



Fundamentals of Analytical Chemistry



Basic Tools of Analytical Chemistry

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The Language of Analytical Chemistry

Analytical Chemistry is the science of,,,

- Analysis,
- Technique,
- Method,
- Development,
- Validation,
- Methodology,
- Procedure,
- Protocol,
- Determination,
- Measurement,
- Calculation,



Basic Tools and Operations of Analytical Chemistry

- Chemicals, apparatus, equipment and instruments

Materials, Standards, Real samples, Additives, Reagents, Solvents, Glass and other wares, Balances, Volumetric wares, Laboratory safety, etc.

- Numbers, units and concentration expressions

Base quantities, SI units, Derived units, Molarity, Molality, Normality, Weight, volume, and weight-tovolume ratios, Converting between units, p-Functions, etc.

- Chemical calculations, stoichiometry and equilibrium

Chemical reactions, Chemical equations, Yield, Theoretical and practical calculations, Calculations based on balanced equations, etc.

- Errors in chemical analyses and measurements

Error sources, Systematic errors (determinate), Random errors (indeterminate), Human errors, Uncertainty, Significant figures, Rounding off, etc.

- Sampling, standardization and calibration

Sample collection, Sample preparation, Standard solution, External standards, Standard additions, Internal standards, etc.

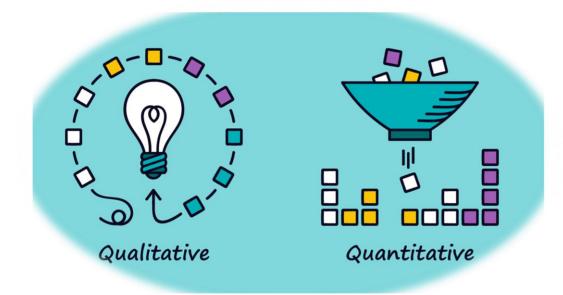
- Methods development and validation

Good laboratory practice, Quality control, Quality assurance, Accuracy, Precision, Sensitivity, Selectivity, Robustness, Ruggedness, Scale of operation, Time, Cost, Laboratory accreditation, etc.

- Statistical data treatment and evaluation

Slope, Intercept, Coefficient of determination, Rejection of results, Detection limits, Statistics software, Making the final decision, etc.

Analytical Chemistry - Objectives

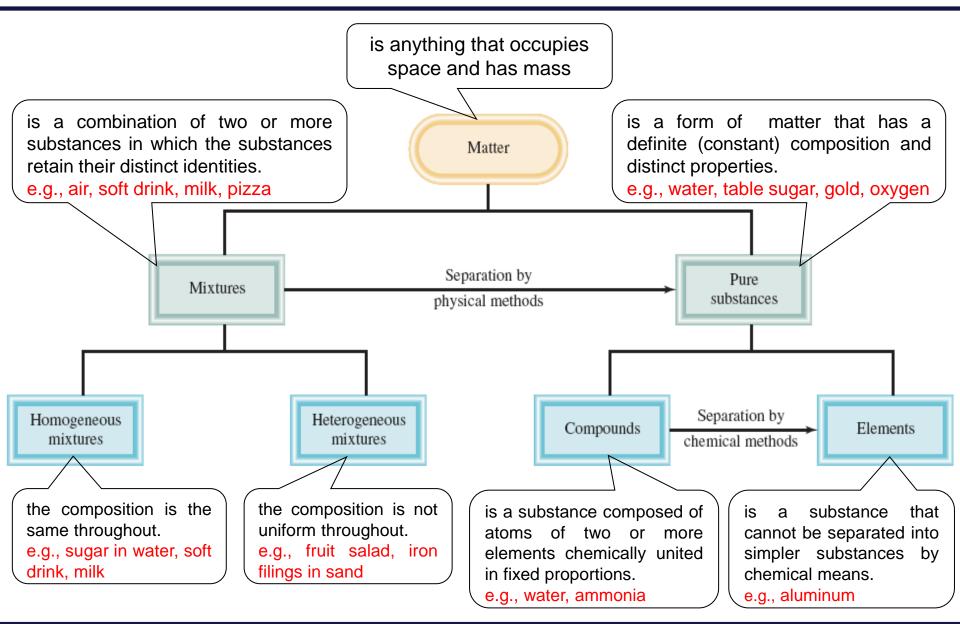


Intrinsic aim attaining analytical information; qualitative and quantitative of the highest quality, accuracy and precision with low uncertainty.

