ATOMIC EMISSION SPECTROSCOPY

Atomic emission spectroscopy (**AES**) is a method of chemical analysis that uses the intensity of light emitted from a flame, plasma, arc, or spark at a particular wavelength to determine the quantity of an element in a sample. The wavelength of the atomic spectral line in the emission spectrum gives the identity of the element while the intensity of the emitted light is proportional to the number of atoms of the element.

Principle:

Atomic-emission spectroscopy (AES) **uses quantitative measurement of the optical emission from excited atoms to determine analyte concentration**. Analyte atoms in solution are aspirated into the excitation region where they are desolvated, vaporized and atomized by a flame, discharge, or plasma.

PROCEDURE:

Atomization and Excitation

Atomic emission requires a means for converting into a free gaseous atom an analyte that is present in a solid, liquid, or solution sample. The same source of thermal energy used for atomization usually serves as the excitation source. The most common methods are flames and plasmas, both of which are useful for liquid or solution samples. Solid samples are analyzed by dissolving in a solvent and using a flame or plasma atomizer.

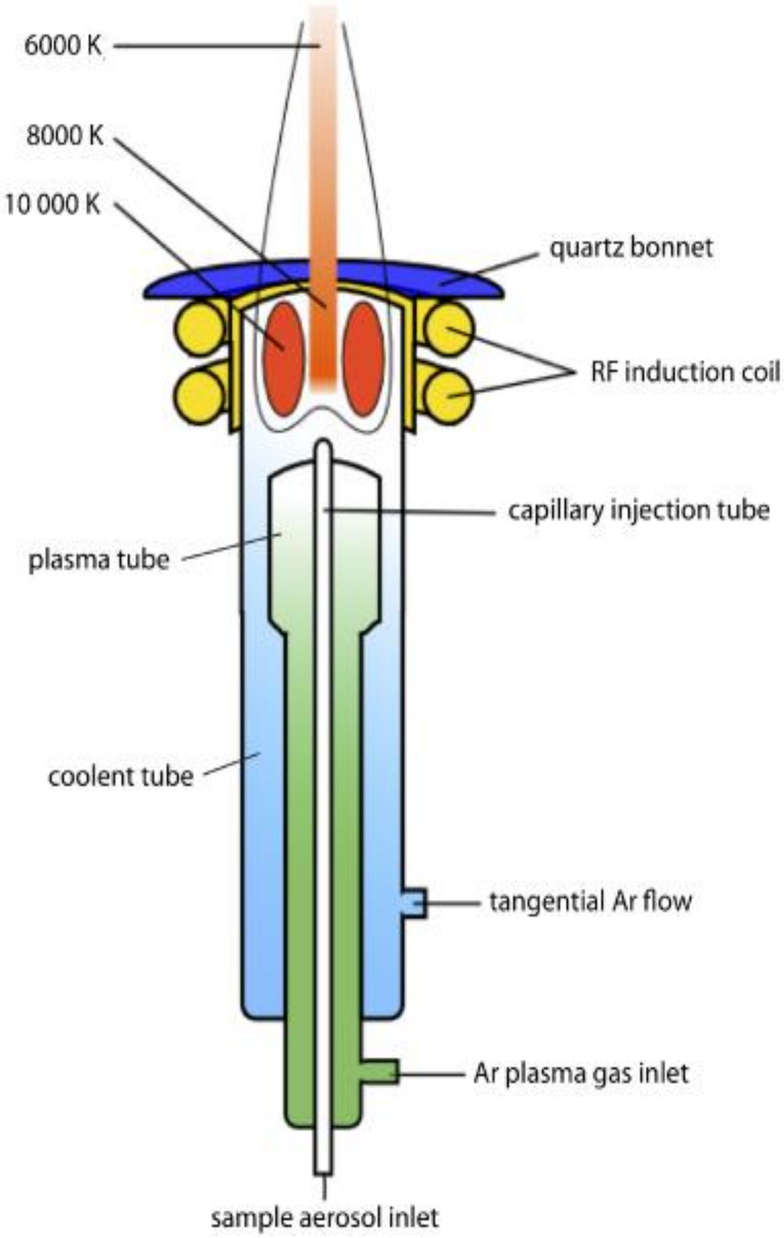
Flame Sources

Atomization and excitation in flame atomic emission is accomplished with the same nebulization and spray chamber assembly used in atomic absorption (Figure 10.4.1). The burner head consists of a single or multiple slots, or a Meker-style burner. Older atomic emission instruments often used a total consumption burner in which the sample is drawn through a capillary tube and injected directly into the flame.

Plasma Sources

A ***plasma*** is a hot, partially ionized gas that contains an abundant concentration of cations and electrons. The plasma used in atomic emission is formed by ionizing a flowing stream of argon gas, producing argon ions and electrons. A plasma's high temperature results from resistive heating as the electrons and argon ions move through the gas. Because a plasma operates at a much higher temperature than a flame, it provides for a better atomization efficiency and a higher population of excited states.

