Identifying an Unknown Compound by Solubility, Functional Group Tests and Spectral Analysis

Purpose Of The Experiment:

Identifying an unknown organic compound through a three-step process involving selective solubility tests, selective functional group tests and spectral analysis.

Background Required:

You should be familiar with techniques for weighing, measuring by volume, and mixing in a test tube, as well as analysis of ^{1}H NMR and ^{13}C NMR spectra.

Background Information:

Organic qualitative analysis is an exercise in spectroscopy. Nuclear magnetic resonance spectroscopy and infrared spectroscopy are the major spectroscopic techniques used by organic chemists. However, much insight can be gained from using simple qualitative tests to determine the identity of unknowns. Structures of unknown compounds can be determined by comparing physical properties, performing functional group tests, and checking melting points of derivatives against those of known compounds reported in the literature. Solubility properties and chemical reactivity become apparent during these qualitative tests.

Spectroscopy has been discussed extensively in the lecture portion of this course.

Organic qualitative analysis involves four types of tests.

1. *Measurement of physical properties* includes determining refractive index, boiling points, melting points, and density.
2. *Solubility tests* can suggest the size and polarity of an unknown compound and the presence of basic or acidic functional groups. A compound's solubility in aqueous acid or base involves ionization of the compound and, therefore, a chemical reaction. The salts produced are water-soluble.
3. *Chemical tests* transform an unknown into a different compound with an accompanying change in appearance. These tests are often called **classification tests** because they identify the possible functional groups present.
4. *Formation of a solid derivative* is a critical step in identifying an unknown. Many compounds have similar physical properties and give similar results in qualitative tests. However, an unknown can undergo reaction to form another compound called a **derivative**. The melting point of the purified derivative allows identification of the unknown.

In this lab we will focus on using Solubility Tests, Chemical Tests and Spectra Analysis to identify two unknown compounds.

Overview:

In this experiment, you will combine both spectroscopy and qualitative tests to identify an unknown organic compound. For this experiment, the possible categories of the unknown are alkane, alkene, alkyl halide, alcohol, phenol, amine, aldehyde, ketone, and carboxylic acid. Each compound will contain only a single type of these functional groups. Each of these functional groups has a unique combination of solubility and reactivity that allows it to be distinguished from the others.

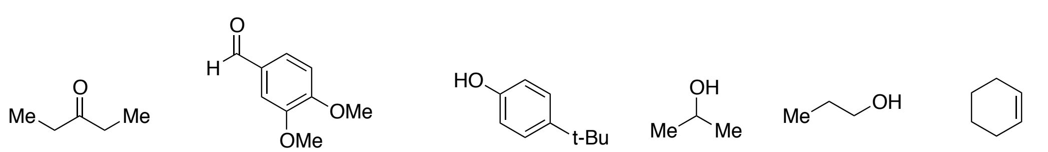
In Part A of the experiment (Week 1), you will use solubility tests to characterize your unknown compound. By comparing the solubility of your unknown in several aqueous solutions (described below), you will be able to limit the possible functional groups on your compound. A flow chart, Figure 2, will help guide you in this effort. In some cases, these tests will be sufficient to identify the functional group(s) of your unknown substance.

In Part B of the lab (Week 2), you will conduct a series of experiments to distinguish between the remaining functional group possibilities to uniquely identify the functional group on your unknown compound. You should note that in most cases, with proper planning and utilization of the information gained in Part 1, only a few functional group tests will be required to uniquely identify the functional group(s) contained within your molecule. You will not need to run all of the chemical tests on each sample. You job is to decide which are needed for each unknown in order to determine its functional group(s). If you are not thoughtful in this process, and try to run all of the tests, you will likely run out of material (see below).

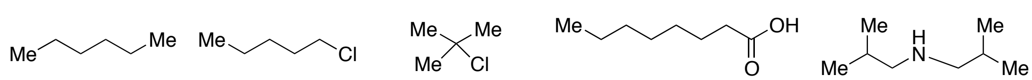
Each group will be given approximately 1 gram of two different unknown samples. You must carefully think about what tests you wish to conduct as not to waste your sample. If you carelessly run too many tests and exhaust your material, you can obtain an additional sample of your unknown from your TA. **Additional sample will cost you 10% of your grade for this lab per additional sample required.** Take-home message: plan your experiments carefully.

For both Part A and Part B, several known compounds will also be available so you can compare your results from your unknown to both known positive and negative tests. Figure 1 lists the known compounds that will be available to you. Tables 1 and 2 outline known substrates for each of the tests.

Figure 1. List of Known Compounds Available For Use As Positive and Negative Standards



3-propanone 3,4-dimethoxybenzaldehyde 4-tert-butylphenol 2-propanol 1-propanol cyclohexene



hexane 1-chloropentane tert-butylchloride octanoic acid diisobuytlamine

In Part C of the lab (take home), once you have correctly identified the functional group present in your unknown compounds, your TA will provide you with the ^{1}H NMR and ^{13}C NMR spectra for your compounds, as well as the compound's molecular formula. From this data, and the results of your experiments above, you will then assign the structure of the unknown and label the spectral data.

