

# CHM 116 made easy

10/11/2020 #Mie: 7:11

Qualitative examination of unknown organic substances enables you to identify the functional groups and to place into its chemical class, any organic compound you will be given.

Qualitative analysis: Preliminary tests, Confirmatory test, Preparation of derivatives

## I PRELIMINARY TESTS.

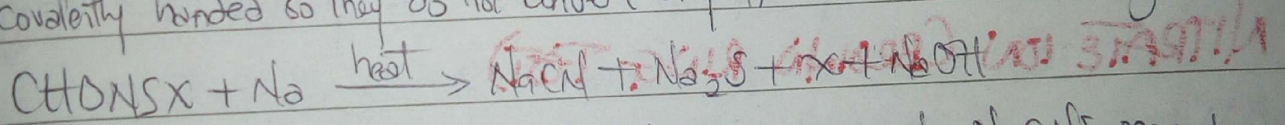
(A) IGNITION TEST: Place sample on a nickel spatula, heat gently, then strongly. Observe whether the substance SUBLIMES, MELTS, VOLATILIZES OR DECOMPOSES without melting.

Also note if the substance burns. If it burns, NON-LUMINOUS FLAME may indicate

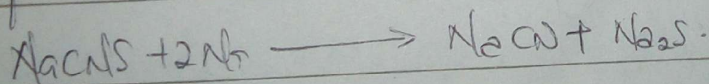
AROMATIC COMPOUNDS. A white or coloured residue is probably a METAL. A black

residue indicates CARBON. To confirm, add a few drops of AMMONIUM NITRATE SOLUTION

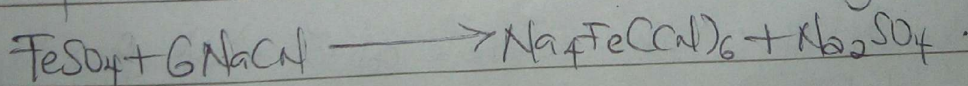
(B) SODIUM FUSION TEST (CLASSAIGNE'S TEST): It is used to detect the presence of Nitrogen, Sulphur, or halogens (Cl, Br, I). When they occur in organic molecules, they are covalently bonded so they do not convert any N, S or X to ionisable inorganic substance



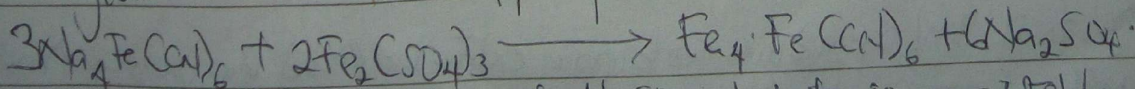
Excess sodium is used, otherwise if S and N are both present, NaCN is may be produced, instead of NaCN and Na<sub>2</sub>S as above. CNS does not give the blue ppt (Prussian Blue), but rather a red-colouration with ferric ions.



Sodium fusion mixture is then extracted with water to give an alkaline solution



Upon boiling, ferric ions react with the Fe(CN)<sub>6</sub> present to form Fe<sub>4</sub>·Fe(CN)<sub>6</sub>, which gives an insoluble, blue ppt "Prussian Blue".



HCl could be used in place of H<sub>2</sub>SO<sub>4</sub> but it is unsuitable because FeCl<sub>3</sub> that would be formed is yellow, making "Prussian Blue" appear greenish.

## TEST FOR NITROGEN.

Add about 0.1g of ferrous sulphate to 2-3ml of the above filtrate, heat the mixture gently, with mixing till it boils. Add dil.  $H_2SO_4$  to dissolve the iron hydroxide making the solution slightly acid.

A blue or greenish colouration or precipitate indicates the presence of N

## TEST FOR SULPHUR

Acidify 2ml of the fusion filtrate with dilute acetic acid, and add a few drops of lead acetate solution. A black precipitate of  $PbS$  indicates the presence of S.

## TEST FOR HALOGEN.

If N and CN or S are present place a few ml of the fusion extract in a beaker, add dilute  $H_2SO_4$  and place a porous pot and boil till the liquid is reduced to half its original volume. Then add dilute  $HNO_3$  and an excess of  $AgNO_3$  solution. A precipitate indicates the presence of a halogen

## NITRATE ION (BROWN RING TEST)

Add ml to conc.  $H_2SO_4$  slowly to 2ml of the sodium carbonate extract. Mix. Pour 2ml of freshly prepared saturated aqueous solution of  $FeSO_4$  slowly. The formation of a dark brown ring indicates  $NO_3^-$ . Red-brown ring indicates Br, violet ring I.

## SULPHATE ION.

Add dil.  $HCl$  to 2-3ml of sodium carbonate extract. Add few drops of  $BaCl_2$ . A heavy white ppt indicates the presence of  $SO_4^{2-}$

## HALIDE ION

Add dil.  $HNO_3$  to 2-3ml of sodium carbonate extract. Add few drops of  $AgNO_3$  reagent. A yellow ppt indicates Br (dissolves less readily in  $NH_3$ ). A yellow ppt indicates I (insoluble in  $NH_3$ ).

