



## Introduction to Atomic Emission Spectrometry

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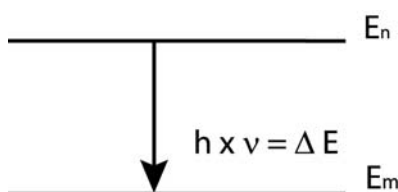
**Keywords:** atomic emission, sample preparation, analysis

### 1 Principle of atomic emission

#### 1.1 General information

A given atom has a large number of possible energy levels. An emission spectrum is produced by an electronic transition from a high energy level  $E_n$  to a lower energy level  $E_m$ . The acceptable transitions are given by the quantum mechanics selection rules. A quantity of energy  $Q$  is transferred to an atom by collision with another particle, resulting in excitation of the atom. An electron from an outer layer of the atom is excited to a higher energy level. Following this electron excitation, the electron returns, in one or several stages, to its original energy level.

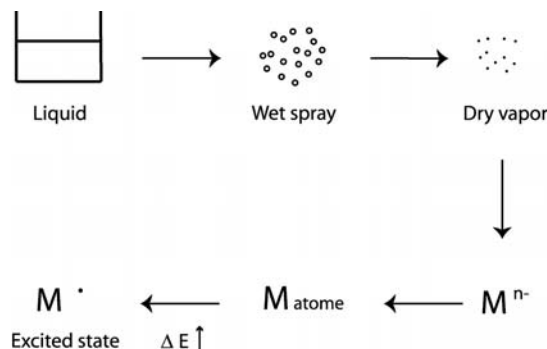
The atomic emission technique measures the energy lost by an atom passing from an excited state to a lower energy state. The energy is released in the form of light rays with a wavelength  $\lambda$ , or more specifically, in the form of a photon with a frequency  $\nu$  carrying energy  $h \times \nu$ .



**Figure 1: Energy transition**

The atomic emission spectrum is composed of discrete spectral lines. The number of photons emitted is proportional to the number of atoms of the element present. To be excited, the sample must be atomized, meaning dissociated into free ions or atoms.

For a liquid sample, the atomization process can be illustrated as follows.



**Figure 2: Transformation of sample**

Depending on the species excited, the lines have different types:

- \* emission from an atom: line I
- \* emission from an ion once ionized: line II
- \* emission from an ion twice ionized : line III

Lines I and II are frequently observed; lines III are rarely observed in the plasma and lines of a higher degree are not observed. This is due to the energies involved.

#### 1.2 Plasma

The emission phenomena takes place in a plasma. A plasma is an electrically neutral highly ionized gas. The gas used is typically argon.

##### 1.2.1 Plasma creation

An argon flow travels through a crystal tube inside a solenoid. The lines of force, generated by the magnetic fields, are directed along the axis of the solenoid inside the tube and take the form of an ellipse on the outside.



An electrical discharge is created to arc the plasma by partially ionising the gas in the torch.

The electrons produced are subjected to the magnetic field induced and circulate along the axis of the crystal tube describing annular circuits. Induced or eddy currents are thus produced. The electron path is stopped by collision, resulting in heating and ionisation of the other gas atoms. The plasma is self maintaining and continuous.

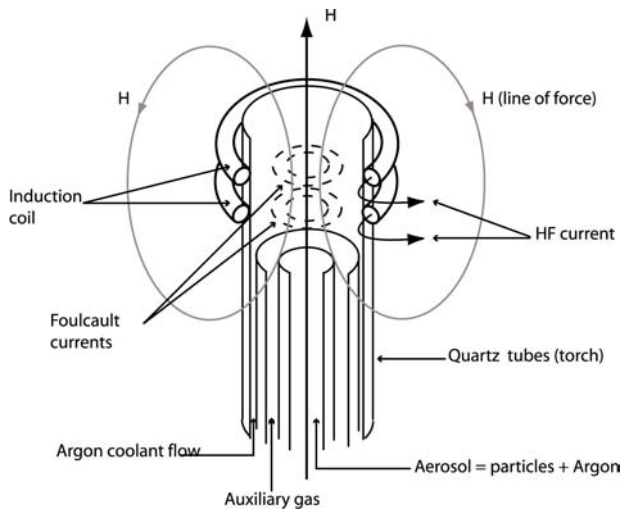


Figure 3 : Magnetic field

### 1.2.2 Plasma gas

The gas generally used is argon, which like all rare gases, is monatomic, chemically inert and has a high ionisation energy (15.6 eV). A certain number of advantages are provided by argon:

- Emission of a relatively simple spectrum producing little spectral interference in emission spectrometry,
- Capacity to atomise, ionise and excite most of the elements of the periodic table,
- Absence of formation of stable composites between argon and elements,
- Lower cost than that of other rare gases as it is the most widely available (1 % in air).

