Analytical chemistry

Lecture № 23

REDOX titration
Part II

BROMATOMETRIC TITRATION titrant sol. $KBrO_3$

Potassium bromate is a powerful oxidizing agent which is reduced smoothly to bromide:

$$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O, \quad E^\circ(BrO_3^-/Br^-) = 1.44\,V.$$

In acidic medium, excess of bromate ions oxidize bromide ions to give bromine according to the reaction

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

This is a very important reaction. It permits us to generate bromine *in situ from* potassium bromate, which is a primary standard.

From a purely analytical standpoint, we now mention some quantitative reactions. They are classified under the following headings:

- oxidization reactions with bromate (***bromatometric titration***) ions and with bromine (***bromometric titration***);
- fixation reactions of bromine on organic molecules either by substitution or by addition.

Scheme of titrations:

$$Red + KBrO_3 + HCl \rightarrow KBr + H_2O + ...$$

At equivalence point

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

$$Ind + Br_2 \rightarrow irreversible\ distruction\ of\ Ind$$

The presence of free bromine, and consequently the end point, can be detected by its yellow colour, but it is better to use indicators such as methyl orange or methyl red. These indicators have their usual colour in acid solution, but are destroyed irreversible by the first excess of bromine. In this case such indicators are named irreversible indicators.

Peculiarities of bromatometric titrations

1. With all irreversible indicators the destruction of the indicator is often premature to at slight extent: a little additional indicator is usually required near the end point.
2. Direct titrations with bromate solution in the presence of irreversible indicators are usually made in sulfuric acid solution, the concentration of which should be at least 1-2 M.

Peculiarities of bromatometric titrations

Preparation of a solution of $KBrO_3$

Potassium bromate is readily available in a high state of purity, the product has an assay value of at least 99,9 percent. The substance can be dried at 120-150°C, in anhydrous, and the aqueous solution keeps indefinitely. It can therefore be employed as a primary standard.

Examples of determinations:

1. Determination of $SbCl_3$

$$3SbCl_3 + KBrO_3 + 9HCl = KBr + 3H[SbCl_6] + 3H_2O$$

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

2. Determination of As_2O_3 and arsenic (III) salts

$$3As_2O_3 + 2KBrO_3 + 9H_2O = 2KBr + 6H_3AsO_4$$

3. Determination of hydrazine

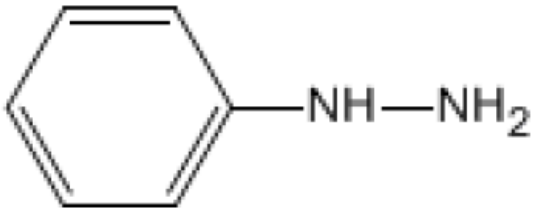
$$3N_2H_4 + 2KBrO_3 = 2KBr + 3N_2 + 6H_2O$$

4. Determination of phenilhydrazine

$$3C_6H_5-NH-NH_2+2KBrO_3+3HCl=2KBr+3[C_6H_5-N\equiv N]Cl+6H_2O$$

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

$$n(\tfrac{1}{4}C_6H_5NHNH_2)=n(\tfrac{1}{6}KBrO_3)$$

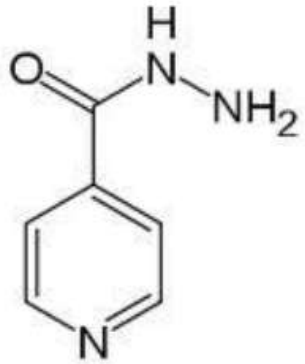


5. Determination of izoniazide

$$3C_5H_4N-CONHNH_2+2KBrO_3=3C_5H_4N-COOH+2KBr+3N_2+3H_2O$$

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

$$n(\tfrac{1}{4}C_5H_4N-CONHNH_2)=n(\tfrac{1}{6}KBrO_3)$$



BROMOMETRIC TITRATION titrant sol. $KBrO_3$ + KBr

Various substances cannot be oxidized directly with potassium bromate, but react quantitatively with an excess of bromine. Acid solutions of bromine of exactly known concentration are readily obtained from a standard potassium bromate solution by adding acid and an excess of bromide:

$$5KBr\,(excess) + KBrO_3 + 6HCl \rightarrow 3Br_2 + 6KCl + 3H_2O$$

$$Analyte + Br_2 \rightarrow .....$$

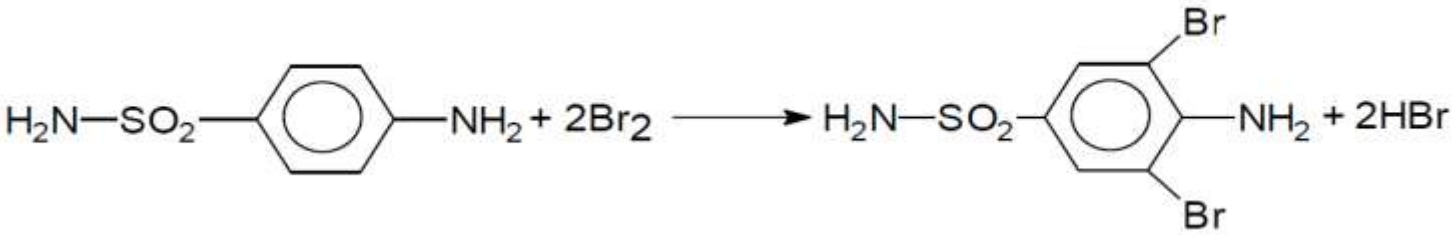
$$Ind + Br_2 \rightarrow irreversible\ distruction\ of\ Ind$$

This method can be used to analyze many unsaturated organic compounds.

