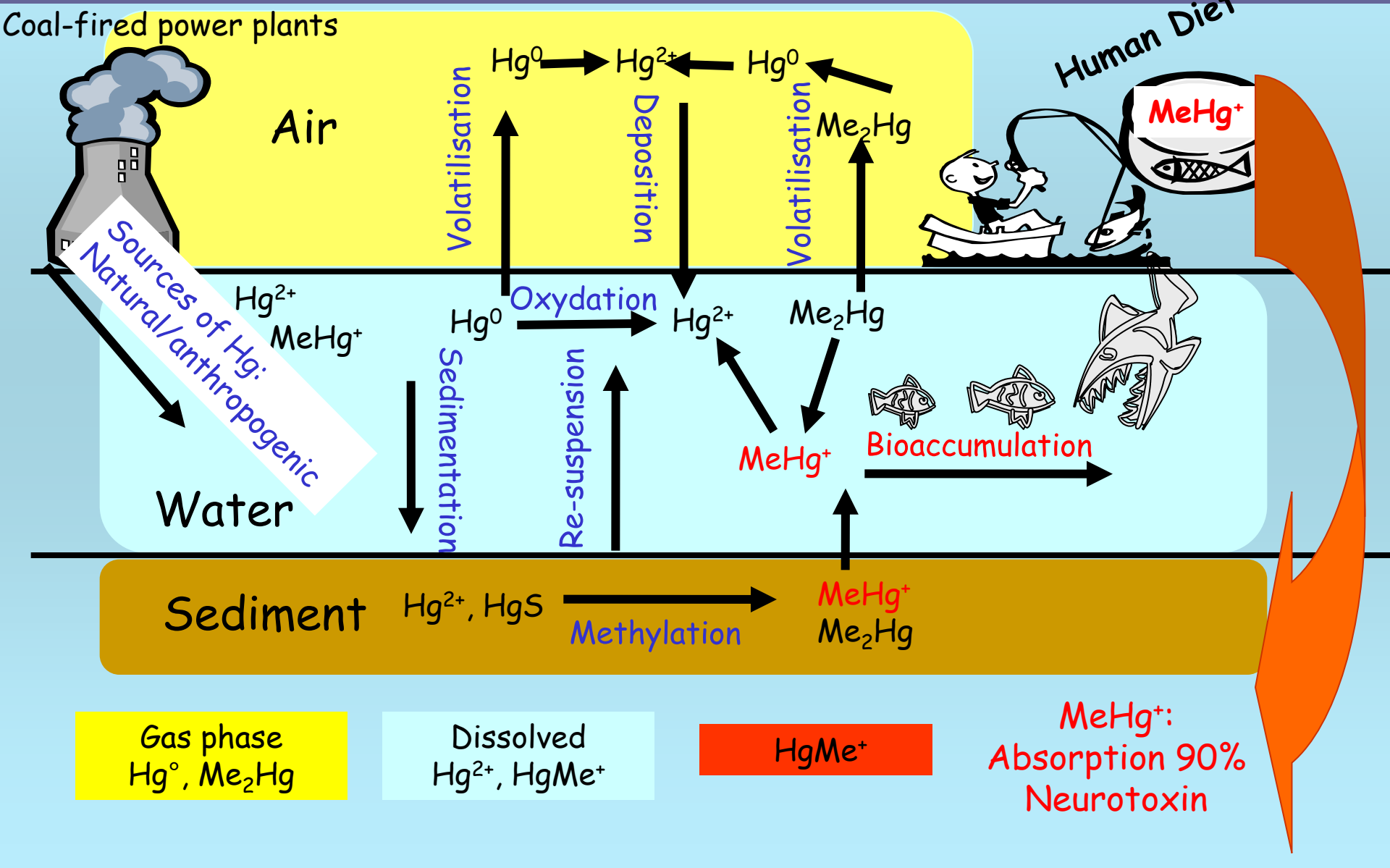
Mercury

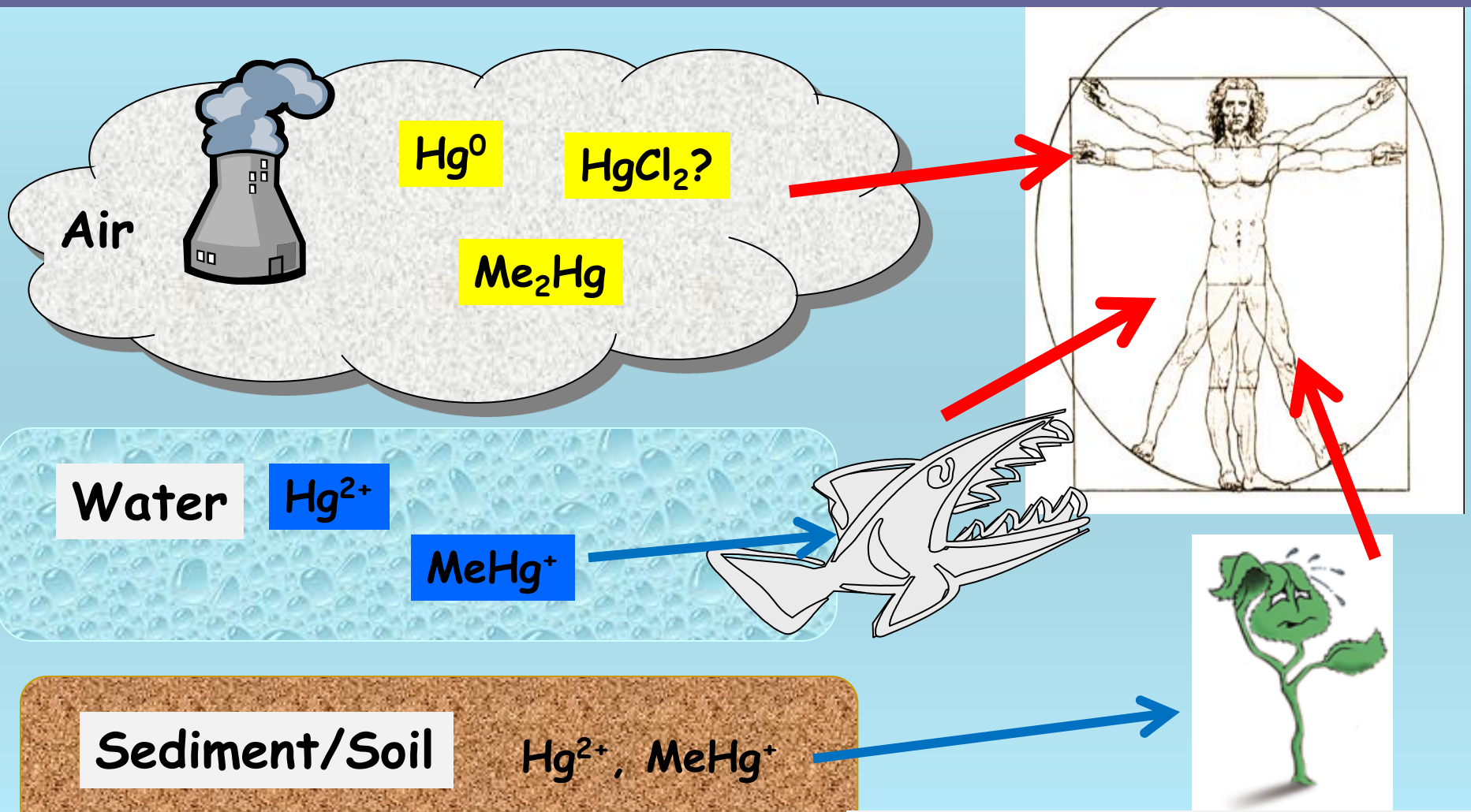
- No known essential biological function
- Industrial use: mercury switches, thermostats, thermometer, medications, preservatives (e.g. as *Thimerosal* in vaccines), antiseptics, pesticides…
- Amalgamates with gold and silver: use in mining and as a dental fillings
- Geogenic as ore (Cinnabar) and as trace element in coal: Partition of volatile Hg into air during coal combustion
- High-level Hg exposure produces serious neurological problems in adults and in children born to mothers with high mercury levels

