EXPERIMENT 9
ESTIMATION OF AMINO GROUPS

Structure

9.1 INTRODUCTION

In Courses CHE-3 (L) and CHE-7 (L) you were introduced to the various techniques for quantitative analysis. We have described different methods which are used in quantitative analysis i.e., gravimetric methods are those in which the weight of a substance is measured, titrimetric methods refer to measurements of a volume, and physiochemical (instrumental) methods are based on the measurement of some physical or chemical property. In the experiments 9 to 14 we will use some of these methods for organic quantitative analysis. In the section 9.2 of this experiment, we will first give you an overview of the organic analysis. This will give you an idea as to how organic quantitative analysis are useful in organic analysis. In section 9.3 though we are giving very a brief introduction to elemental analysis and molecular weight determinations (i.e., determination of empirical and molecular formulae respectively), but we are not giving any experimental details. Because these experiments require the use of more complex or more costly articles of equipment, which are very difficult to provide at graduation level laboratories. After that you will be introduced to the actual experiment in which you will use acetylation and bromination methods for estimation of amino group.

Objectives

After studying and performing this experiment, you should be able to:

- describe the significance of organic quantitative analysis in organic analysis,
- determine the amino group in the given sample by acetylation methods,
- determine amino in the given sample by bromination method.
- describe acetylation and bromination phenomena and perforam acid base and iodemetric titrations.

9.2 AN OVERVIEW OF THE ANALYSIS OF ORGANIC COMPOUNDS

The following is an outline of the methods used in the study of organic compounds.

1. Separation and Purification: Before the properties and structure of an organic compounds can be completely investigated the compound must be pure. Common methods of separation and purification are:

1. Extraction
2. Crystallisation
3. Sublimation
4. Distillation
5. Chromatography

There are various criteria for determining purity. The most commonone for solids is m.p; for liquids, b.p. and more recently infra-red (IR) spectrun has been used as a test for purity. In all cases, the process of purification is repeated until the physical constant or spectrum remains unchanged. Methods of separation and purification of organic compounds, and of testings their purity, are described in the courses 'Chemistry Lab-II'.

(a) After getting pure organic compound, next step is identification and characterisation of the structure of the compound. This, can be achieved by organic qualitative and organic quantitative analysis.

Organic Qualitative Analysis:

Qualitative analysis gives information about the presence of elements such as nitrogen, sulphur or the halogens, and functional groups such as-OH,CO,-COOH, $-NH_2$ etc. Following steps are involved in this process.

i) Physical examination

ii) Elemental analysis

iii) Solubility test

iv) Determination of physical constant

v) Functional group analysis

vi) Preparation of derivation.

We have already discussed these steps in quite detail in the second Block of 'Qualitative Organic Analysis' of course Chemistry Lab-II.

Organic Quantitative Analysis

Having known the constituent elements and the functional groups present in a organic compound, the next important step in its analysis involves quantitative analysis. Permiting the calculations of an empirical formula, which gives the atomic ratio of the elements present. Determination of the relative molecular mass permits the assignment of a definite molecular formula that expresses the actual number of atoms of each element present in the compound. Further quantitative functional group analysis gives the information about the number of functional group present in the substance.

There are two approaches to this. One is so far discussed methods of analysis, traditional, it depends on chemical reactions. The modern method involving spectrometry, is discussed in the course of Spectroscopy (CHE-10). Spectrometric methods are used extensively today because they are faster and are capable of dealing with small amount of compounds with more complex structures. Although the traditional methods now are seldom used alone, they are described in lab courses of our B.Sc. programme for a number of reasons. On occasion, part of the traditional schemes are still quite useful. Also, the required techniques strongly reinforce fundamental chemical and physical principles and exposes the student initially to make the right chemical judgments, an essential skill for productive research. The time invested in learning how to interpret chemical and physical behaviour will be repaid many times over in future work. Last reason is that our laboratories are not equipped with the modern instrumentations.

Now we will concentrate on the organic qualitative analysis.

