AP Chemistry

The Absorption Spectrum of Cobalt(II) Chloride

When hydrogen and other gaseous substances are heated they will emit light with a few characteristic frequencies. In contrast, matter will also absorb discrete frequencies of light. This process is exactly the opposite of emission.

During the absorption of light, an electron undergoes a transition from a lower (usually the lowest) energy level to a higher energy level. The electron gains energy in this process by absorbing a photon, whose energy (E) is given by Planck's equation $E = hv$. The energy of the photon corresponds to the difference in energy between the higher and lower energy levels. As a result of the transition, a component of light with a frequency v is absorbed, and other frequencies are transmitted.

The amount of light absorbed by a substance in solution is dictated by the concentration of that substance: Absorption decreases as the concentration is decreased by dilution. The statement is expressed mathematically in Beer's Law. You must understand the calculation of the concentration of a solution after dilution before you can use or appreciate this law.

Purpose:

You will investigate the absorption of light by a series of solutions of cobalt(II) chloride ($CoCl_2$). You will also receive a solution of this substance whose concentration is unknown but too large for an accurate measurement of the absorption of light. Your task will be to determine the concentration of this solution.

Concept of the Experiment:

The absorbance of a 0.150M solution of $CoCl_2$, will be measured before and after a series of dilutions. For each dilution you will calculate the new concentration of $CoCl_2$. According to Beer's Law, the slope of the best straight line from a graph in which absorbance is plotted against the concentration of $CoCl_2$ will give you k (the constant from Beer's law) for $CoCl_2$ under your experimental conditions. You will obtain the slope by a method called linear regression.

You will also receive a solution of $CoCl_2$ whose concentration is unknown but so large that the absorbance is too great to be reliably measured. You must determine the concentration of $CoCl_2$ in this solution from a measurement of a diluted solution. It will be up to you to discover an appropriate dilution.

Before you measure any of these absorbances, however, you will need to find the correct wavelength for the measurements. This wavelength, which will be the wavelength in the absorption spectrum of $CoCl_2$ at which the maximum absorbance occurs, will allow maximum sensitivity for each measurement.

Procedure:

1. Mark each of 7 dry 18 x 150mm test tubes with one of a series of identification numbers running from 1 – 7.
2. Use Mohr pipets to make the additions of 0.150M $CoCl_2$ and distilled water shown in the table at the top of the next page.

Caution: Never use your mouth to draw liquid into a pipet, even if the liquid is water.

Test Tube #	0.150M $CoCl_2$ Solution (mL)	Distilled Water (mL)
1	5.0	0
2	4.0	1.0
3	3.5	1.5
4	3.0	2.0
5	2.5	2.5
6	2.0	3.0
7	1.0	4.0

3. Thoroughly mix the contents of each test tube. Do not use one of your fingers as a stopper.
4. Obtain the absorption spectrum of aqueous $CoCl_2$ by using the contents of the first test tube and measuring the absorbance at intervals of 25nm between 400 and 600nm. Do not dispose of this solution. Record our results.
5. From these measurements, select the wavelength at which the absorbance is largest. This wavelength will provide maximum sensitivity. Use this wavelength for all subsequent measurements.
6. Remeasure the absorbance of the contents of the first test tube at this wavelength. Measure the absorbances of the contents of the remaining test tubes. Record your results.
7. Label a piece of the available graph paper so that absorbance (A) appears on the vertical axis and the concentration (c) of $CoCl_2$, in mol/L, appears on the horizontal axis.
8. Enter each point on the graph as a small, blackened circle. Do the data appear to conform to a straight line? Use linear regression to calculate the slope of the best straight line that satisfies these points. If you wish, draw a straight line with this slope on your graph. This line should pass through the origin ($A = 0, c = 0$)
9. Now you can begin to work on your unknown. Use the following guidelines in establishing the molar concentration of $CoCl_2$ in this solution.
    a. A portion of this solution must be diluted until the absorbance lies within the range of absorbances that you found in Step 6.
    b. To establish the correct dilution, measure the absorbance after each of a series of successive dilutions. Your final result here may have a large experimental error because errors will accrue during several dilutions.
    c. To eliminate the accumulation of experimental errors, prepare a new sample and obtain the desired absorbance in one dilution rather than a series of dilutions. Clearly, this dilution must be equivalent to the overall dilution obtained in the previous set of trials.
10. Calculate the concentration of $CoCl_2$ in the diluted solution using the absorbance and k. Calculate the concentration of $CoCl_2$ in the original unknown.