❖ **Mercury is a global pollutant!**

The Aquatic Mercury Cycle



Hg Species of Interest – Occurrence, Exposure and Analytical Challenge

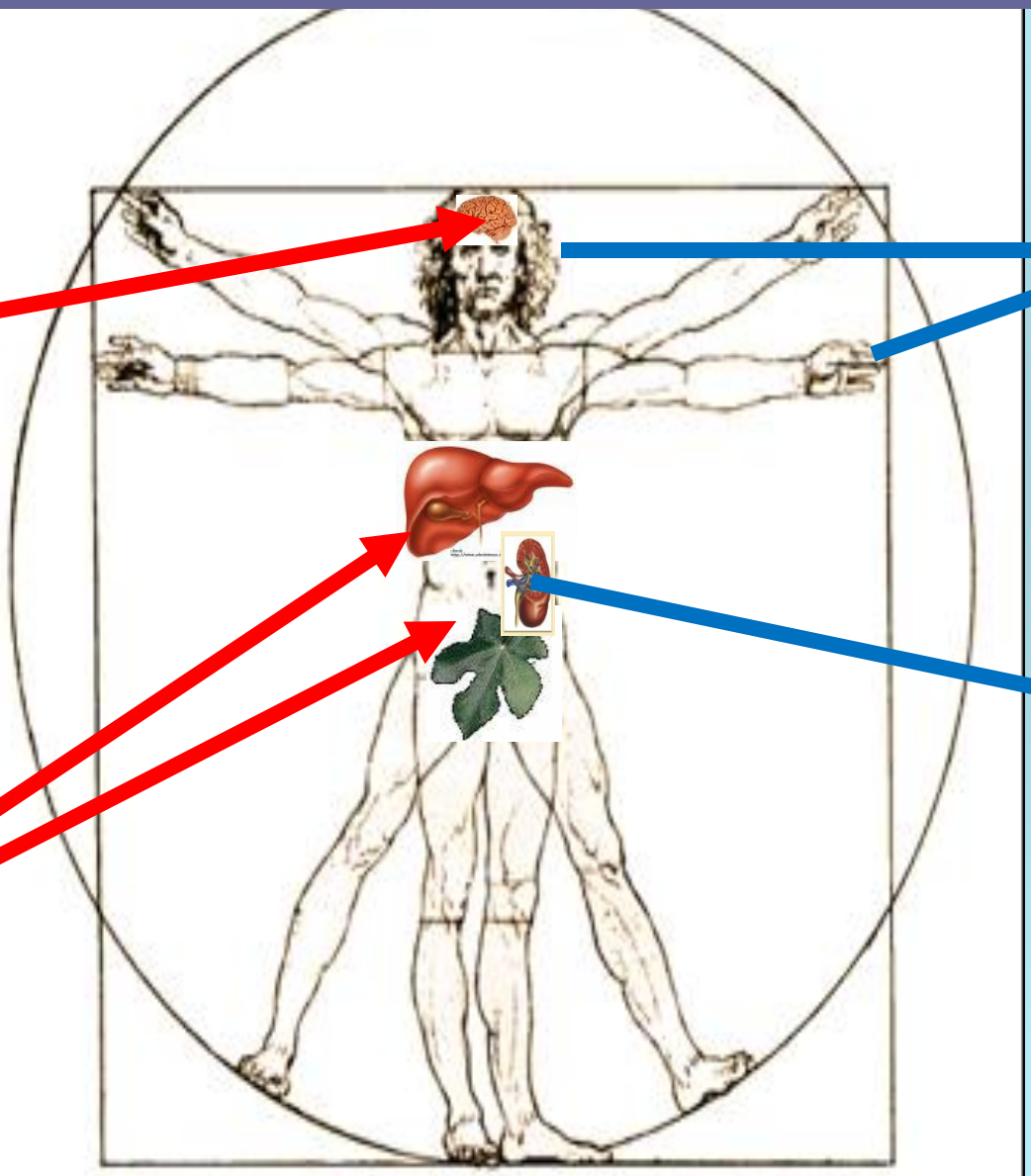


Toxicity of Hg species: Target Organs

IN

Hg (organic): HgMe, $HgMe_2$, HgEt…

Hg (inorganic)



