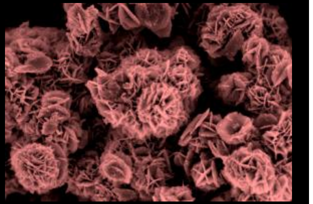

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INTRODUCTION

CEB 4032: ANALYTICAL CHEMISTRY
CFB3032: ANALYTICAL INSTRUMENTATION

TS. CHM. DR. MOHD DZUL HAKIM WIRZAL

Chemical Engineering

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Outline

- Analytical Objectives
- Qualitative Analysis
- Quantitative Analysis
- Analytical Methodology
- Type of equipment which includes Gravimetry, Spectrophotometry, Spectroscopy and Chromatography.
- Basic Tools and Operation
- Data Handling and Statistic
- Errors

Learning Outcomes:

<u>At the end of this chapter</u>:

(1) Objectives of analytical chemistry.

(2) Definition of analytical chemistry, qualitative anlaysis and quantitative analysis.

(3) Type of equipment and basic tools used in analytical chemistry and laboratory safety.

(4) Basic calculation, statistical method and errors in data handling for reliability and significant derived results.

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What is Analytical Chemistry?

The branch of chemistry that deals with the separation, identification and determination of component in a sample.

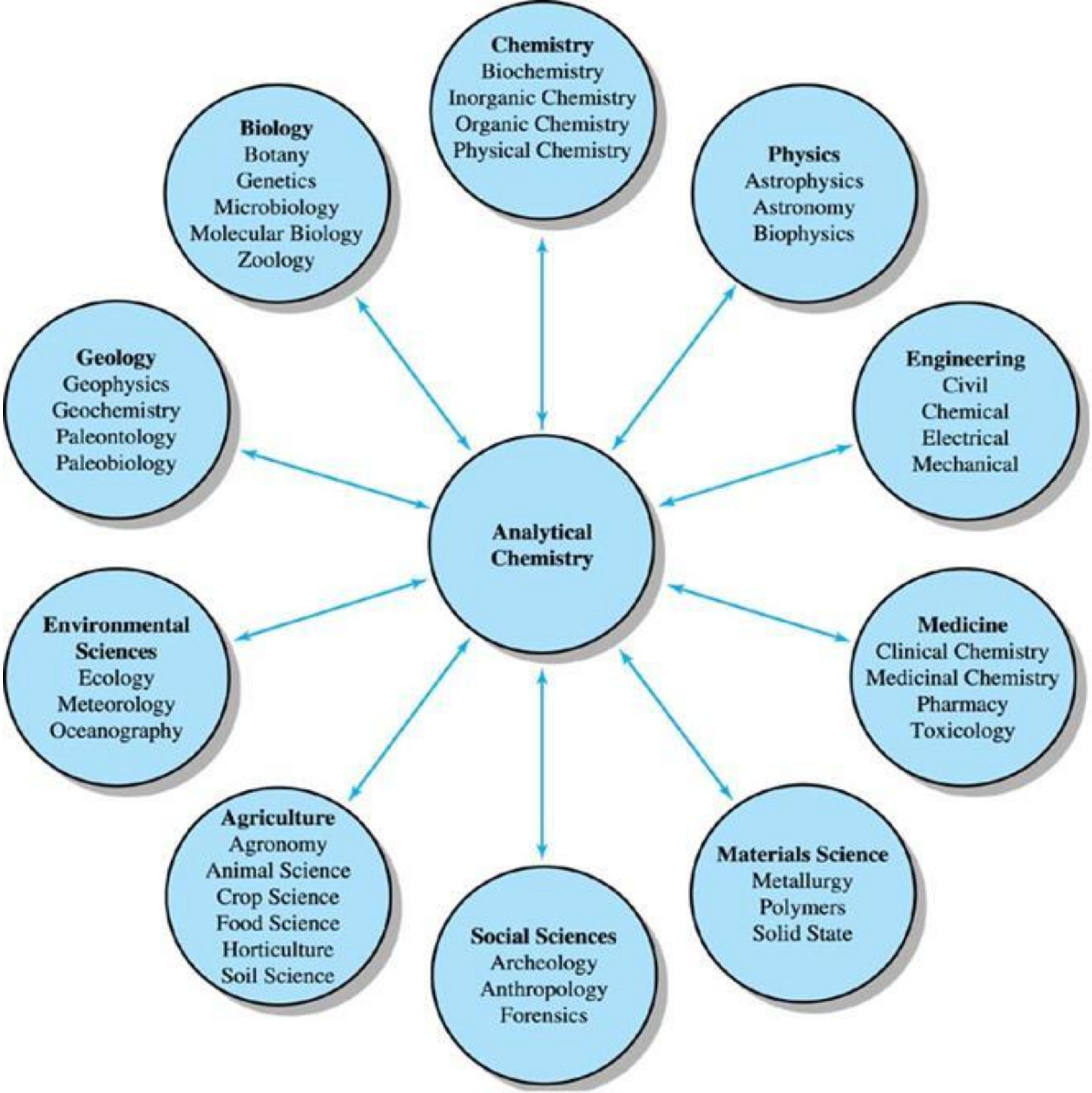
WHY BOTHER LEARNING ANALYTICAL CHEMISTRY??????

LETS THINK AND SHARE

Main Objective of Analytical Chemistry

- Chemicals make up everything we use or consume, and knowledge of the chemical composition of many substances is important in our daily lives.

Examples:
-N content in fertilizer
-contaminants in food
-nutrients in food
-CO in air
-CO_2 in NG
-glucose in blood
-carbon in steel


Chemistry
Biochemistry
Inorganic Chemistry
Organic Chemistry
Physical Chemistry
Biology
Botany
Genetics
Microbiology
Molecular Biology
Zoology
Physics
Astrophysics
Astronomy
Biophysics
Geology
Geophysics
Geochemistry
Paleontology
Paleobiology
Engineering
Civil
Chemical
Electrical
Mechanical
Analytical Chemistry
Environmental Sciences
Ecology
Meteorology
Oceanography
Medicine
Clinical Chemistry
Medicinal Chemistry
Pharmacy
Toxicology
Agriculture
Agronomy
Animal Science
Crop Science
Food Science
Horticulture
Soil Science
Social Sciences
Archeology
Anthropology
Forensics
Materials Science
Metallurgy
Polymers
Solid State

Analytical Objectives

- Measuring the chemical composition of natural and artificial materials.
- Identify the substances which may be present in the material.
- Determine the exact amounts of the identified substance.

Analytical Chemist

- Medicine: basis for clinical laboratory tests which help physicians diagnose disease and chart progress in recovery.

- Industry: testing raw materials, assuring the quality of products whose chemical composition is critical (household products, fuels, paints, pharmaceuticals, etc).

- Environment quality: testing for suspected contamination.

- Nutritional value of food: major components such as protein, carbohydrates, trace amount of vitamins and minerals, calories.

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Qualitative and Quantitative Analysis

Discipline of Analytical Chemistry

Qualitative
(What is it?)

Quantitative
(How much is it?)

Qualitative Analysis

- Identification of elements, ions or compounds present in a sample.
- The sample may be solid, liquid or gas.

Example: The presence of gunpowder residue on a hand generally requires only qualitative analysis.

- Qualitative test may be performed by selective chemical reactions or with the use of instrumentation.

