

GRAVIMETRIC AND COMPLEXOMETRIC DETERMINATION OF NICKEL IN A SOLID SAMPLE

N. Ladislavová, L. Habartová

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INTRODUCTION

In this work, the weight percentage of nickel is to be determined using gravimetric analysis and complexometric titration (chelatology). Regarding the time requirements of this laboratory task, do strictly follow the outlined workflow and focus on time management. To work more efficiently, study the enclosed illustrations and details on the manipulation with laboratory equipment. The following paragraphs describe the theoretical background of both methods utilized, chemicals and equipment required.

SAFETY INSTRUCTIONS

1. If any chemical is stored in the fume hood, it must be worked with therein and it is not permitted to transfer it anywhere around the lab.
2. The use of safety goggles is obligatory.
3. In case of any chemical spill, it is necessary to clean up the workplace regarding the character of the spilt substance.
4. **If there is any skin contact with chemicals, immediately start rinsing the affected area with water (in the sink, not distilled) and alert the assistant.**
5. **In the event of any injury (e.g. burns, cutting hand/fingers on broken glass), alert the assistant right away.**
6. Flammables will be used during the laboratory task, thus, pay attention to the hazard pictograms on the packaging. When working with a flammable substance, do not approach open fire (gas plate) or any other heat source (electric hotplate).
7. Do not put weighted or measured chemicals back into their storage containers, as this would lead to contamination.

GRAVIMETRIC ANALYSIS

CHEMICALS

Hydrochloric acid
[HCl (1:1 V/V)]



- in the fume hood
- corrosive
- in case of skin contact, rinse with water
- for sample dissolution



Bromothymol blue



- on the tables
- pH indicator
- range 6.0 (yellow) – 7.6 (blue)
- dosing with dropper (press finger on the upper hole, dose by slowly releasing the finger)

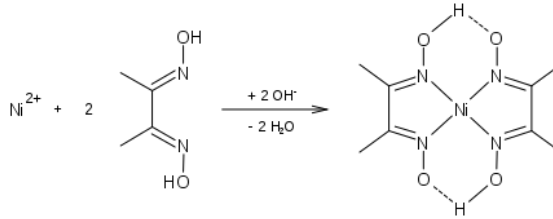
Ammonia
[NH₃ (1:1 V/V)]



- in the fume hood
- corrosive
- in case of skin contact, rinse with water
- for neutralization before nickel precipitation



Dimethylglyoxime
[1% in ethanol]



- on the tables
- complexing agent (precipitating agent)
- flammable – do not expose to open fire



LABORATORY EQUIPMENT

Filter crucible



Volumetric flask¹



Beaker 250 ml



Stirring rod²



Graduated cylinder³



Watch glass⁴



Bulb⁵



Non-graduated pipette 50 ml⁶



Dessicator⁷



Apparatus for filtration



Glass water bottle⁸



¹The volumetric flask is calibrated “to contain” (marked “IN”). In the case of aqueous solutions, the precise volume is obtained when the meniscus of the liquid touches the etched ring graduation marking. If the volume exceeds the marking, the whole content must be disposed of and the flask must be filled up again to avoid distortion of the dilution coefficient.

²During this task, the stirring rod will be used for stirring, to prevent nucleate boiling, and as a “dosing equipment”. While dosing, the liquid is slowly poured onto the rod and flows down to the designated solution. When you filter the precipitate, use the rod to dose the liquid gradually, thereby creating an even layer of the precipitate on the filter. After stirring and as prevention against nucleate boiling, the rod must remain in the respective solution.

³The cylinder is calibrated “to contain” (marked “IN”). To measure the required volume, pay attention to the mutual position of meniscus of the liquid and the cylinder scale.

⁴Watch glass serves as a lid for the beakers and titration flasks during heat treatment. Should the sample be transferred quantitatively, it is necessary to rinse the watch glass, which was in contact with the sample and vapours thereof.

⁵The bulb has three main positions: **A** (on the top, “air”) is designated for deflation. By pressing **S** (in the middle, “suction”), the bulb inflates and the suction pressure pulls the liquid column into the pipette. Position **E** (on the side, “empty”) evens out the pressure and the liquid is released from the pipette. **Do not tilt a pipette with liquid inside and the bulb on under any circumstances.** The liquid may flow into the bulb, causing irreversible damage. The bulb is to be put on the pipette gently, **never insert the pipette deep into the bulb mouth!** The suction system would be damaged, or the pipette may be broken and the bulb destroyed completely.

