2nd Workshop of the EU ASIA-LINK CALIBRE Project, Grenoble, France, 22nd-23rd September 2008

Mercury speciation in continental water

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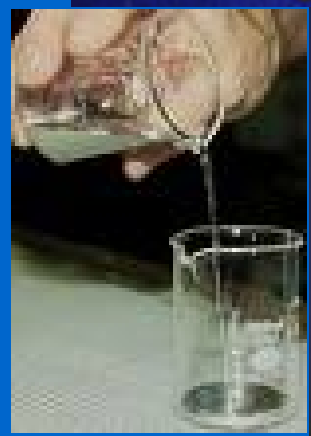
I – Hg Global Overview

Mercury species in the environnement



- **Elemental mercury (Hg^0) :**

Liquid (at roomT°) and volatil

Natural: cinabar (HgS)

Industry : chlor-alkaly, pharmaceutical, chemicals, dental, catalytical…

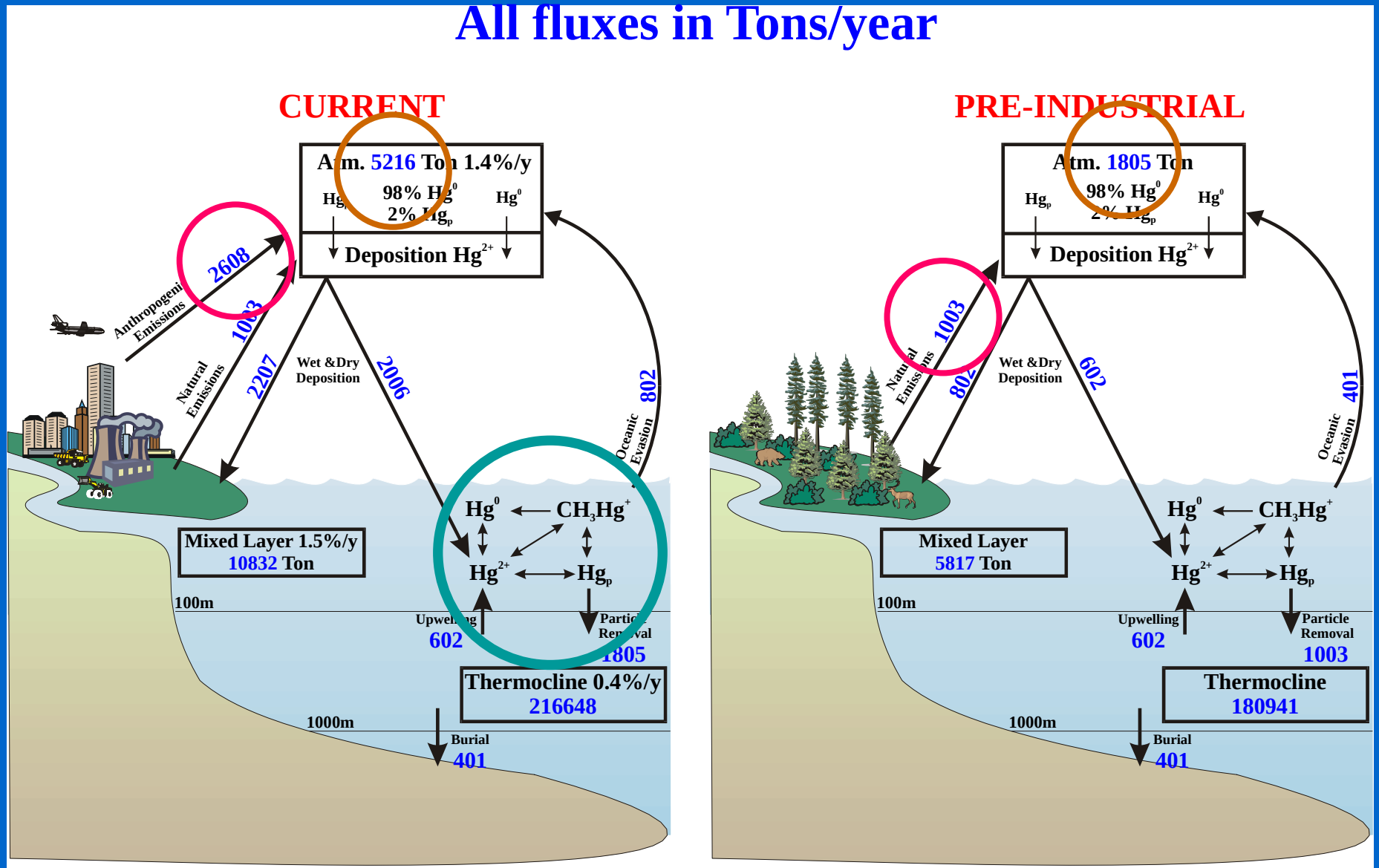
- **Divalent mercury (Hg^{II}) :**

oxidized state, main form in soils, sediments, hydrosystems and biota

MeHg : organic form, toxic, bioaccumulation

Global environmental mercury budget

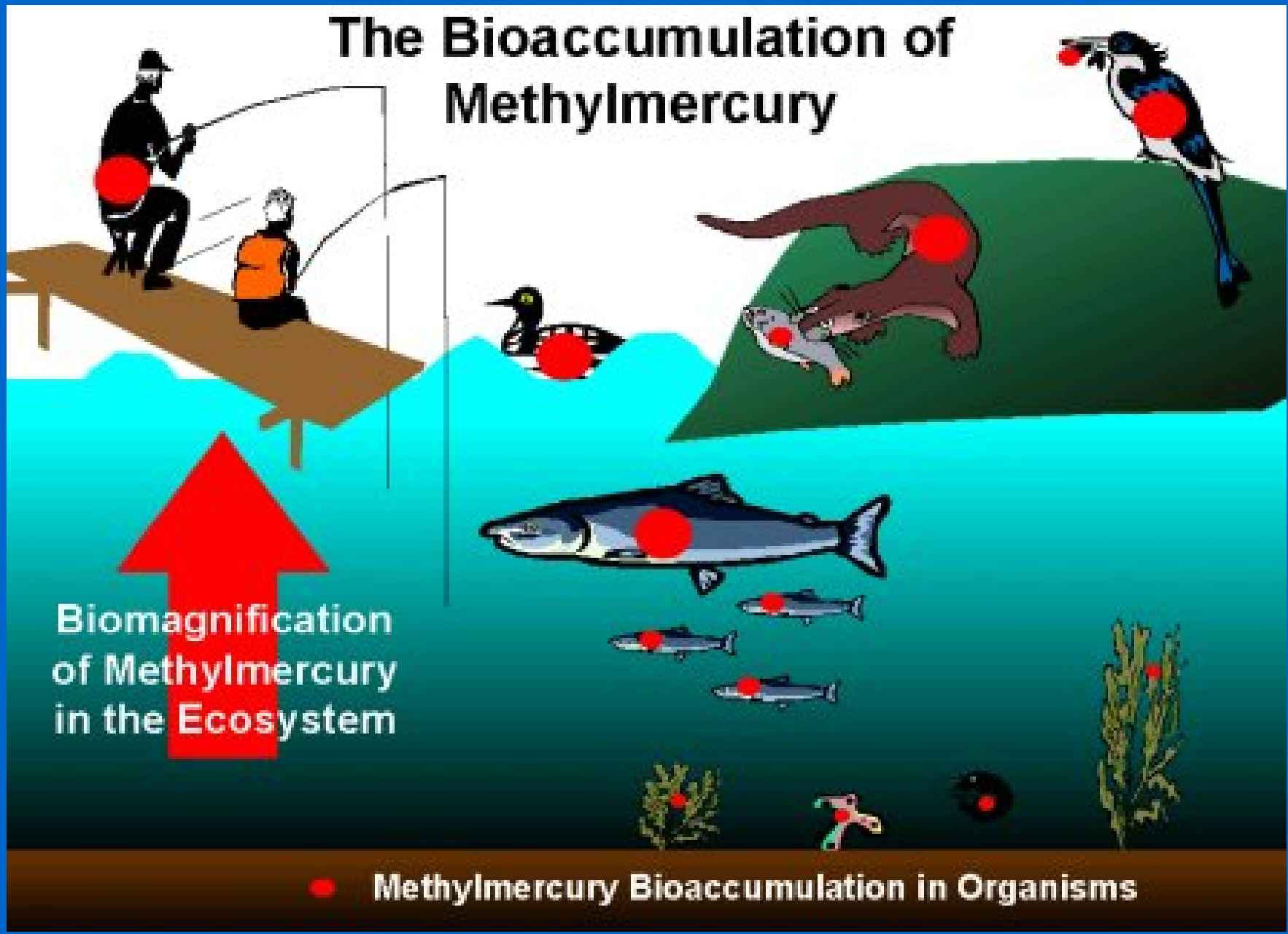
All fluxes in Tons/year



Adopted from Lamborg et al. 2002

Why mercury?

- Hazardous properties of global relevance
  - Impact at local, regional and global scale
  - Once mobilized Hg persists in the environment where it circulates among air, water, sediments and biota
