State of the art of mercury speciation analysis

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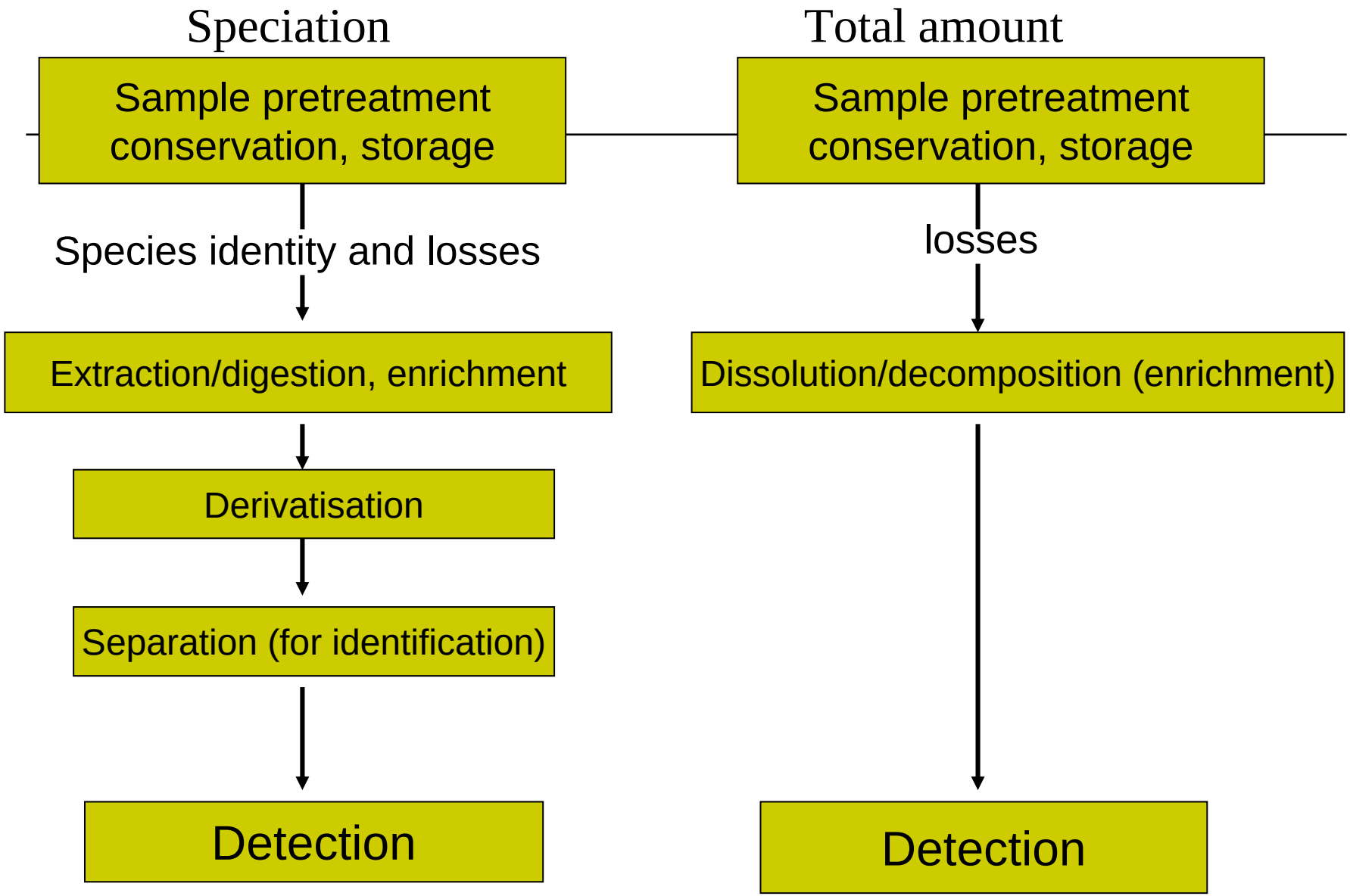
Major mercury species in environmental samples

- Elemental Hg^{o}
- Inorganic mercuric Hg^{2+}
- Inorganic mercurous Hg^{+}
- HgS

- Organic CH_3Hg^{+}
  $C_6H_5Hg^{+}$
  $(CH_3)_2Hg$

- Isotope distribution; Hg binding to proteins or humic acid

Speciation analysis and total amount determination



One of the first papers on Hg speciation analysis

ACTA CHEMICA SCANDINAVICA 21 (1967) 1790–1800

Determination of Methylmercury Compounds in Foodstuffs

II. Determination of Methylmercury in Fish, Egg, Meat, and Liver

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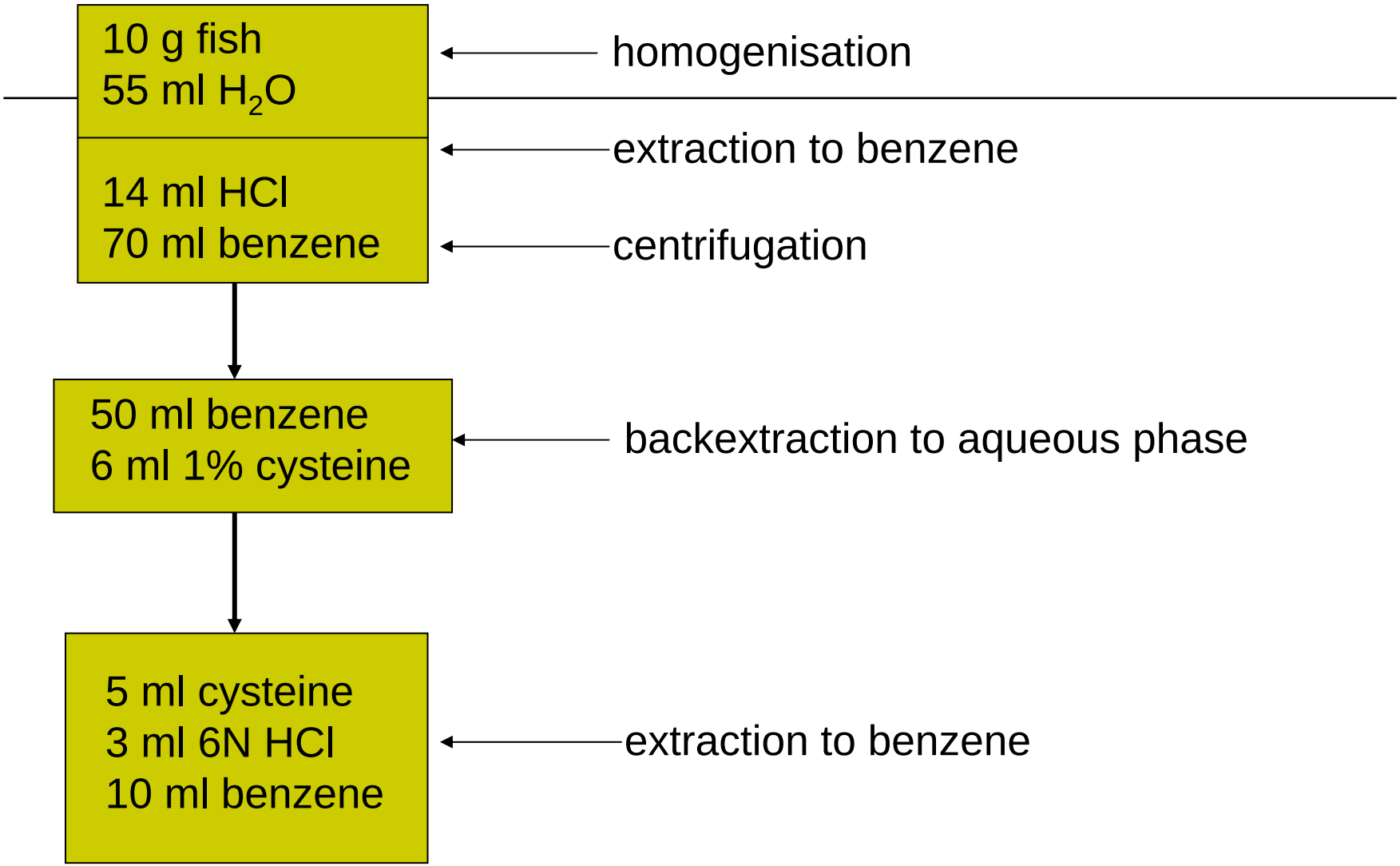
Extraction procedure for CH_3Hg in foodstufs



