

Emission Spectroscopy

BACKGROUND: Spectroscopy is the study of the manner in which light (electromagnetic radiation) interacts with materials. As a scientific discipline, spectroscopy occupies that fertile ground between chemistry and physics. Fundamental investigations in spectroscopy have led to our understandings of the electronic structures of atoms and the geometry and bonding of molecules. Spectroscopy research today focuses on the fundamental aspects of the energetics and mechanisms of chemical reactivity. Applied spectroscopy exploits the fact that the wavelengths (energies) of light that is absorbed or emitted by a material are unique to that material. In various modifications, this principle can allow either qualitative identification of the components in a sample or quantitative determination of the amounts of an element or compound in a sample. In this exercise we will use concepts from both fundamental and applied spectroscopy.

Convenient for the purposes of this experiment, the electronic spectra of the elements fall largely within the range of energies (wavelengths) that are detected by the human eye. In Part A, we will work with five Group I & II elements and use subjective visual sense to determine the colors emitted by these elements, and also use the student spectroscope to determine the specific wavelengths of the spectral lines emitted by these elements. From this information we can determine the identity of the cation in a solution containing a single metal halide.

One of the curious observations of the mid-nineteenth century that defied explanation for nearly fifty years was the fact that unlike the continuous "rainbow" spectra emitted by the sun or a white light, the spectra emitted by a single element consisted of a small number of discrete lines. Finally in 1914, Niels Bohr provided an explanation for this phenomenon. Bohr's quantum mechanical theory suggested that atoms of an element emit radiation when they undergo transitions between two energy states. And further, the two energy states of the atom differ with respect to the orbital radius of the electrons. The theory provides a method to calculate the energy of these states

$$E_n = (-2.18 \times 10^{-18} \text{ J}) (Z^2 / n^2),$$

where Z is the number of protons in the nucleus of atoms of that element, and n is a positive integer identifying the energy state of the atom.

Using the Planck relationship ($\Delta E = hc / \lambda$) and an expression for change in energy ($\Delta E = E_{\text{final}} - E_{\text{initial}}$) scientists were able to confirm the essential validity of the Bohr quantum mechanical model.

In Part B, we will calibrate the wavelength scale of the student spectrometer using the known wavelengths of the helium emission lines. Then using that calibration, students will determine the wavelength of the most prominent lines of hydrogen and calculate the atomic state transition responsible for those hydrogen lines.

Planck's constant, $h = 6.63 \times 10^{-34}$ J-s

Speed of light, $c = 3.00 \times 10^8$ m/s

PART A—QUALITATIVE ANALYSIS OF A METAL:

1. Obtain a clean wooden splint or q-tip and dip it into the KCl solution.
2. Hold the splint in the flame of the Bunsen burner and record the color you see.
3. Repeat the procedure. This time, observe the flame through the student spectroscope and determine the wavelengths of the lines you observe. It may be necessary to dip the stick in the solution several times in order to observe all of the spectral lines. Record the wavelengths emitted by KCl.
4. Obtain a new stick and repeat the procedure with the remaining salt solutions and your unknown.

Note: The unknown samples used in this course contain only a single metal cation. Qualitative analysis of more complex samples containing two, three or even many elements can be accomplished by similar, though more complicated, instrumental techniques. Those techniques are studied and used in later courses.

PART B—SPECTROSCOPIC TRANSITIONS:

1. Place a helium discharge tube into the high voltage supply, turn on the power and observe the emitted light through the student spectroscope.
2. From the measured positions of the helium lines and the table of known wavelengths of those lines, draw a graph of known wavelength (on Y-axis) vs spectrometer scale reading (on X-axis).

Color of helium emission line Accepted Wavelength

red	668 nm
yellow	588 nm
green	502 nm
green	492 nm
blue-green	471 nm
blue-violet	447 nm
violet	403 nm

3. Ask the student assistant to replace the helium discharge tube with a hydrogen discharge tube in the high voltage supply. (Careful, these things can get a little hot.) Observe the lines produced by the hydrogen discharge tube and record the scale reading for each line you see.
4. Using the calibration curve produced in step 2, determine the experimental wavelength of the prominent lines in the hydrogen emission spectra. Remember to record your data to the correct number of significant figures allowed by the scale in your spectroscope.
5. From the experimental wavelength of the red and blue hydrogen emission lines and the Bohr quantum mechanical model, determine the quantum numbers of the initial and final quantum states that correspond to that transition.

Note: The department has two models of student spectroscopes. One has an included wavelength scale and the other has an unmarked linear scale. Since we will be making our own calibration, either model can be used equally well.

ADVANCED QUESTIONS:

1. In Part A above you used the chloride salts of five different Group I & II metals. One might ask if the spectral lines observed are due to emission from the cations (K, Na, Ba, Sr, Ca) or due to the anion. Develop and perform a procedure to establish conclusively that the spectral lines are arising from the emission of the cation and not the anion.
2. The hydrogen emission spectrum also includes additional weak lines in the visible region. Using your spectroscope in a darkened room you may be able to identify one or more of these weak lines. Then determine the spectroscopic transitions that are responsible for these lines.

REPORT: This week, write a detailed introduction including the theory of emission spectroscopy. Be sure to reference your sources. In the data section of your report, include your observations from Part A and your calibration plot and data from part B. Also answer the questions above.

REFERENCES:

1. From your textbook review sections 7.1 - 7.5, pages 292-306. Chemistry, 5th Ed., Zumdahl, Houghton-Mifflin, 2000
2. <http://www.colorado.edu/physics/2000/quantumzone/index.html>
3. Meloan, C.E., James, R.E., Saferstein, R. *Criminalistics: An Introduction to Forensic Science, Lab Manual*, 6th Ed., Prentice Hall, 1990
4. Tyner, K.L., *Exploring Chemistry in Today's World*, Wm. C. Brown, 1993