Experiment 10: Quantitative determination of trace cobalt ions

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2026.04.14

I. Objective

The objective of this experiment is to determine the trace amount of cobalt(II) ions in a compound by means of spectroscopic analysis and complexation reactions using thiocyanate.

II. Technique

In this experiment, the use of volumetric flasks, pipettes, and a spectrophotometer, as well as techniques such as serial dilution, will be introduced and practiced.

III. Introduction

(i) Beer's law

Quantitative analysis in chemistry often makes use of the light-absorbing properties of colored substances and Beer's law. Consider a beam of parallel radiation with radiant power P_0 incident perpendicularly on the surface of a rectangular sample (solid, liquid, or gas). After passing through a path length b, the radiant power is reduced to P due to absorption by the sample, as shown in Figure 10-1.

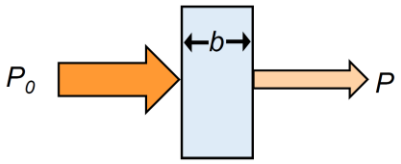


Figure 10-1. Schematic diagram of the absorption of radiant energy by a substance.

The ratio of the radiant power P transmitted through the sample to the incident radiant power P_0 is defined as the transmittance, T (Equation 10–1):

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

Absorbance, A, is further defined as (Equation 10–2):

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

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

Equation 10-3 is known as Beer's law, which states that the absorbance of a dissolved substance is directly proportional to its concentration and the path length of the light passing through the absorbing medium. In this equation, ε is the molar absorptivity (unit: $cm^{-1}M^{-1}$); b is the path length of the light through the cuvette (unit: cm); and c is the concentration (unit: M). This law is applicable only within the low concentration range ($A < 1$). A series of standard solutions with known concentrations is prepared, and their absorbance at the analytical wavelength is measured using a spectrophotometer. A calibration curve is then constructed by plotting absorbance versus concentration. Subsequently, the absorbance of an unknown sample is measured, and its concentration can be determined from the calibration curve, as shown in Figure 10–2.

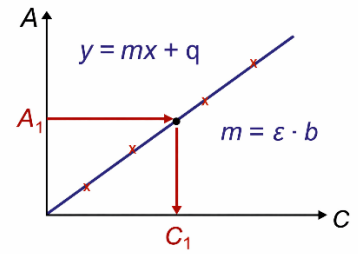


Figure 10-2. Calibration curve of standard solutions.

(ii) Spectrophotometric determination of cobalt ions

For the quantitative determination of metal ions, a reagent is often first added to form a colored complex with the metal ion. The concentration can then be determined based on the proportional relationship between the absorbance of the complex at a specific wavelength and its concentration. In general, light absorption by substances is subject to more interference in the ultraviolet region than in the visible region (400–700 nm). Therefore, species that exhibit strong absorption in the visible region are commonly selected for quantitative analysis. For example, thiocyanate ions (SCN^-) react with cobalt(II) ions to form a blue complex ion, $[Co(SCN)_4]^{2-}$ (Equation 10–4):

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

The visible absorption spectrum of a solution containing the $[Co(SCN)_4]^{2-}$ complex ion is shown in Figure 10-3, with a maximum absorption wavelength at 620 nm (orange light). The solution appears blue, which is the complementary color of orange. When the sample is diluted with water, the concentration of SCN^- decreases, and the $[Co(SCN)_4]^{2-}$ complex readily dissociates. As a result, most cobalt(II) ions exist in the form of the pale pink $[CoSCN]^+$ species, making accurate quantification of Co(II) difficult.

The addition of an organic solvent with a lower dielectric constant, such as acetone or other water-miscible solvents, can suppress the dissociation of the cobalt complex. The acidity of the solution also affects the absorbance of the complex; therefore, hydrochloric acid is added to maintain a constant pH. In this experiment, $KSCN_{(aq)}$, hydrochloric acid, and acetone are added to a solution containing trace amounts of Co(II) ions to form a stable $[Co(SCN)_4]^{2-}$ complex. A wavelength of 620 nm is selected for analysis, at which the complex exhibits a high molar absorptivity (approximately 1.9×10^3 $cm^{-1} \cdot M^{-1}$), allowing accurate determination of trace cobalt ion concentrations in the solution.

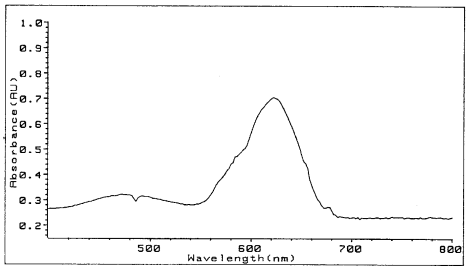


Figure 10-3. Absorption spectrum of $[Co(SCN)_4]^{2-}{}_{(aq)}$.

