Atomic Emission Spectra

Objectives

The objectives of this laboratory are as follows:

- To build and calibrate a simple box spectroscope that is capable of measuring wavelengths of visible light.
- To use this spectroscope to observe and measure the line spectra emitted by mercury, hydrogen and other elements.
- To use Bohr’s theory to identify the electronic transitions that give rise to each wavelength observed in the line spectra of hydrogen.

Background

Atomic Emission Spectra

Electrons in atoms normally occupy the lowest energy states possible. Such an atom is said to be in the ground state. However, electrons can be excited to high energy states when they absorb energy. This energy can be provided by heat, light, or an electrical discharge. The electrons will then return to lower energy states, eventually returning all the way to the ground state. As the electrons return to lower energy states, they release their excess energy. Often, this energy is released in the form of light, with each atom or molecule releasing a single photon of light for each electron energy transition it makes.

For example, in the hydrogen discharge tubes used in this experiment the energy of the electric discharge first dissociates the H₂ molecules into H atoms, then excites the electrons in the H atoms into high energy states. Due to conservation of energy, the amount of energy in an emitted photon will exactly match the amount of energy lost by the electron as it moves to the lower energy state.

Different colors of light are associated with different photon energies. For example, a single photon of blue light has more energy than a single photon of red light. Thus, the color of the light emitted by a particular atom depends upon how much energy the electron releases as it moves down to a lower energy level. The energy levels that are allowed for each atom depend upon the number and arrangement of protons and electrons in the atom. As each element has different energy states available to it, each element releases photons of different color when its atoms return to their lower energy states. Since each atom has many excited states (high energy levels) available to it, several colors of light can be emitted by each element. The set of individual colors emitted by an element is called its spectrum. Since the spectrum of each element is unique, spectra can be used like fingerprints to identify unknown elements.
Wavelengths of Light

Visible light is only one kind of electromagnetic radiation. The wavelength of radiation determines what kind of radiation it is. The human eye is able to detect only a narrow range of wavelengths of electromagnetic radiation, those from about 400 nm to about 700 nm. Radiation with wavelengths less than 400 nm includes ultraviolet, x-ray, or γ-rays, while radiation with wavelengths longer than 700 nm includes infrared radiation, microwaves, and radio waves. In this experiment, we use our eyes to detect the radiation emitted by excited atoms, and therefore we work only with visible light.

The color of light is related to its wavelength (λ), which is related to its frequency (ν) and the energy of its photons (E). Shorter wavelengths of light have higher frequencies and higher photon energies while longer wavelengths of light have lower frequencies and less energy per photon.

\[ \text{Red Orange Yellow Green Blue Violet} \]

\[ \nu \quad \lambda \quad E \]

It is easy to convert between photon energy, wavelength, and frequency using the following relationships:

\[ \lambda \nu = c \quad \text{and} \quad E = h\nu \]

where \( c = \) the speed of light = 2.998 \times 10^8 m/s, and \( h = \) Planck’s Constant = 6.626\times10^{-34}J\cdot s. These two relationships can be combined to give a third relationship:

\[ E = hc / \lambda \]

Thus, the line spectrum of an element can be described by listing the particular wavelengths of light that its atoms emit.

Box Spectroscope

To measure wavelengths in a line spectrum we must first separate them. To the naked eye, the various wavelengths (colors) of light emitted by an element are mixed together and appear as a single color that is a combination of the component colors. However, if we view the light through a prism or a diffraction grating, the individual wavelengths are separated. A diffraction grating is a piece of glass or clear plastic with many very narrow and closely spaced lines on it. As the light emerges after being reflected by the grating, these tiny lines cause the reflected light to interfere with itself in such a way that the different wavelengths of the light to appear in different positions to the left and right of the original direction in which the light was traveling. In this lab, a diffraction grating will be mounted in a simple “box spectroscope” that will be constructed by each student in lab.

Using a light source that contains known wavelengths of light, we can measure exactly where each known wavelength appears along a graph paper scale, which will be mounted opposite to the diffraction grating in the box spectroscope. Since this position has a linear dependence upon the wavelength, a graph of wavelength versus position of the spectral line will yield a
straight line. Once the best-fit straight line has been determined, the equation of this line can then be used to convert positions of other spectral lines to wavelength. For example, using the same box spectroscope, it is possible to view the spectrum of a new element, measure where its spectral lines occur on the graph paper scale, and then read the calibration graph (or use the equation of the line) to determine the wavelength to which each of those positions corresponds. The calibration graph is therefore an integral part of the spectroscope.