BACKGROUND:

The Absorption of Light:

When a substance absorbs light, an electron undergoes a transition from the lowest energy level to a higher energy level. The energy difference between these levels is given by Planck's equation E = hν. Consequently, only one frequency ν causes this transition. Frequency is inversely related to wavelength ($\lambda = c/\nu$); Planck's equation then becomes $E = \frac{hc}{\lambda}$, where c is the velocity of light.

Transmittance and Absorbance:

When light of the correct wavelength shines through a solution of a substance that absorbs light, the intensity of the light diminishes as it passes through the solution because absorption occurs. If the intensities of the light that enter and emerge from the solution are represented by I_O and I, respectively, **transmittance** (T) is defined by the ratio $T = \frac{I}{I_o}$.

A related quantity called the **absorbance** (A) is defined as the negative logarithm of the transmittance. $A = -\log T = -\log\left(\frac{I}{I_o}\right)$

Spectrophotometers:

Absorbance is measured with an instrument called a spectrophotometer. This instrument separates light into its component wavelengths and selectively measures the intensity of the light of a given wavelength after it passes through a solution. All spectrophotometers, regardless of the manufacturer, have certain common fundamental parts. These parts include a source of radiant energy, a prism or grating to isolate the light of a particular wavelength, a device for holding the sample, and a photoelectric cell for measuring the intensity of the light. Your laboratory instructor will explain the operation of the spectrophotometers in your laboratory.

If your spectrophotometer is a Spectronic 20 with a meter, a commonly used instrument in general chemistry laboratories, a word of advise is offered here. The meter on this spectrophotometer is calibrated linearly in percent transmittance (100 T) and logarithmically in absorbance. You will always want to obtain three significant figures in your measurements of absorbance. However, if the absorbance is relatively large, doing so will be difficult on this meter because of the logarithmic scale. Percent transmittance can always be read with high precision, however, if it is above 10%. If you cannot measure an absorbance with three significant figures, measure the percent transmittance with this precision, convert to transmittance by diving by 100, and calculate the absorbance by taking the negative logarithm of the transmittance.

Beer's Law:

This law states that the absorbance is directly related to the concentration (c) of the substance that absorbs light, or $A = kc$ where k is constant. Because A is a dimensionless number $A = -\log\left(\frac{I}{I_o}\right)$ and the unit of measurement for c is mol/L (M), it follows that the unit of measurement for k is L/mol (M^{-1}). This is constant for a given substance at a particular wavelength. Its value may be zero if no light is absorbed at a particular wavelength, or it may be as high as 10^4 M^{-1}.

