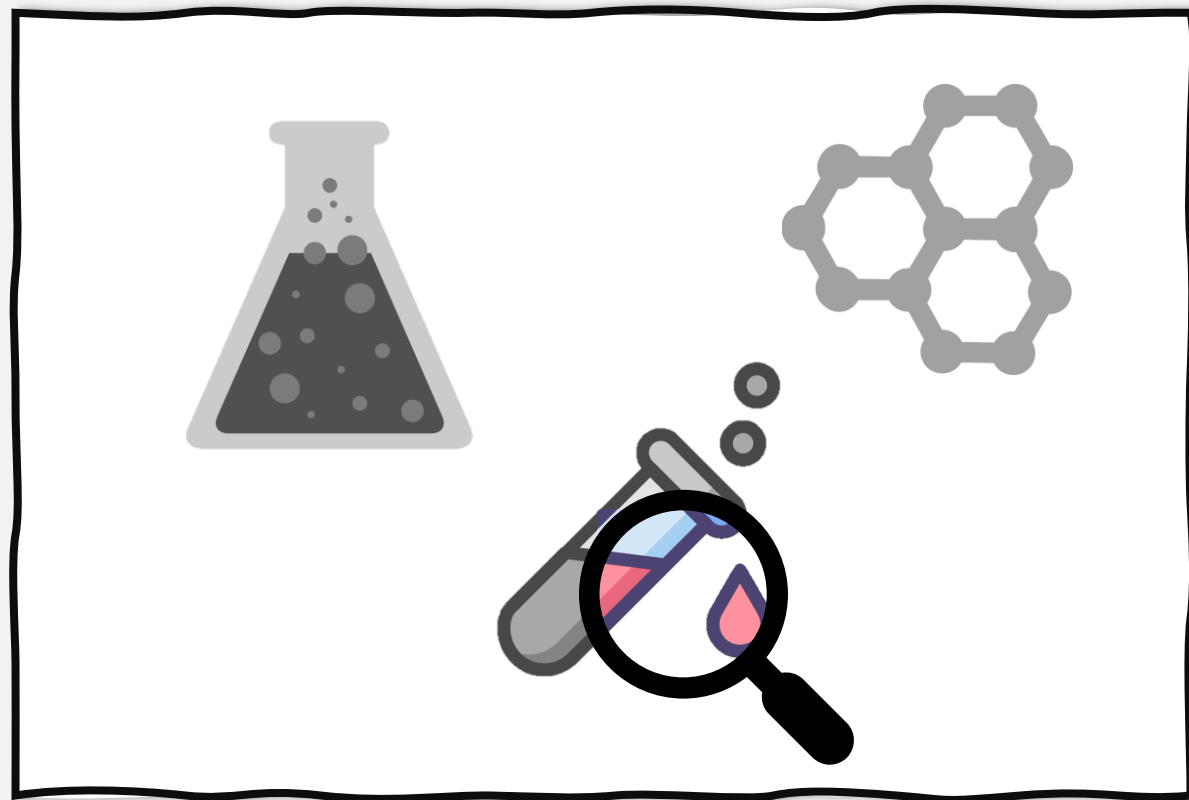


Lab 4: Unknowns

CHEM 242 – Section AA
TA: Hao Nguyen



Liquid unknown

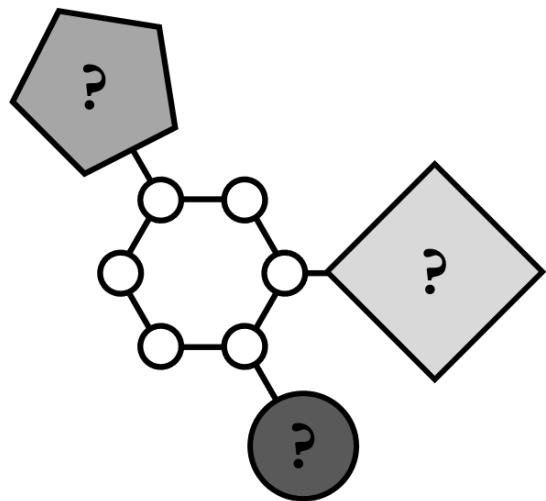


Solid unknown



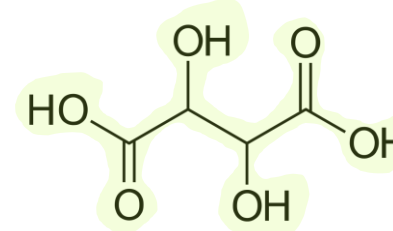
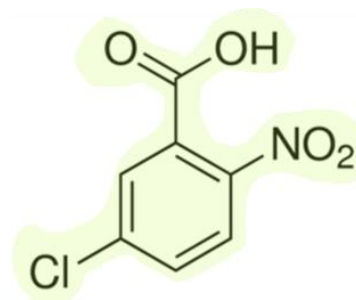
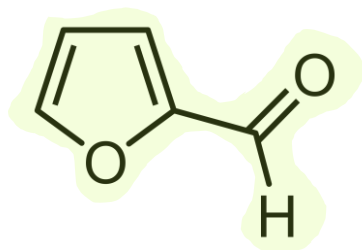
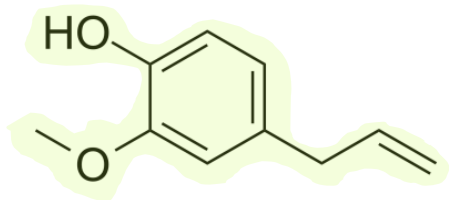
Spectroscopy unknown





Primary functional groups: alcohols, aldehydes, amines, carboxylic acids, esters, ketones, or phenols.

