

8.2. Resonance fluorescence is a type of fluorescence in which the emitted radiation has a wavelength that is identical to the wavelength of the radiation used to excite the fluorescence.

8.3. Fluorescence will occur at longer wavelength (the Stokes shift) than the excitation wavelength when relaxation takes place by combination of fluorescence and vibrational relaxation. This can occur under conditions of elevated temperature or pressure, depending on the system.

8.6. The energy necessary to promote a ground state s electron to the next p level is so high for Cs that only a fraction of Cs atoms are excited at the temperature of a natural gas flame. At the higher temperature of a hydrogen/oxygen flame a much larger fraction of the atoms are excited and thus the Cs line emission is more intense.

8.9. The energies of the 3p states can be obtained from the emission wavelengths shown in Fig.

8.1. For Na we will use an average wavelength of 589.3 nm and for Mg, 280.0 nm.

$$\text{Na: } E_{y1} = \frac{hc}{\lambda} = \frac{6.6262 \times 10^{-34} \text{ Js} * 2.998 \times 10^8 \text{ m/s}}{589.3 \times 10^{-9} \text{ m}} = 3.37 \times 10^{-19} \text{ J}$$

$$\text{Mg: } E_{y2} = \frac{hc}{\lambda} = \frac{6.6262 \times 10^{-34} \text{ Js} * 2.998 \times 10^8 \text{ m/s}}{280.0 \times 10^{-9} \text{ m}} = 7.09 \times 10^{-19} \text{ J}$$

Substituting into Eq. 8.1, for T = 2100 K

$$\frac{N_{j1}}{N_0} = 3 \exp\left(-\frac{3.37 \times 10^{-19} \text{ J}}{1.38 \times 10^{-23} \text{ J/K} * 1800 \text{ K}}\right) = 3.8 \times 10^{-6}$$

(a)

$$\frac{N_{j2}}{N_0} = 3 \exp\left(-\frac{7.09 \times 10^{-19} \text{ J}}{1.38 \times 10^{-23} \text{ J/K} * 1800 \text{ K}}\right) = 1.2 \times 10^{-12}$$

$$\text{(b) } \frac{N_j}{N_0} = 7.6 \times 10^{-4} \text{ (Na), } 8.2 \times 10^{-8} \text{ (Mg) (2950 K)}$$

$$\text{(c) } \frac{N_j}{N_0} = 0.1 \text{ (Na), } 2.5 \times 10^{-3} \text{ (Mg) (7250 K)}$$

9.2. The absorbance of Cr decreases with increasing flame height because chromium oxides are formed to a greater extent as the Cr rises through the flame. The Ag absorbance increases because the Ag becomes more atomized as it rises through the flame. Silver oxides are not formed as readily as chromium oxides. Mg exhibits a maximum as a result of both effects acting in opposition to one another.

9.3. The electrothermal atomizer requires less sample and keeps the sample in the optical beam path for a longer time than does the flame.

9.5. Source modulation is employed to distinguish between the component of light arising from the source and the component of the light arising from the flame background.

9.6. The alcohol reduces the surface tension of the solution, thereby leading to smaller droplets, a greater number of which then reach the flame in a given time interval. Thus a greater number of Ni atoms are present at any instant.

9.8. (1) Use a higher temperature flame (*e.g.* O₂/acetylene). (2) Use a solvent that contains ethanol or other organic substances. (3) Add a releasing agent or a protective agent.

10.2. Flame atomic absorption requires a separate lamp for each element, which is not convenient when several elements need to be determined in a single sample.

10.5. In the presence of air and with graphite electrodes, strong cyanogens (CN) bands render the wavelength region from 350 nm to 420 nm essentially useless. By excluding N₂ from the system with an inert gas, the intensities of these bands are reduced substantially, making possible the detection of several elements with lines in this region.

10.6. By nebulization, by electrothermal vaporization and by a high voltage electric spark.