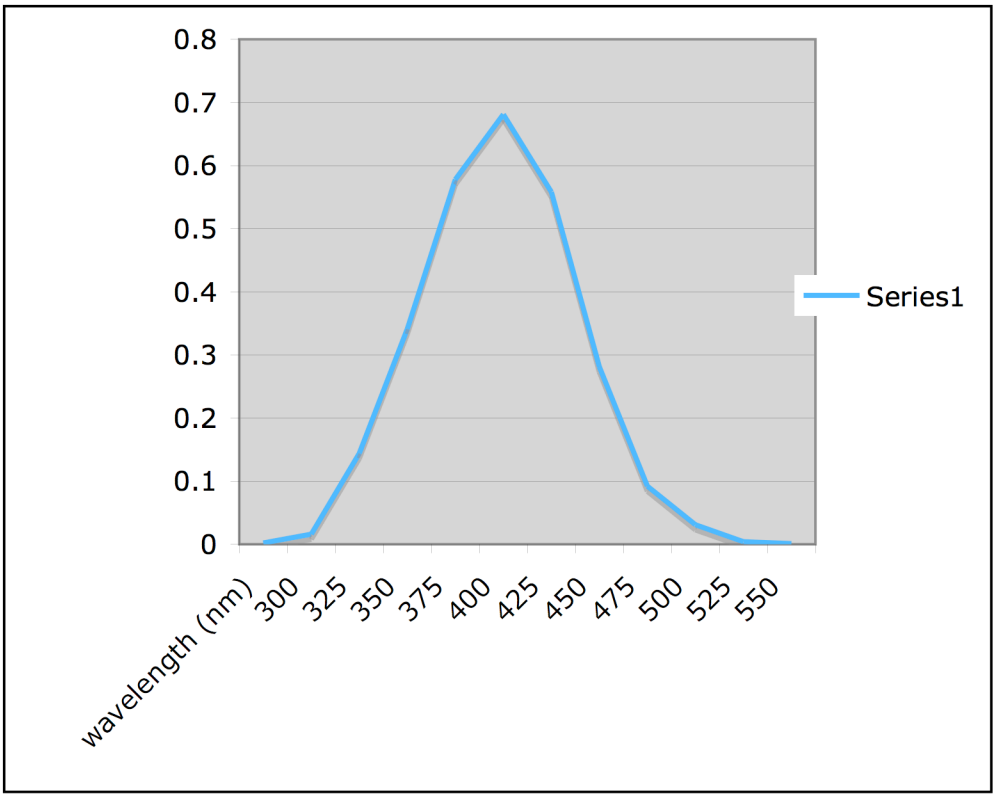
Absorbances Obtained at Various Wavelengths for a Solution of a Hypothetical Substance (c = 0.0120 M)

λ (nm)	A	λ (nm)	A
300	0.002	450	0.558
325	0.016	475	0.281
350	0.144	500	0.092
375	0.341	525	0.031
400	0.578	550	0.004
425	0.681	575	0.001

An Absorption Spectrum:

Suppose the absorbance of a colored substance is a colorless liquid is measured at each of a series of wavelengths. Some typical results are given in the table above, where the absorbance was measured at intervals of 25nm between 300nm and 575nm. These absorbances are plotted against the wavelengths in the graph below. After the data are plotted, the points are connected by a smooth curve. This curve, which represents the best estimate of the absorbance anywhere between 300nm and 575nm, is called the **absorption spectrum**.

Because the concentration of the substance is fixed in this experiment, the change in the absorbance that is shown in graph below indicates the manner in which k from Beer's law is dependent on the wavelength. The value of the constant reaches a maximum at 425nm, where the absorption spectrum for this substance reaches a maximum.



The Determination of k:

The equation for Beer's Law, A = kc, has the same form as the equation for a straight line, y = mx + b. A comparison of these equations indicates that

