Chemical Tests for Unknowns

Chemical tests have been developed as a means of identifying what functional groups are present in an unknown compound. Since IR and NMR spectroscopy has been developed, they are no longer critical to unknown analysis, but they can still be useful for confirming what you have determined by spectroscopy. Some of them look cool too!

In order for a chemical reaction to work as a chemical test, it must

- 1) create a visible result (a color change, a precipitate, etc)
- 2) work in a short amount of time (instantly to 5 minutes)
- 3) only work with one functional group

The following are chemical tests that we will use in this class. Some cover two related functional groups (such as the bromine test for alkenes and alkynes), while other only a specific subcategory of that functional group (such as the iodoform test for methyl ketones).

In some cases there can be false positives (compounds which do not have the functional group still give a result test) or false negatives (compounds which have the functional group give a negative result). If your results do not match what you expected, use your judgment to determine if you should ignore the results or rethink your interpretation of the spectra.

test	functional group	positive result
Baeyer test	alkenes and alkynes	clear purple solution turns to brown precipitate
Bromine test	alkenes and alkynes	brown color disappears
Dinitrophenylhydrazine test	aldehydes and ketones	yellow to orange red precipitate
Ferrox test	any functional group containing oxygen	reddish-purple color
Hydroxamate test	amides and esters	red-purple color appears
Iodoform test	methyl ketones	yellow precipitate
Iron hydroxide test	nitro groups	red-brown precipitate
Jones test	1° and 2° alcohols	orange reagent turns blue-green
Lucas test	2°, 3°, and benzylic alcohols	cloudy solution or separate layer
Tollen's test	aldehydes	silver mirror forms

Summary of functional group tests

Note: There are no chemical tests in this lab for amines, nitriles, or alkyl halides. If you have one of these functional groups, you must rely on spectral data to determine the functional groups.

Lucas test – alcohols

The Lucas reagent contains $ZnCl_2$ in aqueous HCl, which reacts with some alcohols in an S_N1 reaction to produce an alkyl chloride. Which it is first formed it appears cloudy because it is immiscible with water; eventually it separates to form an other layer. The test does not work well on solid alcohols because they do not easily dissolve in the first place, and multifunctional compounds may give unusual results. Phenols also do not react. The test is positive with secondary, tertiary or benzylic alcohols but negative with primary alcohols.

<u>Procedure:</u> Add about 2 drops of a liquid unknown to 0.5 ml of Lucas reagent in a small vial. Shake vigorously, then allow to stand at room temperature. If the alcohol is primary, it will simply dissolve in the reagent. Secondary alcohols will give a cloudy solution and/or separate layer after 2-5 minutes. Tertiary, benzylic, or allylic alcohols will give a cloudy solution and/or a separate layer almost immediately.

Jones test – alcohols

The Jones reagent contains CrO_3 in sulfuric acid solution, which oxidizes primary alcohols to carboxylic acids and secondary alcohols to ketones. Chromium +6 in the reagent is orange, while the resulting chromium +3 is blue-green. This reaction is also the basis for the breathalyzer test for drunk drivers. Aldehydes will also be oxidized to carboxylic acids, and will also give a positive result. Phenols do not react (or give an unusual reaction) in this test.

<u>Procedure:</u> Dissolve about 10 mg (if solid) or 2 drops (if liquid) of unknown in 0.8 ml of acetone in a small vial. Add one drop of Jones reagent and shake. Primary and secondary alcohols react within 10 seconds to form a blue-green precipitate; tertiary alcohols do not react (solution remains orange).

Tollen's test – aldehydes

In this test the aldehyde is oxidized to a carboxylic acid, reducing silver ions to silver metal. Ketones cannot be oxidized, so this is a good way to distinguish ketones from aldehydes.

<u>Procedure:</u> Mix 1 ml of 10% silver nitrate and 0.5 ml of 10% sodium hydroxide in a small test tube. Add 10% ammonium hydroxide dropwise under the dark silver oxide precipitate just dissolves. Then add about 10 mg (if solid) or 2 drops (if liquid) of the unknown and shake well. Allow to stand at room temperature for ten minutes. Formation of a silver coating on the outside of the test tube is a positive test. (Do not allow this mixture to stand overnight – silver fulminate, an explosive compound, may form.)

Dinitrophenylhydrazine test - aldehydes and ketones

In this test an insoluble hydrazone derivative is formed. Saturated compounds usually give yellow precipitates, while aromatic or unsaturated compounds give red-orange precipitates. The test is

positive for both aldehydes and ketones, but not usually for esters. Easily oxidized alcohols may also give a positive test.

<u>Procedure:</u> Add 0.5 ml of 2,4-dinitrophenylhydrazine reagent to a small vial. Add about 10 mg of unknown dissolved in a few drops of ethanol if it is a solid, or 2 drops of unknown if it is a liquid. Allow to stand up to 15 minutes. If a red, orange, or yellow precipitate forms, the test is positive.

Bromine test – alkenes and alkynes

In this test the alkene or alkyne reacts with Br_2 to form an alkyl dibromide, which causes the orange-brown of the Br_2 to disappear. This will be immediate with alkenes, but may take a short while with alkynes. Activated aromatic rings give a false positive in this test.

