Experiment 10

QUANTITATIVE ANALYSIS OF COBALT(II) IONS

Objective

The purpose of this experiment is to determine trace amounts of cobalt(II) ions by quantitative spectroscopic analysis of $[Co(SCN)_4]^{2-}$ complex ions.

Lab techniques

- Preparing a serial dilution concentration of standard solutions
- Operating a volumetric flask, a graduated pipet, and the spectrophotometer

Introduction

I. Beer's Law:

In chemistry, we often use the characteristics of colored substances that absorb light and Beer's law for quantitative analysis. A beam of monochromatic radiation with intensity P_0 travels perpendicularly through a rectangular block of matter (either solid, liquid, or gas) having an optical path length b. After the light is absorbed by the matter, its intensity reduces from P_0 to P (Fig. 10-1).

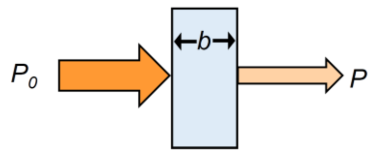

Figure 10-1 An illustration of monochromatic radiation absorption

The ratio P/P_0, called the transmittance (T), is a measure of the fraction of light that passes through the sample (10-1):

$$T = P/P_0 \tag{10-1}$$

The amount of light absorbed is given by the absorbance (A, 10-2), where

$$A = -\log T = -\log(P/P_0) = \log(P_0/P) \tag{10-2}$$

Beer's law (10-3) relates the amount of light being absorbed to the concentration of the substance absorbing the light:

$$A = \varepsilon \cdot b \cdot c \tag{10-3}$$

where ε is the molar absorptivity constant in $cm^{-1}\cdot M^{-1}$ (a characteristic of the substance being monitored), b is the optical path length traveled through the sample in cm, and c is molar concentration in M. Beer's law is a limiting law that describes the absorption behavior of dilute solution ($A < 1$) only. We can measure the absorbance of a series of standard solutions (known concentrations) at a specific wavelength and then plot the absorbance against sample concentrations to obtain a calibration curve. By experimentally measuring the absorbance of a sample solution, we can determine its concentration by using the calibration curve (Fig. 10-2)

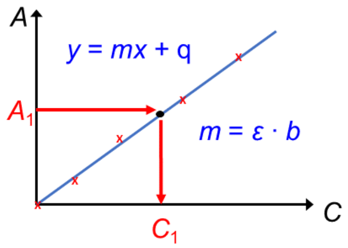

Figure 2 Calibration curve of standard solutions

II. Quantitative spectroscopic analysis of cobalt(II) ions

For quantitative analysis of metal ions, reagents are usually added to form a colored complex with the metal ions, and then analyzed using a spectrophotometer and Beer's law. For the light absorption by general substances, the interference in the ultraviolet region is greater than that in the visible region (400~700 nm). Hence, complexes that have stronger absorption in the visible region are favorable, such as the blue cobalt complex, $[Co(SCN)_4]^{2-}$ (10-4).

$$Co^{2+}(aq) + 4\ SCN^{-}(aq) \rightleftharpoons [Co(SCN)_4]^{2-}(aq) \qquad (10\text{-}4)$$

Referring to the absorption spectrum of $[Co(SCN)_4]^{2-}$, the solution has the strongest absorbance at 620 nm (orange light; Fig. 10-3) and thus appears blue (the complementary color of orange). Dilution of this complex solution with water results in dissociation of $[Co(SCN)_4]^{2-}$ to $[Co(SCN)]^{+}$, which is light pink; this causes errors in subsequent analysis. To prevent dissociation of the cobalt complex, an organic solvent that is miscible with water and has a lower dielectric constant(2) such as acetone is added to the solution. Since the solution's acidity may affect the absorption of the complex, hydrochloric acid is added to maintain the pH of the solution. In the experiment, we add KSCN(aq), hydrochloric acid, and acetone to the solution containing a trace amount of Co(II) ions to obtain stable complex ions, $[Co(SCN)_4]^{2-}$. The complex ions show large molar absorptivity (*ca.* $1.9 \times 10^3\ cm^{-1}\cdot M^{-1}$) at the analytic wavelength of 620 nm. Therefore we use this spectrochemical method to analyze the concentration of Co(II) accurately.

