Experiment 6
Qualitative Tests for Alcohols, Alcohol Unknown, IR of Unknown

In this experiment you are going to do a series of tests in order to determine whether or not an alcohol is a primary (1°), secondary (2°) or tertiary (3°) alcohol. The tests can also determine whether or not there is a secondary methyl alcohol functionality in the molecule. You will do four chemical tests: (1) Chromic Acid Test (or Jones Oxidation), (2) Ritter Test using potassium permanganate (3) the Lucas Test using $ZnCl_2$ and HCl, and (4) the Iodoform Test.

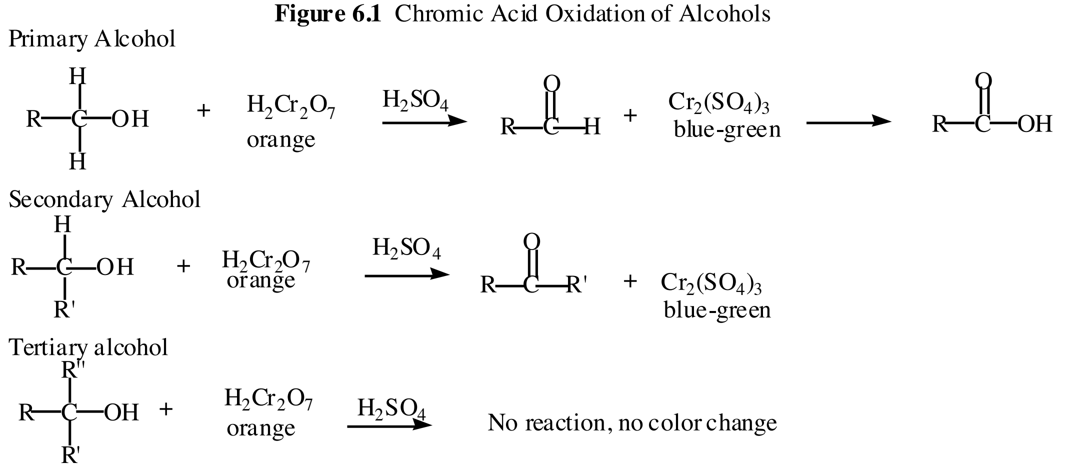
The experiment has three parts, all of which can be done in one laboratory session. First, you will practice all four of the chemical test using known alcohols. You will perform each of the first three tests three times, once with a primary, once with a secondary and once with a tertiary alcohol. The fourth test we will do two times, once with a secondary methyl containing alcohol and once with a not secondary methyl alcohol. The tests on the three known alcohols can be done at the same time. Then you will perform all four chemical tests on your unknown. Finally, you will take an Infrared Spectrum of your unknown. You will identify your unknown alcohol and as many peaks as you can using our IR tables at the back of this manual.
PLEASE RETURN THE REAGENT BOTTLES TO THE CENTRAL BENCH WHEN YOU ARE FINISHED WITH THEM SO THAT OTHERS CAN USE THEM.

Test 1: Chromic Acid Oxidation

This test distinguishes primary and secondary alcohols from tertiary. Chromic acid will oxidize a primary alcohol first to an aldehyde and then to a carboxylic acid and it will oxidize a secondary alcohol to a ketone. Tertiary alcohols do not react. The OH-bearing carbon must have a hydrogen atom attached. Recall, that a carbon is oxidized when it loses a hydrogen or hydrogens or gains a more electronegative atom.

Since the carbon atom is being oxidized in primary and secondary, the orange chromium Cr^{6+} ion is being reduced to the blue-green Cr^{3+} ion. The reactions involved are shown in Figure 6.1.

