Experiment 5: Gravimetric determination of nickel in nickel oxide

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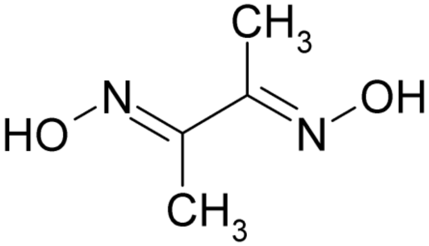
PURPOSE

Determine, gravimetrically, the percentage of Ni in an impure sample of nickel oxide by means of a precipitation of the nickel dimethylglyoximate.

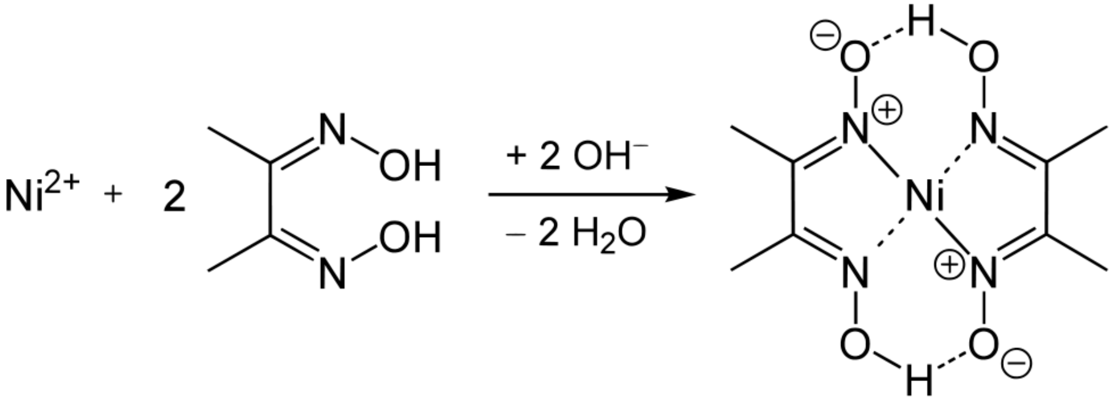
THEORY

Nickel (II) is quantitatively precipitated using a 1% alcoholic solution of the organic compound dimethylglyoxime, $C_4H_6(NOH)_2$, or **DMGO**, in the pH range 5 to 9. The DMGO structure is shown in Figure 1:

Figure 1: Structure of dimethylglyoxime



The reaction, in which two molecules of DMGO chelate the nickel ion, is:



The nickel ion displaces a proton from one oxime group (-NOH) on each of the DMGO molecules, but it is chelated by the electron pairs on each of the four nitrogens, not the electrons on the oxygens. In order to achieve a quantitative determination, all of the nickel (FW 58.70) present in a sample, has to be converted completely to the nickel dimethylglyoximate (FW 288.93).

The nickel oxide sample is not soluble in water, and for that reason 6M HCl is used for that purpose. But since the precipitation takes place in a slightly basic solution, aqueous NH_3 is used to control the pH. The pH of the solution must not drop below 5 to avoid the displacement of the equilibrium in favor of soluble Ni^{2+} ion. After precipitation, the solution is heated in order for the **digestion** to occur. In this process, the precipitate stands in contact with the ***mother liquor*** for some period of time, usually with heating. Digestion promotes slow recrystallization of the precipitate, increasing particle size and expelling impurities from the crystal.

Sintered-glass crucibles of medium (M) porosity are used to filter the precipitate. If coarse (C) porosity is used, a portion of the precipitate may be lost. Fine (F) porosity may be used, but filtration time would be longer. Care should be taken since the dimethylglyoximate is a bulky and slimy precipitate, which is difficult to transfer to a filtering crucible.

PRELABORATORY ASSIGNMENT

1. Explain in your own words what is a ligand and a complex forming reaction?
2. What is a digestion of a precipitate? Mention two benefits of the process.
3. Mention two steps that contribute to the formation of an easy to filter precipitate.
4. Explain how you determine that the precipitate is free from chloride.
5. Justify the use and state six safety considerations (two per chemical), for the use of the following reagents in this experiment:
   a. 6M HCl
   b. 6M NH_3
   c. dimethylglyoxime

APPARATUS AND MATERIALS

Sintered-glass crucibles, M porosity
Vacuum filtration apparatus
3-400 mL beakers
3- stirring rods with rubber policeman
3-watch glasses
50% HNO_3
Ethanol, 30%
bromothymol blue indicator
HCl, 6M
Dimethylglyoxime in ethanol,1%
1M and 6M HCl
6M NH_3
0.1M $AgNO_3$

EXPERIMENTAL

NOTE: You will receive from your Instructor about 2.5 g of a nickel oxide sample of unknown concentration which has already being dried for about one hour at 140 ^{o}C.

