ANALYTICAL CHEMISTRY I 3150/FA

ORGANIC ANALYSIS

a classical way

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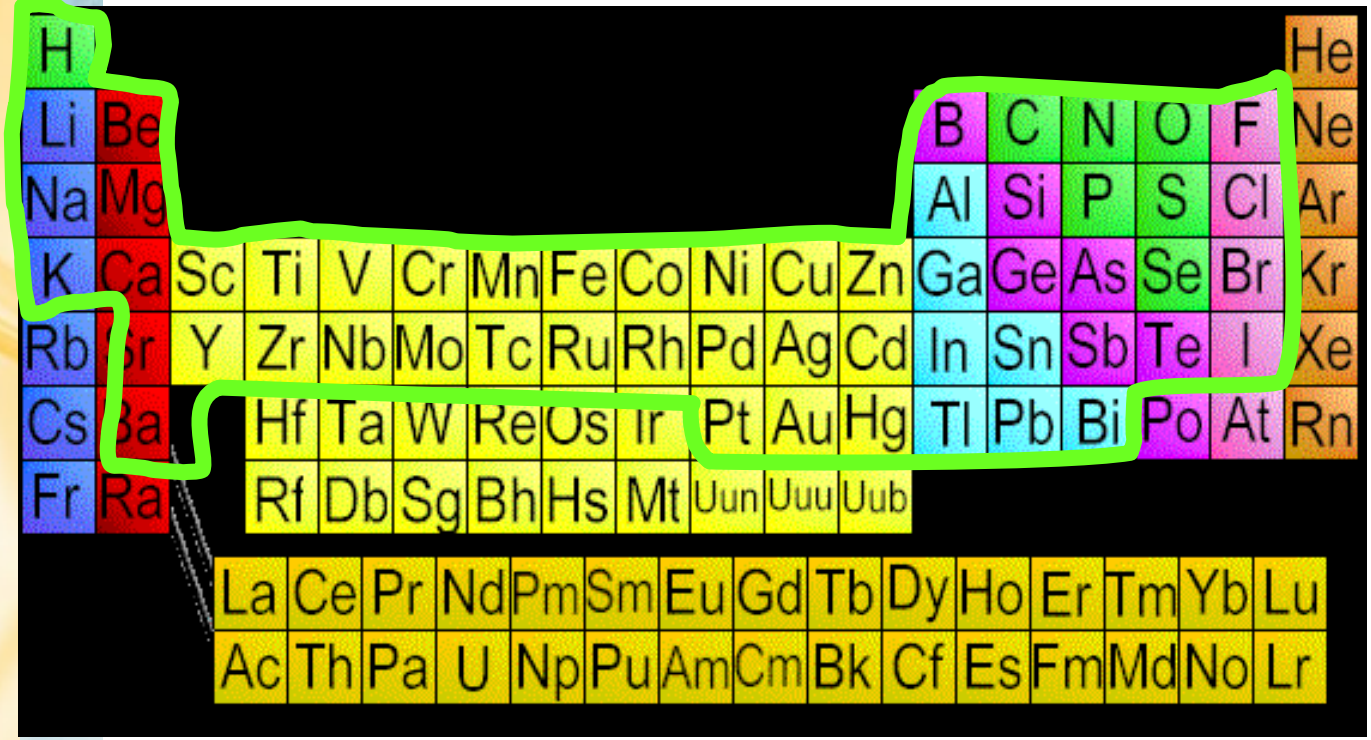
ORGANIC ANALYSIS



Inorganic chemistry =cca 50 elements

- State, other physical properties
- Color
- solubility

IDENTIFICATION PROCEDURE

Classical

1. Purification
2. Physical appearance
3. Physical properties (melting point, boiling point, refractive index, density….spectra)
4. Elemental analysis
5. Confirmation / determination of functional groups
6. Preparation of derivatives - final identification
7. Literature comparison

Instrum

- chromatography (relative method)
- combination of spectral methods: UV-VIS, IR, NMR, MS
- interpretation of results, identification with libraries, structural prediction

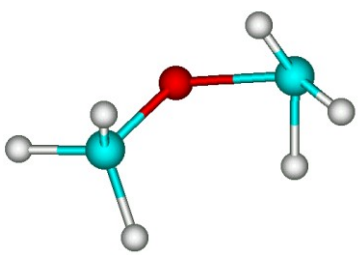
REQUIRED: μg - mg of the analyte

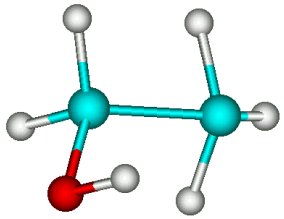
CLASSICAL ANALYSIS OF ORGANIC COMPOUNDS

- Limited number of elements: : C, H, N, O, S, X
- Thermolabile, decomposition within 100-400 ºC
- cca 5.10^{6} compounds - **isomers**:

Compounds with an identical chemical formula

e.g.