(ii) Complexes and Crystal Field Theory (CFT, supplementary reading)

Complexes, also known as coordination compounds, typically consist of a central metal (M) and several ligands (L). Ligands are neutral molecules with lone-pair electrons, such as ammonia (NH_3), or anions, such as chloride ions (Cl^-). The central metal can be either a cation or a neutral atom, and its coordination number may range from two to more than ten; however, four- and six-coordinate complexes are the most common. Four-coordinate complexes may adopt either a square planar or a tetrahedral geometry, whereas six-coordinate complexes are typically octahedral in shape, as shown in Figure 10–4.

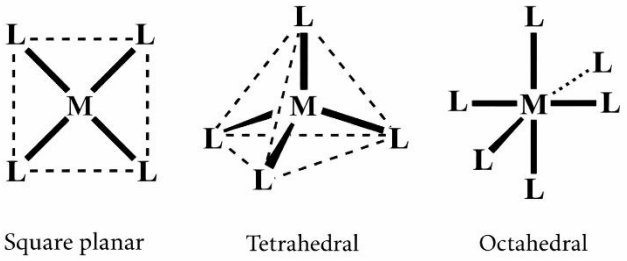


Figure 10-4. Geometries of coordination complexes.

Complexes formed by transition metal elements often exhibit different colors and magnetic properties. To explain these characteristics, several theories have been developed. Among them, crystal field theory (CFT) assumes that ligands act as point charges carrying negative charge, where the donor atoms providing electron pairs interact with the central metal through electrostatic attraction.

Transition metal ions possess five degenerate d orbitals with identical energy but different orientations. Since orbitals represent regions of high electron probability and are negatively charged, the approach of negatively charged ligands causes varying degrees of electrostatic repulsion with the metal d orbitals. As a result, the energies of the d orbitals are raised to different extents upon complex formation. Taking an octahedral complex with coordination number six as an example, the five d orbitals split into two sets of energy levels. The $d_{x^2-y^2}$ and d_{z^2} orbitals point directly toward the ligands, experience greater repulsion, and thus have higher energy. The remaining three orbitals—d_{xy}, d_{yz}, and d_{zx}—do not point directly at the ligands and therefore have lower energy, as shown in Figure 10–5. The energy difference between these two sets is called the crystal field splitting energy (Δ_o), which varies depending on the nature of the ligands and their interaction with the metal. Ligands that produce a large splitting are referred to as strong-field ligands, while those causing a small splitting are weak-field ligands. In strong-field complexes, electrons tend to occupy the lower-energy orbitals, resulting in paired electrons and a low-spin state. In contrast, in weak-field complexes, electrons follow Hund's rule and occupy degenerate orbitals with maximum unpaired spins, leading to a high-spin state.

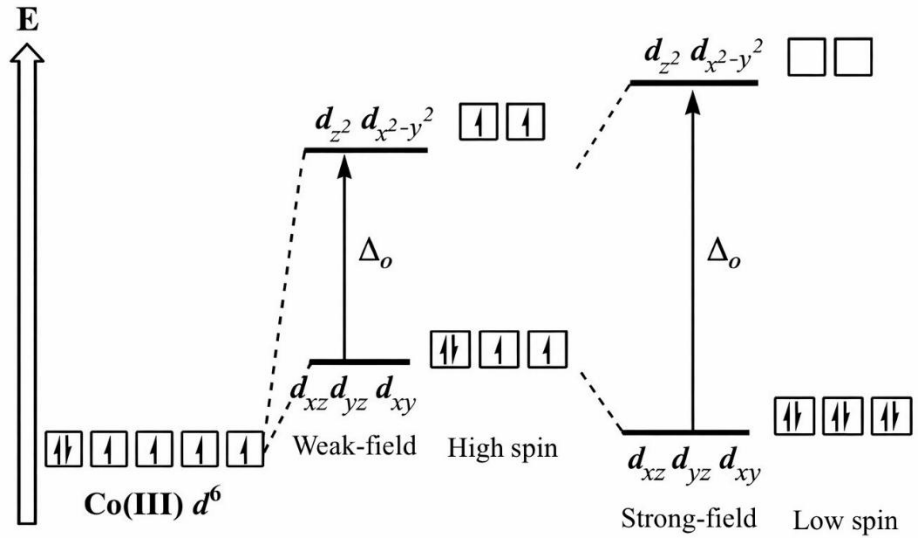


Figure 10-5. Electron configurations of weak- and strong-field octahedral crystal fields.

The d-orbital splitting energy of transition metal complexes typically falls within the visible and ultraviolet regions. Thus, electrons in lower-energy d orbitals can absorb light of appropriate wavelengths and transition to higher-energy orbitals, giving rise to the observed colors of these complexes.

