Elemental analyses, physical, spectral and solubility test give a reasonable idea regarding the identity of unknown compound.

Despite the tremendous importance and ease of spectral analyses, chemical tests are indispensable to complete characterization.

The “wet” tests are commonly used as a method of functional group and compound identification.

Table 9.1: Classification Tests, Listed by Functional Groups.

Table 9.2 lists the classification tests alphabetically by the name of the test.
1. Classification Tests For Alcohols

(a) Sodium Metal

\[
2\text{ROH} + 2\text{Na} \rightarrow 2\text{RO}^-\text{Na}^+ + \text{H}_2(g)
\]

- **Positive Test:** evolution of gas
- The rate is highly variable and depends upon the alcohol structure.
- Precipitation occurs upon adding ether – solid salt precipitating.
- The sample must be water-free.
- Other Functional groups that give positive Test:
  
  \[ \text{R}_2\text{NH, RSH, RC≡C-H, RCO}_2\text{H} \]
(b) Ceric Ammonium Nitrate Oxidation

\[\text{Ceric ammonium nitrate} + \text{alcohol} \rightarrow \text{Product (red)}\]

- **Positive Test:** Color changes from yellow to red first then to colorless solution. (1 min. to 12 hrs)
- Positive for alcohols of 10 or fewer carbons.
- A positive test includes successively the formation, and then the disappearance of the red color.
- Very good test for 1°, 2° alcohol, but slow for 3° alcohol
- **Note:** Phenols give brown or black products.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Time&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Compound</th>
<th>Time&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary alcohols</strong></td>
<td></td>
<td><strong>Diols, triols, . . . , polyols</strong></td>
<td></td>
</tr>
<tr>
<td>Allyl alcohol</td>
<td>6 min</td>
<td>Pinacol</td>
<td>5 sec</td>
</tr>
<tr>
<td>Methyl cellosolve</td>
<td>1.2 hr</td>
<td>Mannitol</td>
<td>38 sec</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>3.6 hr</td>
<td>2,3-Butanediol</td>
<td>1 min</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>4.0 hr</td>
<td>Glycerol</td>
<td>10 min</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>4.1 hr</td>
<td>Propylene glycol</td>
<td>15 min</td>
</tr>
<tr>
<td>2-Methyl-1-propanol</td>
<td>4.1 hr</td>
<td>Diethylene glycol</td>
<td>3 hr</td>
</tr>
<tr>
<td>1-Heptanol</td>
<td>5.0 hr</td>
<td>Ethylene glycol</td>
<td>5 hr</td>
</tr>
<tr>
<td>Ethanol</td>
<td>5.5 hr</td>
<td>1,4-Butanediol</td>
<td>1 hr</td>
</tr>
<tr>
<td>Methanol</td>
<td>7.0 hr</td>
<td>1,4-Butynediol</td>
<td>36 min</td>
</tr>
<tr>
<td>2-Methyl-1-butanol</td>
<td>7.0 hr</td>
<td>1,4-Butynediol (mostly cis)</td>
<td>3 min</td>
</tr>
<tr>
<td>1-Decanol</td>
<td>12.0 hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Secondary alcohols</strong></td>
<td></td>
<td><strong>Carbohydrates</strong></td>
<td></td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>3.7 hr</td>
<td>Glucose</td>
<td>1 min</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>6.0 hr</td>
<td>Fructose</td>
<td>30 sec</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>9.0 hr</td>
<td>Galactose</td>
<td>1 min</td>
</tr>
<tr>
<td>2-Pentanol</td>
<td>17.0 hr</td>
<td>Lactose</td>
<td>5 min</td>
</tr>
<tr>
<td>2-Octanol</td>
<td>16.0 hr</td>
<td>Maltose</td>
<td>8 min</td>
</tr>
<tr>
<td>Diphenylcarbinol</td>
<td>12.0 hr</td>
<td>Sucrose</td>
<td>12 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cellulose—in soluble—in no red</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Starch—in soluble—in no red</td>
<td></td>
</tr>
<tr>
<td><strong>Tertiary alcohols</strong></td>
<td></td>
<td><strong>Hydroxy acids</strong></td>
<td></td>
</tr>
<tr>
<td>tert-Butyl alcohol</td>
<td>&gt;48 hr</td>
<td>Lactic acid</td>
<td>15 sec + CO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>tert-Pentyl alcohol</td>
<td>&gt;48 hr</td>
<td>Malic acid</td>
<td>30 sec + CO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>3-Methyl-3-hydroxy-1-butyne</td>
<td>36 hr</td>
<td>Tartaric acid</td>
<td>1 min + CO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mandelic acid</td>
<td>1 min + CO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Citric acid</td>
<td>1 min + CO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td><strong>Hydroxy ketones</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Hydroxy-2-butanone</td>
<td>15 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methyl-3-hydroxy-2-butanone</td>
<td>10 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Variations in time of consideration can be expected due to variable size of reagent drops and to the age of the reagent.
(c) Jones Oxidation: Chromic anhydride or Chromium Trioxide ($\text{CrO}_3$)