Figure 6.1 Chromic Acid Oxidation of Alcohols



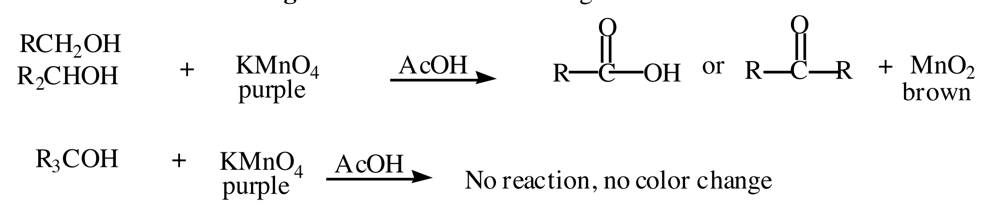
Procedure:

Set-up three small test tubes in your test tube rack. The tubes do not need to be dry. Label the first test tube as a primary alcohol, the next as a secondary alcohol and the third as a tertiary alcohol. Write down in your notebook which alcohols you are going to be using. Add 2 mL of acetone to each test tube and then add 3-4 drops of your test alcohol. Be sure that the drops fall into the acetone and do not remain on the sides of the tube. Add 2 drops of the Chromic Acid Test Reagent (also called the Bordwell-Wellman Reagent). Shake vigorously using a small, tight fitting cork. You should see a color change to a blue or blue-green or similarly colored precipitate within a few seconds to indicate a positive test. Record your results in your notebook.

Test 2: Ritter Test

This test is similar to the Chromic Acid Oxidation and provides the same information. It is the oxidation of primary and secondary alcohols to carboxylic acids and ketones using potassium permanganate ($KMnO_4$). Again, tertiary alcohols cannot be oxidized by this reagent because there is no hydrogen to be lost from the carbon that bears the OH group. In the Ritter Test the Mn^{7+} of $KMnO_4$ (bright purple) is reduced to Mn^{4+}. The Mn^{4+} is brownish in color. The reactions involved are as follows.

Figure 6.2 Potassium Permangante Oxidation



Procedure:

As for the Chromic Acid Oxidation, set-up three small, labeled tests tubes. Add 2 mL acetic acid (CAUTION: Stench!) to each tube. Add 3-4 drops of the test alcohol to each tube and then add **ONE** drop of saturated $KMnO_4$ solution to each test tube. Shake vigorously to mix, using a small cork as before. For the 1° and 2° alcohols you should see a brownish color develop as the purple $KMnO_4$ color disappears. Do not add too much $KMnO_4$. If you add an excess of this reagent, the purple color will persist even though you have a primary or secondary alcohol. With the tertiary alcohol you should see no color change since the purple color remains. Record your observations in your notebook.

Test 3: Lucas Test

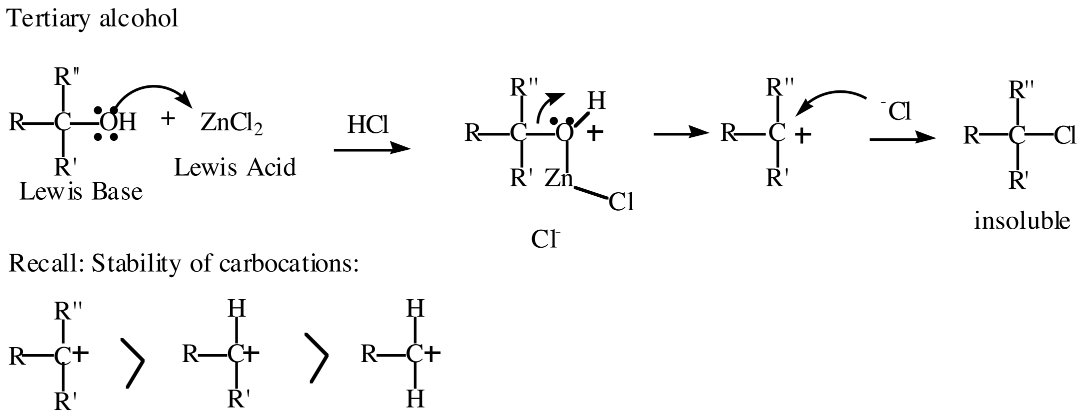
This test distinguishes tertiary, secondary and primary alcohols from each other. It uses zinc chloride as the reagent in concentrated hydrochloric acid (Lucas Reagent). It is based on the rate of formation of insoluble alkyl chloride. An emulsion is formed. This test is reliable only for alcohols that are fairly soluble in water.

