EXPERIMENT

10

Spectra and Beer's Law

INTRODUCTION

One way to determine the identity and concentration of a compound in solution is to observe its color and the intensity of its color. This technique is called colorimetry. For example, compound A gives a blue solution, compound B a pink one. Information about the concentration of the species in solution is obtained by observing the intensity of the color of the solution which is directly related to the concentration of the species in solution. Simple colorimetric measurements may be made with the unaided eye which is very sensitive to both colors and intensity of colors.

If only very small color changes are involved, or if more than one colored species are present in solution, a more accurate way to measure color and intensity is necessary. Such a method is called spectrophotometry. Before describing this method, some facts about light will be reviewed.

Light or electromagnetic radiation can be classified in several ways. Because of its wave nature it is most convenient to refer to the wavelength and frequency of the radiation. Radiation falling within various frequency (or wavelength) regions are particularly designated: ultraviolet, visible, infra-red, etc. The visible region encompasses those wavelengths which are visible to the eye, from about 400 nm to 750 nm. White light is a mixture of all the wavelengths in the visible region. When white light is passed through a prism or diffraction grating it is resolved into its component wavelengths and the resulting pattern is called a spectrum. The visible spectrum consists of all of the colors of the rainbow from violet to red. Each color, as we observe it, consists of a range or band of wavelengths; the red region, for example, extends from about 650 nm to 700 nm. A high quality prism or grating can resolve white light into narrow wavelength bands.

When white light is directed at a colored solution, some of the components of the white light are not transmitted through the solution. They have been absorbed by the solution. The frequencies (or wavelengths) of white light which are transmitted through the solution gives the observed color to the solution (Figure 8-1). The amount of light which is absorbed by a substance in solution is a function of the concentration of the substance in the solution. In order to do quantitative work using spectrophotometry, the light which has been absorbed by the solution must be measured. Sensitive measurements of the color and intensity of light which has been absorbed may be made with a spectrophotometer (*spectro*-many colors, *photo*-light, *meter*-measure).

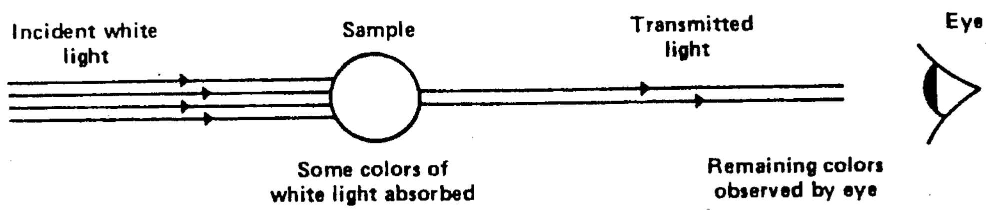

Figure 8-1. Schematic illustration of light absorption.

The spectrophotometer separates light into its component wavelengths, isolates a selected wavelength band, directs this band through a solution and measures the amount of light absorbed. The absorption at various wavelengths can then be recorded.

A plot of the absorbance of a solution versus wavelength of incident light is called an absorption spectrum. Because most compounds have a unique spectrum, determining the spectrum is also a precise way of identifying a compound in solution. The spectrum of a compound resembles a "fingerprint."

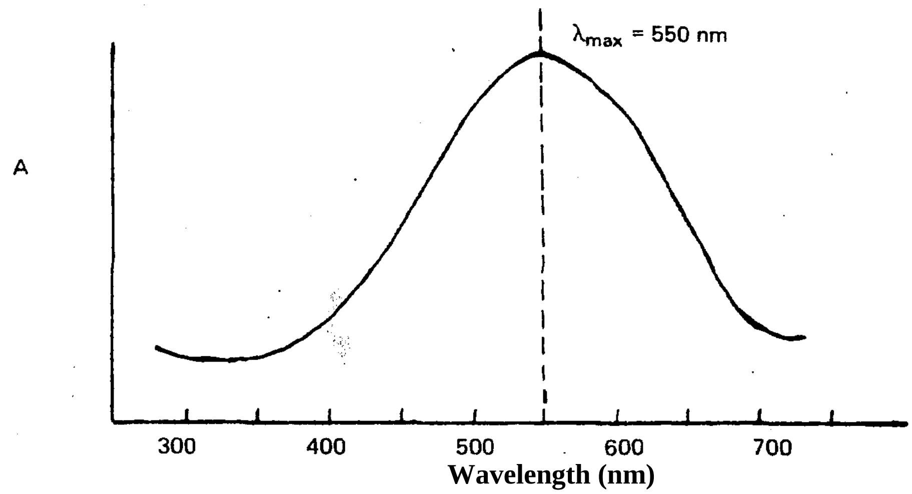

Figure 8-2. A Typical Absorption Spectrum

Quantitative information about the concentration of compounds in solution can be obtained because it is found that the absorbance of a solution is proportional to the molar concentration of the solution and the path length through which the light travels. This may be expressed as

$$A = \varepsilon\, l\, c \qquad (1)$$

where

A = absorbance

c = molar concentration (moles/liter)

l = path length (in this experiment = 1 cm)

