VIRTUAL EXPERIMENT 4: WHAT'S IN THE WATER?

OBJECTIVE: To identify unknown compounds detected in a drinking water sample supplied by contaminated surface water using spectroscopic techniques.

BACKGROUND:

Surface waters are commonly used to supply drinking water for communities both locally and globally. Surface water can contain a number of contaminants and, as a result, requires treatment to make the water safe to drink. In this experiment, a surface water sample that feeds into the drinking water supply has been shown to contain a number of contaminants. These contaminants remained present in detectable quantities following treatment and have been isolated and some of them have been analyzed using Infrared (IR) spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopy. You will use IR and NMR spectrophotometers to obtain spectra for the remaining unknowns. The IR and NMR spectra of each unknown compound will then need to be analyzed and the compounds identified.

Both IR and NMR spectroscopy measures the amount of electromagnetic radiation that is absorbed by a sample. The methods differ, however, in the frequency of electromagnetic radiation utilized. Remember the hydrogen atom absorption line spectrum? In that case, light was absorbed by the hydrogen atom and an electron was promoted to a higher energy level. IR and NMR work on similar principles, but with the following differences. In IR the absorption of a photon in the infrared region leads to an increase in the energy of a molecular vibration (electrons are not affected). In NMR the absorption of a photon in the radio frequency region leads to excitation of a hydrogen nucleus (the proton). In general, the more complex the molecule the more vibrations and H atoms it will have and the more absorption peaks it will have in both the IR and NMR spectra. For the purposes of our experiment NMR spectroscopy will yield two major pieces of information about H containing molecules: (1) how many different kinds of H atoms are present, and (2) the relative numbers of each type of H atom. The absorption peaks of chemically different H atoms will appear at different frequencies in the radio frequency region (the units of frequencies in this case are ppm). The area of each peak is directly proportional to the number of hydrogens of that type. There is one complicating factor in that a peak is sometimes split up into several smaller peaks in approximately the same position. We shall ignore the reason for this but will be careful to add up the areas of all the little peaks to get the ***total area*** for each type of proton. Representative NMR spectra for some sample molecules are shown in Figures 4.1 through 4.3. You should examine them carefully. Look at each structure and determine the number of different hydrogens and the number of hydrogens of each type; correlate this information with the observed spectrum. The most difficult problem at first is determining which hydrogens are chemically the same. The key is to visualize the structure (or actually make a model); if different hydrogen atoms have ***exactly*** the same environment, i.e. the same number and type of surrounding atoms, then they are equivalent.

Infrared spectroscopy is most useful in determining if certain groups (called functional groups) with characteristic vibrations are either present (if an absorption peak is present) or absent (no peak is present). Typical functional groups are C-H, C=O, or O-H and each one of these groups absorbs a different frequency of IR radiation. (Note: the unit of frequency employed in IR is the reciprocal centimeter, cm^{-1}.) Table 4.1 lists some functional groups and their associated IR absorption ranges.

You should know it is possible for two different functional groups to absorb in the same region of the IR. The presence of a peak is, therefore, somewhat ambiguous, especially in the 600 to 1500 cm^{-1} region in that it does not mean that a certain functional group is actually present in the molecule.

However, absence of a peak is conclusive evidence that a certain functional group is not present in the molecule. Figures 4.1 through 4.3 have the IR spectra included as well as the NMR spectra, so look at them and use Table 4.1 to see if you can pick out some peaks that are present because of functional groups that are present in each molecule. Also, look for functional groups in Table 4.1 that are **not** present in the molecule. Does the corresponding region in the IR appear absent of peaks?

Table 4.1: Characteristic IR Absorption Peaks.