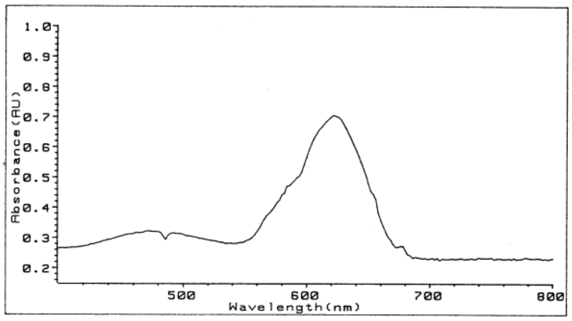

Figure 10-3 Absorption spectrum of $[Co(SCN)_4]^{2-}$

Apparatus

Spectrophotometer (type: SP-830 Plus/SH-U830(S)), cuvette, volumetric flask (10 mL), graduated pipet (2 mL), Erlenmeyer flask (50 mL, 6), cork stopper (6), beaker (100 mL, 2), pipet filler, lens tissue, and NBR gloves.

Chemicals

Acetone, CH_3COCH_3

6 *M* Hydrochloric acid, HCl(aq)

50% Potassium thiocyanate, KSCN

Cobalt(II) sulfate heptahydrate, $CoSO_4·7H_2O$ (used to prepare 0.10 mg/mL standard and unknown concentration cobalt(II) solutions)

Procedure

<table>
<tr><th colspan="2">Procedure</th><th>Illustration</th></tr>
<tr><td colspan="3">I. Preparation of standard sample solutions of $[Co(SCN)_4]^{2-}$</td></tr>
<tr><td>1.</td><td>Wash and oven-dry six 50 mL Erlenmeyer flasks and a test tube; allow them to cool to room temperature.</td><td></td></tr>
<tr><td>2.</td><td>Take ca. 8 mL of 0.10 mg/mL standard cobalt(II) solution using a test tube.

Note: Refer to Table 10-1 to prepare blank and standard sample solutions.</td><td>
<table>
<tr><th>Sample no.</th><th>0.10 mg/mL Co^{2+} (mL)</th><th>6 M HCl (mL)</th><th>50% KSCN (mL)</th><th>Acetone (mL)</th><th>DI water</th></tr>
<tr><td>1</td><td>0</td><td rowspan="6">0.8</td><td rowspan="6">2.0</td><td rowspan="6">4.8</td><td rowspan="6">Add to 10 mL mark</td></tr>
<tr><td>2</td><td>0.50</td></tr>
<tr><td>3</td><td>1.00</td></tr>
<tr><td>4</td><td>1.50</td></tr>
<tr><td>5</td><td>2.00</td></tr>
<tr><td>Unknown</td><td>X ($0.50 \le X \le 2.00$)</td></tr>
</table>
</td></tr>
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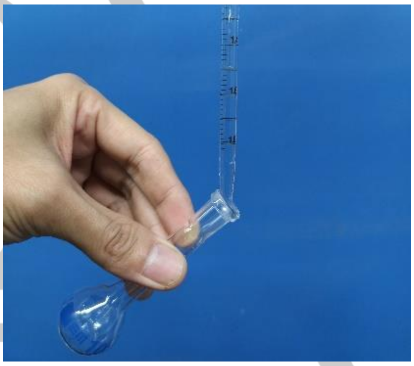
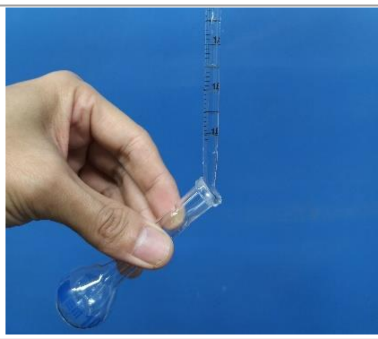
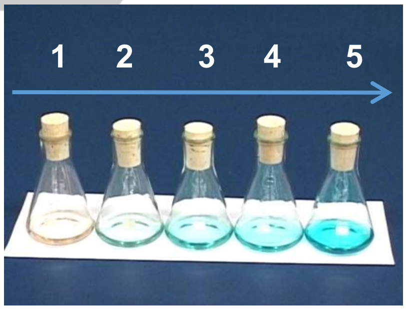
3.	(1) Measure and transfer exactly 0.8 mL of 6 *M* HCl, 2.0 mL of 50% KSCN, and 4.8 mL of acetone into a 10 mL volumetric flask. Dilute it with DI water up to the 10 mL mark and stopper the flask. Pressing the stopper firmly, invert the flask several times to ensure complete mixing of the solution. (2) Pour this blank solution into a clean Erlenmeyer flask. Stopper the flask with a cork to prevent evaporation of acetone.	 
4.	(1) Wash and rinse the volumetric flask with DI water. (2) Use a 2 mL graduated pipet to transfer exactly 0.50 mL of standard cobalt(II) solution to the volumetric flask. Add 0.8 mL of 6 *M* HCl, 2.0 mL of 50% KSCN, and 4.8 mL of acetone. Dilute with DI water up to the 10 mL mark and stopper the flask. Mix the solution thoroughly to obtain a clear, transparent blue solution. (3) Transfer the solution into a clean Erlenmeyer flask. Stopper the flask and set aside. Note: The prepared sample solutions should be transparent and clear blue without precipitate.	  
5.	Repeat step 4, using 1.0, 1.5, and 2.0 mL of standard cobalt(II) solution separately to prepare a series of $[Co(SCN)_4]^{2-}$ standard sample solutions.	
6.	Measure a suitable amount of the unknown concentration cobalt(II) solution (within 0.50~2.00 mL) into a volumetric flask. Follow step 4 to prepare the unknown concentration sample solution.	