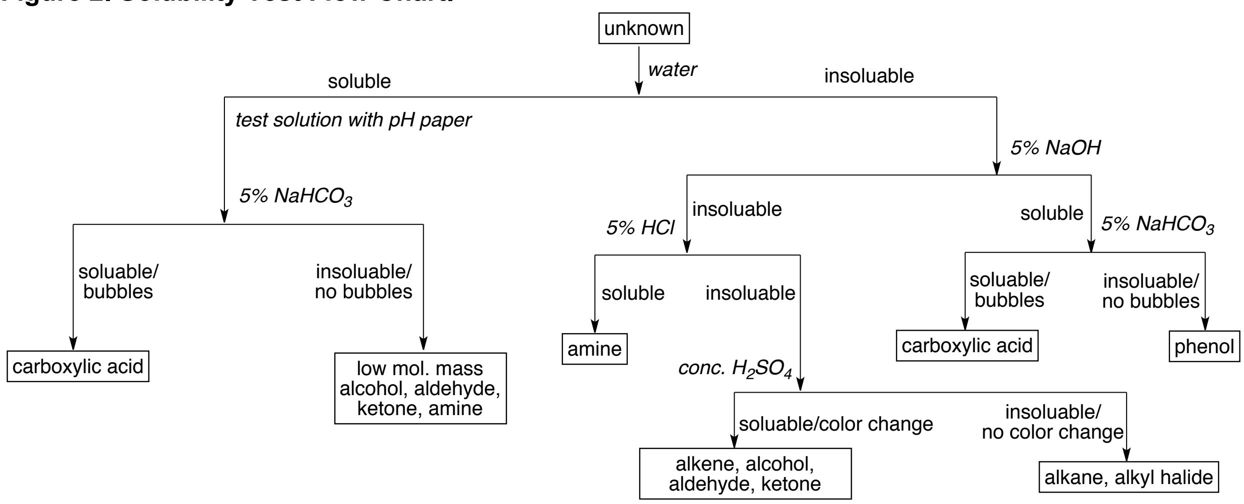
PART A (WEEK 1) - SOLUBILITY TESTS

Organic compounds follow three interdependent rules of solubility:
1. *small organic molecules are more soluble in water than are large organic molecules;*
2. *polar organic molecules, especially those capable of hydrogen bonding, are more soluble in water than are nonpolar molecules; and*
3. *compounds in their ionic forms are more soluble in water than their neutral forms.*

For example, benzoic acid is not soluble in water, yet it is soluble in sodium hydroxide solution and in sodium hydrogen carbonate solution because these bases react with benzoic acid to form the water-soluble benzoate ion. The solubility of carboxylic acids and amines is so characteristic that solubility tests alone differentiate these functional groups from all the others in this experiment.

The solubility flowchart shown in Figure 2 provides the scheme for this experiment. The first test to perform on all unknowns is water solubility.

Figure 2. Solubility Test Flow Chart.



Water

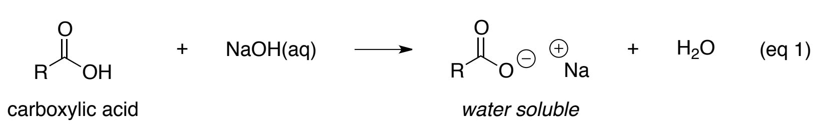
Small, polar organic compounds such as alcohols, aldehydes, ketones, amines, carboxylic acids, and a few phenols are soluble in water. Water-soluble compounds are tested with pH paper to see if they are acidic or basic. A pH of 4 or lower indicates a carboxylic acid. A pH of 8 or higher indicates an amine.

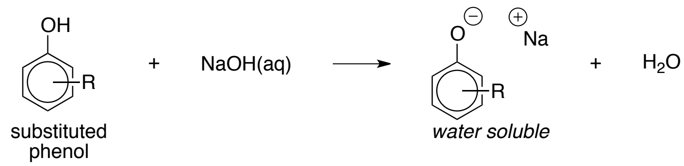
Water-soluble compounds are tested with 5% sodium hydrogen carbonate ($NaHCO_3$) to determine whether or not they are carboxylic acids. Carboxylic acids react with $NaHCO_3$ to produce carbon dioxide bubbles, as shown below in Equation 3.

Large alcohols, aldehydes, ketones, amines, carboxylic acids, and phenols are not soluble in water. Alkanes, alkyl halides, and alkenes are not soluble in water, regardless of their size. These water-insoluble compounds are tested for their solubility in the following reagents.

