




STUDY MATERIALS

chem@YNSir

Qualitative Analysis of a Single Solid Organic Compound Manual for Practical

YASIN NUREE
Department of Chemistry
Dumkal College



Department of Chemistry
Dumkal College
Basantapur, Dumkal
Murshidabad

Sample Number:

Physical Characteristics:

(i) Colour:

(ii) Texture:

(iii) Odour:

Detection of Special Elements (N, Cl, S) by Lassaigne's Method: Lassaigne's Test: A pea sized dry and clean sodium was taken in a fusion tube and heated gently until it melted with a shiny surface. A pinch of the sample was added to it and the mixture was heated gently and then strongly to red hot on a non-luminous flame for about two minutes. Finally the fusion tube was carefully plunged in a mortar containing distilled water (8-10 mL). The mixture was ground thoroughly by a pestle and filtered. The following experiments were performed with this aqueous colourless filtrate.

EXPERIMENT	OBSERVATION	INFERENCE
Test for Nitrogen: To a portion of the filtrate, a few crystals of FeSO_4 were added. (Alternatively freshly prepared FeSO_4 solution may also be added.) The mixture was boiled gently and then acidified with dilute H_2SO_4 .	A deep blue solution or precipitate	Nitrogen present.
Test for Sulphur: To a portion of the filtrate, 1-2 drop of dilute sodium nitroprusside solution was added.	Purple colouration	Sulphur present
Test for halogens (If N and/or S absent): A portion of the filtrate was acidified with concentrated HNO_3 , boiled for 2-3 minutes, cooled and AgNO_3 solution was added. To the precipitate dilute NH_4OH was added.	Curdy white precipitate. Soluble, but reappeared on acidification with dilute HNO_3 .	Chlorine present.

Department of Chemistry
Dumkal College
Basantapur, Dumkal
Murshidabad

If N and/or S present: A portion of the filtrate was acidified with concentrated HNO ₃ and gently boiled till the volume of the solution becomes half. It was then cooled and AgNO ₃ solution is added. To the precipitate dilute NH ₄ OH was added.	Same observation as above	Same inference as above.
--	---------------------------	--------------------------

Middleton's test: Use of Zn & Na₂CO₃ mixture instead of metallic Na [An intimate mixture of Zn dust and Na₂CO₃ (2:3 by weight) may be stored in a bottle.] A pinch of organic sample and the above mixture (200 mg) was heated gently and then strongly to red hot on a non-luminous flame for about three minutes. Then the fusion tube was plunged in a mortar containing distilled water (6-7 mL). The mixture was ground thoroughly by a pestle and filtered. The following experiments were performed with this aqueous filtrate: [When an organic compound is heated with a mixture of zinc powder and Na₂CO₃, the nitrogen and chlorine are converted into NaCN and NaCl respectively, and the sulphur into ZnS (insoluble in water). NaCN and NaCl are extracted with water and detected as in Lassaigne's method, whilst ZnS in the residue is decomposed with dilute HCl and H₂S evolved is identified with lead acetate paper which forms black PbS.]

Solubility Classification

Observations to be made at room temperature

(scale: 100 mg of sample in 3 mL of solvent)

Water	5% HCl	5% NaOH	5% NaHCO ₃	Conclusion
+	NP	NP	NP	Polar compound: low MW aliphatic acids, polyphenols, salts.
-	+	-	-	Basic: amines
-	-	+	+	Strongly acidic: acids, nitrophenols

Department of Chemistry
Dumkal College
Basantapur, Dumkal
Murshidabad

–	–	+	–	Weakly acidic: phenols, imide
–	+	+	+	Bipolar compounds; may contain both amine and carboxylic acid groups, e.g. amino acids, sulphanilic acids etc.
–	–	–	–	Neutral compounds: a) carbonyl (if N absent) b) Nitro/amide (if N present)
‘+’ means soluble; ‘–’ means insoluble; ‘NP’ means not performed				

If the sample is soluble in water, then no need to check the solubility in all other aqueous solvents mentioned above. Report ‘NP’ (Not Performed) in the columns of other solvents. Detection of Functional Groups by Systematic Chemical Analysis: [If nitrogen is present as special element then tests for all the functional groups must be performed.] **If nitrogen is absent as special element, then report as given below: “Since nitrogen is absent as special element, tests for nitrogen containing functional groups aromatic amino ($-NH_2$), aromatic nitro ($-NO_2$), carboxamide ($-CONH_2$) and imide ($-CONHCO-$) are not performed”.** [Perform only the tests for non-nitrogenous functional groups.]

Tests for Nitrogen Containing Functional Groups

(aromatic $-NH_2$, aromatic $-NO_2$, $-CONH_2$ and $-HNCONH-$)

Experiment	Observation	Inference
Test for aromatic $-NH_2$ (azo-dye test): To 1 mL dilute HCl solution / suspension of the sample, 1 mL 2% $NaNO_2$ solution was added under ice cold condition. This cooled diazotized solution was then added to a previously cooled alkaline solution of	Red / orange azo-dye	Aromatic $-NH_2$ present

