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CHEMISTRY 242/244- ANALYTICAL CHEMISTRY- 3Hr.

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1.0 Analytical Chemistry

1.1. What is analytical chemistry?

- Deals with identifying and determining the number and types of components (qualitative) or the chemical composition or the functional groups in a sample as well as determining the relative amount of each of these components (quantitative) in a sample (numerical information)

- An analyte is the substance of interest in a given sample or matter. The determination of analytes in a sample gives us numerical information which is expressed in relative terms of amount of analyte per size of the sample

- Such relative measurements could be expressed as: percentage (%), parts per thousand (ppt),per million (ppm) or per billion (ppb) of the sample, or weights (volume) of analyte per unit sample, and mole fraction of analyte/sample

- Application of chemical analyses can be found everywhere. Examples include measuring the amount of emission of CO_2 in ppb from the burning of hydrocarbons, determining the amount of cholesterol in a particular client, determining the reaction process (mechanism) or reaction rates, measuring the amount of caffeine in kolanut (obi, orji, goro) etc

- Analytical chemistry is important to a chemist or biochemist just as calculus and matrix is to a physicist

1.2 There are two types of analytical chemistry

- (1) Classical or wet chemistry- entire process involves separating analytes by precipitation, extraction, distillation. Qualitative analyses is then done by treating the separated analytes with reagents that gives products that can be recognized by their colors, boiling and melting points, solubilities, odors, optical or refractive indexes and quantitatively by gravimetric (mass of analyte or a product of the analyte is determined) or volumetric determinations (volume or mass of a standard reagent that will completely react with the analyte is measured) and (ii) instrumental analysis- involves the use of instruments to measure a certain characteristics of the analyte such as conductance, electrode potential, light absorption or emission, mass/charge ratio, chromatography, electrophoresis etc are used for analysis.

1.3 The Analytical Process

Akaraogun wants to measure the amount of caffeine in Kolanut. He bought 5 pieces of Kolanut from Kontagora market, cleaned the Kolanut, air dry and measured its weight. He added 20 ml of 80% methanol to the Kolanut and grinded it to a paste. The paste was emptied into a 250 ml conical flask and 80 ml of 80% methanol was added to the paste, stirred and filtered. A brown filtrate was obtained and 1 micro liter of the filtrate was injected into the injection port of a gas chromatography/mass spectrometer for analysis (GC/MS). The GC/MS chromatogram show 8 analytes and were identified by the mass spectral in the library of the GC/MS. The external standard method (using caffeine) was used to estimate the amount of each analyte in the sample. The caffeine in the Kolanut sample was found to be 40mg/g (+/ 0.001) of Kolanut

The entire process used in estimating the amount of caffeine in Kolanut includes:

sampling (choosing the sample), sample preparation, extraction, separation of interfering components (filtration), sample measurement (analysis), identification, interpretation, estimation of analyte with statistical methods, report

These simple steps are employed in wet or instrumental analytical chemistry.

1.4 Calibration Standards

Analytical instrumental processes simply involve measurement of a specific physical characteristic (X) of an analyte that varies with its concentration C_1. The relationship between the physical characteristic and the concentration is desired to be linear: $C_1 = kX$ (k is a proportionality constant)

The calculation of the value of k is important in every analytical process except in gravimetry and colorimetry and it is called the Calibration constant.

1.5 Characteristics of a Calibration Standard

A calibration standard is a pure sample that is very similar to the analyte in composition and structure and physical and chemical characteristics. This sample is exposed to the same condition the analyte will be exposed to and its response will be measured and used to determine the concentration of the analyte. Desirable characteristics of a calibration standard include:

- Stability: (i) easily weighable, (ii) both solutions and the compound from which it is prepared must be stable (iii) Cannot be hygroscopic, deliquescent, efflorescent (iv) cannot undergo chemical change when dried
- Purity: must at least be 99.5% pure
- Solubility: Must be readily soluble in water and common acids or bases

- Availability: must be cheap to purchase and easy to find from suppliers
- Similarity: must be structurally similar to analyte
- Molecular weight: Molecular weight should be as high as possible for easy accurate weighing
- Toxicity: Must have low toxicity level (as low as possible)
- Few chemical compounds meet this criteria and are called primary standards

1.6 Criteria for Choosing an Analytical Method

- The following parameters are needed to determine the best method to be chosen for a given chemical analysis: speed, accuracy, convenience, number of analytes, available equipments, amount of sample available, limits of concentration and concentration range of analyte
- Failure or success of an analysis depends on the method used in the analysis
- There are no special rules to use in choosing the best method.
- Ability to choose correctly is based on experience

1.7 Types of Instrumental Methods

Instrumental methods involve measuring a characteristic (physical or chemical) typical of an analyte with instruments. Common characteristics that are commonly measures are listed in Table 1.1 below

Table 1.1 Common Physical and Chemical Characteristics Used In Instrumental Methods

Characteristics/Properties	**Instrumental Methods**
Emission of Radiation	Emission Spectroscopy (X-ray, UV, Visible, fluorescence, phosphorescence, luminescence
Absorption Radiation	Spectrophotometry, Photometry(X-ray, UV/Visible, IR, NMR, electron spin resonance)
Scattering of Radiation	Turbimetry, nephelometry, Raman spectroscopy
Refraction of Radiation	Refractometry- interferometry

Diffraction of radiation	X-ray, Electron diffraction methods

Table 1 Cont'd

Characteristics/Properties	**Instrumental Methods**
Rotation of Radiation	Polarimetry, circular dichroism,
Electrical Potential	Potentiometry, chronopotentiometry
Electrical charge	Coulometry
Electrical current	Amperometry, polarography
Electrical Resistance	Conductometry
Mass	Gravimetry
Mass to charge ratio	Mass Spectrometry
Rate of a reaction	Kinetic methods
Thermal characteristics	Thermal gravimetry/titrimetry, calorimetry, thermal conductimetric methods
Radioactivity	Activation and isotope dilution methods
Nuclear Spin	Nuclear Magnetic Resonance spectroscopy

1.8 Review of Some Concepts Needed in Quantitative Analysis

- **Chemical Composition**: Most reactions are carried out in aqueous (are mostly solutions of inorganic acids or bases) or non aqueous, or organic solutions. Common behavior of solutes in aqueous media include the following:

- **Electrolytes**: solutes that dissolve in a solvent to form ions that can conduct electric current. Electrolytes can be strong (complete ionization in solvent e.g. hydrochloric acid) or weak (partial ionization in the solvent e.g. acetic acid)

- **Acids and Bases**: Bronsted and Lowry defined an acid as a proton donor and a base as a proton acceptor. Many solvents donate or accept a proton, hence, inducing acid behavior on solutes dissolved in them. For example, $HNO_2 + H_2O \leftrightarrow NO_2^- + H_3O^+$

acid base base acid

$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$

base acid acid base

This shows that water is amphitpropic: can act as an acid or a base

- **Strength of Acids or Bases:** the extent of dissociation of an acid or base in a solvent will determine its strength. Some acids or base are completely dissociated in a solvent (strong acid) while others are partially dissolved (weak acid)

- **Units of Weights and Concentration:**. Mass of a substance is recorded in SI units of pg, ng, µg, mg, g, kg etc. It is necessary to use units that express weight relationship or stochiometry (simple molar ratio of reactants and products) between reaction species in small whole numbers. For example, gram formula weight (formula weight), gram equivalent weight (equivalent weight), gram molecular weight (molecular weight) are employed in chemical analysis

- **Empirical Formulas, Chemical Formula and the Mole: Empirical formula is the smallest whole number ratio of atoms in a substance.** It can be calculated from % composition of a substance. For example, CH_2O can be used to represent formaldehyde (CH_2O), glyceraldehydes ($C_3H_6O_3$), glucose ($C_6H_{12}O_6$)

- Chemical formula is the actual numbers of the atoms in a molecule. We need to know the actual molecular weight of a molecule before we can determine its chemical formula

- **The Mole**: it is a unit that expresses the amount of a substance or sample. It is associated with the chemical formula and it is equal to one Avogadro's number of atoms (6.02×10^{-23}) ions, molecules or electrons. One mole of a substance is equal to the formula weight (sum of the atomic weight of all atoms in the formula) of that substance. For example, the formula weight of water, H_2O is: 2H + O = 1x2 + 16x1 = 18.0g/mol and that of methanol, CH_3OH is: C + 4H +O = 1x 12 + 1x4 + 1x 16 = 32.0 g/mol. This implies that 1 mole of water and methanol weighs 18 and 32 g respectively.

- **Millimole**: Most of the times, millimole (mmol) is used instead of mole in the laboratory. The mmol is the mole divided by 1000.

- **Concentration**: the number of moles of a solute in one liter of solution or the millimoles/milliliter of solution is called the **Molarity.** This is equivalent to the molar analytical concentration and different from equilibrium molar concentration. The equilibrium molar concentration is the concentration of the ions formed by the solute when dissolved in a one molar of the solvent. It is symbolized by placing a square bracket around the specie formula. Molarity is temperature dependent. The volume of a dilute

solution expands by ~ 0.002%/^{o}C when heated around 20^{o}C hence, molarity also decreases by the same amount

- **Normality or Normal Concentration**: the number of equivalents of solute contained in a liter of solution. The equivalent weight is the number of moles or weight of a substance that either contributes or consumes one mole of hydrogen ions in a neutralization reaction. For example: the equivalent weight of HCl is 36.5/1 = 36.5 g/mol. That of H_2SO_4 = 98/2 = 49 g/mol

- For strong acids or bases, the equivalent weight is equal to the molecular weight divided by the number of replaceable hydrogen ions in one mole of the acid or bases

- **Titer:** defines concentration in terms of the weight of some species with which a unit volume of the solution reacts.

- **p-Function:** sometimes, the concentration of a specie in a dilute solution is expressed in terms of its p-value. The p-value is the negative logarithm (base 10) of the molar concentration of this species: pX = -log[X].
  Example: Calculate the p-value of an ion with a concentration of 2.0 x 10^{-4}M?
  Answer: pX = $-\log_{10}[2x\ 10^{-4}] = -\log 2 - \log 10^{-4} = -0.301 - (-3.0) = 2.699$

- **Density and Specific Gravity:** Density is mass/volume (SI unit kg/l or g/ml) and specific gravity is the ratio of the mass to that of an equal volume of water at 4^{o}C (dimensionless, density of water at 4^{0}C =1.0). Specific gravity is the one used in commerce because it does not have a unit.

- **Parts per Million (ppm)/Parts per billion (ppb):** It is more convenient to express concentration of very dilute solution in ppm or ppb.
  ppm = (weight of solute/weight of solution) x 10^{6}
  = (mg of solute/10^{6} mg of water) = mg of solute/L of water = µg/mL

- ppb= (weight of solute/weight of solution) x 10^{9}
  = (mcg of solute/10^{9} mg of water) = mcg of solute/L of water

- Example 1: What is the molarity of K^{+} in a solution that contains 63.3 ppm of $K_2Fe(CN)_6$?
  Answer: 63.3 ppm $K_2Fe(CN)_6$= 63.3 $K_2Fe(CN)_6$ mg/L
  $[K^{+}]$ = (63.3 mg/L $K_2Fe(CN)_6$)(mmol $K_2Fe(CN)_6$/329 mg)(2 mmol K^{+}/mmol $K_2Fe(CN)_6$)(mol/10^{3}mmol) = 5.77 x 10-4 M

- Example 2: What is the molarity of NO_3^{-} in a solution that contains 17.8 ppm of $NaNO_3^{-}$?
  Answer: 17.8 ppm NO_3^{-}= 17.8 NO_3^{-}mg/L
  $[NO_3^{-}]$ = (17.8 mg/L $NaNO_3$)(mmol $NaNO_3$/62mg)(mol/10^{3}mmol)= 2.93 x 10-4 M

- **Molality:** Molality, m, is the # of moles of a solute/kg of solvent. Molality is not temperature dependent and is useful for precise physical measurements.

- **Osmolarity:** total # of moles of particles/L of solution. For non electrolyte like glucose, Osmolarity is the same as the molarity. For strong electrolytes like $CaCl_2$, the Osmolarity is 3 times the molarity since $CaCl_2$ provides 3 ions in solution ($Ca + 2\ Cl^-$)

- **Percentage Composition (parts per hundred):** % composition can be expressed as follows:
  Weight % (w/w) = wt of solute/weight of solution x 100
  Example: Commercial HCL is labeled 37% and its specific gravity (density) is 1.18 g/mL. Find the molarity of the solution and the mass and volume of the solution containing 0.1 mol of HCl?
  Answer: 37% = 37 g in every 100g of solution.
  The mass of one liter of the acid = 1000mL x 1.18 g/mL = 11800 g. Therefore, the mass of HCl in 1 liter = 0.37 x 1180 g = 437g.
  The molarity of HCl = 437g/36.5 g/mol = 12 mol/l = 12.0 M

  (b) 0.1mol = 3.65 g of HCl, since HCl is 37 g/100g of solution, therefore 0.1mol of this solution of HCl = 3.65 g/0.37 g HCl/g solution = 9.8 g solution
  (c) the volume of 0.1 mole of HCl = 9.8g solution/1.18 g/mL = 8.35 mL
  Volume % (v/v) = vol. of solute/vol. of solution x 100
  Weight-Volume % (w/v) = wt of solute /vol. of solution (ml) x 100

- **Solution-Diluent Volume Ratio:** The composition of a dilute solution is sometimes expressed as a ratio of the concentrated solution and the amount of solvent needed to do the dilution: For example a dilution ratio of 1:5 of HCl translates to 1 volume of concentrated HCl to 5 of the diluting solvent

- **Stochiometric Relationship:** A balance equation is needed in order to determine the combining ratio of the reactants and the products. Molar ratios of these substances give what is called the **stochiometry of the reaction**. For example, $H_{2g} + ½O_{2g} \rightarrow H_2O_l$ indicates that 1 mole of hydrogen molecule and half mole of oxygen molecule will give 1 mole of water molecule.

