

**B.Sc. Programme
(Chemistry Major)**

**Laboratory Manual
Gravimetric Estimation/
Organic Preparations**



Compiled by

DEPARTMENT OF CHEMISTRY

G.T.N. ARTS COLLEGE (AUTONOMOUS)

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GRAVIMETRIC ANALYSIS

INTRODUCTION

Gravimetric analysis is a branch of analytical chemistry which involves the estimation of a substance by the process of weighing. The constituent to be estimated is converted into a compound of definite composition and the weight of the compound is determined accurately. From this weight, the weight of the substance is calculated. In this analysis the material to be analysed is precipitated by some suitable reagent which after drying is weighed.

For the technique to be successful, precipitation must be complete, so the substance must be very insoluble, filtration must be easy, the substance must be crystalline rather than colloidal or gelatinous; the final product must be pure, and so the reaction should be specific.

Gravimetric analysis is capable of great accuracy but titrimetric analysis is faster. The choice of method depends on whether the situation demands high accuracy or speed.

APPARATUS COMMONLY USED IN GRAVIMETRIC ANALYSIS:

1. Fused Silica Crucibles:

Fused silica glass crucibles, now a days are being used very widely as these can withstand very high temperature. Even the red hot crucible may be immediately dipped in water without breaking. These crucibles are resistant to most of the strong chemicals except very strong alkalies and HF acid.

2. Sintered glass crucible:

Sintered glass crucible is made of an excellent resistance pyrex glass, and is fitted with sintered ground glass, filter disc at a few millimeter above the lower end. It is generally preferred to collect directly a precipitate which requires only drying. The sintered glass crucibles can be had in various degrees of porosity to suit precipitates of different sizes. G3 is used for most precipitates, while G4 is employed for filtering very fine precipitates. This type of crucible is very convenient to use. However, it cannot withstand temperatures above 400°C.

Such crucibles are never heated directly on the flame. The precipitate in sintered glass crucible are mostly dried at 110°C - 120°C in an electric oven.

Precautions to be taken in using a crucible:

- (1) Always use a clean non luminous flame for heating a silica crucible.
- (2) While heating a silica crucible, the flame should be kept low in the beginning and then gradually raised to dull red.
- (3) Always handle a crucible with clean tongs. Throughout the experiment never touch the crucible with the hand.
- (4) Before lifting a hot crucible with tongs, the tips of the latter must be heated for a while in non luminous flame. If cold tips of tongs are brought in contact with hot crucible, the latter might crack.
- (5) While filtering or washing precipitate in a sintered crucible, the liquid or suspension must be poured gently in the centre of the crucible down a glass rod.

3. Desiccator:

Desiccator is used for cooling crucibles in dry air to avoid absorption of moisture. It contains in its lower part a drying agent like anhydrous calcium chloride or conc. sulphuric acid. The crucible to be kept in a desiccator is placed on porcelain disc having holes of suitable sizes. The upper rim of the desiccator jar and the under rim of its cover are ground and this provides an air-tight fitting

Precautions to be taken in using a desiccators:

- (1) Always keep the desiccator covered, except when actually placing or removing the crucible.
- (2) Red hot crucible must not be kept in a desiccator. The crucible should first be cooled for some time in air and then transferred to the desiccator.
- (3) For opening a desiccator, hold the jar firmly on the table with your left hand. Hold the knob of the cover with your right hand and then pull it aside to slide on the rim of the jar.
- (4) When placing the cover on the table always keeps the greased surface upwards.
- (5) For placing the cover, slide its rim over the rim of the jar.
- (6) For carrying a desiccator, always hold it carefully with both hands.

4. Crucible tongs:

A metallic pair of tongs is needed to transfer the crucible from the desiccator to the flame and vice versa.

Precautions to be taken in using tongs:

- (1) Tips of the tongs must be clean. If dirty, rub them with sand paper then wash under tap and finally heat them for a while in the non-luminous flame.
- (2) When placing clean tongs on the table, its tips must be directed upwards.

Steps involved in gravimetric estimation:

(a) Precipitation:

Precipitation is carried out in a 250 ml. beaker of resistance glass (Pyrex). The conditions of precipitation differ in different cases. But, there are some essential points to be remembered during a precipitation. Precipitant should be added slowly with stirring and without splashing. For this, the reagent is allowed to flow down the side of the beaker or along the glass rod used for stirring. Only a moderate excess of the reagent should be added. A large excess of the reagent may sometime have a solvent action on the precipitate and will also make the washing of the precipitate more difficult.