5% Sodium Hydroxide

Water-insoluble compounds are first tested with 5% sodium hydroxide (NaOH). Sodium hydroxide is a strong base that ionizes strong or weak (Figure 2 *Solubility flowchart*) acids. Thus, both carboxylic acids and phenols are converted to salts and dissolve in aqueous solution. Non-acidic compounds will not dissolve. The reactions of carboxylic acids and phenols are shown in Equations 1 and 2, respectively.





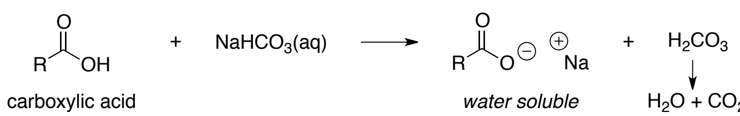
(eq 2)

5% Sodium Hydrogen Carbonate

Water-insoluble compounds that are soluble in 5% NaOH are then tested with 5% sodium hydrogen carbonate ($NaHCO_3$). Strongly acidic compounds such as carboxylic acids react with $NaHCO_3$ to form water-soluble salts, as shown in Equation 3. The reaction also produces bubbles of carbon dioxide (CO_2).

This test is commonly misinterpreted because CO_2 bubbles are tiny. Careful observation is essential.

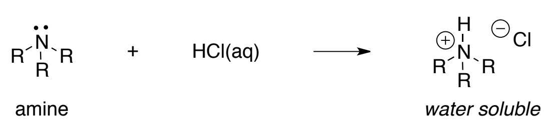
Phenols are less acidic than carboxylic acids and do not react with $NaHCO_3$ to form water-soluble salts. As a result, phenols are insoluble in 5% $NaCHO_3$.



(eq 3)

5% Hydrochloric Acid

Water-insoluble compounds that are insoluble in 5% NaOH are tested with 5% hydrochloric acid (HCl). If a compound is soluble in 5% HCl, it is an amine. Amines are organic bases that react with HCl to form water-soluble amine salts, as shown in Equation 4.



(eq 4)

Concentrated Sulfuric Acid

Water-insoluble compounds that are insoluble in 5% HCl are tested with concentrated sulfuric acid (H_2SO_4). Virtually all organic compounds containing alkene functional groups or oxygen or nitrogen atoms are soluble in concentrated H_2SO_4. These functional groups typically react with H_2SO_4 to form new compounds. Only alkanes, alkyl halides, and some aromatic compounds are insoluble in H_2SO_4.

Table 1 Known Positive And Known Negative Test Compounds For Solubility Tests

solvent	**positive test**	**negative test**
water	isopropanol	3,4-dimethoxybenzaldehyde
5% NaOH	4-tert-butylphenol	3,4-dimethoxybenzaldehyde
5% $NaHCO_3$	octanoic acid	3,4-dimethoxybenzaldehyde
5% HCl	diisobutylamine	3,4-dimethoxybenzaldehyde
H_2SO_4	cyclohexene	hexane

PROCEDURE PART A (WEEK 1)

Preview:

- Perform the water solubility test on the known positive, known negative, and unknown
- Perform subsequent solubility tests
- If the solubility tests point to a carboxylic acid or amine, the classification is complete
- If the solubility tests suggest any other functional groups, you will preform classification tests during week 2 appropriate to those groups until the unknown is narrowed to only one functional group

Equipment:

Microspatula	glass stirring rod
10-mL graduated cylinder	6-10 test tubes, 15 x 125-mm
6-10 test tubes, 10 x 75-mm	test tube rack
pH paper	1.0-mL transfer pipet
Pasteur pipet, with latex bulb	

Solubility Tests:

> **CAUTION—Wear departmentally approved safety goggles at all times while in the chemistry laboratory.**
>
> **Always use caution in the laboratory. Many chemicals are potentially harmful. Follow safety precautions given for all reagents used in this experiment. Prevent contact with your eyes, skin, and clothing. Avoid ingesting any of the reagents.**

Perform all tests in duplicate using an unknown, a known positive, and a known negative. Mix well to make certain that liquid samples are not floating in the meniscus. Allow several minutes for compounds to dissolve. Be patient and observe closely.

Conduct the solubility tests following the pattern shown in Figure 1 above. *Verify your solubility test results with your laboratory instructor before performing the classifications tests in Part 2.* Use clean test tubes for each test.

1. Performing the Water Solubility Test

CAUTION—Unknowns may be flammable, toxic, corrosive, or irritating. Keep away from flames or other heat sources.

Add 1 drops of a liquid sample or about 25 mg of a solid sample to 0.5 mL of distilled or deionized water in a test tube. Tap the tube with your finger to mix or stir gently with a glass stirring rod. Record the sample as soluble or insoluble.

If the unknown is water-soluble, test the solution with pH paper. Also test the pH of water as a control.