Tertiary Alcohols	React immediately to form an emulsion of the alkyl halide and water (cloudy solution).
Secondary Alcohols	React in 5-10 minutes. Heating in warm water and shaking is sometimes necessary with water-insoluble alcohols.
Primary alcohols	These generally take more than one hour to react.

The rate of reaction of the alcohols is determined by the ease of formation of the carbocation intermediate. Tertiary alcohols react quickly because they form a relatively stable tertiary carbocation and secondary alcohols react more slowly because the secondary carbocation is less stabilized than the tertiary carbocation.

The first step, shown below for a tertiary alcohol, involves a Lewis acid- base reaction between zinc chloride and a lone pair of electrons on the alcohol oxygen. In the next step, which is the slow, rate determining step, the HO-ZnCl complex leaves and the carbocation is then attacked by a chloride anion from the HCl solvent to form the insoluble alkyl chloride which forms the cloudy emulsion indicative of a positive test. Again, the overall rate of the reaction is determined by the slow step, which is the breaking of the C-OH-ZnCl bond. This rate is determined by the stability of the carbocation being formed.

Figure 6.3 Lucas Test



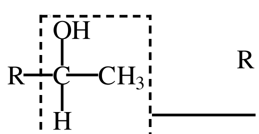
Procedure:

Set-up three small test tubes as above, labeling each of them. Add 0.5 mL of the test alcohol to each test tube. To the first test tube, add 3 mL of the Lucas reagent. Shake vigorously using a small cork to stopper the test tube. Wait at least 10 minutes. If you have a water insoluble alcohol (you see two layers in your test tube) then repeat the experiment using a hot water bath set at 60 °C, immersing the test tube in the water bath immediately after shaking and waiting the 10 minutes with occasional shaking. Also repeat the experiment using a water-soluble alcohol of the appropriate class. Record your results. Repeat on all three classes of alcohol.

Test 4: Iodoform Test

This test is slightly different from the previous three tests. This test does not distinguish 1°, 2°, 3° alcohol but is specific for only one class of alcohol. This is the secondary methyl alcohol. If the alcohol contains a methyl group attached to a carbon that also has a hydrogen and an OH group then it will give a positive iodoform test. The formation of a yellow precipitate indicates a positive test. This is shown in figure 6.4.

Figure 6.4



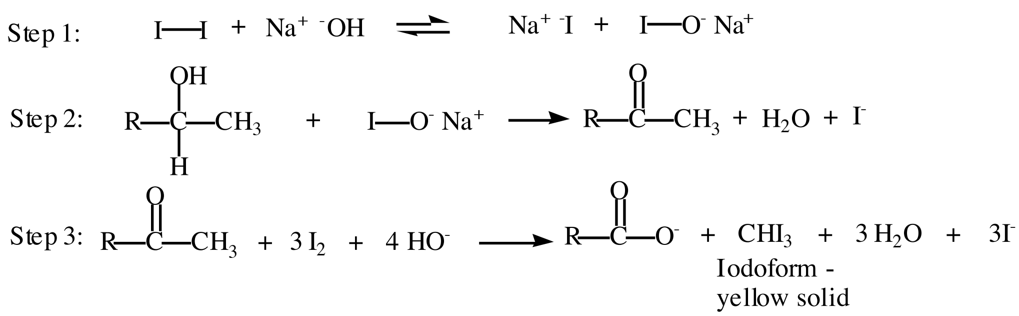
R = H, CH_3, CH_2CH_3, etc

This group must be present in the molecule in order to give a positive iodoform test.