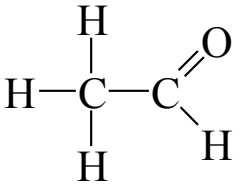




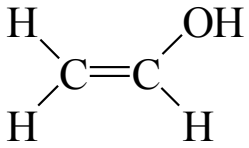
constitutional: C_2H_6O

positional : 1-propanol, 2-propanol

tautomers : *acetaldehyd* *vinylalkohol*



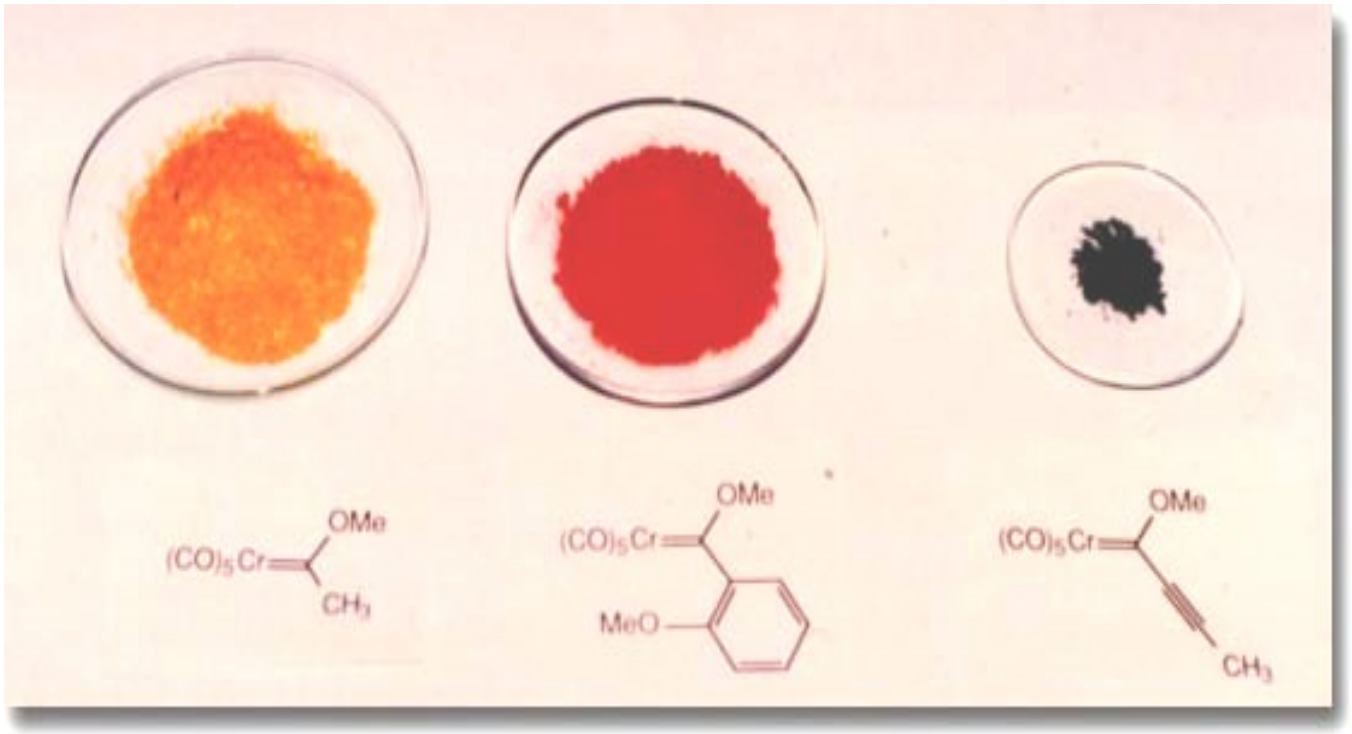
$CH_3\ CH{=}O$



$CH_2{=}CHOH$

- polymers: polystyrene $-(C_6H_5\text{-}C_2H_4)_n-$
- no or low charge, ionic

COLOR



PHYSICAL APPEARANCE

stat (liquid) – relatively small M, polar?, viscous = polymer, polyfunctional compound

(solid) - salts, strongly polar cmpds (crystals), amorphous = polymeric cmpds

colour

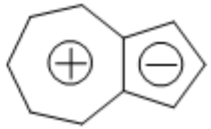
yellowish = $-NO_2$, -NO (s), -N(O)N- (azoxy-), -NH-NH- (hydrazo-), conjugated systems

yellow = α-diketones (s), quinones, nitrophenols, nitroanilines, osazones, azo-cmpds

orange-red = nitroaminophenols, azocompounds, nitrophenyl = hydrazines (NH_2.NH-), hydrazones (NH_2.N=), o-quinones, azo-

violet = azo-cmpds, aminoantraquinones

blue = terpenes, aminoantraquinones, azulenes



green = quinhydrones, nitroso-cmpds in solutions, triphenylmethane dyes

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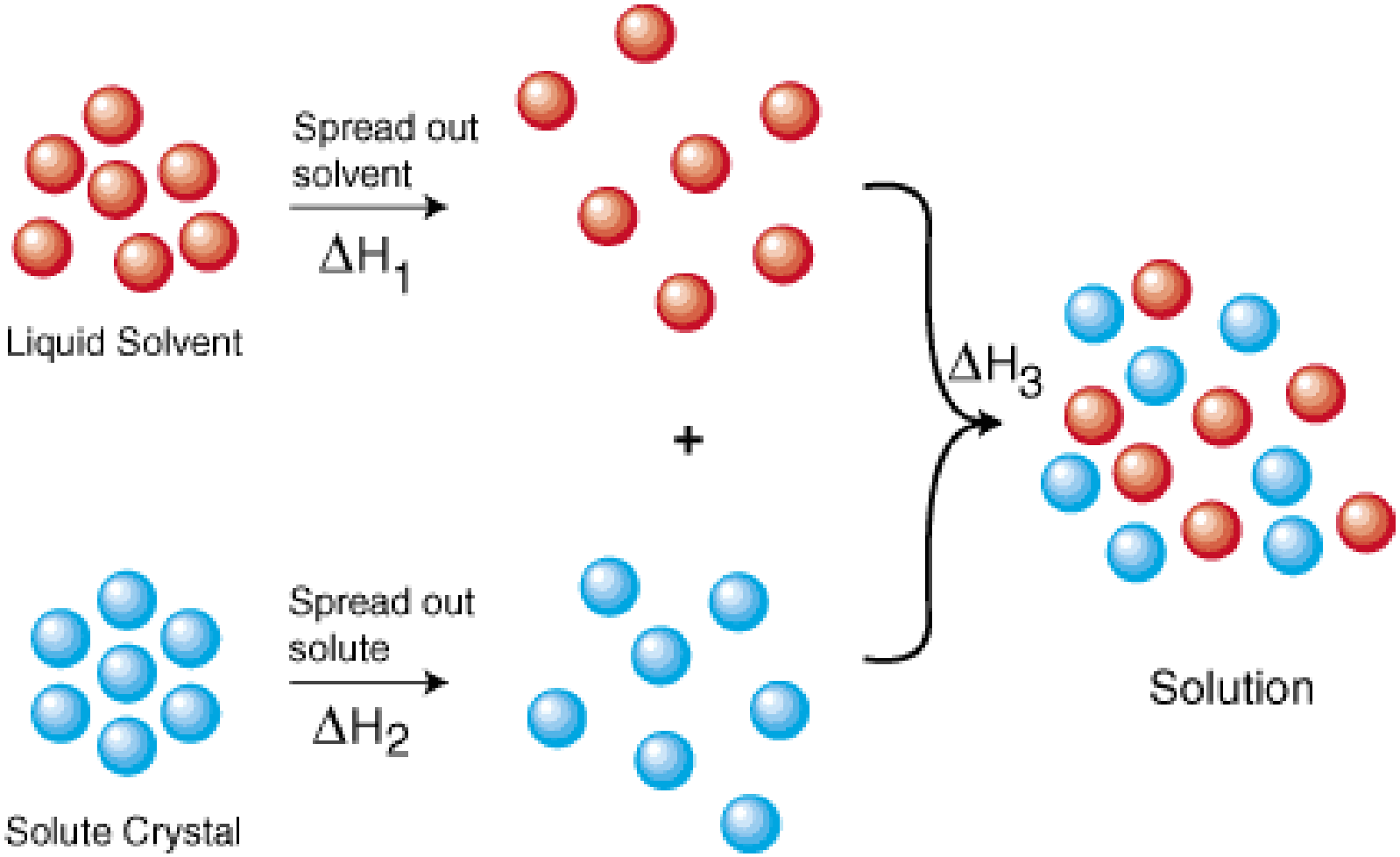
"brown / black" = mixed organic dyes, oxidable or decomposed compounds

INTERMOLECULAR FORCES * STRUCTURE



SOLUBILITY/MISCIBILITY CLASSES

Rules:

- Similis similibus solventur (=like dis

Intermolecular forces

Solubility of homologues

Alcohol solubility chart

Name	Formula	Solubility
Methanol	CH_3OH	miscible
Ethanol	C_2H_5OH	miscible
Propanol	C_3H_7OH	miscible
Butanol	C_4H_9OH	0.11
Pentanol	$C_5H_{11}OH$	0.030
Hexanol	$C_6H_{13}OH$	0.0058
Heptanol	$C_7H_{15}OH$	0.0008