1.9 Tools of the Trade

- Laboratory note Book: record keeping is very important. A laboratory notebook is used to document what was done and observed in the laboratory. Complete statements should be used in documenting information in the lab notebook as well as writing legibly.

- Analytical Balance: Are either single pan or semi- micro balances. The weight capacity is usually between 100-200g with a sensitivity of 0.01 or 0.1 mg. The weighing method is done either by difference (weighing a filter paper or any other vessel) and add the analyte and record the weight again, the difference between the two weights is the weight of the analyte. Alternatively, we can weigh by **tarring** (weight of the filter paper or weighing vessel is made zero) before weighing the sample. This balance is a mechanical balance using built in weights to balance unknown weights.

- Electronic Balance: Unlike the mechanical balance, it does not use built in weight to return the balance to its original position. It uses the electromagnetic force to restore the balance to its original position. The major limitation of this balance is that it is calibrated with a standard at the factory where the force of gravity is different from that of the laboratory where it is been used. Other limitations include effect of electromagnetic radiation from nearby instruments and dust getting into the gap between the coil and the permanent magnet.

- Effect of Buoyancy**:** When the balances are tarred, it is tarred with air on it. When a weight is placed on the pan, it displaces a certain amount of air which makes the weight lighter than what it should be. This also applies to the removable weights used in measurements. There is always a net effect of buoyancy (been lighter) when the density of the object been weighed is not equal to the density of the standard weights. The true mass of the object is then given as

- $m= m_i(1-d_a/d_w)/1-d_a/d$ where d_a = density of air, d_w= density of water, d= density of object to be weighed

- Errors in Weighing: There are various parameters that introduce error to the value of the weights obtained by both analytical and electronic balances. These include human, method and instrumental errors. Examples of the errors are: touching the weighing substance or the substance, keeping substance at temperature higher than the ambient temperature before weighing (error due to convection of air current, cool down hot substances in desiccators to ambient temp), keep pan in its arrested position when loading and weighing, keeping door of the balance open. Others include not placing the balance on a solid support, changing the location of balance very often. Each balance has its tolerance level (margin of error)

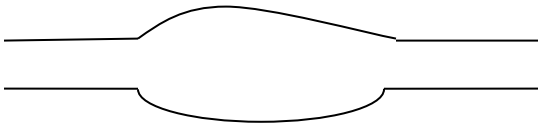
- Piezo-Electric Crystal Detectors**:** measures slightest change in mass using a vibrating quartz crystal. How does it work? When pressure is applied to the crystal, voltage drop will develop across some certain surfaces of the crystal and can be used to detect so many phenomenons such as precise time clocks.

- Burette**:** Various graduated glass cylinders are used to measure volumes of liquids. An example is the burette which is a column of glass with a graduation from 0 -50 mL. The burette should be placed such that the top of the liquid is at the eye level so that the height of the liquid in the burette can be read accurately and the problem of parallax will be avoided. Usually, liquids form concave meniscus and its height should be read at the bottom of the meniscus. A white card can be placed behind the meniscus or a black tape at the bottom of the meniscus for accurate reading. Sources of error in using burette include the presence of bubbles around the stop cock region or not properly rinsing burettes before and after use.

- Digital Titrator: A more convenient and portable device than a burette but less accurate. It is used mostly in field operation where samples are collected. It has a dial and a counter that can be used to know how much solvent is used when collecting samples.

- Volumetric Flask: This is another type of graduated glass cylinders used in volume measurements. It is calibrated to contain a certain amount of water (50, 100 …5000 mL) at 20^{o}C. The bottom of the meniscus is adjusted to the center of the marked line (at the neck of cylinder) on the cylinder. The cylinder is marked "TC 20^{o}C" or "TD" to show the temperature of calibration. This is important because the glass and the solvent expand at different temperature. The volumetric flask is used to prepare sample of known concentration.

- Pipets and Syringes: Are also graduated glass columns but smaller in size compared to a burette. They are used to transfer a certain volume of solution. There are two types of pipets: (i) those with "blown-out " portions at different part of the glass column (ii) the measuring pipets with no "blown-out" portion.

- 

- There are also two types of pipets with "blown-out portions": (a) Transfer pipets (blown-out portion is of different volumes and is at the middle of the pipet) (b) Ostwald-Folin which is similar to the transfer pipet (blow out last drop of solution when used, "blown-out portion is at the end of the glass column). There are two types of measuring pipets: (1) Normal measuring pipet that can deliver variable volumes and (2) the Serological pipet which is calibrated to the top and can only deliver 10 mL solution, (blow out last drop when used). Never use your mouth to draw liquids into a pipet. Use a rubber bulb instead.

- Small Volumes of Solution: Plastic micropipettes are used to deliver small volumes of solution (1-1000 µL). Accuracy is between 1-2% and precision is about 0.5%. For very small volumes, micro syringes are used instead.

- Drying: Glassware and instruments used for drying include: crucibles, evaporating dish and an oven. Different substances and wares have variable drying temperatures. The most common temperature for glassware's and crucibles is 110^{o}C. Dried substances are usually cooled down in desiccators.

1.10 Level of Tolerance (Margin of Error)

- The weighing balances and the volumetric glass wares have different tolerances (error) for every measurements made with them. Table 1.2show tolerance level for Class A buret

Table 1.2

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	±0.1

Chapter 2 Analysis of Experimental Data

2.1 Introduction

The "true" value of any form of measurement cannot be stated with 100% certainty. They all have a measure of uncertainty (error) which may be caused by humans, methods or the instrument. The best effort that can be made is to determine these uncertainties and try to reduce them to a tolerable level. This may include using a known reliable method, measuring the same data in different ways to see if they agree, using statistical analysis etc. The level of reliability of a data is very essential in chemical analysis and must be set by the analyst from the beginning before the data is acquired.

2.2 Essential Terminologies in Chemical Analysis

(1) Reliability of a Data: Often, scientist repeats an analysis 3-5 times. The data obtained may not be exactly the same but will show how reliable these set of data are. Oftentimes, a "central best value" can be determined for this set of data which may be very close to the "true" value of parameter of interest. The "central best value" may be represented by the mean or median.

- (2) Mean: The mean, average or arithmetic mean is one and the same expression: the sum of a set of replicate data/the number of individual results in the set.

- (3) Median: the number at the middle of a set of data (odd set of data) or the data which have half of the set above and below it.
  Example: Calculate the mean and median of 5.1, 5.8, 5.6, and 5.5?
  Mean ($\overline{x}$) = (5.1 +5.8 +5.6 +5.5)/4 = 22/4 = 5.5
  Median(even # of data) = (5.5 +5.6)/2 = 11.1/2 = 5.52 (half of the sum of the middle data)

- (4) Precision: It is the measure of the reproducibility of a data or agreement of a set of measurement obtained in an identical way. There are different ways of expressing precision. The most common way is to find the average of the deviation from the mean or median of the set of the data $\Sigma(x_i - \overline{x})/n$. Absolute values of the deviation is used in the calculation irrespective of the sign. Other methods of expressing precision include measuring the range (spread), the standard deviation or the variance of the data.

- Example: Calculate the mean. Median and the deviation from the mean for the following set of 5.1, 5.8, 5.6, and 5.5?

- The Range of a data: Measures the difference between the highest and lowest value in a data . Using the data in Table 2.1, the Range = 5.8 – 5.1 = 0.7

Table 2.1 Mean and Median

# of Data	Data	Deviation from the Mean	Deviation from the Median
1	5.1	0.4	0.42
2	5.5	0	0.02
3	5.6	0.2	0.08
4	5.8	0.3	0.28
	$\bar{x}$= 22.4/4 =5.5	$\Sigma\,\Sigma^{N}_{i=1}(x_i - \bar{x})^2$n=0.9/4=0.25	0.80/4= 0.2

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- (5) The Range of a data: Measures the difference between the highest and lowest value in a data. Using the data in Table 2.1, the Range = 5.8 – 5.1 = 0.7

- (6) Standard Deviation (σ): This is the square root of the average of square of deviation from the mean. For N number of data, the $\sigma = \sqrt{\Sigma^{N}_{i=1}(x_i - \bar{x})^2/N}$ for large set of data and

  $\sigma = \Sigma(x_i - \bar{x})^2/(N-1)$ for small number of data or degrees of freedom

- (7) Standard Deviation (σ): This is the square root of the average of square of deviation from the mean. For N number of data, the $\sigma = \sqrt{\Sigma(x_i - \bar{x})^2/N}$ for large set of data and $\sigma = \sqrt{\Sigma^{N}_{i=1}(x_i - \bar{x})^2/(N-1)}$ for small number of data. The standard deviation has the same unit as the data and is the preferred choice of expressing precision. Using the data in Table 2.1

- Table 2.2

# of data	Data	Deviation from the Mean	Square of the Deviation from the Mean
1	5.1	0.4	0.16
2	5.5	0	0
3	5.6	0.2	0.04
4	5.8	0.3	0.09
	$\bar{x}$= 22.4/4 =5.5	$\Sigma(x_i - \bar{x})/n$=0.9/4=0.25	$\sigma = \sqrt{0.29/(4-1)} = 0.31$

- (8) Variance: This is the square of the standard deviation (σ^2): The advantage of using variance over the standard deviation is that variance is additive i.e. if there are various causes of variance in a data, the overall variance is the sum of each individual variances of the data ($\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \ldots..$). Using the example in Table 2.2, the $\sigma^2 = (0.31)^2 = 0.96$

- (9) Accuracy: Is defined as the nearness of a data to its accepted value. It is reported as absolute error (E). $E = x_i - x_t$. x_i = observed data x_t = accepted value. Using the example in Table 2.2 and assuming the accepted mean is 0.34, the E= 0.29 – 0.34 = -0.05. the negative sign is retained to show that the error is increasing or decreasing

- (10) Relative Error (RE): Relative error is a more useful parameter than the absolute error. It is expressed as the ratio of the absolute error to the accepted value in % or parts per thousand (ppt.). Using the example above: the absolute error = -0.05, hence the relative error (RE) = -0.05 x100/0.34 = - 14.71 % or -0.05 x 1000/0.34 = 147.1 ppt.

2.3 Classification of Errors

Errors encountered in chemical analysis can be classified into two major typed: Determinate and Indeterminate errors. Precision measurements do not reveal these types of error. Putting one type of error in a certain group is a subjective exercise but determining such error is good for analytical measurements.

- Determinate Errors: These errors are also called Systematic errors. They have values and we may assign a cause for the error. Usually they are unidirectional, i.e. it could either be

low or high. For example, an incomplete step in the analysis of nicotinic acid in a sample involves oxidation with sulfuric acid. This may result to low yield of the nicotinic acid. The cause is assignable.

- Types of Determinate Errors: May include;

- **Instrumental Error**: Any instrument used in measurements has inherent sources of errors. For example, glass wares (burette, volumetric flask etc) slightly volume differences from the one indicated by the manufacturers due to distortion in glass walls and calibration temperatures of the manufacturers. Electrical equipments might have variable voltages at different points in time. Instrumental error can be corrected by constant recalibration of the instrument.

- **Method Error:** may be due to non-ideal physical or chemical behavior of reagents and reactions on which analysis is based. For example, a reaction may be slow or incomplete, side reactions, unstable and non specificity of reagents, using excess reagent than required by theoretical calculation etc. Inherent errors in a method are difficult to detect and is the most serious type of determinate error. Method errors can be minimized in sample calibration with known standards that approximate sample of interest, do independent analysis, blank determinations or using of sample of different size (detect constant errors)

- **Personal Error:** Many measurements need the personal judgment of the analyst. For example, determining meniscus level, color at endpoint, and exact position of a pointer on a scale. There might be variation on values obtained for these measurements from one analyst to another. Errors associated with these decisions are systematic, subjective and unidirectional. Physical handicap, prejudice or bias may contribute to these uncertainties. A good example of personal bias is observed with number bias where we tend to push a number in the direction of a preconceived true value.

- **Gross Mistakes:** These type of errors include arithmetic, transposition, misinterpretation, reading a scale backward or using a wrong scale etc. Self discipline is the antidote to this problem.

- **2.3. 1 Effect of Determinate Errors on Analysis:** Determinate errors can be constant or proportional: Constant Error: A constant error is made for every measurement made during analysis. The magnitude of the error in independent on the number of determinations made but is significant with the size of the quantity to be measured. Constant errors become more significant when the size of the quantity to be measured decreases. Proportional Error: Increases or decreases in proportion of the size of the quantity to be measured. A good example is the presence of interfering ions in a sample.

