Determination of mercury in natural waters.

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Natural waters

- Surface water
- Groundwater
- Drinking water
- Precipitations
- Soil water
The determination of mercury is special and difficult

- The concentrations are very low (ng/l)
- Hg evaporates at room temperature (cold vapor)
<table>
<thead>
<tr>
<th>Method</th>
<th>Approximate LOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV-AFS (without gold trap)</td>
<td>5 ng/l</td>
</tr>
<tr>
<td>CV-ICP-MS</td>
<td>2-10 ng/l</td>
</tr>
<tr>
<td>CV-ICP-OES</td>
<td>100 ng/l</td>
</tr>
<tr>
<td>CV-AAS</td>
<td>15-500 ng/l</td>
</tr>
</tbody>
</table>
Our method

- CV-AFS without gold trap
The analysis consists of

- Sampling and adding $\text{HNO}_3$
- Combined preservation/digestion
- Preparation of calibration standards
- Analysis with the AFS device
The sampling

- 0.5 - 1 l glass or plastic bottles
- with HNO₃ inside (final concentration of HNO₃ is 0.5%)
- For the dissolved Hg, the sample is filtered through a 0.45 µm syringe filter prior to adding HNO₃ and preservation.
Combined preservation/digestion

- 50 ml of the sample is pipetted to the glass jar
- 9 ml HCl is added
- 1.2 ml KBr/KBrO$_3$ solution is added

Hg in sample is oxidized by bromate/bromide reagent. The solution turns yellow and is stable during one week.
Combined preservation/digestion

• Just before analysis add 0.5 ml L-ascorbic acid is added to eliminate the excess of Br
• The color disappears
Preparation of calibration standards

- Stock solution 10 mg/l
- Stock solution 0.1 mg/l (prepare on the day of use)
- Stock solution 1 µg/l (prepare on the day of use)
- Calibration standards 0 ng/l; 5 ng/l, 20 ng/l, 50 ng/l, and 100 ng/l (prepare on the day of use)
Analysis with the AFS device

- The ionic Hg is reduced with SnCl$_2$ to Hg vapour
- The Hg vapour is separated from solution by passing the sample through a gas/liquid separator
- The Hg vapour is purged from solution by an argon gas carrier steam
- Moisture is removed from the gas steam
Analysis with the AFS device

- The Hg (0) is detected by AFS
- Concentration of Hg is determined by AFS at 253.7 nm
- The analysis is automated by means of an autosampler and control software
Specialities of AFS analysis

- There are many contamination sources (reagents, glassware, lab environment etc.)
- Hg may also be lost during handling of the sample
- Skilled analyst is needed
- Analysis is time consuming
• We started on 1995 with CV-AAS
• Our laboratory performed 516 Hg analyses on 2018
• 244 of them were natural waters
• Price - 27 euros
244 natural water samples

- 122 surface water samples
- 23 groundwater samples
- 15 drinking water samples
- 80 precipitation samples
- 3 soil water samples
Eesti Keskkonnauuringute Keskus

Thank you!