A solution at pH 4 of lower suggests a carboxylic acid. A solution at pH 8 or higher suggests an amine.

2. Performing the 5% Sodium Hydroxide Solubility Test

CAUTION—Sodium hydroxide (NaOH) and hydrochloric acid (HCl) are toxic and corrosive.

If your compound is water-soluble, proceed to Part 3.

For water-insoluble compounds, add 1 drops of a liquid sample or about 25 mg of a solid sample to 0.5 mL of 5% NaOH in a test tube. Tap the tube with your finger to mix or stir gently with a glass stirring rod. Record the sample as soluble or insoluble.

To verify that a compound has dissolved, add 5% HCl to the NaOH mixture until the solution is acidic to pH paper. Look for a precipitate, indicating that the water-soluble salt has converted back into the water-insoluble compound.

Solubility in NaOH indicates either the carboxylic acid or phenol.

3. Performing the 5% Sodium Hydrogen Carbonate Solubility Test

a. For Water-Soluble Compounds

Put 1 drops of liquid sample or about 25 mg of solid sample in a dry test tube. Add 0.5 mL of 5% sodium hydrogen carbonate ($NaHCO_3$). Do not stir. Watch for bubbles at the interface of the phases. Then tap the tube with your finger to mix or stir gently with a glass stirring rod. Record the sample as soluble or insoluble.

Generation of bubbles and solubility indicates a carboxylic acid. Solubility without generation of bubbles indicates a low molar mass alcohol, aldehyde, ketone, or amine. Conduct classification tests to determine which functional group is present.

CAUTION—Diethyl ether (ether) is highly flammable and toxic. Keep away from flames or other heat sources. Use a *fume hood*.

If no bubbles were observed, put 1 drop of liquid sample or about 25 mg of solid sample in a dry test tube. Using a ***fume hood***, add about 0.5 mL of ether. Then immediately add 0.5 mL of 5% $NaHCO_3$. Observe whether or not bubbles are generated at the ether-water interface.

Generation of bubbles indicate a carboxylic acid.

b. For Water-Insoluble Compounds

Put 1 drop of liquid sample or about 25 mg of solid sample in a dry test tube. Add 0.5 mL of 5% sodium hydrogen carbonate ($NaHCO_3$). Do not stir. Watch for bubbles at the interface of the phases. Then tap the tube with your finger to mix or stir gently with a glass stirring rod. Record the sample as soluble or insoluble.

Generation of bubbles or solubility indicates a carboxylic acid.

If the compound is not soluble in $NaHCO_3$ but is soluble in NaOH, it is likely a phenol. Confirm the presence of phenol with a phenol classification test.

4. Performing the 5% Hydrochloric Acid Solubility Test

CAUTION—Hydrochloric acid (HCl) is toxic and corrosive.

For compounds insoluble in water and insoluble in 5% NaOH, add 1 drop of a liquid sample or about 25 mg of a solid sample to 0.5 mL of 5% HCl in a test tube. Tap the tube with your finger to mix or stir gently with a glass stirring rod. Record the sample as soluble or insoluble.

If the compound is soluble in 5% HCl, it is most likely an amine.

5. Performing Concentrated Sulfuric Acid Solubility Test

CAUTION—Concentrated sulfuric acid (H_2SO_4) is toxic and oxidizing. Use a *fume hood* when working with H_2SO_4.

If the compound is insoluble in 5% HCl and 5% NaOH, add 1 drop of a liquid sample or about 25 mg of a solid sample to 0.5 mL of concentrated sulfuric acid (H_2SO_4) in a dry test tube. Tap the tube with your finger to mix or stir gently with a glass stirring rod. Do not use a metal spatula.

Record the sample as soluble or insoluble. Interpret a color change or a precipitate as soluble.

If the compound is soluble in H_2SO_4, the sample is an alkene, an alcohol, an aldehyde, or a ketone. Conduct classification tests for each compound type.

If the compound is insoluble in H_2SO_4, the sample is an alkane or an alkyl halide. Conduct classification tests for alkyl halides.

If alkyl halide tests are negative, the compound is an alkane.

Based upon the positive and negative results from the above experiments you should now be able to narrow the possibilities for the functional group(s) present in your unknown sample. You should now carefully decide which experiments are needed during Part B (Week 2) to distinguish those possibilities.

PART B (WEEK 2) - CLASSIFICATION TESTS

Solubility tests (Week 1) alone can indicate whether an unknown compound in this experiment is a carboxylic acid, a phenol, or an amine. The other functional groups must be identified or verified by classification tests.

Classification tests are based on the chemical reactivity characteristic of particular functional groups. The results are intended to be visual and obvious, such as a color change, formation of a precipitate, or evolution of bubbles. Sometimes the results are difficult to interpret or are borderline between positive and negative.