Bohr’s Theory and the Balmer Series

For atoms that contain only one electron, the theory of atomic structure proposed by Niels Bohr can be used to calculate wavelengths for transitions between particular electronic energy levels of the atom. In this experiment, the only one-electron atom we will consider is hydrogen. Applying Bohr’s theory for hydrogen, a close match can be found between the calculated wavelengths and those measured experimentally. To calculate the wavelengths of light emitted by hydrogen atoms, recall that the energy of an electron in the \( n \)th energy level of a one-electron atom is given by:

\[
E_n = -\frac{Z^2R}{n^2}
\]

where \( R \) is the Rydberg Constant (= \( 2.184 \times 10^{-18} \) J), \( Z \) is the nuclear charge, and allowed values for \( n \) are \( n = 1, 2, 3, \ldots, \infty \). For hydrogen, the nuclear charge is +1 so this equation becomes:

\[
E_n = -\frac{R}{n^2}
\]

The change in energy for the electron when it makes a transition from one level to another is given by its subtracting its initial energy from its final energy:

\[
\Delta E_{\text{electron}} = E_f - E_i
\]

By conservation of energy, the energy of the photon emitted as this electron drops to a lower energy level must equal the change in energy for the electron. However, since photon energies must be a positive quantity, thus the absolute value of the change in energy for the electron must be used:

\[
E_{\text{photon}} = |\Delta E_{\text{electron}}|
\]

Once the energy of the photon is known, it is readily converted into a wavelength as discussed earlier.

Because there are many energy levels possible for the electron in a hydrogen atom, and because the electron could jump from any higher \( n \) to any lower \( n \), there are many lines in the spectrum of hydrogen. However, most of these lines occur at wavelengths that our eyes cannot detect (either infrared or ultraviolet). The visible portion of the spectrum (which you will observe in this experiment) was the first to be studied by scientists since it is the only portion that can be seen with the naked eye. This series of spectral lines is named after one of the first scientists to study it, and is called the Balmer series. Note that all of the spectral lines in the Balmer series involve transitions from a higher \( n \) level to the \( n = 2 \) level. You will need this information to complete the calculations for your lab report.
Procedure

Materials and Equipment

Medium-sized box supplied by each student (thinner cardboard is best), diffraction grating, strips of graph paper, box cutters, masking tape, black electrical tape, high voltage power supplies, hydrogen, mercury, helium and other polyelectronic element discharge lamps.

Safety

① Exercise extreme caution with the high voltage supplies as severe shocks are possible! Do not touch the front of the power supply while it is plugged in.
② Do not touch or attempt to remove the discharge tubes from the high voltage supplies. In addition to the risk of electrical shock, the tubes become very hot with use. The power supplies must be turned off and unplugged before changing discharge tubes.
③ View the light emitted by the discharge tubes through glasses or goggles. Both glass and plastic lenses will absorb most of the harmful UV radiation emitted by many atoms.

Part A: Constructing and Calibrating a Box Spectroscope

Construction of Box Spectroscope

- Detailed instructions on how to construct and test the spectroscope will be provided at the beginning of the lab session. However the basic procedure is supplied here.

![Basic Box Spectroscope Design](image)

1. Cut holes (roughly 1.5 cm x 1.5 cm) for the grating and slit on opposite sides of the box. Use the wider sides of the box for your slit and grating, not the narrow sides.

2. Tape the diffraction grating over one of the holes and hold the box up to the light. Aim your spectroscope at a fluorescent ceiling lamp and look through the grating. You should see a rainbow (a continuous color spectrum) on the side (not top) of the box. If you do not see a rainbow on the side of the box, rotate the diffraction grating by 90 degrees.
3. Place a strip of black tape on either side of the opposite hole where the light enters your box to create a “slit” with a width of about 1 mm or less. This should make the rainbow appear much sharper and crisper.

4. Note the approximate position of the rainbow (to the side of the slit), and mark where it starts and ends on your box. Then cut out a cardboard flap on three sides slightly wider than this area. This is where you will be mounting the graph paper scale (see diagram).

5. Use a pen to clearly label some of the lines on your graph paper strip: 1, 2, 3, etc. Write these numbers along the center line of the graph paper strip so that you can clearly read them from inside the box once the strip is mounted in place. It does not matter whether you label each line 0, 1, 2, 3… or every 5th line, or every 10th line, just make sure that the spacing in your numbering scale is consistent.

6. Tape the strip of graph paper over the space you just cut so that you can see the rainbow on the scale. With the flap slightly open you should be able to read the numbers that you wrote from inside the spectrometer.

7. Test your spectroscope by (once again) aiming it at the fluorescent lights in the room. You should now see a complete rainbow appearing clearly on the numbered portion of your graph paper scale. If not, consult with your instructor before continuing.

