GRAVIMETRIC DETERMINATION OF NICKEL IN AN UNKNOWN SOLUTION

AIM

The main objective of this experiment is to determine the concentration of nickel (II) ion in a nickel solution with an unknown concentration by gravimetry.

INTRODUCTION

Nickel (II) forms a precipitate with an alcoholic solution of dimethylglyoxime, $\text{H}_2\text{C}_4\text{H}_6\text{O}_2\text{N}_2$, in a slightly alkaline medium. The formation of the red solid Ni complex, $\text{Ni}((\text{H}_4\text{C}_6\text{O}_2\text{N}_2)_2$ is illustrated below:

$$\text{Ni}^{2+} + 2\text{H}_2\text{C}_4\text{H}_6\text{O}_2\text{N}_2 \rightarrow 2\text{H}^+ + \text{Ni}((\text{H}_4\text{C}_6\text{O}_2\text{N}_2)_2$$

Although the loss of one proton occurs from one oxime group (N-OH) on each of the two molecules of dimethylglyoxime, the chelation reaction occurs due to donation of the electron pairs on the four nitrogen atoms, not by electrons on the oxygen atoms.

This reaction is performed in a buffered solution to keep the pH > 5 by using either an ammonia or citrate solution. Otherwise the equilibrium of the above reaction favors the dissolution of Ni complex back into the mother liquor.

The bulky character of Ni complex limits the mass of nickel that can be handled conveniently and thus the sample mass. Since dimethylglyoxime (DMG) is only slightly soluble in water (0.063 g in 100.0 mL at 25 °C), an alcoholic solution of it is used as the precipitating reagent in the experiment. However it is crucial to avoid the addition of excess amount of DMG as it may crystallize out as well with the Ni complex. It is also important to know that the Ni complex itself is slightly soluble to some extent in alcoholic solutions. Thus, by adding only an optimum volume of the DMG, the errors due to these sources can be minimized.

REAGENTS AND APPARATUS

- Unknown nickel solution, NiSO$_4$ (2 replicates for each student)
- 25.0 mL of 6.0 M HCl for 2 students
- 25.0 mL of 6.0 M NH$_3$ for 2 students
- Concentrated NH$_3$ (in the hood)
- 1.0 % (w/v) dimethylglyoxime in 95 % alcohol (ready)
- 0.1 M AgNO$_3$ (ready)
- 2 sintered glass crucibles (gooch crucible); medium porosity
- 2 beakers of 400.0 mL
- 2 watch glasses
• 100.0 mL graduated cylinder
• 2 glass stirring rods
• Wash bottle

**PROCEDURE**

**A. Preparation of Gooch Crucibles**

1) Clean and dry two gooch crucibles. Make sure that each crucible is marked properly.
2) Dry crucibles in the oven at ~110 °C. Cool the crucibles outside of oven for ~10 minutes and then, store in a desiccator for cooling to room temperature then, weigh to the nearest 0.0010 g.
3) Repeat Step 1 and 2 to bring crucibles to constant mass. (i.e. successive weighings agree within ± 0.0010 g).
   - Always store crucibles in a desiccator when they are not in use.

**B. Preparation and Precipitation of the Nickel Unknown Samples**

1) Take your unknown solution into a 400.0 mL beaker. Treat each unknown solution individually. Add 100.0 mL distilled water using a graduated cylinder.
2) Add concentrated NH₃ (1-2 mL) until a faint odor of NH₃ can be detected in the vapors over the solution (Do this in the hood!)
   - The presence or absence of excess NH₃ is readily established by odor; use a waving motion with your hand to drag the vapor towards your nose.
3) Make the solution slightly acidic with 6.0 M HCl until no odor of NH₃ is smelt (add 2-5 mL acid solution).
   - Slightly acidic means a pH of 4-5 (preferably 5). If care is not taken in this step, much time will be lost.
   - Some minor loss of the Ni²⁺ occurs when checking the pH of the solution before precipitation. It can be considered as a small error and has been minimized in procedure by the sample size used and by the volume of the solution.
4) Heat the solution to 60° to 80 °C (do not boil but feel hot from outside of the beaker,) in a water bath and then, add 20.0 mL of 1.0% (w/v) alcoholic solution of DMG.
   - If a red precipitate forms immediately after adding the DMG, the solution must be already basic (i.e. it’s OK, just proceed!).
5) Then, with a good stirring, introduce sufficient amount of 6.0 M NH₃ until slight excess NH₃ is present as indicated by the odor, plus an additional 1.0 to 2.0 mL. During this treatment a heavy red precipitate must be formed.
   - Use a separate stirring rod for each sample and leave it in its baker throughout.
6) Set your beaker (and stirring rod) in the water bath and carefully cover it with a watch glass. Digest the precipitate for 1 hour at about 60 °C. Later, cool it for at least 1 hr.
   - Before filtering the solutions test them for unprecipitated Ni as follows.
a) Carefully add (without mixing), a few drops of 6.0 M ammonia to each solution.
b) Next add a few drops of the 1% DMG solution.
c) Look for the appearance of NEWLY formed red precipitate.
d) If more precipitate is forming, add a few more drops of 6.0 M ammonia and reheat on the steam bath.

