ELECTIVE-II **Semester - II**

19CHP205B **ANALYTICAL CHEMISTRY** **4H 4C**

Instruction Hours/week:L: 4 T:0 P:0 Marks: Internal:40 External: 60 Total:100

Course objectives

1. To learn about quantitative inorganic analysis.
2. To understand the different colorimetric analysis.
3. To learn about electrochemical methods of analysis.
4. To learn different chromatographic techniques.
5. To understand how to analyze the data obtained.

Course Outcome

1. Known about quantitative inorganic analysis.
2. Understood the different colorimetric analysis.
2. Understood the electrochemical methods of analysis.
3. Understood the different chromatographic techniques.
4. Learned about how to analyze the data obtained.

UNIT-I

Quantitative Inorganic Analysis: Theoretical basis of quantitative inorganic analysis-common ion effect solubility product, effect of acid, temperature and solvent upon the solubility of a precipitate.

Supersaturation-Von Weimarn concept. Formation and treatment of precipitates-co-precipitation and post-precipitation. Precipitation from homogeneous solution. Specific and selective precipitants.

Principles of acid-base, oxidation-reduction, precipitation and complexometric titrations-indicators used in such titrations. Uses of organic reagents in inorganic quantitative and qualitative analysis.

UNIT-II

Data Analysis: Errors in chemical analysis-Defining terms: Mean median, accuracy and precision – classification of errors: Systematic errors and random errors. Improving accuracy of analysis – mean, standard deviation and Q-test. Comparison of results – Least square, 't'-teat, 'F'-test and 'Chi' square test. Validation of analytical methods: Precision, accuracy, robustness, quantification, linearity and range.

UNIT-III

Techniques in Inorganic Chemistry: Colorimetry: Theoretical and practical aspects of colorimetric analysis. Flame emission and atomic absorption spectroscopy – types of atomic spectroscopy – emission methods – absorption methods – fluorescence methods – source and atomizers for atomic spectroscopy – flame atomizers – electrothermal atomizers – principle and applications of atomic absorption spectroscopy. Advantages of atomic absorption spectrometry over flame photometry.

UNIT-IV

Electrochemical Methods of Analysis: Cyclic voltammetry, coulometry and amperometry-principle and applications.

Thermal characterization techniques: Principle and applications of differential thermal analysis (DTA), differentials scanning calorimetry (DSC) and thermogravimetric analysis (TGA) thermometric titration.

UNIT- V

Chromatographic Methods: Classification – techniques and applications in column, size-exclusion, ion exchange, paper and thin layer chromatography.

Gas chromatography and high performance liquid chromatography (HPLC)-principle, equipment design, sample injection system, columns, detectors and applications.

SUGGESTED READINGS:

Text Books:

1. Svehla, G. (2002). *Vogel's Qualitative Inorganic Analysis* (VII Edition). Singapore: Pearson Education.
2. Christian, G. D. (2007). *Analytical Chemistry* (VI Edition). United States: John Wiley & Sons.
3. Skoog, D. A., West, D. M., Holler, F. J., & Crouch, S. R. (2014). *Fundamentals of Analytical Chemistry* (IX Edition). United States of America: Cengage Learning.

Reference Books:

1. Skoog, D. A., Holler, F. J., & Crouch, S. R. (2007). *Principles of Instrumental Analysis* (VI Edition). United States of America: Thomson Brooks/Cole Publishers.

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LECTURE PLAN
DEPARTMENT OF CHEMISTRY

STAFF NAME: Dr. S.RAVI
SUBJECT NAME: Analytical Chemistry SUB.CODE:19CHP205B
SEMESTER: II CLASS: I-M.Sc (CHEMISTRY)

S.No.	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos
		UNIT-I	
1	1	Theoretical basis of quantitative inorganic analysis-common ion effect solubility product,	T1:203, 355-357
2	1	effect of acid, temperature and solvent upon the solubility of a precipitate.	T1: 361
3	1	Supersaturation-Von Weimarn concept. Formation and treatment of precipitates-co-precipitation and post-precipitation.	T1: 344-348
4	1	Precipitation from homogeneous solution. Specific and selective precipitants.	T1: 347
5	1	Principles of acid-base, oxidation-reduction, precipitation and complexometric titrations	T1: 374-376
6	1	indicators used in such titrations	T1: 378-380
7	1	Uses of organic reagents in inorganic quantitative and qualitative analysis.	T1: 349-350
8	1	Recapitulation	
	Total No of Hours Planned For Unit 1=08		
		UNIT-II	
1	1	Errors in chemical analysis-Defining terms: Mean median,	T1:97,98
2	1	accuracy and precision	T1:62-63
3	1	classification of errors: Systematic errors and random errors	T1: 63,64
4	1	Improving accuracy of analysis – mean, standard deviation and Q-test.	T1:72-74, 97-98

5	1	Comparison of results – Least square, 't'-test,	T1:84-88, 100-104
6	1	'F'-test and 'Chi' square test.	T1:84-88
7	1	Validation of analytical methods: Precision, accuracy, robustness, quantification, linearity and range.	T1:135-142
8	1	Recapitulation	
	Total No of Hours Planned For Unit II=08		
		UNIT-III	
1	1	Colorimetry: Theoretical and practical aspects of colorimetric analysis.	T1:790
2	1	Flame emission and atomic absorption spectroscopy	T1:553- 557
3	1	types of atomic spectroscopy – emission methods – absorption methods – fluorescence methods	T1: 558-560, 574-575
4	1	source and atomizers for atomic spectroscopy – flame atomizers – electrothermal atomizers –	T1: 560-564, 569-571
5	1	principle and applications of atomic absorption spectroscopy.	T1: 557-560
6	1	Advantages of atomic absorption spectrometry over flame photometry.	T1: 562-563
7	1	Recapitulation	
	Total No of Hours Planned For Unit III=07		
		UNIT-IV	
1	1	Cyclic voltammetry- principle and applications	T1: 467-469
2	1	Coulometry- principle and applications	T1:471
3	1	Amperometry- principle and applications	T1:472-473
4	1	Principle and applications of differential thermal analysis (DTA)	T2:483-489
5	1	differentials scanning calorimetry (DSC)	T2:489-493
6	1	thermogravimetric analysis (TGA) thermometric titration.	T2:478-482
7	1	Recapitulation	
	Total No of Hours Planned For Unit IV=07		
		UNIT-V	
1	1	Classification – techniques and applications in column chromatography	T1:603-605

2	1	size-exclusion, ion exchange - chromatography	T1:605-607
3	1	paper and thin layer chromatography	T1:608
4	1	Gas chromatography	T1:619-620
5	1	high performance liquid chromatography (HPLC	T1:651-670
6	1	principle, equipment design, sample injection system, columns, detectors and applications	T1:625-630, 665-674, 700-701
7	1	Recapitulation	
8	1	Discussion of previous year end semester question papers	
9	1	Discussion of previous year end semester question papers	
10	1	Discussion of previous year end semester question papers	
	Total No of Hours Planned for unit V=10		
Total Planned Hours	**40**		

Text Books:

1. Christian, G. D. (2007). *Analytical Chemistry* (VI Edition). United States: John Wiley & Sons.
2. Fifields, F.W. D.Kealey, (2000). Principles and Practice of Analytical Chemistry, 5th Edition, Blackwell science Ltd, Japan.

Unit-I

Quantitative Inorganic Analysis: Theoretical basis of quantitative inorganic analysis-common ion effect solubility product, effect of acid, temperature and solvent upon the solubility of a precipitate.
Supersaturation-Von Weimarn concept. Formation and treatment of precipitates-co-precipitation and post-precipitation. Precipitation from homogeneous solution. Specific and selective precipitants.
Principles of acid-base, oxidation-reduction, precipitation and complexometric titrations-indicators used in such titrations. Uses of organic reagents in inorganic quantitative and qualitative analysis.

Introduction

Analytical chemistry is concerned with the chemical characterization of matter and the answer to two important questions: what is it (qualitative analysis) and how much is it (quantitative analysis). Chemicals make up everything we use or consume, and knowledge of the chemical composition of many substances is important in our daily lives. Analytical chemistry plays an important role in nearly all aspects of chemistry, for example, agricultural, clinical, environmental, forensic, manufacturing, metallurgical, and pharmaceutical chemistry. The nitrogen content of a fertilizer determines its value. Foods must be analyzed for contaminants (e.g., pesticide residues) and for essential nutrients (e.g., vitamin content). The air we breathe must be analyzed for toxic gases (e.g., carbon monoxide). Blood glucose must be monitored in diabetics (and, in fact, most diseases are diagnosed by chemical analysis). The presence of trace elements from gun powder on a perpetrator's hand will prove a gun was fired by that hand.

The quality of manufactured products often depends on proper chemical proportions, and measurement of the constituents is a necessary part of **quality assurance**. The carbon content of steel will influence its quality. The purity of drugs will influence their efficacy.

Analytical Chemistry seeks ever improved means of measuring the chemical composition of natural and artificial materials. The techniques of this science are used to identify the substances which may be present in a material and to determine the exact amounts of the identified substance.

Analytical chemists serve the needs of many fields:

● In *medicine*, analytical chemistry is the basis for clinical laboratory tests which help physicians diagnose disease and chart progress in recovery.

● In *industry*, analytical chemistry provides the means of testing raw materials and for assuring the quality of finished products whose chemical composition is critical. Many household products, fuels, paints, pharmaceuticals, etc. are analyzed by the procedures developed by analytical chemists before being sold to the consumer.

● *Environmental quality* is often evaluated by testing for suspected contaminants using the techniques of analytical chemistry.

● The nutritional value of *food* is determined by chemical analysis for major components such as protein and carbohydrates and trace components such as vitamins and minerals. Indeed, even the calories in food are often calculated from its chemical analysis.

Analytical chemists also make important contributions to fields as diverse as forensics, archaeology, and space science.

The discipline of analytical chemistry consists of **qualitative analysis** and **quantitative analysis**. The former deals with the identification of elements, ions, or compounds present in a sample (we may be interested in whether only a given substance is present), while the latter deals with the determination of how much of one or more constituents is present. The sample may be solid, liquid, gas, or amixture. The presence of gunpowder residue on a hand generally requires only qualitative knowledge, not of how much is there, but the price of coal will be determined by the percent of undesired sulfur impurity present

Qualitative tests may be performed by selective chemical reactions or with the use of instrumentation. The formation of a white precipitate when adding a solution of silver nitrate in dilute nitric acid to a dissolved sample indicates the presence of a halide. Certain chemical reactions will produce colors to indicate the presence of classes of organic compounds, for example, ketones. Infrared spectra will give "fingerprints" of organic compounds or their functional groups.

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A clear distinction should be made between the terms **selective** and **specific**:

● A *selective* reaction or test is one that can occur with other substances but exhibits a degree of preference for the substance of interest.

● A *specific* reaction or test is one that occurs *only* with the substance of interest. Unfortunately, very few reactions are truly specific but many exhibit selectivity.

Selectivity may be also achieved by a number of strategies. Some examples are:

1. Sample preparation (e.g., extractions, precipitation)
2. Instrumentation (selective detectors)
3. Target analyte derivatization (e.g., derivatise specific functional groups)
4. Chromatography, which separates the sample constituents

For quantitative analysis, the typical sample composition will often be known (we know that blood contains glucose), or else the analyst will need to perform a qualitative test prior to performing the more difficult quantitative analysis. Modern chemical measurement systems often exhibit sufficient selectivity that a quantitative measurement can also serve as a qualitative measurement. However, simple qualitative tests are usually more rapid and less expensive than quantitative procedures. Qualitative analysis has historically been composed

of two fields: inorganic and organic. The former is usually covered in introductory chemistry courses, whereas the latter is best left until after the student has had a course in organic chemistry.

Common ion effect:

Whenever a solution of an ionic substance comes into contact with another ionic compound with a common ion, the solubility of the ionic substance decreases significantly. For example, this would be like trying to dissolve solid table salt (NaCl) in a solution where the chloride ion (Cl^-) is already present. The amount of NaCl that could dissolve to reach the saturation point would be lowered. This phenomenon is the common ion effect and plays important roles in pharmaceutical and environmental areas. The common ion effect can be explained by Le Chatelier's principle of chemical equilibrium:

We know that weak acids and weak bases slightly ionize in water and equilibrium is established in their solutions. The phenomenon of suppression of the degree of dissociation of a weak acid or a weak base by the addition of a strong electrolyte containing a common ion is known as common ion effect.

For example: let us consider the ionization of a weak base ammonium hydroxide i.e. NH_4OH as:

$NH_4OH\ (aq) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$

The ionization constant for the base will be:

$K_b = [NH_4^+]\,[OH^-] / [NH_4OH]$

If solid NH_4Cl is added to the solution, the concentration of NH_4^+ ions increases. According to Le-Chateliers's principle, the equilibrium shifts to the left. As a result, the concentration of OH^- is considerably decreased and the weak base NH_4OH becomes even weaker in the presence of its salt.

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

(Equilibrium shifts to left side)

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

This phenomenon is known as common ion effect

Calculate the equilibrium concentrations of A and B in a 0.10 *M* solution of a weak electrolyte AB with an equilibrium constant of 3.0 × 10−6.

$$AB \rightleftharpoons A + B \qquad K_{eq} = \frac{[A][B]}{[AB]}$$

Both [A] and [B] are unknown and equal. Let *x* represent their equilibrium concentrations.

The concentration of AB at equilibrium is equal to its initial analytical concentration minus *x*.

$$\begin{array}{rcccc} & \text{AB} & \rightleftharpoons & \text{A} & + & \text{B} \\ & 0.10 - x & & x & & x \end{array}$$

The value of *K*eq is quite small, so we are probably justified in neglecting *x* compared to 0.10. Otherwise, we will have to use a quadratic equation. Substituting into the *K*eq expression,

$$\frac{(x)(x)}{0.10} = 3.0 \times 10^{-6}$$

$$x = [\text{A}] = [\text{B}] = \sqrt{3.0 \times 10^{-7}} = 5.5 \times 10^{-4} M$$

After the calculation is done, check if the approximation you made was valid. Herethe calculated value of *x* can indeed be neglected compared to 0.10.

