Quantitative Analysis (CHEM 201)

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Fall 2007, SH-C162

T &Th: 11:40 am – 1 pm

What do you need?

- Textbook (bcs.whfreeman.com/qca7e)
- Laboratory Manual
- Laboratory Notebook
- Gloves and Safety Glasses
- Calculator
- Access to a computer with Excel and a printer

Analytical Chemistry

- ***Analytical chemistry*** deals with methods for determining the chemical composition of samples of matter.
- ***Qualitative analysis*** – Information about the identity of atomic or molecular species or the functional groups in the sample (What).
- ***Quantitative analysis*** - Numerical information as to the relative amount of one or more of these components (How much).

Quantitative Analysis

Classical

- gravimetric
- volumetric (or titrimetric)

Instrumental

- electroanalytical
- spectroscopic
- chromatographic

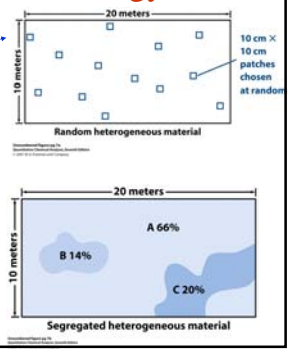
Comparison of Different Analytical Methods

Table 1.1
Comparison of Different Analytical Methods

Method	Approx. Range (mol/L)	Approx. Precision (%)	Selectivity	Speed	Cost	Principal Uses
Gravimetry	10^{-1}–10^{-1}	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^{-1}–10^{-10}	2–5	Good	Moderate	Moderate	Inorg., org.
Spectrophotometry	10^{-1}–10^{-5}	2	Good–moderate	Fast–moderate	Low–moderate	Inorg., org.
Fluorometry	10^{-5}–10^{-9}	2–5	Moderate	Moderate	Moderate	Org.
Atomic spectroscopy	10^{-1}–10^{-8}	2–10	Good	Fast	Moderate–high	Inorg., multielement
Chromatography	10^{-1}–10^{-5}	2–5	Good	Fast–moderate	Moderate–high	Org., multicomponent
Kinetic methods	10^{-1}–10^{-10}	2–10	Good–moderate	Fast–moderate	Moderate	Inorg., org., enzymes

Analytical Terminology

- heterogeneous
- homogeneous
- Analyte: the sample being analyzed



Classification of Analytical Methods According to Size of Sample

Method	Sample Weight (mg)	Sample Volume (μL)
Meso	>100	>100
Semimicro	10-100	50-100
Micro	1-10	<50
Ultramicro	<1	

Constituents

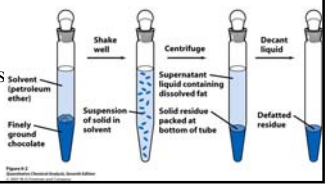
Method	Constituents
major	>1%
minor	0.1-1%
trace	<0.1%

Steps in a Chemical Analysis

- Sampling: representative
- Sample Preparation
- Analyzing the Sample
- Interpreting the Results

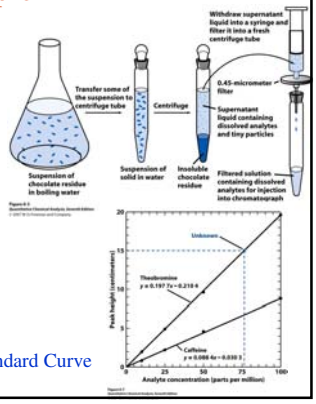
Analyzing the Sample

- Step 1. Obtain a representative bulk sample.
- Step 2. Extract from the bulk sample a smaller, homogeneous laboratory sample.
- Step 3. Convert the laboratory sample into a form suitable for analysis a process that usually involves dissolving the sample.



Analyzing the Sample

- Step 4. Remove or mask species that will interfere with the chemical analysis.
- Step 5. Measure the concentration of the analyte in several aliquots.
- Step 6. Interpret your results and draw conclusions.