⁶The pipette is calibrated “to deliver” (marked “EX”). For correct dosing, hold the pipette under an angle of 45° against the beaker wall. Before use, rinse the whole pipette with distilled water and, subsequently, with a few millilitres of your sample (empty into a waste beaker) to avoid possible contamination.

⁷The desiccator is used to cool down the crucibles. The desiccator must not be open for a longer period; try to minimize the contact of the inside environment with ambient humidity. Do not place crucibles into the desiccator directly after filtration, put them in the oven first. The lid is lubricated, therefore, never put the lid down on the table with the ground glass joint facing the surface. Turn the lid around and rest it on its handle and rim. During transport, **hold the desiccator firmly with both hands.**

⁸To rinse the precipitate, pull the syringe piston and mount the rubber hose onto the glass bottle. May you consider the manipulation with the syringe difficult, you can blow the air into the bottle directly with your mouth.

PRACTICAL REMARKS

1. Do not place any glassware into the oven, as it is designated for crucibles only. If you wish to dry out the glassware, rinse it with ethanol and leave it standing on the table.
2. Analytical balances are placed in the weighing room outside lab D, in the main corridor, between labs B and C. Write down the access code for the weighing room and use only that balance that is assigned to lab D. Each balance exhibits its uncertainty, thus, use only one balance for the whole task. The contribution of the uncertainty will then be constant and the results will not be biased.
3. Weigh the sample and other chemicals differentially, using the weigh boat. Tare the weight of the boat first. After weighing the sample, pour it out into the working container and weigh the boat again (even if there is no visible substance remaining

on it). Subtract the values of the first and final weighing. The result corresponds to the real weight of your sample.

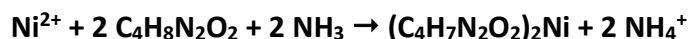
THEORY OF GRAVIMETRIC ANALYSIS

Gravimetric analysis belongs to selective, non-instrumental analytical methods. The basic principle is the transformation of the sample into a precipitate of low solubility and a subsequent formation of a weighing form. To enable analytical calculations, the weighing form is required to have into the defined composition. The selectivity of the method depends on the experiment setup and the selection of the precipitating agent. In the case of inorganic precipitating agents, such as hydrogen sulfide or sulfuric acid, the precipitate needs to be transformed into the weighing form. When using organic agents (dimethylglyoxime and 8-chinolinol), the precipitate form is usually identical with the weighing form. The selectivity of the method allows for the determination of ions of one element even in complex matrices. Within this laboratory task, Ni²⁺ ions will be determined in a simple matrix.

Precipitates may generally adopt two forms: crystalline and amorphous. The crystalline form is more suitable for the analysis due to higher purity and simpler filtration. The quality and purity of a precipitate depend on precipitation conditions. The precipitating agent is usually dosed in small batches while slowly stirring the solution. In many cases, the resulting precipitate is left to age, which allows for its “packing” (recrystallization), thereby facilitating filtration and resulting in higher purity.

In the next step, the precipitate and its mother liquor are separated. For the filtration, a filter paper or crucible may be used. Because it is not necessary to calcine the nickel precipitate, low-pressure filtration through a crucible will be employed. After the crucibles with the precipitate will be dried to constant weight (explained below), the weight percentage of nickel will be calculated.

In this task, nickel will be precipitated by dimethylglyoxime, generating a red complex:



WORKFLOW

Preparation of filter crucibles

In the first step, rinse three crucibles with distilled water and mark the frit bottom with a **pencil** (do not use pens or markers to avoid precipitate contamination). Place the crucibles into the Petri dish, into the oven and **write down the time**. **From now on until filtration, do not touch the crucibles with your hands; use only laboratory pincers for manipulation!!!**

In the morning part of your work, you have two options: Either you take the crucibles out of the oven after one hour, put them into the desiccator for 30 minutes, weigh them afterwards and put them back into the oven for another 30–60 minutes; or you leave them in the oven until the moment your precipitate will be left to age on the electric hotplate (described further). In case you choose the second option, time management is crucial. The ageing of the precipitates lasts 30 minutes, which is the same time required for the crucibles to cool down in the desiccator. If you take the crucibles out of the oven just in time, you may use them for filtration directly after weighing them. The crucibles must be dried to constant weight, meaning that two subsequent measurements after drying and cooling **must not differ by more than 0.5 mg**. If you are unsure, ask the assistant and follow his/her instructions.

Note 1: After rinsing the crucibles and placing them into the oven, you will be given a short test. Comments from the assistant will follow, as well as any questions you may have regarding the task. Do not hesitate to ask anything during the whole task.