Its only limitation is its low thermal conductivity compared to that of molecular gases such as nitrogen or oxygen. During heating, the argon ions transfer energy to the atoms present in the sample solutions.

## 2 Analysis

### 2.1 Introduction

As discussed previously, an atom subjected to a plasma emits characteristic photons. This property makes it possible to perform a qualitative analysis. The number of photons emitted is proportional to the number of atoms of the considered element. This is the basis of the quantitative analysis.

### 2.2 Qualitative analysis

A qualitative analysis consists of searching for the elements in an unknown sample. The lines recorded reveal the presence of an element. An approximate quantification can also be performed. To select the lines, see the wavelength tables. Note that experience will play a major role in interpreting the spectra. This semi-quantitative analysis can be performed very rapidly using the JY Win-IMAGE option.

### 2.3 Quantitative analysis

The quantitative analysis links the energy emitted to the number of atoms contained in the sample. Atomic emission is not an absolute method. The relation existing between the intensity emitted by a line and the concentration of the associated element must be calculated: this is called the line calibration curve. The advantage of ICP-OES is that these calibration curves are, in most cases, linear to several orders of concentration. Great care must be taken in calculating these curves as they will determine the ultimate accuracy of the analysis.

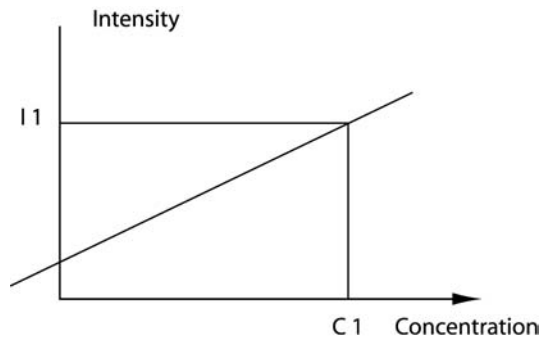


Figure 4: Calibration line

## 2.4 Analytical performance

An emission spectrometer provides a large number of analytical performance features: accuracy, repeatability, reproducibility, selectivity, robustness, sensitivity, detection limit, linearity, dynamic range ...

The main terms are defined below:

**Accuracy:** The accuracy of an instrument is its capacity to give results that are free of systematic error, meaning having a good degree of exactitude. The accuracy is evaluated by the difference between the measured mean value and the true value of element concentration.

**Blank:** Matrix without analytes

**Detection limit:** Smallest concentration which can be detected with certainty with respect to a blank

**Error:** Deviation between the mean value and the true value

**Fidelity:** Capacity of an instrument to give good repeatability.

**Long term stability:** Equivalent to repeatability over a long period of time (several hours).

**Precision:** Corresponds to repeatability and reproducibility.

**Quantification limit:** Concentration corresponding to a given repeatability (for example 5%).

**Repeatability:** Represents the fluctuations of the signal during a single reading under the same measurement conditions.

**Reproducibility:** Represents the fluctuations of the signal when one of the measurement parameters has varied.

**Robustness:** Capacity of plasma to accept different changes without significant variation in element concentration. These changes can come from the matrix, the analytical parameters or the environment.

**Sensitivity:** Slope of the calibration line; signal intensity versus concentration.

**Uncertainty:** Estimation within which the true value is located.

### 2.4.1 Repeatability, reproducibility and accuracy

These three terms are often understood to mean the same thing. Repeatability and reproducibility are expressed as a relative standard deviation. The only difference is the fact that for reproducibility, one of the parameters has varied. Accuracy is a principle that can be difficult to measure. It is evaluated using certified reference materials. It mainly depends on the calibration curve and the preparation of the samples.

