

Experiment 17

Emission and Absorption Spectroscopy

Pre-Lab Assignment

Before coming to lab:

- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise.

Purpose

A handmade spectroscope will be calibrated by measuring the emission spectrum of mercury gas then used to measure the emission spectra of a variety of cations through a flame test and hydrogen and helium gas. Rydberg's constant will be experimentally determined. The absorption spectra of CuSO_4 , CoCl_2 , and KMnO_4 will be measured.

Background

Light (electromagnetic radiation) is transmitted through space as two perpendicular waves, where one direction is electricity and the other is magnetism. In a vacuum, all light travels at the same speed ($c = 3.00 \times 10^8 \text{ m/s}$) but varies in wavelength (λ , meters), the distance between two wave crests, and frequency (ν , 1/s or Hertz), the number of waves that pass through a stationary point in one second. For any given type of light, the product of its wavelength in meters times its frequency in Hz (or 1/s) will equal its speed in m/s, as in Eqn. 1

$$c = \lambda \nu \quad \text{Eqn. 1}$$

Light can be classified into different categories based on its wavelength/frequency. This is called the electromagnetic spectrum (Fig. 1). The visible light spectrum, or the range of wavelengths that the human eye can see, averages between 400-700 nm. Each different color distinguished by the human eye is due to a difference in wavelength.

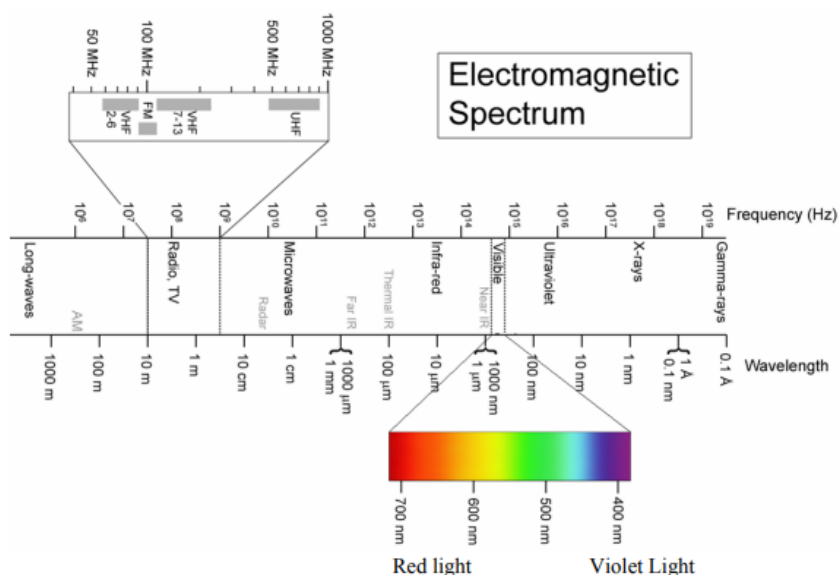


Figure 1: Electromagnetic spectrum

At the turn to the twentieth century, a number of scientists including Albert Einstein, J.J. Thompson, Max Planck, and Niels Bohr postulated that light was actually both a wave (transfer of energy) and a particle (has matter), called wave-particle duality. Light traveled as a wave of tiny, quantized packets called photons. The energy in Joules of a single photon is directly proportional to its frequency in Hz (or 1/s) by Planck's constant (h , 6.626×10^{-34} J·s) as seen in Eqn. 2.

$$E = h \nu \quad \text{Eqn. 2}$$

When combined, Eqn. 1 and 2 become Eqn. 3.

$$E = \frac{hc}{\lambda} \quad \text{Eqn. 3}$$

Niels Bohr postulated that electrons also exhibited wave-particle duality similar to light. As such, electrons in atoms were also confined to quantized shells that ring the nucleus, defined by the principle quantum number, n in what is called the Bohr Model of the atom. (Fig. 2). Electrons could exist on, but not between, the shells. The closer the shell is to the nucleus, the lower in energy.