Department of Chemistry
Dumkal College
Basantapur, Dumkal
Murshidabad

β -naphthol.		
Test for aromatic $-\text{NO}_2$ (in absence of aromatic $-\text{NH}_2$) Reduction followed by azo-dye test: A few pieces of Zn or Sn granules were added to the sample (~50 mg) in concentrated HCl (2 mL). The mixture was boiled gently for 2 minutes. It was then cooled and filtered and diluted with water. Azo-dye test as described above was performed with it.	Red / orange azo-dye	Aromatic $-\text{NO}_2$ present
Test for aromatic $-\text{NO}_2$ (in presence of aromatic $-\text{NH}_2$) However, Mulliken and Barker test can be performed for aromatic $-\text{NO}_2$ group whether or not aromatic $-\text{NH}_2$ group is present in the given sample. Mulliken and Barker test: To a mixture of sample (~50 mg), Zn dust (100 mg) and solid NH_4Cl (100 mg) 50% aqueous ethanol (3 mL) was added. The mixture was boiled gently in a water bath for 5 minutes and then filtered into freshly prepared Tollens' reagent (2 mL).	A grey / black precipitate or silver mirror	Aromatic $-\text{NO}_2$ present
Test for amide ($-\text{CONH}_2$) and imide: A mixture of the sample (~50 mg), 2-3 NaOH / KOH pellets and a few drops of water was heated strongly.	Smell of NH_3 was perceived and the evolved vapour turned phenolphthalein paper temporarily pink.	Amide or imide present

Department of Chemistry
Dumkal College
Basantapur, Dumkal
Murshidabad

Preparation of Tollens' reagent: $\text{Ag}(\text{NH}_3)_2\text{OH}$: A few drops of dilute NaOH solution are added to 1-2 mL of AgNO_3 solution. The resulting precipitate is then dissolved by adding requisite amount of NH_4OH solution.

Tests for Non-nitrogenous Functional Groups

(phenolic $-\text{OH}$, $>\text{CO}$, $-\text{COOH}$)

Experiment	Observation	Inference
Alcoholic solution of the sample is tested with moist blue litmus paper.	Blue litmus paper turns red.	strongly acidic functionality ($-\text{COOH}$) present.
Test for carboxylic acid ($-\text{COOH}$): Sample or its alcoholic solution was added to a saturated solution of NaHCO_3 . Esterification: A solution of the sample in dehydrated alcohol (2 mL) and 2 drops of concentrated H_2SO_4 was warmed on a water bath for 5 minutes. It was cooled and then poured cautiously in a beaker containing 5% solution of NaHCO_3 (10-15 mL).	Effervescence of CO_2 was observed Characteristic fruity smell of ester was perceived.	Acidic functionality ($-\text{COOH}$) present. Carboxylic acid group ($-\text{COOH}$) present.
Test for carbonyl ($>\text{CO}$ or $-\text{CHO}$) (Aldehyde/Ketone): 2,4-Dinitrophenylhydrazine (2,4-DNP) reagent (Brady's reagent) was added to a saturated alcoholic solution of the sample (2 mL). The mixture was shaken vigorously for few minutes and then the inner wall of the test tube was scratched	Orange / yellow crystalline precipitate.	Carbonyl group ($>\text{CO}$) present. Distinction between aldehyde & ketone may be done by Tollens' reagent

Department of Chemistry
Dumkal College
Basantapur, Dumkal
Murshidabad

with a glass rod.		
<p>Test for phenolic –OH group:</p> <p>(a) To an alcoholic/aqueous solution of the sample, few drops of neutral FeCl_3 solution is added.</p> <p>(b) Back Dye Test: To a solution of 1 drop of aniline in dilute HCl, 1 mL 2% NaNO_2 solution was added under ice cold condition. The resulting solution was then added to cold alkaline solution of the sample. [Any one of the above tests, if positive, indicates the presence of phenolic –OH group. To show the absence,, both tests must be performed.]</p>	<p>Permanent or transient purple/red/blue/violet/green colouration. Red precipitate or colouration of azo-dye observed.</p>	<p>Phenolic –OH group present. Phenolic –OH group present</p>

[According to the syllabus, however, **Only One Test For Each Functional Group** is to be reported]

Solid Organic Compounds for Qualitative Analysis

Succinic acid Benzoic acid Phenylacetic acid Phthalic acid Cinnamic acid Anisic acid o-Chlorobenzoic acid Sulphanilic acid Resorcinol Hydroquinone 2-Naphthol Salicylic acid p-Hydroxybenzoic acid Vanillin Benzil Benzophenone Benzoin p-Chlorobenzaldehyde p-Hydroxybenzaldehyde p-Nitrobenzaldehyde p-Toluidine p-Anisidine Aniline hydrochloride p-Chloroaniline m-Dinitrobenzene p-Nitrotoluene p-Nitrophenol p-Nitroaniline o-Nitroaniline m-Nitroaniline p-Nitrobenzoic acid m-Nitrobenzoic acid p-Aminobenzoic acid Benzamide Salicylamide Phthalamide Phthalimide Sulphanilamide Urea

Department of Chemistry
Dumkal College
Basantapur, Dumkal
Murshidabad

Reference Books:

1. Vogel, A. I. *Elementary Practical Organic Chemistry, Part 2: Qualitative Organic Analysis*, CBS Publishers and Distributors.
2. *University Hand Book of Undergraduate Chemistry Experiments*, edited by Mukherjee, G. N. University of Calcutta, 2003.
3. Mann, F.G. & Saunders, B.C. *Practical Organic Chemistry*, Pearson Education (2009).
4. Furniss, B.S., Hannaford, A.J., Smith, P.W.G., Tatchell, A.R. *Practical Organic Chemistry, 5th Ed.*, Pearson (2012).
5. Clarke, H. T., *A Handbook of Organic Analysis (Qualitative and Quantitative)*, Fourth Edition, CBS Publishers and Distributors (2007).
6. *Practical Workbook Chemistry (Honours)*, UGBS, Chemistry, University of Calcutta, 2015.