**Classification Tests for Organic Chemicals**

Always do parallel tests on authentic compounds that will give both positive and negative results. Many reagents are toxic/corrosive. Use care and find out what to do if you contact the reagent.

Selected CLASSIFICATION TESTS for various FUNCTIONAL GROUPS
(protocols on subsequent pages)

<table>
<thead>
<tr>
<th>Group</th>
<th>Test</th>
<th>Positive Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol</td>
<td>dichromate (Jones test)</td>
<td>clear orange → dark ppt indicates 1° or 2° alcohol</td>
</tr>
<tr>
<td></td>
<td>Lucas</td>
<td>1° unreactive</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2° cloudy within 5-15 min, but some 2° fail to react</td>
</tr>
<tr>
<td></td>
<td>iodoform</td>
<td>yellow ppt only for R-CHOH-CH₃</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>dichromate</td>
<td>clear orange → dark ppt (see also alcohols)</td>
</tr>
<tr>
<td></td>
<td>2,4-DNP</td>
<td>heavy yellow to red ppt</td>
</tr>
<tr>
<td></td>
<td>bromine water</td>
<td>decolorization (not always reliable)</td>
</tr>
<tr>
<td>Alkane</td>
<td>Flammability test</td>
<td>flame without much smoke</td>
</tr>
<tr>
<td>Alkyl Halide</td>
<td>AgNO₃/EtOH</td>
<td>precipitate (Cl-bright white, Br-light yellow, I-light tan)</td>
</tr>
<tr>
<td></td>
<td>Na fusion</td>
<td>ppt. with aq. AgNO₃ (colors as above denote Cl, Br, I)</td>
</tr>
<tr>
<td></td>
<td>Flammability test</td>
<td>not flammable</td>
</tr>
<tr>
<td>Alkene**</td>
<td>bromine/CCl₄</td>
<td>&quot;instant&quot; decolorization</td>
</tr>
<tr>
<td></td>
<td>permanganate</td>
<td>purple → brown</td>
</tr>
<tr>
<td>Amine</td>
<td>dil aq. HCl</td>
<td>soluble (or obvious reaction)</td>
</tr>
<tr>
<td></td>
<td>Hinsberg</td>
<td>see text; distinguishes 1°, 2°, 3°</td>
</tr>
<tr>
<td></td>
<td>bromine water</td>
<td>decolorization (can also use tests for alkyl amines)</td>
</tr>
<tr>
<td>Arene</td>
<td>Friedel-Crafts</td>
<td>bright yellow to red colors</td>
</tr>
<tr>
<td></td>
<td>try to ignite</td>
<td>sooty flame if it burns</td>
</tr>
<tr>
<td>Aryl Halide</td>
<td>Na fusion</td>
<td>ppt. with aq. AgNO₃</td>
</tr>
<tr>
<td></td>
<td>Friedel-Crafts</td>
<td>bright yellow to red colors</td>
</tr>
<tr>
<td></td>
<td>Flammability test</td>
<td>sooty flame if it burns</td>
</tr>
<tr>
<td>Carboxylic Acid</td>
<td>aq. bicarbonate</td>
<td>bubbles; unknown becomes soluble</td>
</tr>
<tr>
<td>Ketone</td>
<td>2,4-DNP</td>
<td>heavy yellow to red ppt</td>
</tr>
<tr>
<td></td>
<td>iodoform</td>
<td>yellow ppt only for methyl ketones</td>
</tr>
<tr>
<td>Phenol</td>
<td>bromine water</td>
<td>decolorization</td>
</tr>
<tr>
<td></td>
<td>3M NaOH</td>
<td>soluble or obvious reaction</td>
</tr>
</tbody>
</table>

** Alkenes may give test results expected for alcohols, particularly if wet (e.g., positive Jones test, cloudy Lucas test, broad "OH" band in IR). It's wise to put one drop of Br₂/CCl₄ in 0.5 mL ether (check for persistent color), then add one drop of unknown and check for instant decolorization. An alcohol won't decolorize Br₂ unless it also has a C=C bond.
+ Consult with instructor if considering this reaction.
Classification Tests for Organic Chemicals
Always do parallel tests on authentic compounds that will give both positive and negative results. Many reagents are toxic/corrosive. Use care and find out what to do if you contact the reagent.