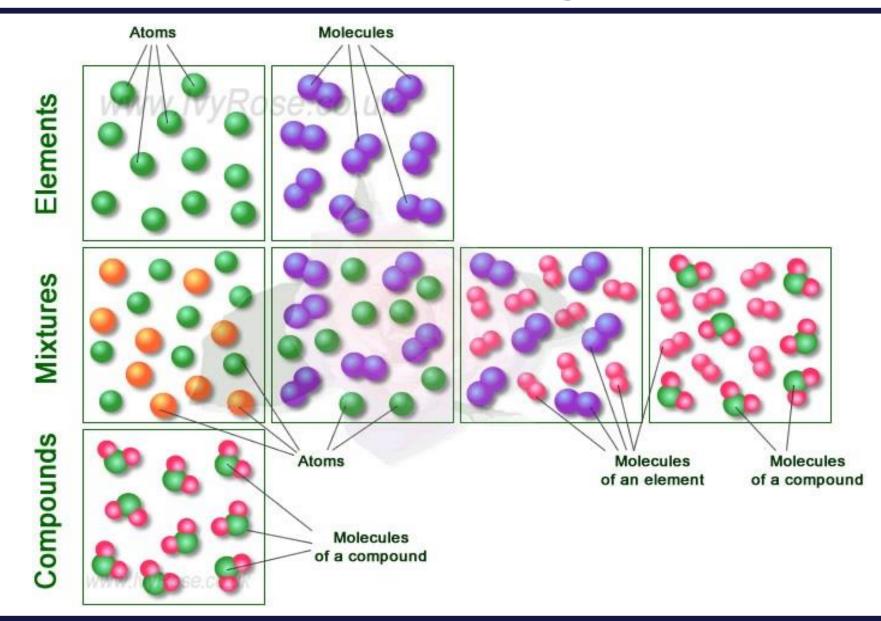
Extrinsic aim

solving analytical problems derived from other fields such as food, biochemistry, health, industry, environment, etc.

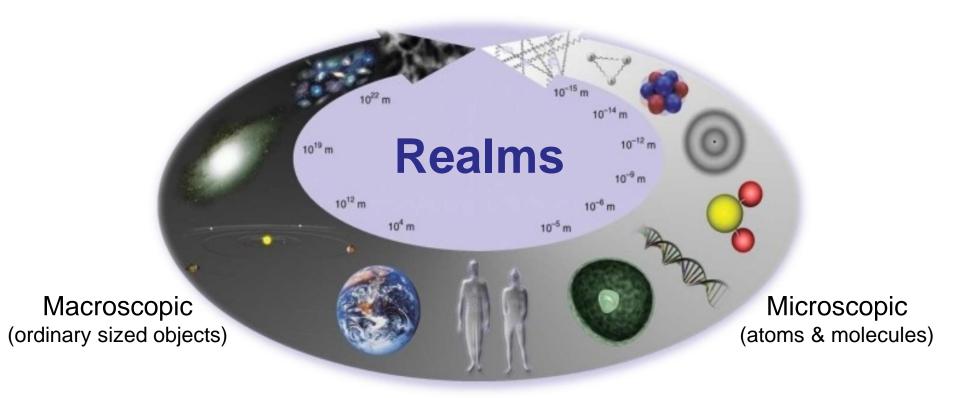
What are you looking for? "Matter"



Classification of matter according to its composition



Units of Measurement



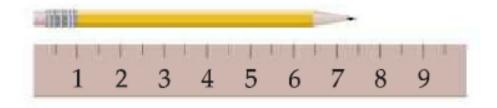
Macroscopic properties, on the ordinary scale, which can be determined directly. e.g., length, mass, volume, temperature.

Microscopic properties, on the atomic or molecular scale, must be determined by an indirect method.

Units

A measured quantity is usually written as a number with an appropriate unit.

7.5 meaningless7.5 cm specifies length



Units are essential to stating measurements correctly.

The units used for scientific measurements are those of the metric units.

The metric system is an internationally agreed decimal system of measurement that was originally based on the mètre des Archives and the kilogramme des Archives introduced by France in 1799.

SI Units (Base Units)

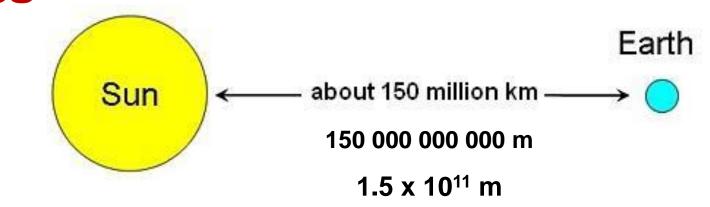
The General Conference of Weights and Measures; the international authority on units, proposed a revised metric system called the **International System of Units** (abbreviated **SI**, from the French Système Internationale d'Unites, 1960).

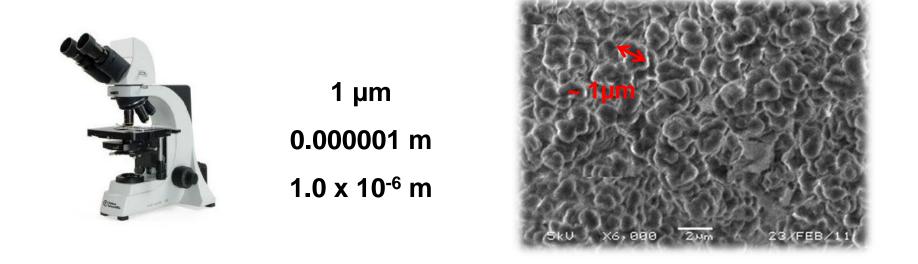
SI Base Units			
Physical Quantity	Name of Unit	Abbreviation	
Mass	kilogram	kg	
Length	meter	m	
Time	second	8	
Temperature	kelvin	К	
Amount of substance	mole	mol	
Electric current	ampere	А	
Luminous intensity	candela	cd	

SI Base Units (seven base units)

- All other units can be derived from these base units.







