

Chapter: 02

Ch.Id:-ASU/GRF/EB/AEHFPOC/2022/Ch-02

DOI: <https://doi.org/10.52458/9789391842697.2022.eb.grf.asu.ch-02>

AIM: TO PERFORM SYSTEMATIC QUALITATIVE ANALYSIS OF ALDEHYDE

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Requirements

Chemicals

1. Sodium bisulphite
2. Schiff reagent
3. Tollen's reagent
4. 2,4 dinitrophenyl hydrazine (2,4-DNP)
5. Fehling's A & B

Glass wares

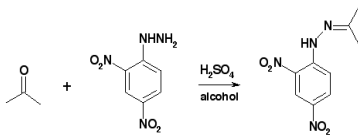
1. Test-tube
2. Stands
3. Brush
4. Holder
5. Glass rod
6. Beakers

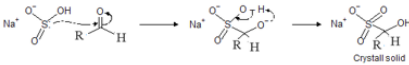
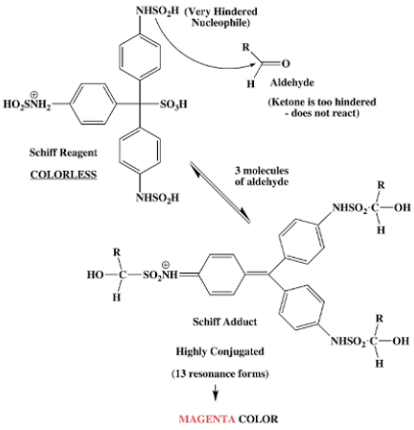
Theory: The carbonyl group is present in aldehydes and ketones; hence, both families of molecules react similarly with numerous chemicals. Commonly, 2,4-DNP is utilized to detect both types of chemicals. Aldehydes react with mild oxidizing agents to form carboxylic acids, whereas ketones, which are more resistant to oxidation, stay unaltered.

The identification of carbonyl compounds (aldehydes and ketones) is facilitated by a number of easily produced derivatives. In this category are oximes, phenylhydrazine, 2,4-dinitrophenylhydrazones, and semicarbazones. These derivatives are attractive because they are easily purifiable crystalline solids with a sharp melting point. In the production of these closely

related derivatives, a conventional nucleophilic addition is performed at the carbonyl carbon, which is then followed by the removal of a water molecule.

Functional Group Test for Aldehydes

S. No.	Identification Test	Observation	Inference
1	<p>2,4-DNP test: Add a solution of one or two drops of the sample dissolved in two ml of CH₃OH to three ml of 2,4 dinitrophenyl hydrazine reagent. If no precipitate appears immediately after vigorous shaking, solution is allowed to stand for 15 minutes.</p>  <p>The diagram illustrates the chemical reaction for the 2,4-DNP test. On the left, an aldehyde (represented by a carbonyl group C=O) reacts with 2,4-dinitrophenylhydrazine (DNPH), which is a benzene ring with nitro groups (NO₂) at the 2 and 4 positions and a hydrazine group (NHNH₂) at the 1 position. The reaction is catalyzed by H₂SO₄ in alcohol. The product is a 2,4-dinitrophenyl hydrazone, where the carbonyl oxygen is replaced by the nitrogen of the hydrazine group, forming a C=N double bond.</p>	Yellow/red ppt (dinitrophenyl hydrazone)	Carbonyl group may be present
2	<p>Sodium bisulphite addition complex: In a clean and dry test tube, given sample (0.3 ml) is poured in it, followed by 1 ml of the sodium bisulphite reagent. Shake the test tube vigorously with the stopper on.</p>	White precipitate	Carbonyl group is confirmed

	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} + \text{NaSO}_3\text{H} \longrightarrow \text{R}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{SO}_3^-\text{Na}^+$ <p>Mechanism</p> 		
<p>3</p>	<p>Schiff's test: To take a sample, put a few drops of Schiff reagent in clean and dry test tube and shake it thoroughly. The presence of aldehyde can be identified by its colour, which can be a deep red, violet, or pink.</p> <p>Note: false positive test is given by Amines</p> 	<p>Pink/violet colour</p>	<p>Aldehyde is confirmed</p>
<p>4</p>	<p>Tollen's test: To one ml of freshly prepared Tollen's reagent, add a single drop or a few crystals of the</p>	<p>Silver mirror or a</p>	<p>Aldehyde is confirmed</p>

	<p>sample. If there is no quick reaction, a low-temperature heating method may be used instead.</p> $\text{R-CHO} + 2[\text{Ag}(\text{NH}_3)_2] \longrightarrow \text{R-COONH}_4 + 2\text{NH}_3 + \text{H}_2\text{O} + 2\text{Ag}$	black precipitate	
5	<p>Fehling solution test: In a clean and dry test tube, both the Fehling solution A and the Fehling solution B combine in proportional amounts. Include three drops of the sample here. Positive test: Heat the tube in a H₂O bath maintained at 60 degrees Celsius for fifteen minutes.</p> $\text{CH}_3\text{CHO} + 2\text{CuO} \longrightarrow \text{CH}_3\text{COOH} + \text{Cu}_2\text{O}$	Brown red precipitate	Aldehyde is confirmed
6	<p>Test with Chromic Acid: The reaction that takes place between aldehydes and chromic acid results in the formation of a precipitate that can range in colour from green to blue. There is no reaction between chromic acid and ketones. A number of primary and secondary alcohols, but not dinitrophenyl hydrazine, also produces a positive result for this test. The appearance of a green or blue precipitate is sign that aldehydes are present in the sample under investigation.</p> <p>➤ Take the specified organic compound and place it in a clean</p>	Green or blue colour precipitate	Aldehyde is confirmed

	<p>and dry test tube.</p> <p>➤ Add 1 ml of chromic acid reagent to the organic substance provided.</p> $\text{R-CHO} + 2\text{CrO}_3 + 3\text{H}_2\text{SO}_4 \longrightarrow 3\text{R-COOH} + 3\text{H}_2\text{O} + \text{Cr}_2(\text{SO}_4)_3$ <p style="text-align: center;">(green colour)</p>		
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Result: The findings of the systemic qualitative testing on aldehydes were observed and reported.