$y = Ax = c$

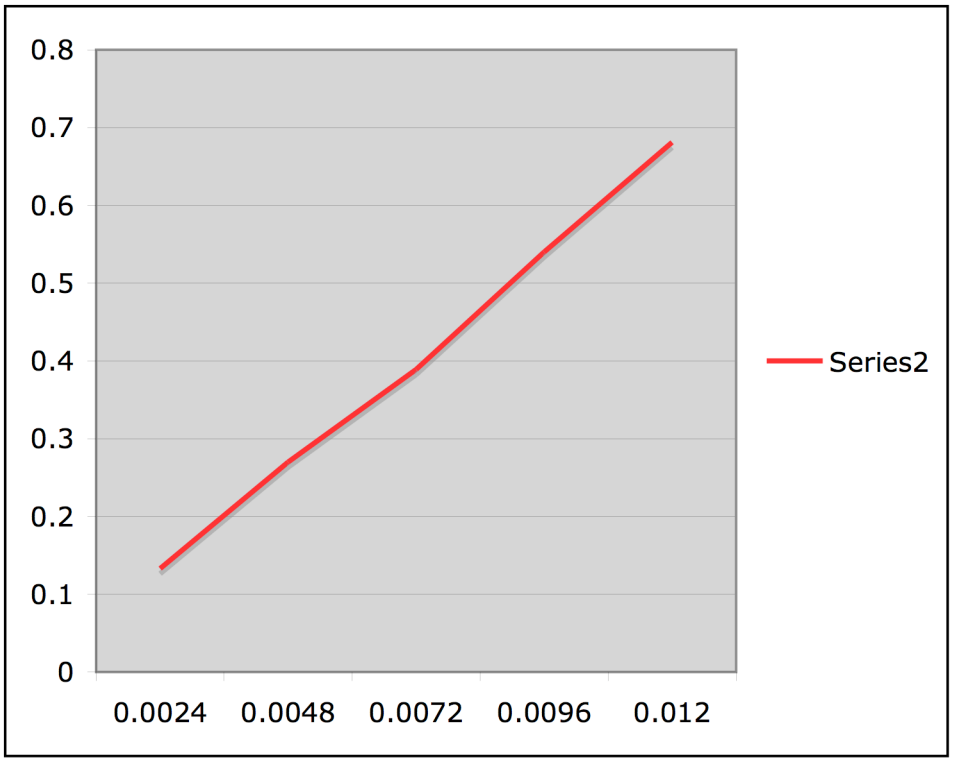
m = slope = k

b = intercept on y axis = 0

Consequently, you should obtain a straight line when you plot the absorbances obtained at various concentrations against those concentrations. Moreover, the slope of that line will be given by k, and the line must pass through the origin (A = 0, c = 0), because the intercept is zero.

Absorbances Obtained at Various Concentrations at 425nm:

c (M)	**A**
0.0120	0.681
0.00960	0.540
0.00720	0.389
0.00480	0.270
0.00240	0.133



Let's use the data table above as an example. You may assume that the hypothetical substance whose absorption spectrum is shown in first graph was used again to obtain these data. The second graph shows the absorbances plotted against the concentrations. A straight line passing through the origin was drawn in an attempt to provide the best fit for all the data. Experimental error is the reason why some of the points deviate from that line.

Any arbitrary point on the line will provide enough information for us to calculate the slope k. For example, we will choose a point with c = 0.0100M and A = 0.557.

The slope is given by $k = \frac{A}{c} = \frac{0.557}{0.0100M} = 55.7M^{-1}$

How do we know whether second graph shows the best straight line? If five different people used their eyes to draw what they considered to be the best straight line, five slightly different straight lines with five slightly different slopes would undoubtedly result. Clearly, visual fitting of data to a straight line is not entirely satisfactory.

An Analysis by Linear Regression:

c (M)	**A**	**cA (M)**	**c^2 (M^2)**
0.0120	0.681	0.0081720	0.0001440
0.00960	0.540	0.0051840	0.0000922
0.00720	0.389	0.0028008	0.0000518
0.00480	0.270	0.0012960	0.0000230
0.00240	0.133	0.0003192	0.0000058
		Sum = 0.0177720	Sum = 0.0003168

$$k = \frac{\sum cA}{\sum c^2} = \frac{0.0177720\ \ M}{0.0003168\ \ M^2} = 56.1\ \ M^{-1}$$

Fortunately, linear regression analysis (also called the method of least squares) provides the means to find an entirely reproducible straight line. If five people treat the data in the third data table by this method, the results will be the same straight line.