9.3 ORGANIC QUANTITATIVE ANALYSIS

The organic quantitative analysis consists of a series of steps that not only helps to establish the identity of the compounds but also provides methods for the determination of amounts or concentration of constituents. There are two main types of quantitative analysis which are generally carried out for organic compounds.

i) Quantitative elemental analysis: This is carried out to find out the relative numbers of the different kinds of atoms, that is to determine the empirical formula. This in turn combined with the molecular formula weight shows the actual numbers of the different kinds of atom, that is, gives us the molecular formula. In recent years it has become possible to find the molecular formulae of some compounds directly by mass spectrometry.

ii) Quantitative functional group analysis: This is carried out to find the relative number of the different kinds of functional groups.

9.3.1 Quantitative Elemental Analysis:

The elements commonly found in organic compounds are carbon, hydrogen, oxygen, nitrogen, halogens, sulphurs, phosphorous and metals. The methods used in the determination of the composition by weight of an organic compound are based on simple principle. Most of our undergraduation laboratories do not have the apparatus to conduct practicals of quantitative elemental analysis, therefore, here we are discussing only the principle part.

Carbon, hydrogen and nitrogen: A known weight of the compound is heated to a high temperature in an excess of dry oxygen. The compound burns to form carbondioxide and water. If nitrogen is present in the organic compound, a mixture of nitrogen oxides (and sometimes nitrogen gas) is also produced; the oxides of nitrogen are subsequently reduced by copper to nitrogen. The weights of carbondioxide, water and nitrogen are then found and percentage composition of carbon, hydrogen and nitrogen can be calculated.

Now a day CHN analysis are carried out by analysers known as CHN analyser, which enable the compound to be analysed automatically (see Fig. 9.1)

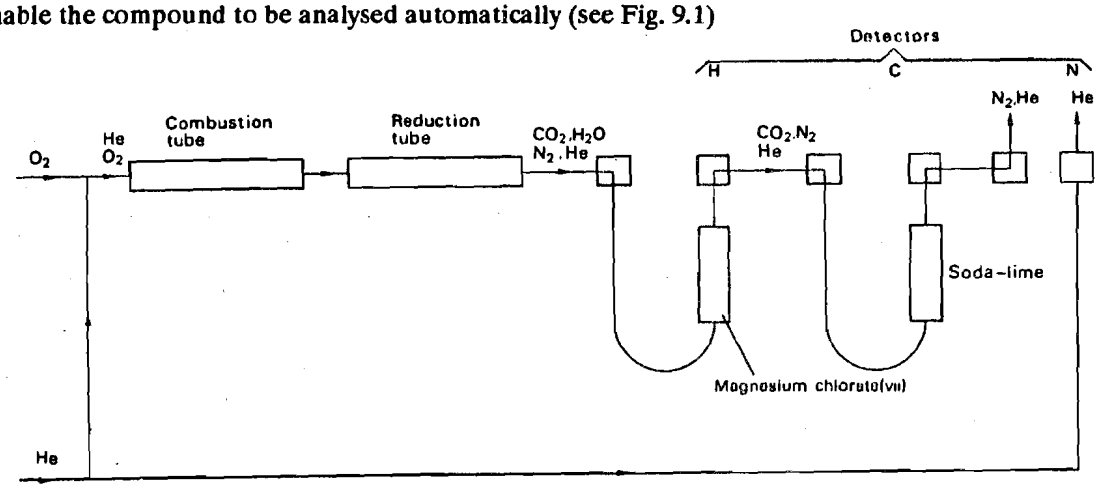


Fig. 9.1: A CHN analyser

Oxygen

It is usually estimated by difference.

Halogens, sulphur and phosphorous

They are usually estimated by the 'oxygen flask' method of combustion. A sample of the compound is wrapped in ashless filter paper and ignited electrically in a flask of

oxygen containing the appropriate absorption liquids for the halogen or sulphur oxides produced. Suitable titration or gravimetric determination gives the amount of these elements present.

Calculation of the Empisical Formula

Once the percentage composition of each element is known, the ratio of the number of atoms of each element present in the compounds can be calculated. This is the **empirical formula.**

The method is to divide the percentage composition of each element by its relative atomic mass and to factorise the resulting numbers so as to obtain simple whole numbers. For example, a compound X, a white solid, was found by analysis to contain 23.30 percent carbon, 8.85 per cent hydrogen and 40.78 percent nitrogen. It was known to contain no other elements, so that the composition of oxygen was 100 – (23.30 + 4.85 + 40.78) = 31.07 per cent then,

Element	% composition	Relative atomic mass	Atomic ratio	Simple atomic ratio
Carbon	23.30	12	$\frac{23.30}{12}=1.94$	2
Hydrogen	4.85	1	$\frac{4.85}{1}=4.85$	5
Nitrogen	40.78	14	$\frac{40.78}{14}=2.91$	3
Oxygen	31.07	16	$\frac{31.07}{16}=1.94$	2

The empirical formula of X is $C_2H_5N_3O_2$. To determine the molecular formula, the relative molecular mass must be found.