Presence of Iron impurities in Copper ore may give false high estimation of copper in the ore.

- **2.3.2 Indeterminate Errors (Random Error):** Occurs when a system of measurement is extended to its maximum limit. The sources and the magnitude of these errors cannot be detected or quantified. The effect of this error on results is that it makes it varies randomly.

2.4 Distribution of Data from Replicate Measurements

Indeterminate errors are often small in size but cannot be eliminated from measurements. To understand how small quantities affect the outcome of replicate data, we may assume that only four errors causes indeterminate error in an experiment. The probability of these errors occurring is the same and can only affect the final result in two ways: (1) cause the outcome to be an additive error or (ii) by subtractive error of a fixed amount, U. The four errors (U) can combine in different ways to result into the indeterminate errors. The magnitude of the indeterminate error can be : (i) One way or equal contribution (Maximum error, $u_1 + u_2 + u_3 + u_4 = 4U$), 2U(4 different ways where 2 will cancel out and 2 will result into the indeterminate error), 0U(6 different ways which cancel each other out) and mirror images of these combinations that result into -2U and -4U respectively. The ratio of the different combinations (6:4:1) is a probability of distribution of how the error will occur. If the number of replicate measurements is large, and the uncertainties becomes smaller and smaller, the distribution of the frequency of the probability of error will look like a bell and is called the Gaussian or normal error curve shown below

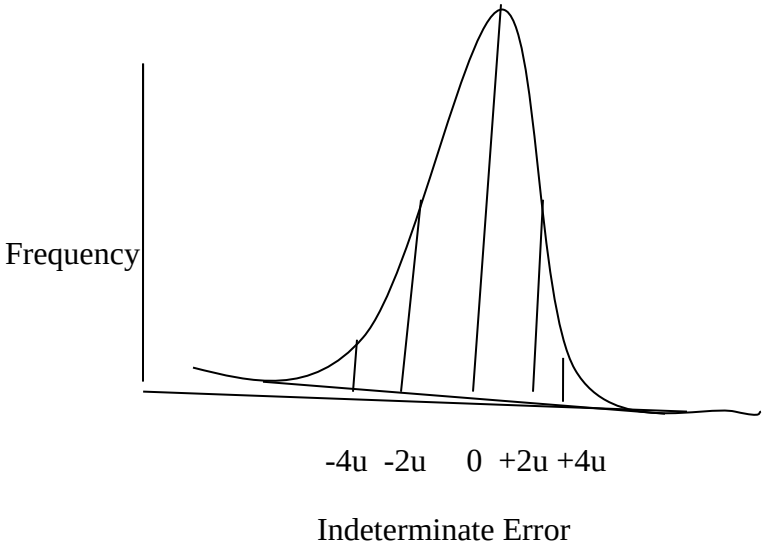


Figure 2.1 Frequency of Error vs. Indeterminate Error

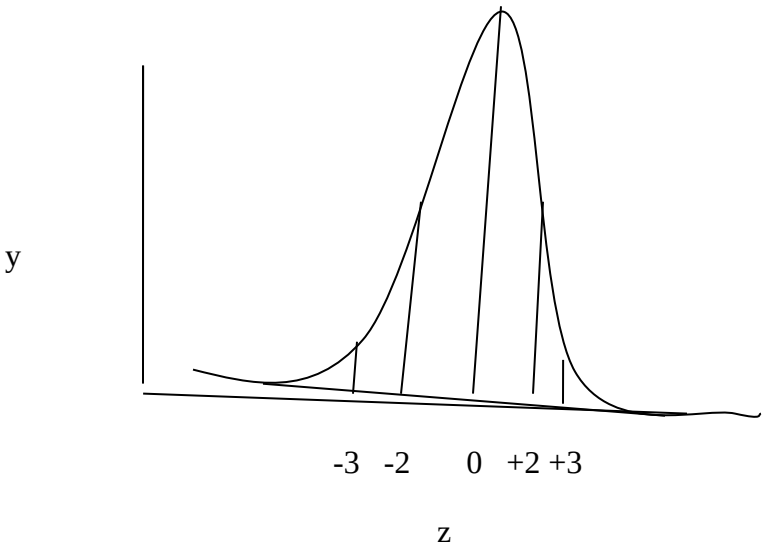
2.4.1 Properties of the Gaussian Curve

- Has a maximum frequency in occurrence of zero indeterminate error

- It has a symmetry on both sides of the maximum indicating that there is an equal frequency of occurrence of both negative and positive errors
- There is an exponential decrease in frequency of error as the magnitude of the error increases which indicates that small indeterminate errors occur more frequently than large ones
- Indeterminate errors in chemical analysis distribute themselves in a way that approximates the Gaussian curve
- This allows statistical techniques to be used in estimating the limits of precision of indeterminate errors from the precision of chemical data.
- Figure 2.1 can be described mathematically as follow

  $\mathbf{y = e^{-(x-\mu)2/2\sigma 2}/\sigma\sqrt{2\pi}}$ **(1)**

  where **x** = values of individual measurements, **μ =** arithmetic mean, **(x-μ)** = deviation from the mean, **y** = frequency of occurrence for each value of (x-μ), **σ =** standard deviation (a constant), **π** = 3.14 (22/7), **e** = Napierian logarithm (2.718).
- The breath of the normal error curve is related to **σ**
- If **z = -(x-μ)/σ, then equation 1 becomes**
- $\mathbf{y = e^{-z2/2}/\sqrt{2\pi}}$ **(2)**
- z gives the deviation from the mean a unit of σ
- **Hence plotting y vs. z will produce the same error distribution curve for all values of σ**



- Figure 2.2 Frequency of Error vs. z

Chapter 3 Application of Statistics to Chemical Analysis

At the end of this chapter, students:

- Would have learnt how to use statistical methods to evaluate data so that judgment about the effect of indeterminate errors can be better assessed.
- Will be able to define the interval around the mean of a set of data within which the true mean is expected to be found with a certain amount of probability (certainty)
- Will be able to determine the number of replications needed for a set of measurement so that the experimental mean can be included with a certain probability within a predetermined interval around the true mean
- Shall be able to use statistical methods as a guide in deciding whether an outlying data should be rejected or accepted in calculating a mean for the set
- Will be able to estimate the probability that two samples analyzed by the same method are significantly different in composition, i.e. to determine that the difference in experimental result is due to determinate or indeterminate error or truly due to differences in composition
- Shall be able to estimate the probability that there is real difference in precision between two methods of analysis

3.1 Confidence Interval

- The true mean (μ) value of a replicate of measurements is an unknown constant. Statistical theory helps us to set a limit around experimental mean ($\overline{x}$) within which we expect to find the true mean with a certain degree of probability
- These limits are called **confidence limits** and the **interval of the limits** is called **confidence intervals** (distance between two limits)
- The size of the interval depends on the **degree of the correctness desired**
- As the probability of desired correctness increases or decreases so also the size of the interval increases or decreases.
- For correctness to be absolutely correct, we must choose and interval about the mean that is large enough to include a possible values of data (x_i). the interval does not have a predictive value and if we do not have to have very large interval is we can accept a 99% level of correctness. We can even make it smaller if we choose lower percentiles of correctness

- The confidence interval obtained from standard deviation, s, for method of measurements also depends in magnitude on the level of certainty with which it is known

- Oftentimes, scientist assumes that the experimental standard deviation, s, is a good approximation of "true" standard deviation, s, may have some level of uncertainty and therefore, a large interval may be needed to obtain a reasonable level of certainty

3.2 Methods of Obtaining Good Approximation of σ

- Variation in the value of σ (theoretical standard deviation) may be reduced if the number of data (N) is large. In this case, value of **s** and **σ** will be the identical. This will be true for $N \geq 2$.

- It is then possible to obtain a good value of "**s**" if the method of analysis is not too long and adequate size of sample is available for replicate analysis

- It is assumed that the indeterminate error is the same therefore **s** will be a good approximation of **σ**

- For time consuming methods of analysis, precision for different set of data will be pooled together to estimate **s**. The estimated **s** is superior to that of any individual set of data

- Example: The mercury in seven samples of fish taken from Esinmirin River was determined by a method based upon absorption of radiation by elemental mercury. The results are given in the table shown below. Calculate a standard deviation for the method, based upon pooled precision data

3.3 Confidence Interval when s is a good approximation of σ

- The breath of a normal error curve is determined by **σ**.

- For any given value **σ,** the area under a part of the normal error curve relative to the total area of the error curve is related to the parameter **z** (**$z = -(x-\mu)/\sigma$**) in the equation **$y = e^{-z2/2}/\sqrt{2\pi}$**

- This ratio is called the confidence level and is reported in percentages

- The ratio also measures the probability for the absolute deviation (**$(x-\mu)$ (deviation from the theoretical mean)** to be less than **$z\sigma$**.

- The various values of **z** are shown in the table below

Table3.1

Sample #	# of Replicates	Results, Hg ppm	Mean ppm, $\bar{x}$	Sum of Squares of Deviation from the Mean $\Sigma(\bar{x}_i - x)^2$
1	3	1.80,1.54, 1.64	1/87	0.0258
2	4	0.96, 0.98, 1.02, 1.10	1.02	0.0116
3	2	2.13, 3.35	3.24	0.0242
4	6	2.06, 1.93, 2.12, 2.16,1.89,1.95	2.02	0.0611
5	4	0.57, 0.58, 0.54,0.49,	0.57	0.0114
6	5	2.35, 2.44, 2.70, 2.48, 2.44	2.48	0.0685
7	4	1.11, 1.15, 1.22, 1.04	1.13	0.0170
	Σ =28			**Σ = 0.2196**

s = √0.0258 + 0.0116 + 0.0242 + 0.0611 + 0.0114 + 0.0685 + 0.0170/28 -7

= 0.10 ppm Hg

- For example, the area encompassed by z = 1.96σ is 95% of the total area. This means that 95 out of 100 times, the calculated absolute deviation (x-μ) will be less than ±1.96σ
- For a single measurement, the confidence limit for the mean of the data μ = x ± zσ. The value of z could be positive or negative
- For N replicates of measurements, the confidence interval decreases by √N, hence the confidence limit for μ = x ± zσ/√N (a)
- This indicates that the confidence interval can be drastically reduced as the number of measurements increases. For example, if N is 4, the confidence interval will be halved. As the value of N increases, then the law of diminishing returns sets in and there will be no more advantage of making more measurements.
- Therefore, it is safe to take averages of 2- 4 measurements to achieve a reasonable confidence interval for any method of analysis.

Table 3.2

Confidence Level, %	Z
50	0.67
68	1.00
80	1.29
90	1.64
95	1.96
96	2.00
99	2.58
99.7	3.00
99.9	3.29

3.4 Confidence Limits when σ is Unknown (Student t-test)

Confidence Interval

- When a new method is developed and used to analyze a set of data, accurate estimation of the σ may be difficult,
- The accurate estimation of σ may also be hampered by length of time for analysis and the amount of sample available
- The same data will be used to estimate the mean and the precision which may introduce a great deal of uncertainty to the value of **s** (standard deviation).
- To account for the great variability of **s**, we may use the **t**-value where $\mathbf{t} = \bar{x}-\mu/\mathbf{s}$ and it is used to measure probability, establish confidence interval, measure differences between results of the same data and also compare results from different experiments
- Unlike **z**, **t** depends on the confidence level (**s**) and the degree of freedom used to calculate **s**
- As the degree of freedom increases **t** → **z**
- Values of **t** can be found in the t-table

- The confidence limit can be derived from the **t-table** as $\mu = \bar{x} \pm ts/\sqrt{N}$

Example: A chemist obtained the following data for the alcohol content in a sample of blood: percent of alcohol; 0.084, 0.089 and 0.079. Calculate the 95% confidence limit for the **mean** assuming (a) no additional knowledge about the precision of the method and (b) that on the basis of previous experience, **s→ σ** 0.006% ethanol.

- Answer: (a) $\bar{x} = (0.084 + 0.089 + 0{,}079)/3 = 0.084$

$$s = \sqrt{(0.00)^2 + 0.005)^2 + 0.005)^2/(3-1)} = 0.005$$

The degrees of freedom = N-1 = 2 and its **t** value at 95% confidence level= ± 4.30

Hence the confidence limit, $\mu = \bar{x} \pm ts/\sqrt{N}$ @ 95% confidence level = 0.084 ± 4.3 x $0.005/\sqrt{3} = 0.084 \pm 0.012$

(b) Since **s→ σ** 0.006% ethanol (a good value of σ is available) then **z** value may be used instead of the t value to estimate the confidence limit @ 95% confidence level by using the equation:

$$\mu = \bar{x} \pm zs/\sqrt{N} = 0.084 \pm 1.96 \times 0.006/\sqrt{3} = 0.084 \pm 0.007$$

3.5 Difference between Two Methods

- The t-test can also be used to compare two methods of analysis. For example, methods A and B were used to analyze 6 blood samples for cholesterol. Each sample is a different blood with different cholesterol content. The results are listed in the Table 3.3. Method B gives a lower result than method A in five of the six samples. Is method B systematically different from method A?

