**Atomic Absorption Spectroscopy**

*Reading assignment: Chapter 9 of Principles of Instrumental Analysis by Skoog, Holler, & Nieman; 1997.*

***Basic principles***

Unlike atomic emission spectroscopy, atomic absorption spectroscopy is based on the absorption of a particular characteristic wavelength by the atomized sample which contains that analyte with this characteristic wavelength. The degree of absorption of that wavelength will therefore be proportional to the concentration of the analyte in the sample. Generally, all absorption techniques used in quantitative analysis are based on Beer’s law.

*Beer’s law*

$$\frac{I}{I°}=10-^{alC}$$

Where *I* and *I°* are the intensities of the characteristic light before and after passing through the “flame” (sample solution with analyte), respectively, *a* is the absorption coefficient (absorptivity), C the concentration of the analyte, and *l* is the flame/sample path length. It should be noted that the relationship between C and the absorption *I/I°* is linear over a limited range of (low) concentrations. The basic principle of operation is therefore to measure the absorption of a set of standards of known concentrations, plot absorption against concentration to obtain a calibration curve, then run the unknown measuring the absorption resulting. The calibration curve could then be used to determine the concentration of the analyte in the sample.

*Absorption and absorbance:*

Absorbance is defined as the logarithm of absorption. It was found that plotting log *I/I°* rather than the absorption, against concentration would give a more linear relationship (e.g. Fig. 1 of last week’s handout).

***Components of a typical AAS (Fig. 1)***

1. Hollow cathode lamp: The principle of operation of this lamp is the creation of a plasma that is capable of sputtering a fork-shaped negatively charged target of the element analyzed for, hence generating the characteristic emission lines (Fig. 3).
2. Nebulizer to carry your sample into the flame (or energy source)
3. Flame (or energy source) that would excite/ atomize elements in your sample.
4. Spectrometer: As in the case of the ICP-OES, the spectrometer consists of a grating and one or more photomultipliers.
5. Amplifier and readout device

***Uses***

The AAS is useful for analyzing for trace elements, particularly those that are **easily volatilized**. However, it can also analyze for major elements (diluting your solution if necessary). We can analyze for 22 different elements in our labs using this instrument. Detection limits are normally on the order of a fraction of ppb (µg/l).

**The Zeeman GFAAS:**

Graphite furnace AA spectrometers use a small graphite tube to atomize the sample (instead of the nebulizer + flame). A Zeeman GFAAS has a strong electromagnet that makes use of the Zeeman effect in order to correct for some interferences (see below). A Zeeman GFAAS therefore has better sensitivity compared to a standard GFAAS.

***Components (Fig. 2)***

1. Hollow cathode lamp
2. Graphite furnace:
3. Zeeman magnet
4. Spectrometer
5. PC

***Operation:***

The lamp is inserted in the GFAAS, warmed, and aligned. A specific line is selected for absorbance measurements in a way that would ensure maximum sensitivity. A known volume of the standard/ sample is introduced into a graphite tube through a capillary tube + syringe. This tube is then heated in a controlled manner to ensure the atomization of the sample. Two types of tubes are used: (a) partitioned (off the wall) tube used regularly for most solutions, and (b) notched tube (platform) used for samples dissolved in organic solvents (Fig. 4).

Heating of the graphite tube follows a specific routine that ensures that the sample undergoes the following processes (Fig. 5):

1. A drying stage: for desolvation of the sample, it is heated to below the boiling point of the solvent. Necessary to ensure good precision.
2. An ashing stage: removes the sample matrix prior to atomization.
3. A stage during which the gas is turned off
4. T ramp stage: a stage during which the T is increased rapidly to the atomization T.
5. A stage of atomization, during which the spectrometer is set to read the resulting absorbance. The gas is still turned off during this stage.
6. A tube clean stage: during which the tube is heated to ensure full atomization and that no material has remained in it.

***Calibration:***

The GFAAS is calibrated by running a set of standards of known concentrations through the furnace, each time recording the absorbance. The standards are selected following the same criteria discussed earlier for ICP-AES. A calibration curve is then plotted. However, unlike in the case of the ICP-AES, the calibration curve is not necessarily linear, and one seldom chooses standards covering the entire analytical range (Fig. 6). Instead, the standards are prepared to cover the expected range of the unknowns. Typically, only 3 or 4 standards are used for the calibration curve.