  - High toxicity, dependant on the chemical form, the pathway of exposure, the amount and the vulnerability of persons exposed


The Bioaccumulation of Methylmercury
Biomagnification of Methylmercury in the Ecosystem
Methylmercury Bioaccumulation in Organisms

MeHg in humans: a worldwide concern

- Elevated MeHg in many fish-eating populations throughout the world
- Notably among coastal, island, river and lakeside populations and those living near reservoirs
- Also: persons who eat large quantities of commercially sold high-end predators
- MeHg exposure knows no geographic or social boundaries

II – Sampling procedure for Mercury and methylmercury analysis

General points on Hg and MeHg sampling and analysis:

Measurment difficulty :

- High analytical Sensibility: Natural waters concentrations

= 1 to 2 ng per water liter

- Complexe Technical analysis : Species separation (MeHg, Hg_{inor}, Hg^0)

Sampling and conditioning

- Imperative to limit the **contamination** during sampling, filtration and storage using **Ultra - clean techniques** (gloves, téflon materials, multiples wash, ultra-clean acid, clean packing ...)

→ **« The minimum handling and quantities of chemical reagents»**

Solutions sampling for Hg and MeHg analysis (teflon bottles)

Acid washed teflon bottles / rince (x3) with sample filtration on acid washed teflon filters
storage in 0.5% ultrapure HCl

Solid sampling for Hg and MeHg analysis

Sampling and storage

- Soils and sediments : teflon shovel/plastic bag
- Organisms (fish) : freezing or formol

Sample preparation

- Lyophilization
- Grinding
- Storage at 4°C

III – Mercury and methylmercury analysis

a) Total Hg in the solid phase

(atomic absorption sectrophotometry)

Detection limit :
0.01 µg.g^{-1}

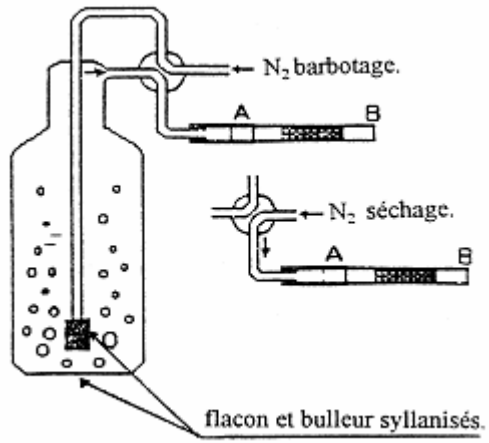
Sample preparation :
lyophilization
grinding to 63µm

10 to 30mg solid sample heated at 550°C : Hg is volatilized
Hg^0 carried by an oxygen flow and amalgamed on a gold trap
Gold amalgan is heated and the Hg vapor is send to an atomic absorption sectrophotometer cell where it is quantified