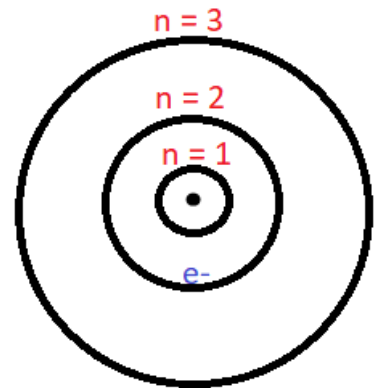


Figure 2: The Bohr Model of the atom

Electrons that absorb energy can “jump” from lower to higher shells. This process is called **excitation** and is the cause of an atom's **absorption spectrum**, or a set of wavelengths that appear as dark lines or bands. An object's visible color is the *complement* of the wavelengths absorbed; for example, an object that absorbs orange wavelengths appears visibly blue as blue and orange are complements. Similarly, electrons that release energy can jump from higher to lower shells in a process called **relaxation** that causes an **emission spectrum**, where a specific set of lines are visible. The wavelengths either absorbed or emitted are proportional to the energy absorbed or released, respectively (Fig. 3). Since the energy shells are unique to a substance, so is its absorption and emission spectra. These can be seen either by heating gaseous elements with electricity or by using metal ions as salts in flame.

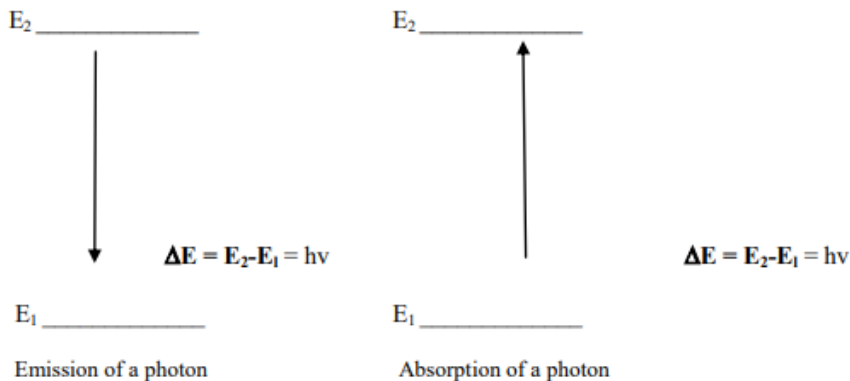


Figure 3: Relaxation of an electron by emission of a photon; excitation of an electron by absorption of a photon

Before the phenomenon of an atom's emission spectrum was properly explained, Johannes Rydberg developed a purely empirical (from experimental data, not theory) equation to calculate the lines seen for the hydrogen atom, seen in Eqn. 4.

$$\frac{1}{\lambda} = -R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{Eqn. 4}$$

Here, R_H is Rydberg's constant ($1.097 \times 10^7 \text{ m}^{-1}$), n_1 is the final shell the electron moves to and n_2 is the initial shell from which the electron moved, both whole number integers ≥ 1 . If the wavelength value is negative, then it and its corresponding energy is being absorbed. If the wavelength is positive, then it and its corresponding energy is being emitted. For hydrogen, the series of emissions that fall within the visible light spectrum are called the Balmer series, where $n_1 = 2$ and $n_2 = 3, 4, 5,$ and 6 . Rydberg's constant can be determined graphically by rearranging Eqn. 4 into a linear form ($y = mx + b$) and plotting $1/n_2^2$ versus $1/\lambda$, as seen in Eqn. 5. The slope of the line will be equal to R_H and the intercept to R_H/n_1^2 when $n_1 = 2$.

$$\frac{1}{\lambda} = R_H \frac{1}{n_2^2} - \frac{R_H}{n_1^2} \quad \text{Eqn. 5}$$

$$y = m \quad x \quad + \quad b$$

Example Problem: Using Rydberg's Equation

An electron moves from the $n = 5$ to the $n = 1$ shells. Calculate the wavelength emitted, in nm. Is this transition visible to the human eye?

Step 1: Use Eqn. 5 to solve for $1/\lambda$.

$$\frac{1}{\lambda} = (1.097 \times 10^7 \text{ m}^{-1}) \left(\frac{1}{1^2} - \frac{1}{5^2} \right)$$

$$\frac{1}{\lambda} = (1.097 \times 10^7 \text{ m}^{-1}) \left(1 - \frac{1}{25} \right)$$

$$\frac{1}{\lambda} = (1.097 \times 10^7 \text{ m}^{-1})(0.96)$$

$$\frac{1}{\lambda} = 10531200 \text{ m}^{-1}$$

Step 2: Take the inverse of both sides to find λ .

$$\lambda = 9.50 \times 10^{-8} \text{ m}$$

Step 3: Convert to nm.

$$9.50 \times 10^{-8} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 95.0 \text{ nm} < 400 \text{ nm}, \text{ so not visible}$$

Procedure

Part I: Spectroscope Instructions

In this experiment you will use a spectroscope, a device to observe spectra, to measure and record both absorption and emission data. A diagram of the scope is shown below (Fig. 4).

