

3.2.2.2. Oxidation-Reduction Titration

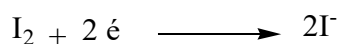
3.2.2.2.1. Iodometric Titrations

Iodimetry: It is a form of redox titration which includes the use of iodine as titrant. In iodimetry, the titrant is iodine (I₂) and the analyte is reducing agent.

Iodometry: Another common titration type is iodometry. Here, a sample is usually mixed with an excess of iodine. The iodine oxidizes a part of a sample. The iodine which is not converted is then titrated with thiosulphate. This is a back titration, as both the reagent iodine (or a mixture of iodate with iodide) must be precisely dosed or weighed, as well as the back titration must be done with a well-defined concentration.

However, these two terms (iodimetry, iodometry) are often confused, and in general both are called IODOMETRY.

Elemental iodine oxidizes certain substances, and is reduced to iodide ion.



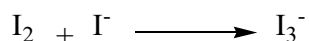
Molecules that reducing iodine to iodide ion: S₂O₃²⁻, Sn²⁺, H₂S

Iodine is a moderate oxidation agent. Very few substances can be titrated with iodine, directly. Only arsenide and thiosulfate are important in direct titration with iodine. Many compounds have the capacity to oxidize iodide to iodine. Thus, these compounds can be titrimetrically analyzed by releasing iodine with thiosulfate. This method is known as indirect titration.



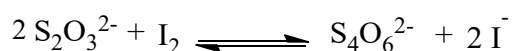
Molecules that iodine-releasing from iodide ion: MnO₄⁻, Cr₂O₇²⁻, H₂O₂, IO₃⁻

Iodine is slightly soluble in water, but since it converts into triiodide in iodide solution, it dissolves in water.

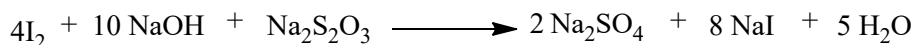
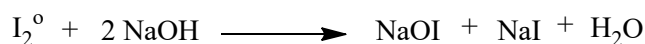


Using the iodide solution as a solvent increases the solubility and decreases the evaporation of iodine. Thus, the stability of the iodine solution is provided.

All indirect iodometric titrations are based on the titration of iodine with thiosulfate. Stoichiometric reaction equation:



The reaction occurs best when the pH is <6. In other words, the reaction media should not be alkaline. In an alkaline media, the iodine converts to the hypoiodite ion and oxidizes the thiosulfate ion to sulphate, and therefore less thiosulfate is consumed to reduce the same amount of iodine in the media.

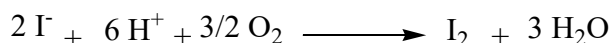


If the iodine needs to be titrated in the weak basic solution, arsenide solution should be used instead of thiosulfate as the standard solution (titrant). In solutions that pH higher than 11, titration cannot be made with iodine solution. On the other hand, the standard solutions of thiosulfate are not stable at acid pH. It gives the best stability when pH=9-10. Oxygen facilitates the decomposition of thiosulphate and this fragmentation is catalyzed by copper ion impurity which is trace amount in the water. Therefore, it is important that the water is pure.

To obtain accurate results in iodometry titrations,

- To prevent oxidation of acidified iodide solution in air
- To prevent reducing amount of elemental iodine due to evaporation

The iodide ion is gradually oxidized by the oxygen of the air in the acid medium.



Substances reduced by the iodide ion in the acid medium and the light catalyzes this reaction. Therefore, before titrating with thiosulfate in the iodometric determination of the oxidation, the system should not be waited longer than the required time for finishing the reaction between amount of oxidant that to be determined and the iodide ion, and should be kept in the dark during this time.

Determination of Endpoint in Iodometry

In iodometry, the endpoint is determined by excess of iodine and its characteristic color when the standard iodine solution is used, and when the thiosulfate solution is used, it is determined by the loss of iodine color. Iodine solution is dark colored due to triiodide ion. Therefore, a drop of 0.1 N iodine solution gives a pale yellow color to 100 ml of cold water. Sensitivity of color change can be increased by placing starch as indicator to the media. In the presence of iodide, iodine is adsorbed by starch to give a characteristic blue color. In the absence of iodide, no color occurs. On the other hand, extraction indicators (chloroform, carbontetrachloride) can be used as indicators. While the sensitivity of the indicators increases with acid, organic compounds and heat reduce this sensitivity.