From the absorption spectra of complexes, the relative crystal field strength of ligands can be determined. Weak-field ligands produce smaller splitting energies and absorb longer wavelengths, whereas strong-field ligands result in larger splitting energies and absorb shorter wavelengths. This relationship is known as the spectrochemical series, with the following order of crystal field strength:

$$I^- < Br^- < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NH_3 < en < CN^- < CO$$

Weak-field ligand
Small splitting energy

Strong-field ligand
Large splitting energy

*en: ethylenediamine, $H_2NCH_2CH_2NH_2$

Complexes containing transition metals often exhibit a variety of colors and magnetic properties—such as paramagnetism and diamagnetism—due to differences in the central metal, ligands, coordination number, or geometry, which lead to variations in d-orbital splitting energy.

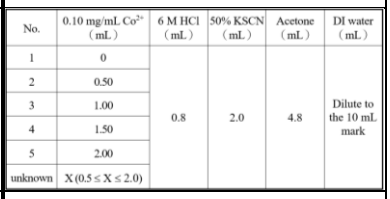
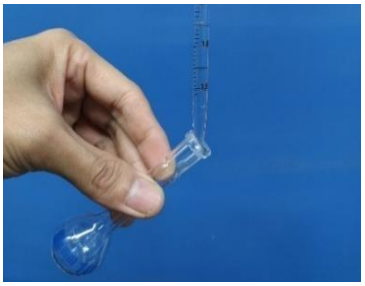
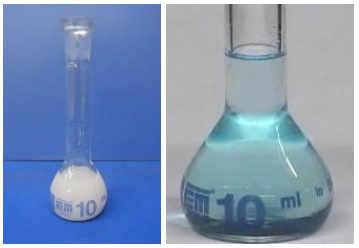
IV. Equipment

Group Equipment/Materials (in Cabinet)	**Provided by Teaching Assistant**
Pipet filler (1)	Cleaning wipes
Graduated pipet (1)	Dropper (6)
10 mL Volumetric flask (5)	Cuvette (1)
Rubber stopper (6)	Spectrophotometer (1) (one device shared by two groups)
Erlenmeyer flask (6)	

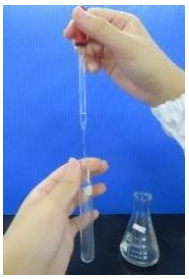
V. Chemicals

50% KSCN	Unknown Co(II) solution
6.00 M HCl	Acetone
0.10 mg/mL standard Co(II) solution	

VI. Procedure

Procedure		Figure
Preparation of standard cobalt(II) solutions ($[Co(SCN)_4]^{2-}$)		
1.	Clean and dry six 50 mL Erlenmeyer flasks and one test tube; allow them to cool before use.	
2.	Use this test tube to obtain approximately 8 mL of the standard cobalt(II) ion solution, and prepare a series of standard cobalt(II) solutions according to Table 10–1.	
3.	(1) Accurately measure 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 to the mark with deionized water, stopper the flask, hold the stopper firmly, and invert several times to ensure thorough mixing. (2) Transfer this Co(II)-free blank solution into a clean, dry Erlenmeyer flask, and stopper it with a cork to prevent acetone evaporation.	
4.	(1) Rinse the volumetric flask thoroughly with deionized water, then add 0.8 mL of 6 M HCl, 2.0 mL of 50% KSCN, and 4.8 mL of acetone into the flask. (2) Rinse a 2 mL graduated pipette 2–3 times with a small portion of the standard cobalt(II) solution, then accurately transfer 0.50 mL of the 0.10 mg/mL standard cobalt(II) solution into the volumetric flask. (3) Add deionized water to the 10 mL mark of the volumetric flask and mix thoroughly. Transfer the resulting clear, transparent blue solution (free of precipitate) into an Erlenmeyer flask and stopper it for storage. **Note:** The rinsing solution contains the heavy metal cobalt. Collect it temporarily in a beaker and dispose of it in the designated waste container after the experiment.	 

No.	0.10 mg/mL Co^{2+} (mL)	6 M HCl (mL)	50% KSCN (mL)	Acetone (mL)	DI water (mL)
1	0	0.8	2.0	4.8	Dilute to the 10 mL mark
2	0.50				
3	1.00				
4	1.50				
5	2.00				
unknown	X (0.5 ≤ X ≤ 2.0)				

