1.Units of concentrations
2. Sampling

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Expressing Concentrations

1. Mass Concentration
2. Molar Concentration
3. Equivalents and Normal Concentration

Mass Concentration

* **WEIGHT/VOLUME (w/v)**
* Mass of solute per Volume of solution
* Milligrams per liter (mg/l)
  * Equivalent to parts per million (ppm) for most natural waters and wastewaters since 1 liter of water has a mass of 1 kg (1E6 mg)
* Grams per cubic meter (g/m^3)
* Trace amounts:
  * Micrograms per liter (µg/L)
  * Nanograms per liter (ng/L)

Mass Concentration

* **WEIGHT/WEIGHT (w/w)**
* Mass of solute per mass of solution
* Parts per million (ppm)=1mg/kg
* Parts per billion (ppb)=1µg/kg
* Parts per trillion (ppt) =1ng/kg
* Assuming the density of water is 1.00 g/mL, 1 liter of solution = 1 kg and hence, 1 mg/L = 1 ppm.
* This is generally true for freshwater and other dilute aqueous solutions.
* Note: In seawater, 1 mg/L ≠ 1 ppm since the density of seawater is 1.03 g/mL.
* 1.00 mg/Lsewater = 1.00 mg/L x 1 mL/1.03 g x 1 L/1000 mL x 1000 mg/g = 0.971 mg/kg or 0.971 ppm

Molarity/Molality

- Molarity-Moles of solute per volume of solution
  - A 1 molar solution of NaCl would contain 58.5 gm per liter of water
- Molality-Moles per mass of water
- Equilibrium constants are based on molar concentrations

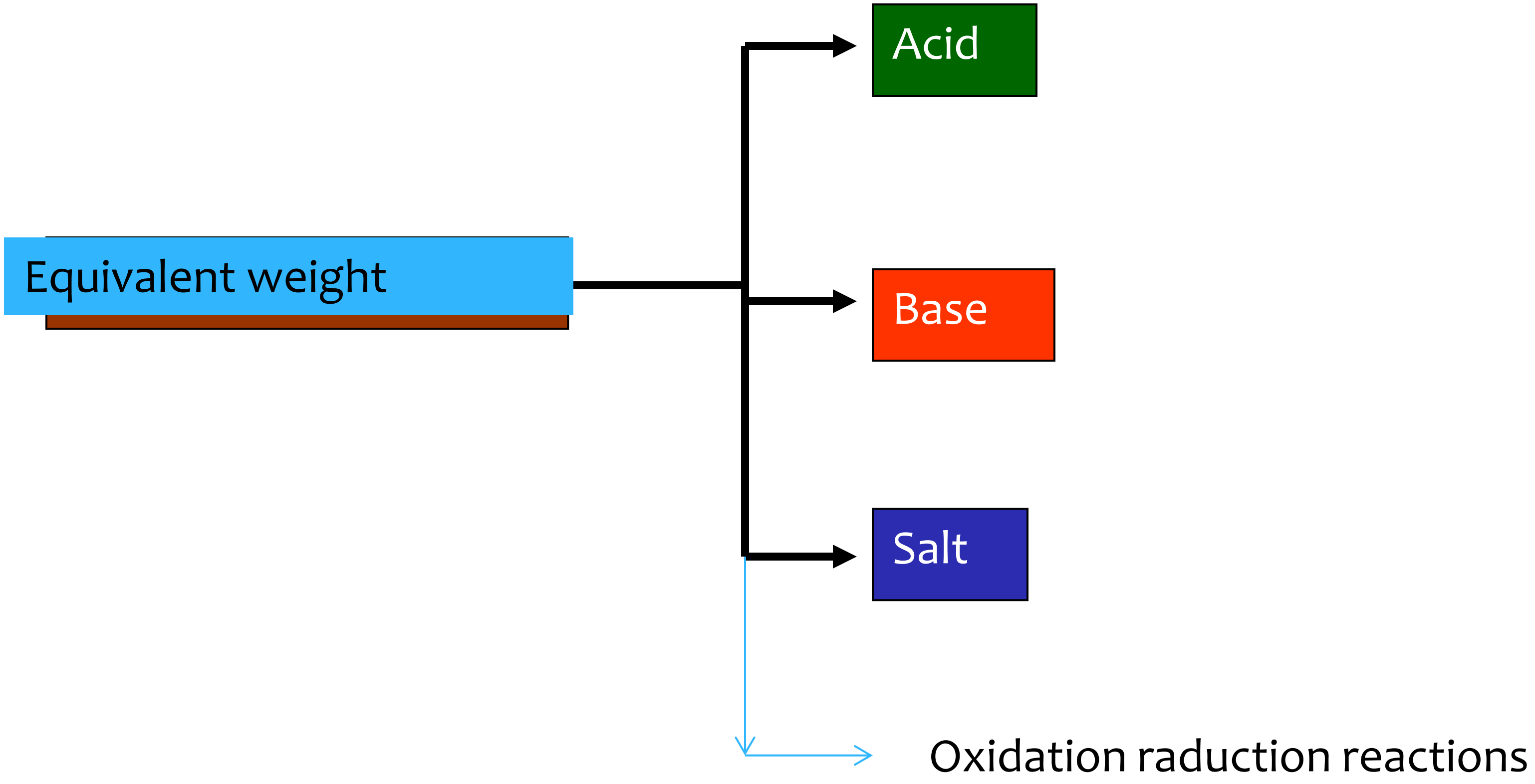
TYPICAL CONCENTRATIONS OF CONCENTRATED ACIDS AND BASES
(as written on the labels of their containers)

