UNIVERSITY OF AGRICULTURE, ABEOKUTA

DEPARTMENT OF ENVIRONMENTAL MANAGEMENT & TOXICOLOGY

EMT 202 - METHODS IN ENVIRONMENTAL ANALYSIS 1

Lecturers: Professor O. Bamgbose, Dr. (Mrs.) Olayinka & Dr. O.S. Olatunji

Synopsis:

Review of fundamental concepts:- What is Environmental Analysis. Importance of Environmental Analysis, Classification of .Units of Concentration. Preparation of Standard Solutions. Statistical Treatment of Analytical Data: Accuracy, Precision, Errors, Mean, Standard Deviation. Reliability of an average value (t-test), F-test, Rejection of outliers (Q-test and 4Q-test). Analysis of Vatriance (ANOVA) Sampling, Techniques, Graph plotting (Centroid method/Least square). Evolution, Loss on Ignition, Gas Absorption, Thermogravimetry, Electrogravimetry, Precipitation from Solution (Conditions for Analytical Precipitation, Digestion, Filtration, Handling of Precipitates, Co-precipitation), Calculations. Acid Base Titrimetry, Primary Standards, Indicators, Titration Curves, Application, Fundamental Principle of Calculation in titrimetry, Non Aqueous Titration: Definition of (Arrhenius, Bronsted lowry, lewis. General Solvent), Standards. Precipitations. Titrimetry: Titration curves, indicators in precipitation titration (Mohrs, Volhard) EDTA, Masking and Demasking, Complexometrix Indicators, Titration methods with EDTA, Titrimetry. Concept of oxidation & Reduction, Oxidation States, Balancing of Redox. Reactions. Standard electrode potentials. Relationship between Concentration and Potential End Point Detection (Self Specific And True Oxidation. Red Indicators Application Draft Practical manual is ready for your perusal and corrections/additional input

LECTURE CONTENT:

1. REVIEW OF FUNDAMENTAL CONCEPTS

What is Analytical Chemistry
Importance of Analytical Chemistry
Classification of Analytical chemistry
Units of Concentration in Analytical Chemistry
Preparation of standard solution

WHAT ANALYTICAL CHEMIST DO/IMPORTANCE OF

Analytical Chemistry deals with the qualitative and quantitative characterization of matter. Analytical Chemists in reality actually check the chemical composition of products. All industrial products are made up of various chemical bits and manufacturers must not only be able to perform the appropriate chemical reactions to convert the starting materials into the desired product but must also ensure that the product has the appropriate chemical composition, therefore the work of the analytical chemist is to devise ways of measuring the relative amounts of the various chemical species that go to make up the particular material and also to be able to identify such chemicals. The job of analytical chemist in an industry can then be categorized as follows

(a) sampling and testing raw materials
(b) testing intermediates
(c) monitoring product quality and
(d) monitoring effluent quality.

Apart from the role of the analytical chemist in the manufacturing and processing industries, there are many other aspects of our complex life-style in which analytical chemists are involved.

2. HELPING TO SAVE LIVES

Laboratories of nearly all hospitals have analytical personnel called clinical chemists involved in the analysis of samples of patients blood, urine, etc for a variety of components to help doctors with their diagnoses. The progress of a patient with a particular disease may be followed by monitoring the concentrations of certain key components of the blood or urine.

3. HELPING TO PROTECT THE CONSUMER THE ENVIRONMENT

It is the job of the public analyst to check the quality of some of the materials that we use in our everyday lives i.e. to see that these products conform to the appropriate legal requirement. This involve analysis of food, drink, medicine, pesticide and also provide service to customs and exercise by examining beer, wines, spirits, oils, petrol, tobacco products and a variety of contrabands, including drugs.

-This is the type of job of the NSO and $FEPA_1$ – and more recently NAFDAC consider the production of water

4. HELPING THE FARMER

Analytical chemists play a role in monitoring the levels of nutrients in soils, giving the farmer information as to how much and of which fertilizer to use/apply. Levels of potentially harmful materials are monitored not only in the soil but also in crops and animals. It is also important to monitor levels of pesticides, weed killers etc applied to crops and soils that could pass along the food chains to human. e.g. as in pesticide residue analysis.

5. **HELPING TO CATCH CRIMINALS**

The work of the police in solving crimes and bringing the culprits to justice is considerably helped by analytical chemists – forensic chemist. Work is based on establishing contact i.e. was – such and-such a person at such – and-such a place dependent on the maxim that every contact leaves its traces e.g. firing of handgun – Sb and Ba high conc on hand. Victims of hit and run,fragments of paints/glass-trace element determination.

Finger prints – no two people have the same finger prints. Analysis of skin, DNA (refer to Clinton and Monica Lewinsky).

6. **HELPING TO ENSURE FAIR PLAY**

The abuse of drugs in connection with sporting events is sufficiently widespread for a number of Laboratories to be involved in checking blood and urine samples for drugs of this type or their metabolites.

- Some competitors resort to artificial means to increase their performance
- Anaebolic steroids – in some cases the competitor may not have a say in the matter, race horse or grey bound. Give examples

There are other areas where analytical chemist are involved e.g. geological surveys, prospecting, coal and gas supply, electricity generation and in fact there are a few of them involved in the teaching and training of analytical chemists of **WHICH I AM ONE.**

CLASSIFICATION OF ANALYTICAL CHEMISTRY

1. Classical Analytical Chemistry (Gravimeric or Tirimetric)

2. Instrumental Analytical Chemistry (IR, UV, NMR AAS, MS, X-ray)

- Gravimetry : is a technique in which analytical results is obtained by weighing.

- Tirimetry: Analytical results is obtained by measurement of volumes of solutions

The use of classical techniques is determined by the level of the analyte in the sample being analysed.

If analyte > 10% major component
0.1-10% Minor Component
0.0001% - 0.1% Trace component
<0.0001% Ultra trace.

If the amount of analyte is present at either the major or minor component level of the sample then classical technique is applicable while for analytes at the trace and ultra trace component level, instrumental technique is used.

UNITS OF CONCENTRATION IN ANALYTICAL CHEMISTRY

At minor and major analyte level the unit of Conc is % and Molarity. % can be mass/mass or mass/volume

Trace and Ultra-trace level units are in ppb and ppm. (parts per million)

ppm can also be / wt or wt /volume\For wt per wt, ppm means 1 part in 10^6 parts

1ppm = 1g analyte per 10^6g sample

=1mg analyte per 10^3g sample.

Or 1mg/kg samplr

1 ppm can also be expressed as Ug/g. (ng/mg,pg/g)

mg = 10^{-3}g, micro = 10^{-6}gm nano = 10^{-9}_{g}, pico = 10^{-12}_{g} femto = 10^{-15}g

IN WEIGHT/VOLUME

1ppm = mg/L ($mg1^{-1}$ **)**
or ng/ul

U=10^{-6}

= 10^{-6} x 10^3ml = 10^{-3}ml = 0.001ml

1ppm = 10^{-4} of a % = 0.0001%

or 10^4ppm = 1%

ppb = 10^{-3}ppm, ppt = 10^{-3}ppb or 10^{-6}ppm.

PREPARATION OF PPM SOLUTION

How do you prepare 100ppm Na solution from NaCl salt.

-What does 100ppm mean

100ppm Na=100mg Na per 1 litre of solution or 100g Na/ml of solution

Formula weight of NaCl = 23 + 355 = 58.5

Na ⟶ NaCl

23g ⟶ 58.5g

1g ⟶ 58.5/23

:.1000mg ⟶ 2.54g

100mg ⟶ 0.254g of Nacl

i.e weighing 0.254g of Nacl and dissolving in 1 litre of water gives 1000ppm Na

Assignment

1. How would you prepare 250ppm Na solution from sodium sulphate solution?
2. 250ppm Ca Soln from calcium carbonate in a 250ml flask

DILUSIONS OF SOLUTIONS

How would you prepare 10ppm Na salt in a 50ml flask from 1000ppm Na

$C_1V_1 = C_2V_2$

1000ppm x Vml = 10ppm x 50ml

Vml = 10 x 50/1000=0.5ml

:. 0.5ml of 1000ppm Na solution diluted to 50ml (made up to mark in a 50ml std flask) gives 10 ppm Na solution

PREPARATION OF STANDARD SOLUTION FOR TITRIMETRY

How would you prepare standard acid solution from concentrated acid.
e.g. How would you prepare 2MH_2SO_4 from H_2SO_4 or 0.2M HCl from Conc HC.

Specify gravity % purity Acid

1.18g/cm^3 36% HCl

1.84g/cm^3 98% H_2SO_4

THERE ARE TWO METHODS

1. Molar mass of H_2SO_4 = 98 S. G = 1.845/cm3

1 molar solution contains the formular weight in solution

:. 1 cm^3 of H_2SO_4 contains 1.84g H_2SO_4

1 litrewill contain 1.84 x 1000 = 1840g

by definition

98g of H_2SO4 in 1 litre solution = 1 molar (1M)

:. 1840g = 1840/98 = 18.76M

assuming 100% purity

but acid is 98% pure

:. Molarity = 18.76 x 98/100 = 18.39M.

$M_1V_1 = M_2V_2$

18.39 x V_1 = 2 x 1

V_1 = 2x 1000/18.39 = 108.75ml

i.e take 108.75ml of conc H_2SO_4 and dilute to 1 litre with distilled water to prepare 2M H_2SO_4

1cm^3 of H_2SO_4 = 1/1.84 = 0.54347826cm^3

:. 98g = 53.26 x 100/98 = 54.34cm^3

but 53.36cm^3 is equivalent to 98% pure acid, for 100% purity then 98 = 53.26 x 100/98 = 54.34cm^3

:. 54.34x2 = 108.69cm^3 made up to 1 litre with distilled water = 2M

Molarity = % purity x S.G x 1000/100 xMM

Molarity = MM

Molarity = 10 x S.G x % P/MM

Supposaing we are using a 250ml standard flask = 108.69/4 in 250ml std flask

ASSIGNMENT

1. Using the 2 methods show how you would prepare 0.2M HCl from Conc HCl S.G = 1.18gl/cm % purity = 36%

2. A student requires 150ml of 3M $HC10_4$ solution, each for the digestion of three meat samples. The student measured 163ml of the conc acid and made it to mark in a ½ litre std flask. Can this preparation be assumed correct?