Determination of the Molecular Formula

As said above, the molecular formula of a compound (the actual number of each kind of atom in the molecule) can be determined from the empirical formula and the relative molecular mass.

For example, the empirical formula of the compound X in above mentioned example was found to be $C_2H_5N_3O_2$. The formula weight is 103. In this case, therefore, the empirical formula is also the molecular formula. On the other hand, if the relative molecular mass had been found to be 206, the molecular formula would have been $C_4H_{10}N_6O_4$.

The determination of relative molecular masses of compounds is described in detail in 'Physical Chemistry' Course (CHE-04). Those of gases are generally determined by the limiting density method, using a gas density balance, while those for volatile liquids and solids are found by Victor Meyer's method in which the volume of vapour from a known weight of compound is determined. The relative molecular mass of an involatile liquid or solid is often found from the depression of the freezing point of a solvent. The relative molecular mass can also be found quickly and with a very high degree of precision by mass spectrometry. Procedure detail of mass spectrometric method is given in the course 'Spectroscopy' (CHE-09).

9.3.2 Quantitative Functionals Group Analysis

The quantitative estimation of the functional groups is based on the stoichiometric equations of the reactions such as neutralisation, acetylation, reduction, oxidation, addition, hydrolysis etc. Function grow analysis not only helps to estimate functionals groups presen in a compound but also provides methods for the determination of amount or concentration of organic Constitutents. In this course, you will be introduced to five such experiments. These experiments are the determination of amino groups, hydroxyl groups, sugars, amino acids, and formaldehyde and analysis of oil and fats.

9.4 DETERMINATION OF AMINO GROUPS

In an organic compound amino groups can be estimated by two methods, one of which is based on an acetylation method, while other is based on bromination method. In acetylation method the excess of free acetic acid left after acetylation of amino group is determined by titration with standard sodium hydroxide solution. In bromination method the excess of bromine is determined after bromination of aromatic amines by the addition of potassium iodide solution and titration of liberated iodine with sodium thiosulphate solution. If the molecular weight of the compound is known, the number of amino groups can then be calculated.

Now you will be introduced to the actual experiment in which you will use above mentioned methods for the determination of amino group in a given sample.

9.4.1 Experiment 9a: Determination of Amino Group by Acetylation Method

Principle

The amino group reacts quantitatively with acetic anhydride in presence of base (pyridine) to form acetyl derivative. The excess of acetic anhydride is then hydrolysed with water and the total free acetic acid is found out by titrating with a standard sodium hydroxide solution using phenolphthalein as an indicator. A control or blank experiment is performed (without using amino compound) by taking same amount of acetic anhydride. The difference in the amount of alkali used in the two experiments is equivalent to the acetic acid used in acetylation. If the molar mass of the compound is known, the number of amino groups in the compound can be calculated.

In organic estimation we frequently employ control blank experiment along with original experiment. Such approach has following advantages.

(1) The absolute concentration of a reagent (for example in Experiment 9, the exact amount of acetic anhydride) need not be determined, since if the same amount of reagent is used in the actual and in the control experiments, the difference gives at once the actual amount used.

(2) The losses of the reagents due to the chemical action or the alkaline glass vessels, slight absorption by the curves etc., are almost identical for the actual and the control experiments and therefore, do not affect the difference in result between the two experiments. Ordinary chemical flask, with reflux water condensers, using rubber stopper can also be used.

$$R(NH_2)_n + n(CH_3CO)_2O \xrightarrow{\text{Pyridine}} R(NHCOCH_3)_n + nCH_3COOH$$

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH$$

excess acetic acid :

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

In this experiment pyridine is used as a solvent because it is inactive towards the reagent, it removes the acid products by salt formation, and it also serves as a catalyst.