Assume that A and B are an ion pair, which can dissociate into A (a cation) and B (an anion). Recalculate the concentration of A in Example 6.4, assuming that the solution also contains 0.20 *M* B.

Solution

We can represent the equilibrium concentration as follows:

	[AB]	[A]	[B]
Initial	0.10	0	0.20
Change (x = mmol/mL of AB dissociated)	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	$0.20 + x$
	≈ 0.10		≈ 0.20

The value of *x* will be smaller now than before because of the common ion effect of B, so we can certainly neglect it compared to the initial concentrations. Substituting in the equilibrium constant expression,

$$\frac{(x)(0.20)}{(0.10)} = 3.0 \times 10^{-6}$$

$$x = 1.5 \times 10^{-6} M$$

The concentration of A was decreased nearly 400-fold.

The common ion effect can be used to make analytical reactions more favorable or quantitative. The adjustment of acidity, for example, is frequently used to shift equilibria.

Titrations with potassium dichromate, for example, are favored in acid solution, since protons are consumed in the reaction. Titrations with iodine, a weak oxidizing agent, are usually done in slightly alkaline solution to shift the equilibrium toward completion of the reaction, for example, in titrating arsenic(III):

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2I^- + 2H^+$$

Solubility product

A substances solubility product is the mathematical product of its dissolved ion concentrations raised to the power of their stoichiometric coefficients.

When substances have limited solubility and their solubility is exceeded, the ions of the dissolved portion exist in equilibrium with the solid material. So-called insoluble compounds generally exhibit this property.When a compound is referred to as insoluble, it is actually not completely insoluble but is **slightly soluble**. For example, if solid AgCl is added to water, a small portion of it will dissolve:

$$\underline{AgCl} \rightleftharpoons (AgCl)_{aq} \rightleftharpoons Ag^+ + Cl^-$$

The precipitate will have a definite solubility (i.e., a definite amount that will dissolve)in g/L, or mol/L, at a given temperature (a saturated solution). A small amount of undissociated compound usually exists in equilibrium in the aqueous phase (e.g., onthe order of 0.1%, although usually less for the precipitations employed for analysis,and depending on *K*sp), and its concentration is constant. It is difficult to measure the undissociated species, and we are interested in the ionized form as a measure of a compound's solubility and chemical availability. Hence, we can generally neglect the presence of any undissociated species.

We can write an overall equilibrium constant for the above stepwise equilibrium, called the **solubility product** *K*sp. *(*AgCl*)*aq cancels when the two stepwise equilibrium constants are multiplied together.

$$K_{sp} = [Ag^+][Cl^-]$$

The "concentration" of any solid such as AgCl is constant and is combined in the equilibrium constant to give *K*sp. The above relationship holds regardless of the presence of any undissociated intermediate; that is, the concentrations of free ions are rigorously defined by the above equation, and we will take these as a measure of a compound's solubility. From a knowledge of the value of the solubility product at a specified temperature, we can calculate the equilibrium solubility of the compounds. (The solubility product is determined in the reverse order, by measuring the solubility.)
The amount of a slightly soluble salt that dissolves does *not* depend on the amount of the solid in equilibrium with the solution, so long as some solid is present. Instead, the amount

that dissolves depends on the *volume* of the solvent. A nonsymmetric salt (one in which the cation and anion are not in the same ratio) such as Ag2CrO4 would have a *K*sp as follows:

$$Ag_2CrO_4 \rightleftharpoons 2\,Ag^+ + CrO_4^{2-}$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

Such electrolytes do not dissolve or dissociate in steps because they are really strong electrolytes. That portion that dissolves ionizes completely. *Therefore, we do not have stepwise* K*sp values*. As with any equilibrium constant, the *K*sp product holds under all equilibrium conditions at the specified temperature. Since we are dealing with heterogeneous equilibria, the equilibrium state is achieved more slowly than with homogeneous solution equilibria.

The *K*spof AgCl at 25◦C is 1.0×10^{-10}. Calculate the concentrations of Ag^+ and Cl^- in a saturated solution of AgCl, and the molar solubility of AgCl.

When AgCl ionizes, equal amounts of Ag^+ and Cl^- are formed; $AgCl \rightleftharpoons Ag^+ + Cl^-$ and $K_{sp} = [Ag^+][Cl^-]$. Let *s* represent the molar solubility of AgCl. Since each mole of AgCl that dissolves gives one mole of either Ag^+ or Cl^-, then

$$[Ag^+] = [Cl^-] = s$$

$$s^2 = 1.0 \times 10^{-10}$$

$$s = 1.0 \times 10^{-5}\ M$$

Effect of acid, temperature and solvent upon the solubility of a precipitate.

The solubility of a precipitate whose anion is derived from a weak acid will increase in the presence of added acid because the acid will tend to combine with the anion and thus remove the anion from solution. For example, the precipitate MA that partially dissolves to give M+ and A− ions will exhibit the following equilibria:

$$\left.\begin{array}{l} MA \rightleftharpoons M^+ + A^- \\ \qquad\quad + \\ \qquad\quad H^+ \\ \qquad\quad \uparrow\downarrow \\ \qquad\quad HA \end{array}\right\} A_T$$

The anion A− can combine with protons to increase the solubility of the precipitates. The combined equilibrium concentrations of A− and HA make up the total analytical concentration AT, of A, which will be equal to [M+] from the dissolved precipitate (if neither

M+ or A− is in excess). By applying the equilibrium constants for the equilibria involved, we can calculate the solubility of the precipitate at a given acidity.

Consider, for example, the solubility of CaC2O4 in the presence of a strong acid.

The equilibria are

$$\underline{CaC_2O_4} \rightleftharpoons Ca^{2+} + C_2O_4^{2-} \qquad K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 2.6 \times 10^{-9} \qquad (11.1)$$

$$C_2O_4^{2-} + H^+ \rightleftharpoons HC_2O_4^- \qquad K_{a2} = \frac{[H^+][C_2O_4^{2-}]}{[HC_2O_4^-]} = 6.1 \times 10^{-5} \qquad (11.2)$$

$$HC_2O_4^- + H^+ \rightleftharpoons H_2C_2O_4 \qquad K_{a1} = \frac{[H^+][HC_2O_4^-]}{[H_2C_2O_4]} = 6.5 \times 10^{-2} \qquad (11.3)$$

The solubility s of CaC_2O_4 is equal to $[Ca^{2+}] = Ox_T$, where Ox_T represents the concentrations of all the oxalate species in equilibrium ($= [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]$). We can substitute $Ox_T\alpha_2$ for $[C_2O_4^{2-}]$ in the K_{sp} expression:

$$\boxed{K_{sp} = [Ca^{2+}]Ox_T\alpha_2} \qquad (11.4)$$

where α_2 is the fraction of the oxalate species present as $C_2O_4^{2-}$ ($\alpha_2 = [C_2O_4^{2-}]/Ox_T$). Using the approach described in Chapter 7 for H_3PO_4 to calculate α's, we find that

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \qquad (11.5)$$

We can write, then, that

$$\boxed{\frac{K_{sp}}{\alpha_2} = K'_{sp} = [Ca^{2+}]Ox_T = s^2} \qquad (11.6)$$

where*K*_sp is the **conditional solubility product**, similar to the conditional formation constant.

Calculate the solubility of CaC_2O_4 in a solution containing 0.0010 M $[H^+]$.

Solution

$$\alpha_2 = \frac{(6.5 \times 10^{-2})(6.1 \times 10^{-5})}{(1.0 \times 10^{-3})^2 + (6.5 \times 10^{-2})(1.0 \times 10^{-3}) + (6.5 \times 10^{-2})(6.1 \times 10^{-5})}$$

$$= 5.7 \times 10^{-2}$$

$$s = \sqrt{K_{sp}/\alpha_2} = \sqrt{2.6 \times 10^{-9}/5.7 \times 10^{-2}} = 2.1 \times 10^{-4}\ M$$

Supersaturation-Von Weimarn concept.

Von Weimarn discovered that the particle size of precipitates is inversely proportional to the relative supersaturation of the solution during the precipitation process:

$$\text{Relative supersaturation} = \frac{Q - S}{S}$$

where$Q$ is the concentration of the mixed reagents *before* precipitation occurs, S is the **solubility**of the precipitate at equilibrium, and$Q - S$ is the **degree of supersaturation**. This ratio, $(Q - S)/S$, relative supersaturation, is also called the **von Weimarn ratio**.

As previously mentioned, when a solution is supersaturated, it is in a state of metastable equilibrium, and this favors rapid nucleation to form a large number of small particles. That is,

High relative supersaturation→ many small crystals *(*high surface area*)*
Low relative supersaturation→ fewer, larger crystals *(*low surface area*)*

Obviously, then, we want to keep Q low and S high during precipitation. Several steps are commonly taken to maintain *favorable conditions for precipitation*:

1. Precipitate from *dilute solution*. This keeps Q low.

2. Add dilute precipitating reagents *slowly*, with effective *stirring*. This also keeps Q low. Stirring prevents local excesses of the reagent.

3. Precipitate from *hot solution*. This increases S. The solubility should not be too great or the precipitation will not be quantitative (with less than 1 part per thousand remaining). The bulk of the precipitation may be performed in the hot solution, and then the solution may be cooled to make the precipitation quantitative.

4. Precipitate at as *low* a *pH* as is possible to maintain quantitative precipitation. As we have seen, many precipitates are more soluble in acid medium, and this slows the rate of precipitation. They are more soluble because the anion of the precipitate (which comes from a weak acid) combines with protons in the solution.

Formation and treatment of precipitates

After preparing the solution, the next step is to do the precipitation. Again, certain conditions are important. The precipitate should first be *sufficiently insoluble* that the amount lost due to solubility will be negligible. It should consist of *large crystals* that can be easily filtered. All precipitates tend to carry some of the other constituents of the solution with them. This contamination should be negligible. Keeping the crystals large can minimize this contamination.

We can achieve an appreciation of the proper conditions for precipitation by first looking at the **precipitation process**. When a solution of a precipitating agent is added to a test solution to form a precipitate, such as in the addition of $AgNO_3$ to a chloride solution to precipitate AgCl, the actual precipitation occurs in a series of steps. The precipitation process involves heterogeneous equilibria and, as such, is not instantaneous. The equilibrium condition is described by the solubility product. First, **supersaturation** occurs, that is, the solution phase contains more of the dissolved salt than it can carry at equilibrium. This is a metastable condition, and the driving force will be for the system to approach equilibrium (saturation). This is started by **nucleation**. For nucleation to occur, a minimum number of particles must come together to produce microscopic nuclei of the solid phase. The higher the degree of supersaturation, the greater the rate of nucleation. The formation of a greater number of nuclei per unit time will ultimately produce more total crystals of smaller size. The total crystal surface area will be larger, and there will be more danger that impurities will be adsorbed.

Although nucleation should theoretically occur spontaneously, it is usually induced, for example, on dust particles, scratches on the vessel surface, or added seed crystals of the precipitate (not in quantitative analysis).

Following nucleation, the initial nucleus will grow by depositing other precipitate particles to form a crystal of a certain geometric shape. Again, the greater the supersaturation, the more rapid the crystal growth rate. An increased growth rate increases the chances of imperfections in the crystal and trapping of impurities.

When the precipitation is performed, a slight excess of precipitating reagent is added to decrease the solubility by mass action (common ion effect) and to assure complete precipitation. A large excess of precipitating agent should be avoided because this increases chances of adsorption on the surface of the precipitate, in addition to being wasteful. If the approximate amount of analyte is known, a 10% excess of reagent is generally added. Completeness of precipitation is checked by waiting until the precipitate has settled and then adding a few drops of precipitating reagent to the clear solution above it. If no new precipitate forms, precipitation is complete.

DIGEST THE PRECIPITATE TO MAKE LARGER AND MORE PURE CRYSTALS

We know that very small crystals with a large specific surface area have a higher surface energy and a higher apparent solubility than large crystals. This is an initial rate phenomenon and does not represent the equilibrium condition, and it is one consequence of heterogeneous equilibria. When a precipitate is allowed to stand in the presence of the **mother liquor** (the solution from which it was precipitated), the large crystals grow at the expense of the small ones. This process is called **digestion**, or **Ostwald ripening**. Small particles have greater

surface energy associated with a greater surface area and display somewhat greater solubility than larger particles. The small particles tend to dissolve and reprecipitate on the surfaces of the larger crystals. In addition, individual particles **agglomerate** to effectively share a common counterion layer (see below), and the agglomerated particles finally *cement* together by forming connecting bridges. This noticeably decreases surface area.

IMPURITIES IN PRECIPITATES

Precipitates tend to carry down from the solution other constituents that are normally soluble, causing the precipitate to become contaminated. This process is called **coprecipitation**. The process may be equilibrium based or kinetically controlled. There are a number of ways in which a foreign material may be co precipitated.

1. Occlusion and Inclusion. In the process of **occlusion**, material that is not part of the crystal structure is trapped within a crystal. For example, water may be trapped in pockets when AgNO3 crystals are formed, and this can be removed to a degree by dissolution and recrystallization. If such mechanical trapping occursduring a precipitation process, the water will contain dissolved impurities. **Inclusion** occurs when ions, generally of similar size and charge, are trapped within the crystal lattice (isomorphous inclusion, as with K+ in NH4MgPO4 precipitation). These arenot equilibrium processes. Occluded or included impurities are difficult to remove. Digestion may helpsome but is not completely effective. The impurities cannot be removed by washing.Purification by dissolving and reprecipitating is helpful.

2. Surface Adsorption. As we have already mentioned, the surface of the precipitate will have a primary adsorbed layer of the lattice ions in excess. This results in **surface adsorption**, the most common form of contamination. For example, after barium sulfate is completely precipitated, the lattice ion in excess will be barium, and this will form the primary layer. The counterion will be a foreign anion, say, nitrate two for each barium. The net effect then is an adsorbed layer of barium nitrate, an equilibrium-based process. These adsorbed layers can often be removed by washing,or they can be replaced by ions that are readily volatilized. Gelatinous precipitates are especially troublesome, though. Digestion reduces the surface area and, therefore, theadsorbed amount.