Selective and Specific reaction:

Selective reaction

-Reaction can occur with other substances but exhibits in degree of preference for the substance of interest.

Specific reaction

-Reaction that occur only with the substance of interest.

*few reactions are specific but many exhibit selective

Quantitative Analysis

- Determination of how much of one or more constituents is present.

Example: Price of diesel will be determined by the percent of sulfur impurity present

- A large portion of this course deals with methods that are used to determine how much a material is present.

- We need to review the general steps that are taken for any quantitative method.

- These steps are taken to insure an accurate and reliable answer.

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Getting Started: Analytical Methodology/Process

1. Plan: Qualitative or quantitative or both; what kind of information have; which technique is suitable/technique to be used.

2. Sampling: Accuracy depends on proper sampling, characteristic of sample is very important, required good representative sample.

3. Sample preparation: depends on analytical techniques.

4. Analytical measurement.

5. Data Analysis: Whether the data make sense or not.

1. Plan/Technique to be Used

1. Accuracy and sensitivity
2. Cost
3. Number of samples to be assayed
4. Number of components in a sample

The approach must produce the results in time and cost effective.

What type of information you need?

- Complete analysis
  - The goal is to determine the amount of each component in a sample.

- Ultimate analysis
  - The amount of each element present without regard to actual composition.

- Partial analysis
  - Determine one or a limited number of species in a sample(the most common approach)

    e.g. Fe in an ore sample

    Presence of lead in a water sample

2. Sampling

1. Must be representative

   -To insure the results reflect average composition.

   e.g. Fe in an ore- minerals and ores are heterogeneous → to assay any single sample may not yield valid results for an entire sample lot.

   Proper sample selection and preparation may help.

2. Sample selection

   - Requires some knowledge as to sample source and history, random sampling may help, powder the sample, blend the sample, etc.

3. Sample Preparation

One must then convert the sample to a form of suitable for the method of analysis:

This may include:

1. Drying to insure an accurate weight
2. Sample dissolution
3. Elimination or masking of potential interferences
4. Conversion of analyte to a single or measureable form

4. Analytical Measurement/Method

It is essential to define clearly the nature of the analytical problem.

In general, the following points should be considered when choosing an method for any measurement.

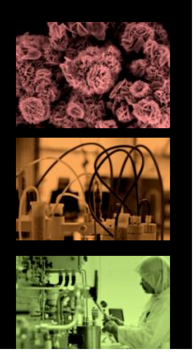
- Accuracy and precision required
- Available sample amount
- Concentration range of the analyte
- Interference in sample
- Physical and chemical properties of the sample matrix
- Number of sample to be analyzed
- Speed

- Classical Methods: Wet chemical methods such as precipitation, extraction, distillation, boiling or melting points, gravimetric and titrimetric measurements.

- Instrumental Methods: Analytical measurements (conductivity, electrode potential, light absorption or emission, mass-to-charge ratio, fluorescence etc.) are made using instrumentation.

Type of Method/Equipment

- Gravimetry → Methods based on a measured weight.
- Titrimetry → Methods based on the measured volume.
- Electrochemical → Approaches that rely on the measurement of potential, current, resistance, charge etc.
- Spectral Methods →Interaction of an analyte with electromagnetic radiation.
- Chromatography →Separation of a material due to its interaction with two different phases.



Different methods provide a range of precision, sensitivity, selectivity, and speed capabilities

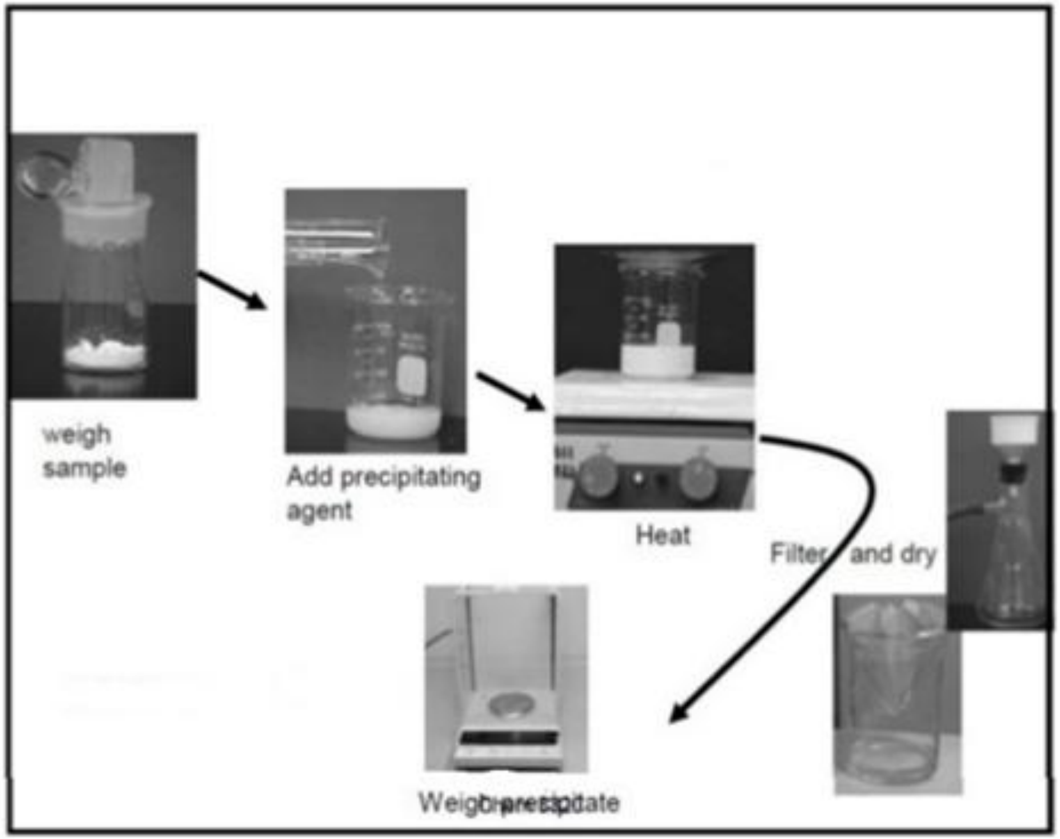
Table 1.1

Comparison of Different Analytical Methods

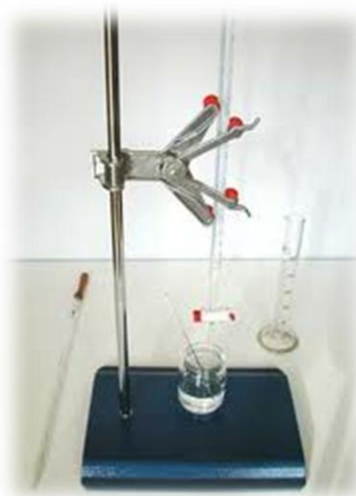
Method	Approx. Range (mol/L)	Approx. Precision (%)	Selectivity	Speed	Cost	Principal Uses
Gravimetry	10^{-1}–10^{-2}	0.1	Poor–moderate	Slow	Low	Inorg.
Titrimetry	10^{-1}–10^{-4}	0.1–1	Poor–moderate	Moderate	Low	Inorg., org.
Potentiometry	10^{-1}–10^{-6}	2	Good	Fast	Low	Inorg.
Electrogravimetry, coulometry	10^{-1}–10^{-4}	0.01–2	Moderate	Slow–moderate	Moderate	Inorg., org.
Voltammetry	10^{-3}–10^{-10}	2–5	Good	Moderate	Moderate	Inorg., org.
Spectrophotometry	10^{-3}–10^{-6}	2	Good–moderate	Fast–moderate	Low–moderate	Inorg., org.
Fluorometry	10^{-6}–10^{-9}	2–5	Moderate	Moderate	Moderate	Org.
Atomic spectroscopy	10^{-3}–10^{-9}	2–10	Good	Fast	Moderate–high	Inorg., multielement
Chromatography	10^{-3}–10^{-9}	2–5	Good	Fast–moderate	Moderate–high	Org., multicomponent
Kinetic methods	10^{-2}–10^{-10}	2–10	Good–moderate	Fast–moderate	Moderate	Inorg., org., enzymes

