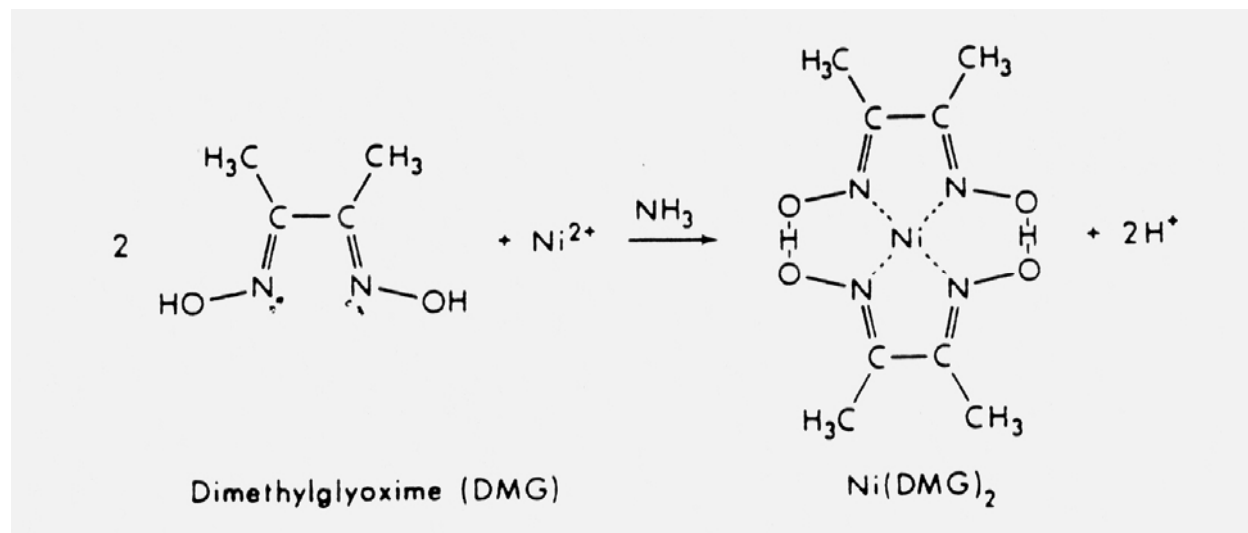


The Gravimetric Determination of Nickel

INTRODUCTION

Nickel(II) forms a precipitate with the organic compound dimethylglyoxime, $C_4H_6(NOH)_2$. The formation of the red chelate occurs quantitatively in a solution in which the pH is buffered in the range of 5 to 9. The chelation reaction that occurs is illustrated below.

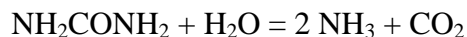


Although the loss of one proton occurs from one oxime group (NOH) on each of the two molecules of dimethylglyoxime, the chelation reaction occurs due to donation of the electron pairs on the four nitrogen atoms, not by electrons on the oxygen atoms. The reaction is performed in a solution buffered by either an ammonia or citrate buffer to prevent the pH of the solution from falling below 5. If the pH does become too low the equilibrium of the above reaction favors the formation of the nickel(II) ion, causing the dissolution of $Ni(DMG)_2$ back into the mother liquor.

Adding tartarate or citrate ions before the precipitation of the red nickel complex prevents interference from Cr, Fe and other metals. These anions selectively form tightly bound soluble complexes with the metals and prevent the formation of insoluble metal hydroxides in the buffered solution.

An alcoholic solution of dimethylglyoxime (DMG) is used as the precipitating reagent during the experiment because DMG is only slightly soluble in water (0.063 g in 100 mL at $25^\circ C$). It is therefore crucial to avoid the addition of too large an excess of the reagent because it may crystallize out with the chelate. It is also important to know that the complex itself is slightly soluble to some extent in alcoholic solutions. By keeping the volume added of the chelating reagent small, the errors from these sources are minimized. The amount of the reagent added is also governed by the presence of other metals such as cobalt, which form soluble complexes with the reagent. If a high quantity of these ions is present, a greater amount of DMG must be added.

The nickel dimethylglyoximate is a precipitate that is very bulky in character. Therefore, the sample weight used in the analysis must be carefully controlled to allow more convenient handling of the precipitate during transferral to the filtering crucible. To improve the compactness of the precipitate, homogeneous precipitation is often performed in the analytical scheme. This is accomplished by the adjustment of the pH to 3 or 4, followed by the addition of urea. The solution is heated to cause the generation of ammonia by the hydrolysis of the added urea, as indicated by the following reaction.