Functional Groups		Range of Absorptions (cm^{-1})
O-H		3500 to 3100 (broad, strong)
C-H	H on benzene ring	3150 to 3000
C-H	H on singly bonded carbon	3010 to 2800
C=O		1750 to 1650 (strong)
C-Cl		850 to 600 (strong)
C-Br		650 to 550 (strong)

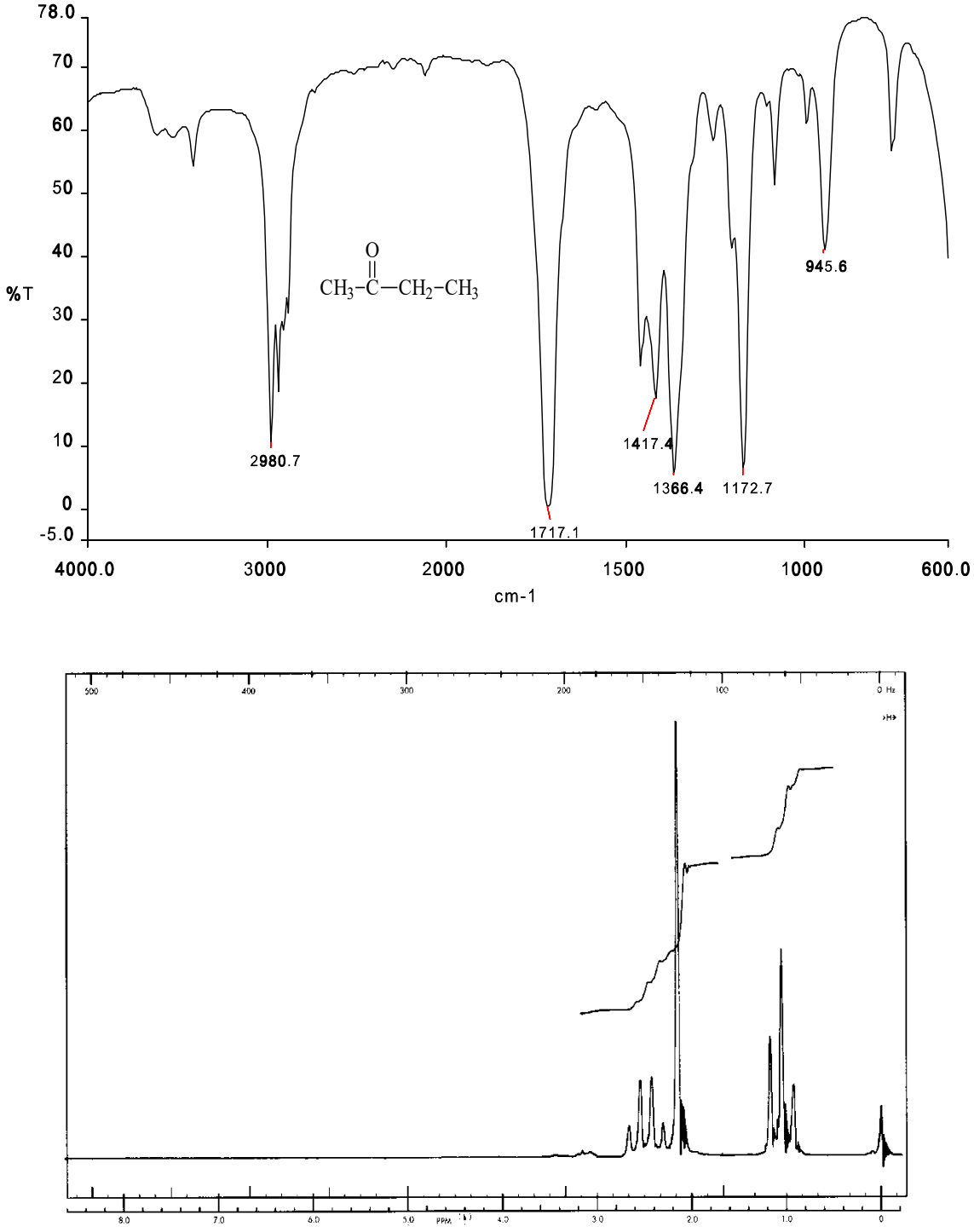


Figure 4.1: IR (top) and NMR (bottom) Spectra of 2-Butanone