- $\mathbf{t = \bar{d}/s_d.\sqrt{n}}$ **and** $\mathbf{s_d = \sqrt{(d_i - \bar{d})^2/n-1}}$

- **where** $\bar{d}$ **= average of the difference between the two methods and** s_d **= the standard deviation of the average difference of the two methods**

Table 3.3 Comparison of two methods for measuring Cholesterol (g/L)

Plasma Sample	**Method A**	**Method B**	**Differences (d_i)**	**$(d_i-\overline{d})^2$**
1	1.46	1.42	0.04	0.004
2	2.22	2.28	-0.06	0.0484
3	2.84	2.67	0.17	0.0121
4	1.97	1.80	0.17	0.0121
5	1.13	1.09	0.04	0.004
6	2.35	2.25	0.01	0.0016
Average Difference of the $\bar{d}$			$\Sigma d_i/N = +0.06$	$\Sigma = 0.0822$
Standard deviation of the differences (s_d)				$\sqrt{0.0822/6-1} = 0.12$

3.6 Comparing two Means

- to see if they are the same or different from each other
- We use the formula $\mathbf{t = (\overline{x_1} - \overline{x_2})/s.\ (\sqrt{n_1 n_2}/\ (n_1+n_2))}$
  $s = \sqrt{\Sigma(x_i - \overline{x_1})^2 + \Sigma(x_j - \overline{x_2})^2/(n_1+n_2 -2)}$ and $\overline{x_1}$ and $\overline{x_2}$ are experimental means of the replicate data

  To establish that there is a difference or no difference between the two sets of data, we must set the Null Hypothesis that μ_1 and μ_2 are identical, and if so,
- $\overline{x_1}-\overline{x_2} = \pm ts((\sqrt{n_1+n_2}/\ (n_1.n_2)$
- If experimental difference is less than the calculated difference at a certain confidence level, then there is no difference between the replicate data. The converse is true.
- Example: The composition of a flake of paint found on the clothes of a hit-and run victim was compared with that of the paint from the car suspected of causing the accident. Do the following data for the spectroscopic analysis for titanium in the paints suggest a difference in composition between the two materials? From previous experience, the

standard deviation for the analysis is known to be 0.35% Ti; that is, s→ σ Paint from clothes %Ti = 4.0, 4.6. Paint from car %Ti = 4.5, 5.3, 5.5, 5.0, 4.9

- Answer: $\bar{x}_1 = 4.0 + 4.6/2 = 4.3$
- Answer: $\bar{x}_2 = 4.5 + 5.3 + 5.5 + 5.0 + 4.9 \ /5 = 5.0$
- $\bar{x}_1 - \bar{x}_2 = -0.7\%Ti$
- $\bar{x}_1 - \bar{x}_2 = \pm ts(\sqrt{n_1 + n_b}/ (n_1.n_b)$ since s→ σ, then

$\bar{x}_1 - \bar{x}_2 = \pm zs(\sqrt{n_1 + n_b}/ (n_1.n_b)$

at 95 and 99% confidence interval, z = 1.96 and 2.58 respectively

$\bar{x}_1 - \bar{x}_2 = \pm 1.96 \times 0.35(\sqrt{2+5}/ (2x.5) = 0.57\%$ (5 out of every 100 data will differ by ≥ 0.57%)

$\bar{x}_1 - \bar{x}_2 = \pm 2.58 \times 0.35(\sqrt{2+5}/ (2x.5) = 0.76\%$ (1 out of every 100 data will differ by ≥ 0.76%)

- The result shows that between 95-99% confidence levels, the observed difference of -0.7% is not from indeterminate error but from real difference in the paint samples. Hence, we could say the suspected car is not the cause of the accident

3. 7 Detection Limit

- We can use the equation $\bar{x}_1 - \bar{x}b = \pm ts((\sqrt{\mathbf{n_1 + n_b}}/ \mathbf{(n_1.n_b)}$ to estimate the detection limit of a measurement (Δx_{min})
- $\Delta x_{min} = \bar{x}_1 - \bar{x}_b > \pm ts \ (\sqrt{\mathbf{n_1 + n_b}}/ \mathbf{(n_1.n_b)}$ where
- $\bar{x}_1$, $\bar{x}_b$ and n_1, nb are the mean and number of data for the result and the blank respectively

Example: A method for the analysis of DDT gave the following results when applied to pesticide –free foliage samples (µg): 0.2, -0.5, -0.2, 1.0, 0.8-0.6, 0.4, 1.2. Calculate the DDT detection limit (99% confidence level) for (a) a single analysis and (b) the mean of five analyses

Answer: $\bar{x}_b = 0.2 -0.5 -0.2 + 1.0 + 0.8 -0.6 + 0.4+ 1.2/8 = 0.3$ µg

$s_b = \sqrt{((0.1)^2 + (0.8)^2 + (0.5)^2 + (0.7)^2 + (0.5)^2 + (0.9)^2 + (0.1)^2 + (0.1)^2)/8-1} = 0.68$ µg

(a) For a single analysis $N_1 = 1$, degrees of freedom = (1+8-2) = 7, hence , $t_{99\%} = 3.5$
$\Delta x_{min} > 3.5 \times 0.68\sqrt{1+8/1x8} > 2.5$ µg of DDT

(b) For 5 analysis N_1 =5, therefore $\Delta x_{min} > 3.11 \times 0.68\sqrt{5+8/5x8} > 1.2$ µg of DDT

3.8 Rejection of Data

- Sometimes we have a result that is larger or smaller (outlying) than the average of a data. We have to decide to either reject or retain the data
- If we set a limit that makes rejection too difficult, we will have a false or bogus result that will have a deleterious effect on the average of the data.
- If we set a limit that makes rejection easy, we will discard result that should not be discarded, hence introduce a bias to the data.
- The **Q** test is the preferred method of deciding whether to retain or reject a measurement. It is about an individual data
- **Q** = (Questionable result – Nearest result to Questionable result)/Range of result(spread)
- If Questionable result – Nearest result to Questionable result) = Gap, then
  Q = Gap/Range
- There is a table of **Q** values at different confidence level which can be used to calculate the values of Q for any data
- If $\mathbf{Q_{(observed)} > Q_{(tabulated)}}$, then, the data should be rejected but if $\mathbf{Q_{(observed)} < Q_{(tabulated)}}$, then the data should be retained
- Example: The amount of chloride ion in a factory waste was determined by titrimetric method. Five replicates were obtained: 12.53, 12.56, 12.47, 12.67 and 12.48. Is 12.67 a bad result?
- Answer: Rearrange the data: 12.47, 12.48, 12.53, 12.56, 12.67
  Q= Gap/Range = 12.67-12.56/12.67-12.47 = 0.11/0.20 = 0.55.
  At 90% confidence level, Q = 0.64, hence, $\mathbf{Q_{(observed)} < Q_{(tabulated)}}$, therefore the questionable result (12.67) should be retained
- The **Q** test is not that helpful for small sets of data (N < 5) because if a result has less than 10% of being real and is included in a data, it will introduce serious bias into the data
- It is better to reexamine existing data to spot sources of error or spend time to repeat the test if more sample is available than out rightly retaining or rejecting the result
- However, If the Q test suggest retaining the result, then report the median rather than the mean because the median has a higher virtue of including all data than the mean

3.9 Comparison of Precision of Measurements (F-test)

- The F-test is used to compare the precision of two identical sets of data
- The sample can be the same sample or different samples that are sufficiently similar so that the sources of indeterminate error are the same
- F –test is based on the null hypothesis that the precision of the two sets of data are identical
- The F-value is the ratio of the variances of the two sets of data
- The experimental F_{exp} value is compared to the maximum F_{tab} value obtained at a certain confidence level from the tables of F values (at specific degrees of freedom) if there are no differences in precisions
- If $F_{exp} > F_{tab}$, then there is a statistical basis for questioning whether the two standard deviations are alike
- The **F-** value can be used to answer two pertinent questions: (1) if $method_1$ is more precise than $method_2$. In this case, the standard deviation of the more precise method is made the denominator and the less precise one the numerator.
  (2) If there is a difference in the precisions of the two methods. In this case, the larger variance is made the numerator. Making the larger of the variances the numerator increased the outcome of the test **less certain,** hence the level of confidence may be decreased
- Example 1: The standard method for the determination of carbon monoxide in gasesous mixtures is known from many hundreds of measurements to have a standard deviation of 0.21 ppm CO. A modification of the method has yielded an s of 0.15 ppm CO for a pooled data with 12 degrees of freedom. A second modification, also based on 12 degrees of freedom, has a standard deviation of 0.12 ppm Co. Is either of the modifications significantly more precise thatn the original?
- Answer: An improvement is claimed by the modification, hence the irvariances are placed as denominators: For the standard method, $s \rightarrow \sigma$, hence the degrees of freedom for the numerator in F_1 and F_2 is assumed to be infinity (∞).
  For Mod_1, $F_1 = (0.21)^2/(0.15)^2 = 1.96$. F_{tab} for 12 degrees of freedom = 2.30
  For Mod_2, $F_2 = (0.21)^2/(0.15)^2 = 3.06$. F_{tab} for 12 degrees of freedom = 2.30
  For Mod_1, , F_1 is slightly less than F_{tab} , hence there is not much deviation and hence the precision is similar with the original method. But for Mod_2, F_2 is > F_{tab} , the deviation is significant, suggestion that it has a greater precision than the original method

- Then, we can ask the question: is Mod_2 than Mod_1? The answer can be obtained by comparing the variances of the two methods and place the larger variance as the numerator: $F_{exp} = (0.15)^2/(0.12)^2 = 1.56$ and $F_{tab} = 2.69$ at 12 degrees of freedom . Since $F_{exp} < F_{tab}$, there is not much difference between the two modifications

Chapter 4 Propagation of Errors

4.1 Introduction

Any result obtained from every experiment has a form of error associated with it. The error could be a determinate or indeterminate error and both have different effects on the result. In some cases, the error will cancel out and in other cases, it will not and accumulates to a significant proportion. These errors may be accumulated in different ways depending on the arithmetic relationship between the term containing the error and the item that is being measured. Errors or uncertainty in results is expressed as standard deviations of replicate determinations.

4.2 Accumulation of Determinate Errors

Method of accumulation of errors in addition/subtraction is different from that of multiplication and division

4.2.1 Addition/Subtraction

If a measurement is represented by the equation $y= a+ b-c$ (1)

where a, b, c are values of three different measurements. Each measurement will have absolute determinates errors Δa, Δa, Δb associated with them respectively.

So, the actual result obtained for each of a, b and c is $y + \Delta y = (a+\Delta a) + (b+ \Delta b) – (c + \Delta c)$ (2)

Subtracting equation (1) from (2) will give the absolute error Δy of the overall measurement as

$$\Delta y = \Delta a + \Delta b – \Delta c$$

This implies that the overall error of a data involving addition or subtraction is determined by the sum/difference of errors associated with the individual measurements that makes up that data

Example: Calculate the error in the result of the following determinations of Cl^- ion in sea water?

+ 0.41 (+0.01), +0.38 (+0.02), - 0.45 (-0.04) ppm

Answer: $y + \Delta y = (a+\Delta a) + (b+ \Delta b) – (c + \Delta c)$

$(+0.41 +0.01) + (+0.38 +0.02) + (- 0.45 -0.04)$ ppm

$\Delta y = \Delta a + \Delta b – \Delta c = (0.01 + 0.02 – (-0.04) = + 0.07$

4.2.2 Multiplication

Consider the product $y = a \times b$ (1)

with associated absolute errors $\Delta a + \Delta b$ and overall error of Δy

: $y + \Delta y = (a+\Delta a)(b+ \Delta b) = ab + a\Delta b + b\Delta a + \Delta a\Delta b$ (2)

Subtracting (1) from (2) $\Delta y = b\Delta a + a\Delta b + \Delta a\Delta b$ (3)

If we divide equation (3) by equation (1):) $\Delta y/y = \Delta a/a + \Delta b/b + \Delta a\Delta b/ab$

$\Delta a\Delta b/ab$ will be a small term compared to $\Delta a/a$ and $\Delta b/b$ because of the larger denominator and the product of two small numbers, hence $\Delta y/y \sim \Delta a/a + \Delta b/b$

This error is a relative error not absolute errors as in the case of addition/subtraction

4.2.3 Division

Consider the product $y = a /b$ (1a) or $yb = a$ (1b)

with associated absolute errors $\Delta a + \Delta b$ and overall error of Δy

: $y + \Delta y = (a+\Delta a)/(b+ \Delta b)$ (2a) or

$(a+\Delta a) = yb + y\Delta b + b\Delta y + \Delta y\Delta b$ (2b). substituting eqn (1b) in (2b),

$(a+\Delta a) = a + y\Delta b + b\Delta y + \Delta y\Delta b$ (3a) and

$\Delta a = y\Delta b + b\Delta y + \Delta y\Delta b$, dividing by eqn (1)

$\Delta a/a = y\Delta b/yb + b\Delta y/yb + \Delta y\Delta b/yb$ (4a)

$= \Delta b/b + \Delta y/y + \Delta y\Delta b/yb$

$\Delta y/y = \Delta a/a- \Delta b/b-\Delta y\Delta b/yb$ assuming that $\Delta y\Delta b/yb <<<<< \Delta a/a- \Delta b/b$, then

$\Delta y/y = \Delta a/a- \Delta b/b$

In general, if $y = ab/c$ then $\Delta y/y = \Delta a/a+ \Delta b/b - \Delta c/c$

Example: Example: Calculate the error in the result of the following determinations of Cl^- ion in sea water?

