

# **CHAPTER 3**

## **Spectrometric methods**

### **3. Spectrometric methods**

When a solution containing a metallic salt (or any other compound) is drawn into a flame (for example, acetylene burning in air), a vapor containing atoms of the metal can form. Some of these gaseous metal atoms may be at a sufficiently high energy level to emit radiation characteristic of the element, for example, the yellow color imparted to a flame by compounds containing sodium atoms. This emission is the basis of flame emission spectroscopy, formerly known as flame photometry.

However, a much larger number of these metal atoms in the gaseous state generally remain in an unexcited state, that is, their ground state. They are capable of absorbing radiant energy corresponding to their own precise resonance wavelength, which is generally that of the radiation they would emit if they were excited from the ground state. Thus, when a flame containing the metal atoms is illuminated by monochromatic radiation of this wavelength, a portion of the photons are absorbed proportionally to the number of atoms present in the flame in their ground state. This is the fundamental principle of atomic absorption spectroscopy (AAS).

When a solution containing a suitable derivative of the metal under study is drawn into a flame, the process leading to metal atoms in the gaseous state can be described as a rapid succession of steps:

1. Evaporation of the solvent, leading to a solid residue.
2. Vaporization of the solid with dissociation into its constituent atoms, initially in the ground state.
3. Excitation of some of the atoms by the thermal energy of the flame raising them to higher energy levels, such that these atoms can emit radiant energy.

The resulting emission spectrum consists of a set of lines originating from excited atoms or ions. These processes are generally represented in the form of a diagram.

Given the energies involved (visible and near-UV light), electrical transitions only affect the outer energy levels of atoms. They correspond to the movement of an electron from an unfilled subshell to a higher-energy unoccupied subshell (absorption) or the return of an electron to the valence subshell (emission). The core energy levels are not involved at all.

#### **3.1. Atomic Absorption Spectrometry (AAS):**

##### **3.1.1. Definition :**

Atomic absorption spectrometry allows the quantification of approximately sixty chemical elements in trace amounts (a few mg/liter). The analysis is based on the absorption of photons by atoms in their ground state, and solutions are generally used for this purpose.

Preparation is therefore often necessary, for example, dissolving an alloy. The method is:

- Quantitative.
- Relative: therefore, a calibration curve must be created. This method has many advantages:
  - It is very selective; there is no spectral interference, or only when it is known.
  - The technique is simple if you know how to prepare the initial solutions.
  - It is very well documented: all the traps are known and listed in the manual supplied with the device.

However, several limitations can be noted:

- For technological reasons and not of principle, certain elements, such as rare gases, halogens... cannot be analyzed by spectrometry, their absorption energy not being between 180 and 1000 nm.
- Concentrations must be on the trace scale in order to remain within the linearity domain of Beer-Lambert's law, as its dynamics are limited.
- The existence of severe chemical interferences sometimes complicates things (example: calcium/phosphorus).
- The non-qualitative aspect of the technique necessitates knowledge of the elements to be dosed in order to choose the appropriate source.
- The preliminary settings are based on parameters that are not always independent.

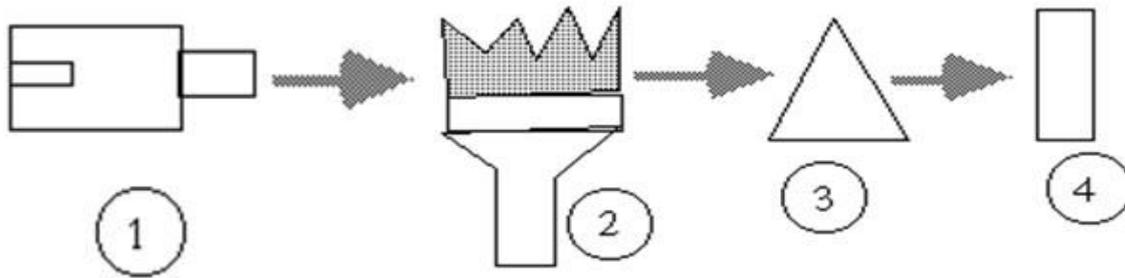
### **3.1.2. Apparatus and principle:**

#### **Equipment:**

The experimental setup used in SAA consists of:

1. A monochromatic source (the hollow cathode lamp).
2. A burner and a nebulizer.
3. A monochromator.
4. A detector.

Figure 11 represents an apparatus for atomic absorption spectrometry.