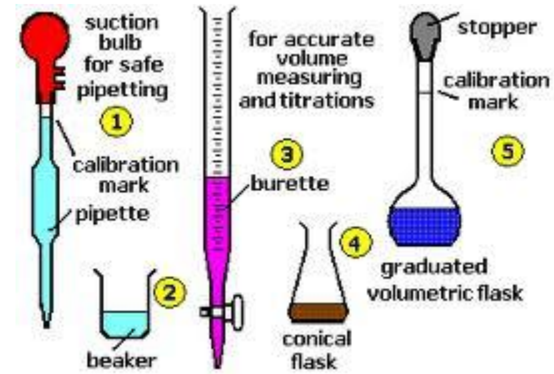
Classical and Instrumentation Methods

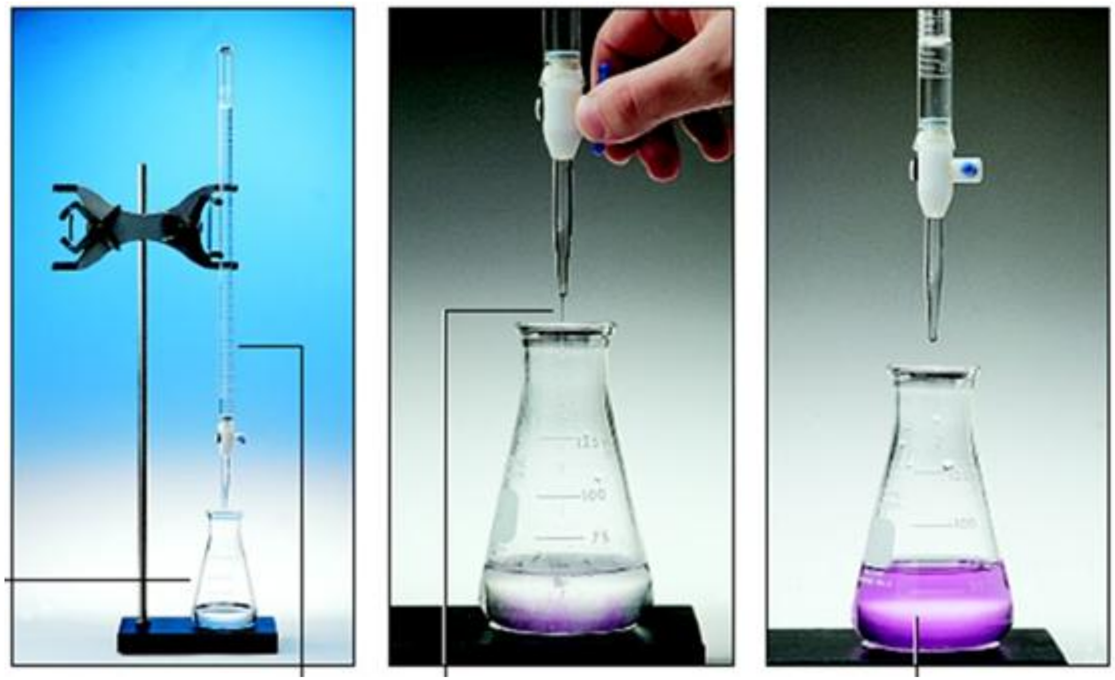
Gravimetric



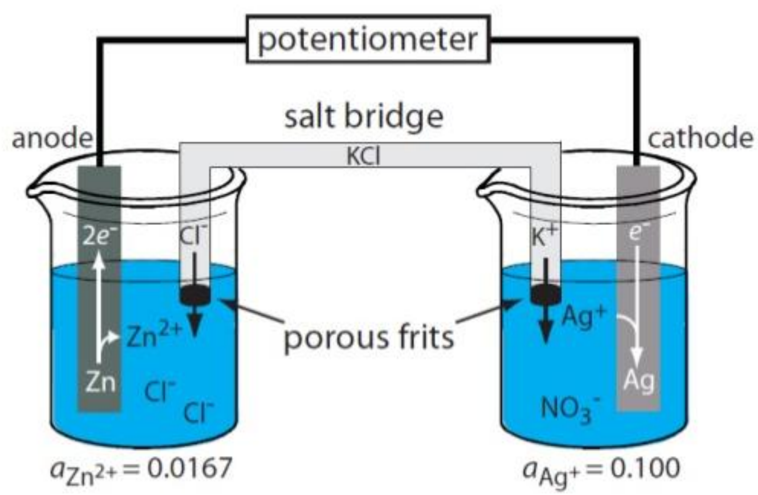
Volumetric



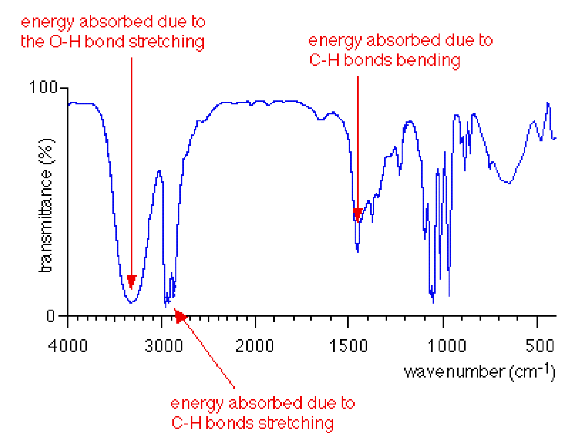

suction bulb for safe pipetting
1
calibration mark
pipette
2
beaker
for accurate volume measuring and titrations
3
burette
4
conical flask
stopper
calibration mark
5
graduated volumetric flask



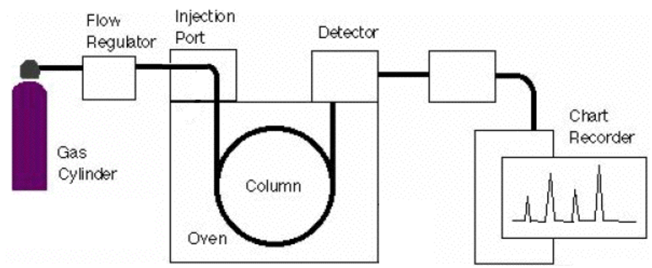
Electrochemical



Spectral Methods



Chromatography



5. Data Analysis/Results

Final step in analysis methodology:

This may include:

- ➢Application of the standard curve
- ➢Elimination of error based on replicates
- ➢Reporting in a standard, useable format.

Verification of method → to analyze a standard reference material of known composition.