0.41 (+0.01) x 0.38 (+0.02)/0.45 (-0.04) ppm

Answer: $\Delta y/y = 0.01/0.41 + 0.02/0.38 - (-0.04)/0.45 = 0.024 + 0.053 + 0.088 = 0.165 = 0.17$

$\Delta y = 0.17 \times y$ and $y = 0.41 \times 0.38/0.45 = 0.346$ hence, the absolute error

$\Delta y = 0.17 \times 0.345 = 0.059$

4.3 Accumulation of Indeterminate Errors

Standard deviation is the most convenient way of representing indeterminate errors however; no particular sign can be attached to these standard deviations when it comes to indeterminate errors. Each of these errors have equal chances of been positive or negative, hence we attach the sign ± to standard deviations of indeterminate errors.

4.3.1 Addition/Subtraction

The most probable error in summation or differences of indeterminate errors in a given data is given by the square root of the individual variances of each of the measurements that constitute that data: $s_y = \sqrt{s_a^2 + s_b^2 + s_c^2}$

Example: Calculate the error in the sum of the result of the following determinations of Cl^- ion in sea water? 0.41 (±0.01), 0.38 (±0.02), -0.45 (±0.04) ppm

Answer: $s_y = \sqrt{s_a^2 + s_b^2 + s_c^2} = \sqrt{(0.01)^2 + (0.02)^2 + (0.04)^2} = \sqrt{(0.0001) + (0.0004) + (0.0016)} = \sqrt{0.0021} = \pm 0.046$ **The sum of the data = 0.34** ± 0.046

4.3.2 Multiplication and Division

Just like we did with determinate errors, we must first of all calculate the relative errors for each measurement ($\Delta a/a$, $\Delta b/b$, $\Delta c/c$) and then relative variance of the result ($s_y = \sqrt{s_a^2 + s_b^2 + s_c^2}$) and finally find the absolute error of the result ($\Delta y = s_y \times y$)

Example: Calculate the error of the result for Cl^- ion from sea water: 0.41 (±0.01) x 0.38 (±0.02)/0.45 (±0.04) ppm?

Answer: relative error = 0.01/0.41 = 0.024, 0.02/0.38 = 0.053, 0.04/0.45 = 0.088

The relative variance: $s_y = \sqrt{s_a^2 + s_b^2 + s_c^2} = \sqrt{(0.024)^2 + (0.053)^2 + (0.088)^2} = \sqrt{(0.00058 + 0.0028 + 0.0077} = 0.0011$

The absolute error = $\Delta y = s_y \times y = 0.0011 \times 0.346 = 0.00038 \sim 0.0004$

4.4 Mixed Operation

Calculate the standard deviation of the following data

1. $[14.3(\pm0.01) - 11.6(\pm0.02)] \times 0.050(\pm0.001)/[820(\pm10) + 1030(\pm5)] \times 42.3(\pm0.4) = 1.725 (\pm?) \times 10^{-6}$
2. $[1.763(\pm0.03) - 0.59(\pm0.02)]/1.89(\pm0.02) = 0.691 (\pm?)$

Answer: (1). First step is to calculate the standard deviation of the sums and differences:

The difference in the Numerator: $s_a = \sqrt{s_a^2 + s_b^2 + s_c^2} = \sqrt{(\pm0.2)^2 + (\pm0.2)^2} = \pm0.28$

The sum in the denominator: $s_a = \sqrt{s_a^2 + s_b^2 + s_c^2} = \sqrt{(\pm10)^2 + (\pm5)^2} = \pm11$

The eqn. now becomes: $[2.7(\pm0.28) \times 0.050(\pm0.001)/1850(\pm11) \times 42.3(\pm0.4) = 1.725 (\pm?) \times 10^{-6}$

The eqn. now includes products and quotients. We should then calculate the relative standard deviation of each quantity: $(s_a)_r = \pm0.28/2.7 = 0.104$, $(s_b)_r = \pm0.001/0.05 = 0.020$, $(s_c)_r = \pm11/1850 = 0.0060$, $(s_d)_r = \pm0.4/42.3 = 0.0095$,
then, $(s_y)_r = \sqrt{s_a^2 + s_b^2 + s_c^2 + s_c^2} = \sqrt{(0.104)^2 + (0.020)^2 + (0.0060)^2 + (0.0095)^2} = 0.106$

The absolute standard deviation = $1.725 (\pm?) \times 10^{-6} \times (\pm0.106) = \pm0.18 \times 10^{-6}$

The answer = $1.7(\pm0.2) \times 10^{-6}$

(2) $[1.763(\pm0.03) - 0.59(\pm0.02)]/1.89(\pm0.02) = 0.691 (\pm?)$

First step is to calculate the standard deviation of the sums and differences:

The difference in the Numerator: $s_a = \sqrt{s_a^2 + s_b^2 + s_c^2} = \sqrt{((\pm0.03)^2 + (\pm0.02)^2} = \pm0.0013$

The eqn. now becomes: $[1.173(\pm0.0013)/1.89(\pm0.02) = 0.691 (\pm?)$

The eqn. now includes quotients. We should then calculate the relative standard deviation of each quantity: $(s_a)_r = \pm0.0013/1.173 = 0.0011$, $(s_b)_r = \pm0.02/1.89 = 0.011$,
then, $(s_y)_r = \sqrt{s_a^2 + s_b^2 + s_c^2 + s_c^2} = \sqrt{(0.0011)^2 + (0.011)^2} = 0.0111$

The absolute standard deviation = $0.691 (\pm?) \times (\pm0.0111) = \pm0.0077$

The answer = $0.691 (\pm0.0077)$

4.5 Propagation of Errors in Exponential Determinations

Consider an experimental result, **a**, expressed as

$y= a^x$, (1), x is the power or root that contains no uncertainty.

The uncertainty Δy due to determinate error Δa in **a**, is determined by taking the derivative of y wrt **a,**

$dy = xa^{(x-1)}da$ (2)

Divide eqn 2 by eqn (1)

$dy/y = xa^{(x-1)}da/a^x$ (3) but $a^{(x-1)} = 1/a$ hence eqn(3) becomes

$dy/y = xda/a$

For finite increments

$\Delta y/y = x\ \Delta a/a$ where Δy is the absolute error of the data while Δy/y is the relative error of the data. This implies that the relative error is the product of the power or root (exponent) of the data and the relative error of the data itself. So if x= 2, the relative error is double of the error of the data and if x = ¼, the relative error will be ¼ of the error of the data itself

This equation applies to indeterminate errors itself where $s_y = x\ s_y$

Example: The standard deviation in measuring the diameter, d, of a sphere is ±0.02 cm. what is the standard deviation in its calculated volume V if d = 2.15 cm?

Answer: $V= 4\pi /3(d/2)^3 = 4\pi /3(2.15/2)^3 = 5.20\ cm^3$

Relative error in volume = $s_v/V = 3 \times s_d/d = 3 \times 0.02/2.15 = 0.028$

Absolute standard deviation in V = 0.028 x 5.20 = 0.15 hence,

$V= 5.2 \pm 0.02\ cm^3$

Example 2: The solubility product K_{sp}, for a silver salt AgX, is $4.0(\pm 0.02) \times 10^{-8}$. What is the uncertainty associated with the calculated solubility of AgX in water?

Answer: Solubility = $\sqrt{K_{sp}} = \sqrt{4.0 \times 10^{-8}}. = 2.0 \times 10^{-4}$, $(s_{a)r} = 0.4 \times 10^{-8}/4.0 \times 10^{-8} = 0.1$

$(s_{y)r} = x.\ (s_{a)r} = 1/2 \times 0.1 = 0.05$ and $(s_{y)} = 2.0 \times 10^{-4} \times 0.05 = 0.1 \times 10^{-4}$ then solubility = $2.0(\pm 0.1) \times 10^{-4}$

4.6 Propagation of Error in Logarithm and Antilogarithm Calculations

If y = log **a**, then the natural logarithm of log **a** = In **a**

So, y= loga = 0.434In **a**. Taking the derivative of y = dy = 0.434da/**a**

For finite values $\Delta y = 0.434\ \Delta a/\mathbf{a}$. this implies that the absolute uncertainty in y is equal to the relative uncertainty in **a**.

The absolute standard deviation = $s_v = 0.434\ (s_a)_r$

Example: Calculate the absolute standard deviation of the following results:
(a) log [2.0(±0.02) $x10^{-3}$] = -0.269±? (b) a = antilog[1.200(±0.003) = 15.849 ±? (c) a = antilog[45.4(±0.3) = 2.5119 x 10^{45} ±?

Answer: (a) $s_v = 0.434\ (s_a)_r = 0.434(0.02\ x10^{-3}/2.0x10^{-3}) = \pm\ 0.004$

Therefore, log [2.0(±0.02) $x10^{-3}$] = -0.269± 0.004

(b) $s_v = 0.434\ (s_a)_r$ (1) rearranging eqn (1) $(s_a)_r = s_a/a = s_v\ /0.434 = 0.003/0.434 = \pm 0.0069$

$s_a =$ 0.0069 x a = 0.0069 x 15.849 = 0.11, therefore, ±

antilog[1.200(±0.003) = 15.849 ±0.11

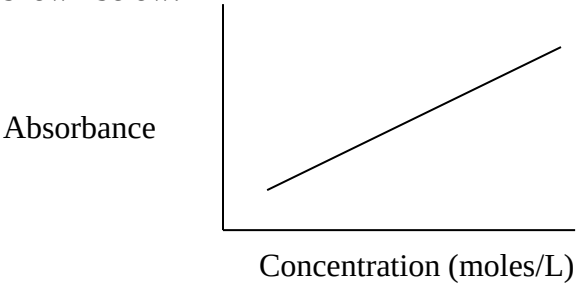
(c) $s_v = 0.434\ (s_a)_r$ (1) rearranging eqn (1) $(s_a)_r = s_a/a = s_v\ /0.434 = \pm 0.3/0.434 = \pm 0.69$

$s_a =$ 0.69 x a = 0.69 x 2.5119 x 10^{45} = 1.7 x 10^{45}, therefore,

antilog[45.4(±0.3) = 2.5119 ±1.7 x 10^{45}

4.7 Calibration Curve

Nearly all analytical method needs a calibration curve. The standard and the sample are treated exactly in the same way. Different concentrations of the chosen standard sample are used to obtain data and the data is plotted against the concentrations to obtain a calibration curve as shown below.



A region of the concentration where all the data points will fit a straight line is the most desired. This region will give a one: one (1:1) correspondence between the size of the desired variable and the concentration of the standard and is then used to estimate the size of an analyte in a sample. Usually, not all data points will fall on a straight line because of indeterminate error. Hence, the scientist need to find the **best straight line** that fits the data. Regression analyses

allow such a line to be obtained and also furnish the uncertainty associated with the line. The regression method is called **method of least squares.**

The **method of least squares** assumes that: (i) there is a linear relationship between the analyte concentration (**independent variable)** and the measured variable (**dependent variable)** (ii) the exact concentration of the standard is known. Therefore, any deviation from such a line is due to indeterminate error in the measured variable and are similar (iii) the error in the measured variable is greater than the one in the independent variable. The linear relationship is represented by the equation:

$y = mx + c$ [m = slope of the line and c = interception i.e. where the value of y = 0]

The deviations from the straight lines, **residuals**, [**$Q = y_i - (mx_i + c)$= vertical distance between the line and each data point],** are random and could be positive or negative. The **method of least squares**' aim is to minimize the sizes of the deviations and therefore, we can find the best straight line of which the squares' of the deviation (so that we only deal with positive numbers) is the minimum.

4.8 Determining the Slope, Intercept and the Standard Deviations (slope, intercept, result)

The slope, intercept and their standard deviations can be derived from the least square method by applying statistical equations. Let us define the following parameters

$A^2 = (\Sigma(x_i-\bar{x})^2 = \Sigma x_i^2 - (\Sigma(x_i)^2/n$, $B^2 = (\Sigma(y_i-y)^2 = \Sigma y_i^2 - (\Sigma(y_i)^2/n$,

$C^2 = (\Sigma(x_i-\bar{\bar{x}})(y_i-\bar{y}) = \Sigma x_i\, y_i - (\Sigma(x_i)\Sigma y_i)/n$

x_i an y_i are pairs of data, $\bar{x_i} = \Sigma x_i/n$ and $y_i = \Sigma y_i/n$ are the mean of the data pairs, n is the number of data pairs that defines the of the calibration curve. Then

$m = AB/A^2$, $c = \bar{y} - b\bar{x}$, s_r = standard deviation of the residuals = $\sqrt{B^2 - b^2A^2/n-2}$

s_m = standard deviation of the slope = $\sqrt{s^2_r}/A^2 = s_r/A$,

s_c = standard deviation of the results based on this calibration curve

$= s_r/b\sqrt{1/m + 1/n + (\bar{y}_c - \bar{y})/b^2A^2}$, $\bar{y}_c$ = mean of the result for the sample, $\bar{y}$ = mean of the standard solution

Exercise

1. Table 3.4 shows the data of a protein standard using Lowry's method to determine the amount of protein in a sample. The absorbance of an unknown sample is found to be 0.246. Calculate the amount of protein in the sample and its associated uncertainty?