ALCOHOLS

Lucas Test (for alcohols of 6 C or fewer): distinguishes between 1°, 2° and 3° alcohols.
Method: Thoroughly mix 2-3 drops of unknown with about 0.5 mL of Lucas Reagent (which is conc HCl saturated with ZnCl₂ — corrosive and smelly!).
Interpretation: 1° alcohols remain soluble (clear), 2° produce cloudiness in 5-20 min (but some take longer!), 3° become cloudy instantly. Ignore color. Note that this test does NOT produce a precipitate!
Interferences: alcohols with > 6 C may give results like 3° because the large alcohol is not soluble in the Lucas Reagent.

Jones (acid dichromate) Test: distinguishes oxidizable (1°, 2°) alcohols from nonoxidizable (3°).
Method: Put 0.5 mL of pure acetone in a small test tube. Thoroughly mix one drop or one small crystal of compound to be tested with the acetone until everything is dissolved. Add one small drop of Jones Reagent and mix well.
Interpretation: Rapid formation of a thick dark bluish-green precipitate indicates reaction. If the liquid part of the mixture remains orange, consider the test to be negative even if there is a light green precipitate.
Interferences: Aldehydes, phenols and amines give a positive test. Certain alkenes and ketones may give a slow, weak positive test. Some 3° alcohols may slowly dehydrate in the reagent and thus give a weak positive test.

Iodoform Test: distinguishes CH₂–CHOH–R from all other kinds
Method, Interpretation: see ketones; probably need warming to assure reaction. Interferences: methyl ketones

ALDEHYDES

Jones (acid dichromate) Test:
Method, Interpretation, Interferences: See alcohols

2,4-dinitrophenylhydrazine (DNP) Test:
Method: [The reagent is made in ethanol and contains H₂SO₄. It reacts with proteins in skin to make long-lasting yellow stains (they wear off in about 2 weeks). Treat the reagent as toxic and corrosive.] In a medium-size test tube, completely dissolve 3 drops or 3 small crystals of compound to be tested in about 2 mL of 95% EtOH. Then add about 2 mL of DNP Reagent. Mix thoroughly with a stirring rod.
Interpretation: Rapid appearance of a thick precipitate is positive (color may range between bright yellow to deep red).
[Can purify & use as solid derivative; see Solid Derivatives document.]
Interferences: Ketones

ALIPHATIC AND AROMATIC HYDROCARBONS AND HALIDES

Sodium Fusion Test for Halogen and/or Nitrogen: (Useful only for a pure compound. Always do a known positive compound in parallel.)
This test can be used if you suspect the presence of halogen or nitrogen in any form in your unknown. Get two Pyrex test tubes ready for their “final journeys” by washing with Alconox and then rinsing numerous times with deionized water. Dry them thoroughly with a clean paper towel. Test your sample and, separately, a positive control (a chemical that contains the element for which you are testing). Clamp the test tube firmly in a screw type clamp with metal jaws. Get a small piece of sodium metal (already cut for you - about 3 x 3 mm), blot away the oil with a paper towel, and put the sodium into the tube. Then add about 4 drops or a small crystal of unknown. Take this to a hood (which must be free of flammable chemicals!) equipped with a Bunsen burner. Heat the tube with a soft flame at first, agitating it vigorously to make sure you have good contact between the molten metal and the compound. Fumes will be emitted and may catch fire. Just let them burn and continue agitating the tube. Eventually change to a very hard, hot flame (lots of gas and lots of air; tube at tip of inner luminous blue cone) and heat the tube until the entire bottom and lower sides glow red (about 1 minute). Let the tube cool. Once cool, add about one mL of methanol and crush any lumps with a clean stirring rod (this will destroy any unreacted sodium metal). As soon as no action is evident (there will usually be none), add 4 mL of deionized water. Agitate with the stirring rod while heating nearly to boiling (be very careful – it’s easy to blow the contents out of the tube as it starts to boil!), then filter through a cone of paper in a previously rinsed glass funnel, capturing the liquid in a clean test tube. This clear filtrate can be used to test for the presence of nitrogen and halogens. Test only for the element(s) you suspect to be present (see below), but do the tests at the same time for your sample and positive control. Use not more than half of your filtrate in case you need to repeat the test (less if doing both halogen and nitrogen).
Classification Tests for Organic Chemicals
Always do parallel tests on authentic compounds that will give both positive and negative results.
Many reagents are toxic/corrosive. Use care and find out what to do if you contact the reagent.

Sodium Fusion Test for Halogen and/or Nitrogen (Cont):

**Halogen:** Put some of your filtrate into a clean test tube and make acidic with 3 M nitric acid (test a drop of filtrate with litmus). Boil this (carefully) for about 20 seconds to get rid of any volatile N- or S-containing compounds. Add one drop of AgNO₃ in water. A heavy precipitate signals halogen: AgCl is white, AgBr is light yellow, and AgI is light tan (you can do parallel color tests with salts of known halides – KCl, KBr, KI).