3. In a laboratory practical class for two hundred pre-degree students involving the titration of 0.312M NH_4OH with 0.078M H_2SO4. Calculate (i) the total volunes of Conc NH_3 and Conc H_2SO_4 that must be dissolved in what volume of water so that each student has $100cm^3$ of NH_4OH and $200cm^3$ of H_2SO_4

STATISTICAL TREATMENT OF ANALYTICAL DATA

INTRODUCTION

Every physical measurement is subject to degree of uncertainty and the determination of this uncertainty is difficult to ascertain. Errors that can be attributed to definite causes are defined as determinate errors or systematic errors. In principle these errors can be eliminated by improved procedures or corrected for if they are reproducible. Indeterminate errors. Are errors that cannot be positively identified and do not have a definite measurable value. They fluctuate in a random manner. Such group of unsuspected and non-reproducible errors which remains beyond control include temperature, fluctuation, electronic noise, mechanical vibration, spillage, reading errors, contamination, variation in sample composition.

Errors generally come from three sources:

1. **Personal**: May be due to ignorance, carelessness or physical limitations for example being colour blind i.e not knowing colour changes. Improper use of technique in transferring samples, personal bias or prejudice i.e lack of objectivity e.g. estimating reading so as to get good precision.

2.Instrumental: This is as a result of the instrument i.e temp fluctuation, electronic noise etc or for example the measuring apparatus not giving the volume specified on them i.e when used at temps different from which they were graduated.

3.Method error: this is most difficult type of error to detect. It can be due to incomplete or slowness of reaction. It may also be due to non-specificity of reagent or little understanding of the chemical procedure e.g. washing of precipitate with too little water causing high weight of the precipitate and washing with too much water causing some of the precipitate to dissolve.

WAYS OF EXPRESSING ERRORS

Absolute error is the difference between a given measurement and the true values (Measured value- True value = Absolute error

Relative Error – is the relationship between absolute error and the true value

x-μ=A E or /E?

R E = x-μ/u

Precision – is a measure of indeterminate error, for example if during a calibration of a 10ml pipette, the following values were obtained. 9.99,9.70,10.32,9.98,10.25 giving an average of X = 9.98 [Poor precision good accuracy because the random error is in a fairly wide range].

It is also possible to have high precision but poor accuracy e.g. 10.55, 10.54, 10.53, 10.52, 10.59, 10.51 X=10.54

METHODS OF EXPRESSING PRECISION

The precision of the method in given by the standard deviation

$\sigma = \frac{\Sigma(x-x)^2}{N}$ where N>50

σ^2 = variance and is used to describe the population distribution.

In general, the frequency distribution is based on a relatively small sample of a much larger population because in real life, we do not deal with the entire population rather an estimate of the population such that instead of standard deviation we use S = standard error.

Where $S = \Sigma(x-x)^2 /n-1$

n = no of measurement in the same experiment

x = value of individual measurement

x = mean of the measurement

Though the parameters were calculated from the sample distribution and the parameters required are in fact those of population distribution, the sample parameters are therefore estimate of the population parameters.

$S = \frac{\Sigma(x-x)^2}{n-1}$ is used when n>10

For values of n<10, the following can be used for estimating the precision

1. Range: poorest estimate of standard deviation and is the difference between the largest and the smallest value (xn-xi)
2. Average deviation ϑ Σlx –xl/n
   It over estimates the standard error
3. Constant factor Dean and Dixon reported a means of finding standard errors for values of n<10 such that S =KnR where Kn is the factor, n is the no of measurement and R = Range

n	Kn	n	Kn
2	0.89	7	0.37
3	0.89	8	0.35
4	0.49	9	0.34

5	0.43	10	0.33
6	0.40		

Thus when the scattered result is not affected by extremes then use S=KnR instead of ϑ whereas if the results are affected by extremes then use Range.

ACCURACY

For every parameter that is being measured, there is a true value (a true value which is not known) how near or close a measurement is to the real value is the accuracy. True value in any analysis is represented byμ such that μ = Ɛx/N where Ɛx = sum of values for each component of the population.
N = total no of component is the population
Estimate of the true value can be obtained by various ways.
The use of mode, median or mean
In laboratory analysis, mean is the most commonly used. The mean is defined as the summation of measurement carried out on each component divided by total no of components.

$$x=\frac{\text{Ɛ}xi}{n}$$

Consider a set of data obtained by an analyst who is evaluating a new method for determining tetraethyl lead in gasoline. The results gPb / gallon of gasoline on the first twenty trials are given below:

4.20	4.28	4.45	4.17	4.30	A
4.22	4.24	4.14	4.23	4.38	
4.23	4.18	4.31	4.23	4.38	
4.27	4.12	4.25	4.33	4.26	

Calculate the mean, average deviation and standard error of the whole data.

Assuming only five readings were taking (A) calculate the standard error using S= KnR and

$$S=\frac{\text{Ɛ}(x-x)^2}{n-1}$$

Reliability of an average value

The t-test is being made use of and this is used in comparing two different unrelated system. To use that t-test, first you must define a confidence limit. It is used to test the quality of a result and for comparing result (two different experiments).
t-isa parameter of a sample and therefore depends on the number of measurement.

$tcf = \frac{x-\mu}{s}$ (single value)

$x-\mu$ = difference between a value and the true value as a function of estimated standard deviation. t is a function of confidence limit and the degree or freedom c=confidence limit f=degree of freedom = (d-1). Therefore for a sample population $t = \frac{x-\mu}{S}\ n$

Confidence limit $C = x \pm \frac{ts}{n}$

Example: In the determination of the concentration of an acid, the following results were obtained

0.4229	0.4323	0.4326
0.4331	0.4378	0.4327
0.4332	0.4323	0.4326

Question: What is the concentration of the acid, if the true concentration is given as $\mu = 0.4327 \pm 0.0005$. Comment on the merit of the method used in collecting the data above.

$x = \frac{x_1 = x_2 \ldots\ldots\ldots\ldots\ldots\ldots x_n}{N} = \frac{3.8895}{9} = 0.4322$

To calculate the standard error we cannot use the formula in which $n \geq 10$ instead we use S =KnR.

S= 0.34 x [0.4378- 0.4229] = 0.005266

Suppose μ is not given $\mu = x \pm ts/n$

$t = \frac{x-\mu}{S}\ n = 0.4322 - 0.4327/0.0005\ 9 = -3$

Degree of freedom = 9 – 1 = 8

Tc,f =t 95% 8 = 2.3

We then compare the t from the table with that calculated.

The method used in collecting the data is good since we have to accept the null hypothesis (Ho: there is merit in the method used in collecting the data). Because the t calculated – 3 is less than the value from table (two tail test).

Comparison of two means

In comparing two different means from an unrelated system we use a formula in which the two means to be tested are parts of.

$t = \frac{x_1 = x_2\ N_1\ N_2}{S\quad N_1 + N_2}$

Where S in this formula is pooled $S = \frac{(N_1-1)\ S_1^2 + (N_2 - 1)S_2^2}{}$

$N_1 + N_2 - 2$

However before a pooled S can be used, an F test must be performed to show that there is no significant difference between the two values of S. If on applying the F test and there is a significant difference then the value of S is calculate from

$$S = \frac{S_1^{2+} S_2^2}{n_1 \quad n_2}$$

F – test

The f-test is used to test if there is a significant difference between the precisions of two methods. f is defined in terms of the variance

$F = S_1^2 / S_2^2$ where the degree of freedom is defined as $V_1 = n_1 - 1$ and $V_2 = n_2 - 1$. If the calculated value is less than value from table it means that there is no significant difference in the precision of the two methods.

Example

1 A new colorimetric procedure for determining the glucose content of blood serum is being developed. This procedure is compared with the standard folin-Wu procedure. From the following data given below determine whether the new method compares well with the standard folin-Wu procedure at the 95% confidence level.

New method	127,	125,	122,	130,	131,	126,	128
Std method	130,	128,	131,	129,	127,	125,	126

$X_1 = 899/7 = 127$ $S = KnR = 0.37 \times (131 - 122) = 3.33$

$X_2 = 896/7 = 128$ $S = KnR = 0.37 \times (131 - 125) = 2.22$

Test of precision $F = S_1^2/S_2^2 = (3.33/2.22)^2 = 2.25$

F6, 6 = 4.28 and since 2.25 is less than 4.28 it means pooled S can be used

$$t = \frac{X_1 - X_2}{S} \qquad \frac{N_1 \quad N_2}{N_1 + N_2}$$

$$\text{Pooled } S = \frac{(N_1-1) S_1^2 + N_2-1) S_2^2}{N_1 + N_2 - 2}$$

$S = (6 \times 11.0889) + (6 \times 4.9284) / (7+7) - 2$

$S = \frac{96.1038}{12} = 2.83$

$T_{12},95\% = \frac{128 - 127}{2.83} \quad \frac{7 \times 7}{7 + 7} = 0.66$ $t_{12,95}$ from table is 2.08

Since $t_{12,95}$ calculated (0.66) is less than $t_{12,95}$ from table, it means that there is no significant difference in the two means and as such we can conclude that the new method and folin-wu procedure compares well.

2 A new method for the determination of cholesterol in serum is being developed in which the rate of depletion of oxygen is measured with an oxygen electrode upon reaction of the cholesterol with oxygen, when catalyzed by the enzyme cholesterol oxidase. The results for replicate analysis are compared with the standard Lieberman colorimetric method. From the following data, determine by the t-test if there is a statistical significance between the two methods at the 95% confidence level.