Note 2: There is 120 °C (248 °F) in the oven, thus, to avoid thermal shock and crucible cracking, you have to put them into the desiccator for 30 minutes every time you take them out of the oven. Only use pincers for the manipulation with your crucibles until your precipitate is ready for filtration. Should you not do so, your results will be influenced by additional humidity and impurities transferred from your skin.

Preparation of the precipitate

Weigh 0.5–0.6 g of your sample into a beaker. In the fume hood, prepare 20 ml HCl into the cylinder. Pour the acid slowly to the sample and stir to obtain a clear green solution. If the solution is grey and turbid, place the beaker covered with a watch glass onto the gas plate and heat up until clear and green; or consult the assistant.

Transfer the clear solution quantitatively into a 250-ml volumetric flask and fill up to the mark with distilled water. Mix well. For the nickel determination, take 50 ml of the sample solution into a 250-ml beaker and fill up to approximately 100 ml with distilled water. Following the aforementioned procedure, prepare 3 beakers with sample solutions.

To assess the pH of the solution, bromothymol blue is used (Fig. 1). Add 3 drops of the indicator into each beaker (adding more or less will result in different colour intensity, yet will not affect the experiment) and neutralize the solution using ammonia. Ideally, the solution should be light blue (pH = 7.5; Fig. 2). Should the solution turn out too dark, you may add a few drops of HCl. This step may be followed only once in case of need, which will prevent the solution from unnecessary over-salting.

Hint: The colour change occurs quite fast. Add ammonia onto the rod and stir well. A blue trace after ammonia addition means that you are getting close to pH = 7.



Fig. 1 – The colour range of the solution with bromothymol blue at individual pH

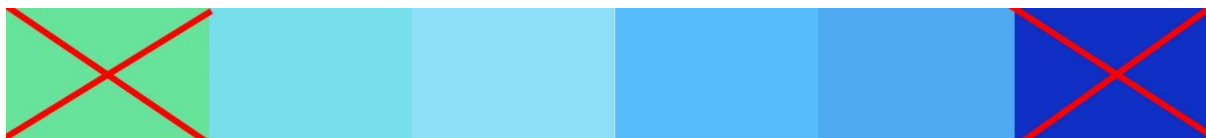


Fig. 2 – The colour range of the solution at the ideal, slightly alkaline pH

Place the neutralized solution onto the electric hotplate and heat up to 50–60 °C (122–140 °F; you can easily hold the beaker with your bare hands) and add 20 ml dimethylglyoxime into the warm solution. Glyoxime is flammable, thus work with it on your table, not in the fume hood close to open fire. Add glyoxime gradually, stir slowly and observe a red voluminous precipitate being formed. After the addition of the precipitating agent, place the beaker onto the hotplate and let sit for at least 30 minutes. **Time delays between the heating, addition of the precipitating agent and sitting on the hotplate should be minimized – the solution must not cool down.**

Hint: To eliminate time delay between precipitation steps, the samples should be precipitated consecutively one by one, not all three simultaneously. Place the solution onto the hotplate, prepare the precipitating agent, take the solution to your table, add the precipitating agent and place the solution back onto the hotplate. Later, the first solution to be filtered is the one that is resting on the hotplate for the longest time.

Before filtration, the following must be prepared:

- dry and weighed crucibles
- aged precipitates
- glass water bottle
- warm distilled water for rinsing (the consumption for the whole task is approx. 300 ml, therefore, two people may use one large beaker of water, which is to be placed onto the hotplate 10–15 minutes prior to filtration)

Connect the apparatus for filtration to the water pump and insert the crucible (lower pressure will help you place the crucible correctly into the rubberneck). Pour the precipitate into the crucible along the rod, creating an even compact layer. This will increase the efficiency of the filtration. The crucible may be maximally filled up to its half. After you filter the whole solution, rinse the beaker (3×) and the rod with warm water from the glass bottle. Disconnect the apparatus from the water pump, take out the crucible and place it into the oven (again, from now on, use pliers

for the manipulation with crucibles). Repeat the whole process with the two remaining precipitate solutions.

Note: When filtering, the sample may get through the frit into the waste filtrate. If your filter bottle contains only the filtrate of the currently filtered sample, you may pour it back into the beaker and filter again. If this is not the case and the filtrates are mixed, you must not repeat the filtration, as it would contaminate the sample. Thus, it is recommended to dispose of the filtrate after each filtration.

After the last crucible is placed into the oven, write down the exact time. One hour later, take out the crucibles, cool them down in the desiccator for 30 minutes and weigh them. Repeat this process until the crucibles reach constant weight (e.g. two subsequent weightings do not differ by more than $0.5 \text{ mg} = 0.0005 \text{ g}$).