Prefixes are used to indicate decimal **multiples** or **fractions** of various units. Prefixes convert the base units into units that are appropriate for the item being measured.

Prefix	Abbreviation	Multiplier
yotta-	Y	10^{24}
zetta-	Ζ	10^{21}
exa-	E	10^{18}
peta-	Р	10^{15}
tera-	Т	10^{12}
giga-	G	10^{9}
mega-	М	10^{6}
kilo-	k	10^{3}
hecto-	h	10^{2}
deca-	da	10^{1}
deci-	d	10^{-1}
centi-	С	10^{-2}
milli-	m	10^{-3}
micro-	μ	10^{-6}
nano-	n	10^{-9}
pico-	р	10^{-12}
femto-	f	10^{-15}
atto-	а	10^{-18}
zepto-	Z	10^{-21}
yocto-	У	10^{-24}

Note that a metric prefix simply represents a number:



Mass: is a measure of the amount of matter in an object (SI unit of mass is the kilogram, kg).

Weight: is the force that gravity exerts on an object (SI unit is Newton, N).

In chemistry, the smaller gram (g) is more convenient:

$$1 \text{ kg} = 1000 \text{ g} = 1 \times 10^3 \text{ g}$$

Derived SI Units

The SI are used to derive the units of other quantities.

For example:

Speed is defined as the ratio of distance traveled to elapsed time.

Speed =
$$\frac{length}{time} = \frac{m}{s}$$

Thus, the SI unit for speed is meters per second (m/s).

Volume

SI-derived unit for volume is the *cubic meter* (m³).

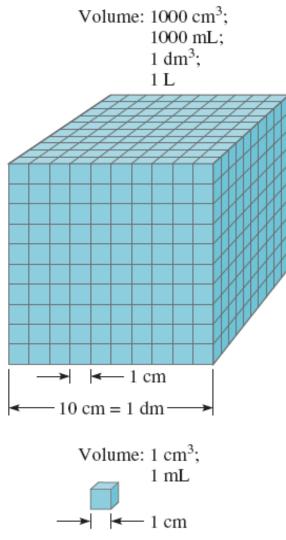
Generally, however, chemists work with much smaller volumes, such as the cubic centimeter (cm³) and the cubic decimeter (dm³):

$$1 \text{ cm}^3 = (1 \times 10^{-2} \text{ m})^3 = 1 \times 10^{-6} \text{ m}^3$$

$$1 \text{ dm}^3 = (1 \times 10^{-1} \text{ m})^3 = 1 \times 10^{-3} \text{ m}^3$$

 $1 m^{3} = 1000 dm^{3}$ $1 L = 1 dm^{3}$ $1 dm^{3} = 1000 cm^{3}$ $1 cm^{3} = 1 mL$

Even though the liter is not an SI unit, volumes are usually expressed in liters (L) and milliliters (mL).



Density

Density is the amount of mass in a unit volume of the substance.

Density =
$$\frac{\text{mass}}{\text{volume}}$$

The SI-derived unit for density is the kilogram per cubic meter (kg/m³).

This unit is awkwardly large for most chemical applications. Therefore, grams per cubic centimeter (g/cm³) and its equivalent, grams per milliliter (g/mL), are more commonly used for solid and liquid densities.

$$1 \text{ g/cm}^3 = 1 \text{ g/mL} = 1000 \text{ kg/m}^3$$

Because gas densities are often very low, we express them in units of grams per liter (g/L): 1 g/L = 0.001 g/mL

Other Derived SI Units

Length = L = m (SI unit, Base quantity) Area = L x L = m x m = m^2 Volume = L x L x L = m x m x m = m^3

Energy = $\frac{1}{2}$ m v² = kg (m/s)² = kg m² s⁻² = J

Pressure = F / A = kg m s^{-2} / m^2 = kg $m^{-1} s^{-2}$ = Pa

Scientific Notation

Chemists often deal with numbers that are either extremely large or extremely small.

Consequently, when working with very large and very small numbers, we use a system called **scientific notation**.

Regardless of their magnitude, all numbers can be expressed in the form $N \times 10^{n}$

where N: is a number between 1 and 10 and

n: the exponent, is a positive or negative integer (whole number).

