Purpose: Emission and absorption spectroscopy is to be explored from different perspectives in a multipart experiment.

Part I: Certain elements are to be identified by their emission line spectra.

Part II: Wavelengths of white light are examined, and the effect of placing colored solutions between the light source and the refraction grating is to be determined.

Part III: Beer’s Law is utilized to create a standard curve for the absorption of light by aqueous solutions of cobalt(II) chloride of various concentrations. The graph is then used to determine the concentration of an unknown cobalt(II) chloride solution.

Introduction:

When energy is emitted (released) in the form of light it produces an emission spectrum. When energy is absorbed in the form of light it produces an absorption spectrum. In this experiment we will focus on the light in the visible region, with wavelengths between 400 and 700 nm. The figure below shows the difference in these three terms: transmit, reflect and refract. If the incoming light (the incident beam) looks different from the transmitted or reflected light, it is because part of the light has been absorbed by the sample. When transmitted light is at an angle different from the angle at which it entered the medium, it is said to be refracted. The color we perceive of a clear solution is based on the light being transmitted through a sample; whereas, the color we perceive of an opaque sample (such as a solid) is based on the light reflected off the surface. Be sure you understand the distinction in the meaning of transmitted, absorbed, reflected light and how they are related.

In Part I of this experiment you will examine the light emitted. In Parts II and III you will examine what is absorbed by a sample and what is transmitted.

PART I: EMISSION SPECTROSCOPY

When ordinary white light is passed through a glass prism it produces a continuous spectrum, that is, one containing all the colors of the rainbow, with one color merging into another. This phenomenon can be explained by considering light as having a continuous distribution of wavelengths traveling through the glass. Light of each wavelength travels through the prism at a different speed and therefore refracted at a different angle. As a result, white light separates out into a rainbow of colors, spanning from violet at a wavelength of 400 nm to red at a wavelength of 700 nm. There are emissions below and above this region, but they would not be visible to our eyes (e.g. ultraviolet, infrared, microwave etc.)
When energy is added to an element, either by passing an electric current or by applying a flame to it, light is emitted. When this light is passed through the glass prism, only certain wavelengths of light are emitted, appearing as a series of colored lines on a black background, instead of the continuous rainbow. This type of spectrum is referred to as an Emission Line Spectrum. It is due to the excitation of electrons of the element to a higher energy level. When the electron drops down to a lower energy level, energy is produced in the form of light at a wavelength corresponding to the energy released. The wavelength is related to the amount of energy released by the following equation:

\[
E = \frac{hc}{\lambda}
\]

where \( E \) is the amount of energy released
\( \lambda \) is the wavelength of the light emitted
\( h \) is Planck’s constant,
\( c \) is the speed of light (also a constant)

With \( \lambda \) in the denominator, this means that the longer the wavelength, the smaller is the energy. Thus, red light (around 700 nm) is lower in energy than violet light (around 400 nm).

Each element has a unique set of emission lines, like a finger print, that can be used for identification. In Part I you will examine the emission line spectra of a few elements and identify the element by comparing the observed spectrum to known spectra provided. This is similar to how scientists are able to identify elements in the stars without having to obtain actual gas or soil samples from the stars.

The instrument you will use is called a spectroscope. The light you examine will pass through a grating that acts like a prism. (See Figure 12.1.)

PART II: ABSORPTION SPECTROSCOPY

In contrast to the emission spectrum, the absorption spectrum of an element appears as a series of black lines on a rainbow background. Each black line is due to the light absorbed as the electron is promoted to a higher energy state.

In Part II you will examine the absorption of light due to a few aqueous solutions of ionic compounds. The samples to be examined are no longer simple systems such as monatomic or diatomic gases that you will examine in Part I, but are ionic compounds dissolved in water. Absorptions for such systems are no longer limited to just transitions of electrons from one energy level to another. They will also involve rotational and vibrational energies that are of nearly the same quantity of energy. These absorptions will appear as bands rather than sharp lines. That is, the lines will merge into blocks of black areas.