Secondary functional groups: nitro groups, aromatic rings, or halogens.



Tests:

Boiling point, melting point, solubility, DNP, cerium, ignition, Beilstein, Lucas, ferric chloride, Tollen, idoform, nitrous acid, sodium bicarbonate, ferric hydroxamate, ferrous hydroxide, ferric chloride, silver nitrate.

Derivative experiments:

3,5-dinitrobenzoate, phenylurethanes and naphthyl urethanes, bromo derivatives, semicarbazone, DNP, oxime, benzamide, acetamide, amine titration, anilide, toluidide, amide, acid titration, saponification.

Caution:

False positives and ambiguous results happen exist !!!



CHEM 242

Unknowns: Liquids and Solids

Order of Operations

Provided to you:

- 1) MP/BP
- 2) Solubility - neutral / base / acid
- 3) DNP / cerium
- 4) Beilstein / ignition
- 5) NMR / IR

Narrow down functional groups to 1-2

Next steps:

- 6) Classification tests
 - Should know functional group at this point

Confirmation:

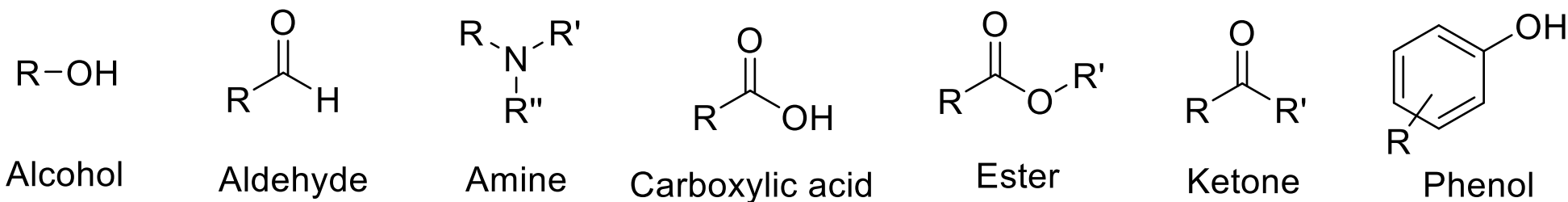
- 7) Derivatives
 - Confirm structure by product MP

Approximate Schedule

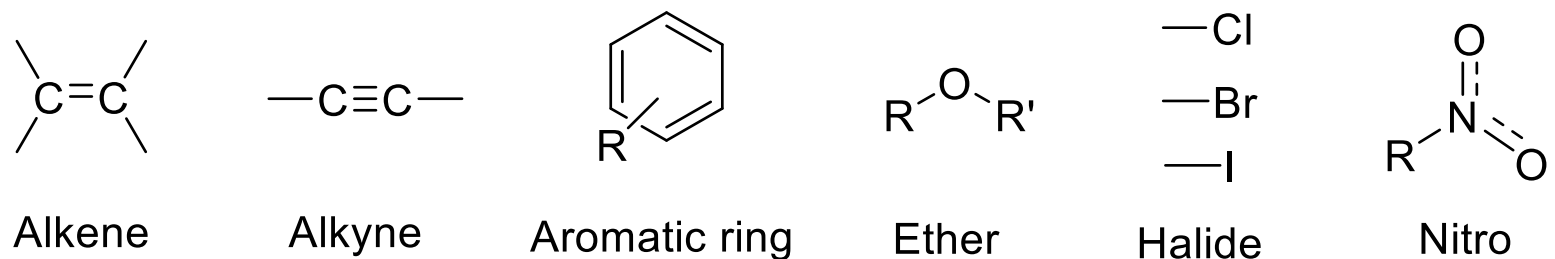
- ▶ Day 1 - introduction, classification tests
- ▶ Days 2-3 - classification tests
 - ▶ You should be prepared to justify why you want to do a test
 - ▶ What relevant information do you already have?
 - ▶ What information would you get?
- ▶ Days 4,6 - derivatives
 - ▶ You should be prepared to explain your reasoning
 - ▶ What functional group does it derivatize?
 - ▶ **DRAW** the general structure you are expecting
 - ▶ Explain why you chose that specific derivative (example - oxime instead of semicarbazone or DNP)
- ▶ Day 5 - discussion day
 - ▶ Choose **either** liquid or solid unknown
 - ▶ What have you done so far, what can you conclude?
 - ▶ What remains to be done?
- ▶ Days 7,8 - finish anything that is missing if needed

Unknown functional groups

Your molecule contains at least one PRIMARY functional group:



Possible SECONDARY functional groups:



Solubility

Procedure: Add 1 drop to 2 mL solution.

Shake in H_2O , NaOH , HCl , NaHCO_3 .