<u>Procedure:</u> Dissolve about 10 mg (if solid) or 2 drops (if liquid) of unknown in about 0.5 ml of dichloromethane on a spot plate. Add 4 drops of 2% Br_2 in dichloromethane solution. If the brown color disappears, the test is positive.

Baeyer test – alkenes and alkynes

In this test the alkene or alkyne is oxidized to a diol (alkene) or diketone (alkyne), which uses up the purple permanganate solution and produces manganese dioxide, a brown precipitate. It may also give a positive test for aryl amines, aldehydes, and alcohols, which can also be oxidized.

<u>Procedure:</u> Dissolve about 10 mg (if solid) or 2 drops (if liquid) of the unknown in about .5 ml of acetone on a spot plate. Add 3 drops of 0.02 M KMnO_4 solution. If the purple color disappears and a brown precipitate is formed, the test is positive.

Hydroxamate test - esters and amides

On heating with hydroxylamine (NH₂OH), esters and amides form hydroxamic acids (N is attached to the C=O), which form colored complexes with Fe^{+3} ions.

<u>Procedure:</u> In a 5 ml conical vial containing a spin vane and a reflux condenser, place 3 drops (if liquid) or 20 mg (if solid) of the unknown, followed by 1 ml of 0.5 M hydroxylamine hydrochloride in ethanol. Heat to reflux for 5 minutes, cool to room temperature, and add 2-5 drops of 5% ferric chloride. If the solution turns a red to purple color, the test is positive.

Neutralization equivalent – carboxylic acids

Strictly speaking, this is not a functional group test, but rather a titration to determine the number of moles of acid in a given mass of the compound. This will allow the molecular weight of a compound (or a multiple thereof) to be determined, and is very useful in narrowing down the possible structures of the unknown. It is essential to use standardized base, which has a very exact

concentration (such as 1.0001 M), and to measure the mass of the carboxylic acid and ml of base as carefully as possible. The amount of water or ethanol used to dissolve the acid is not important.

<u>Procedure:</u> Accurately weigh about 50 mg of the unknown and dissolve it in 15-20 ml of a water/ethanol mixture (most acids have too much hydrocarbon in them to dissolve well in water alone). Add a few drops of phenolphthalein solution. Titrate using a buret and standard 0.01 N NaOH (fill the buret to the 50 ml mark). Using a stir plate is helpful both to stir the solution and have a white background. Determine the ml of base needed for the pink color to persist as accurately as possible.

Calculate the neutralization equivalent by calculating the number of moles of base needed to neutralize the acid (multiply the ml of base by the molarity of the base). Then dividing the mass of the sample (in g) by the number of moles of base. This will give you the molecular weight of the carboxylic acid (or a multiple of it if there is more than one COOH group).

To get an idea of how far off is reasonable, calculate backwards to figure out how many ml of base would be required to neutralize the acid if it had the MW you were expecting. Is the difference within experimental error?

Ferrox test - ethers

This test is used to distinguish ethers from alkanes (which give a negative test), since the C-O bands on the IR may be hard to read. However, it will also give a positive test for any other group containing an oxygen (alcohol, aldehyde, ketone, etc) so it isn't useful for distinguishing ethers from these compounds. You would be wise to use both ether and alkane controls so that you can be sure to see the difference.

<u>Procedure:</u> On a dry spot plate, grind one crystal of ferric ammonium sulfate and a crystal of potassium thiocyanate using a glass rod. Place 2 drops of the unknown in a separate well. Use the glass rod with ground up crystals attached to stir the unknown. If the test is positive, the crystals will dissolve in the unknown, giving a reddish-purple color.

Iodoform test – methyl ketones

This test is used to identify methyl ketones (ketones with a methyl group on one end). It uses the haloform reaction, in which the methyl ketone is oxidized to a carboxylic acid and iodoform, a yellow solid, is produced.

<u>Procedure:</u> Dissolve 50 mg (if solid) or 5 drops (if liquid) of unknown in a small vial. Add 0.5 ml of 10% NaOH, then add the KI/I_2 reagent dropwise with shaking until a definite dark color persists. Then add a few more drops of NaOH to get rid of the iodine color. Allow to stand at room temperature for 15 minutes. Formation of a yellow precipitate is a positive test.

Iron hydroxide test – nitro groups

This test involves oxidation of ferrous hydroxide (whitish blue solid) to ferric hydroxide (red brown solid) by the nitro group. Other functional groups in the compound may interfere with this reaction.

<u>Procedure:</u> Add 0.5 ml of 5% ferrous ammonium sulfate (solution must be a pale blue color - if red, it has already oxidized and is not good!) to about 10 mg (if a solid) or 2 drops (if a liquid) of the unknown. After mixing, add 1 drop of 3 M sulfuric acid followed by 10 drops of 2 M KOH in methanol. Shake vigorously and allow to stand for 5 minutes. Formation of a red-brown precipitate is a positive test; if a blue-green precipitate forms, the test is negative.