

EXPERIMENT 2

GRAVIMETRIC ANALYSIS |

Structure

2.1	Introduction Expected Learning Outcomes	2.3	Experiment 2B: Gravimetrically determine Aluminium as Aluminium 8-hydroxyquinolate Principle Requirements Procedure Observations Calculations Result
2.2	Experiment 2A: Gravimetrically determine Nickel(II) In Nickel Steel as dimethylglyoximate Principle Requirements Procedure Observations Calculations Result	2.4	Summary
		2.5	Further Reading

2.1 INTRODUCTION

As you are aware, that the aim of chemical analysis is to determine the composition of naturally occurring or artificially prepared substances. This usually done in two steps. As a first step, qualitative analysis is performed to identify the different components of a substances. In the second step, the quantitative analysis is performed in which the relative amounts of these components are determined. In this laboratory course, you are required to perform the quantitative analysis of components of known substances only. In this unit we discuss some experiments for gravimetric determination of certain ions to illustrate quantitative analysis. In Unit 1 of this course, we have already described the scheme of qualitative analysis of mixtures of inorganic salts.

Methods of performing quantitative analysis are broadly classified into two types:

- i) Chemical methods which are based on quantitative performance of suitable chemical reactions. Titrimetry or volumetry and gravimetry are the examples of chemical methods of analysis.
- ii) Instrumental methods which require the use of instruments for measuring some physical properties such as electrical or optical properties of substances for determining their composition. Conductometry, potentiometry and colorimetry bare some of the examples of this class.

In the Chemistry Laboratory course (BCHCL 132), you might have performed some experiments on titrimetry, conductometry, potentiometry, and colorimetry. Here, you shall perform some experiment on gravimetry.

In gravimetric analysis, the component to be estimated is converted into an insoluble precipitate which is filtered, dried /ignited and weighed accurately. Knowing the stoichiometry of the chemical reaction involved in precipitation the mass of the precipitate is used to determine the amount of the component in the substance.

Expected Learning Outcomes

After performing the given experiments you should be able to:

- ❖ determine nickel and aluminium as their soluble salts;
- ❖ perform various operations, i.e. precipitation, filtration, washing, drying, ignition, cooling and weighing involved in gravimetric determinations;
- ❖ perform calculations involved in gravimetric determinations; and
- ❖ explain the principle underlying the gravimetric determination of nickel in steel and aluminium as aluminium 8-hydroxyquinolate.

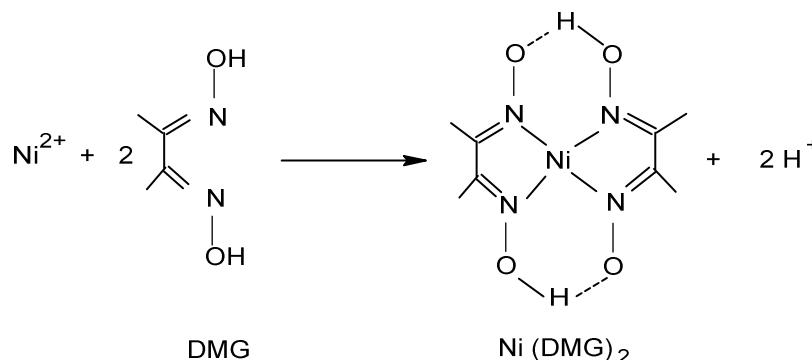
2.2 EXPERIMENT 2A: GRAVIMETRICALLY DETERMINE NICKEL(II) IN NICKEL STEEL AS DIMETHYL GLYOXIMATE

In this experiment you would learn about and perform the determination of nickel in a given sample of steel. Steel is an alloy of iron with other elements primarily carbon though a wide range of elements are used in these alloys. The nature and amount of a given elements is determined by the desired properties and application of steel. The presence of nickel in steel increases its tensile strength and provides it resistance from corrosion.

The complex formation involves the ionization of an oxime group each on the two ligands and the formation of coordinate bonds with nitrogen atoms.

