

## Atomic Absorption Spectroscopy (AAS) and Inductively-coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

After reading this Factsheet you will:

- Be able to recall the uses of AAS and ICP-AES
- Be able to describe the basic functions of the main components of both spectrometers
- Understand the atomic processes that occur during both forms of spectroscopy
- Understand the importance of a calibration curve and how to create one
- Be able to analyse quantitative data produced by AAS and ICP-AES

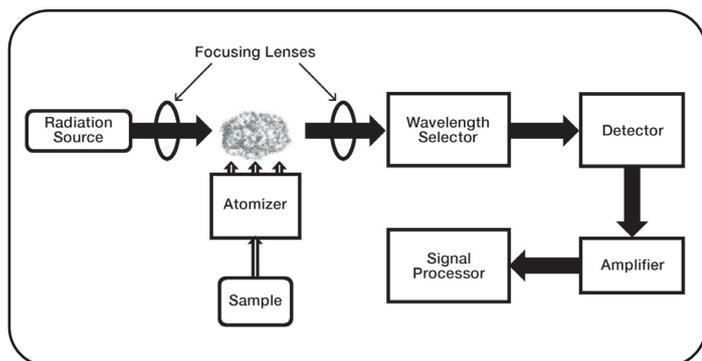
At the simplest level, both AAS and ICP-AES are used for similar applications and rely on the same basic processes of electronic transition and photon absorption and emission. However, the manner in which both spectrometers work is different and this factsheet will look at each separately; focusing on the principles behind the components of the devices.

### Use of AAS and ICP-AES

Both types of spectroscopy are highly selective and can be used in a variety of applications. The most common applications involve the detection of metals within a sample. Some typical applications include:

- Analysis of mineral content in soils and other agricultural media
- Analysis of metal contamination in water sources
- Toxicological studies of body fluids such as urine and blood
- Detection of trace levels of metal catalysts in pharmaceutical products
- Analysis of motor oil to determine engine wear

**Figure 1** The basic components of an Atomic Absorption Spectroscopy



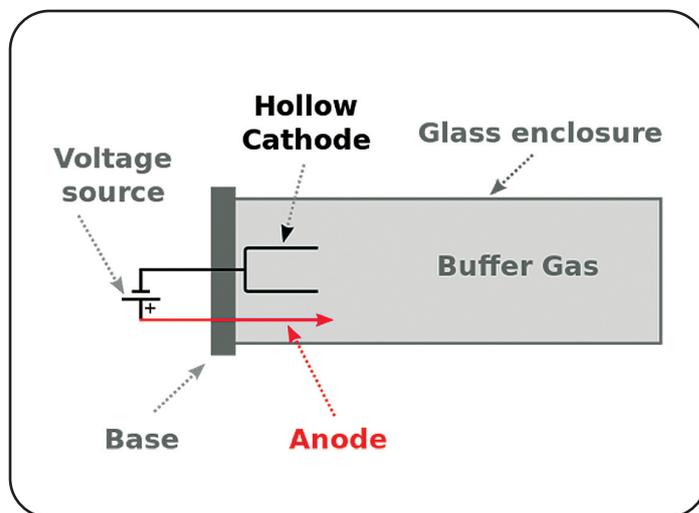
### Atomic Absorption Spectroscopy

In brief, an element-specific radiation source emits light into a vaporised sample of atoms. Atoms of the element under analysis absorb specific frequencies of light and this absorption is detected and amplified by the spectroscopes electronics.

**Figure 1** shows the individual components contained within a typical atomic absorption spectrometer. We will take a more detailed look at some of the key parts:

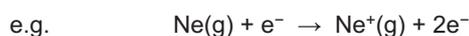
**1. Radiation source:** Commonly, the source of radiation is a hollow cathode lamp which emits frequencies of light specific to the element being detected.

**Figure 2**



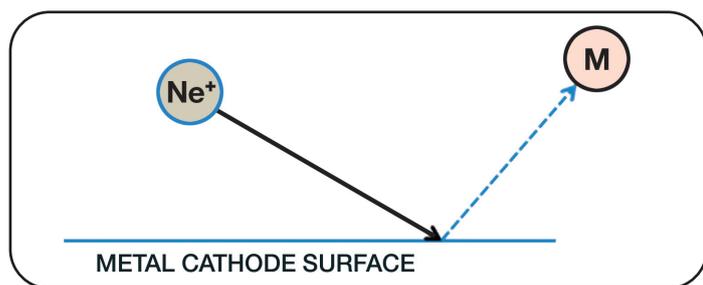
The hollow cathode is made from the element under analysis, i.e., it is made of chromium if the experiment is designed to detect the presence of chromium. The anode is made from tungsten and is a source of high energy electrons. A series of collisions results in the emission of light specific to chromium atoms from the lamp.

a) Electrons emitted from the anode collide with atoms of the buffer gas, typically an inert gas such as argon or neon. This results in formation of gaseous ions.