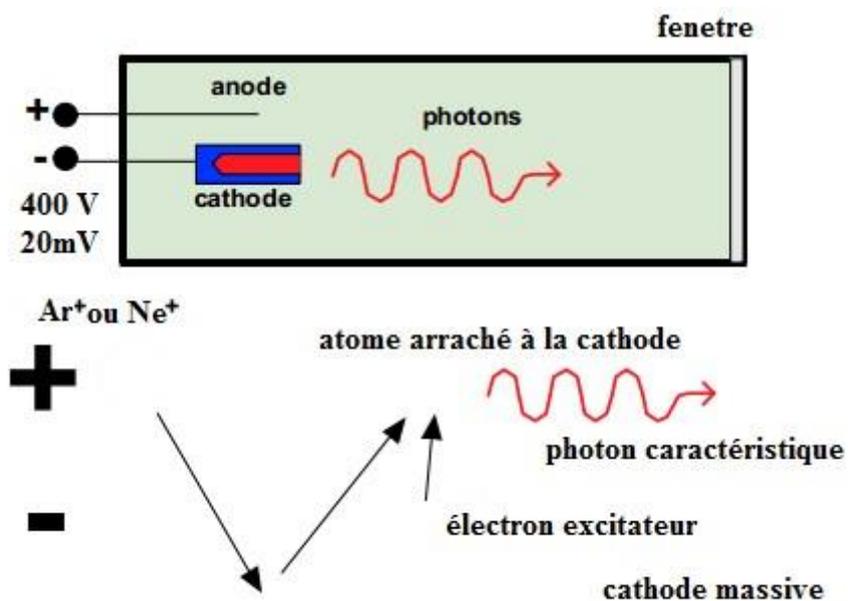


**Figure 11.** Apparatus for an atomic absorption spectrometry.

**A/ Hollow cathode lamp:**

It consists of a sealed glass envelope with a glass or quartz window containing a cylindrical hollow cathode and an anode. The cathode is made of the sample to be analyzed. A high vacuum is created inside the bulb, which is then filled with a noble gas (Ne or Ar) under a pressure of a few millimeters of Hg. When a potential difference is applied between the two electrodes, a discharge is established. The noble gas is then ionized, and these ions bombard the cathode, dislodging atoms from it. These atoms are thus free and are excited by collisions: this results in atomic emission of the element constituting the hollow cathode.

The distinctive feature of the emitted radiation is that it consists of very intense and very fine lines. Figure 12 shows hollow cathode lamps.



**Figure 12.** Diagram of a hollow cathode lamp.

## **B/ Nebulizer:**

When the sample to be analyzed is a solution, it is drawn through a capillary tube into a nebulizer. It is then atomized into an aerosol of fine droplets. This aerosol enters the nebulizer chamber to break up the droplets and remove larger ones. This homogeneous mist then enters the burner.

## **C/ The flame:**

The aerosol enters the burner and then the flame. After a certain distance at the flame's edge, the droplet's solvent is eliminated, leaving behind salts or solid products which are then melted, vaporized, and atomized.

The air-acetylene flame is the most common and allows for the titration of many elements. Its temperature is approximately 2500°C.

## **Principle:**

The absorption of electromagnetic radiation from the visible and UV regions of the spectrum by free atoms results from a change in their electronic structure. This is observed when the characteristic radiation (generally resonance radiation) of an element passes through a cloud of atomic vapor from the sample. The sample is vaporized by drawing the solution into a flame or by evaporation from an electrically heated surface.