(1) Express 568.762 in scientific notation: $568.762 = 5.68762 \times 10^2$ move decimal to left (n>0, +ve)(2) Express 0.00000772 in scientific notation: $0.0000772 = 7.72 \times 10^{-6}$ move decimal to right (n<0, -ve)</td>

Addition & Subtraction

 $(7.4 \times 10^3) + (2.1 \times 10^3) = 9.5 \times 10^3$ $(4.31 \times 10^4) + (3.9 \times 10^3) = (4.31 \times 10^4) + (0.39 \times 10^4) = 4.70 \times 10^4$ $(2.22 \times 10^{-2}) - (4.10 \times 10^{-3}) = (2.22 \times 10^{-2}) - (0.41 \times 10^{-2}) = 1.81 \times 10^{-2}$

Multiplication & Division

 $(8.0 \times 10^4) \times (5.0 \times 10^2) = (8.0 \times 5.0) (10^{4+2}) = 40 \times 10^6 = 4.0 \times 10^7$

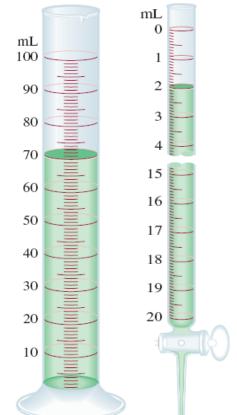
$$\frac{6.9 \ x \ 10^7}{3.0 \ x \ 10^{-5}} = \frac{6.9}{3.0} \ x \ 10^{7-(-5)} = 2.3 \ x \ 10^{12}$$

Significant Figures

In scientific measurements, it is important to indicate the margin of error in a measurement by clearly indicating the number of significant figures, which are the meaningful digits in a measured or calculated quantity.

Measuring the volume using a graduated cylinder with a scale that gives an uncertainty of **1 mL**. If the volume is found to be 6 mL, then the actual volume is in the range of 5 to 7 mL. Represent as (6 ± 1) mL.

For greater accuracy, we might use a graduated cylinder or a buret with **0.1 mL** uncertainty. If the volume of the liquid is 6.0 mL, we may express the quantity as $(6.0 \pm 0.1) \text{ mL}$, and the actual value is somewhere between 5.9 and 6.1 mL.



When significant figures are used, the last digit is understood to be uncertain.

Guidelines for using significant figures

1. Any digit that is not zero is significant. e.g., 845 has 3 sig. fig., 1.234 has 4 sig. fig.

2. Zeros between nonzero digits are significant. e.g., 606 contains 3 sig. fig., 40,501 contains 5 sig. fig.

3. Zeros to the left of the first nonzero digit are not significant.

e.g., 0.08 contains 1 sig. fig., 0.0000349 contains 3 sig. fig.

4. If a number is greater than 1, then all the zeros written to the right of the decimal point count as significant figures.

e.g., 2.0 has 2 sig. fig., 40.062 has 5 sig. fig., 3.040 has 4 sig. fig. If a number is less than 1, then only the zeros that are at the end of the number and the zeros that are between nonzero digits are significant.

e.g., 0.090 has 2 sig. fig., 0.3005 has 4 sig. fig., 0.00420 has 3 sig. fig.

5. For numbers that do not contain decimal points, the trailing zeros (that is, zeros after the last nonzero digit) may or may not be significant. e.g., 400 may have 1 sig. fig., 2 sig. fig., or 3 sig. fig. (ambiguous case) We cannot know without using scientific notation. We can express the number 400 as 4×10^2 for 1 sig. fig., 4.0×10^2 for 2 sig. fig., or 4.00×10^2 for 3 sig. fig.

Determine the number of significant figures in the following measurements: (a) 478 cm, (b) 6.01 g, (c) 0.825 m, (d) 0.043 kg, (e) 1.310×10^{22} atoms, (f) 7000 mL.

(a) 478 cm, 3 sig. fig.

(b) 6.01 g, 3 sig. fig.

(c) 0.825 m, 3 sig. fig.

(d) 0.043 kg, 2 sig. fig.

(e) 1.310×10^{22} atoms, 4 sig. fig.

(f) 7000 mL, This is an ambiguous case; the number of significant figures may be: 4 for (7.000×10^3) , 3 for (7.00×10^3) , 2 for (7.0×10^3) , 1 for (7×10^3) .

Practice Exercise

Determine the number of significant figures in each of the following measurements: (a) 24 mL, (b) 3001 g, (c) 0.0320 m^3 , (d) 6.4×10^4 molecules, (e) 560 kg.

Significant figures in calculations

1. In addition and subtraction, the answer cannot have more digits to the right of the decimal point than either of the original numbers.

Examples:

 $\begin{array}{c}
89.332 \\
+ 1.1 \\
90.432 \\
\hline round off to 90.4
\end{array}$ $\begin{array}{c}
2.097 \\
- 0.12 \\
1.977 \\
\hline round off to 1.98
\end{array}$

If the first digit following the point of rounding off is equal to or greater than 5, we add 1 to the preceding digit. e.g., 8.727 rounds off to 8.73, and 0.425 rounds off to 0.43.

2. In multiplication and division, the number of significant figures in the final product or quotient is determined by the original number that has the *smallest* number of significant figures.

Examples:

$$2.8 \times 4.5039 = 12.61092 \longleftarrow$$
 round off to 13 $\frac{6.85}{112.04} = 0.0611388789 \longleftarrow$ round off to 0.0611

3. The *exact numbers* obtained from definitions, conversion factors or by counting numbers of objects can be considered to have an infinite number of significant figures.