The repeatability and accuracy concepts can be summarised using a target. The true value being the center of the target.

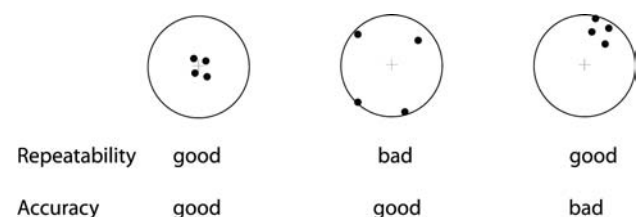
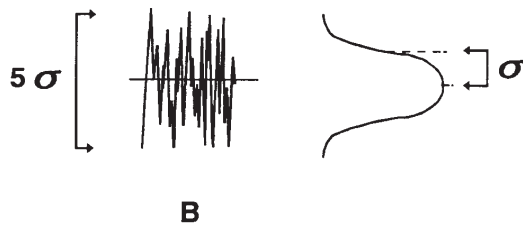


Figure 5: Repeatability and Accuracy

In figure 5 the second case is better than the third, even though the result seems bad (high relative standard deviation).

### 2.4.2 Detection limits (LOD), Quantification limit (LOQ)

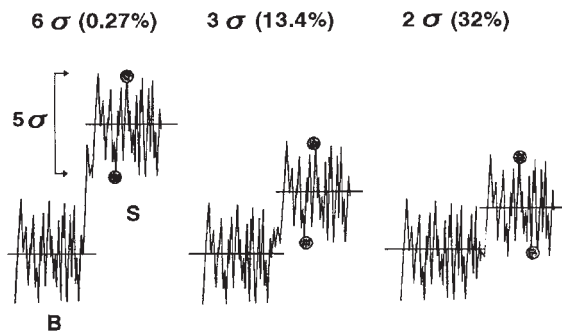
Here, we assume that the fluctuation of the spectral background follows a Gaussian distribution defined by its standard deviation.



**Figure 6: Gaussian distribution of spectral background distribution fluctuations**

The detection limit is derived from the signal that will be statistically possible to extract from the background. This comes down to stating the following question: does a measurement point belong to the background or to the signal?

$k$  corresponds to a safety coefficient. The higher the  $k$ , the easier it will be to differentiate a signal point from a background point.

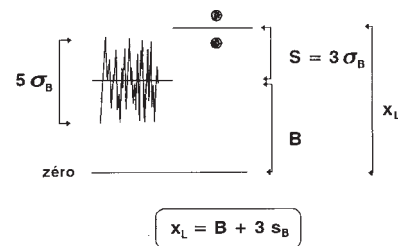


**Figure 7: Detection of a point among the background noise**

The Figure 7 represents the overlap of the fluctuations of background  $B$  and signal  $S$  as a function of the deviation between the two mean values,

expressed in multiples of standard deviation.

Figure 8 shows the influence of the coefficient  $k$  on the percentage of error.



**Figure 8: Smallest detectable signal  $X_L$**

IUPAC recommends applying  $k = 3$ . The percentage of error is then 13%.

Three equivalent formulas are used to express the detection limit:

( $C_L$ , concentration limit) :

- (1)  $C_L = 3 C S_B / S$
- (2)  $C_L = 3 C RSD_B / SBR$
- (3)  $C_L = 3 BEC RSD_B$

Where,

$S$  = net signal of solution

$C$  = concentration of solution measured.

$s_B$  = standard deviation of blank

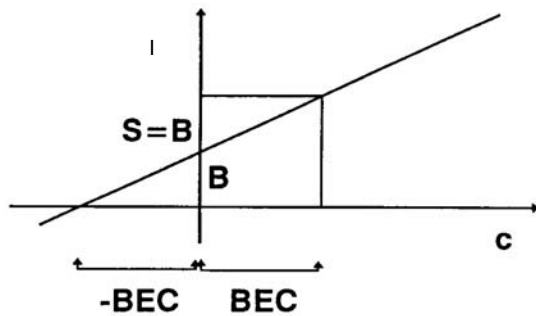
$RSD_B$  = standard deviation relative to blank

$SBR$  = signal to background ratio

$BEC$  = Background Equivalent Concentration

Formula (2) is mainly used for plasma optimisation. Formula (3) is used to calculate the detection limits for a given matrix following a calibration.