3. Isomorphous Replacement. Two compounds are said to be **isomorphous** if they have the same type of formula and crystallize in similar geometric forms. When their lattice dimensions are about the same, one ion can replace another in a crystal, resulting in a **mixed crystal**. This process is called **isomorphous replacement** orisomorphous substitution. For example, in the precipitation of Mg2+ as magnesium ammonium phosphate, K+ has nearly the same ionic size as NH4+ and can replace it to form magnesium potassium phosphate. Isomorphous replacement, when it occurs, causes major interference, and little can be done about it. Precipitates in which it occurs are seldom used analytically. Chloride cannot be selectively determined by precipitation as AgCl, for example, in the presence of other halides and vice versa. Mixed crystal formation is a form of equilibrium precipitate formation, although it may be influenced by the rate of precipitation. Such a mixed precipitate is akin to

a solid solution. The mixed crystal may be spatially homogeneous if the crystal is in equilibrium with the final solution composition (homogeneous coprecipitation) or heterogenous if it is in instaneous equilibrium with the solution as it forms (heterogenouscoprecipitation), as the solution composition changes during precipitation.

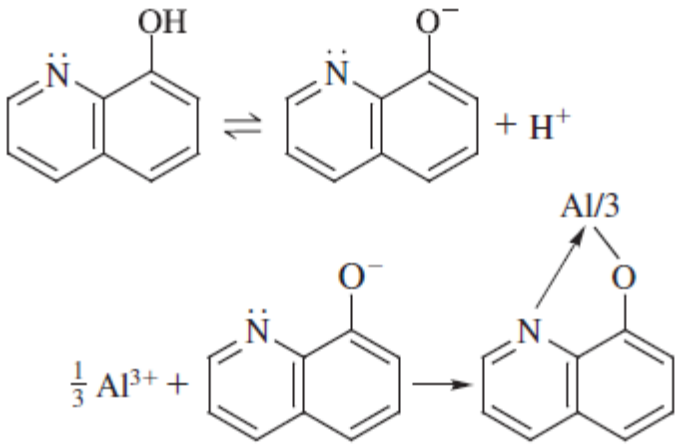
4. Postprecipitation. Sometimes, when the precipitate is allowed to stand in contact with the mother liquor, a second substance will slowly form a precipitate with the precipitating reagent. This is called **postprecipitation**. For example, when calcium oxalate is precipitated in the presence of magnesium ions, magnesium oxalate does not immediately precipitate because it tends to form supersaturated solutions. But it will precipitate if the solution is allowed to stand too long before being filtered. Similarly, copper sulfide will precipitate in acid solution in the presence of zinc ions without zinc sulfide being precipitated, but eventually zinc sulfide will precipitate. Postprecipitation is a slow equilibrium process.

Precipitation from homogeneous solution.Specific and selective precipitants.

The first step in performing gravimetric analysis is to prepare the solution. Some formof preliminary separation may be necessary to eliminate interfering materials. Also,we must adjust the solution conditions to maintain low solubility of the precipitate and to obtain it in a form suitable for filtration. Proper adjustment of the solution conditions prior to precipitation may also mask potential interferences. Factors that must beconsidered include the volume of the solution during precipitation, the concentration range of the test substance, the presence and concentrations of other constituents, thetemperature, and the pH.

Although preliminary separations may be required, in other instances the precipitation step in gravimetric analysis is sufficiently selective that other separations are not required. The pH is important because it often influences both the solubilityof the analytical precipitate and the possibility of interferences from other substances.

For example, calcium oxalate is insoluble in basic medium, but at low pH the oxalateion combines with the hydrogen ions to form a weak acid and begins to dissolve.8-Hydroxyquinoline (oxine—also known as 8-quinolinol) can be used to precipitate alarge number of elements, but by controlling pH, we can precipitate elements selectively.Aluminum ion can be precipitated at pH 4, but the concentration of the anionform of oxine is too low at this pH to precipitate magnesium ion; magnesium oxinatehas a much greater solubility product.



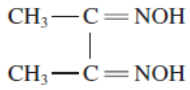
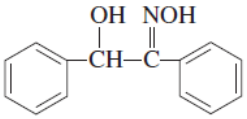
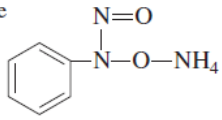
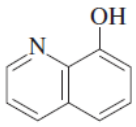
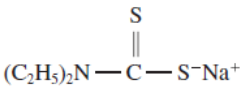
A higher pH is required to shift the ionization step to the right in order to precipitate magnesium. If the pH is too high, however, magnesium hydroxide will precipitate, causing interference.

All the precipitating agents we have talked about so far, except for oxine, cupferrate, and dimethylglyoxime, have been inorganic in nature. There are also a large number of organic compounds that are very useful precipitating agents for metals. Some of these are very selective, and others are very broad in the number of elements they will precipitate. Organic precipitating agents have the advantages of giving precipitates with verylow solubility in water and a favorable gravimetric factor. Most of them are **chelating agents** that form slightly soluble, uncharged **chelates** with the metal ions. A chelating agent is a type of complexing agent that has two or more groups capable of complexing with a metal ion. The complex formed is called a chelate. Since chelating agents are weak acids, the number of elements precipitated, and thus the selectivity, can usually be regulated by adjustment of the pH. The reactionscan be generalized as (the underline indicates what is precipitated):

$$M^{n+} + nHX \rightleftharpoons \underline{MX_n} + nH^+$$

There may be more than one ionizable proton on the organic reagent. The weaker the metal chelate, the higher the pH needed to achieve precipitation. Some of the commonly used organic precipitants are listed in Table. Some of these precipitates are not stoichiometric, and more accurate results are obtained by igniting them to form the metal oxides. Some, such as sodium diethyldithiocarbamate, can be used to perform group separations, as is done with hydrogen sulfide.

Some Organic Precipitating Agents

Reagent	Structure	Metals Precipitated
Dimethylglyoxime		Ni(II) in NH_3 or buffered HOAc; Pd(II) in HCl ($M^{2+} + 2HR \rightarrow \underline{MR_2} + 2H^+$)
α -Benzoinozime (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ ($M^{2+} + H_2R \rightarrow \underline{MR} + 2H^+$; $M^{2+} = Cu^{2+}$, MoO_2^{2+}, WO_2^{2+}) Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) ($M^{n+} + nNH_4R \rightarrow \underline{MR_n} + nNH_4^+$) Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) ($M^{n+} + nHR \rightarrow \underline{MR_n} + nH^+$)
Sodium diethyldithiocarbamate		Many metals from acid solution ($M^{n+} + n$NaR $\rightarrow \underline{MRn} + n$$Na^+$)
Sodium tetraphenylboron	$NaB(C_6H_5)_4$	K^+, Rb^+, Cs^+, Tl^+, Ag^+, Hg(I), Cu(I), NH_4^+, RNH_3^+, $R_2NH_2^+$, R_3NH^+, R_4N^+. Acidic solution ($M^+ + NaR \rightarrow \underline{MR} + Na^+$)
Tetraphenylarsonium chloride	$(C_6H_5)_4AsCl$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-. Acidic solution ($A^{n-} + n$RCl $\rightarrow R_nA + n$$Cl^-$)

Principles of acid-base, oxidation-reduction, precipitation and complexometric titrations-

There are four general classes of volumetric or titrimetric methods.

1. *Acid–Base.* Many compounds, both inorganic and organic, are either acids or bases and can be titrated, respectively, with a standard solution of a strong base or a strong acid. The end points of these titrations are easy to detect, either by meansof an indicator or by following the change in pH with a pH meter. The acidity and basicity of many organic acids and bases can be enhanced by titrating in a *nonaqueous solvent*. The result is a sharper end point, and weaker acids and basescan be titrated in this manner.

2. *Precipitation.* In the case of precipitation, the titrant forms an insoluble productwith the analyte. An example is the titration of chloride ion with silver nitratesolution to form silver chloride precipitate. Again, indicators can be used to detectthe end point, or the potential of the solution can be monitored electrically.

3. *Complexometric.* In complexometric titrations, the titrant is a reagent that forms a water-soluble complex with the analyte, a metal ion. The titrant is often a **chelating agent**.6 Ethylenediaminetetraacetic acid (EDTA) is one of the mostuseful chelating agents used for

titration. It will react with a large number of metalions, and the reactions can be controlled by adjustment of pH. Indicators can beused to form a highly colored complex with the metal ion.

4. *Reduction–Oxidation.* These "redox" titrations involve the titration of an oxidizingagent with a reducing agent, or vice versa. An oxidizing agent gains electronsand a reducing agent loses electrons in a reaction between them. There must bea sufficiently large difference between the oxidizing and reducing capabilities ofthese agents for the reaction to go to completion and give a sharp end point; that is,one should be a fairly strong oxidizing agent (strong tendency to gain electrons)and the other a fairly strong reducing agent (strong tendency to lose electrons).Appropriate indicators for these titrations are available; various electrometricmeans to detect the end point may also be used.

An acid–base titration involves a **neutralization** reaction in which an acid is reacted with an equivalent amount of base. By constructing a **titration curve**, we can easily explain how the **end points** of these titrations can be detected. The end point signals the completion of the reaction. A titration curve is constructed by plotting the pH of the solution as a function of the volume of titrant added. *The titrant is always a strong acid or a strong base*. The analyte may be either a strong base or acid or a weak baseor acid.

The calculations of titration curves simply involve computation of the pH from the concentration of the particular species present at the various stages of the titration. The volume changes during the titration must be taken into account when determining the concentration of the species.

Detection of the End Point: Indicators

Carrying out the titration process is of little value unless we can tell exactly when the acid has completely neutralized the base, i.e., when the equivalence point has been reached. Therefore, we wish to determine accurately when the equivalence point is reached. The point at which the reaction is *observed to be complete* is called the **end point**. A measurement is chosen such that the end point coincides with or is very close to the equivalence point. The difference between the equivalence point and the end point is referred to as the **titration error**; as with any measurement, we want to minimize error. The most obvious way of determining the end point is to measure the pH at different points of the titration and make a plot of this versus milliliters of titrant. This is done with a pH meter.

It is often more convenient to add an **indicator** to the solution and visually detecta color change. An indicator for an acid–base titration is a weak acid or weak base that is highly colored. The color of the ionized form is markedly different from that of then onionized form. One form may be colorless, but at least one form must be colored.These substances are usually composed of highly conjugated organic constituents thatgive rise to the color.
Assume the indicator is a weak acid, designated HIn, and assume that thenonionized form is red while the ionized form is blue:

$$\underset{\text{(red)}}{\text{HIn}} \rightleftharpoons \text{H}^+ + \underset{\text{(blue)}}{\text{In}^-}$$

We can write a Henderson–Hasselbalch equation for this, just as for other weak acids:

$$\text{pH} = \text{p}K_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

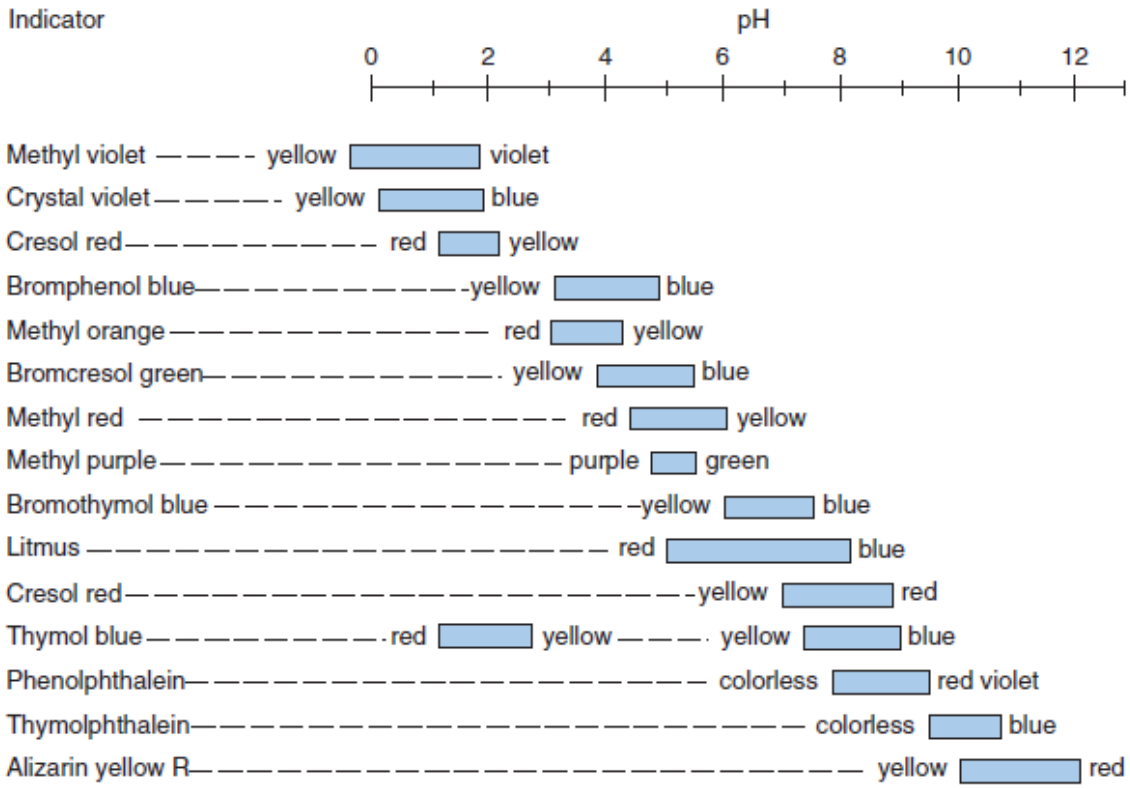
The indicator changes color over a pH **range**. The transition range depends on the ability of the observer to detect small color changes. With indicators in which both forms are colored, generally only one color is perceived if the ratio of the concentrationof the two forms is 10:1, if the molar absorptivities (Chapter 16), i.e., color intensities,of each are not too different; only the color of the more concentrated form is visuallysensed. From this information, we can calculate the pH transition range required togo from one color to the other. When only the color of the nonionized form is seen,[In−]/[HIn] = 1/10 . Therefore,

$$\text{pH} = \text{p}K_a + \log \frac{1}{10} = \text{p}K_a - 1$$

When only the color of the ionized form is observed, [In−]/[HIn] = 10/1 and

$$\text{pH} = \text{p}K_a + \log \frac{10}{1} = \text{p}K_a + 1$$

So the pH in going from one color to the other has changed from p*Ka*− 1 to p*Ka*+ 1.This is a pH change of 2, and *most indicators require a transition range of about two pH units*. During this transition, the observed color is a mixture of the two colors. Midway in the transition, the concentrations of the two forms are equal, and pH = p*Ka*. Obviously, then, *the p*Ka*of the indicator should be close to the pH of the* near*equivalence point*.