$$RNH_2 + (CH_3CO)_2O + C_5H_5N \longrightarrow RNHCOCH_3 + (C_5H_5NH)^+ (CH_3COO)^-$$

$$HOH + (CH_3CO)_2O + 2C_5H_5N \longrightarrow 2(CH_3COO)^- + 2(C_5H_5NH)^+$$

Requirements

Apparatus		Chemicals
Burette (50 cm^3)	- 1	Aniline
Conical flask (250 cm^3)		Acetic anhydride
Conical flask (Q.F) (250 cm^3)	- 1	Pyridine
or Round bottom flask (Q.F) 250 cm^3	- 2	Sodium hydroxide
Weighing bottle	- 1	Alcohol
Funnel (small)	- 1	Phenolphthalein
Test-tube	- 1	Soda-lime
Burette stand	- 1	
Water-bath	- 1	
Reflux condenser	- 2	

Solution Provided

i) **Sodium hydroxide solution, 1 *M*:** It is prepared by dissolving 40 g NaOH in distilled water in 1dm^3 flask. This solution can be standardised with either 0.5*M* oxalic acid solution using phenolphthalein indicator.

ii) **Phenolphthalein indicator:** Dissolve 1.0g of phenolphthalein in 100 cm^3 of ethanol and then dilute with 100 cm^3 of water.

Procedure

i) **Preparation of acetylating reagent:** Mix 20 cm^3 of acetic anhydride (AR) and 60 cm^3 of pure and dry pyridine as required in a dry conical flask. Fill the solution in a dry burette.

ii) Take two 250 cm^3 conical flasks (Q.F) marked 'A' and 'B' fitted with reflux condensers. Weigh accurately about 1 g of sample aniline and transfer it to flask 'A'. Then add 10 cm^3 of acetylating reagent to the flask 'A' and also to the blank flash 'B'. Heat the two flasks on boiling water-bath for 45 minutes.

iii) Add 20 cm^3 of distilled water through the condensers in both flasks so that the water rinses down the condenser tube and the walls of the flasks. Shake the contents of the flasks and heat for 2 minutes more. Cool the flasks under running water.

iv) Titrate the contents of each flask separately with 1 *M* sodium hydroxide solution using phenolphthalein as indicator. The difference between the volumes of alkali used in the two titrations corresponds to the anilin which has reacted. Repeat both blank an actual titrations to get at least two concordant readings in each case. Record the observation in Observation Tables I and II for blank and originals titrations; respectively.

Observations

Mass of the weighing bottle	$= m_1$	= .....g
Mass of the bottle+aniline	$= m_2$	= .....g
Mass of the bottle (after transferring the compound)	$= m_3$	= .....g
Mass of aniline transferred	$= m_2 - m_3$	$= m$ =
Molar mass of aniline	$= M_m$	= 93 g mol^{-1}

Observation Table I
Acetylating Reagent vs. Sodium Hydroxide Solution
(Blank Titration)

Sl. No.	Volume of Acetylating reagent in cm^3	Burette		Volume of NaOH in cm^3 (Final-Initial)
		Initial	Final	
1	10			
2	10			
3	10			

Volume of NaOH used in neutralising 10 cm^3 of acetylating reagent = V_1 =..... cm^3

Pyridine can be dried over KOH

Standardisation of sodium hydroxide solution

Sodium hydroxide is not a primary standard. It is to be standardised. It can be standardised by titrating against standard oxalic acid solution using phenolphthalein as indicator. The procedure is given below:

(1) **Preparation of standard oxalic acid Solution**
Oxalic acid solution, 0.5 *M* : Dissolve 8 g of oxalic acid in water in 250 cm^3 volumetric flask and make up to mark.

(2) **Standardisation of sodium hydroxide solution :** Pipette out 20 cm^3 of standard oxalic acid solution (0.5 M) into a 100 cm^3 conical flask. Add 2-3 drops of phenolphthalein indicator. Titrate with sodium hydroxide solution taken in the burette. Swirl the conical flask after each addition. Continue the titration till a permanent purple colour is obtained as the end point. If M_1 and V_1 are the molarity and volume of oxalic acid solution, whereas M_2 and V_2 are the molarity and volume of sodium hydroxide solution, then the molarity of sodium hydroxide would be given by the following formula (as per stiochiometric equation

$(COOH)_2 + 2OH^- \longrightarrow 2H_2O + CO_2$

Molarity of NaOH $= M_2 =$

$$\frac{2M_1V_1}{V_2} = 40\frac{M_1}{V_2}$$

The experiment can also be carried out in two 250 cm^3 conical flask with out testing reflux condensers; since very little evaporation of the acetylating mixture, from an open conical flask would occur during heating on the water-bath.