- Reactive solubility

= an ACID dissolves in a BASE or a BASE dissolves in an AC

Solvents

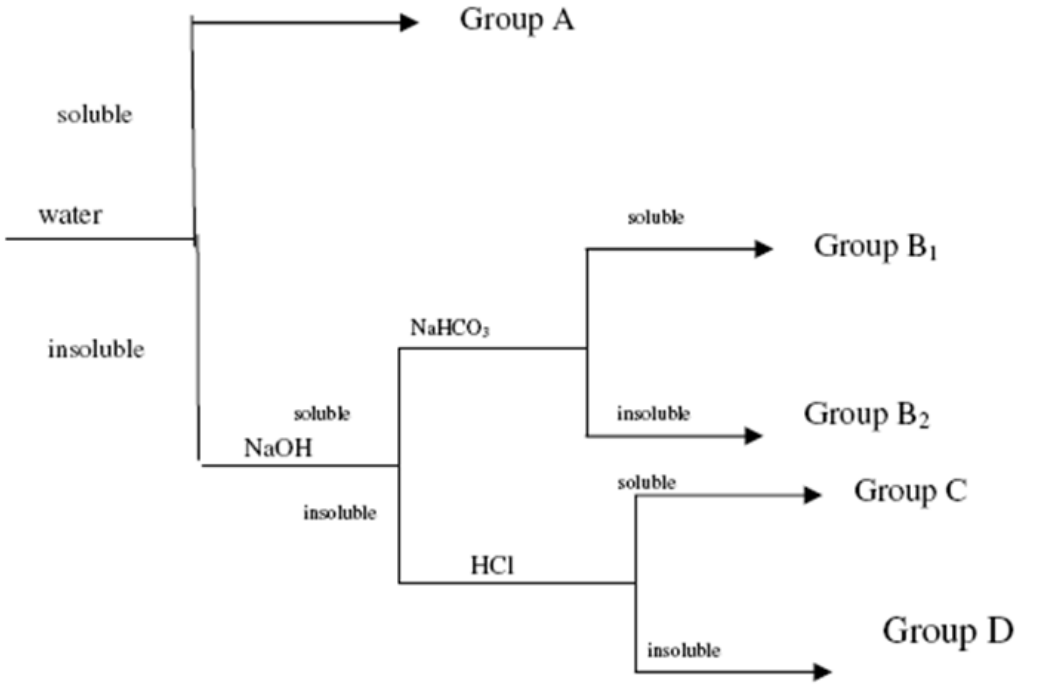
- ❑ **Polar (water)**
- ❑ **low polar (ether)**
- ❑ **Reactive** (5% HCl, 5% NaOH, 5% $NaHCO_3$, konc.H_2SO_4)

SOLUBILITY CLASSES

- Similis similibus solventur
- Acid-base reactions

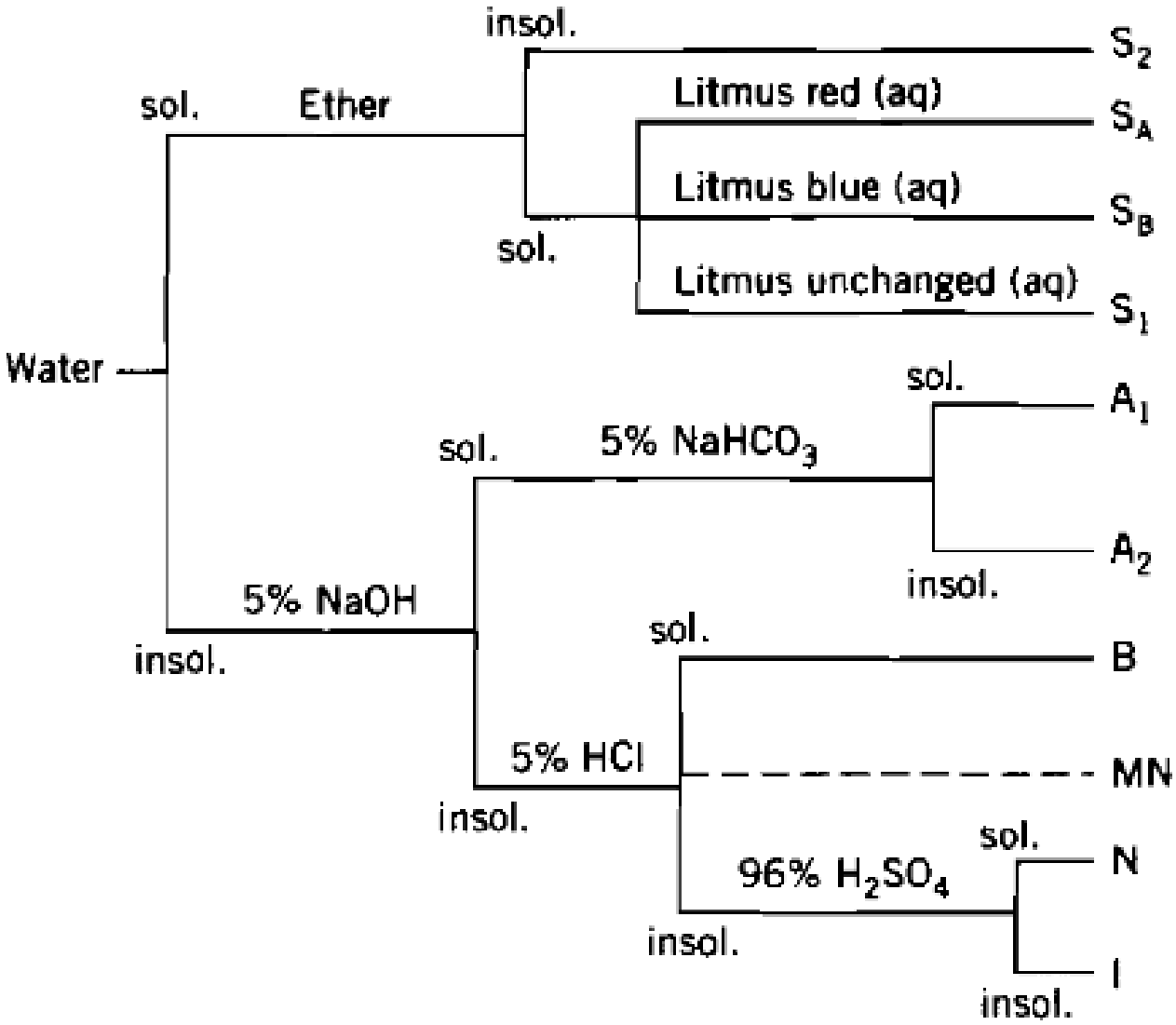
Solvent	Characteristics
Soluble in Water	Lower members of homologous series of O or N containing compounds (alcohols, ketones, amines, carboxylic acids, amines having <5 C atoms
Insoluble in water but soluble in 5% NaOH and 5% $NaHCO_3$	Carboxylic acids with 5 or more carbons, phenols with electron withdrawing groups and β-diketones
Insoluble in water, insoluble in 5% $NaHCO_3$, but soluble in 5% NaOH	Phenols
Insoluble in water, insoluble in 5% NaOH, 5% $NaHCO_3$, but soluble in 5% HCl	Amines

SOLUBILITY CLASSES



Group A	Lower members of homologous series of O or N containing compounds (alcohols, ketones, amines, carboxylic acids, amines having <5 C atoms
Group B_1	Carboxylic acids with 5 or more carbons, phenols with electron withdrawing groups (more acidic) and β-diketones (more acidic)
Group B_2	Phenols
Group C	Basic compounds (amines)
Group D	Hydrocarbons, alkyl halides, highly alkylated *(containing 5 or more carbon atoms)* alcohols, aldehydes, ketones.

