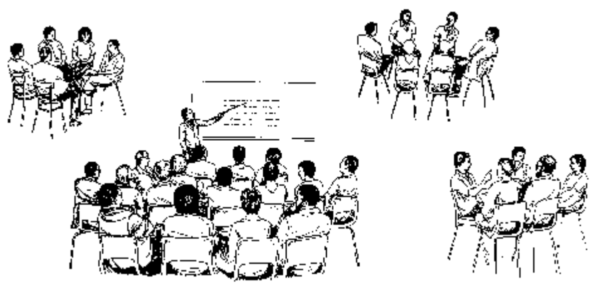
Instrumentation, Analytical Techniques and Sampling

ENHL 232

Lecture 1



Introduction

Objectives of the session:

- Provide an overview about
  - The basic units of metric system
  - Concentration units
  - Dilution calculations
  - Interpretation of data
  - Statistical Calculations

The Importance of Units

- Numbers are meaningless without units
- The basic units of metric system:
  - Length in meter
  - Mass in kilogram
  - Volume in liter

Unit of Prefixes and their Values

Prefix	Symbol	Exponential value
Kilo	k	10^{3}
Hecto	h	10^{2}
Deca	da	10
Deci	d	10^{-1}
Centi	c	10^{-2}
Milli	m	10^{-3}
Micro	μ	10^{-6}
Nano	n	10^{-9}
Pico	p	10^{-12}

Concentration Units

- Molarity (M)
  - The number of moles of a certain species contained in one liter of the solution
  -
  -

Concentration Units

- Normality (N)
  - Normality is the number of equivalents of solute per liter of a solution
  - N= equivalent of solute/v of solution (l)
  - Normality of a solution depends on the reaction taking place
  - For normality to be calculated the stoichiometric equation must be known

Concentration Units

-
  - where X may be
    - acidity of a base
    - basicity of an acid
    - number of electrons gained or lost by a redox reagent

Types of reactions

- Acid-base neutralization
  -
- Oxidation-reduction reactions
  -
- Precipitate formation
- Complex formation

pFunction or the negative logarithm function

- Mostly, the function is the concentration of the studied species
- The symbol of the studied species in terms of its concentration is enclosed in brackets

Percent

- Weight percent
  - weight percent = (weight solute/weight solution) x 100 with same weight units such as gram-gram, mg-mg, Kg-Kg
  - For solid such as ores or tissue samples:
    - Weight percent = (grams substance determined/ grams total sample) x 100

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Percent

- Volume percent
  - Used if both the solute and the solvent are liquids
    - Volume percent = (volume solute/volume solution) x 100 with same volume units such as ml-ml or liter-liter
- Weight-volume percent
  - Used in the preparation of approximate concentrations of solutions:
    - Weight-volume percent = (g solute/ml solution) x 100

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Parts per thousand, parts per million, and parts per billion

- 1 ppm = 1 g of analyte per million grams of water
- 1 ppb = 1 g of analyte per billion grams of water

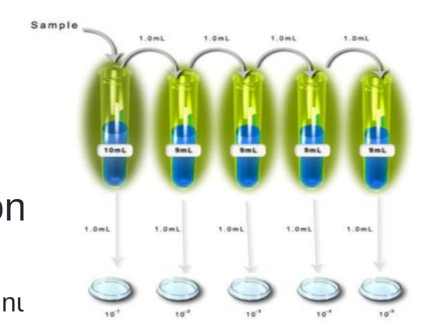
Parts per unit methods of expressing concentrations and equivalent expressions

Expression	Parts per unit part	Equivalent quantities	
		Solids	Liquids
Percent (%)	10^2	g/100 g	g/100 ml
Parts per thousand (ppt)	10^3	g/1000 g	g/1000 ml
		g/Kg	g/L
		mg/g	mg/ml
Milligram percent (mg %)	10^5	g/10^5g	g/10^5 ml
		g/100 Kg	g/100 L
		mg/100 g	mg/100 ml
Parts per million (ppm)	10^6	g/10^6 g	g/10^6 ml
		g/10^3 Kg	g/10^3 L
		mg/Kg	mg/L
		µg/g	µg/ml
Parts per billion (ppb)	10^9	g/10^9 g	g/10^9 ml
		g/10^6 Kg	g/10^6 L
		mg/10^3 Kg	mg/10^3 L
		µg/Kg	µg/L
		ng/g	ng/ml

Dilution Calculations

- It is often necessary for experimental needs to dilute our sample so as to have a lower concentration
- The dilution process

Involves adding water
to a known concentration
and volume of the sample
that is a higher concentration
value



  - Number of moles in diluted sample = nu sample
  -

Interpretation of Data

- Precision and accuracy

Precision: the variability among replicate measurements, i.e., how close the values in a series of results are to each other

Accuracy: the difference between the obtained value and the true value

SUPPOSE YOU MEASURED THE MASS OF A ROCK TO BE 8.2 GRAMS AND THE VOLUME TO BE 2.3 CM3.
HOW ACCURATELY CAN YOU DETERMINE ITS DENSITY?