► POSITIVE: clear liquid phase

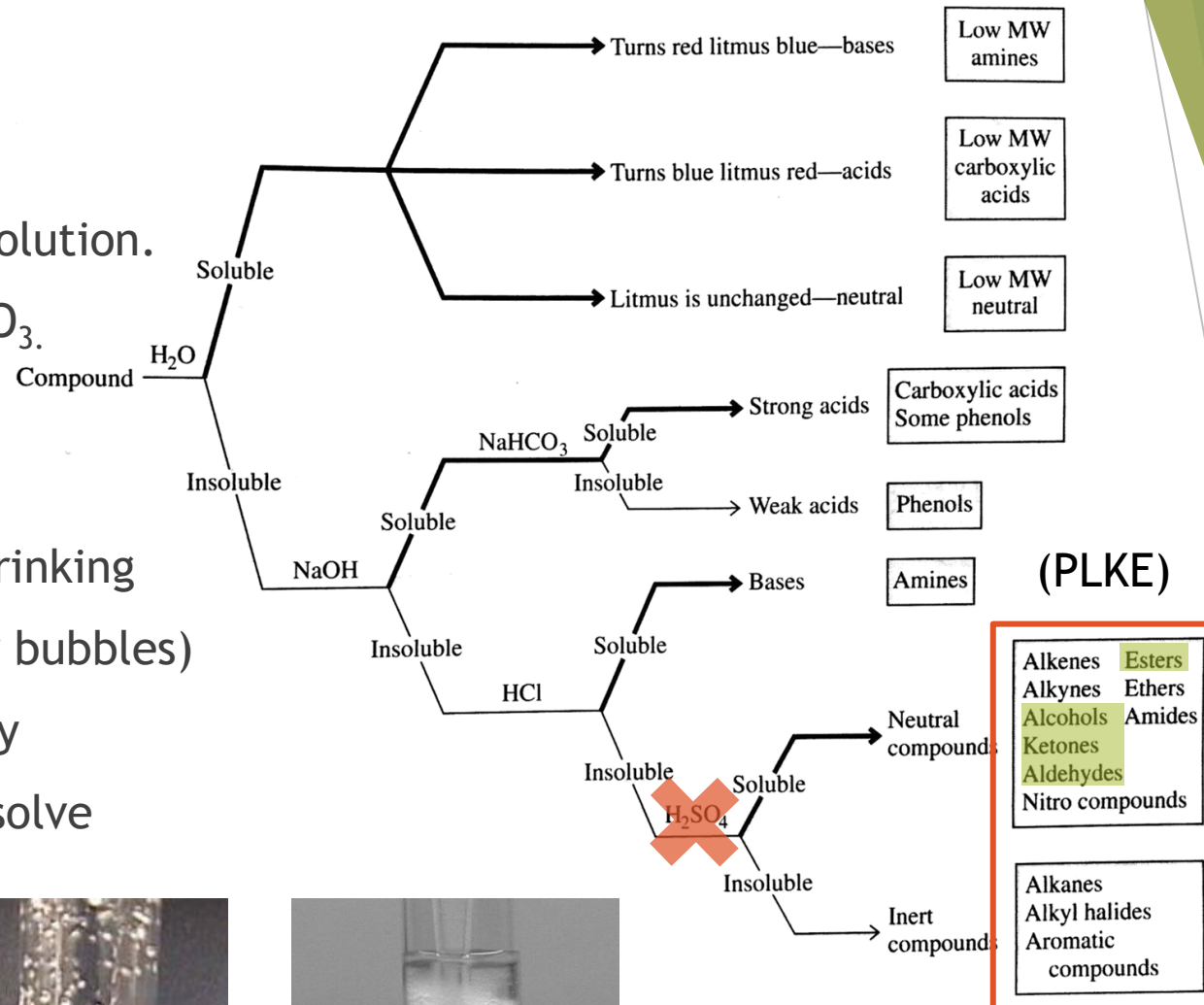
► NEGATIVE

Solid: floating pieces, not shrinking

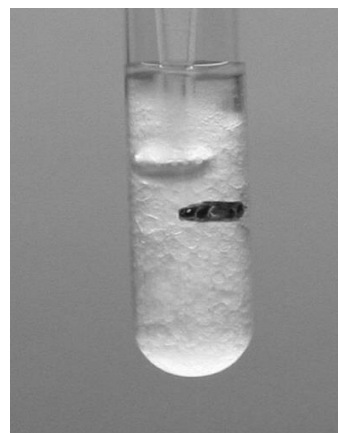
Liquid: “oil” bubbles (not air bubbles)

NOTES: may see partial solubility

may need to wait to dissolve



clarenium.blogspot.com



hazardid.com

→ What are possible functional groups?

(-) H_2O (+) NaOH

(-) HCl (+) NaHCO_3

DNP: Aldehydes & Ketones

Procedure: Add 1 drop to 1 mL DNP solution.

