



PRINCIPLES RELATED TO PRACTICAL CHEMISTRY

ANALYSIS OF ACIDIC RADICALS

Group	Group reagent	Group radicals	Colour & Observation
1.	Dil. H_2SO_4 or dilHCl	(i) CO_3^{2-} -	Brisk effervescence in cold with evolution of colourless and odourless gas.
		(ii) SO_3^{2-}	Colourless gas with suffocating odour (smell of burning sulphur)
		(iii) S^{-2}	A colourless gas with smell of rotten egg.
		(iv) NO_2^-	A light brown gas.
		(v) CH_3COO^-	Colourless vapours with smell of vinegar.
2.	Conc. H_2SO_4	(i) Cl^-	Colourless gas with pungent smell which fumes in air.
		(ii) Br^-	Reddish brown fumes which intensify on addition of MnO_2 .



		(iii) I^-	Violet pungent fumes evolved which intensify on addition of MnO_2 and condense as black.
		(iv) NO_3^-	Light brown vapours with pungent smell and intensify on addition of Cu turnings/paper bits.
		(v) $C_2O_4^{2-}$	Colourless, odourless gas burns with blue flame at the mouth of test tube and turns lime water milky.
3.	$BaCl_2$	SO_4^{2-}	White precipitate of $BaSO_4$, insoluble in conc. HCl.
	C_2H_5OH and conc. H_2SO_4	BO_3^{3-}	Green edged flame of $(C_2H_5)_3BO_3$.
	Conc. HNO_3 and $(NH_4)_2MoO_4$	PO_4^{3-}	A canary yellow precipitate of $(NH_4)_3PO_4 \cdot 12MoO_3$.
	Sand and conc. H_2SO_4	F^-	Waxy white deposit of silicic acid <i>i.e.</i> H_4SiO_4 or $Si(OH)_4$.



Analysis of Basic Radicals

Group	Group Reagent	Basic Radicals	Colour and Composition of Precipitate
1.	DilHCl	Ag^+ Pb^{+2} Hg_2^{2+}	AgCl — White PbCl_2 — White Hg_2Cl_2 — White
2.	H_2S in presence of dilHCl	Hg^{+2} Pb^{+2} Bi^{+3} Cu^{+2} Cd^{+2} As^{+3} Sb^{+3} Sn^{+2} Sn^{+4}	HgS — Black PbS — Black Bi_2S_3 — Black CuS — Black CdS — Yellow As_2S_3 — Yellow Sb_2S_3 — Orange SnS — Brown SnS_2 — Yellow



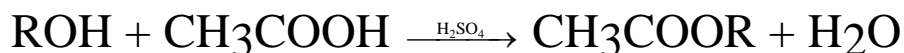
3.	NH ₄ OH in presence of NH ₄ Cl	Fe ⁺³ Cr ⁺³ Al ⁺³	Fe(OH) ₃ — Reddish Brown Cr(OH) ₃ — Green Al(OH) ₃ — White
4.	H ₂ S in presence of NH ₄ OH	Mn ⁺² Co ⁺² Ni ⁺²	MnS — Buff CoS — Black NiS — Black
5.	(NH ₄) ₂ CO ₃ in presence of NH ₄ OH	Ba ⁺² Sr ⁺² Ca ⁺²	BaCO ₃ — White SrCO ₃ — White CaCO ₃ — White
6.	Na ₂ HPO ₄	Mg ⁺²	Mg(NH ₄)PO ₄ — White
Zero	NaOH	NH ₄ ⁺	NH ₃ gas



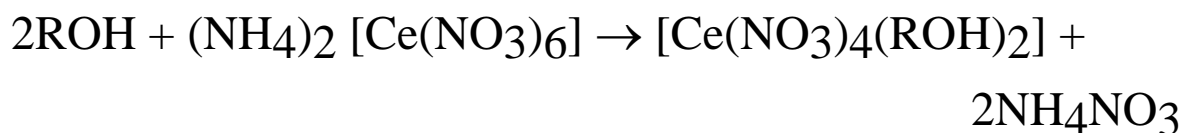
Detection of functional group

1. Test for alcoholic group

(i) **Ester test:** Warm the given liquid with acetic acid in presence of sulphuric acid. A fragrant smell indicates the formation of ester.



(ii) **Ceric ammonium nitrate test:** Shake a few drops of ceric ammonium nitrate with 1 ml of organic compound. A red colour is produced (phenol give a green or brown colour).