A slow increase in the concentration of ammonia in the solution causes the pH to rise slowly and results in the gradual precipitation of the complex. The result is the formation of a more dense, easily handled precipitate. Once the filtrate has been collected and dried, the nickel content of the solution is calculated stoichiometrically from the weight of the precipitate.

REAGENTS AND APPARATUS

- 3-Sintered Glass Crucibles; medium porosity (see instructor for these)
- 3-400 mL beakers
- 3-Watchglasses and glass hooks
- 1-Rubber Policeman and glass stirring rod
- Whatman No. 40 filter paper; medium porosity
- Unknown Ni ore sample
- Nitric Acid (concentrated)
- Hydrochloric Acid (concentrated)
- 20% Tartaric Acid solution (prepared by student)
- 1:1 Ammonium Hydroxide solution (prepared by student)
- 1% alcoholic dimethylglyoxime solution
- Urea (solid, ACS reagent grade)
- Acidic AgNO₃ (already prepared)
- pH paper

PROCEDURE

****Week in advance*** Dry the unknown sample at 140 °C for three hours.*

Part A –Preparation

1. Sintered-glass crucibles of medium (M) porosity are recommended for filtering many

precipitates if the precipitate may be dried at temperatures below approximately 250 ° C. These types of crucibles will be used in this experiment. To clean the crucible, first remove any visible dirt with detergent solution by brushing, taking care not to scratch the fritted glass disk in the bottom of the crucible; then rinse. Assemble the filter flask, filter holder, and crucible. Connect the filter flask with rubber suction tubing to the aspirator. Fill the crucible about halfway with 6M hydrochloric acid and, using gentle suction, draw the acid slowly through the crucible. Rinse the crucible several times with distilled water in a similar manner. When finished filtering, empty the receiving flask and rinse it several times to minimize acid vapors in the room.

2. Dry the crucible in the home microwave oven. Set the power at 100% and set time to two minutes. Place the crucibles in the microwave on the glass plate and start the microwave. When the microwave stops, turn the crucibles over using crucible tongs. Continue drying the crucibles and turning them over until water is no longer visible on the sides and then dry them one more time. Weigh. Repeat drying in microwave until the weights agree within +/- 0.4 mg (constant weight). Always store the crucibles in the desiccator when they are not in use. Alternatively, the crucibles may be dried for a week in a drying oven.

PART B – Sample Dissolution: *(If microwave digestion is not available, see the "Alternate Decomposition Method" at the end of this document)*

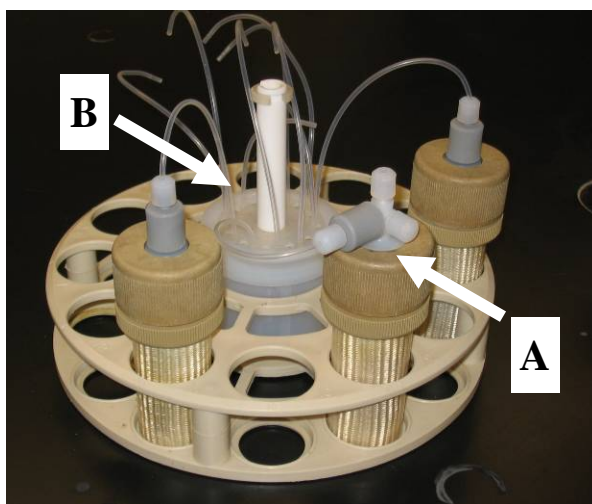


Figure 1. Microwave carousel with three vessels. The vessel labeled A is the control vessel. Note that all vessels are attached to the overflow reservoir in the event a rupture membrane fails. Rupture membranes are placed inside the grey fitting on each vessel.

1. Accurately weigh three 1.0 to 1.2-g samples of the dried unknown into clean, dry Teflon PFA microwave vessels (Figure 1). Add 10 mL of concentrated nitric acid and 5 mL hydrochloric acid (in the hood). These acids should be added only after the lids to the vessels have had new rupture membranes inserted and are ready to be closed.