SOLUBILITY CLASSES



SOLUBILITY

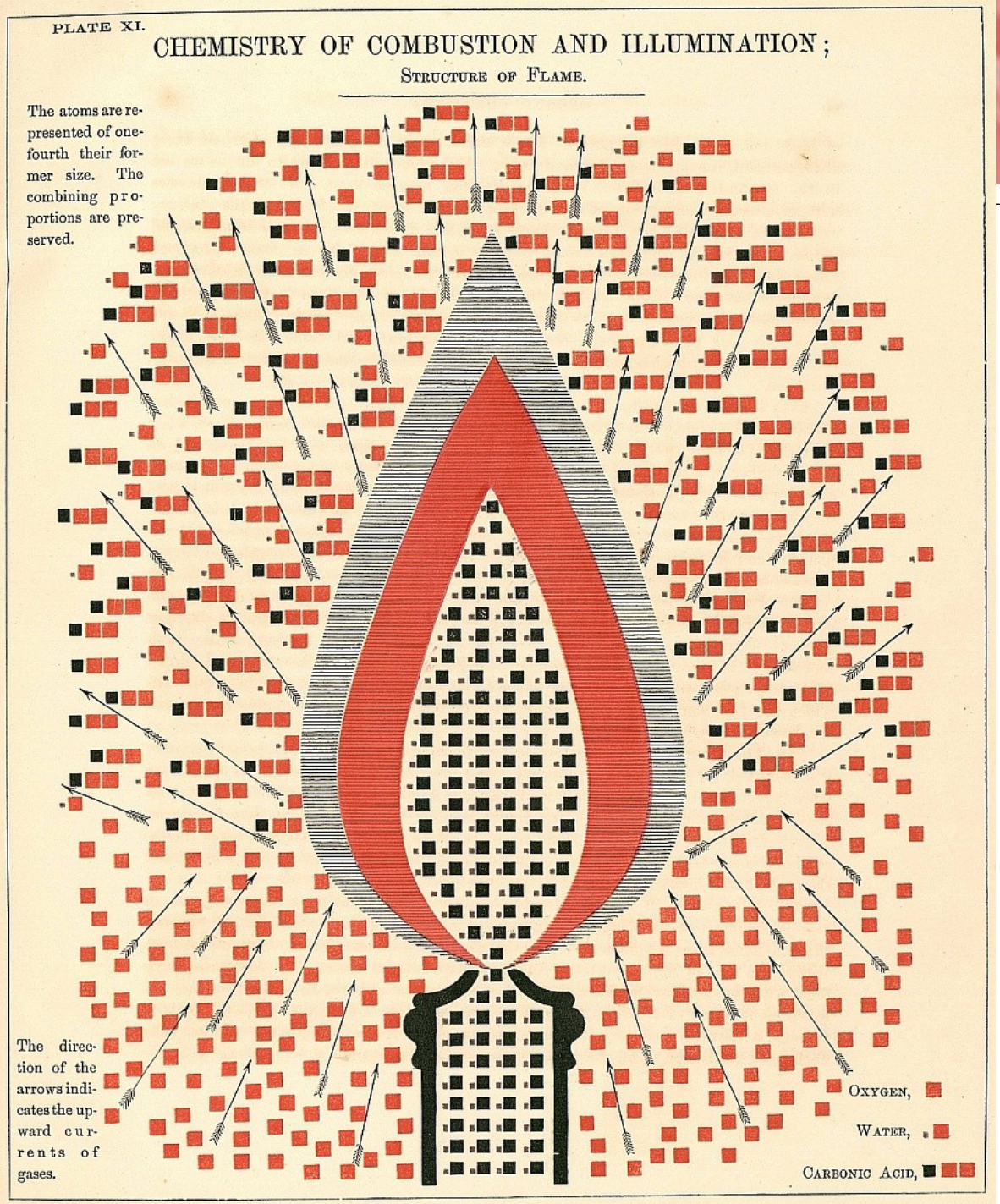
S_2	Salts of organic acids (RCO_2Na, RSO_3Na); amine hydrochlorides (RNH_3Cl); amino acids
	; polyfunctional compounds with hydrophilic functional groups: carbohydrates (sugars), polyhydroxy compounds, polybasic acids, etc.
S_A	Monofunctional carboxylic acids with five carbons or fewer;
S_B	Monofunctional amines with six carbons or fewer.
S1	Monofunctional alcohols, aldehydes, ketones, esters, nitriles, or fewer.
A1	Strong organic acids: carboxylic acids with more than six withdrawing groups in the ortho and/or para position(s);
A2	Weak organic acids: phenols, enols, oximes, imides, more than five carbons; /3-diketones (1,3-diketones); nitro
B	Aliphatic amines with eight or more carbons; anilines (only one nitrogen); some ethers.
MN	Miscellaneous neutral compounds containing nitrogen or carbon atoms.
N	Alcohols, aldehydes, ketones, esters with one functional group fewer than nine carbons, ethers, epoxides, alkenes, alkynes, (especially those with activating groups).
I	Saturated hydrocarbons, haloalkanes, aryl halides, other diaryl ethers.
Acyl	halides and carboxylic acid anhydrides have not been classified because of their high reactivity.

ELEMENTAL ANALYSIS

PLATE XI.

CHEMISTRY OF COMBUSTION AND ILLUMINATION;

Structure of Flame.