Situations to be considered in Iodometry

1. Titration should be carried out in cold. Otherwise;
 - a) I_2 evaporates from the reaction medium.
 - b) The reaction between oxygen (O_2) and iodide (I^-) is accelerated.
 - c) The colour of starch indicator weakens, and to detect the endpoint becomes difficult.
2. The starch must be added in the back titration (in the titration of iodine with thiosulfate) after the majority of iodine has been titrated. If added early;
 - a) Since starch will remain in acid medium for a long time, it is hydrolyzed and does not act as an indicator.
 - b) Starch and concentrated iodine form irreversible complex in the medium. Endpoint cannot be determined.
3. Titration should be shaken continuously. Otherwise it fragmentises to $\text{S}_2\text{O}_3^{2-}$.

4. The erlenmeyer which the titration is made, should be kept in the dark. If not kept, iodine is released by the effect of light.

5. Iodine should not be contacted with materials such as rubber and cork stopper.

6. Titrations should not be made in alkaline media.

Iodometrically quantified substances:

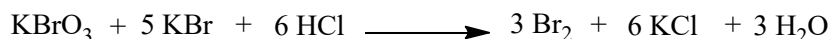
Ascorbic acid, dimercaprol, phenazone (antipyrine), halazone, hydrogen peroxide, isoniazid, nitrofurazone, novalgin, potassium benzyl penicillin, cephalixin, cephaloridine and so on.

3.2.2.2 Bromometry (Titrations with KBrO₃ Solution)

Titrations such as these are made based on the addition and substitution reactions of organic materials with free bromine. Bromine is also good oxidizing agent like iodine. However, since the standard bromine solution does not remain stable for a long time, the bromine required for titration is formed from KBrO₃ and KBr.



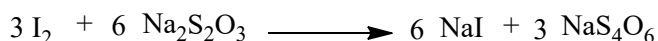
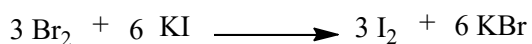
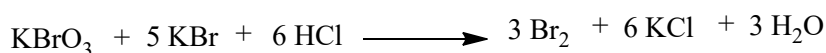
A part of bromine oxidizes the substance to be quantitated. Excess of bromine is calculated by titrating iodine (I₂), which is released when potassium iodide is added to the medium, with standard thiosulfate (S₂O₃²⁻) solution (using starch). By this method, substances can be determined such as phenol, salicylic acid, sulfamides, resorcinol, isoniazid.



KBrO₃ equivalent weight = KBrO₃ (167.02)/6 = 27.84

For 0.1 N bromine solution, 2.784 g KBrO₃ is weighed and completed with distilled water to 1000 ml.

Total equation:



3.2.2.3 Permanganometry

Permanganate is a strong oxidizing agent and is a self-indicator. **Self indicator** is actually a chemical substance which can mark the end point of a titration or any other reaction along with self-participation in the reaction. So permanganate is widely used in titrations. The standard permanganate solution is used for quantification of reducing agents. Using this method, Fe⁺², oxalate, arsenic, antimony, nitrite and ferrocyanide ions and H₂O₂, calcium lactate and calcium gluconate samples can be quantified.

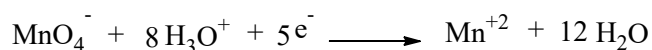
Properties of Permanganate solution:

0.1N KMnO₄ solution is used in Permanganometric titrations. There are situations to be considered during the preparation of the solution. Permanganate solution is easily degraded by heat. It can decompose by contacting with filter paper or rubber stopper, resulting in an oxidation reaction. The solution should be stored in closed colored bottles, away from heat and light, to prevent degradation. Nevertheless, it is recommended that the prepared solutions are not stored for a long time and that fresh solutions are used.