2. One vessel in each set of samples which are to be decomposed must be a control vessel (labeled A in Figure 1, see instructor for instructions on use of this vessel). The purpose of this vessel is to allow monitoring of the reaction pressure, preventing vessels from rupturing and preventing you from losing samples. If several students are decomposing 3 samples each, up to 12 vessels may be placed in the MDS-2000 microwave at a time, of which only 1 must be a control vessel. If more than 3 vessels are placed in the microwave, increase the power setting 5% for each additional vessel above three.
3. Place the vessels in the microwave carousel and then place the carousel in the microwave digestion system. Press **f2**: program new method. Next choose **1** for standard digestion and then **1** for Teflon PFA vessel. Enter any file name. Digest the samples at 50% power for two minutes. Allow five to ten minutes for cooling. Repeat the digestion and cooling periods two more times. Carefully, open the vessels **in the hood**. Nitrogen dioxide gas will escape from the vessels. Be sure to let the samples cool before opening them completely (approx. 10-15 min.)! If undigested sample is still present in the bottom of the vessel, replace the lid and repeat the digestion procedure until all materials have been decomposed.
5. Once completely decomposed, place the open vessels in the microwave and, using standard digestion, digest for one minute at 50% power to drive off excess nitric acid. Repeat until formation of the reddish brown nitrogen dioxide gas ceases. Cool samples in the hood (if 6 vessels are placed simultaneously in the microwave, increase the power to 65%, following other directions identically).
6. Quantitatively transfer the samples to 400 mL beakers and dilute to 150 mL with distilled water. Add 60 mL of 20% tartaric acid solution. Heat the solution to nearly boiling and add 1:1 ammonium hydroxide slowly until the solution is alkaline (**IN THE HOOD**). The final solution should smell distinctly of ammonia after blowing away the vapors from above the solution and its color will turn from a light green to aqua. If the addition of ammonia causes any precipitate to form, dissolve it by adding hydrochloric acid, add more tartaric acid solution, and neutralize again with ammonia.

AVOID STARTING THE FOLLOWING STEP UNLESS YOU HAVE AT LEAST 2 HOURS REMAINING IN THIS PERIOD.

PART C – Precipitation

1. Make each of the samples slightly acidic with hydrochloric acid (pH = 5). Add 15 mL of 1% dimethylglyoxime and 4 - 5 grams of urea to each sample. Cover each beaker with a watch glass and heat for about an hour at 80 - 85 degrees Celsius. If a red precipitate does not start forming after 15 minutes, add more urea. Do not allow the solutions to heat to boiling. If the solutions begin to boil, remove them from the heat source and allow them to cool below boiling before continuing to heat on a lower setting.
2. Cool to room temperature during the lab period and check the pH with pH paper. Use the pH paper in a frugal and proper manner (see your instructor for the proper manner to use it). If

the solution is not above pH 7, add a drop of ammonium hydroxide and check again. Filter the solution through one of your previously weighed crucibles.

3. Test the filtrate on all samples for the completeness of precipitation by adding a little more dimethylglyoxime (2 - 3 mL). If any red precipitate forms, reheat the solution on the hot plate after raising the pH to 7. When you are finished filtering, wash the precipitate with cold water to which a few drops of ammonia have been added (do not use distilled water without this precautionary measure). Continue washes until the washings are free from chloride ion (use acidic AgNO_3).
4. Dry the precipitate in the oven at 130°C to constant weight.

OR

Dry the precipitate in the home microwave oven to constant weight. Use 100% power for one minute intervals. Carefully turn the crucible to allow all portions to be dried, though you should not turn the crucible completely upside down as the precipitate may fall out.

5. Calculate your results and report them as % Ni in the sample. Report the 95% confidence interval for your measurements.
6. **Clean the crucibles by dissolving the precipitate with ~3 ml of 6M hydrochloric acid. Precipitate that is adhered to the sides of the crucible can be dissolved by rolling the crucible so that the 6M HCl solution coats the crucible walls. After the precipitate has dissolved, pour the solution into the Nickel waste container. Only a few mL of HCl should be used in order to minimize the volume of waste produced. Rinse each crucible thoroughly with distilled water (these rinses do not need to go in the waste container) and return them to the instructor.**

Information, Helps And Hints for Ni Determination

Preparation:

- Remember, advance preparation in this experiment is especially crucial. Plan ahead carefully to avoid wasting your time.
- The unknown should be dried for 3 hours at $130\text{-}140^\circ\text{C}$.
- When cleaning your crucibles before use, refer to your lab manual for details. Remember that 6 M HCl is used in this process and that care should be exercised. When finished cleaning your crucibles, also clean the acid out of the filtering apparatus with liberal use of water. As a general rule, you should always clean the filtering flask once finished with them.
- **DO NOT** store wet crucibles in your desiccator. Only do so after having dried the crucibles at least 30-40 minutes in the conventional oven or one heating cycle in the microwave.
- Please do not let your crucibles sit in the microwave while cooling. Constant weight means that no more than ± 0.4 mg difference is seen between the last two massing operations.