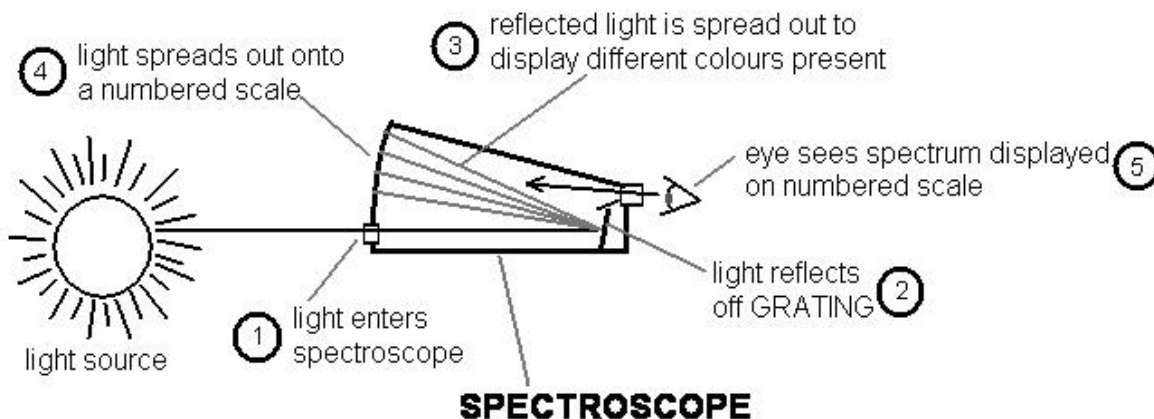


Fig. 4: Diagram of a spectroscope

(<http://wikieducator.org/images/f/f4/Chemistry - Observing Light Spectrum 3.JPG>)

To use the scope, look into the viewing hole on the smaller end and align the slit on the opposite end with a light source. Light enters the slit and strikes the grating, a piece of plastic that works like a prism. Most of the light passes through the grating to your eye, but part of it undergoes diffraction: it is broken up into its component wavelengths and projected back onto the scale. Through the grating you will see spectral lines superimposed on the scale from which you can read their approximate wavelengths.

Part II: Spectroscope Calibration

1. Using your spectroscope, look through the slit while pointing the grating at the mercury vapor lamp. You should see three bright lines on your scale: yellow, bright green, and blue. Record the scale positions on your data sheet as accurately as possible. More faint lines may be visible; do not record these. Since moving the box will shift the lines, try to be as consistent and still as possible.
2. Plot a calibration graph of the known wavelengths (x-axis) versus the scale readings (y-axis). Add a trendline and record the equation to use in Part III.

Part III: Spectral Analysis of Gas Lamps

1. Using your spectroscope, read and record the scale positions and colors of the emission lines from the helium lamp. Helium will have many lines. Record the brightest five that you see.
2. Using your trendline equation from your calibration graph in Part II, convert the scale reading for each observed line to wavelength in nm.
3. Repeat Steps 1-2 for the hydrogen lamp. Record the brightest three lines that you see.
4. Calculate the expected emission wavelengths for the Balmer series of hydrogen ($n_1 = 2$ and $n_2 = 3, 4, 5,$ and 6). Match your observed wavelengths to the closest expected wavelength to find n_2 for each. One of the boxes will be blank (you are calculating four wavelengths but observed only three).
5. Plot $1/\text{wavelength}$ versus $1/n_2^2$ for your three observed wavelengths. Determine R_H and compare it to the known value.