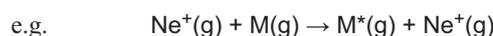


b) The newly-formed gaseous ions are accelerated towards the cathode and collide with the metallic surface. This process results in metal atoms being ejected from the surface of the cathode in a process known as **sputtering** (**Figure 3**).

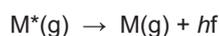
Figure 3



c) a multitude of collisions are now possible between the ions and atoms present inside the chamber. Some of these collisions may result in the metal atoms becoming excited as their electrons are promoted to higher energy levels.



d) the excited metal atoms relax to a lower energy state and emit photons of light specific to that element.

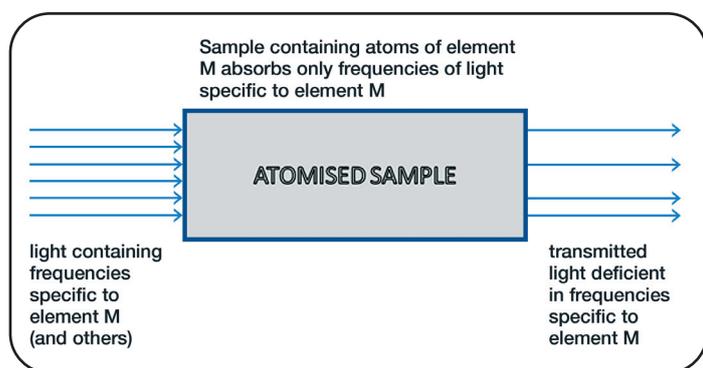


The product of the above processes is a beam of light emitted from the lamp which contains frequencies from all the atoms present in lamp; however, the intensity of the frequencies emitted by the metal atoms is high and this allows them to be selected for at a later stage and reduces interference from frequencies emitted by other elements (e.g. the buffer gas).

**2. Atomiser:** The light emitted from the hollow cathode lamp is focused and shone into the sample. The sample is prepared by injecting it into the spectroscope where it is nebulised (turned into a fine vapour) and passed into a flame atomiser. This flame (typically produced by burning an ethyne and oxygen mixture) causes molecules and ions in the sample to be converted to atoms.

These atoms absorb photons of light of specific frequencies emitted from the hollow cathode lamp. If the sample contains atoms of the elements under analysis then those frequencies of light specific to that element will be absorbed from the radiation source (**Figure 4**).

Figure 4



**3. Wavelength selector:** Commonly known as a **monochromator**. This component functions to filter out all of the frequencies of transmitted light that are not specific to the element being analysed; this serves to reduce interference from unwanted frequencies. Light passing from the monochromator to the detector will contain only (or mainly) frequencies of light specific to the element being analysed at varying intensities depending on how much has been absorbed by the sample.

**4. Detector:** The detector and subsequent electronics provide an output in which the intensity of the transmitted light from the sample is measured relative to the intensity of light transmitted in the absence

of the sample. This numerical value is called **absorbance** and is measured at a given wavelength/frequency of transmitted light.

Absorbance is related to the concentration of the element in the sample according to the **Beer-Lambert Law** (general form given below); the relationship is directly proportional.

$$\text{Absorbance} = \log(I_0/I) = \epsilon cl$$

where,  $I_0$  is the intensity of transmitted light in the absence of a sample (blank)

$I$  is the intensity of transmitted light from the sample

$\epsilon$  is the molar extinction coefficient (a species-dependent constant of proportionality)

$c$  is the concentration of the species in the sample

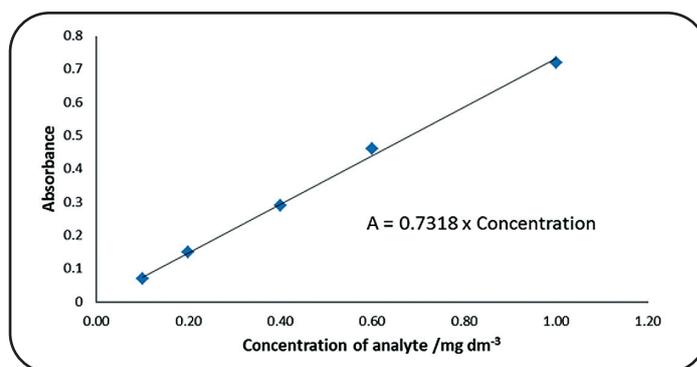
$l$  is the length of the light path through the sample

Given the directly proportional relationship between absorbance and concentration, it is possible to quantify an analyte within a sample provided the absorbance of a series of reference standards is also determined prior to testing the sample. This can be achieved by creating a **calibration curve**.

### Calibration curve and sample analysis

The creation of a calibration curve is a quick and simple way to determine the concentration of an analyte in a sample. The method involves determining the absorbance values for a reference sample of the same analyte at a number of different concentrations. According to the Beer-Lambert Law, this should yield a directly proportional relationship and a graph of absorbance (y-axis) against concentration (x-axis) can be plotted and used to determine the concentration of the analyte in an unknown sample (**Figure 5**).

Figure 5



Once the calibration curve has been created, samples can be tested and the concentration of the analyte in each can be calculated by using the gradient of the calibration curve.