GC-Chromatograms from methylmercury extracts using an ECD detector

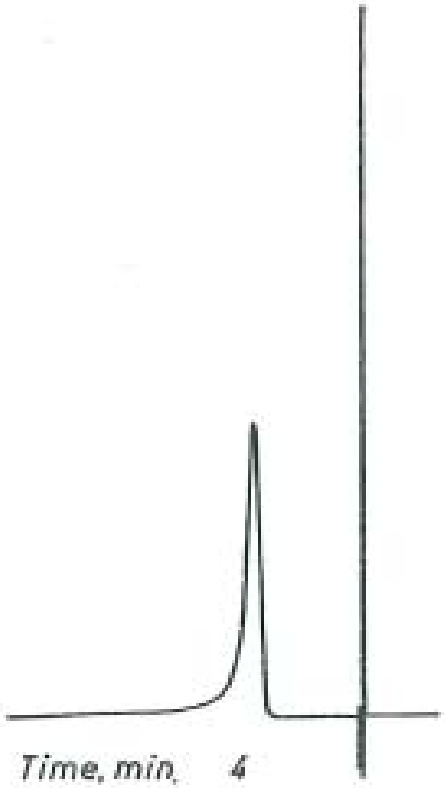


Fig. 1. Gas chromatogram of a purified cod extract (10 g sample).

Fig. 2. Gas chromatogram of a purified fillet of beef extract (50 g sample).

Acta Chem. Scand. 21 (1967) No. 7

Present status for CH_3Hg^+ in food

- Extraction/enrichment: Similar as 1967 but faster and simpler with new techniques
- Separation: Often capillary GC-better detection limits but requires derivatisation. Capillary electropheresis is available.
- Detection: Hg-specific- AFS; AES; AAS and ICP-MS- more tolerant to interferences, improving accuracy compared to ECD.

Present status of Hg speciation analysis

- Most work for CH_3Hg^+ in various matrices
- Methods focused on measurement part
- LC-MS for identification of species
- ICPMS for species specific isotope dilution
- *In-situ* speciation analysis:

  Hg-species in humic substances

  Determination of labile Hg forms

In-situ speciation-an example

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Geological and anthropogenic factors influencing mercury speciation in mine wastes: an EXAFS spectroscopy study

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EXAFS study for Hg speciation in mine wastes

Identified species at Hg concentrations of 80 µg/g and higher

HgS (cub)

HgS (hex)

HgO

$Hg_3O_2SO_4$

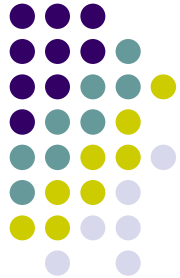
$HgCl_2$

$Hg_3S_2Cl_2$

Hg_2OCl

Important for estimating mobility, reactivity and potential bioavailability of Hg species in mine impact regions

Mercury Speciation Analysis in Soils and Sediments



Species of interest:

- Methylmercury (CH_3Hg^+ , $MeHg^+$)
- Inorganic mercury (Hg^{2+})
- Metallic mercury (Hg^0),
- Dimethylmercury $(CH_3)_2Hg$
- Phenylmercury ($C_6H_5Hg^+$)

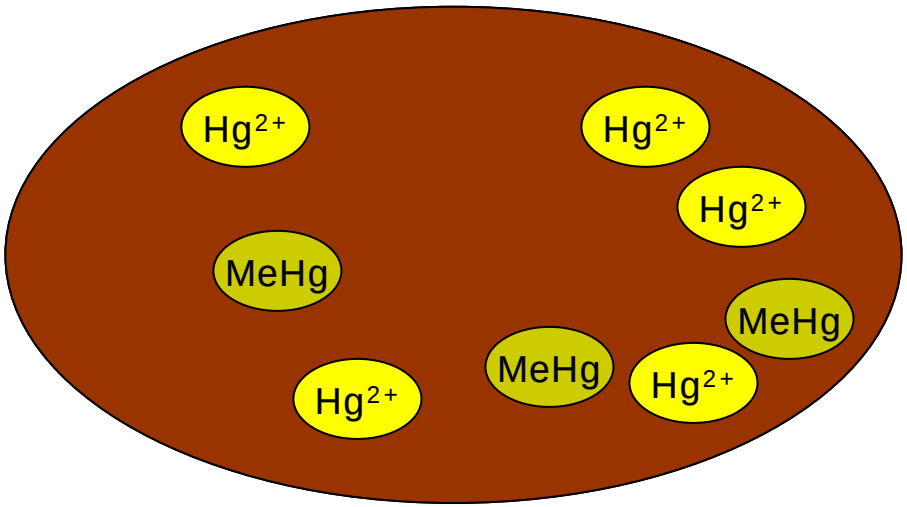
Total Hg

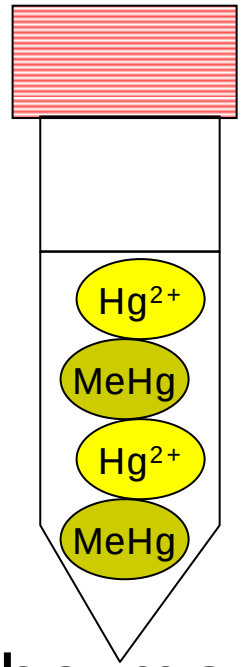
Soil/sediment background levels:

$MeHg^+$: ~1 ng g^{-1}

TotHg (~Hg^{2+}): ~100 ng g^{-1}

Extraction/Preconcentration





Extraction of Hg species from the matrix is the most critical step in soil/sediment Hg speciation analysis

Criteria:

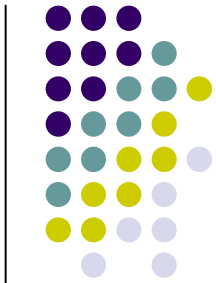
Hg species should be separated from the matrix without loss, contamination or change of speciation

Extraction / Preconcentration

- Solid-Liquid extraction:
  - Acid leaching
    Dilute mineral acids: HCl, H_2SO_4
    Ion-pair reagents: NaCl, KBr…
  - Alkaline digestion
    MeOH/KOH
    TMAH
  - Solvent extraction
    Toluene, DCM…

+ $MeHg^+$ extraction yield
- Hg^{2+} extraction yield
- Laborious
- Solvent use

Extraction/Preconcentration



- Vapor distillation
  - \+ $MeHg^+$ yield
  - \- Risk for $MeHg^+$ artifacts during processing
- Microwave assisted acid/organic extraction
  - \+ Fast
  - \+ Yield
  - \- $
- Supercritical fluid extraction (SFE)
- Accelerated solvent extraction (ASE)

US EPA Hg Test Methods

Method ID	Description
245.5 IO-5 7472 7470A PP-007 7474 7471A 1631B	Total Hg
1630	Methyl Mercury in Water by Distillation...CVAFS
3200	Organic, inorganic and total mercury in soil
6800	Elemental & Speciated Isotope Dilution MS

Determination and Validation

Analytical techniques:

- GC-AFS
- GC-ICP-MS
- HPLC-ICP-MS

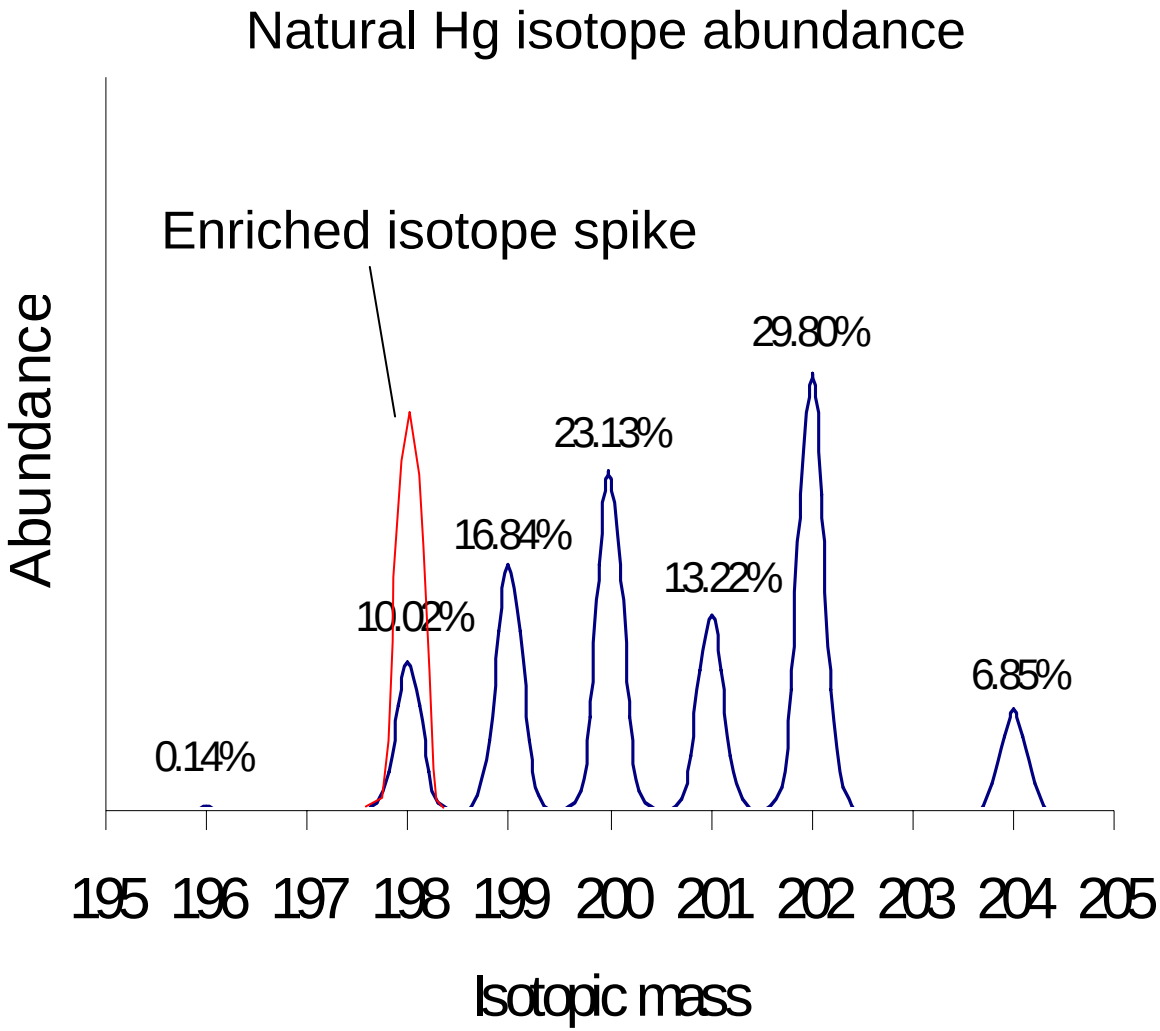
Quantification methods:

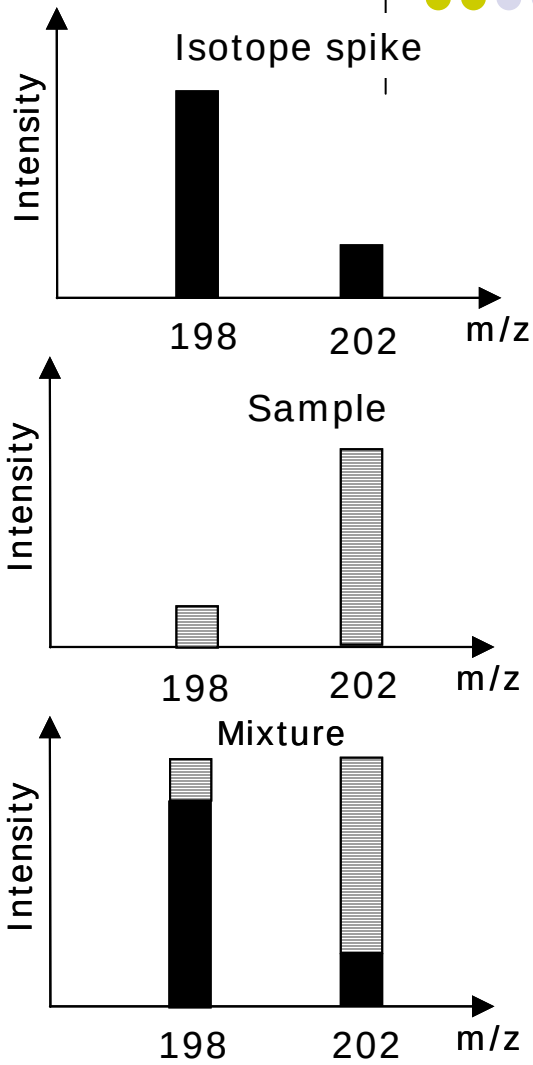
- External calibration
- Internal calibration
- Standard addition
- Isotope dilution

Validation:

- Extraction efficiency
- Certified reference materials

Isotope Dilution





Isotope Dilution

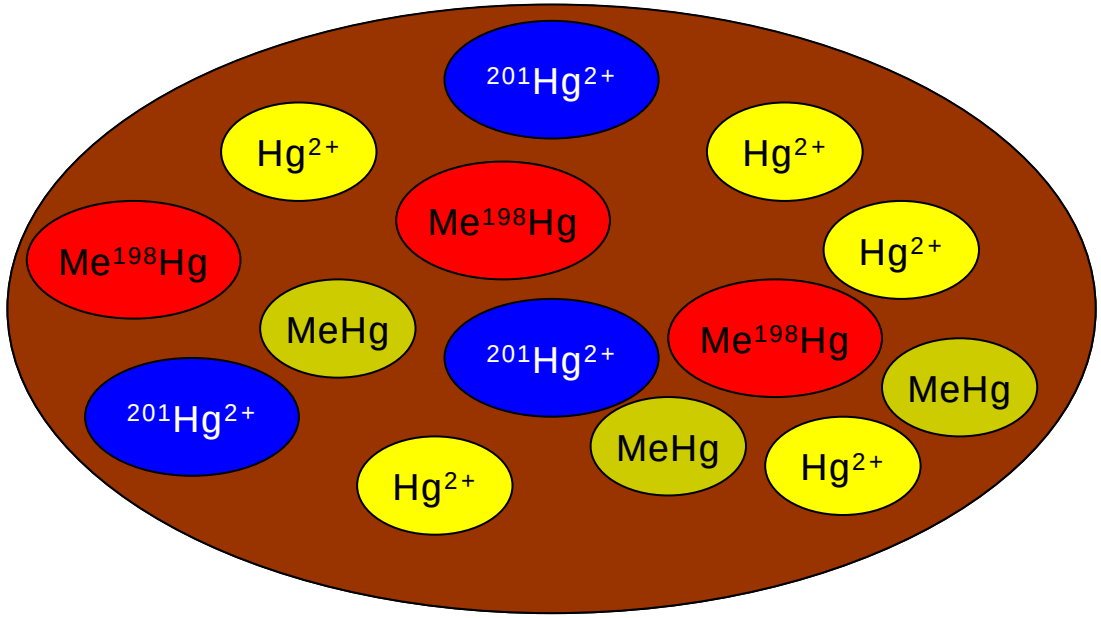
Criteria:

- ✓ Homogeneous mixture between isotope spike and sample
- ✓ Isotope spike and intrinsic analyte must be extracted with equal efficiency

\+ Increased accuracy and precision
\+ Non-quantitative extraction yields automatically corrected for-simplified analysis
\- Requires mass selective detector

Species-Specific Isotope Dilution

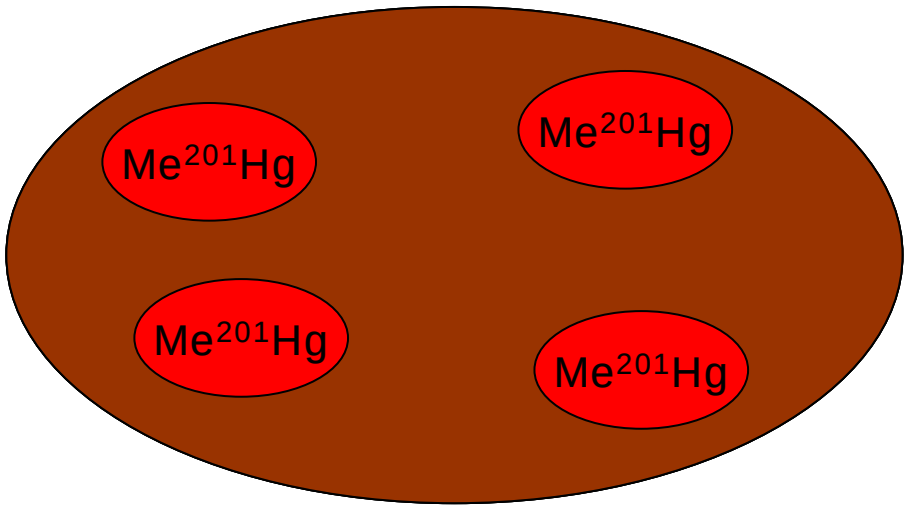
- Species specific isotope dilution calibration using isotope labelled Hg species: $Me^{198}Hg^{+}$, $^{201}Hg^{2+}$

