School of Chemistry
University of Hyderabad

CH104 Quantitative Analysis Lab

LAB-MANUAL

Course website - http://chemistry.uohyd.ernet.in/~mvr/ch104

CH104 Quantitative Analysis (Lab)

Introduction

In this course you will learn basic volumetric and gravimetric methods of chemical analysis. Volumetric involves measurement of volumes of reagents participating in a chemical reaction. Gravimetric involves measurement of weights of solid precipitates resulting from a chemical reaction.

The usual questions which are answered by doing a quantitative chemical analysis are: (i) What is the concentration of substance *A* in the given solution. (ii) What is the percentage by weight of substance *A* in the given sample. These are important questions in many contexts in chemistry as well as other fields of science dealing with any type of material.

What you will learn in this one semester course (about a dozen 3 hour laboratory sessions) is a small part of analytical science. You will become familiar with the theoretical basis of some of the most commonly used analytical procedures, and with practice you will be able to produce a reliable result from your work in the laboratory. You will be always on the look out for possible sources of errors in your measurements because a result which is not reliable is no result at all.

Suggested Reading: (i) Vogel's Textbook of Quantitative Inorganic Analysis, 4th Edition, Revised by J. Bassett, R. C. Denney, G. H. Jeffery, and J. Mendham, Longmann (1982); (ii) Quantitative Analysis, R. A. Day and A. L. Underwood, 5th Edition, Prentice-Hall (1988).

General Instructions:

(i) For each lab period you will be given the detailed procedure in advance. Record your observations in the data sheets provided. Submit a detailed report as per the instructions. The report should be prepared on A4 size sheets and attached to the printed procedure sheets and submitted the following week. The reports should be preserved in a folder till the end of the course. Follow a simple style, write neatly and legibly.

(ii) Read the background material either from the above references or any other source before coming to the lab.

(iii) Work safely: wear a lab coat, wear goggles, don't pipette corrosive substances with mouth – use an aspirator.

(iv) Work neatly and quietly – keep your bench space and common bench space and the balances clean and tidy. Untidy work may attract negative marking.

(v) Note your measurements (weights, titre values) in the sheet given as and when you take a reading. Get it signed by the instructor before leaving the lab.

Your work will be continuously evaluated based on the accuracy of the results, lab report and viva. There will be no lab exams.

This lab manual and additional material is at the `Course website -`
`http://chemistry.uohyd.ernet.in/~mvr/ch104`

Experiment 1 : Check the accuracy and precision of your volumetric measurements.

Method: Measure out known volumes of distilled water using various volumetric apparatus and determine their weights accurately, correct to 1 mg. Calculate the volume using density. Repeat the measurement several times.

Density of pure water at different temperatures :

Temp. / °C	21	23	25	27	29	30
Density / g cm^{-3}	0.9970	0.9965	0.9960	0.9955	0.9949	0.9946

Procedure: Clean the glassware (burette, pipette, measuring jar, conical flask) thoroughly. Rinse with distilled water and drain. If the glassware is clean the water will drain out completely without forming droplets on the glass surface.

Familiarize yourself with the use of burette, pipette, standard flask, measuring jar and the analytical balance.

Note the weight of a conical flask accurately (correct to 1 mg). Measure out accurately a known volume of distilled water (for example, 5 ml, 10 ml etc.) into the conical flask using your burette. Record the weight. Calculate the volume using density. Compare the calculated volume with the value read from the burette. Repeat with different initial and final burette readings.

Do the above experiment with your pipette, standard flask, measuring jar. Repeat at least once.

Record your observations in tabular form.

Wt of empty flask (g)	Initial burette reading (ml)	Final burette reading (ml)	Measured volume (ml)	Wt of flask + water (g)	Calculated volume (ml)

Wt of empty flask (g)	Volume measured with pipette / standard flask / measuring jar (ml)	Wt of flask + water	Calculated volume(ml)

Record your conclusion.

Study Question: Describe the meaning of the terms: (i) accuracy, (ii) precision.

Experiment 2 : Acid base titration. Standardisation of sodium hydroxide with potassium hydrogenphthalate.