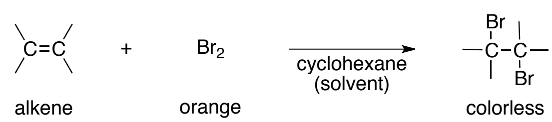
There are two inviolable rules when performing classification tests. First, perform the test exactly as described. If the procedure says add 3 drops, do not add 4 or 5. Second, always perform tests in duplicate. Perform the test on a known compound that will result in a positive test (**known positive**); perform the test on a known compound that will result in a negative test (**known negative**); and perform the test on the unknown compound. This direct visual comparison of the results of testing the unknown against a known positive test and a known negative test confirms that the reagents are good and you are performing the test properly.

No classification test is always accurate in every case. A compound may produce a **false positive** if the test is positive even though the compound giving the test *is not* of the expected type. For example, some phenols give a positive test for aldehydes. A **false negative** occurs if the test is negative even though the compound undergoing the test *is* the expected type. For example, less reactive aldehydes or very insoluble aldehydes may fail to give a positive test for aldehydes.

The following classification tests are performed in this experiment and are among those tests commonly performed in qualitative organic analysis.

Bromine in Cyclohexane

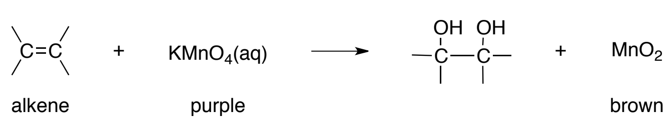
Alkenes react with bromine (Br_2) in cyclohexane, an orange solution, to produce colorless vicinal dibromides, as shown in Equation 5. This test is commonly used for water-insoluble compounds. Alkenes with strong electron-withdrawing groups may fail to react. Phenols, phenyl ethers, and some aldehydes and ketones also react to decolorize bromine in cyclohexane.



(eq 5)

Potassium Permanganate

Alkenes are oxidized to diols by dilute potassium permanganate ($KMnO_4$), as shown in Equation 6. The purple color of $KMnO_4$ disappears and is replaced by the brown color of manganese dioxide (MnO_2). Because $KMnO_4$ is a strong oxidizing agent, aldehydes, some primary and secondary alcohols, phenols, and aromatic amines can also react.



(eq 6)

Silver Nitrate in Ethanol

Alkyl halides react with silver nitrate ($AgNO_3$) in ethanol by the S_N1 mechanism. Tertiary, allylic, and benzylic halides give an immediate precipitate at room temperature, as shown in Equation 7. Secondary halides require several minutes to give a precipitate, primary halides require hours.

$$\underset{\text{alkyl halide}}{R{-}X} + AgNO_3 + HOEt \longrightarrow R{-}OEt + HNO_3 + \underset{\textit{precipitate}}{AgX(s)} \qquad \text{(eq 7)}$$

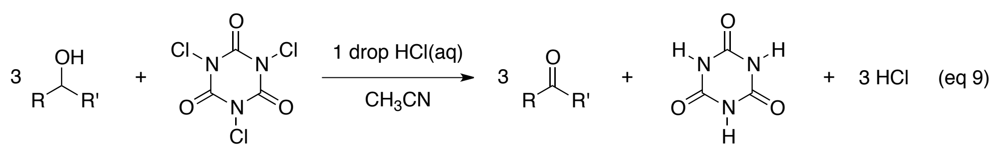
Sodium Iodine in Acetone

A saturated solution of sodium iodide (NaI) in acetone reacts rapidly with primary, allylic, and benzylic chlorides or bromides by the S_N2 mechanism. Secondary halides react slowly, while tertiary halides are unreactive. The corresponding alkyl iodides and a precipitate of sodium chloride or sodium bromide result, as shown in Equation 8.

$$\underset{X = Br,\ Cl}{R{-}X} + NaI \xrightarrow[\text{acetone}]{} R{-}I + \underset{\textit{precipitate}}{NaX(s)} \qquad \text{(eq 8)}$$

TCICA Test

In acid solution, 1,3,5-trichloroisocyanuric acid (TCICA) slowly releases chlorine, which is an oxidizing agent. The reaction is rapid in the presence of an oxidizable compound such as a primary of secondary alcohol, as shown in Equation 9. The produce is isocyanuric acid, which is very soluble in water but precipitates from the solvent acetonitrile. The time it takes for isocyanuric acid precipitate to appear is characteristic of the type of alcohol. Secondary alcohols react fastest, within 15-30 seconds; primary alcohols produce a precipitate usually within 3-7 minutes, although some can take up to 20 minutes; tertiary alcohols are not oxidizable at room temperature and produce no precipitate within an hour.