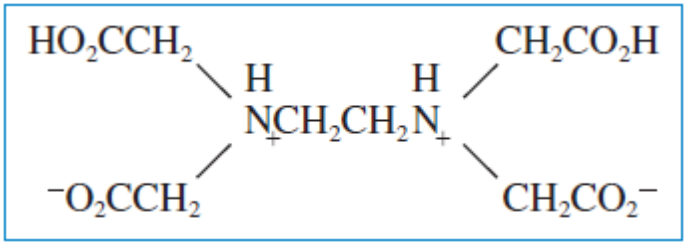
Since an indicator is a weak acid or base, the amount added should be kept minimal so that it does not contribute appreciably to the pH and so that only a small amount of titrant will be required to cause the color change. That is, the color change will be sharper when the concentration is lower because less acid or base is required to convert it from one form to the other. Of course, sufficient indicator must be added to impart an easily discernible color to the solution. Generally, a few tenths percent solution (wt/vol) of the indicator is prepared and two or three drops are added to the solution to be titrated.

Complexometric titrations

Simple complexing agents such as ammonia are rarely used as titrating agents because a sharp end point corresponding to a stoichiometric complex is generally difficult to achieve. This is because the stepwise formation constants are frequently close together and are not very large, and a single stoichiometric complex cannot be observed. Certain complexing agents that have two or more complexing groups on the molecule, however, do form well-defined complexes and can be used as titrating agents. Schwarzenbach demonstrated that a remarkable increase in stability is achieved if a bidentate ligand (one with two complexing groups) is used. For example, he showed replacing ammonia with the bidentate ethylenediamine,NH2CH2CH2NH2 (en), results in a highly stable Cu(en)2 2+ complex.
The most generally useful titrating agents are aminocarboxylic acids, in which the amino nitrogen and carboxylate groups serve as ligands. The amino nitrogens are more basic and are protonated (−NH3+) more strongly than the carboxylate groups. When these groups bind to metal atoms, they lose their protons. The metal complexes formed with these multidentatecomplexing agents are often 1:1, regardless of the charge on the metal ion,

because there are sufficient complexing groups on one molecule to satisfy all the coordination sites of the metal ion.

An organic agent that has two or more groups capable of complexing with ametalThe protons in ion is called a **chelating agent**. The complex formed is called a **chelate**. The chelatingagent is called the *ligand*. Titration with a chelating agent is called a **chelometric titration**, perhaps the most important and practical type of complexometric titrations.The most widely used chelating agent in titrations is **ethylenediaminetetraaceticacid (EDTA)**. The formula for EDTA is

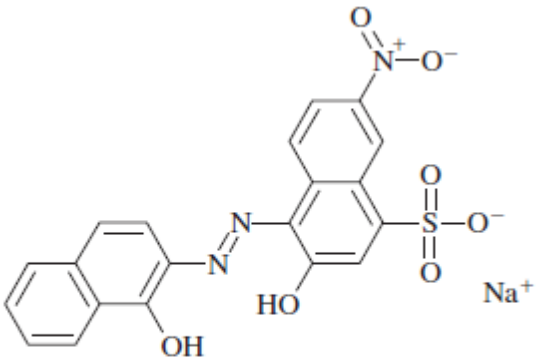


Each of the two nitrogens and each of the four carboxyl groups contains a pair of unshared electrons capable of complexing with a metal ion. Thus, EDTA contains six complexinggoups.

Detection of the End Point: Indicators—They Are Also Chelating Agents

We can measure the pMpotentiometrically if a suitable electrode is available, for example, an ion-selective electrode (see Chapter 13), but it is simpler if an indicator can be used. Indicators used for complexometric titrations are themselves chelating agents. They are usually dyes of the *o*, *o*_-dihydroxyazo type.

Eriochrome Black T is a typical indicator. It contains three ionizable protons, so we will represent it by H3In. This indicator can be used for the titration of Mg2+ with EDTA. A small amount of indicator is added to the sample solution, and it forms a red complex with part of the Mg2+; the color of the uncomplexed indicator is blue. As soon as all the free Mg2+ is titrated, the EDTA displaces the indicator from the magnesium, causing a change in the color from red to blue:



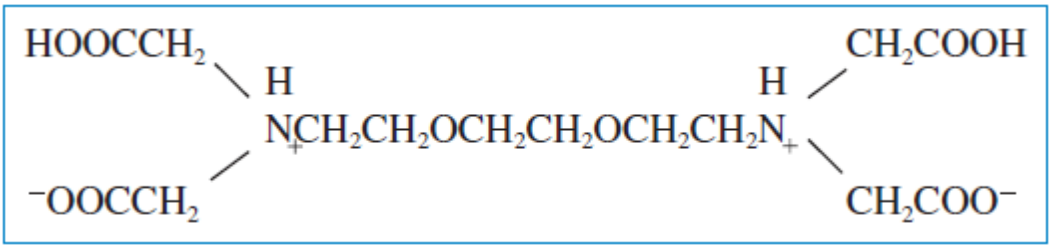
Eriochrome Black T

$$MgIn^- + H_2Y^{2-} \rightarrow MgY^{2-} + HIn^{2-} + H^+$$
(red) (colorless) (colorless) (blue)

This will occur over a range of pMg values, and the change will be sharper if the indicator is kept as dilute as possible but is still sufficient to give a good color change. Of course, the metal–indicator complex must be less stable than the metal–EDTA complex, or else the EDTA will not displace it from the metal. On the other hand, it must not be too weak, or the EDTA will start replacing it at the beginning of the titration, and a diffuse end point will result. In general, *the Kf for the metal–indicator complex should be 10 to 100 times less than that for the metal–titrant complex*.

Since Eriochrome Black T and other indicators are weak acids, their colors will depend on the pH because their ionized species have different colors. Thus, indicators can be used over definite pH ranges. It should be emphasized, though, that although complexometricindidators respond
to pH, their mechanism of action does not involve changes in pH, as the solution is buffered. But the pH affects the stability of the complex formed between the indicator and the metal ion, as well as that formed between EDTA and the metal ion. An indicator is useful for indication of titrations of only those metals that form a more stable complex with the titrant than with the indicator at the given pH. This may sound complex but suitable indicators are known for many titrations with several different chelating agents.

There are a number of other useful reagents for complexometric titrations. AEGTA allows the notable example is ethyleneglycolbis (*β*-aminoethyl ether)-N, N, N_, N_-tetraacetic acid (**EGTA**). This is an ether analog of EDTA that will selectively titrate calcium in the presence of magnesium



REDOX titration Indicators

Obviously, the end point can be determined by measuring potential with an indicating electrode relative to a reference electrode and plotting this against the volume of titrant. But as in other titrations, it is usually more convenient to use an indicator that can be observed with the naked eye.

SELF-INDICATION

If the titrant is highly colored, this color may be used to detect the end point. For example, a 0.02 *M* solution of potassium permanganate is deep purple. A dilute solution of potassium permanganate is pink. The product of its reduction, Mn2+, is extremely faint pink, nearly colorless. During a titration with potassium permanganate, the purple color of the MnO4 − is removed as soon as it is added because it is reduced to Mn2+. As soon as the titration is complete, a fraction of a drop of excess MnO4−solution imparts a definite pink color to the solution, indicating that the reaction is complete. Obviously, the end point does not occur at the equivalence point, but at a fraction of a drop beyond. The titration error is small and can be corrected for by running a blank titration, or it is accounted for in standardization.

STARCH INDICATOR

This indicator is used for titrations involving iodine. Starch forms a complex with I2 that is a dark-blue color. The color reaction is sensitive to very small amounts of iodine and is not very reversible. In titrations of reducing agents with iodine, the solution remains colorless up to the equivalence point. A fraction of a drop of excess titrant turns the solution a definite blue.

REDOX INDICATORS

The above two methods of end-point indication do not depend on the half-reaction potentials, although the completeness of the titration reaction and hence the sharpness Compare redox indicators with of the end point do. Examples such as these first two methods of visual indication are few, and most other types of redox titrations are detected using **redox indicators**. These
are highly colored dyes that are weak reducing or oxidizing agents that can be oxidized or reduced; the colors of the oxidized and reduced forms are different. The oxidation state of the indicator and hence its color will depend on the potential at a given point in the titration. A half-reaction and Nernst equation can be written for the indicator:

$$Ox_{ind} + ne^- \rightleftharpoons Red_{ind}$$

$$E_{ind} = E^0_{ind} - \frac{0.05916}{n} \log \frac{[Red_{ind}]}{[Ox_{ind}]}$$

The half-reaction potentials during the titration determine *E*In and hence the ratio of [Redind]/[Oxind]. This is analogous to the ratio of the different forms of a pH indicator being determined by the pH of the solution. So the ratio, and therefore the color, will change as the potential changes during the titration. If we assume, as with acid–base indicators, that the ratio must change from 10/1 to 1/10 in order that a sharp color change can be seen, then *a potential equal to 2 × (0.05916/*n*) V is required*. If *n* for the indicator is equal to 1, then a 0.12V change is required. If *E*0 ln*is near the equivalence point potential* of the titration, where there is a rapid change in potential in excess of 0.12 V, then the color change occurs at the equivalence point. Again, this is analogous to the requirement that the p*Ka*value of an acid–base indicator be nearthe pH of the equivalence point.

Redox Indicators

Indicator	Color		Solution	E^0 (V)
	Reduced Form	Oxidized Form		
Nitroferroin	Red	Pale blue	1 *M* H_2SO_4	1.25
Ferroin	Red	Pale blue	1 *M* H_2SO_4	1.06
Diphenylaminesulfonic acid	Colorless	Purple	Diluted acid	0.84
Diphenylamine	Colorless	Violet	1 *M* H_2SO_4	0.76
Methylene blue	Blue	Colorless	1 *M* acid	0.53
Indigo tetrasulfonate	Colorless	Blue	1 *M* acid	0.36

Redox indicators for appropriate indication of the end point have a transition range over a certain potential, and this transition range must fall within the steepequivalence point break of the titration curve. The redox indicator reaction must beboth *rapid*, and it must be *reversible*. If the reaction is slow or is *irreversible* (slowrate of electron transfer), the color change will be gradual and the end point will notbe sharp.

Possible questions

2 mark questions

1. A. State and explain common ion effect with suitable examples
2. What is meant by solubility product. What are its applications
3. Explain the terms (i) precipitation (ii) co-precipitation (iii) Post precipitation
4. Explain Von Weimarn concept. Explain the process involved during the precipitation

5. Differentiate co-precipitation and post precipitation

8 mark questions

1. Explain the principle and types of acid base titrations
2. Describe the complexometric titrations with suitable indicators
3. Explain the use of organic reagents in inorganic quantitative analysis
4. Discuss in detail about (i) Oxidation-reduction titration (ii) Precipitation titrations.
5. Discuss the uses of organic reagents in inorganic qualitative analysis.
6. Explain the factors affecting the different stages of precipitation

KARPAGAM ACADEMY OF HIGHER EDUCATION

CLASS: IMSc CHEMISTRY COURSE NAME: ANALYTICAL CHEMISTRY

COURSE CODE: 18CHP205B UNIT: I (Quantitative Inorganic Analysis) BATCH:2018-2020

Analytical Chemistry

S.No	Question	a	b	c	d	Answer
1	Analytical chemists serve the needs of many fields. In *medicine*, analytical chemistry is the basis for	clinical laboratory tests	testing raw materials	testing for suspected contaminants	nutritional value of *food*	clinical laboratory tests
2	Analytical chemists serve the needs of many fields. In *industry*, analytical chemistry is the basis for	clinical laboratory tests	testing raw materials	testing for suspected contaminants	nutritional value of *food*	testing raw materials
3	Analytical chemists serve the needs of many fields. In *Environmental science*, analytical chemistry is the basis for	clinical laboratory tests	testing raw materials	testing for suspected contaminants	nutritional value of *food*	testing for suspected contaminants
4	Analytical chemists serve the needs of many fields. In *Food Industry*, analytical chemistry is the basis for	clinical laboratory tests	testing raw materials	testing for suspected contaminants	nutritional value of *food*	nutritional value of *food*
5	In Analytical chemistry clinical laboratory tests are carried out in	Medicinal field	Industry	Environmental science	Food Industry	Medicinal field
6	In Analytical chemistry testing of raw materials are carried	Medicinal field	Industry	Environmental science	Food Industry	Industry

	out in					
7	In Analytical chemistry testing of contaminants are carried out in	Medicinal field	Industry	Environmental science	Food Industry	Environmental science
8	In Analytical chemistry testing of nutritional value are carried out in	Medicinal field	Industry	Environmental science	Food Industry	Food Industry
9	The test is one that can occur with other substances but exhibits a degree of preference for the substance of interest	Selective reaction	Specific reaction	Targeted reaction	Spot test	Selective reaction
10	The test is one that occurs *only* with the substance of interest	Selective reaction	Specific reaction	Targeted reaction	Spot test	Specific reaction
11	Whenever a solution of an ionic substance comes into contact with another ionic compound with a common ion, the solubility of the ionic substance	Increases significantly	Decreases significantly	Remains the same	Cannot be determined	Decreases significantly
12	The suppression of dissociation of a weak electrolyte by the addition of a strong electrolyte having a common ion is called	Solubility product	Common ion effect	Ionic product of water	Dissociation constant	Common ion effect
13	The dissociation of acetic acid may be suppressed by the addition of	Ammonium chloride	Sodium chloride	Ammonium phosphate	Sodium acetate	Sodium acetate
14	The dissociation of ammonium Hydroxide may be suppressed by the addition of	Ammonium chloride	Sodium chloride	Ammonium phosphate	Sodium acetate	Ammonium chloride

