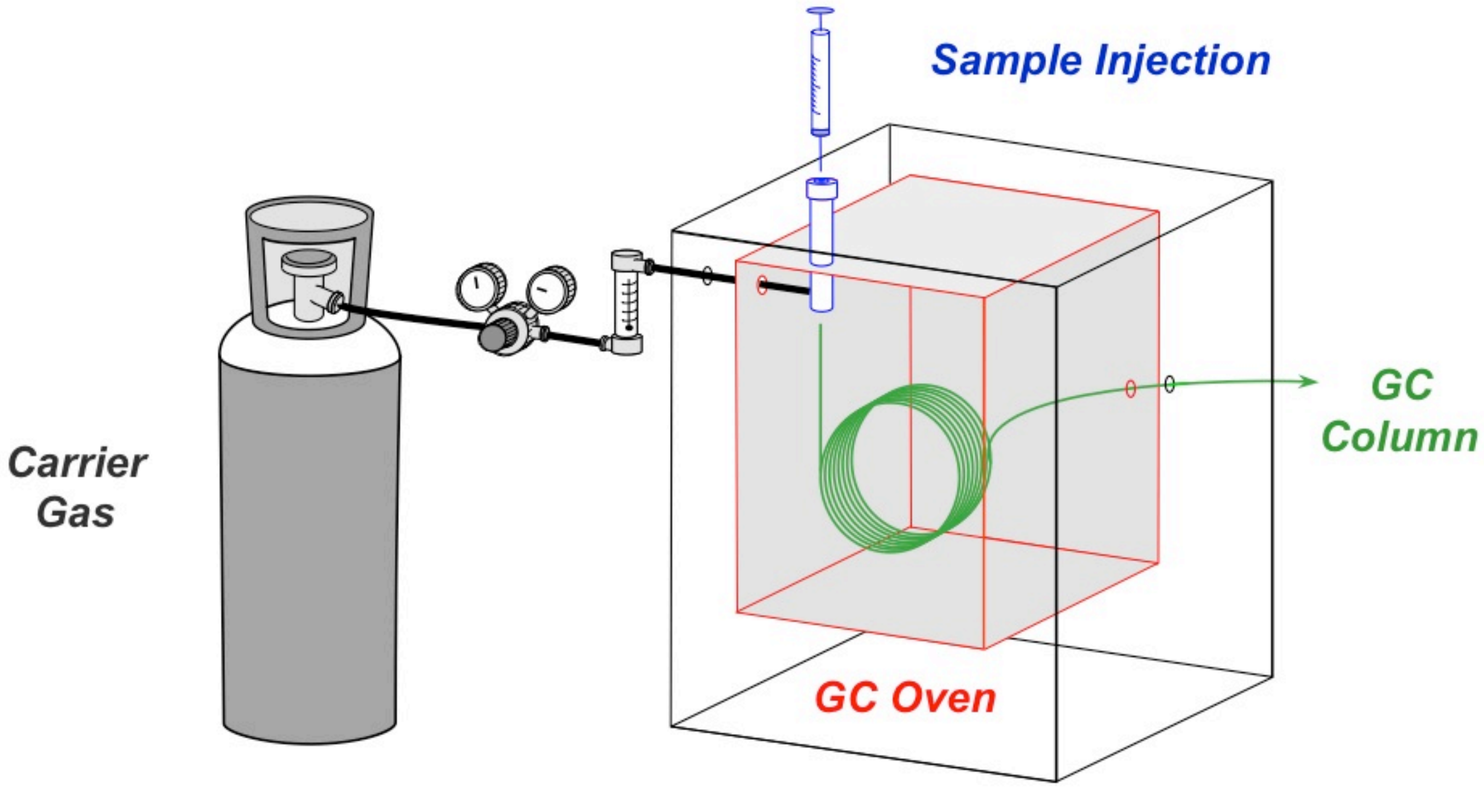


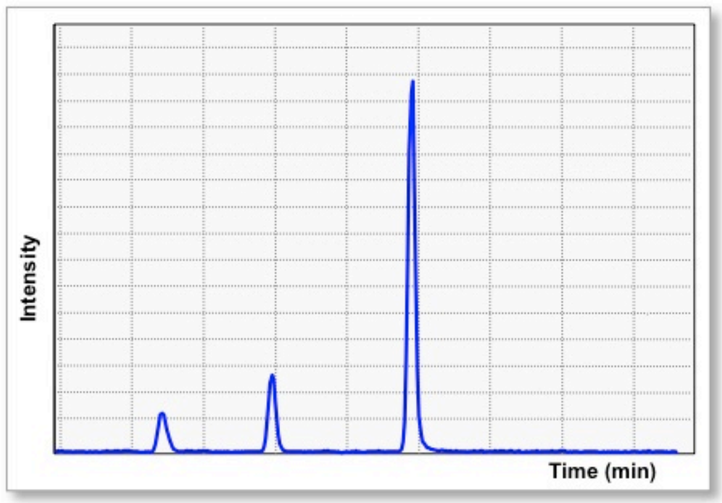
Classical elements /species analyzed by GC-ICPMS



GC-ICPMS coupling: Gas Chromatography

⇒ Analytical technique for the separation of chemical species from a complex mixture, likely to be volatilized by heating without any degradation.





Elution to the Detector

Gas chromatography (GC) is based on a partition equilibrium of analytes between:

- a solid **stationary phase** (column filled with a silicone-based material)
- a **mobile phase** (inert carrier gas: He, N_2, …).

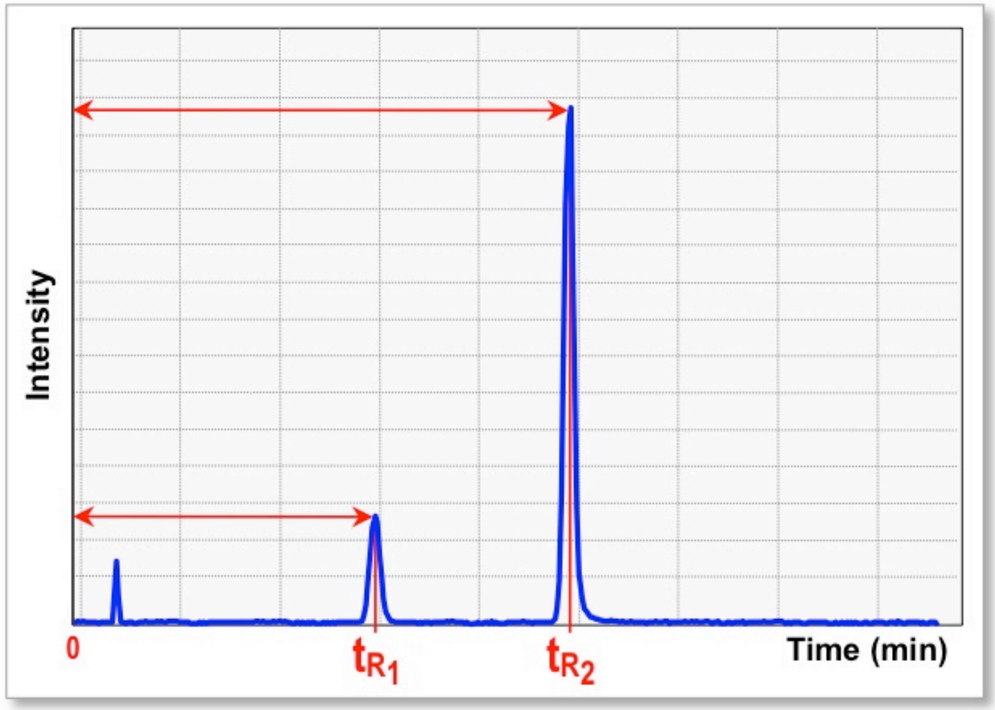
Analytes are eluted to the detector as a function of:

- their chemical affinity with the stationary phase
- their **boiling point** (for derivatized Hg species)

Final sample preparation and injection has to be achieved in **organic solvent**

Chromatographic parameters: **Retention time** (t_R)

The retention time is the characteristic time it takes for a particular analyte to pass through the system (from the column inlet to the detector).
t_R is defined at the maximum intensity of the peak



⇒ t_R is theoretically independent of the concentration and of the injected amount.

⇒ Under fixed experimental conditions, t_R is reproducible and allows the **identification** of the analytes by comparison with injections of standard solutions.

Chromatographic parameters:

General factors influencing the quality of the GC separation & analysis:

- Column geometrical factors

  Length, Internal diameter, coiling up

- Column filling

  Stationary phase regularity, type and quantity

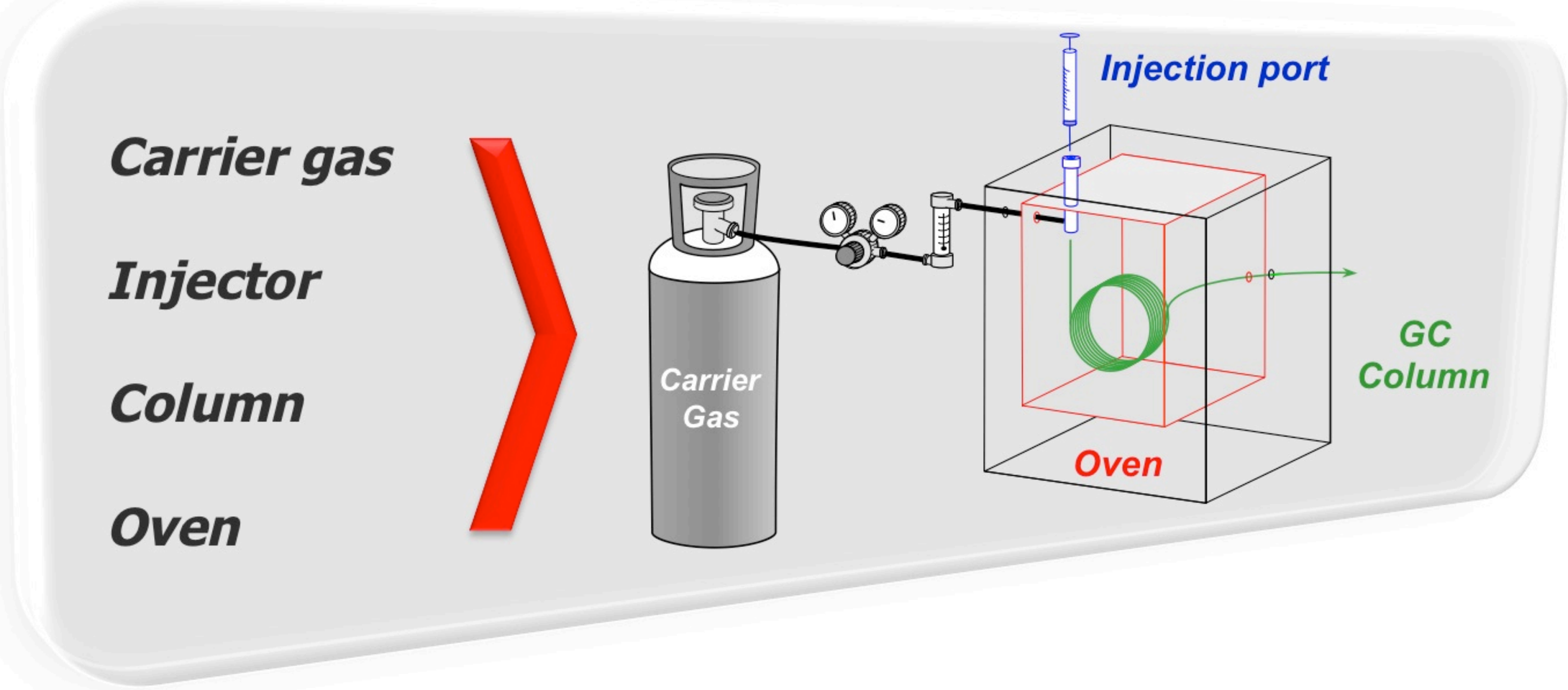
- Mobile phase:

  Type of gas and flow

- other factors

  Oven heating program, amount of sample injected

⇒ Optimized design of the GC system



Carrier gas:

Chemically inert with the analytes
High purity grade
Compatibility with the employed detector

→ Typical carrier gases include **helium**, nitrogen, argon, hydrogen and air.

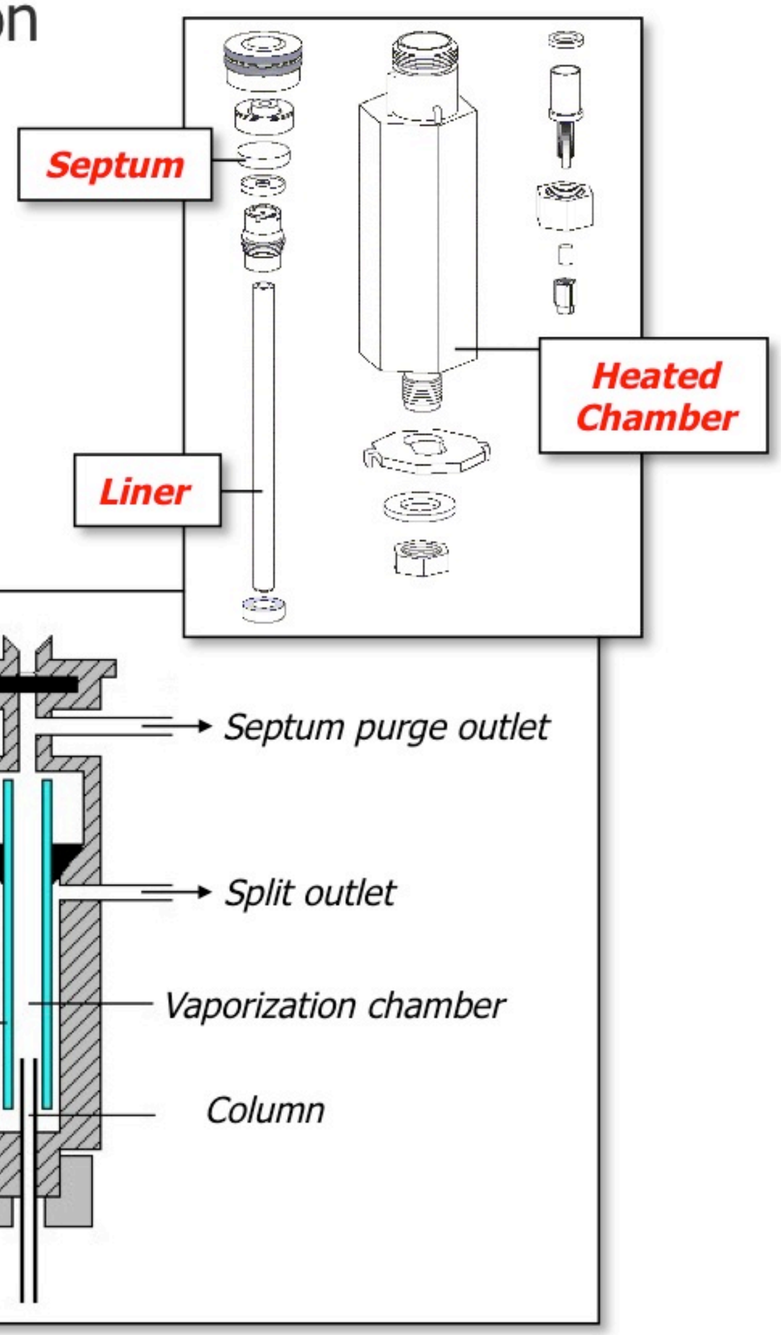
→ The carrier gas flow depends on the type of column used (capillary, filled column) and influenced both separation of the analytes and duration of the analysis.

Injector:

The injector provides the means to efficiently introduce the sample in the GC column

- No degradation of the analytes prior to the separation
- Repeatable injection of microvolumes

→ The injector is
- connected to the head of the GC column
- **thermoregulated**
- flushed by the carrier gas



→ Sample injection through a **septum**

Thermolite® septa for Hg species analysis

→ Analytes are volatilized in the **liner**

Injection mode: Split

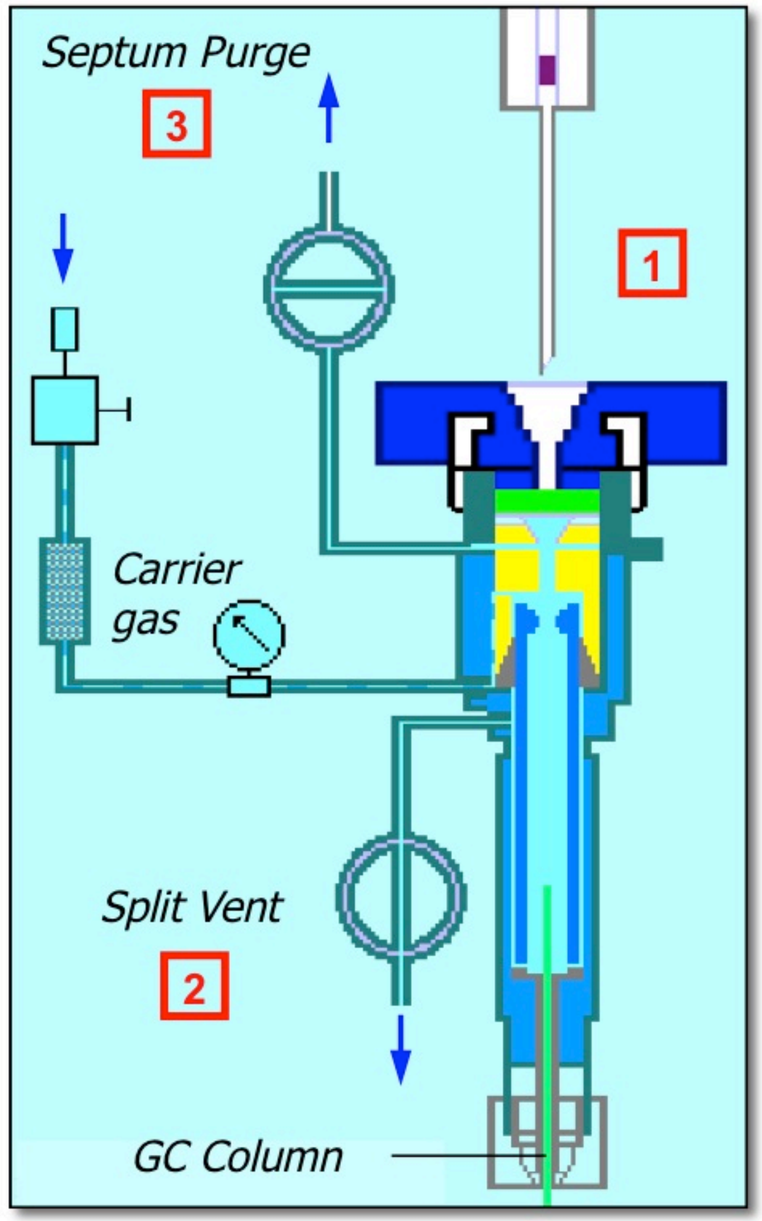
A part of the sample/carrier gas mixture in the injection chamber is exhausted through the split vent.

⇒ Split injection is preferred when working with samples with high concentrations.

1- Injection and **vaporization** in the liner

2- Split of the sample/carrier gas mixture

3- Septum Purge to remove heavier elements



For GC-MC/ICPMS application:

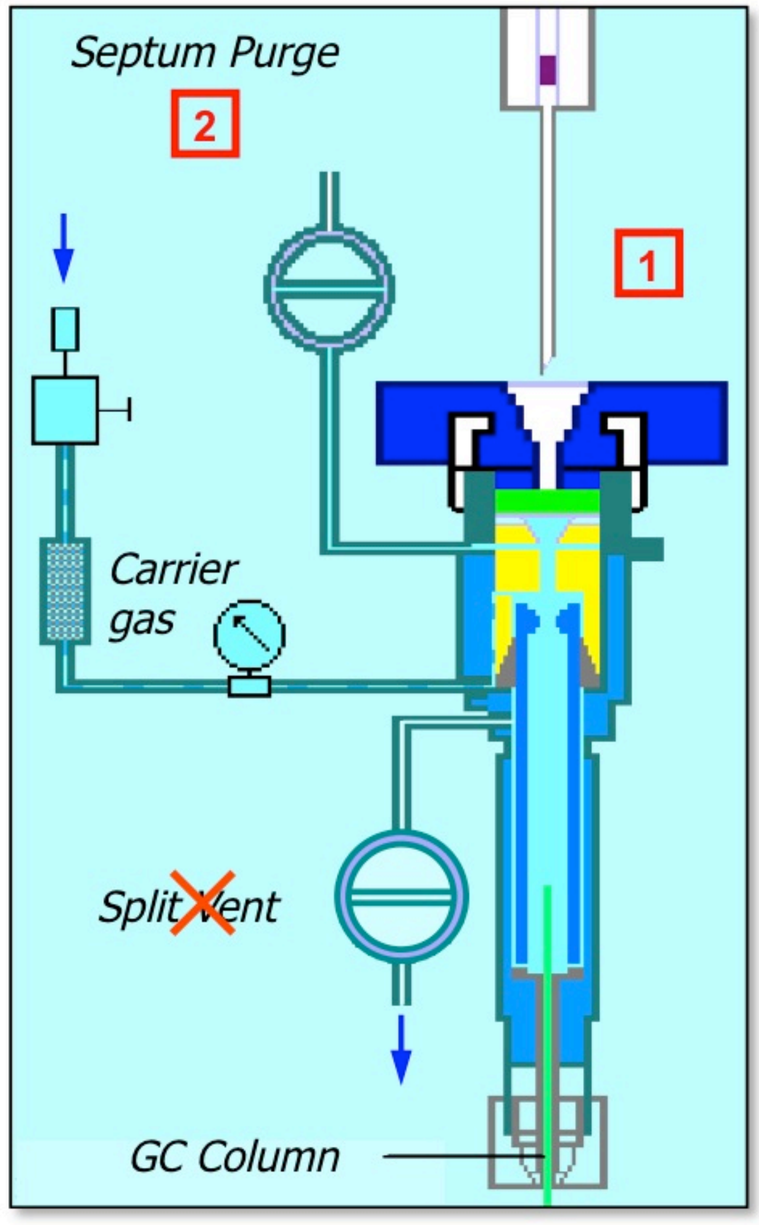
The split mode can induce isotopic fractionation

Injection mode: Splitless

The carrier gas sweeps completely the sample into the column.
⇒ Splitless injection is dedicated to trace analysis with low amounts of analytes.

1- **Injection** and **vaporization** in the liner

2- **Septum Purge** to remove heavier elements



Limitation : Maximum injection volume of 3µL.

The Inlet must be **cleaned** on a regular basis (septum replacement, ferrules fragment removal)

Injection mode:

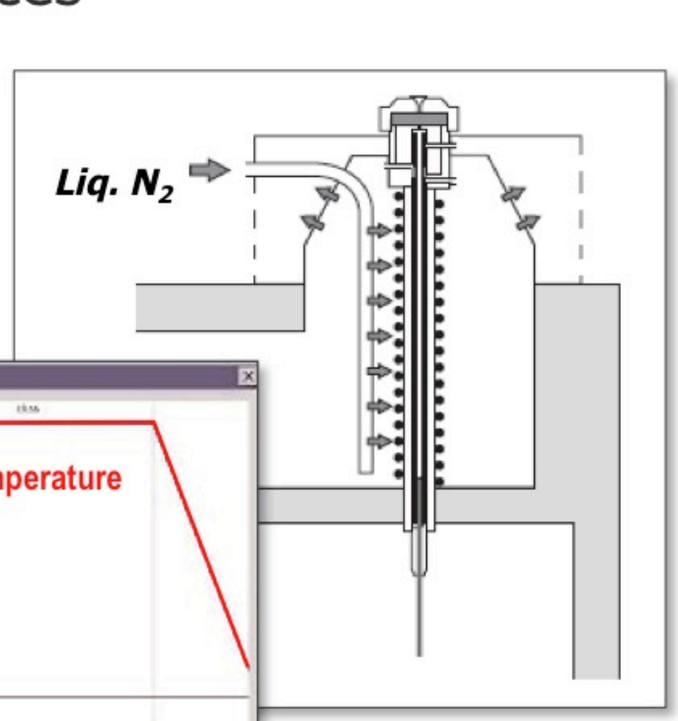
- **PTV Injector:** Programmable Temperature Vaporization injector

A programmed temperature gradient is applied to perform a pre-separation of target analytes from other components of the sample (solvent, matrix, heavy compound…)

Simultaneous cold/cryo trapping of the analytes and venting of the solvent
⇒ **large volume or multiple injection**

Advantages:

- Improve chromatographic resolution and analytical performances
- Increase injection volume up to ~100-200 µL
- Reduce solvent & matrix effects
- Prevent GC column against aging, clogging and bleeding



Limitations:

- Cost
- Liquid nitrogen supply
- Helium carrier gas
- Analytes losses via the solvent vent

GC column:

1- Capillary column characteristics:

- Internal diameter : 0.2 to 0.32 mm
- Length : 15 to 100 meters
- Tubing : **Fused silica, Stainless steel**
- Carrier gas flow: 0.5-2 mL min^{-1}

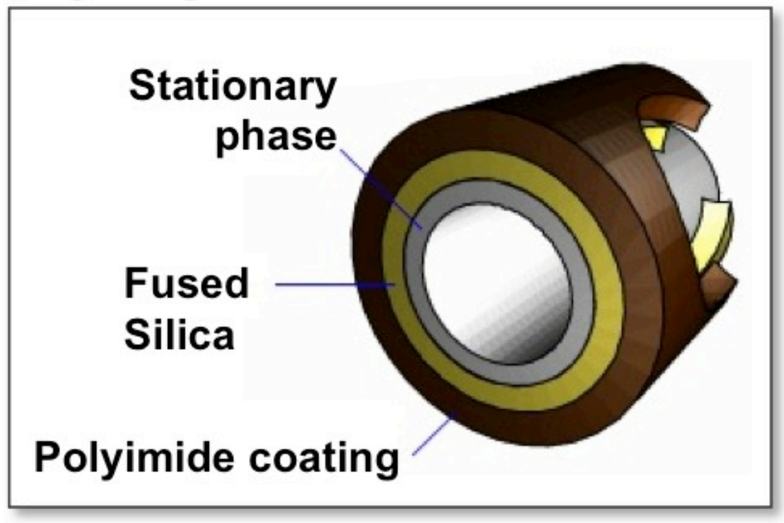
2- Semi-capillary column characteristics:

- Internal diameter : 0.53 mm
- Length : 5 to 50 meters
- Tubing : **Fused silica, Stainless steel**
- Carrier gas flow: 1-30 mL min^{-1}

⇒ Chromatographic resolution will depend on:

- Internal diameter
- Length
- Type of the stationary phase and thickness

Capillary column cross section



Applications and required conditions for speciation analysis and GC separation

- Target analytes must be **volatile** and **thermally stable**.
- Non volatile target analytes must be easily **alkylated**, without any modification of the original speciation and species distribution in the sample.

Example of chemical species of environmental interest :

Mercury	**Tin**	**Lead**	**Selenium, ...**
Hg^{2+}	Sn^{4+}	Pb^{2+}	
$Me_xHg^{(2-x)+}$	$Me_xSn^{(4-x)+}$	$Me_xEt_yPb^{(4-x-y)+}$	Me_2Se
$Et_xHg^{(2-x)+}$	$Et_xSn^{(4-x)+}$		Me_2Se_2
	$Bu_xSn^{(4-x)}$		
	$Ph_xSn^{(4-x)}$		

For these elements, only the fully substituted species, plus Hg°, are volatile and can be directly analyzed, without any sample prep with using a GC-(MC)/ICPMS

Ex : Hg°, Me_2Hg, Et_2Hg, Et_4Sn, Me_4Pb, etc...

GC column:

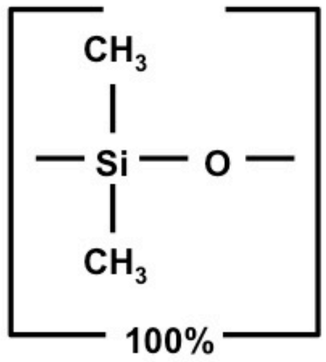
Most frequently used capillary column for Hg, Sn, Pb, Se Speciation & GC/ICPMS coupling:

⇒ **DB5, DBMS, HP5, MXT1, ...**

Preference :

Semi-capillary **MXT-1** column : - Siltek treated Stainless steel (or Silcosteel)
- non polar phase 100% dimethyl polysiloxane
- T° range: -60 to 430°C

RESTEK

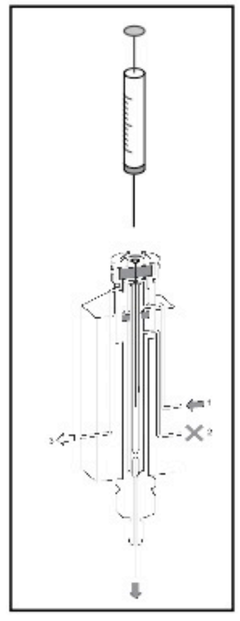


Similar columns:
DB-1, DB-1MS, HP-1, HP-1MS, Ultra-1, SPB-1, Equity-1, MDN-1, CP-Sil 5 CB, VF-1ms

- Robustness
- Easy installation and maintenance
- Flexible Chromatographic resolution:

⇒ Peak width suitable for isotopic measurements

GC-CPMS coupling: Advantages & Limitations



+ Gaseous phase sample introduction

100% of the sample is transferred into the ionization source (plasma).

⇒ The transient signal obtained (chromatographic peak) improves significantly the analytical performances of the method (**ALD < 1pg**).

The signal treatment and statistics have to be carefully conducted in order to maintain that benefit for isotopic measurement.

+ Chromatographic separation

The sequential elution of the analytes reduced isobaric interferences and matrix effects in the plasma.

Enhanced stability of the ionization source and background noise due to the continuous introduction of the GC mobile phase (Carrier gas).

+ GC-MC/ICPMS coupling

New and promising analytical tool to push back the frontier of scientific knowledge on Hg metrology and environmental issues (natural transformation mechanisms, source tracking, ...).

Limitations of GC/ICPMS coupling

- **Stability of the target analytes** during the chromatographic process

  ⇒ Species preservation and absence of isotopic fractionation

- **Chromatographic organic solvent**

  induces plasma disturbance and carbon deposits on the cones

- **GC-(MC)/ICPMS interface**

  Only 3 couplings are commercially available (Agilent, Thermo, Perkin Elmer)

  Customization still needed to fully optimize the mass spectrometer

  (mass calibration, mass bias correction, GC-ICPMS control and communication script,...)

- **GC-(MC)/ICPMS Analysis Run time**

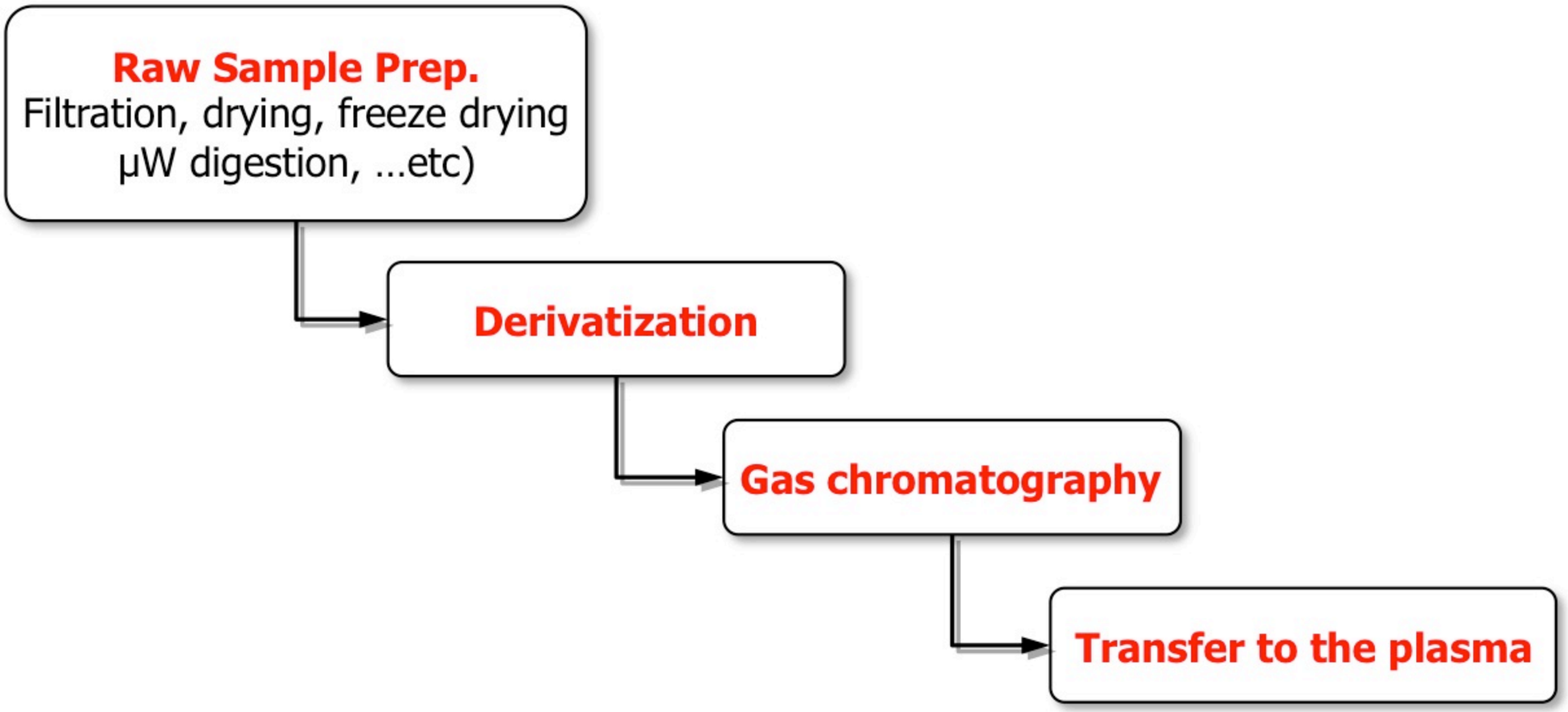
  Isotopic measurements on transient signal ⇒ "Slow" GC run (15-20 min), needed for replicated analyses + bracketing standards

- **GC-(MC)/ICPMS Data treatment**

  Transient signal treatment for isotopic measurements is time consuming

  Need for customized Chromatographic integration software or calculation sheets.

Speciation scheme for GC-(MC)/ICPMS analysis



Each step of the sample prep. protocol has to preserve the chemically integrity of the target analytes and avoid any fractionation process.

Soft extraction methods for Hg speciation

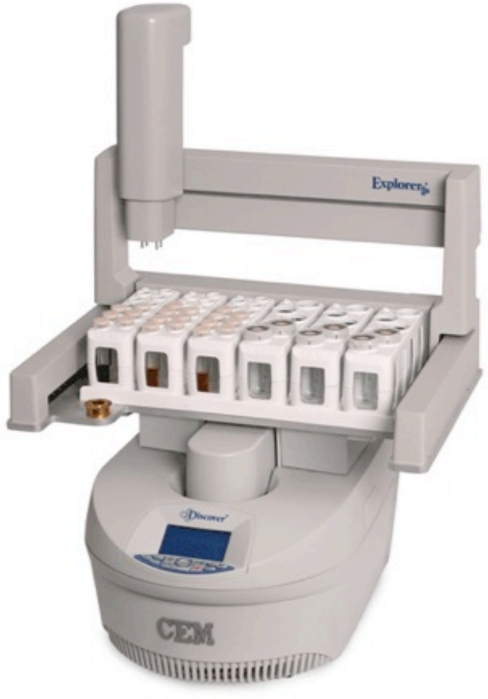
Objective: preservation of the chemically integrity of the target Hg species.

Hot plate digester:

- Acidic or Alkaline digestion
- T max ~75-80°C
- Closed glass or Teflon vessel (Savillex)

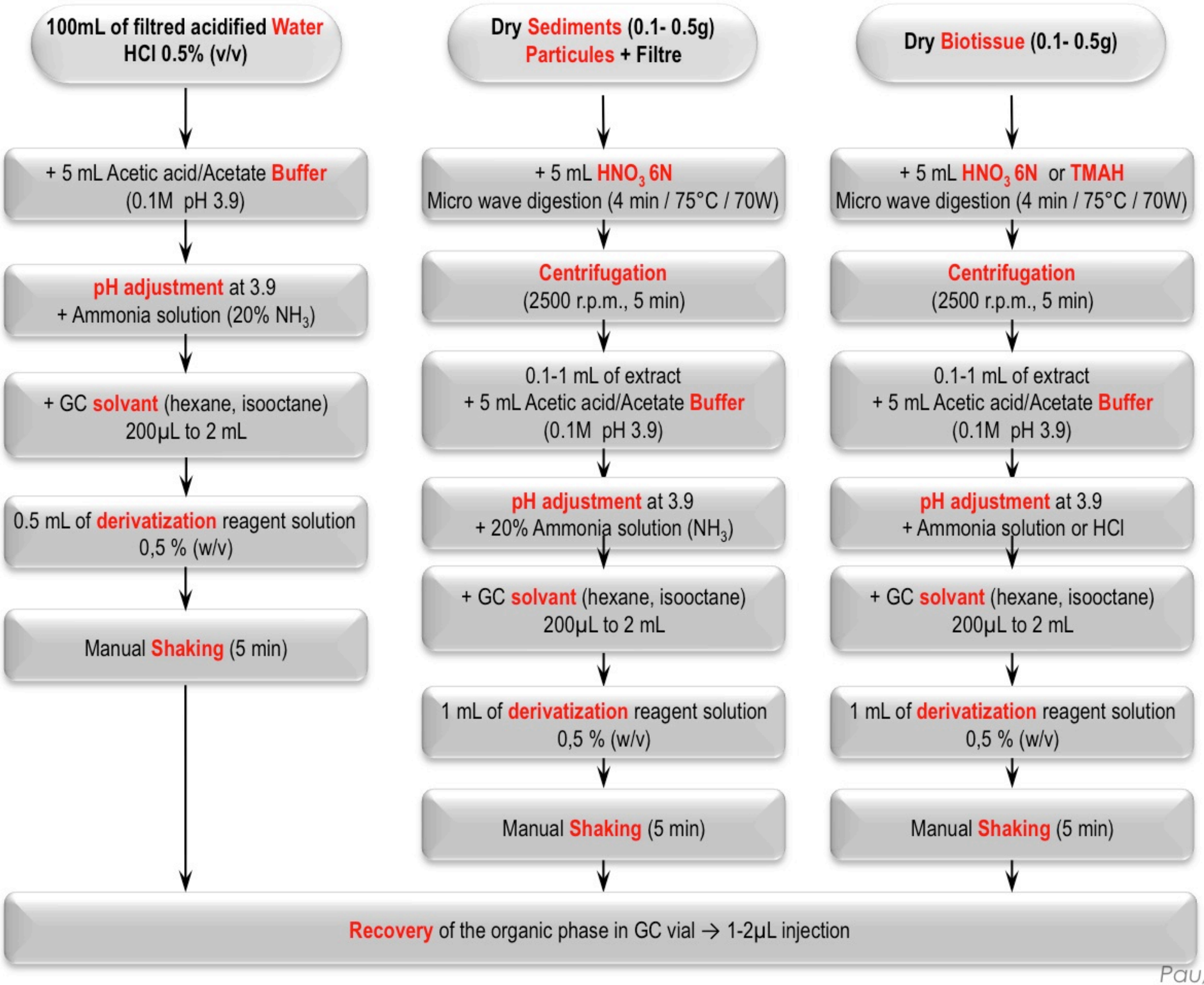
Assisted Micro wave digestio

- Acidic or Alkaline digestion
- Programmable Heating
-Semi- closed glass vessel



Avoid sonication processes to solubilize the sample:
Significant risk of methylmercury degradation

Soft extraction methods for Hg speciation (Hg^{2+}, CH_3Hg^+)



Soft extraction methods for Hg speciation (Hg^{2+}, CH_3Hg^+)

Some critical points:

- Specific pH adjustment using a pH meter for each sample
  - precision required: 10^{-2} pH unit
  - acceptable range: 3.8 - 4.1
  - frequent calibration of the instrument

- Vessel and vials must be compatible with the entire chemical prep protocol regarding :
  - the nature of material (glass, Teflon, polypropylene)
  - the decontamination protocol (acid resistance)
  - the tightness (manual shaking)
  - the centrifugation step
  - the liq/liq extraction step & the recovery of the organic phase (narrow neck)

Wheaton vials
+ Teflon lined PP cap

Significant risk of cross contamination :
The material and ancillary instruments should be dedicated to the isotopic composition analyses

Derivatization reaction

Alkylation Reactions

Reactions in aqueous solution

Hg species **Ethylation** ($NaBEt_4$) :

$$2NaBEt_4 + Hg^{2+} \longrightarrow 2BEt_3 + HgEt_2 + 2Na^+$$

$$NaBEt_4 + MeHg^+ \longrightarrow BEt_3 + MeHgEt + Na^+$$

Hg species **Propylation** ($NaBPr_4$) :

$$2NaBPr_4 + Hg^{2+} \longrightarrow 2BPr_3 + HgPr_2 + 2Na^+$$

$$NaBPr_4 + MeHg^+ \longrightarrow BPr_3 + MeHgPr + Na^+$$

Hg species **Phenylation** ($NaBPh_4$) :

$$2NaBPh_4 + Hg^{2+} \longrightarrow 2BPh_3 + HgPh_2 + 2Na^+$$

$$NaBPh_4 + MeHg^+ \longrightarrow BPh_3 + MeHgPh + Na^+$$

Derivatization reaction

Alkylation Reactions

Driving parameters

pH effect

- Optimum alkylation of Hg species occurs at pH 3.9
- Lower pH ⇒ parasitic reactions producing alkanes will reduce Hg derivatization efficiency
- higher pH ⇒ reaction rate is slow down

Kinetic of the reaction

- Reaction time ranges from 5 to 30 min depending on the type of matrix and reagent

Limitations

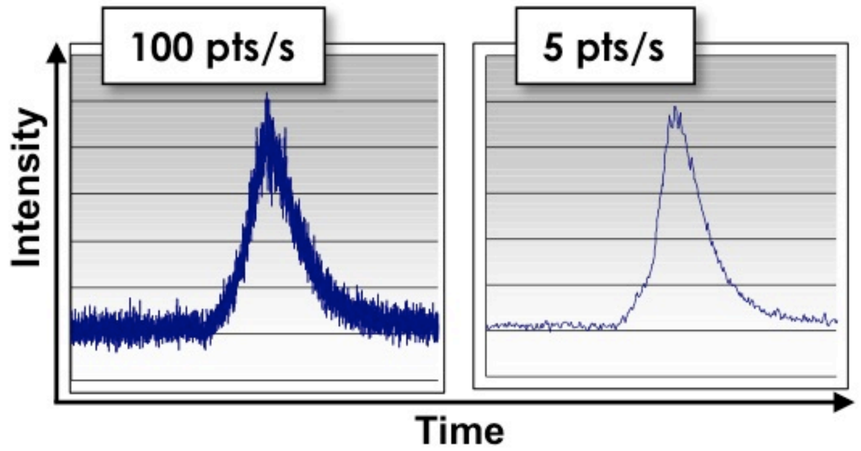
- Purity grade of derivatizating reagents is variable depending on suppliers and lots
- Reagent stability
- A post-derivatization liquid/liquid extraction is needed to transfer the substituted Hg species in the GC solvent.