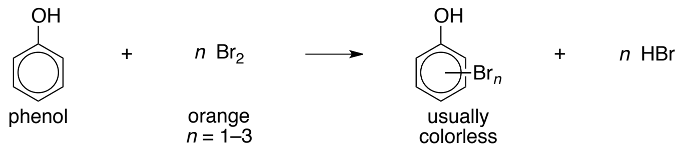
primary or secondary alcohol — TCICA — aldehyde or ketone — isocyanuric acid *(precipitate)*

Iron(III) Chloride

Many phenols react with iron(III) chloride ($FeCl_3$) solution to give brightly colored complexes. Many of these complexes are short-lived; the color may fade soon after it forms. Some phenols may not react at all, so a negative iron(III) chloride test is inconclusive. Aldehydes or ketones with significant enolic character can also give colored complexes with $FeCl_3$.

Bromine in Water

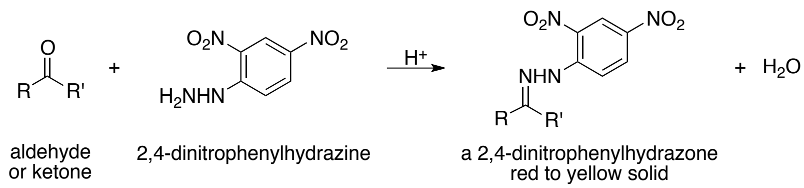
Phenols are activated toward electrophilic aromatic substitution and react with Br_2 in the absence of catalyst, as shown in Equation 10. The disappearance of the bromine color, and often the appearance of a precipitate of the brominated phenol, constitute a positive test. Other activated aromatic compounds, such as phenyl ethers and anilines, can also react with Br_2.



(eq 10)

2,4-Dinitrophenylhydrazine

Aldehydes and ketones rapidly form yellow, orange, or red precipitates with 2,4-dinitrophenylhydrazine (DNP) reagent, as shown in Equation 11.



(eq 11)

Schiff Test

In a complex series of reactions that is not completely understood, Schiff reagent reacts only with aldehydes to produce a purple fuchia solution. A faint pink color results from the initial reaction and does not constitute a positive test. The Schiff test is the most sensitive rest for aldehydes. However, the Schiff test is subject to giving false positives and false negatives.

Table 2 Known Positive And Negative Test For Functional Group Classification Tests

		compound	
functional group	test	positive test	negative test
alkane	by exclusion—alkanes are insoluble in aqueous reagents and in H_2SO_4, and are negative for alkyl halide tests		
alkene	bromine/cyclohexane	cyclohexene	hexane
	$KMnO_4$	cyclohexene	hexane
alkylhalide	$AgNO_3$/ethanol	2-chloro-2-methylpropane	2-propanol
	NaI/acetone	1-chlorobutane	2-propanol
alcohol	TCICA test	2-propanol	2-chloro-2-methylpropane
phenol (to confirm)	$FeCl_3$	4-tertbutylphenol	1-propanol
	bromine/H_2O	4-tertbutylphenol	2-propanol
amine	soluble in HCl—this group is determined by the series of solubility tests: if water soluble, solution is basic to pH paper; if water is insoluble, then soluble in HCl		
aldehyde	2,4-DNP	3,4-dimethoxybenzaldehyde	1-propanol
	Schiff test	3,4-dimethoxybenzaldehyde	1-propanol
ketone	2,4-DNP	3-propanone	1-propanol
carboxylic acid	soluble in NaOH and in $NaHCO_3$—this group is determined by the series of solubility tests: if water-soluble, solution is acidic to pH paper; if water-insoluble, then soluble in NaOH and soluble in $NaHCO_3$ with gas evolution		

Preview:

- Based on the data you collected in Week 1 of the lab, you should have decided which experiments you need to conduct to distinguish the functional groups present in your unknown compound.
- In this experiment, you will identify two unknowns by functional groups using solubility tests and classification tests. Table 2 list known positive and known negative compounds for classification tests.
- Note: You should not run all of the experiments listed below on each unknown sample. You must use the solubility data from Week 1 to decided which tests are nessary for your compounds.

Equipment

250-mL beaker	microspatula
glass stirring rod	6-10 test tubes, 15 x 125-mm
10-mL graduated cylinder	6-10 test tubes, 10 x 75-mm
hot plate	test tube rack
pH paper	thermometer, -10 to 260°C
1.0-mL transfer pipet	tongs
Pasteur pipet, with latex bulb	

Procedure Week 2. Performing the Bromine in Cyclohexane Test for Alkenes

CAUTION—Bromine (Br_2) is toxic and oxidizing. It causes severe burns. Always use a *fume hood* when working with Br_2. Acetone and cyclohexane are flammable and irritating. Keep away from flames or other heat sources.

Place 1 mL of cyclohexane in a small test tube. Add 3 drops of Br_2/H_2O. Mix until the bromine color appears in the top cyclohexane layer.

For liquid samples, add 2 drops of sample to the Br_2/H_2O. Tap the tube with your finger to mix or stir gently with a glass stirring rod. Note and record whether or not the orange color disappears.

