

CHEMISTRY 268H. Identification of Unknowns - 2. (rev 2/08)

Finish working on the first unknown if necessary and begin working on the second unknown during this week. You will be given two lab periods (you may use the last day of lab if necessary) in which to work on the second unknown. This experiment requires considerably more planning than was done for the previous experiment. Help to keep the stink down – see “Waste Disposal”.

Solubility tests for this experiment are essential – these must be done before trying to do any classification tests. The solubility behavior of the sample will direct you to a smaller number of possible functional groups and thus save you much time and effort. If you get to a point in the solubility tree that requires knowing whether N or S is present, ask your TA. Because you will not do the sodium fusion test you will not test for these elements. As with all of these tests, do them carefully and make careful observations. Misinterpretation can lead you down the wrong path.

Unknown 2. Treat all unknowns as if they are toxic. Keep them out of you and off of you. Review the previous handout. The second unknown will be an alcohol, aldehyde, alkene, amide, amine, carboxylic acid, ester, or ketone and will be listed in the tables in the reference, "CRC Handbook of Tables for Organic Compound Identification, 3rd Ed" (not in the tables in Williamson). This handbook is available for use in the Organic Lab. Please do not write in the book.

Purity of the sample. Most unknowns should be reasonably pure. For solids, MP is a sensitive test of purity. If a solid unknown has more than a 2° MP range consider it to be impure. If a sample is just slightly impure you can probably carry out the tests without interference from the small amount of impurity. The MP however will be a key part of the identification, so recrystallization would be in order in such a case. For a liquid, determine the bp and carry out the tests assuming that the sample is pure enough. If problems arise in interpreting the data, a GC can be run afterward to assess purity and a distillation done to purify the sample. This is time-consuming so do it only as a last resort (if a distillation is done it must be done in a hood – consult your instructor before proceeding.)

Strategy. The same general approach used in identifying the first unknown should be used for the second as well, the main difference being the addition of complete solubility tests.

Classification tests to be used for the second unknown include those for the first unknown plus the following: for alkenes, bromine in methylene chloride, and potassium permanganate; for carboxylic acids, litmus test; for esters, alkaline iron(III) hydroxamate; for unsubstituted amides, hydroxamic acid test, p. 772 (large handout, Chapter 70 from previous edition) and for substituted amides, hydrolysis and characterization of the amine and acid (this test is time consuming and should be done only if necessary) - note that the test for anilides will not be done; for amines, the Hinsberg test, p. 589-590. Derivatives for the second unknown include the following: for alcohols, 3,5-dinitrobenzoates and phenylurethanes; for aldehydes and ketones, 2,4-dinitrophenylhydrazones and semicarbazones; for alkenes, no derivatives; for carboxylic acids, p-toluidides, anilides, and amides; for esters and amides, no derivatives; for amines, benzamides, acetamides (no picrates). Note that for some compound types,

derivatives are not easily obtained. Esters and amides can be hydrolyzed and their components derivatized, but this is difficult and time consuming. If you have no derivative easily available to you, you must determine your other physical constants (e.g., mp, bp, density of unknown) and do the chemical tests especially carefully. **WARNING:** some derivatizing reagents are highly energetic and will react vigorously under certain conditions. For example, a carboxylic acid chloride may react violently with water and alcohols. When working with these and other compounds of unknown reactivity, be especially careful. If aqueous solutions for example are added to a reagent which can react violently with water, add the solution dropwise to the cooled solution, with swirling between each addition. Never point the reaction tube toward anyone. Note that occasionally a particular derivative may not work or the derivative may be an oil instead of a solid. In that case make the other derivative. If more information is needed it may be helpful to make both.