Bromine Br_2 is a red-brown liquid at ordinary temperature. It is very volatile. It gives very dense red-brown vapors that are highly toxic to mucous membranes. In the liquid state, it is particularly corrosive. It results in very serious burns on the skin. Its chemical analysis exhibits great analogies with iodine. Dibromine aqueous solutions are very unstable, because of bromine's volatility.

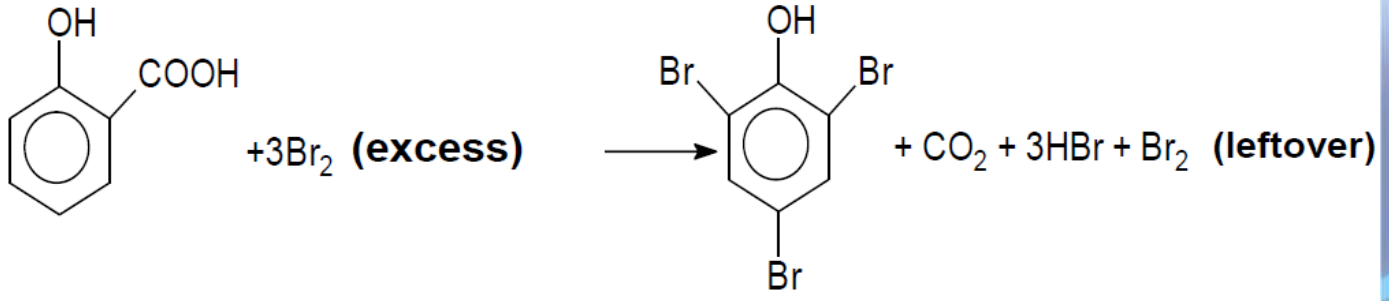
Determination of streptocide

$$5KBr(excess) + KBrO_3 + 6HCl \rightarrow 3Br_2 + 6KCl + 3H_2O$$



Determination of salicylic acid

Salicylic acid can be substituted rapidly and quantitatively with bromine produced from bromate and bromide in acid solution. The determination involves treating salicylic acid with an excess of potassium bromate and potassium bromide, when bromination is complete the unreacted bromine is then determined by adding excess potassium iodide and back titrating the liberated iodine with standard sodium thiosulphate