2. Answer: Plot the data using the least square methods. Determine the slope, intercepts and their uncertainties: m= 0.0163, s_m = 0.00022; c = 0.1040, s_c = 0.0026; s_y = 0.0059
3. From y= mx +c, x = y-c/m (x= absorbance of the unknown)
4. x = 0.246± (0.0059) – 0.1040(±0.0026)/0.0163(±0.00022) = 0.142(±0.0064/0.0163 (±0.00022)
5. x = 0.142(±4.5%)/0.0163(±1.3%) = 8.7 (±4.7%) = 8.7 (±0.0.04) µg of protein

Table 3.4 Spectrophotometer Readings for Protein Analysis by Lowry Method

Sample (µg)	**Absorbance of three independent samples**	**Range**	**Average with all data**
0	0.099, 0.099, 0.1	0.001	0.0993
5	0.185, 0.187, 0.188	0.003	0.1887
10	0.282, 0.272, 0.272	0.0.010	0.2753
15	0.342, 0.345. 0.347	0.005	0.3447
20	0.425, 0.425, 0.423	0.002	0.4267
25	0.483, 0.488, 0.496	0.013	0.4890

Chapter 5 Sampling Procedure

5.1 Introduction

Samples that are analyzed in laboratories are as homogeneous as possible while the ones found in nature are mostly heterogeneous and needs to be treated one way or the other to fit what is required in the laboratory. Some of the treatments that is often employed are: sampling, producing a homogeneous sample, and drying.

Sampling: A sample is a representative of a given bulk material that is exactly alike in properties (size, reactivity's, color, etc) and composition like the bulk material. For example, when people want to celebrate an occasion, the celebrant chooses a brand of cloth that he/she will like his guest to wear to the occasion. Some bundles of the clothing material are bought and distributed among the guest as sample to be taken to the market so that they can buy can buy the same type of cloth. The initial bundle distributed to the guests is called a **sample**. Usually, substances that need to be analyzed are not in the right condition or size suitable for a laboratory analyses', hence, a small portion of it that is similar in all ways to the original substance is taken to the laboratory for processing and analysis. This portion is also called a **sample**. The procedure of choosing this particular sample is called **Sampling.**

5.2 Sampling Procedure

Sampling may be done by: (i) taking a small portion of a large sample based on statistical probabilities that predicts that the sample is similar to the bulk from which it is taken (ii) taking a small portion on **'as needed'** bases (iii) analyzing the whole sample. Procedures (ii) and (iii) are prone to giving false or unreliable results and also not cost and time effective. The first option is the best way to choose a sample because the limitations of the process of selection and the level of acceptability of result based on such selection are known ahead of time. Usually, random sampling is done which limits human bias in choosing the samples for analysis.

Samples in the real world are usually heterogeneous and non uniform throughout its bulk. Hence, the major problem in sampling procedure is the physical nature of the sample itself. The greatest problem is found with solids relative to gases or liquids. The problems with gases usually involve contamination from previous use of storage tanks or gases reacting with containers. Problems of homogeneity may only occur if there are variations in conditions surrounding the gas. For liquids, the major problem is homogeneity which can be solved by stirring. With solids, homogeneity is problematic for many reasons: localization of some components, presence of some components in a section and not throughout the sample, structural differences in different part of the sample etc. The sampling process will therefore be different for each solid. The process may include taking a large number of samples from the original sample. These smaller samples are then crushed and mixed properly by suitable procedures (tabling process, grinding

etc) to obtain what is called an **average sample (200-300 g).** The same process must be used to produce replicate samples for analysis.

5.3 Problems that Accompanies Sampling Procedure

There many hazards that accompany the sampling procedure: emission of excessive or poisonous gases, corrosive chemicals, fire outbreak, ignitable elements, volatile or inflammable materials, radioactivity etc. The sampler must be protected in all situations: having prior knowledge of the type of sample, providing adequate dressing gear, antidotes to toxic substances must be on site, adequate preventative procedures must be taught prior to sampling time etc. Sometimes, the sample composition may change after sampling due to internal changes, reaction with air or moisture or the container. For example, ion-exchange may occur on glass interface, hence plastic containers is preferable as a container for the samples.

5.4 Common Terminologies used in Sampling Processes

A Lot: Material from which samples are taken: river, ore etc

Bulk or Gross Sample: The sample taken from the lot for analysis or archiving. The size of the gross sample is determined by cost, the level of uncertainty desired between the composition of the gross and lot sample, degree of heterogeneity of the lot, and the particle size at which heterogeneity starts. At one end of the spectrum, liquids and gases heterogeneity starts at the molecular level with the size of the particle size in the range of 10^{-5} or less. At the other extreme of the spectrum are solids with particle size in the order of one centimeter or greater. In between these extremes are colloids and solidified metals like alloys. The number of, **n**, of the particle of the material to be taken as a sample must be of the same particle size and its magnitude depends on the level of uncertainty desired and the degree of heterogeneity of the material. The gross sample of liquids and gases may be small in size and may require taking multiple samples from different parts of the liquids. Example large volume liquids exposed to the atmosphere may have different amount of oxygen at different depth of the water. For solids, sampling may be done will transferring the material. Conning and quartering (splitting into 4 equal parts) or rolling and quartering are common methods used in sampling gross samples of solids.

Laboratory Sample: Smaller samples taken from the bulk sample.

Test Portions: These aliquots taken from the laboratory sample for analysis

Random Sample: A lot is divided into real or imaginary sections from which samples are taken in random fashion based on a table of random numbers

Highly Segregated Materials: Materials with different compositions at different regions of the material.

Composite Sample: samples constructed from a highly segregated material based on the same ratio of segregation of the original sample: for example, if the material has three regions in the ratio of 2:3:5, the sample should also be taken in the same ratio 2:3:5

5.5 Sampling Statistics

If the overall standard deviation = s_o, sampling procedure standard deviation = s_s and the analytical procedure standard deviation = s_a,

Then, $s^2_o = s^2_a + s^2_s$ which implies that the sampling and analysis variances are additive. It then point out that if one std is large and the other one very small, it is not necessary to try to reduce the deviation in the larger one because the overall effect will be negligible and will not worth the effort.

5.6 Sample Preparation

Laboratory scale sample is prepared from the gross sample. The method applied in this case may include, grinding (to reduce the size), mixing, dividing and drying (determine the amount of moisture) to produce a homogeneous sample.

There are different types of grinders that can be used to grind coarse samples to smaller sizes or fine particles: mortar and pestle (steel or percussion mortar, agate mortar), ball mill. Drying of solids is done a 110^0C until a constant mass is obtained. The dried sample can then be dissolved in the appropriate solvents for analysis. Inorganic solids that do not dissolve easily are digested or fused with acid (non oxidizing acids: HCl, HBr, HF, H_3PO_4, dilute H_2SO_4, dilute $HClO_4$. Substances that do not dissolve in non oxidizing acids may be digested with oxidizing acids such as concentrated HNO_3, H_3PO_4, or $HClO_4$ in a microwave bomb digester.

Inorganic samples that do not dissolve in acids can be fused by a hot inorganic flux (Na_2CO_3, Na_2O_2, NaOH, KOH, NaB_4O_7, LiB_4O_7,

Sometimes organic compounds need to be decomposed before analysis. This is called **ashing.** Ashing could be dry (solids) or wet ashing (liquids).

Oftentimes, the amount of substance available may be very small (trace amount). This may need to be **pre-concentrated** before been analyzed. Techniques like ion exchange may be used such a case. Also, we might need to remove interfering substances before pre-concentrating a sample. This is called **sample clean up.**

It may be necessary sometimes to **derivatize** a sample before analyzing it. The reason is to make the analyte suitable for detection. For example, we may need to make a sample volatile for GC analysis or florescent for UV detection.

5.7 Forms of Moisture in Samples

Most of the time, samples contain water either as a contaminant or parts of its structure. The ones that are part of the chemical composition are called **essential water**, and they exist in Stochiometric proportion while the ones that are not part of the chemical composition are called **non-essential water,** and not in Stochiometric proportions. Examples of essential water are the water of crystallization or water of constitution (water given off if a substance when heated). Non essential water includes: adsorbed, sorbed, occluded and solid solution.

Determination of Moisture in Samples

There are two methods of determining water content of a sample: direct and indirect methods.

Indirect method: Drying of a sample in an oven at low temperature (100-110^{0}C) is the most common method used in determining the water content of a sample. The disadvantages include: (i) not high enough heat at drying temperature to completely remove all water molecules (ii) sample decomposition (reduces sample weight), (iii) air oxidation (increases sample weight), and (iv) given-off of volatile components

Direct Method: This includes collecting water that is driven off a sample in a water adsorbent such as magnesium perchlorate. The adsorbent weight before and after drying the sample is determined by subtraction. Other methods include chemical methods (Karl Fisher), chromatographic (GC), Infra red, and distillation.

Chapter 6 Gravimetric Analysis

6.1 Introduction

Gravimetric analyses involve using the weights of a product to determine that of the sample. It is also called **quantitative analysis by weight**. The composition of the product and sample are known and are also chemically related to each other. Gravimetric processes involve isolating the desired analyte and manipulate it to get it in its most stable purest form and in a format that can be weighed. The weight of the analyte is then calculated from chemical formula and the atomic weights of the elements that make up the analyte.

There are many methods used in gravimetric analysis: (1) **precipitation methods**: Here, the analyte to be determined is made to react with other reagents that produces an insoluble product, which can be filtered and treated to give a stable desired product of known composition. The product is then weighed, manipulated and reported in the desired format (2) v**olatilization methods**: this is applicable to a volatile analyte. The sample is heated up to volatize the analyte. The weight of the analyte or left over sample (nonvolatile part) may be used to estimate the desired data (3) **electro-analytical methods**, (4) **extraction methods**, and (5) **chromatographic methods**.

The disadvantage of gravimetric analysis is that it is time consuming and the advantage is that it can be isolated and the number and amount of impurities present in the analyte can be determined.

6. 2 Scope of Gravimetry

Mass measurement is the most important aspect of gravimetry and it can be done with high degree of accuracy. Therefore, gravimetric method is commonly used in analytical chemistry. The only instrument used in gravimetry is a balance. Most precipitating agents are non specific; hence, reaction conditions must be adequately controlled to avoid co-precipitation of interfering ions. Tables of precipitating anions, cation are organic reagents are available in the literature.

6.3 Calculations in Gravimetric Analysis

The general approach is to compare moles of product (analyte) to that of the sample. Sometimes, the analyte sought is the product or a part of the product that is weighed, or is chemically related to the product. In all cases, the weight of the product must be converted to that of the analyte sought by a gravimetric factor. For example if the amount of Fe in $Fe_2(SO_4)_3$ is to be determined by precipitation as $BaSO_4$: $Fe_2(SO_4)_3 + 3Ba^{2+} \rightarrow 2Fe^{3+} + 3BaSO_4$.

The Gravimetric factor: 2x fw. Fe/3 fw. BaSO4

Determination of Cl^- ion by precipitation with Ag+

Example:

- How many grams of Cl^- (At. Wt= 35.45 g/mol) are contained in a precipitate of AgCl (Formula Wt. = 143.3 g/mol) that weighs 0.204 g?
- Answer: to solve the problem, we will need to (i) convert metric mass to that of chemical mass (ii) obtain the stochiometry of the reaction i.e. amount of analyte and sample in the process: $Ag^+ + Cl^- \rightarrow AgCl$ (s).
  Mole ratio $Cl^-/AgCl$ =>
- conversion to chemical mass (moles) stochiometry

$[0.204\ g\ AgCl \times \frac{1\ mol\ AgCl}{1\ mole\ 143.3\ g\ AgCl}] \times [\frac{1\ mol\ Cl^-}{1\ mole\ AgCl}] \times [35.45\ g\ Cl^-/mol\ Cl^-] = 0.05g\ Cl$

conversion to metric unit (g)

- **Gravimetric factor**: in obtaining the amount of Cl^{-1} in the above example we employed conversion to chemical mass, stochiometry of the reaction and the conversion to metric unit parameters to obtain the desired result. These conversion ratios are called the gravimetric factor.

The gravimetric factor = (a/b x formula weight of product/formula weight of sample)

(where a/b is the theoretical mole ratio of productsought/sample)

The weight of the product is thus calculated as:

wt of product x (a/b x formula weight of sought/formula weight of substance weighed)

(Where a/b is the theoretical mole ratio of product/sample)

Example 2

At elevated temperatures, $NaHCO_3$ is converted to Na_2CO_3:

$2NaHCO_3 \text{ -=> } Na_2CO_3 + CO_{2g} + H_2O_g$ (1)

Ignition of 0.718 g of impure $NaHCO_3$ yielded a residue weighing 0.4724g. Calculate the percentage purity of the sample assuming any impurity is non volatile?