(b) Filtration:

Filtration is usually done in special filter papers. The diameter of the filter paper used is determined by the bulk of the precipitate. The entire precipitate should not occupy more than $\frac{1}{3}$ of the capacity of the filter. The quality of the filter paper used is determined by the nature of the precipitate.

Whatman No. 41 with very loose texture gives very fast filtration and is best suited for coarse and gelatinous precipitates like that of $\text{Al}(\text{OH})_3$, and $\text{Fe}(\text{OH})_3$. Whatman No. 40 with moderately open texture gives fairly rapid filtration, This is suitable for majority of precipitates like BaSO_4 , MgNH_4PO_4 , etc. Whatman No. 42 with very close texture is adopted for very fine precipitates. The paper should be folded carefully and fitted in the Funnel, so that the top of the paper should be atleast 1 cm below the rim of the funnel.

The upper portion of the filter paper should fit tightly on the sides of the funnel. If the paper is fitted correctly in the funnel the stem of the funnel will remain filled with liquid during the filtration. The funnel is so mounted that the tip of the funnel stem just touches the side of the vessel (beaker) receiving the filtrate. The liquid to

be filtered is then poured down a glass rod into the filter directing the liquid against the side of the filter and not to the apex. The end of the glass rod should be directed to the side of the filter where there is a double fold. The rod should be very close to but should not touch the filter. The filter should never be filled more than 2 with the liquid.

Note on filtration by using sintered glass crucibles:

The sintered glass crucible is fitted into a glass adapter by means of rubber ring. The stem of the adapter is passed through a rubber stopper, which is fitted tightly into the mouth of large filter flask. The side tube of filter flask is connected to a suction pump through empty flask. The pump is turned on and sintered glass filter disc is washed repeatedly with distilled water under maximum suction. The crucible is then moved from the adapter and placed in an air oven at a temperature to which the precipitate is to be finally heated. It is then cooled in a desiccator and weighed. The operations of heating, cooling and weighing. The operations of heating, cooling and weighing are repeated till the weight becomes constant.

(c) Washing the precipitate :

Filtration and washing of precipitate should be done by decantation. After the precipitate has settled, the supernatant liquid into the filter along a glass rod without disturbing the precipitate, as much as possible. After the supernatant, liquid has been poured through the filter; about 20 to 25ml of the washing liquid is added and stirred thoroughly. The precipitate is allowed to settle once again and the clear liquid is decanted into the filter. The process is repeated three or four times. Washing by decantation is very effective because it ensures that all portions of the precipitate comes into intimate contact with the washing liquid, which is not the case if the washing is carried out in the filter. Repeated washing with small volumes of liquid is much more effective than washing with the same total volume of liquid applied in one or two stages. The liquid added to the filter should be allowed to drain as completely as possible before adding the next lot.

(d) Drying and incineration:

These operations are peculiar to gravimetric analysis. In cases where the substance to be finally weighed has the same composition as the precipitate, it has to be dried at a suitable temperature. It is here that sintered crucibles are particularly useful. (For filtering organic compounds Buckner funnels are used).

When incineration of the filter paper and ignition of the precipitate are necessary the filter with the funnel is covered up with a piece of paper and placed in an oven kept at about 110°C. When thoroughly dry the funnel is taken out and the filter paper removed. The filter paper is then suitably folded and incinerated (burnt to ash) in a weighed silica crucible. The weight of ash may be neglected. The ash may have to be suitably treated if the burning has altered the composition of the precipitate sticking to the paper. The main bulk of the precipitate is then heated to the required temperature, cooled in a desiccator and weighed.

Crucible and their lids should be handled only by clean crucible tongs. Hot Crucible and lids should never be placed directly on the table but on porcelian tiles.

GRAVIMETRIC ESTIMATIONS

EXPERIMENT-1

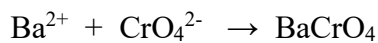
Estimation of Barium as barium chromate

Aim:

To Estimate the weight of Barium in the whole of the given BaCl₂ solution.