***IMPORTANT WARNING!:* DIMETHYLGLYOXIME WILL TRIGGER AN EXPLOSIVE REACTION WHEN MIXED WITH ACIDS SUCH AS NITRIC ACID (HNO_3). THESE CHEMICALS MUST BE STORED ON SEPARATE WASTE CONTAINERS. REFER TO THE MSDS OR ASK YOUR INSTRUCTOR IF YOU HAVE QUESTIONS ON HOW TO PROPERLY DISPOSE THESE CHEMICALS.**

First laboratory period:

1. Wash two sintered-glass crucibles with 50% HNO_3 in order to remove any organic residue. **CAUTION: Use the fume hood.** Fill the crucible about halfway with the acid. Using gentle vacuum, draw the acid slowly through the crucible. Fill halfway again and interrupt the vacuum briefly to allow for the acid to remain in contact with the crucible for a few minutes. Wash several times with distilled water.

2. Wash the crucibles now with 6M NH_3. This will form NH_4NO_3 with any nitrate residue from the acid that may still remain. In the next step, the crucibles will be heated and the NH_4NO_3 will evaporate.

3. Dry the crucibles in the oven for one hour at 100 ^{o}C. Cool in the desiccator for 30 minutes and weigh in the analytical balance. Heat for 30 minutes again, cool and weigh. Repeat the process of heating for 30 minutes. Cool and reweigh until constant weight is attained (two consecutive weighing agrees within ±0.4 mg (0.0004g). Record the last weighing as the correct mass of the sample. Store crucibles in the desiccator until ready to use.

4. Obtain the 2.5 g of the unknown nickel oxide sample (See NOTE above). Weigh two 1.0000 g samples and dissolve in 30 mL of 6M HCl, in 400 mL beakers. Cover with watch glasses and heat in a hot plate for 30 minutes in the fume hood. After this process, a carbon residue may be present; do not filter. Cool to room temperature.

5. Dilute each sample with 250 mL of distilled water.

6. Add 3 drops of bromothymol blue. Slowly, and while stirring, add 6M NH_3 (**in the fume hood**) until the solution changes from yellow to blue. Add 15 mL of the 1% DMGO solution. Leave the stirring rod inside the beaker until the experiment is finished.

7. Heat in a hot plate for 30 minutes, from 60 to 80 ^oC. Cool to room temperature, for at least one hour, using a cold water bath to speed the cooling process.

8. Cover the beakers with a watch glass and put them aside in your locker until the next laboratory period.

   NOTE: Handle the beakers with care since the precipitate tends to climb over its walls.

Second laboratory period:

1. Filter each solution. Place a crucible (at constant weight) in the vacuum filtration apparatus, and apply gentle vacuum. If possible, first decant the cool supernatant from the beaker into the crucible, retaining the precipitate in the beaker. Transfer the precipitate to the crucible by pouring the rest of the solution. Use a wash bottle and a rubber policeman. **NOTE: Do not fill the crucible to the top since the precipitate tends to climb over its walls.**

2. If some precipitate is still adhered to the walls of the beaker, add 5 mL of hot 1M HCl (in the fume hood), plus one drop of bromothymol blue, 5 mL of the DMGO solution and finally, 5ml of 6M NH_3. By now, the solution should appear as blue-violet.

3. Pour the resulting solution into the crucible. After the filtration process has ended, close the vacuum. Discard the filtrate, and wash the filtering flask with tap water and then with distilled water.

4. Wash the precipitate in the crucible with four portions of distilled water, or until the washings are free from chloride (Cl^-). To test for chloride presence$^-$, use 2 ml of the filtrate, add 5 drops of 6M HNO_3 and two drops of 0.1M $AgNO_3$. If turbidity appears, wash the precipitate once again until the test produces a crystalline solution.

5. Wash the precipitate in the crucible with 30.0 mL of the 30% ethanol solution.

6. Drain the crucible dry with strong vacuum. Place in a beaker in order to be dried in the oven.

Third laboratory period:

1. Dry the crucibles in an oven for two hours at 140 ^oC, cool in the desiccator for 30 minutes and weigh.
2. Repeat the procedure, heating for 30 minutes. Cool and reweigh until constant weight is attained.

CALCULATIONS

1. Determine the mass of $Ni(DMGO)_2$ recovered.
2. Using the stoichiometric factor, determine the mass of Ni in the sample.
3. Determine the percentage of Ni for each sample.
4. Determine the average percentage of Ni.
5. Determine the relative average deviation (rad) in ppt.

QUESTIONS

1. What would happen to your results if the sample contains traces of Fe^{+2}?
2. A student precipitates the nickel sample without heating. Does this affect his results? Explain.
3. What is the limiting reagent in this reaction?
4. What causes the red color of the precipitate?
5. Why do you need to remove the chloride ions from the precipitate?