### **3.1.3 Atomization:**

The goal is to obtain atoms in their ground state, relate the absorption caused by these atoms to their number, and then relate this number to their concentration in the solution being analyzed. To obtain free atoms, two methods are possible depending on the elements being analyzed.

If mercury or elements that can form hydrides need to be measured, these are easily released in atomic form. For other elements, atomization is necessary. To obtain free atoms from a sample, one technique involves heating the sample so that the thermal energy dissociates the particles (atoms, ions, or molecules). Other methods are also detailed in the implementation section. In many cases, vigorous heating and a high temperature will be required to obtain isolated atoms.

The atomic absorption method requires atoms to be in their ground state in order to observe the characteristic spectral lines of the element. However, one might think that atomization in a flame primarily provides atoms in excited states, since the flame temperature is usually in the range of 2000 to 3000 K.

### 3.1.4. The absorption law in SAA:

The absorption intensity depends directly on the number of light-absorbing particles according to Beer-Lambert's law, according to which absorbance is proportional to the specific absorption coefficient  $a$ , the optical path  $l$  (flame length), and the concentration  $c$ .  $A = al c$ . or  $A = \log I_0/I$ .

$I$ : Intensity after absorption by atoms.  $I_0$ : Initial intensity of the light source.

### 3.1.5. Sample separation method:

To access free atoms, several methods exist depending on the state of the product, but some of it will inevitably need to be destroyed. Furthermore, the number of states obtained must be representative of their proportion in the product to yield a quantitative result. Several methods exist for obtaining free atoms from a sample:

- Heat the sample in such a way that the thermal energy dissociates the particles (atoms, ions, or molecules). In many cases, vigorous heating and high temperatures will be required to obtain isolated atoms.
- Subjecting the sample to a bombardment of electrons or ions: electric arc or spark or cathodic sputtering (metals and alloys) in which the atoms will then be excited and ionized, which will lead rather to an emission spectrometry.
- Heat the sample in a very high temperature oven or introduce it into a flame or plasma capable of dissociating the particles.

### 3.1.6. Measuring cells:

The most commonly used absorption cells in spectrometry are the flame and the graphite furnace, which are capable of providing free atoms in sufficient proportion to use the absorption technique from elements present in solution.

#### 3.1.6.1 The flame:

When using a flame, the solution is nebulized by means of a capillary tube and a venturi which provides a fine aerosol of the solution (droplets of a few microns in diameter), carried into the flame by the gases which feed it.

It should be noted that only a few percent of the solution ends up in the flame after complex phenomena of more or less strong vaporization of free atoms capable of absorbing radiation.

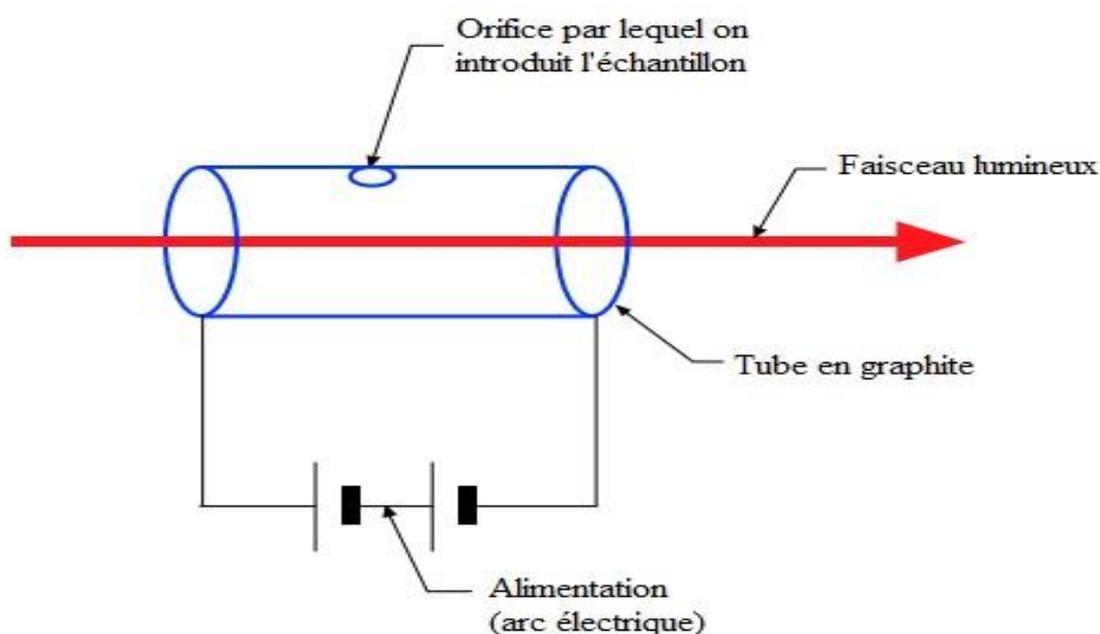
This is why we are obliged to prepare standards with a composition (a matrix) as close as possible to that of the samples in order to best control the physico-chemical phenomena (nebulization, vaporization, chemical reactions) which are involved in obtaining free atoms in the ground state.