	MESS-2	IAEA-142	DORM-1	DORM-2
Valeur certifiée	0,092 ± 0,009	0,126 ± 0,016	0,798 ± 0,074	4,36 ± 0,26
Valeur trouvée	0,089 ± 0,001	0,120 ± 0,006	0,854 ± 0,013	4,41 ± 0,04

b) MeHg in the solid phase
(Ethylation-gaz chromatography-CVAFS)

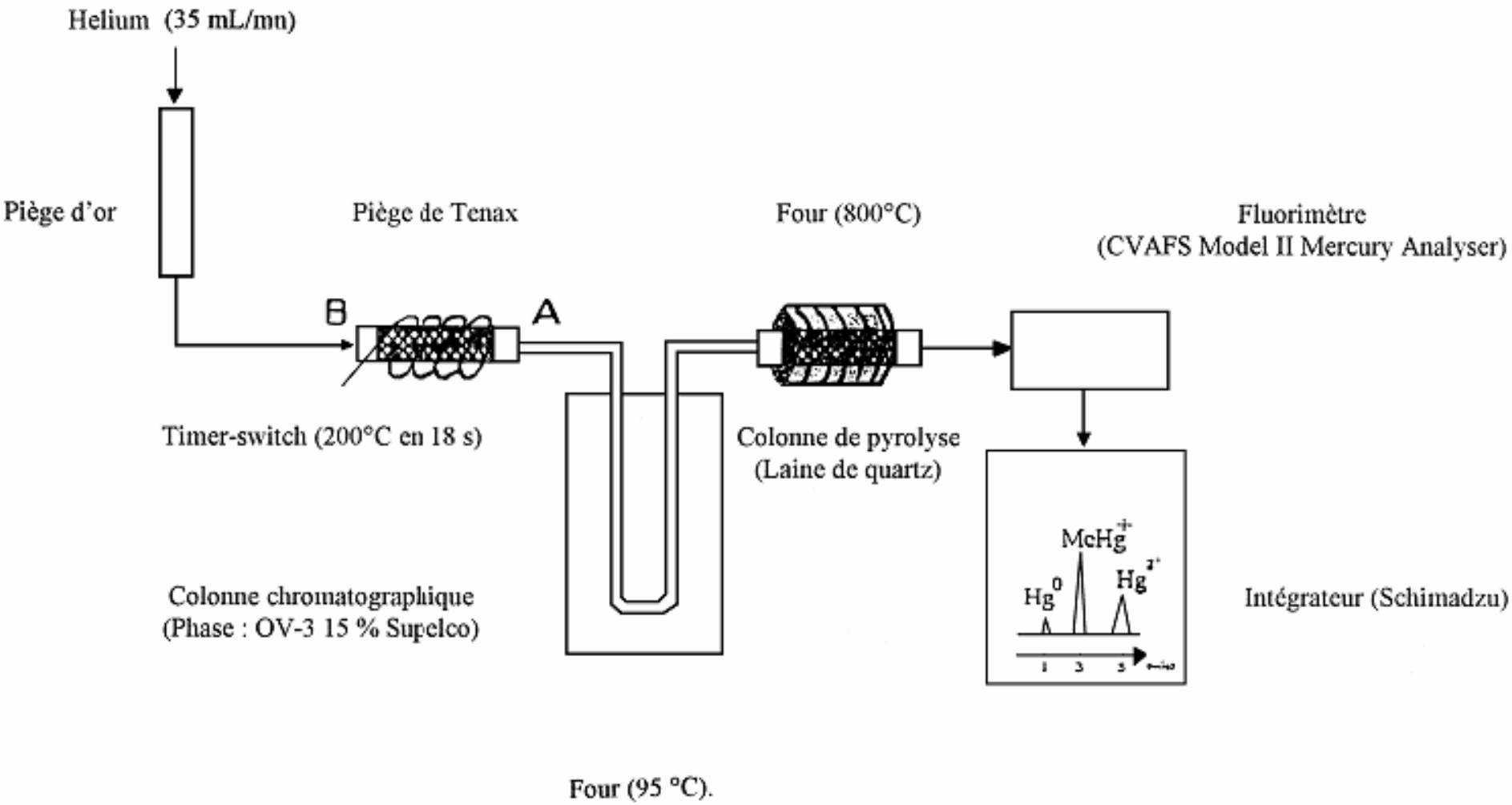
- Sample solubilization in alkalin (organisms)
  or acid solution (sediments)
- Ethylation of monomethylmercure (MMHg)
  in solution with sodium tetraethylborate (NaBEt4) :
  formation of volatil MHgEt and $HgEt_2$
- Fixation on a adsorbing support (Tenax®)
  under nitrogen flow