Observation Table II
Sample + Acetylating Reagent vs. Sodium Hydroxide Solutio
(Actual Titration)

Sl. No.	Sample + 10 cm^3 Acetylating reagent in cm^3	Burette		Volume of NaOH in cm^3 (Final-Initial)
		Initial	Final	
1				
2				
3				

Volume of sodium hydroxide used in neutralising the

sample +10 cm^3 of acetylating reagent $= V_2$ =..... cm^3

Calculations

Mass of the sample $= m$ g =..... g

Difference of sodium hydroxide

Solution required for OT-I & OT-II $= V_1 - V_2$ cm^3=..... cm^3

1000 cm^3 M_2 NaOH = M_2 g mol. NaOH = M_2 g mol. CH_3COOH = M_2 g mole NH_2, where M_2 = molarity of sodium hydroxide solution

$$(V_1 - V_2) \text{ cm}^3 \text{ of } M_2 \text{ NaOH} = \frac{M_2 \times (V_1 - V_2)}{1000} \text{ g mol. of } NH_2$$

or

$$= \frac{16 \times M_2 \times (V_1 - V_2)}{100} \text{ g of } NH_2$$

As you know, this is due to m g of sample, therefore, for 100 gms of the sample you will have (% of the NH_2) group

$$\% NH_2 = \frac{16 \times M_2 \times (V_1 - V_2) \times 100}{m \times 1000}$$

=..... %

ii) The number of amino group (NH_2) in the sample (aniline) can be calculated as follows:

From above

$$\text{m g of sampl} \equiv \frac{16 \times M_2 \times (V_1 - V_2)}{1000} \text{g of } NH_2 \text{ group}$$

$$\text{93 g (1 g mol) of amine contain} = \frac{16 \times M_2 \times (V_1 - V_2) \times 93}{1000 \times m} NH_2 \text{ group}$$

Since 16.03 g mass is due to the one NH_2 group

$$\text{Therefore, aniline contains} = \frac{16 \times M_2 \times (V_1 - V_2) \times 93}{1000 \times m \times 16} NH_2 \text{ group (s)}$$

=..... NH_2 group(s)

Result

The percentage of amino group in the sample of aniline =..... %

The number of amino group(s) in the sample of aniline = ...

9.4.2 Experiment 9b: Determine Aniline by Bromination Method

Principle

Aniline and some of its derivatives having free *ortho* and *para* positions can be estimated by bromination method. The method involves the following steps:

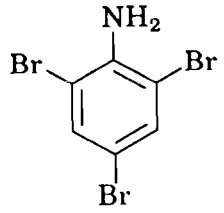
(a) **Bromination of aniline by bromination mixture:**

Aniline reacts with bromine to form 2, 4, 6– tribromoaniline. Since the yield is quantitative, it is used for the estimation of aniline. The bromine required is obtained by treating a mixture of potassium bromide and potassium bromate with dilute hydrochloric acid. The bromine so liberated reacts with aniline to produce tribromoaniline while excess of bromine remains unreacted.

$$5\,KBr + KBrO_3 + 6HCl \longrightarrow 6KCl + 3Br_2 + 3H_2O$$

The number of bromine molecule consumed by various phenols is given against the name of the phenol given below:

Phenol - three,
Cresol - three,
o- and *p*- Nitrophenol - two,
m-Nitrophenol - three,
Resorainol - three,
Salicylic acid - three,
Naphthol - one.



2, 4, 6-Tribromoaniline

(b) **Determination of unreacted bromine:**

The unreactive bromine is treated with potassium iodide, the equivalent iodine thus liberated is determined iodometrically with sodium thiosulphate (hypo) solution using starch as indicator.

$$2KI + Br_2 \longrightarrow 2KBr + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

Sodium tetrathionate

Requirements

Apparatus		Chemicals
Burette (50 cm^3)	- 1	Aniline (AR)
Pipette (25 cm^3)	- 1	Potassium bromide (AR)
Conical flask (250 cm^3)	- 1	Potassium bromate anhydrous (AR)
Vol. flasks (250 cm^3)	- 2	Potassium iodide (AR)
		Sodium thiosulphate
Weighing bottle	- 1	conc. hydrochloric acid
Funnel (small)	- 1	
Test-tube	- 1	

