GUIDE FOR M.Sc. INORGANIC CHEMISTRY PRACTICALS

For use by students of M.Sc. Chemistry – Semesters 1 & 2, Mahatma Gandhi University.
(2001 admission onwards)

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M.Sc. Chemistry Practical Syllabus for semesters 1 & 2

CH-205 INORGANIC CHEMISTRY – PRACTICALS-I (60 + 60 hours)

A – Qualitative analysis

I. Separation and identification of four metal ions including two less familiar elements such as Tl, W, Se, Mo, Ce, Th, Ti, Zr, V, U and Li. (Na, K and eliminating anions not to be given. A minimum of 5 mixtures containing 5 different rare ions have to be analysed by a student)

B – Quantitative analysis

II. Complexometric titration for the estimation of hardness of water, Zn, Mg, Ca, Ni ions.

III. Colourimetric estimation of Fe, Cu, Ni, Mn, Cr, NH_4^+, phosphate and nitrate ions.

References

1. Vogel – A Text Book of Qualitative Inorganic Analysis – Longman
2. Kolthoff & Stenger – Volumetric Analysis – Intersience
3. Vogel – A Text Book of Quantitative Inorganic Analysis – Longman
4. Kolthoff & Sandell - Text Book of Qualitative Inorganic Analysis.
5. G. Schwarzen Back "Complexometric Titration" Interscience.

Note to Examiners:

1. Candidates may be asked to report four metal ions present in the given mixture.
2. While reporting the scheme of analysis the student is expected to indicate the chemistry involved in the relevant reactions.
3. The candidates may be asked to give the procedure for the quantitative analysis giving the chemistry behind the experiments.
4. Each student has to carry out I, II and III experiments for the practical examination.

COLOURIMETRIC ANALYSIS

COLOURIMETRIC ESTIMATION OF NICKEL

Aim: To determine the mass of nickel present in the whole of the given solution colourimetrically as the glyoxime complex.

Principle: [Ref: (1) Cumming and Kay, Quantitative chemical analysis, 10th edn., (1948), p 271. (2) Vogel's textbook of quantitative inorganic analysis, 4th edn., ELBS (1978), p 747.]

When dimethyl glyoxime is added to an alkaline solution of a nickel salt which has been treated with an oxidizing agent such as bromine or sodium hypochlorite, a red colour is produced. The red complex soluble in water contains nickel in a higher oxidation state (regarded as III or IV). The complex has absorption maximum at 445 nm. [This should be distinguished from glyoximate of nickel(II), which is insoluble in water but soluble in chloroform].Full colour development requires a few minutes after adding reagents and has to be measured within 10 to 15 minutes.

Chemicals required: (per student)

(1) Pure nickel ammonium sulfate, about 1gram.
(2) Bromine water or 1% sodium hypochlorite solution, about 10 cm^3.
(3) Concentrated ammonia solution.
(4) 1% solution of dimethyl glyoxime in ethanol.

Apparatus required:

(1) One 1000 cm^3 volumetric flask (common for all students).
(2) Two 100 cm^3 volumetric flasks.
(3) Eight 50 cm^3 volumetric flasks.
(4) 10 cm^3 graduated pipette.
(5) Funnel, beaker.
(6) Photoelectric colourimeter / spectrophotometer.

Procedure:

(<u>Note</u>*: Colours are developed in the solutions for calibration and estimation simultaneously. Switch on the colourimeter at least 30 minutes before use Set zero using the blank solution. Do not switch off or change settings till all readings are taken.*)

<u>Standard nickel solution</u> is prepared by dissolving 0.673 g of pure nickel ammonium sulfate, accurately weighed, in distilled water and making up to 1000 cm^3. Make up 10 cm^3 of this solution to 100 cm^3. One cubic centimeter of this solution contains 0.01 mg of nickel.

Transfer the <u>given solution for estimation</u> quantitatively into a 100 cm^3 volumetric flask and make up to the mark using distilled water.