THE SCIENTIFIC METHOD

The “scientific method” of coming up with an explanation for our observations is different from a nonscientific method in that we must confirm our preliminary guess at an explanation with experimental evidence. The “scientific method” can be loosely outlined as follows:
1. Making observations – recording observations and data with an aim to recognize any patterns that might appear. It could also be recognizing some observation or data that do NOT fall in a previously established pattern.

2. Formation of a Hypothesis – forming an educated guess to explain the pattern we noted.

3. Testing the hypothesis – designing experiments to test our hypothesis. The experiments must be such that results are reproducible and such that the hypothesis is proven valid or invalid.

4. Formation of a Theory – If the experimental results repeatedly support our hypothesis, the hypothesis becomes theory. If not, we can either discard the hypothesis or revise it and redesign experiments to test the revised hypothesis.

In Part II you will make some observations of how certain colored solutions absorb light. You will propose a hypothesis as to the relationship between the color of the solution and the color that is apparently being absorbed. You will then devise a plan to prove your hypothesis.

PART III: THE USE OF BEER'S LAW AND A STANDARD CURVE TO DETERMINE THE CONCENTRATION OF A SOLUTION

Beer’s Law states that at a given wavelength, the intensity of absorption of a solution is directly proportional to the concentration of the solution. The intensity of absorption is called absorbance (A).

\[
A = \varepsilon l c
\]

where

- \( A \) = absorbance
- \( \varepsilon \) = molar absorptivity (or molar extinction coefficient)
- \( l \) = the path length (diameter of the cuvet)
- \( c \) = concentration of the solution

Note that \( \varepsilon \) (pronounced epsilon) is a unique property of the solute and is constant for a given substance. \( l \) is also a constant as all the cuvets (glass tubes holding the sample being examined) have the same diameter. Thus we can combine the two constants (\( \varepsilon \) and \( l \)) and rewrite the equation as

\[
A = k c
\]

where \( k \) is a constant (\( \varepsilon \) times \( l \))

You should recognize that this is an equation of a straight line:

\[
y = mx + b \quad \text{where} \quad y = \text{absorbance (A)}
\]

- \( m \) = slope \( (k = \varepsilon \times l) \)
- \( b \) = y-intercept = zero

Thus, if we plot absorbance \( \text{versus} \) concentration we should get a straight line, and the slope is equivalent to \( \varepsilon l \). The equation also tells us that absorbance is directly proportional to the concentration (i.e. the more concentrated the solution, the higher is the absorbance, proportionally.) This is the essence of Beer’s Law.
The instrument you will use in this section is called a spectrophotometer. You will set it to the wavelength you wish to examine and then record the absorbance of aqueous solutions of cobalt(II) chloride (CoCl₂).

You will be given a set of cobalt(II) chloride (CoCl₂) solutions with known concentrations (called standard solutions). You will measure the absorbance of these solutions and prepare a standard curve (also called calibration graph) of absorbance vs. concentration (molarity of CoCl₂). Once you have such a standard curve, you will be able to determine the concentration of a solution by measuring its absorbance and reading the concentration off the graph. The slope will also allow you to calculate $\varepsilon$ of CoCl₂.

**Procedure**

*You will perform the entire experiment with a partner. You do not have to do Parts I, II and III in order. As there is a limited number of instruments available, you will be assigned to do certain parts first.*

**Part I: Emission Spectroscopy**

*Do not take more than 5 minutes on Part I. You will need considerably more time for the other two parts.*

1. Three discharge tubes, labeled X, Y and Z, have been set up for your viewing with the spectroscope. If you don't see anything through the eyepiece, get help from your instructor to re-align the spectroscope.

2. Compare the spectra you observed with known spectra posted at each spectroscope and determine the identity of the gas in each discharge tube. The possible gases are as follows:
   - hydrogen, helium, mercury, neon

3. Record your conclusion on the Calculations & Results page.
Part II: Absorption Spectroscopy

This part of the experiment should take no more than 30 minutes.

1. Observe the white light from either a fluorescent tube or incandescent light bulb through the eyepiece of the spectroscope. For our purpose, it does not matter which light source you are using. With the colored pencils provided, shade in the appropriate colors onto the Calculations & Results Page, being careful of where (at which wavelengths) each color appears. These are colors that are transmitted by the light bulb. The wavelengths that appear in the spectroscope are in units of nm (nanometers).