15	The common ion effect can be explained by	Solubility product	Gaussian distribution	Le Chatelier's principle	Faradays laws	Le Chatelier's principle
16	When the product of ionic concentrations of a salt exceeds the solubility product then the salt will	precipitate	Be more soluble	Ionize more	Dissociate more	precipitate
17	When the product of ionic concentrations of a salt is lower than the solubility product then the salt will	Precipitate	Be more soluble	coagulate	peptise	Be more soluble
18	Von Weimarn discovered that during the precipitation process the particle size of precipitates is inversely proportional to the	concentration of the mixed reagents *before* precipitation	degree of supersaturation.	relative supersaturation of the solution:	Degree of dissociation	relative supersaturation of the solution:
19	when a solution is supersaturated, it is in a state of metastable equilibrium, and this favours	Dissociation of the electrolyte	rapid nucleation to form a large number of small particles	vapourisation	sublimation	rapid nucleation to form a large number of small particles
20	When von Weimarn ratio is very high, then it favours	many small crystals with high surface area	many large sized crystals with high surface area	fewer, larger crystals with low surface area	fewer, larger crystals with large surface area	many small crystals with high surface area
21	When von Weimarn ratio is very low, then it favours	many small crystals with high surface area	many large sized crystals with high surface area	fewer, larger crystals with low surface area	fewer, larger crystals with large surface area	fewer, larger crystals with low surface area

22	To maintain *favorable conditions for precipitation*:	*Q value should be* low	*Q value should be* high	*Q value should be* zero	*Q value should be* negative	*Q value should be* low
23	To maintain *favorable conditions for precipitation*:	*S value should be* low	*S value should be* high	*S value should be* zero	*S value should be* negative	*S value should be* high
24	One among the following is required To maintain *favorable conditions for precipitation*:	*dilute solution*	Without effective *stirring*	*Cold solution*	High PH	*dilute solution*
25	One among the following is required To maintain *favorable conditions for precipitation*:	*Concentrated solution*	effective *stirring*	*Cold solution*	High PH	effective *stirring*
26	One among the following is required To maintain *favorable conditions for precipitation*:	*Concentrated solution*	Without effective *stirring*	*Hot solution*	High PH	*Hot solution*
26	One among the following is required To maintain *favorable conditions for precipitation*:	*Concentrated solution*	Without effective *stirring*	*Cold solution*	Low PH	Low PH
27	During a precipitation process the first step is	*Super saturation*	Nucleation	*Ostwald ripening*	Digestion	*Super saturation*
28	During a precipitation process once the solution is supersaturated, which takes place	*Coagulation*	Nucleation	*Ostwald ripening*	Digestion	Nucleation
29	During a precipitation	*Coagulation*	Nucleation	*Ostwald*	supersaturation	*Ostwald ripening*

	process after the nucleation which takes place			*ripening*		
30	If the solution phase contains more of the dissolved salt than it can carry at equilibrium.	*Coagulation*	Nucleation	*Ostwald ripening*	supersaturation	supersaturation
31	A minimum number of particles must come together to produce microscopic nuclei of the solid phase. This is called	*Coagulation*	Nucleation	*Ostwald ripening*	supersaturation	Nucleation
32	The process which is usually induced, for example, on dust particles, scratches on the vessel surface, or added seed crystals of the precipitate	*Coagulation*	Nucleation	*Ostwald ripening*	supersaturation	Nucleation
33	Larger crystals grow in the expense of the smaller crystals, the process is called	*Coagulation*	Nucleation	*Ostwald ripening*	supersaturation	*Ostwald ripening*
34	Larger crystals grow in the expense of the smaller crystals, the process is called	*Coagulation*	Nucleation	*Digestion*	supersaturation	Digestion
35	When Precipitates tend to carry down from the solution other constituents that are normally soluble, causing the precipitate to	*Co-precipitation*	Post precipitation	Occlusion	Inclusion	*Co-precipitation*

	become contaminated. This is called					
36	The process in which the material that is not part of the crystal structure is trapped within a crystal	*Co-precipitation*	Post precipitation	Occlusion	Isomorphism	Occlusion
37	The process in which the material that is not part of the crystal structure is trapped within a crystal	*Co-precipitation*	Post precipitation	Inclusion	Isomorphism	Inclusion
38	Which occurs when ions, generally of similar size and charge, are trapped within the crystal lattice	*Co-precipitation*	Post precipitation	Inclusion	Isomorphism	Inclusion
39	the surface of the precipitate will have a primary adsorbed layer of the lattice ions in excess and is termed as	*Surface adsorption*	Post precipitation	Inclusion	Isomorphism	*Surface adsorption*
40	Two compounds are said to be **isomorphous** if they have the	Different formula and crystallize in similar geometric forms	same type of formula and crystallize in different geometric forms	same type of formula and do not form crystals	same type of formula and crystallize in similar geometric forms	same type of formula and crystallize in similar geometric forms
41	when the precipitate is allowed to stand in contact with the mother liquor, a second substance will slowly form a precipitate with the precipitating reagent	*Co-precipitation*	Post precipitation	Inclusion	Isomorphism	Post precipitation
42	8-Hydroxyquinoline is otherwise called	*Oxine*	EDTA	*DDT*	DMG	*Oxine*

43	Oxine is also called	8-Hydroxyquinoline	Ethylene diammine tetra acetic acid	*Dimethyl glyoxime*	Oxalic acid	8-Hydroxyquinoline
44	The complexing agent that has two or more groups capable of complexing with a metal ion is called	Chelate	Chelating agent	*Double salt*	Peptising agent	Chelating agent
45	The product formed when a complexing agent forms a complex with a metal	Chelate	Chelating agent	*Double salt*	Peptising agent	Chelate
46	Usually the chelating agents are	Weakly basic	Weakly acidic	*Strongly basic*	Strongly acidid	Weakly acidic
47	Dimethyl glyoxime is used to precipitate	Nickel	Iron	*Potassium*	Magnesium	Nickel
48	Mostly 8-Hydroxyquinoline is used to precipitate	Nickel	Iron	*Potassium*	Magnesium and aluminium	Magnesium and aluminium
49	If the titrant and the analyte are a weak acid and a base respectively, then it is called	*Acid–Base titration*	*Precipitation titration*	*Complexometric. titration*	*Reduction–Oxidation titration*	*Acid–Base titration*
50	If the titrant forms an insoluble product with the analyte, then it is called	*Acid–Base titration*	*Precipitation titration*	*Complexometric. titration*	*Reduction–Oxidation titration*	*Precipitation titration*
51	If the titrant is a reagent that forms a water-soluble complex with the analyte, a metal ion	*Acid–Base titration*	*Precipitation titration*	*Complexometric. titration*	*Reduction–Oxidation titration*	*Complexometric. titration*
52	The titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa is called	*Acid–Base titration*	*Precipitation titration*	*Complexometric. titration*	*Redox titration*	*Redox titration*

53	Substances which are used to find the end point of a titration ae called	Indicators	Chelating agents	*Chelates*	Catalysts	Indicators
54	In an indicator the ionised form and the unionised form will have	Same colour	Different colour	*Same structure*	Same morphology	Different colour
55	The indicator which has an working range in basic PH	Methyl orange	Phenolpthalein	*Crystal violet*	Cresol red	Phenolpthalein
56	The indicator which has an working range in acidic PH	Methyl orange	Phenolpthalein	*Alizarin yellow*	Thymolpthalin	Methyl orange
57	Erichrome Black T is a	Weak acid	Chelating agent	*Complexometric titration indicator*	Weak base	*Complexometric titration indicator*
58	Which can be used aa an indicator for complexometric titrations	Methyl orange	Phenolpthalein	*Alizarin yellow*	Erichrome Black T	Erichrome Black T
59	Using EDTA which can be estimated	Calcium	sodium	*Potassium*	Lithium	Calcium
60	Using EDTA which can be estimated	Magnesium	sodium	*Potassium*	Lithium	Magnesium

Unit-II

Data Analysis: Errors in chemical analysis-Defining terms: Mean median, accuracy and precision – classification of errors: Systematic errors and random errors. Improving accuracy of analysis – mean, standard deviation and Q-test. Comparison of results – Least square, 't'-teat, 'F'-test and 'Chi' square test. Validation of analytical methods: Precision, accuracy, robustness, quantification, linearity and range.

Data Analysis: Errors in chemical analysis-Defining terms: Mean median, accuracy and precision

Accuracy is the degree of agreement between the measured value and the true value. An absolute true value is seldom known. A more realistic definition of accuracy, then, would assume it to be the agreement between a measured value and the *accepted* true value.

We can, by good analytical technique, such as making comparisons against a known standard sample of similar composition, arrive at a reasonable assumption about the accuracy of a method, within the limitations of the knowledge of the "known" sample (and of the measurements). The accuracy to which we know the value of the standard sample is ultimately dependent on some measurement that will have a given limit of certainty in it.

Precision is defined as the degree of agreement between replicate measurements Good
of the same quantity. That is, it is the repeatability of a result. The precision may be accuracy.
expressed as the standard deviation, the coefficient of variation, the range of the data,or as a confidence interval (e.g., 95%) about the mean value. Good precision does notassure good accuracy. This would be the case, for example, if there were a systematicerror in the analysis. The volume of a pipet used to dilute each of the samples may bein error. This error does not affect the precision, but it does affect the accuracy. Onthe other hand, the precision can be relatively poor and the accuracy may be good;admittedly, this is very rare. Since all real analyses are unknown, the higher the degreeof precision, the greater the chance of obtaining the true value. It is fruitless to hopethat a value is accurate despite the precision being poor; and the analytical chemiststrives for repeatable results to assure the highest possible accuracy.

These concepts can be illustrated with targets, as in Figure 3.1. Suppose you are at target practice and you shoot the series of bullets that all land in the bull's-eye (lefttarget). You are both precise and accurate. In the middle target, you are precise (steadyhand and eye), but inaccurate. Perhaps the sight on your gun is out of alignment. In theright target you are imprecise and therefore probably inaccurate. So we see that goodprecision is needed for good accuracy, but it does not guarantee it.As we shall see later, reliability increases with the number of measurementsmade. The number of measurements required will depend on the level of uncertaintythat is acceptable and on the known reproducibility of the method.

Determinate Errors—They Are Systematic

Two main classes of errors can affect the accuracy or precision of a measured quantity.

Determinate errors are those that, as the name implies, are determinable and that presumably can be either avoided or corrected. They may be constant, as in the case of an uncalibrated pipet that is used in all volume deliveries. Or, they may be variable but of such a nature that they can be accounted for and corrected, such as a buret whose volume readings are in error by different amounts at different volumes.

The error can be proportional to sample size or may change in a more complex manner. More often than not, the variation is unidirectional, as in the case of solubility loss of a precipitate due to its solubility (negative error). It can, however, be random in sign, i.e., a positive or negative error. Such an example is the change in solution volume and concentration occurring with changes in temperature. This can be corrected for by measuring the solution temperature. Such measurable determinate errors are classed as **systematic errors**.

Some common determinate errors are:

1. *Instrumental errors.* These include faulty equipment such as uncalibrated glassware.

2. *Operative errors.* These include personal errors and can be reduced byexperience and care of the analyst in the physical manipulations involved.Operative errors can be minimized by having a checklist of operations.Operations in which these errors may occur include transfer of solutions,effervescence and "bumping" during sample dissolution, incomplete dryingof samples, and so on. These are difficult to correct for. Other personalerrors include mathematical errors in calculations and prejudice in estimatingmeasurements.

3. *Errors of the method.* These are the most serious errors of an analysis. Most ofthe above errors can be minimized or corrected for, but errors that are inherentin the method cannot be changed unless the conditions of the determinationare altered. Some sources of methodical errors include coprecipitationof impurities, slight solubility of a precipitate, side reactions, incompletereactions, and impurities in reagents. Sometimes correction can be relatively simple, for example, by running a **reagent blank**. A blank determination is ananalysis on the added reagents only. It is standard practice to run such blanksand to subtract the results from those for the sample. But a good blank analysisalone cannot guarantee correct measurements. If the method, for example,responds to an analyte present in the sample other than the intended analyte,the method must be altered. Thus, when errors become intolerable, anotherapproach to the analysis must be made. Sometimes, however, we are forcedto accept a given method in the absence of a better one.

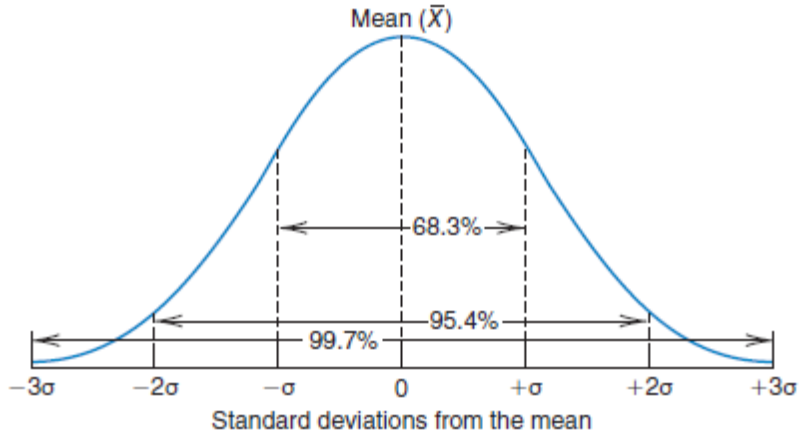
Determinate errors may be *additive* or *multiplicative*, depending on the nature of the error or how it enters into the calculation. In order to detect systematic errors in an analysis, it is common practice to add a known amount of standard to a sample (a "spike") and measure its recovery and note that good spike recovery cannot also correct for response from an unintended analyte(i.e., an interference). The analysis of reference samples helps guard against method errors or instrumental errors.