The mechanism of the reaction is somewhat complex (Figure 6.5) and will be studied in detail in the second semester. Only the outline of the mechanism is shown here. Notice that the first step is the formation of the mild oxidizing agent sodium hypoiodite, NaOI, from sodium hydroxide and iodine. NaOI oxidizes the alcohol to a carbonyl in the second step. NaOI is similar to sodium hypochlorite, NaOCl, which is the active ingredient in household bleach. Notice that the oxidation state of the halogen is +1, not the usual –1. In the second step, the alcohol is oxidized to a ketone (loss of two hydrogens) and the oxidation state of the iodine changes from +1 to –1 (gain of 2 electrons). In the third step, which really consists of several individual steps, the methyl ketone is converted to the anion of a carboxylic acid (with one carbon less than the alcohol) and iodoform (yellow precipitate). Only the second and third steps involve oxidation/reduction.

Note that the initial product formed is a methyl ketone derivative and acetone contains this functionality. Acetone therefore gives a positive Iodoform Test. Be sure that your test tube does not contain any traces of acetone.

Figure 6.5 Iodoform Test



Procedure:

We will do the iodoform test only twice with known alcohols, once with an alcohol that contains the methyl secondary alcohol functionality and once with a compound that does not. You will need two medium-sized test tubes. Make sure there is no acetone present in your test tubes. Acetone also gives a positive Iodoform Test.

To each test tube, add 4-5 drops of test alcohol, 2 mL H_2O, 2 mL 10% sodium hydroxide solution. If your alcohol does not fully dissolve, add 1 mL of ethanol.

Add a 10% solution of iodine (I_2) in potassium iodide (KI) dropwise. Keep adding the dark iodine solution with stirring until you see a faint yellow color persisting in the test tube. Note the reaction that is occurring. As you add the I_2 to the NaOH solution, you are forming your sodium hypoiodite reagent. Add enough iodine so that you have a slight excess of iodine as evidenced by a persistent yellow or brownish color.

You should see a yellow precipitate starting to form within five minutes. Sometimes you may need to heat the mixture to 60 °C in a water bath.

Unknown Alcohol

When you have finished all four tests and are confident that you can perform them accurately and can distinguish a positive test from a negative one, then get an unknown alcohol from the teaching assistant. Record your unknown number in your notebook and then repeat all four tests on your unknown. Your goal is to classify it as a primary, secondary or tertiary alcohol.

Record the results of the four tests in your notebook and on your Unknown Report Sheet.

Infrared Spectrum of Your Unknown

Once you have identified your unknown as a 1°, 2°, or 3° alcohol, then you will also take its infra-red spectrum to establish its identity. Place the spectrum in your laboratory notebook and identify as many absorbances as you can using the IR correlation table given at the back of this manual and in the textbook. Positive identification can be made by comparing your spectrum to that of the authentic alcohol. These are given in Appendix 6.2. Another source is of spectra is http://webbook.nist.gov/gov/chemistry. The National Institute of Standards and Technology (NIST) provides gas-phase spectra and the absorbances due to the O-H stretching frequency will be much narrower and at higher wavenumbers (cm^{-1}). Why? The rest of the spectrum will be very similar to that of the liquid phase.

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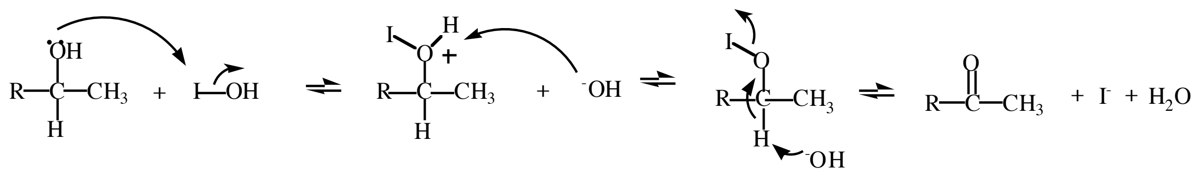
Appendix 6.1: A possible mechanism for hypoiodite oxidation of Alcohols.