2. With the help of your partner, examine what happens when a colored solution is placed between the light source and the slit of the spectroscope. In particular, note which colors disappeared when a colored solution is put in place. These are the colors that are absorbed. One partner should slowly lower and raise the colored solution in front of the slit while the other partner is looking through the eyepiece. Record your observations on the Calculations & Results page.

**NOTE:** One or more colors may disappear. You will find it easier to note which color(s) disappeared by keeping your eye on one color (such as red) and when your partner lowers the sample, see whether that color disappeared. Then go to the next color (such as orange) and repeat until you have gone through entire spectrum, one color at a time. This is probably easier than to just look at the entire rainbow of colors at the same time and try to discern which color disappeared.

![Diagram of the Spectroscope](image)

**Figure 12.1: The Spectroscope**

3. Discuss with your partner what you observed regarding the relationship between the color of the solution and the color(s) that disappeared. Relate the colors to the color wheel that is posted at each spectroscope.

4. You and your partner should propose a hypothesis as to what the relationship is and design an experiment to test your hypothesis. The test should be one that you can perform using the equipment available to you. Write on the Calculations & Results page your hypothesis and what you predict the results would be for the test and then present it to your instructor. If your instructor suggests changes in your hypothesis and plan, you should record it as well before you test your hypothesis.

*(continued next page)*
5. Perform the test and record your observations. As the conclusion to this section, state whether your hypothesis has been confirmed or whether it requires revision. Provide a brief explanation. If it requires revision, propose a revised hypothesis.


Figure 12.2: Spectrophotometer (UNICO 1100 RS Model)

The instructions below are written specifically for UNICO 1100 RS Model. If you are using a different model, please see your instructor.

1. You and your partner MUST be checked out by your instructor on the operation of the spectrophotometer before you proceed. RECORD THE INSTRUMENT ID # on which you are working. This is written in black ink on the instrument.
2. First check that the wavelength is set at 520 nm.
3. Using the MODE SELECTOR (see Fig. 12.2) set the mode to A (Absorbance). All your readings should be done in this mode.
4. We are interested in the absorbance of the CoCl₂ only and not of the solvent (water) which does absorb slightly at this wavelength. For this reason, pick up the cuvet containing water, wipe the outside of the cuvet with Kimwipes (a special lintless tissue paper) to remove fingerprint and other contaminants, insert it into the cell holder and close the lid. Press BLANK ADJUST (0A/100%T) once. After a few seconds, BLA will appear in the display window. It will then blink a few times and then 0.000 will appear. You have just set the instrument to an absorbance reading of 0.000 for water. This is like placing an empty beaker on the balance pan and “taring” it to zero. The water in this experiment is referred to as the blank (BLA).
5. Each of the four CoCl\(_2\) solutions is labeled by its concentration, with units of M (mole/liter). Wipe the outside of each cuvet with Kimwipe just prior to use. Record the absorbance of each. Note that absorbance has no units. (A is not a unit.)

6. Your instructor will assign EACH student an unknown CoCl\(_2\) solution. Record the unknown number immediately into the Data Table in your lab notebook. You do not need to record your partner’s unknown number or absorbance. Record the absorbance of your unknown solution and return it to the exact location where you had found it.

Sample of Data Table for Part III:

<table>
<thead>
<tr>
<th>Unknown ID #:</th>
<th>Spectrophotometer #:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration of CoCl(_2)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0125 M</td>
<td></td>
</tr>
<tr>
<td>0.0250 M</td>
<td></td>
</tr>
<tr>
<td>0.0500 M</td>
<td></td>
</tr>
<tr>
<td>0.1000 M</td>
<td></td>
</tr>
<tr>
<td>Unknown</td>
<td></td>
</tr>
</tbody>
</table>

The Standard Curve

*Review Appendix 3 on the preparation & interpretation of graphs. You are expected to have learned how to prepare graphs properly from Experiment 6.*

Prepare a standard curve of Absorbance vs. Concentration for the four standard solutions of CoCl\(_2\). (Be sure to review what that means. Is Absorbance to be plotted on the x- or y-axis?) Choose your scales wisely and use a very sharp pencil. The title of the graph is *Standard Curve: Absorbance vs. Concentration of CoCl\(_2\).* Be sure to turn in your graph along with your lab report.

