Determination of heavy metals by the method of AAS

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**Atomic Absorption Spectroscopy - AAS**

One of the most widespread analytical methods is the following:

- quantitative & qualitative determination of more than 70 elements
- category samples
  - environmentals samples (drinking water, waste water, soil, etc)
  - foods (milk, wine, etc)
  - biological samples (blood, urine, tissues, etc)
- samples of little quantity in mL or μL
- low LOD that is referred in ppb - ppm
Parts of the AAS

1. Line source
2. Atomizer
3. Monochromator
4. Processor
5. PC
Line source

lamps - Hollow cathode
lamps - EDL

The parts of the lamp are the following
Method Atomization (AAS)

3 different techniques of atomization applied in depending of element, element concentration and type of sample.

- **Flame Atomization**
  - temperatures 2000 up to 4800°C
  - LOD in ppm

- **Graphite Furnace Atomization**
  - temperatures 2000 up to 2400°C
  - LOD in ppb

- **Chemical Atomization** that leads to the creation of Hydrides
  - suitable only for volatile elements (e.g. Hg, As)
Atomization in Graphite Furnace

The process of atomization takes place on a graphite that enters into the furnace. We can see the schematic representation of the graphite furnace.
Perkin Elmer Analyst 800

Provides

- Two adapted systems of atomization with atomizing technique change
  1. Furnace Graphite
  2. Flame System
- Temperature system of standardization - TGFA & STPF
- Background correction in a magnetic field (TGFA)
- Background correction in a deuterium lamp (flame)
- Autosampler with the big sample capacity
- FIAS - flow injection analysis system
Main steps of Graphite Furnace atomization program

- Autosampler – volume sample 10-20μL

- Electrical graphite heating in four distinctive stages:
  1. Dry (10-100 seconds)
  2. Ash (10-100 seconds)
  3. Fire/Atomize (1-3 seconds)
  4. Cleaning in 2400°C for a few seconds

Figure 8-6 Profile of an atomic line showing definition of the effective line width Δλ₁/₂.
Chemical modifiers

- They are used in the graphite furnace technique order do minimize the chemical burdens of the substrates of the sample as well as the tissues of the graphite furnace in the analysis of the metals

**Aim:**
- It reduces the volatility of the metals and by this way it allows the increase of the pyrolysis temperature without the metal’s loss that is subjected to analysis
- It increases the volatility of the substrate of the sample with the result of having better distance during the sample’s preheating

<table>
<thead>
<tr>
<th>Metal</th>
<th>Chemical Modifier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb &amp; Cd</td>
<td>NH₄H₂PO₄ and Mg(NO₃)₂</td>
</tr>
<tr>
<td>Cr, Fe</td>
<td>Mg(NO₃)₂</td>
</tr>
<tr>
<td>As, Mn</td>
<td>Pd and Mg(NO₃)₂</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
</tr>
</tbody>
</table>
### Applications for drinking water

<table>
<thead>
<tr>
<th>No</th>
<th>Metals</th>
<th>Legal limit for drinking water (ppb)</th>
<th>Method of determination</th>
<th>Linearity (ppb)</th>
<th>LOQ (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Arsenic</td>
<td>10</td>
<td>Furnace</td>
<td>50</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>Lead</td>
<td>10</td>
<td>Furnace</td>
<td>50</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>Cadmium</td>
<td>5</td>
<td>Furnace</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>Chromium</td>
<td>50</td>
<td>Furnace</td>
<td>25</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>Nickel</td>
<td>20</td>
<td>Furnace</td>
<td>50</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>Manganese</td>
<td>50</td>
<td>Furnace</td>
<td>50</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>Iron</td>
<td>200</td>
<td>Furnace / Flame</td>
<td>100/2000</td>
<td>1/20</td>
</tr>
<tr>
<td>8</td>
<td>Zinc</td>
<td>-</td>
<td>Flame</td>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>Copper</td>
<td>2000</td>
<td>Flame</td>
<td>2000</td>
<td>10</td>
</tr>
</tbody>
</table>

1. LOQ: limit of quantitation

**Note:** Conservation of the samples in the refrigerator after being acidified
Example – As in drinking and surface waters

<table>
<thead>
<tr>
<th>No</th>
<th>T(°C)</th>
<th>Ramp time (s)</th>
<th>Hold time(s)</th>
<th>Internal Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>110</td>
<td>1</td>
<td>20</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>130</td>
<td>20</td>
<td>30</td>
<td>250</td>
</tr>
<tr>
<td>3</td>
<td>1100</td>
<td>10</td>
<td>40</td>
<td>250</td>
</tr>
<tr>
<td>4</td>
<td>2100</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>2450</td>
<td>1</td>
<td>5</td>
<td>250</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wave Length</th>
<th>Slit width</th>
<th>Read time</th>
<th>Delay time</th>
</tr>
</thead>
<tbody>
<tr>
<td>193.7 nm</td>
<td>0.7L</td>
<td>3 sec</td>
<td>0.5 sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Modifier/ volume</th>
<th>Volume sample</th>
<th>Sensitivity Check 50 ppb</th>
<th>Linearity (ppb)</th>
<th>Legal limit for drinking water</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pd+Mg(NO)_3$ - $5 \mu l$</td>
<td>20 \mu l</td>
<td>0.11 Abs</td>
<td>50 ppb</td>
<td>10 ppb</td>
</tr>
</tbody>
</table>
Example of Fe’s measurement

- From the working solution the other five standards solutions are produced, which are used for the calibration
- This line is the result of calibration
- From this absorption the concentration of the unknown sample is measured
Accreditation of laboratory

- Determination of reproducibility with quality control, natural and spiked samples
- Determination of repeatability
- Determination of recovery
- Determination of SD (standard deviation)
- Determination of limit of detection (LOD) and limit of quantitation (LOQ)
- External Quality Control

Our laboratory is certified in six metals (As, Pb, Cd, Ni, Cr, Mn) for samples of drinking and surface waters according to ISO 17025
Accreditation of laboratory

For each metal a control chart must be formulated

**Control chart Cr 50ppb**

20 measurements measured on 20 different days
AAS - Advantages

- The general function is simple and automatized to a great extent
- The detection limits are adequate for a wide sample range - environmental and clinical samples
- Good repeatability in measurements
- Affordable market cost
- Functioning cost is low
AAS - Restrictions

- Species variations cannot be determined (Cr$^{3+}$-Cr$^{6+}$). Only total metal concentration.

- For solid and organic samples a procedure of elaboration is demanded that includes dissolution with powerful acids in a special machine of digestion suitable for high pressures and temperatures.
Thank you