Method: Potassium hydrogenphthalate is a monobasic acid. The neutralization reaction with sodium hydroxide is represented as,

$HK(C_8H_4O_4)$ + NaOH = $NaK(C_8H_4O_4)$ + H_2O.

The equivalent weight of each reagent in the above reaction is its molecular weight. A solution having known concentration of the acid is prepared by dissolving the solid in water. This is the standard solution. A known volume is then titrated against sodium hydroxide using phenolphthalein as indicator. Phenolphthalein is colorless in acid and red in alkali. At the end point the colorless solution containing the indicator becomes red.

Procedure:

Preparation of the standard solution: Clean a 100 ml standard flask. Rinse it three times with small quantities of distilled water. Put a clean and similarly rinsed funnel on top. Transfer about 2 g of potassium hydrogenphthalate to a clean dry weighing bottle and note the weight accurately. Carefully transfer the solid to the funnel. Weigh the bottle again. With the help of glass rod carefully add distilled water to the funnel taking care to bring all the solid into the flask. Rinse the funnel several times with small quantities of distilled water and remove the funnel. Gently swirl the flask to dissolve the solid completely, adding more water if necessary. After the solid has completely gone into solution, carefully add more distilled water to the standard flask till the level touches the graduation. You will have to add the water drop by drop when you are close to the graduation mark. View without parallax. *If you added too much water you will need to repeat from start.* Stopper the flask and mix the solution by gently inverting it and reversing several times. Calculate the normality of the solution. *This is the procedure which you will follow also for future experiments for the preparation of standard solutions.*

Standardisation of sodium hydroxide: Clean a burette and rinse three times with small quantities of distilled water. Rinse it again three times with small quantities of sodium hydroxide solution. Fill it with the sodium hydroxide solution. Note the initial reading.

Clean a conical flask and rinse it three times with distilled water. Pipette 20 ml of your standard solution into the conical flask. Add a few drops of the indicator (phenolphthalein). Titrate by carefully running in the solution from the burette. Gently swirl the flask during the titration. Stop when the colour changes to red. Note the burette reading. *The end point is obtained within one drop of the alkali.* Repeat till two consecutive titre values are same. *This is the general procedure for titrations. In future the description will be more concise, omitting washing, rinsing etc. But remember to do them!*

Calculate the normality of sodium hydroxide, using $V_{\text{acid}}N_{\text{acid}} = V_{\text{alkali}}N_{\text{alkali}}$ where V denotes volumes and N denotes normality.

Study Questions: (i) What is a standard solution? What are primary and secondary standards? What are the main characteristics of a reagent used as primary standard for titrations? (ii) Why do you rinse the burette with the reagent but not the titration flask? (iii) For more accurate work, a known amount of the acid in solid form is directly added to the titration flask, dissolved in some distilled water (volume not precisely known) and titrated against the alkali. How will you calculate the normality of the alkali in this case?

Experiment 3 : Acid base titration. (i) Standardisation of hydrochloric acid. (ii) Estimation of sodium carbonate. (iii) Estimation of sodium carbonate and sodium bicarbonate in a mixture.

Method: Indicators change colour within well defined pH ranges: phenolphthalein changes from colourless to red in the range 8.0 - 9.6; methyl orange changes from red to yellow in the range 3.1 - 4.4. The pH just after the neutralization point depends upon the strength of the acid / base, ie., their pK_a / pK_b.

Hydrochloric acid is standardized against previously standardized sodium hydroxide using phenolphthalein as indicator: $HCl + NaOH = NaCl + H_2O$.

The decomposition of carbonate by acid takes place in two steps: (i) $CO_3^{2-} + H^+ = HCO_3^-$. (ii) $HCO_3^- + H^+ = H_2O + CO_2$. At the end of step (i), the pH will be near about 8 or 9. After the complete neutralization, the next drop of HCl will bring down the pH to near about 3 or 4.

The Na_2CO_3 content of the given sample is determined by titration against standard hydrochloric acid using methyl orange as indicator: $Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$. The equivalent weight of Na_2CO_3 is half its molecular weight (M). This means $M/2$ g of Na_2CO_3 is equivalent to 1000 ml of 1 N HCl. It also means that the molarity of a solution of Na_2CO_3 is half its normality.