Enzymatic 101, 102, 99, 98, 103, 100, 97, 102, 98, 101, 99

Colorimetric 112, 114, 105, 107, 106, 108, 109, 110, 113, 106, 109

xc	x-x	$(x-x)^2$	xc	x-x	$(x-x)^2$
101	1	1	112	3	9
102	2	4	114	5	25
99	-1	1	105	-4	16
98	-2	4	107	-2	4
103	3	9	106	-3	9
100	0	0	108	-1	1
97	-3	9	109	0	0
102	2	4	110	1	1
98	-2	4	113	-4	16
101	1	1	106	-3	9
99	-1	1	109	0	0

Ɛx – 1100 Ɛx – 1199

X = 100 X = 109

S = 38 / 10 = 1.95 S = 90/10 = 3.0

$F = = S_1^2 / S_2^2 = 3^2 / 1.9^2 = 2.37$

F10, 10 = 2.98 which is greater than 2.37 calculated then we can use pooled S

$$\text{Pooled S} = \frac{(11-1)\ 9 + (11-1)\ 1.95^2}{11 + 11 - 2}$$

$$t = \frac{109 - 100}{2.53} \frac{11 \times 11}{11 + 11} = 8.34$$

$t_{20\ 95}$ = 2.09 which is less than calculated value of 8.34. Therefore there is a significant difference between the two methods i.e both methods are not comparable.

Test for outliers

In analytical chemistry at times values are obtained which may appear usually high or low and as such there is a temptation in discarding such figures from a personal bias. The test for outliners eliminates this bias and gives a statistical treatment for such data.

There are two of such tests.

1. Q-test for values of n<than 10
2. 4D test for values of N>10

Q-test

In dealing with less than 10 results there is often a single result, which deviates from the mean, far more than any other. If there is a known cause for the error the result should be rejected. Frequently the cause is uncertain and judgement must be made whether to include the result as valid or to reject it.

Q90	0.94	0.76	0.64	0.56	0.51	0.47	0.44	0.41
n	3	4	5	6	7	8	9	10

$$Qn = \frac{\text{Suspect value – nearest value to it}}{\text{Largest value – smallest value}}$$

$$= \frac{Xn - Xn-1}{\text{Range}}$$

For lowest result too low

Q_L = Nearest value – Lowest values = Xn+1- Xn
Range R

If the calculated Q is greater than the Q from table then the figure must be rejected.

Consider the data

0.4229 0.4323 0.4326 0.4331
0.4332 as obtained for determination of acid concentration, check for outliers.

Qn = 0.4378 – 0.4332 = 0.31
0.0149 (0.4378 – 0.4229)

Since 0.31 is less than 0.44 at Q90 when n = 9 then it means the highest figure 0.4378 is okay and should not be rejected.

For $Q_{L=}$ 0.4323 – 0.4229 = 0.63
0.0149

Since 0.63 is greater than 0.44 then we reject the figure indicating that 0,4229 is too low we then go on to test the next lowest figure.

4D Test

For sample data where N is large (N>10), a particular data can be rejected by using the 4Dtest. The average deviation and the mean are calculated without using the value being targeted for rejection. If the difference between the rejected value and the mean of the data is greater than 4 times the average deviation then the value can be rejected.

In the determination of % alcohol of a batch of beer bottles, the following results were obtained.

	4.50	4.10	3.80	3.60	4.70	4.90	5.20	4.00	5.90	(5.90)
	3.50	4.20	4.30	3.70	4.40	5.00	4.60			
/x-x/	0.2	0.2	0.5	0.7	0.4	0.6	0.9	0.3		
	0.8	0.1	0.0	0.6	0.1	0.7	0.3			

X = 4.3

Ɛx = 64.5
Ɛ lx-xl = 6.4 / 15
= 0.4266

(sV – Ɛx) < [Ɛlx –xl] (a) Should the value 5.90 be rejected

n n-1

5.9 – 4.3 4[0.4266] (b) what is the % alcohol in the batch of beer bottle
1.6 1.7064

Then the value should therefore not be rejected
(b) Mean = $\frac{X_1 + \ldots\ldots\ldots\ldots X_n}{N} = \frac{64.5 + 5.9}{16} = 4.4\%$

Linear Least Squares

It is usual to plot graphs involving analytical data in particular calibration curves. One normally assumes the best points by eye fitting (intuitively) and a straight line is drawn through these points, however there still exist some scatter

A better graph that will take cognizance of all the points can be drawn using the least square method e.g $y = mx + c$

Where m is slope and x and y are variables and c is the intercept on the y-axis. It has been shown that the best straight line through a series of experimental points is that line for which the sum of squares of deviations of the points from the line is minimum (method of least squares).

The final useful equation is given as

$$m = \frac{\Sigma x_1 y_1 - (\Sigma x_1 \Sigma y_1)/n}{\Sigma x_1^2 - (\Sigma x_1)^2/n}$$

Example

Riboflavin (vitB) is determined in a cereal sample by measuring its florescence intensity in 5% acetic acid solution. A calibration curve was prepared by measuring the fluorescence intensities of a series of std of increasing concentration. From the data collected, use the method of least squares to obtain the best straight line for the calibration curve and hence determine the concentration of riboflavin in the sample solution with a fluorescence intensity of 15.4

x0	2	4	7	9	using the least square method.
y0	20	45	70	85	Determine the straight line equation

the best fits the set of data below.

Riboflavin µg/ml x1	Fluorescence intensity arbitrary units (y_1)	x_1^2	x_1y_1
0.00	0.0	0.00	0.00
0.100	5.8	0.01	0.58

0.200	12.2	0.04	2.44
0.400	22.3	0.16	8.92
0.800	43.3	0.640	34.64

Σx_1 1.500 $\Sigma y_1 = 83.6$ $\Sigma x_1^2 = 0.850$ $\Sigma x_1 y_1 = 46.58$

$(\Sigma x_1)^2 = 2.250$

$x = \frac{\Sigma x_1}{n} = 0.300$ $y = \frac{\Sigma y_1}{n} = 16.72$

$m = \frac{46.58 - (1.50 \times 83.6) / 5}{0.850 - 2.250 / 5} = 53.75$

$C = y - mx$

$C = 16.72 - (53.75 \times 0.30) = 0.60$

Straight line equation

$= y = 53.75x + 0.60$

Sample concentration is given by $15.4 = 53.8x + 0.6x = 0.275$ glml

To draw an actual plot, take two arbitrary values of x sufficiently far apart, calculate the corresponding value of y and join the two points.

Reference Text

Fundamentals of analytical chemistry - Skoog & West

Statistical methods in Agriculture and Experimental Biology - R.Mead, R.N. Curnow & A.M. Hasted

Statistical for Analytical Chemistry - J.C. Miller & J.N. Miller

Biostatistical Analysis - Jerold H. Zar

GRAVIMETRY

Gravimetry is a technique for the determination of the conc of an analyte in a sample obtained by weighing. Conventionally, gravimetry involves precipitation of analyte from solution by the addition of a ligand or precipitant. The precipitante is then filtered, washed, dried and weighed. From the weight of the ppt, conc of the analyte in the sample can then be estimated.

Types of Gravimetry

(1) EVOLUTION METHOD

(a) Moisture content determination (b) Loss on ignition (det. of CO_2

(a) Moisture Content Determination

It is at times necessary in carrying out analysis to require the dry weight of the sample and such to determine the mixture content of the sample. The principle involves drying a known amount of a sample at 105^{o}C to constant weight. The procedure for moisture content determination is as follows:

Step i: Take a clean and dry container and dry at 105^{o} for 4 hours
Step ii Cool in a desiccators to room temp.
Step iii Weigh the container
Step iv Return the container back to the oven and dry again at 1050C for 30mins.
Step v Cool the container in a desiccators to room temp
Step vi: Weigh the container W_1 (Weight of container)
Repeat step iv, v and vi until the difference between successive weights is not more than 5%
Step vii Weigh the container and small amount of sample (1-5g) W_2
Step viii Dry the container and the sample at 150^{o}C for 8hrs.
Step ix Repeat steps iv, v, vi until constant weight is obtained = W_3.(wt of container + Dried sample)

Weight of sample = $W_2 - W_1$
Weight of moisture = W_2-W_3
%Moisture = W_2-W_3/W_2-W_1x100
This method can be applied to moisture determination of detergents, food, plants, salts,
Industrial materials and geological samples.

Take for example, a farmer needs for cultivation of cocoa pods a fertilizer containing at least 15% moisture contents. From the data given below 3 fertilizes available in the Lagos market advise the farmer on which fertilizer is best for his purpose.

Brand of	Weight of dried porcelain boat.	Wt of boat + fertilizer Wt of boat +Fertilizer Before oven treatment	
	fertilizer after		8hrs
	in the oven		
Pfizer XII	43.5178	46.5700	48.1579
Onne K2	44.3246	47.0760	46.9219
CPL GG3	47.1931	49.7300	49.2989

(b) Loss on Ignition

Consider the standard decomposition of the limestone in a furnace at 600 – 800^{o}C

C_aCO_3 --------- CO_2 + CaO. The ignition method is a measure of the amount of CO_2 lost. The procedure is as follows: In ignition experiment, a platinum crucible is preferably used to porcelain crucible (since platinum can withstand higher temp.). The steps are similar to that of moisture content determination.

Wt of crucible = W_1

Wt of crucible + Limestone = W_2

Wt of Limestone = $W_2 – W_1$

Wt of CO_2 loss = $W_2 – W_3$

% CO_2 loss = W_2-W_3 x 100/1

W_2-W_1

$CaCO_2$ = 40 + 12 + 12 + 48 = 100

CO_2 = 12 + 32 = 44

44g of CO_2 = 100g $CaCO_3$

44g of CO_2 = 100g $CaCO_3$

1g of CO_2 = 100/44 = 2.27g

G. F x % CO_2

From the percentage loss (CO) it is possible to calculate the equipment amount of calcium carbonate equal to CO_2 as shown above.