It is always a good idea to run a blank.

Indeterminante Errors

The second class of errors includes the **indeterminate errors**, often called accidental or random errors, which represent the experimental uncertainty that occurs in any measurement. These errors are revealed by small differences in successive measurements made by the same analyst under virtually identical conditions, and they cannot be predicted or estimated. These accidental errors will follow a random distribution; therefore, mathematical laws of probability can be applied to arrive at some conclusion regarding the most probable result of a series of measurements.

It is beyond the scope of this text to go into mathematical probability, but we can say that indeterminate errors should follow a **normal distribution**, or **Gaussian curve**. Such a curve is shown in. The symbol σ represents the *standard deviation* of an infinite population of measurements, and this measure of precision defines the spread of the normal population distribution as shown in Figure. It is apparent that there should be few very large errors and that there should be an equalnumber of positive and negative errors.



Indeterminate errors really originate in the limited ability of the analyst to control or make corrections for external conditions, or the inability to recognize the appearanceof factors that will result in errors. Some random errors stem from the intrinsic natureof things, for example, consider that a sample of the radionuclide 129I is taken. Theisotope is long lived, and in a short time there will not be a perceptible change in itsnumber. But, if a sufficient amount is taken, then based on the half-life, you can expecta decay to occur every 60 s. In reality, this may not occur every 60 s, but can fluctuate,with an average of 60 s. Sometimes, by changing

conditions, some unknown errorwill disappear. Of course, it will be impossible to eliminate all possible random errorsin an experiment, and the analyst must be content to minimize them to a tolerable orinsignificant level.

Indeterminate errors are random and cannot be avoided.

"Undetectable errors are infinite in variety, in contrast to detectable errors, which by definition arelimited."

Significant Figures: How Many Numbers Do You Need?

The last digit of a measurement has some uncertainty. You can't include any more digits.

The weak link in the chain of any analysis is the measurement that can be made with the least accuracy or precision. It is useless to extend an effort to make the other measurements of the analysis more accurately than this limiting measurement. The number of significant figures can be defined as **the number of digits necessary to express the results of a measurement consistent with the measured precision**.Since there is uncertainty (imprecision) in any measurement of at least ±1 in the last significant figure, the number of significant figures includes all of the digits that are known, plus the first uncertain one. In reported answers, it generally does not make sense to include additional digits beyond the first uncertain one. Each digit denotes the actual quantity it specifies. For example, in the number 237, we have 2 hundreds, 3 tens, and 7 units. If this number is reported as a final answer, it implies that uncertainty lies in the units digit (e.g., ±1).

The digit 0 can be a significant part of a measurement, or it can be used merely to place the decimal point. The number of significant figures in a measurement is independent of the placement of the decimal point. Take the number 92,067. This number has five significant figures, regardless of where the decimal point is placed. For example, 92, 067 μm, 9.2067 cm, 0.92067 dm, and 0.092067m all have the same number of significant figures. They merely represent different ways (units) of expressing one measurement. The zero between the decimal point and the 9 in the last number is used only to place the decimal point. There is no doubt whether any zero that *follows* a decimal point is significant or is used to place the decimal point. In the number 727.0, the zero is not used to locate the decimal point but is a significant
part of the figure. Ambiguity can arise if a zero *precedes* a decimal point. If it falls between two other nonzero integers, then it will be significant. Such was the case with 92,067. In the number 936,600, it is impossible to determine whether one or both or neither of the zeros is used merely to place the decimal point or whether they are a part of the measurement. It is best in cases like this to write only the significant figures you are sure about and then to locate the decimal point by scientific notation. Thus, 9.3660 × 105 has five significant

figures, but 936,600 contains six digits, one to place the decimal. Sometimes, the number may be written with a period at the end to denote all digits are significant, e.g., 936,000. to avoid amiguity.

List the proper number of significant figures in the following numbers and indicatewhich zeros are significant.
0.216; 90.7; 800.0; 0.0670

Solution

0.216 three significant figures
90.7 three significant figures; zero is significant
800.0 four significant figures; all zeros are significant
0.0670 three significant figures; only the last zero is significant _

If a number is written as 500, it could represent 500 ± 100. If it is written as 5.00×10^2,then it is 500 ± 1.

The significance of the last digit of a measurement can be illustrated as follows.

Assume that each member of a class measures the width of a classroom desk, using the same meter stick. Assume further that the meter stick is graduated in 1-mm increments. The measurements can be estimated to the nearest 0.1 division (0.1 mm) by interpolation, but the last digit is uncertain since it is only an estimation. A series of class readings, for example, might be

565.4 mm
565.8 mm
565.0 mm
566.1 mm

565.6 mm *(*average*)*

Standard Deviation—The Most Important Statistic

Each set of analytical results should be accompanied by an indication of the **precision** of the analysis. Various ways of indicating precision are acceptable.

The standard deviation σ of an infinite set of experimental data is theoretically given by

$$\sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{N}}$$

where*xi* represents the individual measurements and μ represents the mean of an infinite number of measurements (which should represent the "true" value). This equation holds strictly only as $N \rightarrow \infty$, where N is the number of measurements. In practice, we must calculate the individual deviations from the mean of a limited number of measurements, x, in

which it is anticipated that $x \rightarrow \mu$ as $N \rightarrow \infty$, although we have no assurance this will be so; x is given by_*(xi/N)*. average, x = _*(xi/N)*

For a set of N measurements, there are N (independently variable) deviations from some reference number. But if the reference number chosen is the estimated mean, x, the sum of the individual deviations (retaining signs) must necessarily add up to zero, and so values of $N - 1$ deviations are adequate to define the Nth value. That is, there are only $N - 1$ independent deviations from the mean; when $N - 1$ values have been selected, the last is predetermined. We have, in effect, used one degree of freedom of the data in calculating the mean, leaving $N - 1$ **degrees of freedom** for calculating the precision.

As a result, the **estimated standard deviation** s **of a finite set of experimental data** (generally N <30) more nearly approximates σ if $N - 1$, the number of degrees of freedom, is substituted for N ($N - 1$ adjusts for the difference between x and μ).

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

The value of s is only an estimate of σ, and it will more nearly approach σ as the number of measurements increases. Since we deal with small numbers of measurements in an analysis, the precision is appropriately represented by s.

Example

Calculate the mean and the standard deviation of the following set of analytical results: 15.67, 15.69, and 16.03 g.

Solution

x_i	$x_i - \bar{x}$	$(x_i - \bar{x})^2$
15.67	0.13	0.0169
15.69	0.11	0.0121
16.03	0.23	0.0529
$\sum$ 47.39	$\sum$ 0.47	$\sum$ 0.0819

$$\bar{x} = \frac{\sum x_i}{N} = \frac{47.39}{3} = 15.80$$

$$s = \sqrt{\frac{0.0819}{3 - 1}} = 0.20 \text{ g}$$

THE STUDENT *t*-TEST——ARE THERE DIFFERENCES IN THE METHODS?

Frequently, the analyst wishes to decide whether there is a statistical difference between the results obtained using two different procedures, that is, whether they both indeed measure the same thing. The *t*-test is very useful for such comparisons. In this method, comparison is made between two sets of replicate measurements made by two different methods; one of them will be the *test method*, and the other will be an *accepted* or benchmark method. In a similar manner, we may be comparing the blood concentration of a particular analyte in a population of diabetic patients vs. those measured in a control group. A statistical *t* value is calculated and compared with a tabulated value for the given number of tests at the desired confidence level
(Table 3.1). If the calculated *t* value *exceeds* the tabulated *t* value, then there is a *significant difference* between the results by the two methods at that confidence level. If it does not exceed the tabulated value, then we can predict that there is no significant difference between the methods at the confidence level we have chosen. This in no way implies that the two results are identical.

There are several ways and several different types of situations in which a *t*-test can be used. Consider the following cases:

1. You have taken a certified single sample for which the analytical result is exactly known or is known with a degree of certainty much higher than you expect from your test method. You analyze the same sample by the test method a number of times with an objective to determine if there is no difference between the certified value and the mean value obtained by your method at a specified degree of certainty.

2. The situation is the same as above except that the uncertainty of the certified value or the standard deviation of measurements by a reference method is not negligible. You compare repeated measurements of the same single sample made by the reference method with repeated measurements made by the test method. This is often referred to as *t-test by*

comparison of the means. The number of measurements in the two measurement sets need not be the same.

3. Often the intent is to compare a newly developed method with another, and a certified reference standard is not available. Further, even if a reference standard is available, it can only check a method at only one concentration and it will be desirable to check the applicability of the method spanning the entire range of concentrations in which the method is to be used. You take a *number of different samples* spanning the concentration range of interest. All samples are divided in two parts; one set is analyzed by the benchmark method and the other by the test method. The pairs of analytical results thus generated are subjected to the *paired t-test* to determine if the two methods produce results that are statistically different at a specified confidence level. This test is also useful in other situations. For example, it can be used to answer the question: Does a new drug cause a statistically different change in blood pressure
compared to another? A number of people are studied and each person is examined twice for a change in blood pressure: once after administration of drug 1 and another time after administration of drug 2. Necessarily, equal numbers of sampled data exist for each measurement set in a paired *t*-test.

4. You want to compare two sample populations that are unrelated to each other. Is coal from West Virginia statistically different in its sulfur content compared to coal from Pennsylvania? Are post-mortem brain tissue data for aluminum content statistically different in Alzheimer affected subjects compared to control subjects? Note that unlike the preceding example, in this case, two different sample populations are tested and the numbers in each population do not have to be equal. This type of *t*-test can be subdivided in two groups: (a) when the variance or standard deviations of the two sample sets being compared are statistically the same (as determined, e.g.,
by the *F*-test), the two sample sets are said to be *homoscedastic*, (b) when the variance of the two sample sets are statistically different, the sample populations are *heteroscedastic*.

Rejection of a Result: The Q Test

When a series of replicate analyses is performed, it is not uncommon that one of the results will appear to differ markedly from the others. A decision will have to be made whether to reject the result or to retain it. Unfortunately, there are no uniform criteria that can be used to decide if a suspect result can be ascribed to accidental error rather than chance variation. It is tempting to delete extreme values from a data set because they alter the calculated statistics in an unfavourable way, that is, increase the standard deviation and variance (measures of spread), and they may substantially alter the reported mean. The only reliable basis for rejection occurs when it can be decided that some specific error may have been made in obtaining the doubtful result. No result should be retained in cases where a known error has occurred in its collection.

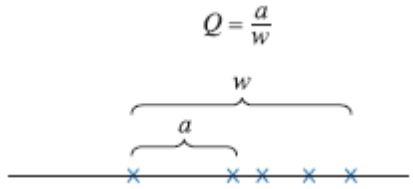
Experience and common sense may provide just as practical a basis for judging the validity of a particular observation as a statistical test would be. Frequently, the experienced analyst

will gain a good idea of the precision to be expected in a particular method and will recognize when a particular result is suspect.

Additionally, an analyst who knows the standard deviation expected of a method may reject a data point that falls outside 2*s* or 2.5*s* of the mean because there is about 1 chance in 20 or 1 chance in 100 this will occur. A wide variety of statistical tests have been suggested and used to determine whether an observation should be rejected. In all of these, a range is established within which statistically significant observations should fall. The difficulty with all of them is determining what the range should be. If it is too small, then perfectly good data will be rejected; and if it is too large, then erroneous measurements will be retained too high a proportion of the time. The ***Q* test** is, among the several suggested tests, one of the most statistically correct for a fairly small number of observations and is recommended when a test is necessary. The ratio *Q* is calculated by arranging the data in increasing or decreasing order of numbers. If you have a large data set, you will find the Data/Sort function in Excel very helpful to arrange the data either in ascending or descending order. The difference between the suspect number and its nearest neighbour *(a)* is divided by the range *(w)*, the range being the difference between the highest number and the lowest number. Referring to the figure in the margin, $Q = a/w$. This ratio is compared with tabulated values of *Q*. If it is equal to or greater than tabulated value, the suspected observation can be rejected. The tabulated values of *Q* at the 90, 95, and 99% confidence levels are given in Table 3.3. If *Q* exceeds the tabulated value for a given number of observations and a given confidence level, the questionable measurement may be rejected with, for example, 95% confidence tha tsome definite error is in this measurement.

Rejection Quotient, *Q*, at Different Confidence Limits[a]

No. of Observations	Confidence Level		
	Q_{90}	Q_{95}	Q_{99}
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568
15	0.338	0.384	0.475
20	0.300	0.342	0.425
25	0.277	0.317	0.393
30	0.260	0.298	0.372



Linear Least Squares—How to Plot the Right Straight Line

The analyst is frequently confronted with plotting data that fall on a straight line, as in an analytical calibration curve. Graphing, that is, curve fitting, is critically important in obtaining accurate analytical data. It is the calibration graph that is used to calculate the unknown concentration. Straight-line predictability and consistency will determine the accuracy of the unknown calculation. All measurements will have a degree of uncertainty, and so will the plotted straight line. Graphing is often done intuitively,that is, by simply "eyeballing" the best straight line by placing a ruler through the points, which invariably have some scatter. A better approach is to apply statistics to define the most probable straight-line fit of the data. The availability of statisticalfunctions in spread sheets today make it straightforward to prepare straight-line, or even nonlinear, fits. We will first learn the computations that are involved in curvefitting and statistical evaluation.