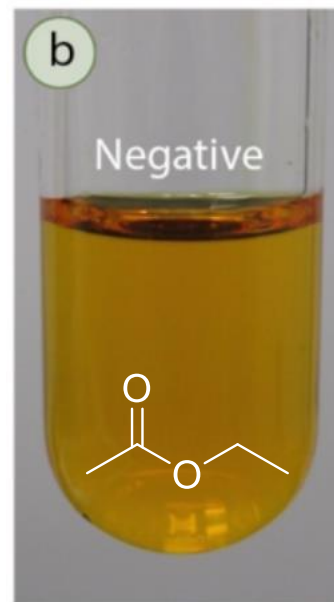
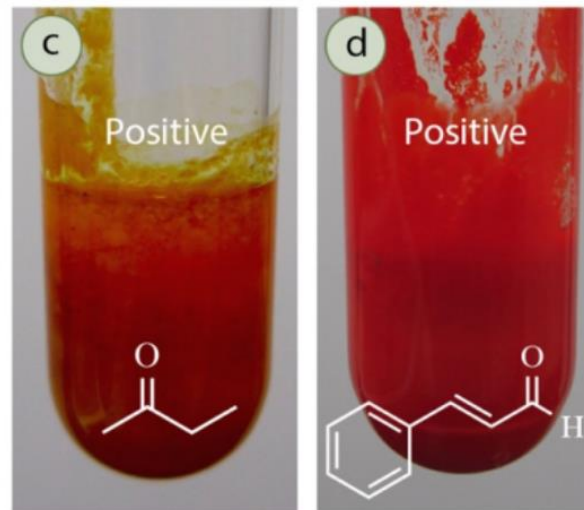
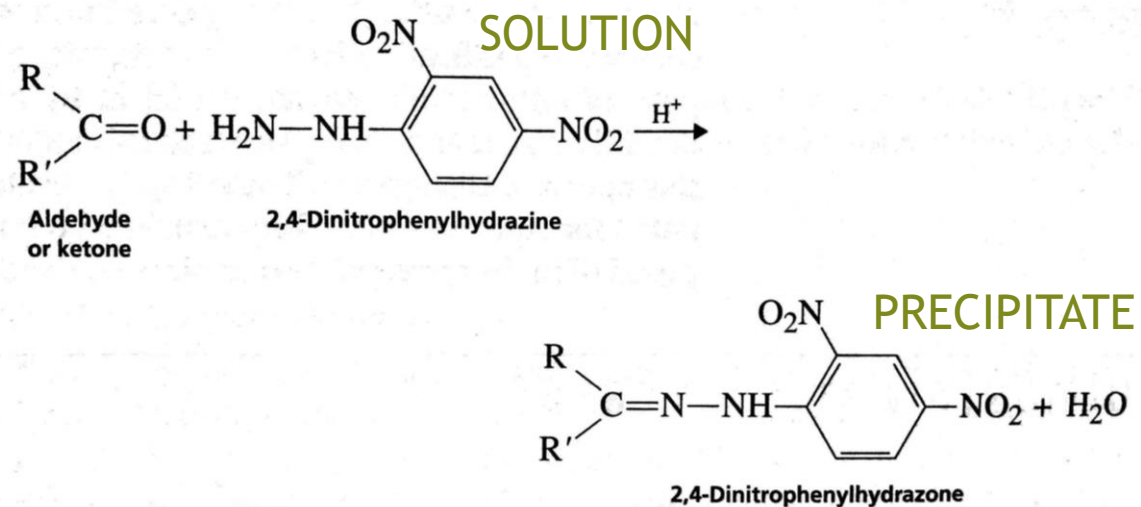
Dissolve solid first in minimum 95% ethanol.

- ▶ POSITIVE: yellow to red precipitate
- ▶ NEGATIVE: clear colored solution (no change)

NOTES: this test is NOT for carbonyl groups

Beware of acetone false positives!