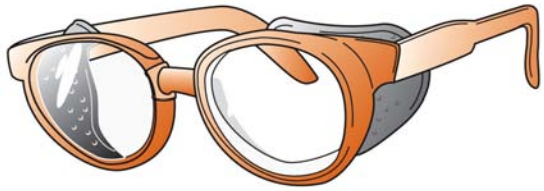


Calibration Curve/Standard Curve

Safe, Ethical Handling of Chemicals and Waste

- The primary safety rule is not to do something that you (or your instructor or supervisor) consider to be dangerous.
- proper clothing
- food & drink in lab **NO WAY!!!!!**
- disposal of solids and liquids
  - always ask instructor for the proper procedure

Eye Protection at all Times



Chemical hazards label (NFPA)

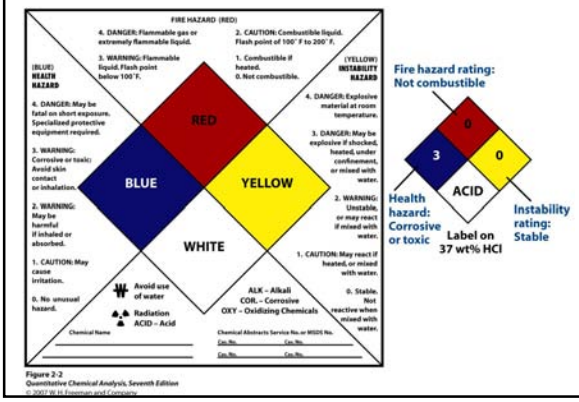


Figure 2-2
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LABEL ALL CONTAINERS

Lab Notebooks

- Laboratory data will be recorded directly in the notebook. Entries will be made using a ballpoint pen.
- Be complete, accurate documents of the experiment and be understandable – can be served as a legal document for your work
- Format refers to the syllabus

Analytical Balance

Figure 2-3a
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Analytical Balance

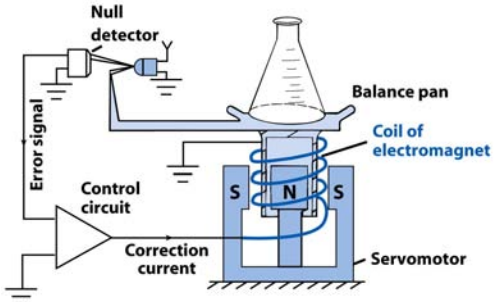

Figure 2-3b
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Table 2-1 Tolerances for laboratory balance weights[a]

Denomination	Tolerance (mg)		Denomination	Tolerance (mg)	
Grams	Class 1	Class 2	Milligrams	Class 1	Class 2
500	1.2	2.5	500	0.010	0.025
200	0.50	1.0	200	0.010	0.025
100	0.25	0.50	100	0.010	0.025
50	0.12	0.25	50	0.010	0.014
20	0.074	0.10	20	0.010	0.014
10	0.050	0.074	10	0.010	0.014
5	0.034	0.054	5	0.010	0.014
2	0.034	0.054	2	0.010	0.014
1	0.034	0.054	1	0.010	0.014

a. Tolerances are defined in ASTM (American Society for Testing and Materials) Standard E 617. Classes 1 and 2 are the most accurate. Larger tolerances exist for Classes 3–6, which are not given in this table.

Table 2-1
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Analytical Balance

Unknown samples & primary standard materials

Tare: the mass of the empty vessel, set to 0

Weighing-by-difference (esp. hygroscopic reagents)

Weigh bottle + Reagent (1)
Remove necessary amount of reagent (2)
Weigh bottle + Remaining reagent (3)
Mass of reagent removed = (1) –(2)

Common Sources of Error

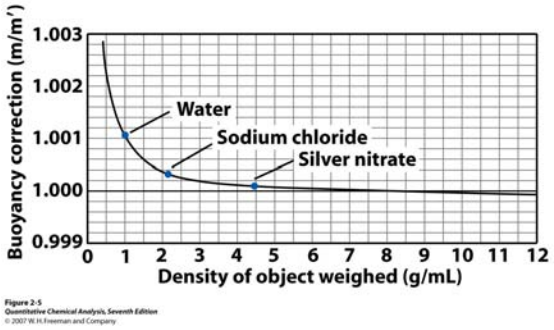
- Non-leveled balance
- Improper sample handling including without cooling the sample completely
- Finger prints
- Unclosed balance cover
- Buoyancy-induced errors (inherent)

Buoyancy

$$m = \frac{m'(1 - d_a/d_w)}{(1 - d_a/d)}$$

where m => true mass of object being "weighed"
m'=> mass read by balance
d_a=> density of air
d_w=> density of the calibration weight
d => density of object being "weighed"

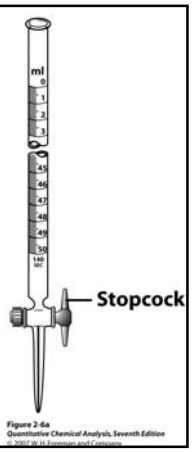
Buoyancy Correction



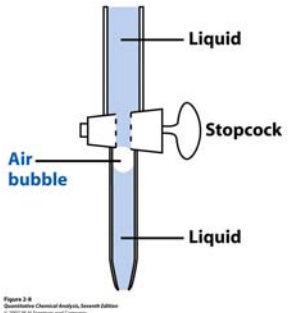
Burets

Buret reading tips:

1. Allow time for draining.
2. Read the bottom of the concave meniscus.
3. Avoid parallax.
4. Account for the thickness of the marking lines in your readings.