Take for example a sample of marble which gave on ignition 13% of CO_2. what could be the corresponding weight of marble from which the CO_2 was lost.

2. **Gas Absorption Method**

The absorption method is used for the determination of carbon and hydrogen in organic compounds, The organic sample is combusted in a tube in an atmosphere of oxygen, such that carbon is converted to CO and hydrogen is converted to H_2O. These oxidation products are absorbed in weighed U-tubes containing $MgCIO_4$ (Magnesium chlorate) and slaked lime respectively. The gain in weight of the tubes give the amount of H_2O and CO_2 and hence the percentage of hydrogen and carbon indirectly.

The calculation

The formula weight of H_2O = 18g
18g of H_2O = 2g of H
:. 1g of H_2O = 2/18 = 0.111g
%H = 2/18 x Wt of water / x 100 Wt of sample

Similarly

% Wt H_2O = 18g
44g of CO_2 = 12g of C
:. 1g of CO = 12/44
:. % of C = 12/44 x Wt of CO_2x100
Wt of sample

E.g 0.0475g of an organic compound on combustion gave 0.14513g of CO_2 and 0.01726g of H_2O. Given that the molecular mass of this compound is 72. Determine the % H. and % C and hence the molecular formular of the compound.

44g of CO_2 = 12g of C
1g of CO_2 = 12/44g = 0.27g
% of C = 0.27 x 0.14513/0.0475 x 100 = 83.33%

18g of H_2O = 2g of H
1g of H_2O = 2/18 = 0.111g
% of H = 0.111 x 0.07126 / 0.0475 x 100
= 16.6%

C	H	
83.33/12	16.67/1	Molecular mass of compound = 72.
6.94/6.94	16.67/6.94	:. $(CH_{2.4})n$ = 72
1	2.4	12n + 2.4n = 72
		14.4n = 72

n=72/14.4

n=5.

:. Molecular formula = C_5H_{12}

3. THERMOGRAVIMETRY

This is the change in weight of a sample recorded as a function of temperature. A thermogram is useful for evaluating the thermal stability of compound and also for qualitative identification of compounds. It is also useful for estimating the drying temp of gravimetry precipitates.

4 ELECTROGRAVIMETRY

Analyte is electrically deposited over a previously weighted electrode and the gain in weight of electrode is a measure of the concentration of the analyte.

5. **PRECIPITATION OF ANALYTE FROM SOLUTION**

In general a weighed sample is dissolved in an excess of precipitating reagent. The ppt that is formed is then filtered, washed, dried or ignited and weighed. From this weight and the composition of the ppt it is then possible to calculate taking into consideration the wt of the sample taken, the % of the desired substance in the original sample.

In carrying out precipitation of analyte from solution the following requirement must be met

(i) The ppt that is formed must be of extremely low solubility such that no appreciable loss occurs when it is collected by filtration.

(ii) the physical nature of the ppt must be such that it can be readily separated from the solution by filtration and can be washed free of soluble impurities i.e. ppt particles do not pass through the filtering medium and that the particle size is unaffected by the washing process.

The individual steps in gravimetric analysis are:

(i) Preparation of solution (ii) Precipitation (iii) Filteration (iv) Washing

(v) Drying or Igniting (iv) Weighing (vii) Calculations

The following steps occur in precipitation formation

(a) Ion pair formation (b) Ion cluster formation (c) Nucleation (d) Crystal growth

ION PAIR FORMATION

(i) On the addition of $BaCl_2$ to sulphate soln, ion pairs are formed Ba^{2+} + SO_4^{2-}

ION CLUSTER FORMATION

Since many ion paira would exist in solution by electrostatic action, some of the ion pairs come together to form ion clusters.

Ba^{2+} + SO_4^{2+-} Ba^{2+} + $SO4^{2-}$ Ba^{2+} $SO_4^{2-}Ba^{2+}SO_4^{2-}Ba^{2+}$

When there are 6-8 ion pairs in a Cluster, a ion cluster then reaches a critical size called NUCLEUS. The process of ppt is therefore started by a formation of very tiny particles of ppt refereed to as NUCLEI

The process of forming the nuclei is referred to as NUCLEATION. There are 2 types of nucleation

Homogeneous Nucleation: this involves the ppt ions that are in solution i.e. Ba^{2+} and SO_4^{2}-. In homogeneous nucleation, the nucleation rate exceeds the ppt crystal growth rate resulting in many tiny colloidal ppt partices which are difficult to filter.

Heterogeneous Nucleation: Apart from the ppt ions it also involves impurity ions in soln (i.e induced on dust particles, scratches on a vessel's surface or added seed crystals) in this case ppt cystal growth rate exceeds nucleation rate resulting in the formation of shiny needle like crystals. Therefore in any pptn, the aim must be at achieving heterogeneous nucleation which is done by adding the precipitation in drops and stirring.

Crystal Growth: Following nucleation, the initial nucleus will grow by pptn of other ppt particles to form a crystal of certain geometric shape**.** This comes about as a result of the cartons and anions in the solution colliding with the nucleus and getting attached to the surface by chemical bonding. E.g. if silver chloride nucleus is formed by a slow addition of silver to excess sodium chloride.

CI ions will be adsorbed on the ppt surface awaiting the arrival of more Ag^+ ions to continue the crystal growth.

Factors Favouring Analytical Precipitation: The formation of good crystal is the aim of every analytical pptn. In this respect it has been found that the particle size of ppt is inversely proportional to the super-saturation ratio of a solution during pptn.

SSR = Q – S/S Q-is the molar conc of the mixed reagent before any pptn occur . S – is the molar solubility when the system has come to equilibrium.

At low SSR, heterogeneous nucleation takes place which favours the formation of crystals of large particle size. At high SSR, homogeneous nucleation is favoured which brings about formation of many crystals of small particle size.

To make SSR low, Q must be low and S must be high, to ensure this, the following must be done, pptn is done from dilute solution (low Q). Slow addition of ppting reagent with effective stirring, avoids locally high concentration of ppting reagent thereby, keeping Q low.
Precipitation from hot solution because S increases with temp and therefore increase in S leads to the low SSR.

DIGESTION: Small particles will be expected to dissolve rapidly than large crystal i.e. smaller crystal have a greater solubility. Therefore when a ppt is allowed to stand in the presence of a mother liquor, (i.e. solution from which it is being pptated) the larger crystals grow at the expense of the smaller ones, this process is called DIGESTION. During this process the smaller particles tend to dissolve and re-precipitate on the surface of a larger crystal. This results in a mild improvement in the filterability of the ppt as well as its purity.

Occlusion: This occurs when foreign ions are trapped inside the crystal as it is formed. E.g. during the formation of a crystal of $BaSO_4$ by the addition of $BaCl_2$ to sodium sulphate. Barium sulphate is pptd by the slow addition of $BaCl_2$ to the sulphate solution.

$BaCl_2 + Na_2SO_4 \quad BaSO_4 + 2NaCl$

The sulphate ions will be in excess forming the 1^0 adsorbed layer which is neutralized by a secondary layer of Na^+ As more $BACl_2$ is added the loosely bound Na^+ is replaced by Ba^{2+} ions and the crystal continues to grow.

If the rate of growth is very rapid all the Na^+ ions may be replaced by Ba^{2+}ions meaning that part of the Na^+ ions will be occluded in the $BaSO_4$ crystals. Occlusion may also take place by mechanical entrapment of solvent in imperfection (holes) in the crystal. The solvent may contain dissolved impurities. Occluded impurities may be

removed by dissolving the ppt and re-ppting. However such occluded impurities cannot be removed by washing.

Surface Adsorption: This is as a result of the surface of the ppt having a 1^0 adsorbed layer of the lattice ions in excess for e.g. after pptation of $BaSO_4$, the lattice ion in excess will be Ba^{2+} and there will be a counter ion for this i.e. NO_3. The net effect is an adsorbed layer of $Ba(NO_3)_2$. This adsorbed layer can be removed.

POST PRECIPITATION

During the period a ppt is in contact with the liquor, there is a possibility of a 2^{nd} substance forming a ppt with the ppting agent, e.g. calcium Oxalate is ppted in the presence of Mg^{2+} ions. Magnesium Oxalate $Mg(COO)_2$ does not immediately ppt because it tends to form super saturated solution.
However it will be ppted eventually if the soln is allowed to stand for too long a period before being filtered.

Filteration

The choice of a filtering medium is controlled by the nature of the ppt as well as question of cost. There are various types of filter paper for different types of ppts.

	Filter paper	**Examples**
Colloidal ppt	Whatman 42	$BaSO_4$
Small sized xtals	Whatman 40	AgCl
Large sized xtals	Whatman 41	$Fe_2O_3.xH_2O$ or $MgNH_4SO_4$.

The size of the filter paper selected for a particular ppt is determined by the bulk of the ppt and not by the volume of the liquid to filter.

Other methods of filteration is the use of Gooch crucible and the sintered glass crucible.

Drying and Weighing of precipitates

Dry the ppt at a temp in which it is stable, then dry to constant weight.

Calculation:

The weight of the elements or ion to be determined is calculated from the wt of the ppt with the aid of gravimetric factor (G. F) G F is the ratio of the formula weight of substance sought (being determine) to that of the substance weighed.

G.F = Substance sought / substance weighed
e.g. if we are to determine the amount of sulphur in a sample of Barium sulphate
Sample Weighed = W
Wt of ppt = w

Formula weight of $BaSO_4$ contains ome mass of sulphus :. W wt of ppt will contain

(at. Mass of sulphur) x w
fwt of $BaSO_4$ = G. F x w

% Amount of S in sample will be G.F x w/W x 100/1

Substance Sought	**Substance Weighed**	**G.F**
K	$KClO_3$	$K/KClO_3$
K_2O	$KClO_3$	$K_2O/2KClO_3$
SO_3	$BaSO_4$	$SO_3/BaSO_4$
MgO	$Mg_2P_2O_7$	$2MgO\|Mg_2P_2O_7$
Fe	Fe_2O_3	$2Fe/Fe_2O_3$

Example 1

Ortho Phosphate is determined by weighing ammonium phosphomolybatate $(NH_4)_{3.}\ PO_4.\ 12MoO_3$
Calculate % of phosphorus in the sample and % of P_2O_5 if 1.1682g of ppt were obtained from 0.2711g of sample.