ACID/BASE NAME	WT%	DENSITY (sp. gr) (g/ml)	MOLARITY
Acetic acid	99.7%	1.05 g/ml	17.4
Ammonium hydroxide (aqueous ammonia)	28%	0.89 g/ml	14.6
Hydrochloric acid	37%	1.18 g/ml	12.0
Nitric acid (HNO_3)	70%	1.40 g/ml	15.6
Phosphoric acid	85%	1.69 g/ml	14.7
Sulfuric acid	96%	1.84 g/ml	18.0

Normality

- The number of “equivalent weights” of solute per liter of solution
  - Another way to express concentration
  - Used when it’s important to know how many “reactive groups” are present in a solution rather than how many molecules

Equivalent Weight



Normality

- Key to understanding N
  - *Reactive groups and equivalent weight*
    - Used in reference to acids and bases
      - Acids dissociate in solution to release H^+ ions
      - Bases dissociate to release OH^- ions
        - Both are reactive groups
    - For an acid:
      - 1 equivalent weight is equal to the number of grams of that acid that reacts to yield 1 mole of H^+ ions, that is, 1 mole of reactive groups
    - For a base:
      - 1 equivalent weight is equal to the number of grams of that base that supplies 1 mole of OH^-, that is , 1 mole of reactive groups

Equivalents and Normal Concentration

* The equivalent weight of an element or radical is equal to its atomic weight divided by the valence it assumes in compounds. The definition is based on reaction type.
* Advantage is that the number of equivalents of reacting constituents is equal to the number of equivalents of product.
* Disadvantage is that a single substance can have two different equivalent weights because the substance is involved in different reactions
* A one normal solution contain one equivalent weight of a substance per liter of solution

Normality

* For example, HCl has one reacting unit (H^+) when reacting with a base like NaOH but sulfuric acid has two reacting units (two protons) when reacting completely with a base.

Acid/base	z	M.W.	E.W.
HCl	1	36.5	36.5
H_2SO_4	2	98.1	49.0
$CaCO_3$	2	100	50.0
$Al(OH)_3$	3	78.0	26.0

* For oxidation reduction reactions, z is the number of moles of e- transferred per mole of oxidant or reductant in the balanced half reaction

Balanced half reaction	z
$Fe^{3+} \rightarrow Fe$	3
$I_2 \rightarrow 2\,I^-$	2
$2\,S_2O_3^{2-} \rightarrow S_4O_6^{2-}$	1

Expressions for normality are shown below. Notice the similarity to molar solution definition.

$$\text{normality} = N = \frac{\text{number of equivalents of solute}}{\text{1 liter of solution}} = \frac{\text{equivalents}}{\text{liter}}$$

where

$$\text{number of equivalents of solute} = \frac{\text{grams of solute}}{\text{equivalent weight of solute}}$$

then

$$N = \frac{\text{grams of solute}}{\text{eq wt solute} \times \text{L solution}} = \frac{\text{grams}}{\text{eq wt} \times \text{L}}$$

Examples

What is the *normality* of a solution containing 98.0 grams of H_2SO_4 in 1 liter of solution?

- The relationship between N and *M*:
  - N=z * *M*

Expressing Concentrations in Terms of another Compound

- Elements can exist in different forms
  - Nitrogen
    - Ammonium (NH_4^+)
    - Nitrite (NO_2^-)
    - Nitrate (NO_3^-)
  - Phosphorous
    - Ortho (PO_4^{3-})
    - Monohydrogen (HPO_4^{2-})
    - Dihydrogen ($H_2PO_4^-$)

Sampling

The Key to Analysis

What do I mean by "sampling"?