Part IV: Spectral Analysis of Flame Tests

1. Place a small quantity of NaCl crystal on the tip of a nichrome wire attached to a cork. You may need to wet the wire first in order to make the solid stick.
2. Using a Bunsen burner and holding the cork, position the wire so that the end holding the crystal is in the center of the flame. Meanwhile have your partner use the spectroscope to read and record on your data sheet the scale positions and colors for each observed emission line. You may need multiple samples to record every emission line.
3. Wash the wire with dilute hydrochloric acid and then deionized water.
4. Repeat Steps 1-3 with LiCl and SrCl₂ crystals. Be careful to not cross-contaminate the reagents.
5. Using the trendline prepared in Part II, convert each scale reading to wavelength in nm.

Part V: Spectral Analysis of Absorption Spectra

1. Using your spectroscope, observe the spectrum from a white light ordinary light bulb.
2. Place the test tube of KMnO_4 solution between the light bulb and your spectroscope. Read and record on your data sheet the wavelength region most strongly absorbed by the sample by shading the regions on the scale where visible light *can* be seen.
3. Repeat Step 2 with the solutions of CuSO_4 and CoCl_2 .
4. Using the trendline prepared in Part II, convert each scale reading for the region *absorbed* to wavelength in nm.

Experiment 17—Data Sheet

Name: _____

Part II: Spectroscope Calibration

Mercury

Color	Scale Reading	Wavelength (nm)
Blue		435.8
Green		546.1
Yellow		579.0

Trendline Equation (from graph): _____

Part III: Spectral Analysis of Gas Lamps

Helium

Color	Scale Reading	Wavelength (nm) use trendline equation

Show calculation for scale reading to wavelength:

Hydrogen

Color	Scale Reading	Wavelength (nm) use trendline equation

Show calculation for scale reading to wavelength:

n₁	n₂	Calculated Wavelength (nm) use Rydberg's Equation	Experimentally Observed Wavelength (nm) from previous table
2	3		
2	4		
2	5		
2	6		

Show calculation for calculated wavelength:

Matched n_2	$1/n_2^2$	Experimentally Observed Wavelength (nm) from previous table	$1/\text{wavelength}$ (1/nm)

Trendline Equation (from graph): _____

Experimental R_H value: (m^{-1}) _____

Percent Error (%): _____
show calculation:

Part IV: Spectral Analysis of Flame Tests

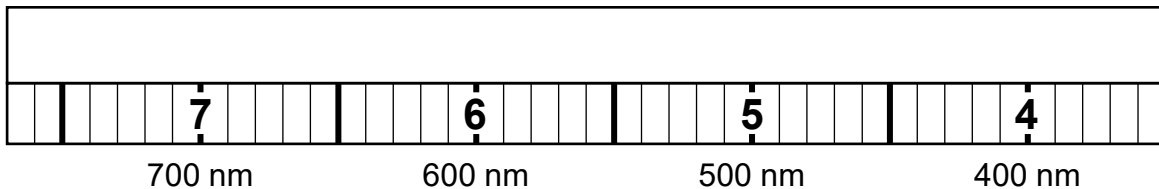
Compound	Color	Scale Reading	Wavelength (nm) Use trendline equation
NaCl			
LiCl			
SrCl ₂			

Show calculation for scale reading to wavelength:

Part V: Spectral Analysis of Absorption Spectra

1. White Light

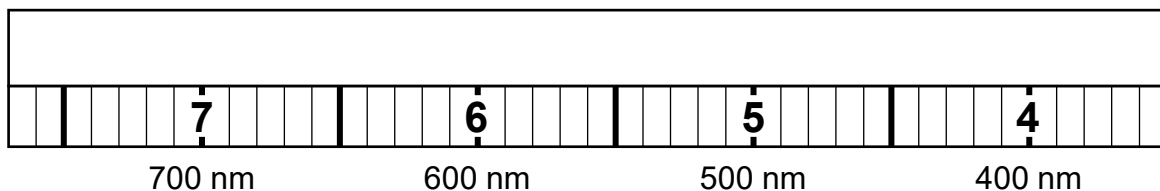
- a. Shade in regions above scale where visible light was seen for the white light source:



2. KMnO_4

- a. Color of KMnO_4 solution without spectroscope: _____

- b. Shade in regions above scale where visible light was seen for KMnO_4 :



- c. What color(s) were missing from the full spectrum of visible light (the rainbow)?