2.2.1 Principle

In the gravimetric determination of nickel in steel, the Ni(II) ions are brought in solution by dissolving the steel sample in concentrated acid. These are then precipitated from a slightly alkaline medium with an alcoholic solution of dimethylglyoxime (H₂DMG). The medium is made alkaline by subsequent addition of aqueous ammonia solution. With the reagent nickel form a pure stable compound which may be conveniently weighed. The formation of the nickel complex, bis (dimethylglyoximate) nickel(II) can be represented as



This stable complex is rarely soluble and is of known composition. The precipitate is washed with cold water and dried at 110-120 °C to volatilise any unwanted reagent in it.

The presence of iron in the solution interferes with the determination as the ferrous ions also form a red coloured complex with dimethylglyoxime. Therefore, while bringing nickel ions into solution the ferrous ions are oxidized to ferric ions by nitric acid. These are then masked with the help of tartarate or citrate ions which keep Fe(II) ions in solution and do not let them complex with DMG.

The generation of hydrogen ions in the process of complex formation suggested that in acidic medium the reverse reaction would be significant. Therefore, the complex formation is carried out in alkaline solution.

2.2.2 Requirements

Apparatus	Number	Chemical
Beaker (400 cm ³)	1	Nickel steel (analyte sample)
Beaker (250 cm ³)	2	Hydrochloric acid(AR: 6 M)
Weighing bottle	1	Dimethylglyoxime in ethanol
Watch glass	1	1% (w/v)
Glass rod	1	Dilute ammonia solution (6 M)
Policeman rod (glass rod with rubber tip)	1	Whatman filter paper 41
Glass funnel	1	Tartaric acid 15% (w/v)
Tripod stand	1	Concentrated ammonia
Wash bottle	1	
Gooch sintered glass crucible	1	
Desiccator	1	
Analytical / Electronic balance	1	
Wire gauze	1	

Solutions Provided: Procedures for the preparation of these solutions are given for the sake of information. These solutions would be prepared for you by the counselor.

Dimethylglyoxime solution (1%). It is prepared by dissolving 1 g of dimethylglyoxime in 100 cm³ of 95% ethanol.

Dilute ammonia solution (6M): It is prepared by carefully adding 100 cm³ of liquor ammonia to 100 cm³ of water taken in a 250 cm³ beaker.

15% (w/v) tartaric acid: It is prepared by dissolving, 15 g of tartaric acid in about 60 cm³ of water taken in a 250 cm³ beaker and making up the volume to 100 cm³.



Gooch crucible

2.2.3 Procedure

The procedure for gravimetric determination of nickel in steel can be divided into the following steps:

- a) Bringing nickel present in steel into solution as Ni(II) ions and oxidizing iron to Fe(III) ions
- b) Selective precipitation of Nickel ions with DMG in alkaline medium
- c) Filtration and washing of the precipitate.
- d) Cooling and weighing the precipitate

Follow the instruction given below in the sequential order to accomplish these tasks.

- a) Bringing nickel present in steel into solution as Ni(II) ions and oxidizing Fe(II) to Fe(III) state.
- b) Selective precipitation of Nickel ions with DMG in alkaline medium.
 - i) Dilute the solution to about 250 cm³ in a 400 cm³ beaker and add 5g of tartaric acid or 30 cm³ of 15% (w/v) solution of tartaric acid (if tartaric acid is not available you may use citric acid)

Neutralize the solution with dilute aqueous ammonia solution. You should obtain a totally clear solution in this process (in case a precipitate appears or if the solution is not clear when it is made ammoniacal, then acidify the solution back and add more tartaric (or citric acid.)
 - iii) In case any insoluble material is still there filter it and wash with hot water containing a little ammonia/ammonium chloride solution.)
 - iv) The solution becomes highly ammoniacal then you must acidify by adding dilute hydrochloric acid. You may use a litmus paper on pH paper to monitor the process. There should be no smell of NH₃ ,
 - v) Warm the solution to 60-80 °C and add 20-25 cm³ of 1% ethanolic solution of dimethylglyoxime, immediately followed by dilute ammonia solution dropwise until the liquid is slightly ammoniacal,
 - vi) Stir well and keep the beaker on a water bath for 20-30 minutes and allow the solution stand for about an hour; the temperature should come down to room temperature during this time.
- c) Filtration and washing of the precipitate
 - i) Take a constant weight Gooch crucible and filter the precipitate obtained above
 - ii) Test the filtrate for complete precipitation by adding a little DMG solution to a few drops of the filtrate
 - iii) Wash the precipitate with cold until free form chloride ions, The presence of chloride ions can be tested by collecting a few drops of

the filtrate in a test tube, acidifying with HNO_3 , and adding a few drops of 0.1 M AgNO_3 . A white precipitate or turbidity indicates the presence of chloride ions. The washing is said to be complete when there are no chloride ions