Detector's acquisition frequency

The ICPMS acquisition frequency is a key parameter for transient signal characterization and treatment.

It directly influences:

- the chromatographic peak's definition :
  20 to 30 points of acquisition are necessary to well characterized a symmetric chromatographic transient signal (100pts for asymmetric peak).



- the analytical performances :
  Too high acquisition frequency increases the background noise and decreases in turn the performances.

⇒ A good compromise has to be found between

Chromatographic resolution

Analytical performances

$$\sigma^2 = \sigma^2_{\text{shot noise}} + \sigma^2_{\text{flicker}} + \ldots$$

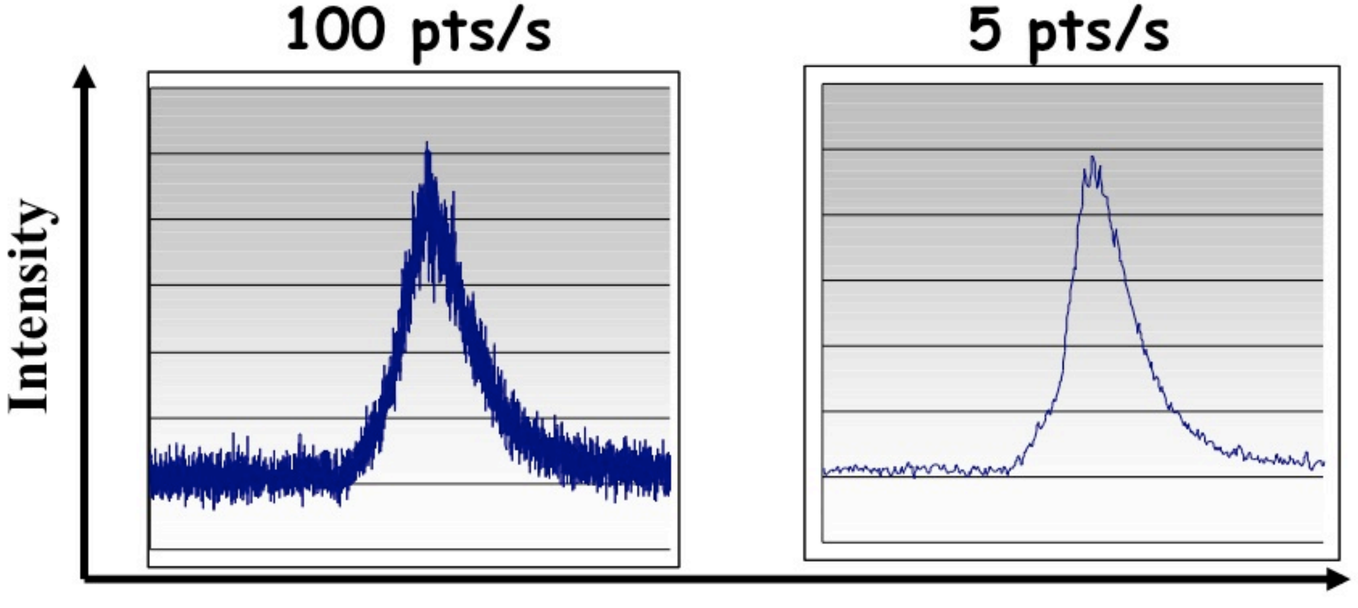
• The acquision time directly affects the shot noise value. In a first approximation, the shot noise varies according to the law :

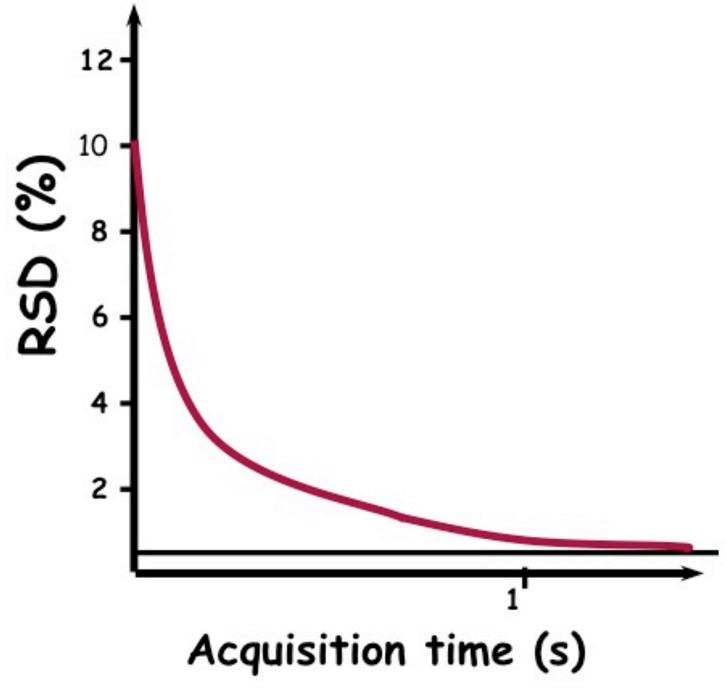
$\sigma_{\text{shot noise}} = k.\ (1/\sqrt{t})$, where t is the acquision time and k a constant.

•Hence **increasing the acquisition time allows reducing the shot noise**

⇒ According to this approximation, the LOD can be improved by a factor 2 when increasing the acquisition time by a factor 4.

⇒ In ICPMS (quad), the shot noise becomes negligible after 1 – 2 s of integration.





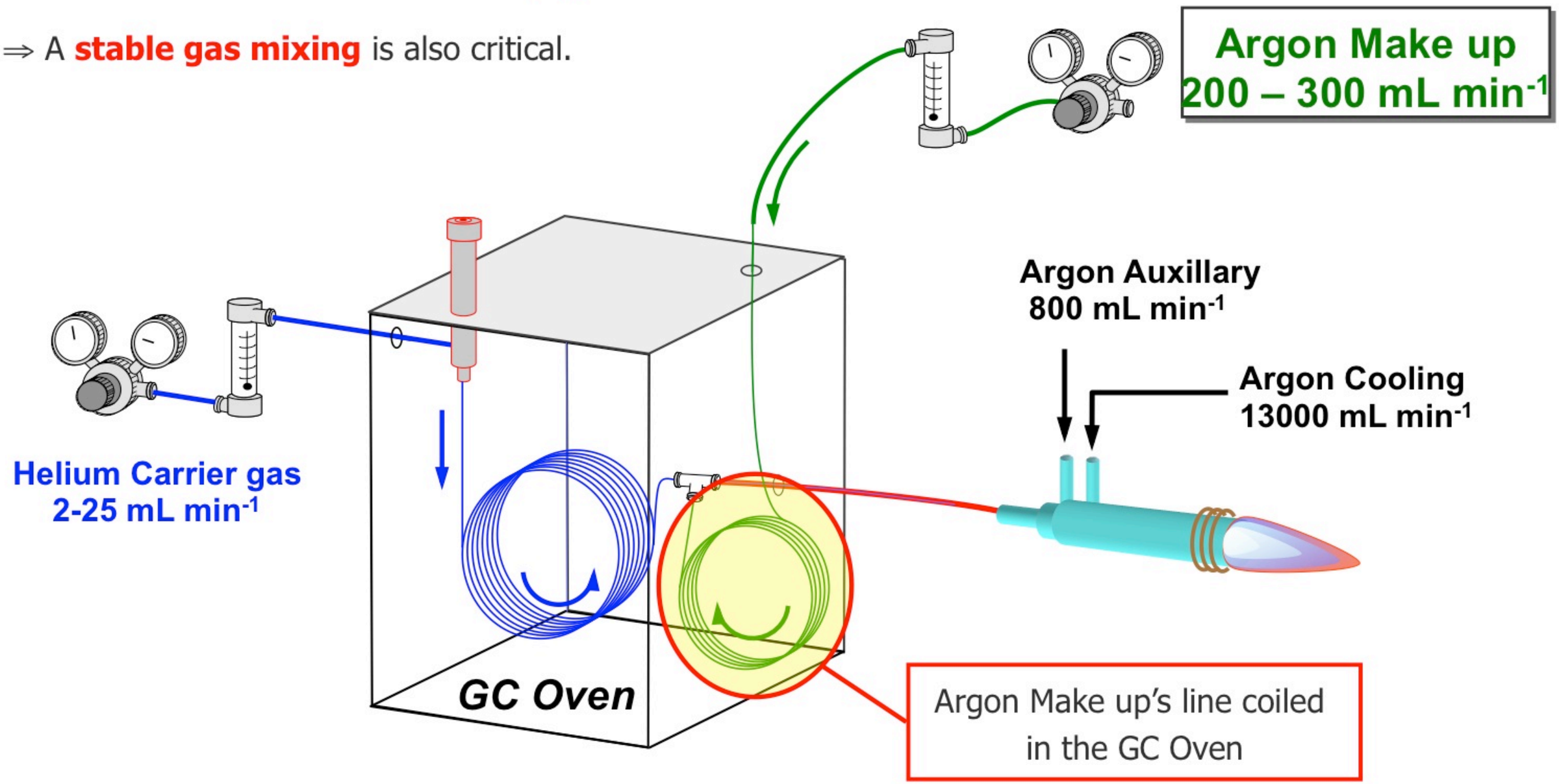
Principle:

Objective n°1: Efficient introduction of the GC carrier gas in the Plasma

ICPMS Argon flows act as a mechanical barrier for the GC's analytes introduction in the plasma.

⇒ The addition of an Argon **Make up gas** is essential.

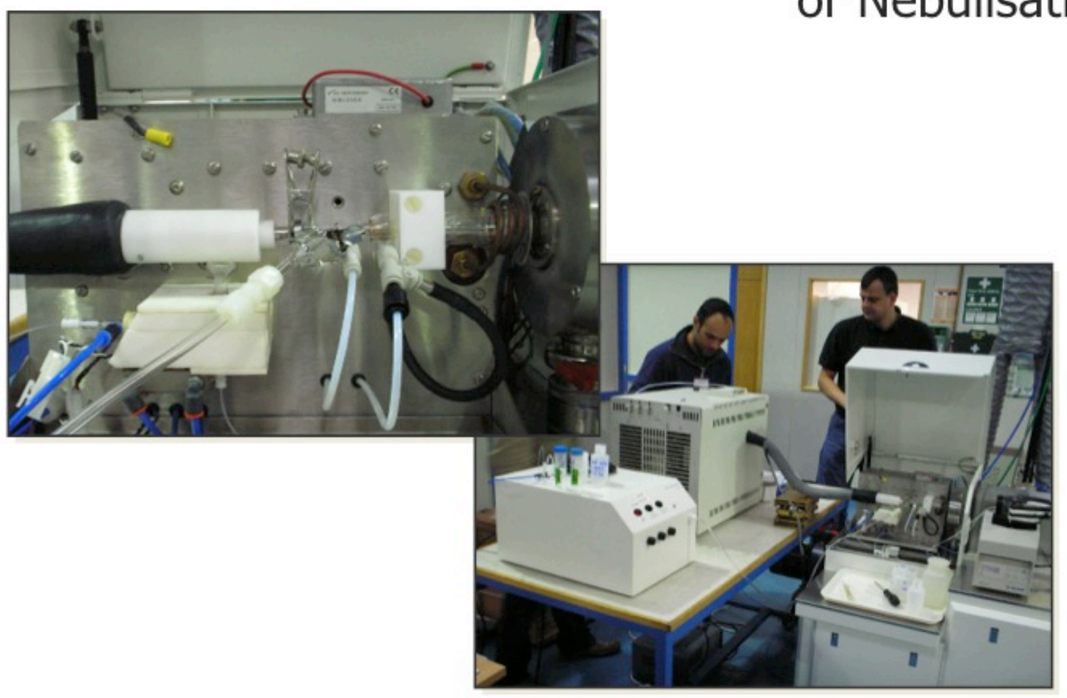
⇒ A **stable gas mixing** is also critical.



Principle:

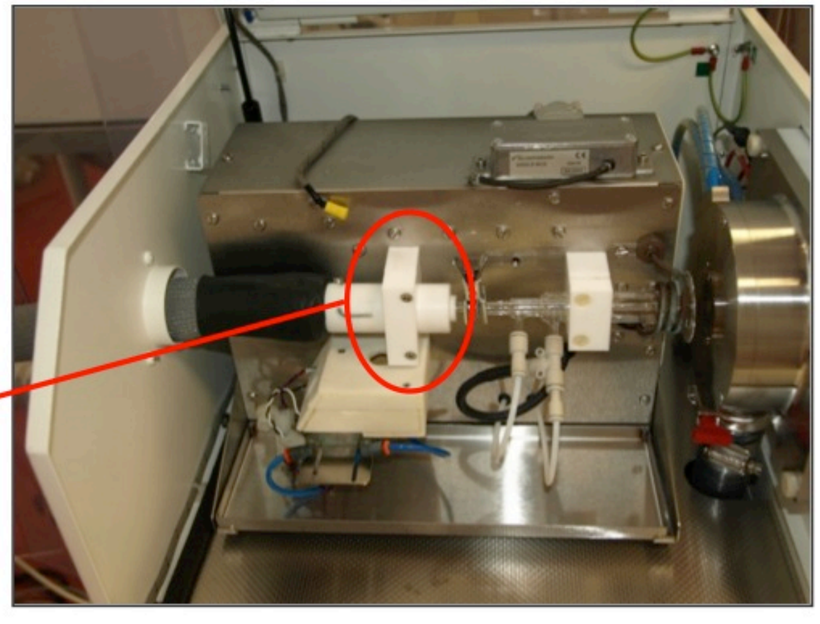
Objective n°2: Dual sample introduction system via the double inlet torch

- Simultaneous connection of a Desolvating nebuliser system
  or Nebulisation spray chamber



⇒ Continuous internal standard introduction
- Bias correction
- Signal optimization
- Signal stability monitoring

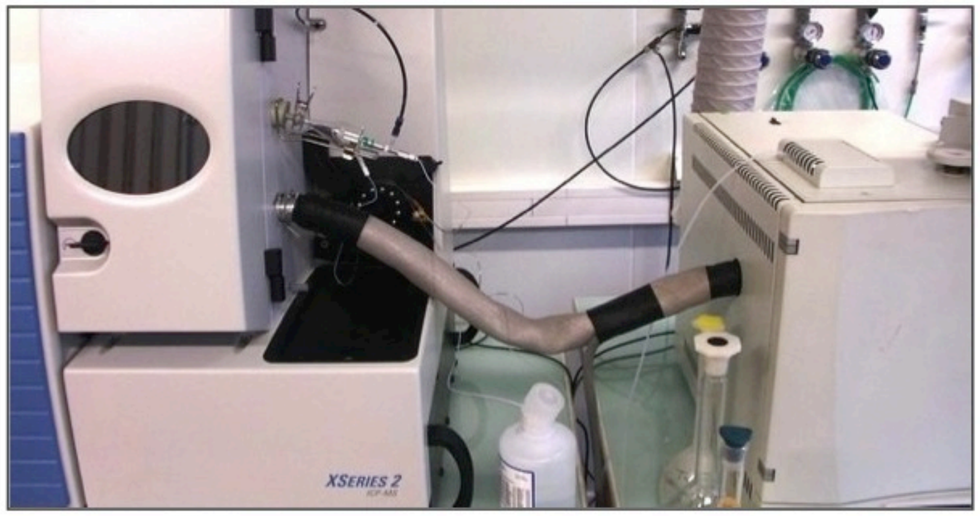
- Transfer line's **holder** is necessary to not disturb the **torch positioning**



Commercial GC-ICPMS Interfaces

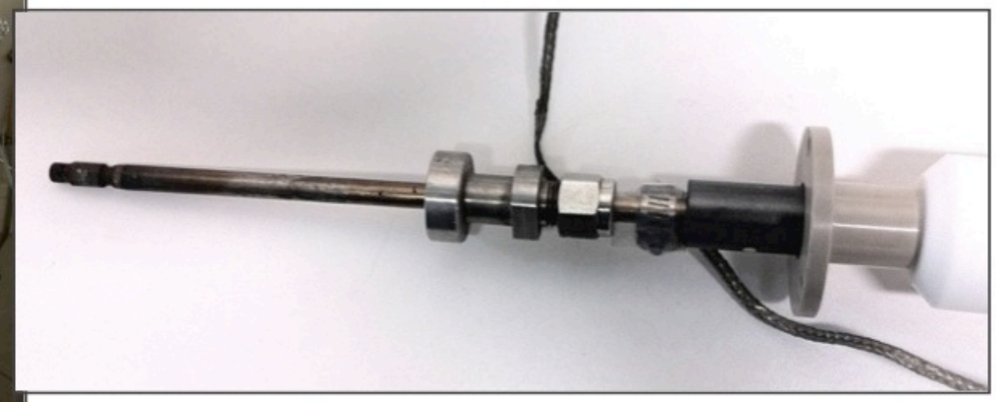
Thermo SCIENTIFIC

T max = 300°C



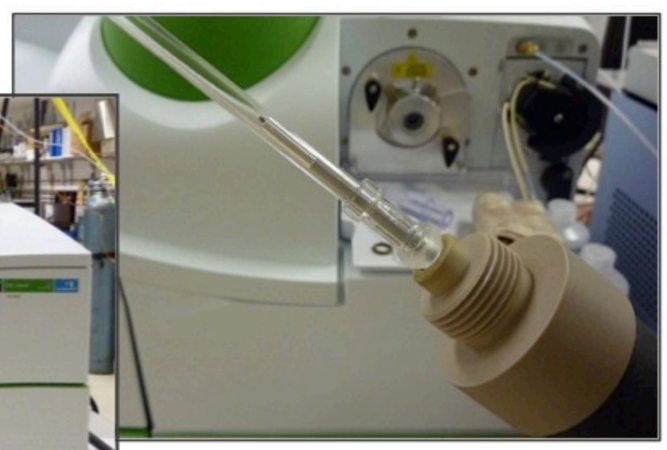
Agilent Technologies

T max = 300°C



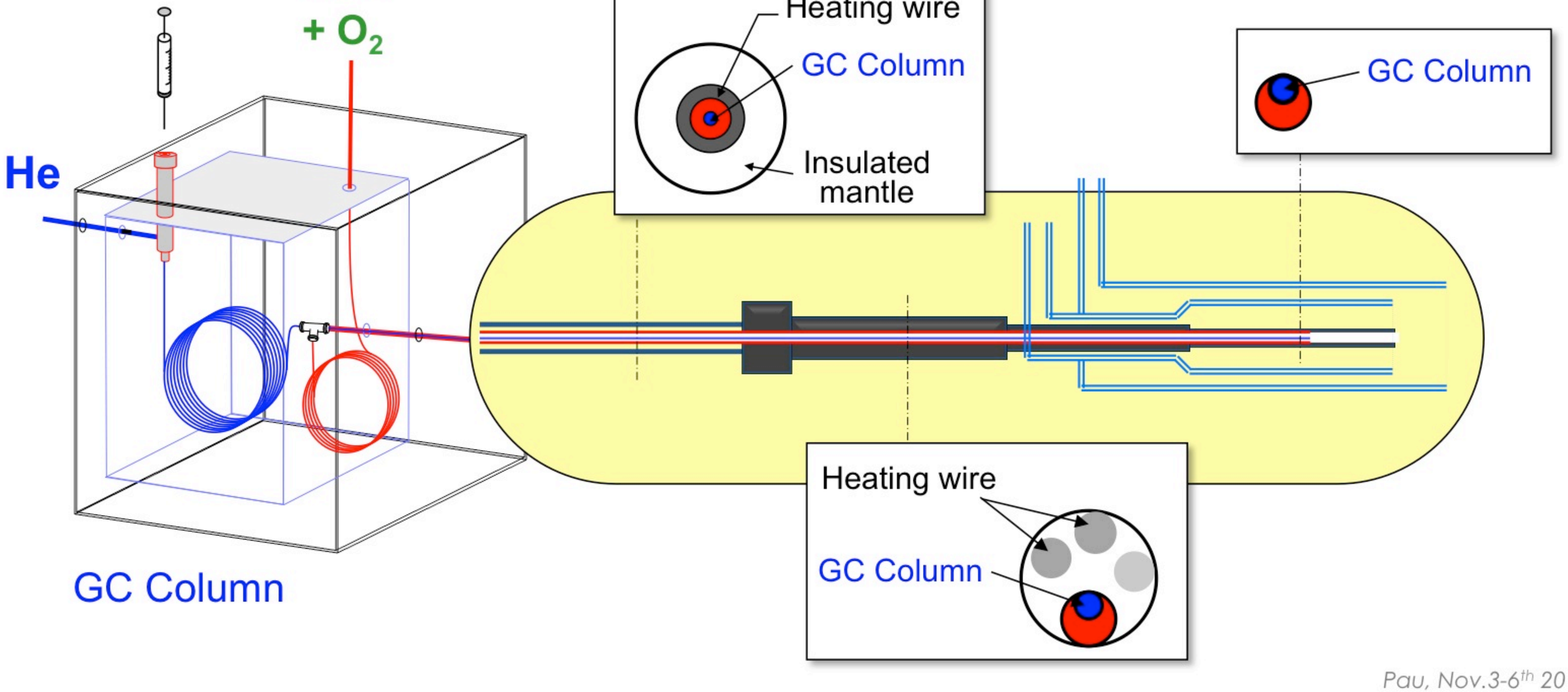
PerkinElmer

T max = 300°C



Dry Plasma interface :

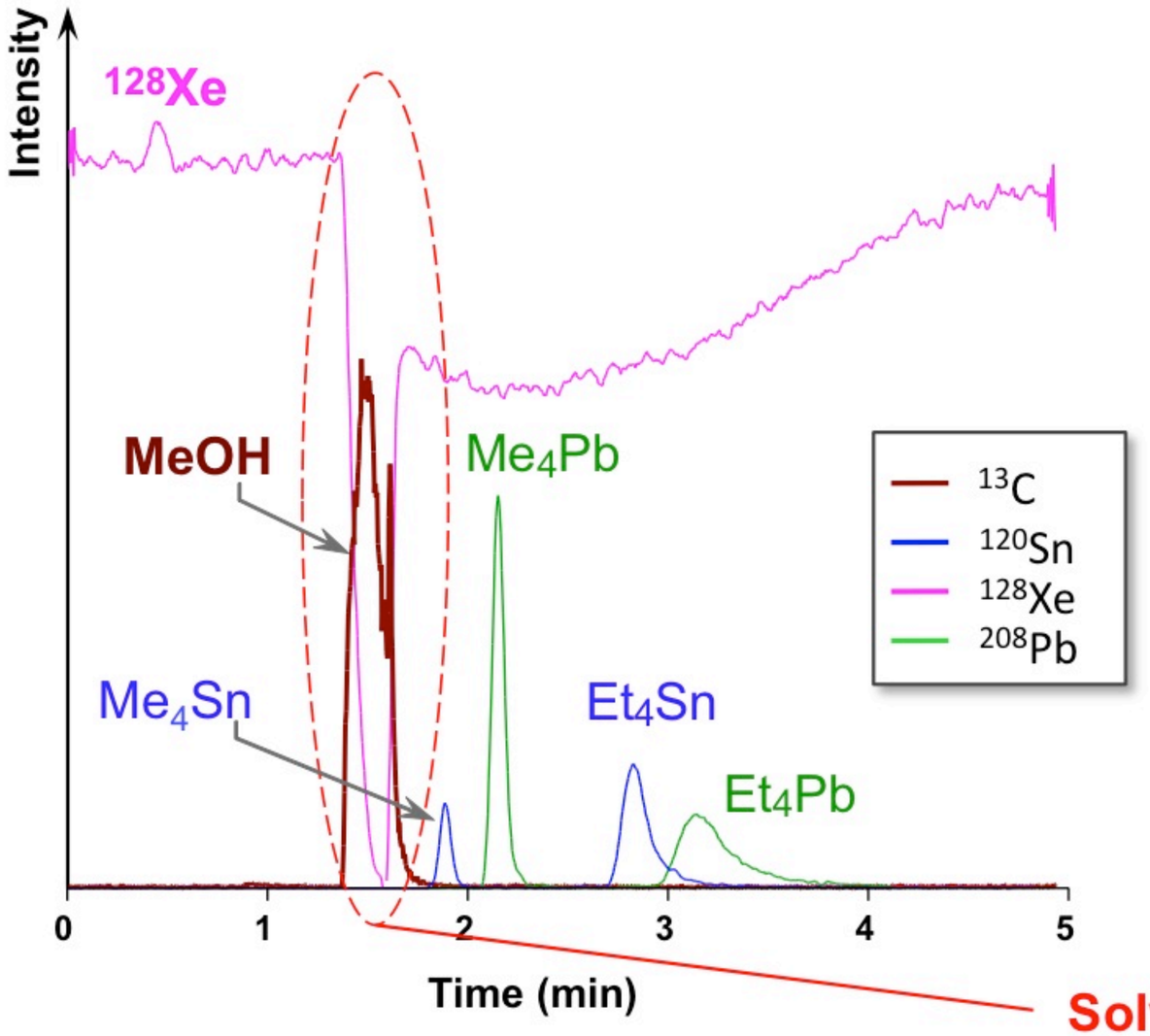
⇒ Need for O_2 introduction to avoid carbon deposits
⇒ Need for a gaseous Internal standard for signal optimization



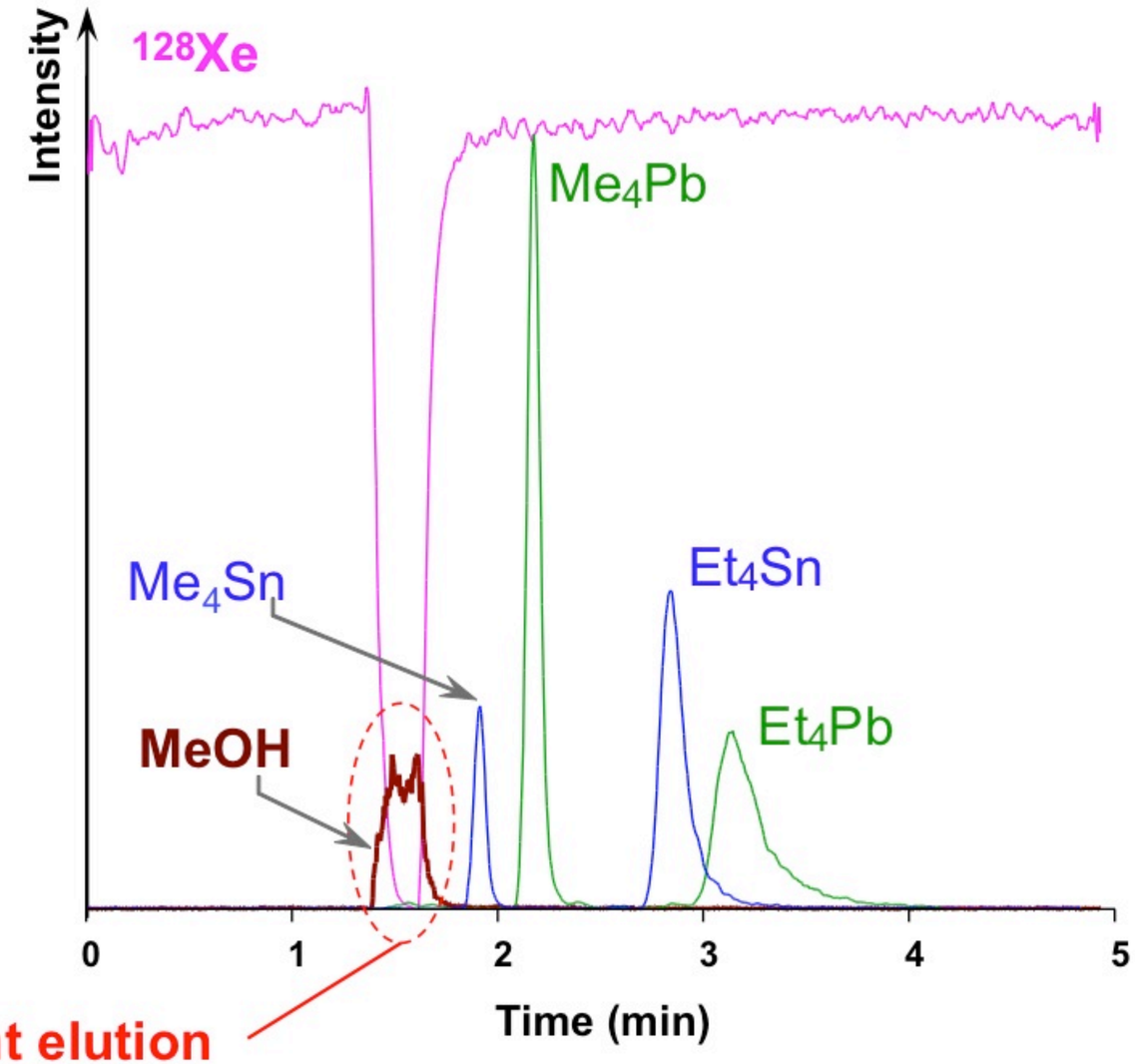
Example of potential plasma disturbance during GC solvent elution :
2µL of gaseous organometallic standards in methanol

⇒ **Solvent effect** reduced by addition of O_2

Without O_2 addition



With O_2 addition

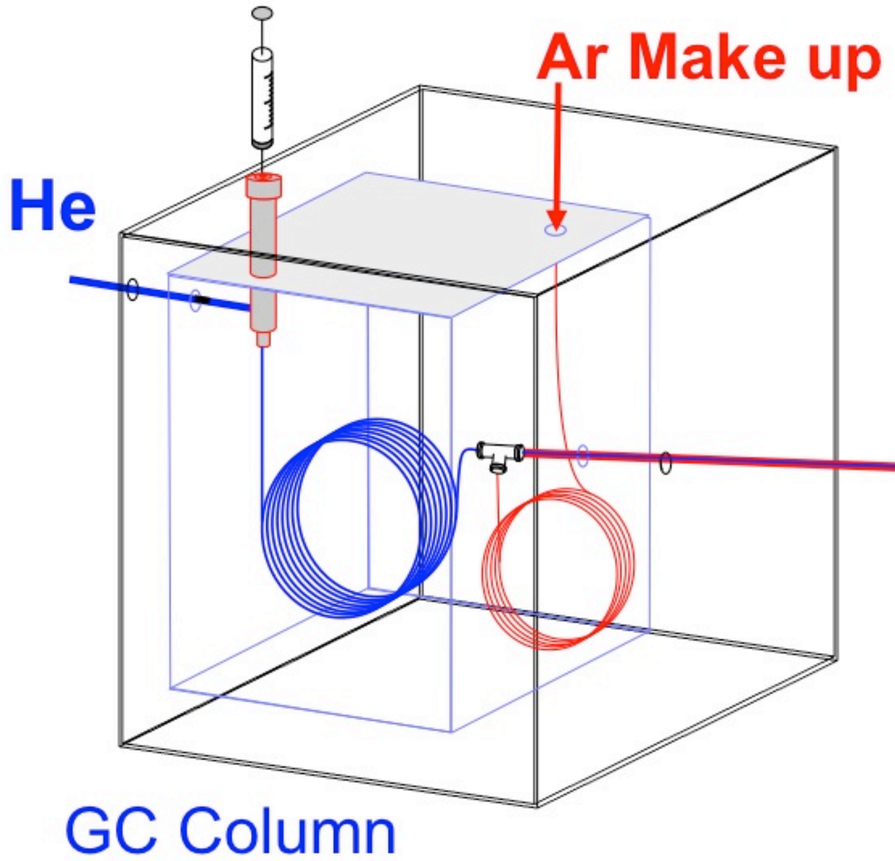


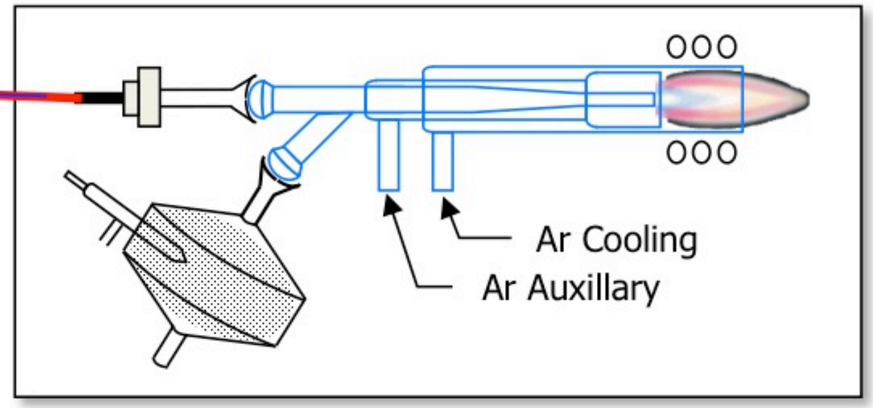
Solvent elution

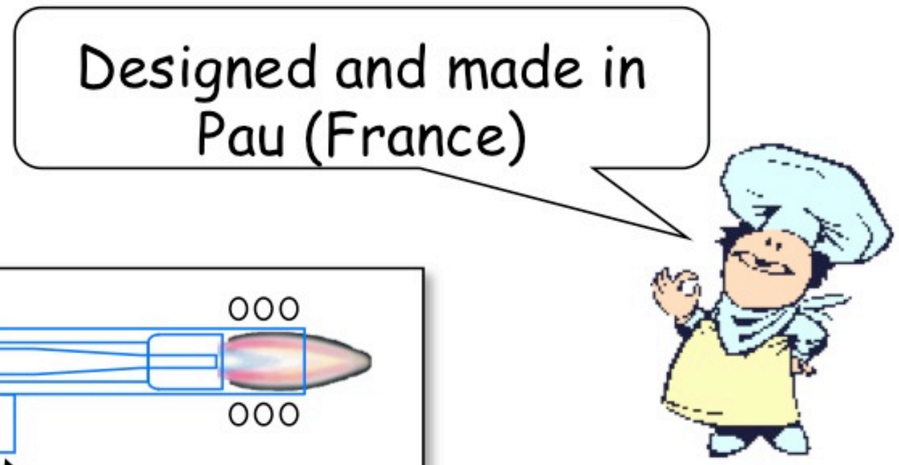
Wet Plasma interface :

Simultaneous introduction via a double inlet torch: - GC flow in the torch axis

- Liquid aerosol with a 45° angle







Avantages: *Continuous nebulization of Standard aqueous (or desolvated) solution*

⇒ Online signal optimization

Dissolved O_2 avoid any Carbon deposit

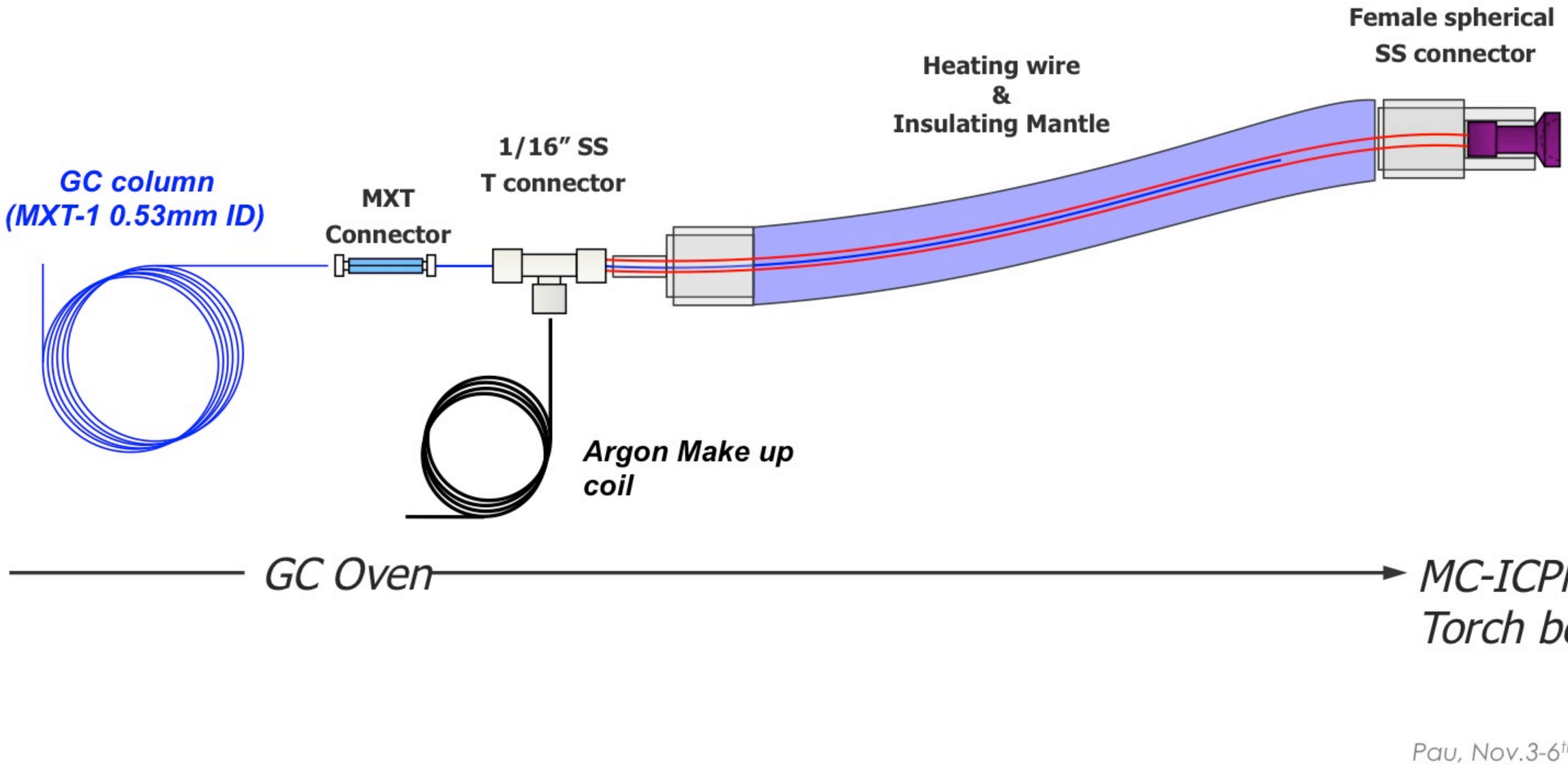
Signal stability control, mass bias correction

Semi-Quantification with internal liquid standard (± 30%)

Wet or dry plasma configuration

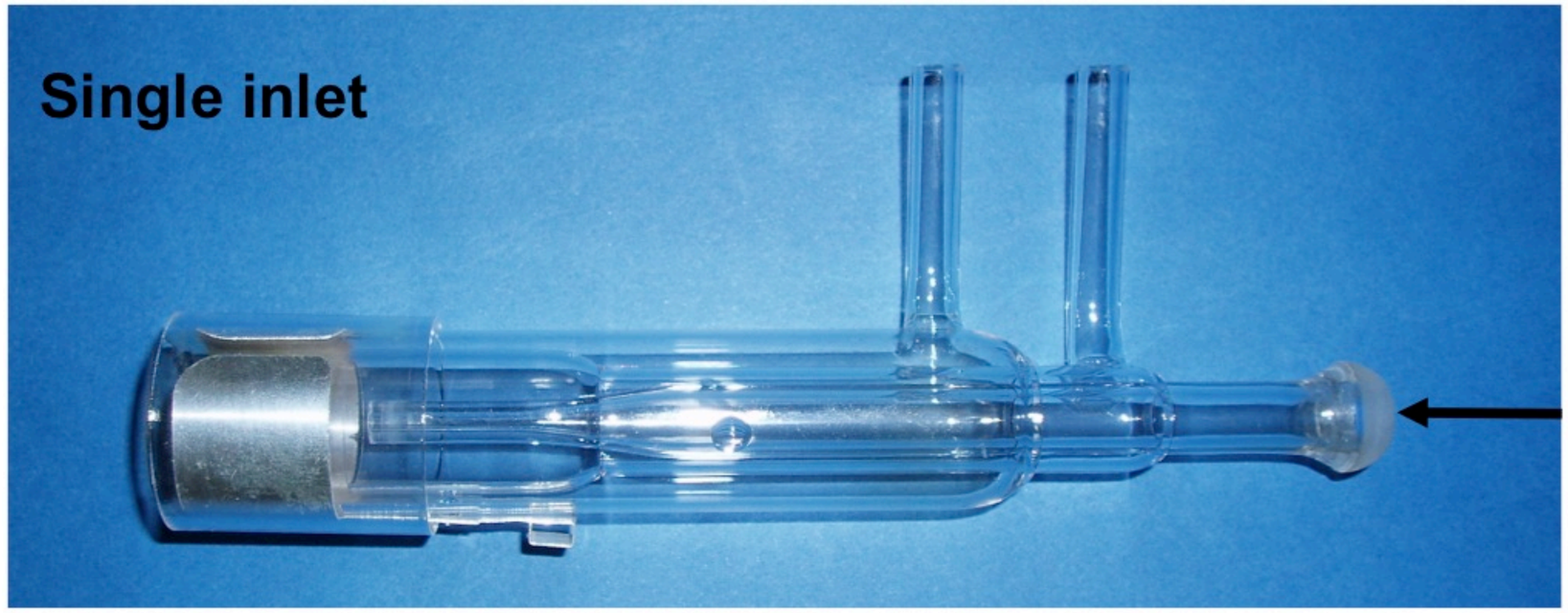
Dry/Wet Plasma interface :

- **Outer tubing: 1/16" passivated Stainless Steel tubing** *(Siltek / Silcosteel, Restek)*
- **Inner tubing: 0.28 mm ID MXT1 Stainless Steel Guard column** *(Restek)*
- **GC column connection: passivated & low dead volume connector** *(Restek)*
- **1/16" Stainless Steel tubing**