Example (1)

The inch is defined to be exactly 2.54 centimeters; that is,

1 in = 2.54 cm

Thus, the "2.54" in the equation should not be interpreted as a measured number with 3 significant figures. In calculations involving conversion between "in" and "cm", we treat both "1" & "2.54" as having an infinite number of significant figures.

Example (2)

If an object has a mass of 5.0 g, then the mass of nine such objects is,

5.0 g x 9 = 45 g

The answer has two significant figures because 5.0 g has two significant figures. The number 9 is exact and does not determine the number of significant figures.

Example (3)

The average of three measured lengths; 6.64, 6.68 and 6.70 is,

 $\frac{(6.64 + 6.68 + 6.70)}{3} = 6.67333 = 6.67$ (two decimals because 3 is an exact number and not measured value).

Carry out the following arithmetic operations to the correct number of significant figures:

(a) 11,254.1 g + 0.1983 g,

$$+ 0.1983$$
 g
 $+ 0.1983$ g

(b) 66.59 L – 3.113 L,

$$\begin{array}{r}
66.59 \text{ L} \\
- 3.113 \text{ L} \\
63.477 \text{ L} \longleftarrow \text{ round off to } 63.48 \text{ L}
\end{array}$$

(c) 8.16 m x 5.1355, 8.16 m \times 5.1355 = 41.90568 m \leftarrow round off to 41.9 m

(d) 0.0154 kg ÷ 88.3 mL,

 $\frac{0.0154 \text{ kg}}{88.3 \text{ mL}} = 0.000174405436 \text{ kg/mL} \longleftarrow \text{round off to } 0.000174 \text{ kg/mL} \text{ or } 1.74 \times 10^{-4} \text{ kg/mL}$

(e) $2.64 \times 10^3 \text{ cm} + 3.27 \times 10^2 \text{ cm}$.

First we change 3.27×10^2 cm to 0.327×10^3 cm

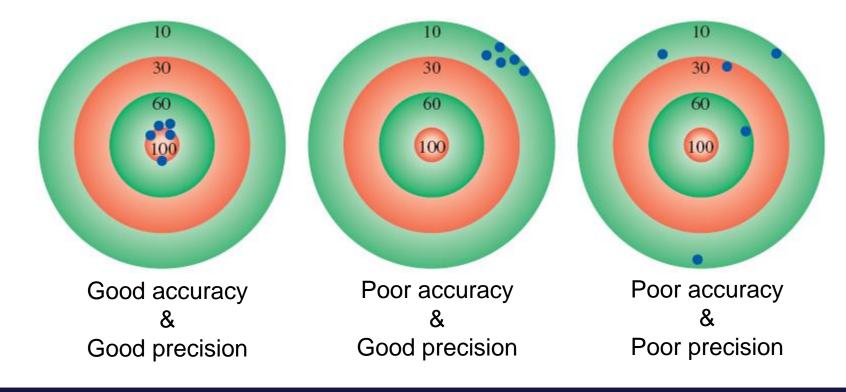
 $(2.64 \text{ cm} + 0.327 \text{ cm}) \times 10^3$

 2.97×10^3 cm.

Accuracy & Precision

Accuracy tells us how close a measurement is to the true value of the quantity that was measured.

Precision refers to how closely two or more measurements of the same quantity agree with one another.



Example,

Three students are asked to determine the mass of a piece of copper wire. The true mass of the wire is 2.000 g.

The results of two successive weighings by each student are:

	Student A	Student B	Student C
	1.964 g	1.972 g	2.000 g
	1.978 g	1.968 g	2.002 g
Average value	1.971 g	1.970 g	2.001 g

Therefore, **Student B's** results are more precise than those of **Student A**, but neither set of results is very accurate. **Student C's** results are not only the most precise, but also the most accurate, because the average value is closest to the true value.

Highly accurate measurements are usually precise too. On the other hand, **highly precise measurements do not necessarily guarantee accurate results**. For example, an improperly calibrated meterstick or a faulty balance may give precise readings that are in error.

Dimensional Analysis

The procedure we use to convert between units in solving chemistry problems is called *dimensional analysis* (also called the *factor-label method*).

Dimensional analysis is based on the relationship between different units that express the same physical quantity.

For example, by definition 1 in = 2.54 cm

we can write the conversion factor as $\frac{1 in}{2.54 cm}$ or as $\frac{2.54 cm}{1 in}$

Convert 12.00 in to cm?

$$12.00 \text{ in } \times \frac{2.54 \text{ cm}}{1 \text{ in }} = 30.48 \text{ cm}$$

In general, to apply dimensional analysis we use the relationship

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given quantity \times conversion factor = desired quantity
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and the units cancel as follows:

$$\frac{\text{given unit}}{\text{given unit}} = \text{desired unit}$$

A person's average daily intake of glucose (a form of sugar) is 0.0833 pound (lb). What is this mass in milligrams (mg)?