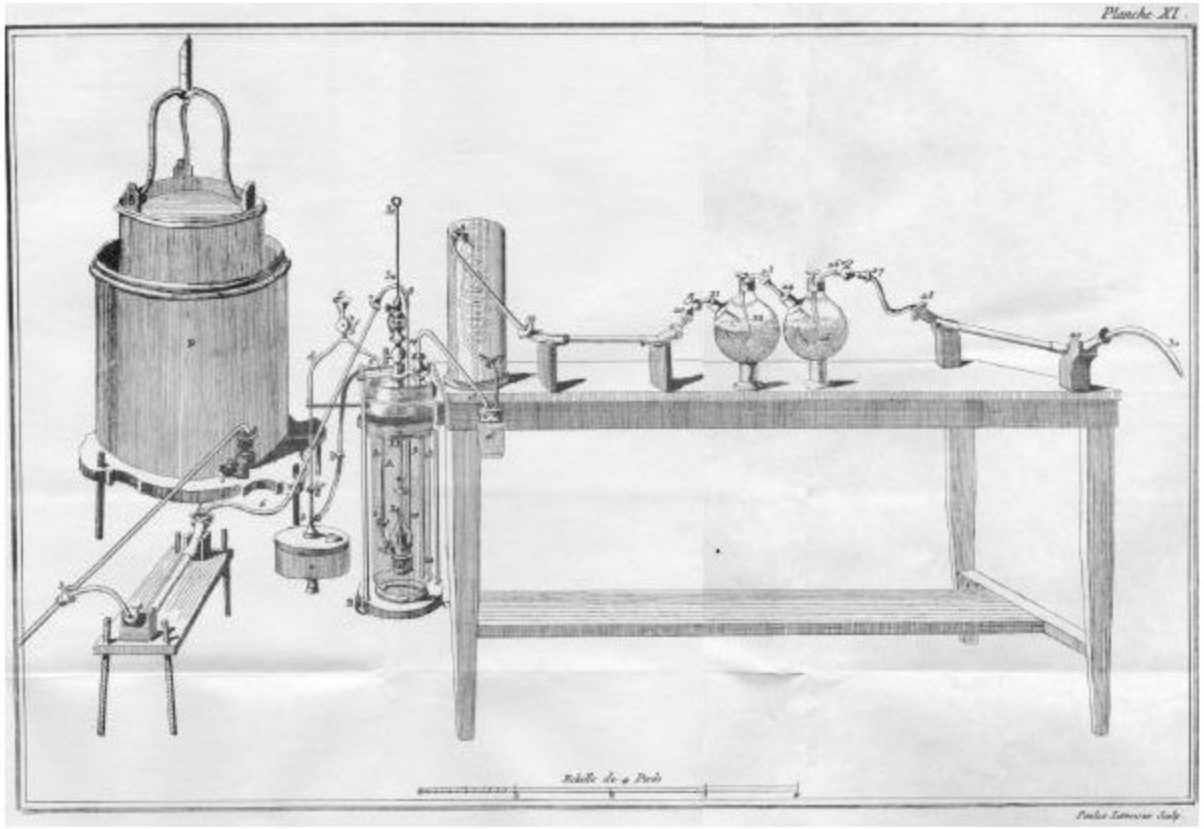


THERMAL DECOMPOSITION

A. Lavoisier

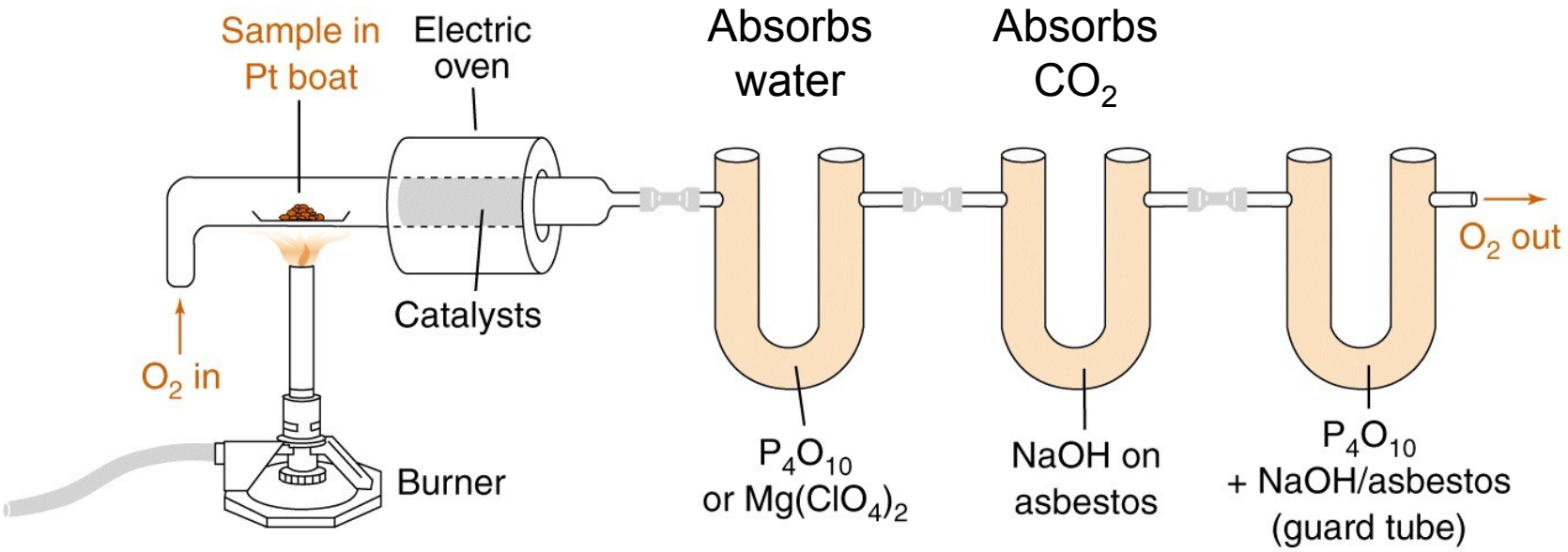
Lavoisier's Oil Analysis

"Traité Élémentaire de Chimie" (1789) vol. II, chap.VII, p. 493-501



http://www.chem.yale.edu/~chem125/125/history/Analysis/Liebiganal.html

COMBUSTION ANALYSIS (QUANTITATIVE ANALYSIS)



Find the empirical formula for a 13.72 mg organic compound that produced 6.97 mg of water and 28.44 mg of carbon dioxide

D.C. Harris, *Quantitative Chemical Analysis, 6th Ed., p.691*

MINERALIZATION

In organic compounds the elements commonly occurring along with carbon and hydrogen, are oxygen, nitrogen, sulphur, chlorine, bromine and iodine. The detection of these elements depends upon **converting them to water-soluble ionic compounds** and the application of specific tests (the conversion is called „mineralisation"). There can be performed an oxidative mineralisation (e.g. catalysed with CuO) or reductive mineralisation (with Na or Mg).

Lassaigne's test after reductive mineralisation

C, H, O, N, S, X -> X- CN- S(2-) CNS-

PROCEDURE

Place a little of the compound (50 mg or 2 - 3 drops) into a fusion tube. Add a reaction mixture (magnesium powder+potassium carbonate) in the fusion tube tip but keep there a gap for hot air to escape.

Heat the fusion tube gently at first by flame of a gas burner. Then heat up the reaction mixture. When charring begins, heat the bottom of the tube to dull redness (but avoid melting of the glass!). Finally plunge the tube, while still hot, into a clean dish test tube half-filled with cold distilled water (6 mL) kept in a test tube stand. The fusion tube breaks and the content is released into the water.