A schematic diagram of the inductively coupled plasma source (ICP) is shown in Figure 10.7.210.7.2. The ICP torch consists of three concentric quartz tubes, surrounded at the top by a radio-frequency induction coil. The sample is mixed with a stream of Ar using a nebulizer, and is carried to the plasma through the torch's central capillary tube. Plasma formation is initiated by a spark from a Tesla coil. An alternating radio-frequency current in the induction coil creates a fluctuating magnetic field that induces the argon ions and the electrons to move in a circular path. The resulting collisions with the abundant unionized gas give rise to resistive heating, providing temperatures as high as 10000 K at the base of the plasma, and between 6000 and 8000 K at a height of 15–20 mm above the coil, where emission usually is measured. At these high temperatures the outer quartz tube must be thermally isolated from the plasma. This is accomplished by the tangential flow of argon shown in the schematic diagram.


6000 K
8000 K
10 000 K
quartz bonnet
RF induction coil
capillary injection tube
plasma tube
coolent tube
tangential Ar flow
Ar plasma gas inlet
sample aerosol inlet

Selecting the Wavelength and Slit Width

The choice of wavelength is dictated by the need for sensitivity and the need to avoid interferences from the emission lines of other constituents in the sample. Because an analyte’s atomic emission spectrum has an abundance of emission lines—particularly when using a high temperature plasma source—it is inevitable that there will be some overlap between emission lines. For example, an analysis for Ni using the atomic emission line at 349.30 nm is complicated by the atomic emission line for Fe at 349.06 nm.