The total amount of carbonate and bicarbonate in the mixture is determined by titration against standard hydrochloric acid using methyl orange as indicator: $CO_3^{2-} + HCO_3^- + 3H^+ = 2H_2O + 2CO_2$. Another titration using phenolphthalein as indicator will give the concentration of carbonate. $CO_3^{2-} + H^+ = HCO_3^-$. If the above titre values are V_m and V_p respectively, then carbonate is equivalent to $2V_p$ and bicarbonate is equivalent to $V_m - 2V_p$. *Note that in the second titration the pH change is relatively slow near the neutralization point, therefore the colour change is not sharp and the titration has to be done slowly*.

Procedure:

(i) *Standardization of hydrochloric acid*: Transfer 25 ml of sodium hydroxide solution to a 250 ml conical flask using a pipette. Dilute with a little water (about 10 ml) and add 1-2 drops of phenolphthalein. Titrate against hydrochloric acid taken in a burette. Repeat till concordant titre values are obtained. Calculate the normality of the acid using the given normality of sodium hydroxide.

(ii) *Estimation of Na_2CO_3 content of the given sample*:

A : Weigh accurately about 0.6 g of the sample (w g) into a 100ml standard flask. Dissolve in distilled water and make upto the mark with distilled water. Titrate 25 ml of this solution against standard hydrochloric acid (normality, N_a) using 1-2 drops of methyl orange as indicator. When the colour becomes very faint yellow, continue the titration dropwise until the colour becomes orange or a faint pink. Repeat the titrations till concordant values (V_a) are obtained. Calculate the normality ($N_b = V_aN_a/25$) of the sodium carbonate solution and the percentage purity of the sample. [Amount of Na_2CO_3 in the weighed sample, $m = (100/1000) \text{ x } (N_b/2) \text{ x } M$; percentage purity = $100m/w$].

B : Repeat the above experiment by accurately weighing about 0.15 g of the solid sample to a 250 ml titration flask (ie., conical flask), dissolving it in water and diluting to about 40 ml and titrating as before. Calculate the percentage purity. The amount of Na_2CO_3 in the weighed sample is, $m = (N_a \text{ x } V_a /1000) \text{ x } (M /2)$.

Estimation of Na_2CO_3 and $NaHCO_3$ in a mixture: Accurately weigh about 2.0 g of the mixture and prepare a solution in distilled water in a 250 ml standard flask. Slowly titrate 25 ml of this solution against standard hydrochloric acid using phenolphthalein as indicator. Repeat to concordance (V_p ml). Now titrate the same volume using methyl orange as indicator. Repeat to concordance (V_m ml). Calculate the number of equivalents, in the titrated volume(ie., 25.0 ml), of Na_2CO_3 ($E_{carb} = N_a \text{ x } 2 \text{ x } V_p/1000$) and $NaHCO_3$ [$E_{bicarb} = N_a \text{ x } (V_m - 2V_p)/1000$]. Hence calculate the respective amounts and percentages in the given sample.

Study Questions: (i) Look up the molecular structures of the indicators used in this experiment. What chemical reactions cause the colour changes in each case? (ii) Make a plot of the change in pH when 25.0 ml of a 0.100 M solution of NaOH is titrated against 0.100 M HCl. (Use a graph paper! Mark enough points to get a smooth curve!!)

Experiment 4 : Acid base titration. (i) Determination of total alkali content of a commercial detergent. (ii) Determination of acetic acid content of commercial vinegar.

Method : Aqueous solutions of detergents are alkaline due to the presence of free soda ash (Na_2CO_3) and due to hydrolysis of fatty acid salts. Total alkali content can be obtained by titration against standard hydrochloric acid. Similarly, the total acid content of vinegar (mainly acetic acid) can be determined by titration against standard sodium hydroxide.

Procedure :

(i) *Determination of total alkali content of a commercial detergent*: Transfer about 0.5 g of detergent (accurately weighed) into a 250 ml conical flask and dissolve in about 30 ml distilled water. Titrate against standard hydrochloric acid using methyl orange as indicator. Calculate the total alkali content and express it as so many grams of Na_2CO_3 per 100 g. Express this also in terms of Na_2O. Repeat the experiment at least once to check the precision of your result. *Note*: *You may need to standardize the given hydrochloric acid*.