- A positive test for $1^\circ$, and $2^\circ$ alcohols consists in the changes from an orange-red color ($\text{Cr}^{+6}$) to opaque suspension with green to blue color ($\text{Cr}^{+3}$) in 2 sec.
- $3^\circ$ alcohols give no visible reaction within 2 sec. remaining orange

**Note:** Aldehydes give positive result.
(d) Lucas Test (HCl/ZnCl₂)

- Substrates that easily give rise to cationic character at the carbon bearing the hydroxyl group undergo the Lucas test readily.

\[
\text{R}_2\text{CHOH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{R}_2\text{CHCl} + \text{H}_2\text{O} \\
\text{R}_3\text{COH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{R}_3\text{CCl} + \text{H}_2\text{O}
\]

- **Pos. Test:** Formation of insoluble layer or emulsion in 5-10 min

- **Note:** Primary alcohols do not give positive result.
Since the Lucas test depends on the appearance of the alkyl chloride as a second liquid phase, it is normally applicable only to alcohols that are soluble in the reagent.

This limits the test in general to monofunctional alcohols lower than hexyl and certain polyfunctional molecules.

Allyl alcohol, although a primary alcohol, yields a carbocation that is relatively stable.

Thus, allyl alcohol reacts rapidly with the Lucas reagent and the reaction is accompanied by the evolution of heat. Addition of ice water to the reaction results in the formation of the allyl chloride as a separate layer.
(e) Periodic Acid (HIO₄) Test for detection of Vicinal Diols and Related Compounds
The iodic acid is detected with 5% AgNO₃ solution – an immediate precipitation of silver iodate occurs.

\[
\text{HIO}_3 + \text{AgNO}_3 \rightarrow \text{HNO}_3 + \text{AgIO}_3(s)
\]

iodic acid \hspace{1cm} \text{silver nitrate} \hspace{1cm} \text{silver iodate (white)}

Olefins, 2\textsuperscript{o} alcohols, 1,3-glycols, ketones and aldehydes are not affected by HIO₄ under the test condition.
(f) Acetyl Chloride

- **Positive Test:** Evolution of heat and HCl gas and formation of ester as a top layer.

  - $\text{ROH} + \text{H}_3\text{C} = \text{C} = \text{Cl} \rightarrow \text{H}_3\text{C} = \text{C} = \text{O}R + \text{HCl}(g)$
  
  - $\text{ArOH} + \text{H}_3\text{C} = \text{C} = \text{Cl} \rightarrow \text{H}_3\text{C} = \text{C} = \text{OAr} + \text{HCl}(g)$

- $3^o$ alcohols form primarily alkyl chloride due to the reaction of the liberated HCl on another molecule of the alcohol.

- Other functional groups that give positive test: $1^o$ and $2^o$ amines.
TCICA Test

- The TCICA test is utilized to distinguish between 1\textsuperscript{o}, 2\textsuperscript{o} and 3\textsuperscript{o} alcohols.

- The trichloroisocyanuric acid (TCICA) is a strong oxidizing agent – it is reduced to cyanuric acid which is a white solid.
<table>
<thead>
<tr>
<th>Class</th>
<th>Reaction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^o$ alcohols</td>
<td>1-15 min.</td>
</tr>
<tr>
<td>$2^o$ alcohols</td>
<td>0.1-1 min.</td>
</tr>
<tr>
<td>$3^o$ alcohols</td>
<td>do not react within 5 h.</td>
</tr>
<tr>
<td>ketones</td>
<td>do not react within 4 h.</td>
</tr>
<tr>
<td>aliphatic aldehydes</td>
<td>react in 1-1.5 min.</td>
</tr>
<tr>
<td>aromatic Aldehydes</td>
<td>react in 2-3 h.</td>
</tr>
<tr>
<td>phenols</td>
<td>react in 1-15 sec.</td>
</tr>
<tr>
<td>sugars</td>
<td>react in 1-5 min.</td>
</tr>
</tbody>
</table>
2. Classification Tests For Aldehydes and Ketones (a) 2,4-Dinitrophenyl Hydrazine