ELEMENTAL ANALYSIS

1. NITROGEN (CYANIDES)

To a portion (2 mL) of the 'fusion' filtrate add 0.2 g of powdered ferrous sulphate crystals. Boil the mixture for a half a minute, cool and acidify by adding dilute sulphuric acid dropwise. Formation of a **bluish-green precipitate** (Prussian blue) or a blue solution indicates that the original substance contains nitrogen. If no precipitate appears, allow to stand for 15 minutes, filter and inspect filter paper.

$$Fe^{3+} + FeS + 6\ CN^- \rightarrow Fe[Fe(CN)_5]^- + S^{2-}$$

2. SULPHUR (SULPHIDE)

To the cold 'fusion' filtrate (1 mL) add a few drops of cold, freshly prepared, dilute solution of sodium nitroprusside. The latter may be prepared by adding a small crystal of the solid to 2 mL of water. Production of a **rich purple** colour indicates that the original substance contains sulphur. This test is very sensitive.

$$S^{2-} + [Fe(CN)_5NO]^{2-} \rightarrow [Fe(CN)_5NOS]^{4-}$$

3. HALOGENS (HALIDES)

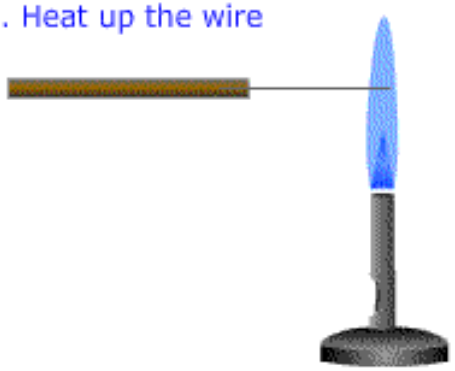
Acidify a portion (1 mL) of the 'fusion' filtrate with 2M nitric acid, and if nitrogen and/or sulphur are present, boil for 1 - 2 minutes.* Cool and add aqueous silver nitrate (1 mL), compare with a blank. Formation of a heavy, **white or yellow precipitate** of silver halide indicates halogen. If a positive result is obtained: acidify the remaining portion of the 'fusion' filtrate with dilute sulphuric acid, boil and cool. Add carbon tetrachloride (1 mL) and a few drops of freshly prepared chlorine water. Shake the mixture.

$$Ag^+ + X^- \rightarrow AgX$$

BEILSTEIN TEST FOR HALOGENES

Flame tests

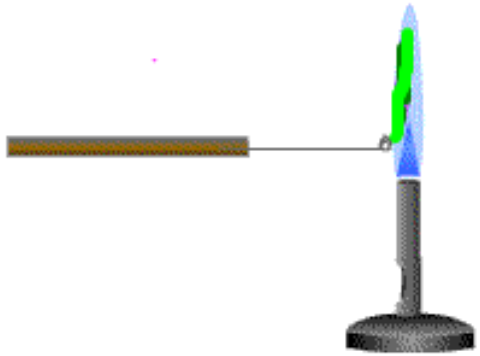
1. Heat up the wire



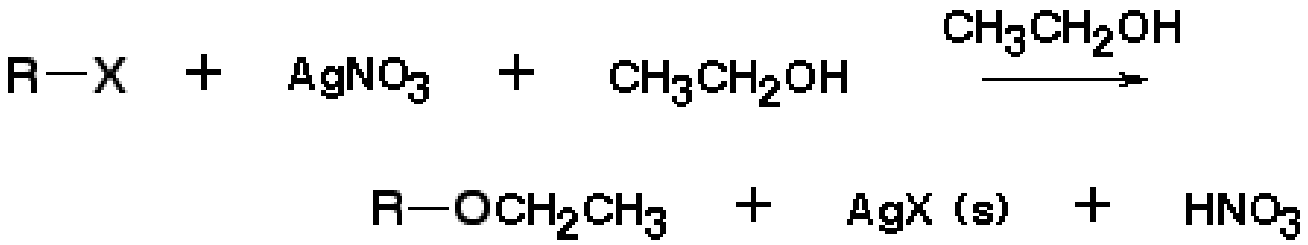
2. Dip the wire

3. Dip the wire

4. Hold sample in the edge of a hot flame



SILVER NITRATE REACTION FOR HALOGENES



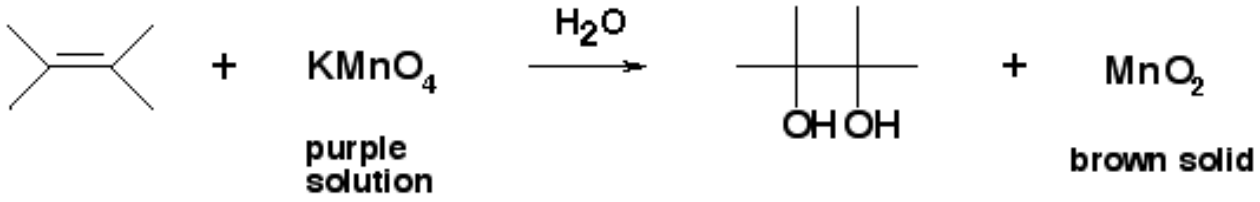
Procedure

Place approximately 0.25 mL of each compound into a test tube. Add 2 mL of a 1% ethanolic silver nitrate solution to the material in each test tube, noting the time of addition. After the addition, shake the test tube well to ensure adequate mixing of the compound and the solution. Record the time required for any precipitates to form. If no precipitates are seen after 5 minutes, heat the solution on the steam bath for approximately 5 minutes. Note whether a precipitate forms in the test tube. Continue slow reactions for up to 45 minutes at room temperature.

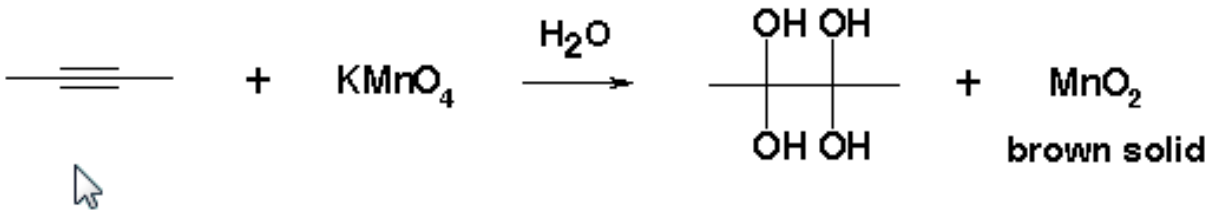
TESTS FOR FUNCTIONAL GROUPS

BAYER (PERMANGANATE) TEST FOR UNSATURATION

Alkene



Alkyne

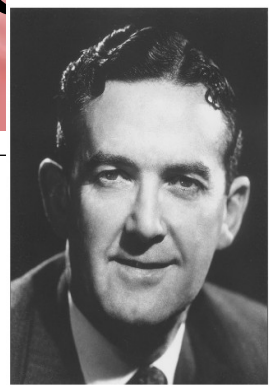


Standards
Cyclohexane, Cyclohexene and Bromobenzene.