(ii) *Determination of the acetic acid content of vinegar*: Transfer using a graduated pipette 20.0 ml of vinegar into a 100 ml standard flask. Make up to the mark with distilled water. Titrate 25 ml of this solution against standard sodium hydroxide solution using phenolphthalein as indicator. Calculate the total acid content and express it as grams of acetic acid per 100 g of vinegar (assume a density of 1.00).

Study Question: How will you prepare 250.0 ml of exactly 0.1000 N hydrochloric acid if you are given the concentrated acid which is approximately 12 M ?

Experiment 5: Redox titration. (i) Standardization of potassium permanganate. (ii) Estimation of iron.

Method : In acid solution the reduction of MnO_4^- corresponds to the following stoichiometry :

$$MnO_4^- + 8H^+ + 5e \leftrightarrows Mn^{2+} + 4H_2O.$$

The equivalent weight is therefore one-fifth the molecular weight. Solutions of potassium permanganate can be standardized against a standard solution of sodium oxalate:

$$C_2O_4^{2-} + 2H^+ \leftrightarrows H_2C_2O_4$$

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$$

Since the oxidation corresponds to the half reaction, $C_2O_4^{2-} \leftrightarrows 2CO_2 + 2e$, the equivalent weight of sodium oxalate is half its molecular weight.

Fe^{2+} in acidified aqueous solution is quantitatively oxidized by MnO_4^- and this forms the basis for the determination of iron (which should be present in solution in the ferrous state).

$$MnO_4^- + 5Fe^{2+} + 8H^+ = Mn^{2+} + 5Fe^{3+} + 4H_2O$$

The equivalent weight of Fe^{2+} is its molecular weight, *ie.*, one-fifth a mole of MnO_4^- is equivalent to 1 mole of Fe^{2+}.

Potassium permanganate titrations are self-indicating since permanganate has a pink colour even in very dilute solution while the products of the reaction are almost colourless.

Procedure :

(i) *Standardization of potassium permanganate*:

Preparation of potassium permanganate solution: Weigh about 1.5 g of potassium permanganate into a beaker (approximate weight will do). Dissolve it in water and transfer to a 500 ml reagent bottle. Add enough water so that the total volume is approximately 500 ml. Label it as 0.1 N potassium permanganate.

Preparation of standard solution of sodium oxalate: Accurately weigh about 1.7 g of sodium oxalate into a 250 ml standard flask. Dissolve it in distilled water and make up to the mark. Calculate the normality.

Titration of sodium oxalate against potassium permanganate: Transfer 25.0 ml of the standard sodium oxalate solution to a 250 ml conical flask using a pipette. Add approximately 100 ml of distilled water followed by approximately 40 ml of dilute (3M) sulphuric acid. Rapidly titrate against potassium permanganate solution taken in a burette. When the first pink colour appears in the solution, stop the titration and allow to stand till the colour disappears (about 1 minute). Then warm the solution to 50-60° C. Continue the titration adding one drop at a time till a faint pink colour persists for at least 30 s. The solution should be warm till the end of the titration. Calculate the normality of potassium permanganate.

(ii) *Estimation of iron in the given solution*: Quantitatively transfer the given ferrous salt solution to a 100 ml standard flask. Add 10 ml of dilute sulphuric acid and make up the volume with distilled water. Pipette 25.0 ml of this solution to a conical flask, add 25 ml dilute sulphuric acid and titrate against standard potassium permanganate to a permanent pale pink colour. Calculate the amount of iron in the given sample.

NOTE: *Preserve the potassium permanganate solution for next week's experiment*!

Study Questions: (i) If 0.165 g of sodium oxalate is weighed into a beaker, dissolved in dil. H_2SO_4, the solution warmed and titrated against 0.156 N $KMnO_4$, what will be the titre value? (ii) 0.565 g of a sample of iron ore is dissolved in conc. HCl and reduced to Fe(II) with stannous chloride. The solution is titrated against 0.106 N $KMnO_4$. If the titre value is 23.7 ml, calculate the percentage of iron in the ore. Write balanced equations for the reactions involved in this experiment.

Experiment 6: Redox titration. Estimation of hydrogen peroxide.