ε = a proportionality constant called the *molar absorption coefficient* which depends on the material being studied.

The expression is known as the Beer-Lambert Law. It has the mathematical form of a straight line, $y = mx + b$, where $y = A$, $x = c$, $m = \varepsilon l$ and $b = 0$. A plot of absorbance, A, versus concentration, c, should result in a straight line. Such a graph is called a Beer's Law plot (Figure 8.3). The usual method of employing Beer's Law is to measure the absorbances of various concentrations of a compound at the wavelength at which the absorption of that compound is a maximum.

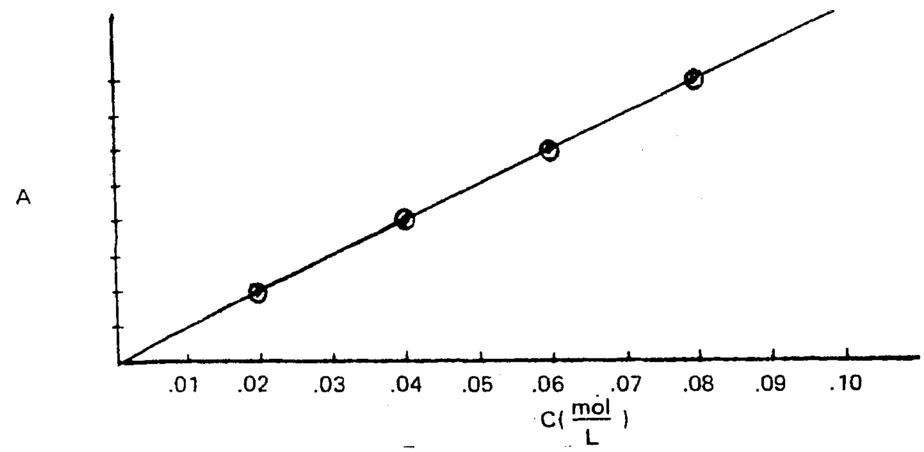

Figure 8-3. A Typical Beer's Law Plot

In this experiment, the absorption spectrum (absorbance vs. wavelength) of a complex ion of copper, $Cu(NH_3)_4^{2+}$, is determined. The complex ion is prepared by adding an excess of NH_3 to a solution containing Cu.

$$Cu^{2+} + 4\ NH_3 \rightarrow Cu(NH_3)_4^{2+} \qquad (2)$$

A Beer's Law plot (absorbance vs. concentration) for $Cu(NH_3)_4^{2+}$ at the wavelength where the complex ion has a maximum absorbance is then constructed.

In order to construct the Beer's Law plot it is necessary to calculate the concentration of the $Cu(NH_3)_4^{2+}$ in each of the prepared solutions. The concentration unit used is molarity, M, which is defined as the number of moles of solute (n) per liter of solution (V).

$$M = \frac{n}{V} \qquad (3)$$

Equation (3) can be rewritten

$$n = M\ V \qquad (4)$$

A sample of the Cu^{2+} solution of volume V_1 and molarity M_1 contains $M_1\ V_1$ moles of Cu^{2+}.

$$n_{Cu_{2+}} = M_1\ V_1 \qquad (5)$$

If excess NH_3 is added to the Cu^{2+} solution, all of the Cu^{2+} reacts with the added NH_3 according to equation (2), and the moles of Cu^{2+} equals the moles of $Cu(NH_3)_4^{2+}$

$$n_{Cu^{2+}} = n_{Cu(NH_3)_4^{2+}} \qquad (6)$$

The molarity of $Cu(NH_3)_4^{2+}$ in the final solution, M_2, is equal to the moles of $Cu(NH_3)_4^{2+}$ in the final solution divided by the total volume of the final solution, V_2

$$M_2 = \frac{n_{Cu(NH_3)_4^{2+}}}{V_2} \qquad (7)$$

Finally, the molarity, in moles/liter, of a solution of $Cu(NH_3)_4^{2+}$ of unknown concentration will be determined using the Beer's Law plot.