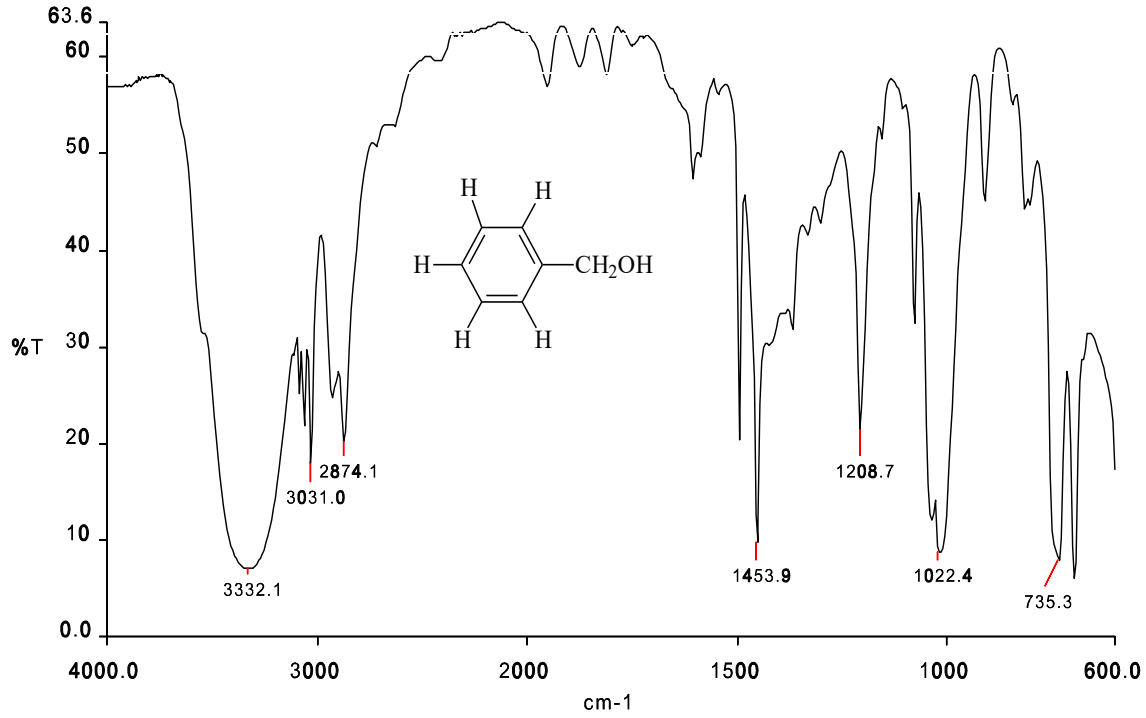


Figure 4.2: IR Spectrum of Benzyl Alcohol

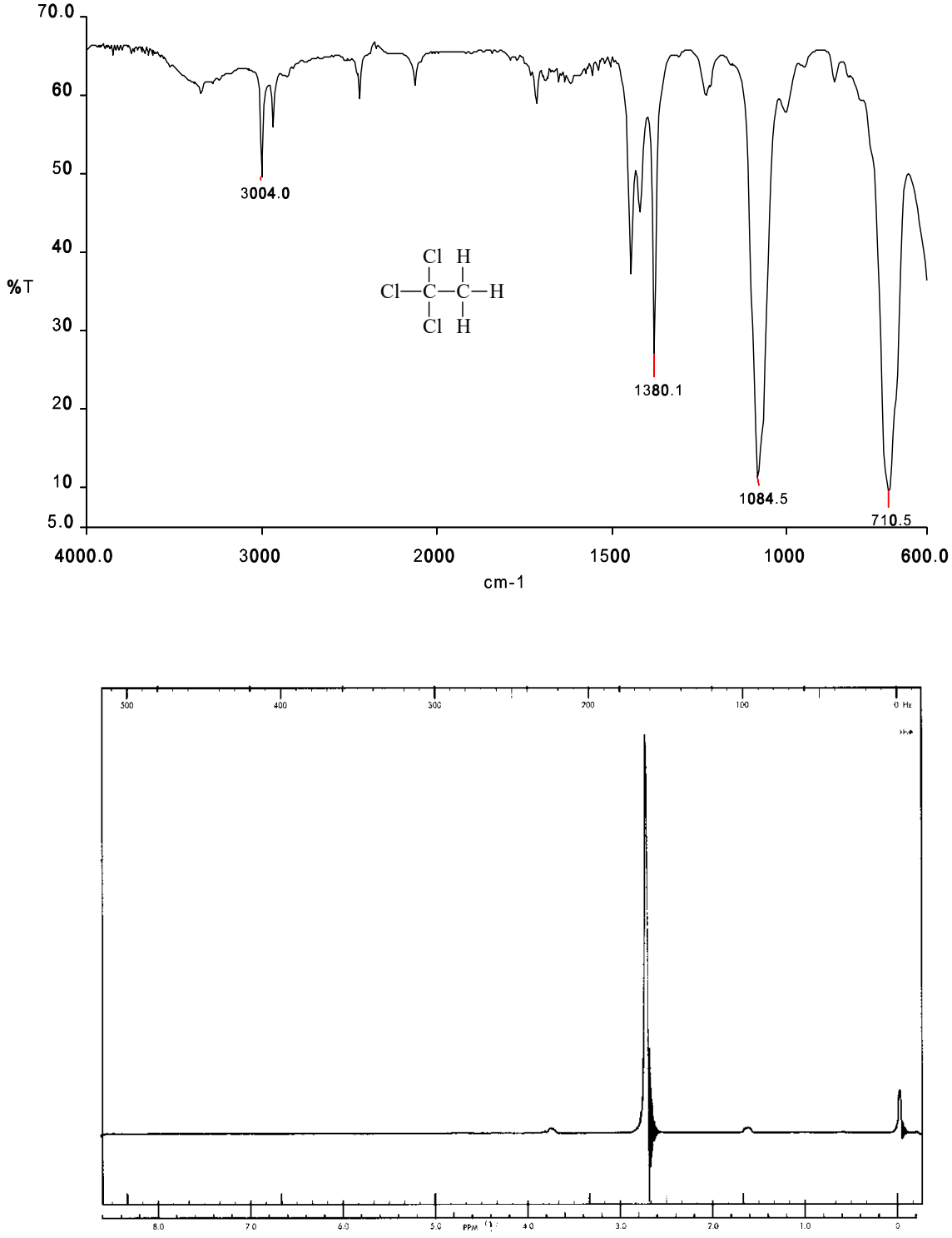
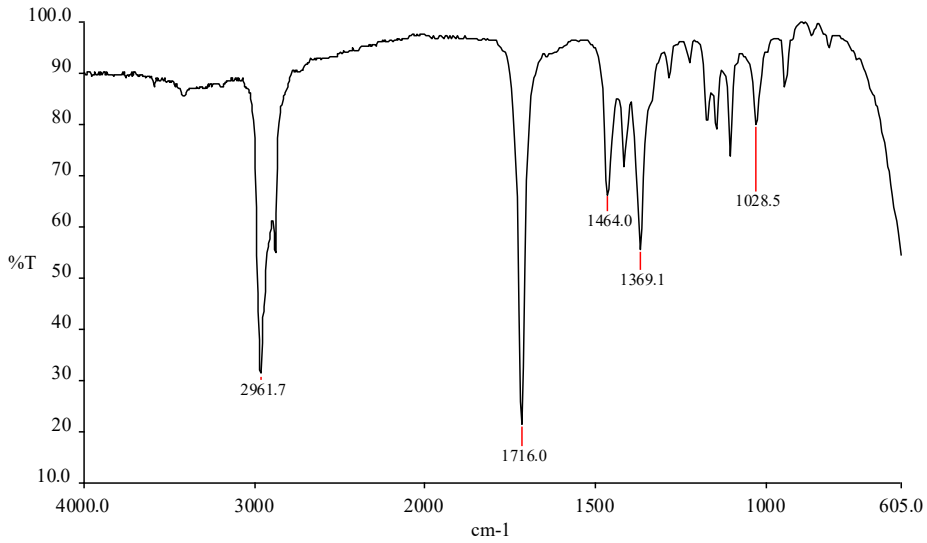