**Nitrogen:** *Always do a positive control along with this test.* Put some of the filtrate into a clean test tube. To this add about 25 mg of solid ferrous ammonium sulfate or ferrous sulfate, 4 drops of 2 M KF, and one drop of 3 M NaOH. Boil gently for about one minute. There should be a bluish precipitate. If not, add 2 more drops of 3 M NaOH and boil again. Add 2 drops of FeCl₃ and boil again. Then add 3 M sulfuric acid dropwise with good mixing until the precipitate has just dissolved. Allow the solution to stand. If an intense, deep blue color (Prussian Blue) forms, nitrogen is definitely present. Any other color is an ambiguous result, but likely negative.

Flammability test (pertains to all):

**Method:** Put a watch glass inside your desk hood. Put a small shred of paper towel in the middle to act as a wick. Physically stopper any nearby flasks that have organic liquids in them, and move them far from the hood. Verify that your neighbors on both sides have done the same. Ask an instructor to verify that it is safe to light a flame. Pour about 1 mL of the compound to be tested into the watch glass, strike a match, and attempt to ignite the liquid.

**Interpretation:**
- Flame without much smoke: likely an alkane
- Flame with heavy, sooty smoke: likely aromatic hydrocarbon
- Not flammable: probably an alkyl or aryl halide

**Interferences:** most other compounds – be sure that you have ruled out all other classes

ALKENES

Bromine absorption test:

**Method:** Work in a small test tube. Put in it about 0.5 mL of hexanes or diethyl ether. To this add 1 M Br₂ in CCl₄ dropwise with good mixing until the color persists for at least 30 sec. Immediately add one drop or crystal of the compound to be tested and mix well.

**Interpretation:** Instant loss of color in a positive test. Very slow loss of color is negative.

**Interferences:** Easily oxidized compounds – mainly aldehydes. Alkanes that have allylic or benzylic H atoms react very fast via a free radical mechanism due to effect of room light.

Aq. permanganate test:

**Method:** Work in a small test tube. Put in it about 0.5 mL of water and one drop/crystal of the compound to be tested. Add one drop of aq. KMnO₄. Mix thoroughly.

**Interpretation:** Change from clear and purple to cloudy and yellow or brown is positive.

**Interferences:** easily oxidized compounds like aldehydes and some alcohols.

ALKYL HALIDES (not aromatic)

Silver Nitrate Test:

**Method:** Work in a small test tube. Dissolve the compound to be tested in about 1 mL of 95% EtOH. Add one drop of 0.1 M AgNO₃ in ethanol and mix well

**Interpretation:** slow formation of a precipitate is a positive test. Halides react fastest to slowest in the order 3°>2°>1°. If no precipitate is evident after a few minutes, warming the mixture may elicit a reaction. The Na fusion test is often more reliable.

**Interferences:** Halide salts from fingerprints or dirty glassware, left-over HCl from separation attempts.

Sodium Fusion Test:

**Method, Interpretation:** see Aliphatic and Aromatic Hydrocarbons and Halides
Classification Tests for Organic Chemicals
Always do parallel tests on authentic compounds that will give both positive and negative results.
Many reagents are toxic/corrosive. Use care and find out what to do if you contact the reagent.

AMINES

Odor Test:
Method: sniff carefully
Interpretation: odor like fish, rotting flesh or ammonia suggests an aliphatic amine. The more revolting the odor, the more likely that you have a small, water-soluble amine. Aromatic amines smell more like mothballs than rotting flesh.
Interferences: confusion with other unpleasant odors

