State of the art of mercury speciation analysis

Wolfgang Frech, Lars Lambertsson, Tom Larsson and Erik Björn, Department of Chemistry, Analytical Chemistry, Umeå University, S-90187 Umeå, Sweden
Major mercury species in environmental samples

- Elemental Hg\(^0\)
- Inorganic mercuric Hg\(^{2+}\)
- Inorganic mercurous Hg\(^+\)
- HgS
- Organic CH\(_3\)Hg\(^+\)
  C\(_6\)H\(_5\)Hg\(^+\)
  (CH\(_3\))\(_2\)Hg

- Isotope distribution; Hg binding to proteins or humic acid
Speciation analysis and total amount determination

**Speciation**
- Sample pretreatment
  - conservation, storage
- Species identity and losses
  - Extraction/digestion, enrichment
    - Derivatisation
    - Separation (for identification)
    - Detection

**Total amount**
- Sample pretreatment
  - conservation, storage
- Losses
  - Dissolution/decomposition (enrichment)
  - Detection
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

GUNNEL WESTÖÖ

Department of Food Hygiene, National Institute of Public Health, Stockholm, Sweden
Extraction procedure for CH$_3$Hg in foodstufs

- **Homogenisation**
- **Extraction to benzene**
- **Centrifugation**
- **Backextraction to aqueous phase**
- **Extraction to benzene**
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).

Present status for CH$_3$Hg$^+$ 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 electrophoresis 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$_3$Hg$^+$ 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

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

Christopher S. Kim\textsuperscript{a,*}, James J. Rytuba\textsuperscript{b}, Gordon E. Brown Jr.\textsuperscript{a,\textsuperscript{c}}

\textsuperscript{a}Surface and Aqueous Geochemistry Group, Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA

\textsuperscript{b}US Geological Survey, 345 Middlefield Road, MS 901, Menlo Park, CA 94025, USA

\textsuperscript{c}Stanford Synchrotron Radiation Laboratory, SLAC, 2575 Sand Hill Rd., MS 99, Menlo Park, CA 94025, USA

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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$_3$O$_2$SO$_4$
HgCl$_2$
Hg$_3$S$_2$Cl$_2$
Hg$_2$OCl

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 ($\text{CH}_3\text{Hg}^+$, MeHg$^+$)
- Inorganic mercury (Hg$^{2+}$)
- Metallic mercury (Hg$^0$),
- Dimethylmercury ($\text{CH}_3\text{Hg}$),
- Phenylmercury ($\text{C}_6\text{H}_5\text{Hg}^+$)

Total Hg

Soil/sediment background levels:
- MeHg$^+$: $\sim 1$ ng g$^{-1}$
- TotHg ($\sim$Hg$^{2+}$): $\sim 100$ 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, H₂SO₄
    - Ion-pair reagents: NaCl, KBr...
  - Alkaline digestion
    - MeOH/KOH
    - TMAH
  - Solvent extraction
    - Toluene, DCM...

  + MeHg⁺ extraction yield
  - Hg²⁺ 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

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<td>6800</td>
<td>Elemental &amp; Speciated Isotope Dilution MS</td>
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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

Natural Hg isotope abundance

Enriched isotope spike

--

Sample

Isotopomer standard

Mixture

Isotope spike

--

Intensity

m/z
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
Determination of volatile Hg species in gaseous samples

Tom Larsson, Dept. of Analytical Chemistry, Umeå University
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 ($\text{CH}_3\text{Hg}^+$)
Forms ionic complexes with e.g. halogens: $\text{CH}_3\text{HgX}$
Water soluble, relatively volatile

Dimethyl mercury ($\text{(CH}_3)_2\text{Hg}$)
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
Species specific isotope enriched gaseous Hg tracers

Permeation tubes

Mixing chamber

Ethylation of ionic Hg species on capsule filter support

Gas flow direction

Gaseous sample

(CH3)2Hg

Hg0

CH3HgX

(CH3)2198Hg

CH3200HgCl

201HgCl2

202Hg0

Tenax TA tube

Au/Pt tube

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

- a: Hg⁰
- b: (CH₃)₂Hg
- c: CH₃HgX
- d: HgX₂
SSID with permeation tubes

Biogeochemical studies

 Soil remediation
 Petroleu industry

 Carrier gas

 Biochemical reactions

 Sediment sample containing 1µg/g \( ^{199}\text{Hg}^{2+} \) (aq)
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. Initial isotope compositions for Hg$^{2+}$ and CH$_3$Hg$^+$.
   - The ratio between added and reference isotope is 2 for both species.

2. 25% degradation of CH$_3$Hg$^+$ into Hg$^{2+}$.

3. Isotope compositions after species transformation.
   - For CH$_3$Hg$^+$ the isotope ratio is still 2.
   - For Hg$^{2+}$ the ratio is altered and correction is necessary.

\[ \text{CH}_3^{^{196}\text{Hg}^+} \]

\[ ^{198}\text{Hg}^{2+} \]

- Reference isotope (202)
- Added isotope for Hg$^{2+}$ (198)
- Added isotope for CH$_3$Hg$^+$ (196)
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
Determination of CH$_3$Hg$^+$ in tuna

- Only national metrology institutes and invited expert laboratories
- High concentration (4.3 mg kg$^{-1}$) of CH$_3$Hg$^+$, fairly easy extractable matrix, high relative concentration (>90%) of CH$_3$Hg$^+$ 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.

CCQM-P39 results

CCQM-P39 methodologies


Fig. 2. Overview of the methodology applied by the CCQM-P39 participants.
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$_3$Hg$^+$ 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…?)