For solid samples, place 30 mg of solid into a test tube. Add 5 drops of acetone. Add the acetone solution to the Br_2/H_2O. Tap the tube with your finger to mix or stir gently with a glass stirring rod. Note and record whether or not the orange color disappears.

If the orange color disappears quickly, the sample may be an alkene.

NOTE: Phenols, phenyl ethers, and some aldehydes and ketones may test positive.

Performing the Potassium Permanganate Test for Alkenes

CAUTION—1% Potassium permanganate ($KMnO_4$) is corrosive and oxidizing.

If your sample is water-soluble, place 1-2 mL of water into a small test tube. If your sample is water-insoluble, place 1-2 mL of 95% ethanol into a small test tube.

Add 2 drops of a liquid sample or about 30 mg of a solid sample. Add 2 drops of 1% $KMnO_4$. Tap the tube with your finger to mix or stir gently with a glass stirring rod. Let the mixture stand 10-20 s. Note and record whether or not the purple color disappears.

If the purple color disappears and a brown color or precipitate appears, the compound may be an alkene.

Note: The brown color or precipitate may not appear. Aldehydes, some primary and secondary alcohols, phenols, and aromatic amines may test positive.

Performing the Silver Nitrate in Ethanol Test for 2° and 3° Alkyl Halides

CAUTION—Silver nitrate ($AgNO_3$) in ethanol is flammable, toxic, and oxidizing. It also stains the skin. Keep away from flames or other heat sources.

Place 1 mL of 2% $AgNO_3$ in ethanol into a small test tube.

For liquid samples, add 2 drops of sample to the 2% $AgNO_3$. Tap the tube with your finger to mix or stir gently with a glass stirring rod.

For solid samples, place 30 mg of solid into a test tube. Add 5 drops of ethanol. Add this ethanol solution to the 2% $AgNO_3$ in ethanol. Tap the tube with your finger to mix or stir gently with a glass stirring rod. Note and record whether or not a precipitate forms.

An immediate precipitate indicates a tertiary, allylic, or benzylic halide.

Performing the Sodium Iodide in Acetone Test for 1° and 2° Alkyl Halides

CAUTION—Sodium iodide (NaI) in acetone is flammable and irritating. Keep away from flames or other heat sources.

Place *exactly* 1.0 mL of NaI in acetone into a small test tube. Add 3 drops of a liquid sample. Tap the tube with your finger to mix or stir gently with a glass stirring rod. Allow the tube to stand 3-6 min at room temperature. Note and record whether or not a precipitate forms.

A white precipitate indicates a primary, allylic, or benzylic halide.

Performing the TCICA Test for Alcohols

CAUTION—1,2,5-trichloroisocyanuric acid (TCICA) is corrosive and oxidizing. Acetonitrile is toxic. 5% Hydrochloric acid (HCl) is toxic and corrosive.

Place 0.5 mL of the TCICA test solution into a small test tube. Add 1 drop of 5% HCl. Tap the tube with your finger to mix or stir gently with a glass stirring rod.

For liquid samples, add 1 drop of the sample. Tap the tube with your finger to mix or stir gently with a glass stirring rod.

For solid samples, dissolve about 20 mg of solid in 1-2 drops of acetonitrile. Add this solution to the TCICA/HCl solution.

Note and record whether or not a precipitate forms.

The formation of a precipitate within one min indicates a secondary alcohol; the formation of a precipitate between 3-20 min indicates a primary alcohol.

Performing the Iron(III) Chloride Test for Phenols

CAUTION—Iron(III) chloride ($FeCl_3$) is toxic and corrosive. Ethanol is flammable and toxic. Keep away from flames or other heat sources.

Place 1 mL of 95% ethanol into a small test tube. Add 2 drops of a liquid sample or about 30 mg of a solid. Add 3-5 drops of 3% $FeCl_3$. Tap the tube with your finger to mix or stir gently with a glass stirring rod. Note and record any formation of a brightly colored solution.

The presence of bright color, even briefly, indicates a phenol.

NOTE: Some aldehydes or ketones also give colored complexes with $FeCl_3$.

Performing the Bromine in Water Test for Phenols

CAUTION—Bromine (Br_2) is toxic and oxidizing. It causes severe burns. Always use a *fume hood* when working with Br_2. Ethanol is flammable. Keep away from flames or other heat sources.

Place 1 mL of 95% ethanol into a small test tube. Add 5 drops of a liquid sample or about 30 mg of a solid.

Add a drop of water. Tap the tube with your finger to mix or stir gently with a glass stirring rod.
Add 1 drop of Br_2/H_2O. Tap the tube with your finger to mix or stir gently with a glass stirring rod.
Note and record whether or not the orange color disappears.
The disappearance of the orange color indicates a phenol.