PROCEDURE

I. Operating Instructions for the Spectrophotometer

1. Flip the power switch (in the back) on to turn on the instrument. The pilot lamp will light. Allow five minutes warm up time. At this point, go on to part II below: The Spectrum of $Cu(NH_3)_4^{2+}$

GENERAL INSTRUCTIONS for making absorbance measurements:

2. Set the wavelength to the desired value.
3. Fill a cuvette 3/4 full with distilled water. Wipe the cuvette with a kimwipe to remove any fingerprints or spilled solution. Insert the tube in the sample compartment. Line up the marking on the tube with the marking on the instrument. Close the cover and blank the instrument.
5. Fill a second cuvette with your sample; clean the tube and place it in the sample compartment.
6. Record the absorbance value.
7. Every time the wavelength is changed, repeat steps 2-6.

II. The Spectrum of $Cu(NH_3)_4^{2+}$

1. Obtain two 50mL burets from the stockroom.
2. Fill one buret with 2.5M NH_3 , and the second with 0. 1M $CuSO_4$ solution.
3. Place 10 mL of the stock 0.1M $CuSO_4$ solution into a 50mL graduated cylinder. Add 5mL 2.5M NH, from the buret, and fill the graduated cylinder to 50mL with distilled water. Mix the solution thoroughly by pouring it into a beaker and stirring it well.
4. Set the wavelength to 420 nm. Fill a cuvette with distilled water. Blank the instrument as described above in part I under General Instructions.
5. Measure and record the absorbance of the $Cu(NH_3)_4^{2+}$ solution at 420 nm.
6. Remove the $Cu(NH_3)_4^{2+}$ solution from the spectrophotometer.
7. Set the wavelength at 430 nm. Blank the instrument as before, with distilled water.
8. Measure and record the absorbance of the $Cu(NH_3)_4^{2+}$ solution.
9. Repeat steps 6 to 8 at 10 nm intervals to 650 nm.
10. Plot the absorption spectrum of $Cu(NH_3)_4^{2+}$ and determine λ_{max} for $Cu(NH_3)_4^{2+}$.

III. Beer's Law Plot

11. Using the burets, measure 1mL 0.1M $CuSO_4$ and 5mL 2.5M NH_3 into a 50mL graduated cylinder. Bring the volume to 50mL with distilled water. Pour the solution into a beaker and stir thoroughly.
12. Place the solution in a cuvette. Measure and record the absorbance at 600 nm. (Make sure the instrument is standardized before taking the reading.)
13. You will be making a total of 10 solutions, varying the quantity of $CuSO_4$ in each, and measuring the absorbance of each solution. To do this, repeat the procedure in steps 11–12 using 2 mL of 0. 1 M $CuSO_4$ solution, 5mL of 2.5M NH_3 solution, and enough water to make a total of 50mL of solution. For the following solutions, use 3, 4, 5, 6, 7, 8, 9, and 10 mL of 0. 1 M $CuSO_4$ and 5 mL of NH_3, and bring the total volume up to 50 mL with water. (See the data table for the amounts of $CuSO_4$and NH_3 in each solution.)
14. Measure and record the absorbance of each solution. Observe the change in intensity of color as the solutions become more concentrated.
15. Construct a Beer's Law Plot from the data and calculate ε 1 for $Cu(NH_3)_4^{2+}$.

IV. Determination of an Unknown Solution

16. Obtain a solution of $Cu(NH_3)_4^{2+}$of unknown molarity from the instructor.
17. Place the unknown solution in a cuvette, measure and record the absorbance of the unknown solution at 600 nm. Make sure the instrument is blanked before taking the reading.
18. Using the Beer's Law plot constructed in step 14, determine the molarity of the unknown $Cu(NH_3)_4^{2+}$ solution to the appropriate significant figures.