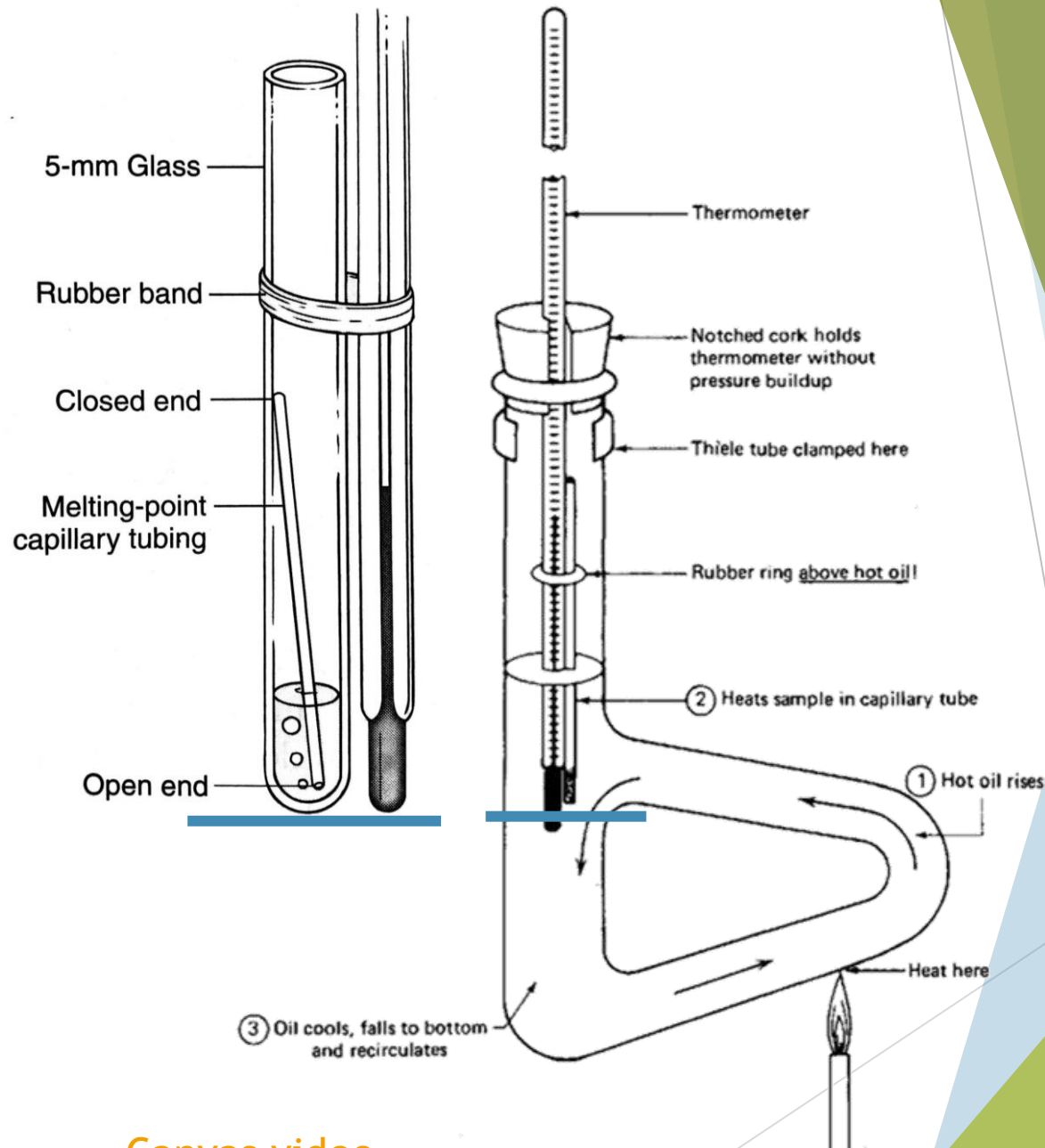
May be slow to precipitate



Boiling Point

Procedure:

- 1) Fill bottom of test tube with liquid
 - 2) Add a capillary with open tip down
 - 3) Use rubber band to attach to thermometer
 - Make sure bottoms are leveled so the measured temperature is near to sample
 - 4) Place sample inside Thiele tube with oil
 - 5) Heat side arm using flame past boiling point to steady stream of bubbles
 - 6) Remove heat and as setup cools, watch liquid goes up capillary.
 - Why does liquid go up capillary tube?
- Narrow down possible compounds $\pm 6^\circ \text{C}$



[Canvas video](#)

Beilstein: Halogens

Procedure:

- 1) Make a Cu wire with ring on one end
- 2) Heat ring over flame to remove contaminants
- 3) Dip wire in liquid or solid. Can wet wire with DI water for solids to stick
- 4) Burn sample over Bunsen burner
 - ▶ POSITIVE: Bright green flame
 - ▶ NEGATIVE: Orange flame

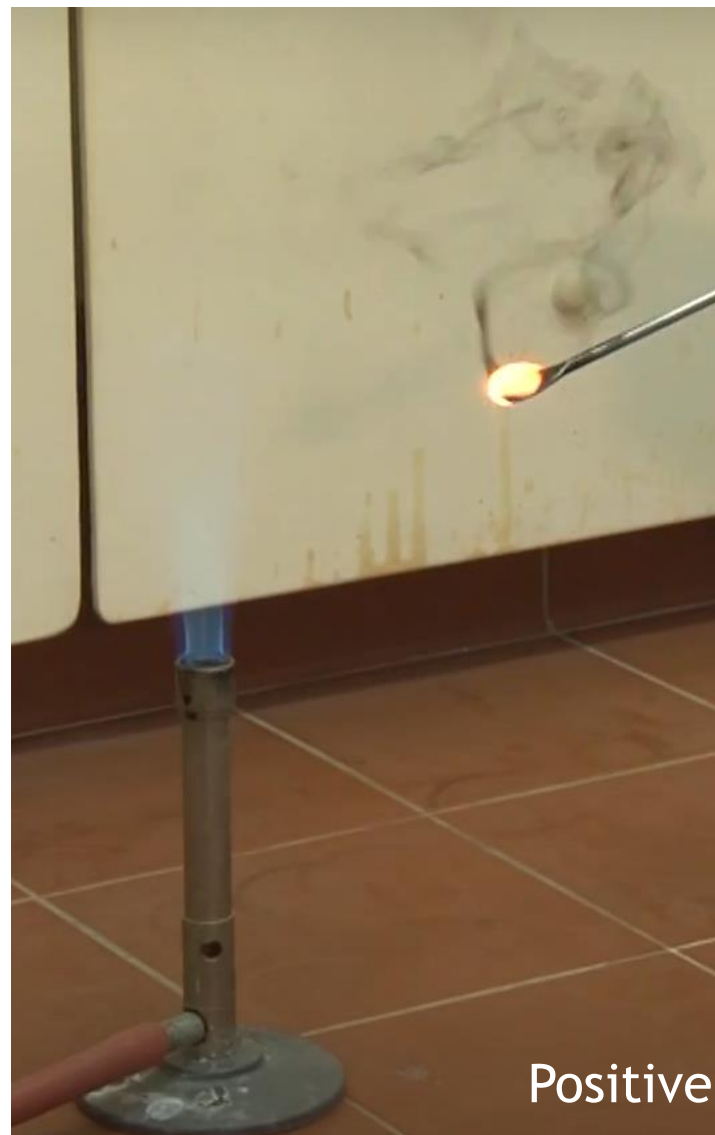
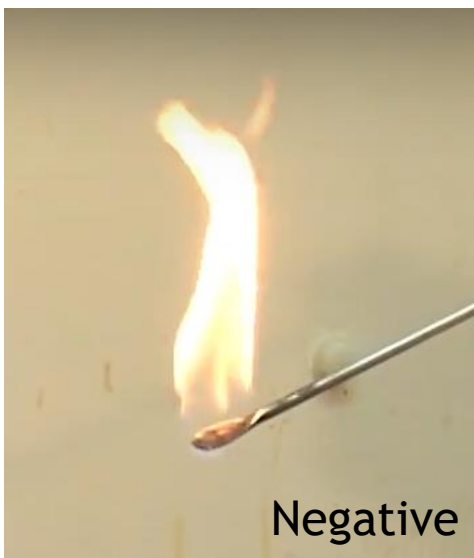


