Trace–Level Automated Mercury Speciation Analysis

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   2. Brooks Rand Labs
Aims:

1. Automated low-level methyl Hg determination
2. Coupling automated system with ICP-MS
3. Determination of higher MW Hg species

EPA 1630 Methyl Mercury in Water (and biological/sediment extracts) by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS (ICP-MS)

Brooks Rand Labs Automated Methylmercury System
Methyl Hg bioaccumulates – speciation in multiple compartments of the environment

- Hg methylation in sediment
- Methyl Hg in surface water is a predictor of fish Hg
- Low trophic level organisms < 90% methyl Hg

Superfund site, Berlin NH
Surface water
Periphyton
Benthic organisms – mayfly, caddisfly, dragonfly, crayfish
Juvenile fish – minnows, bass
“Snack-size” fish – smallmouth bass, perch
Swallows, bats
Sediment
Porewater
Add buffer and derivatizing agent (NaBEt₄)

↓

Hg species to react with ethylating agent $t = 17\text{ min}$

↓

Purge ethylated Hg species from solution and preconcentrate on Tenax trap $t = 17\text{ min}$

↓

Dry Tenax trap $t = 7\text{ min}$

↓

Thermal desorption and separation by packed column GC with detection by AFS $t = 6\text{ min}$
Advancements to EPA 1630

Detection by ICP-MS: Species-specific isotope dilution:

Enriched isotope spike: $\text{CH}_3^{201}\text{Hg}$

Correction for:
- ✓ matrix effects / ethylation efficiency
- ✓ species transformation
- ✓ inorganic Hg ($^{199}\text{Hg}$)
Advancements to EPA 1630

High MW Hg species
vaccines, pesticides, cosmetics, biological samples

Derivatizing agents – propylation, butylation, phenylation
Internal standards – spike with high MW Hg species
MERX-M Automated Methylmercury System

Brooks Rand Labs

- Autosampler for 72 40mL vials
- Gas pressurized liquid transfer to purge vessel for aspiration of volatile Hg species
- Three Tenax traps rotate between loading, heating and drying, enabling a 6.5 min. sample time.
- IR heating to volatilize Hg from trap
- Packed column gas chromatography and pyrolysis
- Atomic fluorescence detection
Manual method: ~30 samples in 8 hrs., 8 hrs. of analyst time

Automated method: 72 samples in 10 hrs., 2 hrs. of analyst time
Configuring MERX-M to AFS/ICP-MS detection

Autosampler
Sample + buffer + ethylating agent

Packed column GC and Pyrolysis

Purge and Trap

AFS detector

ICP-MS

Sample

Make-up gas

Y-connector

N₂ for purging & drying traps

Ar-Xe for trap desorption / column carrier gas

Trigger out from MERX to ICP-MS
Atomic Fluorescence Detection:
Brooks Rand Model III CVAFS

ICP-MS detection:
Thermo Element 2 magnetic sector ICP-MS
Agilent 7500 quadrupole ICP-MS
Trace-Level Automated Mercury Analysis

Methyl Mercury

![Graph showing the analysis of mercury species](image_url)

- **CH$_3$Hg$^+$**
- **Hg$^0$**
- **Hg$^{2+}$**
Method detection limit

7 calibration standards

LOD: Limit of Detection – 3 times $\sigma_{\text{blank}}$ (n=9)
LOQ: Limit of Quantitation – 10 times $\sigma_{\text{blank}}$ (n=9)

MDL: Method Detection Limit - 3 times $\sigma_{\text{std at LOQ}}$ (n=8)  
0.5pg (12.5 pg/L)
Methyl Hg determination

EPA recommends MDL of 20 pg/L

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$Hg$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AFS</td>
</tr>
<tr>
<td>MDL (pg/L)</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Carryover

pg CH$_3$Hg blank / 1000 pg std

<table>
<thead>
<tr>
<th>AFS</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17 %</td>
<td>0.18%</td>
</tr>
</tbody>
</table>
### Methyl Hg in Standard Reference Materials

<table>
<thead>
<tr>
<th></th>
<th>Certified Value (µg/g)</th>
<th>AFS (µg/g)</th>
<th>ICP-MS (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TORT-2</td>
<td>0.152 ± 0.013</td>
<td>0.143 ± 0.007</td>
<td>0.152 ± 0.003</td>
</tr>
<tr>
<td>DOLT-4</td>
<td>1.33 ± 0.12</td>
<td>1.21 ± 0.01</td>
<td>1.34 ± 0.017</td>
</tr>
<tr>
<td>DORM-2</td>
<td>4.47 ± 0.32</td>
<td>4.04 ± 0.05</td>
<td>4.23 ± 0.063</td>
</tr>
</tbody>
</table>
n-propyl Hg

Packed column GC

1 ng CH$_3$Hg, C$_3$H$_7$Hg
Capillary GC: ↑ resolution and ↓ retention time

- Gradient heating
- Higher theoretical plates

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**GC parameters**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Agilent 6890N GC</td>
<td></td>
</tr>
<tr>
<td>Inlet mode</td>
<td>Splitless</td>
</tr>
<tr>
<td>Column</td>
<td>Agilent HP-1Megabore 0.53mm ID</td>
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<tr>
<td>GC flowrate</td>
<td>15 mL/min</td>
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</tbody>
</table>
Configuring MERX-M to capillary GC with AFS/ICP-MS detection

- Sample
- Autosampler: Sample + buffer + ethylating agent
- Purge and Trap: Ethylated Hg from sample
- Make-up gas to GC
- Ar(-Xe) carrier gas
- Capillary GC
- Packed GC (bypassed) and pyrolysis unit
- Trigger out from MERX to capillary GC and ICP-MS
- ICP-MS: Separated Hg species to ICP
- AFS detector: Separated Hg species to AFS

High MW Hg species

Trace-Level Automated Mercury Analysis
Capillary GC heating program
Trace-Level Automated Mercury Analysis

Capillary GC

- GC coupled with ICP-MS
- Run time < 4 min

GC coupled with AFS

- Run time 6 min

High MW Hg species

CH$_3$Hg$^+$, Hg$^0$, Hg$^{2+}$, C$_3$H$_7$Hg$^+$
Method Detection Limits

EPA recommends MDL of 20 pg/L

<table>
<thead>
<tr>
<th></th>
<th>Methyl Hg pg/L</th>
<th>Propyl Hg pg/L</th>
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<tbody>
<tr>
<td>packed GC</td>
<td></td>
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</tr>
<tr>
<td>AFS</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>ICP</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>capillary GC</td>
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<td></td>
</tr>
<tr>
<td>AFS</td>
<td>6</td>
<td>13</td>
</tr>
<tr>
<td>ICP</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
Trace –Level Automated Mercury Analysis

Carryover

![Graph showing % carryover for different methods and types of mercury species.](image)
Summary:

1. Automated system achieved MDL of < 2 pg/L, reducing analyst time from 8 hrs. for a 30 sample run to 2 hrs. for a 72 sample run.

2. Connection to ICP-MS achieved similar MDL as AFS, and enabled the use of isotope dilution.

3. Capillary GC decreased run time (4 min) relative to packed GC (10 min) for high MW weight Hg species (propyl Hg).
Thanks!

Funding: Dartmouth Superfund Research Program