Summary Steps in an Analysis

1. Plan/ Technique to be used

Define the Problem

Factors

- What is the problem—what needs to be found? Qualitative and/or quantitative?
- What will the information be used for? Who will use it?
- When will it be needed?
- How accurate and precise does it have to be?
- What is the budget?
- The analyst (the problem solver) should consult with the client to plan a useful and efficient analysis, including how to obtain a useful sample.

Select a Method

Factors

- Sample type
- Size of sample
- Sample preparation needed
- Concentration and range (sensitivity needed)
- Selectivity needed (interferences)
- Accuracy/precision needed
- Tools/instruments available
- Expertise/experience
- Cost
- Speed
- Does it need to be automated?
- Are methods available in the chemical literature?
- Are standard methods available?

2. Sampling

Obtain a Representative Sample

Factors

- Sample type/homogeneity/size
- Sampling statistics/errors

3. Sample Preparation

Prepare the Sample for Analysis

Factors

- Solid, liquid, or gas?
- Dissolve?
- Ash or digest?
- Chemical separation or masking of interferences needed?
- Need to concentrate the analyte?
- Need to change (derivatize) the analyte for detection?
- Need to adjust solution conditions (pH, add reagents)?

Perform Any Necessary Chemical Separations

- Distillation
- Precipitation
- Solvent extraction
- Solid phase extraction
- Chromatography (may be done as part of the measurement step)
- Electrophoresis (may be done as part of the measurement step)

4. Analytical Measurement

Perform the Measurement

Factors

- Calibration
- Validation/controls/blanks
- Replicates

5. Data Analysis and Results

Calculate the Results and Report

- Statistical analysis (reliability)
- Report results with limitations/accuracy information

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The way you perform an analysis will depend on your experience, the equipment available, the cost, and the time involved.

Good laboratory practice (validation) is required to assure accuracy of analyses.

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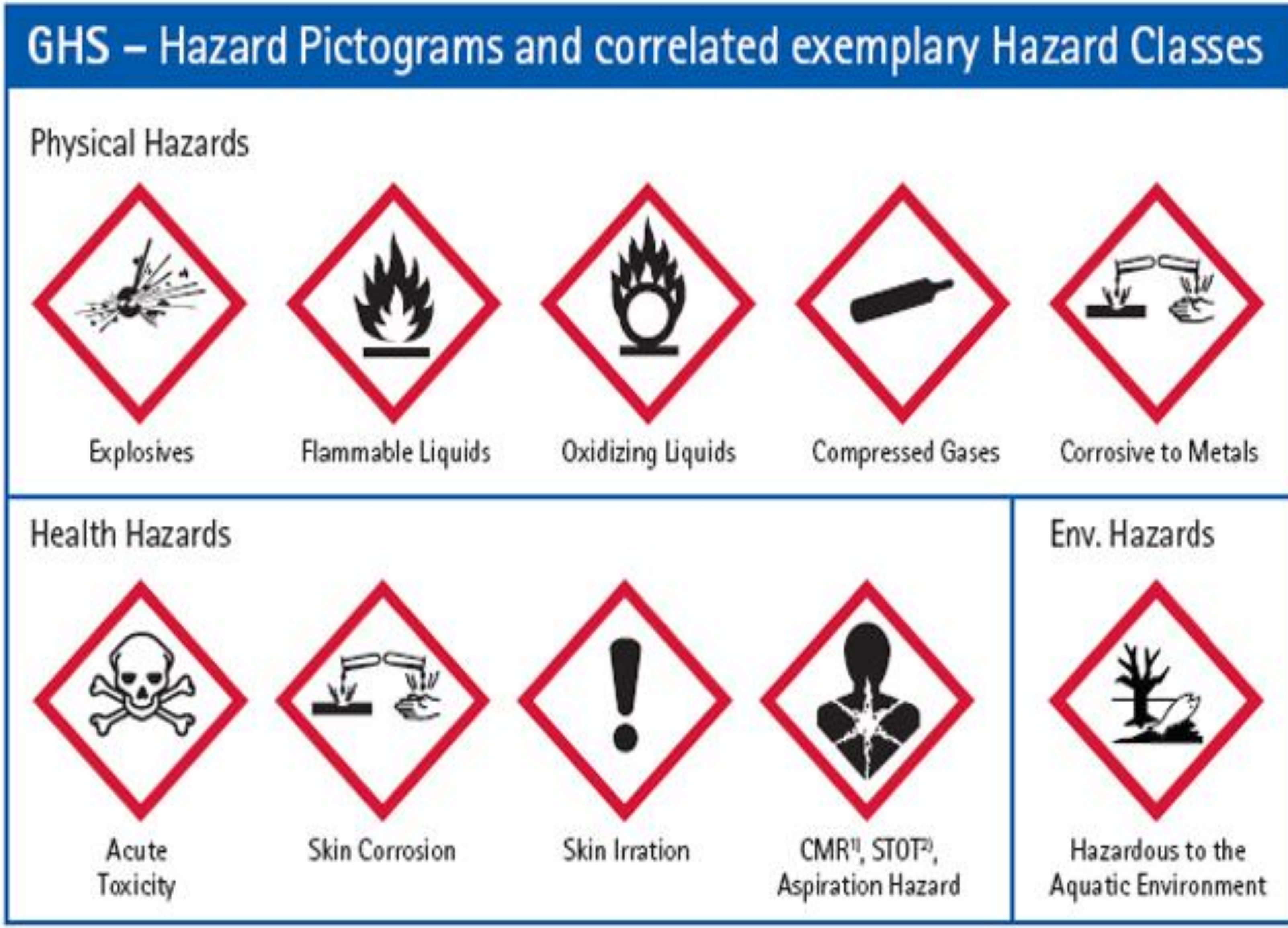
Safe, Ethical Handling of Chemicals and Waste

- Safety should come first.
- Before working, familiarize yourself with safety features of your laboratory.
- Wear goggles or safety glasses all the time → protect your eyes.
- Wear lab coat, long pants and covered shoes.
- Rubber gloves→ protect hands from chemicals.
- Clean up any chemical spills immediately.
- Chemicals with hazardous fume should always be used under a fume hood.
- Label all the vessels.



1) carcinogenic, germ cell mutagenic, toxic to reproduction / 2) specific target organ toxicity

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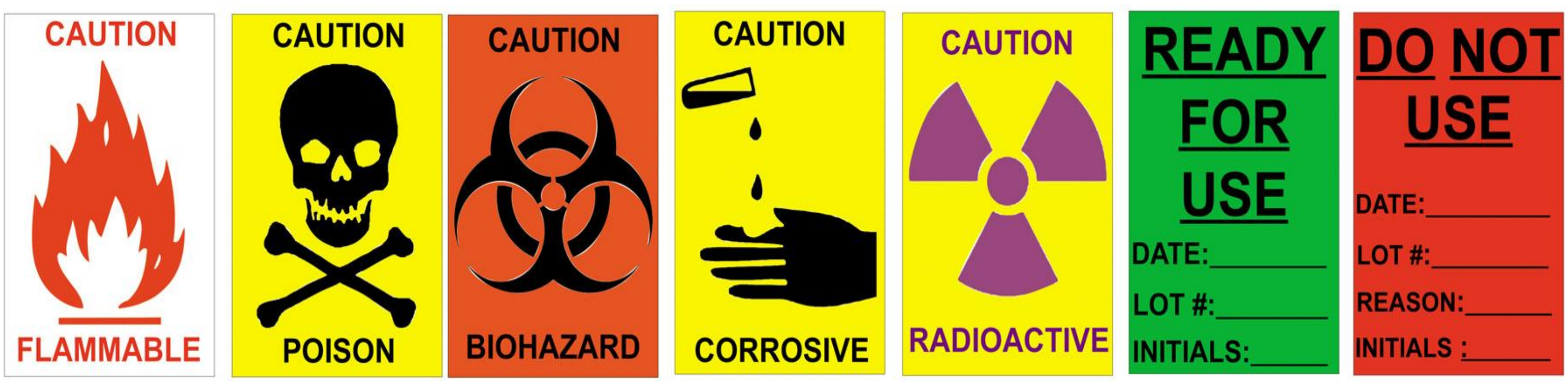
CAUTION
HIGHLY TOXIC CHEMICAL
Use by Authorized Personnel Only