Ignition: Aromaticity

Procedure: Burn compound on spatula

- ▶ POSITIVE: Dark, black smoke
- ▶ NEGATIVE: Clean, yellow flame

NOTES: can be positive for double/triple bonds
can be difficult to interpret



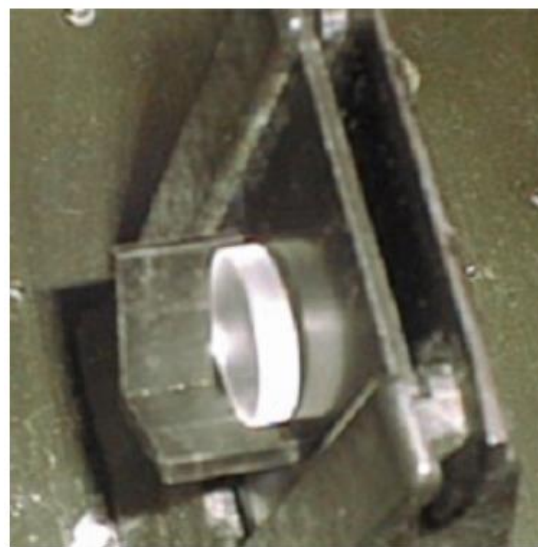
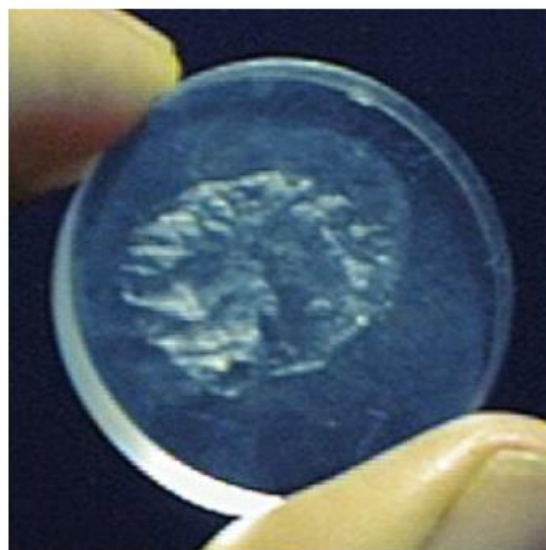
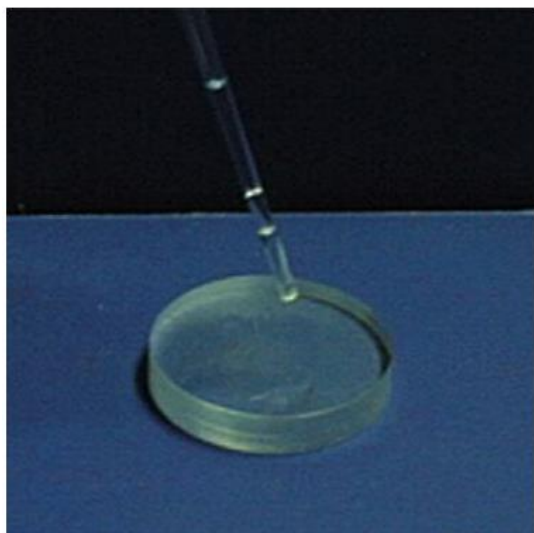
IR: solid film

Procedure

NOTE: solid must be soluble in methylene chloride

- 1) Dissolve 50 mg solid in 1 mL CH_2Cl_2
- 2) Add 3-5 drops onto a salt plate
- 3) Let solvent evaporate
- 4) Run IR with solid film (no second salt plate)