Permanganate solution oxidizes the chloride ion found in the medium as impurity. The trace amount of iron ion present in the medium catalyzes the reaction. Therefore; In the titration of iron-containing preparations with permanganate solution, should be ensured that no chlorine ions are present in the medium or should be taken precautions to prevent oxidation.

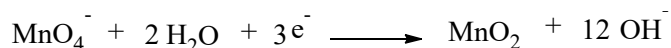
One of the most important points in the titration with permanganate is that no indicator is used. Permanganate gives two different reactions depending on whether the medium is acidic or basic.

1) Acidic Medium: Titrations are continued until the characteristic pink color of KMnO₄ disappears. The moment when the color is lost indicates the equivalent point. Reaction equation in acidic medium;



Valence of manganese ion: 5

2) Neutral or Basic Medium: In the titrations made in this medium, the moment when the pink color is formed determines the equivalent point. Reaction equation;



Valence of manganese ion: 3

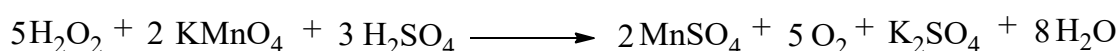
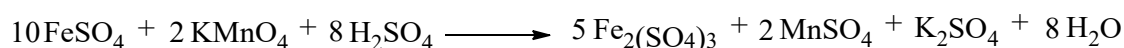
Permanganometric titrations can be examined in two parts.

1) Direct Titration: The sample containing the reducing agent is directly titrated with the standart KMnO₄ solution.

Example:

The purity of FeSO₄ and H₂O₂ samples is determined by the adjusted KMnO₄ solution.

The reaction equations that occur during titrations are as follows.



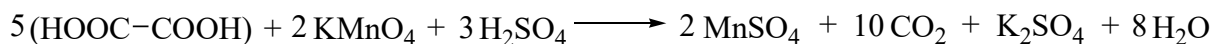
Siderite (FeCO₃), hematite (Fe₂O₃), ferroammonium sulfate (Fe(NH₄)₂(SO₄)₂·6H₂O), oxalic acid, sodium perborate (NaBO₃) can be quantified using this method.

- 2) **Indirect Titration:** The reducing agent reacts with a substance such as ammonium oxalate and it is precipitated as its oxalate. Based on this precipitate, titration is carried out with permanganate solution in an acid medium.

Example:

This method is especially used the quantitation of calcium lactate and calcium gluconate. These precipitated oxalates are filtered off and the precipitate is dissolved in H₂SO₄ and the oxalate ion is titrated with the standard permanganate solution.

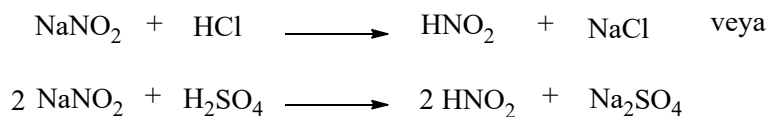
The total reaction equation is as follows.



In addition, rare earth elements such as nitrite (-NO₂), copper (Cu), zinc (Zn), lead (Pb), and phosphorus, sodium compounds can be quantified by indirect titration.

3.2.2.3. Nitrite Titration

Nitrite titration is a titration method used particularly for the assay of primary aromatic amines. This process is known as the diazo reaction for the primary aromatic and aliphatic compounds. The diazo reaction is the reaction of primary aromatic and aliphatic amines to form diazonium salts with nitrous acid. Since nitrous acid is a weak acid and unstable, it is formed in situ and gives reaction in the reaction medium. For this, sodium nitrite is reacted with a mineral acid.

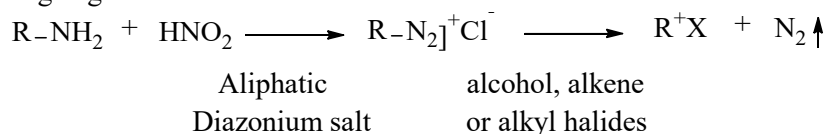


For the titration; the sample is titrated with standardized NaNO₂ solution in acidic medium. Nitrous acid reacts with all amines, gives water-soluble diazonium salts with only primary aromatic amines and gives water-insoluble compounds with secondary and tertiary amines.