Air Bubble in Tip



Reading a Buret

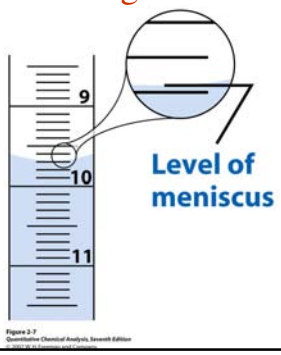


Table 2-2 Tolerances of Class A burets

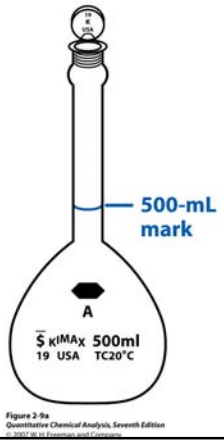
Buret volume (mL)	Smallest graduation (mL)	Tolerance (mL)
5	0.01	±0.01
10	0.05 *or* 0.02	±0.02
25	0.1	±0.03
50	0.1	±0.05
100	0.2	±0.10

Volumetric Flasks

sizes: 5 mL to 2 L

TC 20°C => to contain at 20°C

TD 20°C => to deliver at 20°C



Volumetric Flasks

when to use volumetric flasks

- to make standard solution where an analytical balance was used to weigh the solid to be dissolved
- to make quantitative dilutions using volumetric pipets

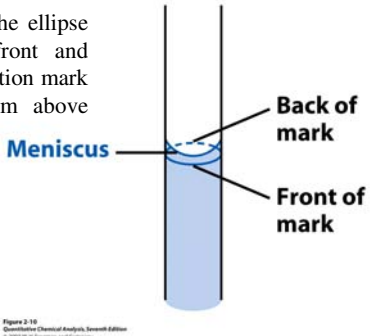
Volumetric Flasks

when not to use volumetric flasks

- to make solutions where an analytical balance is not used for weighing the sample (exception to this would be for a large size sample in a large flask)

Volumetric Flasks – Proper position of the meniscus

- At the center of the ellipse formed by the front and back of the calibration mark when viewed from above and below



Volumetric Flasks

Table 2-3 Tolerances of Class A volumetric flasks

Flask capacity (mL)	Tolerance (mL)
1	±0.02
2	±0.02
5	±0.02
10	±0.02
25	±0.03
50	±0.05
100	±0.08
200	±0.10
250	±0.12
500	±0.20
1 000	±0.30
2 000	±0.50

Table 2-3
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Pipets – Transfer & Measuring

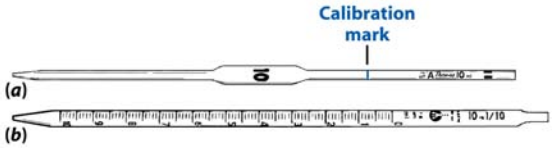

Figure 2-11
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Table 2-4 Tolerances of Class A transfer pipets

Volume (mL)	Tolerance (mL)
0.5	±0.006
1	±0.006
2	±0.006
3	±0.01
4	±0.01
5	±0.01
10	±0.02
15	±0.03
20	±0.03
25	±0.03
50	±0.05
100	±0.08

Table 2-4
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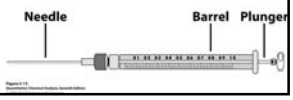
Pipets and Syringes

Using a Transfer Pipet

- **NEVER PIPET BY MOUTH**
  - **use a bulb or pipet aid of some description**
- **NEVER BLOW OUT LAST DROP**
  - designed to retain some liquid in tip

Using a Syringe

- used to deliver a small volume



Micropipets

Figure 2-12c
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Figure 2-12ab
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Table 2-5 Manufacturer's tolerances for micropipets

Pipet volume (µL)	At 10% of pipet volume		At 100% of pipet volume	
	Accuracy (%)	Precision (%)	Accuracy (%)	Precision (%)
Adjustable Pipets				
0.2–2	±8	±4	±1.2	±0.6
1–10	±2.5	±1.2	±0.8	±0.4
2.5–25	±4.5	±1.5	±0.8	±0.2
10–100	±1.8	±0.7	±0.6	±0.15
30–300	±1.2	±0.4	±0.4	±0.15
100–1 000	±1.6	±0.5	±0.3	±0.12
Fixed Pipets				
10			±0.8	±0.4
25			±0.8	±0.3
100			±0.5	±0.2
500			±0.4	±0.18
1 000			±0.3	±0.12

SOURCE: Data from Hamilton Co., Reno. NV.