Method : Potassium permanganate is reduced by hydrogen peroxide in presence of acid as follows:

$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{2+} + 5O_2 + 8H_2O$

Therefore, 1 ml of 1N $KMnO_4$ is equivalent to 0.5 milli-moles of H_2O_2.

Procedure : Transfer 10.0 ml of the hydrogen peroxide solution to a 250 ml standard flask using a burette or pipette with an attached rubber bulb (DO NOT SUCK WITH MOUTH). Make up to the mark with distilled water. Mix well. Pipette 25.0 ml of this solution into a conical flask, dilute with about 100 ml water, add 20 ml 3 M sulphuric acid and titrate with 0.1 N potassium permanganate to the first permanent faint pink colour. Repeat to concordance. Calculate the weight of H_2O_2 per litre of the given solution. Calculate also the 'volume strength', i.e., the number of ml of oxygen at s.t.p. that will evolve by decomposition of 1 ml of the solution.

Note: *If you prepare fresh potassium permanganate you will have to standardise it as described in the previous experiment.*

Study Question: Write half reaction for the oxidation of hydrogen peroxide. How does this reaction differ from the decomposition reaction? The decomposition reaction is catalysed by MnO_2. Traces of MnO_2 may form in permanganate titrations if sufficient acid is not present. How will this affect the accuracy of the determination?

Experiment 7: Redox titration. (i) Standardisation of ammonium ferrous sulphate using potassium dichromate. (ii) Estimation of barium as chromate by back titration with potassium dichromate.

Method : Potassium dichromate, though not as powerful an oxidizing agent as the permanganate, has the advantage that it is more stable in solution and can be obtained in pure enough form for use as a primary standard. However, it is not self-indicating because of the green colour of the product (Cr^{3+}(aquo)).

$Cr_2O_7^{2-} + 14H^+ + 6e \leftrightarrows 2Cr^{3+} + 7H_2O$

The equivalent weight is one-sixth the molecular weight.

Barium can be precipitated as chromate and the precipitate dissolved in dilute acid.

$2BaCrO_4 + 2H^+ = 2Ba^{2+} + Cr_2O_7^{2-} + H_2O$

A known excess of Fe(II) solution of known concentration is then added which will be quantitatively oxidized by the $Cr_2O_7^{2-}$. The excess Fe(II) is titrated against standard potassium dichromate.

Procedure:

(i) *Standardisation of ammonium ferrous sulphate*:

Preparation of standard solution of potassium dichromate: Weigh accurately about 1.2 g of potassium dichromate into a 250 ml standard flask. Dissolve and make up to the mark with distilled water. Mix well. Calculate the normality.

Preparation and standardisation of ammonium ferrous sulphate solution: Weigh about 10 g of ammonium ferrous sulphate into a 500 ml reagent bottle. Dissolve in about 200 ml of distilled water and add about 50 ml of 3 M sulphuric acid and mix well. Pipette 25.0 ml of the solution to a conical flask, add 0.5 ml of N-phenylanthranilic acid indicator. Add about 20 ml 3 M sulphuric acid, dilute with about 20 ml water and titrate with 0.1 N potassium dichromate until the colour changes from green to violet - red. Repeat to concordance.

(ii) *Estimation of barium in the given solution*: Transfer the given solution quantitatively to a 100 ml standard flask and make up to the mark with distilled water. Pipette 25.0 ml of this solution to a beaker. Add 1 ml of 6M acetic acid and 10 ml of neutral 3M ammonium acetate. Heat to boiling and add drop-wise, with constant stirring, a slight excess of ammonium chromate (or potassium chromate) solution using a dropper. Place the beaker on a water bath till the precipitate settles. Test for completeness of precipitation by adding a little more of the reagent. Allow to cool. Filter carefully, discard the filtrate and wash the precipitate with water. Transfer the precipitate along with the filter paper to a conical flask. Dissolve the precipitate in dilute sulphuric acid. Add 50.0 ml of the previously standardized Fe(II) solution. Titrate the excess Fe(II) against standard potassium dichromate. Calculate the amount of barium in the given solution.

Study Question : Calcium in a sample of chalk, for example, can be estimated by converting to oxalate or chromate, which are both insoluble in water. Outline a suitable procedure for these experiments based on redox titrations.