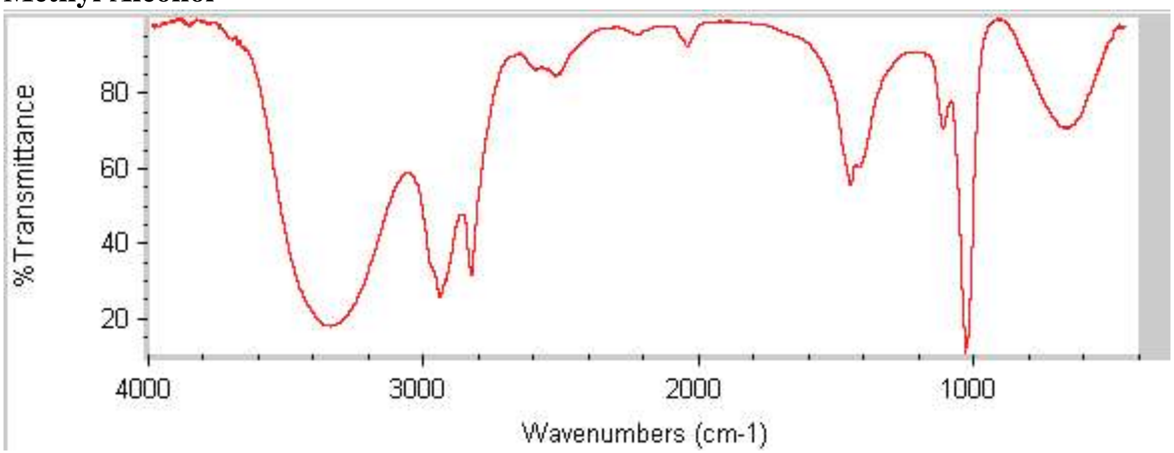
Figure 6.6

$$I{-}I + Na^{+}\,{}^{-}OH \rightleftharpoons Na^{+}\,{}^{-}I + I{-}OH$$

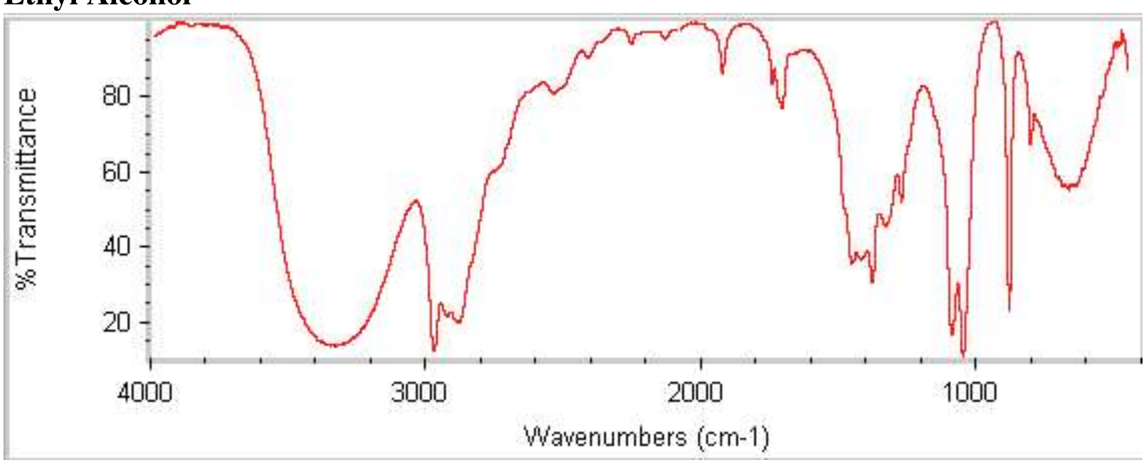


Appendix 6.2 Infrared Spectra of Unknown Alcohols.