### 3.6.1.2. The graphite furnace:

The tube temperature is programmed. The atomization process takes place in several stages:

- A drop of the sample is introduced into the tube.
- Heating up to 500-600°C allows mineralization (elimination of organic matter).
- Rapid heating up to 2000-3000 K: atomization is rapid (1 to 2 seconds) and the absorption signal is in the form of a peak that must be integrated.
- This method has a particular advantage: it uses very little solution. In fact, a single drop of sample may be sufficient for the titration.

Figure 13 shows a diagram of the graphite furnace.



**Figure 13.** Diagram of the graphite furnace.

### 3.1.7 Some applications:

Anaerobic digestion allows for the analysis of numerous inorganic materials (rocks and ores, metals, alloys, etc.). It is therefore very well suited to the study of archaeological material. Examples include:

- In metallurgy: the analysis of alterations in bronzes and the effects of silver cleaning products.
- Analysis of the major constituents of archaeological ceramics.
- Measuring Ca, Sr, Zn levels in bones.
- Analysis of trace elements for stone identification.
- The degradation of the lenses.

### **3.2. Atomic emission spectrometry:**

#### **3.2.1 Definition and advantages:**

Atomic emission spectrometry (AES) is a general method for quantifying elements based on the study of radiation emitted by atoms in an excited, usually ionized, state. Several processes are used to separate samples into their constituent elements, notably through the use of very high temperatures generated by plasmas. Since the spectra are much more complex than those obtained with flame emission spectroscopy, instruments with very high-quality optics are required to resolve line interference and matrix effects.

The analytical range of this highly sensitive technique covers a wide dynamic range. Used since its inception in metallurgical laboratories, it has become an indispensable tool in chemical analysis.

It has reached a point of automation where inexperienced staff can use it.

Spectrometers are capable of routinely analyzing several elements simultaneously or sequentially. Mass spectrometry coexists with atomic absorption, to which it is more complementary than competitive. Finally, it is less expensive than mass spectrometry applied to elements but is not suitable for analyzing light elements.

Atomic emission techniques offer two major advantages:

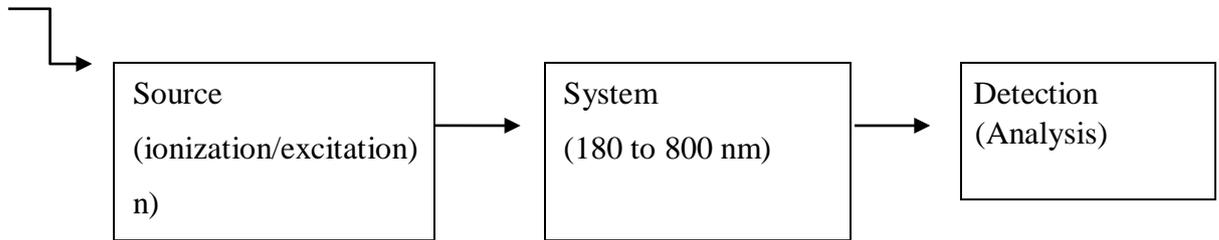
- Some elements can be analyzed with greater sensitivity and less interference.
- Atomic emission spectroscopy allows for qualitative analyses, unlike absorption spectroscopy. In emission spectroscopy, the sample itself is the light source. This means that several elements can be analyzed simultaneously, resulting in significant time savings and therefore cost savings, even though a multi-element emission spectrometer is considerably more expensive than an atomic absorption spectrometer.