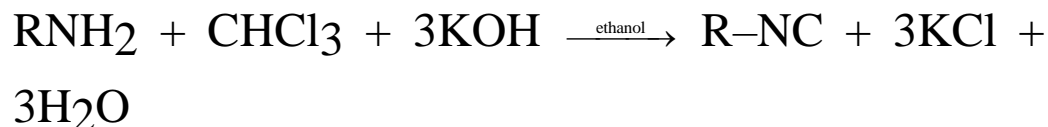
2. Test for carboxylic group

(i) **Litmus test:** Place a small quantity of organic compound or its aqueous solution on a piece of moist blue litmus paper. If paper turns red carboxylic acid may be present.

3. Test for Amino group

(a) Test for primary amine

Carbylaminetest : Heat the organic compound with alcoholic KOH and chloroform in a test tube.

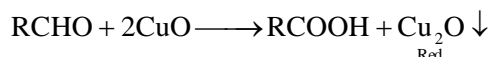


This test is applicable to aliphatic and aromatic primary amines.

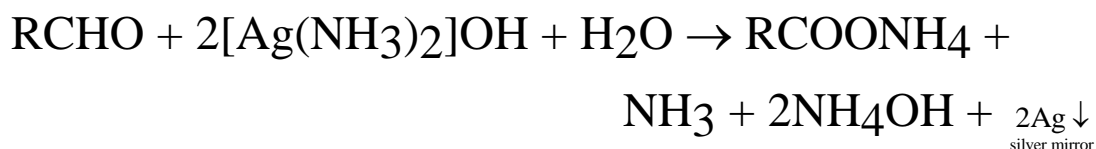


4. Test for aldehyde group

(i) **Fehling's test:** Mix equal volumes of Fehling's (A) and Fehling's (B) solution in a test tube. Add a small amount of the organic compound and boil for sometime. A red precipitate of Cu_2O is obtained

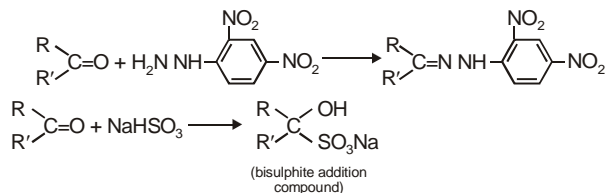


(ii) **Tollen's test:** Take about 5 ml of Tollen's reagent in a test tube. Add a small quantity of organic compound and heat on a water bath. A shining silver mirror is formed on inner walls of the test tube.



5. Test for ketonic group

(i) Ketones unlike aldehyde do not restore the pink colour of Schiff's reagent nor do they reduce Fehling solution or ammonical AgNO_3 solution. However they form crystalline precipitate with 2, 4-dinitrophenyl hydrazine and also with sodium bisulphite reagent.

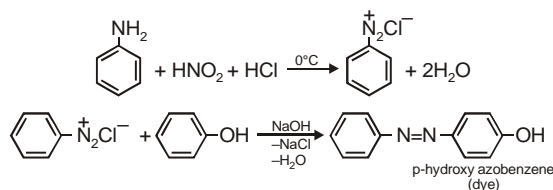


6. Test for phenolic group

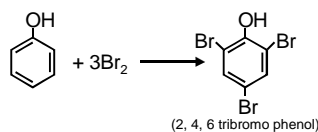


(i) **Neutral FeCl₃ test:** When phenols are treated with neutral FeCl₃ solution they form coloured complexes. The colour of complex may be violet, red, blue or green. This is a characteristic reaction of compounds having enolic group (=C–OH). All enols respond to this test.

(ii) **Aniline dye test:** To this cold solution, add organic compound already dissolved in sodium hydroxide solution. A red or orange precipitate is obtained



(iv) **Bromine water test:** Take aqueous or alcoholic solution of organic compound in test tube. Add excess of bromine water. A yellowish white precipitate is obtained.

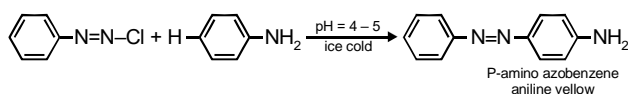
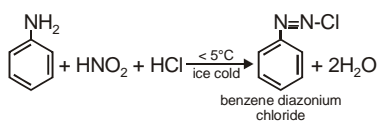
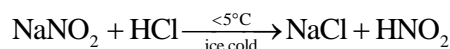


PREPARATION OF ANILINE YELLOW



It is prepared by the coupling of benzene diazonium chloride with aniline in fairly acidic medium (pH 4 – 5) at a temperature below 5°C. Its colour is yellow.