The reactions of nitrous acid with amines:

Reaction with primary amines;

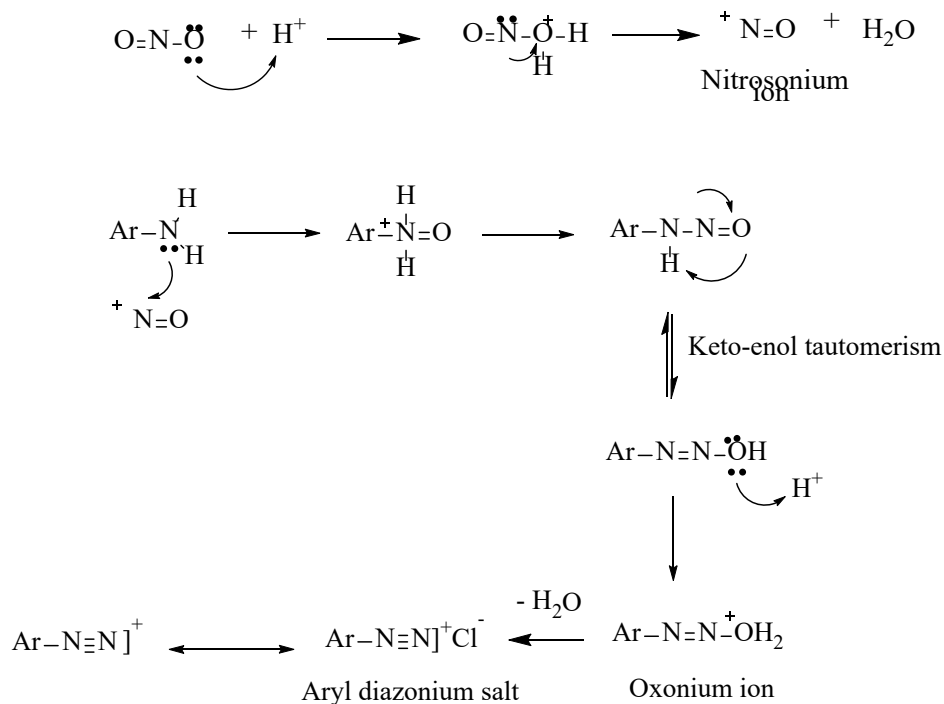
Primary aliphatic amines provide the diazonium salts with nitrous acid. However, even at very low temperatures, this salt is self-decomposed by decomposing nitrogen gas to produce alcohols corresponding to primary aliphatic amines. Quantitative quantification can be made by measuring the volume of the nitrogen gas released.



Because the products are a mixture, this reaction has no importance.

Primary aromatic amines give aryl diazonium salts with nitrous acid. This salt is very stable when the reaction medium is kept below 5°C. This reaction is called the diazo reaction, the method is called nitrite titration. Quantitative analyses of compounds which has primary aromatic amine groups, such as sulfonamides, local anesthetics, can be carried out with this method.

Reaction mechanism;



Chemical reactions are important in terms of the spreading of electron density in the molecule and the formation of new bonds between molecules. Therefore, electron densities around atoms have become important. If the chemical structure of a molecule is written in accordance with the Lewis form, the electrons indicated by the dot show the free valence electrons. Thus, it is possible to calculate the formal charge of each atom in the molecule. To calculate the formal charge;

Formal charge = total number of valence electrons in free atom - [total number of nonbonding electrons + total number of bonding electrons/2]

Example:

$\text{Ar}-\text{N}\equiv\text{N}]^+$ Calculate the Formal Charges (FC) of two nitrogen atoms.