- Pos. Test: formation of yellow, orange or red ppt.
- The precipitate may be oily at first and become crystalline on standing.
- Certain allyl alcohol derivatives may be oxidized by the reagent to aldehydes or ketones, which then give a +ve test.
- Esters give a negative test.
- The melting point of the solid should be checked to be sure it is different from that of 2,4-Dinitrophenyl hydrazine (198°C)
- If recrystallization is necessary, solvents containing reactive carbonyl groups, such as acetone, should not be used as they may result in the formation of another hydrazone.
(b) Phenyl hydrazine and p-Nitrophenyl hydrazine.

Positive Test: formation of yellow ppt.

(c) Hydroxylamine Hydrochloride

The liberation of hydrogen chloride can be detected by the change in color from orange to red of a pH indicator.
(d) Sodium Bisulfite (NaHSO₃)

Positive Test: formation of ppt; good for aldehydes, all give ppt

Only some ketones give positive results (ppt)

This reaction is greatly inhibited by the steric constraints about the carbonyl group.
(e) Iodoform Test (For Methyl Ketones)

Positive Test: Yellow ppt for methyl ketones

Disadvantages: Some compounds that can be easily oxidized to methyl ketones give also positive results
The principal types of compounds that give a positive test:

The test is negative for the following type:

In such compounds the reagent removes the acetyl group and converts it to acetic acid, which resists iodination.
Acetoacetic acid is unstable, acidic aqueous solutions decompose to give CO$_2$ and acetone.

give positive iodoform test
To distinguish between aliphatic and aromatic aldehydes, the TCICA test can be utilized.

- Aliphatic aldehydes react in 1-1.5 min
- Aromatic aldehydes react in 2-3 h
3. Tests that give positive results with aldehydes and negative results with Ketones

(a) Jones Oxidation: Chromic anhydride or Chromium Trioxide (CrO₃)

A positive test for 1°, and 2° alcohols and Aldehydes consists in the changes from an orange-red color (Cr⁺⁶) to opaque suspension with green to blue color (Cr⁺³) in 2 sec.

\[
3RCH₂OH + 4CrO₃ + 6H₂SO₄ → 3 \text{carboxylic acid} + 9H₂O + 2Cr₂(SO₄)₃ (\text{intense blue to green})
\]

\[
3R₂CHOH + 2CrO₃ + 3H₂SO₄ → 3 \text{ketone} + 6H₂O + 2Cr₂(SO₄)₃ (\text{intense blue to green})
\]

\[
3RCH = H + 2CrO₃ + 3H₂SO₄ → 3 \text{carboxylic acid} + 3H₂O + Cr₂(SO₄)₃ (\text{blue to green})
\]
(b) Tollens Reagents Ag(NH$_3$)$_2$OH

\[
\begin{align*}
\text{aldehyde} + 2\text{Ag(NH}_3\text{)}_2\text{OH} &\rightarrow 2\text{Ag(s)} + \\
\text{Tollens reagent} &\quad \text{salt of the carboxylic acid}
\end{align*}
\]

- **Positive Test:** Formation of silver mirror (Ag$^0$) or colloidal (granular) gray or black Ag precipitate.

- If no reaction takes place in the cold, solution should be warmed slightly on a steam bath or in a hot-water bath.

- However, excessive heating will cause the appearance of a false positive test by decomposition of the reagent.

- False-negative tests are common with water insoluble aldehydes.