Exactly 2, 4, 6, 8 and 10 cm^3 each of the standard nickel solution are pipetted into five different 50 cm^3 volumetric flasks. 10 cm^3 distilled water is taken in another 50 cm^3 volumetric flask to be used as blank to set the spectrophotometer. Two suitable volumes (say 5 cm^3 and 7 cm^3) of the given solution are taken in two other 50 cm^3 volumetric flasks. Add about 20 cm^3 of distilled water, 2 cm^3 of saturated bromine water (or 1% sodium hypochlorite solution) and 2 cm^3 of ammonia solution to each flask and mix well. Then add 2 cm^3 of 1% dimethyl glyoxime solution to each flask, mix and make up using distilled water. Keep for 5 minutes and measure the absorbance at 445 nm. Plot the absorbance against volume of standard nickel solution to obtain the calibration curve.

Using the absorbance values for the given solution, find the corresponding volume equivalent to the standard nickel solution from the calibration curve. Mass of nickel in this volume and hence mass of nickel in the whole of the given solution is then computed.

Result:
Mass of nickel in the whole of the given solution = (1) _____ g.

(2) _____ g.

Calculation:

(a) Calibration:

Mass of nickel ammonium sulfate weighed = w g.
∴ mass of nickel per cm^3 of standard solution, (m) = (0.01 / 0.673) × w mg.

(b) Estimation:

Volume of made up solution used for colour development = v cm^3.
Volume corresponding to standard solution from graph = V cm^3.
Mass of nickel corresponding to V cm^3.standard = V.m = x mg.
∴Mass of nickel corresponding to v cm^3 given solution = x mg.
∴Mass of nickel in the whole of the given solution = (x / v) × 100 mg.

Note to instructor: The first 1000 cm^3 of standard solution is sufficient for all students together. Give a volume between 8 and 12 cm^3 from this for estimation to each student. If 100 cm^3 volumetric flasks are used in place of 50 cm^3 flasks for developing colour, the volumes of nickel solutions and reagents used in the procedure must be doubled.

COLOURIMETRIC ESTIMATION OF FERRIC IRON
(Ammonium thiocyanate method)

Aim: To determine the mass of ferric iron present in the whole of the given solution colourimetrically as the thiocyanate complex.

Principle: When treated with excess of thiocyanate ions, ferric salt solutions produce red colour proportional to the amount of iron present.

$$Fe^{3+} + 6CNS^- \rightarrow [Fe(CNS)_6]^{3-}$$

A calibration curve can be obtained by plotting the absorbance against concentration for a set of standard solutions after developing the colour using thiocyanate. The concentration of an unknown solution can then be obtained by developing its colour under similar conditions and measuring its absorbance. The colour fades with time due to reduction of ferric iron by thiocyanate ions. Therefore readings have to be taken immediately after developing the colour.

Chemicals required: (per student)

(1) Ferric alum [$NH_4Fe(SO_4)_2\ 12H_2O$; molar mass =482.2] – 1 g
(2) approx. 5 N HCl (iron-free) - 100 cm^3
(3) 20% amm. thiocyanate solution - 100 cm^3

Apparatus required:

(1) Ten 100 cm^3 volumetric flasks.
(2) 10 cm^3 graduated pipette.
(3) Funnel, beaker.
(4) Photoelectric colourimeter / spectrophotometer.

Procedure:

(*Note: Colours are developed in the solutions for calibration and estimation simultaneously. Switch on the colourimeter at least 30 minutes before use. Set zero using the blank solution. Do not switch off or change settings till all readings are taken*)

A standard iron solution containing 0.1 mg iron per milliliter is prepared as follows: 0.8634 g ferric alum is weighed into a 100 cm^3 volumetric flask. 10 cm^3 of conc. HCl (iron-free) is added to prevent hydrolysis. It is then made up to 100 cm^3. 10 cm^3 of this solution is pipetted into another volumetric flask and made up to 100 cm^3. This solution now contains 0.1 mg iron per milliliter.

Transfer the given solution quantitatively into a 100 cm^3 volumetric flask and make up to the mark using distilled water.

2, 4, 6, 8 and 10 cm^3 of standard iron solution are taken in 5 different 100 cm^3 volumetric flasks. 10 cm^3 of distilled water is taken in another volumetric flask to be used as blank to set the spectrophotometer. Two suitable volumes (say 4 cm^3 and 6 cm^3) of the given solution are also taken in two other volumetric flasks. 5 cm^3 of 5 N HCl and 5 cm^3 of 20% amm. thiocyanate solution are added to each and made up to 100 cm^3. The absorbances are measured at 480 nm. Plot the absorbance against volume of standard iron solution to obtain the calibration curve.