Answer: From eqn ,1 mole ratio of $NaHCO_3$: CO_{2g}: H_2O_g = 2:1:1

(wt of sample – wt of residue) = weight of CO_{2g} and H_2O_g in the $NaHCO_3$ sample

= 0.7184 – 0.4724 = 0.2460g

% $NaHCO_3$ = 0.2460 x [2(fw $NaHCO_3$ /fw(CO_{2g} + H_2O_g)]/0.7184 x100

= 0.2460 x [2(84.01/ (44.01 + 18.02)]/0.7184 x100 = 92.75 %

Example 3

A method for measurement of soluble organic carbon in sea water involves oxidation of the organic material to CO_2 with $K_2S_2O_8$ followed by gravimetric determination of CO_2 trapped by a column of NaOH coated asbestos. A water sample weighing 6.234 g produced 2.378 mg of CO_2. Calculate the ppm carbon in the seawater?

Answer: Mole ratio of C: CO_2= 1:1. Volume of water = (6.234 – 0.002378) mL = 6.232 mL

mg of C in seawater/ml = 2.378 x (1/1) x (12/44)]/6.232 = 0.10406 mg/ml

ppm of C in seawater = mg/L of C in seawater = 0.1041x 1000 = 104.1

Precipitation Method

Precipitation method is the most important step in gravimetric analyses. The analyte that is sought must be insoluble and can be recovered by filtration. Sometimes, the analyte to be weighed has a different form from how it was precipitated (e.g., Magnesium is precipitated as ammonium magnesium phosphate (Mg (NH_4) $PO_4.6H_2O$) and weighed as pyrophosphate ($Mg_2P_2O_7$). The following factors that define a good precipitating method include: insolubility, minimum loss during washing and filtration, appreciable size of the analyte that can be retain during filtration, convertible to a pure form of the analyte with known composition, and stable to temperature of drying.

Often times, the precipitated analyte is not pure. Co-precipitation (soluble substances that comes down with the analyte during precipitation) depends on the substances in solution before and after precipitation, the size of the particles of the analyte, solubility, temperature, reactants concentration, and the rate at which reactants are mixed. The colloidal properties (particle size) are shown by particles with sizes ranging from 0.1µm (10^{-3} mm) and 0.1nm (10^{-7} mm) and it depends on the chemical composition of the precipitate and the conditions that exist at the time of precipitation. Normal filter paper can retain particles in the range of 10^{-2} mm = 10 µm.

Drying or Ignition of Precipitates (Thermogravimetry)

Precipitates are heated to a constant weight and cooled before being weighed. The heat dries the precipitate by removing water and other volatile co-precipitates or sometimes decomposes the precipitate to give a compound of known composition. There are four types of water: (i) adsorbed water (present on all solid phases due to humidity), (ii) occluded water (present in solid solution or cavities of crystals), (iii) sorbed water (present in compounds with large internal

surfaces, hydrous oxides), (iv) essential water (water of crystallization, $CaCl_2.2H_2O$). Different substances have different ignition or drying temperatures.

Precipitating Agents

Gravimetric methods have been developed for almost all inorganic cation, anions and neutral species and some organic substances (cholesterol in cereals, nicotine in pesticides etc). These agents are often non specific and selective. Inorganic precipitating agents include NH_3, H_2S, NaCl, HNO_3, $H_2C_2O_4$ etc. which often forms slightly soluble salts or oxides. There are reducing agents that convert the precipitates to the elemental forms ($H_2C_2O_4$, SO2, H_2 etc. There are two types of organic agents: those that form coordination complexes (non-ionic) and those that form ionic complexes. Examples include: 8-hydroxyquinoline, dimethylglyoxime, sodium tetraphenylboron, α-Nitrosoϐ-napthol etc.

Advantages and Disadvantages of Gravimetric Analysis

Table 6.1

Advantages	**Disadvantages**
No calibration needed (only gravimetric factor needed	Time consuming
Sensitivity and accuracy is seldom affected by type of instruments used in analysis.	May only be affected by the difficulties encountered in separation technique (coagulation, time to precipitate, solubility etc.
	Accuracy cannot be generalized because of many sources of errors which may vary from one analysis to the other
Gravimetric agents are often selective	Gravimetric agents are rarely specific

Volatilization Method

This method is commonly used for water and carbon dioxide analysis. There are two methods for water analysis: (i) Direct method: involves igniting the sample and collecting the water on solid desiccants. The change in mass of the desiccant is measured and is recorded as the weight of water (ii) indirect method: the sample is weighed and dried and allowed to cool. The difference in weight before and after drying is recorded as the weight of water assuming no other volatile substance is in the sample.

Chapter 7 Titrimetric Analysis: Acid Base Titrations

Titration of strong acid with strong base, titration of weak acid with a strong base, titration of a weak base with strong acid, titration with diprotic systems, finding the end points, Complexometric titrations (EDTA titrations)

7.1 Introduction

Acid-base titrations are routine reactions in all fields of chemistry and biochemistry. For example, the protein *Ribonuclease* has 124 amino acids (AA) which act as an enzyme that cuts molecules of ribonucleic acids (RNA) into smaller units. Near pH of 9.6, the enzyme has no net charge. 16 of the AA of Ribonuclease can be protonated and 2o can lose protons when titrated with an acid or a base respectively. A plot of pH against the volume of titrant added can be plotted to obtain a titration curve for this enzyme. Form the curve one will be able to determine the pKa for each titrable group which can help us to understand the environment around each AA's.

7.2. Titration of a Strong Acid with a Strong Base

The titration process involves adding a standardized titrant to an unstandardized analyte. Hence, a titration curve can be obtained for the titration process. Usually, the pH of the analyte changes as the titrant is added, hence, we can plot change in pH against the volume of titrant that is added

The equation that represents the titration of strong acid with strong base is shown in equation1

$$\mathbf{H^+ + OH^- \leftrightarrow H_2O} \quad \mathbf{(1)}$$

The equation can be used to calculate the composition and pH after each addition of the titrant. At the equivalent point, the equilibrium constant of this equation, $K_e = 1/K_w$ (K_w = dissociation constant of water) and one can say that the reaction has 'gone to completion'; therefore, any amount of acid or base added will consume a stoichiometric amount of base or acid respectively. It is possible to calculate the amount or acid or base needed to reach the equivalence point (V_e). For example, if 20.00 mL of 0.001000M NaOH is titrated with 0.002M HCl, the volume of HCl needed to reach the equivalence point, $(V_e)(0.01000M) = (20.00\ mL)(0.001000M) = 10.00\ mL$

mmol of acid at equivalence point mmol of base at equivalence point

In the titration of any strong base or acid, there are three regions of the titration curve which represent three different types of calculations:

(i) the region before the equivalence point (pH is determined by excess base, $[OH^-]$, in the solution. For example, if 2 mL of 0.002M HCl has been added to 20 mL of 0.001000 M NaOH, then, concentration of $[OH^-]$ remaining can be calculated thus,

$[OH^-] = (10.00- 2.00)/10.00)(0.001000)(20.00/20.00 + 2.00) = 0.0073$ M

(10.00- 2.00)/10.00)= fraction of NaOH remaining

(0.001000) = initial concentration of NaOH

(20.00/20.00 + 2.00) = dilution factor = initial volume of NaOH/total volume of solution

(ii) The region at the equivalence point where the amount of acid (H^+) is just sufficient to react with all the bases in the solution to make water. Some of the water will redisslves to give equal concentrations of H^+ and OH^- (x moles each as shown in equation 2). The pH is determine by the dissociation of water, K_w

$$\mathbf{H_2O \leftrightarrow H^+ + OH^-} \qquad \mathbf{(2)}$$

x x

$K_w = [H^+][OH^-] = 1.0\ x^2\ 10^{-14}$ M and

$[H^+] = K_w/[OH^-]\ x = 10^{-7}$ M. Therefore, pH = 7.00

(iii) The region after the equivalence point where excess acid is been added. The pH is determined by the excess acid in the solution. The concentration of the excess acid, H^+ can be calculated. For example is 10.2 mL of acid has been added, the concentration of the acid $[H^+]$ can be calculated thus;

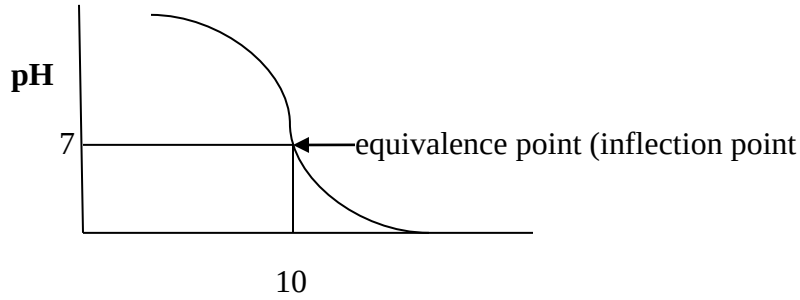
$[H^+] = (0.00200)(0.2000/20.00 +10.2) = 0.000013$ M $= 1.3 \times 10^{-5}$ M

pH = -log$[H^+]$ = 4.89

(0.00200) = initial concentration of the acid, $[H^+]$

(0.2000/20.00 +10.2) dilution factor = volume of excess H^+/total volume of solution

A plot of the three regions against the volume of acid added is shown below



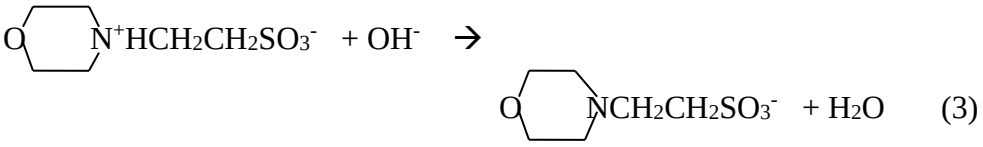
Volume of acid added (mL)

There is a sudden change in pH near the equivalence point and it is where the slope is the steepest (maximum slope, $\delta pH/\delta V_a$ or $\delta y/\delta x$). Therefore, the equivalence point is a point of inflection ($\delta^2 y/\delta x^2 = 0$). The equivalence point has a pH = 7.00 which is only true for strong acid-strong base titrations. This is not true for weak acid-weak base titrations.

7.3 Titration of a Weak acid with a Strong base

The titration of 50.0 mL of 0.020 M MES (2-(N-morphorlino) ethanesulfonic acid) with 0.100 M NaOH will be used to explain what happens when a weak acid reacts with a strong base

The titration reaction is shown below



$$O(C_4H_8)N^+HCH_2CH_2SO_3^- + OH^- \rightarrow O(C_4H_8)NCH_2CH_2SO_3^- + H_2O \quad (3)$$

Reaction 3 is the reverse of the K_b reaction for a base A^-, hence, the equilibrium constant for this reaction $K = 1/K_b = 1/(K_w/K_a) = 7.1 \times 10^7$. The value of K is very large and therefore, we can say that the reaction will go to completion after each addition of the base (OH^-)

From the onset, we can calculate the volume of the base (V_b) that will be needed to reach the equivalence point:

$(V_b(mL))(0.10\ M) = (50.0\ mL)(0.020\ M)$ and (4)

$V_b = 10.0$ mL

There four regions of the titration curve (pH vs Volume of titrant) for a weak acid-strong base titration, viz;

(1) ***Before any base is added:*** The solution is completely and acid (HA) in water. The acid is weak and is partially dissociated. The pH is determined by the equation:

$HA \leftrightarrow H^+ + A^-$ (5) the equilibrium constant is K_a

F-x x x (F= 0.020 M)

Before adding any base, we have a solution of 0.0200 M HA with $K_a = 10^{-6.15}$, therefore,

$x^2/0.020 - x = K_a$ and $x = 1.19 \times 10^{-4}$

(2)***From the first addition of the base until immediately before the equivalence point:*** there are unreacted acid (HA) and A^- (A^- is produced by reaction 3) in solution. This situation (HA and A^- coexisting in the same solution is called a buffer – a weak acid and its conjugate base). We can

use the Henderson- Hasselbalch equation to obtain the pH of this solution:
$pH = pK_a + \log[A^-]/[HA]$

For example, when 3.0 mL of OH^- is added to the weak acid solution

$$HA + OH^- \leftrightarrow A^- + H_2O \quad (6)$$

Titration reaction	HA	+ OH^- ↔	A^- + H_2O
Relative initial quantities (HA ~ 1):	1	3/10	-
Relative final quantities:	7/10	-	3/10

(Remember that volume of base at equivalence point is 10.0 mL)

Therefore, the pH of the solution after the addition of 3.0 mL of the base is:

$pH = pK_a + [A^-]/[HA] = 6.15 + \log[3/10]/[7/10] = 5.78$

When the volume of the titrant added is ½ V_b, then,

$pH = pK_a + \log [1/2]/[1/2] = pK_a + \log 1 = pK_a$. One can then say that by looking at a titration curve, one can determine an approximate value of the pK_a of that acid by finding the pH at ½V_b

(3) ***At the Equivalence Point:*** All of HA has been converted to A^-. The situation is similar to dissolving A^- in water right from the beginning. However, the situation is a weak-base situation described by equation 7

$$A^- + H_2O \leftrightarrow HA + OH^- \quad (7) \text{ equilibrium constant is } K_b$$

Here, the exact amount of OH^- needed to consume all the acid has been added

Titration reaction	HA	+ OH^- ↔	A^- + H_2O
Relative initial quantities (HA ~ 1):	1	1	-
Relative final quantities:		-	1

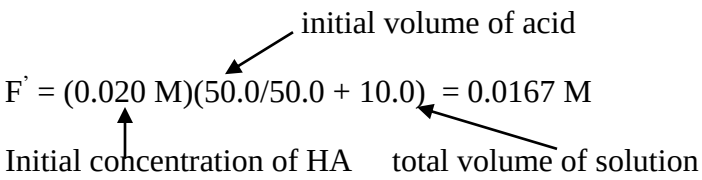
(Remember that volume of base at equivalence point is 10.0 mL)

The resulting solution only contains A^-. the pH of a weak base can be estimated by writing the equation of a weak base with water (7):

$$A^- + H_2O \leftrightarrow HA + OH^- \quad (7)$$

F-x x x and $K_b = K_w/Ka$

Here the formal concentration of the base (A^-), F, is no more 0.020 M. It has been diluted by the volume of the acid (50.0 mL), therefore,



Therefore, $x^2/(F'-x) = K_b = K_w/Ka = 10^{-14}/10^{-6.15} \sim 1.43 \times 10^{-8}$ and $x = 1.54 \times 10^{-5}$ M

Remember that $K_w = [H^+][OH^-]$ and $[H^+] = K_w/[OH^-]$, therefore,

$pH = -\log K_w/x = 9.18$

(4) ***Beyond the equivalence Point:*** excess OH^- (NaOH) is added to a solution containing A^-. Here, the pH is determined by OH^-. The pH is calculated neglecting the contribution of A^-.