- **Note:** Diphenylamine and aromatic amines, as well as 1-naphthol and certain other phenols, give a positive Tollens test.
(c) Fuchsin Reagent

- In this test, the reagent should not be heated and the solution tested should not be alkaline.
- Advisable to perform simultaneous test on a known aldehyde and a known ketone for comparison.
- The development of a light pink color in the reagent is not a positive test for aldehydes.
(d) Bendicts solution and Fehling’s Solution

- **Positive Test**: yellow or yellowish green ppt.
- All aldehydes give positive result **except** aromatic aldehydes (negative)
(e) Purpald Test

- If the unknown is an aldehyde, the color will change from yellow to green to orange to deep rust.
- Acetone will give a negative test.
- False positives may occur with dioxane, 1,4-butanediol, and diethylamine.
4. Classification Tests for Unsaturation "alkenes & alkynes"

- Alkanes are not usually characterized chemically because they are quite inert to most classification reactions.
- Alkanes fall into solubility class I.
- Mostly, rely on physical and spectral characterization.

(a) Bromine in CCl₄

- **Pos. Test:** Bromine color discharged without evolution of gas (HBr).
- Alkenes & alkynes give positive results.
- If HBr is evolved, it indicates phenols, enols & enolizable compounds.

- Bromine color is discharged by amines to produce a salt, which could be mistaken for addition.
(b) Baeyer Test (KMnO₄ aqueous)

Positive Test: Purple color discharges, and brown color PPT (MnO₂) appears

Note: Aldehydes and alcohols also give positive result
Notes: since the ionic characters of the Br₂ and KMnO₄ reactions are very different, there is some complementary character between the two tests.

For example, some alkenes bearing electron-withdrawing groups undergo rapid reaction with KMnO₄ but often slow or negligible reaction with Br₂.

![Chemical structures and reactions](image)

A few tetrasubstituted olefins such as C₆H₅CBr=CBrc₆H₅ and (C₆H₅)₂C=C(C₆H₅)₂ fail to give positive tests with Br₂ in CCl₄ or KMnO₄ solution.
5. Tests for Alkyl Halides

- Aliphatic halides are often detected initially by qualitative halogen analysis.

- (a) Ethanolic Silver Nitrate & (b) Sodium Iodide in Acetone

- Both tests involve displacement of halogen:
  - AgNO$_3$/ethanol test proceeds by a carbocation ($S_N$1) process
  - NaI/acetone test proceeds by a direct displacement ($S_N$2)

\[
\text{AgNO}_3/\text{ethanol test: } R_3\text{CX} > R_2\text{CHX} > R\text{CH}_2\text{X} \\
\text{NaI/acetone test: } R_3\text{CX} < R_2\text{CHX} < R\text{CH}_2\text{X}
\]
(a) Ethanollic Silver Nitrate Solution

- The reaction of alkyl halide with silver nitrate yields a silver halide precipitate

\[
\text{RX} + \text{AgNO}_3 \xrightarrow{\text{CH}_3\text{CH}_2\text{OH}} \text{AgX(s)} + \text{RONO}_2
\]

- **Pos. Test:** formation of ppt. indicates 2° and 3° RX
- 1° RX, Ar-X, and vinyl halides give negative Result.
- **Note:** alkylic and benzylic RX give positive result
- The identity of the halogen can sometimes be determined from the color of the silver halide: AgCl (white); AgBr (pale yellow); AgI (yellow)
(b) Sodium Iodide in Acetone Test

- The NaI test can be used to test for the presence of bromine or chlorine.
- Sodium halide (NaX) precipitates from the solution.

Positive Test: precipitate forms

- Indications: 1°, 2° RX, allylic and benzylic halides.
- Not good for ArX, vinyl halides, HCCl₃, and 3° RX

Since reactivity toward alcoholic silver nitrate is often very different from reactivity toward sodium iodide in acetone, both tests should be used with any halogen compound.
6. Tests for Amines and Amine Salts

(a) Acetyl Chloride

- $1^\circ \ & 2^\circ$ amines react with acetyl chloride to produce amides which often precipitate from the solution when added to $\text{H}_2\text{O}$, along with heat evolution.

- $3^\circ$ amines give only heat.