CAUTION
FLAMMABLE
CAUTION
POISON
CAUTION
BIOHAZARD
CAUTION
CORROSIVE
CAUTION
RADIOACTIVE
READY FOR USE
DATE:
LOT #:
INITIALS:
DO NOT USE
DATE:
LOT #:
REASON:
INITIALS :

What do we use in a Analytical Lab?

Basic Tools:

-Chemicals

-Balances

-Glassware

-Heating apparatus

-Instruments

-Miscellaneous: filter paper, tongs, stir rods, beaker, etc

Handling of Chemicals

- The key is to limit contamination of chemicals and reagents.
- Never return excess chemicals to original bottle.
- Keep the workplace and balances clean.
- Not everything goes down the drain.

Analytical Balance

- Electronic balance → to balance the load on the pan.
- Capacity → 100-200 g
- Sensitivity → 0.01-0.1 mg
- Sensitivity → the smallest increment of mass that can be measured.
- Chemical should never be placed directly on the weighing pan.


APX-100
Denver Instrument
ZERO

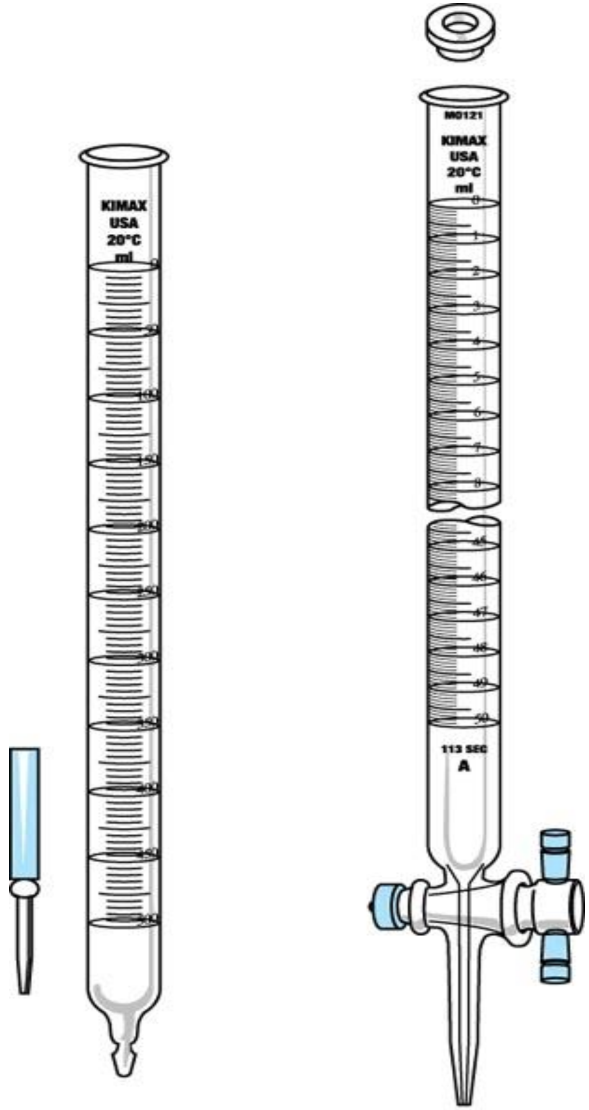
Using a Balance

- Always weight chemicals in a clean ‘vessel’, not on the pan!
- Vessel → glassware, weighing dish, or weighing paper (put on the balance).
- Samples normally need to be weight at ambient temperature (room temperature to get an accurate reading).
- Balance need to be calibrated and leveled to work properly.
- Using tongs, tissue or paper towel vessel.

Glassware and Apparatus

- Burets → measure the volume of liquid precisely
- Volumetric Flasks → calibrated flasks to contain a particular volume
- Pipets → deliver known volumes of liquid (calibrated).
- Syringes → dispenses tiny volumes (accuracy and precision ~ 1%)
- Desiccator→ closed chamber containing a drying agent called desiccant
- Filters → filter and collect precipitate

Burets



(a) (b)