## SOLUBILITY TESTS

A water-soluble substance might be ammonium salt, alkali salt of an acid, salt of an amine or mono and disaccharides or lower aliphatic compounds.

A basic compound should be soluble in acid and be precipitated from the acidic solution upon addition of excess alkali.

An acidic compound should dissolve in alkali and be precipitated from the alkaline solution upon the addition of excess acid.

A neutral organic compound does not dissolve in either acid or alkali, but will dissolve in ethyl alcohol or other organic solvent.

If the substance is basic, an amine is indicated.

If the substance is acidic, a carboxylic acid or a phenol is indicated.

Neutral substances include esters, aldehyde, ketones, amines, nitric compounds, carbohydrates, alkyl and aryl halides.

## II CONFIRMATORY TESTS.

(i) ISOCYANIDE REACTION: The product is poisonous & has an unpleasant odour.

(ii) NITROUS ACID: Dissolve the substance in dilute HCl, cool in ice. Next add 2-naphthol in NaOH(aq); ppt of brilliant red dye indicates that the substance is a primary aromatic amine.

(iii) TEST FOR CARBOXYLIC ACID: Add few drops of a saturated aqueous soln of  $\text{NaHCO}_3$ . An evolution of bubbles indicates carboxylic acid.

(iv) TEST FOR PHENOL: Dissolve in water or alcohol, add one drop of ferric chloride reagent. It will give an intense colour.

(v) TEST FOR AMMONIUM SALTS AND AMIDES: Boil with aqueous NaOH, test the issuing vapour. The gas with characteristic smell of ammonia indicates the presence of simple amide.

## (v) TEST FOR NITRO COMPOUNDS

Reduction to hydroxylamine. Confirmatory test can be made with Tollens' reagent or Fehling's solution.

## TEST FOR KETONES AND ALDEHYDES

Dissolve the substance in a little alcohol and add a few ml of an alcohol solution of 2,4-dinitrophenylhydrazine reagent. Warm and cool.

A ppt indicates an aldehyde or ketone.

## (vi) TEST FOR REDUCING PROPERTIES i.e. aldehyde groups

(a) Fehling's solution: Mix equal vol. of Fehling's A & B. add a few drops of mixture to the organic compound in solution and warm. Disappearance of the blue colour & precipitation of red or yellow ppt of  $\text{Cu}_2\text{O}$  indicates red. agent.

(b) Ammoniacal  $\text{AgNO}_3$  i.e. Tollens' reagent: add dilute  $\text{NH}_4\text{OH}$  solution in drops to  $\text{AgNO}_3$  containing a few drops of  $\text{NaOH}$  until the ppt  $\text{Ag}_2\text{O}$  almost completely dissolved. A silver mirror indicates a reducing agent.

Some amines give positive result.

vii Iodoform test: for the presence of compounds containing  $\text{C}-\text{CH}_3$  or  $\text{CH}_3-\text{CH}(\text{OH})-$  groups (eg acetone  $\text{CH}_3\text{COCH}_3$ , ethyl alcohol  $\text{CH}_3\text{CH}_2\text{OH}$  - but not methyl alcohol  $\text{CH}_3\text{OH}$ ). Dissolve in water & add 1ml of bich  $\text{NaOH}$ . Add iodine solution with shaking until the dark brown colour of iodine persists.

A fine yellow crystalline ppt of iodoform (characteristic smell) is positive. M. pt:  $119-121^\circ\text{C}$ .

viii Molisch's Test for sugar: A trace of 1ml of water is added to 2ml of Naphthol in alcohol or chloroform. 1ml of conc.  $\text{H}_2\text{SO}_4$  is then cautiously added. A violet ring (or purple colour on gently mixing) indicates the presence of sugar.

x) Test for esters: hydroxamic acid formation.

To a few drops of an ester, add hydroxylamine hydrochloride and  $\text{NaOH}$  solution and gently boil. Cool & acidify with dil.  $\text{HCl}$  and add few drops of ferric chloride solution. A violet or deep-red brown colour gives positive results.

xi) Test for unsaturation:

Add very dilute bromine water or neutral potassium permanganate solution. An immediate decolourization of the reagent indicates an unsaturated compound.

## TECHNIQUES FOR SEPARATION AND IDENTIFICATION OF SOME ORGANIC COMPOUNDS.

Distillation is used to separate substances with different boiling points.

Electrophoresis is used to separate mixture according to differences in their particle size and their electrical charge.

Chromatography is a method of separation of substances based on differences in their polarity and adsorption on a stationary phase.

## SEPARATION OF CATIONS INTO GROUPS.

### GROUP I

Solids:  $\text{AgCl}$ ,  $\text{PbCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$  heat with water.

