7. Atomic Emission and Absorption Spectroscopy

Atomic emission and absorption spectroscopy are important analytical tools in clinical biochemistry, e.g. for the determination of the concentrations of metals (Ca, Mg, Na, K) in blood and urine.

Electronic transitions of atoms and the absorption and emission of electromagnetic radiation are due to the different energy levels of the atomic orbitals, e.g. Sodium

Wavelength differences (in Å) associated with transitions between the different energy levels of Na
The electronic configuration of Na in the ground state is $1s^22s^22p^63s^1$.
When excited (e.g. in a flame) its valence electron may undergo a transition to the 3p orbital, i.e. to give the configuration $1s^22s^22p^63s^03p^1$.
When the atom returns to its ground state it can emit a photon, which gives rise to the characteristic yellow emission of sodium (590 nm).
Each element has its own characteristic spectral lines, which can be used for its identification and quantification, e.g.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>589.6</td>
</tr>
<tr>
<td>Cd</td>
<td>480.0</td>
</tr>
<tr>
<td>Hg</td>
<td>546.1</td>
</tr>
<tr>
<td>V</td>
<td>437.9</td>
</tr>
<tr>
<td>Al</td>
<td>309.3</td>
</tr>
</tbody>
</table>

The analysis of a sample involves a number of steps:

Solution of analyte
↓
↓ Nebulization
↓
Spray (aerosol)
↓
↓ Heating (desolvation)
↓
Gaseous molecules
↓
↓ Heating (dissociation)
↓
Atoms
↓
↓ Heating (excitation)
↓
Excited atoms $\Rightarrow$ Light ($h\nu$)
What temperature would be necessary to excite atoms and observe their spectral lines?

Example: Na D-line, 590 nm

A typical flame temperature is 2000 °C (2273K). The population of the excited state relative to the ground state can be calculated according to the Boltzmann distribution (eq. 3.6):

$$\frac{N_{\text{excited}}}{N_{\text{ground}}} = \exp\left(-\frac{\Delta E}{kT}\right) = \exp\left(-\frac{hc}{\lambda kT}\right)$$

$$= 2.18 \times 10^{-5}$$

Although the population of the excited state is very small, the sodium D-line can be observed because of its high transition probability.

For the observation of spectral lines from all elements, however, the temperature of a flame is insufficient. To obtain higher sensitivity one must go to much higher temperatures, >5000K.

Such temperatures can be achieved by the method of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).
Inductively coupled plasma torch

Plasma state: Fourth state of matter consisting of free electrons and charged cations.

Argon plasma is produced by a spark from a Tesla coil. When the plasma flow reaches the radiofrequency induction coil at the tip of the torch, the magnetic field causes the cations and electrons to flow in opposite circular paths. As they collide with one another, temperatures up to 10,000 K are produced.
Sample injection

The sample is carried into the observation region at the tip of the torch as an aerosol with argon as the carrier gas.

Detection limit 0.02-40 ng/ml (nM range)
Advantage: all elements can be determined simultaneously from one measurement.
Disadvantages: many spectral lines and possible interference, high cost
Atomic Absorption Spectroscopy (AAS)

The technique of atomic absorption spectroscopy is in principle the reverse of atomic emission spectroscopy, i.e. the absorption of radiation is measured rather than its emission. However, there are a number of important technical differences.

a) Burning
Because absorption is measured rather than emission, it is not necessary to excite the atoms of the sample. The sample must just be heated in a burner to 2000-3000 K so that atomisation occurs (dissociation of all molecules).
b) Radiation source
Because AAS is an absorption method, a light source for irradiation is required. In order to reduce interference, to increase specificity and sensitivity, a lamp is chosen which corresponds to the element being analyzed for.

Hollow cathode lamp

Each hollow cathode lamp consists of a tungsten anode (+) and a cup-shaped cathode (-) made from the element to be investigated. When a voltage is applied, light is emitted from the cathode at wavelengths characteristic for that element.
For example, if one wishes to measure the Na concentration, one uses a Na vapour lamp and measures the absorbance of the Na D-line.

One measures the intensity of the line from the lamp before and after passage through the sample and calculates the absorbance according to eq. (6.2). If the instrument is calibrated using samples of known concentration, the concentration of the sample can be determined using Beer's law (eq. 6.5).
Application: Lead Poisoning

Pb$^{2+}$ inhibits enzymes responsible for the production of haem.

High blood lead levels
⇒ Reduced level of haemoglobin
⇒ Oxygen starvation, Anaemia
⇒ Brain damage

Monitoring of blood lead levels in children is important for ensuring proper brain development (e.g. possible link between hyperactivity and delinquent behaviour and high blood lead levels).

0.48-1.21 µmol/L Pb may impair cognitive development in children

NHMRC recommendations (1993)
- Max. blood lead level goal for all Australians: 0.48 µmol/L
- If in a community 5% of pre-school children have > 0.72 µmol/L, public health action should be taken to investigate lead sources.

With a 10km radius of the Sydney CBD 7% of children had blood lead levels >0.72 µmol/L.
Units in Analytical Chemistry

Parts per million = ppm

1 ppm = \(1\ g/10^6\ g\) of solution

If the solvent is water (density = 1 g/ml),

\[1\ ppm = 1\ g/10^6\ ml\ of\ solution = 10^{-3}\ g/L\]

e.g. For lead,

Atomic mass = 207.2 g mol\(^{-1}\)

\[1\ ppm = 10^{-3}\ g/L = \frac{10^{-3}}{207.2}\ mol\ L^{-1}\]

\[= 4.8 \times 10^{-6}\ mol\ L^{-1}\]

\[= 4.8\ \mu\text{mol/L}\]