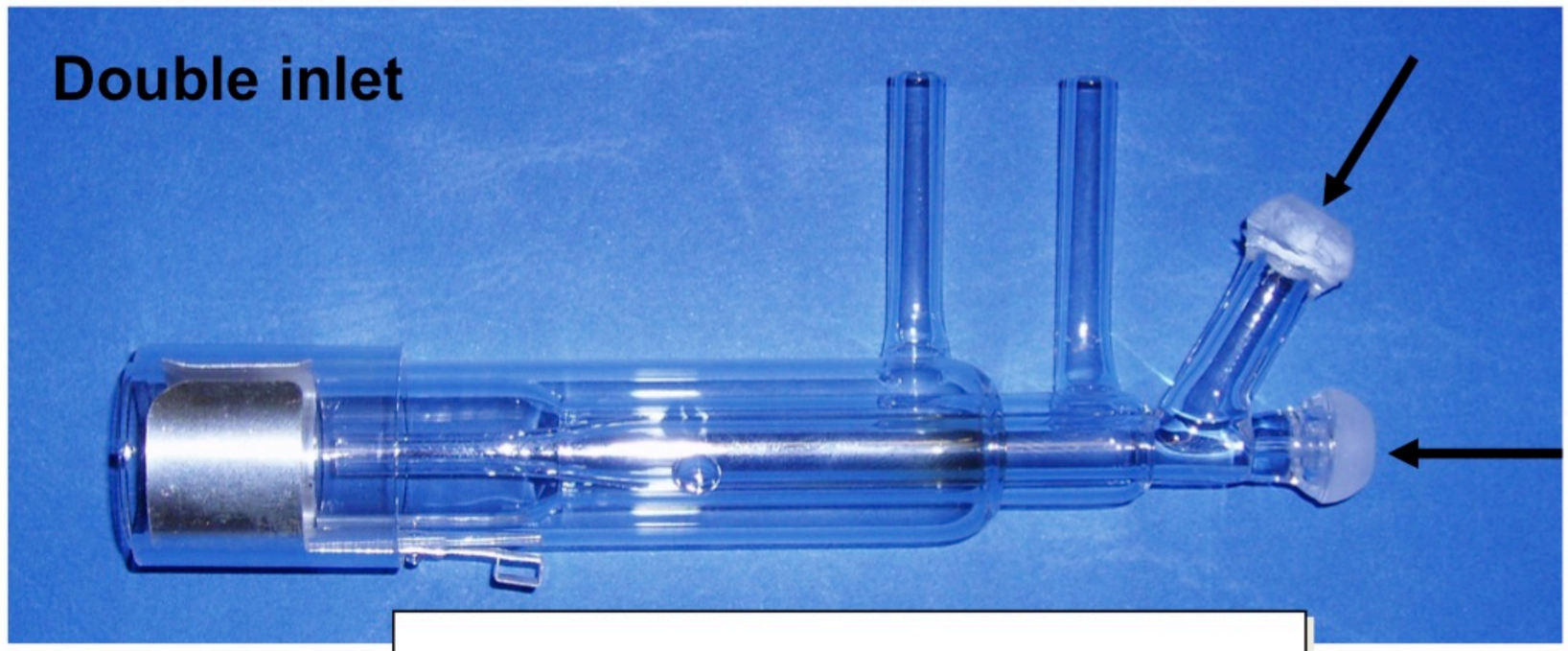
Torch design for dual-inlet introduction

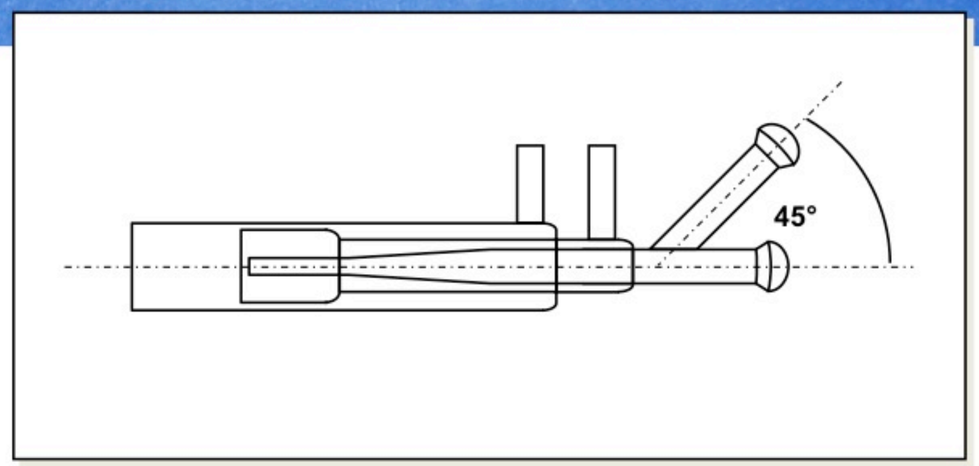
Standard torch
X7 et XII



Torch for GC/ ICPMS X7 et XII

(collaboration LCABIE / Thermo)

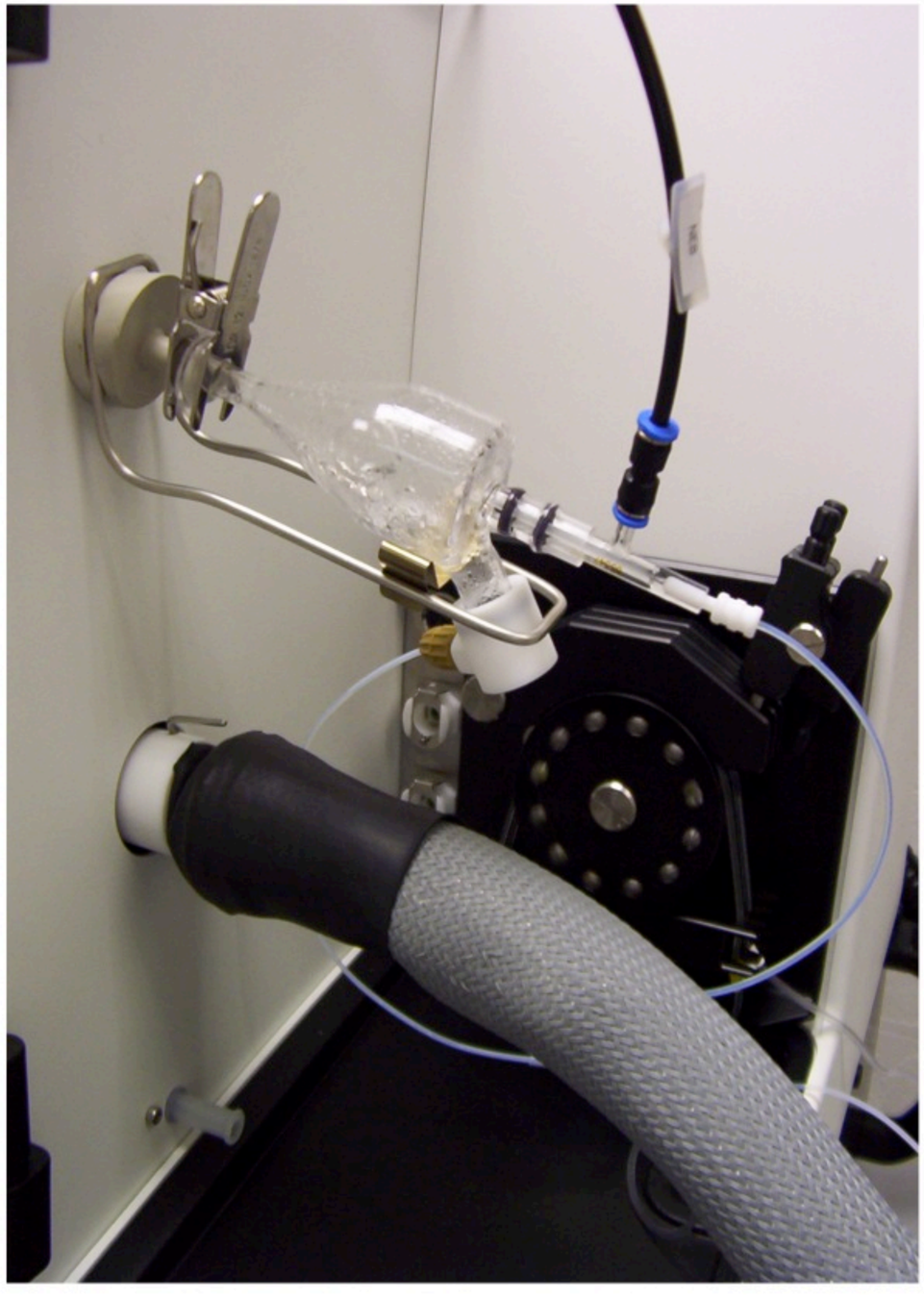




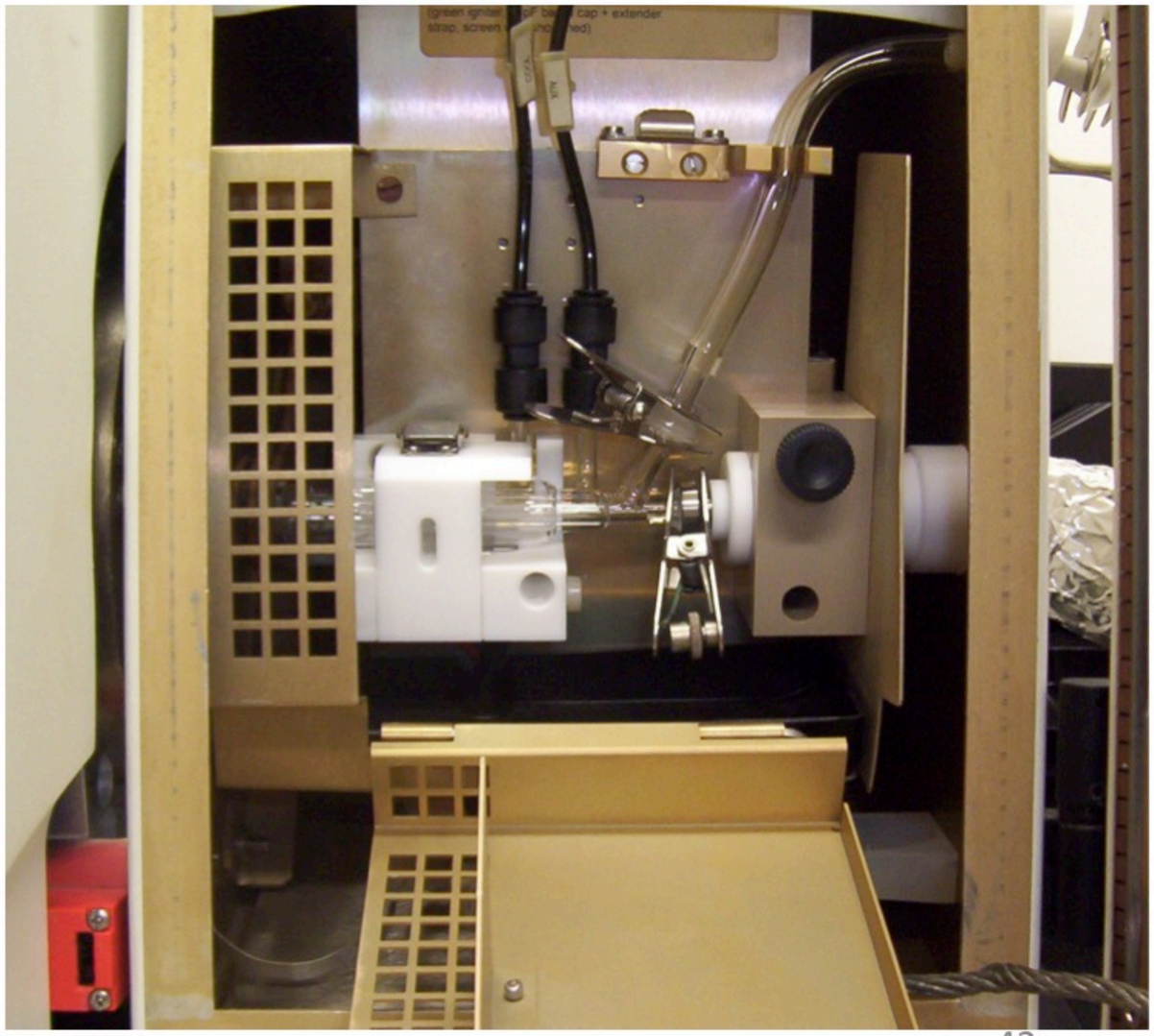
Thermo GC-ICP-MS

XSeries ICP-MS and Focus GC

- Three legged GC-ICP-MS torch
- Autotune & Performance; reporting with aqueous solution
- Gas or solution analyses without reconfiguring the interface
- On-line addition of aqueous internal standards
- Robust wet plasma conditions for GC-ICP-MS analysis



Realisation modified torch box with GC coupling



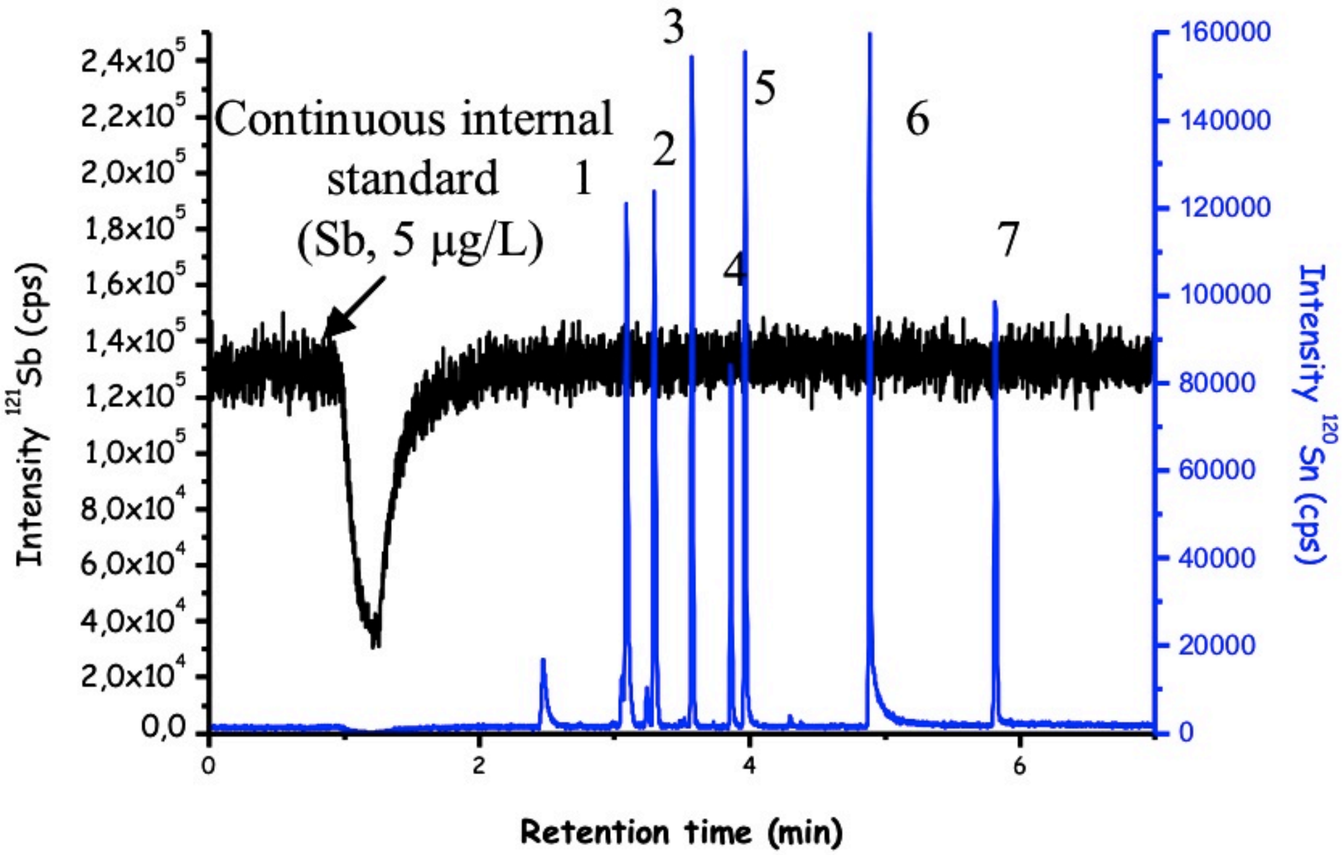
GC-ICPMS coupling: GC transfer line

GC

Injector	Splitless, 250 °C
Column	DB 1, 30 m, i.d. 0,32 mm, df 0,25 µm
Carrier gas	Helium, 4 mL/min
GC program	80°C / ramp 50°C/min / 280°C

ICP/MS

Power	1250 W
Gas flows	Plasma gas : 15 l/min Auxiliary Gas : 1 L/min Blend gas : 0,85 l/min + Xe
Internal standard	Xenon 50 ppmv in Ar, 5 mL/min
mode	Time Resolved Analysis



GC-ICP-MS determination of 7 organotin compounds (1: MBT, 2:TPrT, 3: DBT, 4: MPhT, 5: TBT, 6: DPhT, 7: TPhT)

Analytical performance

Limits of detection < 10 fg for organo-tin compounds

Example of **Operating Conditions** for Hg species analysis – Wet Plasma

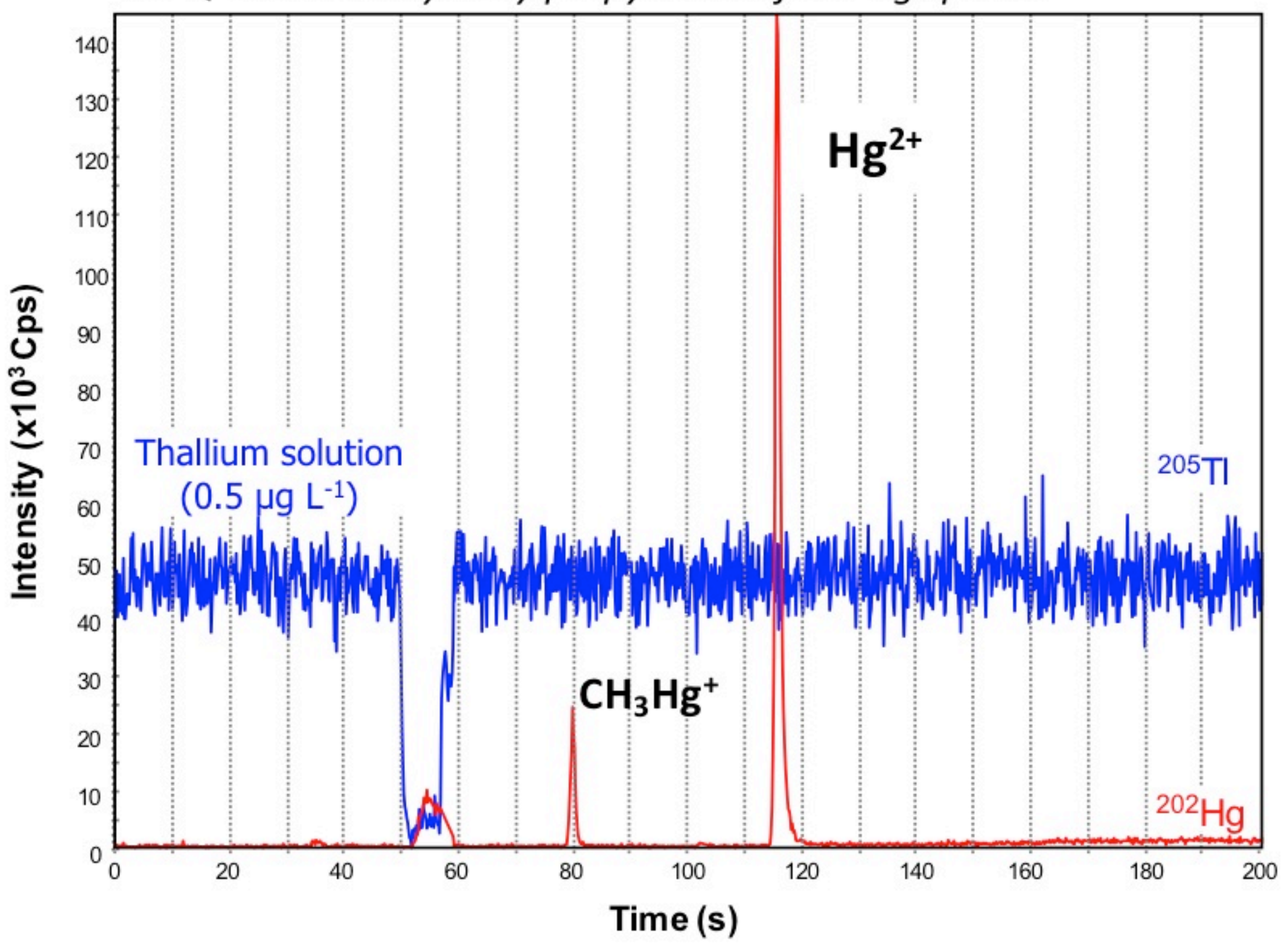
GC Parameters

Injector	**Splitless; 250°C**
Column	**MXT-1; 30m lgth; 0.53mm ID d_f 1µm**
Carrier gas	**Helium, 25 mL min^{-1}**
Make up gas	**Argon, 280 mL min^{-1}**
GC program	**60°C/2min – 40°C/min – 250°C**

ICP-MS parameters

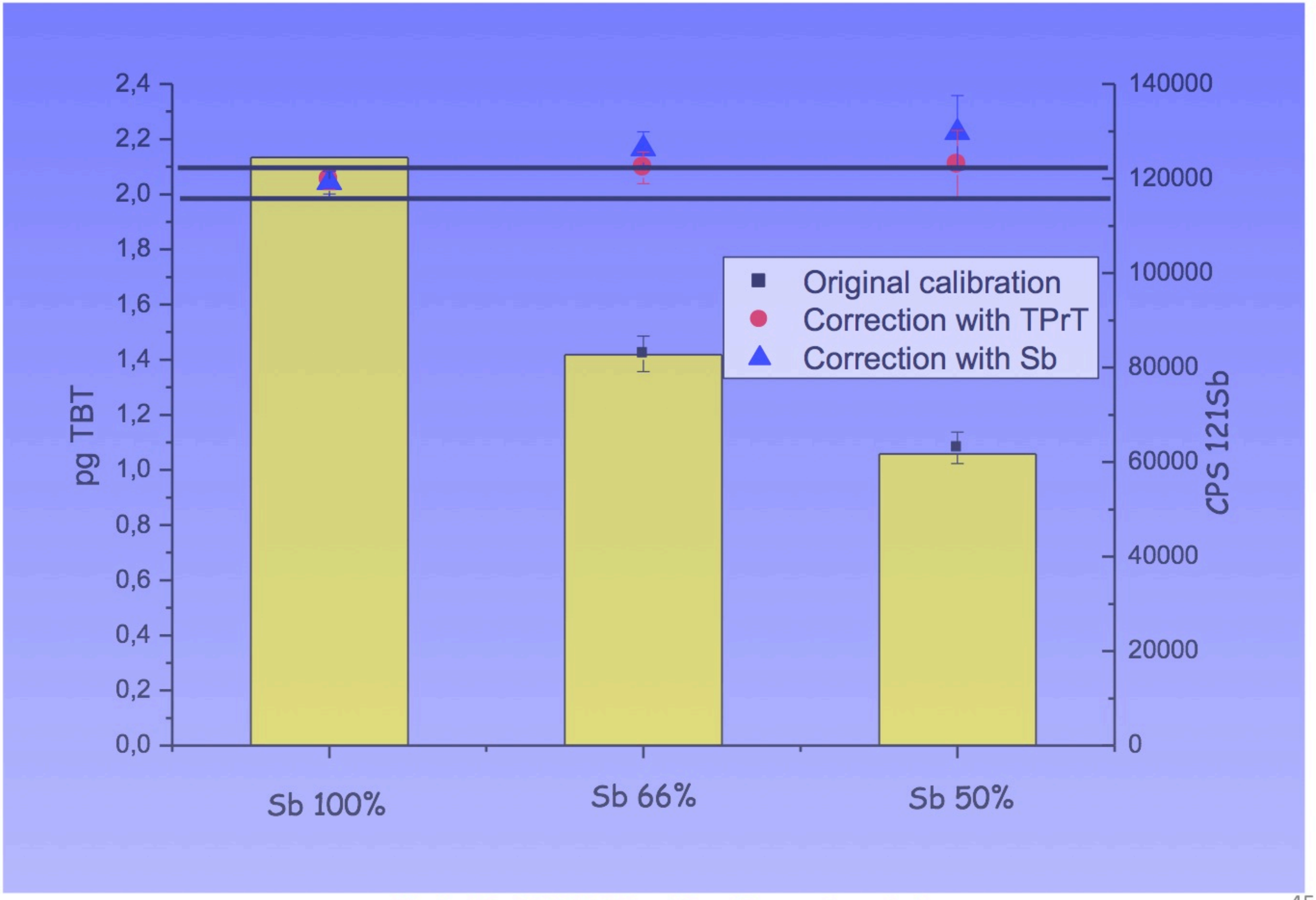
Power	**1270 W**
Gas Flow	**Cooling: 14 L min^{-1} Auxiliary: 0.8 L min^{-1} Nebulizer: 0.5 L min^{-1}**
Spray Chamber	**Cyclonic**
Nebulizer	**Meinhard concentric, self aspirating**
Isotopes	**^{198}Hg ; ^{199}Hg ; ^{200}Hg ; ^{201}Hg ; ^{202}Hg ; ^{203}Tl; ^{205}Tl**

GC-Q-ICPMS analysis by propylation of the Hg species



Drift correction with internal standards

Instrument sensitivity changed by « de-tuning » the extraction lens

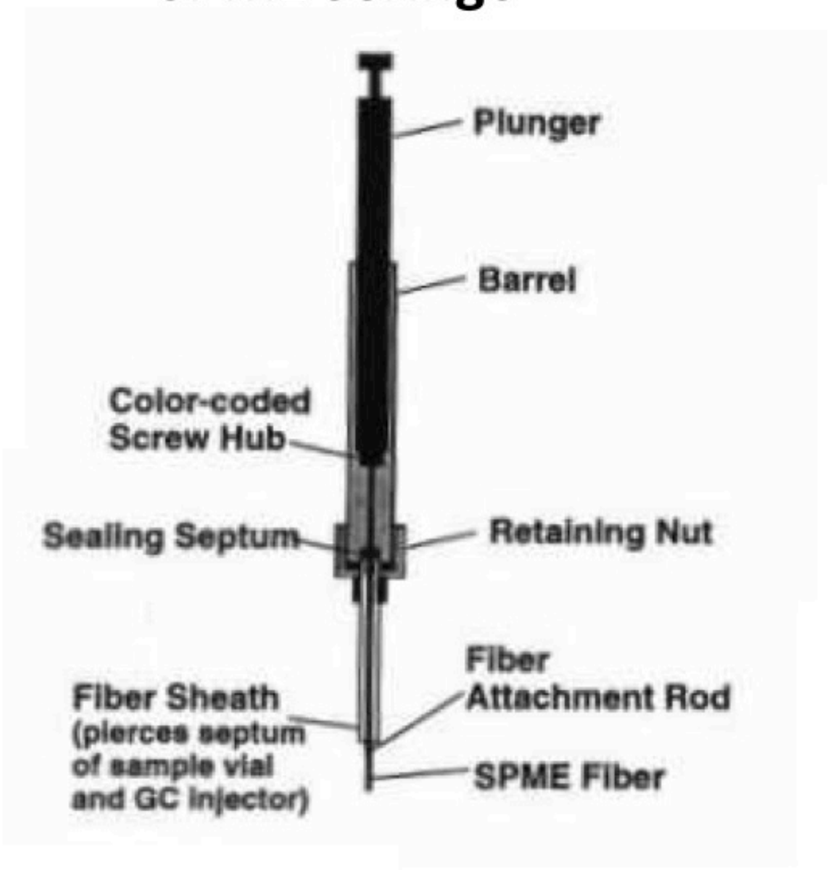


Data for TBT, injection 2 pg absolute

SPME/GC/ICPMS

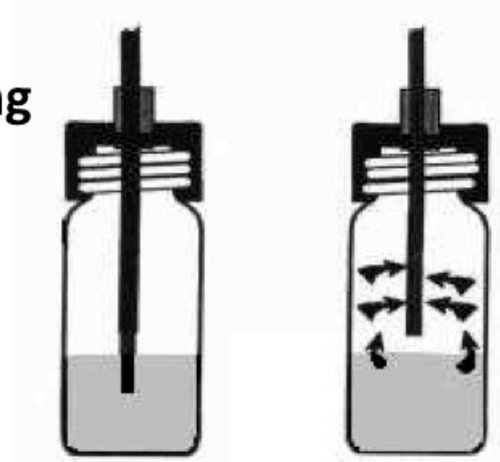
Definition: SPME (Solid Phase Micro Extraction) is a preconcentration technique, allowing analyte preconcentration on a fiber prior injection into a GC.
The extraction yield (preconcentration) is not total as a result of an equilibrium between the fiber, the solution un the head space. It depends on the matrix, the species, the volume of the solution, the fiber type, the temperature and the mixing of the solution.

SPME seringe



Preconcentration principles

Direct sampling



Head space sampling

SPME/GC/ICPMS

The $GC_{capillaire}$/ICPMS interface is similar as shown previously. A special liner must however be used

<u>Advantages</u> :

- Very low limits of detection (pg/l organoSn)
- No solvent
- No sovent injection into the detector
- Can be automated (analyse *on-line*)

<u>Drawbacks</u>:

- Equilibrium time (10-40 min) depending on the species and the sampling mode (direct or head space)
- Internal standard or standard addition are mandatory to conterbalance matrix effects that likely affect the extraction yield.
- Poor reproducibility

SPME/GC/ICPMS

Organo-Sn

Pretreatment

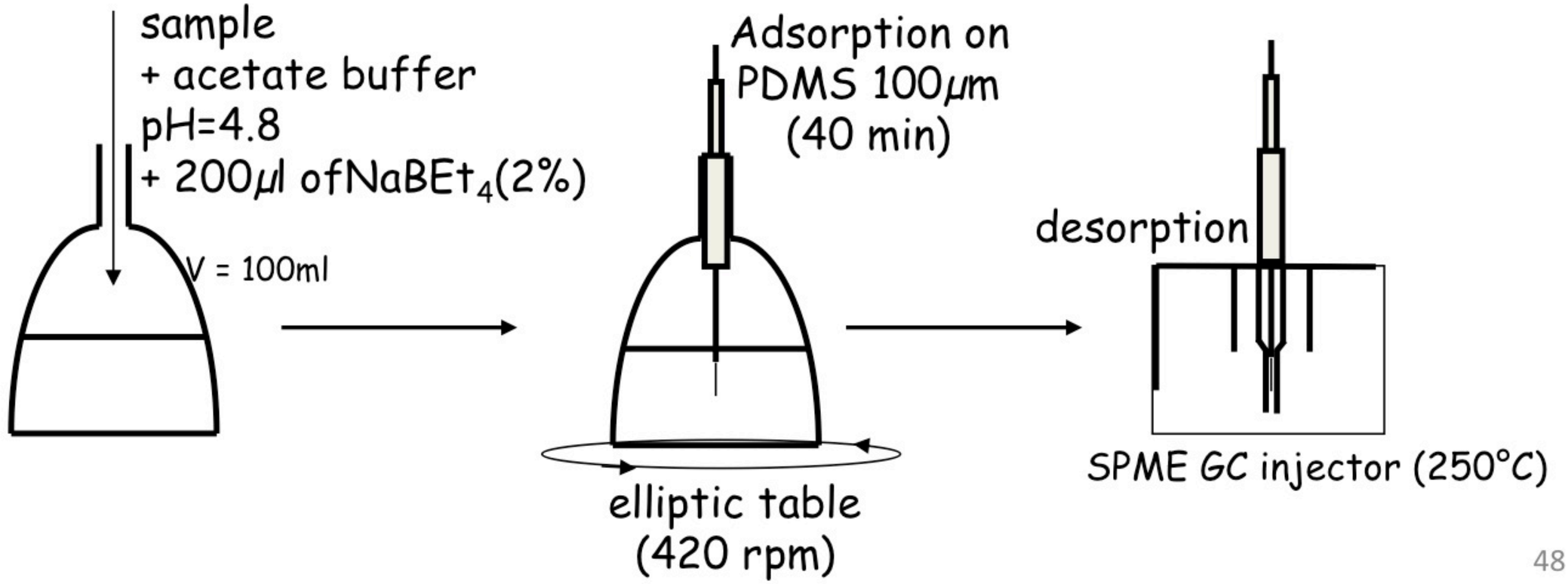
Aqueous matrix
filtration

Solid matrix
extraction

CH_3COOH
Sédiment, sludge

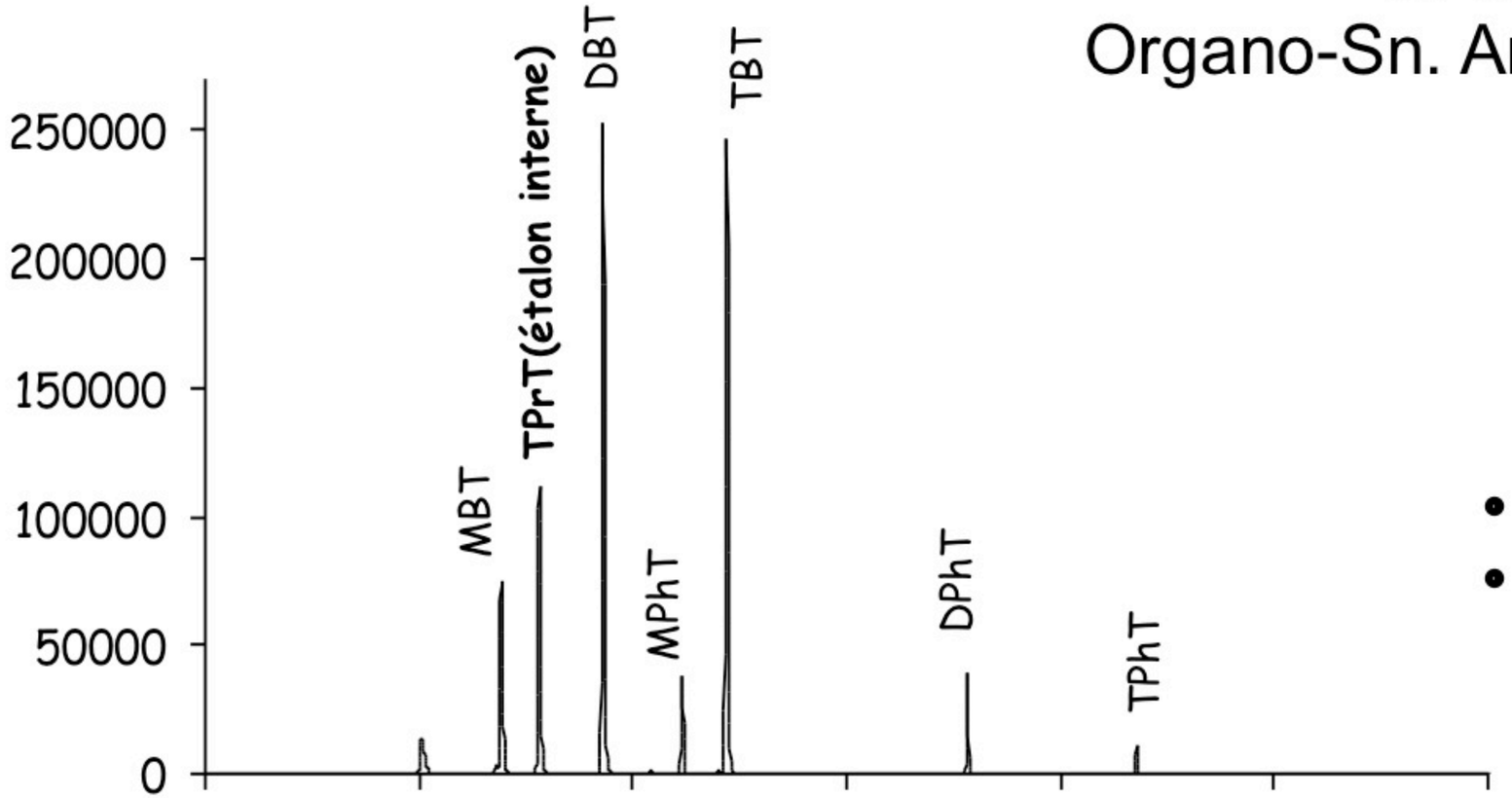
HCl/MeOH (0.1M)
biological tissue

derivatization



SPME/GC/ICPMS

Organo-Sn. Analytical performances



- injection of 50 ng(Sn)/l
- ^{120}Sn

	MBT	**DBT**	**TBT**	**MPhT**	**DPhT**	**TPhT**
Limites de détection pg(Sn)/l	2	0.7	0.6	4	6	20
Repétabilité (%)	7	7	3	10	14	20
Linéarité ng(Sn)/l	De la limite de détection à 400					

Isotope dilution /GC/ICP/MS

Objectives

- High precision and high accuracy analysis
- Monitor reactivity and transfert of a given species in the environment (Biogeochemical cycles understanding)

Principle

- It consists in adding a specific isotope incorporated in the same chemical form than the species to be analysed.
  e.g : add $^{201}HgMe^{+}$ to quantify $HgMe^{+}$

Advantages : the isotopically enriched chemical species behave similarly than the analytes... Then :

- The analytical bias related to sample preparation (some molecular degradation, adsorption, etc...) are counterbalanced
- Matrix effects occuring into the ICPMS (and sample introduction) are also corrected.