1 lb = 453.6 g 1 mg = 10⁻³ g

pounds \longrightarrow grams \longrightarrow milligrams

Conversion factors

453.6 g	and	1 mg
1 lb		$1 \times 10^{-3} g$

? mg = 0.0833
$$\text{ls} \times \frac{453.6 \text{ g}}{1 \text{ ls}} \times \frac{1 \text{ mg}}{1 \times 10^{-3} \text{ g}} = 3.78 \times 10^4 \text{ mg}$$

Practice Exercise

A roll of aluminum foil has a mass of 1.07 kg. What is its mass in pounds?

An average adult has 5.2 L of blood. What is the volume of blood in m³?

1 L = 1000 cm³ 1 cm = 1 x 10⁻² m, 1 cm³ = $(1 x 10^{-2})^3 m^3$, 1 cm³ = 1 x 10⁻⁶ m³.

Conversion factors

$$\frac{1000 \text{ cm}^3}{1 \text{ L}} \text{ and } \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \qquad \frac{1 \times 10^{-6} \text{ m}^3}{1 \text{ cm}^3}$$

?
$$m^3 = 5.2 \, \underline{\nu} \times \frac{1000 \, \mathrm{cm}^3}{1 \, \underline{\nu}} \times \frac{1 \, x \, 10^{-6} \, m^3}{1 \, \mathrm{cm}^3} = 5.2 \times 10^{-3} \, \mathrm{m}^3$$

Practice Exercise

The volume of a room is $1.08 \times 10^8 \text{ dm}^3$. What is the volume in m³?

Liquid nitrogen is obtained from liquefied air and is used to prepare frozen goods and in low-temperature research. The density of the liquid at its boiling point (-196°C or 77 K) is 0.808 g/cm³. Convert the density to units of kg/m³.

1 kg = 1000 g and 1 cm = 1 x 10^{-2} m or 1 cm³ = 1 x 10^{-6} m³

Conversion factors

$$\frac{1 \text{ kg}}{1000 \text{ g}}$$
 and $\frac{1 \text{ cm}^3}{1 \times 10^{-6} \text{ m}^3}$

? kg/m³ =
$$\frac{0.808 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ cm}^3}{1 \times 10^{-6} \text{ m}^3} = 808 \text{ kg/m}^3$$

Practice Exercise

The density of the lightest metal, lithium (Li), is 5.34 x 10^2 kg/m³. Convert the density to g/cm³.

The speed of sound in air is about 343 m/s. What is this speed in miles per hour (mi/h) and in km/h?

Conversion factors: 1 mi = 1609 m, 1 min = 60 s, 1 hour = 60 min

$$343 \frac{m}{s} \times \frac{1 \text{ mi}}{1609 \text{ m}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ hour}} = 767 \frac{\text{mi}}{\text{hour}}$$

$$343 \frac{m}{s} \times \frac{1 \text{ km}}{1000 \text{ m}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ hour}} = 1234.8 \frac{\text{km}}{1 \text{ hour}}$$

Laboratory Materials and Reagents

Materials used in the manufacture of common laboratory apparatus.

Material	Max. Working Temperature °C	Chemical Inertness	Notes
Borosilicate glass	200	Attacked somewhat by alkali solutions on heating	Trademarks: Pyrex (Corning Glass Works); Kimax (Owens-Illinois)
Soft glass		Attacked by alkali solutions	Boron-free. Trademark: Corning
Alkali-resistant glass			
Fused quartz	1050	Resistant to most acids, halogens	Quartz crucibles used for fusions
High-silica glass	1000	More resistant to alkalis than borosilicate	Similar to fused quartz Trademark: Vycor (Corning)
Porcelain	1100-1400	Excellent	
Platinum	1500	Resistant to most acids, molten salts. Attacks by aqua regia, fused nitrates, cyanides, chlorides at > 1000°C. Alloys with gold, silver, and other metals	Usually alloyed with iridium or rhodium to increase hardness. Platinum crucibles for fusions and treatment with HF
Nickel and iron		Fused samples contaminated with the metal	Ni and Fe crucibles used for peroxide fusions
Stainless steel	400-500	Not attacked by alkalis and acids except conc. HCl, dil. H_2SO_4 , and boiling conc. HNO ₃	
Polyethylene	115	Not attacked by alkali solutions or HF. Attacked by many organic solvents (acetone, ethanol OK)	Flexible plastic
Polypropylene	120	Translucent. Has replaced polyethylene for many purposes	
Polystyrene	70	Not attacked by HF. Attacked by many organic solvents	Some what brittle
Teflon	250	Inert to most chemicals	Useful for storage of solutions and reagents for trace metal analysis. Is permeable to oxygen

The Analytical Balance

The balance measures mass. The analytical balance is indispensible tool in all laboratory.

Modern **electronic balances** offer convenience in weighing and are subject to fewer errors or mechanical failures than are **mechanical balances**, which have become largely obsolete.

Zero-point Drift Greater precision equals greater cost.