Experiment 8: Redox titration. Iodometry – (i) Standardisation of sodium thiosulphate. (ii) Estimation of copper.

Method : Iodometry involves titration of iodine liberated in chemical reactions against a standard solution of a reducing agent (usually sodium thiosulphate).

$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$

One mole of I_2 is equivalent to 2 moles of thiosulphate. The equivalent weight of sodium thiosulphate is the same as its molecular weight.

Potassium iodate can be used as primary standard for sodium thiosulphate. Its equivalent weight is one-sixth the molecular weight:

$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$

An example of a reaction in which iodine is liberated :

$2Cu^{2+} + 4I^- = 2CuI + I_2$

The above reaction can be used for the estimation of copper in a solution of a Cu(II) salt.

A freshly prepared starch solution is commonly employed as indicator in iodometric titrations. It produces a blue colour in presence of iodine.

Procedure :

(i) *Standardisation of sodium thiosulphate*:

Preparation of standard solution of potassium iodate : Accurately weigh about 0.35 g of potassium iodate into a 100 ml standard flask. Dissolve in distilled water and make up to the mark. Mix well. Calculate the normality.

Preparation and standardisation of sodium thiosulphate solution : Dissolve about 12 g of sodium thiosulphate in about 500 ml water and store in a reagent bottle. Pipette 25.0 ml of potassium iodate into a conical flask. Add 10 ml of a 10% solution of potassium iodide, followed by 3 ml of 1M sulphuric acid. Titrate the liberated iodine with sodium thiosulphate solution. When the colour has become pale yellow, dilute to about 100 ml with distilled water, add 2 ml of starch solution and continue the titration until the blue solution turns colourless. Repeat to concordance. Calculate the normality of sodium thiosulphate.

(ii) *Estimation of copper in the given Cu(II) salt* : Weigh out accurately about 5 g of the salt into a 250 ml standard flask. Dissolve in distilled water and make up to the mark. Mix well. Pipette 25.0 ml of this solution into a conical flask. Add 10 ml of a 10% solution of potassium iodide. Titrate the liberated iodine with standard sodium thiosulphate using starch indicator as before. Repeat to concordance. Calculate the percentage of copper in the given salt.

Study Questions : (i) In solutions containing iodine and an iodide, the following equilibrium is obtained : I_2 (*aq*) + I^- $\leftrightarrows$ I_3^-. Will this affect the accuracy of the above titrations? Explain. (ii) Iodide is slowly oxidized by oxygen in presence of light. Write a balanced equation. How will you minimize the error due to this reaction in your work. (iii) Iodine has appreciable volatility. How will you minimize the error due to this? (iv) You have analysed a pure copper(II) salt. What complications may arise when you try to apply this procedure to estimate the percentage of copper in an ore?

Experiment 9: Redox titration. Iodometry – Estimation of hydrogen peroxide

Method : Iodide in an acidified solution is slowly oxidized by hydrogen peroxide. The reaction is greatly speeded up by small amounts of ammonium molybdate.

$H_2O_2 + 2H^+ + 2I^- = I_2 + 2H_2O$

Procedure : Transfer 10.0 ml of the given hydrogen peroxide solution to a 250 ml standard flask using a burette or pipette with a rubber aspirator (DO NOT SUCK WITH MOUTH). Make up to the mark with distilled water. Mix well. Take 10 ml of a 10% solution of potassium iodide in a stoppered bottle and add 100 ml of 1M sulphuric acid. Pipette 25.0 ml of the hydrogen peroxide solution into this bottle, stopper it and allow the mixture stand for 15 minutes. Titrate the liberated iodine against standard (0.1 N) sodium thiosulphate. Add 2 ml of starch solution when the solution is pale yellow and continue the titration till the blue colour is discharged. Repeat to concordance. Calculate the weight of H_2O_2 per litre of the given solution.

In another experiment, pipette 25.0 ml of the hydrogen peroxide into a conical flask. Add 100 ml 1M sulphuric acid, 10 ml of a 10% solution of potassium iodide and 3 drops of 3% solution of ammonium molybdate. Titrate the solution immediately with standard sodium thiosulphate as before. Repeat to concordance. Calculate the weight of H_2O_2 per litre of the given solution.

