

QUALITATIVE ANALYSIS (EXPERIMENT 54)

The purpose of this experiment is fairly straightforward: you will be issued two unknown substances. The first is called the “chemical unknown” which, as the name implies, you will identify by chemical tests given in chapter 54 of PLKE and IR spectroscopy only. The other unknown is called the “spectroscopy unknown” that you will identify by using NMR, IR and mass spectroscopy without any chemical tests. Since you are doing all of these tests strictly to identify the identities of the two unknowns without regard to yield or other quantitative considerations, the whole process is called “qualitative analysis”, which is something that a lot of environmental and forensic chemistry labs do.

The “chemical unknown” may be an alcohol, aldehyde, amine, carboxylic acid, ester, ketone, or phenol. This unknown may also contain one or more "secondary" functional groups, such as a nitro group, aromatic rings or halogen. It is also *possible* for your unknown to contain **more than one** primary functional group, e.g., a ketone *and* a phenol.

The “spectroscopy unknown” may be an alcohol, aldehyde, amine, carboxylic acid, ester, ketone, phenol, halide, aromatic or ether. It *may* also contain *two* of these groups. You will simply obtain IR, NMR and mass spectra of your sample using the instruments in the instrument room. Your instructor will teach you how to use the mass spectrometer at a later date.

You will work on finding the identity of your two unknowns over the next five lab periods (from April 25 to May 9). During the last three “qualitative analysis” lab sessions, you will also work on experiment 64 (Michael and aldol condensation reactions).

On the first day of this experiment, you will perform the following tests, so that you will have a chance to familiarize yourself with some of the different functional group classification tests using known compounds. Once this is done you can start analyzing your unknowns.

PLKE chapter reference	Test name	Samples to be tested
54B	Beilstein	Benzoic acid and bromobenzene
54D	2,4- dinitrophenylhydrazine (2,4-DNP)	Acetone and ethanol
54D	Chromic acid	Ethanol, butraldehyde and acetone
54A	Solubility	4-nitrobenzoic acid and vanillin (use 1M HCl, 5% NaHCO ₃ and 1M NaOH as the solvents)

There should be a total of 13 tests.

• **Pre-lab:**

Read: This handout, and the parts of PLKE experiment 54 mentioned in the write-up below. The "Identification of Unknowns" contains much of the information you will need to identify your unknowns. Eventually, you should also read PLKE Appendix 2 on the preparation of derivatives.

Prepare for class on Wednesday, April 25: The overall "Purpose" and, specifically for the known compounds tests (the table above), the "Materials and methods" section, which should contain the structure of all reagents and "known" compounds to be tested. A table format would be good. For each test you should also state what a positive test would look like. Below the table, write the *chemical equation* of the 2,4-DNP test (you do not need the chemical equation for the others). You do **not** have to have a procedure written for each test.

• **During lab:**

As you do the experiments record all experimental results in your notebook — write down what you *observe*, **not just** that it was a positive or negative test.

IDENTIFICATION OF THE CHEMICAL UNKNOWN

Where to start:

On day 1, begin your analysis by determining the physical properties of the unknown. For boiling point determination, it is recommended that you try the semi-microscale direct method (reflux method) as described in section 13.2 (p. 695) of PLKE. To monitor the temperature, use the temperature probe with the LabPro interface and laptop.

Then expand into using chemical tests; classification as described in PLKE 54A should enable you to narrow down the list of possible functional groups for your unknown (see the helpful diagram on p. 455 of PLKE but **ignore the sulfuric acid section**).

Safety issue: For the Beilstein and ignition tests remember to use flames only in the hood and away from flammable organic solvents).

Finally, the infrared spectrum will provide important evidence for the presence of various functional groups. You should assign as many of the significant peaks as possible but do not attempt to identify all the peaks in your spectrum.

Note that for the chemical unknown you can take an IR but you cannot run an NMR or mass spec of this compound!

Give your completed preliminary report to your instructor. The instructor will indicate in a timely fashion any results that you should re-check before proceeding.

Once you have completed the preliminary report, you will begin with the identification proper. The "Identification Report" form is included in this handout.

It may be helpful to consult the Merck Index for additional information that might help you to identify your unknown.

Using the information you have gathered from the preliminary tests, solubility tests and the IR spectrum, classification tests should be selected from procedures 54B through 54I, as appropriate for the functionality or functionalities you suspect. It is always a good idea to run positive and negative controls when conducting classification tests. See the following list for tests that you may run:

1. Test for a halide: Beilstein Test (p. 461)
2. Test for a nitro group (p. 463)
3. Test for multiple bonds: Bromine in methylene chloride (p. 466)
4. Test for aromaticity: Ignition test (p. 469)
5. Test for aldehydes and ketones: 2,4-dinitrophenylhydrazine (p. 471) and chromic acid test (p. 473)
6. Test for carboxylic acids: pH of aqueous solution (p.477) and sodium bicarbonate (p. 477) and neutralization equivalent (p. 478)
7. Test for phenols: NaOH (p. 479) and ferric chloride (p. 480)
8. Test for amines: pH of aqueous solution (p. 484) and acetyl chloride (p. 484)
9. Test for alcohols: acetyl chloride (p. 487) and chromic acid (p. 489)
10. Test for esters: ferric hydroxamate (p. 492)

The classification tests should enable you to decide what main functional group(s) is (are) present in your unknown. The tables for the identification of unknowns are on the web site: <http://faculty.northseattle.edu/jpatterson/pdf/239unkderivlist.pdf>. These tables can be used to find candidates with melting points or boiling points similar to your unknown. Unknowns suspected of containing more than one primary functional group should be checked under all suspected functional groups.

Finally, the preparation of a derivative (PLKE Appendix 2 p. 971) and the determination of their melting points should enable you to positively identify your unknown. **You are required to prepare at least one pure derivative for your unknown.**

IDENTIFICATION OF THE SPECTROSCOPY UNKNOWN

Some time during the five periods you have to work on the qualitative analysis experiment, take an NMR, IR and mass spectrum of your spectroscopy unknown. You cannot do any chemical tests on this unknown and you cannot determine its boiling point.

For NMR, prepare the sample by dissolving 3-4 drops of the unknown in 0.7 mL of deuterated chloroform (CDCl_3).

For IR, place 1-2 drops of the unknown on the salt plate, and sandwich with another salt plate.

For mass spectroscopy, dissolve 1 drop of your unknown in 10 mL of methylene chloride. See instructor for GC-MS use.

• Post-lab and Lab Result Report: (Due Monday, May 14, at the beginning of lab)

Photocopy the entire lab in your notebook. Make sure there are tables that clearly show the melting point/boiling point of your unknown and its derivative are present, as well as the chemical equation of the creation of your derivative. Make sure that your spectra (all of them) are also photocopied, and clearly labeled as to sample and solvent (if appropriate).

No conclusion or abstract is required, but a diagram similar to the one on p. 455 of PLKE and the analysis of your spectra (including tables of peak assignments) should be present in your report.

What I will be looking for in your chemical unknown report is how you narrowed down the potential candidates for your compound after each step.

UNKNOWN REPORT FORMS

Once you have identified your unknown you will fill out and turn in the "Identification Report" and "Preliminary Report" forms (located on the web site). You must also submit the vial with the derivative you prepared, clearly labeled with your name, the date, the name of the derivative and its melting point.