5.	Repeat step 4 using standard cobalt(II) solution volumes of 1.00, 1.50, and 2.00 mL, respectively, to prepare a series of standard cobalt(II) solutions.	
6.	(1) Rinse the pipette twice with the unknown cobalt(II) solution. (2) Transfer an appropriate volume of the unknown cobalt(II) solution into a volumetric flask. Add the reagents as described in Step 4 and dilute to the 10 mL mark with deionized water. Measure its absorbance together with the previously prepared standard solutions. **Note:** The volume of the unknown solution should be between 0.50 and 2.00 mL.	
Absorbance measurement		
7.	(1) Turn on the spectrophotometer and allow it to warm up for 15 minutes. (2) Prepare two pieces of lens tissue and one cuvette.	
8.	Instrument blank calibration: Press the function key “A/T/C” until the display shows “A” (absorbance mode). Set the analytical wavelength to 620 nm, then press the “BLANK” key to perform the blank calibration.	
9.	Blank solution calibration: (1) Use a dropper to rinse the cuvette twice with approximately 1 mL of blank solution (No. 1), then fill the cuvette to about one-third of its height with the blank solution. (2) Wipe the outside of the cuvette with lens tissue, place it into the sample holder, and align the white mark on the cuvette with the reference mark on the spectrophotometer to ensure a fixed optical path. Close the sample compartment lid. (3) Press the “BLANK” key again to subtract the background of the blank solution. The absorbance reading on the display should be “0.000.”	 

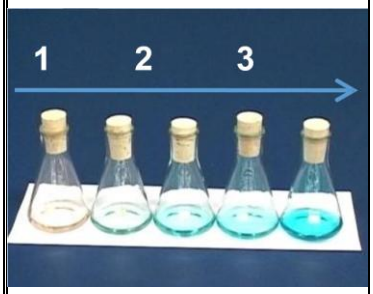
10.	(1) Pour the blank solution from the cuvette back into the original Erlenmeyer flask for storage. (2) Rinse the cuvette twice with a small amount of sample solution No. 2 using a dropper, then fill the cuvette to about one-third of its height with the sample solution and measure its absorbance. (3) Measure the absorbance of sample solutions No. 3–5 and the unknown solution in sequence. **Note:** Begin measurements with the most dilute solution, and measure the unknown solution last. If its absorbance falls outside the range of the standard solutions, adjust the sample volume and prepare it again so that the absorbance lies within the calibration curve range.	
11.	Since the waste solution contains heavy metals and organic solvents, it should be disposed of in the designated waste container after the experiment for centralized treatment.	
12.	(1) After the experiment, clean the cuvette, volumetric flask, graduated pipette, and return them to their original places. (2) Turn off the spectrophotometer and cover it with a dust cover.	

Table 10-1. Preparation of standard cobalt(II) solutions.

No.	0.10 mg/mL Co^{2+} (mL)	6 M HCl (mL)	50% KSCN (mL)	Acetone (mL)	DI water (mL)
1	0	0.8	2.0	4.8	Dilute to the 10 mL mark
2	0.50				
3	1.00				
4	1.50				
5	2.00				
unknown	X ($0.50 \leq X \leq 2.00$)				

References

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

Experiment 10: Quantitative determination of trace cobalt ions

Name: _____ **Student ID:** _____

Department: _____ **Group:** _____ **Date:** _____

I. Experimental Data (show detailed calculations)

1. **Analysis wavelength λ_{max}:** _____
2. **Standard cobalt(II) solution concentration:** _____
3. **Absorbance measurement of standard cobalt(II) solution:**

Standard Co^{2+} solution (mL)	Concentration after dilution (mg/mL)	Absorption

4. **Absorbance measurement of the unknown cobalt(II) solution:**

Unknown Co^{2+} solution number	Unknown Co^{2+} solution (mL)	Absorption

II. Experimental result

1. **Construct a calibration curve with absorbance as the y-axis and cobalt(II) ion concentration as the x-axis**
   Note: MS-Excel may be used for plotting. Select a scatter plot displaying data points only, then add a trendline with the linear regression equation and the R^2 value. Print the data table and the graph, and include them in the experimental report.

2. **Determine the cobalt(II) ion concentration of the unknown solution from the calibration curve, its dilution factor, and the measured absorbance.**
   Unknown Co^{2+} solution number: _____
   Co^{2+} concentration of the unknown solution: _____

III. Conclusion

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_____

IV. Question and Discussion

1. At the end of the experiment, a student found that the first standard cobalt(II) solution had not been measured in absorbance mode during spectrophotometric analysis; instead, the recorded value was the transmittance, T = 40.8%. Is it necessary to repeat this measurement, or is there another way to correct the data?

2. An acidic solution contains 0.420 mg of Fe^{3+}. After color development with KSCN, the solution is diluted to 100 mL. At the analytical wavelength of 480 nm, an absorbance of 0.530 is measured using a cuvette with an inner path length of 1.0 cm. What is the molar absorptivity (ε) of the $FeSCN^{2+}$ complex ion? Based on the analytical wavelength, determine the color of this solution.