Study Questions : (i) Why do you use a stoppered bottle in the above experiment. (ii) The presence of ammonium molybdate also speeds up the air oxidation of HI. Will this affect the accuracy of the above determination? If yes, how will you minimize the error?

Experiment 10 : Precipitation titration – Argentometry. Standardisation of silver nitrate and estimation of chloride

Method : AgCl formed by the reaction between silver and chloride ions in aq. solution is a sparingly soluble precipitate (solubility product 1.2 x 10^{-10}).

$Cl^- + Ag^+ = AgCl$

At the equivalence point $[Ag^+] = [Cl^-] = 1.1 \times 10^{-5}$ M. If a solution of chloride is titrated against $AgNO_3$, and if one plots the concentration of Ag^+ ions against volume of $AgNO_3$ added, a rapid change in Ag^+ concentration occurs in the neighborhood of the equivalence point. This forms the basis for this precipitation titration.

The end point can be detected in different ways: by the formation of a coloured precipitate (Mohr's method), by the formation of a soluble coloured compound (Volhard's method), by using adsorption indicators (Fajan's method), or by the turbidity method (Gay Lussac's method and its modern versions). We will use the Mohr's method in this introductory experiment. In this method, potassium chromate solution is used as indicator which produces the sparingly soluble, red silver chromate (solubility product 1.7 x 10^{-12}) at the end point.

Procedure :

Preparation of standard solution of sodium chloride: Weigh accurately about 1.4 g of the pure dry salt into a 250 ml standard flask. Dissolve it in distilled water and make up to the mark. Calculate the molarity.

Preparation and standardization of silver nitrate: Weigh about 3.4 g of silver nitrate into a 250 ml reagent bottle and dissolve it in 200 ml water. Pipette 25.0 ml of the standard solution of sodium chloride into a 250 ml conical flask. Add 1 ml of a 5% solution of potassium chromate. Slowly titrate against the silver nitrate until the red colour formed by the addition of each drop begins to disappear more slowly. Continue the titration dropwise until a persistent faint reddish-brown colour is obtained. This is the end point. Repeat the titration till concordant values (agreeing within 0.1 ml) are obtained.

Estimation of chloride: Transfer the given solution quantitatively to a 100 ml standard flask and make up to the mark with distilled water. Do a Mohr titration as before. Calculate the amount of chloride present in the given solution.

NOTE: For accurate results with Mohr's method a blank titration is to be performed by adding 1 ml of the indicator to a volume of water equal to the final volume in the previous chloride titration and then adding silver nitrate solution until the colour of the blank matches with that of the chloride titration. The volume of silver nitrate added (~ 0.03 – 0.10 ml) is to be subtracted from the original titre value.

Study Questions : (i) Which is the more soluble salt, AgCl or Ag_2CrO_4 ? (ii) In a solution which is saturated with respect to both the salts, what is the relation between the concentrations of chloride and chromate ions? (iii) What is the purpose of the blank titration in the NOTE attached to the above procedure?

Experiment 11 : Gravimetry – Analysis of barium chloride crystals

Note : This is a group experiment involving three gravimetric determinations, *viz*., barium, chloride, and water of hydration. Each group consists of three students (neighbouring students at the lab bench). If the last group so formed has less than three students, then one or two students from the neighbouring group will belong to both groups. Each group will submit a joint report on the percentage of Ba, Cl and H_2O in barium chloride. An empirical formula should be proposed consistent with the above results.

Determination of water of hydration

Method : Water of hydration is usually lost when a hydrated salt is heated above 100º C. The percentage of the water of hydration can be determined by weighing the sample before and after dehydration. Heating is done in a porcelain crucible. The crucible, after heating, should be cooled to room temperature in a desiccator before weighing.

Procedure : Heat a clean crucible to dull redness for a few minutes and keep it in a desiccator for about 15 minutes. Weigh the crucible. Transfer about 1.5 g of barium chloride into the crucible and weigh again. Heat the covered crucible gradually until its bottom becomes a dull red. Maintain at this temperature for about 10 minutes, allow to cool in a desiccator and weigh. Repeat the heating, cooling and weighing till the weight becomes constant (within about 0.5 mg). Calculate the percentage of water in barium chloride. Do a duplicate determination.