Principle and outline:

Ba²⁺ may be precipitated as barium chromate, by the addition of K₂CrO₄ in presence of an acetate buffer (pH 5.5)



The precipitate is filtered, dried and weighed as BaCrO₄

Make up the given barium salt solution to 100ml in a volumetric flask. Pipette out 20ml of this solution into a clean 200ml beaker carrying a glass rod and watch glass. Dilute to 100ml. Add 1ml of 6 N acetic acid and 10ml of neutral ammonium acetate solution. Heat to boiling. Add 1ml of 10% K₂CrO₄ solution slowly with stirring. Digest for 30 minutes on a hot water bath. Allow the precipitate to settle down by setting it aside. Add a drop of potassium chromate through the side and test completion of precipitation. If there is no further precipitation, cool it to room temperature. Filter through a previously cleaned, weighed sintered glass crucible. Wash the precipitate thoroughly with hot water until the washings are free from chromate ions (test with BaCl₂ solution; wash until, no yellow precipitate is obtained with washings). Dry at 120°C to constant weight and weigh as K₂CrO₄. From the weight of Barium chromate, the weight of barium in the whole of the given solution is calculated. Knowing that 253.34 gms of K₂CrO₄ contains 137.36 gm of Barium.

Calculation: crucible A:

Weight of empty sintered crucible = w_1 gms

Weight of sintered crucible + BaCrO_4 = w_2 gms

Weight of BaCrO_4 = $(w_2 - w_1)$ gms

253.34gms of BaCrO_4 contains 137.36gm of Barium

$(w_2 - w_1)$ gms of BaCrO_4 contains = $137.36 \times (w_2 - w_1) / 253.34$

20ml of the solution contains x gm of Barium

100ml of the solution contains = $x \times 100/20$

(Same calculation should be followed for crucible B)

Result:

Weight of Barium in the whole of the given solution

Weight of lead in the whole of the given solution = (i) gms

(ii) gms.

EXPERIMENT-2

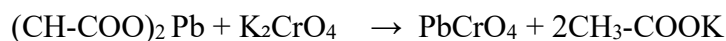
Estimation of lead as lead chromate

Aim:

To Estimate the weight of lead in the whole of the given lead acetate solution.

Principle and outline:

The given lead acetate solution is made upto a definite volume. Lead present in a definite volume of the made up solution is precipitated as lead chromate by adding potassium chromate solution.



The precipitate is filtered using sintered glass crucible, washed, dried and weighed. From the weight of lead chromate, the weight of lead in the whole of the given solution is calculated knowing that 323.21 gms of lead chromate contains 207.21 gms of lead.

Procedure:

The given lead acetate solution is made upto 100ml. in a standard measuring flask. 20ml. of the made up solution is pipetted out into a 250ml, beaker. Ammonium hydroxide is added drop by drop till a permanent precipitate is formed. Dilute acetic acid is then added to make the solution slightly acidic. It is then diluted to 125ml. and heated to boiling. To the hot solution a 4% solution (about 10ml.) of potassium chromate is added in slight excess with constant stirring. The mixture is then boiled for 5 to 10 minutes to make the precipitate granular. The precipitate is then allowed to settle. The supernatant liquid must be coloured slightly yellow. This indicates that potassium chromate solution is sufficient. The precipitate is then filtered through a previously weighed sintered glass crucible (G4). It is washed with hot water, dried at 120°C, cooled and weighed. It is heated to constant weight. A duplicate experiment is conducted.

From the weight of lead chromate, the weight of lead in the whole of the given solution is calculated.

Calculation:**Crucible A:**

Weight of empty sintered glass crucible = w_1 gms

Weight of sintered crucible + PbCrO_4 = w_2 gms

Weight of PbCrO_4 = $(w_2 - w_1)$ gms

323.21 gms. of PbCrO_4 contains 207.21 gms of Pb

$(w_2 - w_1)$ gms of PbCrO_4 contains = $207.21 \times (w_2 - w_1) / 323.21$

= (gms of Pb)

20ml of the solution contains x gm of Barium

100ml of the solution contains = $x \times 100 / 20$

(Same calculation should be followed for crucible B.)

Result:

Weight of lead in the whole of the given solution = (i) gms

(ii) gms.