OUT

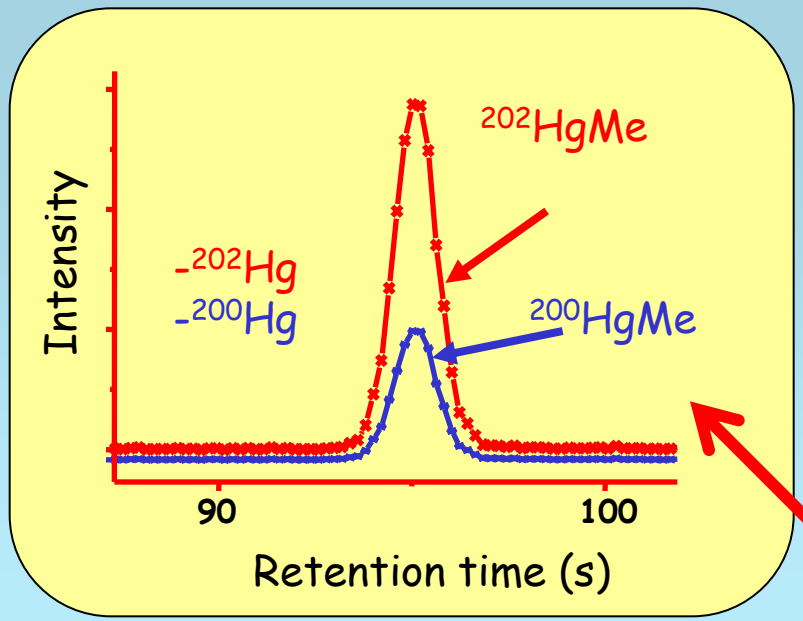
Hg (organic): Hair, fingernails

Hg (inorganic) Urine, Faeces

Focus on Hg speciation: MeHg

(Since Minamata in the 1950's)!