Let us say 0.10 ml of the base is added after the equivalent point, a total of 10.10 ml would have been added so far; the new concentration of $[OH^-]$ will be:

$$[OH^-] = (0.10 \text{ M})(0.10/50.0 + 10.1) = 1.55 \times 10^{-4} \text{ M}$$

$pH = -\log K_w/[OH^-] = 10.22$

7.4 Complexation Reactions – EDTA Metal Complexation

Metal ions acts as *Lewis* acids (electron acceptor) and can bind with *ligands* (*Lewis bases; electron donors*) to form metal complexes called *chelates.* The metal ions are usually (i) p- block metal ions e.g. Mg or (ii) d-block species e.g. Co, Fe and the ligands are usually p-block species such as $[BrF_4]^-$. The ligands are either neutrally charged or anionic species are can bind metals through one atom (monodentate, e.g. CN^-) or multiple atoms (multidentate, adenosine triphosphate (ATP))

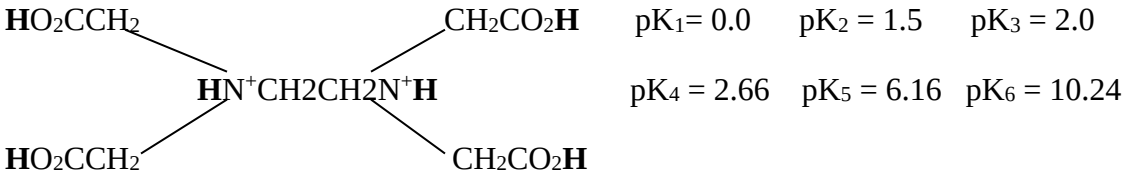
A good example of a multidentate chelating compound is ethylenediamine tetraacetate (EDTA, $((COOH)_2)H_2NCH_2CH_2NH_2(COO^-)_2$) which binds metal ions through two ligand atoms (bidentate) and ATP which is a physiological tetradentate compound that binds with Mg^{2+} ion.

Some metal complexes are not analytically useful because they are unstable and expensive e.g. ATP, while others such as Nitrilotriacetic acid (NTA), trans-1,2 Diaminocyclohexanetetracetic acid (DCTA) are very useful in analytical titrations are often form strong 1:1 complexes with metals. Titration based on metal-complex formation is called *complexometric titrations* and the equilibrium constant for such a reaction is called *formation or stability constant (*K_f).

EDTA Complexes

EDTA is the most commonly used chelator is complexometric titrations. It can be used to analyze almost all elements in the periodic table either by direct titration or by indirect series of reactions. It has six replaceable protons (hexaprotic, $H_6Y_2^+$) which give six different pK_a values.

pK_{1-4} = carboxylic protons and pK_{5-6} = ammonium protons



The neutral EDTA is tetraprotic and can be represented as H_4Y. The formation constant K_f can be represented by the following equilibrium equation

$$M^{n+} + Y^{4-} \leftrightarrow MY^{n-4} \quad \text{and } K_f = [MY^{n-4}]/[M^{n+}][Y^{4-}] \quad (1)$$

There are seven different forms of neutral EDTA forms usually present in solution. K_f is defined for the Y^{4-} specie in equation 1. The K_f for each of the seven forms are very large and often larger for more positively charged metal ions. Metal-EDTA complexes at pH < 10.24 are not stable. Most of the EDTA at this pH's is not the neutral Y^{4-} form but exist as HY^{3-}, H_2Y^{2-} etc. The fraction of each form can be calculated: $[Y^{4-}] = \alpha_{Y4-}[EDTA]$ (2)

(α_{Y4-} is constant and [EDTA] = total concentration of all forms of EDTA);

and the formation constant of each form (*conditional formation constant or effective formation constant*) can also be estimated.

$$K_f = [MY^{n-4}]/[M^{n+}][Y^{n-4}] = [MY^{n-4}]/[M^{n+}]\,\alpha_{Y4-}[EDTA] \quad (3)$$

If a buffer is used to make pH constant, then α_{Y4-} (Appendix A, Table 1) will also be a constant and therefore,

$$K'_f = \alpha_{Y4-}K_f = [MY^{n-4}]/[M^{n+}][EDTA] \quad (4)$$

where K'_f is the conditional formation constant

For a titration reaction to be effective it must go to completion and its stability constant must be large. Each metal-EDTA complexes has a specific pH (fixed by a buffer) at which it can form a stable complex with large stability constant useful for complexometric titration. Therefore, selective titration of metal-EDTA can be made and used to estimate the concentration of metals in a mixture. For example, a solution containing Fe^{3+} and Ca^{2+} could be selectively titrated at pH = 4. Fe^{3+} forms a complex with EDTA at this pH while Ca^{2+} does not.

EDTA Titration Curves: EDTA titration curve is similar to the titration curve of a strong acid-weak base titration curve. The acid is replaced by the metal and EDTA is the weak base. The titration curve has three regions and can be represented by the equation:

$M^{n+} + EDTA \leftrightarrow MY^{n-4}$ (6) where $K'_f = \alpha_{Y4}\text{-}K_f$

If $K'_{f\,is}$ large, the reaction is considered to have gone to completion at each point of titration.

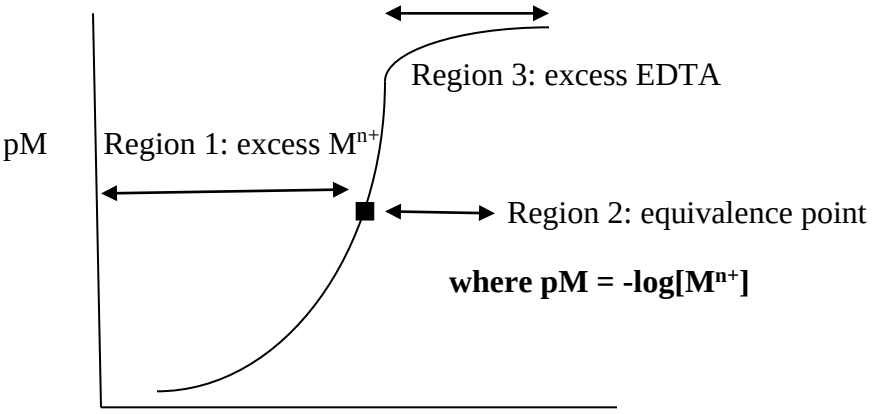
The titration curve natural regions are as follow:

Region 1: occurs before the equivalence point: Here, there is excess metal ion (M^{n+}) in solution after the addition of EDTA. The dissociation of the metal complex, MY^{n-4} is negligible hence; the concentration of free metal ion is equal to the concentration of the excess, unreacted M^{n+}

Region 2: this is the equivalent point: here, there is exactly the same amount of the metal ions and EDTA in solution ($[M^{n+}] = [EDTA]$). There are small amount of M^{n+} ions in solution due to slight dissociation of the MY^{n-4} ion.

$MY^{n-4} \leftrightarrow M^{n+} + EDTA$ (7)

Region 3: occurs after the equivalence point: here, there are excess EDTA in solution and all the metal ion have formed the complex MY^{n-4}. The concentration of free EDTA is equal to the concentration of excess EDTA added after the equivalence point.



7.5 Titration Calculation: Calculating the Titration Curve

The titration reaction of 20.0 mL of 0.0200M Fe^{2+} is with 0.0200M EDTA (buffered at pH = 10), can be written as:

$Fe^{2+} + EDTA \rightarrow MgY^{2-}$ (8)

The $K'_f = \alpha_{Y4}\text{-}K_f$ for the reaction = (0.36)(2.09 x 10^{14}) = 7.5 x 10^{13} (values of α_{Y4}- and K_f are from Apendix A)

The value of K'_f is large; hence it is safe to assume that the reaction goes to completion with the addition of titrant. The equivalence point will be 20.0 mL of EDTA. We can plot a graph of pM vs. mL of EDTA

Region 1 of the titration curve: Metal ion is in excess

If we start by adding 5.00 mL of EDTA to the Fe^{2+}, the equivalence point will be 20.0 mL of EDTA and the excess [Fe^{2+}] that will remain will be:

$[Fe^{2+}] = (20.0 - 5.0/20.0)(0.0200)(20/20.0+5.0) = 0.012$ M and pM = 1.03

Fraction Remaining,(¾) *original concentration of Fe^{2+}* *Dilution factor*

pM for other volumes below 20.0 mL can be calculated in a similar way

Region 2: Equivalence Point

At the equivalence point, 20.0 mL EDTA has been added and all the metal complexes are in the form of FeY^{2-} with very little dissociation into equal amount of Fe^{2+} and EDTA:

$FeY^{2-} \leftrightarrow Fe^{2+} + EDTA$ (9) Initial volume of Fe^{2+}

$[FeY^{2-}] = (0.0200)(20/(20.0+20)) = 0.01$ M and

Original concentration of Fe^{2+} *Dilution factor* *total volume of solution*

Concentration of Fe^{2+} at equivalence point is small and unknown

From equation 9, at equivalence point

	Fe^{2+}	EDTA	$[FeY^{2-}]$
Initial concentration of Fe^{2+}	0	0	0.01
Final concentration of Fe^{2+}	X	x	0.01-x

$K'_f = [FeY^{2-}]/[Fe^{2+}][EDTA] = 0.01\text{-}x/x^2 = 2.08 \times 10^{14}$ (K'_f from Table 2 in Appendix A)

$x = 1.4 \times 10^{-8}$ M

$pFe^{2+} = -\log [1.4 \times 10^{-8}] = 7.85$

Region 3: After the equivalence point

All the Fe^{2+} is binded and exists as FeY^{2-} and there are excess EDTA in this region. The concentration of the excess EDTA and FeY^{2-} can be calculated as follows: at volume 21.0 ml of EDTA, there is an excess of 1.o mL of EDTA

Original concentration of EDTA dilution factor

$[EDTA] = (0.020)(1.0/(20.0+21.0) = 4.9 \times 10^{-4}$M

Volume of excess EDTA total volume of solution

Original concentration of Fe^{2+} dilution factor

$[FeY^{2-}] = (0.020)(20.0/20.0+21.0) = 9.8 \times 10^{-3}$M

Original volume of Fe^{2+} total volume of solution

At equivalence and past equivalence point, little amount of FeY^{2-} will dissociate into equal amount of Fe^{2+} and EDTA:

$FeY^{2-} \leftrightarrow Fe^{2+} + EDTA$

Therefore,

$K'_f = [FeY^{2-}]/[Fe^{2+}][EDTA] = 2.08 \times 10^{14}$

$= [9.8 \times 10^{-3}]/ [Fe^{2+}][4.9 \times 10^{-4}] = 2.08 \times 10^{14}$

$[Fe^{2+}] = 9.8 \times 10^{-3}]/ [2.08 \times 10^{14}][4.9 \times 10^{-4}] = 9.62 \times 10^{-14}$

For a solution containing 2 or more metals, it is possible to use complexometric titration with EDTA to determine their concentrations in the mixture since each metal will have different conditional formation constant, $K'_f = \alpha_{Y4}\text{-}K_f$ which is pH dependent. α_{Y4}- decreases as pH decreases but and its value determines whether a titration is possible. However, at high pH value (high α_{Y4}-), the end point is very sharp but one must be careful not to make the pH to high which will inadvertently precipitate the metal as an hydroxide.