Hinsberg Test: for aliphatic and aromatic amines; distinguishes 1°, 2° and 3° amines if R group is not extremely large
Method: Work in a large test tube closed with a rubber stopper. Liquid: use 5 drops. Solid: use what fits on the narrow end of a scoopula. Mix with 0.5 mL of benzenesulfonyl chloride. Cautiously note the unpleasant odor of this reagent – you will need to verify that it has disappeared later. Add 4 mL of ~6 M KOH (NaOH is OK if no KOH), stopper, and shake vigorously by hand until the reaction is complete. Test the pH occasionally with litmus paper – it must stay alkaline. Add more KOH if necessary, 1-2 mL at a time. Reaction is over when all of the oily benzenesulfonyl chloride is gone, and its odor is gone as well. Note whether the solution still smells strongly of the suspected amine. If a solid is present, recover it by filtration on appropriate-size funnel and wash it with about 2 mL of water. SAVE combined filtrates – see (b) below.
Interpretation:
(a) substantial amount of solid recovered? take a little and see if it dissolves in 2 mL of 3 M NaOH after warming to “hot water” temperature. If it does dissolve, you have a 1° amine [see (b) below]. If it fails to dissolve, you have a 2° amine. The solid perhaps can be used (after recrystallization from EtOH/water) as a solid derivative if its mp is high enough. [Saved filtrate can be discarded.]
(b) reaction mix clear (or had little solid) and had no strong odor? add 6 M HCl until solution (or saved filtrate) is distinctly acidic to litmus paper. A precipitate indicates that a 1° amine was present. If its predicted mp is high enough, harvest this solid and use as solid derivative (after recrystallizing from EtOH/water). No precipitate from this acidic mixture indicates that no amine was present.
(c) reaction mix clear or cloudy but smells of amine? you had a 3° amine. Verify by making some of reaction mix acidic – NO precipitate should form.
Interferences: large R groups interfere with above solubility behaviors. Alcohols react slowly with benzenesulfonyl chloride but make liquid products that do not precipitate after acidification (but they don’t smell like amines!).

Bromine Absorption by Aromatic Amines (Aniline and Relatives):
Method: dissolve one drop or one crystal in 10 mL of ethanol or methanol. Stir vigorously while dripping in Br₂-saturated water.
Interpretation: Rapid loss of Br₂ color suggests presence of aromatic amine. Interferences: phenols

CARBOXYLIC ACIDS

Odor Test
Method: sniff carefully
Interpretation: odor like vinegar, rancid fat, or old socks suggests a volatile carboxylic acid (normally a liquid).
Interferences: confusion with other unpleasant odors

Aq. NaHCO₃ (Bicarbonate) Test:
Method: mix a little of the compound to be tested with about 1 mL of aq. NaHCO₃
Interpretation: Formation of bubbles, and dissolving of the compound, are positive tests. If an acid reacts slowly, it may take a while for it to dissolve and for bubbles to become evident.
Interferences: all water-soluble compounds will dissolve in the bicarbonate solution, but only acids will give bubbles. Strongly acidic (but not ordinary) phenols will also produce bubbles.
Classification Tests for Organic Chemicals

Always do parallel tests on authentic compounds that will give both positive and negative results. Many reagents are toxic/corrosive. Use care and find out what to do if you contact the reagent.

ESTERS

Odor Test:
Method: sniff carefully
Interpretation: pleasant, flowery odor suggests an ester. Interferences: confusion with odors of ketones

Ferric Hydroxamate Test:
Method: Work in a medium test tube. Dissolve one drop or one small crystal of compound to be tested in 0.5 mL of 0.5 M hydroxylamine hydrochloride in EtOH. Add 2 drops of 6 M NaOH. Heat in a boiling water bath for 5 min, cool a few seconds, and mix in 1 mL of 1 M HCl. If cloudy add up to 1 mL of EtOH. Add 10% aq. FeCl₃ dropwise with good mixing
Interpretation: A red to blue color is a positive test. Interferences: none

KETONES

2,4-dinitrophenylhydrazine (DNP) test:
Method, Interpretation: see aldehydes Interferences: Aldehydes

Iodoform Test: distinguishes methyl ketones from all other kinds
Method: Work in a large test tube using 3 drops of liquid or about 0.1 g of solid. Depending on its solubility, dissolve compound to be tested in 2 mL of water or methanol. Add 1 mL of 3 M NaOH, mix well. Dropwise with good mixing, add iodoform reagent (I₂ + KI in water) until brown color persists (up to 4 mL; if no yellow precipitate appears, heat to ~ 60 °C and add more I₂ until brown color persists for 2 min). Add 3 M NaOH dropwise until brown color is just gone (yellow is OK). Add 10 mL of water and mix. Allow up to 15 min for precipitate formation.
Interpretation: Positive test is formation of a lemon-yellow precipitate after the brown color vanishes.
Interferences: Alcohols of the structure CH₃-CHOH-R

PHENOLS

Aq. FeCl₃ Test:
Method: dissolve 1 drop or 1 small crystal of compound to be tested in 1 mL of water or a mixture of water and ethanol. Add one drop of 5% - 10% aq. FeCl₃.
Interpretation: A red, blue, green or purple color is a positive test. Interferences: none

Bromine Absorption:
Method: dissolve one drop or one crystal in 10 mL of ethanol or methanol. Stir vigorously while dripping in Br₂-saturated water.
Interpretation: Rapid loss of Br₂ color suggests presence of phenol Interferences: aromatic amines (aniline and relatives)