To begin, we know that the best straight line must pass through the origin. Although this constraint is not necessary, it simplifies the arithmetic and lessens the tedium of the calculations. The equation for this line will be y = mx, and the slope m will be given by

$$m = \frac{\sum xy}{\sum x^2}$$

The quantity $\sum xy$ in the numerator is the sum of the products of each x and y, and the $\sum x^2$ in the denominator is the sum of the squares of each x. In terms of the equation for Beer's Law, k becomes $k = \frac{\sum cA}{\sum c^2}$

The data in the third data table are subjected to linear regression analysis in table above. Note that k obtained in this manner differs slightly from the one derived from a visually fitted straight line. As a result, the best procedure is to use linear regression to calculate the slope and then to draw a straight line with that slope.

How to Use Your Spectrophotometer:

Basic Operation

Simple Operation Instructions are also printed on the front panel of the spectrophotometer.

Sample Preparation and Analysis

A. Spectrophotometer Warm-up

1. Turn on the spectrophotometer by turning on the Power Switch (located on the rear panel). Allow 15 minutes for the instrument to warm up. To skip warm-up, press the 0 Abs/100%T button.
2. Select the desired wavelength by turning the Wavelength control knob.

B. Sample Preparation

3. Make a blank reference solution by filling a clean cuvet half full with distilled/deionized water or other specified solvent. Wipe the cuvet with tissue to remove the fingerprints or droplets of liquid.
4. Insert the blank cuvet into the Sample Compartment. Close the lid.
5. Set 0A or 100%T with the 0A/100%T button.
6. Remove the blank cuvet. Set it aside in case the 0A/100%T will need to be adjusted again (e.g., change the wavelength).

C. Sample Analysis

7. Rinse a second cuvet with a small amount of the sample solution to be tested. Fill the cuvet half full and wipe the exterior of the cuvet clean with tissue.
8. Put the sample cuvet in the Sample Compartment. Close the lid.
9. Read the %T or A from the Digital Display window. Remove the sample cuvet or test tube.
10. If the same sample is to be tested at other wavelengths, repeat steps 2 to 9 for each wavelength.
11. For each new sample analyzed, repeat steps 2 to 10.

To Make the Standard Curve:

1. Repeat steps 4 – 9 at different wavelengths. A common standard curve might have readings taken every 20 nanometers from 340 to 900 nanometers. Graph wavelength versus absorbance to determine at which wavelength the solution absorbs the strongest.

Features and Components

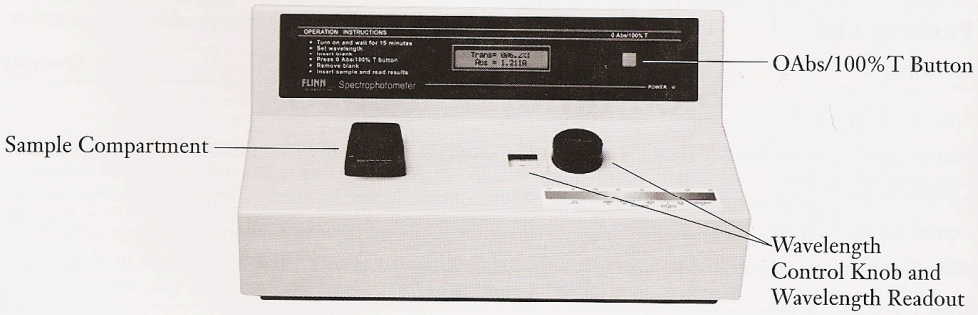


Figure 2. Flinn Scientific Spectrophotometer

Flinn Scientific Spectrophotometer Operation Panel

0A/100%T Button

Adjusts Digital Display reading to 100%T or 0.000A when blank reference solution is in Sample Compartment.

Sample Compartment

Accepts 10 mm cuvet or 10 mm square cuvet (the square cuvet adapter is required).

Wavelength (Wavelength Control) Knob

Selects the desired wavelength in nanometers (nm).

Wavelength Readout Window

Displays desired wavelength.