Mass measured to 2 significant digits

What's wrong with this calculation?

Density = Mass/Volume = 8.2 gm/2.3 cm^3 = 3.56521739 gm/ cm^3

Volume measured to 2 significant digits

Not science but fiction!

Maybe this doesn't look as impressive, but it is a better answer.

Density = Mass/Volume = 8.2 gm/2.3 cm^3 = 3.57 gm/ cm^3

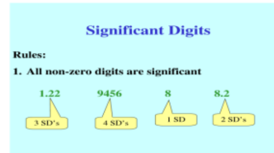
No fictional digits – well, maybe the 7 is stretching it. It is reasonable to carry an extra digit or two in intermediate calculations

Density = 3.6 gm/ cm^3

It is better to keep only the number of digits of your weakest measurement for your final answer.

Interpretation of Data

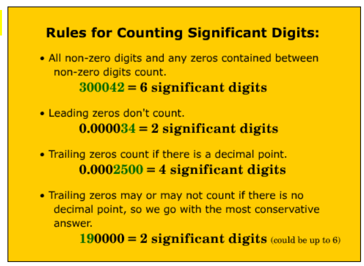
- There are <u>three rules</u> on determining how many significant figures are in a number:
  - **Non-zero digits** are always significant.



  - **Any zeros between two significant d**
    significant.

Number	Significant Digits
28.09	4
1008.91	6
3.005	4
2.03	3

  - **A final zero in the decimal**
    significant.



Interpretation of Data

- 26.38 would have four significant figures and 7.94 would have three
- 0.005 (5.00×10^{-3})
- 0.0304 (3.040×10^{-2})

Interpretation of Data

- Absolute and relative uncertainty
  - The uncertainty of a value may be expressed in absolute or relative terms

Interpretation of Data

- Significant figures in numerical computations
  - A chain is only as strong as its weakest link
  - For addition and subtraction, the weak link is the number of decimal places in the number with the smallest number of decimal places

Interpretation of Data

- The weak link for multiplication and division is the number of significant figures in the number with the smallest number of significant figures

Interpretation of Data

- Example:

  8.9 g / 12.01 g/mol = 0.74 mol

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  8.9444 g
+18.52   g
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 27.46   g
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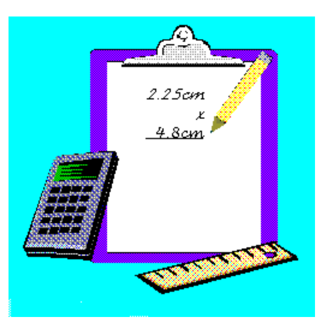


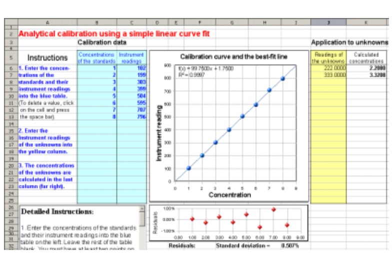
Interpretation of Data

- Rounding data
  - Always round the computed results of a chemical analysis in an appropriate way
  - A good guide to follow when rounding a 5 is always to round to the nearest even number 6

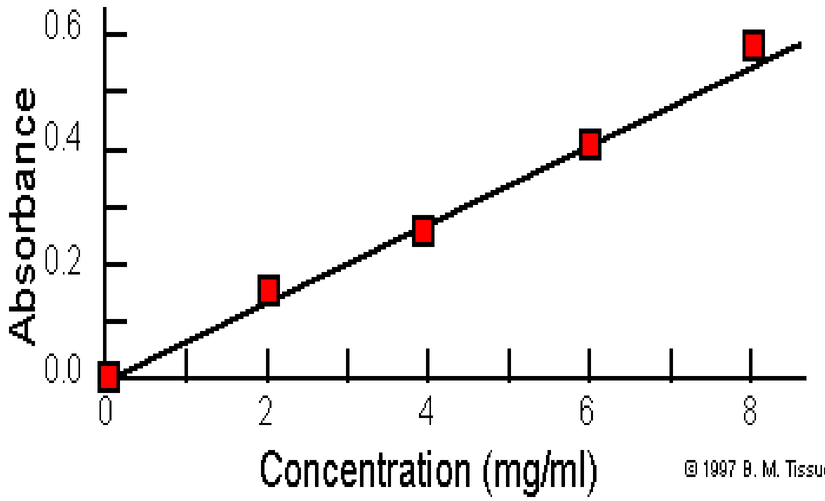
Calibration

- Making measurements with any analytical method instrument requires calibration to ensure the accura of the measurement
- Two common calibration procedures:

  Working curve: Standard addition



Working Curve



Standard Addition

- An analyst usually divides the unknown sample into two portions, so that a known amount of the analyte (a spike) can be added to one portion
- The original and the original plus spike, are then analyzed
- The sample with the spike will show a larger analytical response than the original sample due to the additional amount of analyte added to it

Internal Standard Method

- Instead of using the analyte itself as the calibrant, another substance is used
- It is possible to determine the analyte concentration from a single measurement
- Any losses of analyte will be reflected in similar losses of internal standard

Introduction to Statistics

- The average is synonymous with the arithmetic mean
  - Obtained by adding the results of a number of replications and dividing this sum by the number of replications

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N}$$

Introduction to Statistics

- The average is an important component of reported results but on itself is insufficient
- HOWEVER the extent of the variations within any set of values should also be considered
- From the deviations an average deviation, may be calculated
- The average deviation is the arithmetic mean of the absolute values of the individual deviations

Introduction to Statistics

- Another mean of expressing precision is with standard deviations
  - This is defined as the square root of the sum of the squares of the absolute deviations of the individual samples divided by one less than the number of samples

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}}$$

Standard Deviation and Variance

Deviation just means how far from the normal

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- Standard Deviation
- The Standard Deviation is a measure of how spread out numbers are.
- Its symbol is σ (the greek letter sigma)
- The formula is easy: it is the square root of the Variance. So now you ask, "What is the Variance?"
- Variance
- The Variance is defined as:
- The average of the squared differences from the Mean.
- To calculate the variance follow these steps:
- Work out the Mean (the simple average of the numbers)Then for each number: subtract the Mean and square the result (the *squared difference*).Then work out the average of those squared differences. (Why Square?)
- Example
- You and your friends have just measured the heights of your dogs (in millimeters):
- The heights (at the shoulders) are: 600mm, 470mm, 170mm, 430mm and 300mm.
- Find out the Mean, the Variance, and the Standard Deviation.
- Your first step is to find the Mean:
- Answer:
- Mean = 600 + 470 + 170 + 430 + 300 = 1970 = 3945
- so the mean (average) height is 394 mm. Let's plot this on the chart: Now, we calculate each dogs difference from the Mean:
- To calculate the Variance, take each difference, square it, and then average the result:
- So, the Variance is 21,704.
- And the Standard Deviation is just the square root of Variance, so:
- Standard Deviation: σ = √21,704 = 147.32... = 147 (to the nearest mm)
-
- And the good thing about the Standard Deviation is that it is useful. Now we can show which heights are within one Standard Deviation (147mm) of the Mean:
- So, using the Standard Deviation we have a "standard" way of knowing what is normal, and what is extra large or extra small.
- Rottweilers are tall dogs. And Dachshunds are a bit short ... but don't tell them!
- Now try the Standard Deviation Calculator.

But ... there is a small change with Sample Data

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- Our example was for a Population (the 5 dogs were the only dogs we were interested in).
- But if the data is a Sample (a selection taken from a bigger Population), then the calculation changes!
- When you have "N" data values that are:
- The Population: divide by N when calculating Variance (like we did)
- A Sample: divide by N-1 when calculating Variance
- All other calculations stay the same, including how we calculated the mean.
- Example: if our 5 dogs were just a sample of a bigger population of dogs, we would divide by 4 instead of 5 like this:
- Sample Variance = 108,520 / 4 = 27,130
- Sample Standard Deviation = √27,130 = 164 (to the nearest mm)
- Think of it as a "correction" when your data is only a sample.
- Formulas
- Here are the two formulas, explained at Standard Deviation Formulas if you want to know more:
-
  The "Population Standard Deviation":
- The "Sample Standard Deviation": Looks complicated, but the important change is to divide by N-1 (instead of N) when calculating a Sample Variance.
-
- *Footnote: Why *square* the differences?
- If we just added up the differences from the mean ... the negatives would cancel the positives:
- 4 + 4 - 4 - 4= 04So that won't work. How about we use absolute values?
- |4| + |4| + |-4| + |-4| = 4 + 4 + 4 + 4 = 444That looks good, but what about this case:
- |7| + |1| + |-6| + |-2| = 7 + 1 + 6 + 2 = 444Oh No! It also gives a value of 4, Even though the differences are more spread out!
- So let us try squaring each difference (and taking the square root at the end):
- √4^2 + 4^2 + 4^2 + 4^2= √64= 444 √7^2 + 1^2 + 6^2 + 2^2= √90= 4.74...44That is nice! The Standard Deviation is bigger when the differences are more spread out ... just what we want!
- In fact this method is a similar idea to distance between points, just applied in a different way.
- And it is easier to use algebra on squares and square roots than absolute values, which makes the standard deviation easy to use in other areas of mathematics.

Questions

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