***Types of Interference:***

1. Chemical interference: arises from the formation of chemical compounds containing the analyte, which are either very volatile or very stable. These compounds will therefore not atomize with most of the analyte resulting in weaker absorbance. Chemical interference therefore leads to underestimation of the analyte concentration.
2. Physical interference: arises from (i) thermal gradients that may develop within the graphite tube, (ii) the “splattering” of the sample so that its occurrence in different locations within the tube results in a different set of atomizations, (iii) different behaviors of the sample components during the “dry” stage, (iv) incandescence of the graphite tube.
3. Spectral interference: results from (i) the light source emitting spectral lines that are not resolved by the monochromator; (ii) the presence of molecular species that produce spectral lines close to that of the analyte. Spectral interference is known as “background”.

***Correcting for interference:***

*Chemical interference* is corrected for through the use of ***chemical modifiers***, and/ or the use of a pyrolytic platform. The chemical modifier is an element or compound added to the sample to ensure that the analyte is not vaporized during the drying or ashing stages. A pyrolytic platform on the other hand is used when the analyte forms a stable compound that resists atomization at the selected temperature. Together with the modifier, it is designed to permit a higher ashing T for volatile compounds, or to breakdown those analyte - containing compounds that are otherwise stable at atomization temperatures.

*Physical interferences* are avoided by ensuring that the sample and standards all have the same viscosity and surface tension. If the sample is one with a very low surface tension and spreads easily in the graphite tube, then the use of a platform may be necessary. Generally, physical interferences can be minimized through the use of an automated sample dispenser, and by ensuring that the electrodes are kept clean (hence maintaining constant T throughout the tube). Incandescence is a problem that may arise at very high T of atomization (> 2700°C). It is minimized or avoided by proper alignment of the tube (to ensure that any emissions from the tube wall do not reach the PMT), or by chemical modification, which often results in the reduction of the T of atomization.

Spectral interference (background) is dealt with through the application of a strong magnetic field (Zeeman technique) which has the effect of splitting and shifting the background peaks (arising from salts and other compounds that vaporize in the optical path of the light source, hence scattering it). Chemical modification is also very helpful as it will prevent the appearance of atomic and non-atomic absorption lines simultaneously, hence increasing the sensitivity of the AAS.

***Zeeman Effect:***

Is the splitting of atomic spectral lines under the influence of a strong magnetic field. Two types of splitting occur: (i) normal Zeeman effect, where one spectral line splits into 3 lines, one at the same λ as the original line, and is known as “π”, and two other lines of lower intensity on each side of the original line known as “σ” (Fig. 7a), and (ii) anomalous Zeeman effect which is obtained by varying the intensity or orientation of the magnetic field, producing several “groups” of peaks (Fig. 7b).

The technique involves measuring absorbance while (a) the magnetic field is turned off, then (b) while the field is on. These two readings allow for the identification of the background intensity and correcting for it. It also has the advantage of having the background absorbance measured at the same time as the main analyte line.

Magnetic sensitivity ratio (MSR) = Zeeman sensitivity/ normal AAS sensitivity.

Although the analyte signal is itself subdued by Zeeman magnet, the benefits of background corrections by this method far outweigh this reduction in absorbance signal.

***Advantages of GF atomization***

1. More than 100 X better sensitivity compared to the flame AAS.
2. Lower interferences
3. Smaller amount of sample used; hardly any waste!
4. Tolerant of a variety of samples (concentrated acids; organics; aqueous solutions; …. etc.).

***Limitations/ (Sources of error)***

1. Not suitable for some refractory elements (e.g. Hf and Zr)
2. Not suitable for those elements that combine with C at high T.
3. The memory effect is substantial. It is therefore very critical to ensure that the tube is cleaned between runs.
4. The technique has a limited ability to form chemical species with appropriate spectral lines amenable to detection.
5. The background correction is critical. Background absorption is one of the main sources of error.
6. It is fairly time consuming
7. Incandescence of the tube.
8. Elemental emission.



Fig. 3: The Hollow cathode lamp.

*Source:* [*http://upload.wikimedia.org/wikipedia/en/1/1e/Hollow\_Cathode\_Lamp.png*](http://upload.wikimedia.org/wikipedia/en/1/1e/Hollow_Cathode_Lamp.png)