Sample preparation for fish tissue
(case of Methyl mercury determination)

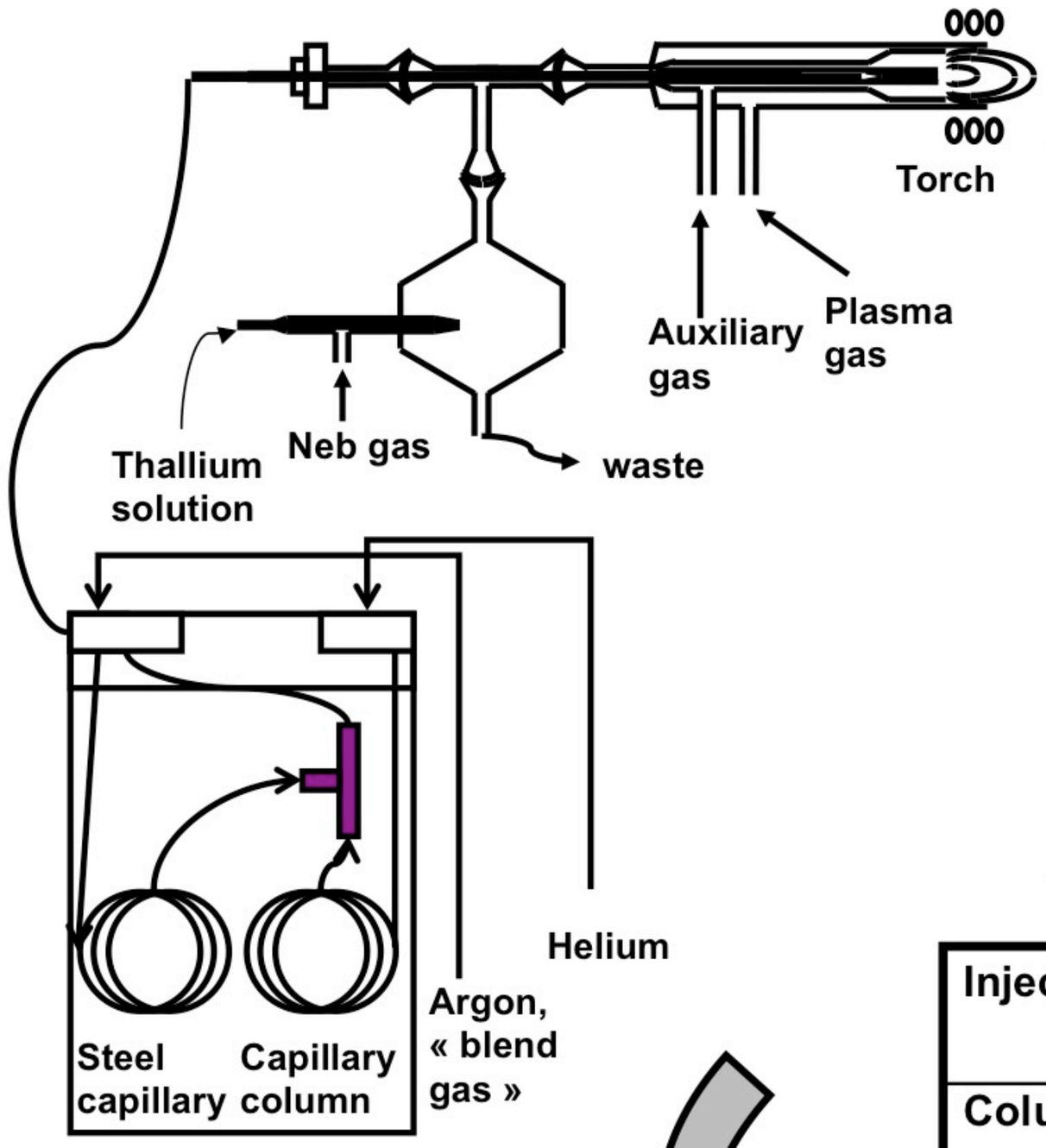
$^{201}HgMe^{+}$ synthesis

Spike of $^{201}HgMe^{+}$ into the sample

Microwave digestion

Derivatization/Extraction:

- **acetate buffer 0.1 M, pH=4.0**
- **$NaBEt_4$ (0.06 % w/w)**
- **Shaken 5 min.**
- **Centrifugation 2500rpm; 5min.**



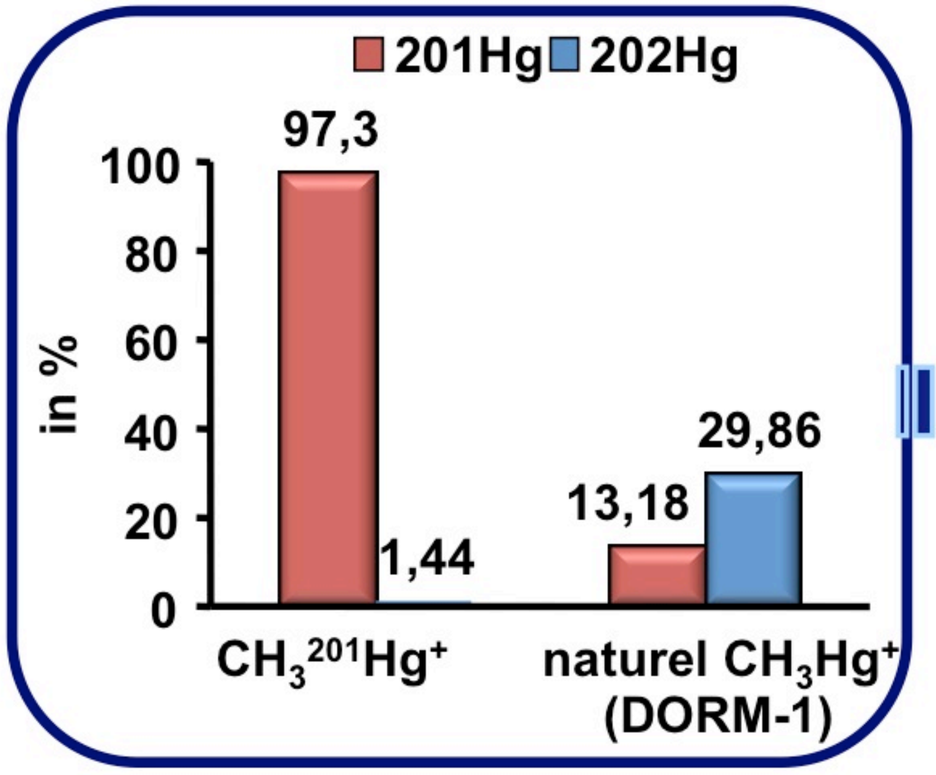
ICP-MS Parameters

Power	1250 W
Gas Flow	Plasma : 15 L/min Auxiliary : 1 L/min Nebulizer : 0.6 L/min
Spray Chamber	Cyclonic
Nebulizer	Meinhard concentric, self aspirating
Isotopes	^{198}Hg ; ^{199}Hg ; ^{200}Hg ; ^{201}Hg ; ^{202}Hg ; ^{204}Hg ; ^{126}Xe ; ^{203}Tl ; ^{205}Tl
Dwell time	Hg isotopes : 20 ms Xe and Tl : 5 ms

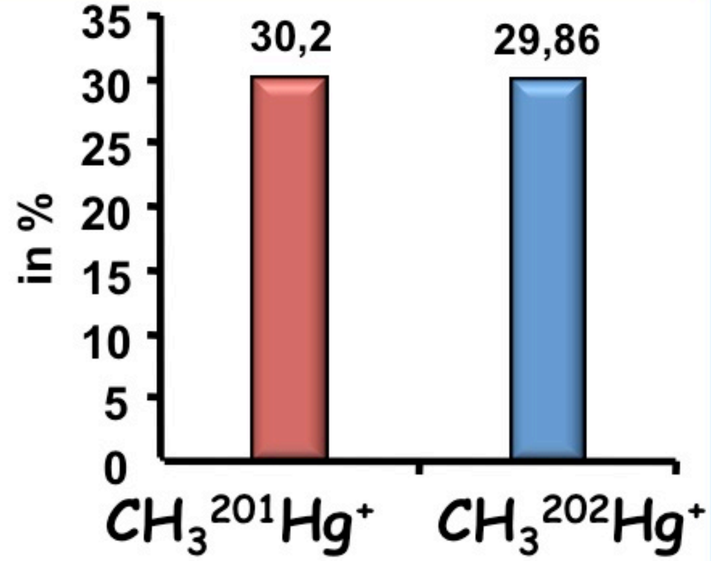
GC Parameters

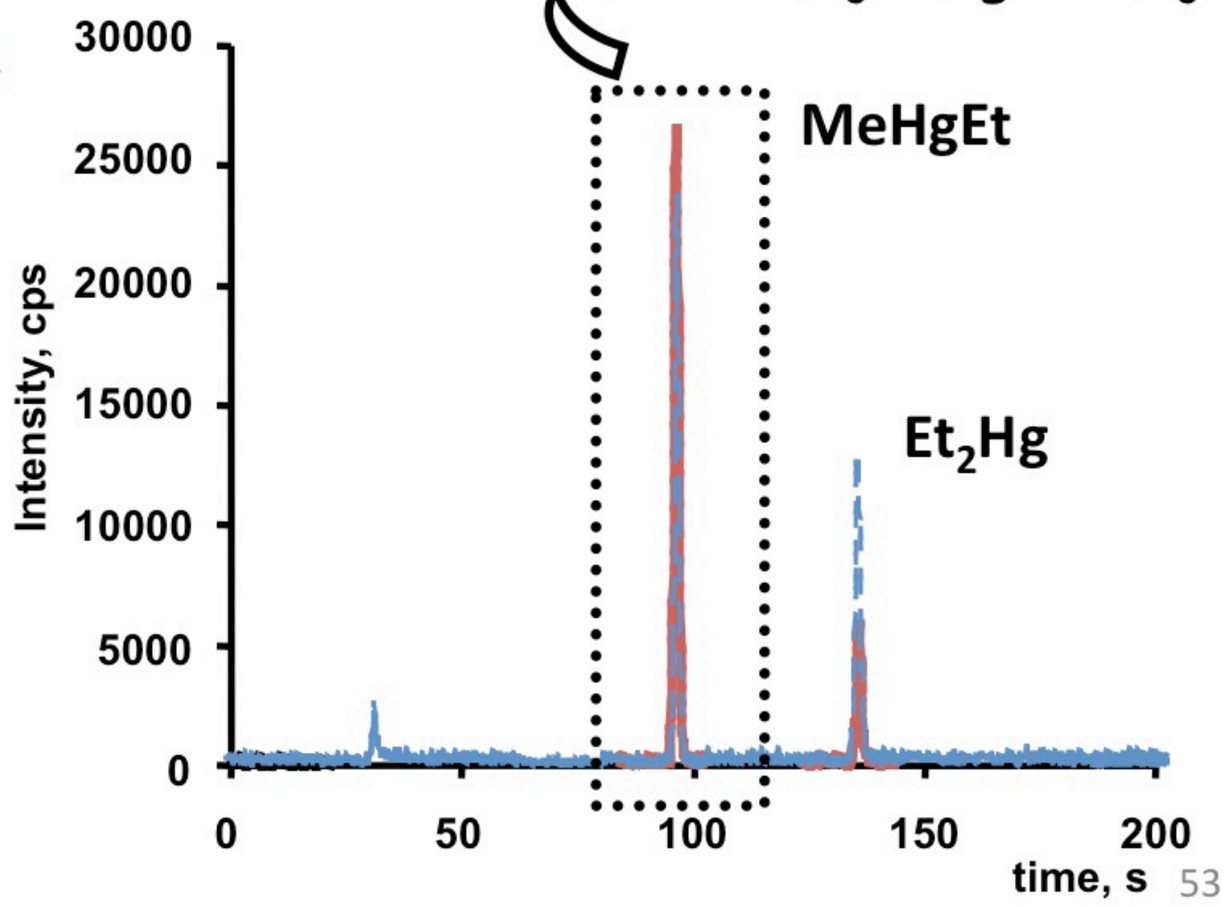
Injector	Splitless, 200 °C
Column	MXT Silcosteel ; 30 m ; i.d. 0.53 mm ; d_f 1.0 µm
Carrier gas	Helium, 25 mL/min
Make up gas	Argon, 300 mL/min
GC program	60 °C/ramp 50 °C/min/180 °C

Determination du methylmercure par dilution isotopique : DORM-1



DORM -1 après ajout $CH_3{}^{201}Hg^+$





Determination of methylmercury by speciated isotope dilution: DORM-1

Isotope dilution equation

$$c = \frac{c' w' A_r (RY' - X')}{w A_r' (X - RY)}$$

(‘) « enriched spike »

w and w’: weight of solution
c and c’: concentration
Ar and Ar’: relative atomic mass of the element
X and X’: isotope abundance (atom %) isotope 201
Y and Y’: isotope abundance (atom %) isotope 202
R = isotope ratio ($^{201}Hg/^{202}Hg$)

Critical parameters:
isotope ratio (R) and spike concentration (c’)

	Concentration of CH_3Hg^+ (µg/g)	
	Determined (n=5)	Certified
DORM-1	0.712 ± 0.036	0.731 ± 0.060

Analytical performance

1. **Precision of 0.9 % for $^{202}Hg/^{201}Hg$ (50 pg $MeHg^+$, n= 5)**

2. **Accuracy of 0.2 % for $^{202}Hg/^{201}Hg$ (50 pg $MeHg^+$, n= 5)**

3. **Absolute detection limits (as Hg) in the fg range**

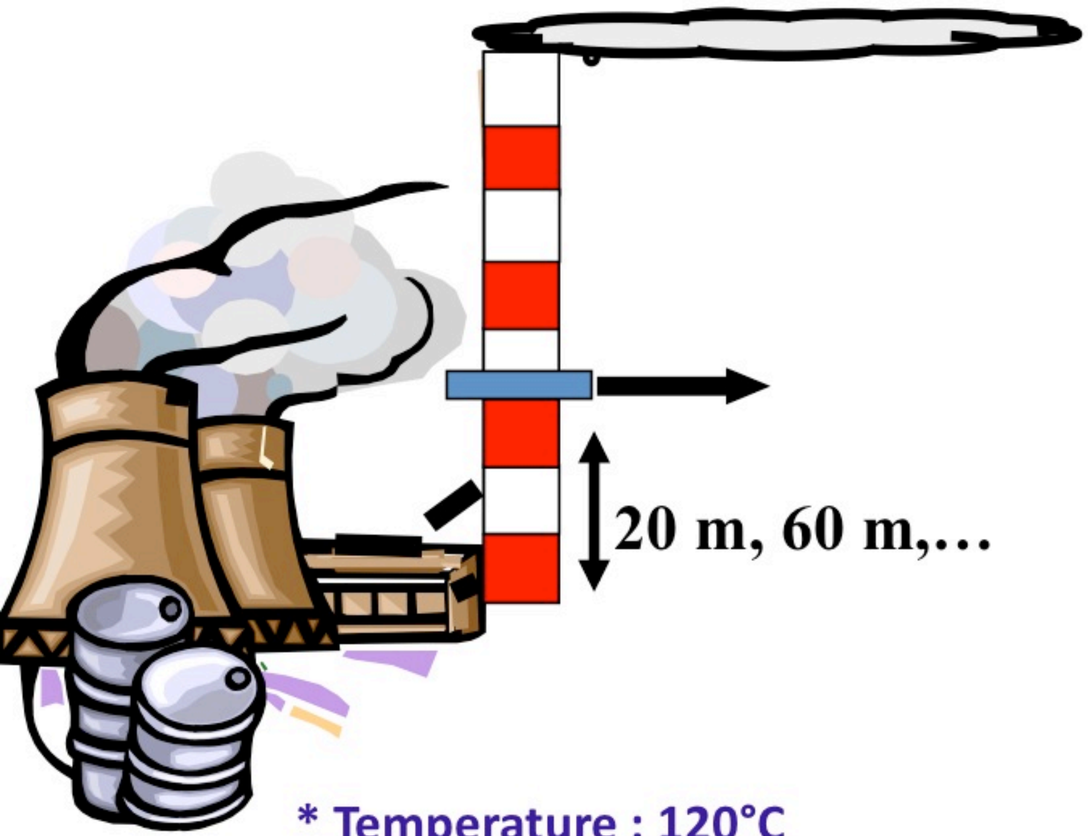
^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{204}Hg
250	194	192	220	143	596

Mass bias correction ($^{205}Tl/^{203}Tl$)

Detector dead time (35 ns)

Volatile metal speciation in the atmosphere (natural or industrial chimney stack).

Speciation in industrial chimney stack



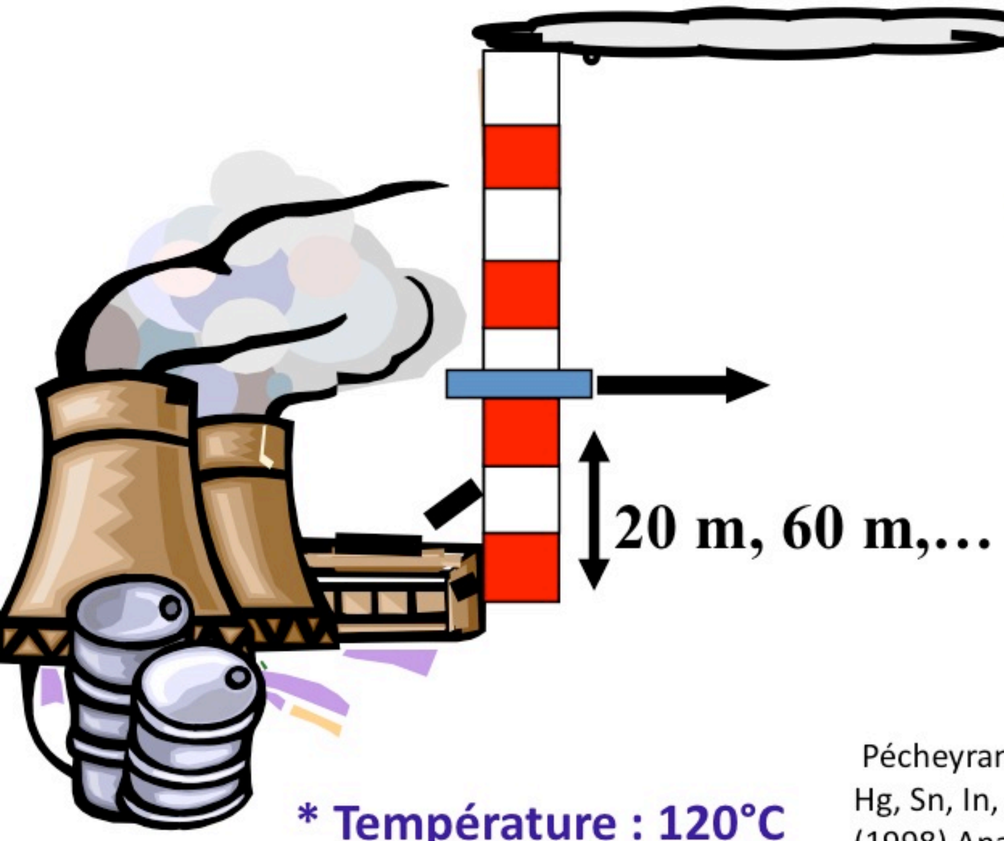
* Temperature : 120°C
* CO_2 = 11 % (vol.)
* H_2O = 8 %
* SO_2 = 800 ppm

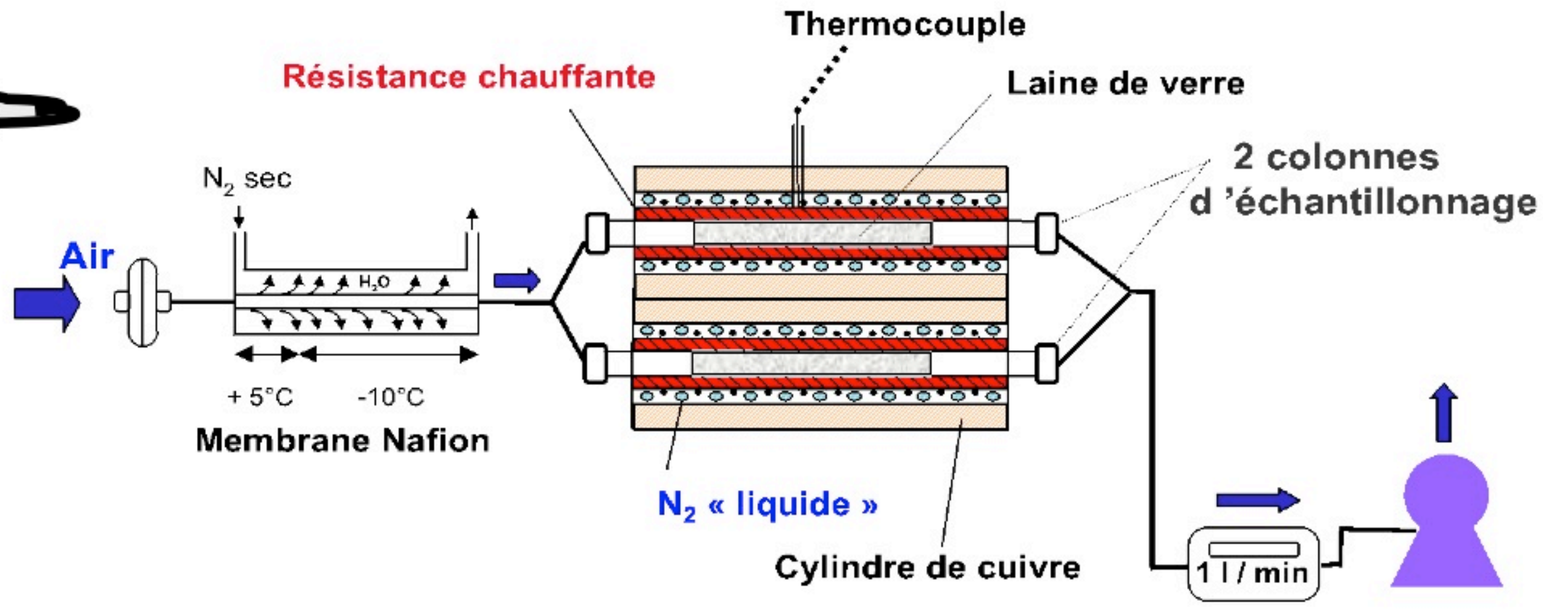
Which chemical species in the gas phase (not associated to particles)?

Which amounts?

Sampling device for speciation in the atmosphere

An universal cryo-sampler





Filtre 0.1 µm	Piège à eau -10°C	Piège cryogénique -180°C	Régulateur de débit	Pompe

* Température : 120°C
* CO_2 = 11 % (vol.)
* H_2O = 8 %
* SO_2 = 800 ppm

Pécheyran, C., Quetel, C.R., Martin Lecuyer, F.M., Donard, O.F.X. Simultaneous Determination of Volatile Metal (Pb, Hg, Sn, In, Ga) and Nonmetal Species (Se, P, As) in Different Atmospheres by Cryofocusing and Detection by ICPMS (1998) Analytical Chemistry, 70 (13), pp. 2639-2645.

Pécheyran, C., Lalère, B., Donard, O.F.X., Volatile metal and metalloid species (Pb, Hg, Se) in a European urban atmosphere (Bordeaux, France)(2000) Environmental Science and Technology, 34 (1), pp. 27-32.

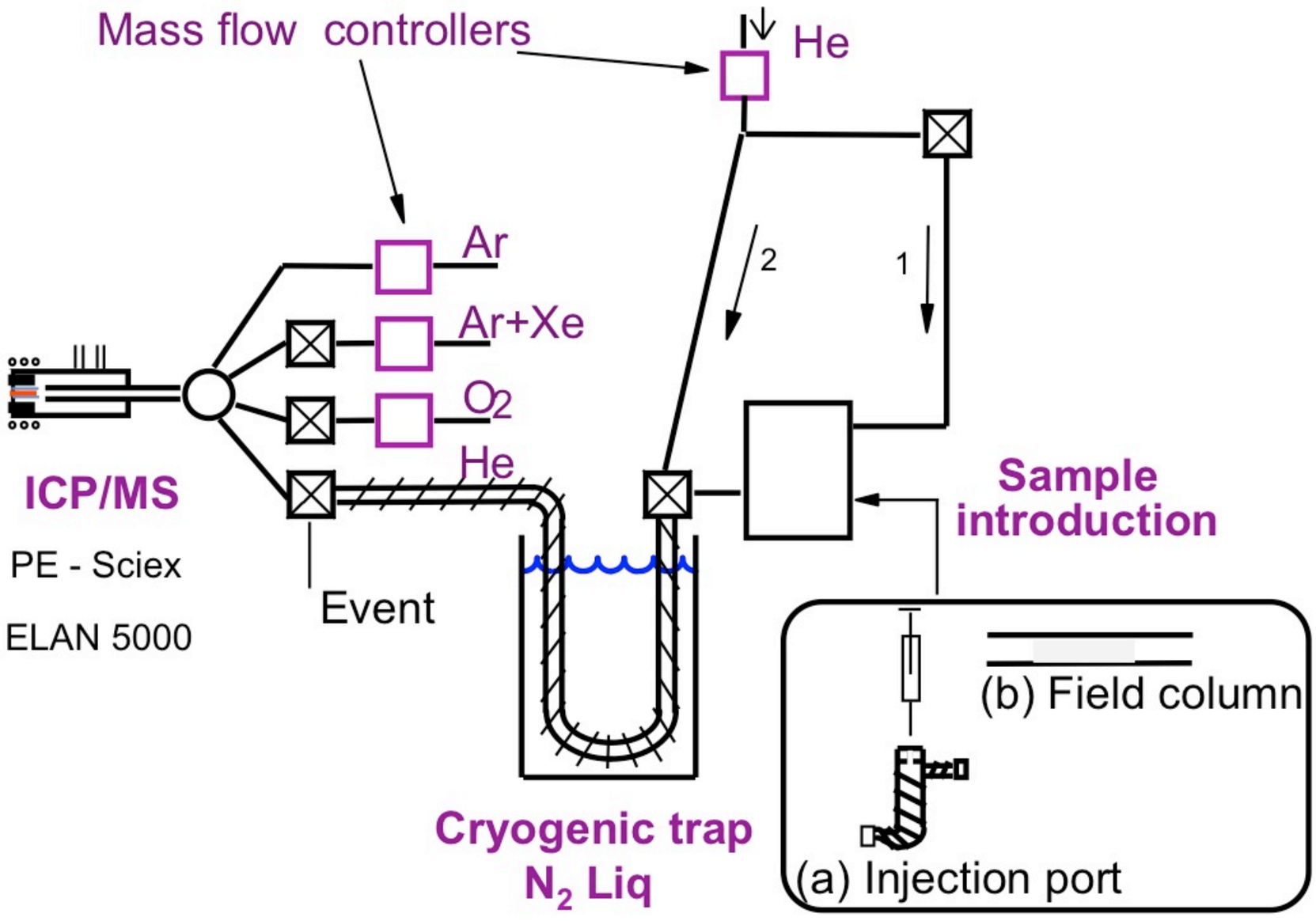
Pavageau, M.-P., Pécheyran, C., Krupp, E.M., Morin, A., Donard, O.F.X.
Volatile metal species in coal combustion flue gas (2002) Environmental Science and Technology, 36 (7), pp. 1561-1573.

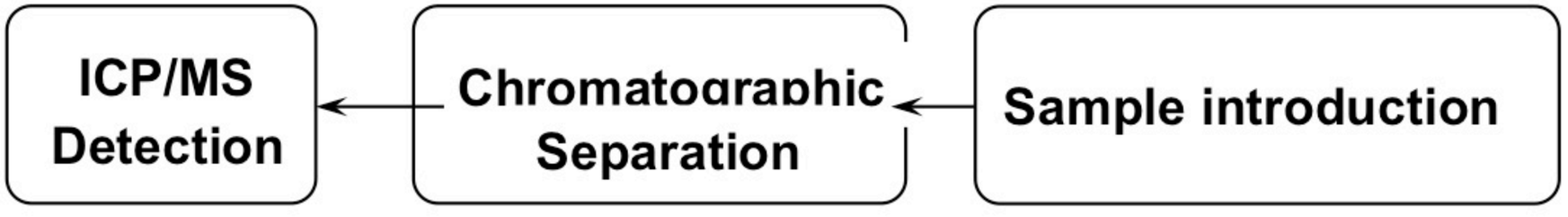
Pavageau, M.P., Krupp, E., de Diego, A., Pécheyran, C., Donard, O.F.X. Cryogenic trapping for speciation analysis (2003) Comprehensive Analytical Chemistry, 41, pp. 495-531.

Pavageau, M.-P., Pécheyran, C., Demange, M., Donard, O.F.X. Phosphine emission measurements from a tobacco factory using cryogenic sampling and GC-ICP-MS analysis (2003) Journal of Analytical Atomic Spectrometry, 18 (4), pp. 323-329.

Pavageau, M.-P., Morin, A., Seby, F., Guimon, C., Krupp, E., Pécheyran, C., Poulleau, J., Donard, O.F.X.
Partitioning of Metal Species during an Enriched Fuel Combustion Experiment. Speciation in the Gaseous and Particulate Phases(2004) Environmental Science and Technology, 38 (7), pp. 2252-2263.

Crytrapping- Low-temperature GC /ICPMS





Crytrapping- Low-temperature GC /ICPMS

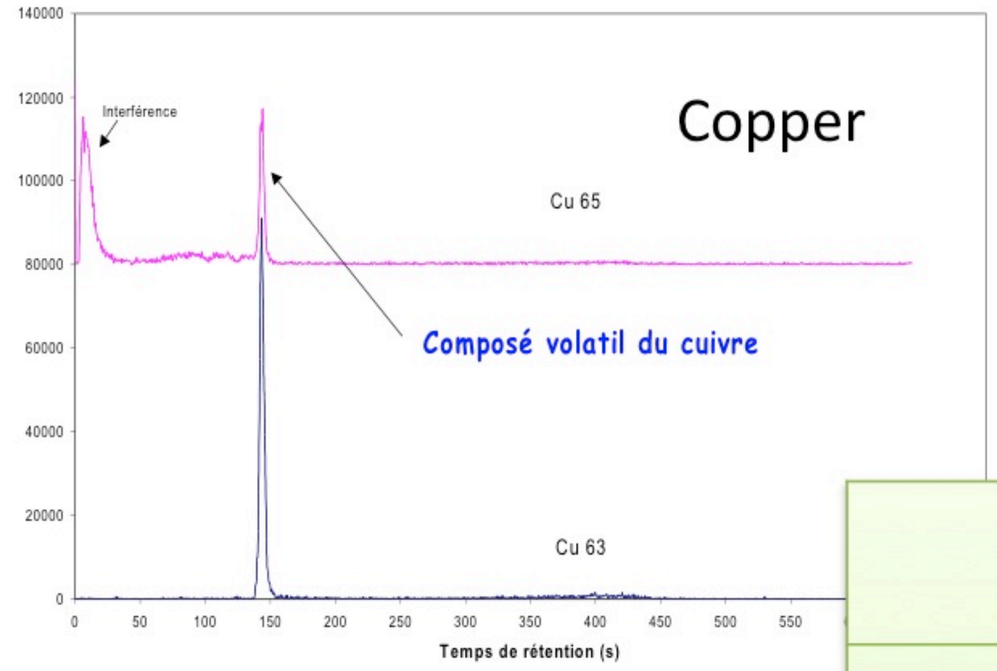
Absolute limit of detection, 3xSD, (pg as metal)

Element	GC/ICP/MS	GC/AAS	
Lead	0.07	10	*Forsyth, 1985*
Tin	0.2	10	*Jantzen, 1991*
Mercury	0.8	50	*Puk, 1994*
Selenium	2.5	100	*Jiang, 1982*

Isotope ratio

	Pb	Sn	Hg	Se
Isotopes	208/206	120/118	202/200	78/77
Measured *	2.19	1.37	1.30	3.17
n = 5	± 0.02	± 0.01	± 0.01	± 0.12
Theoretical	2.22	1.37	1.29	3.10

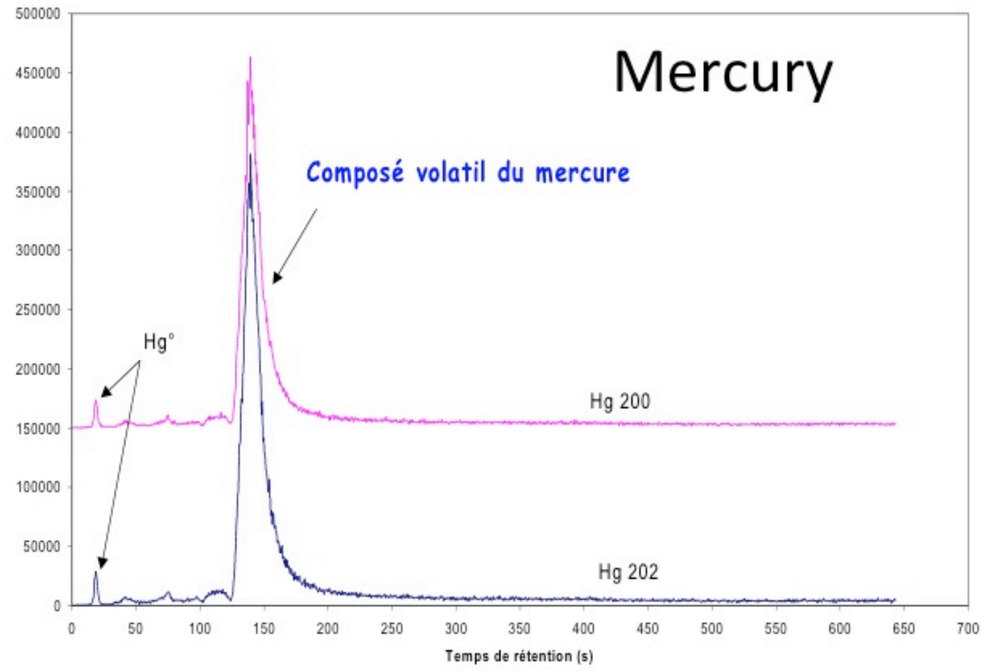
Spéciation of volatile metal species in a chimney stack



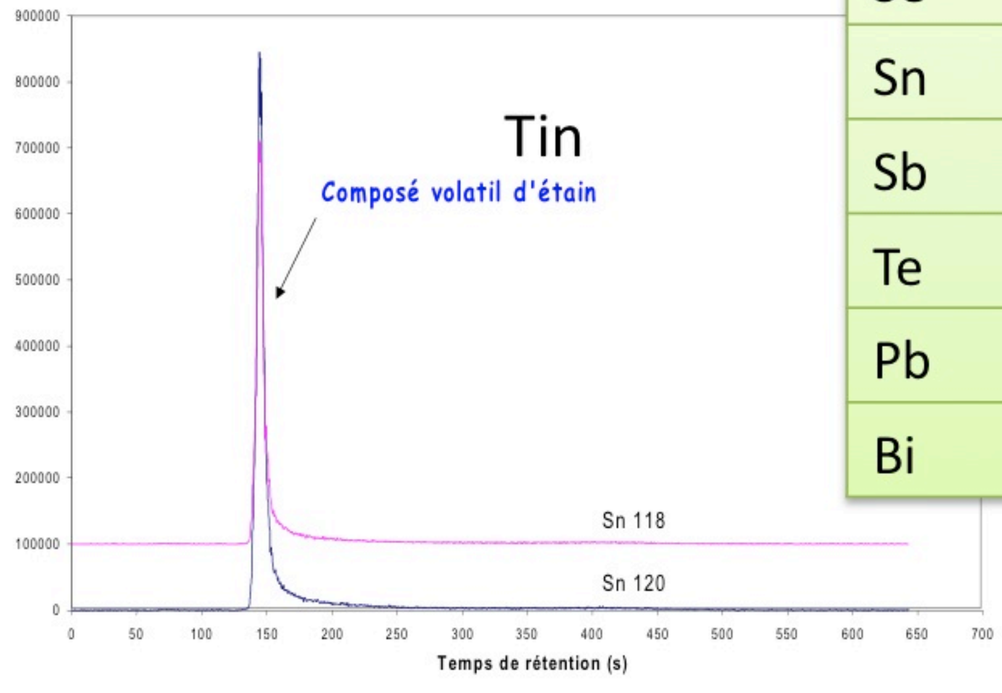
Composés volatils du cuivre

Detected at the emission of a coal power plant

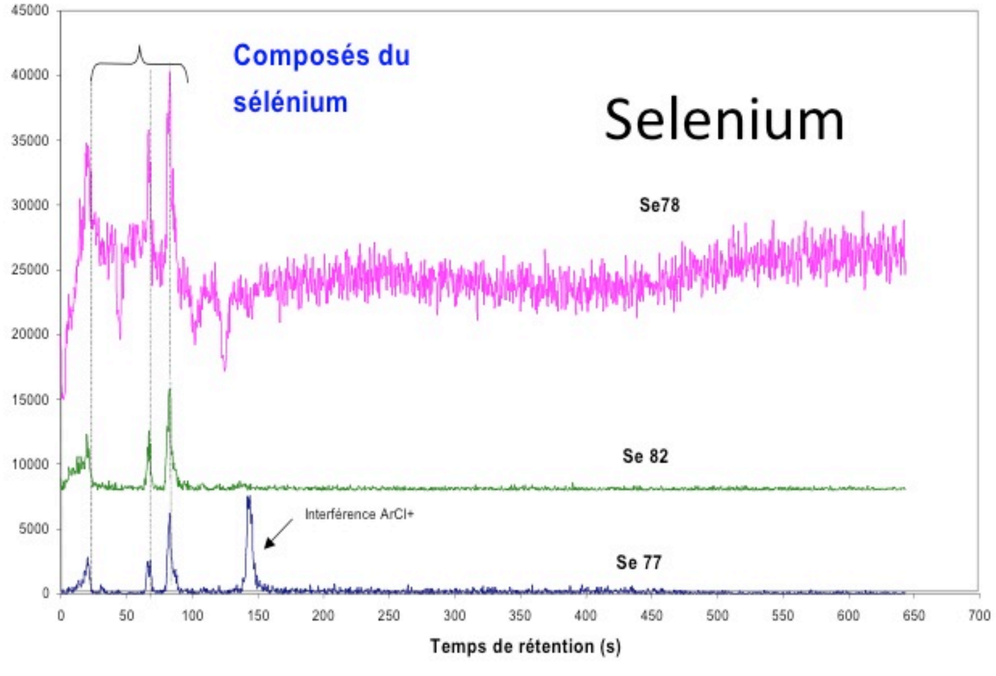
	LOD (fg)	LOD (pg/m^3)
As	229	45,9
Se	1600	319,5
Sn	29	5,7
Sb	3	0,7
Te	23	4,6
Pb	23	4,5
Bi	2	0,5



Composés volatils de mercure

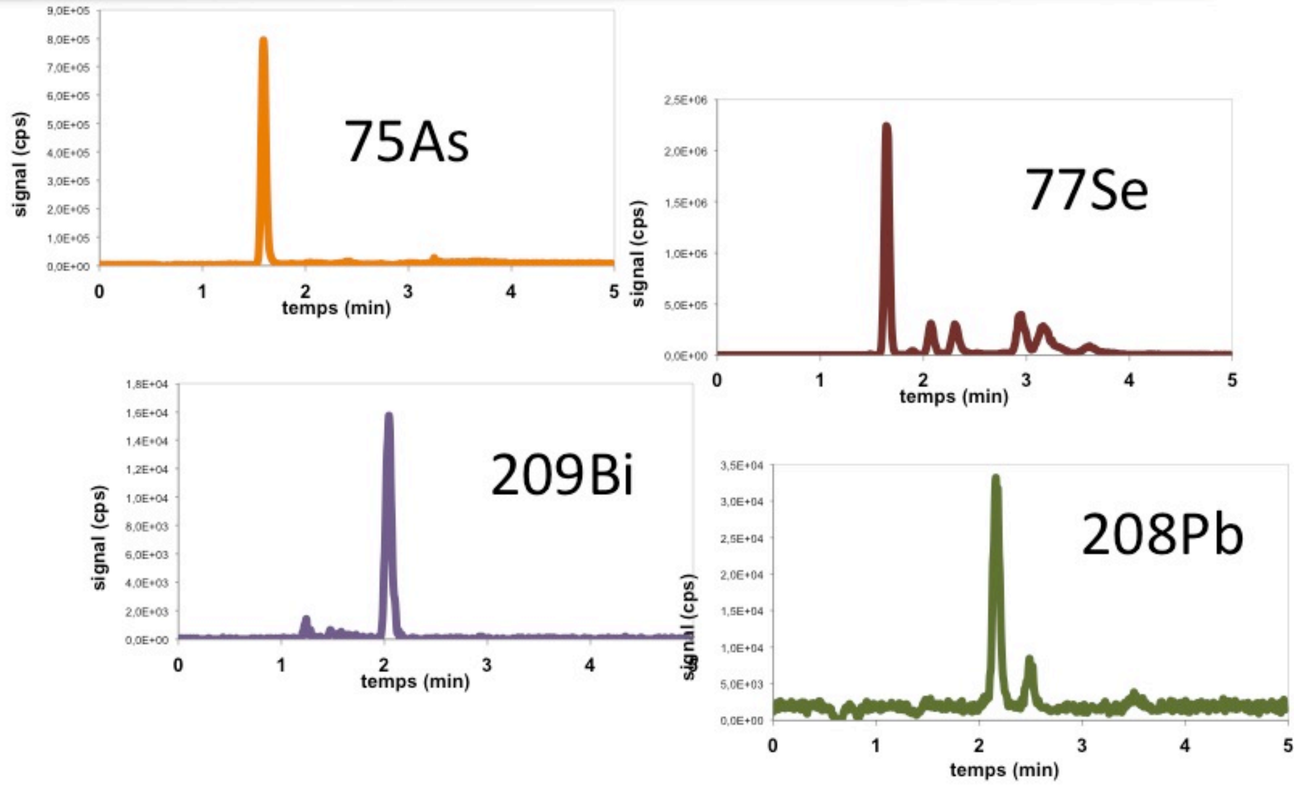


Composé volatil d' étain



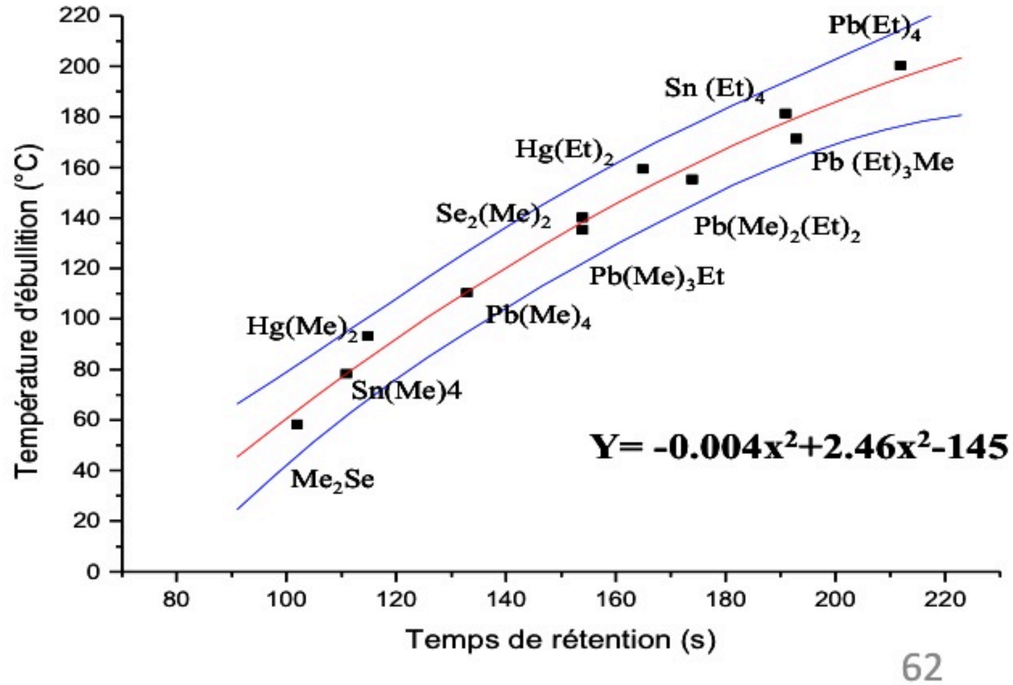
Composés volatils du sélénium

Spéciation of volatile metal species over duck manure storage



New species could be identified...

