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ASSAY OF PHENOL

Bromometric method

Redox Titration

Assistant Lecturer

Sahar Mohammed Shakir

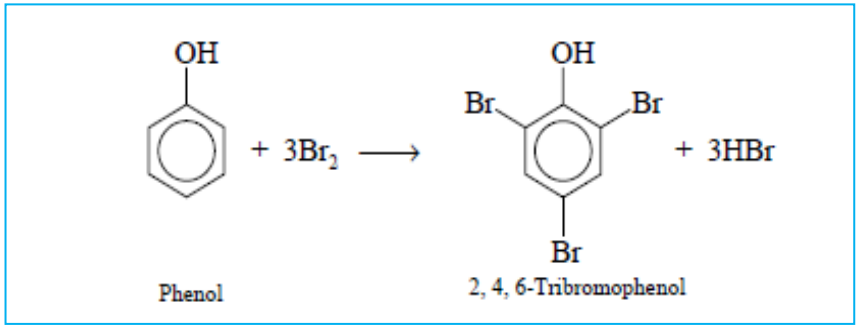
Assistant Lecturer

Abdul Hafeedh Hameed

Theoretical aspect :

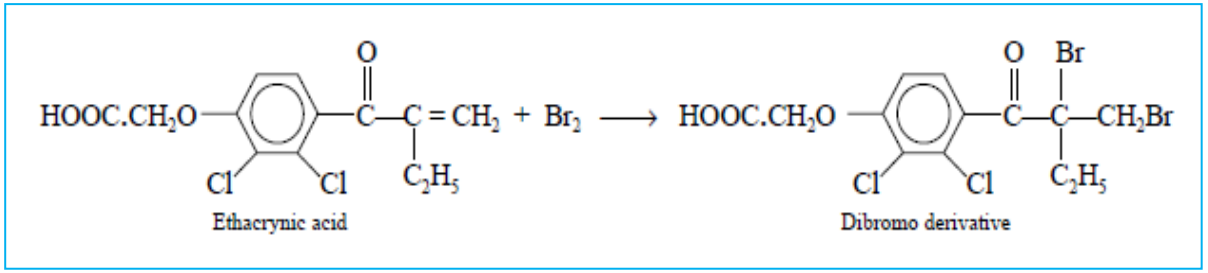
In Redox assays the use of Bromine in place of iodine is carried out as an oxidizing agent for specific cpd.s, because it is reduced quantitatively by the readily oxidized pharmaceutical organic substances in a reaction which results in either ;

a- Water -insoluble bromine substitution products, such as;



Or,

b- Water-insoluble bromine-addition products, such as :



Name of experiment : **PHENOL ASSAY**

Aim of experiment : Determination of the amount of phenol in a sample by Redox Titration .

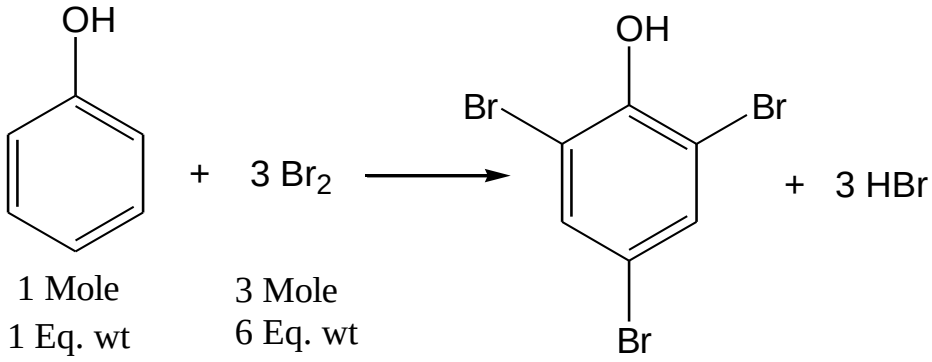
Chemical Principle :

Phenol is assayed by using excess of standard solution of bromine and then determination of the excess unreacted bromine using potassium iodide & standard solution of sodium thiosulfate (Bromometric method).

Br_2 solution, (Koppeschaar's solution) , is produced by mixing potassium bromate , $KBrO_3$, (1^o std. soln.) with an excess of potassium bromide , KBr , in acidified solutions.

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

5 Mole 1 Mole 3 Mole



1 Mole
1 Eq. wt

3 Mole
6 Eq. wt

white ppt.

2,4,6-tribromophenol

Then the liberated iodine quantitatively produced by the oxidation of KI (iodide) with excess unreacted bromine may be assayed by titrating against sodium thiosulfate solution.

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

Br_2: Excess unreacted (1 Mole); 2 KI: (2 Mole); I_2: Free iodine

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

I_2: (1 Mole); $2\,Na_2S_2O_3$: (2 Mole); $Na_2S_4O_6$: Sodium tetrathionate

Chemical Factor :

2 moles of $Na_2S_2O_3$ ≡ 1mole of I_2 ≡ 1 mole of Br_2

So,

6moles of $Na_2S_2O_3$ ≡ 3moles of I_2 ≡ 3moles of Br_2 ≡ 1mole of Phenol

6Eq.wt of $Na_2S_2O_3$ ≡ 6Eq.wt of I_2 ≡ 6Eq.wt. of Br_2 ≡ 1Eq.wt of Phenol

6 x 1000 mL of 1 N Br_2 ≡ 94.11 g of phenol

6000 mL of 0.1 N Br_2 ≡ 9.411 g of phenol

1 mL of 0.1 N Br_2 ≡ (9.411 / 6000) g of phenol

1 mL of 0.1 N Br_2 ≡ 0.001569 g of phenol.