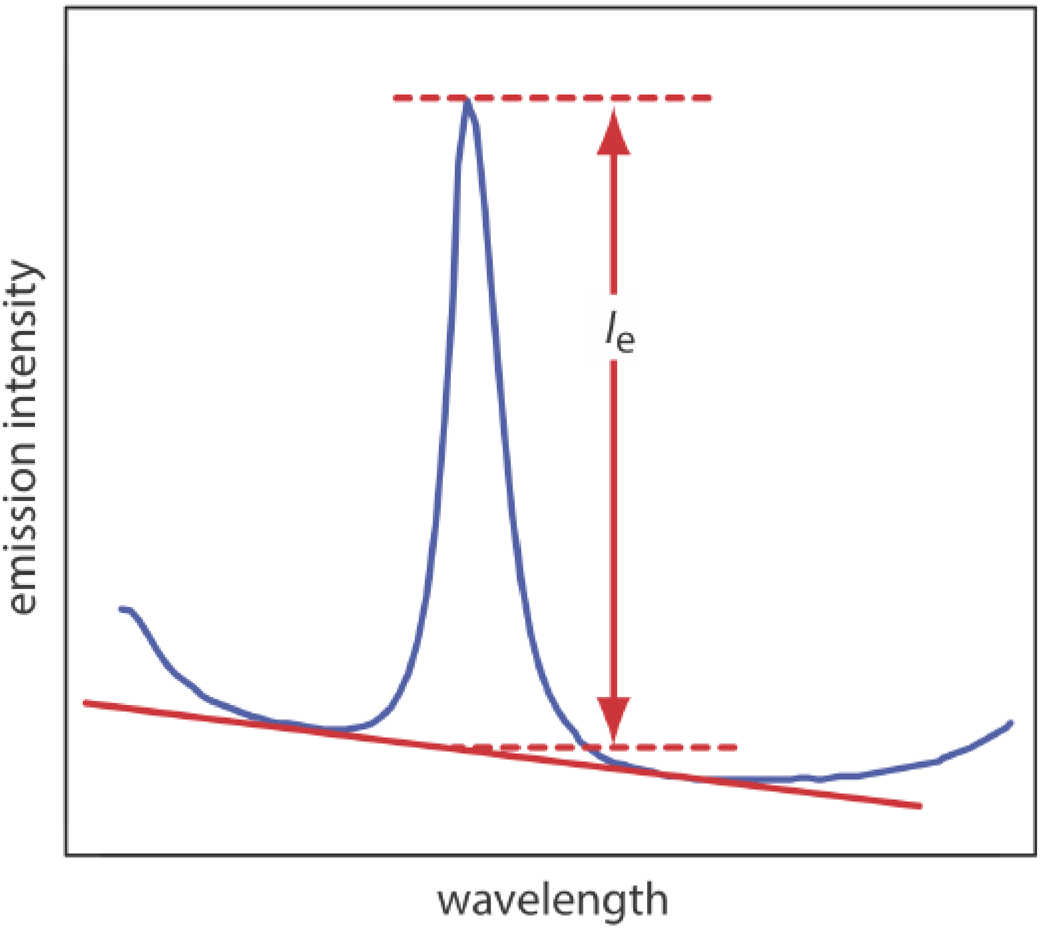
A narrower slit width provides better resolution, but at the cost of less radiation reaching the detector. The easiest approach to selecting a wavelength is to record the sample’s emission spectrum and look for an emission line that provides an intense signal and is resolved from other emission lines.

Preparing the Sample

Flame and plasma sources are best suited for samples in solution and in liquid form. Although a solid sample can be analyzed by directly inserting it into the flame or plasma, they usually are first brought into solution by digestion or extraction.

Minimizing Spectral Interferences

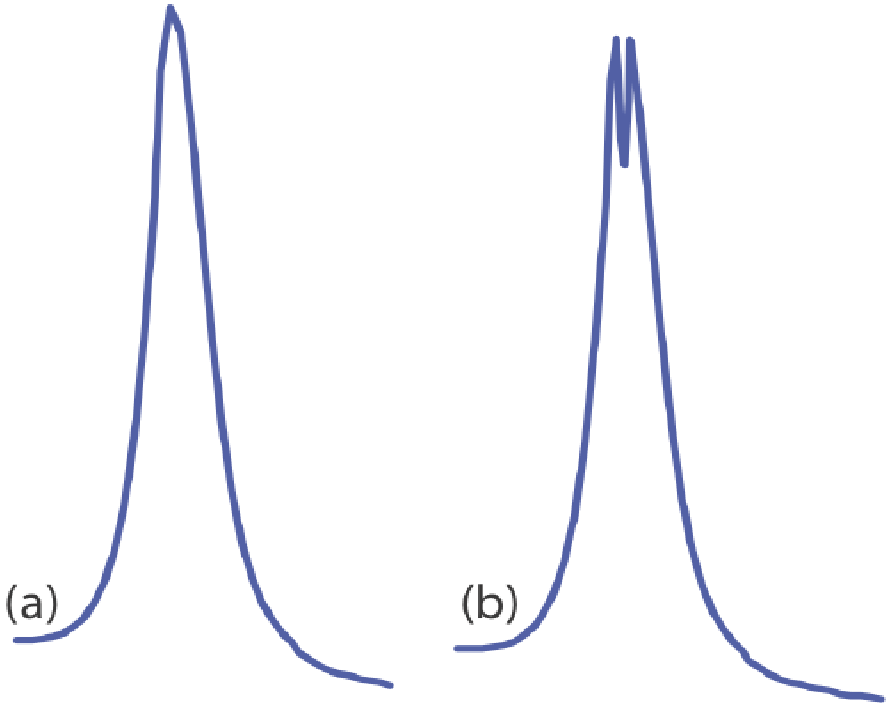
The most important spectral interference is broad, background emission from the flame or plasma and emission bands from molecular species. This background emission is particularly severe for flames because the temperature is insufficient to break down refractory compounds, such as oxides and hydroxides. Background corrections for flame emission are made by scanning over the emission line and drawing a baseline (Figure 10.7.410.7.4). Because a plasma’s temperature is much higher, a background interference due to molecular emission is less of a problem. Although emission from the plasma’s core is strong, it is insignificant at a height of 10–30 mm above the core where measurements normally are made.