ORGANIC PREPARATIONS

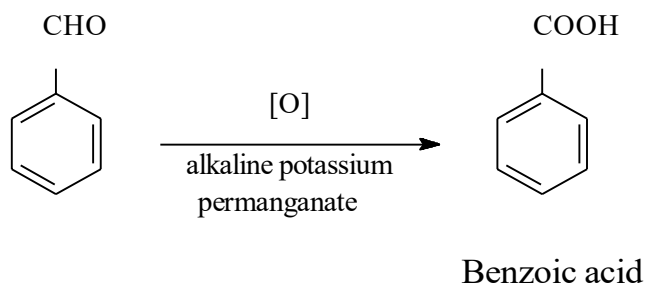
OXIDATION

Preparation of benzoic acid from benzaldehyde

Chemicals Required

- | | | |
|------|------------------------|-------|
| i. | Benzaldehyde | 2.5ml |
| ii. | Sodium carbonate | 2.5g |
| iii. | Potassium permanganate | 3g |

Reaction



Procedure

About 2.5g of sodium carbonate is dissolved in about 20ml of water in a round bottom flask. Benzaldehyde (2.5ml) and a few porcelain bits are then added to it. The flask is fitted with a water condenser and heated over the wire gauze. When the mixture begins to boil, a saturated solution of 3g of potassium permanganate is added to the flask from the top of the condenser till the solution in the flask remains pink in colour. The contents are refluxed for one hour and then cooled. It is then transferred to a beaker and solid sodium metabisulphite is added to the beaker followed by dilute sulphuric acid till all the product of manganese dioxide dissolves and the solution becomes acidic. The precipitate of benzoic acid is filtered and dried. A portion of the sample is recrystallised from hot water.

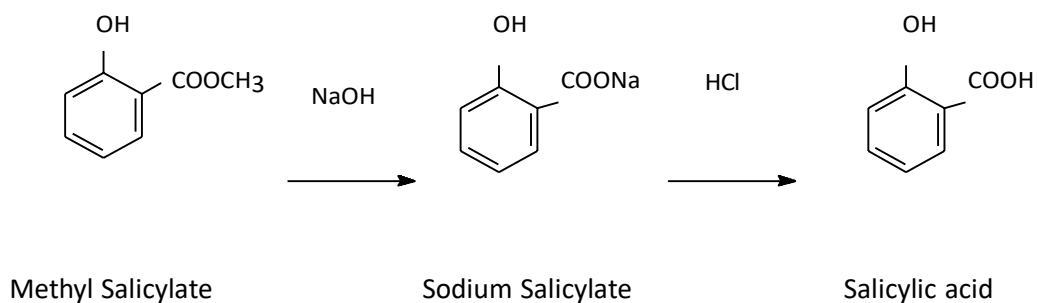
HYDROLYSIS

Preparation of salicylic acid from methyl salicylate

Chemicals Required

- i. Methyl salicylate 2.5ml
- ii. Sodium hydroxide 15ml

Reaction



Procedure

Methyl salicylate (2.5ml), 15ml of sodium hydroxide and a few porcelain bits are taken in a round bottom flask. The flask is fitted with water condenser and the contents are boiled till the oily drops are not seen. The contents are cooled and transferred into a beaker. Concentrated hydrochloric acid is added to the solution in small quantities with vigorous stirring till the solution is acidic. Salicylic acid is precipitated and the contents are cooled well. The precipitate is filtered and washed with water. A portion of the sample is recrystallised from hot water.

NITRATION

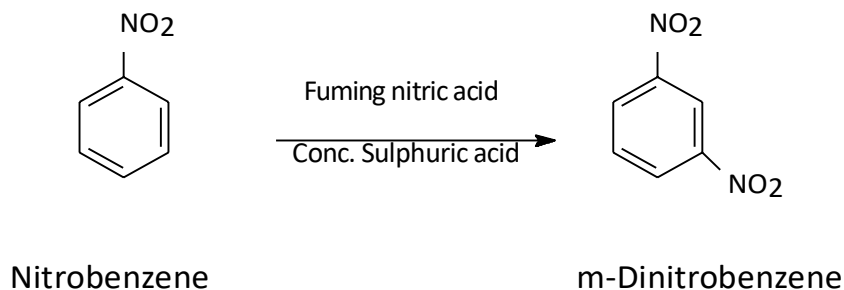
Preparation of m-dinitrobenzene from nitrobenzene

Chemicals Required

i.	Nitrobenzene	5.0ml
ii.	Fuming nitric acid	6ml
iii.	Concentrated sulphuric acid	3.5ml.