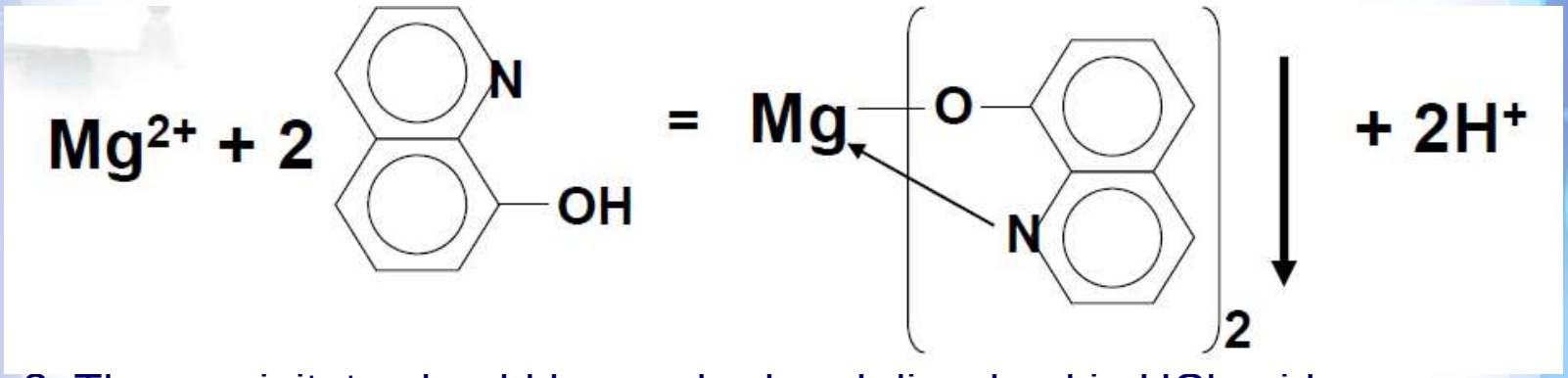


$$Br_2(leftover) + 2KI(excess) \rightarrow I_2 + 2KBr$$

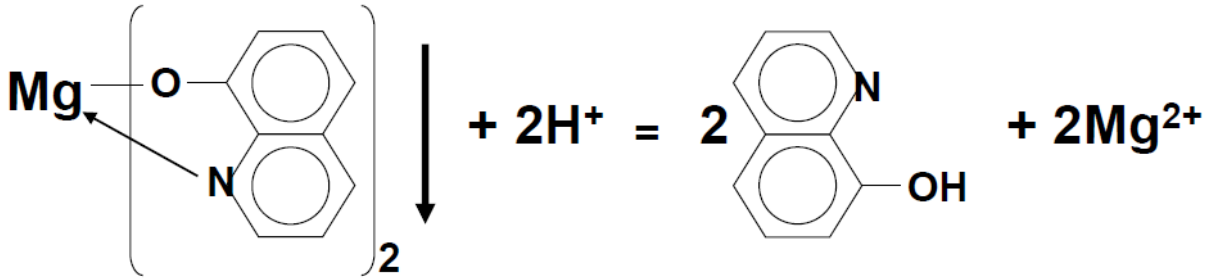
$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Determination of magnesium salts

1. Analyte is treated with 8-hydroxyquinoline (oxine) at pH 5 to precipitate magnesium oxinate:

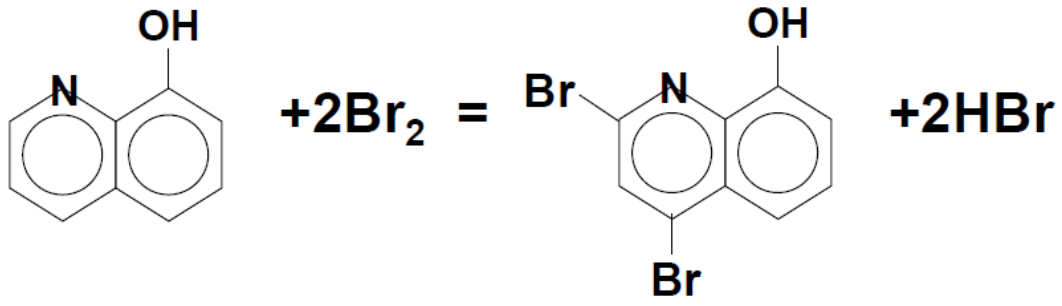


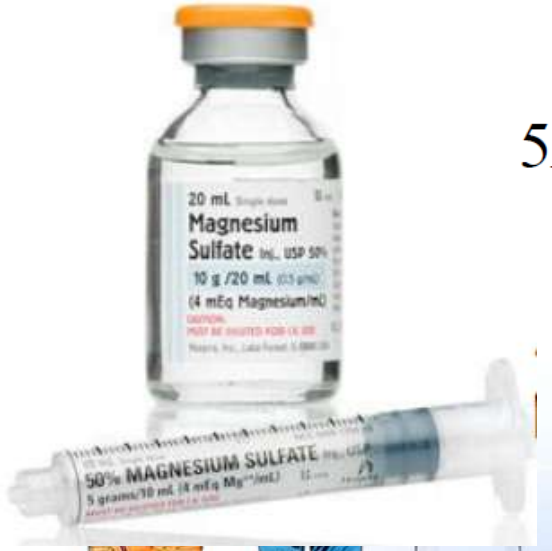
2. The precipitate should be washed and dissolved in HCl acid



3. 8-hydroxyquinoline is titrated by bromometric method

$$5KBr(excess) + KBrO_3 + 6HCl \rightarrow 3Br_2 + 6KCl + 3H_2O$$





Measured excess of standard bromate is added to the solution that contains the sample plus an excess of potassium bromide. After acidification, the mixture is allowed to stand in a glassstoppered vessel until the bromine/analyte reaction is judged complete. To determine the excess bromine, an excess of potassium iodide is introduced so that the following reaction occurs:

$$2I^- + Br_2 \rightarrow I_2 + 2Br^-$$

The liberated iodine is then titrated with standard sodium thiosulfate

Substitution Reactions

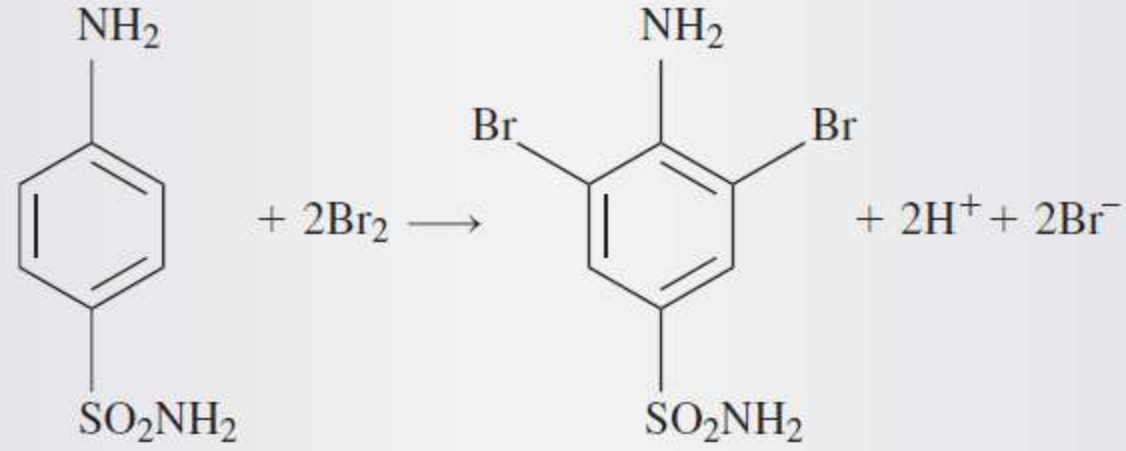
Bromine is incorporated into an organic molecule either by substitution or by addition. In halogen substitution, a hydrogen in an aromatic ring is replaced by a halogen. Substitution methods have been successfully applied to the determination of aromatic compounds that contain strong ortho-para-directing groups, particularly amines and phenols.

A 0.2981-g sample of an antibiotic powder was dissolved in HCl and the solution diluted to 100.0 mL. A 20.00-mL aliquot was transferred to a flask and followed by 25.00 mL of 0.01767 M $KBrO_3$. An excess of KBr was added to form Br_2, and the flask was stopped. After 10 min, during which time the Br_2 brominated the sulfanilamide, an excess of KI was added. The liberated iodine titrated with 12.92 mL of 0.1215 M sodium thiosulfate. Calculate the percent sulfanilamide (172.21 g/mol) in the powder.

Molecular model of sulfanilamide.

In the 1930s, sulfanilamide was found to be an effective antibacterial agent. In an effort to provide a solution of the drug that could be conveniently administered to patients, drug companies distributed sulfanilamide elixir containing a high concentration of ethylene glycol, which is toxic to the kidneys. Unfortunately, over one hundred people died from the effects of the solvent. This event led to the rapid passage of the 1938 Federal Food, Drug, and Cosmetic Act, which required toxicity testing prior to marketing and listing of active ingredients on product labels.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$



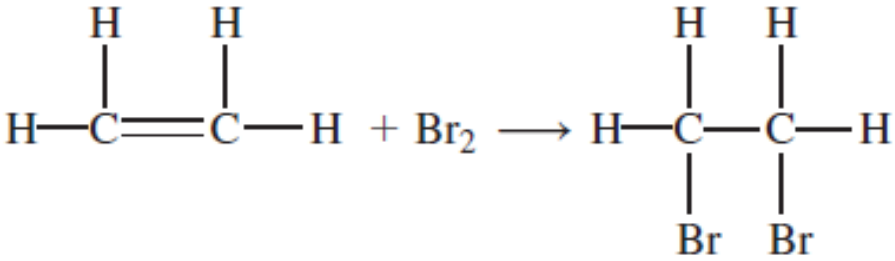
sulfanilamide

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2 \qquad \text{(excess KI)}$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2S_4O_6^{2-} + 2I^-$$

Addition Reactions

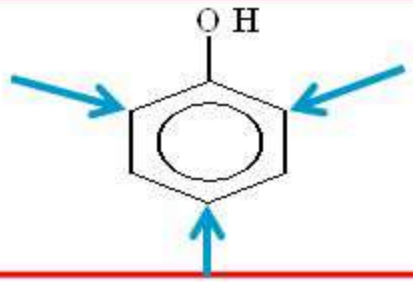
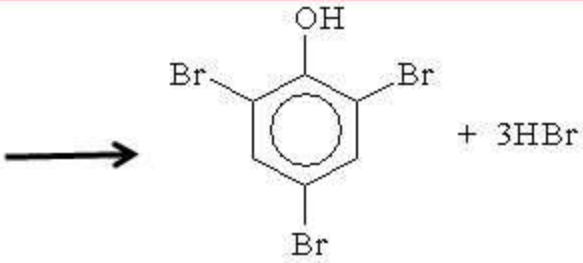
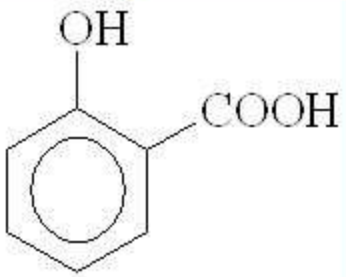
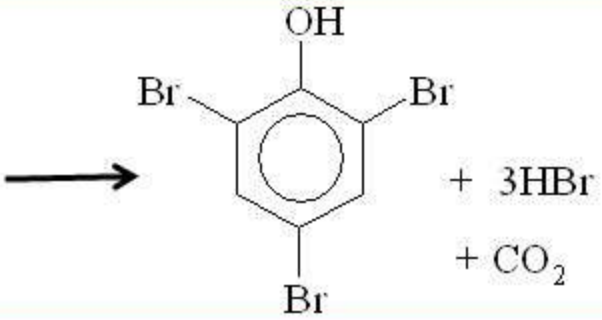
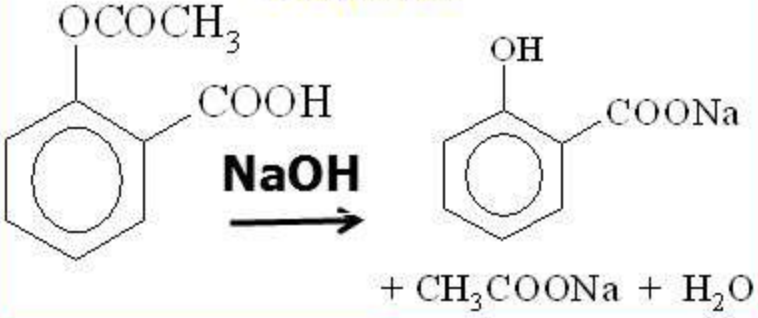
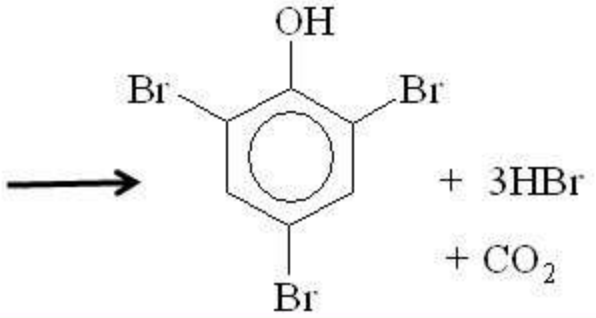
In addition reactions, olefinic double bonds are opened. For example, 1 mole of ethylene reacts with 1 mole of bromine in the reaction