- **Note**: ROH give also positive result (heat).
(b) Nitrous Acid

- Reaction of amines with nitrous acid (HONO) classifies the amine not only as 1°, 2°, or 3°, but also as aliphatic or aromatic.

\[
\text{RNH}_2 + \text{HONO} + 2\text{HCl} \rightarrow [\text{RN}_2^+\text{Cl}^-] \xrightarrow{\text{H}_2\text{O}} \text{diazonium salt} \quad \text{(unstable at 0°)}
\]

\[\text{N}_2(\text{g}) + \text{ROH} + \text{RCl} + \text{ROR} + \text{alkene}\]

\[
\text{ArNH}_2 + \text{HONO} + \text{HCl} \rightarrow \text{ArN}_2^+\text{Cl}^- \xrightarrow{\text{H}_2\text{O}} \text{N}_2(\text{g}) + \text{ArOH} + \text{HCl}
\]

1° aliphatic amine  nitrous acid  diazonium salt  spontaneous

1° aromatic amine  nitrous acid  diazonium salt  (stable at 0°C)
The diazonium salt of the primary aromatic amine reacts with sodium 2-napthol to produce a red-orange azo dye.

\[
\text{ArN}_2\text{Cl}^+ + \text{NaO}^-\text{Na}^+ + \text{NaOH} \rightarrow \text{N} = \text{N} - \text{Ar} + \text{NaCl} + \text{H}_2\text{O}
\]

The reaction involves the diazonium salt of the primary aromatic amine and sodium 2-napthol. The product is an azo dye, which is red-orange in color.

2° amines undergo a reaction with nitrous acid to form N-nitrosoamine, which are usually yellow solids.

\[
\text{R}_2\text{NH} + \text{HONO} \rightarrow \text{R} - \text{N} = \text{N} - \text{O} + \text{H}_2\text{O}
\]

The reaction involves 2° amine and nitrous acid. The product is an N-nitrosoamine, which is yellow in color (oil or solid).
3° aliphatic amines do not react with nitrous acid, but they form a soluble salt. The reaction mixture gives an immediate positive test on the starch-iodide paper for nitrous acid.

\[
R_3N + H^+ \rightarrow R_3NH^+
\]

3° aliphatic amine (soluble)

3° aromatic amines react with nitrous acid to form the orange-colored hydrochloride salt of the C-nitrosoamine. Treating the solution with base liberates the blue or green C-nitrosoamine.
Although nitrous acid is useful for characterizing amines, other functional groups also react.

A methylene group adjacent to a keto group is converted to an oximino group and alkyl mercaptans yield red S-alkyl thionitrites.
(c) Hinsberg Test

Based on the reaction of the amine with benzenesulfonyl chloride and can be used to distinguish among 1°, 2°, and 3° amines.

- 1° amines: give solution that produce ppt after addition of HCl.

\[
RNH_2 + C_6H_5SO_2Cl + 2NaOH \rightarrow C_6H_5SO_2NR^-Na^+ + NaCl + 2H_2O
\]

1° amine   benzenesulfonyl chloride   (soluble)

\[
H^+ \rightarrow C_6H_5SO_2NHR
\]

sulfonamide (insoluble)
2° amines: give ppt – acidification of the solution does not dissolve the sulfonamide (i.e., the PPT is not soluble in NaOH or HCl)

\[
\begin{align*}
R_2NH + C_6H_5SO_2Cl + NaOH & \rightarrow C_6H_5SO_2NR_2 + NaCl + H_2O \\
2^\circ \text{amine} & \quad \text{benzenesulfonyl chloride} \\
& \quad \text{sulfonamide (insoluble)} \\
& \quad \overset{H^+}{\text{No Reaction}}
\end{align*}
\]

3° amines: undergo reaction with benzenesulfonyl chloride to produce quaternary ammonium sulfonate salts, which yield sodium sulfonate and insoluble 3° amines in basic solution.

- Acidification of the reaction mixture results in the formation of sulfonic acids and soluble amine salts

\[
\begin{align*}
R_3N + C_6H_5SO_2Cl & \rightarrow C_6H_5SO_2NR_3^+Cl^- \overset{2NaOH}{\rightarrow} \\
3^\circ \text{amine} & \quad \text{benzenesulfonyl chloride} \\
\overset{2HCl}{\rightarrow} C_6H_5SO_3H + R_3NH^+Cl^- + 2NaCl
\end{align*}
\]
If the amount of the solid is in sufficient quantity, it may be saved, purified, and used as a derivative for that unknown.

The results of the Hinsberg test must not be used alone in classifying amines. The solubility of the original compounds must also be considered.

If the original compound is amphoteric, which means that it is soluble in both acids and alkalies, the Hinsberg method fails to distinguish among the types of amines.
(d) Nickel Chloride and 2-Hydroxy-5-Nitrobenzaldehyde – Test for Primary Amines

- $1^\circ$ aliphatic amines react quickly with 2-hydroxy-5-nitrobenzaldehyde, followed by nickel chloride to form an immediate precipitate, whereas $1^\circ$ aromatic amines usually requires 2-3 min to give a definite precipitate.