#### **2.2 Principle of atomic emission analysis:**

An atomic emission spectrometer comprises (Figure 14):

- A device for introducing and dissociating the sample into the state of atoms or ions;
- An optical system to separate the different optical emissions;

- A system for detecting and analyzing emitted radiation;
- A computer system to provide the user interface.



**Figure 14.** Basic design of an atomic emission spectrometer.

As with flame emission spectroscopy, the light source of the spectrometer is the sample itself, with all its atoms excited simultaneously. Therefore, a compositional analysis, at least a qualitative one, can be performed even if the sample is initially unknown. This marks a significant difference from atomic absorption spectroscopy, which can only analyze the elements for which the instrument has been specifically designed (by choosing a hollow cathode lamp). With a single sample, a multi-elemental analysis can be obtained in just a few minutes, unlike with atomic absorption spectroscopy.

However, it is only possible to truly measure the levels of elements for which calibration has been carefully performed.

Each atom, after being brought to an excited state, can lose its excess energy by emitting one or more photons whose energies can take on distinct and characteristic values. The dispersive system thus produces a multitude of radiations with different wavelengths and intensities. Since the matrix (all the other elements present and the solution) of a sample is also emissive, the identification of an element, which may be present in ultratrace amounts, as well as its quantification, relies on measurements taken at several wavelengths (a kind of fingerprint).

### **3.2.3. Application of atomic emission spectrometry:**

The sheer number of elements that can be measured by atomic emission makes this analytical method indispensable. It allows for the quantification of pre-selected elements or the identification of elements present in any sample. Beyond analytical applications in industry in general—for example, the detection of wear metals found in used engine oils from automobiles or aircraft without disassembly—it is undoubtedly in the environmental field that it has become essential.

This can include analyses of plant or animal production (meat, milk), water, air (dust emitted by incinerators), or finally soils, for which certain elements are present in enormous concentration ratios (related to the spreading of industrial sludge on agricultural land).

This method has also found various applications in the fields of forensics and clinical medicine (analysis of tissues or biological fluids). One of its advantages is the linearity of the response over a very wide range of concentrations, which allows for the analysis of complex matrices with minimal preparation. Thus, with a single solution, it is possible to go from quantifying one concentrated element to another present in trace amounts.

### **3.2.4. Flame emission spectroscopy:**

Two main methods of flame emission spectroscopy are now used. The original method, known as **flame photometry**, is now mainly used for the analysis of alkali metals, particularly in tissues and fluids of biological origin.

The instrument used is simply a flame emission spectrometer; the flame serves as the radiation source, and the hollow cathode lamp and signal modulation device become unnecessary. Flame emission spectroscopy can prove more sensitive than flame absorption spectroscopy. This is particularly evident for elements whose resonance lines correspond to relatively low energies (generally wavelengths above 400 nm). Thus, for example, flame emission spectroscopy shows high sensitivity in the case of sodium (emission line at 689.0 nm) and lithium (at 670.8 nm).

### 3.2.4.1. Flame photometer:

Flames provide much weaker sources of excitation than electric currents. Consequently, a flame spectrum contains only a few emission lines. Furthermore, cold flames are generally used, for example, those produced by air-propane mixtures. In a flame photometer, the emitted radiation is separated by an optical filter (usually an interference filter), and the photodetector generates electrical signals. Figure 15 shows the schematic diagram of a single-beam flame photometer.

