## Spectroscopic Determination of a Complex Ion's Stoichiometry by Job's Method

**ABSTRACT**

This experiment is adapted from Angelici's classic experiment, but uses $Fe(H_2O)_{6-n}(SCN)_n^{3-n}$ as the complex ion. A series of solutions are prepared with different mole fractions of metal cation and ligand. If the resulting complex is highly coloured (as is often the case with transition metal complexes), measurement of the visible spectra of these solutions can give information about the identity of the complex ion(s) (MLnx+) formed in solution, a procedure called "Job's Method".

**Equipment**

No special equipment required.

**Safety Hazards**

No particular hazards. Thiocyanate salts are toxic. Care must be taken with concetrated $HNO_3$.

| | |
|---|---|
| **Year Level**: | 2nd year introductory inorganic |
| **Student time required**: | 2 hours is solutions are provided, 3 hours if students make their own |
| **Instructor time required**: | ~1 hour?? |

| | |
|---|---|
| **Technician notes?** | Available upon request |
| **Study question solutions?** | Available upon request |
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# Chemistry 2351: Inorganic Chemistry I Laboratory Manual

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# Experiment Four:

# Spectrophotometric Determination of a Complex Ion's Stoichiometry: The Job's Method

## Purpose of the Experiment

The purpose behind this experiment is to determine the formula of a complex ion in solution using Job's Method of Continuous Variation.

## Introduction

The compositions of many different coordination complexes have been identified, even some that are non-isolable in the solid state. The fact that a coordination complex has not been isolated does not necessarily imply that the metal-ligand interactions are weak. In many instances, complex equilibria make it difficult to selectively crystallize each of the species separately from solution. For example, while coordination complexes of Ni(II) and $NH_3$ in water have the general formula $[Ni(H_2O)_{6-n}(NH_3)_n]^{2+}$ (n = 0-6) depending on the relative ligand concentrations, only $[Ni(NH_3)_6]^{2+}$ is generally isolable. The identity of the other species must be established and verified by other techniques.

The formulae of highly coloured complex ions may be determined in solution using spectrophotometric techniques. Consider the general reaction between a metal ion $M^{z+}$ and a ligand L that form the coordination complex $[ML_n]^{z+}$ (eq. 1):

$$\mathbf{M^{z+} + n\,L \rightleftharpoons [ML_n]^{z+}} \qquad \textbf{(1)}$$

Assuming there are no other species in solution absorbing radiation of a particular frequency, the Beer-Lambert law (eq. 2) may be used to calculate the concentration of the complex ion:

$$\mathbf{A_{obs} = \ell[\epsilon_M c_M + \epsilon_L c_L + \epsilon_{MLn} c_{MLn}]} \qquad \textbf{(2)}$$

$A_{obs}$ = total absorbance of all species in solution
$\ell$ = pathlength of the cell (taken as 1 cm in this experiment)
$\epsilon_M$, $\epsilon_L$, $\epsilon_{MLn}$ = molar extinction coefficients of the absorbing species
$c_M$, $c_L$, $c_{MLn}$ = concentration of the absorbing species

The procedure used in this experiment is known as the Job's Method of Continuous Variations. The method will be applied to the reaction of $Fe^{3+}$ with $SCN^-$ in water (eq. 3), and the student must determine the empirical formula of the complex ion that is produced under the specified conditions. A series of solutions of various concentrations of ligand ($SCN^-$) and metal ion ($Fe^{3+}$) are prepared and examined spectrophotometrically to determine the concentration ratio that generates the highest concentration of complex ion. By plotting the absorbance of each solution against the mole fraction of ligand, the ligand concentration that corresponds to the maximum concentration of complex ion may be determined.

$$[Fe(H_2O)_6]^{3+} + n\ SCN^- \rightarrow [Fe(H_2O)_{6-n}(SCN)_n]^{3-n} + n\ H_2O \qquad (3)$$

## Experimental Procedure

***Special Notes and Safety Precautions***

There are several reagents used in this experiment that require special attention. Concentrated $HNO_3$ is very corrosive towards tissue and clothing; care must be exercised when using this reagent. Wash all exposed areas with copious amounts of water. The reagent KSCN is toxic and must be handled accordingly. Do not breathe the dust and wash any exposed areas with water.