Figure 4.3: IR (top) and NMR (bottom) Spectra of 1,1,1-Trichloroethane

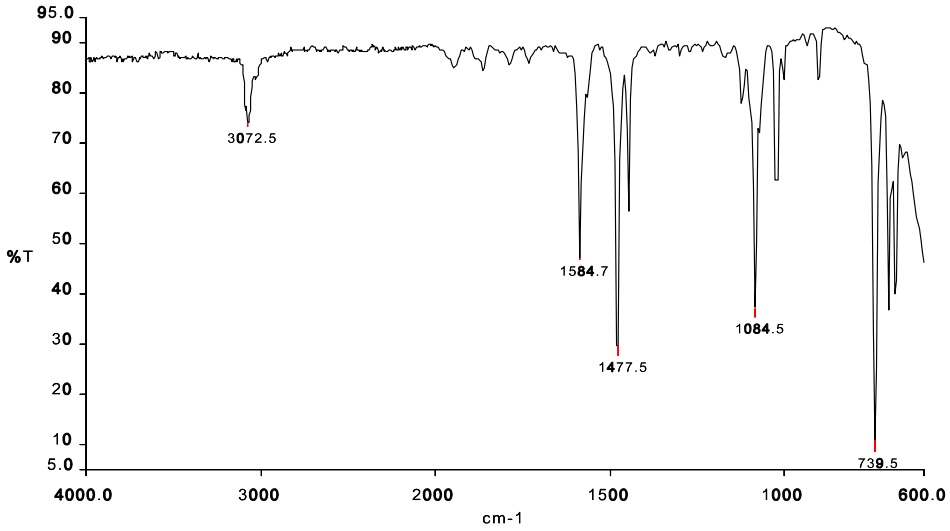
PRELAB ASSIGNMENT:

1. For the two IR spectra below place a check mark in the blanks provided if the functional group indicated may be present.

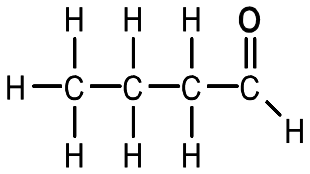
a) O-H _____ C=O _____ C-Cl _____ C-H _____ C-H(benzene) _____

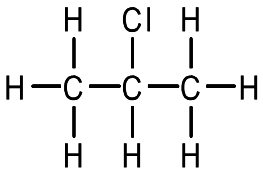


b) O-H _____ C=O _____ C-Cl _____ C-H _____ C-H(benzene)_____



2. How many different hydrogens does each of the following molecules have? What ratio of the area of the peaks would you predict?





PROCEDURE:

The instructor(s) will demonstrate the use of the instruments and help you to obtain the spectra of one liquid unknown. In addition, you will be given the IR and NMR spectra of the other unknown compounds for a total of three unknown compounds detected in a drinking water sample supplied by contaminated surface waters. The possible compounds and their structures are given in Figure 4.4 below. Your three unknowns could be any combination of them.