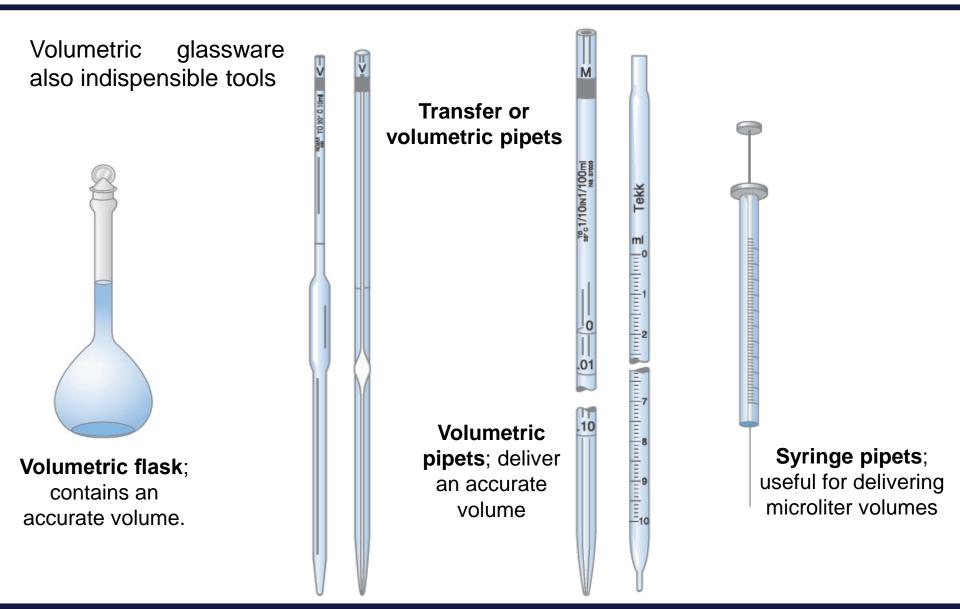
Single-pan mechanical balance



Electronic analytical balance

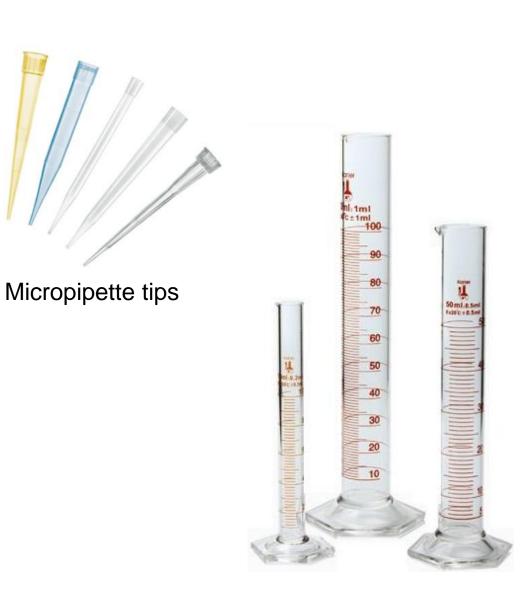


Volumetric Glassware

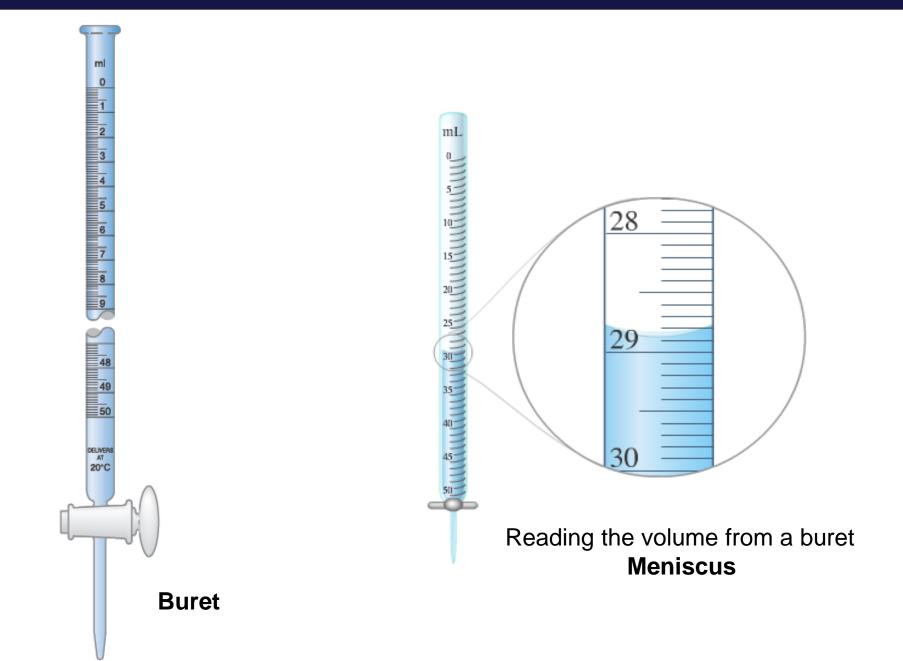




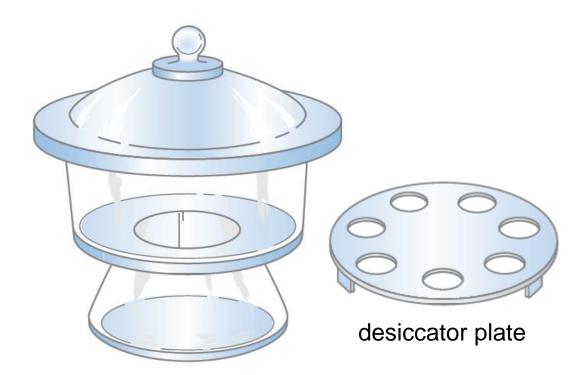
Single-channel and multichannel **micropipettes**



Graduated cylinders



Other Apparatus



Desiccator; used to keep samples dry while they are cooling and before they are weighed and to dry a wet sample. Dried or ignited samples and vessels are cooled in the desiccator. Some common drying agents

- CaCl₂ (anhydrous)
- CaSO₄
- CaO
- MgClO₄ (anhydrous)
- Silica gel
- AI_2O_3

Furnaces and Ovens

Muffle furnace; used to ignite samples to high temperatures, either to convert precipitates to a weighable form or to burn organic materials prior to inorganic analysis Up to about 1200°C

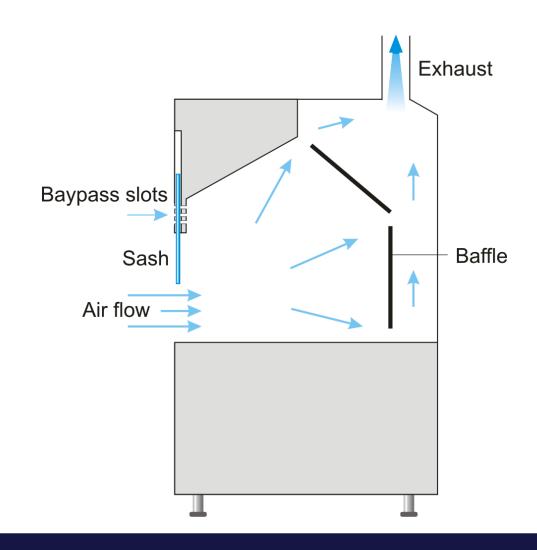




Drying oven; used to dry samples prior to weighing. These ovens are well ventilated for uniform heating. The usual drying temperature is about 110°C. Up to temperatures of 200 to 300°C.



Fume hood; used when chemicals or solutions are to be evaporated. e.g., perchloric acid or acid solutions of perchlorates are to be evaporated, the fumes should be collected, or the evaporation should be carried out in fume hoods.



Laboratory Safety

Before beginning any of the experiments, you must familiarize your self with laboratory safety procedures.



Laboratory safety consists guidelines and rules for,,,

- Personal protection,
- Laboratory protocol,
- Operation in the laboratory,
- Recommended laboratory techniques,
- Chemical hazards,
- Chemicals handling,