SPECTRA AND BEER'S LAW

Name________________________________

Unknown Number:_______________________

DATA

Spectrum of $Cu(NH_3)_4^{2+}$

λ	A	λ	A	λ	A
420		500		580	
430		510		590	
440		520		600	
450		530		610	
460		540		620	
470		550		630	
480		560		640	
490		570		650	

Beer's Law

ml 0.1 M $CuSO_4$	moles $CuSO_4$	ml 2.5M NH_3	moles NH_3	moles $Cu(NH_3)_4^{2+}$ formed	conc $Cu(NH_3)_4^{2+}$	conc $Cu(NH_3)_4^{2+}$ x 10^2	A
1		5					
2		5					
3		5					
4		5					
5		5					
6		5					
7		5					
8		5					
9		5					
10		5					

Unknown

Absorbance of unknown $Cu(NH_3)_4^{2+}$: ______________________

RESULTS

λ_{max} for $Cu(NH_3)_4^{2+}$	
εl for $Cu(NH_3)_4^{2+}$	
Molarity of Unknown $Cu(NH_3)_4^{2+}$ solution	

Calculation of εl: (slope of graph; but remember that the x-axis is labeled Concentration $\times 10^2$)

Calculation of molarity of unknown $Cu(NH_3)_4^{2+}$ solution (using your value for εl in the Beer-Lambert law, equation (1) above):

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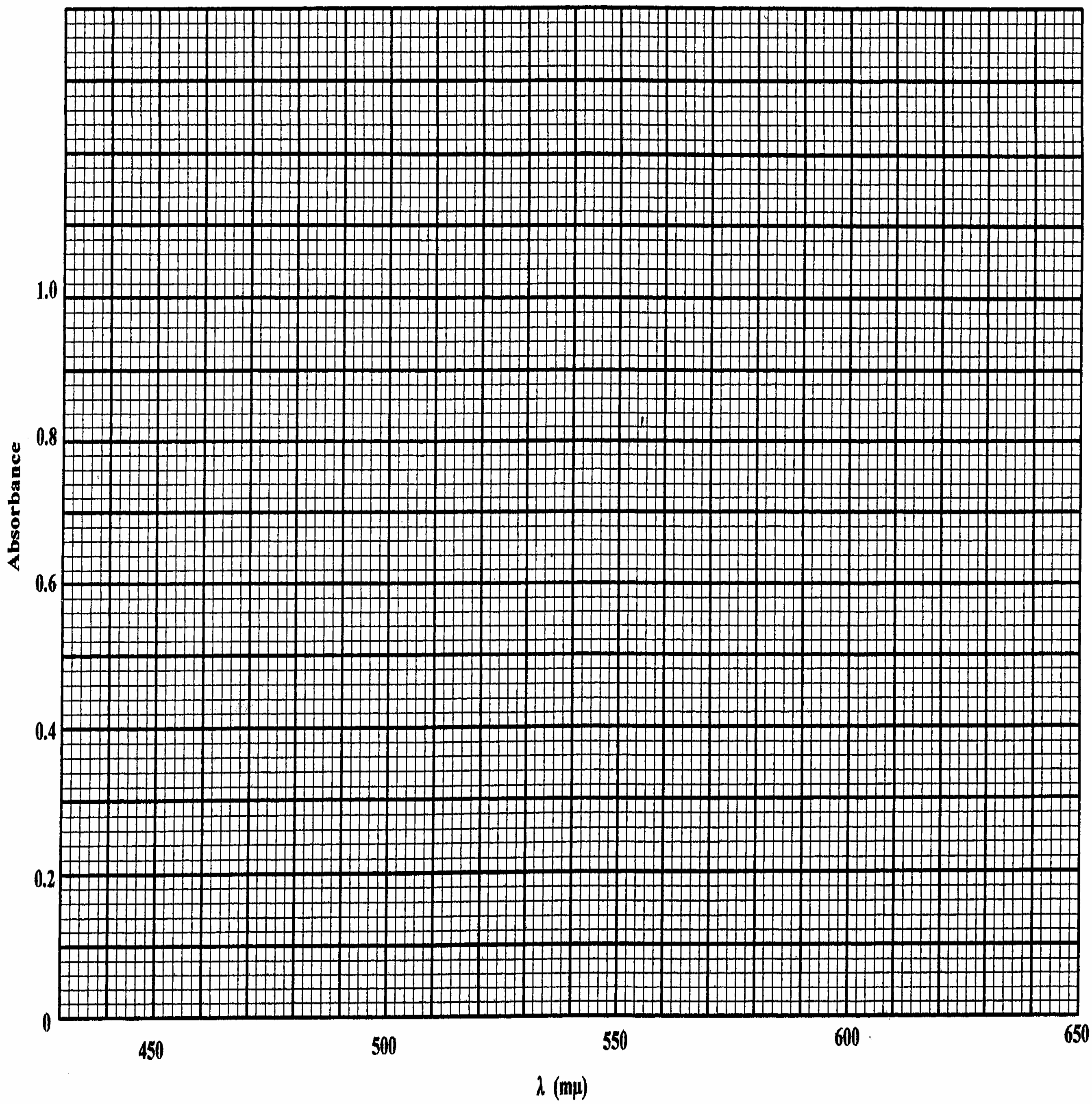