Normal for baselines to
be lower in solid IR



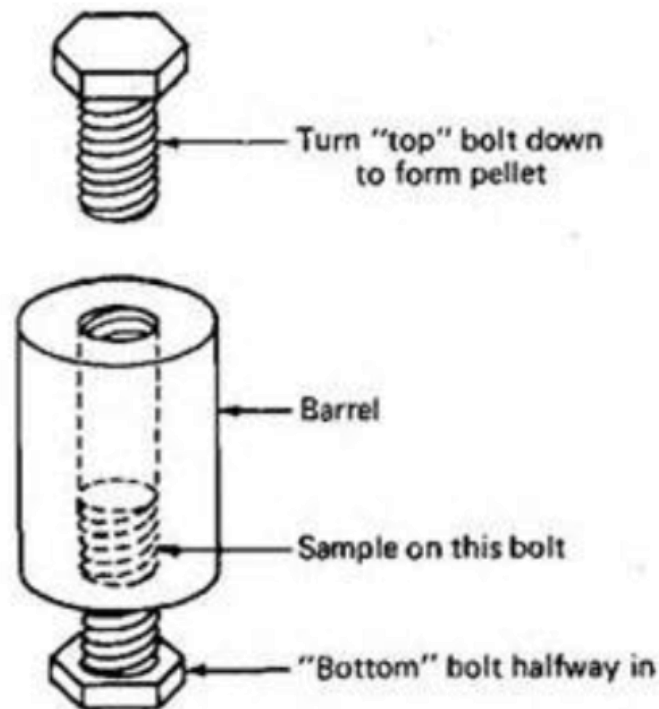
IR: solid pellet

[Canvas video](#)

- Solid is dispersed within a salt pellet

Procedure:

- 1) Grind 1 mg solid and 75 mg KBr with mortar and pestle to fine powder
- 2) Screw in the bottom bolt into metal barrel
- 3) Add your ground sample
- 4) Tighten top screw with wrench and wait for 1 min.
 - Salt fuses under high pressure
- 5) Loosen and remove screws carefully
 - Pellet inside should be translucent
- 6) Run IR with pellet inside barrel



IR: Nujol mineral oil

If all else fails, try this method

NOTE: oil has strong CH absorption

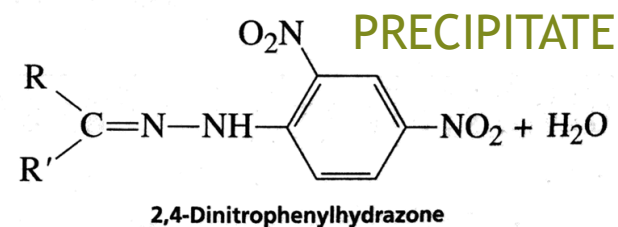
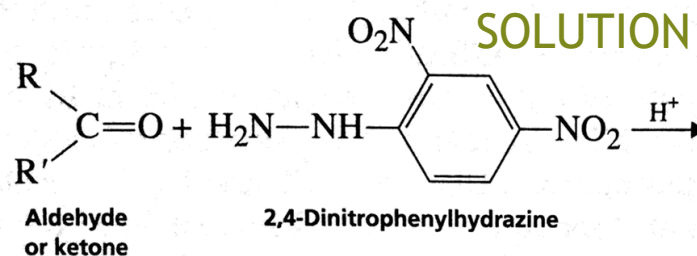
- Want to distinguish sample aromatic CH ($>3000\text{ cm}^{-1}$) and aliphatic CH ($<3000\text{ cm}^{-1}$)

Procedure

- 1) Grind a few mg solid with mortar and pestle
- 2) Add a few drops of Nujol mineral oil
- 3) Run between salt plates like a liquid sample to collect spectrum



Derivatives



- ▶ Reaction between unknown and known compound
- ▶ Use melting point to distinguish products
- ▶ Ex. DNP derivative

ALDEHYDES (Solid)	MP	Derivatives		
		Semi-carbazone	2,4-DNP	Oxime
Phenylethanal (phenylacetaldehyde)	33	163	121	100
1-Naphthaldehyde	34	221	255	98
Piperonal (1,3-benzodioxole-5-carboxaldehyde)	35-39	234	266	146
2-Methoxybenzaldehyde (o-Anisaldehyde)	34-40	215	254	92
4-Diethylaminobenzaldehyde	37-41	241		93
3,4-Dichlorobenzaldehyde	39-42		301	120
3,4-Dimethoxybenzaldehyde	40-43	177	261	95
2-Nitrobenzaldehyde	42-44	256	301	102 (154)
4-Chlorobenzaldehyde	45-50	233	254	110(146)
2,3-Dimethoxybenzaldehyde	48-52	231		99

Obtaining your derivative

- ▶ Tell me unknown codename, solid or liquid, and which derivative
- ▶ Describe procedure and include key steps in your own words
- ▶ Be ready to answer questions to check your understanding of the procedure
- ▶ Melting point will be provided

Discussion day

- ▶ Prepare 4-5 min presentation for liquid or solid
- ▶ Optional 1 slide to show data/structures
- ▶ Covering the following:
 - 1) General properties (e.g. MP, BP)
 - 2) Chemical tests
 - 3) Spectroscopy
 - 4) Ambiguous results
 - 5) Derivatives
 - 6) Possible compounds
 - 7) Next steps
- ▶ Contribute to group discussion with comment or question twice

Questions?



CHEM 242

Unknowns: Spectroscopy

NMR

Tips:

- ▶ TMS may or may not be present. Reference to 0 ppm if it is
- ▶ Similar groups of hydrogens may overlap
- ▶ Beware of deuterium exchange: broad (lower integration) or missing peaks
- ▶ Watch out for impurities. Reference NMR impurities table
- ▶ Final integrations need to match molecule (3H for -CH_3 etc.)

Questions?