Depending on the availability of burettes (required later in the experiment; see below), students may need to work in pairs or groups of three. In any event, ***each student is required to submit his own individually prepared report*** (do NOT submit a group report, or several copies of the same report).

***Preparation of Stock Solutions***

Prepare aqueous solutions of $Fe(NO_3)\bullet 9H_2O$, KSCN, and $HNO_3$ in 100 or 200 mL volumetric flasks with the following concentrations (the prepared solutions need not have these exact concentrations -- as long as they are close and known exactly): $[Fe^{3+}] = 3.00 \times 10^{-3}$ M; $[SCN^-] = 3.00 \times 10^{-3}$ M; $[HNO_3] = 0.500$ M. (these may have been pre-prepared by the instructor as well)

***Using the Spectrophotometer***

There are several types of spectrophotometers. Be sure to ask the instructor if you are unsure how to use the one you are assigned.

***Preparation of Sample Solutions***

Ten solutions containing various volumes of the three solutions (prepared, as above) will be measured. Using three burettes for your stock solutions, prepare the following solutions. (use a small beaker or test tube and thoroughly mix each solution after all three reagents have been added)

| **Solution** | **Volume $Fe^{3+}$** (mL) | **Volume $SCN^-$** (mL) | **Volume $HNO_3$** (mL) |
|---|---|---|---|
| 1 | 0.0 | 16.0 | 4.0 |
| 2 | 1.0 | 15.0 | 4.0 |
| 3 | 3.0 | 13.0 | 4.0 |
| 4 | 5.0 | 11.0 | 4.0 |
| 5 | 7.0 | 9.0 | 4.0 |
| 6 | 9.0 | 7.0 | 4.0 |
| 7 | 11.0 | 5.0 | 4.0 |
| 8 | 13.0 | 3.0 | 4.0 |
| 9 | 15.0 | 1.0 | 4.0 |
| 10 | 16.0 | 0.0 | 4.0 |

Record the absorbance of the ten solution mixtures at 447 nm. Before recording the absorbance of each solution, rinse the cuvette several times with small portions of the solution to be analysed, wipe clean and then insert into the compartment. After each measurement, discard the solution into a waste container and wash the cuvette with DDW. Make all measurements on the same instrument.

## Data Processing

For each of the ten solutions calculate the mole fraction of $SCN^-$ (eq. 4):

$$\boldsymbol{X_{SCN^-} = (\#\ mol\ SCN^-) / (\#\ mol\ SCN^- + \#\ mol\ Fe^{3+})} \qquad \textbf{(4)}$$

Tabulate the absorbance data along with the mole and mole fraction calculations. Plot absorbance *vs.* mole fraction of $SCN^-$ and determine the mole fraction of ligand at the maximum absorbance, $X_{SCN^-, MAX}$. If the plot is curved in the region of the maximum absorbance, extrapolate the two straight-line portions of the curve until they intersect. The mole fraction of metal ion (ie. $Fe^{3+}$) at the maximum absorbance, $X_{Fe^{3+}, MAX}$, is easily calculated using the following relationship (eq. 5):

$$\boldsymbol{X_{Fe^{3+}, MAX} = 1 - X_{SCN^-, MAX}} \qquad \textbf{(5)}$$

The ratio of $X_{SCN^-, MAX}$ to $X_{Fe^{3+}, MAX}$ gives the value of $n$ in equation 3.

## Reference

For a general reference on the method of Job, see: R.J. Angelici Synthesis and Technique in Inorganic Chemistry, 2nd ed., Philadelphia : Saunders, 1977.

# CHEMISTRY 2351 REPORT SHEET
# Experiment 4:
# Spectrophotometric Determination of a Complex Ion's Stoichiometry by Job's Method

NAME:_______________________________

DATE: _______________________________

Attach to this report page:

1. A table giving absorbance and a visual observation of each solution

2. A plot of absorbance *vs*. mol fraction (of $SCN^-$)

Provide the formula(s) for the major complex(es) formed in this study. Be sure to include calculations to support this formulation.

How can the colouration (or lack thereof) of the solutions be explained?

Assuming the $SCN^-$ is coordinating to $Fe^{3+}$ via the nitrogen, how would you expect $\Delta_O$ to change as the number of $SCN^-$ ligands about the metal increases or decreases, and why?