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Manipulating buret stopcock

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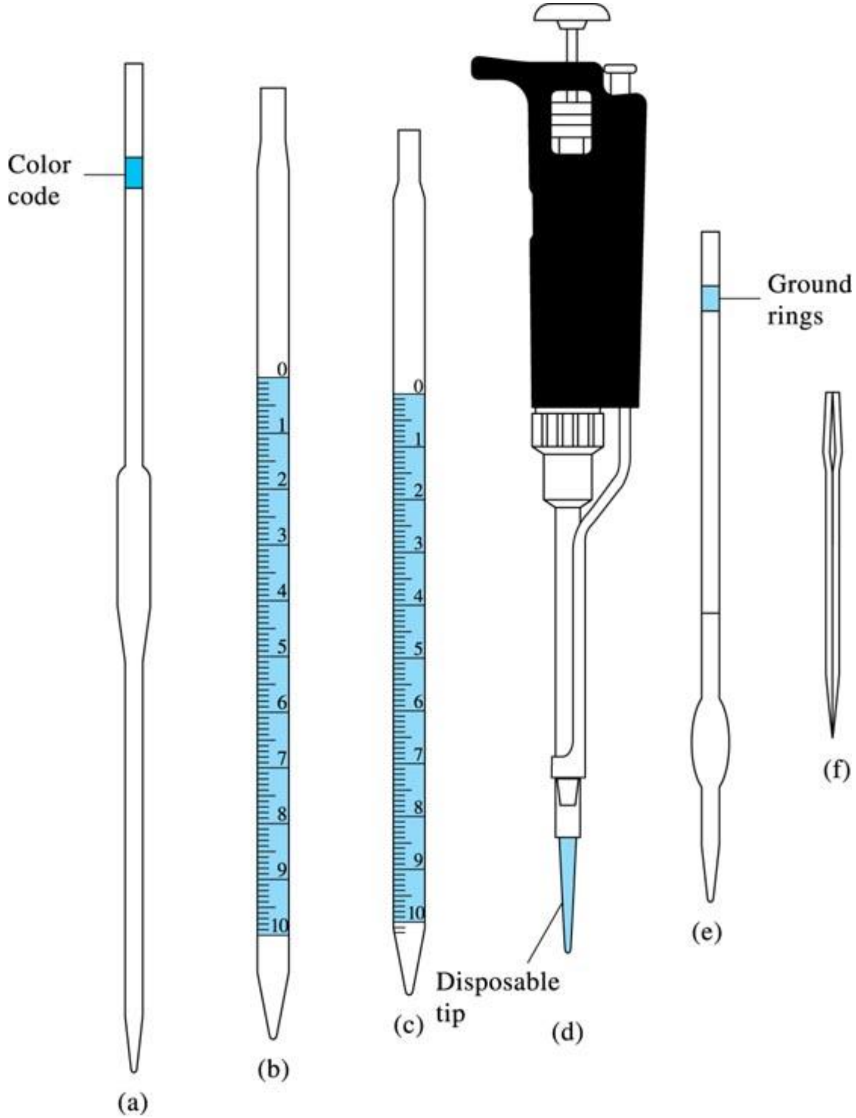
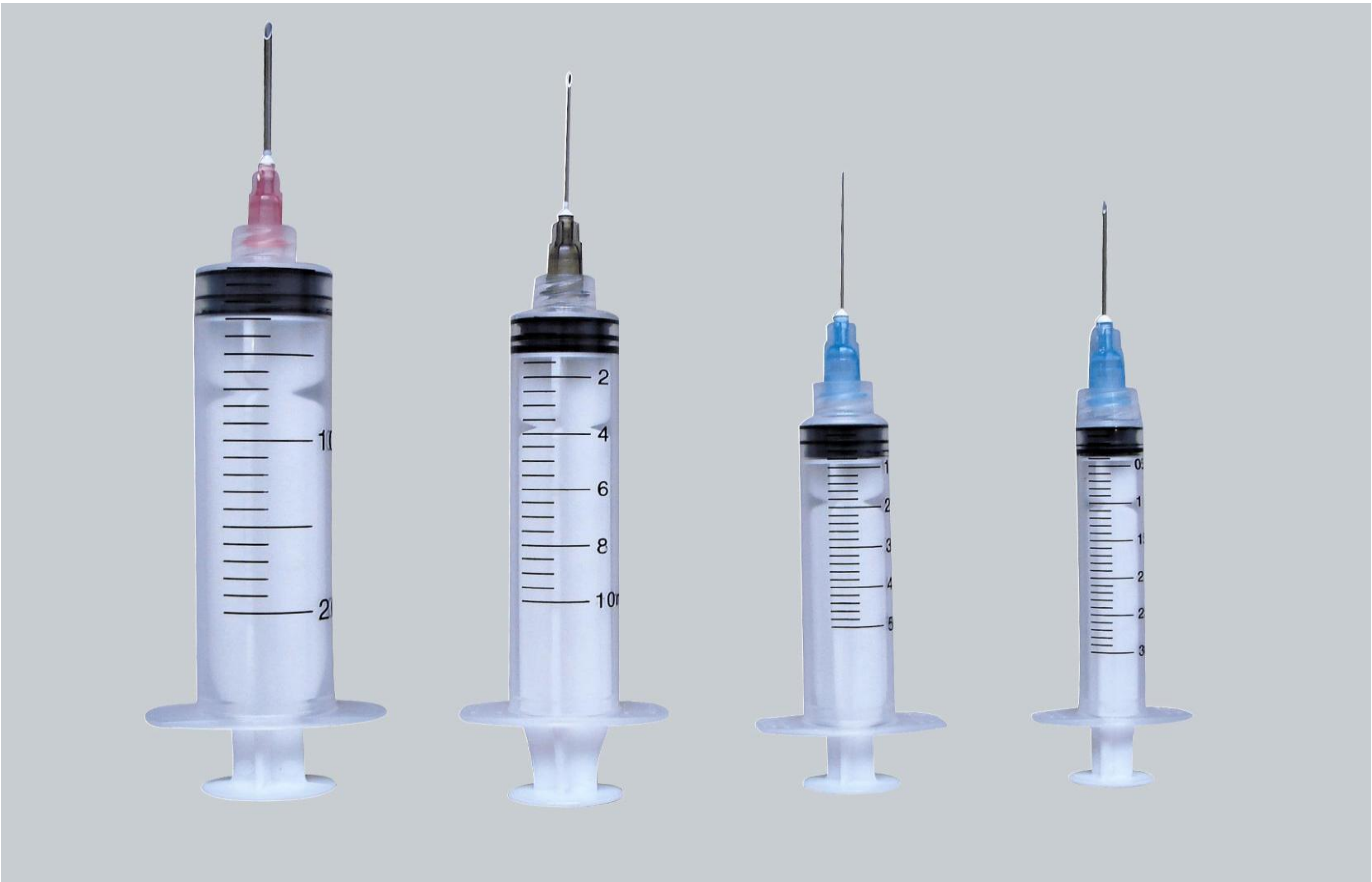
Volumetric Flasks