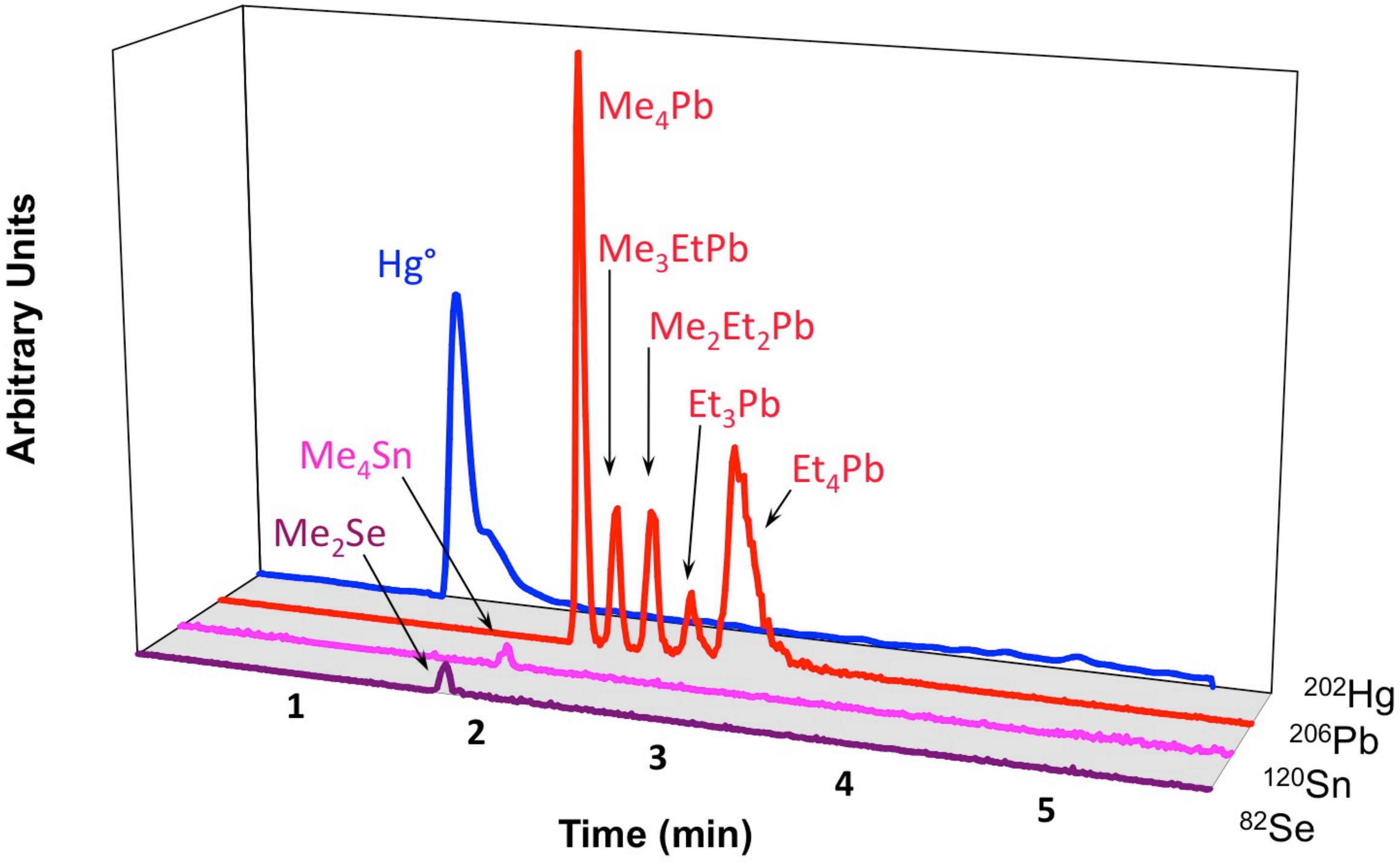
Using **QSAR model** (theoretical chemistry) , improved by determining real boiling point temperature of volatile organometallic species



Spéciation of volatile metal species over duck manure storage

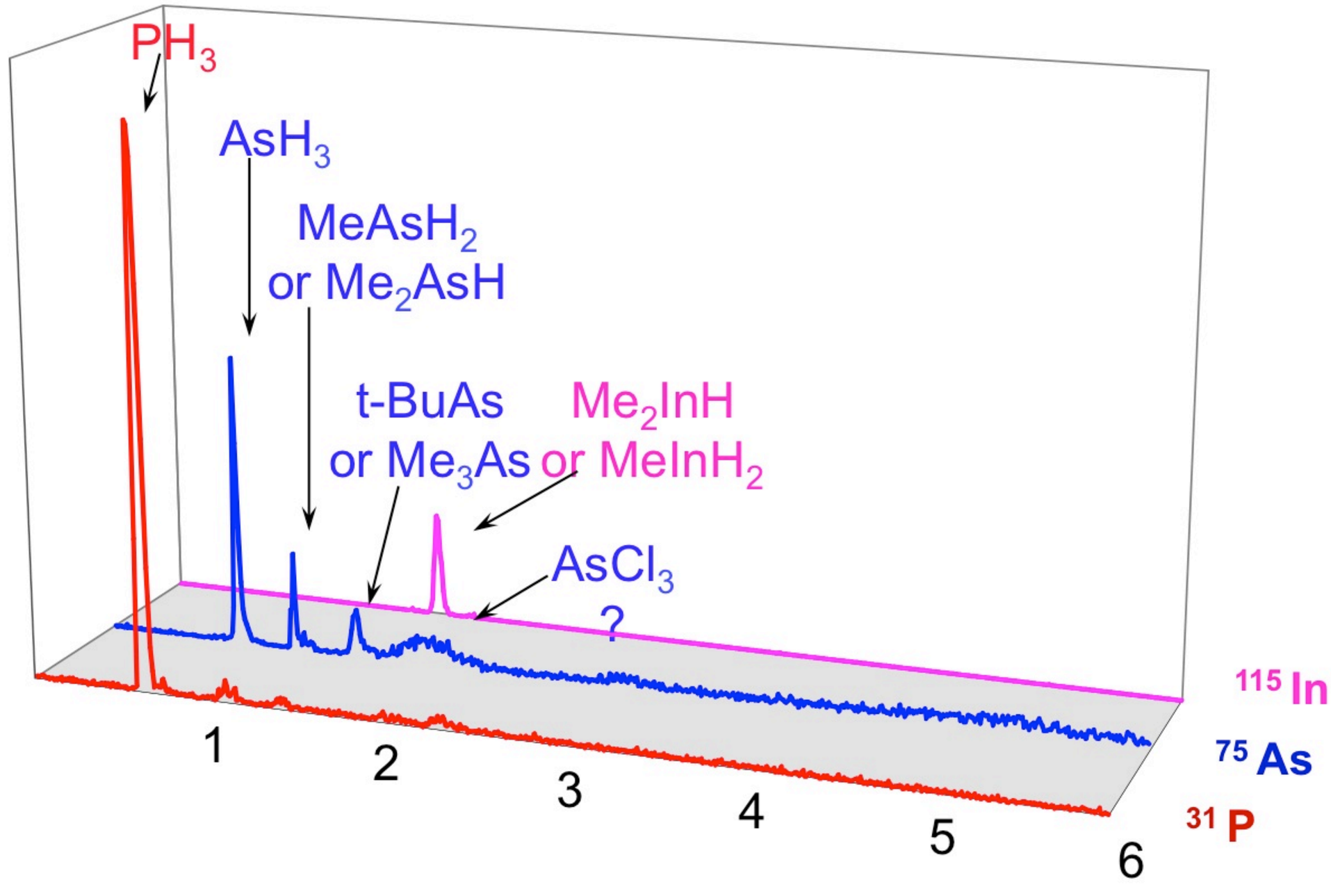
Elément	Espèce **identifiée** ou proposée	Temps de rétention (s)	Température d'ébullition (°C) (Téb cal 1)
As	**$As(Me)_3$**	97	55
Se	**$Se(Me)_2$**	101	62
	SeEtMe	113	82
	$Se(Et)_2$	125	100
	CSe_2 ou MeSeSMe	137	119
	$Se_2(Me)_2$	149	133
	SeSEtMe ou $Se(Pr)_2$	171	159
	Se_2MeEt ou $SeSEt_2$ ou EtSeSEt	186	175
	Se_2MeEt ou $SeSEt_2$ ou EtSeSEt	204	191
Sn	**Sn $(Me)_4$**	111	77
	Sn $(Et)_4$	182	176
Sb	Sb1	97	57
	$Sb(Me)_3$	108	76
Te	**$Te(Me)_2$**	113	83
	TeEtMe	126	103
	$Te(Et)_2$	160	147
	$TeSMe_2$	170	158
	CTe_2 ou TePrEt	182	170
	Te4	198	185
	Te_2Me_2	206	192
Pb	**$Pb(Me)_4$**	130	108
	$Pb(Me)_3Et$	148	134
	$Pb(Et)_4$	200	193
Bi	**$Bi(Me)_3$**	124	99

Urban air sample collected in a day care center (Bordeaux, April 1996)



Air monitoring in the semi conductor industry

air sample collected above wasted oil of CBE pump



Concepts of isotope ratio determination in fast transient signals

Hyphenation with the ICPMS family

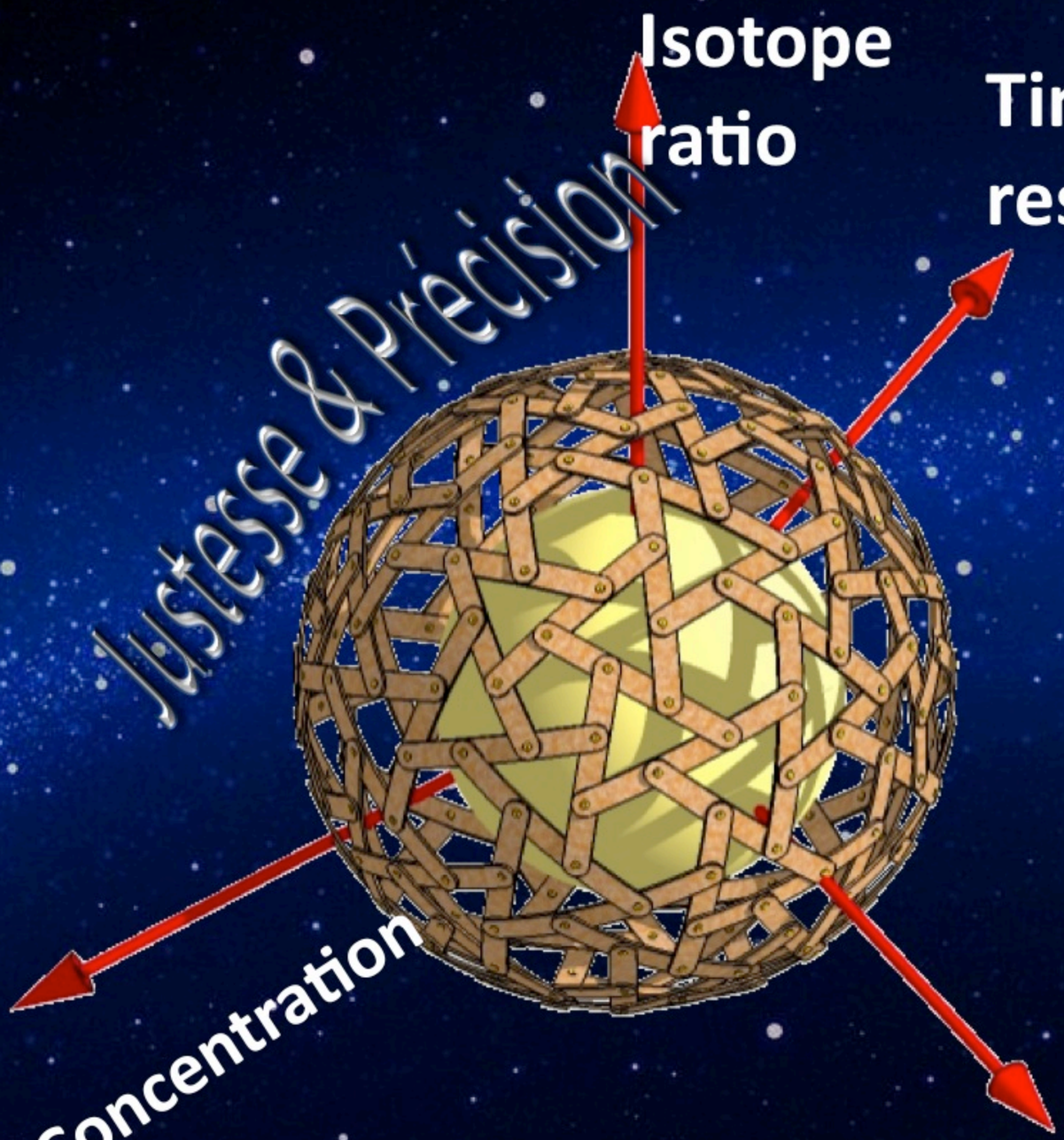
Speciation &
Laser ablation

=

Short transient signals

VLADSTUDIO

Concepts of isotope ratio determination in fast transient signals

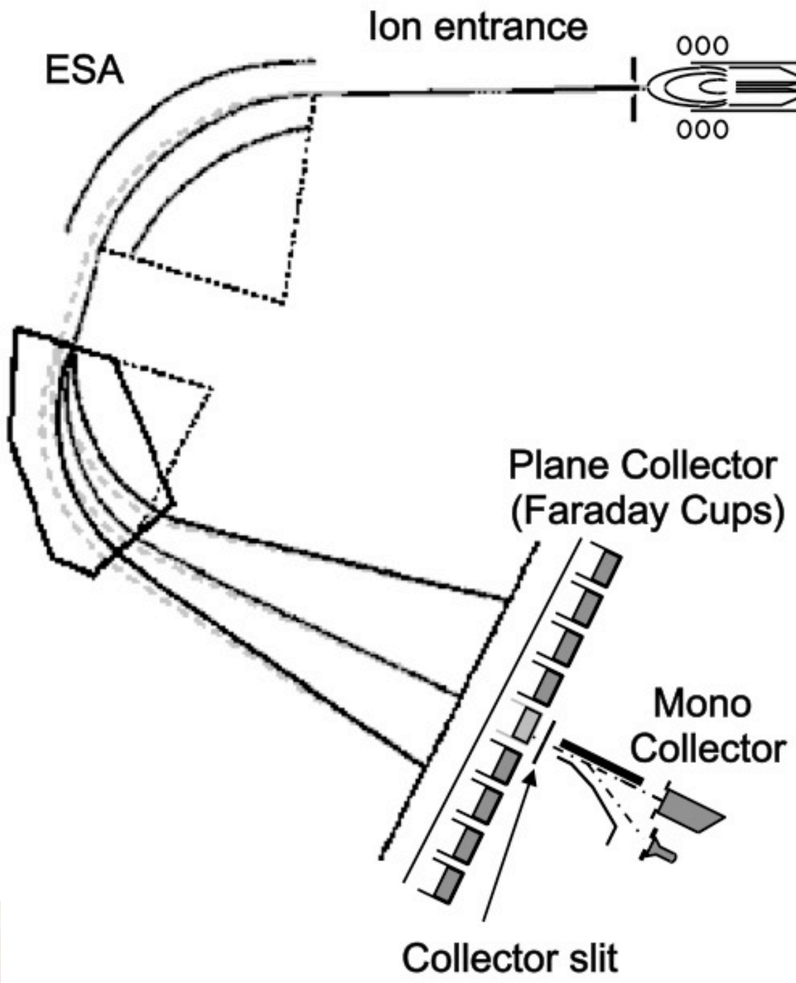


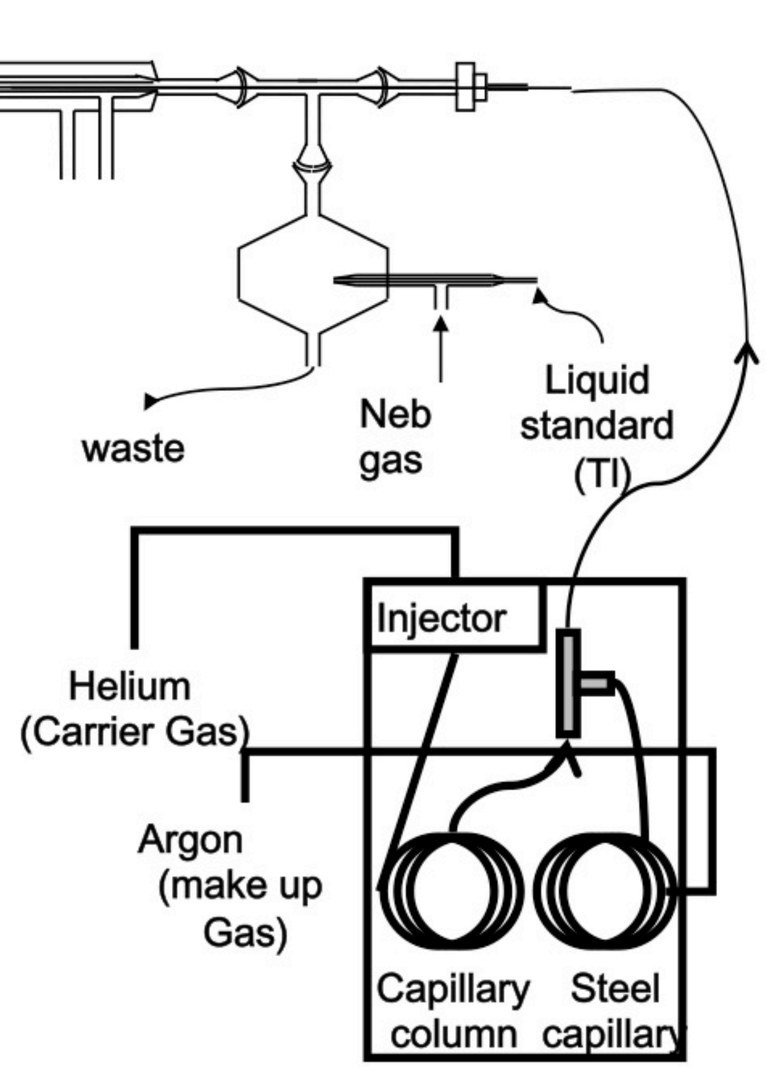
MC-ICPMS

Gas chromatographie

VLADSTUDIO

Concepts of isotope ratio determination in fast transient signals

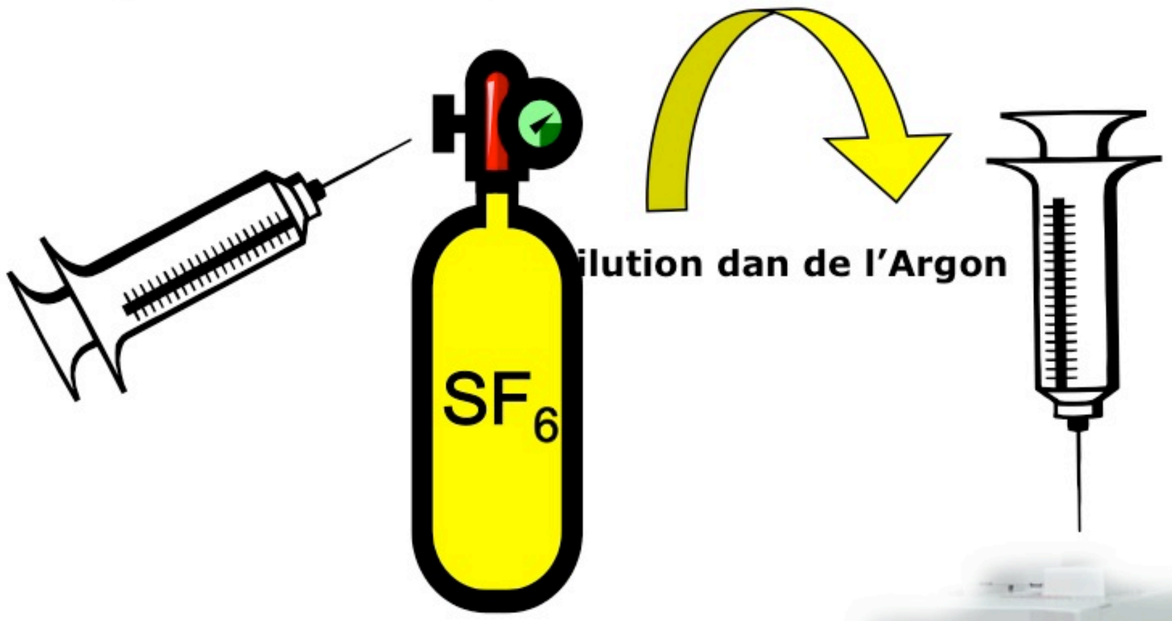




VG Axiom ICP-MC-MS

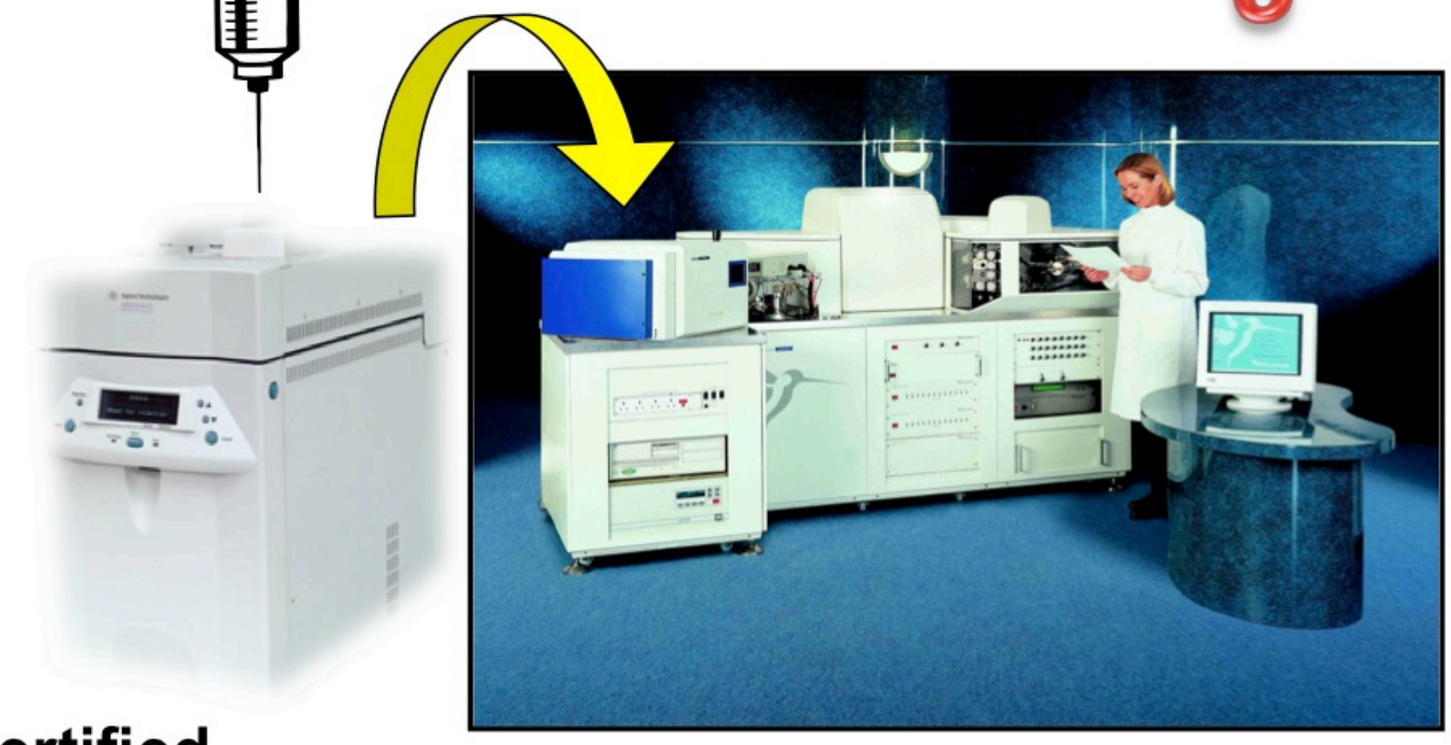
Concepts of isotope ratio determination in fast transient signals

SF_6 standard **(PIGS 2010,IRMM)**



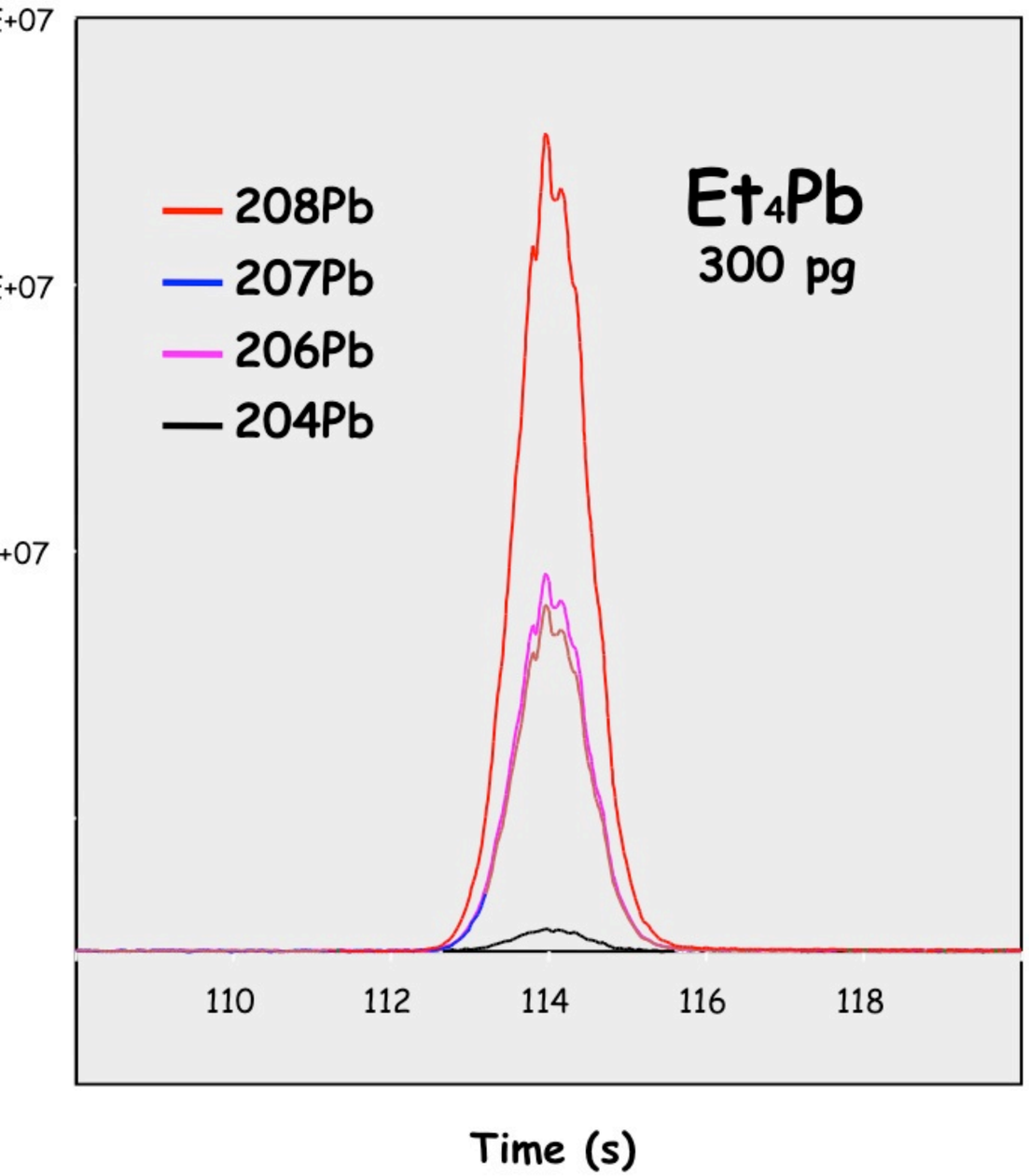
Ethylation of NIST SRM981 (certified Pb) in solution

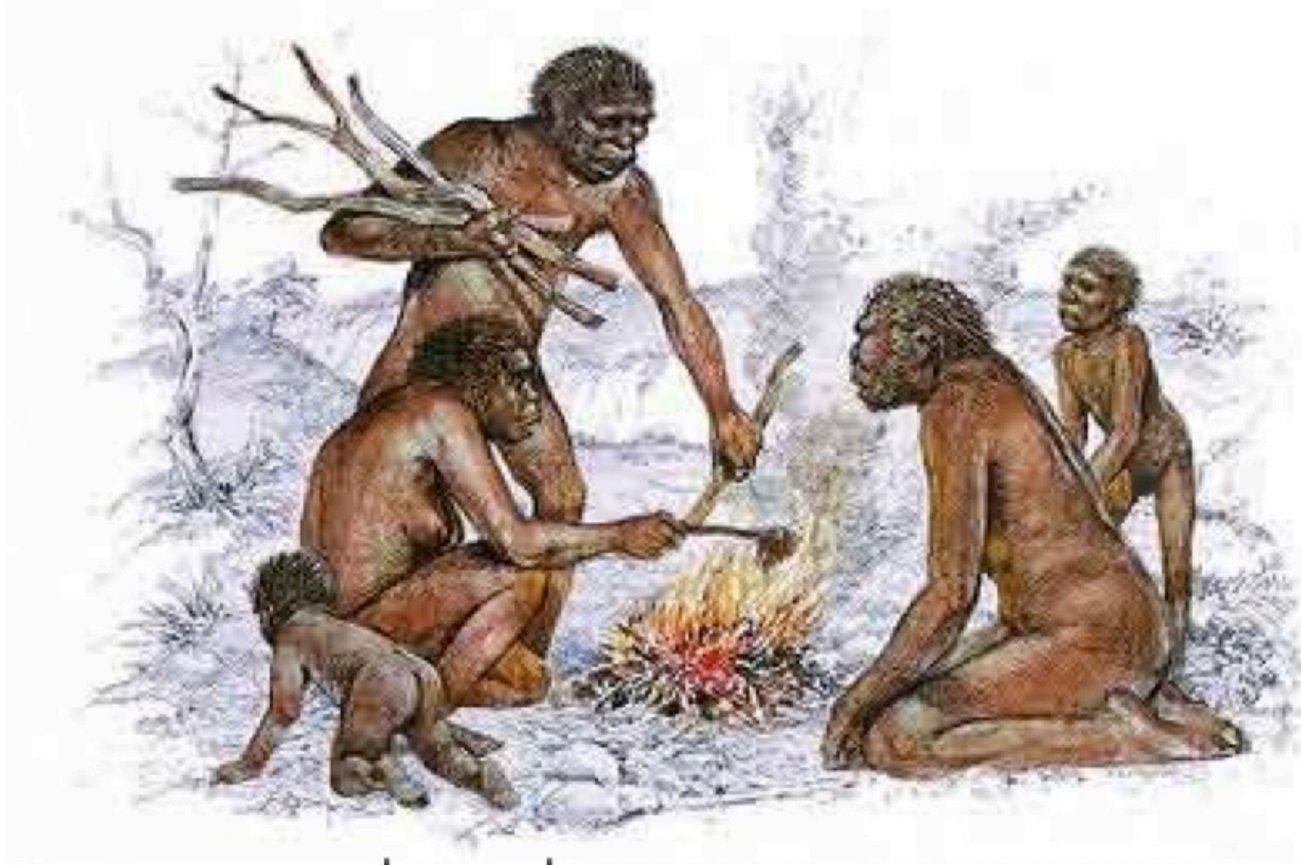
$PbEt_4$ and SF_6

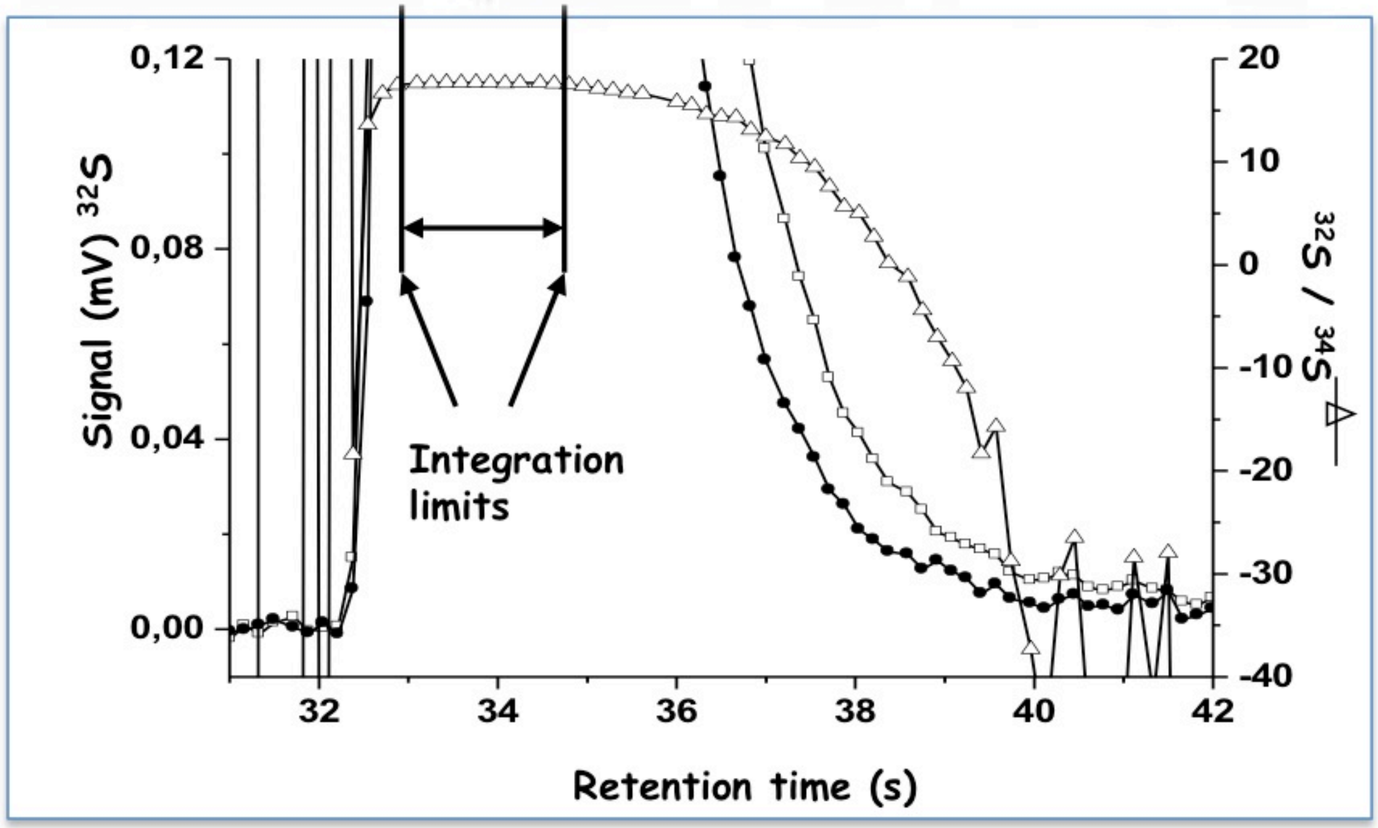


GC-MCICPMS detection (Micromass, Thermo)

Concepts of isotope ratio determination in fast transient signals







Concepts of isotope ratio determination in fast transient signals

NIST 981 (Isotopically certified reference material (Pb))

IR obtained for 3s transient signal- Injection of 300 pg

n=5	208/207	208/206	208/204	207/206	207/204	206/204
Certified	2,3704	2,1681	36,721	0,9147	15,491	16,937
Mean	2,3670	2,1704	36,983	0,9169	15,624	17,040
Error (3xSD)	0,0049	0,0036	0,6522	0,0005	0,3010	0,3189
Precision @ 2xRSD (ppm	1373	1118	11757	389	12843	12476

This was 13 years ago...

Concepts of isotope ratio determination in fast transient signals

- **Peak Apex:**

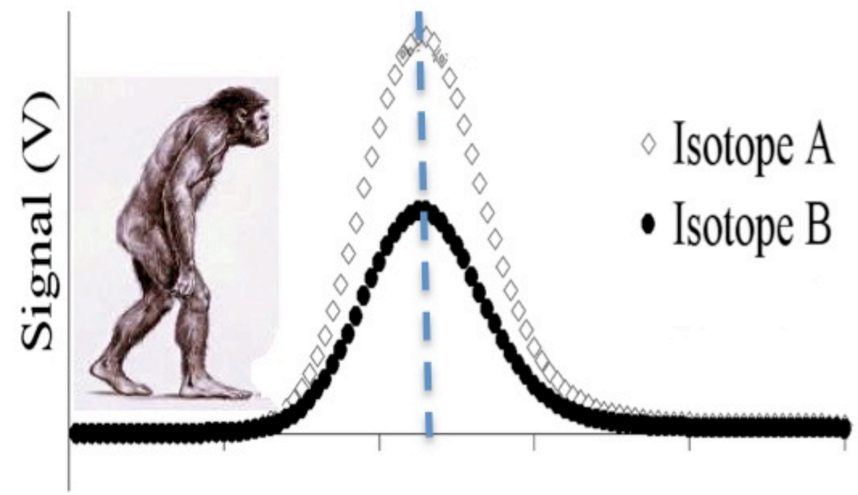
$R_{A/B}$= ratios at maximum

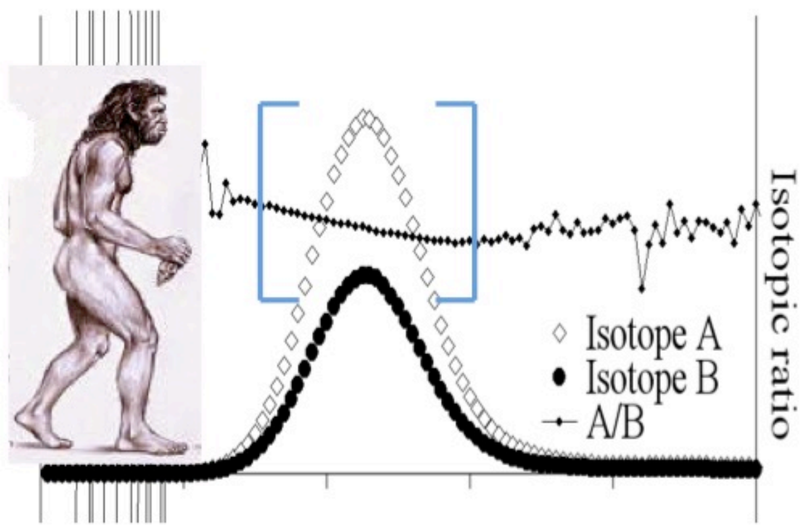
- **Average(point par point):**

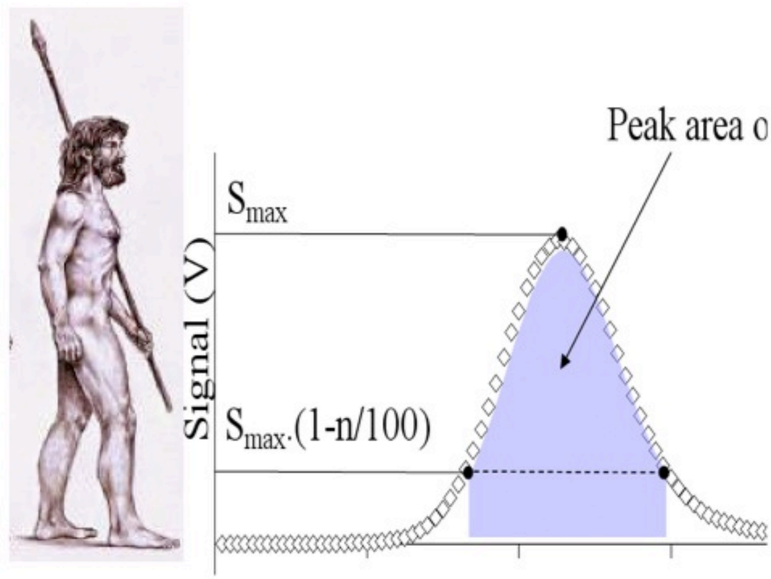
$R_{A/B}$= mean ration~ 20 pts

- **Area integration**

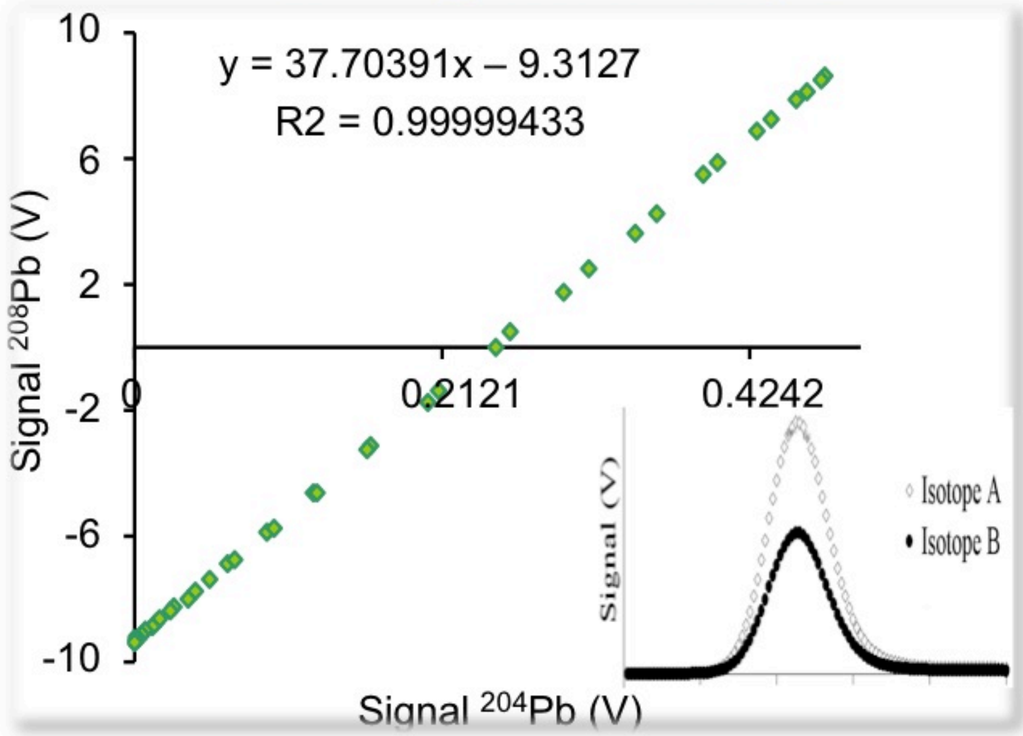
$R_{A/B}$= ratio of the peak areas (>90%)







- **Linear Regression Slope**



- *Fietzke et al.(2008), JAAS: Sr by LA / MC-ICP-MS*

- *Natural weighting of the most significant points.*
- *Precision improvement >10*
- *Independent of the chemical form*
- *Excellent results even at low concentration*

Concepts of isotope ratio determination in fast transient signals

- Linear Regression Slope method

SRM NIST 981, (injection of 1,2 ng as Pb)

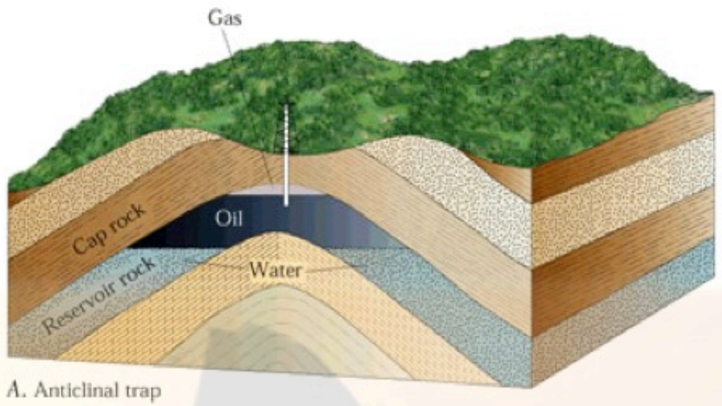
		$^{208/204}Pb$	$^{207/204}Pb$	$^{206/204}Pb$	$^{208/206}Pb$	$^{207/206}Pb$
	NIST 981 ref. value	36,72185	15,49161	16,93736	2,1681 ± 0.00033	0,91464 ± 0.0008
	measured , n = 7	36,72093	15,49127	16,93699	2,16809	0,914641
Correction (Tl+ Bracketing)	accuracy bias. (‰)	**-0.025**	**-0.022**	**-0.022**	**-0.005**	**0.00068**
	$2RSD_{Ext}$, (ppm)	**234**	**190**	**209**	**49**	**69**

Anal. Chem. http://dx.doi.org/10.1021/ac301251b

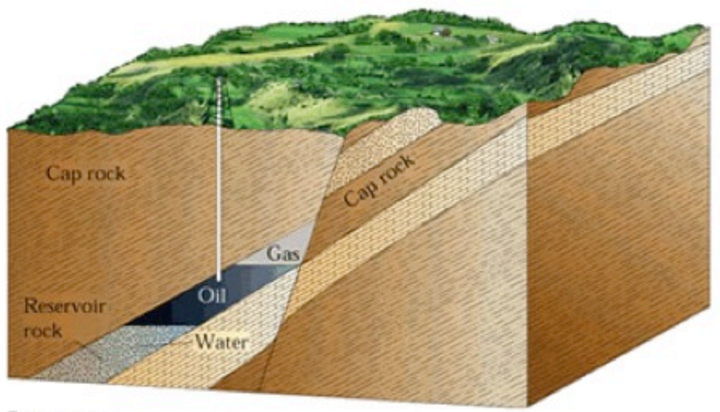
Using speciation techniques for dating crude oil formation

Timing crude oil generation

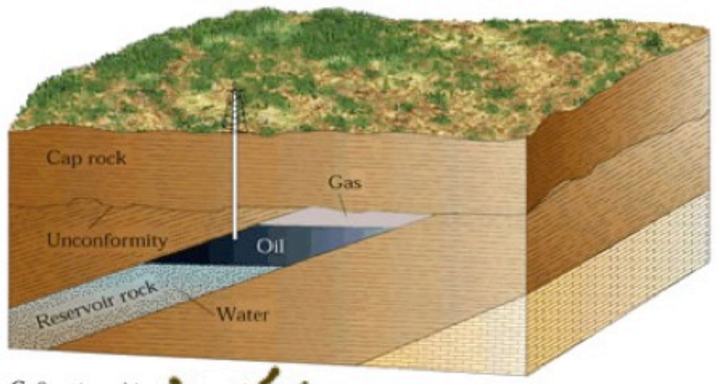
This information is useful to better understand the petroleum system and to find new petroleum reservoirs…



A. Anticlinal trap



B. Fault trap



C. Stratigraphic trap

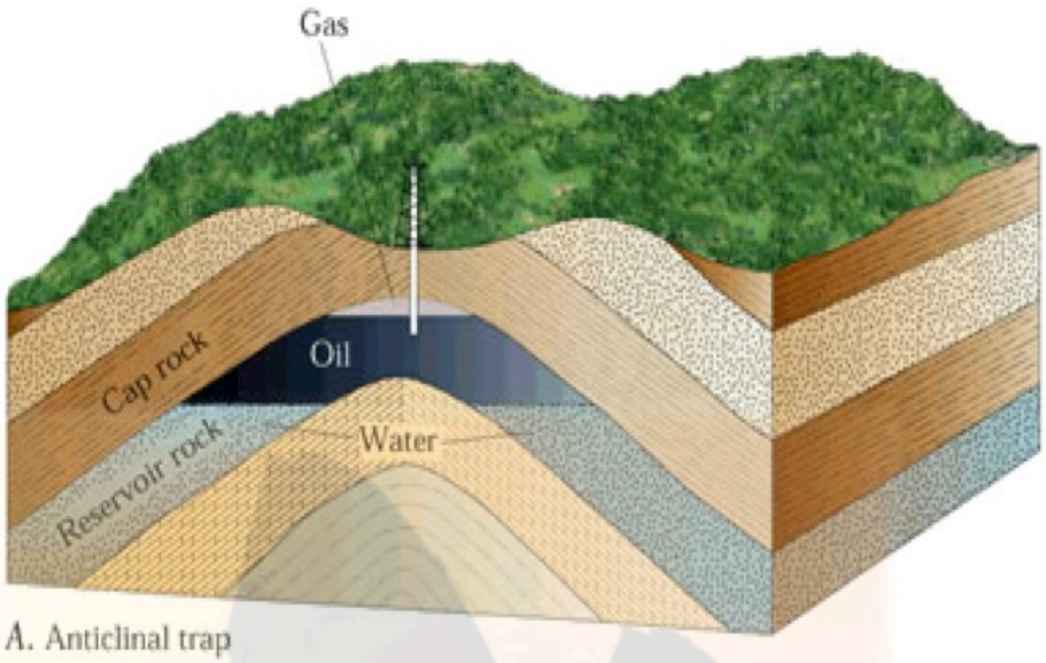
Probability of success

Ps = (Charge factor) x (Trap factor) x **(Time factor)**

- Ps < 15 % — High risk
- 15 % < Ps < 30 % — Medium risk
- 30 % < Ps < 50 % — Low risk
- Ps > 50 % — « Very Low » risk

U-Pb, Th-Pb geochronometers ?