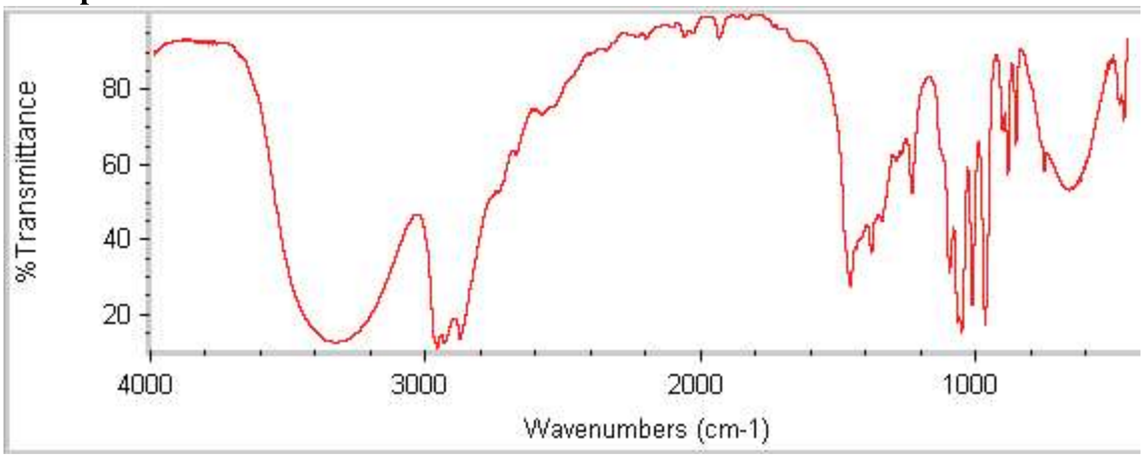
Methyl Alcohol



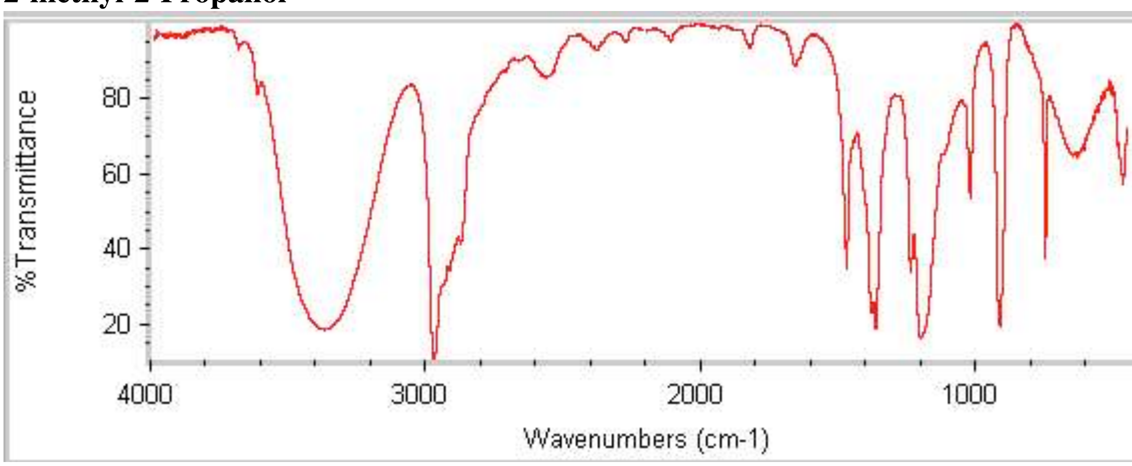
Ethyl Alcohol



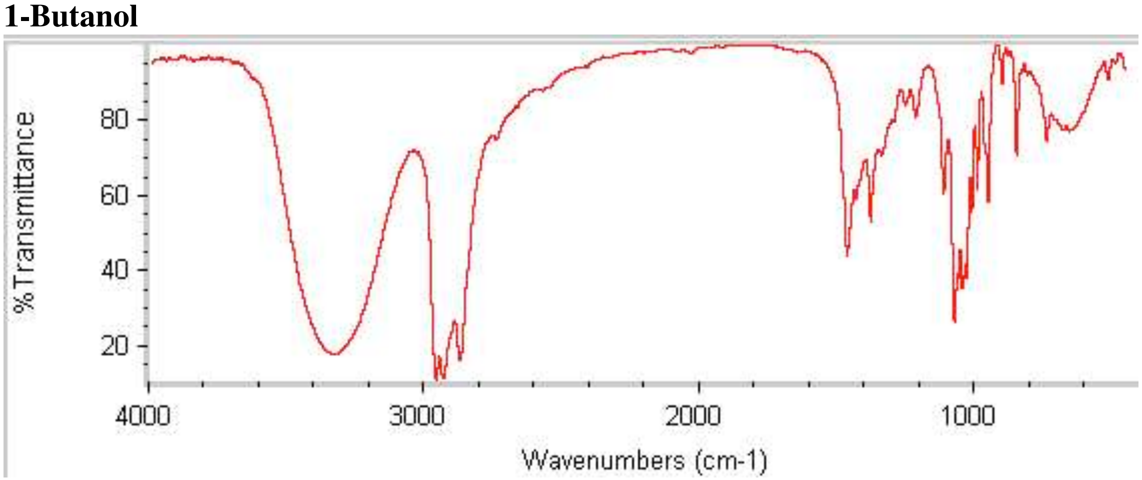
1-Propanol