Detection limit :2 to 4 ng.g^{-1}
Sample preparation : lyophilization
grinding to 63µm

b) MeHg in the solid phase

Hg volatils disorbed by heat / Gaz chromatography seperation / Pyrolysis and CVAFS detection



c) Total Hg in the liquid phase

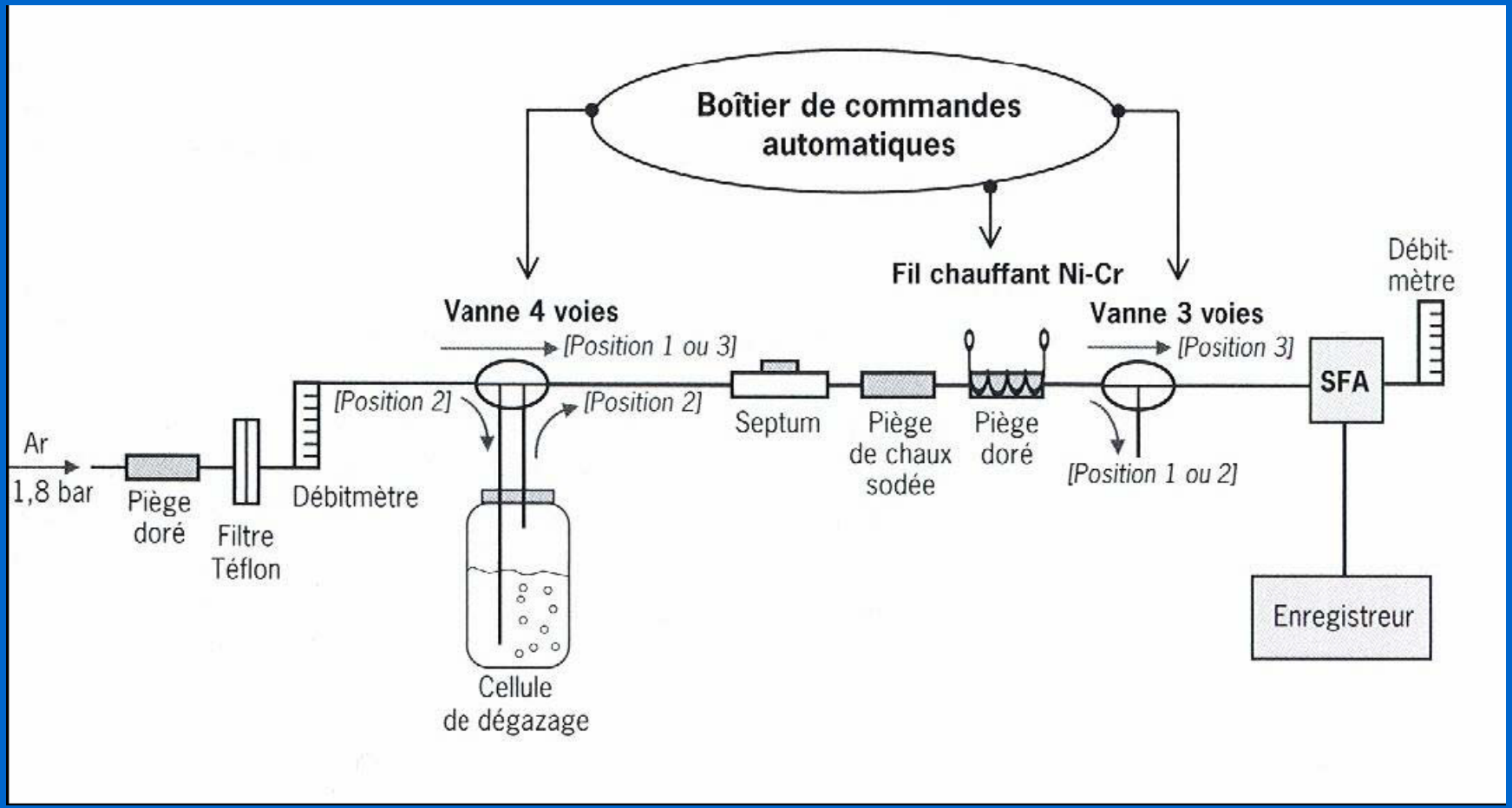
(Cold vapor atomic fluorescence spectrophotometry)