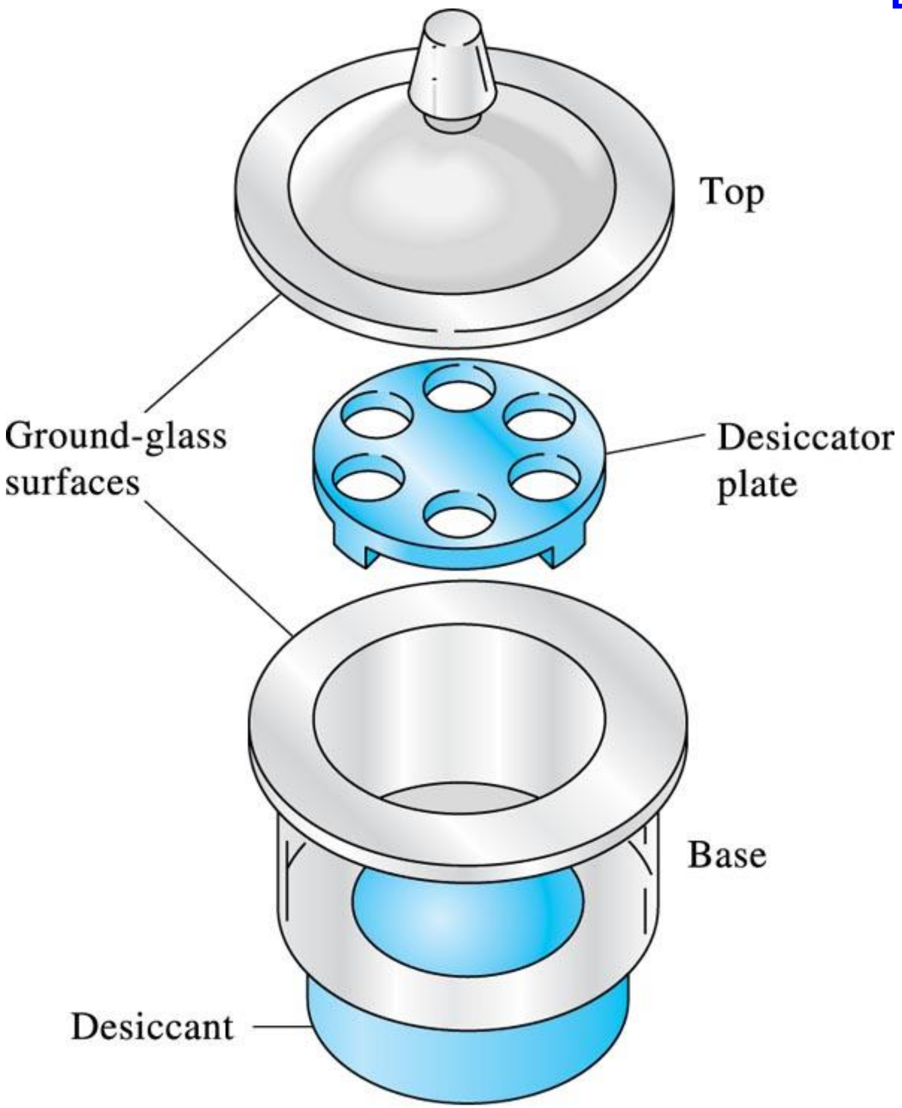


Pipets and Micropipets

Syringes



Desiccator



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Filter Paper

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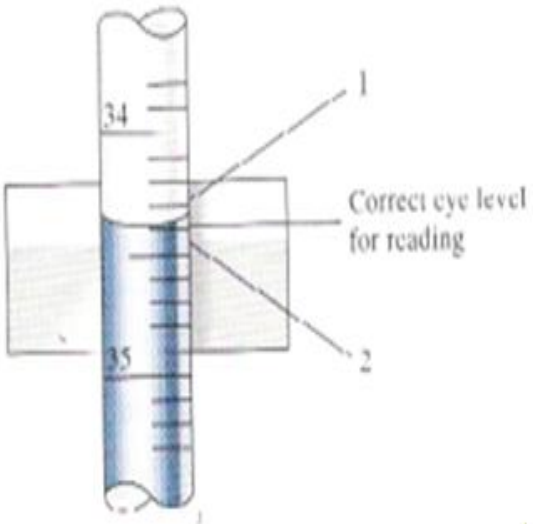
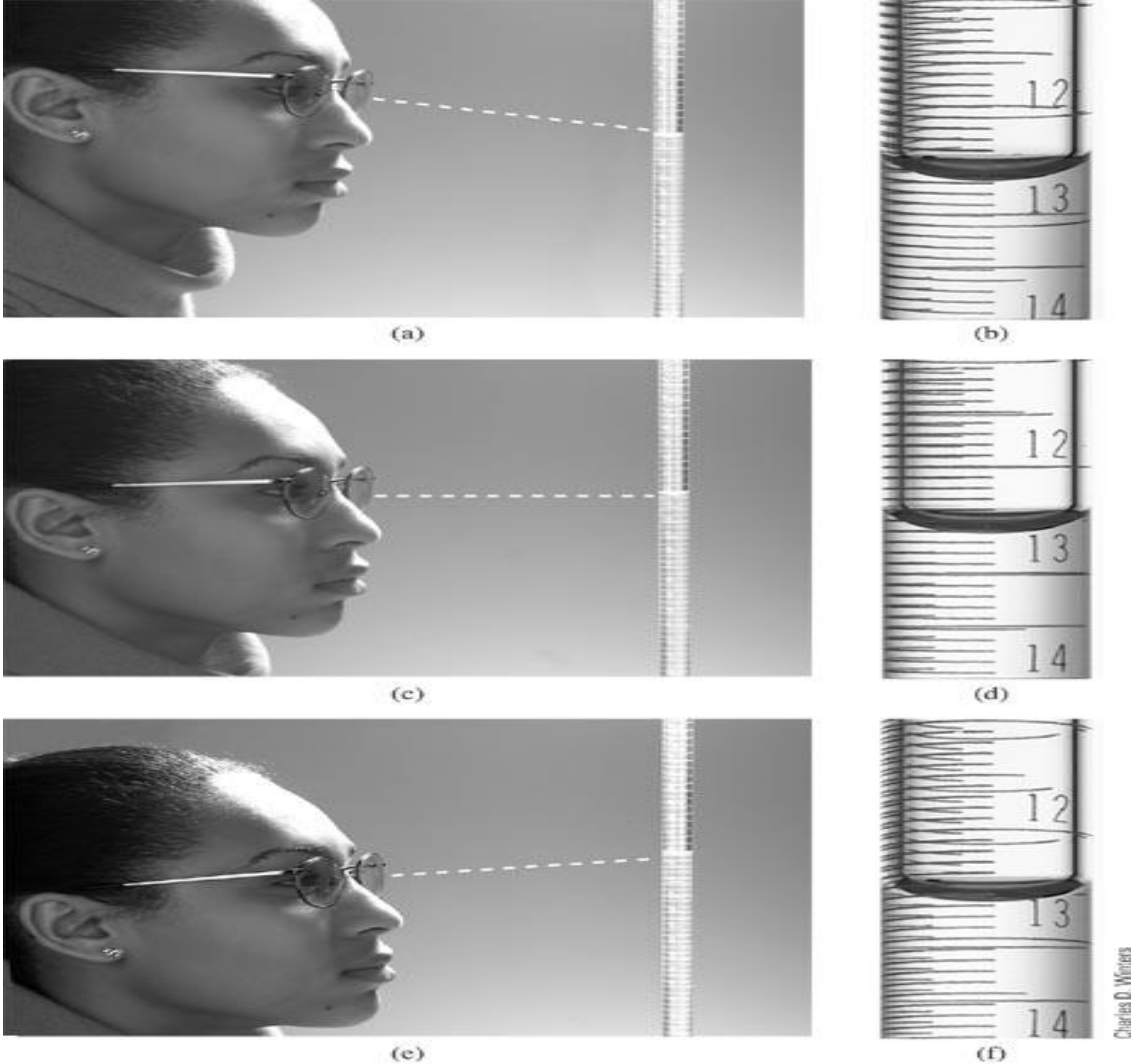
Washing by decantation and transferring the precipitate

Dispensing an aliquot

Reading Volume

- Meniscus → the curved surface of a liquid at its interface with the atmosphere.
- Read the bottom of the concave of the meniscus.
- Make sure your line of sight is level with meniscus.
- Parallax→ apparent displacement of a liquid level or of a pointer as an observer changes position.
- Parallax occurs when an object is viewed from a position that is not at a correct angle to the object.




(a)
(b)
(c)
(d)
(e)
(f)
12
13
14
Charles D. Winters

The Lab Notebook

- To record what you did and what you observed during the experiment.
- Should be understandable to someone else.
- Contains
  - -Experiment objective and purpose
  - -List of glassware and chemicals
  - -Safety info on chemicals
  - -Flow chart of procedures
  - -Data
  - -Analysis and conclusions

08

Gravimetric Determination of Chloride

The chloride in a soluble sample was precipitated as AgCl and weighed as such.

Sample masses	1	2	3
Mass bottle plus sample, g	27.6115	27.2185	26.8105
-less bottle, g	27.2185	26.8105	26.4517
mass sample, g	0.3930	0.4080	0.3588
Crucible masses, empty	~~20.7925~~	~~22.8311~~	~~21.2488~~
	20.7926	22.8311	~~21.2482~~
			21.2483
Crucible masses, with AgCl, g	~~21.4294~~	~~23.4920~~	~~21.8324~~
	~~21.4297~~	~~23.4914~~	21.8323
	21.4296	23.4915	
Mass of AgCl, g	0.6370	0.6604	0.5840
Percent Cl -	40.10	40.04	40.27
Average percent Cl -		40.12	

Relative standard deviation 3.0 parts per thousand

Date Started 1-10-03

Date Completed 1-16-03

Calculation Used in Analytical Chemistry

Some Important Units of Measurement

SI Units

- A standardized system of units known as the International System of Units (SI).
- This system is based on the seven fundamental base units.
- Numerous other useful units, such as volts, hertz, coulombs, and joules, are derived from these base units.