Reaction

m-dinitrobenzene is prepared by the nitration of nitrobenzene



Nitration is effected by fuming nitric acid in the presence of concentrated sulphuric acid.

Procedure

Fuming nitric acid is (6 ml) taken in a round bottom flask and 7ml of concentrated sulphuric acid is added little by little carefully. The flask is cooled during addition. Nitrobenzene (5ml) is then added in small quantities to the nitrating mixture. Shaken well and heated for about 45 minutes, by immersing in a boiling water bath. The contents of the flask are then poured into water contained in a beaker. The mixture is stirred well. m-Dinitrobenzene separated as solid, is filtered off at the pump, washed with water and dried. A portion of the sample is recrystallised from alcohol.

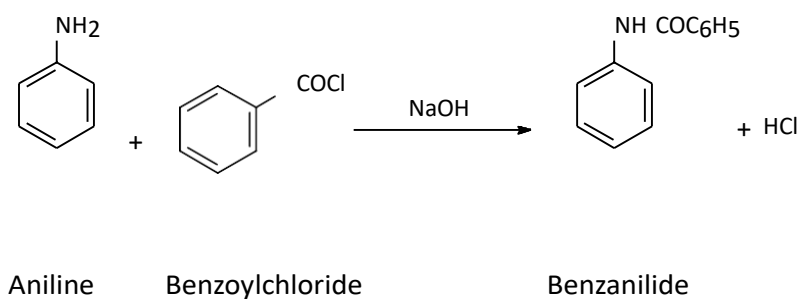
BENZOYLATION

Preparation of benzanilide from aniline

Chemicals Required

- | | | |
|------|----------------------|------|
| i. | Aniline | 5ml |
| ii. | Benzoyl chloride | 5ml |
| iii. | 10% sodium hydroxide | 50ml |

Reaction



Procedure

Aniline (5ml) is taken in a conical flask fitted with a cork. About 5ml of sodium hydroxide and 0.5ml of benzoyl chloride are added to the flask. The flask is corked well and the contents are shaken vigorously. After cooling, again 5ml of sodium hydroxide and 0.5ml benzoylchloride are added and shaken well. The process is repeated till all the benzoyl chloride is added. If the mixture smells that of benzoylchloride, some more sodium hydroxide must be added. The whiteprecipitate of benzanilide formed is filtered and dried. A portion of the sample is recrystallised from alcohol.

PREPARATION OF REAGENTS

1. Phenolphthalein

5g of phenolphthalein is dissolved in 500ml of alcohol. Then 500ml of water is added with constant stirring. Any precipitate formed is filtered off and the clear filtrate is used.

2. Methyl Orange

0.5g of the free acid or the sodium salt is dissolved in a litre of cold water. Any precipitate formed is filtered off and the clear filtrate is used.

3. Borsche's reagent

1 gram of 2,4-dinitrophenylhydrazine is refluxed with 100ml of methyl alcohol till dissolved.

4. Fehling's Solution A

6.9g of copper sulphate crystals are dissolved in 40ml of water and diluted to 100ml.

5. Fehling's Solution B

15g of Sodium hydroxide and 36g Sodium potassium tartrate (Rochelle Salt) are dissolved separately in 30ml of water each, mixed and diluted to 100ml after cooling. Equal volume of A & B are mixed before use.

6. Molisch's reagent

10g of Alpha-naphthol is dissolved in 100ml of rectified spirit.

7. Neutral ferric chloride

About 1g of ferric chloride is dissolved in 100ml water. Sodium carbonate solution is added little by little to the above solution till the slight turbidity persists even after shaking. The precipitate is filtered off and the filtrate is used as neutral ferric chloride solution.

8. KMnO_4 solution

1gm of potassium permanganate solid is dissolved in 100ml of distilled water.

9. Tollen's reagent

About one ml of silver nitrate solution is taken in a test tube. Two drops of NaOH is added and then dil. NH_4OH is added drop by drop until the precipitate is just redissolved.