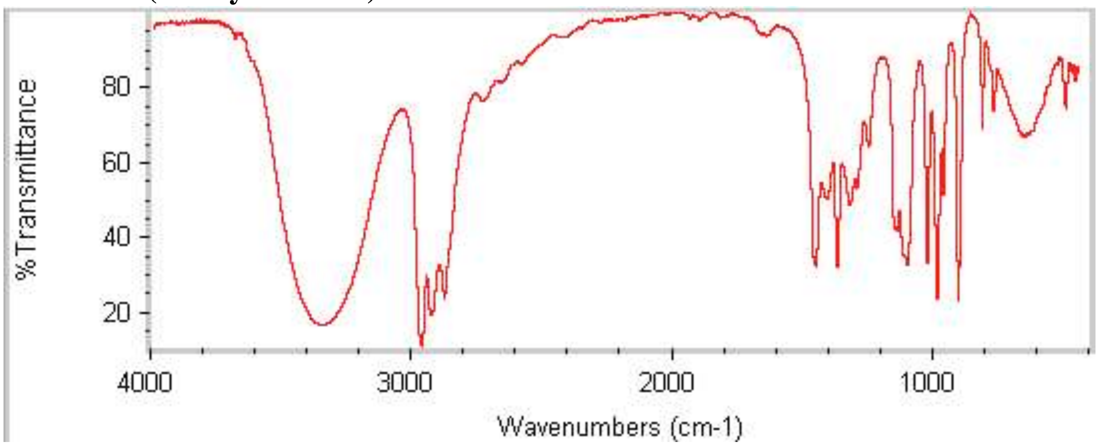
2-methyl-2-Propanol



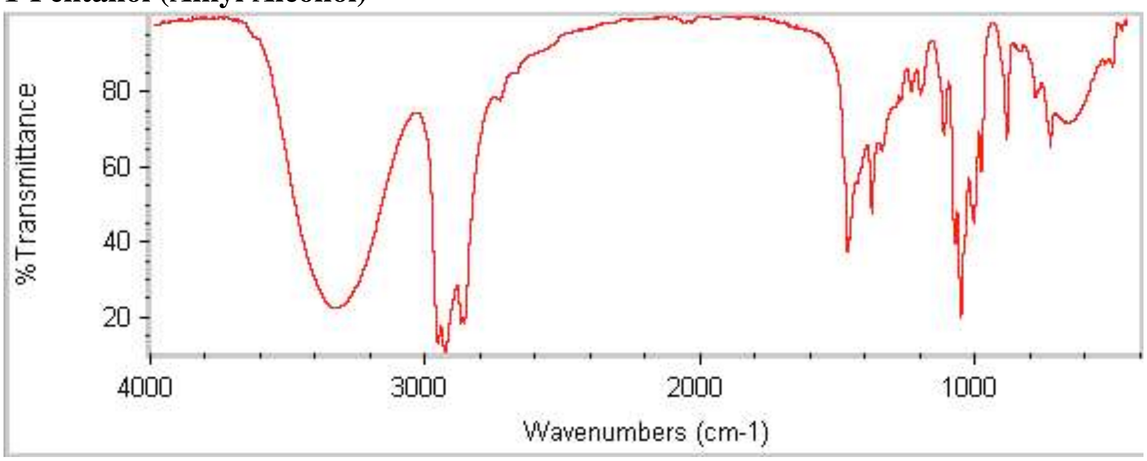
1-Butanol



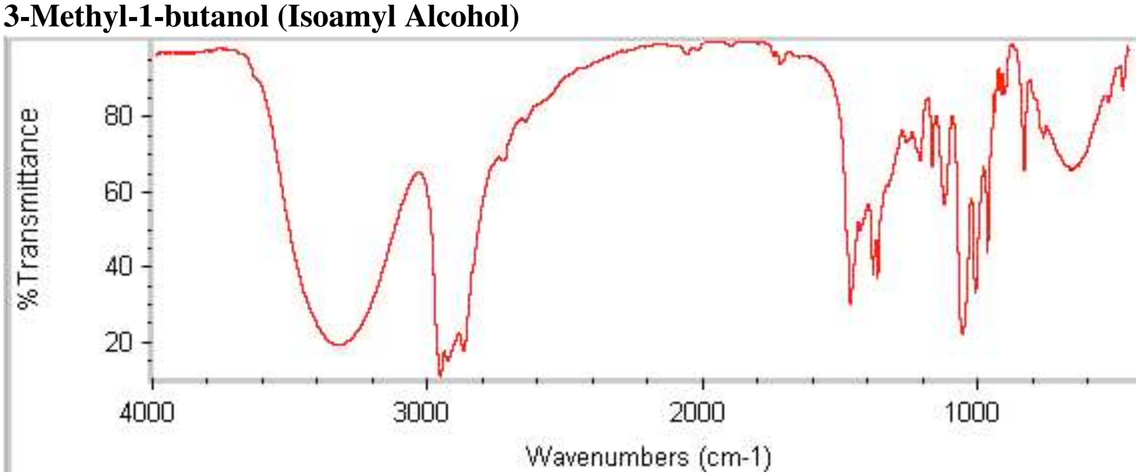