Table 2-5
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Other Volume Tools

graduated cylinder

- use for less accurate volume measurements

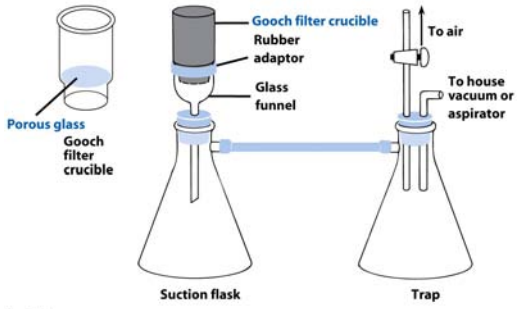
beakers or flasks

- inacurrate graduations (usually $\pm$ 5%)

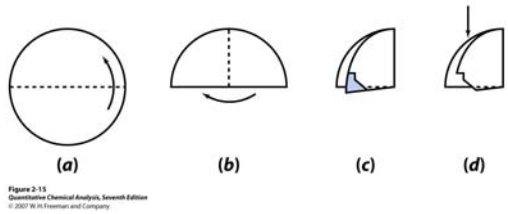
RULE OF THUMB

- **use a set of tools for an analysis which will keep a consistent number of significant figures**

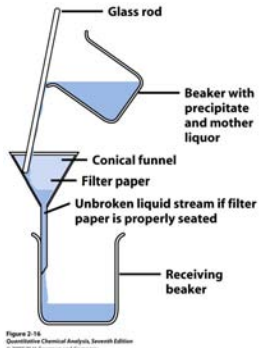
Filtration



Folding Filter Paper

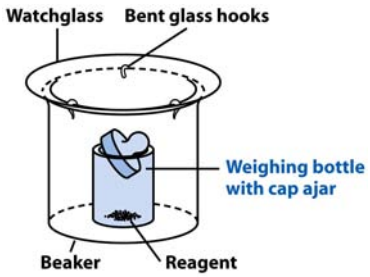


Filtration



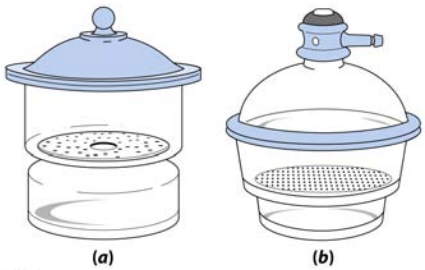
Drying

protecting sample while in oven



Drying

Desiccators



Desiccants

Table 2-6 Efficiencies of drying agents

Agent	Formula	Water left in atmosphere (μg H_2O/L)[a]
Magnesium perchlorate, anhydrous	$Mg(ClO_4)_2$	0.2
"Anhydrone"	$Mg(ClO_4)_2 \cdot 1\text{–}1.5H_2O$	1.5
Barium oxide	BaO	2.8
Alumina	Al_2O_3	2.9
Phosphorus pentoxide	P_4O_{10}	3.6
Calcium sulfate (Drierite)[b]	$CaSO_4$	67
Silica gel	SiO_2	70

*a. Moist nitrogen was passed over each desiccant, and the water remaining in the gas was condensed and weighed. [A. I. Vogel, A Textbook of Quantitative Inorganic Analysis, 3rd ed. (New York: Wiley. 1961), p. 178.] For drying gases, the gas can be passed through a 60-cm-long Nafion tube. At 25°C, the residual moisture is 10 μg/L. If the drier is held at 0°C, the residual moisture is 0.8 μg/L. [K. J. Leckrone and J. M. Hayes. "Efficiency and Temperature Dependence of Water Removal by Membrane Dryers." Anal. Chem. **1997,** 69, 911.]*

*b. Used Drierite can be regenerated by irradiating 1.5-kg batches in a 100 × 190 mm Pyrex crystallizing dish in a microwave oven for 15 min. Stir the solid, heat a second time for 15 min. and place the hot, dry material back in its original container. Use small glass spacers between the crystallizing dish and the glass tray of the oven to protect the tray. [J. A. Green and R. W. Goetz, "Recycling Drierite," J. Chem. Ed. **1991,** 68, 429.]*