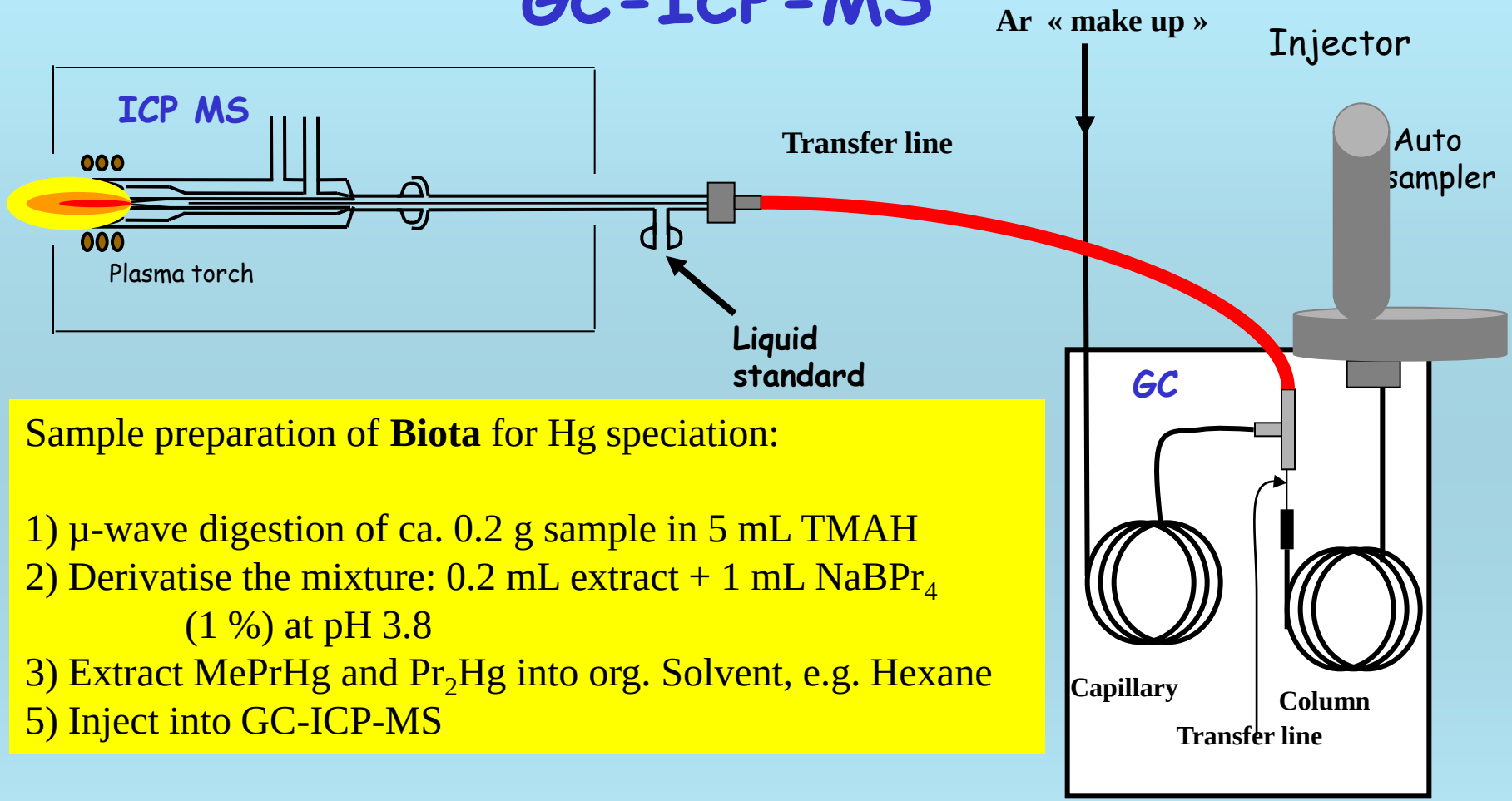
- Methylmercury speciation methods, eg:
  derivatisation with $NaBPr_4$ ($MeHg^+$ → MeHgPr)
  followed by Gas Chromatographic separation and
  Hg-specific detection (Pyro-AFS or ICP-MS)



- Highly selective
- Most sensitive
  (LOD in the
  femtogram range!)
- Highly precise
- Highly accurate

GC-ICP-MS

Useful method for Hg/HgMe speciation: GC-ICP-MS



Sample preparation of **Biota** for Hg speciation:

1) µ-wave digestion of ca. 0.2 g sample in 5 mL TMAH
2) Derivatise the mixture: 0.2 mL extract + 1 mL $NaBPr_4$ (1 %) at pH 3.8
3) Extract MePrHg and Pr_2Hg into org. Solvent, e.g. Hexane
5) Inject into GC-ICP-MS

Ethylation of mercury species with $NaBEt_4$:

$$MeHg^+ + NaBPr_4 \longrightarrow MePrHg$$

$$Hg^{2+} + NaBPr_4 \longrightarrow Pr_2Hg$$

Sample preparation for Hg speciation: Hg^{2+} vs $HgMe^{+}$ in soil/sediments

Challenge: High amounts of Hg^{2+} versus traces of $MeHg^{+}$ (1%) - artefact production of MeHg from Hg2+ due organic matter during sample preparation

Strategy:

Separation of Hg and HgMe by extraction

- **take 3 mL sample extract/digest**
- **add 1.5 mL CH_2Cl_2 and 100 µL HCl (conz)**
- **Shake 5 min**
- **Repeat once**
- **Derivatise and analyse the organic extract for MeHg**

Sample preparation for Hg speciation: Focus on Hg^{2+} vs $HgMe^{+}$

Extraction efficiency and species integrity?

- Aim: To transfer all Hg species from the sample matrix (water, biota, sediment...) into a “measurable form”, i.e. a liquid for chromatographic species separation

Questions:

- Does the species react quantitatively with the reagent ($MeHg^{+}$ → MeEtHg)?