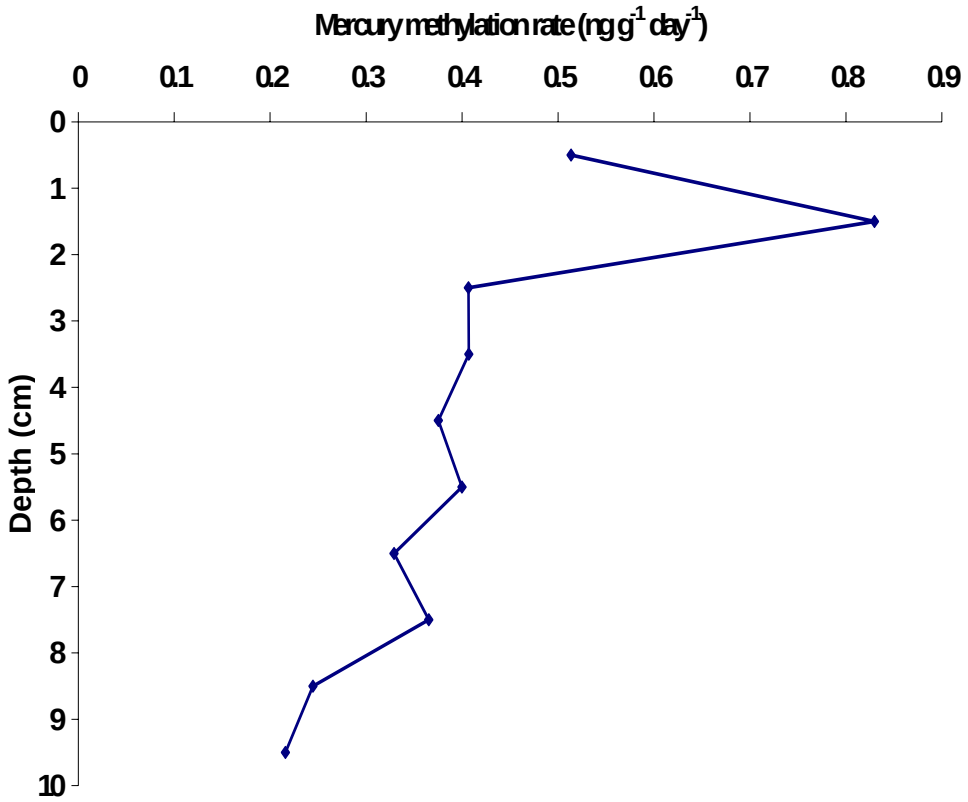


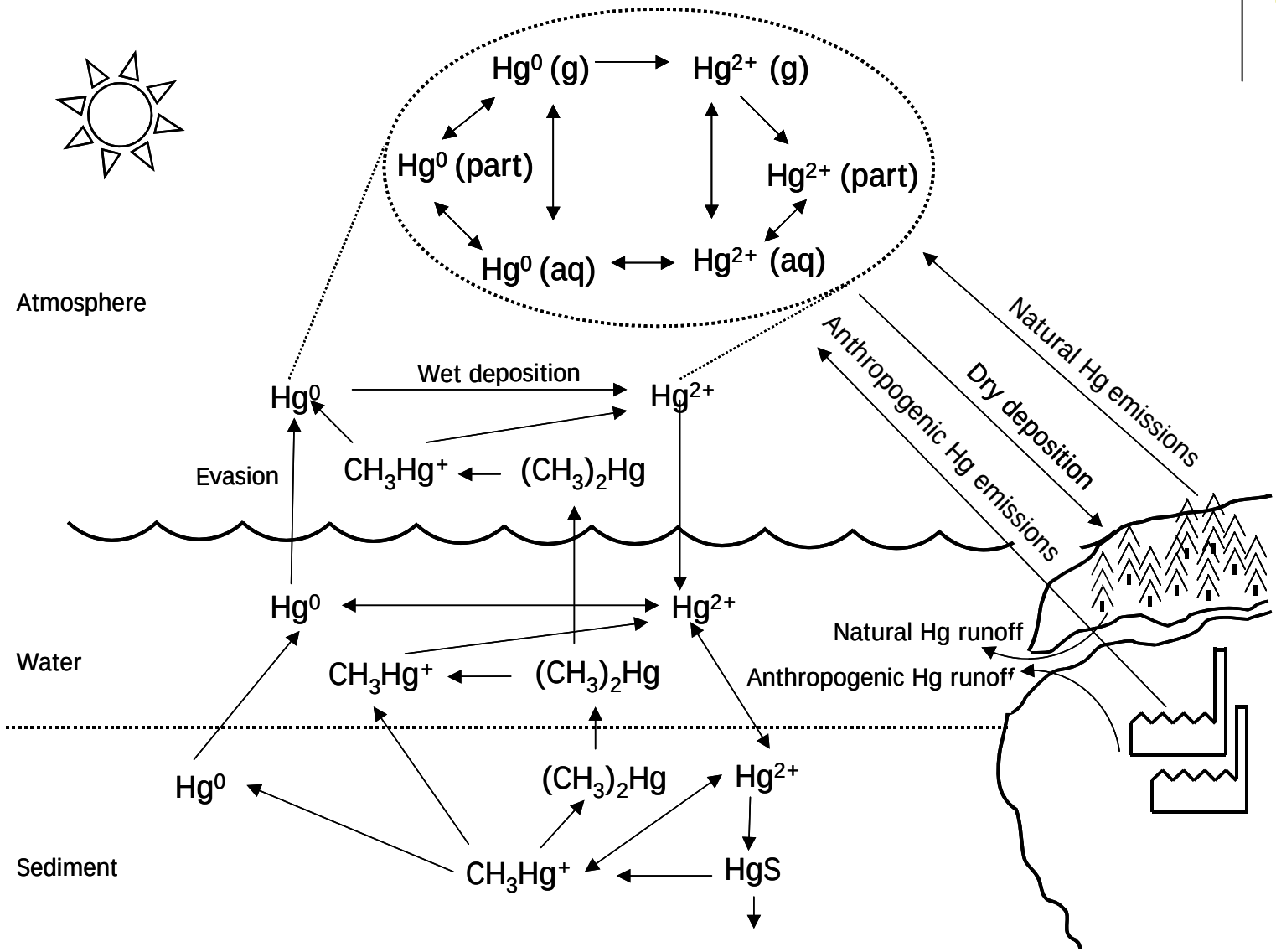
- Correction for species interconversion artefacts possible

Isotope Labelled Hg Species: Tracer Applications

- Net Hg methylation potential in contaminated sediments






Hg0 (g)
Hg2+ (g)
Hg0 (part)
Hg2+ (part)
Hg0 (aq)
Hg2+ (aq)
Atmosphere
Wet deposition
Hg0
Hg2+
Evasion
CH3Hg+
(CH3)2Hg
Natural Hg emissions
Dry deposition
Anthropogenic Hg emissions
Hg0
Hg2+
Water
CH3Hg+
(CH3)2Hg
Natural Hg runoff
Anthropogenic Hg runoff
Hg0
(CH3)2Hg
Hg2+
Sediment
CH3Hg+
HgS