CALCULATION

$$M_{\text{precipitate}} = 288.94 \text{ g}\cdot\text{mol}^{-1}$$

$$M_{\text{nickel}} = 58.6934 \text{ g}\cdot\text{mol}^{-1}$$

Calculate the weight percentage of nickel in your sample.

COMPLEXOMETRIC TITRATION (CHELATOMETRY)

CHEMICALS

Chelaton 3



- on the tables
- disodium salt of ethylenediaminetetraacetic acid (disodium EDTA; Na_2EDTA ; $\text{C}_{10}\text{H}_{16}\text{N}_2\text{Na}_2\text{O}_8$)
- preparation of the titrant (titrating agent, standard solution)



Lead chloride
[PbCl_2]



- in the weighing room
- determination of the exact concentration of the titrant
- $M = 278.1 \text{ g}\cdot\text{mol}^{-1}$



Nitric acid
[$1 \text{ mol}\cdot\text{l}^{-1} \text{ HNO}_3$]



- in the fume hood
- corrosive – in case of skin contact, rinse with water



Xylenol orange



- on the tables
- indicator for the determination of the exact concentration of the titrant



Hexamethylenetetramine



- on the tables
- a.k.a. urotropin, methenamine
- pH control



Hydrochloric acid
[HCl (1:1 V/V)]



- in the fume hood
- corrosive – in case of skin contact, rinse with water
- sample dissolution



Ammonium buffer solution



- in the fume hood
- pH adjustment before sample titration



Murexide



- on the tables
- indicator for the sample titration

LABORATORY EQUIPMENT

Stirring rod



Titration flask



Watch glass



Stock cylinder



Burette¹



¹Before titration, rinse the burette with distilled water and the titrant (disodium EDTA from the stock cylinder). To facilitate manipulation, pour the titrant into a beaker first, then into the burette. If using a funnel, do not forget to remove it from the burette prior to titration.

THEORY OF COMPLEXOMETRIC TITRATION

Complexometric titration is based on the reaction of a titrating agent (titrant, standard solution) with the analyte, or with an auxiliary agent.

Depending on the character of the reaction, the complexometric titration may be as follows:

- neutralization (acidi and alkalimetry)
- redox titration (mangano and iodometry)
- complexometry (chelatometry)
- precipitation (argentometry)

For the determination, the knowledge of molar ratios and of the exact concentration of the titrating agent is required. The addition of the titrant into the solution shifts the whole system towards the equivalence point. The equivalence point represents the moment, in which the whole sample is consumed and there is nothing more left for the titrant to bind to. For the molar ratio of 1:1, the titration goes as follows:

$$n(M) = n(\text{titrant})$$

The equivalence point may be indicated by a colour change of the solution, colour change of an indicator or a change of electrode potential in the case of instrumental methods. After the equivalence point is reached, the titration ends and the consumption (volume) of the titrant is documented. The lower the volume between the equivalence point and titration end, the more precise the determination.

Example: You observe a colour change in the equivalence point, but one more drop of the titrant is added to the solution. The result is thereby biased, because the consumed volumes in the equivalence point and at the end of titration (closing the burette) do not match. Therefore, it is advisable to repeat the titration multiple times.

Regarding the laboratory task, the following text will discuss complexometric titration, specifically chelatometry.

Complexometric reactions are based on the formation of little dissociated and highly water-soluble metal complexes. Within this laboratory task, the titrant is disodium salt of ethylenediaminetetraacetic acid ($\text{Na}_2\text{H}_2\text{Y}$, EDTA, or Chelaton 3; Fig. 3).

Structural formula of disodium EDTA

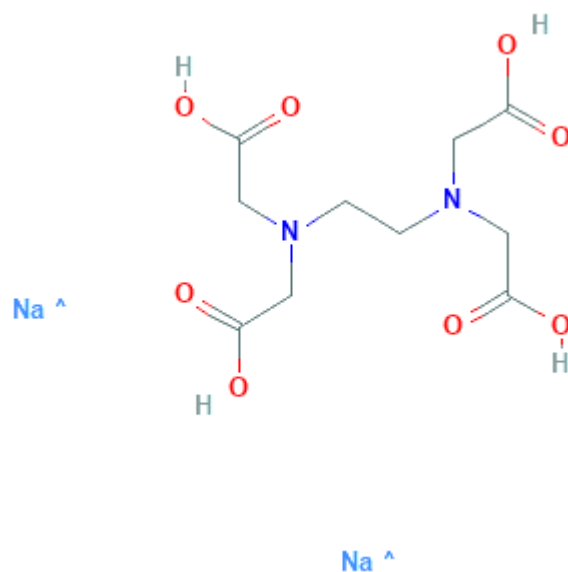
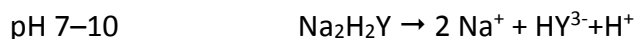