Performing the 2,4-DNP Test for Aldehydes and Ketones

CAUTION—2,4-Dinitrophenylhydrazine (2,4-DNP) solution is corrosive and irritating. It stains skin and clothing.

For liquid samples, place 1 drop of sample into a clean, dry test tube. Add up to 20 drops of 2,4-DNP solution. Tap the tube with your finger to mix or stir gently with a glass stirring rod.
For solid samples, add about 30 mg of solid into a clean, dry test tube. Add 0.5 mL of ethanol. Tap the tube with your finger to mix or stir gently with a glass stirring rod. If the unknown does not dissolve, prepare a warm-water bath by placing 175-200 mL of tap water into a 250-mL beaker. Use a hot plate to heat the water to 40°C. Place the test tube into a warm-water bath and swirl the tube until the unknown is dissolved. Cool the solution to room temperature. Add up to 20 drops of 2,4-DNP solution. Tap the tube with your finger to mix or stir gently with a glass stirring rod.

Note and record whether or not a precipitate forms.
An immediate, brightly colored precipitate indicates an aldehyde or ketone.

Preforming the Schiff Test for Aldehydes.

CAUTION – Schiff solution contains pararosaniline hydrochloride, sodium hydrogen sulfite, and HCl. Schiff solution is toxic, irritation and a suspected carcinogen.

Add 1 drop of a liquid sample or about 15 mg of a solid sample a clean, dry test tube. Place 2 mL of

Schiff solution in a test tube. Mix well. After 5 min, mote the color of the solution and record your observation.

A fuchsia color indicates an aldehyde.

Cleaning Up And Getting the Spectra

Once you believe you have identified the functional groups present in your unknown, check with your TA to see if you have determined them correctly.

After your TA has confirmed your assignment, you should clean-up your work area and rinse any remaining unknown compound into the organic waste using acetone. DO NOT PUT YOUR UNKNOWN INTO THE WASTE UNTIL YOU HAVE CLEARED IT WITH YOUR TA. If you have misassigned your functional groups and disposed of your unknown, you will be penialized to obtain an additional sample.
Thoroughly rise the vials you unknowns came in, and them present them to your TA for inspection. Once your TA is satisfied that you have cleaned-up properly, they will give you the spectra so you can complete Part 3 of the lab.

Wash your hands with soap or detergent before leaving the laboratory.

Part C. Using Spectra To Identify Your Unknown Compound.

In Parts A and B, you used solubility and chemical reactivity test to identify the functional group(s) contained within your unknown compound. Using these results in conjunction with molecular formula and the spectra data that you have received, please fully identify the unknown compound. Assign the ^{1}H and ^{13}C NMR spectra completely.

In your lab report, please state the identity of each of your unknown compounds along with the unknown number. Discuss the relevance of the solubility and chemical tests to this structural assignment.

Pre-Laboratory Assignment

1. What risks do you run by not performing the qualitative tests in duplicate?

2. (a) Why is it important to have clean test tubes before running a test?
   (b) Before which tests should acetone *not* be used to clean the test tubes?

3. Why is water solubility the first test to run?

4. Why run solubility tests before running the functional group classification tests?

5. Determine the functional group present in these unknown:
   (a) Unknown A is soluble in water and gives bubbles with5% $NaHCO_3$.
   (b) Unknown B is insoluble in water, insoluble in 5% NaOH, but soluble in 5% HCl.
   (c) Unknown C is insoluble in water, insoluble in 5% NaOH, insoluble in 5% HCl, soluble with a color change in conc. H_2SO_4, and decolorizes both $KMnO_4$ (aq) and bromine in cyclohexane.
   (d) Unknown D is soluble in water, does not produce bubbles with 5% $NaHCO_3$, gives a precipitate with 2,4-DNP, and gives a fuchsia color with the Schiff test.

6. In each of the following cases, describe the *next* test you would perform.
   (a) Unknown X is insoluble in water, 5% NaOH, 5% HCl, and conc. H_2SO_4.

   (b) Unknown Y is insoluble in water, soluble in 5% NaOH, and insoluble in 5% $NaHCO_3$.

   (c) Unknown Z is insoluble in water, insoluble in 5% NaOH, insoluble in 5% HCl, and soluble in conc. H_2SO_4.

7. If your unknown is soluble in water and does not produce bubbles with 5% $NaHCO_3$, what steps would you follow to determine if your unknown is an amine?

Post-Laboratory Questions

1. Record the solubility results for each unknown that you tested. Describe your observations and briefly explain your conclusions.
2. Record the results of the classification tests that you conducted for each unknown you tested. Describe your observations and briefly explain your conclusions.
3. For each of your unknowns, list the functional group to which it belongs next to its identification code.
4. You suspect that your unknown contains halogen, so you perform the silver nitrate in ethanol test and the sodium iodide in acetone test, both of which are negative. Do these results prove that your compound does not contain a halogen? Briefly explain.