School of Chemistry and Biochemistry,
TIET, Patiala Applied Chemistry (UCB008)
Tutorial Sheet (Atomic Spectroscopy -Part-II)

SOLUTIONS

1. **Which analytical technique AAS or AES is more sensitive to change in temperature and Why?**

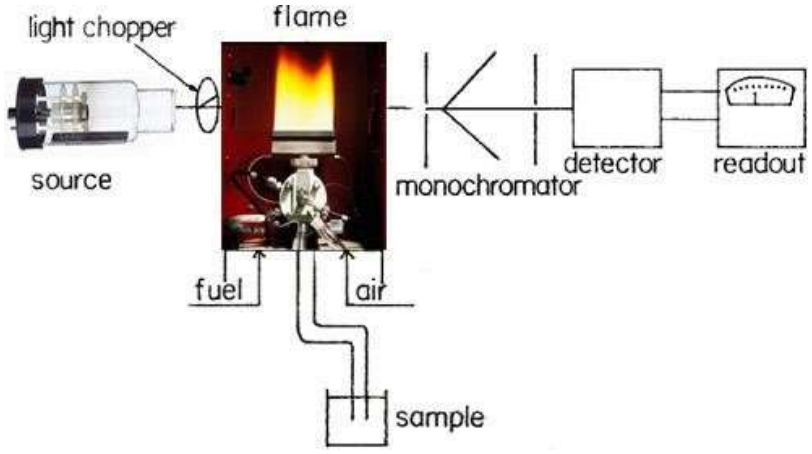
   The AES (Atomic Emission Spectroscopy) technique is more sensitive to changes in temperature than AAS (Atomic Absorption Spectroscopy) because higher temperature will result in the excitation of a large number of atoms to the higher energy electronic state. As the population of the excited atoms increases, the emission intensity will be higher.

2. **In AAS, sometime it is imperative to use O_2 or N_2O oxidant for the fuel-oxidant mixture. What is that condition when we need to use such strong oxidants?**

   The strong oxidants like O_2 or N_2O is used when the analyte/sample under investigation requires more energy for atomization.

3. **What is the principle of atomic absorption spectrometer?**

   The atomic absorption spectrometer works on the principle of absorption spectroscopy where the intensity of the transmitted light is measured. The AA spectrometer contains several components as given by the following diagram:



   Light source: Hollow cathode lamp produces very narrow emission lines at the exact wavelengths that are absorbed by the sample/analyte. The cathode is made up of metal (which is to be analyzed) whose spectrum is emitted by the lamp.

   Chopper: The continuous incident light, from the hollow cathode lamp, is "chopped" using a rotating half-mirror into a pulsating signal so that the detector sees intensities in an alternate manner. At one instance, the detector observes both the source light and the flame emission and the other instance, the detector

observes only the flame emission.

Atomizer: It consists of both nebulizer and a premix burner which carries out atomization of molecules followed by their excitation. The flame is formed by a mixture of fuel and oxidant that are chosen as per the sample/experimental requirement.

Monochromator: The monochromator consists of slits and grating (a dispersion device) that isolate the wavelength of interest and block any stray radiation entering into the detector.

Detector: It detects the light intensities from the source as well as from the flame emission. Typically, a photomultiplier tube (PMT) is used as a detector.

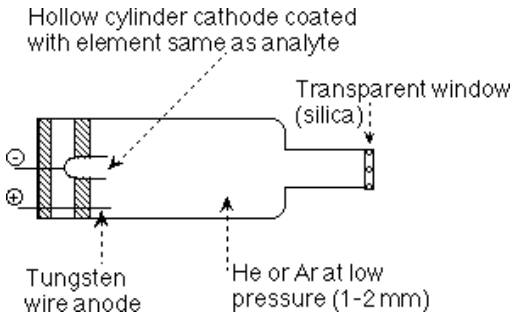
Read-out Components: It consists of data recorder and data analysis components.

4. What is the role of a monochromator in the atomic absorption spectrometer?

The monochromator consists of slits and grating that isolate the wavelength of interest i.e. isolates a single atomic resonance line from a spectrum of emission lines coming from the hollow cathode lamp and allows it to fall onto the detector. Additionally, it blocks any stray radiation entering into the detector.

5. Describe the process sputtering.

The hollow cathode lamp consists of a cathode and an anode in a sealed glass cylinder that is filled with Argon or Neon or Helium at low pressure (~1-2 mm). Applying a high voltage across the anode and the cathode results in intense, narrow emission lines. At the same time, the filler gas i.e. Argon or Neon or Helium gets ionized at the anode which accelerate towards the cathode. The fast-moving, positively-charged Ar^+ or Ne^+ or He^+ strike the surface of the cathode, physically dislodge some metal atoms from the cathode surface and form an atomic cloud. This process is known as sputtering.



6. What is the role of inert gas (He or Ne) in the Hollow Cathode?

Following are the roles of the filler inner gas in the hollow cathode:

(i) The inert gas is monoatomic so that it does not generate any molecular continuum spectra.

(ii) It causes sputtering i.e. dislodges metal atoms from the cathode surface.

(iii) It is the main source of current carrying capacity in the hollow cathode lamp.

7. For the same concentration of Nickel, the absorbance at 352.4 nm was found to be about 30% greater for a solution that contained 50% ethanol than for an aqueous solution in AA. Explain?

The surface tension of ethanol is lower than that of water so, it can form uniform and finer aerosols which increases the amount of sample that reaches the flame. Consequently, the absorbance of Nickel solution containing 50% ethanol is greater than its aqueous solution.

8. What type of metals can't be easily detected by AAS? Give two examples.

The metals which are prone to oxidation and form stable oxides in flame cannot be easily detected by AAS e.g. Aluminium (Al), Titanium (Ti), Molybdenum (Mo), Tungsten (W) etc.

9. Why does Beer's law apply in the case of AA, but not in the case of flame photometry?

Beer's law states that the absorbance of a sample is directly proportional to its concentration. In the case of Atomic Absorption (AA), the absorbance depends on the number of atoms in the ground state and the intensity of the transmitted radiation is measured. Higher the number, greater will be the sample absorbance. However, in flame photometry, the intensity of the emitted radiation is measured and hence, Beer's law is not applicable.

10. What are the essential differences between atomic absorption and flame photometry?

S. No.	Atomic Absorption Spectroscopy	Flame Photometry
1.	Intensity of transmitted light is measured	Intensity of emitted light is measured
2.	Intensity depends on the number of atoms in the ground state	Intensity depends on the number of atoms in the excited state
3.	Follows Beer's law	Does not follow Beer's law
4.	Transmission intensity is independent of the flame temperature	Emission intensity is dependent on the flame temperature

11. Sodium atom absorbs at 589 nm. Calculate the energy gap between the ground and excited state. At a temperature of 2000 K, what is the ratio of excited state to ground state population (N^*/N_o)? Given that A =2, k_B = 1.38 × 10^{-23} J K^{-1} mol^{-1}

Please solve it yourself to get answer = [$N^*/N_0 = 1.3 \times 10^{-5}$]