Fig. 3 – Structural formula of disodium EDTA

The dissociation of disodium EDTA is represented by the following equations:



The dissociation schemes show that H⁺ influences the reaction equilibrium. Therefore, it is necessary to add buffers to the sample solution. This phenomenon, however, may be taken advantage of when determining two or more metals in one solution at different pH.

In chelatometry, the colour change in the equivalence point is caused by the fact that the titrant first binds all free metal ions within the solution and then it forms a complex with ions in the metallochromic indicator. The basic assumption is that the metal-titrant complex is more stable than the metal-indicator complex and that the colour transition between MInd⁻ and HInd²⁻ is sufficiently evident.

WORKFLOW

Determination of the exact concentration of the titrant

The exact concentration of your titrant is required for the calculation of the weight percentage of nickel in your sample.

Prepare a standard solution of disodium EDTA with a concentration of $0.02 \text{ mol}\cdot\text{l}^{-1}$. Using a pipette, transfer 50 ml Na_2EDTA into the stock cylinder and fill up to the 500 ml mark with distilled water. Mix well.

In the next step, the exact concentration of the prepared solution will be determined. **Perform the determination 3x.** Put 0.12 g PbCl_2 into a titration flask, add 50 ml distilled water and 2–3 drops HNO_3 . Bring to a simmer on a gas plate (wait until PbCl_2 is dissolved completely), remove the flask from the gas plate, add another 50 ml distilled water. Once the solution is **cool**, add **xylene orange** and **hexamethylenetetramine** (urotropin). The solution should turn purple (Fig. 4).

Caution! If the solution looks turbid after the addition of urotropin, add few more drops of HNO_3 .

For the titration, use your standard solution, adding it dropwise until the solution turns yellow (Fig. 5). If you are unsure about the titration end, write down the current titrant consumption and add urotropin into the solution. When no colour change is observed, you reached the end of titration.

Caution! The colour change is not immediate, it takes several seconds, thus, add the titrant dropwise while continuously mixing the solution.



Fig. 4 – The colour range of the solution after the addition of urotropin prior to the titration



Fig. 5 – Color range after the titration

Determination of nickel in the sample

The weight percentage of nickel in the sample will be determined 3×.

Weigh 0.2–0.3 g of the sample into the titration flask and add 2–5 ml distilled water. Dissolve the sample by adding HCl (continue adding until the solution stops foaming) and bring to a short simmer on the gas plate (do not forget to cover the flask with a watch glass). Let the flask cool down to ambient temperature. Rinse the walls and watch glass into the flask and add 50 ml distilled water. Adjust the pH by adding ammonium buffer solution until the solution turns light blue (Fig. 6)



Fig. 6 – The colour range of the solution at the ideal, slightly alkaline pH

Add another 50 ml distilled water and murexide. Titrate the resulting yellow solution (Fig. 7) until it turns purple (Fig. 8). If you are close to the equivalence point, the solution colour starts turning red-brown. In the case you observe this transition, it is recommended to close the burette and mix the solution well for 5–10 seconds (the time delay of the colour change is not immediate). If the colour does not change, add another drop of the titrant and repeat the procedure. Should you be unsure of the end of the titration, write down the titrant consumption and add another drop thereof. If the colour does not change, the last value written down corresponds with the end of titration. In the opposite case (colour change is observed), write down the titrant consumption and add another drop thereof.

The next two solutions need to be prepared with such amount of the sample, which would assure the consumption of the titrant of 25 ml. For example, if in the case of $m_1 = 0.2300$ g the titrant consumption reached $V_1 = 17.2$ ml, the next titration requires to weight and dissolve 0.3343 g of the sample.



Fig. 7 – The colour range of the solution after the addition of murexide prior to titration



Fig. 8 – Color range corresponding to the end of titration

CALCULATIONS

$$M_{(\text{PbCl}_2)} = 278.1 \text{ g}\cdot\text{mol}^{-1}$$

$$M_{(\text{Ni})} = 58.6934 \text{ g}\cdot\text{mol}^{-1}$$

Calculate the weight percentage of nickel.

Calculate the average result at the very end, not continuously during the calculations.

All values should be listed to four decimal places.