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 concentration of standard solutions.
- Operating a volumetric flask, graduated pipet, and spectrophotometer.

Introduction

I. Beer's Law:

A beam of monochromatic radiation with intensity P_o 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 particles, its intensity is reduced from P_o to P (Fig. 10-1).

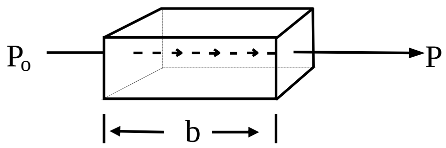


Figure 10-1 An illustration of monochromatic radiation absorption

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

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

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

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

Beer's law 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 (a characteristic of the substance being monitored), b is the optical path length traveled through the sample, and c is molar concentration. Beer's law is a limiting law which describes the absorption behavior of dilute solution (< 0.01 M) only.

When the molar absorptivity and path length are known for a solution sample, we can calculate its molarity by analyzing its absorbance at a specific wavelength. Alternatively, 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.

II. Quantitative spectroscopic analysis of cobalt ions

Reagents that form colored complexes with metal cations are commonly used for quantitative analysis of metal cations by employing a spectrophotometric method. For a solution containing many substances, quantitative results are usually poorer in the UV region than those in the visible region (400-700 nm), mainly because of greater interference (due to the absorbance of carriers, impurities etc.) in the UV region. Hence, complexes that have stronger absorption in visible region are favorable, such as blue cobalt complex, $[Co(SCN)_4]^{2-}$:

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

Since the solution has the strongest absorbance at 620 nm (orange light; refer to Fig. 10-2), it appears blue. The molar absorptivity of $[Co(SCN)_4]^{2-}$ is 1.9×10^3 $cm^{-1}\cdot M^{-1}$ at 620 nm when the solution contains 50% acetone, 10% KSCN, and 0.48 M hydrochloric acid. Dilution of this complex solution with water results in dissociation of $[Co(SCN)_4]^{2-}$ to $[Co(SCN)]^{+}$, which is light pink in color; 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 complexes are stable at low pH values, hydrochloric acid is also added.

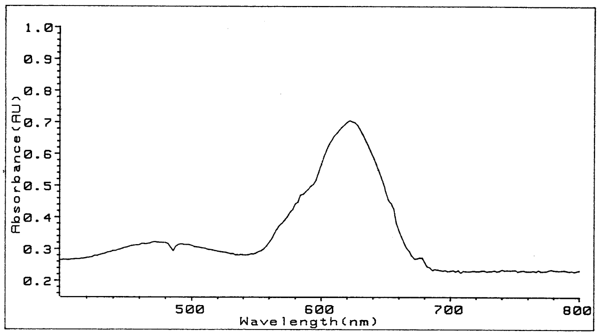


Figure 10-2 Absorption spectrum of $[Co(SCN)_4]^{2-}$

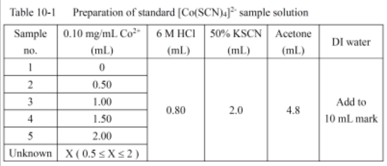
Apparatus

Volumetric flask (10 mL), graduated pipet (2 mL), Erlenmeyer flask (50 mL, 6), cork stoppers (6), pipet filler, spectrophotometer (SP-830 Plus/SH-U830(S)), cuvettes, lens cloth, and latex glove.