In choosing a scale for the x-axis, do *not* use 0.0125M as an increment. It will make it unnecessarily difficult to read values off your graph.

Calculations for Part III:

1. Based on your standard curve what is the molarity of your unknown? Report it on the Calculations & Results page. The molarity should be the same as those of the knowns.

2. Calculate the slope from your graph by selecting two points. Review Appendix 3 on how to select the points. Please do not use your data points even if they lie on the curve. The number of significant figures of your coordinates should be the same as those of your data points. As you perform your calculation of the slope, keep track of your sig. fig. and units!

*(continued next page)*
3. Read the y-intercept from your graph, to the same decimal places as your data points for the y-axis.

4. Write a general equation for the standard curve as described on the Calculations & Results page.

**Post-Lab Questions:** See questions on pp. 113-114.
Calculations & Results: Name: ________________________________
Partners’s Full Name: ________________________________
Lab Sec: ______

Part I: Emission Spectroscopy
Identity of Gases: X = ___________ Y = ___________ Z = ___________

Part II: Absorption Spectroscopy
Using the color pencils provided, color the box below to match the wavelengths observed in the spectroscope.

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|

400 450 500 550 600 650 700 nm

Describe the color of the solution (transmitted) and the color(s) that disappeared (absorbed) when each of the following solutions were placed between the light source and the slit.

<table>
<thead>
<tr>
<th>Color of solution</th>
<th>Color(s) that Disappeared from the Rainbow</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄ (aq)</td>
<td></td>
</tr>
<tr>
<td>NiCl₂ (aq)</td>
<td></td>
</tr>
<tr>
<td>FeCl₃ (aq)</td>
<td></td>
</tr>
</tbody>
</table>

State your hypothesis to explain the relationship between the color transmitted and colors that are absorbed and how they are related to the color wheel:

Proposed plan to test your hypothesis, including predicted results:

State the observations from your test and state whether it shows that your hypothesis is valid.
Name: _______________________

Part III: Determination of the Concentration of an Unknown Solution of Cobalt(II) Chloride

1. Using your graph, determine the molarity of your unknown.

   Unknown # _________  Molarity = _________

2. Calculate the slope from your graph.

   Give the coordinators of these two points. Review the appendix for the proper format and treatment of significant figures.

   (_______, _______)  (_______, _______)

   Show calculations for the slope: *Keep track of your sig. fig. at all steps in your setup. This will tell you how many sig. fig. and what the units should be in your final answer.*

   Ans. The slope is ____________________________.

3. Read the y-intercept from your graph.

   Ans. The y-intercept is ________________________.

4. The general equation of a straight line is $y = mx + b$. What is the equation of your line, written in terms of $A$ (absorbance) and $c$ (concentration), instead of $x$ and $y$? Fill in your values of $m$ and $b$, and with the proper units. (No calculations needed here.)

   *(See Appendix 3, page A-15 Exercise 3, part c.)*

   Ans. The equation is ____________________________.
Post-Lab Questions:  

Name: __________________________

Your instructor will specify whether answers to these questions are to be turned in at the end of the lab period or at the beginning of the prelab the following week.

1. a) What is the color at 520 nm in the spectrum you prepared in Part II? Ans. __________

   b) What is the color of the solution you analyzed in Part III? Ans. __________

   c) What is the color transmitted through your unknown solution? Ans. __________

   d) What is the color absorbed by your unknown solution? Ans. __________

   e) Why would it be incorrect to say that the color reflected by the cobalt(II) chloride solutions is pink (which can be considered a light red)? What is a better way of describing what the pink/light red represents? **Answer in sentences. Write legibly.**

2. What does Beer’s Law tell us about the relationship between the absorbance and concentration of a solution? Does your standard curve in Part III show that Beer’s Law is valid? **Explain in sentences. Write legibly.**

(continued next page)
3. Explain briefly why each of these graphs would not fit Beer’s Law. Specifically what part of the graph is not in agreement with Beer’s Law? Answer each part briefly with one sentence. Write legibly.

a)

b)

c)