Example 2
An ore is analyzed for a magnese content by converting the Mn to Mn_3O_4 and weighing it. If a 1.52g sample yield Mn_3O_4 weighing 0.12g. what will be the % Mn_2O_3 and % Mn in the sample.

Example 3
A mixture containing only BaO and CaO weigh 4.00g, the oxides were converted to the corresponding mixed sulphates by first making the mixture ammonical followed by adding 2M sulphuric acid until pptation was complete. The ppt was filtered and dried. The ppt was found to weigh 8.00g. Calculate the % Ba and Ca in the original mixture.

Example 4

In setting up a fertilizer plant, an industrialist requires a phosphate rock mineral containing at least 55% phosphate as P_2O_5. From the gravimetric data of the analysis of three rock minerals below, advise the industrialist on the sample best suited for this purpose.

Sample	Sample wt	Name of ppt	formiu;a of ppt	weight of
Sultan xk	0.434g	Gumoline phosphomolybdate	$(C_9H_7N)_{2.}H_3PO_4.12MoO_3$	$5.098x10^{-3}$kg
Soloto AlayeOS	1680mg	Ammonium phrsphomolybdate	$(NH_4)_3P_4O_{10}.12Mo.O_3$	7.578gOwellw zT
	1.290x10^{-3}kg	Molybdophosphate	$P_2O_5.24MoO_3$	16.67x10^3mg

TITRIMETRIC ANALYSIS

This is a quantitative analysis based upon the measurement of volume and is referred to as volumetric/ titrimetric analysis.

Titration; is a process by which the quantity of analyte in a solution is determined from the amount of a standard reagent it consumes. A titration is performed by carefully adding the reagent of known concentration until reaction with the analyte is judged to be complete. The volume of standard reagent is then measured.

Usually an indicator is added to ascertain the end of the reaction. Any reaction to be used for titrimetric analysis must satisfy or have the following properties.

The reaction must be rapid or occur instantaneously such as A+B= prodts.

If A&B did not react readily then we use excess of one of the reactant (Back titration)

The reaction must be stoichiometric i.e the equation for the reaction must be known.

The reaction must be specific without any interference from other substances present in the solution.

There must be a suitable indicator in order to know the end reaction (indicators usually measure changes in the physico-chemical properties of the solution) eg pH, colour change, potential change, conductivity.

Types of Titrimetry

Acid-base titrimetry (Acidimetry/ Basimetry)

Precipitation

Complexometric (chelometric) titrimetry.

Oxidation/reduction Titrimetry.

Acidimetry/ Alkalimetry

This involves the addition of an acid to a known volume of alkali in the presence of an indicator.

A solution that is being titrated (i.e solution in conical flask) is referred to as TITRAND, while the solution that is used in titrating (solution in the burette) is the TITRANT.

The reagent of known concentration that is used in a titration is called a STANDARD SOLUTION.

The concentration of a standard solution is established either directly or indirectly;

(1) By dissolving a carefully weighed quantity of the pure reagent and diluting to an exact volume.

(2) By titrating the solution containing a weighed quantity of a pure compound with the reagent solution.

In either method, a highly purified chemical compound called A PRIMARY STANDARD is required as the reference material. The process whereby the concentration of a standard solution is determined by titration of a primary standard is called STANDARDIZATION.

PRIMARY STANDARD

Primary standards must have the following properties

- Must be obtained in the analytical pure state.
- Must be stable (i.e. it should not be attacked by the constituents of the atmosphere).
- Absence of hydrate water.
- Must be soluble in cold water or in slightly warming

The substance must have molecular weight to minimize error in weighing.

A primary standard must be colourless or white in order to avoid interference with indicator colour changes.

Practically, few substances meet or even approach these requirements and as a result, the no of primary standard substances available to the chemist is limited. In some instances, it is necessary to use less pure substances in the absence of primary standard.

In such circumstance the percentage purity of secondary standard must be known.

Acidimetry standard

Anhydrous sodium carbonate dried at 270°c for 1 hr.

Borax ($Na_2B_4O_7.10H_2O$) dried at 55°c for 1hr.

Alkalimetry standard

These are usually weak organic acids

Sulphanic acid (NH2SO3H)

It is not a stable and should be prepared fresh since it undergoes hydrolysis if left overnight

NH2SO3H+ H2O = HH4SO4

Potassium Hydrogen Iodate KH $(IO_3)_2$ strong acid with high molecular weight, not hygroscopic, its low solubility in H_2O is a major disadvantage.

Potassium Hydrogen phthalate $KHC_8H_4O_4$

Acid Base Visual Indicator

pH = -log[H+]

Ht+=0.01M

pH = - log [H+] = -log [10^{-2}] =2

Acid- base indicators are generally organic compounds which behave as weak acids or bases. The dissociation or association reaction of indicators is accompanied by internal, structural re- sarrangement that is responsible for the changes in colour.

A typical acid-base indicator reaction can be represented as follows:

H_2O+HIn = H_3O+ In

Acid Colour Base colour

In+ H_2O = InH +OH

The equilibrium expression

Ka= [H_3O+] [In]/ [HIn]

Log Ka = log [H_3O+] +log [In]- log HIn

-log [H_3O+] = -log Ka+ log [In]/ [HIn]

pH= pKa+ log [In]/ [HIn]

A colour change depends on acid-base ratio.

A ten-fold excess of one form is required before the colour of the specie becomes predominant.

pH = pKa +log (1/10)

pH = pKa + log (10/1)

pH=pKa+_ 1

The idea that an indicator changes its colour form pKa + 1 to pKa-1 interval is referred to as transition range.

E .g

What is the transition range for an indicator with an acid dissociation constant of 1.0 x10^{-5}

Solution

pH= -log [1 x 10-5] ±1

pH= 5±1

T R =4 – 6

EXAMPLES OF ACID-BASE INDICATORS

Common names	**Transition Range**	**Acid colour**	**Base colour**
Thymol Blue	1.2 - 2.8	Red	Yellow
Methyl Orange	3.1 - 4.4	Red	Yellow
Methyl Red	4.2 - 6.3	Red	Yellow
Phenolphthalein	8.0 - 9.6	Colourless	Red
Bromocresol green	3.6 - 5.2	Yellow	Blue

Neutralization curves

When both reagent and analyte are strongly dissociated, the net neutralization reaction can be expressed as,

H_3O + OH- = 2H_2O

E.g HCl + OH = Cl^- + H_2O

Strong acid	strong base	conjugate base	conjugate acid

STRONG ACID VS STRONG BASE

H3O+ is accounted for by acid and water
OH- is accounted for by base and water

$HCl + H_2O = H_3O^+ + Cl$
$H_2O + H_2O = H_3O^+ + OH^-$

For strong acids in which dissociation is complete, the hydrozomium ($H_3O^{+)}$ ion concentration is equivalent to the molarity of the acid.

$[H_3O^+] = M_{HCl}$

For strong base, the OH- is equivalent to the molarity of the acid

$[OH^-] = M_{NAOH}$

For basic solution the pH is calculated from the ionic product of water

$Kw = [H_3O^+][OH^-]$
$\log Kw = \log [H_3O^+] + \log [OH^-]$
$-\log Kw = -\log [H_3O^+] - \log [OH^-]$
$pkw = pH + pOH$

Plot the curve for the titration of 50ml of 0.005M HCL with 0. 1M NaOH

Initial solution = 5×10^{-2} M HCl and since HCl is completely dissociated.

$[H_3O^+] = 0.05$
$pH = -\log 0.05 = 1.30$

50ml of 0.05M HCl with 0.10M NaOH (pH)

Volume of base
0.0 1.30
5

On adding 5ml of NaOH, $[H_3O^+] = \frac{(50 \times 0.05) - (5 \times 0.1)}{\text{Vol of acid + vol of base}} = 55$

Vol. of NaOH	0.0	10.0	20.0	24.0	24.90	25.0	25.10	25.0	30.0
pH	1.30	1.60	1.60	1.60	2.87	3.87	7.00	10.12	11.12	11.80

Equivalent point

$M_1V_1 = M_2V_2$

$0.05 \times 50 = 0.1 \times V_2$
$V_2 = 0.05 \times 50 / 0.1 = 25$ ml
$[H_3O^+] = [OH^-]$, pH=7

All the acid have been consumed and the base is now in excess

$$[OH^-] = \frac{[25.10 \times 0.1] - [50 \times 0.05]}{75.1}$$

Question
What volume of 0.01m NaOH must be added to 5ml of 0.005M HCl to make the resulting solution have a Ph of 10.796

Weak acid Vs strong base
$HA + H_2O = H_3O^+ + A^-$
$Ka = [H_3O^+][A^-]/[HA]$
$\log Ka = \log [H_3O^+] + \log [A^-]/[HA]$
$pH = pKa + \log [A^-]/[HA]$
$pH = pKa + \log [salt] / [acid]$ Henderson- Hasselbach equation

pH in the equyivalence pt region becomes smaller as the acid becomes weaker i.e. the reaction between the acid and the base becomes less complete. End pt is observed at pH> 7, pH interval is 8-10, such that the indicator that is applicable is PHENOLPHTHALEIN.