Black residue due to  $\text{Mg(OH)}_2$  formed.  $\text{Hg}_2\text{Cl}_2$  confirmed. Add dil  $\text{NH}_4\text{OH}$ . Solution may contain  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ . Acidify with dil  $\text{HNO}_3$ . White ppt indicates silver  $\text{Ag}$ .

White crystals of  $\text{PbCl}_2$  may separate. Test clear solution by adding dilute  $\text{CH}_3\text{COOH}$  and  $\text{K}_2\text{CrO}_4$ . Yellow ppt of  $\text{PbCrO}_4$  indicates lead.

## GROUP IIA

Solids  $\text{Bi}(\text{OH})_3$  &  $\text{Pb}(\text{OH})_2$ ; Boil gently with 1-3ml of  $\text{Mg}(\text{OH})_2$ .  
White ppt turns black on addition of  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Indicates Bismuth  
Solution  $\text{Na}_2\text{PbO}_2$ . Add sol.  $\text{CH}_3\text{COOH}$  &  $\text{K}_2\text{CrO}_4$ . Yellow ppt indicates lead  
If blue, it contains copper.  
Acidify with  $\text{CH}_3\text{COOH}$  & add  $\text{K}_4\text{Fe}(\text{CN})_6$ . Brown ppt confirms copper  
Add  $\text{KCN}$  until blue color disappears. Pass thd, yellow ppt indicates cadmium

## GROUP IIB

Solids:  $\text{As}_2\text{S}_3$ ; boil with conc.  $\text{HCl}$   
Boil with  $\text{Zn}$  dust and add dil.  $\text{NaOH}$ . Test gas with  $\text{AgNO}_3$  paper. Brown  
color indicates Arsenic  
Dilute and pass thd orange ppt indicates Antimony  
Add iron wire warm. Pour clear liquid  $\text{HgCl}_2$  solution. White ppt indicates  
tin

## GROUP III

Solids:  $\text{Fe}(\text{OH})_3$ . warm with  $\text{NaOH}$  &  $\text{H}_2\text{O}$ , then boil. ~~crystal~~  
Brown dissolved in  $\text{HCl}$  and  $\text{KCN}$ . A blood-red color is obtained that indicates iron  
If yellow contains chromium. Acidify with  $\text{CH}_3\text{COOH}$  & add lead acetate. Yellow  
precipitate indicates chromium.  
Add  $\text{HCl}$  until just acid. Then add ammonia gas. White ppt indicates Aluminum

## GROUP IV.

Solids: treat with cold dilute  $\text{HCl}$   
Add amyl alcohol & solid  $\text{Ni}(\text{SO}_4)$ . Blue amyl alcohol layer indicates cobalt  
Make alkaline with ammonia & dimethylglyoxime scarlet red ppt indicates Nickel

\* Aqua-regia:  
a mixture of nitric & HCl  
that dissolves gold or platinum.  
Borate:  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

Solid: Brown  $\text{MnO}_2$ . Dissolved in 1:1  $\text{HNO}_3$  & then add solid sodium bisulfate  
purple solution indicates Manganese

Solution: may contain  $\text{Na}_2\text{ZnO}_2$ . Acidify with dilute  $\text{CH}_3\text{COOH}$  and  
pass  $\text{H}_2\text{S}$  white ppt indicates Zinc

## GROUP V

Solid:  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ . Dissolves in hot dilute  $\text{CH}_3\text{COOH}$  &  $\text{K}_2\text{CrO}_4$

Solid: yellow  $\text{BaCrO}_4$  add a drop of conc. HCl. Apply flame test: green  
flame indicates barium.

Add saturated  $\text{CaSO}_4$  heat, white ppt indicates strontium. Add 1 drop  
conc. HCl. Apply flame test crimson flame indicates strontium

Add dilute  $\text{CaSO}_4$  norm and allow to stand. white ppt indicates  
Calcium. Apply flame test. Brick-red flame.

## GROUP VI

Solid:  $\text{MgCl}_2$ ,  $\text{NaCl}$ ,  $\text{KCl}$ . Dissolve in water.

Add 2 drops of magnesia reagent & dil. aq. Blue ppt indicates Magnesium

Add magnesium uranyl acetate & allow to stand. yellow ppt indicates Sodium

Add sodium cobaltinitrite. yellow ppt indicates potassium

## EXAMINATION FOR ANIONS.

Preparation of solution: Boil the solid with excess sodium carbonate for a few minutes

SULPHATE: Acidify with HCl & boil to remove  $\text{CO}_2$  &  $\text{BaCl}_2$ . white ppt

Reducing agents: Acidify with  $\text{H}_2\text{SO}_4$ . add few drops of  $\text{KMnO}_4$ . Decolorizes.

Oxidizing agent: acidify with conc. HCl & add  $\text{MnCl}_2$ . Brown colour.

Nitrates: mix solid with  $\text{CaCO}_3$  & 1 drop conc.  $\text{H}_2\text{SO}_4$ . Take up paste on platinum  
wire & hold at base of Bunsen flame. Green colouration indicates  
borate.