- iv) Dry the precipitate by keeping the crucible at 100-120 °C in an oven for 45-60 minutes.
- v) Transfer the crucible to a desiccator containing fused calcium chloride and allow it to cool.
- vi) Take out the crucible from the desiccator and weigh the crucible with the precipitate.
- vii) Keep the crucible again in the oven for about 10 minutes, cool in the desiccator and weigh it again.
- viii) Repeat the heating –cooling –weighing cycle till a constant mass is obtained.

Precautions

- If the tartaric acid solution is not clear it must be filtered
- The pH of the solution from which the precipitation is to be done should be carefully controlled
- The amount of precipitating agent added should be controlled. If you use excess of DMG then a portion of the precipitate may dissolve as the alcohol content of the solution increases to a great extent.

2.2.4 Observations

Mass of steel taken

- i) Mass of empty weighing bottle = g
- ii) Mass of empty weighing bottle + steel = g
- iii) Mass of empty weighing bottle after transferring = g
the steel in to beaker

Mass of the empty crucible

- iv) 1st reading of mass of empty crucible =g
- v) 2nd reading of mass of empty crucible =g

Mass of crucible + $\text{Ni}(\text{DMG})_2$ (precipitate)

- vi) 1st reading of mass of crucible + precipitate =g
- vii) 2nd reading of mass of crucible + precipitate =g

You may need to take more reading if the mass of the crucible does not become constant.

2.2.5 Calculations

The mass of steel taken = ii) – iii) g = w g

Mass of Ni(DMG)₂ (precipitate) = vii) – v) = p g

Mass of Ni (DMG)₂ contain one mole of Ni²⁺ ions.

Thus,

288.7 g (1 mole) of Ni (DMG)₂ would contain = p [58.7/288.7] g of Ni²⁺ ions

Thus the mass of Ni in the given sample of steel = p[58.7/288.7] g =g

% of Nickel in the given sample of steel = 100 (mass of Nickel /mass of steel taken)%, so

$$\%Ni^{2+} = \frac{p}{w} \times 100$$

Substituting the values in the expression, we get, the percentage of Ni in the given sample of steel.

2.2.6 Result

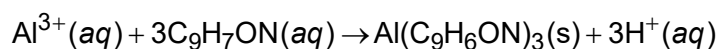
The percentage of nickel in the given sample of nickel steel is found to be = %

2.3 EXPERIMENT 2 B: GRAVIMETRICALLY DETERMINE ALUMINIUM AS ALUMINIUM 8-HYDROXYQUINOLINATE

In Experiment 2a you performed the determination of nickel ions as dimethylglyoximate in nickel steel. In this experiment, you will perform the determination of aluminium ions as aluminium 8-hydroxyquinolate or oxinate.

2.3.1 Principle

Aluminium ions are precipitated as aluminium(III) oxinate from ammonium acetate-acetic acid buffered solution at pH 5.0 by the addition of 8-hydroxyquinoline (oxine) solution in acetic acid. The precipitate is filtered through a sintered glass crucible, washed with water, dried at 130 – 140°C in an electric oven and weighted as aluminium (III) oxinate.



2.3.2 Requirements

Apparatus	Number	Chemical
Beaker (400 cm ³)	1	Potash alum
Beaker (250 cm ³)	2	Concentrated Hydrochloric acid
Weighing bottle	1	Acetic acid

Watch glass		Ammonium acetate
Glass rod	1	8-Hydroxyquinoline
Rubber policeman	1	Whatman filter paper 41
Glass funnel		
Tripod stand	1	
Pair of tongs		
Wash bottle	1	
Gooch sintered glass crucible (G4)	1	
Desiccator	1	
Water bath		
Analytical / Electronic balance	1	
Wire gauze	1	

2.3.3 Procedure

Weigh out accurately about 0.5 g of potash alum from a weighing bottle into a 400 cm³ beaker. Dissolve in 20–25 cm³ of distilled water. Alternatively, take 25 cm³ of the solution prepared by your counselor. Add 1 cm³ of conc. HCl and dilute the solution to 150cm³. Add 5–6 cm³ of 8-hydroxyquinoline (oxine) reagent (a 10% solution in 20% acetic acid) and heat to 70 – 80°C. Slowly add 25 cm³ of 2 M ammonium acetate solution dropwise and with constant stirring to ensure complete precipitation. If the supernatant liquid is yellow to orange in colour, it means enough 8-hydroxyquinoline has been added. Heat the contents on boiling water bath for half an hour so that the precipitate becomes granular and of easily filterable form. Allow to cool.