SI Base Units

Physical Quantity	Name of Unit	Abbreviation
Mass	kilogram	kg
Length	meter	m
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	cd

Prefixes for Units

Prefix	Abbreviation	Multiplier
giga-	G	10^{9}
mega-	M	10^{6}
kilo-	k	10^{2}
deci-	d	10^{-1}
centi-	c	10^{-2}
milli-	m	10^{-3}
micro-	μ	10^{-6}
nano-	n	10^{-9}
pico-	p	10^{-12}
femto-	f	10^{-15}
atto-	a	10^{-18}

The *ångstrom unit, Å*, is a non-SI unit of length that is widely used to express the wavelength of very short radiation such as X-rays (**1 Å = 0.1 nm = 10^{-10} m**). Typical X-radiation lies in the range of 0.1 to 10 Å.

The Mole

- The mole (mol) is the SI unit for the amount of a chemical species.

- It is always associated with a chemical formula and represents Avogadro's number (6.022×10^{23}) of particles represented by that formula.

- The molar mass (M) of a substance is the mass in grams of one mole, g/mol of the substance.

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Example 1

How many mole and milimoles of benzoid acid (MW = 122.1 g/mol) are contained in 2.00 g of the pure acid?

Answer

Amount of HBz = 2.00 g / 122.1 g/mol

= 0.0164 mol

In millimoles = 0.0164 mol x (1000 mmol/1 mol)

= 16.4 mmol

Example 2

How many grams of Na^+ (MW = 22.99 g/mol) are contained in 25.0 g of Na_2SO_4 (MW = 142.0 g/mol)?

Answer

From chemical formula, 1 mol of Na_2SO_4 contains 2 mol of Na^+

Number of mol of Na_2SO_4 = 25 g / 142 g/mol
= 0.1761 mol

Number of mol of Na^+ = 0.1761 mol x 2
= 0.3521 mol

Mass of Na^+ = 0.3521 mol x 22.99 g/mol
= 8.10 g

Solutions and Their Concentrations

- **Expressing Solution Concentrations**
  - **Molar Concentration**
    - The molar concentration (c_x) of a solution of a chemical species X is the number of moles of the solute species that is contained in one liter of the solution (*not one liter of the solvent*).

$$c_x = \frac{no.\ mol\ solute}{no.\ L\ solution}$$

    - Molar concentration, or molarity M, has the dimensions of mol L^{-1}.

Example 3

Calculate the molar concentration of ethanol in an aqueous solution that contained 2.30 g of C_2H_5OH (MW = 46.07 g/mol) in 3.50 L of solution.

Answer

No of mol of C_2H_5OH = 2.30 g / 46.07 g/mol

= 0.05 mol

Molar concentration of C_2H_5OH = 0.05 mol / 3.5 L

= 0.0143 mol/L

= 0.0143 M

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- **Percent Concentration**
  - Chemists frequently express concentrations in terms of percent (parts per hundred).
  - Three common methods are:

$$\text{weight percent (w/w)} = \frac{\text{weight solute}}{\text{weight solution}} \times 100\%$$

$$\text{volume percent (v/v)} = \frac{\text{volume solute}}{\text{volume soln}} \times 100\%$$

$$\text{weight/volume percent (w/v)} = \frac{\text{weight solute, g}}{\text{volume soln, mL}} \times 100\%$$

- **Parts Per Million and Parts Per Billion**

$$c_{\text{ppm}} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \text{ ppm}$$

$$c_{\text{ppb}} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \text{ ppb}$$

– *parts per billion* (ppb)

– *parts per thousand* (ppt)

- 1 ppm = 1 mg/L
- 1 ppb = 1 μg/L

Example 5

What is the molarity of K^+ in a solution that contains 63.3 ppm of $K_3Fe(CN)_6$ (MW = 329.3 g/mol)?

Answer

63.3 ppm of $K_3Fe(CN)_6$ = 63.3 mg/L of $K_3Fe(CN)_6$

Molarity of $K_3Fe(CN)_6$

$$= 63.3 \text{ mg/L} \times \frac{1\ mol}{329.3\ g} \times \frac{1\ g}{1000\ mg}$$

$= 1.9223 \times 10^{-4}$ mol/L

From the chemical formula, 1 mol of $K_3Fe(CN)_6$ contains 3 mol of K^+, thus,

Molarity of K^+ = 1.9223×10^{-4} mol/L x 3

= 5.7669×10^{-4} mol/L

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Chemical Stoichiometry

- Stoichiometry is defined as the mass relationships among reacting chemical species.

- This section provides a brief review of stoichiometry and its applications to chemical calculations.

Empirical Formulas and Molecular Formulas

- An empirical formula gives the simplest whole-number ratio of atoms in a chemical compound.
- In contrast, a molecular formula specifies the number of atoms in a molecule.
- Two or more substances may have the same empirical formula but different molecular formulas.

- For example, CH_2O is both the empirical and the molecular formula for formaldehyde.

- It is also the empirical formula for such diverse substances as acetic acid ($C_2H_4O_2$), glyceraldehyde ($C_3H_6O_3$), and glucose ($C_6H_{12}O_6$).

- The empirical formula is obtained from the percent composition of a compound.

- In addition, the molecular formula requires a knowledge of the molar mass of the species.

Example 6: Stoichiometric Calculations

What mass of $AgNO_3$ (MW =169.9 g/mol) is needed to convert 2.33 g of Na_2CO_3 (MW=106.0 g/mol) to Ag_2CO_3 ?

Given:

$$Na_2CO_3(aq) + 2AgNO_3(aq) \rightarrow Ag_2CO_3(s) + 2NaNO_3(aq)$$

Answer

- Step 1: Mol of Na_2CO_3

$$n_{Na_2CO_3} = 2.33\ \cancel{g\ Na_2CO_3} \times \frac{1\ mol\ Na_2CO_3}{106.0\ \cancel{g\ Na_2CO_3}}$$
$$= 0.02198\ mol\ Na_2CO_3$$

- Step 2: The balanced equation reveals that

$$n_{AgNO_3} = 0.02198\ \cancel{mol\ Na_2CO_3} \times \frac{2\ mol\ AgNO_3}{1\ \cancel{mol\ Na_2CO_3}}$$
$$= 0.04396\ mol\ AgNO_3$$

- Step 3: Mass of $AgNO_3$

$$m_{AgNO_3} = 0.04396\ \cancel{\text{mol AgNO}_3} \times \frac{169.9\ \text{g AgNO}_3}{\cancel{\text{mol AgNO}_3}}$$
$$= 7.47\ \text{g AgNO}_3$$

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End of Topic

Exercise 1

Q1:

Calculate the mass of Ag_2CO_3 (MW = 275.7 g/mol) formed when 25.0 mL of 0.200 M $AgNO_3$ (MW = 169.9 g/mol) are mixed with 50 mL of 0.0800 M Na_2CO_3 (MW = 106 g/mol)?

Q2:

Exactly 0.2220 g of pure Na_2CO_3 (MW = 106 g/mol) was dissolved in 100.0 mL of 0.0731 M HCl (MW = 36.46 g/mol).

a. What mass in grams of CO_2 (MW = 44 g/mol) were evolved?
b. What was the molarity of the excess reactant (HCl or Na_2CO_3)?