Table 2-6
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SI Prefixes

- especially useful in this course

mega	M	10^6
kilo	k	10^3
centi	c	10^{-2}
milli	m	10^{-3}
micro	μ	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}

Solution Terminology

- solute
- solvent
- aqueous solution (the solvent is water)
- Liter
- atomic weight
- molecular weight (or formula weight)

Molarity

$$\text{Molarity} \Rightarrow M = \frac{\#\text{ moles A}}{\#\text{ liters solution}}$$

or

$$\text{Molarity} \Rightarrow M = \frac{\#\text{ millimoles A}}{\#\text{ milliliters solution}}$$

Useful Algebraic Relationships

$$\#\text{ of } mol\text{ A} = \frac{\text{Wt of A}\,(g)}{\text{Fw of A}\,(g/mol)}$$

Or

$$\#\text{ of } mol\text{ A} = \text{Vol. of A}\,(L) \times M \text{ of A in the soln.}\,(mol/L)$$

$$\#\text{ of } mmol\text{ A} = \frac{\text{Wt of A}\,(mg)}{\text{Fw of A}\,(g/mol)}$$

Or

$$\#\text{ of } mmol\text{ A} = \text{Vol. of A}\,(mL) \times M \text{ of A in the soln.}\,(mmol/mL)$$

Preparing Solutions

EXAMPLE: Describe the preparation of 1.00 L of 0.100 M NaOH solution (f.w. 40.00) from reagent grade solid.

Dilution

#moles solute in conc. soln
equals
#moles solut in dil. soln

therefore

$$M_{conc}\ V_{conc} = M_{dil}\ V_{dil}$$

Examples

- How can one prepare 500 mL 1.0 M HCl solution from concentrated HCl solution (12M)?

Percent Composition

$$\text{w - w\%} = \frac{\text{wt of a solute}}{\text{wt of solution}} \times 10^2$$

$$\text{v - v\%} = \frac{\text{vol of a solute}}{\text{vol of solution}} \times 10^2$$

$$\text{w - v\%} = \frac{\text{wt of a solute}}{\text{vol of solution}} \times 10^2$$

Examples-
Converting weight percent into Molarity

- Calculate the molarity of concentrated sulfuric acid (Strength = 95.5-96.5%, **Density** = 1.84 g/mL)?

- P.13

- **Acetic Acid, Glacial, 100% 17 M**
  Ammonia, 29% 15 M
  Hydrochloric Acid, 37%, 12 M
  Nitric Acid, 70%, 16 M
  Phosphoric Acid, 85%, 15 M
  Perchloric Acid, 71%, 11 M
  Sodium Hydroxide, 50%, 19 M
  Sulfuric Acid, 96%, 18 M (36 N)

Parts per Million (ppm)

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

Parts per Billion (ppb)

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

Preparing Solutions

$$M1 \times V1 = M2 \times V2$$

$$C1 \times V1 = C2 \times V2$$

Stoichiometry Calculations

Based on the quantity of a product produced or reactant consumed on a reaction, we can calculate an unknown quantity using stoichiometric relations.

1. Gravimetric methods
2. Titrimetric/Volumetric Methods

Ex. $CaCO_3 + HCl \rightarrow Ca^{2+} + Cl^- + H_2O + CO_2$ (g)
$Ca^{2+} + EDTA^{4-} \rightarrow CaEDTA^{2-}$

Examples-
Converting ppm into Molarity

- How much 0.01 M EDTA solution need to titrate 100 ppm $CaCO_3$ containing water? (FW of $CaCO_3$=100; EDTA:Ca^{2+} =1:1)

Types of Solutions

- strong electrolyte
- weak electrolyte
- non-electrolyte

Formal Concentration

- used for systems which separate (ionize) in solution
- same form for equation as molarity, substitute formula weight for molecular weight for those substances which do not form molecules

Useful Algebraic Relationships

$$n = \frac{W(g)}{FM(g/mol)}$$

$$M = \frac{n}{V}(mol/L)$$ Molarity

$$n = M \times V$$

Molality => m

$$\text{molality} => m = \frac{\#\ \text{moles A}}{\#\ \text{kilograms solvent}}$$

- this concentration unit is temperature independent as the mass does not change with temperature whereas volume does
- used in freezing point depression/boiling point elevation
- not commonly used.