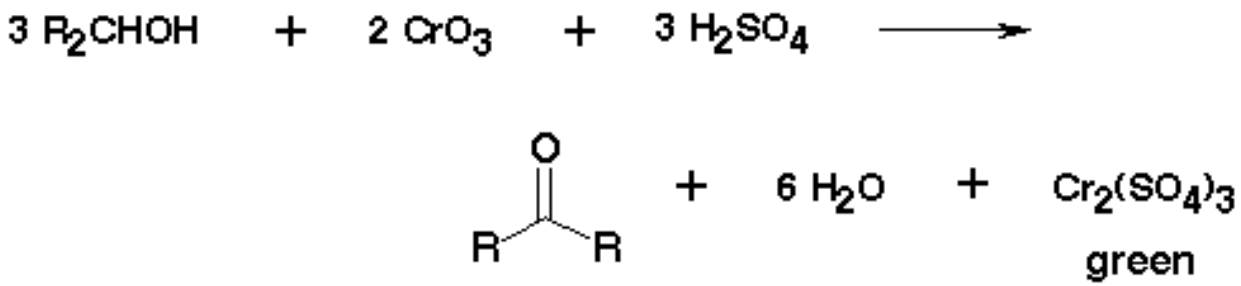
Procedure
Dissolve 1 drop or 0.02 grams of the unknown in 0.5 mL reagent grade acetone. Add a 1% aqueous solution of potassium permanganate dropwise with shaking. If more than one drop of reagent is required to give a purple color to the solution, unsaturation or an easily oxidized functional group is present. Run parallel tests on pure acetone and, as usual, the standards listed above.

Positive Test
The disappearance of the $KMnO_4$'s purple color and the appearance of a brown suspension of MnO_2 is a positive test.

CHROMIC ACID (JONES) TEST FOR ALCOHOLS



SIR EWART RAY
HERBERT JONES
1911 — 2002

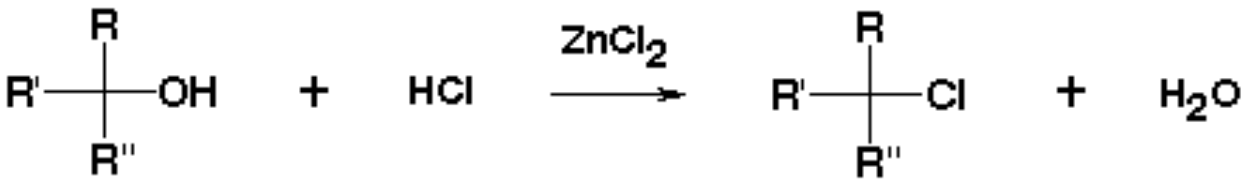


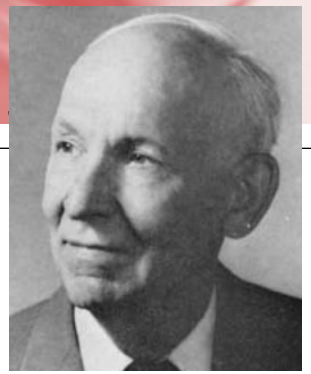
Standards
1-Butanol, 2-Butanol, t-Butyl alcohol

Procedure
Dissolve 10 mg or 2 drops of the unknown in 1 mL of pure acetone in a test tube and add to the solution 1 small drop of Jones reagent (chronic acid in sulfuric acid). A positive test is marked by the formation of a green color within 15 seconds upon addition of the orange-yellow reagent to a primary or secondary alcohol. Aldehydes also give a positive test, but tertiary alcohols do not. The Jones reagent will already be prepared for you.

Positive Test
A positive test for aldehydes and primary or secondary alcohols consists in the production of an opaque suspension with a green to blue color. Tertiary alcohols give no visible reaction within 2 seconds, the solution remaining orange in color. Disregard any changes after 15 seconds.

LUCAS TEST FOR ALCOHOL





Howard Lucas
1885—1963

Standards
1-Butanol, 2-Butanol, t-Butyl alcohol.

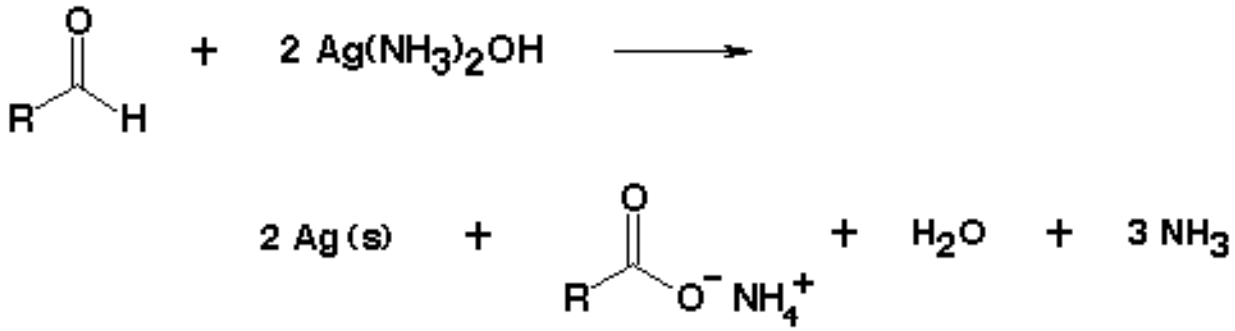
Procedures
To 0.2 mL or 0.2 g of the unknown in a test tube add 2 mL of the Lucas reagent at room temperature. Stopper the tube and shake vigorously, then allow the mixture to stand. Note the time required for the formation of the alkyl chloride, which appears as an insoluble layer or emulsion. The Lucas reagent is already prepared for you.

Positive test
Appearance of a cloudy second layer or emulsion

- 3° alcohols: immediate to 2-3 minutes
- 2° alcohols: 5 -10 minutes
- 1° alcohols: no reaction

TOLLENS TEST FOR ALDEHYDES

Aldehyde



Standards

Cyclohexanone and Benzaldehyde

Procedure

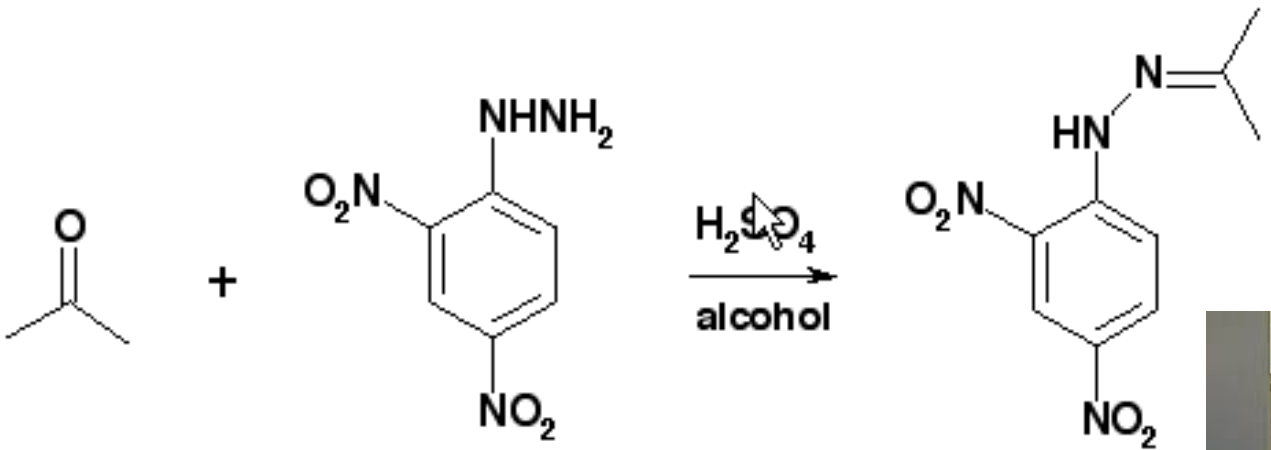
Add one drop or a few crystals of unknown to 1 mL of the freshly prepared Tollens reagent. Gentle heating can be employed if no reaction is immediately observed.