Procedure :

1- Preparation of the unknown sample*:

a- Dissolve 2 g of phenol sample in a sufficient amount of H_2O.

b- Complete the volume with H_2O to 1000 mL in a graduated flask.

2- By using a bulb pipette transfer exactly 25 mL of the unknown sample to a 500 mL glass stoppered iodine flask.

3- Add 50 mL of standard 0.1 N Br_2 solution from the burette to the iodine flask.

4- Add 5 mL of conc. HCl & stopper immediately**.

5- Shake for 15 minutes then allow standing in dark place for 15 minutes.

6- Add 5mL of 20% (w/v) KI solution, stopper & shake well.

7- Remove the stopper; wash it & the neck of the flask carefully with DW

8- Add 5 mL of chloroform with shaking***.

9- Titrate with 0.1 N $Na_2S_2O_3$ with shaking until a faint yellow color.

10- Add 1 mL of starch mucilage (freshly prepared), as indicator.

11- Complete the titration until the discharge of the blue color.

12- Carry out a blank titration simultaneously* * * *.

13- Do your calculations as follows;

a- Correction of volumes to 0.1 N $Na_2S_2O_3$ & 0.1 N Br_2 solutions.

$$N_1 \cdot V_1 = N_2 \cdot V_2$$

b- Calculate the amount of excess bromine from the amount of thiosulfate needed for back titration of free iodine.

V_2 = mL of $Na_2S_2O_3$ utilized by I_2.

= mL of excess Br_2 .

c- Calculate the volume of bromine reacted with phenol.

Volume of total 0.1 N Br_2 solution added (corrected) = 50 mL

50 mL - V_2 = V_3 mL of $Na_2S_2O_3$ which represent volume of Br_2 reacted with phenol.

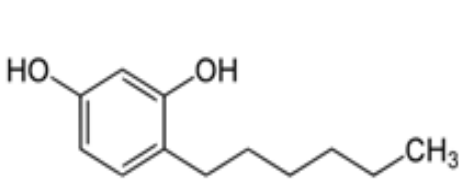
d- Calculate the amount of phenol by using the chemical factor

Each 1 mL of 0.1 N Br_2 ≡ 0.001569 g of phenol.

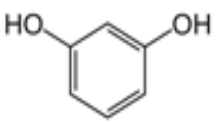
V_3 x 0.001569 = g of Phenol in 25 mL unknown sample.

Notes :

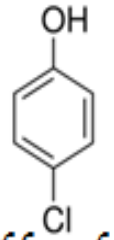
*** A number of phenolic cpd.s assayed by this manner, *e.g.*: Hexylresorcinol , Resorcinol , p - Chlorophenol and preparations containing these phenols as well as Salicylic acid.**



Hexylresorcinol



Resorcinol



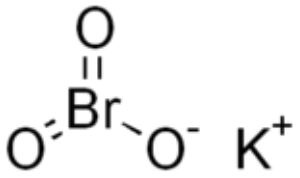
p-Chlorophenol

The determination involves treating phenol with an excess of potassium bromate and potassium bromide ; when bromination of the phenol is completed the unreacted Br_2 is then determined by adding excess potassium iodide and back titrating the liberated I_2 with standard sodium thiosulfate.

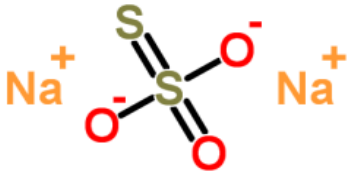
** The flask must be stoppered at all times after the addition of reagents to prevent the loss of bromine.

*** Chloroform is added to dissolve the precipitate of Tribromophenol which would otherwise interfere with clear observation of the end point, especially in the assay of old colored phenol.

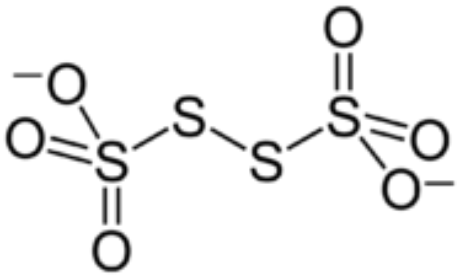
**** A blank determination is always performed simultaneously to account for the losses caused by the Br_2 as well as I_2 vapors due to the interaction of excess Br_2 on potassium iodide.



Potassium Bromate



Sodium Thiosulfate



Tetrathionate

Example :

The volume of 0.105 N $Na_2S_2O_3$ needed to discharge the yellow color of phenol sample assayed by bromometric method was 28 mL, & the volume needed for the blank experiment was 47.5 mL , knowing that each 1 mL of 0.1 N bromine solution is equivalent to 0.001569 g of phenol.

Calculate the weight of phenol in the sample.

References :

* J . Mendham , R . C. Denney , J . D. Barnes , M . Thomas , *Determination of Phenol* , **Vogel's Textbook of Quantitative Chemical Analysis,** 6th edition, 2000 .

* Samira Finjan Hassan , Amer Nadem , May Mohammed Jawad , *Assay of Ascorbic Acid* , **A Laboratory manual on Practical Medical Chemistry for 4th year students,** University of Baghdad , College of Pharmacy , Department of Pharmaceutical Chemistry , 2010 .