2-Butanol (s-Butyl Alcohol)



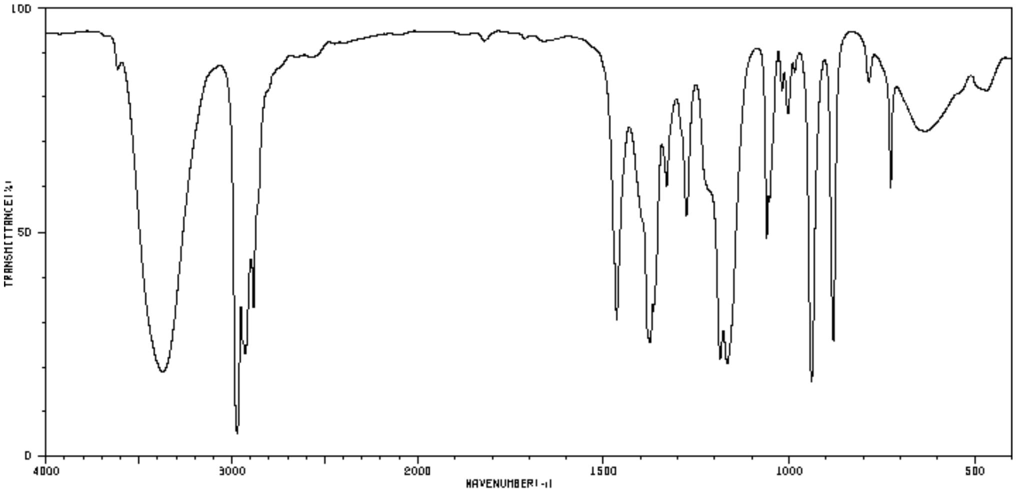
1-Pentanol (Amyl Alcohol)



3-Methyl-1-butanol (Isoamyl Alcohol)



2-Methyl-2-butanol



Cyclohexanol