Technique:

- **DO NOT LABEL THE TEFLON VESSELS WITH TAPE. LABEL ONLY THE OUTER PROTECTIVE SLEEVE!!!!**
- Be observant in your digestion of samples. The directions in the lab are designed for 3 samples. If more than 3 samples are used, the temperature program must be adjusted as specified in the procedure.
- Be especially careful to remember to place the rupture membranes in the microwave sample vessel. Failure to do this will cause problems.
- Extreme caution should be observed when opening microwave vessels. This operation should be performed in the fume hood. Open the fitting only slightly to allow pressure to escape.
- When driving off the excess nitric acid from your samples (Step 5), be especially careful to avoid boiling too rapidly, as sample spatter will cause errors.
- Quantitative transfer of the sample into a 400 mL beaker must also be considered. Rinsing the microwave vessel walls at least three times with small portions of deionized water is essential. Be careful, however, not to use too much water in the transfer as the volume of liquid can have a very nasty habit of becoming too great for the 400 mL beaker. If this happens, a transfer to a larger beaker is necessary (greater manipulations = greater errors).
- When starting the precipitation step, slightly acidic means a pH of 4-5 (preferably 5). If care is not exercised in this step, much time will be lost. The use of HCl which has been diluted to about 1M is recommended.
- Yes. Some minor loss of the Ni^{+2} occurs when checking the pH of the solution before precipitation of the complex. It has been recognized as a small error and has been minimized in procedural considerations by the sample size used and by the volume of your solution at the stage in which the pH has been adjusted.
- Quantitative transfer and washings are extremely important in the filtration process. When it is desired to save the filtrate, be sure that the receiving flask has been scrupulously cleaned.
- When filtering, either the precipitated Nickel dimethylglyoximate or the residues that may occur during the sample preparation using suction filtration, it may be useful to review filtering procedures in your text. Be certain to remember the use of the rubber policeman to aid the transfer of the precipitate.
- Do not heat the precipitate to temperatures much greater than 130 °C for fear of decomposing the compound.
- When finished, please clean your crucibles as described at the end of the Procedure section. Return them as soon as possible after completion of the experiment.

Alternate Decomposition Method (requires 1 additional 4 hour labperiod)

PART A -- PREPARATION

1. Dry the unknown solid sample at 140° C for 3 hours while completing the following steps.
2. Scintered-glass crucibles of medium (M) porosity are recommended for filtering many precipitates if the precipitate may be dried at temperatures below approximately 250° C. To clean the crucible, first remove any visible dirt with detergent solution by brushing; then rinse. Assemble the filter flask, filter holder, and crucible. Connect the filter flask with rubber suction tubing to the aspirator. Fill the crucible about halfway with 6 M hydrochloric acid and, using gentle suction, draw the acid slowly through the crucible. Wash the crucible several times with distilled water.
3. Dry the crucible for 1 hour in an oven at 130°C using a beaker, glass hooks and a watch glass (While the crucibles are drying, proceed with the sample dissolution step). Remove the crucibles and place in the desiccator. Cool for 30 minutes or longer. Weigh. Dry at 130°C for 30 minutes, remove to desiccator, cool for 30 minutes and reweigh. Repeat this process until consecutive weights agree within +/- 0.4 mg (constant weight). Always store the crucibles in the desiccator when they are not in use.

PART B -- SAMPLE DISSOLUTION

1. Weigh three 1.0 to 1.2-g samples of the dried unknown into 400 mL beakers. Add 20 mL of concentrated nitric acid (in the hood) carefully down the sides of the beakers, using a measuring pipet (Mohr or Serological). Boil the solutions in the hood until formation of the reddish brown nitrogen dioxide gas ceases.
2. Approximately half the nitric acid should have evaporated at this point. Cool to room temperature and, in the hood, add 15 mL of concentrated hydrochloric acid down the sides of the beakers. Bake to dryness on the hot plate to dehydrate any silicic acid to silica (be careful that the contents do not pop!!!; i.e., remove the beakers off with 1-2 mL of liquid remaining).
3. Allow the beakers to cool before adding another 10 mL of concentrated hydrochloric acid and dilute each sample with 15-20 mL of water. Heat gently until all salts dissolve. If any residue is present (probably silica), filter immediately through a medium porosity filter paper and wash the precipitate with water. Catch the filtrate and washings in a 400 mL beaker.
4. Dilute each sample to 150 mL with water, and add 60 mL of 20% tartaric acid solution (Citric acid or ammonium citrate may be used for the same purpose). Heat the solution to nearly boiling and add 1:1 ammonium hydroxide slowly until the solution is alkaline (IN THE HOOD). The final solution should smell distinctly of ammonia after blowing away the vapors from above solution. If the addition of ammonia causes any precipitate to form, dissolve it by adding hydrochloric acid, add more tartaric acid solution, and again neutralize with ammonia. Any white or gray precipitate is probably silica and should be removed by filtration (see your text for proper filtration procedures).

PRECIPITATION: Complete the precipitation and filtering steps as outlined in Part C of the microwave decomposition procedure.