**Calibration of Spectroscope using the Line Spectrum of Mercury**

8. Aim your box spectroscope at one of the mercury emission lamps set up in the room. You should see four bright lines or spots on the scale: a deep violet or purple line, a bright blue line, a bright green line, and a bright yellow line (in that order). Note that the violet line can be hard to see and should be just beyond the bright blue line. The exact wavelengths of these four bright lines are given in the table below.

<table>
<thead>
<tr>
<th>Color</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>deep violet</td>
<td>404.7 nm</td>
</tr>
<tr>
<td>bright blue</td>
<td>435.8 nm</td>
</tr>
<tr>
<td>bright green</td>
<td>546.1 nm</td>
</tr>
<tr>
<td>bright yellow</td>
<td>579.0 nm</td>
</tr>
</tbody>
</table>

9. Write the exact position and color of each these lines on your scale on your report form. Remember you should always estimate one decimal place beyond the markings on the scale of any instrument, for example, record “8.2” rather than just “8”. The units on the graph paper scale are non-standard, and may simply be called “graph paper units” (gpu).

10. **Data Analysis:** Using Microsoft Excel®, plot a graph of the exact wavelength of the four lines given above versus their recorded positions on your spectroscope scale. Wavelength should be on the y-axis and line position on the x-axis. Apply a trendline to this data and obtain the equation and $R^2$ value of this line. Staple this graph to your lab report.

This graph is called a calibration curve. It will allow you to find the exact wavelength of unknown spectral lines. Write the calibration equation on your spectroscope for easy reference, and record it on your Report Form as well. By using this equation you can easily convert a measured line position (in gpu) into a wavelength (in nm).
Part B: The Line Spectrum of Hydrogen – A Single Electron Atom

1. Now aim your box spectroscope at one of the hydrogen emission lamps set up in the room. Record the colors and positions of the lines you see on your Report Form, being careful to record them in the order they appear from left to right. You should see at least three lines clearly: bright red, bright aqua and bright blue. You may also be able to see a deep violet line (after the blue line). When finished, use your calibration equation to determine the wavelengths of each of the lines you observed. These are your experimental wavelengths.

2. **Data Analysis:** Using the equations of Bohr’s Theory, calculate the wavelengths of the first four lines in the Balmer series. These are your theoretical wavelengths. Record your results on your Report Form.

3. **Data Analysis:** Compare your theoretical wavelengths with your experimental wavelengths. Then identify which electronic transition (from \( n = ? \) → \( n = 2 \)) is responsible for each of the colored lines you observed in the hydrogen spectrum. Calculate your percent error for each line, and record your results on your Report Form. Recall that:

\[
\% \text{ error} = \left( \frac{\lambda_{\text{theoretical}} - \lambda_{\text{experimental}}}{\lambda_{\text{theoretical}}} \right) \times 100
\]

Part C: The Line Spectrum of a Polyelectronic Element

1. Finally, aim your box spectroscope at either a helium lamp or one of the other polyelectronic element lamps set up in the room. Record the color of the 4-6 brightest spectral lines you see and their corresponding positions on the spectroscope (in the order they appear from left to right). When you have finished, use your calibration equation to determine the wavelengths of the lines you observed. These are your experimental wavelengths.

2. **Data Analysis:** Go to the NIST government website at [http://physics.nist.gov/PhysRefData/Handbook/element_name.htm](http://physics.nist.gov/PhysRefData/Handbook/element_name.htm). Select the name of the element you chose, then click on the box labeled “Strong Lines”. Scan the wavelength column for the wavelengths you measured to see if you can find any close matches. Note the following:
   - The tabulated wavelengths are given in units of Angstroms (1 Å = 10\(^{-10}\) m). The wavelengths you have measured in lab are in nm (1 nm = 10\(^{-9}\) m). Thus, you must convert the numbers in the NIST table to nm by dividing them by 10. (i.e. 5890 Å = 589.0 nm)
   - Each element actually emits hundreds of wavelengths of light, but only some of those wavelengths are emitted with enough intensity (brightness) for our eyes to see them. The tabulated wavelengths include those that we cannot see with the naked eye, so you must scan down the “Intensity” column in the table of wavelengths to look for those lines that have high values for intensity. Look for those spectral lines that are significantly more intense than most since they are the ones you are likely to have seen in lab. Note that this means the wavelengths may not match perfectly.

3. **Data Analysis:** Record the tabulated wavelength for the intense line nearest to each wavelength you observed. These tabulated values are your actual (true) wavelengths. Then calculate the percent error for each of your measured experimental wavelengths.