Minimizing Chemical Interferences

Flame emission is subject to the same types of chemical interferences as atomic absorption; they are minimized using the same methods: by adjusting the flame's composition and by adding protecting agents, releasing agents, or ionization suppressors. An additional chemical interference results from ***self-absorption***. Because the flame's temperature is greatest at its center, the concentration of analyte atoms in an excited state is greater at the flame's center than at its outer edges.

If an excited state atom in the flame’s center emits a photon, then a ground state atom in the cooler, outer regions of the flame may absorb the photon, which decreases the emission intensity. For higher concentrations of analyte self-absorption may invert the center of the emission band (Figure 10.7.510.7.5).



Chemical interferences when using a plasma source generally are not significant because the plasma’s higher temperature limits the formation of nonvolatile species. For example, $\mathrm{PO}3-4$is a significant interferent when analyzing samples for Ca^{2+} by flame emission, but has a negligible effect when using a plasma source. In addition, the high concentration of electrons from the ionization of argon minimizes ionization interferences.

Standardizing the Method

The emission intensity is proportional to the population of the analyte’s excited state, N∗�∗. If the flame or plasma is in thermal equilibrium, then the excited state population is proportional to the analyte’s total population, *N*, through the Boltzmann distribution.

A calibration curve for flame emission usually is linear over two to three orders of magnitude, with ionization limiting linearity when the analyte's concentrations is small and self-absorption limiting linearity at higher concentrations of analyte. When using a plasma, which suffers from fewer chemical interferences, the calibration curve often is linear over four to five orders of magnitude and is not affected significantly by changes in the matrix of the standards.