Wash-bottle for dist. water - 1

Burette stand - 1

Solutions Provided:

i) **Sodiumthiosulphate solution 0.1*M*:** It is prepared by dissolving 6.25g of sodium thiosulphate pentahydrate in 250 cm^3 distilled water in a volumetric flask.

ii) **Potassium iodide soltuion, 20 per cent:** Dissolve 20g of A.R. potassium iodide in 100 cm^3 of distilled water.

iii) **Starch indicator solution:** Make a paste of 1.0g of starch with a little water and pour the suspension, with constant stirring into 100 cm^3 of boiling water.

Procedure

1. **Preparation of Brominating solution (0.2 *M*):** Weigh 1.4 gm of A.R. potassium bromate and 9 gm of potassium bromide A.R. in water and make up the volume to 250 cm^3 in a volumetric flask. Fill the solution in a burette.

2. **Preparation of standard solution aniline:** Weigh accurately about 0.5 g aniline in a weigh bottle. Transfer this to a 250 cm^3 volumetric flask. Weigh the weighing bottle again and find the exact mass of aniline transferred by difference. Dissolve it in water and make up the volume to 250 cm^3.

3. **Titration with brominating solution (Blank titration)**
Pipette out 25 cm^3 of brominating solution in a 250 cm^3 conical flask and add 25 cm^3 of distilled water, 5 cm^3 of concentrated hydrochloric acid and 5 cm^3 of KI solution. Shake the contents of the conical flask, the solution will become dark-brown due to liberation of iodine. Titrate this with sodium thiosulphate solution until the solution acquires light yellow colour and then add 5-6 drops of starch solution and continue the titration with sodium thiosulphate solution carefully. At the end point blue colour disappears. Repeat the titration to get at least two concord readings to ensure a correct and exact measurement. Record the observations in observation Table I. This titration is used to determine the volume of brominating solution which is equivalent to 1 cm^3 of sodium thiosulphate solution.

4. **Titration with standard aniline solution**
Pipette out 25 cm^3 of standard aniline solution in a 250 cm^3 conical flask and add 25 cm^3 of distilled water and 5 cm^3 concentrated HCl. Brominating mixture (taken in burette) is now added to this solution till it achieves light yellow in colour and then add 5 cm^3 of KI solution. Liberated iodine is titrated against sodium thiosulphate solution using starch as an indicator. Repeat the titration to get at least two concordant readings. Records the observation in Observation Table II

5. **Titration with unknown aniline solution (Actual titration):**
Take out 25 cm^3 of unknown aniline solution in a 250 cm^3 conical clask and titrate similarly as described in case of standard aniline solution. Repeat titration to get at least two concerdant reading. Record the observations in Observation Table III.

Volume of brominating mixture used in each set of titration should preferably be same.

Observations

Mass of the weighing bottle $= m_1$ =..... g

Standardised of sodium thiosulphate solution

Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) is not a primary standard. It has to be standardised. It can be standardised by titrating against standard potassium dichromate solution iodometrically using starch as indicator. The procedure is given below:

1) **Preparation of standard dichromate solution** The dichromate solution can be prepared by weighing accurately about 1.226 g $K_2Cr_2O_7$, dissolving in water and making up to 250 cm^3 in a standard flask.

2) **Standardisation of sodium thiosulphate solution** Into a 250 cm^3 conical flask, pipette 20 cm^3 of standard potassium dichromate solution (0.016 *M*). Add 10 cm^3 of 1 M sulphuric acid and 1 g of sodium hydrogen carbonate into the conical flask with gentle swirling. Then add 0.5 g potassium iodide or 10 cm^3 of 5% KI solution, swirl, cover the flask with watch glass and allow the solution to stand for 5 minutes in a dark place. Titrate against sodium thiosulphate solution taken in the birutte, until a light pale yellow colour is obtained. Add 2 cm^3 of starch solution and continue the titration till the blue colour of starch iodine complex disappears. If M_1 and V_1 are the molarity and the volume of $K_2Cr_2O_7$ used whereas M_2 and V_2 are the molarity and volume of thiosulphate required for titration, then the molarity of $Na_2S_2O_3$ solution could be obtained as follows:

As per the stoichiometric equation

$$Cr_2O_7^{2-} + 14H^+ + 6S_2O_3^{2-} \longrightarrow 2Cr^{3+} + 3S_4O_6^{2-} + 7H_2O =$$

$$\frac{M_1V_1}{M_2V_2} = \frac{1}{6}$$

$$\text{or } M_2 = \frac{6M_1V_1}{V_2}$$

or Molarity of thiosulphate solution $= M_2$

$$= 120\frac{M_1}{V_2}$$

(since $V_1 = 20\,cm^3$)

Mass of the bottle + aniline $= m_2$ =..... g

Mass of the bottle

(after transferring the aniline) $= m_3$ =..... g

Mass of aniline transferred $= m_2 - m_3 = m$ =..... g

Molar mass (M_m) of aniline = 93 g mol^{-1}

Observation Table I
Brominating solution vs. Sodium thiosulphate Solution
(Blank Titration)

Sl. No.	Volume of brominating solution in cm^3	Burette reading		Volume of $Na_2S_2O_3$ solution in cm^3 (Final-Initial)
		Initial	Final	
1	25			
2	25			
3	25			

Observation Table II
Standard Aniline Solution vs. Sodium Thiosulphate Solution

Sl. No.	Volume of aniline solution in cm^3	Volume of Brominating solution in cm^3	Burette reading		Volume of $Na_2S_2O_3$ solution in cm^3 (Final-Initial)
			Initial	Final	
1	25				
2	25				
3	25				

Observation Table III
Unknown Aniline Solution vs. Sodium Thiosulphate Solution
(Actual titration)

Sl. No.	Volume of unknown aniline solution in cm^3	Volume of Brominating solution in cm^3	Burette reading		Volume of $Na_2S_2O_3$ solution in cm^3 (Final-Initial)
			Initial	Final	
1	25				
2	25				
3	25				

Calculations:

i) Mass of aniline in standard solution = m g

ii) Volume of sodium thiosulphate used in blank experiment against 25 cm^3 brominating solution = V cm^3 =..... cm^3

iii) Volume of sodium thiosulphate used for standard aniline solution = V_1 cm^3 =..... cm^3

iv) Volume of sodium thiosulphate used for unknown aniline solution = V_2 cm^3 =..... cm^3

V cm^3 of sodium thiosulphate solution =25 cm^3 brominating solution

Hence 1 cm^3 of sodium thiosulphate = $\frac{25}{V}$ cm^3 brominating solution

Therefore, V_1 cm^3 of sodium thiosulphate

$$= \frac{25}{V} \times V_1 \text{ cm}^3 \text{ brominating solution}$$

Hence, volume of brominating solution used for 25 cm^3 of standard aniline solution

$$= V - \frac{25}{V} \times V_1 \text{ cm}^3 = V_3 \text{ cm}^3$$

Similarly, volume of brominating solution used for 25 cm^3 of unknown aniline solution

$$= V - \frac{25}{V} \times V_2 \text{ cm}^3 = V_4 \text{ cm}^3$$

Using relation,

$$\frac{\text{mass of aniline in unknown solution}}{\text{mass of aniline in standard solution}} = \frac{\text{volume of brominating solution used in unknown aniline solution}}{\text{volume of brominating solution used in standard aniline solution}}$$

$$\text{mass of aniline in unknown solution} = \frac{m \times V_4}{V_3} = \ldots \text{ g per } 250 \text{ cm}^3$$

$$\text{The strength of aniline in unknown solution} = \frac{\text{Strength of standard aniline solution} \times V_4}{V_3}$$

$$= \frac{4 \times m \times V_4}{V_3} = \ldots\ldots\ldots\ldots\ldots\ldots \text{g dm}^{-3}$$

Result

The amount of aniline in given unknown solution is g.

The strength of aniline in given unknown solution g dm^{-3}.

The percentage purity of aniline can also be calculated by the following formula:

$$\% \text{ purity of aniline} = \frac{(V - V_2) \times M \times M_m \times 100}{m \times z \times 2000}$$

where,

V = volume of sodium thiosulphate used in blank experiment.

V_2 = volume of sodium thiosulphate used in sample of aniline.

M = Molarity of sodium thiosulphate solution.

M_m = Molar mass of aniline.

m = mass of aniline taken in g

z = number of bromine atoms substituted in aniline.