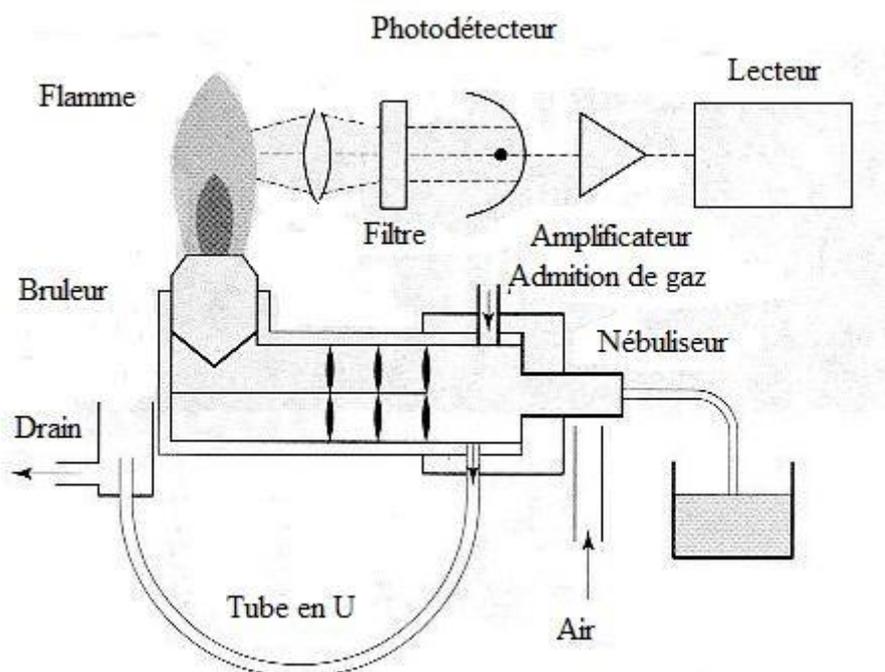
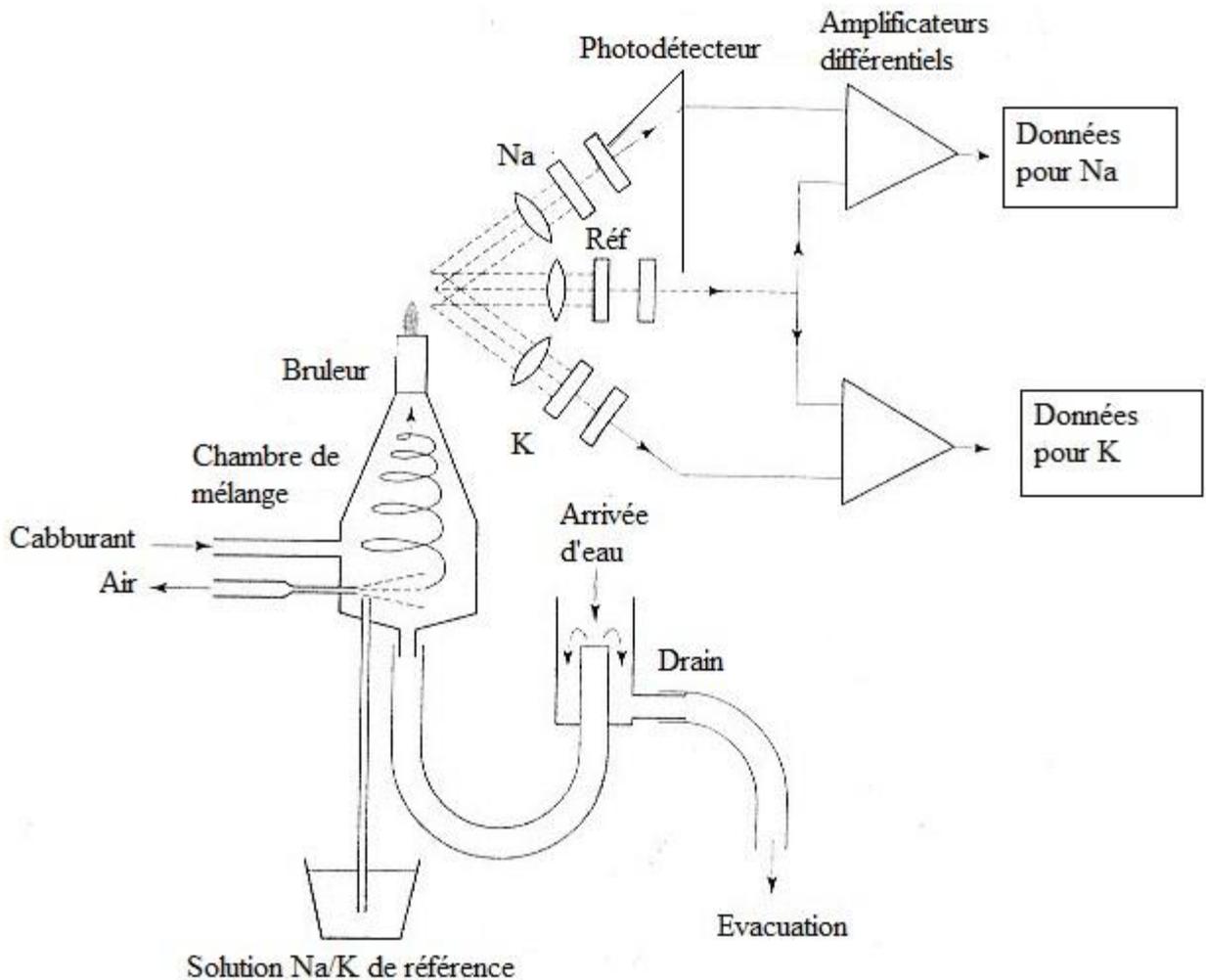