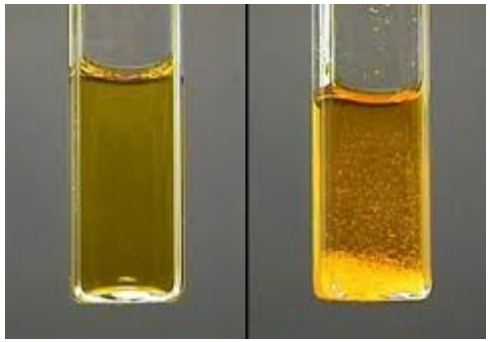
Tollens reagent: Into a test tube which has been cleaned with 3M sodium hydroxide, place 2 mL of 0.2 M silver nitrate solution, and add a drop of 3M sodium hydroxide. Add 2.8% ammonia solution, drop by drop, with constant shaking, until almost all of the precipitate of silver oxide dissolves. Don't use more than 3 mL of ammonia. Then dilute the entire solution to a final volume of 10 mL with water.

Positive Test

Formation of silver mirror or a black precipitate is a positive test.

2,4-DNPH TEST FOR ALDEHYDES AND KETONES





Standards
Cyclohexanone, Benzophenone, and Benzaldehyde

Procedure
Add a solution of 1 or 2 drops or 30 mg of unknown in 2 mL of 95% ethanol to 3 mL of 2,4-dinitrophenylhydrazine reagent. Shake vigorously, and, if no precipitate forms immediately, allow the solution to stand for 15 minutes.
The 2,4-dinitrophenylhydrazine reagent will already be prepared for you.

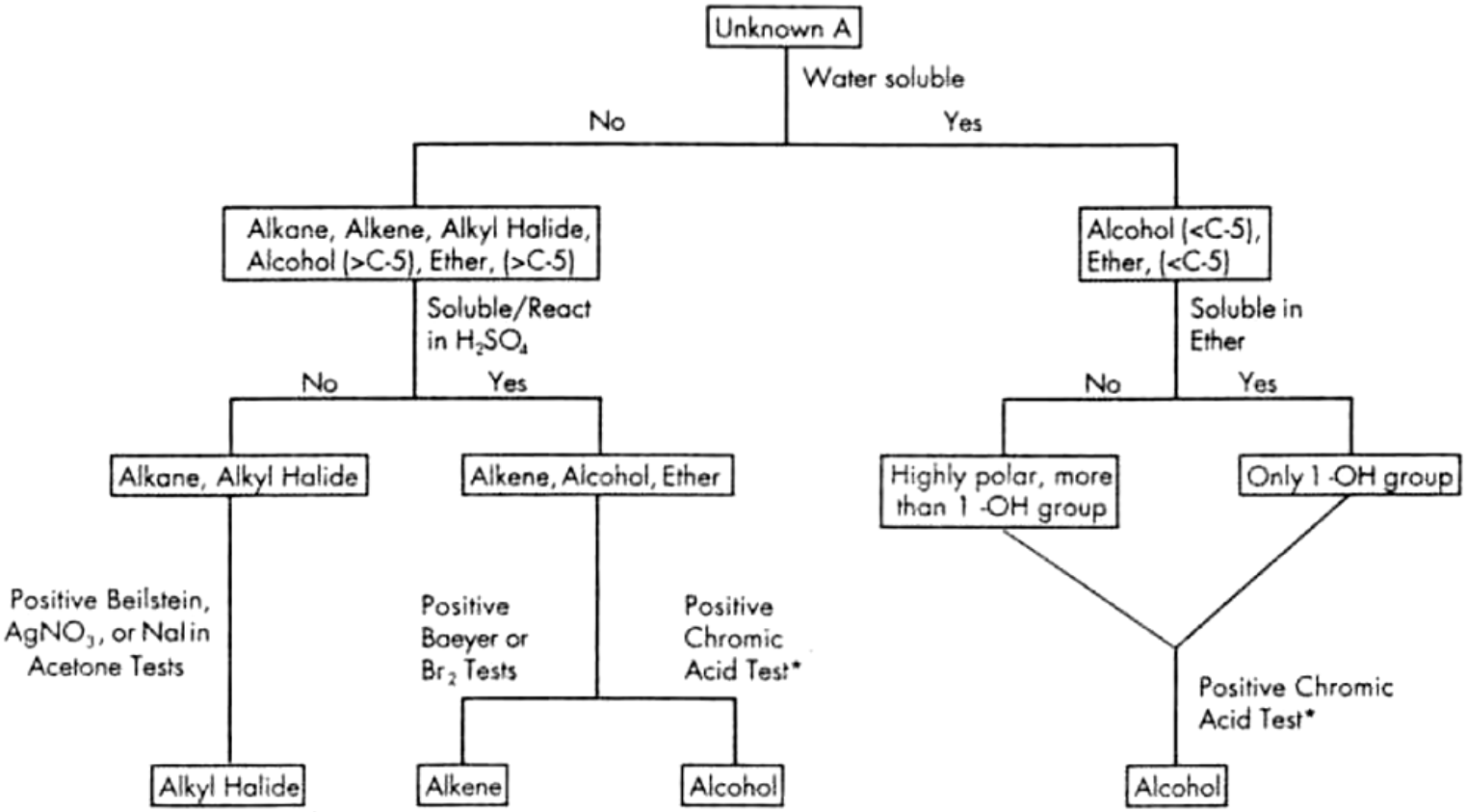
Positive test
Formation of a precipitate is a positive test.

LABORATORY EXERCISE No.3

- Moodle links - quiz
- Laboratory exercise No.3 manual

- sample A = elemental analysis
- sample B = functional analysis
- flowcharts 1/2/3

LABORATORY EXERCISE No.3



FLOW CHART

For Alkane, Alkene, Alkyl Halide, Alcohol, and Ether

SOURCES


www.wellesley.edu/Chemistry/chem211lab/Orgo_Lab_Manual/Appendix/ClassificationTests/unsaturation.html
Online Lab Manual Home
site map
read first
about course
lab manual
appendix

PHYSICAL PROPERTIES

TABLE 1.1 Some Physical Properties

Property	Using the Property to Distinguish Substances
Color	Is the substance colored or colorless? What is the color, and what is its intensity?
State of matter	Is it a solid, liquid, or gas? If it is a solid, what is the shape of the particles?
Melting point	At what temperature does a solid melt?
Boiling point	At what temperature does a liquid boil?
Density	What is the substance's density (mass per unit volume)?
Solubility	What mass of substance can dissolve in a given volume of water or other solvent?
Electric conductivity	Does the substance conduct electricity?
Malleability	How easily can a solid be deformed?
Ductility	How easily can a solid be drawn into a wire?
Viscosity	How easily will a liquid flow?