Identifying Spectroscopy Unknown

1) MS

- ▶ Nitrogen?
- ▶ Halogens: Br or Cl
- ▶ Calculate # of carbons
- ▶ Possible chemical formulas
- ▶ Degree of unsaturation

2) IR

- ▶ Functional groups
- ▶ Solids: film, pellet, oil techniques

3) NMR

- ▶ Rest of the molecule, hydrocarbon

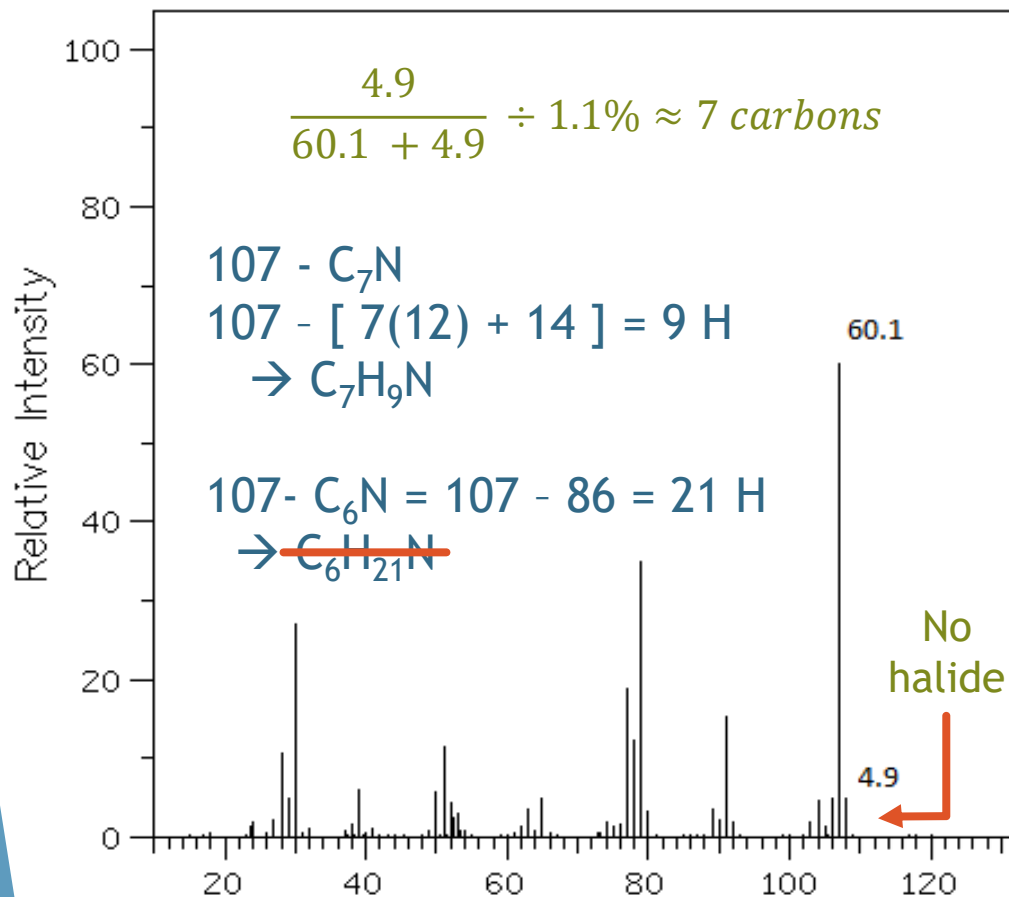
Your spectroscopy unknown can be any molecule!

It is not confined the unknowns list for liquids and solids.

Also today:
Classification tests

Mass Spectrometry

(Mass of molecular ion: 107 Nitrogen



Nitrogen

- ▶ Odd MW = odd # nitrogens (likely 1)
- ▶ Even MW = even # nitrogens (likely 0)

Halogen

- ▶ Intensity MW : M+2 peaks
- ▶ 3:1 ³⁵Cl : ³⁷Cl
- ▶ 1:1 ⁷⁹Br : ⁸¹Br

Carbon

- ▶ Estimate by peak intensities:

$$\frac{(M+1)}{(MW) + (M+1)} \div 1.1\%$$

- ▶ 1.1% = ¹³C abundance

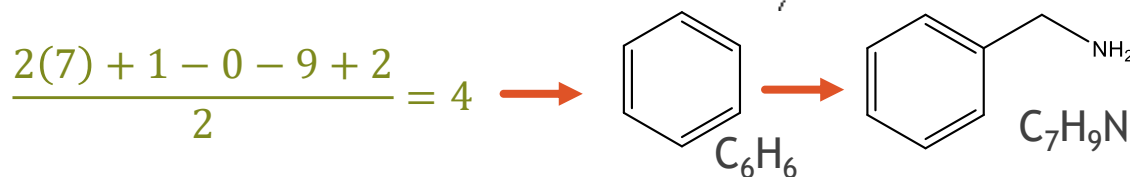
Chemical formulas

- ▶ Trial and error
- ▶ Don't forget oxygen! Reference IR

Degree of unsaturation

- ▶ For C=C, C≡C, rings

$$\frac{2C + N - X - H + 2}{2}$$



What should you do?

1. Lab manual has enough information
2. Plan what to ask before coming to your meeting with TA
3. Keep notes!!!!
4. Keep track on timeline and deadlines.
5. This is a long project (it would take 3-4 weeks for in person lab), so invest your time and use your time wisely.

What can your TA do to help you?

1. Give you your test results **only** during 1-on-1 meeting during lab time
2. Answer related questions through email, office hours
3. Be your emotional support.