APPLICATION OF ACID- BASE TITRIMETRY

Determination of proteins
The sample under test is digested with sulphuric acid to convert the nitrogen of the protein to ammonium hydrogen sulphate (NH_4HSO_4). Potassium sulphate is added to the digest in order to raise the boiling point of the sulphuric acid. Also to hasten the digestion, selenioum powder or copper salt is added as catalyst, the digestion is carried out in a fume cupboard until digest is colourless. The digestion flask is allowed to cool to room temp then the extract is transferred into a distillation unit and ammonia gas is liberated from the digest by the addition of ammonium hydroxide .
$NH_4HSO_4 + NaOH \longrightarrow NH_3 + NaHSO_3 + H_2O_2$

The ammonia liberated is then distilled over into a flask containing standard acid solution

$NH_3 + HCl \longrightarrow NH_4Cl + HCl$ excess

The excess HCl unreacted with ammonia is then titrated with a standard base e.g NaOH

$HCl + NaOH \longrightarrow NaCl + H2O$

QUESTION
0.1172g of fish muscle was digested with sulphuric acid to convert the N_2 to NH_4HSO_4 in the presence of selenium powder as catalyst. The digestion continued until the digest was colourless. The extract (digest) was then distilled and the NH_3 produce collected into 58.5ml ofn 0.03M HCl. The excess unneutralized acid was then titrated with 15ml of 0.011M NaOH.

Given that % protein= $\frac{\text{Millimoles of } NH_3 \times 6.42 \times 100/1}{\text{Wt of sample in mg}}$
Calculate the % protein on the fish muscle

Solution
NH_3HSO_4 +NaOH ---------- NH_3 + $NaHSO_4$
NH_3+HCl ---------- NH_4Cl + HCL excess
HCl + NaOH ---------- NaCl+ H2O
Mmoles of HCl = 5.85x 0.03 = 1.755
Excess HCl = 15 x 0.011 = 0.165 (excess HCl)
NaOH = HCl 1:1
1.755- 0.165

$$\% \text{ protein} = \frac{\text{mmoles of } NH_3 \times 6.42 \times 100}{\text{Wt of sample (mg)}}$$

$$= \frac{1.59 \times 6.42 \times 10}{0.1172 \times 10^3 \times 1 \times 1}$$

CALCULATION UNDER ACID –BASE TITRIMETRY

Recall that by designation a mole is the formula wt of a substance expressed in grammes
i.e. mole = g/ fwt----------(1)
Molarity is the no of moles of solute present in 1 litre of solution
i.e. molarity M - moles / litre ----------(2)

In chemical analysis it is however more convenient to use mmoles(mmol) instead of moles because most analytical determination are concerned with rather quality of solution. Therefore mmoles analytical determination are concerned with rather small

quality of solution. Therefore mmoles can be the formula Wt of a substance expressed in milligrams (mg).

Mmole= mg/fwt----------(3)

Therefore molarity of solution becomes no of mmoles of solute present in 1ml of the solution

M= mmoles/ mlitre= mmoles/ml ----------(4)

We can re- write eqn 4, such that we have Ml x m = mmoles.

Substitute eqn 3 into eqn (4) then Ml x M = mg/fwt ----------(5)

Expressing everything in terms of molarity. Ml x M x Fwt =mg ----------(6)

Calculations in titration can occur in 4 steps, consider the equal aA+ Bb

Product where a, b represents no of moles of titrant & titrand respectively.

A- titrant, B – titrand. To calculate mmoles of A

Mmoles of A can be calculated from the vol and molarity of the titrant.

Mmoles A= Ml_A x M_A

To calculate mmoles of B

The mmoles of B can be calculated from mmoles of A using the combining ratio R given as R = mmoles of A/ mmoles of B = a/b

So that mmoles B= mmoles A x b/a

Mmoles B = Ml_A x M_A x R

Weight of B

From eqn 3, mg B = mmoles B x Fwt B

Mg B = ML_Ax M_A x FwtB x R

To calculate % of B= Wt of B / Wt of sasmple x 100/1

% of B = MlA x MA x Fwt B x R / Mg of sample x100/1

Examples

(1) A 0.475g sample containing (NH4)2 SO4 was dissolved in water and made alkaline with KOH, the liberated NH3 was distilled into exactly 50ml of 0.10 M HCl. The excess HCl was titrated with 11.1ml ofn 0.121 M NaOH. Calculate the % ammonium sulphate in the sample.

(2) Exactly 0.4104g of primary KHP V(potassium hydrogen phalate)(204.22) was dissolved in water. If the solution required 36.0ml of NaOH solution, what is the molarity of NaOH.

KHP+NaOH ---------- NaKHP +OH

Mmoles of KHP = mg/fwt = 0.4104 x 10^3/204.22 = 2.0096 mmoles

Mmoles of NaOH = Mmoles of KHP x b/a = 2.0096mmoles

Molarity of NaOH = mmoles / ml = 2.0096/36= 5.5 x 10^{-2} M .

PRECIPITATION TITRIMETRY

The formation of a ppt can be used as the basis for titration provided there provided there in a suitable way of determining the end point. It is also important that the system reaches equilibrium rapidly after each addition of titrant. Most precipitation titration involves the use of AgNO3 (silver nitrate) as the titrant and as such pptn titreimetry is commonly referred to as ARGENTOMETRIC TITRATION. It has been used for the analysis of Ag^+ ions as well as other ions such as Cl^-, Br^-, I^- thiocyanate.

$Hal^- + AgNO_3 \longrightarrow$ AgHal ppt

A titration curve can also be prepared for pptn titration in a manner similar to that of acid- base titration by plotting pX against vol of $AgNO_3$ (where pX is similar pH) i.e pCl, pI, pBr.

E.g plot the curve for the titration of 50ml of 0.005M Br with 0.010M AgNO3, using the following volumes of AgNO3 0.00, 10, 20, 23, 24.90, 24.95, 25, 25.05, 25.10, 27.00, 30.0.

At the initial pt, pBr= -log [0.005] =2.30

After addition of 5ml, pBr= [50x0.005]—[5x0.01]/55= 3.636×10^{-3}

At the equivalence point, neither Br^- nor Ag^+ is in excess.

.: $[Ag^+] = [Br^-]$ equal to the solubility product

$[Ag^+]\ [Br^-] = 5.2 \times 10^{-13}$

$[Ag^+] = [Br^-] = \sqrt{5.2 \times 10^{-13}} = 7.2 \times 10^{-7}$

[pBr] = 6.14

Note that p[Ag] [Br] = 12.28

After the equivalence pt, e. g. addition of 35ml of AgNO3, all the Br ions would have been ppted and therefore the $AgNO_3$ will be in excess

.: pAg= [35x0.01]- [50x0.005]/85=1.176×10^{-3}

pAg= 2.93, : pBr = 12.28-2.93 = 9.35

vol of AgNO3	0.00	5.0	25.05	35
pBr	2.30	2.44	6.14	9.35

Ksp AgI = 8.3×10^{-17}

Ksp AgBr = 5.2×10^{-13}

Ksp AgCl= 1.1×10^{-10}

The titration curve is similar for normal acid –base titration however; the curve can be plotted in terms of pAg against volume of AgNO3.

INDICATORS IN PRECIPITATION TITRIMETRY

There are two types of indicators

Formation of a colour compound

a) Mohr's and Volhard's indicator
b) Adsorption indicator

Formation of a colour compound

a) Mohr's Method: In this method chloride is titrated which standard silver nitrate solution and a soluble chromate salt is added as indicator. This produces a brick red ppt, after the pptn of Cl^- is complete. The excess Ag^+ in solution reacts with the indicator to precipitate red silver chromate.

$$CrO_4^{2-} + 2Ag^+ \longrightarrow Ag_2CrO_4^-$$

Yellow Brick red

The colour change indicates the end pt, the conc. of the chromate indicator is very important i.e, the $Ag_2CrO_4^-$ should just start ppting at the equivalence pt.
Ksp $Ag_2CrO_4 = 1.1 \times 10^{-12}$
Ksp $AgCl = 1.1 \times 10^{-10}$

Ag chromate is less soluble and is therefore expected to ppt completely before the commencement of the pptn of the AgCl. Furthermore since at initial stage, the Cl^- concentration is high, therefore pptn of Ag chromate should be expected. For the indicator to be suitable, the conc of the Ag chromate must be adjusted such that its solubility product is slightly higher than that of the AgCl. Therefore, by inserting the $[Ag^+]$ in the ksp equation for the Ag chromate, it is possible to calculate the conc. of the CrO_4^- at which pptn is expected to start

$[Ag^+]\ [Cl^-] = 1.0 \times 10^{-10}$
$[Ag^+] = 1.0 \times 10^{-5}$
$Ag_2CrO_4 = [Ag]^2\ [CrO_4^{2-}] = [1.0 \times 10^{-5}]^2\ [CrO_4^{2-}] = 1.0 \times 10^{-12}$
$CrO_4^{2-} = 1.0 \times 10^{-12} / 1.0 \times 10^{-10} = 0.011M.$
Therefore, the conc. of the indicator must be 0.011M if the colour change is to occur at the equivalence pt, if the conc. id > than this (0.011) then the Ag_2CrO_4 will begin to ppt before the equivalence pt ie the end pt is observed much earlier.
If the conc is lower than 0.011M, then it will take much more time before the equivalence pt is arrived at (beyond the equivalence pt).
In practice, the end pt occurs slightly beyond the equivalence pt because an excess of Ag+ is required to ppt the Ag_2CrO_4. Also sufficient Ag_2CrO_4 must be formed before the brick red colour dominates the yellow solution. This is corrected for by running an INDICATOR BLANK, the Ag+ consumption of a Cl- free suspension of CaCO3 is measured in the same volume of solution and same volume of indicator. The blank titration mixture serves as a colour standard for subsequent titration. The blank titre (end pt) is then subtracted from the other titre values.