Using the absorbance values for the given solution, find the corresponding volume equivalent to the standard iron solution from the calibration curve. Mass of iron in this volume and hence mass of iron in the whole of the given solution is then computed.

Result:
Mass of iron in the whole of the given solution = (1) _____ g.

(2) _____ g.

Calculation:

Calibration:

Mass of ferric alum weighed = w g.
∴ mass of iron per cm^3 of standard solution, (m) = (0.1 / 0.864) × w mg.

Estimation:

Volume of made up solution used for colour development = v cm^3.
Volume corresponding to standard solution from graph = V cm^3.
Mass of iron corresponding to V cm^3.standard = V.m = x mg.
Mass of iron corresponding to v cm^3 = x mg.
∴Mass of iron in the whole of the given solution = (x / v) × 100 mg.

Note to instructor: Solution remaining from the first 100 cm^3 of standard solution can be used for giving unknown to students. Give a volume between 8 and 12 cm^3 from this for estimation to each student.

COLOURIMETRIC ESTIMATION OF FERRIC IRON
(Thioglycolic acid method)

Aim: To determine the mass of ferric iron present in the whole of the given solution colourimetrically as the thioglycolic acid complex.

Principle: [Ref: Vogel's textbook of quantitative inorganic chemistry, 4th edn., ELBS, p 743.]

The use of thioglycolic acid (mercapto acetic acid, $HSCH_2COOH$) for the determination of Fe is of importance because it is relatively free from interference giving a red-purple colour with Fe(III) which can be measured at 535 nm. Precipitation of Al(III) and Cr(III) ions, if present, can be prevented by the addition of ammonium citrate. The reaction with Fe(III) is represented as:

$$Fe^{3+} + 2\ HSCH_2COOH + 3\ OH^- \rightarrow [Fe(OH)(SCH_2COO)_2]^{2-} + 2\ H_2O$$

Chemicals required: (per student)

(1) Ferric alum [$NH_4Fe(SO_4)_2\ 12H_2O$; molar mass =482.2] – 1 g
(2) approx. 6 N H_2SO_4 : Add 1 cm^3 of conc. sulphuric acid to 5 cm^3 of water in a small beaker and mix well.
(3) Thioglycolic acid solution: Dissolve 10 cm^3 of analytical grade thioglycolic acid in water and dilute to 100 cm^3
(4) Ammonium hydroxide solution: Take 25 cm^3 of conc. ammonia solution and dilute to 100 cm^3.

Apparatus required:

(1) Ten 100 cm^3 volumetric flasks.
(2) 10 cm^3 graduated pipette.
(3) Funnel, beaker.
(4) Photoelectric colourimeter / spectrophotometer.

Procedure:

(*Note: Colours are developed in the solutions for calibration and estimation simultaneously. Switch on the colourimeter at least 30 minutes before use. Set zero using the blank solution. Do not switch off or change settings till all readings are taken*)

A standard iron solution containing 0.1 mg iron per milliliter is prepared as follows: 0.8634 g ferric alum is weighed into a 100 cm^3 volumetric flask. 5 cm^3 of 6 N H_2SO_4 is added to prevent hydrolysis. It is then made up to 100 cm^3. 10 cm^3 of this solution is pipetted into another volumetric flask and made up to 100 cm^3. This solution now contains 0.1 mg iron per milliliter.

Transfer the given solution quantitatively into a 100 cm^3 volumetric flask and make up to the mark using distilled water.

2, 4, 6, 8 and 10 cm^3 of standard iron solution are taken in 5 different 100 cm^3 volumetric flasks. 10 cm^3 of distilled water is taken in another volumetric flask to be used as blank to set the spectrophotometer. Two suitable volumes (say 4 cm^3 and 6 cm^3) of the given solution are also taken in two other volumetric flasks. 5 cm^3 of thioglycolic acid solution and 5 cm^3 of ammonia solution are added to each and made up to 100 cm^3. The absorbances are measured at 535 nm. Plot the absorbance against volume of standard iron solution to obtain the calibration curve.

Using the absorbance values for the given solution, find the corresponding volume equivalent to the standard iron solution from the calibration curve. Mass of iron in this volume and hence mass of iron in the whole of the given solution is then computed.