Determination of volatile Hg species in gaseous samples

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Overview

Volatile species

Methods

Analytical problems

Species specific isotope dilution with permeation tubes

Volatile Hg species

Inorganic forms

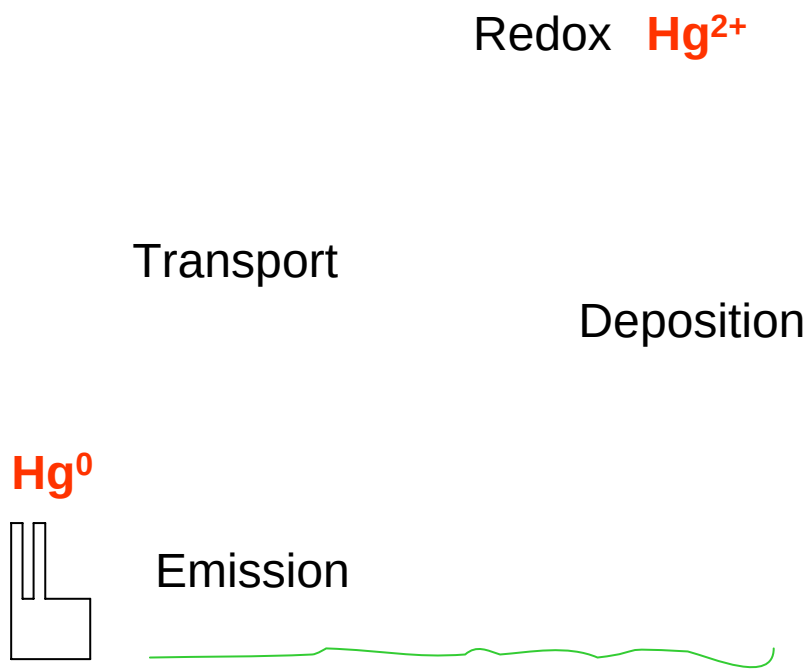
Elemental mercury (Hg^0)

Reduced state, non polar, volatile and rather stable

Divalent mercury (Hg^{2+})

Forms ionic complexes of low volatility, with e.g. halogens: HgX_2

Oxidised state, water soluble, reactive properties



Volatile Hg species

Organic forms

Oxidised forms, generally very toxic, bioaccumulated

Methyl mercury (CH_3Hg^+)

Forms ionic complexes with e.g. halogens: CH_3HgX

Water soluble, relatively volatile

Dimethyl mercury ($(CH_3)_2Hg$)

Non polar, volatile and stable

Methods

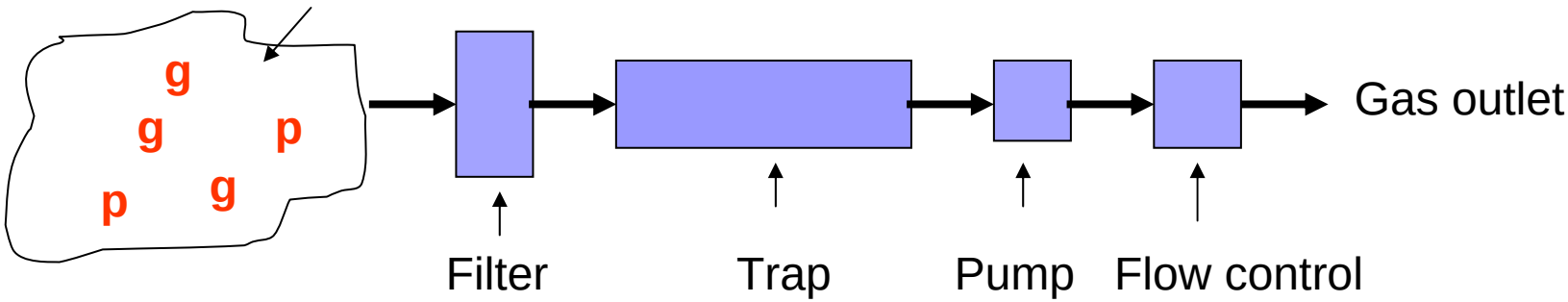
Sample collection

Passive non exhaustive

e.g. small portable devices based on diffusion of mercury vapor

Active exhaustive

Sample containing gaseous (g) and particulate (p) forms of Hg



Methods

Preconcentration of volatile Hg species

- Tot-Hg
  - Amalgamation on noble metals
- Non polar Hg species
  - Solid adsorbents, molecular sieves, cryotrapping
- Ionic Hg species
  - Liquid impingers, mist chambers, denuders

Separation and detection

- Gas chromatograph coupled to ICPMS or CVAFS

Analytical problems

Accuracy of results relies on quantitative or known recoveries in all procedural steps of conventional techniques

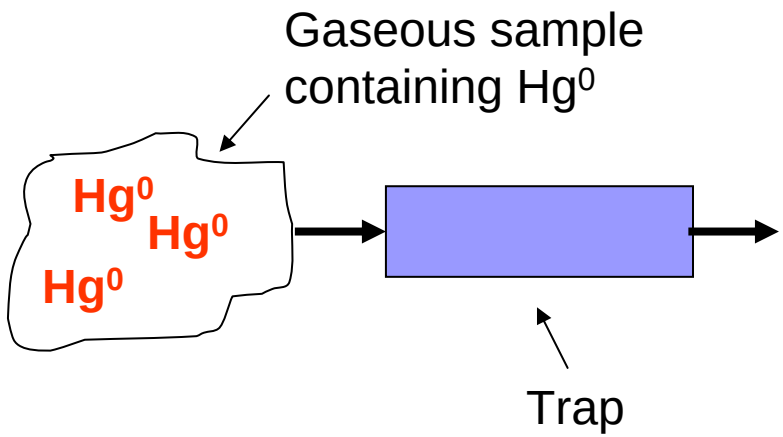
Simultaneous collection of several Hg species – requires compromise (non quantitative) conditions

Matrix effects or changes in environmental conditions leading to losses or alterations of Hg species:

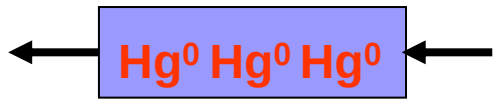
No CRMs available

Analytical problems

Non quantitative collection efficiency



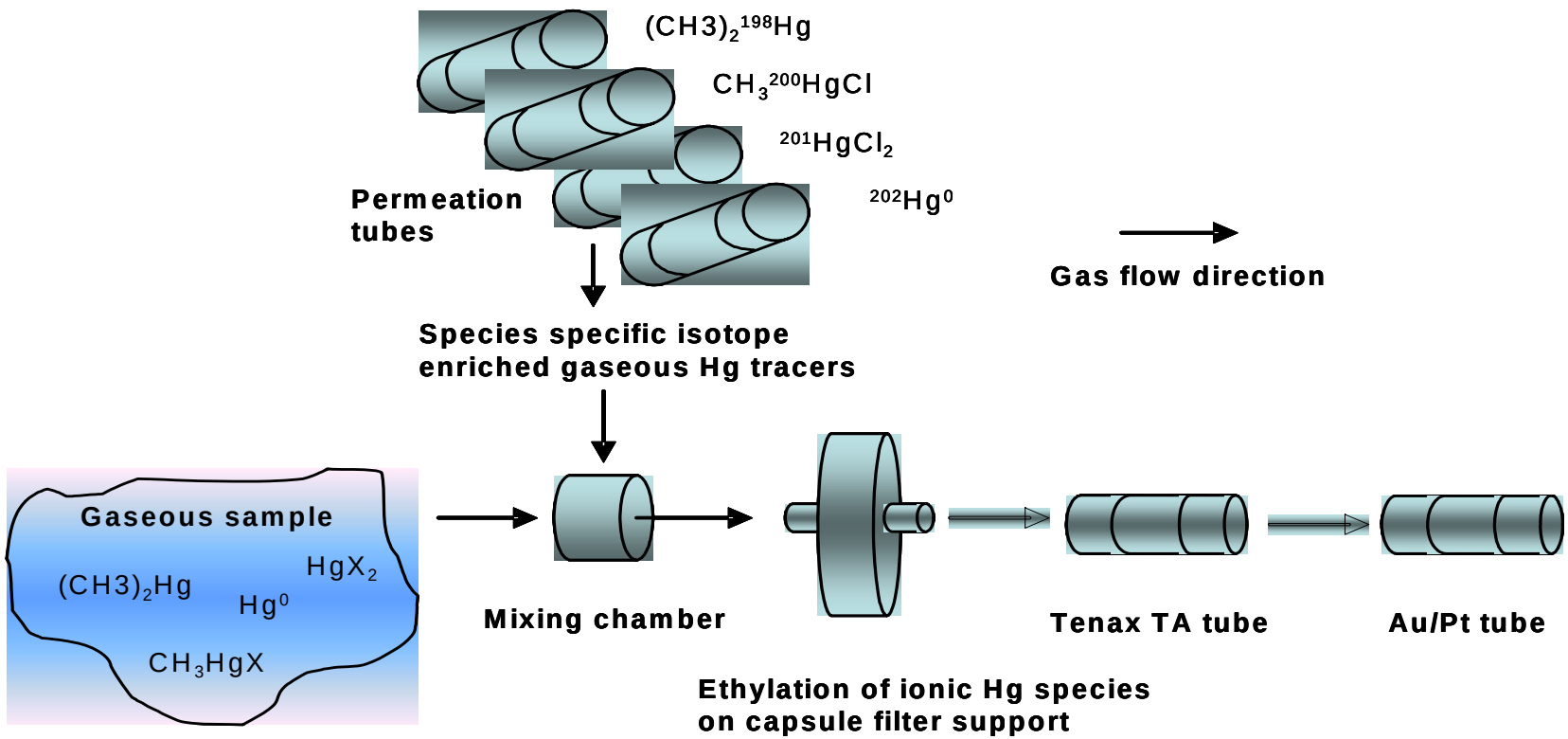
Non quantitative elution efficiency



Transformation reactions

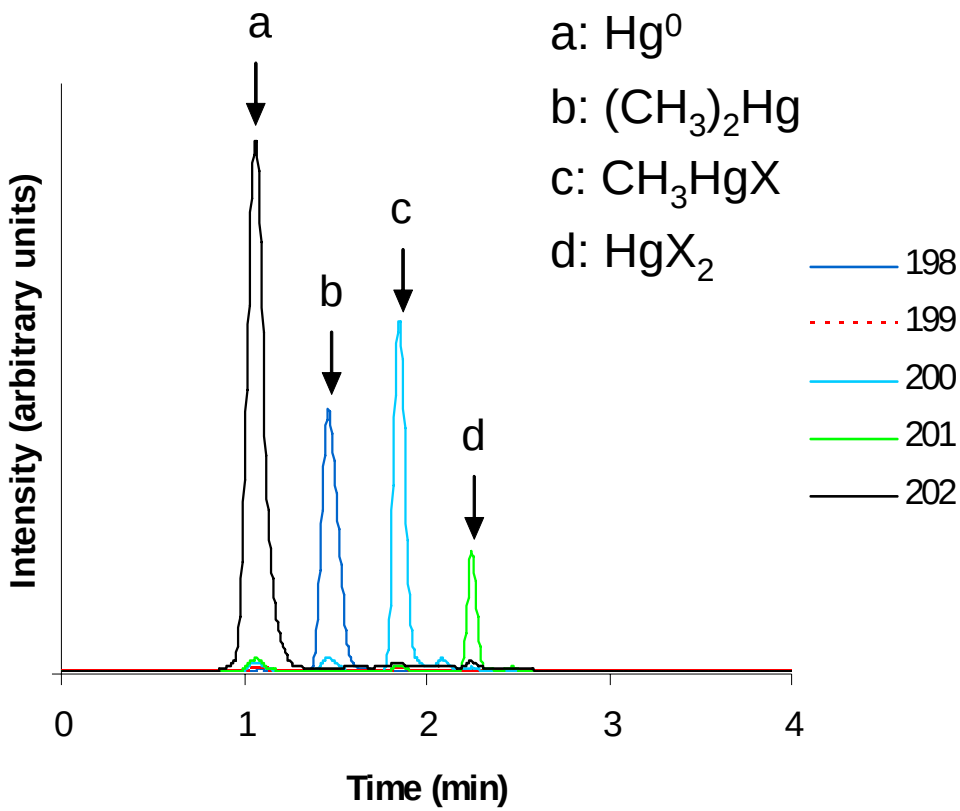
SSID with permeation tubes

Experimental setup for determination of volatile Hg species



SSID with permeation tubes

GC-ICPMS chromatogram for tracers emitted from permeation tubes

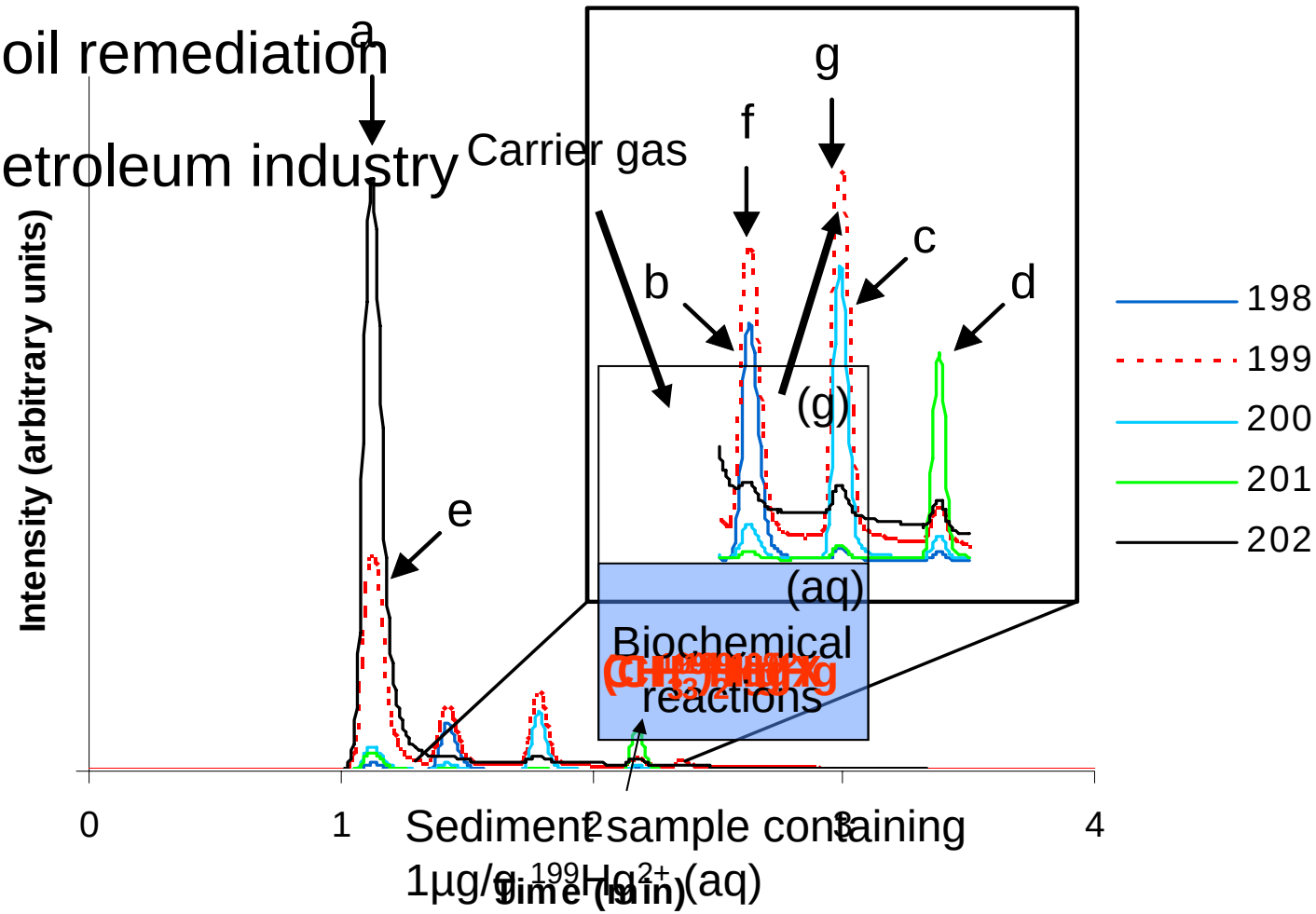


SSID with permeation tubes

Biogeochemical studies

Soil remediation

Petroleum industry



Reliability of speciation analysis

Speciation analysis is in general complex with several uncertainty factors.