II. Calibration curve and spectrophotometric analysis

7.	(1) Turn on the spectrophotometer and allow it to warm up for at least 15 minutes. (2) Prepare 2 lens tissues and 1 photometric cuvette.	
8.	**Zero set** (1) Press the "A/T/C" button and set it to A (Absorbance mode). (2) Set the analytical wavelength (*i.e.* 620 nm). (3) Press the "BLANK" button to zero the absorbance reading.	
9.	**Blank adjustment** (1) Use a dropper to take a small amount of the blank solution to rinse one cuvette twice, then fill it with the blank solution to about 1/3 the height of the cuvette. (2) Wipe the outer wall of the cuvette with a lens tissue. Place the cuvette in the cuvette holder and align its white mark to the mark on the holder to fix the light path. Close the lid. (3) Press the "BLANK" button for blank adjustment. The absorbance reading should be "0.000".	 Transfer soln  Align the mark
10.	**Absorbance measurement** (1) Start measuring the standard sample solutions from low to high concentrations; then the unknown concentration sample. (2) Rinse the cuvette twice with the sample solution; then add the solution to about 1/3 the height of the cuvette. (3) Wipe the cuvette with a lens tissue, place it in the cuvette holder, and align the marks. Close the lid and read the "Absorbance". Note: If the absorbance of the unknown sample solution is not in the range of the calibration curve, reduce or increase its amount	

11.	The liquid waste contains heavy metal ions and organic solvents. Dispose of it into the designated waste container.	
12.	(1) After finishing the experiment, return the cuvette to the lab instructor. Turn off and cover the spectrophotometer.	

Table 10-1 Preparation of standard $[Co(SCN)_4]^{2-}$ sample solutions

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<tr><th>Sample No.</th><th>0.10 mg/mL Co^{2+} (mL)</th><th>6 M HCl (mL)</th><th>50% KSCN (mL)</th><th>Acetone (mL)</th><th>DI water</th></tr>
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References

1. Marczenko, Z. *Separation and Spectrophotometric Determination of Elements*; John Wiley & Sons: New York, 1985.
2. Skoog, D. A.; West, D. M.; Holler, F. J. *Fundamentals of Analytical Chemistry*; 5th ed., Saunders College Publishing: Chicago, 1988.