We should note that a straight line is a model of the relationship between observations and amount of an analyte. One can always blindly apply least squares fitting (see below) to any random set of numbers. That does not necessarily mean a linear model is appropriate. Perhaps one should be fitting logarithms, or should be fitting sigmoids. We fit models to data, not data to models. To some extent, we prefer systems that are linear because they're easier to deal with. However, with facile availability of computation, we need not always avoid nonlinearity.If a straight-line relationship is assumed, then the data fit the equation

$y = mx + b$

where*y* is the *dependent variable*, *x* is the *independent variable*, *m* is the *slope*, ofthe curve, and *b* is the *intercept* on the ordinate (*y* axis); *y* is usually the measuredvariable, plotted as a function of changing *x* (see Figure 3.4). In a spectrophotometriccalibration curve, *y* would represent the measured absorbances and *x* would be theconcentrations of the standards. Our problem, then, is to establish values for *m* and *b*.

LEAST-SQUARES PLOTS

It can be shown statistically that the best straight line through a series of experimentalpoints is that line for which the *sum of the squares of the deviations (the residuals) ofthe points from the line is minimum*. This is known as the **method of least squares**. If *x*is the fixed variable (e.g., concentration) and *y* is the measured variable (absorbance ina spectrophotometric measurement, the peak area in a chromatographic measurement,etc.), then the deviation of *y* vertically from the line at a given value of *x (xi)* is ofinterest. If *yl*is the value *on the line*, it is equal to *mxi + b*. The square of the sum ofthe differences, *S*, is then

$S = \_(yi - yl)^2 = \_[yi - (mxi + b)]^2$

This equation assumes no error in *x*, the independent variable.

Tests of Significance—Is There a Difference?

In developing a new analytical method, it is often desirable to compare the results ofthat method with those of an accepted (perhaps standard) method. How, though, canone tell if there is a significant difference between the new method and the acceptedone? Again, we resort to statistics for the answer.

Deciding whether one set of results is significantly different from another dependsnot only on the difference in the means but also on the amount of data available and thespread. There are statistical tables available that show how large a difference needs tobe in order to be considered not to have occurred by chance. The *F*-test evaluates differencesbetween the spread of results, while the *t*-test looks at differences between means.

THE *F*-TEST

This is a test designed to indicate whether there is a significant difference between two different. methods based on their standard deviations. *F* is defined in terms of the variances ofthe two methods, where the **variance** is the square of the standard deviation:

$$F = \frac{s_1^2}{s_2^2}$$

where$s_1^2 > s2^2$. . There are two different degrees of freedom, $v1$ and $v2$, where degreesof freedom is defined as $N - 1$ for each case.If the calculated *F* value from Equation 3.10 exceeds a tabulated *F* value at theselected confidence level, then there is a significant difference between the variancesof the two methods.

Validation of Analytical Methods

First identify the problem and the Method validation is the process of documenting or proving that an analytical methodprovides analytical data acceptable for the intended use.

The basic concept of the validation process encompasses two aspects:

- The**problem** and the data requirements
- The**method** and its performance characteristics

VALIDATION PROCESS

The need to validate a method and the procedure to be followed are matters ofprofessional judgment; fairly well-prescribed procedures and guidelines are nowavailable that aid in decision making.

- Selectivity
- Linearity
- Accuracy
- Precision
- Sensitivity
- Range
- Limit of detection
- Limit of quantitation
- Ruggedness or robustness

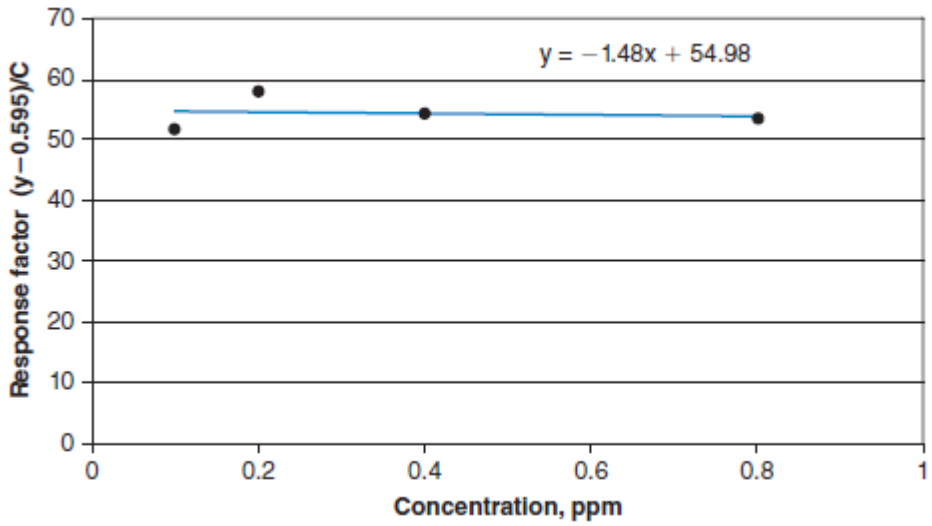
SELECTIVITY

The **matrix** is everything in the Selectivity is the extent that the method can measure the analyte of interest inthe matrices of the samples being analyzed without interference from the matrix(including other analytes). Matrix effects may be either positive or negative. Theanalytical response of the analyte in the presence of potential sample components iscompared with the response of a solution containing only the analyte. The selectionof an appropriate measurement methodology is a key consideration. Methods, evenpreviously validated in general terms, may not be assured to be valid for a particularsample matrix.

LINEARITY

A linearity study verifies that the response is linearly proportional to the analyteconcentration in the concentration range of sample solutions. The study should beperformed using standard solutions at five concentration levels, in the range of 50to 150% of the target analyte concentration. Five concentration levels should allowdetection of curvature on the calibration curve. Each standard should be measured atleast three times.

Linearity data are often judged from the coefficient of determination *(r*2*)* andthe *y* intercept of the linear regression line. An *r*2 value of >0.998 is considered asevidence of acceptable fit of the data to the regression line. The *y* intercept should be asmall percentage of the analyte target concentration, for example, <2%. While thesestatistical evaluations are a practical way to assess linearity, they do not guaranteeit. You should always do a visual inspection of the calibration curve. The linearitywill often deviate somewhat at high and low values. (This is the reason *weighted*least-squares plots may be preferred. In one mode of weighted least squares, thepoints with the least relative deviation are given more weight in the regression line.)One way of evaluating the range of linearity is to plot a *response factor* (RF) versusconcentration.



Response factor = *(*signal − *y* intercept*)/*concentration

If a plot with zero slope is obtained, this indicates that a linear response is obtained over this concentration range. A response factor change over the calibration concentrationrange within, for example, 2 to 3%of the target-level response factor or the average RFmay be considered acceptable linearity. In Figure the regression line is $y = mx + b$.The y intercept is 0.595. A plot of the response factor versus concentration is shown. The slope of the line is −1.48 RF/1 ppm. This corresponds to −1.0 overthe concentration range 0.1 to 0.8 ppm, which is 1.8% of the average RF value of 54.4.This is acceptable linearity.

If a calibration curve deviates from linearity over the 50 to 150% target-levelrange, selection of a narrower range of, for example, 80 to 120% may provide thedesired linearity.

ACCURACY

Accuracy of a method is the closeness of the obtained value to the true value for thesample. This is probably the most difficult parameter to validate. One should considerthe sampling and sample treatment, in addition to the measurement method accuracy.Accuracy of the method can be determined in one of three ways. The most preferredfirst, in order, these are:

(a) Analysis of a reference material
(b) Comparison with results using another method known to be accurate
(c) Recovery studies

(a) is preferred; if one can't do (a) then (b) is second choice and (c) third choice.

Recovery studies are performed by spiking (adding) a known amount of the analyteeither to a blank matrix (a sample that has an unmeasurable level of the test analyte)or by spiking a sample in which the background analyte is measured by the sameprocedure and subtracting from the total *(*sample + spike*)* value to obtain the recovery.The spiked samples should be prepared at three levels, the extremes and the midrange.They should be prepared at least in triplicate.Good spike recovery cannot, however, ensure lack of positive interferences.

Abetter validation method is to perform the analysis by *two independent methods*, inwhich the second method is an accepted procedure known to be accurate for thesample matrix of interest. Ideally, even the sample treatment should be different. Youcan often find in the scientific iterature (journals, reference books, standard methodsbooks) a method that is applicable to your sample (but that may not be appropriate touse because of expense, unavailability of equipment, etc.). If none can be found thathas been applied to your sample matrix, but one is known to be generally applicableand accurate, then use this. If results by your method and the second method agree, thatis good evidence they both work for your sample. If there is disagreement, then it isnot possible to draw any conclusions since either

may give erroneous results with yourparticular sample, although it is probably more likely your new method is the culprit.

PRECISION

The precision of an analytical method is obtained from multiple analyses of ahomogeneous sample. You can determine overall precision of the method, includingsample preparation. Such precision data are obtained by one laboratory on one day,using aliquots of the homogeneous sample that have been independently prepared.

Such intralaboratory precision is called *repeatability*. Interlaboratory precision, ifappropriate, is also determined as part of a measurement of *reproducibility* or*robustness* of the method (see below).You can also determine the precision of different steps of the analysis, forexample, the precision of injecting a sample into a gas chromatograph determinedfrom multiple injections of the same sample solution. Again, statistical considerationsdictate that at least seven measurements should be made for each evaluation step.

SENSITIVITY

The sensitivity is determined by the slope of the calibration curve and generally reflects the ability to distinguish two different concentrations. You can measure the slope or measure samples of closely related concentrations at high, intermediate, andlow concentrations. The sensitivity and precision will govern how many significantfigures should be reported in a measurement. Do not report 11.25% when the methodcan at most distinguish a 0.1% difference.

RANGE

The working range of a method is the concentration range over which acceptableaccuracy and precision are obtained. Usually it also includes linearity. The acceptableaccuracy and precision are generally specified in establishing a method. The precisionwill, of course, vary with the concentration, becoming poorer at low concentrations as well as sometimes at high concentrations, as in spectrophotometricmeasurements.

RUGGEDNESS/ROBUSTNESS

We have defined the precision of a method. *Repeatability* is the long-term precisionover several weeks for an analysis conducted in the same laboratory. *Ruggedness* refersto the precision of one lab over multiple days, which may include multiple analysts,multiple instruments, different sources of reagents, different chromatographic columns,and the like. A ruggedness study will identify those factors that will contribute tovariability of the results and should not be changed. This is related to *robustness* or*reliability* of the method, which refers to how sensitive it is to deliberate or uncontrolledsmall changes in parameters, such as the size of the sample, the temperature, pH of thesolution, reagent concentration, time of reaction, and so forth. It includes an evaluationof the stability of reagents, standards, and samples with time. Each parameter should betested separately, unless statistically more sophisticated factorial analysis experiments
for varying several parameters at once are designed, which we will not go into here.

Reproducibility (or *transferability*) is the analysis of the same sample between labs, in which a homogeneous sample is analyzed by multiple labs with one lab serving as the primary comparison lab. A reproducibility study generally focuses on *bias* between labs, besides precision. One strives for a bias that is within defined acceptable limits.

SUGGESTED MATERIALS

1. Svehla, G. (2002). *Vogel's Qualitative Inorganic Analysis* (VII Edition). Singapore: Pearson Education.
2. Christian, G. D. (2007). *Analytical Chemistry* (VI Edition). United States: John Wiley & Sons.
3. Skoog, D. A., West, D. M., Holler, F. J., & Crouch, S. R. (2014). *Fundamentals of Analytical Chemistry* (IX Edition). United States of America: Cengage Learning.

Section-A
(Online examination)
20x1= 20 Marks

Possible questions

1. Explain with suitable examples the terms (i) Mean (ii) Median (iii) Mode
2. What are errors. Explain the classification of errors
3. Write notes on (i) Systematic errors (ii) Random errors
4. Compare and contrast systematic errors and random errors
5. Explain the terms accuracy and precision with examples.
6. Find the standard deviation for the following data series: 12, 6, 7, 3, 15, 10, 18, 5
7. What is meant by "Q' test. Determine whether 167 is an outlier in this set of data? Test at the 167, 180, 188, 177, 181, 185, 189
8. What is meant by "t" test. Explain the steps involved in the calculation of "t" test.
9. Explain the Validation of analytical methods: Precision, accuracy, robustness, quantification, linearity and range.
10. Write notes on Least square, 'F'-test and 'Chi' square test.