1 2

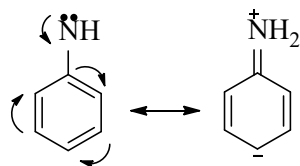
$$(1) \text{ FC} = 5 - (0 + 8/2) = +1$$

$$(2) \text{ FC} = 5 - (2 + 6/2) = 0$$

In this case, the structure is; $\text{Ar}-\text{N}^+\equiv\text{N}$:

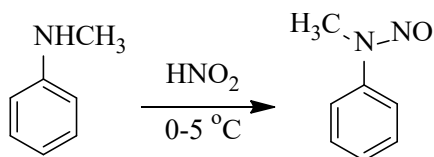
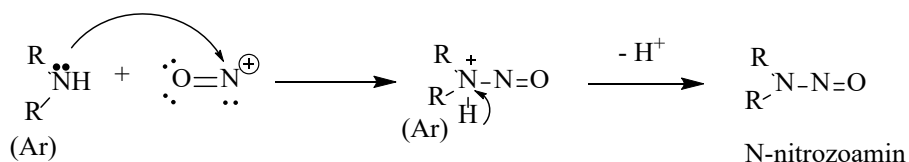
Diazonium salts are important for synthesis; these compounds can be converted into various functional groups.

The free electron pair on nitrogen atom in aromatic amines forms a double bond between nitrogen and carbon by delocalization (resonance, mesomerism) with the ring. In aliphatic amines there is no electron exchange, so the carbon-nitrogen bond is very easy to rupture and cannot be stabilized.



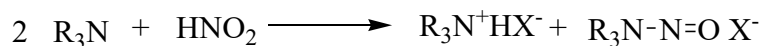
Reaction with secondary amines;

Secondary aliphatic and aromatic amines generate N-Nitrosamines with nitric acid. Nitrosamines are known to be potent carcinogens. These compounds differ from yellow to red color in the reaction medium and are separated into an oily layer. They are insoluble in water, but can be dragged with water vapor.

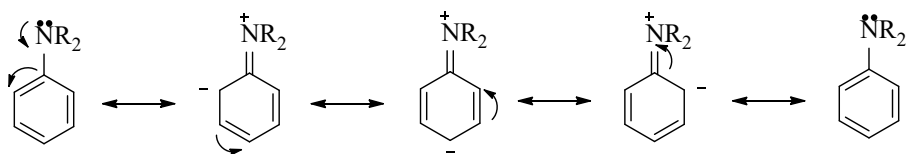


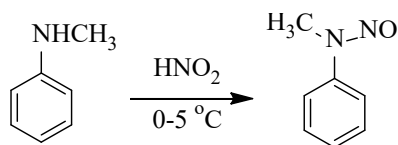
Reaction with tertiary amines;

The diazo reaction is difficult with tertiary aliphatic amines, since the reaction is in a state of equilibrium. The product is stable only at low temperatures, otherwise it may be decomposed to the aldehyde.



Tertiary aromatic amines do not react with nitrous acid unless there are strong electron release groups such as dialkylamino in the aromatic nucleus. The nitrosonium cation is bound primarily from the *para* position due to the steric hindrance, but it may also be the *ortho* isomer by forcing of the reaction conditions if the *para* position is closed, but there is no *meta* isomer.

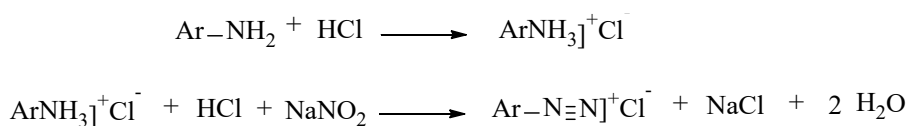




Points to be considered in the application of Nitrite Titration:

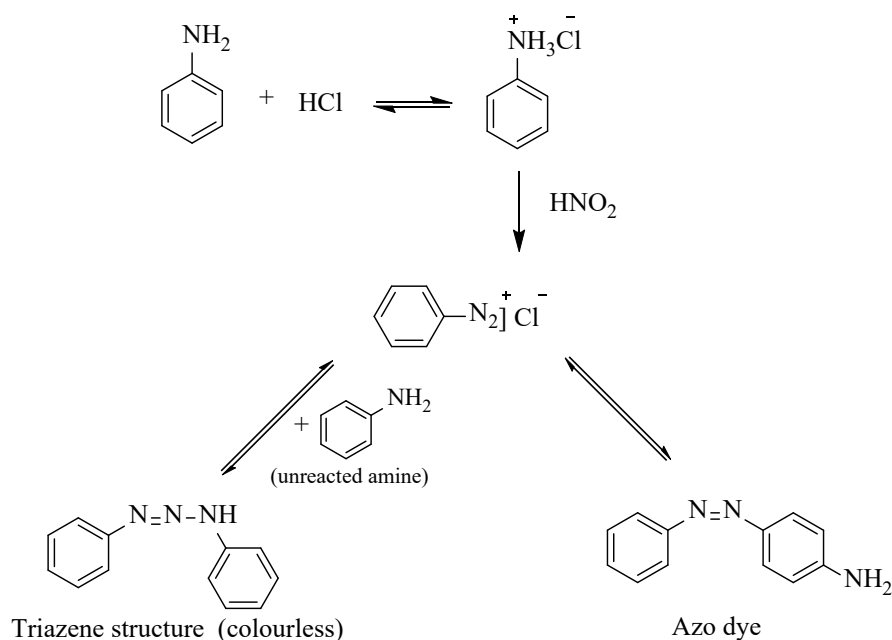
- Since the nitrous acid which used in the diazotation is not resistant to heat, the reaction of the primary aromatic amines with this acid should be carried out at a temperature not exceeding 5°C. If the medium temperature is high then 5°C, the nitrogen is separated from the medium as aeriform and the resulting diazonium salt is also degraded.

- During titration, the mixture in the erlenmeyer flask should be shaken well to ensure that nitrous acid reacts rapidly with an equal amount. Otherwise, nitrous acid is present more in some part of the solution and the wrong result can be obtained.



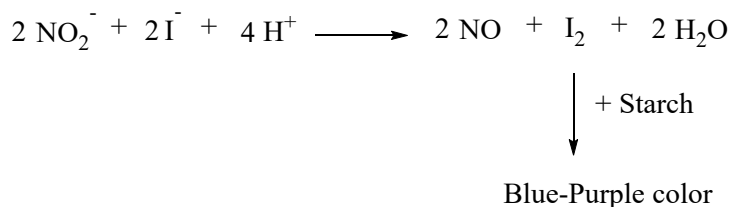
As seen in the above titration equation, 2 equivalent acids should be used. One of them forms salt with amine and the second forms nitrous acid from sodium nitrite. In practice, it is desirable to use 2.5-3 times more acid. The reason is that to prevent the coupling reaction of the unreacted amine by preventing the pH of the solution from getting closer the neutral limit near the end of the reaction.

- The reaction slows down near the end of the titration. Therefore, the titration should be carried out slowly, especially around the equivalence point. The reaction medium must be acid in the diazotization process. Otherwise reaction do not occur, byproducts may occur.



Endpoint Titration

In these titrations, the end point of the titration is determined with external indicator. This indicator is starch iodide paper. When the diazotization reaction is over, which the equivalence point is passed, the nitrite ion is excess of in the reaction medium. There is no appropriate internal indicator to detect this moment. For this reason, one drop of the reaction medium is withdrawn with a glass rod towards the end of the titration, and dropped on the starch iodide paper, it is examined whether the iodine is formed.



After the amine groups of the compound is completely converted to diazo structure the added sodium nitrite remains unreacted and a drop that withdrawn at this time from the reaction medium leaves a blue-purple stain on the starch iodide paper. This is the color that starch gives with iodine, which is formed by the reaction between nitrous acid and KI.

As the paper can be colored with air during standby, titration is continued until a blue-violet color is formed immediately on the indicator paper.

Questions

1. Define the terms equivalence point, standardized solution, indicator, normality, molarity, valence factor (n factor), primary standard, factor (f).
2. Classify the titrimetric analysis reactions according to the principles on which they are based.
3. What kind of indicators are used in the acid-base reaction?
4. Define the acid-base terms according to Bronsted, Arrhenius and Lewis.
5. Explain the reason of the titration preference in anhydrous media by giving an example.
6. Classify the oxido-reduction titrations and explain each of them.
7. What should be considered in iodometry?
8. Which titration method is made by using the diazo reaction? Explain by showing on a sample molecule.
9. How does the nitritometric determination of compounds containing primary, secondary and tertiary amine groups practice?
10. Which chemical substances are used in titrimetric methods as the autoindicator? Write direct and indirect titration methods by using this substance.