Sampling is "the taking of samples".

Why would I take "samples"?

Usually to get a representation of the whole.

The Blind Men and the Elephant

6 blind men are brought to the zoo and asked to describe an elephant.

The first man goes forward and grabs the elephant’s trunk and says, “An elephant is like a large snake, thick and tubular.”

The second man goes forward and bumps into the elephant’s ribs and says, “An elephant is hard and flat like a brick wall.”

The third man goes forward and grabs the elephant’s tusk and declares, “An elephant is like a great spear.”

The Blind Men and the Elephant

The fourth man goes forward and grabs the elephant's tail and cries, "Why, an elephant is just like a rope, thin and rough and wiry."

The fifth man steps forward and grabs the elephant's ear, declaring, "An elephant is like a fan, thin and flat and flexible."

The sixth man steps up and grabs the elephant's leg and says, "An elephant is like a tree."

A sample must…

…contain enough pieces of the whole to allow a description of the whole.

In the case of the blind men, if you combine all six of them, you might get some sense of the true size and shape of the elephant. But you would need even more information to understand its exact functions and nature.

2 Types of Samples

Grab sample – scoop out a sample with a cup! (or the equivalent. Single sample, single time, single place.

Composite sample – Provides a more representative sampling of heterogeneous matrices in which the concentration of the analytes of interest may vary over short periods of time and/or space.

Grab Samples

* May be used where population is not changing suddenly or changing a great deal over time.

e.g. Deep well → water quality is uniform

→ Single grab sample would be enough

* Must be used for particular analyses:
  * Residual chlorine.
  * Fecal coliform.

Composited Samples

* Mainly used in evaluating the efficiency of wastewater treatment facilities.

  24 h composite sample, take @every 1-2 hrs. and collect in a container. The mixed sample is analyzed. Each sample volume should be proportional to flow at that time.

Composite Samples

- Frequently used to estimate average values over a 24-hour period.
  - BOD_5 loading to aeration tanks.
  - TSS leaving the WWTP in the effluent.
- Gives information over a longer period of time or space.
- Permit samples are often flow proportional composites.

Composite Samples

* Consideration must be given to sample handling and storage during compositing.
* We don't want the sample characteristics to change while we are sampling.
* Refrigeration often used to slow biological activity.
* Chemicals may also be added as preservatives.

How to Composite

- Simple Composite – Add equal volumes of samples collected from different times or locations. Mix thoroughly.
- Flow Proportional Composite – Volume of each subsample based on flow.
  - Estimate total volume of sample required.
  - Estimate total flow over sampling period.
  - Calculate sample volume per flow.

Simple vs Flow Proportional

Time	Flow (MGD)	NH_3 -N	Simple	Flow Prop.
Midnight	10	12	12	120
4 a.m.	15	15	15	225
8 a.m.	18	20	20	360
Noon	28	40	40	1120
4 p.m.	26	37	37	962
8 p.m.	14	14	14	196
NH_3-N Conc, (mg/L) in Sample =			23.0	26.9
Avg Daily Flow		18.5	MGD	
Total Lbs - Simple		3549		
Total Lbs - Proportional		4146		
Difference of		**15%**		

Determine those parameters in situ.

-Temperature

-Redox Potential

-Dissolved

Gases

Determine those parameters immediately after sample collection.

-pH

-Electrical Conductivity

-Turbidity

-Alkalinity

What may happen during sample transportation ?

Certain cations are subject to loss by adsorption on, or ion exchange with the walls of the glass containers,these includes: Al,Cd,Cr,Cu,Fe,Pb,Mn, Ag,and Zn.

Those are best collected in a separate clean bottle and acidified with nitric acid to pH below 2.0 to minimize precipitation and adsorption on container walls.

What may happen during sample transportation ?

Biological activity taking place in a sample may change the oxidation state of some constituents

Changes caused by growth of microorganisms are greatly retarded by keeping the sample at a low temperature (<4 C) but above freezing.

Preservation and Storage

General Consideration

1-Start microbiological examination of water samples as soon as possible after collection.

2-Ice samples preferably at <10 C during transport if they can't be analyzed within 1h after collection.

3-Analyze samples on day of receipt whenever possible and refrigerate overnight if arrival is too late for analyzing on same day.

Preservation and Storage

4-Do not exceed 24h holding time from collection to analysis for coliform bacteria.

5-Do not exceed 8h holding time for heterotrophic plate counts.