Result:
Mass of iron in the whole of the given solution = (1) _____ g.

(2) _____ g.

Calculation:

Calibration:

Mass of ferric alum weighed = w g.

$\therefore$ mass of iron per cm^3 of standard solution, (m) = (0.1 / 0.864) $\times$ w mg.

Estimation:

Volume of made up solution used for colour development = v cm^3.

Volume corresponding to standard solution from graph = V cm^3.

Mass of iron corresponding to V cm^3 standard = V.m = x mg.

Mass of iron corresponding to v cm^3 = x mg.

$\therefore$ Mass of iron in the whole of the given solution = (x / v) $\times$ 100 mg.

Note to instructor: Solution remaining from the first 100 cm^3 of standard solution can be used for giving unknown to students. Give a volume between 8 and 12 cm^3 from this for estimation to each student.

COLOURIMETRIC ESTIMATION OF CHROMIUM(VI)
(Diphenyl carbazide method)

Aim: To determine the mass of Cr(VI) present in the whole of the given solution colourimetrically as the diphenyl carbazide complex.

Principle: When treated with diphenyl carbazide, Cr(VI) salt solutions produce a red-violet colour of unknown composition proportional to the amount of Cr(VI) present. A calibration curve can be obtained by plotting the absorbance against concentration for a set of standard solutions after developing the colour using diphenyl carbazide. The concentration of an unknown solution can then be obtained by developing its colour under similar conditions and measuring its absorbance.

Chemicals required: (per student)

(1) Potassium dichromate, 600 mg.
(2) approx. 6 N H_2SO_4, 50 cm^3.
(3) Diphenyl carbazide, 100 mg.
(4) Acetone, 25 cm^3.

Apparatus required:

(1) One 1000 cm^3 volumetric flasks.
(2) Ten 100 cm^3 volumetric flasks.
(3) 10 cm^3 graduated pipette.
(4) Funnel, beaker.
(5) Photoelectric colourimeter / spectrophotometer.

Procedure:

Fresh reagent is prepared by dissolving 100 mg diphenyl carbazide in 25 cm^3 acetone.

A standard Cr(VI) solution containing 0.01 mg Cr per milliliter is prepared as follows: 0.2829 g potassium dichromate is weighed into a 1000 cm^3 volumetric flask and made up with distilled water. 10 cm^3 of this solution is pipetted into another volumetric flask and made up to 100 cm^3. This solution now contains 0.01 mg Cr per milliliter.

Transfer the given solution quantitatively into a 100 cm^3 volumetric flask and make up to the mark using distilled water.

2, 4, 6, 8 and 10 cm^3 of standard Cr(VI) solution are taken in different 100 cm^3 volumetric flasks. 10 cm^3 of distilled water is taken in another volumetric flask to be used as blank to set the spectrophotometer. Two suitable volumes (like 4 cm^3 and 6 cm^3) of the given solution are taken in two other

volumetric flasks. 4 cm^3 of 6 N H_2SO_4 and 2 cm^3 of diphenyl carbazide solution are added to each and made up to 100 cm^3. The absorbances are measured at 540 nm. Plot the absorbance against volume of standard Cr solution to obtain the calibration curve.

Using the absorbance values for the given solution, find the corresponding volume equivalent to the standard Cr solution from the calibration curve. Mass of Cr in this volume and hence mass of iron in the whole of the given solution is then computed.

Result:

Mass of chromium in the whole of the given solution = (1) _____ g.

(2) _____ g.

Calculation:

Calibration:

Mass of potassium dichromate weighed = w g.

∴ mass of chromium per cm^3 of standard solution, (m) = (0.01 / 0.2829) × w mg.

Estimation:

Volume of made up solution used for colour development = v cm^3.

Volume corresponding to standard solution from graph = V cm^3.

Mass of chromium corresponding to V cm^3 standard = V.m = x mg.

Mass of chromium corresponding to v cm^3 = x mg.

∴Mass of chromium in the whole of the given solution = (x / v) × 100 mg.

Note to instructor: Solution remaining from the first 1000 cm^3 of standard solution can be used for giving unknown to students. Give a volume between 8 and 12 cm^3 from this for estimation to each student.