PH CONTROL

The pH of the medium must be neutral or nearly neutral. If the pH is <6 then the reaction;

$2H^+ + 2Cr_2O_4^{2-} \rightarrow Cr_2O_7^{2-} + H_2O$ take place

Dicromate

The silver di-chromate formed is more soluble than the chromate and as such the indicator reaction in acid solution requires substantially larger Ag+ conc meaning that the equivalence pt will be observed far beyond the expected equivalence pt.
If the pH is >10, Ag2O is ppted from this rxn $2Ag+ + 2OH^- \rightarrow 2AgOH + Ag_2O + H_2O$.
This leads to removal of Ag+ from solution and therefore larger[Ag+] (vol of $AgNO^{2-}$) would be needed for Ag_2CrO_4 to be ppted.

b) VOLHARDS METHOD:-

This is an indirect method for determination of halide ions. It is usually carried out in acidic medium, this represents an advantage over the mohr's method because ions such as CO_3^{2-}, Oxalates, arsenates which form slightly soluble Ag+ salts in neutral media do not interfere.

$Hal^- + Ag^+ \rightarrow AgHal^- + Ag$ excess
Ag^+ excess + $SCN^- \rightarrow AgSCN$

Iron (lll) ferric alum serves as the indicator, imparting a red coloration to the solution with the first slight excess of thiocyanate
$Fe^{3+} + SCN^- \rightarrow [Fe(SCN)]^{2+}$
The titration is carried out in acid solution to prevent pptn of Fe3+ as the hydrated oxide. Agcl is contrast to other Ag halide is more soluble than Ag thiocyanate (other halides are less soluble).

As a result of the reaction
$AgCl_{(s)} + SCN^- \rightarrow AgSCN + CL^-$

This causes the end point with a volhard determination of chloride to fade i.e. an over consumption of thiocyanate ion and therefore a negative error for the analysis may result.

This error may be removed by 2 methods,

The first method involves the use of the maximum allowable indicator conc.(0.2M fe3+) or by isolation of the ppted AgCL before back titration i.e the AgCL is filtered, time of filtration is a disadvantage.

A better method of removing the AgCl ppt is by adding few ml of Nitrobenzene, this coagulates the AgCl thereby as a protective coating and removing the AgCl from contact with the solution.

ADSORPTION INDICATOR

These are organic compound mostly weak acids which are adsorbed on or desorbed from the surface of the ppt formed during titration. Ideally the adsorption or desorption occurs near the equivalence pt and the results not only in a colour change but also a transfer of colour from the solution to the solid (or the reverse)

Before the attainment of the end pt, the halide ion is in excess thereby forming the 1^{o} adsorbed layer
Since the indicator is in the anionic form, no colour change is observed. At the end pt or slightly beyond the end pt. Ag+ is in excess, therefore the ppt particle becomes positively charged by the strong adsorption of the Ag+. Therefore the retention of the indicator ions in the counter ion layer occurs, this result in the colour of the adsorbed indicator being discharged (colour change is an adsorption and not formation of a ppt)

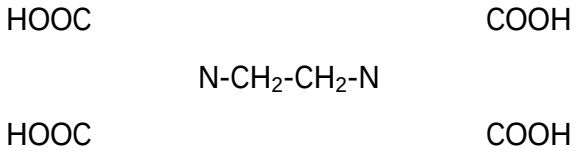
Examples of adsorption indicator are fluorescein, dibromo Fluorescein and Eosin

COMPLEXOMETRIC TITRATION

This is the titration between a metal ion and a ligand to form a soluble complex. The ligand is referred to as a chelating agent (a chelate is produced when a metal ion co-ordinate with two or more donor groups of a single ligand). Chelating agents are referred to as bi, ter, quadric, quinque and sexadentate depending on the donor group available for co-ordination.

EDTA

Ethylenediaminetetraacetic acid is the most important reagent used for complexometric titrations



It is the most widely used of the polyamino-carboxylic acids.

The free acid can be represented as H4Y i.e. it is tetraprotic. Ionization of EDTA solution occurs as follows:

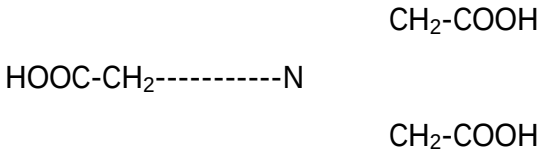
$H_4Y = H^+ + H_3Y^-$ $\quad Ka = 1.0x10^{-2} = \frac{[H^+][H_3Y^-]}{[H_4Y]}$ $\quad pk1 = 2.0$

$H_3Y^- = H^+ + H_2Y^{2-}$ $\quad Ka_2 = 2.2x10^{-3} = \frac{[H^+][H_2Y^{2-}]}{[H_3Y^-]}$ $\quad pk2 = 2.67$

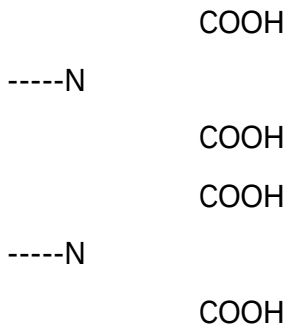
$H_2Y^{2-} = H^+ + HY^{3-}$ $\quad Ka_3 = 6.9x10^{-7} = \frac{[H^+][HY^{3-}]}{[H_2Y^{2-}]}$ $\quad pk3 = 6.17$

$HY^{3-} = H^+ + Y^{4-}$ $\quad Ka_4 = 5.5x10^{-11} = \frac{[H^+][Y^{4-}]}{[HY^{3-}]}$ $\quad pk4 = 10.26$

The pk values indicate that the first two protons are lost much readily than the remaining two. In addition to the four acidic hydrogens, each nitrogen atom has an unshared pair of electrons. The other reagents used for complexometric titration include Nitrilotriacetic acid (NTA)

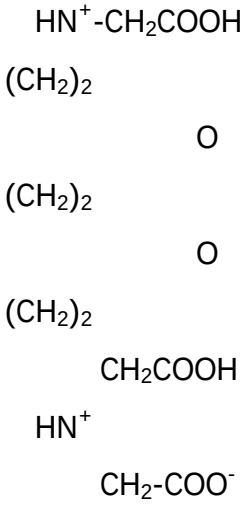


Diaminocyclohexanetetraactic acid (DCTA)

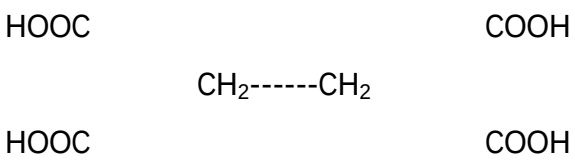


Ethyleneglycolbis(2-methyl)tetraacetic acid (EGTA)

$CH_2\text{-}COO^-$



Ethylenetetraacetic acid (ETA)



Important features of EDTA

It forms a 1:1 ratio with metalions regardless of the charge on the cation

M^{+}	+	H_2Y^{2-}	MY^{3-}	+	$2H^{+}$
M^{+2}	+	H_2Y^{2-}	MY^{2-}	+	$2H^{+}$
M^{3+}	+	H_2Y^{2-}	MY^{-}	+	$2H^{+}$
M^{4+}	+	H_2Y^{2-}	MY	+	$2H^{+}$

This can be represented by the general equation $M^{x+} + H_2Y^{2-} = MY^{(x-4)} + nH^{+}$

FORMS OF EDTA SPECIES AS A FUNCTION OF pH

As pH increases, EDTA ionizes; at low pH we have more of unionized form. H_2Y^{2-} is the predominant species in moderately acidic media (pH 3-6). From pH 6-10, HY^{3-} is the major component. Only at pH>10 does Y^{4-} exist. The pure acid H_4Y has poor solubility in water, hence the sodium salt is often used. $Na_2H_2Y.2H_2O$

FORMATION CONSTANTS OF METALS EDTA COMPLEXES

The formation of metal-EDTA chelate can be written as $M^{2+} + H_2Y^{2-} = MY^{2-} + 2H^+$. The equilibrium constant of metal-EDTA is called the formation constant or k_f or stability constant

$k_f = \frac{[MY^{2-}][H^+]}{[M^{2+}][H_2Y^{2-}]}$ k_f depends on [H+] concentration, hence the dependence on pH

The larger the k_f, the larger the stability of the complex and hence the reaction will proceed readily.

EDTA TITRATION

The larger the k_f the more stable the chelate MY^{2-} the farther to the right the equilibrium will be and the larger will be the end point interval. The larger the k_f the lower the pH at which titration can be performed.

LIMITATION OF EDTA

Its main disadvantage is that it is an unselective reagent as it titrates any metal

Selectivity of EDTA as a titrant:

EDTA can be made selective by

(i) Proper adjustment of pH

(ii) By change of valence

(iii) By masking and demasking

(i) Minimum pH for effective titration of metal cation with EDTA

	Fe^{3+}, Hg^{2+}, In^{3+}, Se^{3+}	pH<4
Log KMY	Ni^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, Fe^{2+}, Mn^{2+}, Cd^{2+}	pH 4-6
	Ca^{2+}, Mg^{2+}, Sr^{2+}	pH>7

How would you determine Fe^{2+} in the presence of Fe^{3+}

**Adjust pH to about 5 then titrate

How do you determine total iron

**Take aliquot adjust pH to 5 –titrate only Fe^{2+}

Take aliquot adjust pH to 3 – titrate only Fe^{3+}

Masking and demasking

A + B → product

A + Ms → AMs -A is no more free

AMs + B No product is formed because A is masked

The masking effect can be removed by demasking

AMs + X → A + MsX

How can zinc and nickel be determined in a nickel-zinc alloy?