Here we will focus on two main factors:

- Extraction efficiency of species
- Species transformations

Using SSID to improve reliability

Prerequisites for accurate SSID

- Standards must be available
- Equilibration between standard and analyte in the sample must be achieved

Species transformations

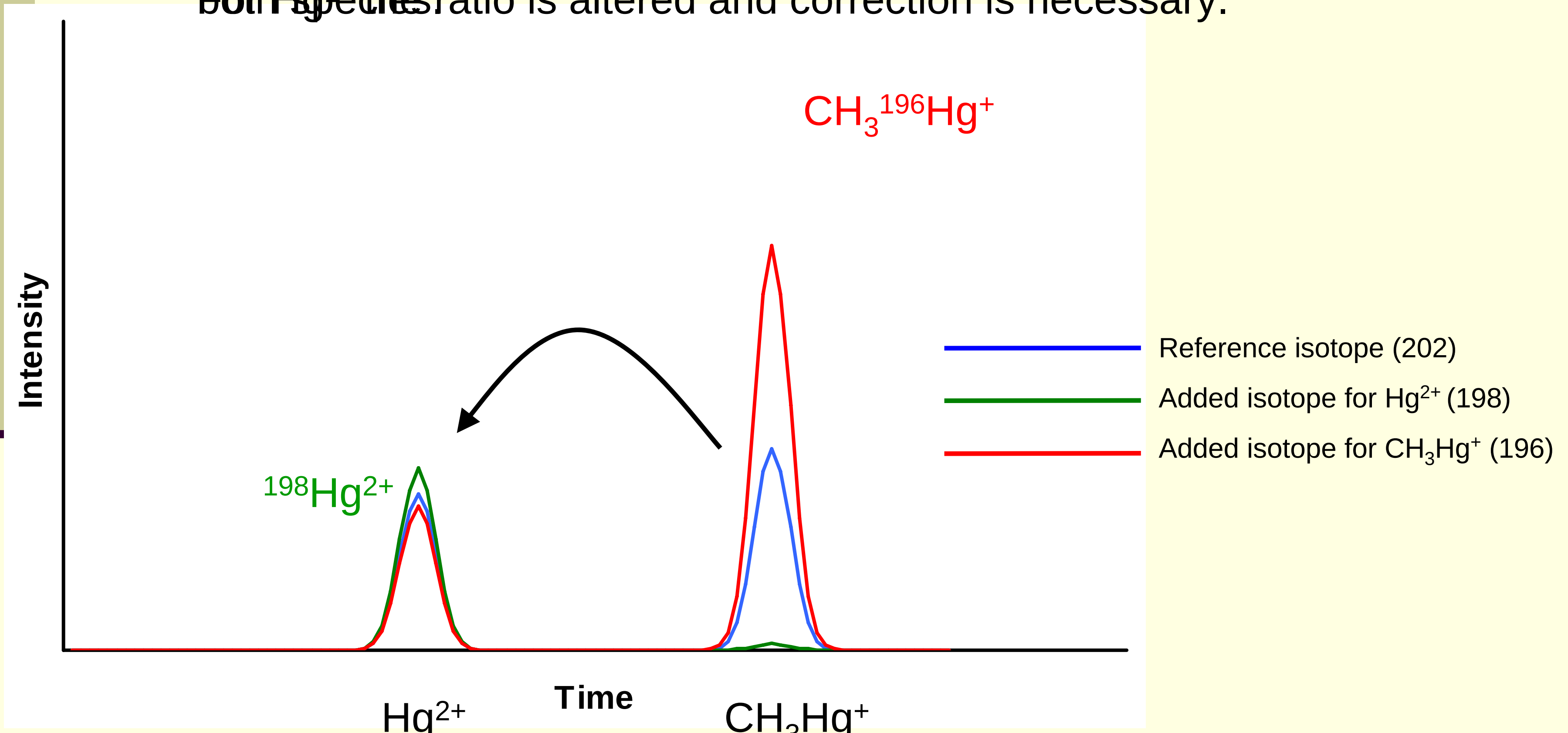
Moderate degradation of species are accurately compensated for by the conventional ID equation if the prerequisites are fulfilled.

Correction for formation of species requires additional calculation schemes.

Species transformations

1. Isotope composition of Hg species and CH_3Hg^+.
The ratio between added and reference isotope is 2 for both species.

2. 25% decomposition of CH_3Hg^+ into Hg^{2+}.
For CH_3Hg^+ the isotope ratio is still 2.
For Hg^{2+} the ratio is altered and correction is necessary.



Extraction efficiency of species

Normally, equilibration between standard and analyte is not be achieved until after the initial extraction of analyte from the solid material.

Isotope standards can not be used to explicitly quantify extraction efficiency but are still useful to study the extraction process.

Extraction efficiency of species

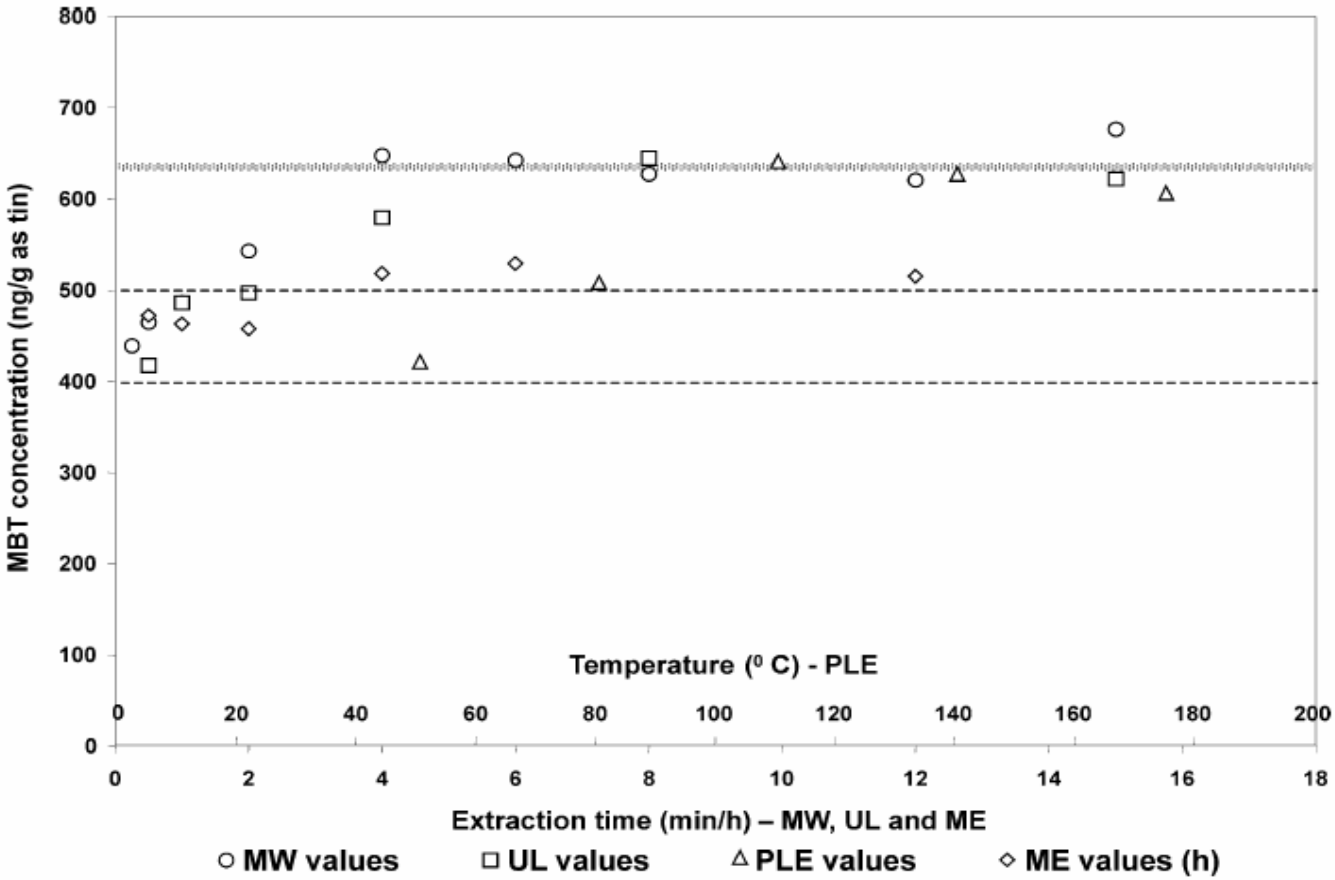


Figure 3. Study of MBT extraction efficiency from the PACS-2 certified reference sediment, using different extraction techniques operated under different conditions and analysis by GC-ICP-MS with double isotope-labelled spike. Dashed lines correspond to the 95% confidence interval of the certified value (ng/g) in the sediment.