The literature contains numerous references to the use of bromine for the estimation of olefinic unsaturation in fats, oils, and petroleum products.

The determination of glycerol. Dihydroxyacetone is formed

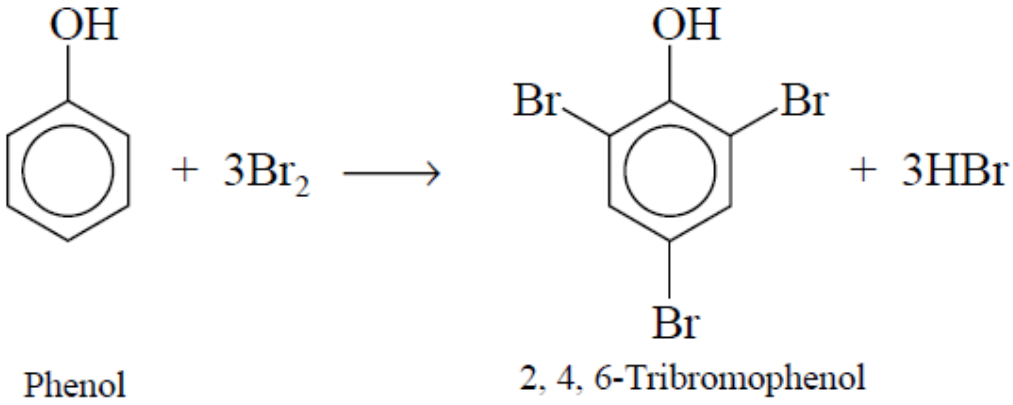
Bromometric determinations
(Bromine substitution method)

Compound	substitution products	Reaction time (min)
Phenol 		45
Salicylic acid 		45
Aspirin 		45

Phenol

Phenol interacts with bromine whereby the former undergoes bromination to yield a waterinsoluble 2, 4, 6-tribromophenol. This reaction takes place quantitatively.

$$5KBr(excess) + KBrO_3 + 6HCl \rightarrow 3Br_2 + 6KCl + 3H_2O$$



Phenol

2, 4, 6-Tribromophenol

$$KBrO_3 + 6KI + 6HCl = 3I_2 + 6KCl + KBr + 3H_2O,$$

Materials Required: Phenol -0.5 g; 0.1 N potassium bromate: 25.0 ml; potassium iodide (powdered): 1.0 g; dilute hydrochloric acid (10%) -10.0 ml; potassium iodide (10% w/v in water) : 10 ml; chloroform -10.0 ml; 0.1 N sodium thiosulphat ; starch solution.