The Background Equivalent Concentration ( $BEC$ ) is represented on the figure 9. It corresponds to the concentration for which the signal is equal to the background ( $S = B$  or  $SBR = 1$ ).



**Figure 9 : Background Equivalent Concentration (BEC)**

BEC is the absolute value of the ordinate of the origin of the calibration curve when no background correction is applied. If a background correction is applied, use formula (2).

For the detection limit, RSD is expressed:

$$RSD = (1/k)\sqrt{2}$$

Therefore, for  $k = 3$ ,  $RSD = 47\%$ .

To define the quantification limit, you define the maximum desired RSD, for example 5 or 10%.

RSD = 10%, for LOQ = 4.5 LOD

RSD = 5%, for LOQ = 10 LOD

RSD = 2% for LOQ = 30 LOD

Generally, the minimum LOQ used = 3 LOD.

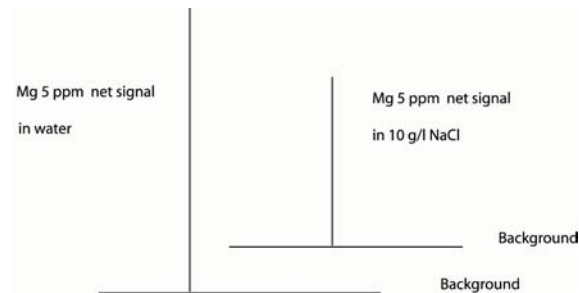
The detection limit is an estimation.

The quantification limit is a measurement.

The detection limit can be calculated in water or in a special matrix. It is very important to know the detection and quantification limits for each of the applications.

### 2.4.3 Robustness

Depending on the composition of the matrix, the same concentration of an element will not give the same signal. For example, 5 ppm of Mg in water or in NaCl 10 g/L does not give the same net intensity.



**Figure 10: Influence of matrix**

To minimize this difference, the most robust plasma possible must be used. The robustness can be evaluated by the ratio between two lines (an ionic line and an atomic line). For this purpose, we use the ratio provided by two Magnesium lines: Mg II 280 nm/ Mg I 285 nm.

The higher the ratio, the more robust is the plasma. A plasma is robust when the ratio of magnesium is greater than 6. In this case, the plasma is in thermodynamic equilibrium.

## 3 Sample Preparation

The samples are usually introduced into the plasma in solution form but solids, finely divided, can also be used. Care should be taken in obtaining a solution of a solid sample since there is a risk of loss of element, or contamination. The final solution obtained by the analyst depends on the nature of the sample and the concentration of elements to be determined.

Two main types of sample preparation are used for ICP analysis:

- Acid Digestion.
- Dry attack.



### 3.1 Acid Digestion

Acids, whether singly or in a mixture, use their oxidising or reducing properties. Care must be taken with respect to possible loss of volatile elements. For example, loss of As, Se, Sn in the form of chloride in the presence of HCl. Creation of precipitates of Ca, Ba, Pb also represents a possible error in the presence of H<sub>2</sub>SO<sub>4</sub>. Open and closed microwave systems are increasingly used in laboratories.

### 3.2 Dry attack

Alkaline fusion is often used, as well as high-temperature calcination (450 - 600 °C) with acid recovery of ashes. Care must be taken with respect to contaminants introduced by the reagents. Losses by volatilisation and insolubilisation can be more than negligible.

### 3.3 Remarks

- Whatever the type of solution, the quantity of acid or flux must be as low as possible to ensure minimum perturbation of the plasma. Certain acids are preferable to others as they perturb the plasma less.

Order of preference (from more favorable to least favourable): HNO<sub>3</sub>, HCl, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>.

- Caution, HF requires a specific sample introduction system.

- Na has a high depressive effect on sensitivity.

- The presence of hydrofluoric acid can result in the formation of Ca, Mg Mn... fluoride precipitates. This occurs frequently during mineralization of geological products, even after evaporation of the hydrofluoric acid. This can be avoided by adding a few drops of boric acid.



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