- Hydroxylamine and hydrazines substituted on only one nitrogen atom give positive tests.

- Amides do not give precipitates.

- The test is not applicable to amino acids.
(e) Sodium Hydroxide Treatment of Ammonium Salt and Amine Salts

- Amine salts can be detected by treating the salt with NaOH to liberate ammonia or amine.

\[
\begin{align*}
\text{R-COONH}_4^+ + \text{NaOH} & \rightarrow \text{R-COONa}^+ + \text{NH}_3 + \text{H}_2\text{O} \\
\text{RNH}_3^+X^- + \text{NaOH} & \rightarrow \text{RNH}_2 + \text{NaX} + \text{H}_2\text{O}
\end{align*}
\]

- Moistened pink litmus paper placed in the vapor above the solution will turn blue if ammonia or a volatile amine is present.
Sodium Metal

- The active hydrogen on 1° and 2° amines undergo reaction with sodium to form salt and liberate hydrogen gas.

\[
2\text{RNH}_2 + 2\text{Na} \rightarrow 2\text{RNH}^-\text{Na}^+ + \text{H}_2(\text{g}) \quad \text{1° amine}
\]
\[
2\text{R}_2\text{NH} + 2\text{Na} \rightarrow 2\text{R}_2\text{N}^-\text{Na}^+ + \text{H}_2(\text{g}) \quad \text{2° amine}
\]
7. Tests for Amino Acids

(a) Ninhydrin Test:

- α-amino acids and β-amino acids react with ninhydrin to give a positive test which is blue or blue-violet color.

- Ammonium sals (NH$_4^+$Cl$^-$) give a positive test.

- Some amines, such as aniline, yield orange to red colors, which is considered a negative test.

- Proline, hydroxyproline, and 2-, 3-, and 4-aminobenzoic acids fail to give a blue color but produce a yellow color instead.
(b) Copper Complex Formation

- Reaction with copper(II) sulfate solution yields a moderate- to deep-blue liquid or a dark-blue solid.
8. Tests for Aromatics

- If the molecule already contains reactive chemical substituents (acids, amines, ethers, carbonyl compounds, etc.,) use the corresponding classification test for that particular group.
- New substituents can be added onto the aromatic ring or existing substituents can be modified, such that the new compound may be more readily characterized.

(a) Fuming Sulfuric Acid

![Chemical Reaction]

This test is good for aromatics with no other functional groups.

**Pos. Test:** the aromatic compound dissolves completely in H₂SO₄ with the evolution of heat (Fuming)

**Caution:** use this reagent with relatively inert compounds only and must be done in the hood.
(b) Chloroform and Aluminum Chloride

\[ 3\text{ArH} + \text{CHCl}_3 \xrightarrow{\text{AlCl}_3} \text{Ar}_3\text{CH} + 3\text{HCl} \]

- Aromatic compound
- Triaryl methane

\[ \text{Ar}_3\text{CH} + \text{R}^+ \rightarrow \text{Ar}_3\text{C}^+ + \text{RH} \]

- Triaryl methane
- Triaryl carbocation (colored)

- Aromatics give colored solution or powder.
- **Positive Test:** (Orange, red, blue, purple, green)
- Non aromatics give yellow color (Negative result)
(c) Azoxybenzene and Aluminum Chloride

- The color of the solution or precipitate is dependent on the functional groups present on the aryl group.
- Aromatic hydrocarbons and their halogen derivatives produce a deep-orange to dark-red color in solution or give a precipitate.
- Fused aromatic ring (such as naphthalene, anthracene, and phenanthrene) produce brown color).
- Aliphatic hydrocarbons give no color or, at most, a pale yellow.
9. Tests for Ethers

- Ethers are only a little more polar and slightly more reactive than either saturated hydrocarbons or alkyl halides.

- **Caution:** Ethers form extremely explosive peroxides upon standing, specially when exposed to air and/or light. Liquid ethers that shows solid precipitates should not be handled.