J. R. Encinar *et al, TRAC*, 2003, **22**, 108

CCQM Pilot Study 39

(Comité Consultatif pour la Quantité de Matière)

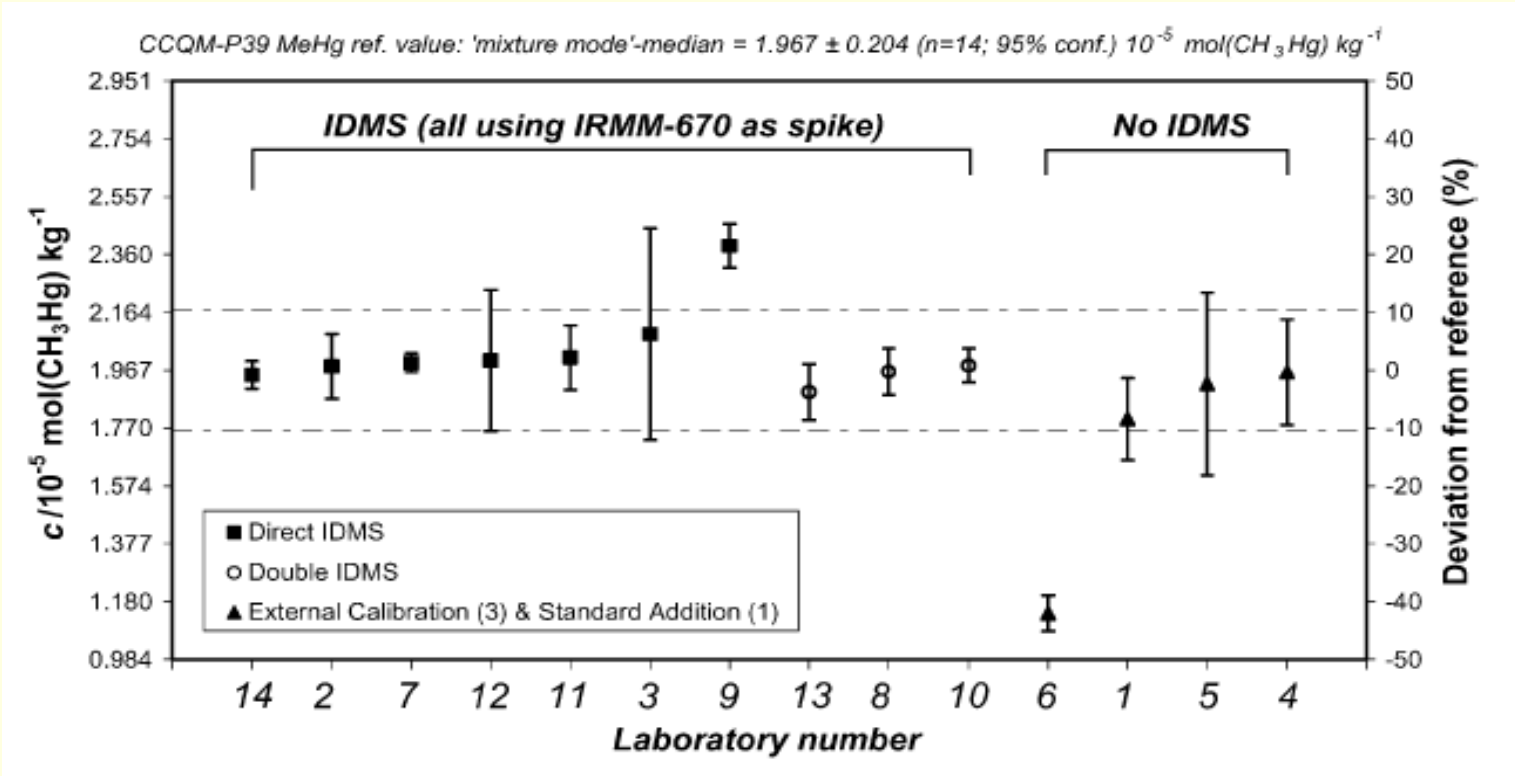
Determination of CH_3Hg^+ in tuna

- Only national metrology institutes and invited expert laboratories
- High concentration (4.3 mg kg^{-1}) of CH_3Hg^+, fairly easy extractable matrix, high relative concentration (>90%) of CH_3Hg^+ compared to Hg^{2+}
- Direct SSID possible by the supply of a certified $CH_3{}^{202}Hg^+$ standard

Thus, this study shows the reliability of speciation analysis data when the conditions are very favourable.

C. R. Quetel *et al*, *J. Anal. At. Spectrom*., 2005, **20**, 1058

CCQM-P39 results



C. R. Quetel *et al*, *J. Anal. At. Spectrom*., 2005, **20**, 1058

CCQM-P39 methodologies

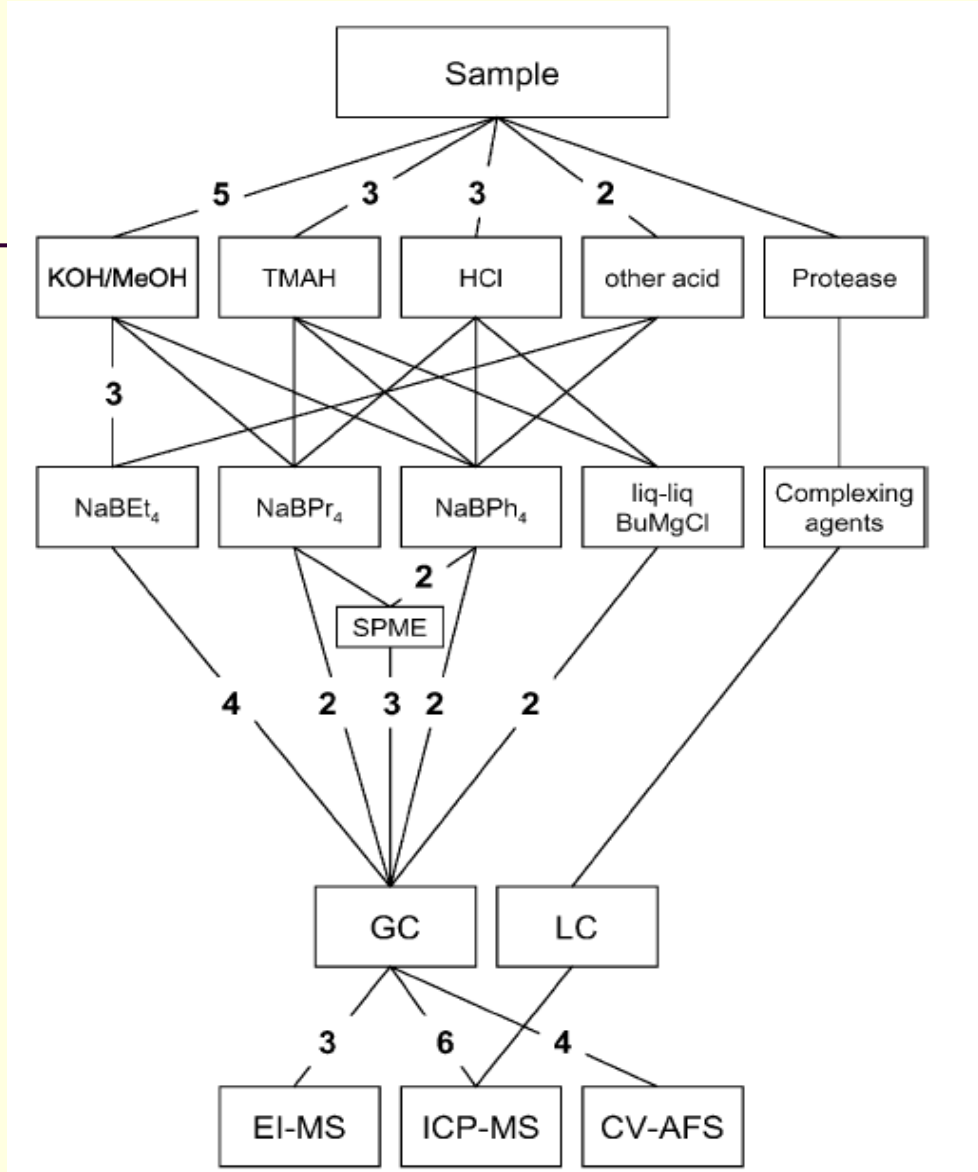


Fig. 2 Overview of the methodology applied by the CCQM-P39 participants.

C. R. Quetel *et al*, *J. Anal. At. Spectrom*., 2005, **20**, 1058

Speciation data in legislation?

For speciation analysis, the difficulty of analysis and the possibilities for method validation are very different for different species and sample types.

For some speciation analysis, e.g. the determination of CH_3Hg^+ in soils and sediments, there are available:

- CRMs
- Standard methods
- Accredited laboratories
- Promising results from proficiency testing

Speciation data produced under such premises should be useful for legislation and in court proceedings (or…?)