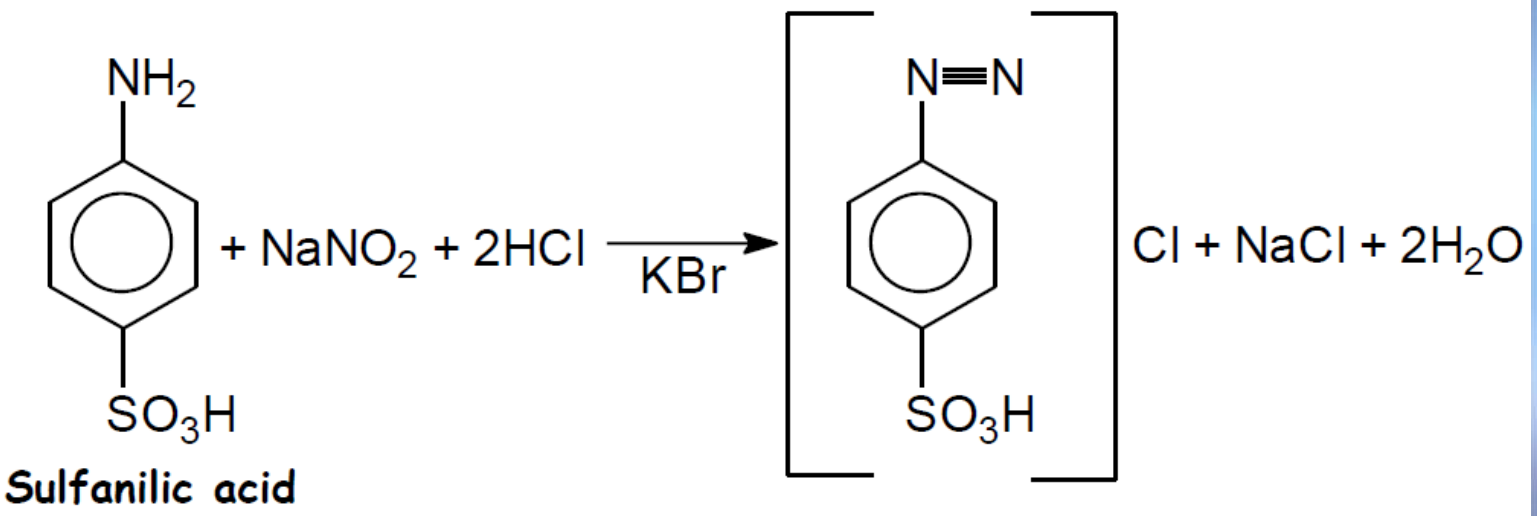
Procedure: Weigh accurately 0.5 g of phenol and dissolve in sufficient water to produce 500 ml in a volumetric flask. Mix 25.0 ml of this solution with 25.0 ml of 0.1 N potassium bromate in a 250 ml iodine flask and add to it 1 g of powdered KI and 10.0 ml of dilute hydrochloric acid. Moisten the glass stopper with few drops of KI solution and place it in position. Set it aside in a dark place for 20 minutes while shaking the contents frequently in between. Add to it 10 ml of KI solution, shake the contents thoroughly and allow it to stand in the dark for a further duration of 5 minutes. Add 10 ml chloroform and titrate with the liberated iodine with 0.1 N sodium thiosulphate using freshly prepared starch as an indicator.

NITRITOMETRIC TITRATION titrant $NaNO_2$

Preparation and standardization of $NaNO_2$ solution

Sodium nitrite is not a standard compound. Firstly the solution is prepared with approximately concentration and then it is standardized.

Standardization (1 variant)



Sulfanilic acid

$$n(HO_3S-C_6H_4-NH_2)=n(NaNO_2)$$

The nitrous acid, generated on the introduction of sodium nitrite solution into the acidic reaction mixture, reacts with the primary amino group of sulphanilamide quantitatively, resulting into the formation of an unstable nitrite that decomposes ultimately with the formation of a diazonium salt. The diazonium salt thus produced is also unstable, and if the reaction mixture is not maintained between 5-10°C, it shall undergo decomposition thereby forming phenol products which may react further with nitrous acid.

Standardization (2 variant)

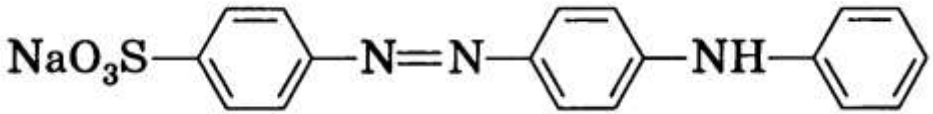
$$2KMnO_4(excess) + 5NaNO_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + 5NaNO_3 + K_2SO_4 + 3H_2O + KMnO_4(left)$$

$$2KMnO_4(leftover) + 10KI(excess) + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5I_2 + 3H_2O$$

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

$$n(\tfrac{1}{5}\,KMnO_4) - n(Na_2S_2O_3) = n(\tfrac{1}{2}\,NaNO_2)$$

Tropeolin 00



$$2KI + 2NaNO_2 + 4HCl = I_2 + 2NO + 2KCl + 2NaCl + 2H_2O.$$

Nitrous acid is formed by the interaction of sodium nitrite and hydrochloric acid as follows:

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

The end-point in the sodium nitrite titration is determined by the liberation of iodine from iodide which may be expressed by the following equations:

$$KI + HCl \longrightarrow HI + KCl$$

$$2HI + 2HNO_2 \longrightarrow I_2 + 2NO + 2H_2O$$

In other words, the small excess of HNO_2 present at the end-point can be detected visually by employing either starch-iodide paper or paste as an external indicator. Thus, the liberated iodine reacts with starch to form a blue green colour which is a very sensitive reaction. Besides, the end-point may also be accomplished electrometrically by adopting the dead-stop end-point technique, using a pair of platinum electrodes immersed in the titration liquid.