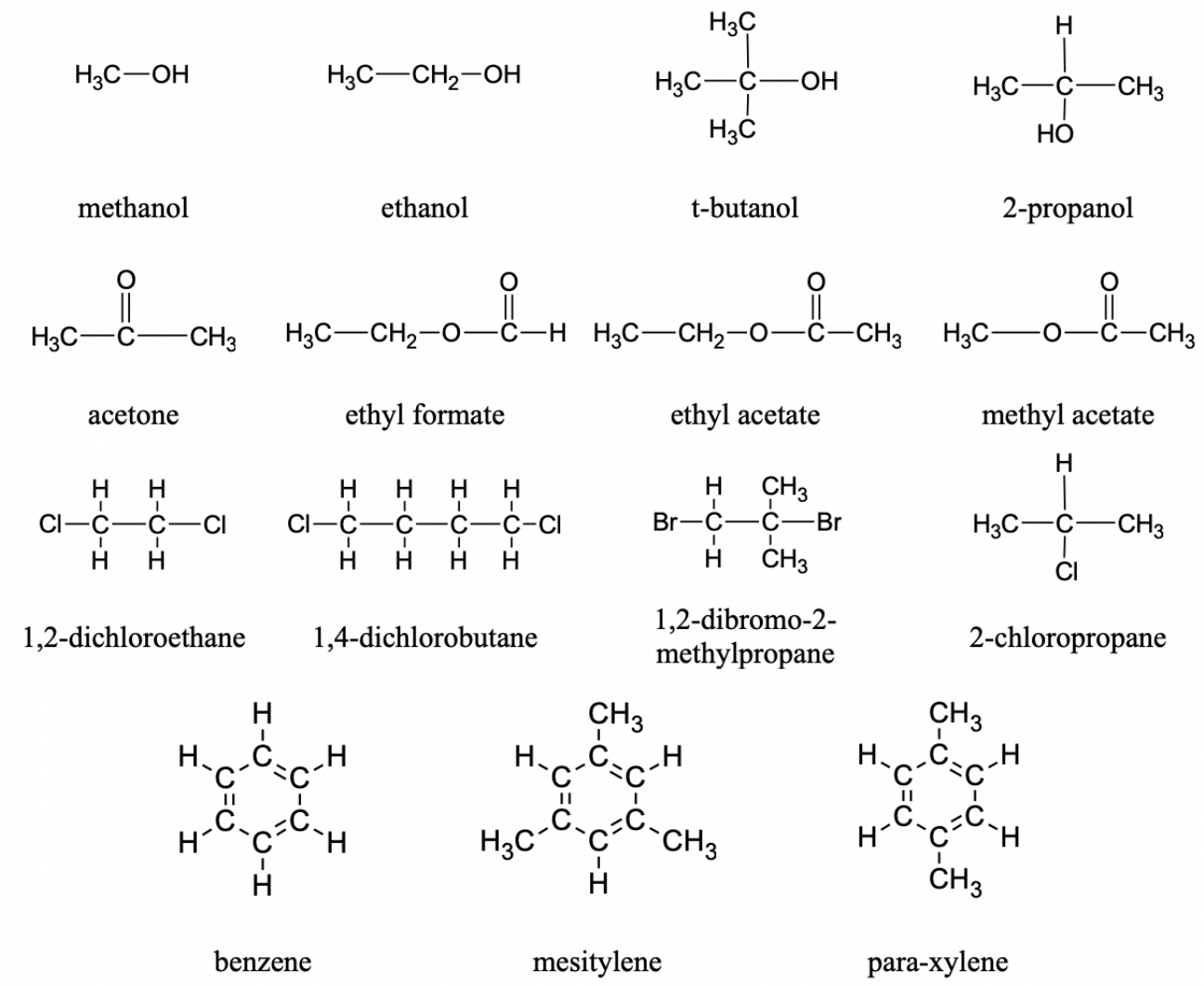


Figure 4.4: Possible Compounds for the Identification of Unknowns

RESULTS WORKSHEET

NOTE: The following results tables will be available in D2L for use in submission of the formal report for this experiment. Remember that all tables and figures within your report must have both a number and a descriptive title.