Trace metal in petroleum products



A. Anticlinal trap

=> better understand the petroleum system, find new petroleum reservoirs, etc...

Les **métaux** dans les **huiles**, **bitumes** et **kérogène** donnent des **informations clés** :

- oil migration
- **oil-oil and oil-source rock correlation**
- **Biodégradation**
- **Maturity**
- depositional environment
- **Time of oil expulsion**

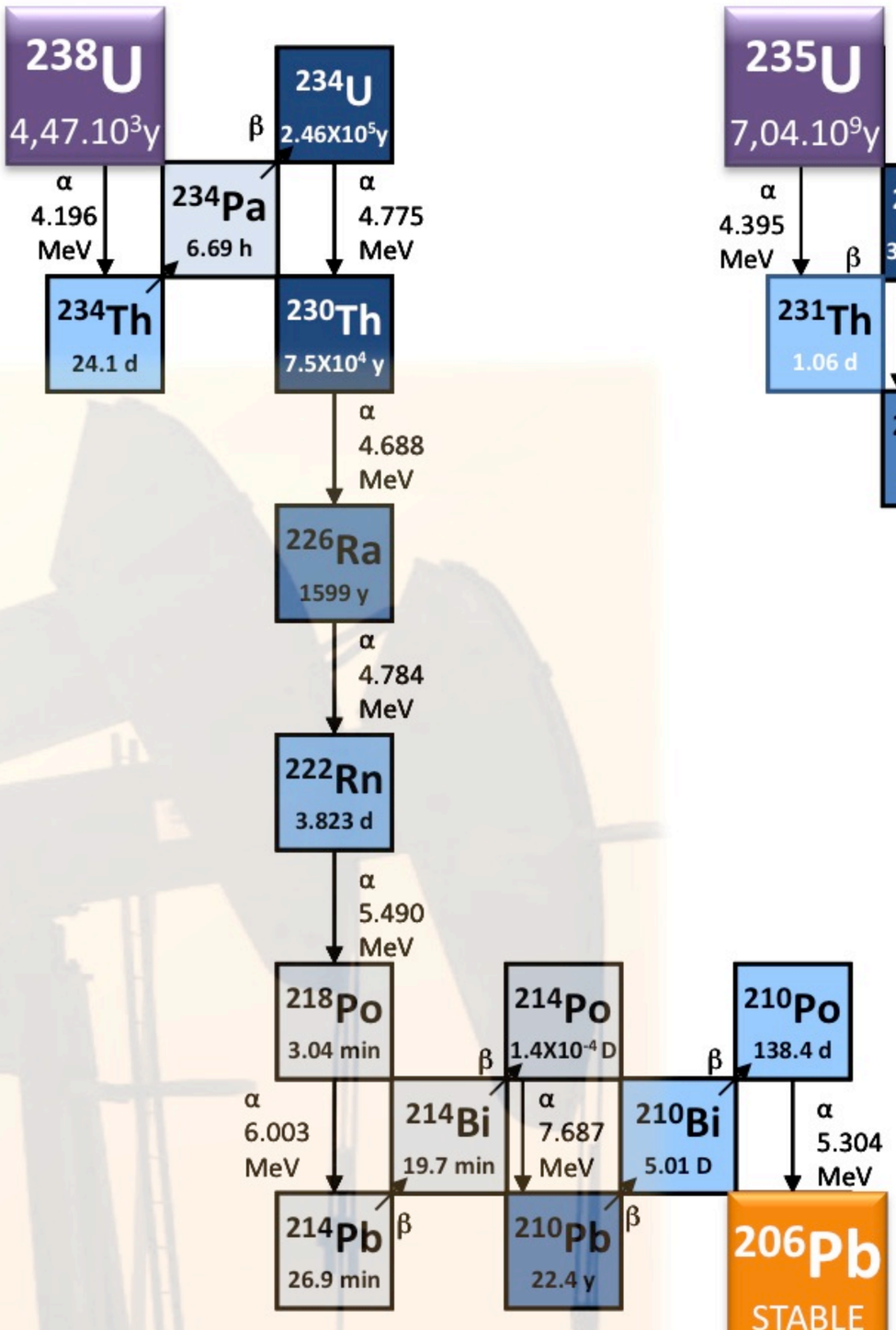
Probability of success

Ps = (Charge factor) x (Trap factor) x **(Time factor)**

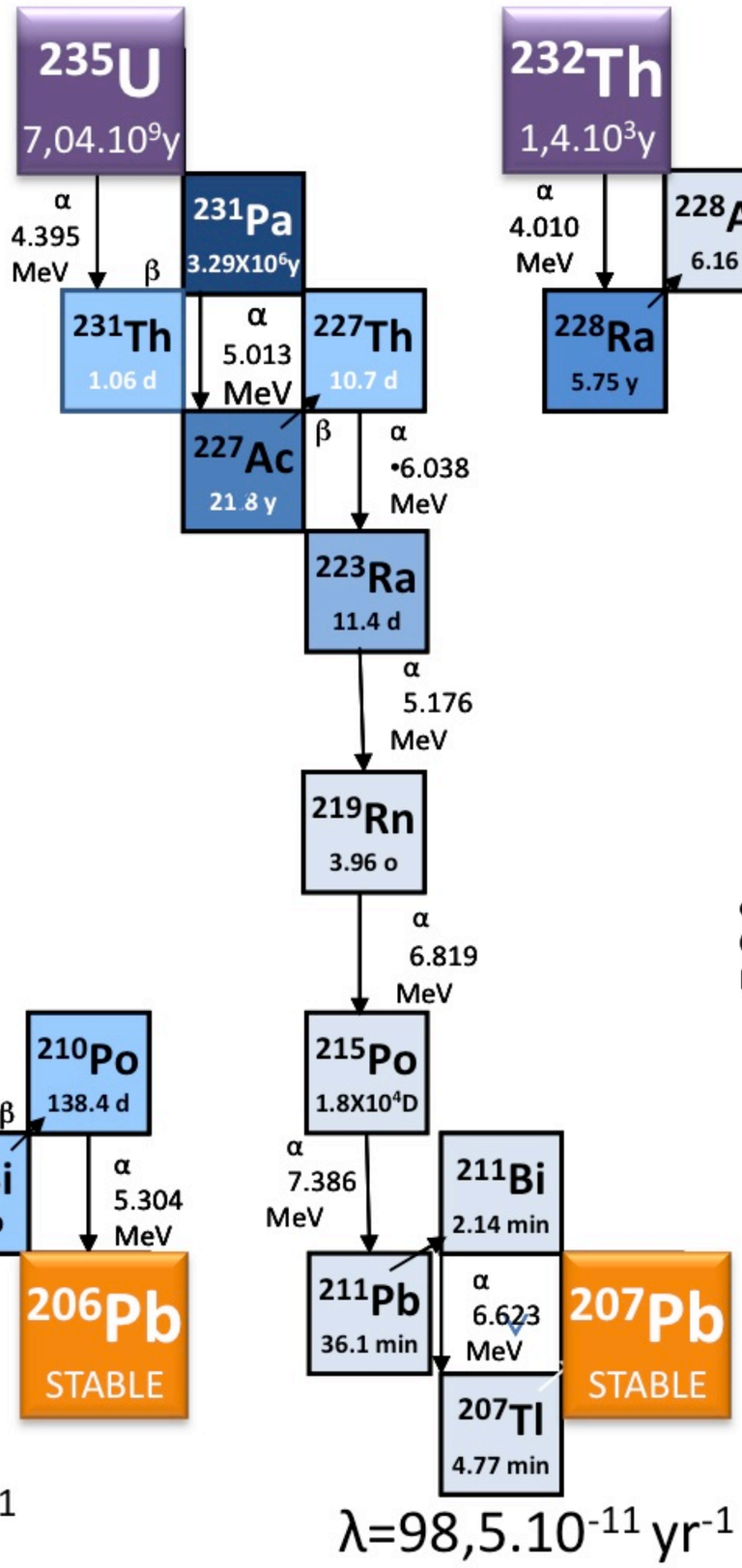
- Ps < 15 % — High risk
- 15 % < Ps < 30 % — Medium risk
- 30 % < Ps < 50 % — Low risk
- Ps > 50 % — « Very Low » risk

U-Pb, Th-Pb géochronometers?

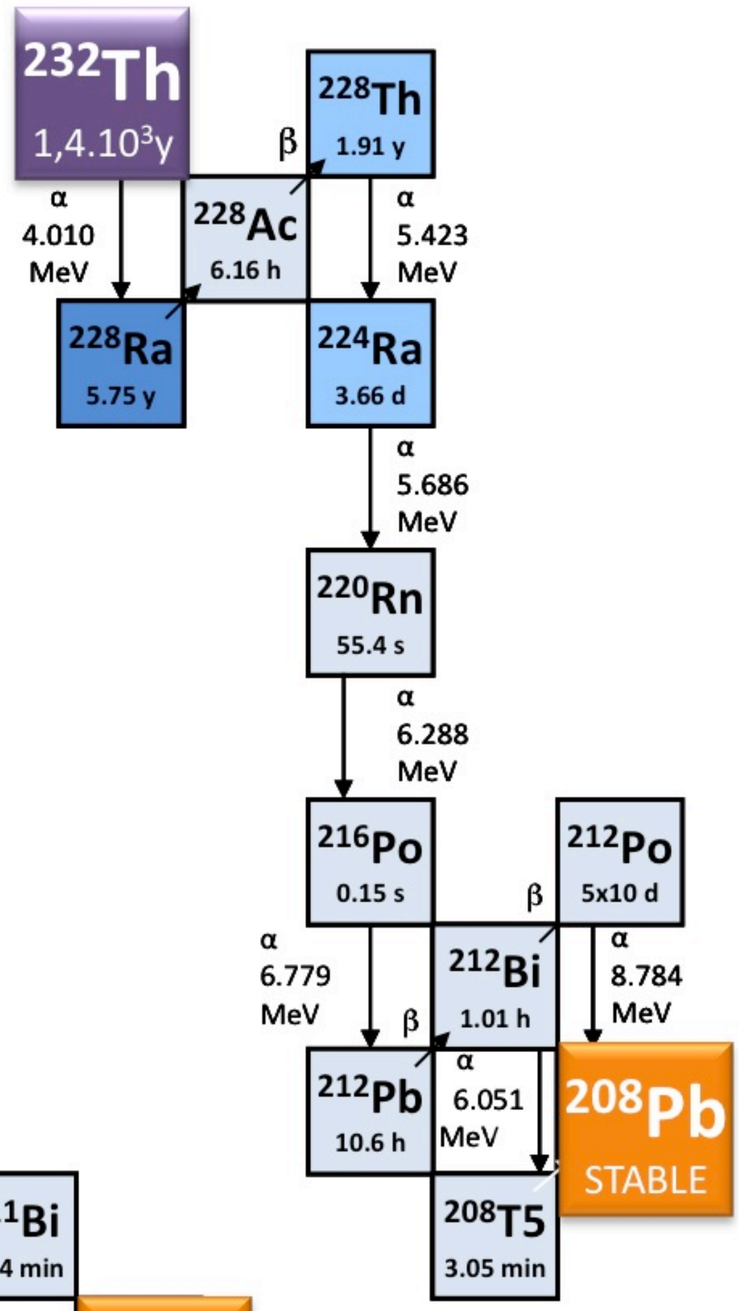
U-Pb, Th-Pb geochronometers



λ=15,5.10^{-11} yr^{-1}



λ=98,5.10^{-11} yr^{-1}



λ=4,95.10^{-11} yr^{-1}

^{204}Pb non radiogenic

U-Pb, Th-Pb geochronometers

In a closed system…

$$\left(\frac{^{206}Pb}{^{204}Pb}\right)_t = \left(\frac{^{206}Pb}{^{204}Pb}\right)_i + \left(\frac{^{238}U}{^{204}Pb}\right)_t (e^{\lambda_1 t} - 1)$$

$$t = \frac{1}{\lambda_1} \ln \left(\frac{\left(^{206}Pb/_{^{204}Pb}\right)_t - \left(^{206}Pb/_{^{204}Pb}\right)_i}{\left(^{238}U/_{^{204}Pb}\right)_t} + 1 \right)$$

$$\left(\frac{^{207}Pb}{^{204}Pb}\right)_t = \left(\frac{^{207}Pb}{^{204}Pb}\right)_i + \left(\frac{^{235}U}{^{204}Pb}\right)_t (e^{\lambda_2 t} - 1)$$

$$t = \frac{1}{\lambda_2} \ln \left(\frac{\left(^{207}Pb/_{^{204}Pb}\right)_t - \left(^{207}Pb/_{^{204}Pb}\right)_i}{\left(^{235}U/_{^{204}Pb}\right)_t} + 1 \right)$$

$$\left(\frac{^{208}Pb}{^{204}Pb}\right)_t = \left(\frac{^{208}Pb}{^{204}Pb}\right)_i + \left(\frac{^{232}Th}{^{204}Pb}\right)_t (e^{\lambda_3 t} - 1)$$

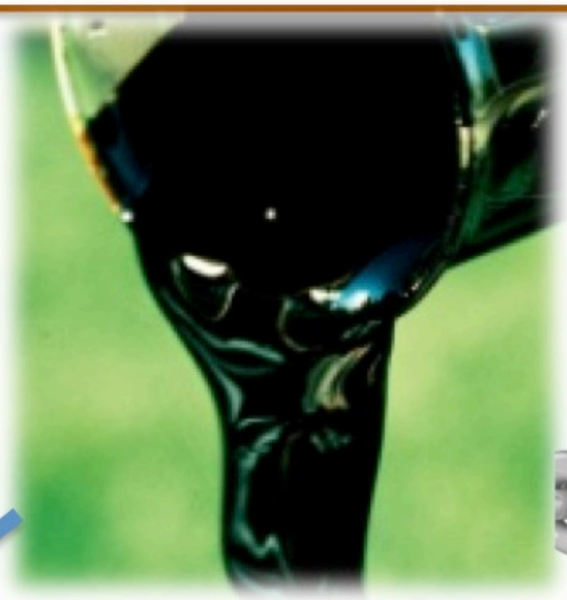
$$t = \frac{1}{\lambda_3} \ln \left(\frac{\left(^{208}Pb/_{^{204}Pb}\right)_t - \left(^{208}Pb/_{^{204}Pb}\right)_i}{\left(^{232}Th/_{^{204}Pb}\right)_t} + 1 \right)$$

- Based on natural radioactivity of uranium and thorium
- Good precision to date samples older than 30 Ma.
- Needs precise and accurate determination of Pb isotope ratio

Pb isotope ratios in crude oil : an analytical challenge…

Very complex matrix…

Low concentrations (ppb)…



Mineralization

↓

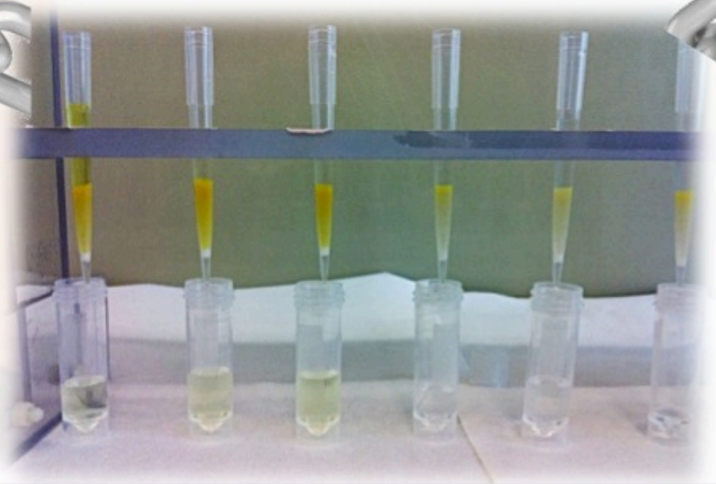
- Dry ashing
- Acid digestion

↓

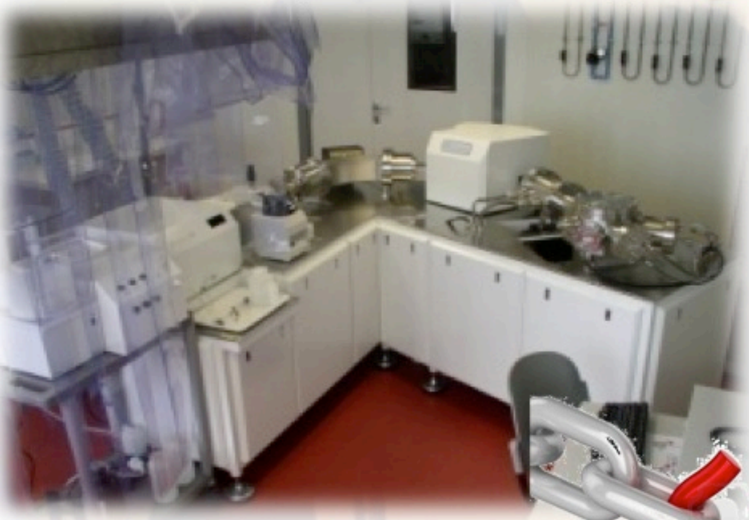
- Time consuming
- Risk of contamination
- Large sample dilution

No Certified Reference crude oils for Pb Isotope ratios

Pb isolation



MC-ICPMS & data processing



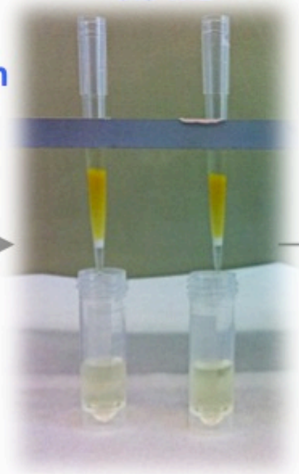
A « conventional » analytical approach in geochemistry…

0.5 g of crude oil +
$HNO_3 + H_2O_2$

Acid Evaporation

Solid dissolution
HBr 0.5 M

Pb purification:
AG1-X8 resin
0.5 mL



Resin cleaning:
4 mL 0.25M HNO_3,
then 2mL H_2O

Resin conditioning:
2 mL 0.5M HBr

Sample loading:
10 mL 0.5 M HBr

Matrix removal:
2 mL 0.5M HBr + 0.2 mL HCl

Sample elution:
4 mL 6M HCl

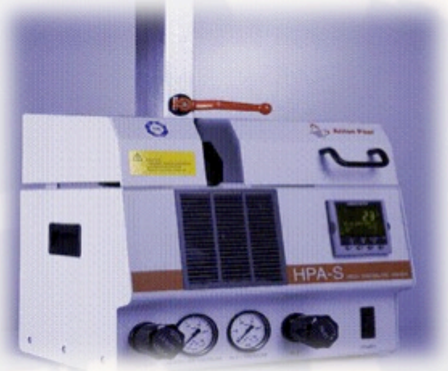
Acid Evaporation

Solid dissolution
HNO3 2%

Ok

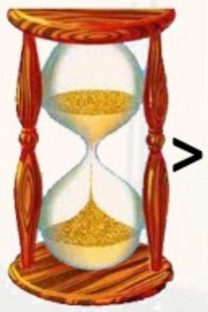
Q-ICP-MS: concentration checking

Total Pb Q-ICPMS (Perkin Elmer, Elan DRC-II)



HPAS digestion
Differents API Crude Oil: 0.5 g
Kerogene: 6 – 100 mg

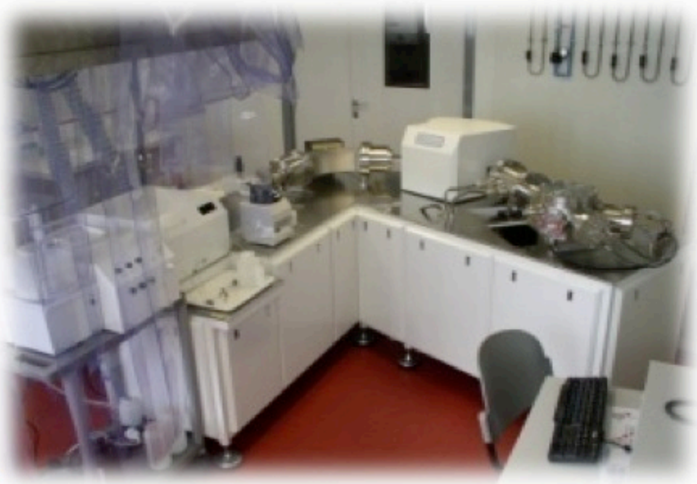
P: 100 bar
T: 300 °C



>18 h

Pb Isotopic ratio analysis by DSN/MC-ICP-MS, Nu plasma, NU Instruments

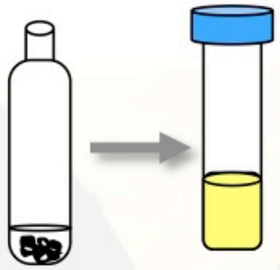
Due to the **low Pb concentrations** in crude oil sample (5-200 ppb), **DSN** was used for all MC-ICPMS measurements.

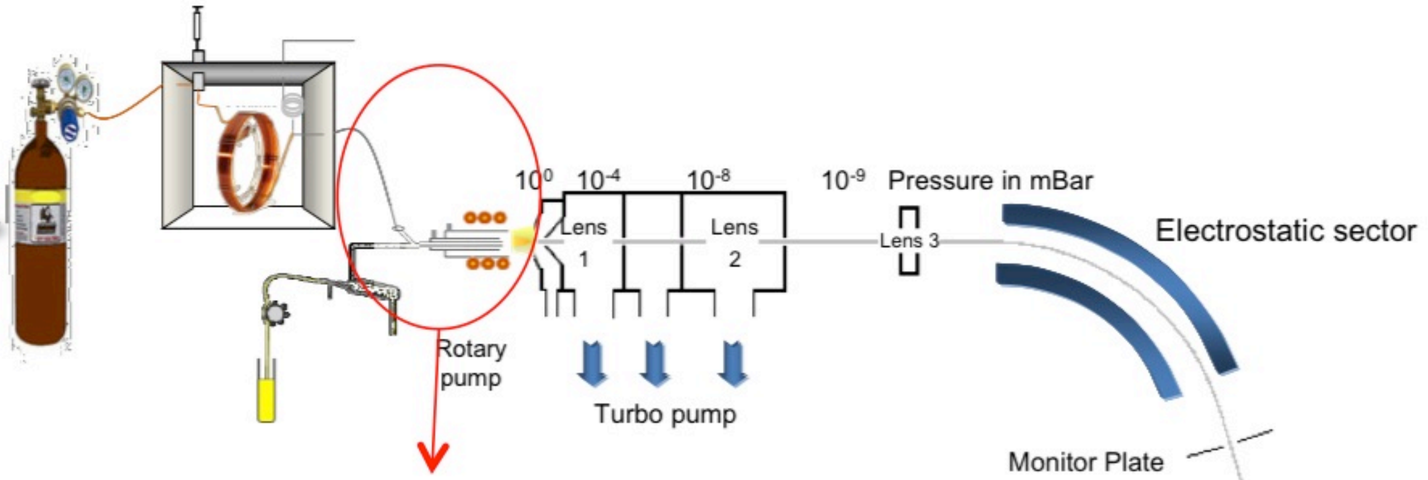


J. Anal. At. Spectrom., 2012, **27**, 1447-1456

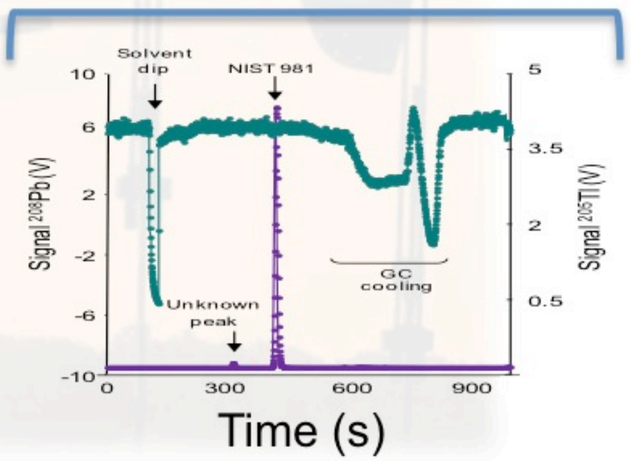
Using speciation techniques for Pb isotope ratios determination.

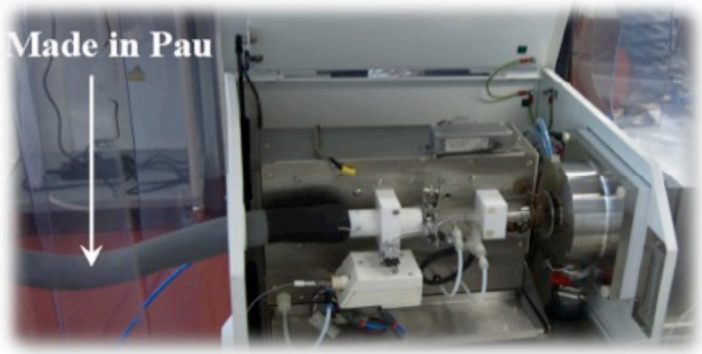
Mineralization | Derivatization | GC separation | MC-ICPMS detection

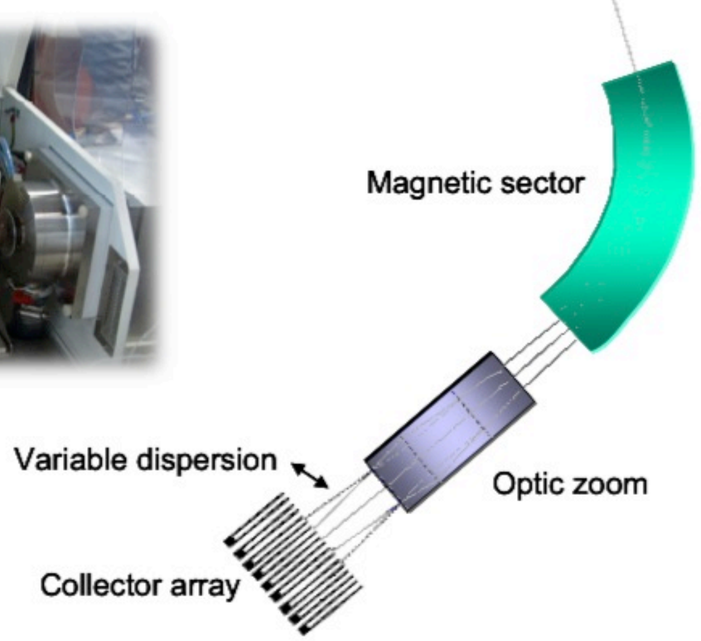




Data reduction







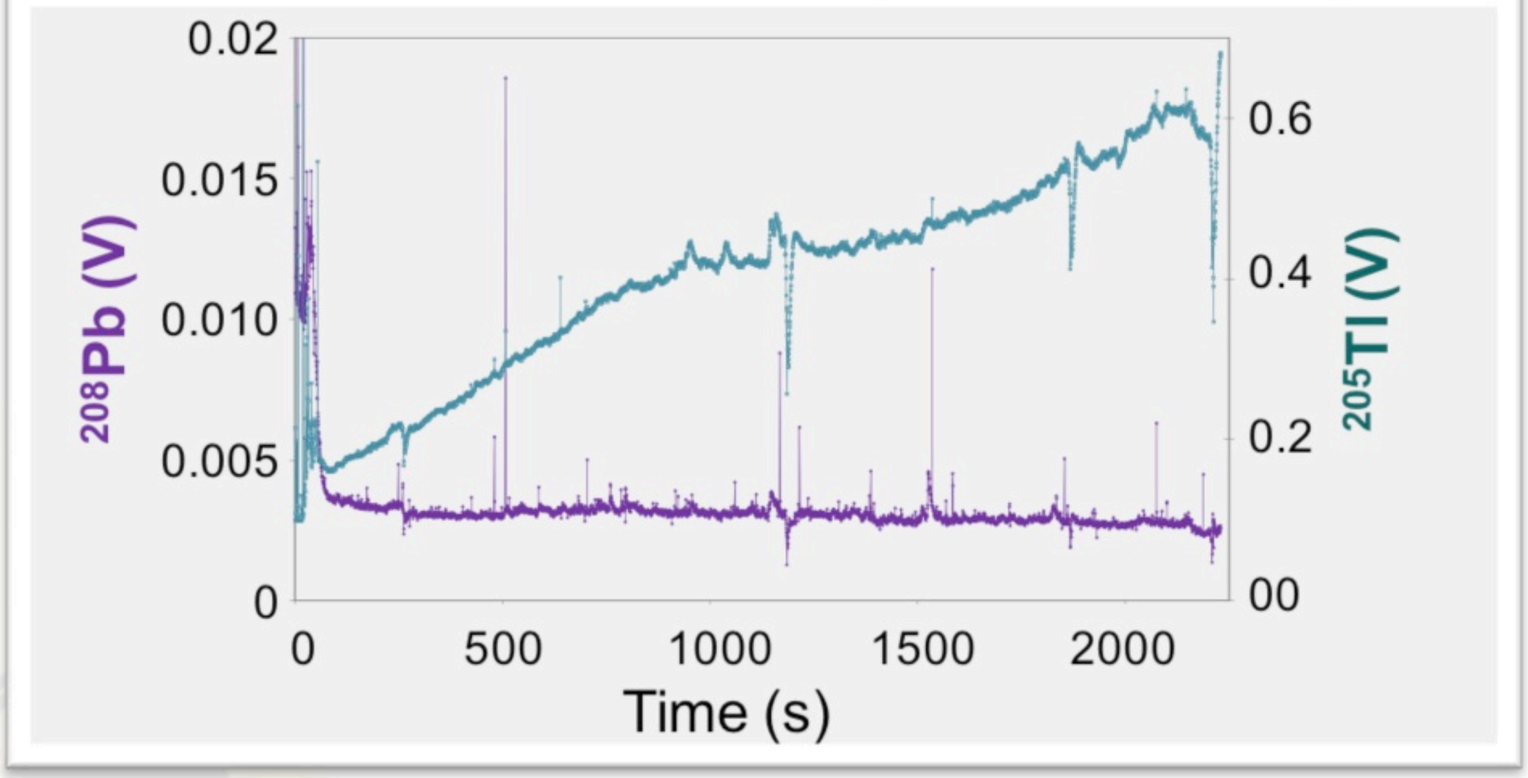
Nu Plasma HR

Anal. Chem. http://dx.doi.org/10.1021/ac301251b

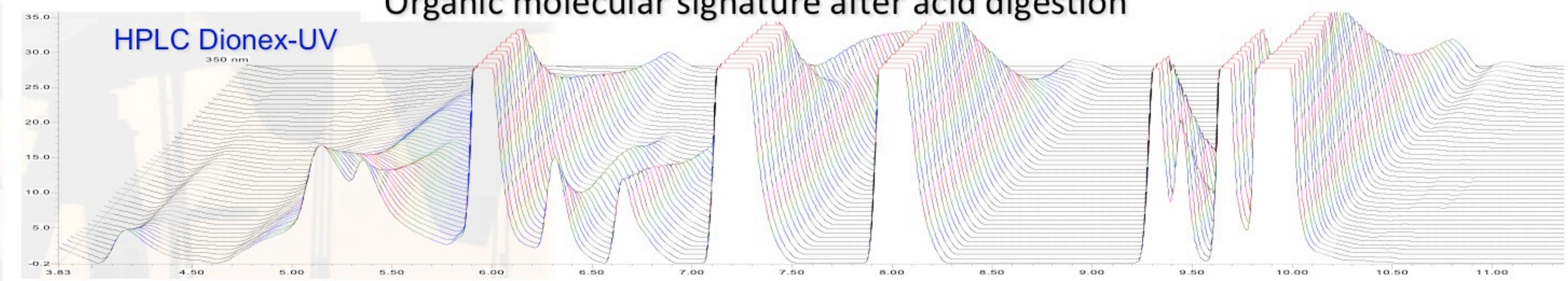
A « conventional » analytical approach in geochemistry…

Remaining matrix effect when analyzing crude oils.

Tl and Pb wash out profile after a purified crude oil digest



Organic molecular signature after acid digestion



Membrane coating by remaining organic compounds?
Tl accumulation in the DSN Membrane?

→ **Very long washout**

J. Anal. At. Spectrom., 2012, **27**, 1447-1456

A « conventional » analytical approach in geochemistry…

	(Wash	- Blank	- Nist 981	- Blank	- **Sample**)$_n$
Time (min)	**10->120**	**3,3**	**13**	**3,3**	**13**

Analysis time : 80-180 min/sample

Results for SRM NIST 981 (20 ng mL^{-1})

with a double mass bias correction : Tl correction + sample bracketing

	$^{208/204}$Pb	$^{207/204}$Pb	$^{206/204}$Pb	$^{208/206}$Pb	$^{207/206}$Pb
Certified Reference Value	36.7219	15.4916	16.9374	2.1681	0.9146
Mean, n = 17	36.7218	15.4916	16.9373	2.1681	0.9146
2RSD$_{Ext}$ (ppm)	107	94	64	52	26

Using speciation techniques for Pb isotope ratios determination.

Fast alternative to conventional sample preparation and MC-ICPMS analysis

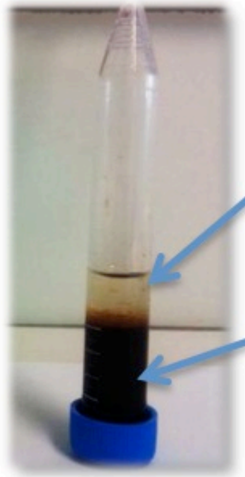
Two-step matrix separation after sample mineralization

1. **Derivatization** with $NaBEt_4$

$Pb^{2+} + NaBEt_4 \rightarrow Et_4Pb$

pH=4,9 (acetate buffer)

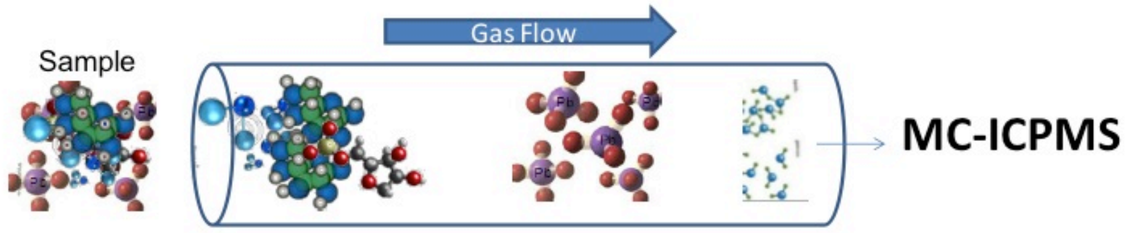
Extraction in isooctane (5-10 min)



Isooctane (0,5 ml) + Et_4Pb

Sample digest

2. **Gas Chromatography** to separate Et_4Pb from the matrix

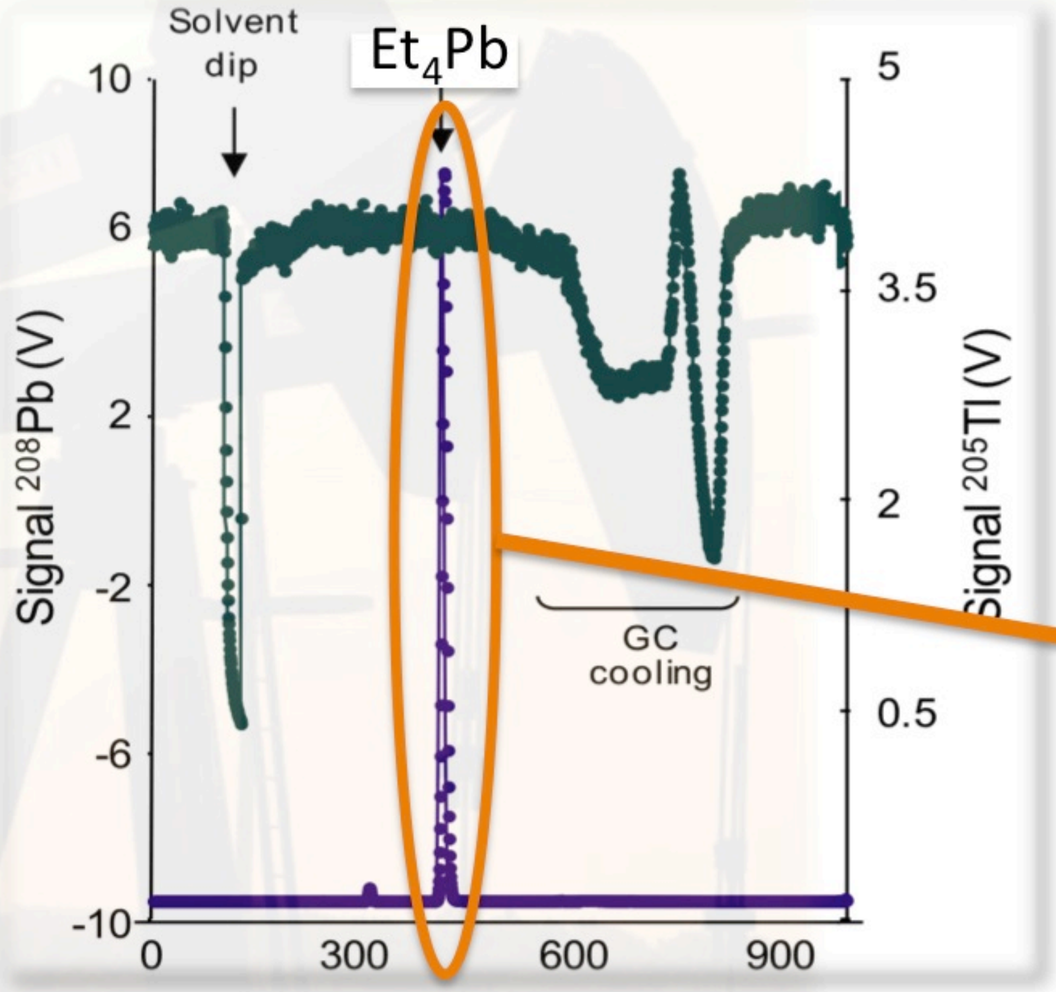


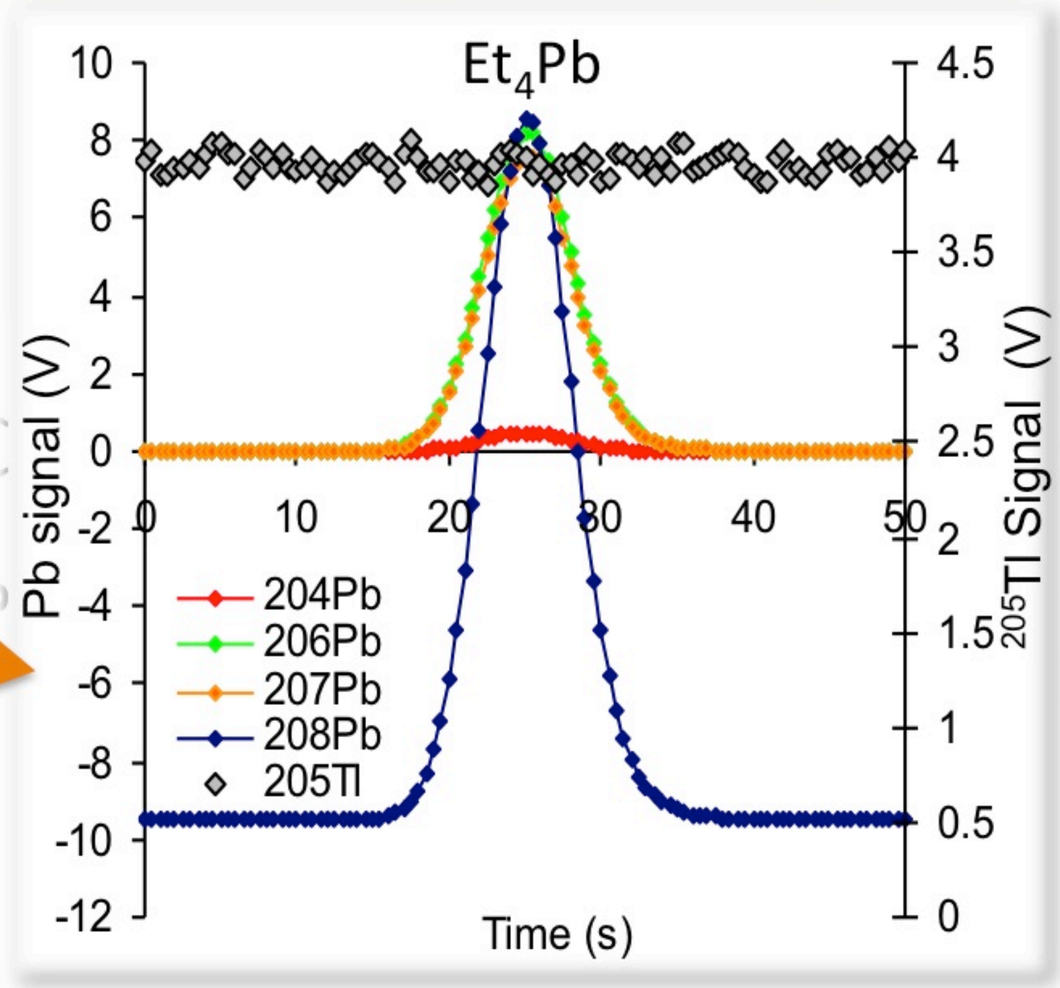
Ethylation of Pb with $NaBEt_4$, Pb extraction in isooctane and the extract is introduced in the MC-ICPMS coupled to a Gas Chromatograph

Anal. Chem. http://dx.doi.org/10.1021/ac301251b

Using speciation techniques for Pb isotope ratios determination.