Determination of reducing agents (e.g $FeSO_4$)

$$2FeSO_4 + 2Na\overset{+3}{N}O_2 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2\overset{+2}{N}O\uparrow + Na_2SO_4 + 2H_2O$$

$$NO_2^- + \bar{e} + 2H^+ \rightarrow NO\uparrow + H_2O$$

$$E^0_{NO_2^-/NO} = +1.20\ B$$

$$n(FeSO_4) = n(NaNO_2)$$

Determination of oxidizing agents (e.g. $KMnO_4$)

$$2KMnO_4 + 5Na\overset{+3}{N}O_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + 5Na\overset{+5}{N}O_3 + K_2SO_4 + 3H_2O$$

$$NO_2^- - 2\bar{e} + H^+ \rightarrow NO_3^- + H_2O$$

$$E^0_{NO_3^-/NO_2^-} = +0.94\ B$$

$$n(\tfrac{1}{5}\,KMnO_4) = n(\tfrac{1}{2}\,NaNO_2)$$

DIAZOTIZATION TITRATION

The diazotization titration is nothing but the conversion of the primary aromatic amine to a diazonium compound. This process was first discovered in 1853 and was applied to the synthetic dye industry. The reaction mechanism was first proposed by Peter Griessin. In this method, the primary aromatic amine is reacted with the sodium nitrite in acidic medium to form a diazonium salt. This method is first used in the determination of dyes.

$$ArNH_2 + NaNO_2 + 2HCl \xrightarrow{[KBr]} [Ar - N \equiv N]Cl + NaCl + 2H_2O$$

The principle involved in this method is that the primary aromatic amine present in the sample reacts with the sodium nitrite in the presence of acid such as hydrochloric acid to obtain a diazonium salt. The diazonium salt thus produced is also unstable, and if the reaction mixture is not maintained between 5-10°C, it shall undergo decomposition thereby forming phenol products which may react further with nitrous acid.

Conditions 1.Acidic solution, because diazo compounds are stable only in acidic solution.

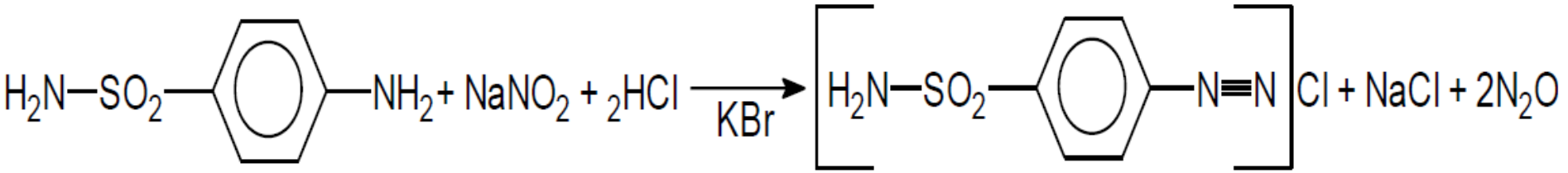
2.Low temperature.

3.Slow titration.

4.Presence of catalyst – KBr.

5.Indicator – tropeoline 00 (red solution turns yellow).