For example, a 25.00 cm<sup>3</sup> sample of river water was tested for the presence of lead (Pb). An atomic absorbance spectroscope was set up using a hollow lead cathode lamp and calibrated using a reference of lead(II) nitrate. A calibration curve was created (**Figure 5**) and then subsequent testing of the river water yielded an average absorbance of 0.37.

$$\text{Concentration of Pb in sample} = 0.37 / 0.7318 = \mathbf{0.51 \text{ mg dm}^{-3}}$$

$$\text{Mass of Pb in sample (25.00 cm}^3\text{)} = 0.51 \times 0.025 = \mathbf{0.0126 \text{ mg}}$$

(or 12.6 μg)

In order to analyse a sample for multiple metallic elements, the hollow cathode lamps must be exchanged to test for each element and separate calibration curves also need to be made for each.

### Inductively-coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

In ICP-AES, samples are atomised in an inductively-coupled plasma rather than in a flame. An inductively-coupled plasma torch is constructed and works in the following manner:

1. A quartz containment tube that is cooled by compressed air or water is surrounded by an induction coil, typically made of copper wire.
2. When activated, a high-power radio frequency signal flows in the coil generating an intense, rapidly-oscillating magnetic field within the containment tube.
3. Argon gas flows through the containment tube and a discharge arc from a Tesla coil is used to 'spark' the plasma by ionising argon atoms.
4. The argon ions and electrons interact with the oscillating magnetic field generating energy which leads, through a series of processes, to further ionisation of argon atoms via particle collisions. A stable plasma can be produced in the manner with a torch temperature of 6000-10000 K.

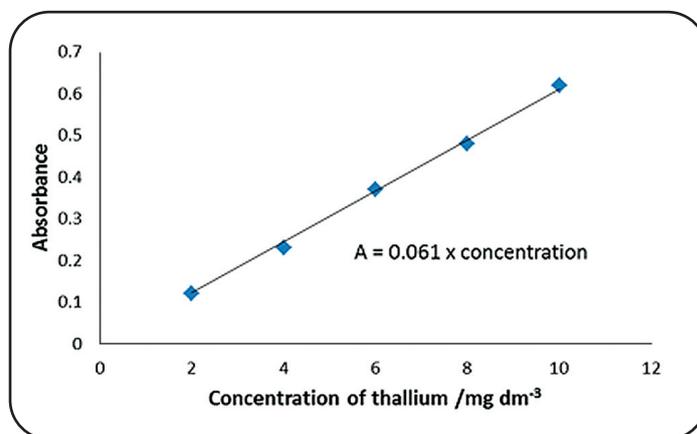
Once the ICP torch is lit, a carrier gas is used to bring a nebulised sample into the containment tube. In the plasma, the extremely high temperatures cause molecules to atomise and atoms to ionise into cations and electrons. These electrons undergo rapid recapture and ionisation with the ions/atoms in the plasma and, in doing, emit photons of light at frequencies specific to the element.

The emitted light contains all the frequencies capable of being emitted by the elements in the sample. A series of special detectors (called charge-coupled devices) are able to analyse all the frequencies simultaneously meaning that the elemental composition of an entire sample can be determined in one single, quick procedure (compare to AAS in which hollow cathode lamps need to be exchanged to detect different elements).

The intensity of the emitted light is related to the concentration of the atoms of that element present in the sample and the concentrations can be quantified by creating calibration curves using known reference samples (in the same manner described previously).

### Questions

1. Briefly describe the purpose of the hollow cathode lamp and monochromator in AAS.
2. Outline two differences between AAS and ICP-AES.
3. The following AAS calibration curve was created for thallium:



A 25.00 cm<sup>3</sup> sample of blood from a police enquiry was analysed via AAS for the presence of thallium. The blood sample was prepared by being made up to 250.00 cm<sup>3</sup> in volumetric flask using a buffer solution. A small quantity of the prepared sample was taken from the flask and its absorbance measured. The prepared sample had an absorbance of 0.41. Determine the concentration of thallium in the original blood sample in μg cm<sup>-3</sup>.

### Answers

1. Hollow cathode lamp – emits light comprising frequencies specific to the element being analysed.  
Monochromator – filters out frequencies of light unrelated to the element being analysed.
2. AAS involves absorption of specific frequencies of light; ICP-AES involves emission of specific frequencies of light.

AAS requires hollow cathode lamp to be changed in order to test for different elements; ICP-AES can detect all elements in a sample at the same time.

AAS uses a flame (burning fuel) to atomise samples; ICP-AES uses an inductively-coupled plasma to atomise samples.

3. Absorbance of 0.41 corresponds to a concentration of  $0.41/0.061 = 6.7 \text{ mg dm}^{-3}$

Analysed sample had been diluted by a factor of 10 so concentration in the original sample =  $67 \text{ mg dm}^{-3}$

Convert to μg cm<sup>-3</sup>: convert from mg to μg by multiplying by 1000; convert from dm<sup>-3</sup> to cm<sup>-3</sup> by dividing by 1000. Overall there is no change to the numerical value so concentration is **67 μg cm<sup>-3</sup>**