Table 4.2: Infrared Spectroscopy

Predict the appearance of the IR spectra of the compounds in Figure 4.4 by filling in the following table. Indicate the presence of a functional group by marking the box; leave the box empty if the group is not present.

Molecule	**Functional Groups**					
	O-H	**C-H (benzene ring)**	**C-H (singly bonded carbon)**	**C=O**	**C-Cl**	**C-Br**
methanol						
ethanol						
t-butanol						
2-propanol						
acetone						
ethyl formate						
ethyl acetate						
methyl acetate						
1,2-dichloroethane						
1,4-dichlorobutane						
1,2-dibromo-2-methylpropane						
2-chloropropane						
benzene						
mesitylene						
para-xylene						

Table 4.3: Nuclear Magnetic Resonance (NMR) Spectroscopy

Predict the NMR spectrum for each of the compounds in Figure 4.4 by filling in the following table.

Molecule	Number of Peaks	Ratio of Areas
methanol		
ethanol		
t-butanol		
2-propanol		
acetone		
ethyl formate		
ethyl acetate		
methyl acetate		
1,2-dichloroethane		
1,4-dichlorobutane		
1,2-dibromo-2-methylpropane		
2-chloropropane		
benzene		
mesitylene		
para-xylene		

Table 4.5: NMR Spectra of Unknown Compounds

Tabulate the number of peaks and the relative areas for the NMR spectrum of each unknown compound. When you are measuring the areas of the NMR peaks (also called the *integrations*), measure carefully and be aware that **these numbers are not perfect**; you can expect up to 10 % error in them.

#	Sample ID	Number of Peaks	Ratio of Areas
1			
2			
3			

Table 4.4: Infrared Spectra of Unknown Compounds
Analyze the spectrum of each unknown compound. If there is a peak present in the spectrum of the unknown compound that corresponds to one of the functional groups listed below, report it by marking the appropriate box. You may want to use a ? to indicate the groups that may possibly be present.

From Table 4.1, remember O-H peaks must be strong and broad, C=O peaks must be strong, etc. There are many other functional groups that absorb in the C-Cl and C-Br regions, so those peaks are relatively weak evidence.

#	Sample ID	Functional Groups					
		O-H	C-H (benzene ring)	C-H (singly bonded carbon)	C=O	C-Cl	C-Br
1							
2							
3							

1. **Identification of unknowns:** Use the information from the tables above to identify your unknowns. Remember to weigh which evidence is strongest when making your determinations.

#	Sample ID	Most likely compound	Other possibilities?
1			
2			
3			

2. **In a few sentences or bullet points each, briefly explain how you identified each unknown:**

Worksheet: Either type or print and write in your results on pages 9-11. Use your phone camera or a phone scanner app to take legible pictures of your completed worksheet pages (9-11). Upload these in a Word doc or PDF (not .jpg or .heic) to the D2L dropbox folder.

See the instruction below for completing the formal lab report for this lab.

DATA ANALYSIS:

1. Correlate the data in results tables 4.4 and 4.5, based on the IR and NMR spectra of your unknown compounds, with the data in results tables 4.2 and 4.3 which were produced by predicting the IR and NMR spectra of possible compounds.

2. Identify your three unknown compounds.

3. Incorporate the spectra of your unknowns as figures in your formal lab report. **Number the tables and figures in your report as they appear in your report, not as they appear in the lab manual.**

DISCUSSION:

1. **Provide a full explanation** of how you determined the identity of each unknown compound, citing specific examples from your results. In particular, is there any ambiguity or uncertainty in the identification of an unknown? (i.e. Were you able to narrow it to two or three compounds but no further?). Be sure to cite specific evidence from your data tables and figures (spectra) to facilitate your discussion.

2. Briefly discuss the implications of the presence of each of the compounds that you identified in the drinking water supply and any potential human health effects.

3. Briefly discuss the implications of the presence of each of the compounds that you identified in the surface waters and any potential environmental effects.