Determination of streptocide



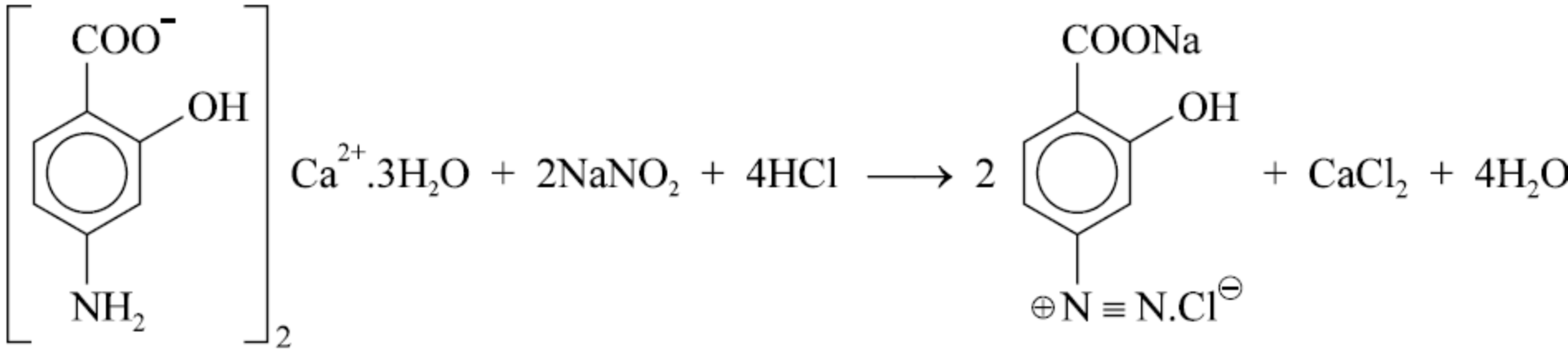
$$n(C_6H_8N_2SO_2) = n(NaNO_2)$$

In general, aromatic primary amino moiety (*i.e., Ar-NH_2), as present in a host of sulphadrugs viz.,* succinyl sulphathiazole, sulphamethoxazole, sulphaphenazole and other potent pharmaceutical substances, for instance sodium or calcium aminosalicylate, isocarboxazid, primaquine phosphate, procainamide hydrochloride, procaine hydrochloride and dapsone react with sodium nitrite in an acidic medium to yield the corresponding diazonium salts.

CALCIUM AMINOSALICYLATE

Materials Required: Calcium aminosalicylate -0.5 g; hydrochloric acid (~− 11.5 N) -10.0 ml; potassium bromide: 1.0 g; 0.1000 M sodium nitrite; starch-iodide paper.

Procedure: Weigh accurately about 0.5 g of calcium aminosalicylate, into a funnel placed in the mouth of a 250 ml volumetric flask. Wash through with 10 ml of hydrochloric acid and enough DW to dissolve, add 1.0 g potassium bromide and make up the volume upto 250 ml mark. Pipette 50 ml into a conical flask, cool to below 15°C (in ice-bath) and titrate gradually with 0.1 M sodium nitrite solution while shaking the contents of the flask vigorously and continuously until a distinct blue colour is achieved when a drop of the titrated solution is placed on a starch-iodide paper 5 minutes after the last addition of the 0.1 M $NaNO_2$ solution. Care must be taken to add $NaNO_2$ solution at the rate of 0.1 ml near the end of the titration.



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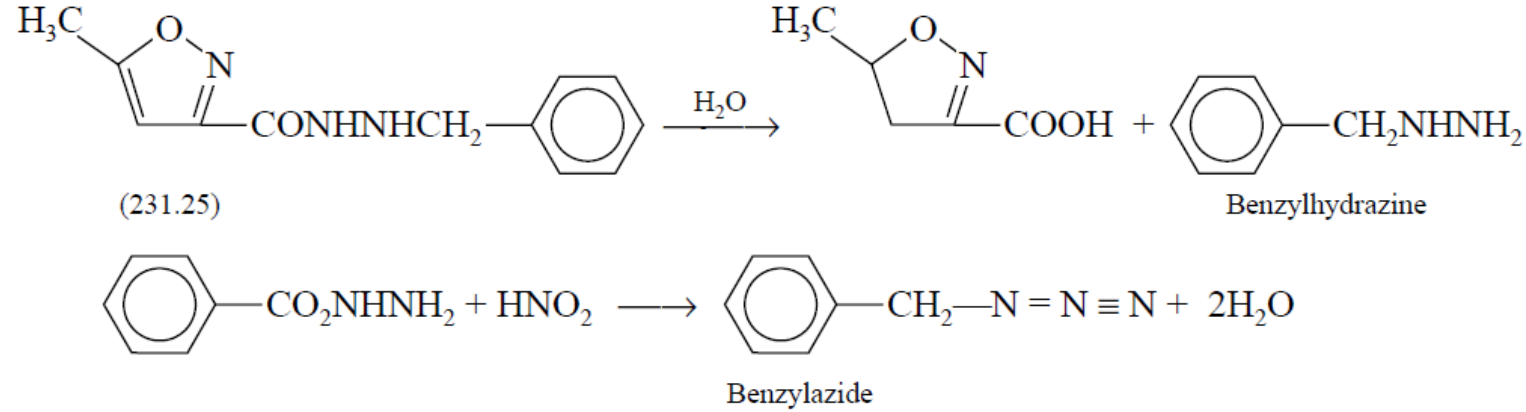
ISOCARBOXAZID

Materials Required: Isocarboxazid: 0.5 g; glacial acetic acid (17.5 N): 20.0 ml; hydrochloric acid (~11.5 N): 20.0 ml; 0.1 M sodium nitrite; starch-iodide paper.

Theory: The estimation is based on the fact that isocarboxazid undergoes rapid cleavage in acidic medium to produce benzylhydrazine. The latter reacts quantitatively with nitrous acid ($NaNO_2$ and HCl) to give rise to benzylazide.



Procedure: Weigh accurately about 0.5 g of isocarboxazid and dissolve it in 20 ml of glacial acetic acid. Add to it 20 ml of hydrochloric acid and 50 ml of DW. Cool to about 15°C in an ice-bath and titrate slowly with 0.1 M $NaNO_2$ while shaking vigorously and continuously until a distinct blue colour is obtained on a starch-iodide paper that lasts for 5 minutes after the final addition of the 0.1 M $NaNO_2$ solution to the titrated solution. Add $NaNO_2$ solution very carefully at the rate of 0.1 ml at a time as the end-point is approached.