7) Filter through filtering crucible that has been previously brought to constant mass. Wash the precipitate with water until it is free of chloride.
   • Test the washings for Cl by collecting a small portion on a watch glass, add few drops of 0.1 M AgNO\textsubscript{3}. Washing is judged complete when little or no turbidity develops. Washing is repeated 3-5 times.

8) After filtering, place the crucible in a beaker and dry at ~110 °C for 1 hr and then, put them in your desiccator. Cool and weigh. Repeat heating, cooling and weighing until the mass of each crucible is constant (i.e. successive weighing agree within ± 0.0010 g).
   • Do not heat the precipitate to temperatures over 130 °C (Ni complex may decompose).

9) Once a constant mass is reached, rinse the crucible with water and then put it into dilute HCl solution for the cleaning process.

10) Rinse each crucible thoroughly with distilled water and return them to the technician.

**CALCULATIONS**

1) On the basis of the two separate results, calculate and report the followings:
   i) mg nickel in each unknown sample.
   ii) mean mg nickel value in the unknown sample.
   iii) standard deviation and % relative error (%RSD).

2) Your assistant will send true value of nickel unknown to your e-mail address. Do not forget to write true value to your data sheet.

3) Calculate percent relative error. If the experimental mean is larger or smaller than the true value, then write the possible sources of positive or negative error(s) in the discussion part.

**PRE-LAB STUDIES**

Read Gravimetry chapter from your text book.

1) Define coprecipitation and explain coprecipitation errors.
2) What are the differences between gооch crucibles and the porcelein ones?
3) What are the difference(s) between colloidal and crystalline suspensions? Which factors determine the particles size of precipitates? Explain briefly.
4) What is the difference between ‘adsorption’ and ‘absorption’?
5) Write at least three ways in order to maximize the crystalline suspension.
6) Describe the preparation of 25.0 mL of 6.0 M NH\textsubscript{3} from concentrated NH\textsubscript{3}.*
7) Describe the preparation of 25.0 mL of 6.0 M HCl from concentrated HCl.*

* Density and mass percent values are written on the labels of the bottles containing concentrated solutions of NH\textsubscript{3} and HCl placed in the hood. These values are also listed in the web page.
POST-LAB STUDIES

1) What is the importance of pH control in the determination of nickel by gravimetry?
2) Why do we perform chloride test?
3) What is the name of alcohol used in this experiment? Why the amount of alcohol content should be controlled?
4) Write the chelation reaction between nickel and DMG and how does the chelation reaction occur? Explain.
## REPORT SHEET

### GRAVIMETRIC DETERMINATION OF NICKEL IN AN UNKNOWN SOLUTION

<table>
<thead>
<tr>
<th>Unknown solution</th>
<th>Replicate 1</th>
<th>Replicate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of empty gooch crucible, g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass of gooch crucible and precipitate, g</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Constant mass of empty gooch crucible, g (m₁)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass of gooch crucible and precipitate, g</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Constant mass of gooch crucible and precipitate, g (m₂)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mg of Ni(DMG)₂, (m₂-m₁)*1000</td>
<td></td>
<td></td>
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<tr>
<td>mg of nickel, X±s (% RSD)</td>
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</tbody>
</table>

The following information (true values) will be sent to your e-mail address:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of NiSO₄ unknown, M</td>
<td></td>
</tr>
<tr>
<td>mL NiSO₄</td>
<td></td>
</tr>
</tbody>
</table>

**TA’s Name and Signature:**