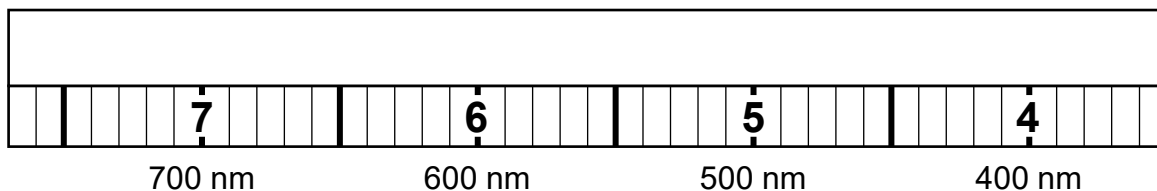
- d. Dark region where visible light wavelengths were absorbed (nm):

_____ nm to _____ nm

If you observed more than one dark region, list the other(s) below:

3. CuSO_4

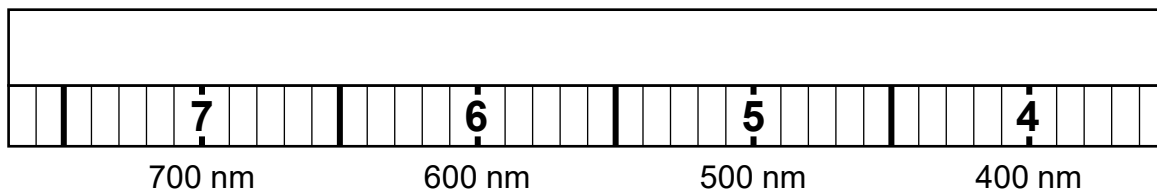
- a. Color of CuSO_4 solution without spectroscope: _____
- b. Shade in regions above scale where visible light was seen for CuSO_4 :



- c. What color(s) were missing from the full spectrum of visible light (the rainbow)?
- d. Dark region where visible light wavelengths were absorbed (nm):
_____ nm to _____ nm
- If you observed more than one dark region, list the other(s) below:

4. CoCl_2

- a. Color of CoCl_2 solution without spectroscope: _____
- b. Shade in regions above scale where visible light was seen for CoCl_2 :



- c. What color(s) were missing from the full spectrum of visible light (the rainbow)?
- d. Dark region where visible light wavelengths were absorbed (nm):
_____ nm to _____ nm
- If you observed more than one dark region, list the other(s) below:

This page intentionally left blank for double-sided printing.

Experiment 17—Post-Lab Assignment

Name: _____

1. Helium has many emission lines in the visible light region, though you observed only the most intense ones. Match your observed wavelengths from Part III to the published values below. Priority should be given to the most intense lines. Many of the boxes will remain blank.

Wavelength (nm)	Intensity	Observed Wavelength (nm)	Wavelength (nm)	Intensity	Observed Wavelength (nm)
388.9	1000		471.3	40	
396.5	80		492.1	50	
400.9	10		501.6	100	
402.6	70		504.8	15	
412.0	35		541.1	50	
414.4	15		587.56	1000	
438.8	30		587.59	10	
443.8	10		656.0	100	
447.1	100		667.8	100	
468.6	300		706.5	70	

2. Using your measured emission lines in Part IV, calculate the energy in J from the observed wavelength for NaCl, LiCl, and SrCl₂.

3. For NaCl, calculate the percent error between your measured emission line's wavelength in Part IV and the tabulated value of 588.9 nm.
4. Based on your data for Part V, explain why KMnO_4 solutions appear visibly purple. (Hint: Careful! Remember that the process responsible for causing the visible color of a solution is a different process than the colors seen in the gas discharge tubes or flame tests).
5. The amount of energy required to completely remove an electron from a hydrogen atom can be found by assuming it is being taken from the $n = 1$ level to the $n = \infty$. Calculate this amount of energy, in J. (Hint: what numerical value does $1/\infty$ approach?)

Experiment 17—Pre-Lab Assignment

Name: _____

For all calculations, show all work and draw a box around the final answers.

1. The background reading mentions four equations. Which one of these equations works **only** for the hydrogen atom? Circle one option:

Eqn. 1

Eqn. 2

Eqn. 3

Eqn. 4

2. Explain the difference between an absorption and an emission spectrum for an element.

3. The wavelength of green light is around 510 nm.

- a. What is the frequency of green light, in Hz?

- b. What is the energy of a single photon of green light, in J?