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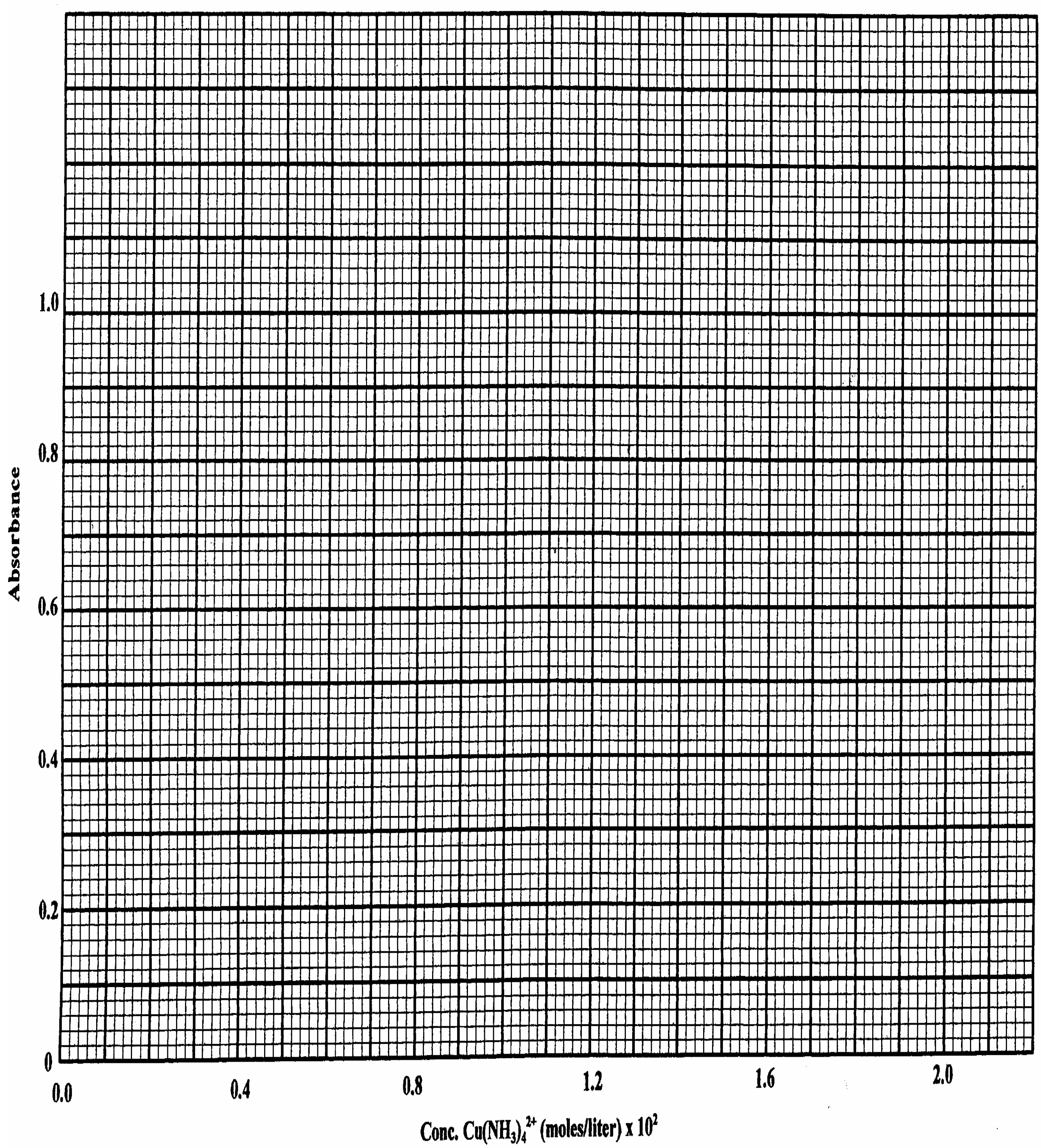
Absorbance
1.0
0.8
0.6
0.4
0.2
0
0.0
0.4
0.8
1.2
1.6
2.0
Conc. Cu(NH3)4 2+ (moles/liter) x 10 2