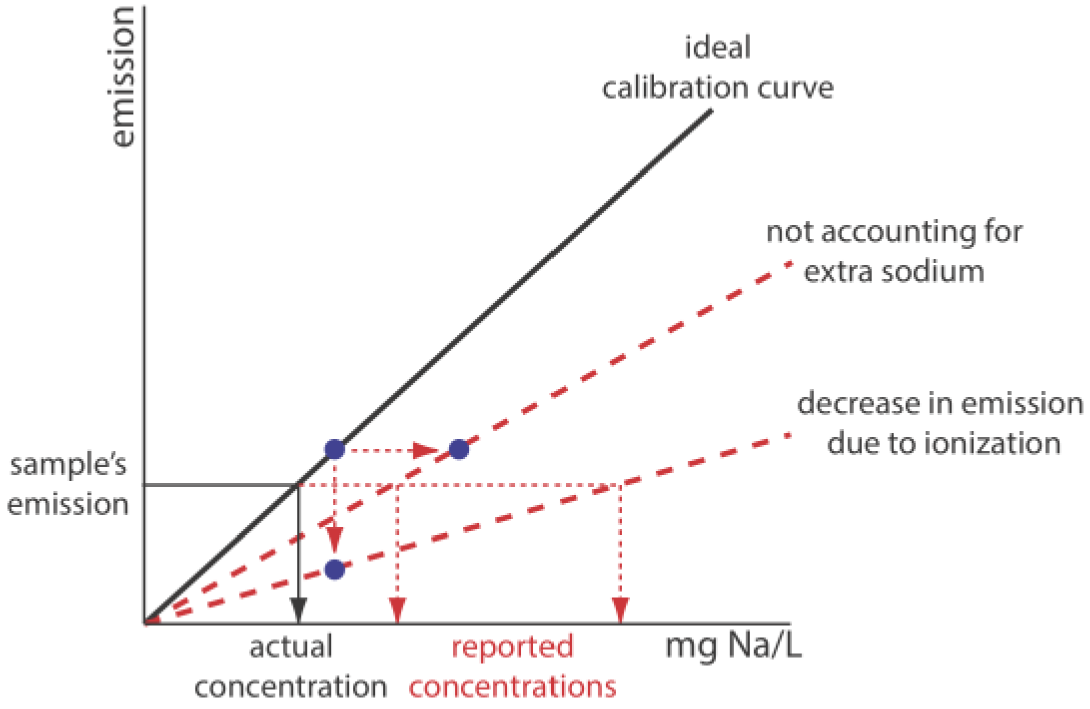
Emission intensity is affected significantly by many parameters, including the temperature of the excitation source and the efficiency of atomization. An increase in temperature of 10 K, for example, produces a 4% increase in the fraction of Na atoms in the 3*p* excited state, an uncertainty in the signal that may limit the use of external standards. The method of internal standards is used when the variations in source parameters are difficult to control. To compensate for changes in the temperature of the excitation source, the internal standard is selected so that its emission line is close to the analyte's emission line. In addition, the internal standard should be subject to the same chemical interferences to compensate for changes in atomization efficiency. To accurately correct for these errors the analyte and internal standard emission lines are monitored simultaneously.

Applications:

Determination of Sodium in a Salt Substitute

A sample is prepared by placing an approximately 10-g portion of the salt substitute in 10 mL of 3 M HCl and 100 mL of distilled water. After the sample has dissolved, it is transferred to a 250-mL volumetric flask and diluted to volume with distilled water. A series of standard additions is prepared by placing 25-mL portions of the diluted sample into separate 50-mL volumetric flasks, spiking each with a known amount of an approximately 10 mg/L standard solution of Na^+, and diluting to volume.

After zeroing the instrument with an appropriate blank, the instrument is optimized at a wavelength of 589.0 nm while aspirating a standard solution of Na^+. The emission intensity is measured for each of the standard addition samples and the concentration of sodium in the salt substitute is reported in µg/g.

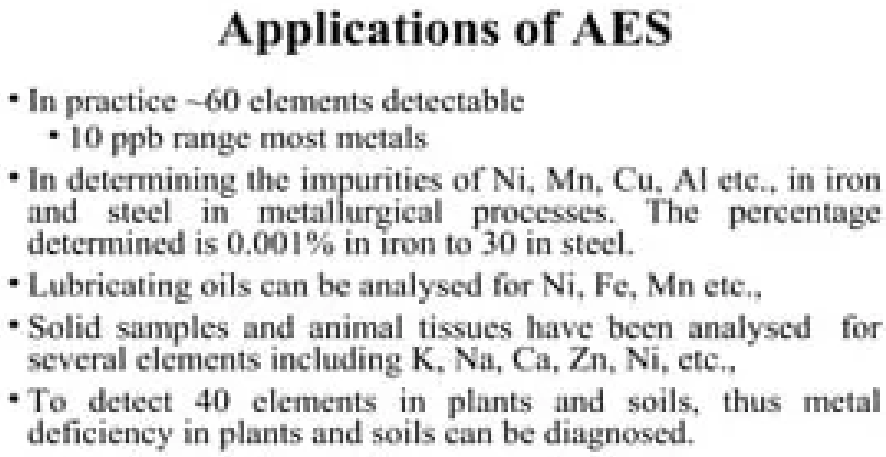


Chapter 10

ATOMIC EMISSION SPECTROMETRY

Advantages emission Spectrometer over absorption methods:

1. Lower interelement interference because of higher temperature.
2. Emission spectra are obtained under a single set of excitation conditions and several elements can be recorded simultaneously.
3. Multielement can be analyzed from very small sample.
4. Low concentration refractory compounds can be determined
5. Nonmetals can also be determined by plasma sources.
6. Very high concentration range (linear range) for plasma sources.



Applications of AES

- In practice ~60 elements detectable
  - 10 ppb range most metals
- In determining the impurities of Ni, Mn, Cu, Al etc., in iron and steel in metallurgical processes. The percentage determined is 0.001% in iron to 30 in steel.
- Lubricating oils can be analysed for Ni, Fe, Mn etc.,
- Solid samples and animal tissues have been analysed for several elements including K, Na, Ca, Zn, Ni, etc.,
- To detect 40 elements in plants and soils, thus metal deficiency in plants and soils can be diagnosed.

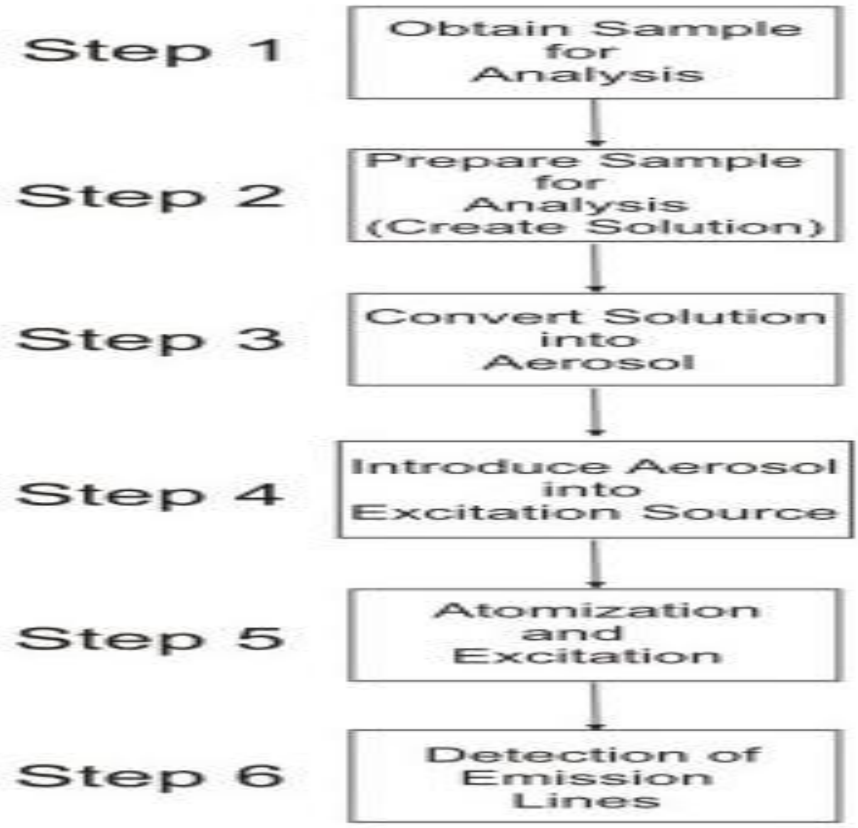

Step 1
Obtain Sample for Analysis
Step 2
Prepare Sample for Analysis (Create Solution)
Step 3
Convert Solution into Aerosol
Step 4
Introduce Aerosol into Excitation Source
Step 5
Atomization and Excitation
Step 6
Detection of Emission Lines

Diagram of ICP-AES