(a) Hydroiodic Acid (Zeisel's, Alkoxyln method)

\[
\begin{align*}
R'OR + 2HI & \rightarrow R'I + RI + H_2O \\
ArOR + HI & \rightarrow RI + ArOH
\end{align*}
\]

\[
\begin{align*}
Hg(NO_3)_2 + 2R'I & \xrightarrow{H_2O} HgI_2 + 2R'OH + 2HNO_3
\end{align*}
\]

- **Positive Test:** Orange or Orange-red color indicating: ether with R equal to 3 carbons or less.

- **Note:** Ethyl and methyl esters give also positive result.

- The test must be done in the hood.
(b) Iodine Test for Ethers and Unsaturated Hydrocarbons

- Positive test: the color of the solution changes from purple to tan.
- Aromatic hydrocarbons, saturated hydrocarbons, fluorinated hydrocarbons and chlorinated hydrocarbons do not react.
- Unsaturated hydrocarbons produce a light-tan solid, while retaining the purple color of the iodine solution.
10. Tests for Phenols

- As with alcohols, the acidic hydrogen in phenol can be detected with sodium (hydrogen gas is evolved) or with acetyl chloride (an ester layer is formed).

\[
\text{ArOH} + \text{H}_3\text{C}\text{C}\text{C}\text{Cl} \rightarrow \text{H}_3\text{C}\text{C}\text{OAr} + \text{HCl}(g)
\]

- Phenols undergo reaction with yellow ceric ammonium nitrate to produce brown or black products.

\[
(\text{NH}_4)_2\text{Ce(NO}_3)_6 + \text{ArOH} \rightarrow (\text{NH}_4)_2\text{Ce(NO}_3)_5 + \text{HN}_3
\]
- Phenols reduce potassium permanganate solution and undergo oxidation to quinones.
- The manganese is reduced from +7 which gives a purple solution to +4 which is brown.

![Chemical reaction]

- The TCICA test can be utilized to identify aldehydes, alcohols and phenols.
- The trichloroisocyanuric acid is reduced to cyanuric acid, a white solid. Phenols react in 1-15 sec.
(a) Bromine water

Positive Test: decolorization of bromine.

This is good for water soluble phenols.
(b) Ferric Chloride – Pyridene Reagent

Positive Test: Production of blue, violet, purple, green, or red-brown colors

- Good for all types of Ar-OH.
- The test must be done in the hood.
11. Test For Nitro Compounds

(a) Ferrous Hydroxide Reduction

\[
\begin{align*}
\text{RNO}_2 & \quad + \quad 6\text{Fe(OH)}_2 & + & 4\text{H}_2\text{O} & \longrightarrow & \text{RNH}_2 & + & 6\text{Fe(OH)}_3 \\
\text{nitroalkane} & \quad \text{ferrous hydroxide} & & \quad \text{(green)} & & \quad \text{ferric hydroxide} & & \quad \text{(red-brown to brown)}
\end{align*}
\]

- **Positive Test:** indicated by the change in color from green to red-brown or brown due to the oxidation of iron from+2 to +3.

- A negative test is indicated by a greenish precipitate.

- **Note:** Nitroso compounds, quinones, hydroxylamines alkyl nitrates give also positive results.
(b) Zinc and Ammonium Chloride Reduction

\[
\begin{align*}
RNO_2 + 4[H] & \xrightarrow{Zn/\text{NH}_4\text{Cl}} RNHOH + H_2O \\
\text{nitro compound} & \quad \text{hydroxylamine}
\end{align*}
\]

\[
RNHOH + 2\text{Ag(NH}_3)_2\text{OH} \rightarrow RNO + 2H_2O + 2\text{Ag(s)} + 4\text{NH}_3
\]

Tollens reagent

- Test the solution with Tollens Reagent
- **Positive Test:** formation of metallic silver
- Only 3° aliphatic nitro compounds and aromatic nitro compounds are reduced by Zn/NH₄Cl to the hydroxylamine.
- The hydroxylamine is then detected by the formation of metallic silver in the Tollens test (or formation of a black or grey precipitate).
(c) Treatment of Aromatic Compounds with Sodium Hydroxide

- The number of nitro groups on an aromatic ring can be determined by the reaction with NaOH.
- In the reaction with NaOH:
  - Mononitro aromatic compounds yield no color change or a very light yellow.
  - Dinitro aromatic compounds produce a bluish-purple color.
  - Trinitro aromatic compounds give a red color.
- The color of the solution is due to a Meisenheimer complex.

![Meisenheimer complex reaction diagram]
THE END