Elution time per sample	≈ 13 min
Peak duration	**~23 s**
Integration time	**0,5 s (46 points/peak)**
Mass bias correction	Tl external correction + Standard Bracketing (NIST 981)



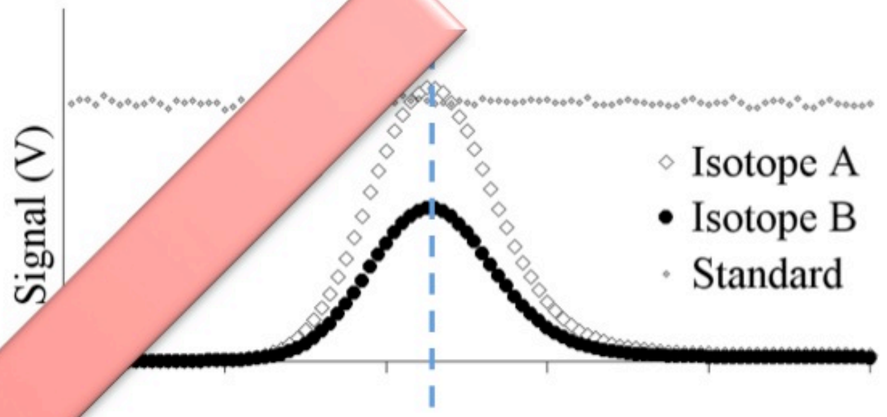


Anal. Chem. http://dx.doi.org/10.1021/ac301251b

How to calculate Isotopic Ratios ?

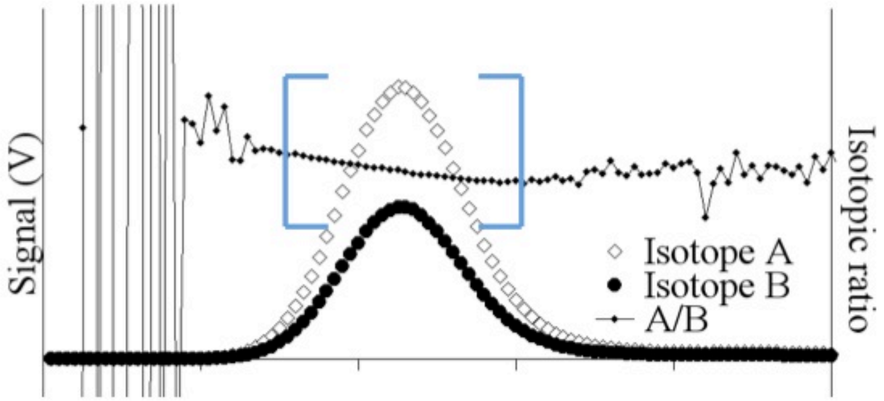
- **Peak Apex:**

$R_{A/B}$= Intensities ratios of [illegible]num



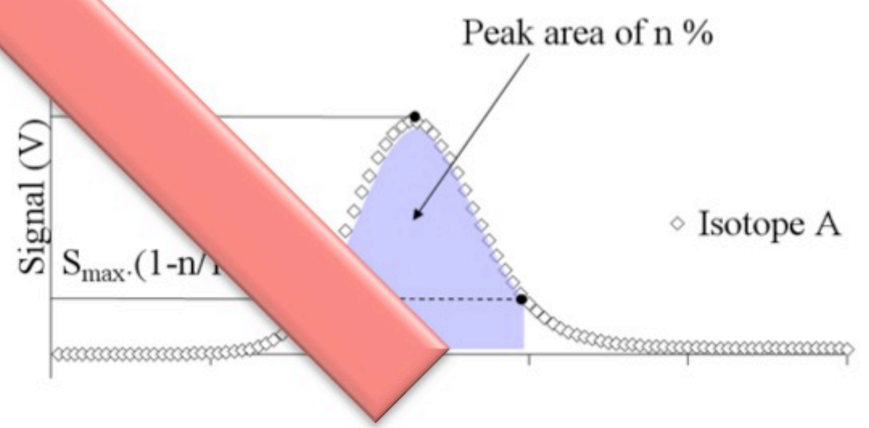
- **Average (point by point):**

$R_{A/B}$= average of isotopic ratios ~ 20 pts



- **Peak area integrati[illegible]**

$R_{A/B}$= ratio of peak [illegible] >90%)

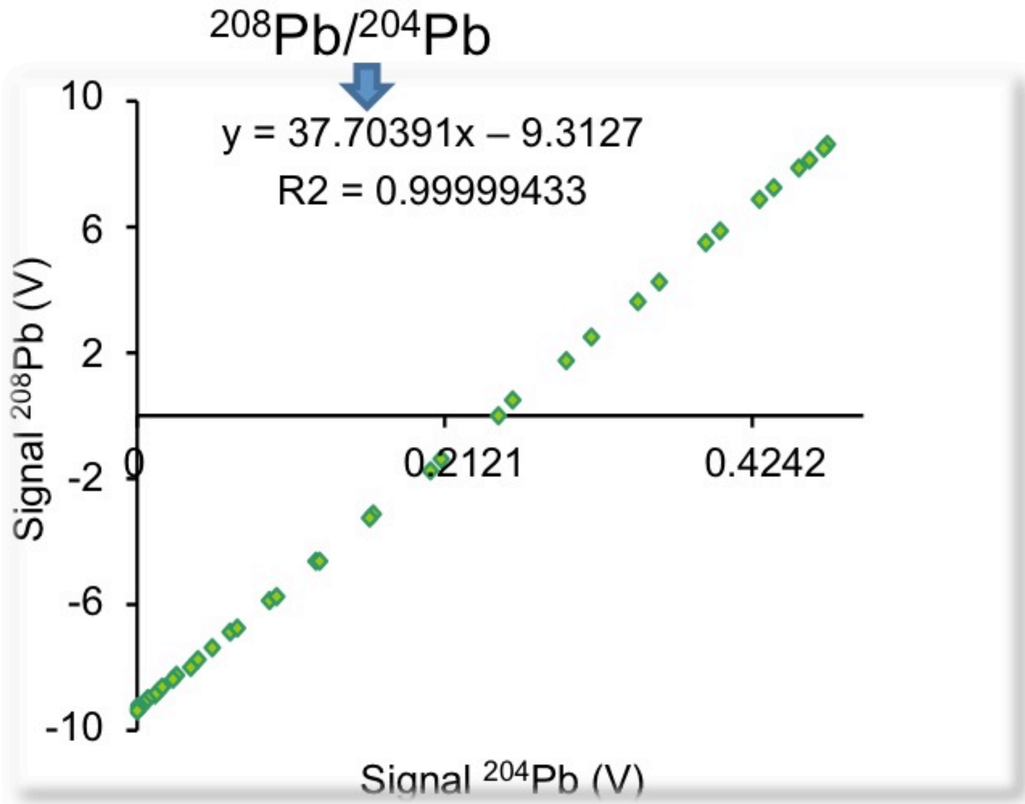


Using speciation techniques for Pb isotope ratios determination.

Data processing

Linear Regression Slope

- *Fietzke et al.(2008), JAAS: Sr by LA / MC-ICP-MS*
- *Epov et al.(2010), Anal. Chem: Hg by GC / MC-ICP-MS*
- *Sanabria et al (2012), Anal Chem, Pb by GC/MC-ICP-MS*
- *Precision improved by ≈ 10*



Results obtained for the measurement of SRM NIST 981, (1,2 ng as Pb was injected)

		$^{208/204}Pb$	$^{207/204}Pb$	$^{206/204}Pb$	$^{208/206}Pb$	$^{207/206}Pb$
	NIST 981 Certified Reference Value	36,72185	15,49161	16,93736	2,1681 ± 0.00033	0,91464 ± 0.0008
	Measured, n = 7	36,72093	15,49127	16,93699	2,16809	0,914641
Corrected (Tl+ Bracketing)	Deviation to the CRV (‰)	**-0.025**	**-0.022**	**-0.022**	**-0.005**	**0.00068**
	$2RSD_{Ext}$, (ppm)	**234**	**190**	**209**	**49**	**69**

Anal. Chem. http://dx.doi.org/10.1021/ac301251b

Analysis of real-life samples: oil, asphaltens, kerogens, etc…

Comparing pneumatic nebulisation (DSN) with GC methods.

Isotope ratios obtained for one crude oil, two asphaltenes, three kerogens

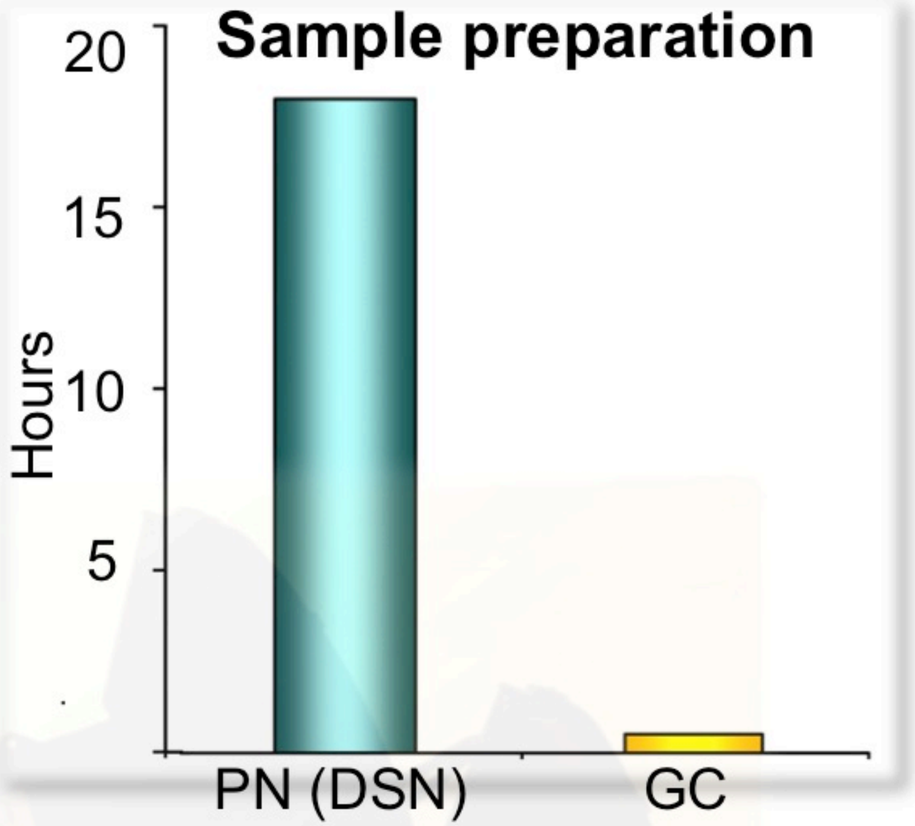
Sample	$^{208/204}Pb$	$^{207/204}Pb$	$^{206/204}Pb$
Kero1, **pneumatic nebulization** (DSN) (n = 4)	38.2677 ± 0.0017	16.0729 ± 0.0005	18.6581± 0.0038
Kero1. **GC** (n = 5)	38.2648 ± 0.0118	16.0739 ± 0.0031	18.6553 ± 0.0115
Kero2, **pneumatic nebulization** (DSN) (n = 2)	38.3174 ± 0.0218	16.2224 ± 0.0089	22.8335 ± 0.1144
Kero2, **GC** n = 2	38.3198 ± 0.0048	16.2235 ± 0.0036	22.6573 ± 0.0136
Kero3, **pneumatic nebulization** (DSN) (n = 2)	38.3508 ± 0.0030	16.1600 ± 0.0013	20.9620 ± 0.0015
Kero3, **GC** (n = 4)	38.3424 ± 0.0114	16.1570 ± 0.0042	20.9242 ± 0.0219
Asph1, **pneumatic nebulization** (DSN) (n = 2)	38.6146 ± 0.0039	16.1212 ± 0.0016	19.1545 ± 0.0022
Asph1, **GC** (n = 2)	38.6105 ± 0.0005	16.1210 ± 0.0002	19.1486 ± 0.0016
Asph2, **pneumatic nebulization** (DSN) (n = 2)	38.4428 ± 0.0042	16.0769 ± 0.0015	18.7759 ± 0.0019
Asph2, GC (n = 1)	38.4365	16.0763	18.7680
COil1, **pneumatic nebulization** (DSN) (n = 2)	38.6613 ± 0.0013	16.1343 ± 0.0001	19.1747 ± 0.0006
COil1, GC (n= 3)	38.5861 ± 0.0187	16.1136 ± 0.0065	19.0904 ± 0.0678

Analytical uncertainty represents SD of reproducibility

Sanchuña Ortega. Submitted article Anal. Chem.

Anal. Chem. http://dx.doi.org/10.1021/ac301251b

Analysis of real-life samples: oil, asphaltens, kerogens, etc…



Sample Preparation time

Wet and dry plasma: Column separation, acid evaporation

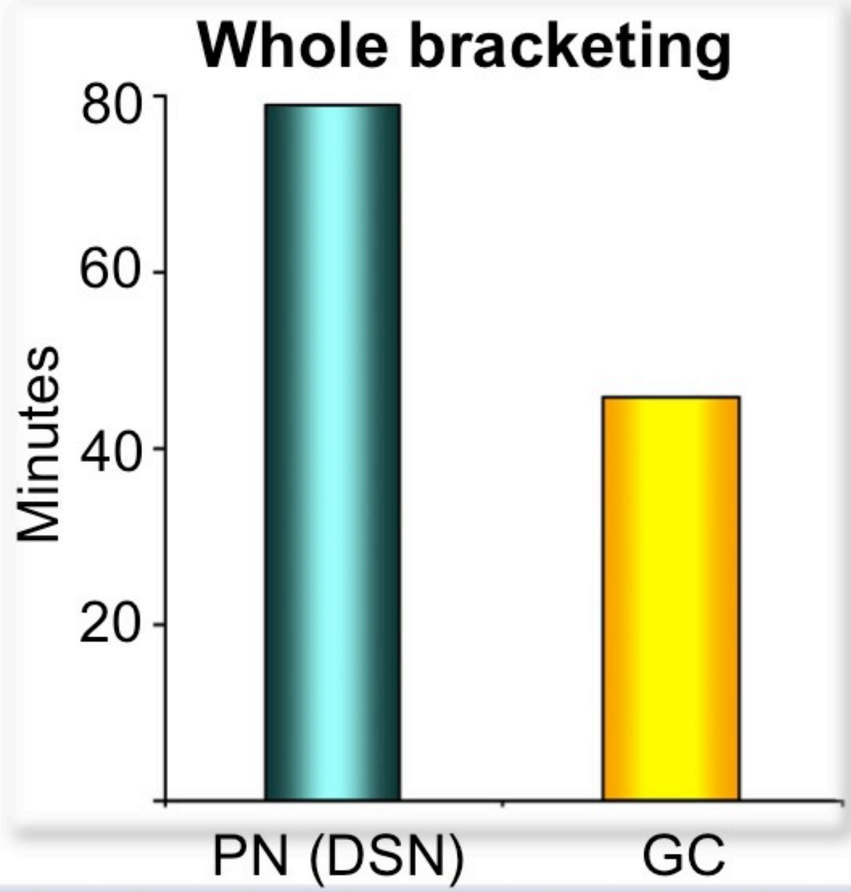
GC: Ethylation and isooctane extraction

15 times faster!!!

Measurement Protocol

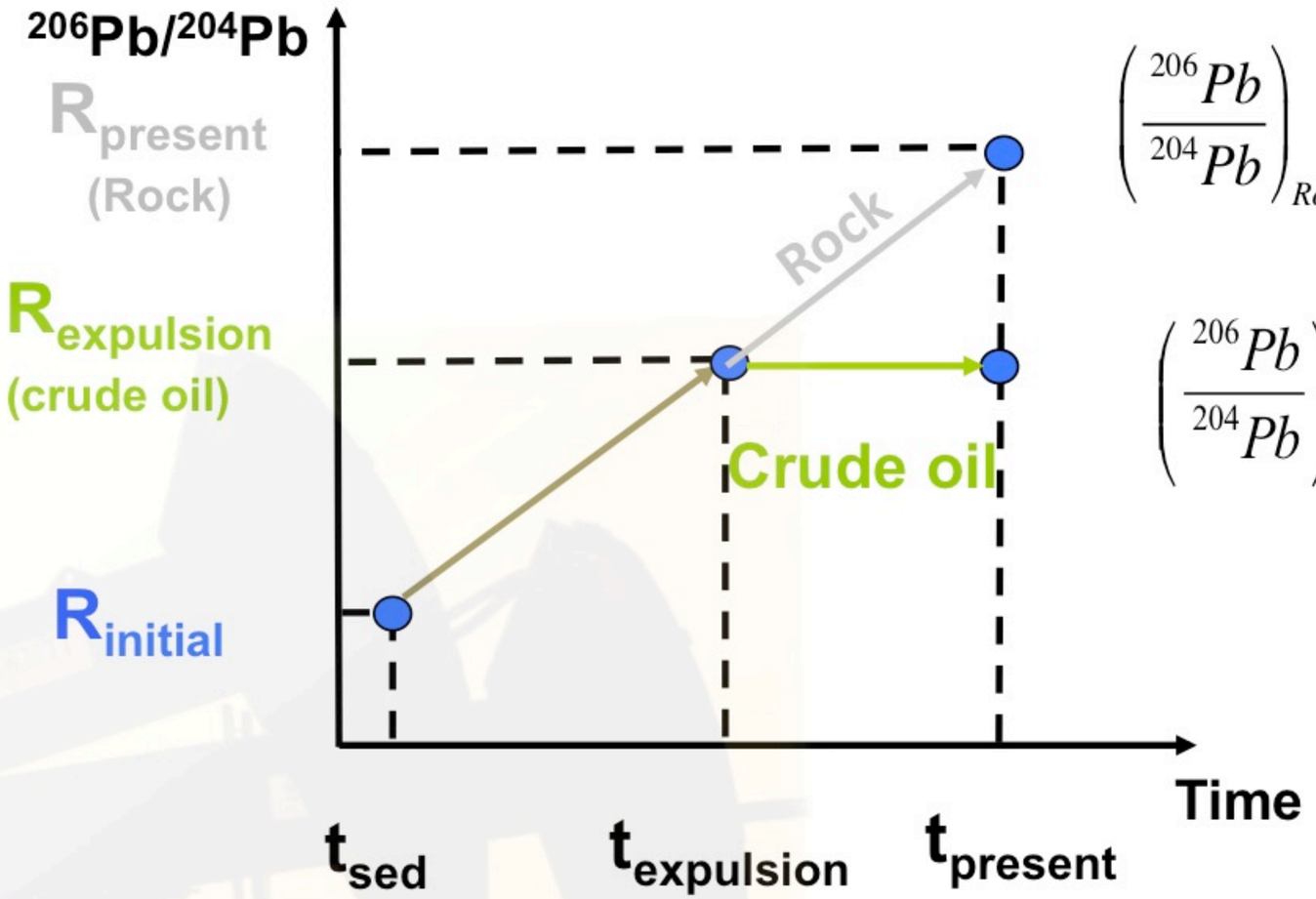
Wet and dry plasma: Wash + Blank + NIST981 + wash + blank + sample + wash + blank + NIST981

GC: NIST981 + Sample + NIST981



Anal. Chem. http://dx.doi.org/10.1021/ac301251b

Dating petroleum generation …



$$\left(\frac{^{206}Pb}{^{204}Pb}\right)_{Rockpresent} = \left(\frac{^{206}Pb}{^{204}Pb}\right)_{Rockgeneration} + \left(\frac{^{238}U}{^{204}Pb}\right)_{Rockpresent}(e^{\lambda t} - 1)$$

$$\left(\frac{^{206}Pb}{^{204}Pb}\right)_{COpresent} = \left(\frac{^{206}Pb}{^{204}Pb}\right)_{COgeneration} + \left(\frac{^{238}U}{^{204}Pb}\right)_{COpresent}^{\mathbf{0}}(e^{\lambda t} - 1)$$

$$\left(\frac{^{206}Pb}{^{204}Pb}\right)_{COpresent} = \left(\frac{^{206}Pb}{^{204}Pb}\right)_{Rockgeneration}$$

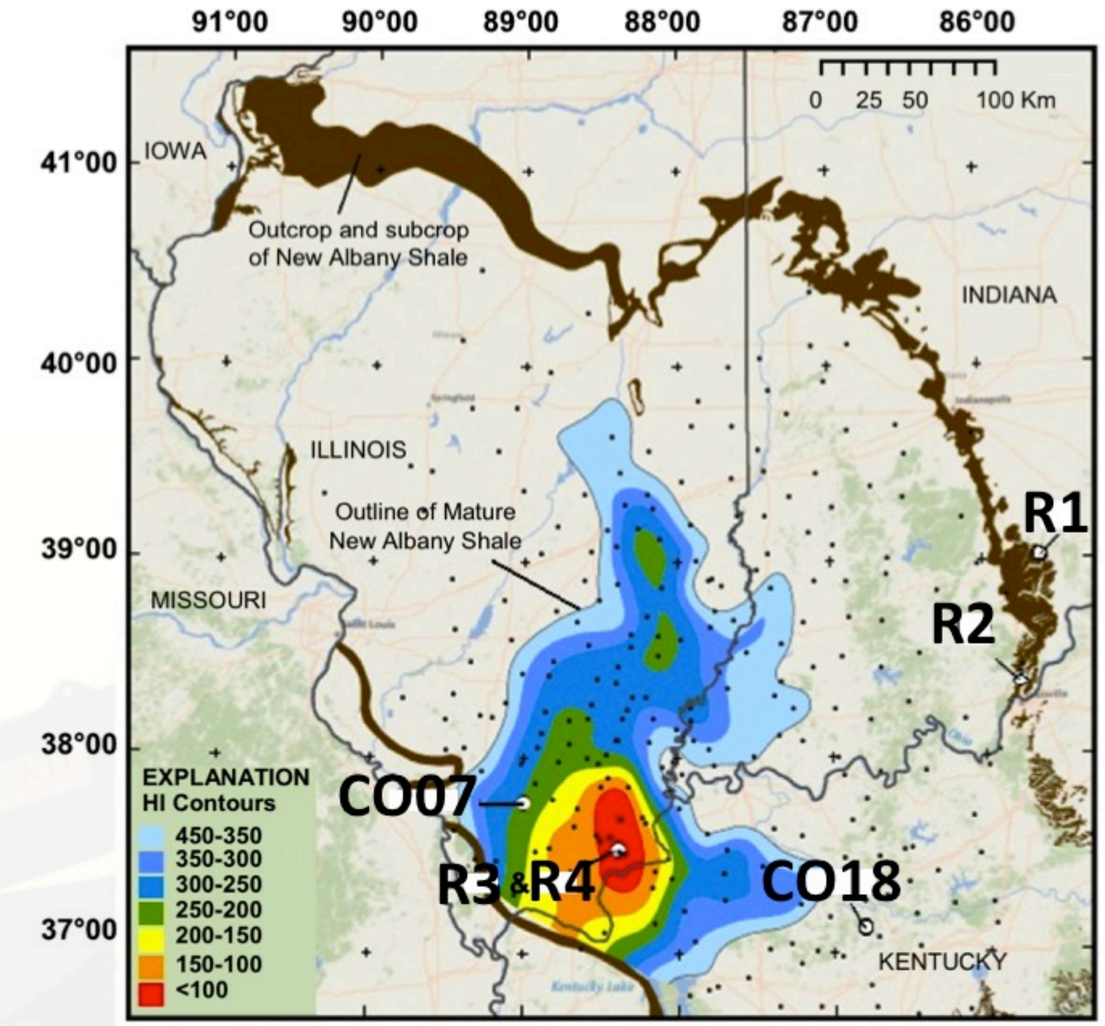
$t_{generation}$ expression:

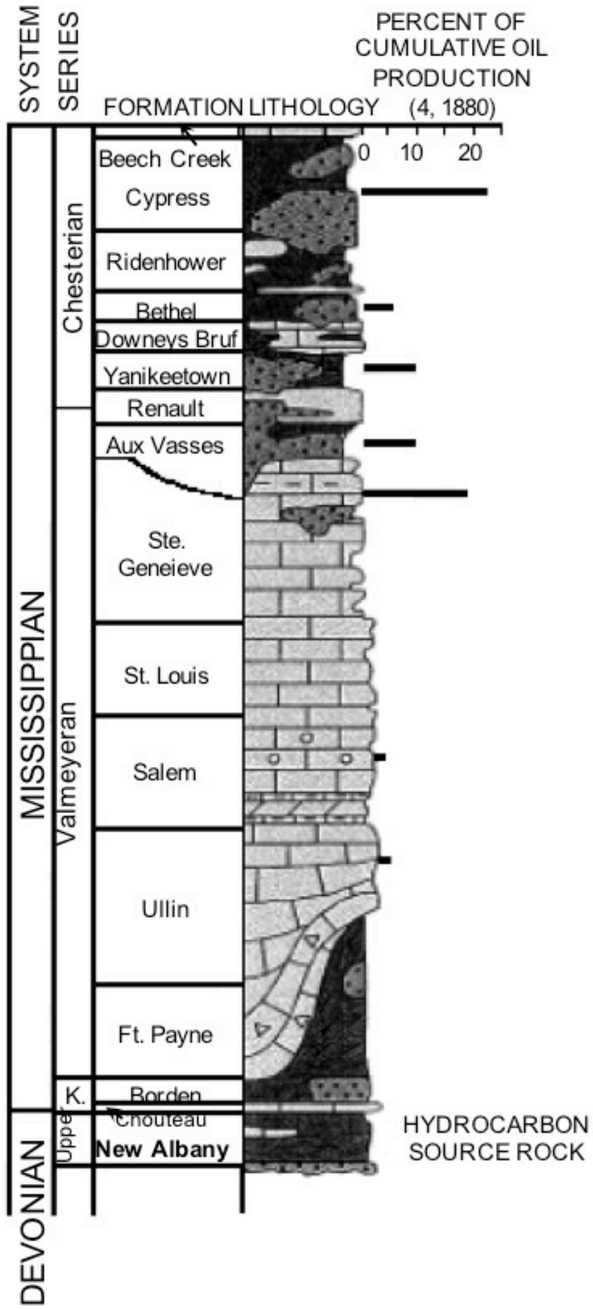
$$t_{generation} = \frac{1}{\lambda}\ln\left[\frac{\left(^{206}Pb/_{^{204}Pb}\right)_{Rockpresent} - \left(^{206}Pb/_{^{204}Pb}\right)_{COpresent}}{\left(^{238}U/_{^{204}Pb}\right)_{Rockpresent}}\right]$$

Sanabria Ortega, Article in preparation, Science

Dating petroleum generation …

New Albany Shale – Illinois Basin





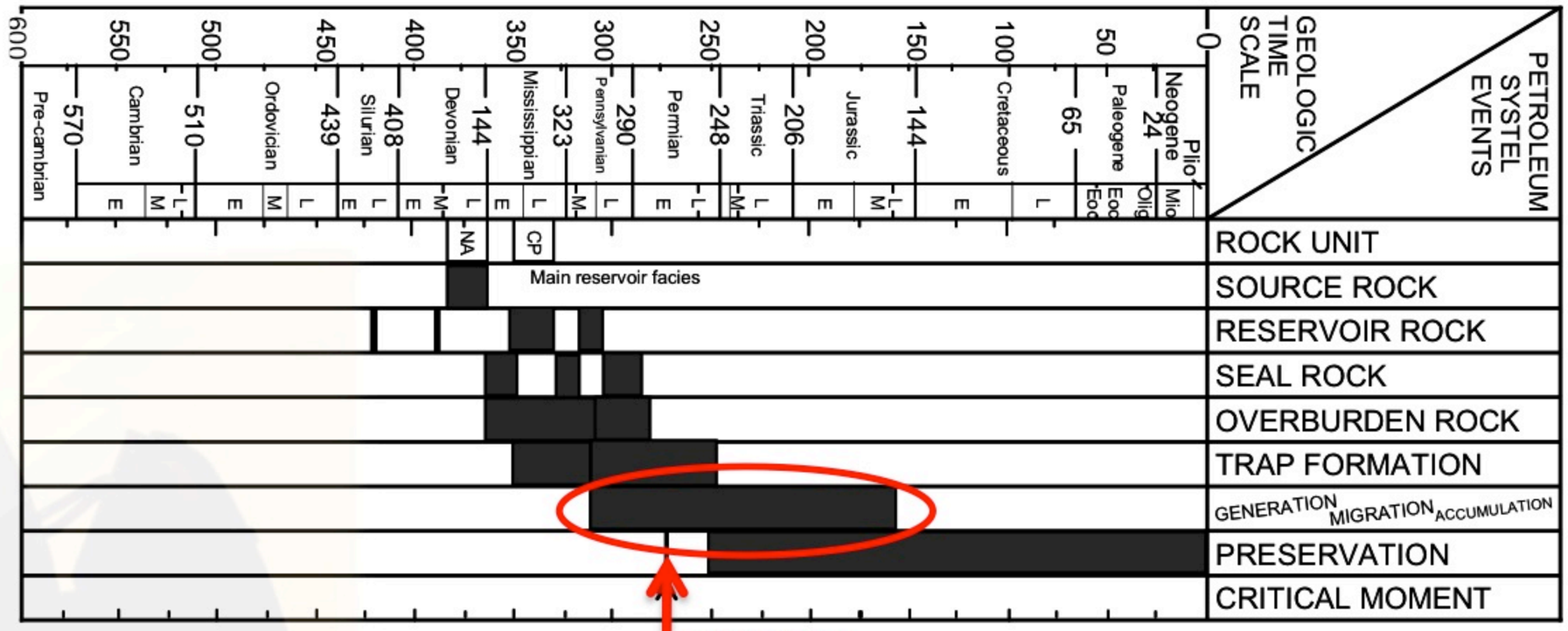
- Extends cross Illinois, southwestern Indiana and western Kentucky
- Time-Transgresive unit
- Consits of brownish-black, organic-rich and greenish-gray organic-poor shale
- Near the southern depocenter, the black shale incorporate more than 2.5% wt% organic carbon which are typical of the oil prone type II kerogen.
- Samples availables: 4 Source rocks, 2 crude oil

Sanabria Ortega, Article in preparation, Science

Dating petroleum generation …

Ages of crude oils and their asphaltenes measured with the U/Pb chronometer

Events chart
Illinois basin



Sample	Crude Oil C007		Asphaltene AS007		Crude Oil C018		Asphaltene AS018	
	$^{238}U/^{204}Pb$ $^{206}Pb/^{204}Pb$	$^{235}U/^{204}Pb$ $^{207}Pb/^{204}Pb$	$^{238}U/^{204}Pb$ $^{206}Pb/^{204}Pb$	$^{235}U/^{204}Pb$ $^{207}Pb/^{204}Pb$	$^{238}U/^{204}Pb$ $^{206}Pb/^{204}Pb$	$^{235}U/^{204}Pb$ $^{207}Pb/^{204}Pb$	$^{238}U/^{204}Pb$ $^{206}Pb/^{204}Pb$	$^{235}U/^{204}Pb$ $^{207}Pb/^{204}Pb$
Rock R1	136 ± 23	110 ± 30	128 ± 12	94 ± 8	196 ± 20	230 ± 28	180 ± 17	204 ± 44
Rock R2	285 ± 10	290 ± 11	284 ± 8	288 ± 8	294 ± 9	305 ± 10	292 ± 9	301 ± 13
Rock R3	253 ± 11	252 ± 13	251 ± 8	248 ± 8	270 ± 10	283 ± 13	267 ± 9	276 ± 17
Rock R4	277 ± 6	277 ± 8	275 ± 4	274 ± 4	289 ± 5	299 ± 7	285 ± 5	294 ± 10

Conclusion…

- An alternative method for Pb isotope ratio determination have been developed by GC-MC-ICPMS.
  - Precision < 200 ppm
  - Accuracies around -0.020 ‰

  } **1.2 ng of Pb**

  - Analytical process reduced by a factor 15.
  - Good performance for the analysis of complex matrices.

- The U-Pb geochronometer was successfully used, for the first time, to estimate the age of crude oil generation.

- Geochemistry approaches revisited with speciation techniques.