A Note on Semicarbazone Derivatives: Sometimes, a semicarbazone forms immediately, even before addition of pyridine, and thus can be confused for unreacted unknown. The temptation in such a case is to add methanol until the solid dissolves to produce a clear solution as described in the book. In no case should you add more than 0.5 mL of methanol. In some other cases, the semicarbazones do not crystallize well. Try the usual methods - scratching, cooling, letting it stand for a long time. If it still does not crystallize, try saturating the hot solution with a little warm water or try running the reaction again, this time using less methanol. If all else fails, try this alternate method: For HOH sol unk, add 3 drops unk to 0.4 mL reagent and 0.1 g sodium acetate. Mix well, heat, cool to crystallize. For HOH insol unk, dissolve 3 drops of unk in 0.7 mL ethanol, add HOH dropwise to produce cloudiness, add 0.4 mL reagent and 0.1 g sodium acetate, heat, and cool to crystallize.

IR spectroscopy. Take good care of the salt plates. They are fragile and are easily etched by samples contaminated by water. Clean the salt plates after use and return them to their containers. Do not just leave them in the instrument. As good practice, you should clean them before use as well. Assuming that the previous person cleaned them is a bad assumption. Dichloromethane should be used to clean the plates in the hood. At no time should water or water-containing solvents come into contact with the plates. Liquids are taken as a thin film between NaCl plates. Solids are taken as a fluorolube mull.

NMR spectroscopy. Once you have narrowed the identity of the 2nd unknown down to a few possibilities or less, you will either run an NMR or be given a copy of the NMR spectrum.

Warnings: (1) Acetone is a ketone. If glassware is contaminated with acetone, you will get false positive results for ketones and methyl ketones. (2) Some unknowns may contain two functional groups. (3) The Beilstein test is very sensitive. Impurities can give a positive test. Interpret its results with care.

SAFETY: As is true with any laboratory chemicals, the reagents and unknowns in this experiment should be considered to be toxic and should not be inhaled or allowed to come into contact with the skin. Remember that many organic chemicals pass quickly through the skin to cause systemic poisoning.

WASTE DISPOSAL: Be sure to place wastes in the proper containers. By now you should be able to determine the appropriate waste containers for each type of waste that you generate. The following containers will be available: Nonhalogenated Liquid Waste (nonhalogenated organic solvents and solutions), Halogenated Liquid Waste (any liquid containing halogenated compounds or solvents - Iodoform Test waste, acid chloride wastes), Acidic Waste (2,4-DNP Test waste - H₃PO₄, waste from thionyl chloride tests), Solid Waste. Do not dispose of pipets contaminated with unknowns or reagents directly in the glass waste box - rinse them with a little acetone first, then leave them in the hood in the container labeled as such.

CLEAN-UP: Reminder. As always, do not leave chemical spills unattended. Leaving spills puts your fellow students and the lab personnel at risk. Clean up balance and hood areas immediately after using them. Cap all reagent bottles after use. Dispose of glass in the glass waste containers only.

General comments on chromatography: There is no need to use chromatography unless you suspect that the sample is impure. For solids, MP is a much more sensitive indication of purity than is TLC. For liquids, GC is more informative than BP. Whenever using chromatography, much care must be used in the interpretation of results. In TLC or GC what does one peak in the chromatogram signify? It is tempting to assume that this means that the sample is pure but this would be an incorrect assumption. It means that there is at least one component in the sample. Under a given set of chromatography conditions, an impurity or several impurities may have the same retention time or R_f value as the principle compound. Why then even bother with chromatography? Because seeing more than one peak certainly indicates that the sample is impure. Also, if the chromatogram is run under several different sets of conditions and still shows only one peak in all cases, it can be more definitely, although still not with complete certainty, assumed that the compound is pure. For example if a sample shows one peak under three very different GC conditions (different column material, temp, column length) it can be pretty safely assumed that the compound is pure. If chromatography is used in this experiment to determine or confirm the purity of an unknown, interpret the results carefully and do not make erroneous assumptions.

Gas chromatography can be used to analyze only compounds which are volatile (high vapor pressure, easily evaporated, usually liquids) enough and stable enough at the column temperature used. As a rule, use a column temperature as low as possible that will give reasonable retention times. If too high a temperature is used all components will pass through the column quickly and with the same retention time (on top of one another). If you decide that GC would be helpful, consult with the instructor.