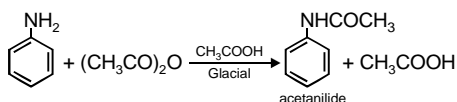
Chemical reaction



Preparation of Acetanilide

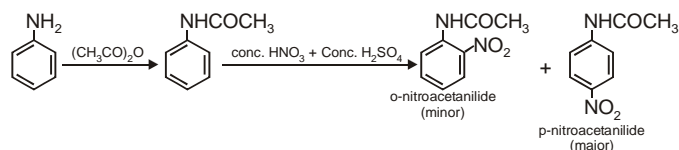
It is prepared by acetylation of aniline with acetic anhydride in the presence of glacial acetic acid. Its colour is white and melting point is 114°C.

Chemical reaction



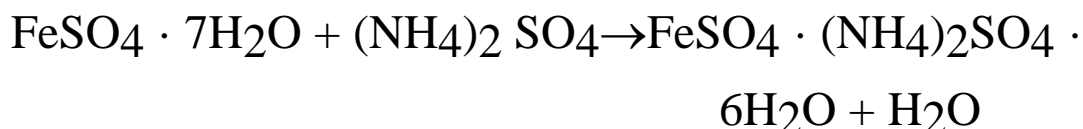
Preparation of P-nitroacetanilide

Aniline cannot be nitrated directly because nitric acid is strong oxidising agent oxidises the amino group. Therefore amino group is first protected by acetylation process and then acetanilide formed is nitrated using conc. HNO_3 + conc. H_2SO_4 . A mixture of o- and p-nitroacetanilide obtained.



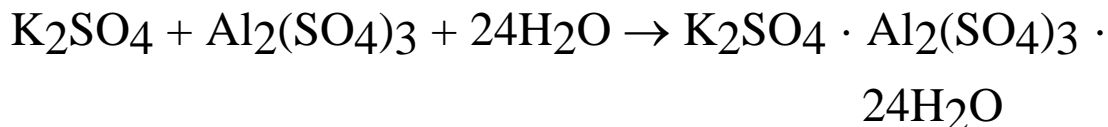
Preparation of Mohr's salt:

Mohr's salt is prepared by dissolving an equimolar mixture of hydrated ferrous sulphate and ammonium sulphate in minimum amount of water containing a little sulphuric acid. On vapourising the resulting solution to crystallisation point and then keep it aside for cooling, a green crystal of ferrous ammonium sulphate separate out.



Preparation of Potash Alum

When a solution containing an equimolar quantities of potassium sulphate and aluminium sulphate is heated to crystallisation point and then cooled slowly colourless crystal of potash alum separate out.

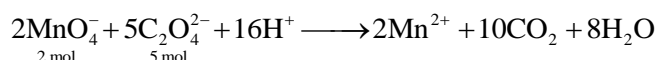


SOME TYPICAL REDOX TITRATIONS

(1) Titration of oxalic acid against KMnO_4 : Oxalic acid $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ is titrated against KMnO_4 in the presence of dilute H_2SO_4 keeping the temperature of



oxalic acid solution between 60 – 70°C. Oxalic acid on oxidation with acidified KMnO_4 produces CO_2 according to the reaction.



The solution is kept hot to expel CO_2 produced so as to avoid back reaction.

The stoichiometric ratio in this titration is evidently (2: 5).

Suppose 20 ml of oxalic acid solution require 25 ml of 0.05 M KMnO_4 solution for titration then the

concentration of oxalic acid solution = $\frac{25 \times 0.05 \times 5}{20 \times 2} = 0.156 \text{ M}$

accordingly the amount of oxalic acid (mole wt 126)

would be $0.156 \times 126 = 19.656 \text{ g L}^{-1}$.

(2) Titration of Mohr salt against KMnO_4 : Mohr salt

$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ is titrated against KMnO_4 in presence of dilute sulphuric acid when FeSO_4 of the Mohr salt is oxidised to $\text{Fe}_2(\text{SO}_4)_3$. KMnO_4 solution is added to a known volume at Mohr salt solution containing dilute H_2SO_4 gradually in small amounts. Rapid addition of KMnO_4 results in the formation of hydrated $\text{MnO}_2 \cdot \text{H}_2\text{O}$ which is brown in colour