Figure 15. Simple flame photometry apparatus.

### 3.2.4.2. Essential elements of a flame photometer:

Air, at a given pressure, is introduced into an atomizer or, by the Venturi effect, draws in the sample solution, which mixes with the air as a fine mist. This mist then enters the burner or, at a small mixing chamber, joins the fuel (often propane), which is delivered to the burner at constant pressure, where combustion occurs. The radiation emitted by the flame passes through a lens, then an optical filter (usually an interference filter) which allows only the characteristic radiation of the element being studied to reach the photodetector (a photomultiplier tube). The output signal is recorded by a digital system.

Figure 16 shows the schematic diagram of a double-beam flame photometer. The signal corresponding to the internal lithium salt-based standard solution is continuously recorded to ensure high accuracy during a single measurement. The optical reference system uses an interference filter that transmits only the lithium line. The ratio of the Na<sup>+</sup> and Li<sup>+</sup> or K<sup>+</sup> and Li<sup>+</sup> line intensities can be obtained from appropriate photodetectors. The electronic circuit is designed to allow direct reading of sodium and potassium concentrations. In addition to these features, the instrument includes an integrated dilution device that automatically dilutes all types of samples (serum, blood plasma, and urine), thus eliminating the need for lengthy manual predilution procedures.



**Figure 16.** Double beam flame photometry apparatus.

To convert the results obtained in terms of emitted radiation intensities into analytical concentrations, one can follow one of the following methods:

- Calibration curve method.
- Method of known additions.
- Internal standard method.

### **3.2.5. Plasma source emission spectroscopy:**

The use of plasma as an atomizing agent in emission spectroscopy has seen significant development over the past 25 years, and the scope of this technique has been considerably broadened. A plasma can be defined as a cloud of ionized gas, composed of ions, electrons, and neutral particles; typically, more than 1% of the atoms are ionized.

In this method, the gas, often argon, is ionized under the influence of a strong electric field, either by direct current or radio frequency. Both types of discharge produce a plasma: direct current plasma (DCP) or inductively coupled plasma (ICP). Plasma sources allow the atomization conditions to be reproduced with a degree of precision far superior to that achievable with conventional arc or spark spectroscopy.