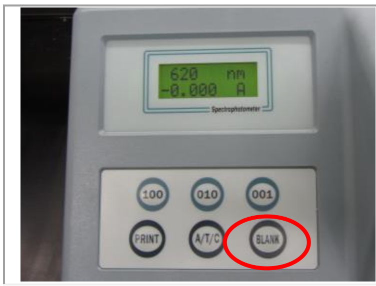
Chemicals

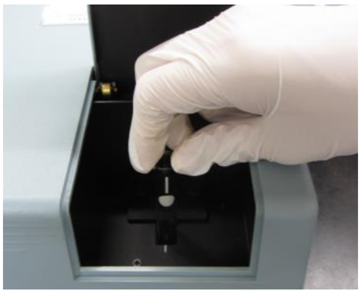
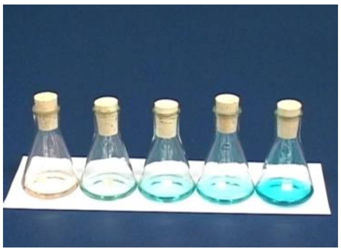
Acetone, CH_3COCH_3
50% Potassium thiocyanate, KSCN
0.10 mg/mL Standard cobalt(II) solution, cobalt(II) sulfate, $CoSO_4$
6 M Hydrochloric acid, HCl(aq)
Unknown cobalt(II) solution

Procedure

<table>
<tr><th colspan="2">Procedure</th><th>Illustration</th></tr>
<tr><td colspan="3">I. Preparation of standard solution 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 cobalt(II) standard solution with test tube.
Note: Refer to Table 10-1 to prepare blank and standard sample solution.</td><td>
Table 10-1 Preparation of standard $[Co(SCN)_4]^{2-}$ sample solution
<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">0.80</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 ($0.5 \le X \le 2$)</td></tr>
</table></td></tr>
<tr><td>3.</td><td>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 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. Pour this blank solution into a clean Erlenmeyer flask. Stopper the flask with a cork to prevent evaporation of acetone.

Note: Refer to the experiment skills videos to learn how to use a volumetric flask.</td><td></td></tr>
</table>

4.	Wash and rinse the volumetric flask with DI water. Use a 2 mL graduated pipet to transfer 0.50 mL of standard cobalt(II) solution to 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 10.0 mL mark and stopper the flask. Mix the solution thoroughly to obtain a clear, transparent blue solution. Transfer the solution into a clean Erlenmeyer flask. Stopper the flask and set aside. Note: Refer to the experiment skills videos to learn how to use a graduated pipet.	 Blank  Sample
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 cobalt(II) solution (within 0.5~2 mL) into a volumetric flask. Follow step 4 to prepare an unknown sample solution.	
II. Spectrophotometric analysis		
7.	Turn on the spectrophotometer and allow it to warm up for at least 20 minutes. Note: Refer to the experiment skills videos to learn how to operate a spectrophotometer.	
8.	**Zero set** (1) Press Mode key “A/T/C” and set to A (Absorbance). (2) Set the analytical wavelength (i.e. 620 nm). (3) Press “BLANK” key to zero set.	

9.	**Blank adjustment** (1) Rinse the cuvette twice with blank solution; then add solution to 1/2 height of cuvette. (2) Wipe the cuvette with lens cloth. (3) Place cuvette in cuvette holder and align in same direction to control the path of the light. (4) Close lid and press “BLANK” to adjust blank.	
10.	**Absorbance measurement** (1) Start testing standard sample solution from low concentration to high; then the unknown sample. (2) Rinse the cuvette twice with sample solution; then add solution to 1/2 height of cuvette (3) Wipe cuvette with lens cloth and place in cuvette holder. (4) Close 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 the amount of the unknown solution and follow step 4 to prepare another test sample solution.	 
11.	(1) After finishing the experiment, hand out the cuvette to lab instructor. Do not leave the cuvette in the spectrophotometer. Turn off and cover the spectrophotometer. (2) The liquid waste contains heavy metal ions and organic solvent. Dispose it into the designated waste container.	

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.

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

Sample no.	0.10 mg/mL Co^{2+} (mL)	6 M HCl (mL)	50% KSCN (mL)	Acetone (mL)	DI water
1	0	0.80	2.0	4.8	Add to 10 mL mark
2	0.50				
3	1.00				
4	1.50				
5	2.00				
Unknown	X (0.5 ≤ X ≤ 2)				