- Disposal of chemicals,
- Instructions on material safety data sheets (MSDSs),
- Safety equipment,
- Emergency procedures.

- Chemicals Safety

Use, handling, storage and disposing of hazardous chemicals.

- Biological Safety

Use of biological agents such as human, animal and plant pathogens; human blood and blood components; recombinant/synthetic nucleic acids; cell and tissue cultures; etc. in addition to the receipt, possession, use, and transfer of biological materials.

- Facilities and Construction Safety

Guidelines for construction and renovation for good health and safety practices, even for small construction or renovation projects.

- Fire Safety

The Fire Safety includes building evacuation, fire prevention methods and the use of portable extinguishers.

- Radiation Safety

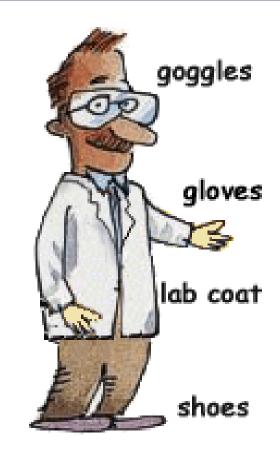
The use of sources of radiation in various teaching, research, and operating activities.

Safety Wears and Protective Equipment

Personal protection

Characteristic hazardous wastes are materials that are known or tested to exhibit one or more of the following four hazardous traits:

- Ignitability (i.e., flammable)
- Reactivity (explosions)
- Corrosivity
- Toxicity



Chemicals life cycle...

The total chemical life cycle defines the stages of a chemical's **purchase**, **use**, and **disposal**.

Rule 1: Purchase of Chemicals

Don't buy or store chemicals you don't need.

Rule 2: Chemicals Storage

Store chemicals in their original containers.

Rule 3: Chemicals Handling

Always wear appropriate safety gear and work in a safe environment.

Rule 4: Chemicals Disposal

Always dispose of chemicals safely.