Analytical chemistry in 5 dimensions

Concentration

LASER ABLATION/ICPMS

Molecular structure

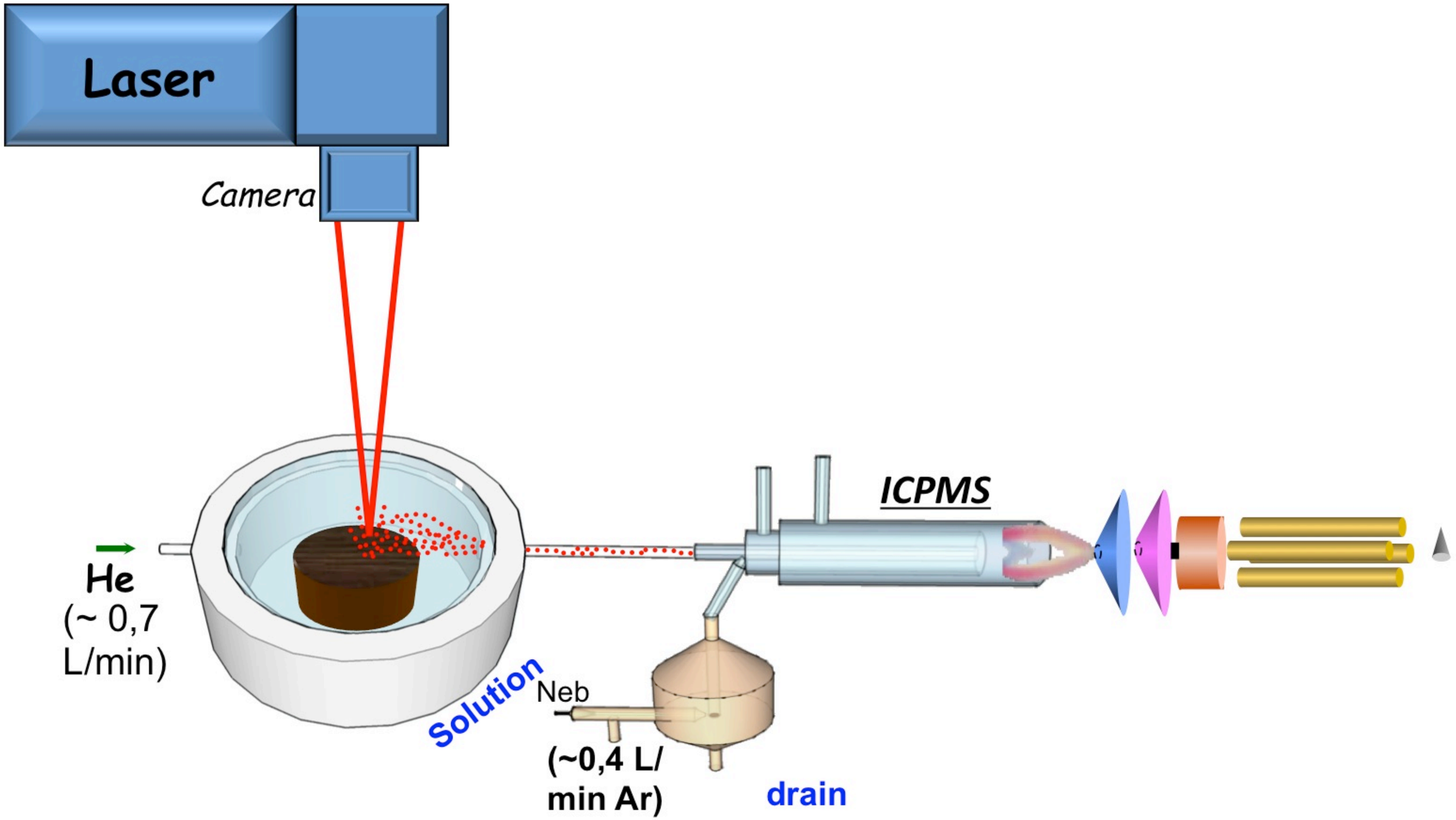
Isotope

INFORMATION

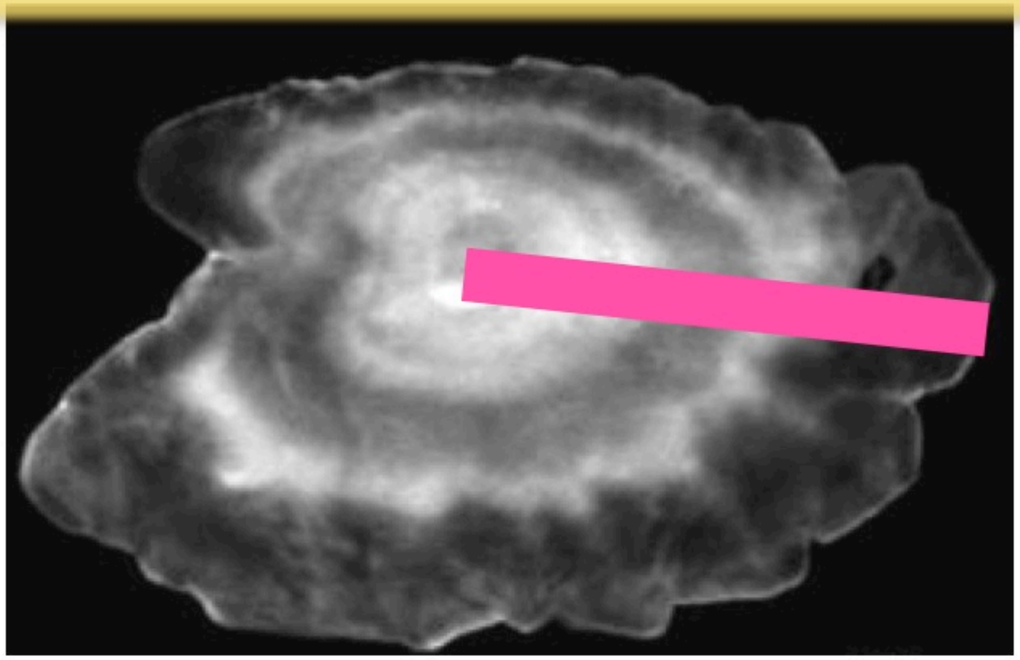
Spatial resolution

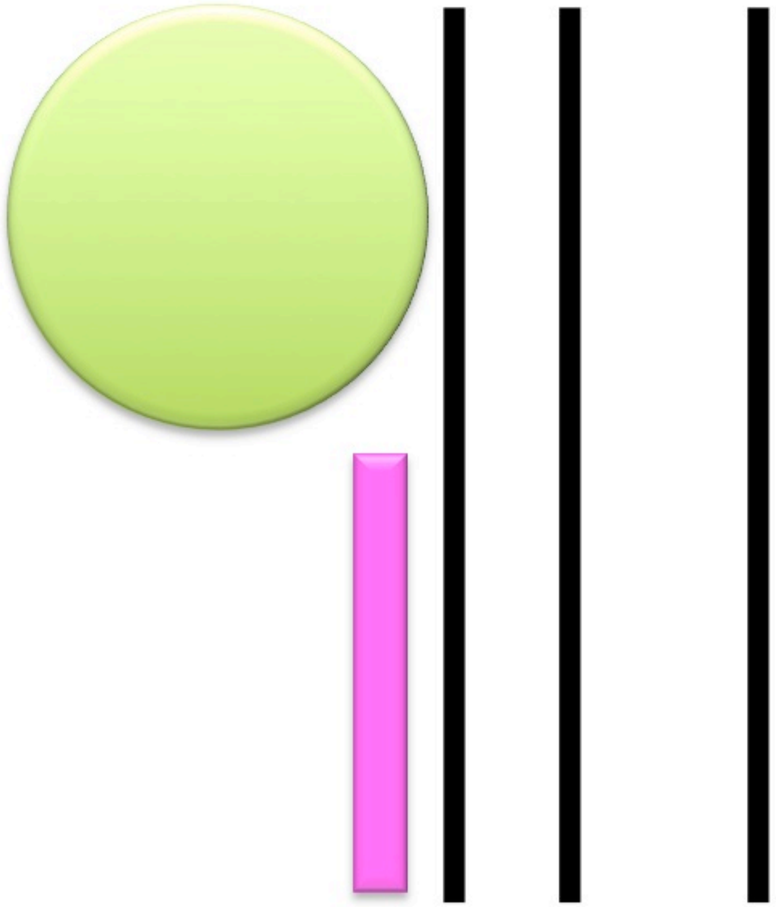
Time resolution

Laser ablation-ICPMS set up

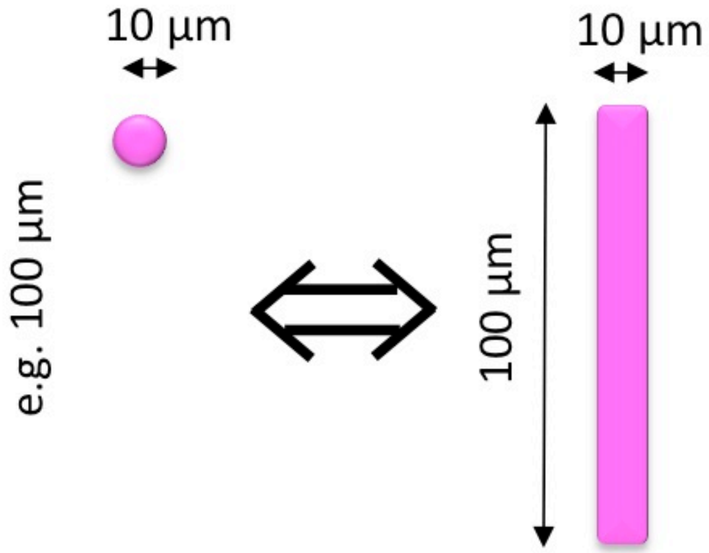


Simulating a sharp blade laser beam

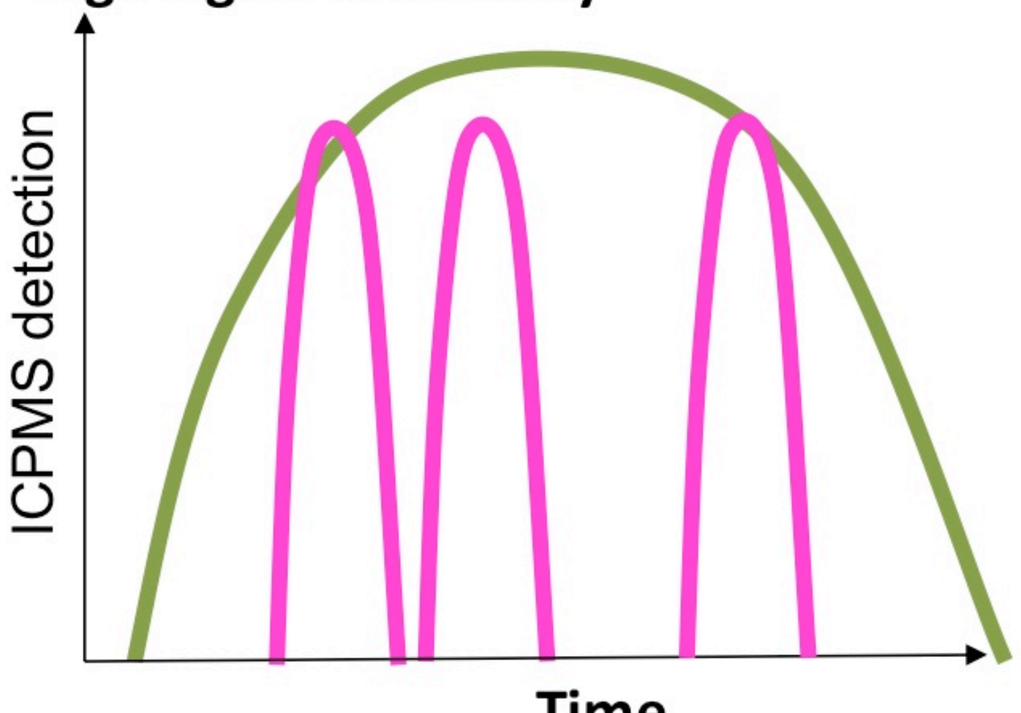




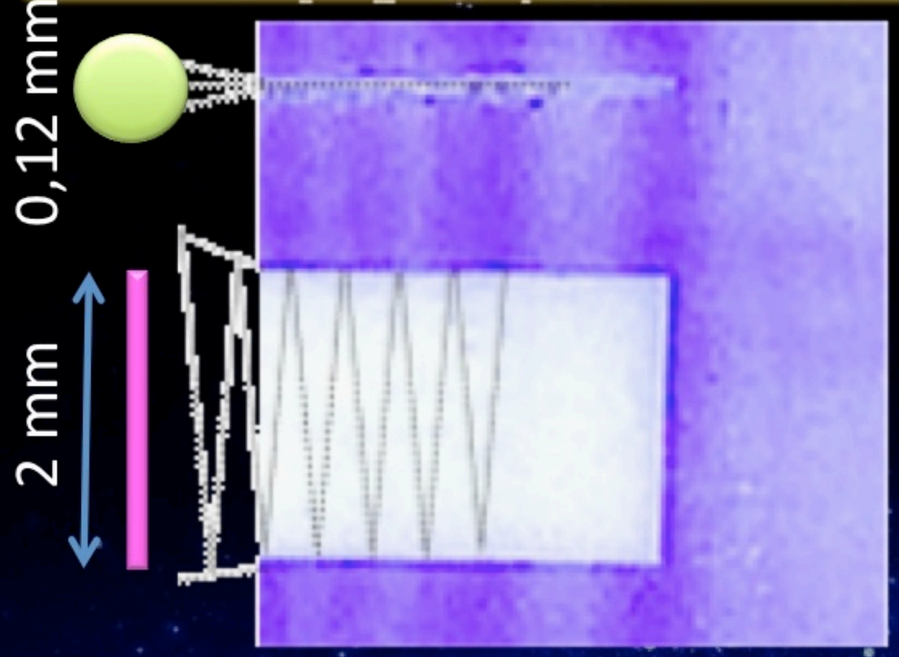
Scanning with a virtual sharp blade…



Large spot vs sharp blade ablation :
-> better spatial resolution while keeping high signal sensitivity



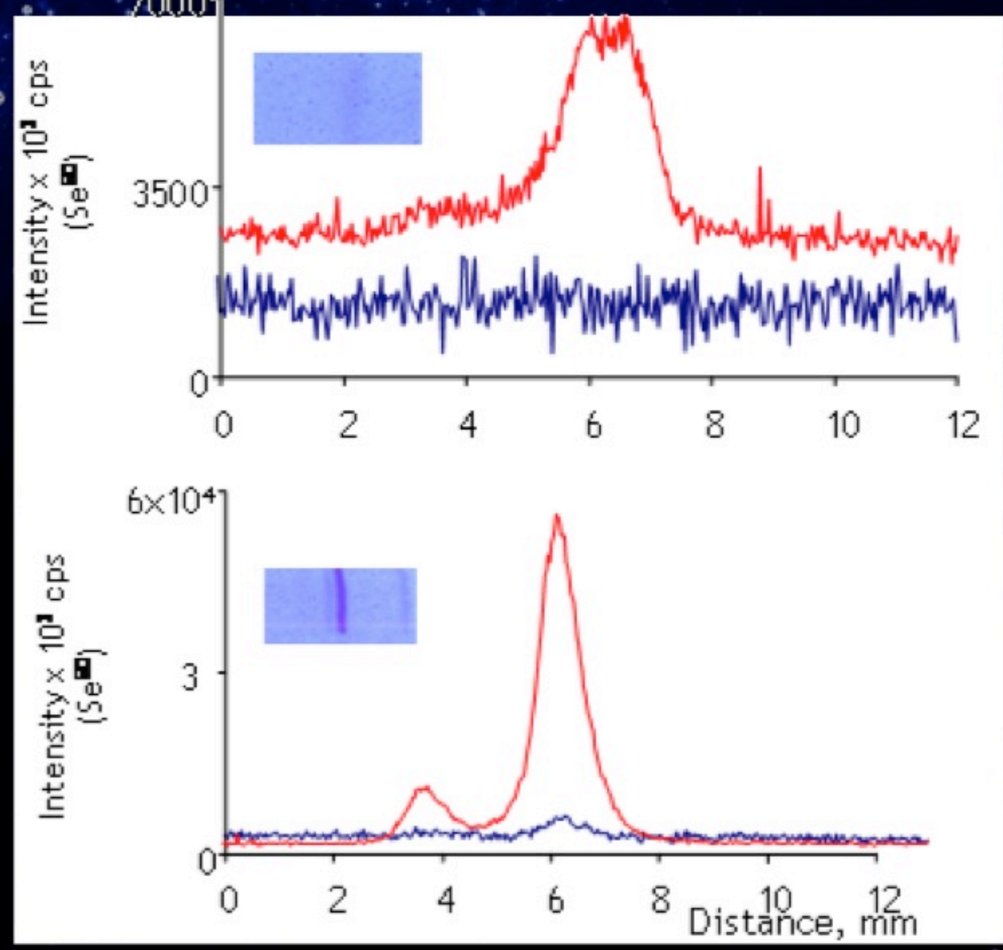
Application to ultra trace metallo-protein identification



Proteins previously separated on gel electrophoresis

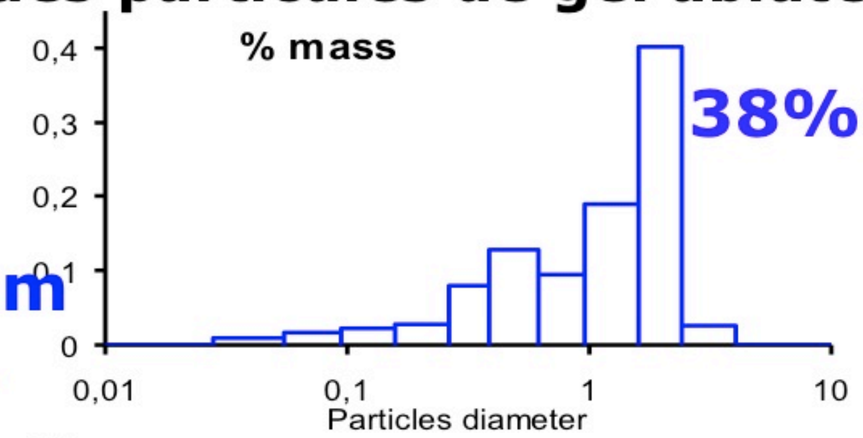
Improvement factor >40

$V_{fsLA} = 27 \times V_{nsLA}$



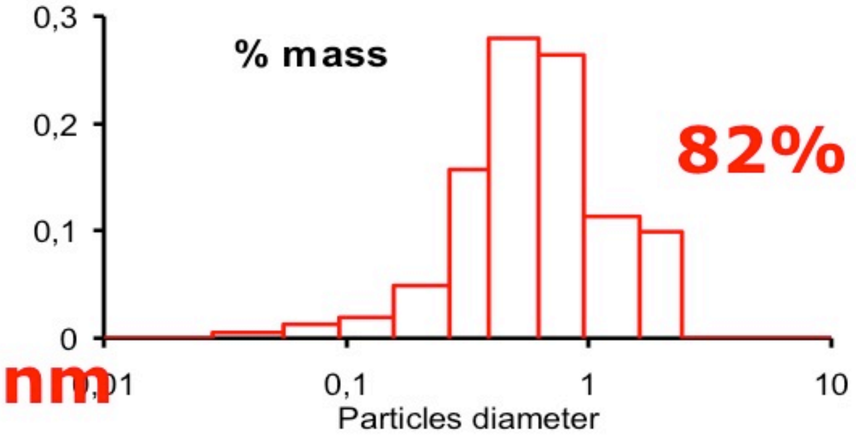
Taille des particules de gel ablaté

266 nm ns LA



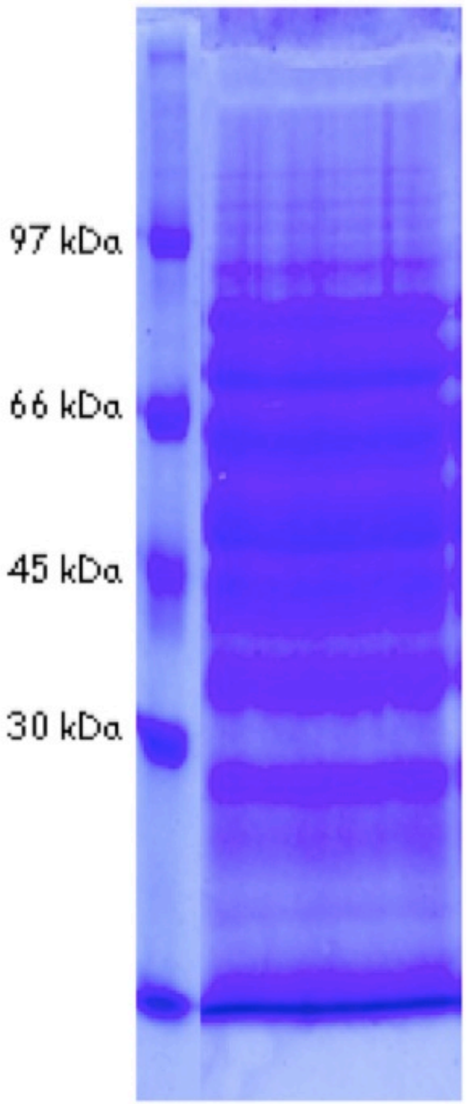
38% < 1µm

1030 nm fs LA

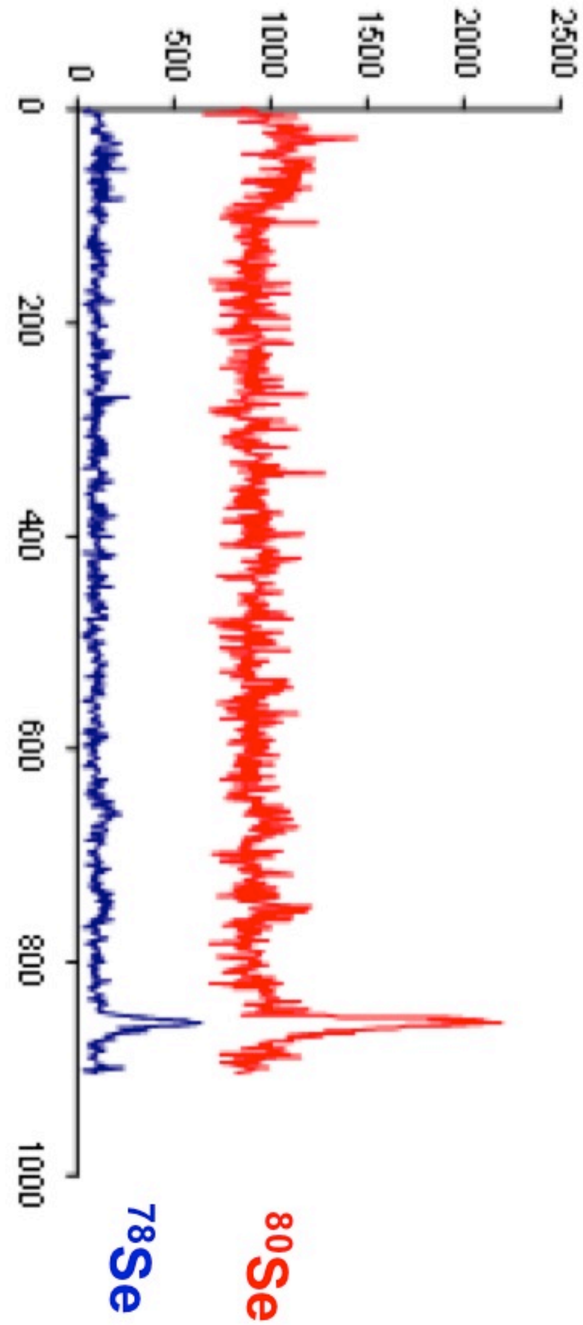


82% < 1µm

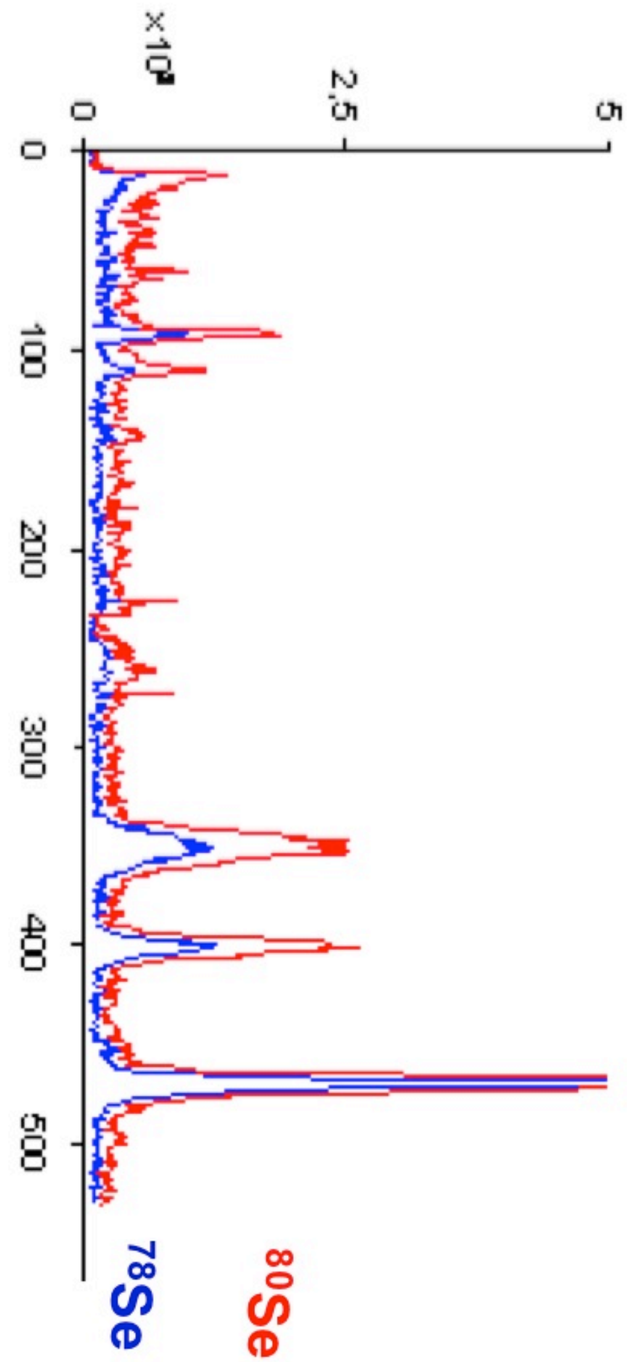
Application in proteomics :
Toward the identification of new preoteins…



266 nm ns laser



Alfamet laser



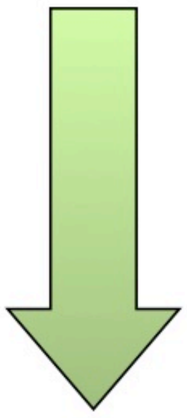
In collaboration with R. Lobinski and S. Mounicou

Short pulses (8 ns)

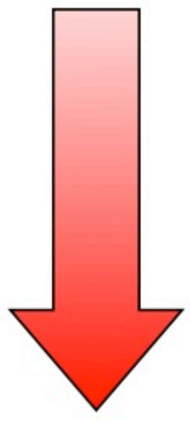
CETAC LSX 100,
266 nm, 20 Hz, 1 mJ
laser beam diameter : 130 µm

Ultra short pulses 360 fs

ALFAMET,
10000 Hz, 35 µJ
Virtual beam shape
2000 µm x 20 µm



Collision cell

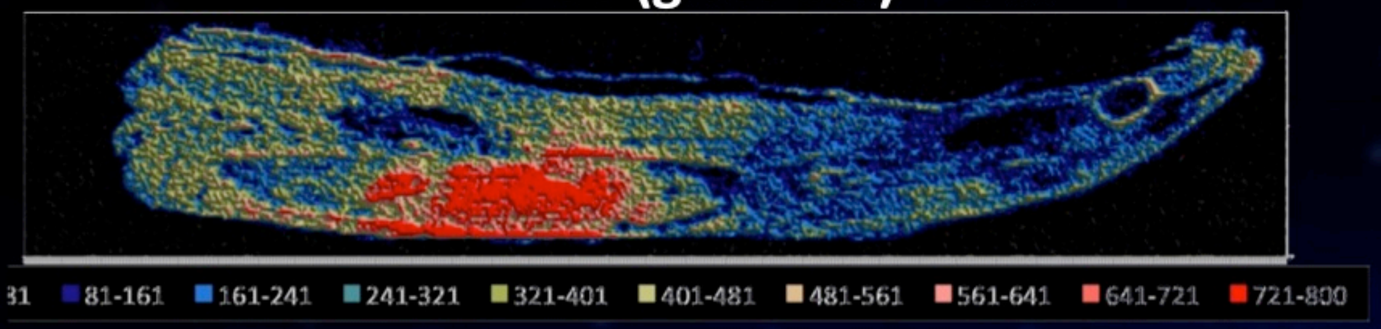


LOD = 1 ppb

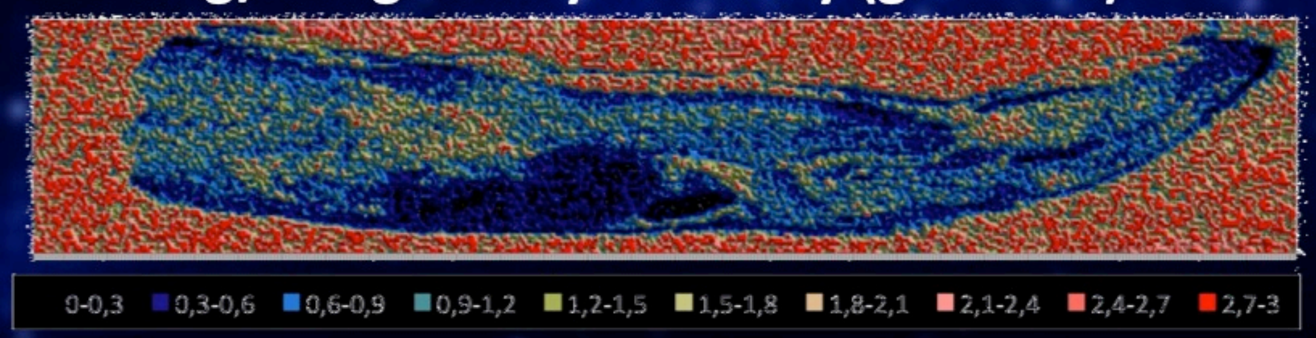
LOD = 0.02 ppb

Isotopic speciation imaging by fsLA/ICPMS.

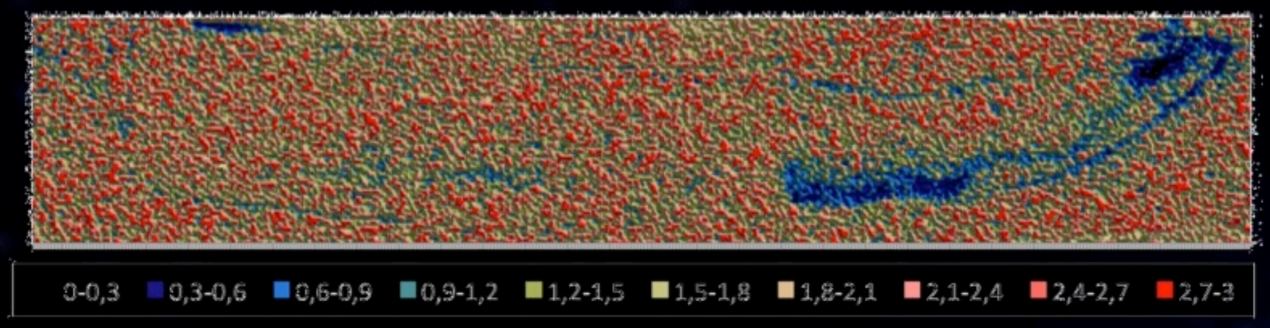
^{77}Se (glass eel) – 8 h



^{202}Hg/^{201}Hg Methyl mercury (glass eel)



^{202}Hg/^{199}Hg Inorganic mercury (glass eel)

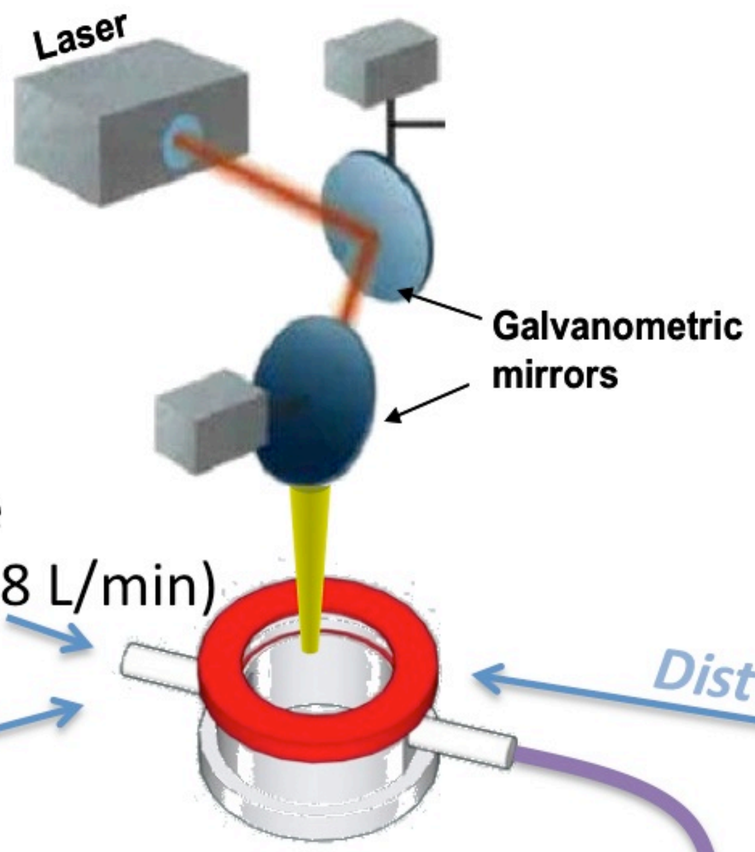


Glass eel grown in water spiked with isotopicall enriched methyl mercury (201HgMe+) and isotopically enriched inorganic mercury (199Hg2+).

Identification of the bioaccumulation sites (better understanding of the metabolism and detoxification processes...)

FsLA- 2D-SF-ICPMS : Simultaneous isotopic and trace element information

IR-Vis-Uv Fs Laser



- gas flow rate tuning
- split adjustment
- Plasma viscosity
- + and other parameters

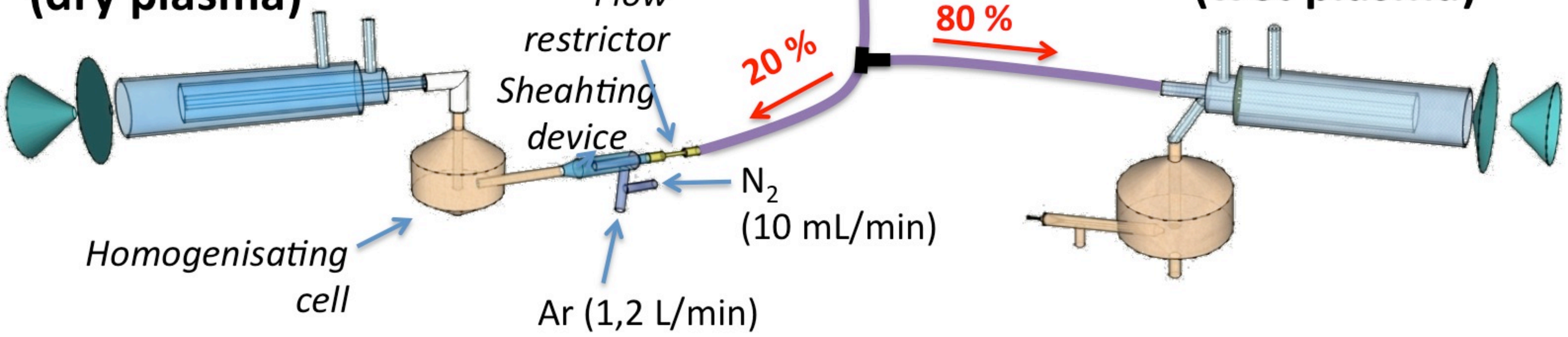
- Stability
- Sensitivity
- Accuracy

Distance : 2 m

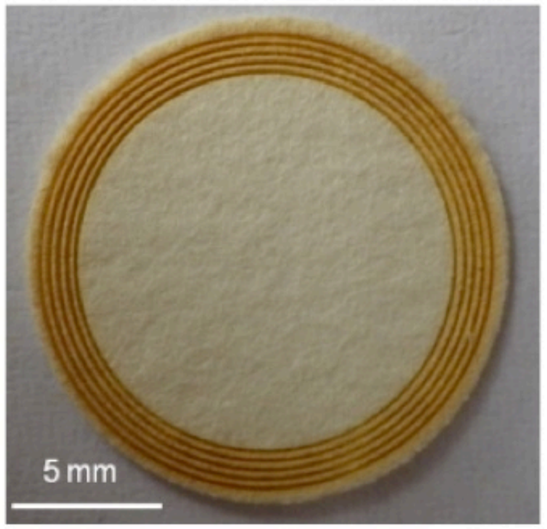
Distance : 10 m

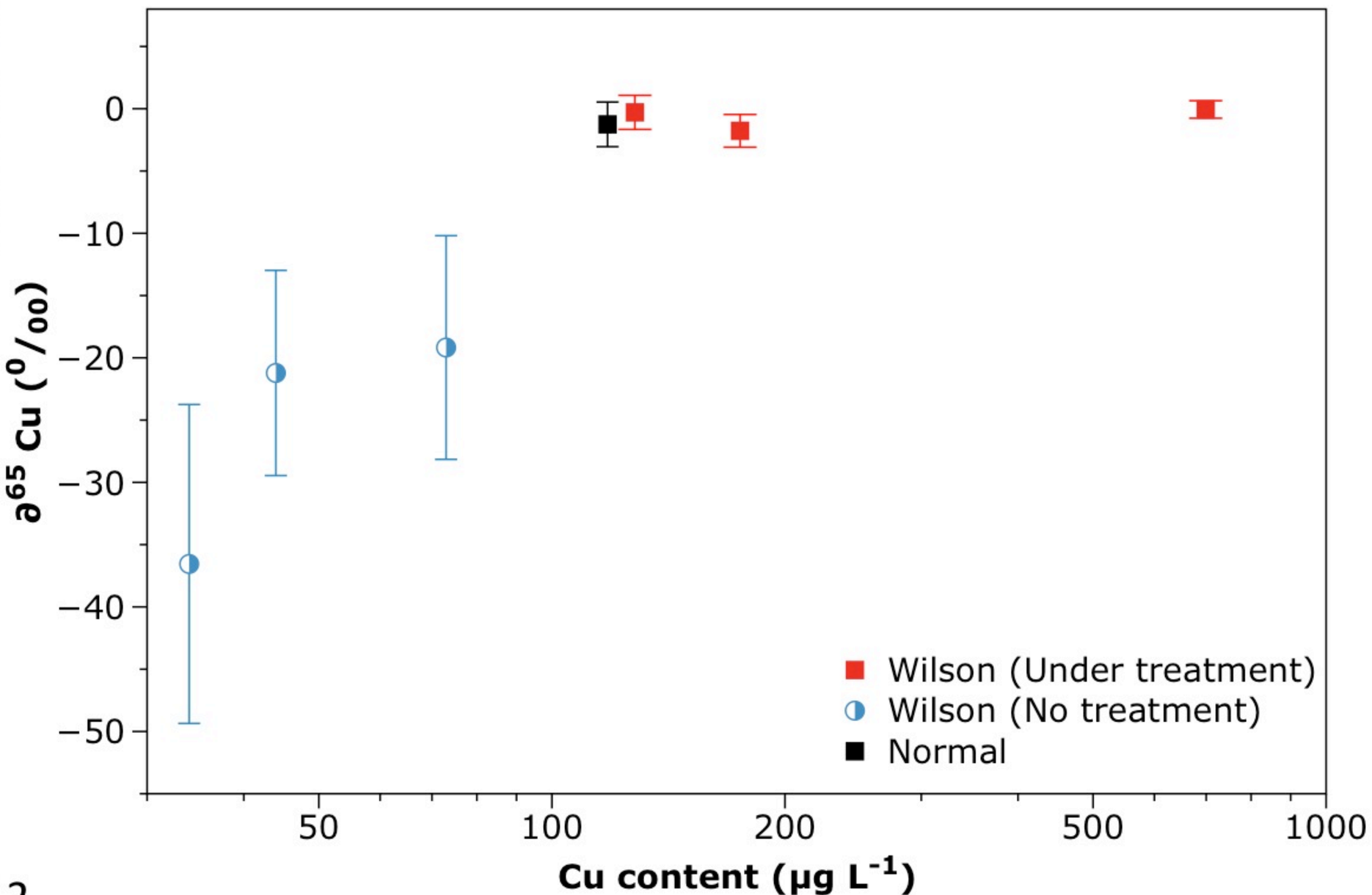
Jet-HR-ICPMS (dry plasma)

MC-ICPMS (wet plasma)



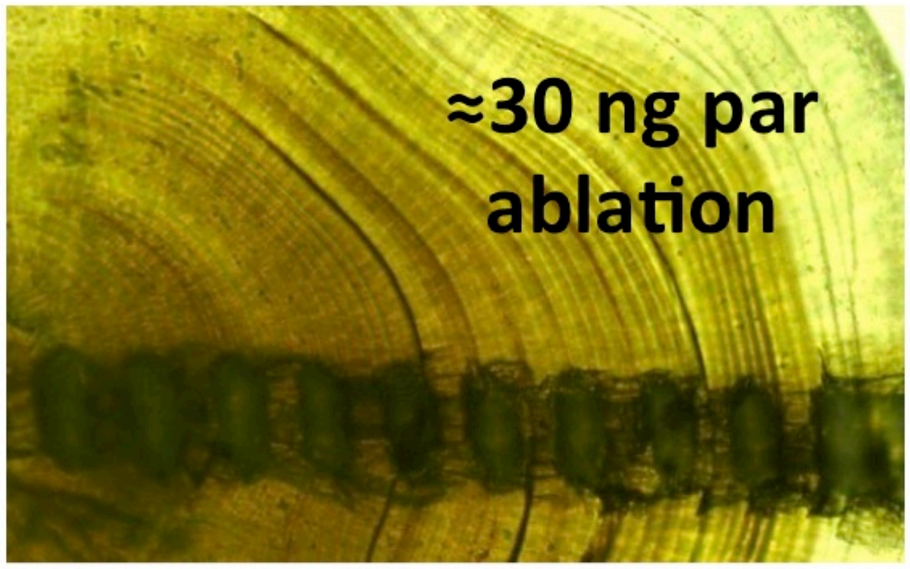
Development of a minimally invasive test for early diagnosis of Wilson's disease



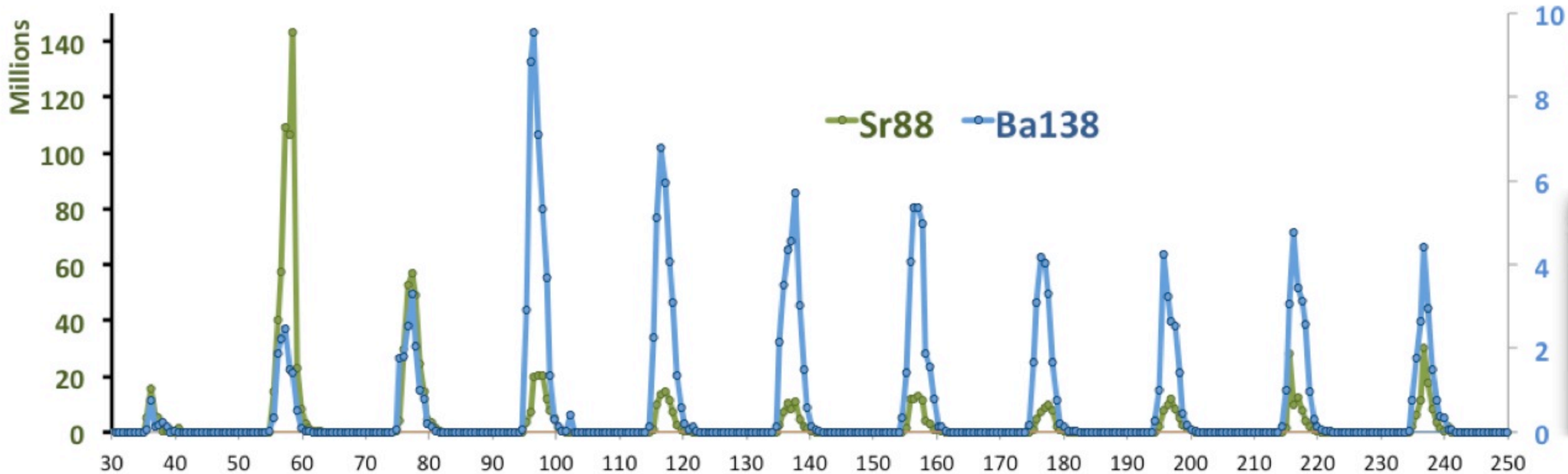


Resano et Al, JAAS, 2012

FsLA- 2D-SF-ICPMS :
Simultaneous isotopic and trace element information

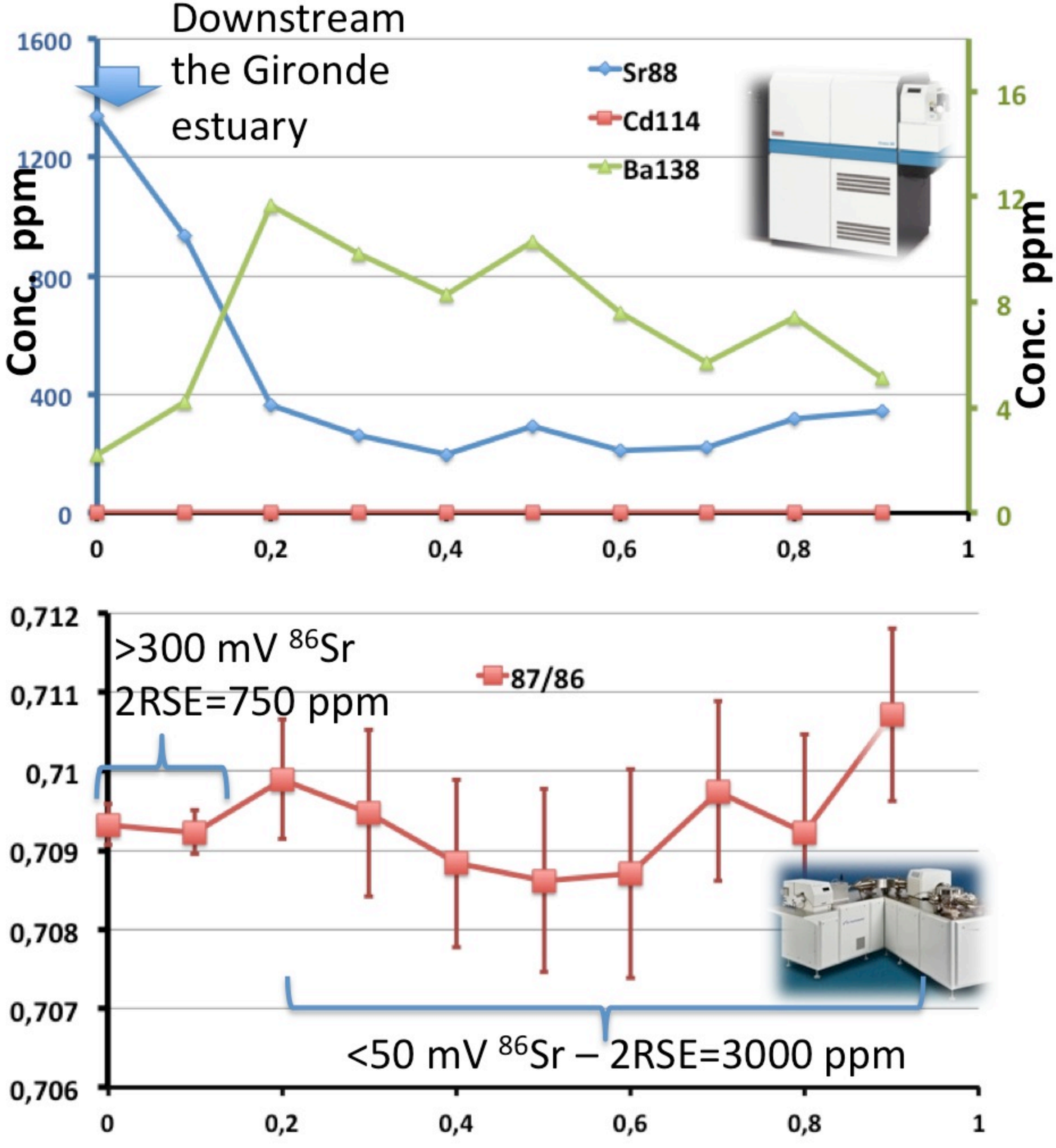


MC-ICPMS



Jet HR-ICPMS

FsLA- 2D-SF-ICPMS : Simultaneous isotopic and trace element information



Typical LODs with fsLA/Jet-HRICPMS

Sr =40 ppb *i.e.* ***1,2 femtograms***

Ba = 6 ppb *i.e.* ***180 attograms***

Cd = 4 ppb *i.e.* ***120 attograms***

Versatile approach with complementary information. Relevant when some geochemical signatures are not significantly pronounced (here 87/86Sr)