- Oxydation of all dissolved Hg species by 0.1 ml BrCl addition to a 50 ml sample solution
- Reduction of all mercury species to Hg^0 with $SnCl_2$
- Degazing in Hg^0 from the solution under Argon flow
- Amalgamation of Hg^0 on a gold trap (preconcentration)
- Heat of the gold trap
- Quantification with CVAFS

Detection limit :0.1 ng.L^{-1}
Sample preparation : filtration 0.45µm
Stored in 0.5% suprapure HCl

c) Total Hg in the liquid phase

(Cold vapor atomic fluorescence spectrophotometry)



D) MeHg in the liquid phase

(Hydride generation / CVAFS)

- Volatils hydrides generation by sodium tetrahydroborure (NaBH4) addition.

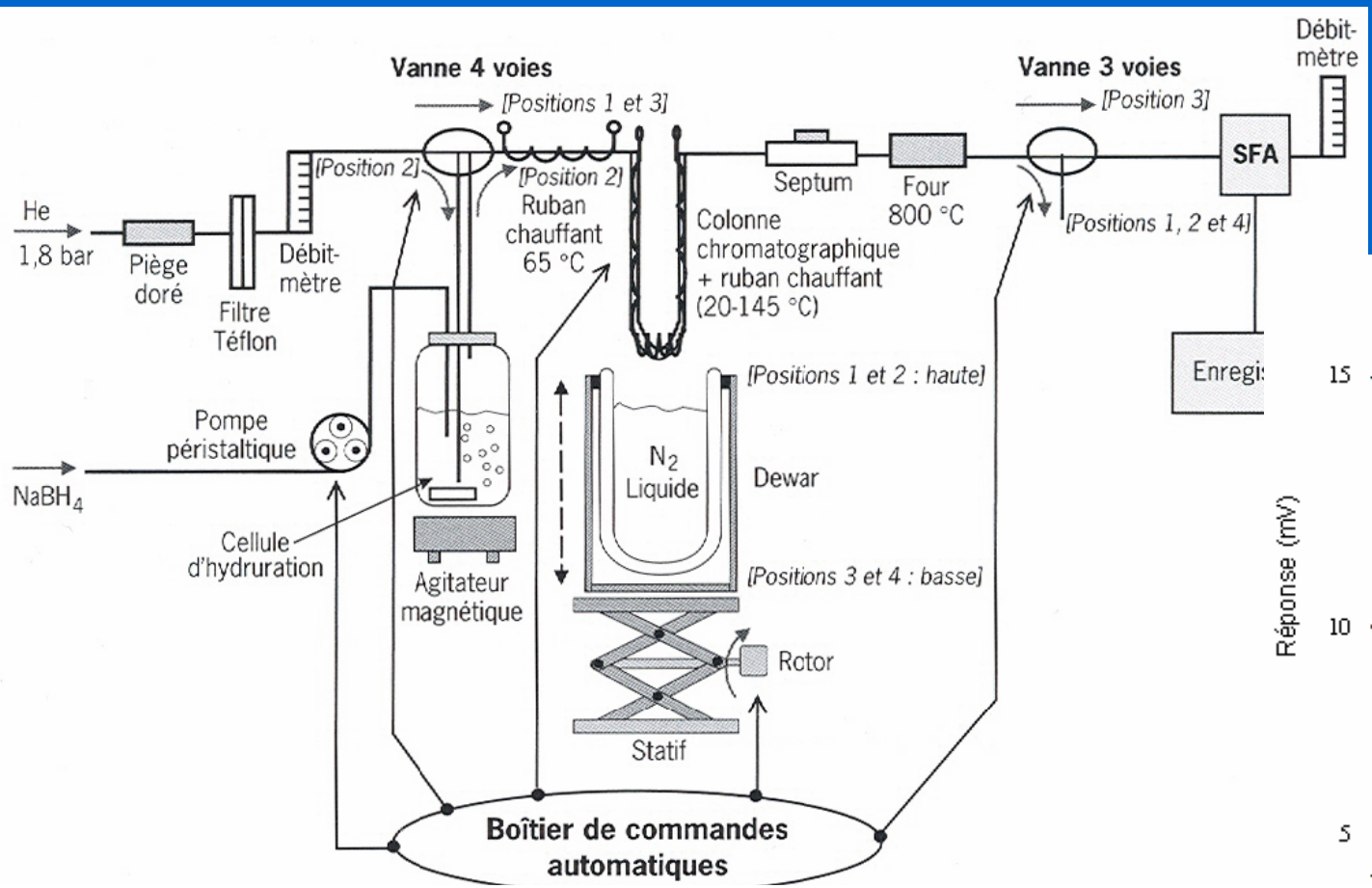
$MeHg^+$ + NaBH4 + 3 H2O = **MeHgH** + 3 H_2 + H_3BO_3 + Na^+