Study Questions : (i) Why do you have to heat the empty crucible before weighing? (ii) Why do you need to cool the crucible in a desiccator rather than just in open air? (iii) The above determination falls under the category of volatalisation or evolution methods in gravimetry. Another example of this method is the conversion of many metal compounds to oxides by thermal decomposition. What requirements are to be met for such decompositions to be used in gravimetric analysis? What weight of Al_2O_3 will be obtained by the decomposition of 2.5000 g of $(NH_4)_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$?

Determination of chloride

Method : Chloride is precipitated and weighed as AgCl. Conditions for such precipitations for gravimetry are to be carefully controlled to minimize errors due to solubility and coprecipitaion. Further, the precipitate should be obtained in a form that will settle and filter easily.

Procedure : Clean a sintered glass crucible (Grade 4) and keep in an oven (about 120º C). Weigh out accurately about 0.4 g of barium chloride into a 250 ml beaker provided with a stirring rod and watch glass. Dissolve in about 150 ml water and add 0.5 ml concentrated nitric acid. Add 0.1 M silver nitrate slowly and with constant stirring. Only a slight excess should be added, checking for completeness by allowing the precipitate to settle and and adding a few drops of silver nitrate to the supernatent. Heat the suspension nearly to boiling with constant stirring and maintain at this temperature until the precipitate coagulates and the supernatent liquid is clear. Confirm that the precipitation is complete. Keep the beaker aside in a dark corner for an hour. Take out the crucible from the oven and allow to cool in a desiccator. Note the weight. Again keep it in the oven for 10 minutes and weigh it after cooling in the desiccator. Repeat till the weights agree within about 0.5 mg. Set up the crucible for filtration by suction. Collect the precipitate of AgCl on the crucible. Use a glass rod fitted with a rubber tip (the ‘policeman’) to dislodge the last small particles sticking to the beaker. Wash the precipitate several times with small amounts of very dilute nitric acid - a few ml of the washings collected in a test tube should not give a turbidity with 1 or 2 drops of 0.1 M HCl. Dry the crucible with the precipitate in an oven (about 120º C) for 1 hour. Allow to cool in a desiccator and weigh. Repeat the heating and cooling until constant weight is attained. Calculate the percentage of chloride in the sample.

Study Questions : (i) It is advised that the above experiment should be done in subdued light. Why? (ii) Why is it important to wash the precipitate in gravimetric experiments? In the above experiment what would happen if the washing is incomplete?

Determination of barium

Method : Barium is precipitated as $BaSO_4$. The precipitate is filtered using ash-less filter paper and then ignited in a crucible and weighed as $BaSO_4$.

Procedure : Heat a porcelain crucible to redness and keep in a desiccator to cool. Weigh accurately about 0.2 g of barium chloride into a 250 ml beaker and dissolve it in about 100 ml water. Heat to boiling, add a slight excess of hot 0.5 M sulphuric acid slowly and with constant stirring. Digest on a steam bath until the precipitate has settled. Confirm that precipitation is complete by adding a few drops of 0.5 M sulphuric acid to the supernatent. Set up a funnel for filtration with Whatman (No. 40) filter paper. The precipitate should be quantitatively transferred to the filter paper using jet of water from the wash bottle and a 'policeman' if necessary. Wash the precipitate several times with small portions of hot water. Continue the washing until about 5 ml of the filtrate gives no turbidity with a drop or two of dilute silver nitrate solution.

Weigh the cooled crucible. Transfer the filter paper with the precipitate to the crucible. Dry the paper by keeping the loosely covered crucible over a low flame. Gradually increase the heat till the paper chars and the volatile matter is expelled. Take care that the paper does not burst into flame. When the charring is complete, raise the temperature till the crucible becomes a dull red and burn off the carbon with free access of air. After the precipitate becomes white, keep the crucible for 10 minutes at red heat. Cool in a desiccator and determine the weight. Repeat heating and cooling till constant weight is obtained. Calculate the percentage of barium in the sample.

Study Questions : (i) Why is the treatment of the precipitated $BaSO_4$ different from that of AgCl? (ii) Can you suggest a faster method for drying precipitates?