(a) Obtain a solution of the alloy by dissolving a known weight of the alloy in a known volume of HNO_3

(b) Take an aliquot of the alloy solution and adjust pH to 4-9 (e.g. pH 5)

(c) Titrate with EDTA – this gives titre value for both Zn + Ni = T_1

(d) Add KCN to an aliquot of the alloy solution, CN^- forms a complex with Zn

Zn^{2+} + $4CN^-$ solution $Zn(CN)_4^{2-}$

Then adjust pH to 4-7 and titrate with EDTA, end point given concentration of

(Ni^{24})= T2 (Zn^{2+}) = $T_2 – T_1$

OR

Using only one aliquot,

Add CN^- to mask Zn^{2+}. Then titrate with EDTA, T1 = [Ni2+]

Then add formaldehyde to damask Zn2+ from the cyano-complex

Zn(CN)42- + HCHO → Zn2+ + HCOCN

Standardization of EDTA

EDTA solutions are standardized using metal salt solution i.e. zinc sulphate or Ca^{2+} solution

COMPLEXOMETRIC INDICATORS

Metal-Ion Indicators

These are organic dyes that form coloured chelates with metal ions in concentration range that is characteristics of the particular cation and dye.

The metal ion indicator can also bond with protons to give species that impart to the solution colours that resembles those of the metal complex. They can function as acid base indicators.

Eriochrome Black T is widely used

Eriochrome black T indicator reaction

$Mn+ + In + EDTA \rightarrow M\text{-}EDTA$

At the end point In-EDTA

For metal – ion indicator to be suitable for EDTA titration, the k_f of the metal indicator complex should be less than one- tenth that of the metal-EDTA complex. The principle depends on colour of uncomplexed indicator being different from that of complexed indicator. Other indicators are calgmagite, solochrome black T, murexide etc.

TITRATION METHODS WITH EDTA

Several procedures are employed in the application of EDTA to volumetric analysis. These include:

Direct Titration

Direct titration with EDTA, using metal ion indicators for end point detection. These are limited to those reaction in which methods for end point detection exists and to those metal ions that reacts rapidly with EDTA

Back Titration

Used for cations that have high k_f with EDTA and for which a satisfactory indicator is not available. The excess EDTA is determined by back titration with standard Mg^{2+} solution

Note: the metal EDTA complex must be more stable than the magnesium EDTA complex.

Displacement Titration

An excess of a Mg-EDTA complex is added. The metal ion forms a more stable complex than that of the mg-EDTA complex added.

$MgY^{2-} + M^{2+} \dashrightarrow MY^{2-} + Mg^{2+}$

The liberated Mg is then titrated with standard EDTA solution.

Tutorial Question

Calculate the concentration of EDTA if 46.35ml of EDTA reacted with 31.69ml of 0.01470M Mg^{2+} solution?

Mmoles Mg^{2+} = mmoles EDTA

$$\text{Mmoles} = \text{ml} \times M = \frac{31.69 \times 0.01470}{46.35} = 0.01M$$

OXIDATION REDUCTION TITRATION

Students are advised to revise the concept of oxidation and reduction, oxidation states, balancing of redox reaction, standard electrode potentials.

Oxidation involves electron loss, reduction involves electron gain. Both processes occur simultaneously i.e. no of electrons gained must equal to no of electron lost.

$Ox_1 + Red_2 = Red_1 + Ox_2$

An oxidizing agent is the substance that is reduced while a reducing agent is the substance that is oxidized. E.g. consider the reaction

$CuO + H_2 = Cu + H_2O$

$Cu^{2+} \rightarrow Cu + 2e$

$H2 - 2e \dashrightarrow 2H^{+}$

CuO is the oxidizing agent, while H_2 is the reducing agent

Consider the reaction of the type

$aOx + ne \rightarrow bRed$

And from Nerst equation

$$E = E^0 - \frac{2.303RT}{NF} \log \frac{[Red]^b}{[Ox]^a}$$

At 25^0C, $\frac{2.303RT}{F} = 0.059$

$$E = E^0 - \frac{0.059}{N} \log \frac{[Red]^b}{[Ox]^a}$$

E^0 = a constant called the standard electrode potential characteristics of the particular reaction

R = the gas constant = $8.314JK^{-1}mol^{-1}$

T = absolute temperature

N = no of electrons participating in the reaction as defined by the equation describing the half cell reaction

Ln = natural logarithm = $2.303\log_{10}$

The electrode potential because it is a measure of the driving force of a half reaction is affected by content ratio, and this relationship between concentration and electrode potential is given by the Nerst equation.

Consider the reaction $Cd^{2+} + 2e = Cd_{(s)}$

$$E = E^0 - \frac{0.059}{2} \log \frac{1}{[Cd^{2+}]}$$

The activity of an element in the elemental state is unity

$$Fe^{3+} + e = Fe^{2+}$$

$$E = E^0 - \frac{0.059}{2} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

**Calculate the potential of the half equation

n that E^0 $Cr_2O_7^{2-}/Cr^{3+}$ = 1.33 and pH = 2.

First the reaction must be balanced

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

6+ 3+

$Cr^{6+} + 3e \quad Cr^{3+}$ but $2Cr^{3+} = 6e$

$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$

$$E = 1.33 - \frac{0.059}{N} \log \frac{[Cr^{3+}]}{[Cr_2O_7^{2-}][H^+]^{14}}$$

At pH = 2 : - $[H^+] = 1 \times 10^{-2}M$

$$E = 1.33 - \frac{0.059}{6} \log \frac{[10^{-2}]}{[10^{-3}][10^{-2}]^{14}}$$

$$E = 1.33 - \frac{0.059}{6} \log 1 \times 10^{27}$$

= 1.33 - (9.83 x 10-3 x 27)

= 1.34 - 1.33 - 0.2655 = 1.06V

** Calculate the potential of the half equation

$MnO_4^- \rightarrow Mn^{2+}$

Carried out at pH of 3.3, given $[MnO_4^-] = 2.5 \times 10^{-3}M$; $[Mn^{2+}] = 5.0 \times 10^{-3}$, and E^0 $MnO_4^-/Mn^{2+} = 1.51V$

$$E = 1.51 - \frac{0.059}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$= \frac{5 \times 10^{-3}}{(2.5 \times 10^{-3})(500 \times 10^{-4})}$$

$$= \frac{5 \times 10^{-3}}{9.765 \times 10^{-3}} = 5.12 \times 1026 \quad \log = 26.71$$

$0.0118 \times 26.71 = 0.315$

$E = 1.5.1 - 0.315 = 1.1954V$

Reagents for Oxidation Reduction titrimetry

Potassium permanganate MnO_4^-

Cerium ammonium nitrate Ce^{4+}

Ammonium sulpahte, Ammonium nitrate, Ammonium hydroxide

Potassium dichromate $Cr_2O_7^{2-}$

Potassium bromated BrO_3^-

Potassium iodate IO_3^-

Periodic acid $H_4IO_6^-$

Sodium thiosulphate $Na_2S_2O_3$

(a) Write balanced equation for the reaction of $KMnO_4$ in acidic medium with the following

(i) Fe^{2+}, Fe^{3+} (ii) $C_2O_4^{2-} \rightarrow 2CO2 + 2e^-$ (iii) $H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$

(b) Write a balance equation for the reaction of $Cr_2O_7^{2-}$

(c) Balance the reaction $IO_3^- + I^- + H^+ \rightarrow I_2 + H_2O$

(d) In the reaction between MnO_4^- and I^- to give Mn^{2+} and I_2. The I_2 produced was titrated with $Na_2S_2O_3$.

What is the mole ratio between MnO_4^- and $S_2O_3^{2-}$, if 27.4ml of 0.052M $KMnO_4$ required 25ml of $Na_2S_2O_3$ for the complete reaction? What is the molarity of the $Na_2S_2O_3$.

END POINT DETECTION (OXD – RED. INDICATORS)

End point detection in many Oxd-Red. Titrations re readily observed by making the solution of the analyte a part of the cell.

Ref electrode/analyte solution/indicating electrode

The end point is determined from a plot of the measured potential as a function of titrant volume.

Advantageous when dialong with coloured solution

CHEMICAL INDICATORS

There are three types

(1) Self indicator –

(2) Specific indicator – Indicator action is based on reaction with one of the reagent in the titration.

(3) True – oxidation reduction indicators – responds to the potential of the system rather than to the appearance or disappearance of a particular species during the titration

SELF INDICATORS

These apply to highly coloured titrant e.g. $KMnO_4$: during titration with an appropriate reducing agent, the violet colour of the MnO_4^- is removed as it is added because of its reduction to Mn2+. When the reaction is complete, a fraction of a drop of excess $KMnO_4$ imparts a pink colour to the solution, this indicates the end point.

SPECIFIC INDICATORS

Starch forms a dark – blue complex with tri-iodide ion. This complex serves to signal the end point in titration in which iodine (yellowish). Addition of starch turns the solution dark – blue. At the end point all the iodine has been consumed and the starch tri-iodide complex no longer exist, solution becomes colourless. Similarly KSCN has been used in the titration of iron (III) with solution (III) sulphate, the end point involves disappearance of the iron (III) thiocyanate complex owing to a marked decrease in the iron (III) concentration at end point.

TRUE OXIDATION – REDUCTION INDICATORS

The action of the indicator depends on the change in the potential of the system. The oxidized form of the indicator has a different colour from the reduced form.

$$In\ Ox + ne \rightarrow In\ Red$$

Then

$$E = E^0 - \frac{0.059}{n} \log \frac{[In\ Red]}{[In\ Ox]}$$

A colour change of the oxidized form of the indicator to the reduced form involves a change in the ratio of the reactant concentration of about 100.

When $\frac{[In\ Red]}{[In\ Ox]} > 1$ changes to $\frac{[In\ Red]}{[In\ Ox]}$

: - condition for the colour change of a typical indicator can be found from the Nerst equation

$$E = E^0 - \frac{0.059}{n} \log \frac{[In\ Red]}{[In\ Ox]}$$

$$E = E^0 - 0.059/N \log 1/10 \text{ or } 10/1$$

Each indicator changes colour over a particular potential range. If E^0 is near the equivalence point, Potential of the titration, then the colour change occurs at the equivalence point.

Examples

Indicator	Oxidized	Reduced	Transition point
Phenathroline	Pale blue	Red	1.11
Diphenylamine	Violet	Colourless	0.76
Methylene blue	Blue	Colourless	