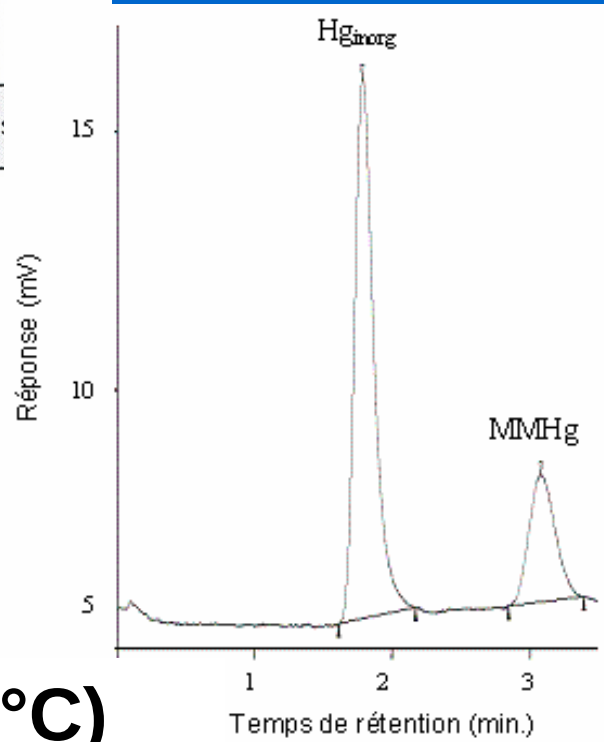
Hg^{2+} + 2 NaBH4 = **Hg°** +B_2H_6 + 2 Na^+ + H_2

- **Limit of the method : interaction with dissolved organic matter**

Detection limit : 5 pg.L^{-1}
Sample preparation : filtration 0.45µm
Stored in 0.5% suprapure HCl

D) MeHg in the liquid phase





Cryogenic preconcentration (-196°C)

Gazeous chromatographic separation

Pyrolysis and CVAFS detection

Conclusion

- **Mercury and methyHg analysis needs :**
  - **Sampling precaution ultra clean techniques**
  - **Use of ultra pure reagents for storage and analysis**
  - **Highly sensitive but complicated techniques**