Filter the precipitate through a constant weight sintered glass crucible of porosity G4. Wash the precipitate first with hot water and then with cold water. Continue washing till the filtrate is almost colourless. Dry the precipitate at 130 – 140°C in an electric drying oven. Cool in a desiccator and weigh as Al(C₉H₆NO)₃. Repeat the process of heating, cooling and weighing till the weight becomes constant.

2.3.4 Observations

Weight of potash alum

- | | | |
|---|---|---|
| i) Weight of empty weighing bottle | = | g |
| ii) Weight of weighing bottle + potash alum | = | g |
| iii) Weight of weighing bottle after transferring | = | g |

Weight of sintered crucible

iv) 1st weight of sintered crucible = g

v) 2nd weight of sintered crucible = g

Weight of sintered glass crucible + precipitate

vi) 1st weight of crucible + precipitate = g

vii) 2nd weight of crucible + precipitate = g

2.3.5 Calculations

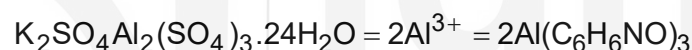
Calculate the percentage of aluminium ions in potash alum as follows:

Weight of potash alum taken for experiment = ii) – iii) g

$$= w \text{ g}$$

Weight of $\text{Al}(\text{C}_9\text{H}_6\text{NO})_3$ formed = vii) – v) g = x g

You know that one mole of potash alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$) contains two moles of aluminium ions which are converted into two moles of aluminium(III) 8-hydroxyquinolate. Thus,



$$948.76 \text{ g} \qquad \qquad \qquad = 2 \times 26.98 \text{ g} \quad = 2 \times 459.43 \text{ g}$$

$$w \text{ g} \qquad \qquad \qquad = y \text{ g} \quad = x \text{ g}$$

Hence, weight of Al^{3+} ions in x g of $\text{Al}(\text{C}_9\text{H}_6\text{NO})_3$

$$y = \frac{26.98}{459.43} \times x \text{ g}$$

Now this y g of Al^{3+} ions are present in w g of the potash alum taken for analysis. Hence, percentage of Al^{3+} ions is potash alum

$$\begin{aligned} \% \text{Al}^{3+} &= \frac{y}{w} \times 100 \\ &= \frac{26.98 \times x}{459.43 \times w} \times 100\% \end{aligned}$$

$\% \text{Al} = \frac{26.98 \times \text{weight of } \text{Al}(\text{C}_9\text{H}_6\text{NO})_3 \text{ formed}}{459.43 \times \text{weight of potash alum taken}} \times 100\%$

Compare this value with the theoretical percentage of Al^{3+} ions (5.69%, calculated in Experiment 4) in potash alum.

If you have performed the experiment carefully, the experimental and the calculated values should agree within 0.5% with each other. Following a similar procedure, you can calculate the percentage of Al^{3+} ions in any other substance.

2.3.6 Result

You can report your result in any one of the following forms as instructed by your counselor.

Weight of $\text{Al}(\text{C}_9\text{H}_6\text{NO})_3$ formed = g

or

Percentage of aluminium ions in potash alum = %

2.4 SUMMARY

In this unit we described the gravimetric estimation of nickel and aluminium ions present in a water soluble compound. We discussed how to perform various operations involved in gravimetric determinations and also how to calculate the percentage of these ions in their compounds.

2.5 FURTHER READING

1. Vogel's Qualitative Inorganic Analysis, G. Svehla, Orient Longman, Sixth edition, 1987.
2. A Text Book of Quantitative Inorganic Analysis, A.I. Vogel, J. Bassett, R.C. Denney, G.H. Jeffery, J. Mendham, Longman, Fourth edition, 1978.