KARPAGAM ACADEMY OF HIGHER EDUCATION

CLASS: IMSc CHEMISTRY COURSE NAME: ANALYTICAL CHEMISTRY

COURSE CODE: 18CHP205B UNIT: II (Data Analysis) BATCH:2018-2020

Analytical Chemistry

S.No	Question	a	b	c	d	Answer
1.	Determinate Errors are otherwise called as	Systematic errors	Accidental errors	Random errors	False errors	Systematic errors
2.	Indeterminate Errors are otherwise called as	Systematic errors	Accidental errors	Determinant errors	False errors	Accidental errors
3.	Indeterminate Errors are otherwise called as	Systematic errors	Random errors	Determinant errors	False errors	Random errors
4.	Example for an Instrumental errors	uncalibrated glassware	personal errors	Inherent in the method	small differences in successive measurements	uncalibrated glassware
5.	Which is an operative error	uncalibrated glassware	personal errors	Inherent in the method	small differences in successive measurements	personal errors
6.	Which is called Errors of the method	uncalibrated glassware	personal errors	Experimental conditions	small differences in successive measurements	Experimental conditions
7.	Experimental conditions is an example for	Errors of the method	operative error	Instrumental errors	Random errors	Errors of the method
8.	Coprecipitation of impurities during precipitation is	Errors of the method	operative error	Instrumental errors	Random errors	Errors of the method
9.	small differences in successive measurements	Errors of the method	operative error	Instrumental errors	Random errors	Random errors
10.	slight solubility of a precipitate is	Errors of the method	operative error	Instrumental errors	Random errors	Errors of the method

11.	side reactions is an example for	Errors of the method	operative error	Instrumental errors	Random errors	Errors of the method
12.	Incomplete reactions is an example for	Errors of the method	operative error	Instrumental errors	Random errors	Errors of the method
13.	Impurities in reagents is an example for	Errors of the method	operative error	Instrumental errors	Random errors	Errors of the method
14.	uncalibrated glassware is an example for	Errors of the method	operative error	Instrumental errors	Random errors	Instrumental errors
15.	Personal errors is an example for	Errors of the method	operative error	Instrumental errors	Random errors	Operative errors
16.	Which is not an Errors of the method	Personal error	Impurities in reagents	Incomplete reactions	slight solubility of a precipitate	Personal error
17.	Which is not an Errors of the method	uncalibrated glassware	Impurities in reagents	Coprecipitations of impurities	slight solubility of a precipitate	uncalibrated glassware
18.	Which is not an Errors of the method	small differences in successive measurements	Impurities in reagents	Coprecipitations of impurities	slight solubility of a precipitate	small differences in successive measurements
19.	Determinant errors are	Additive and multiplicative	Subtractive	divisive	Subtractive and divisive	Additive and multiplicative
20.	The number of digits necessary to express the results of a measurement consistent with the measured precision is called	Accuracy	Validation	Robstness	Significant figures	Significant figures
21.	Calculate the mean of the following set of analytical results: 15.67, 15.69, and 16.03 g.	15.67	15.69	16.03	15.80	15.80
22.	Calculate the median of the following set of analytical results:	15.67	15.69	16.03	15.80	15.69

	15.67, 15.69, and 16.03 g.					
23.	The technique used to decide whether there is a statistical difference between the results obtained using two different procedures	't' test	'Q'Test	'F'Test	Validation	't' test
24.	There is a *significant difference* between the results measured by the two methods, then	*t* value *exceeds* the tabulated *t* value	*Qt* value *exceeds* the tabulated *t* value	*'q'* value *exceeds* the tabulated 'q' value	*t* value remains the same as the tabulated *t* value	*t* value *exceeds* the tabulated *t* value
25.	The two sample sets are said to be *homoscedastic*	when the standard deviations of the two sample sets being compared are statistically the same	when the standard deviations of the two sample sets being compared are statistically different	when the standard deviations of the two sample sets is equal to zero	when the standard deviations of the two sample sets are equal to 100	when the standard deviations of the two sample sets being compared are statistically the same
26.	The two sample sets are said to be *heteroscedastic*	when the standard deviations of the two sample sets being compared are statistically the same	when the standard deviations of the two sample sets being compared are statistically different	when the standard deviations of the two sample sets is equal to zero	when the standard deviations of the two sample sets are equal to 100	when the standard deviations of the two sample sets being compared are statistically different
27.	Rejection of a result is pertained to	't' test	'Q'Test	'F'Test	Validation	'Q'Test
28.	In the equation of the straight line $y = mx + b$; *'y' is the*	Dependent value	Independent value	slope	intercept	Dependent value
29.	In the equation of the straight line $y = mx + b$; *'x' is the*	Dependent value	Independent value	slope	intercept	Independent value
30.	In the equation of the straight	Dependent value	Independent value	slope	intercept	slope

	line $y = mx + b$; *'m' is the*					
31.	In the equation of the straight line $y = mx + b$; *'b' is the*	Dependent value	Independent value	slope	intercept	Intercept
32.	In the equation of the straight line $y = mx + b$; *'dependent value is*	y	x	m	b	y
33.	In the equation of the straight line $y = mx + b$; *'Independent value is*	y	x	m	b	x
34.	In the equation of the straight line $y = mx + b$; *'slope' is*	y	x	m	b	m
35.	In the equation of the straight line $y = mx + b$; *'Intercept' is*	y	x	m	b	b
36.	In a spectrophotometric calibration curve the equation of the straight line $y = mx + b$; *'y' represents*	measured absorbances of the test solutions	concentrations of the standards	Absorbance of concentrated solutions	Absorbance of dilute solutions	measured absorbances of the test solutions
37.	In a spectrophotometric calibration curve the equation of the straight line $y = mx + b$; *'x' represents*	measured absorbances of the test solutions	concentrations of the standards	Absorbance of concentrated solutions	Absorbance of dilute solutions	concentrations of the standards
38.	The best straight line through a series of experimental points is that line for which the *sum of the squares of the*	Method of least squares	't' test	'Q'Test	'F'Test	Method of least squares

	deviations (the residuals) of the points from the line is minimum. This is known as					
39.	The test which evaluates differences between the spread of results,	Method of least squares	't' test	'Q'Test	'F'Test	'F'Test
40.	The analytical response of the analyte in the presence of potential sample components is compared with the response of a solution containing only the analyte. This is called	Selectivity	Linearity	Range	Sesitivity	Selectivity
41.	Which is not related to validation process of a method	Selectivity	Linearity	Range	Standard deviation	Standard deviation
42.	Which is not related to validation process of a method	Selectivity	Linearity	Range	Median	Median
43.	The study which verifies that the response is linearly proportional to the analyte concentration in the concentration range of sample solutions.	Selectivity	Linearity	Range	Median	Linearity
44.	The parameter which is often judged from the coefficient of determination *(r*2*)* and the *y* intercept of the linear regression line.	Selectivity	Linearity	Robustness	Precision	Linearity
45.	The most preferable method to determine the accuracy of	Analysis of a reference material	Comparison with results using	Recovery studies	Range of linearity	Analysis of a reference material

	a method is		another method known to be accurate			
46.	The study which is performed by spiking (adding) a known amount of the analyte either to a blank matrix	Recovery studies	Linearity studies	To determine precision	To determine standard deviation	Recovery studies
47.	Which is determined using the slope of the calibration curve	Selectivity	Linearity	Range	Sesitivity	Sesitivity
48.	Which will govern how many significant figures should be reported in a measurement.	Sensitivity and precision	Accuracy	Range of linearity	robustness	Sensitivity and precision
49.	The concentration range over which acceptable accuracy and precision are obtained is called	The working range of a method	Accuracy	Range of linearity	robustness	The working range of a method
50.	Which refers to the precision of measurement in one lab over multiple days, which may include multiple analysts, multiple instruments	The working range of a method	Accuracy	Range of linearity	robustness	robustness
51.	A list of 5 pulse rates is: 70, 64, 80, 74, 92. What is the median for this list	70	80	74	64	80
52.	The plot between *response factor* (RF) versus concentration is used to evaluate	Selectivity	Range of Linearity	Robustness	Precision	Range of Linearity
53.	The mean of a sample is	always equal to the	always smaller	computed by	computed by	computed by

		mean of the population	than the mean of the population	summing the data values and dividing the sum by (n - 1)	summing all the data values and dividing the sum by the number of items	summing all the data values and dividing the sum by the number of items
54.	Since the mode is the most frequently occurring data value, it	can never be larger than the mean	is always larger than the median	is always larger than the mean	must have a value of at least two	must have a value of at least two
55.	If a data set has an even number of observations, the median	can not be determined	is the average value of the two middle items	must be equal to the mean	is the average value of the two middle items when all items are arranged in ascending order	is the average value of the two middle items when all items are arranged in ascending order
56.	The most frequently occurring value of a data set is called the	Range	Median	Mean	Mode	Mode
57.	A researcher has collected the following sample data. 5, 12, 6, 8, 5, 6, 7, 5, 12, and 4, the The median is	6	5	7	8	6
58.	A researcher has collected the following sample data. 5, 12, 6, 8, 5, 6, 7, 5, 12, and 4, the The mode is	6	5	7	8	5
59.	A researcher has collected the following sample data. 12, 6, 8, 6, 7, 12, and 4, the The median is	6	5	7	8	7
60.	A researcher has collected the following sample data. 5, 12, 6, 8, 5, 6, 7, 5, 12, and 4, the The mean is	6	5	7	8	7

Unit-III

Techniques in Inorganic Chemistry: Colorimetry: Theoretical and practical aspects of colorimetric analysis. Flame emission and atomic absorption spectroscopy – types of atomic spectroscopy – emission methods – absorption methods – fluorescence methods – source and atomizers for atomic spectroscopy – flame atomizers – electrothermal atomizers – principle and applications of atomic absorption spectroscopy. Advantages of atomic absorption spectrometry over flame photometry.

Techniques in Inorganic Chemistry:

Flame emission and atomic absorption spectroscopy

As in molecular spectroscopy, atomic spectroscopy is divided broadly into absorption and emission spectroscopy. The notable differences are that atomic spectrometry is always carried out in the gas phase. The measurement conditions require elevated temperatures; with the exception of Hg, Cd and the inert gases, elements are not present as a monoatomic gas at room temperature. Also, as the name implies, we measure atoms; atomic spectroscopy is then a form of elemental analysis.

Atomic spectrometry is widely used in many laboratories for trace element analyses. Environmental samples are analyzed for heavy-metal contamination, and pharmaceutical samples may be analyzed for metal impurities. The semiconductor industry requires precise doping of some elements into others and composition must be accurately known. The steel industry needs to determine minor components, as well as major ones. The composition of a batch of steel frequently must be confirmed (and amended as needed) before the molten mass is poured out. The particular technique used in any given application will depend on the sensitivity required, the number of samples to be analyzed, and whether multielement measurements are needed.

Flame Emission Spectrometry

In this technique, the source of excitation energy is a flame. The sample is introduced into the flame in the form of a solution. A flame is a low-energy source, and so the emission spectrum is simple and there are few emission lines. In practice, the technique is inexpensive and attractive for only a few elements. As a direct result of the work of Kirchoff and Bunsen in the early 1860s, the analytical utility of measuring the characteristic radiation emitted by specific elements excited in flames was realized. The earliest such instrument was used for the measurement of sodium in plant ash using a Bunsen flame. The difficult part in such an instrument was how best to introduce the sample into the flame. It wasn't until 1929, when Lundegardh utilized a nebulizer to introduce a significant fraction of the sample reproducibly into the flame, that a breakthrough was made. Characteristic atomic emission lines were dispersed by a quartz prism spectrograph and recorded photographically. Use of optical filters and electrical photodetectors improved convenience and precision in later years, and such instruments became widely useful for measuring Na, K, Li, and Ca. Work on many other elements then became possible with the use of grating spectrometers equipped with more

sensitive photomultiplier detectors. But the commercial development of the more broadly applicable AAS technique in the 1960s essentially restricted the scope of flame emission spectrometry and arrested its further development.

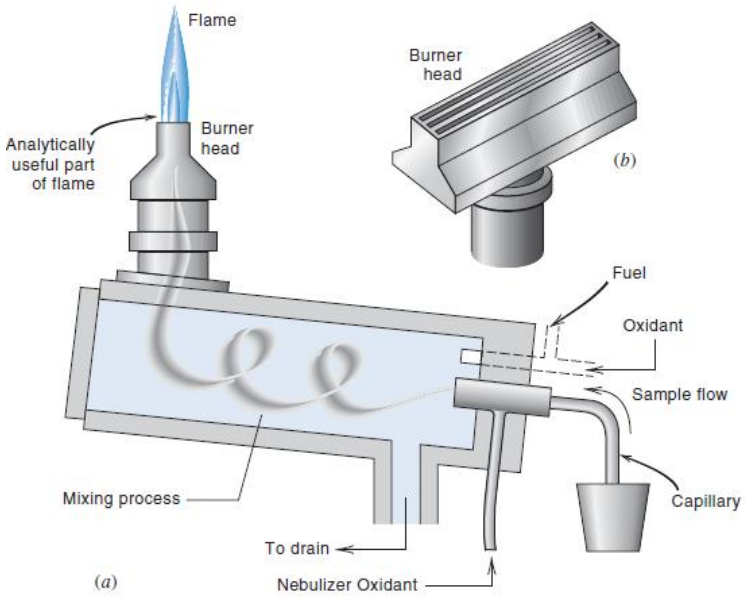
Most commercial instruments in use today are dedicated to the measurement of Li, Na, K, Ca, and Ba, using interference filters centered at 670, 589, 766, 622, and 515 nm, respectively, and thus they are commonly called **flame photometers**. Calcium is actually measured by the emission of molecular CaOH, as this emission at 622 nm is more intense than the emission by atomic Ca at 423 nm. A propane-air flame (temperature 1900–2000◦C) is commonly used. Butane-air or natural gas-air flames can also be used; these flames are not as hot and the measurement is less sensitive. With a propane-air flame, the best of current instruments claim LODs of 0.02 mg/L for Na and K to 10mg/L for Ba. Most analyze one element at a time; the filter is manually changed to switch the target element, but some, such as the BWBTech XP Flame Photometer, are capable of providing simultaneous multiple readouts using multiple detection channels. The formation of CaOH is much affected by the presence of Ba, however, and the two generally cannot be simultaneously determined. The atomic emission line of Ca at 423 nm is less susceptible to interference by Ba but is not commonly used because of lower sensitivity. Many such shortcomings of flame emission measurement can be overcome with higher temperature and more reducing flames such as air-acetylene and higher-resolution spectrometric detection. In many ways, flame emission as practiced today in the form of flame photometry (FP) is a step backward from the heights previously attained because incorporation of high temperature flames and high-resolution spectrometry is not cost competitive relative to the more broadly applicable flame AAS technique.

BURNERS USED FOR FLAME SPECTROMETRY AND DESIRABLE FLAME CHARACTERISTICS

In early years, there was considerable debate on the superiority of the two main types of burners. In one type, the fuel (propane/acetylene) and the oxidant (air/oxygen/nitrous oxide) are premixed and the solution is nebulized by the flow of the premixed gas before the flame. This is the type of arrangement pioneered by Lundegardh. Much of the liquid that is aspirated by the nebulizer actually tends to form large droplets and simply drains from the burner. In the second type of burner, often called a **total consumption burner**, the fuel and oxidant gases are not premixed. The design is basically that consisting of three concentric tubes that terminate in a nozzle. The outermost typically carried the fuel, the next one the oxidant, and the central tube, a capillary, was the sample inlet. The Venturi suction created by the fuel-oxidant flow aspirates the sample into the flame; the name derives from the fact that the entire aspirated sample enters the flame.

Notwithstanding the superiority the "total consumption" name may imply, the **premix burner**, sometimes called the **laminar flow burner**, ultimately produces better results. It is the only type of burner in present use. The primary reason for the difference is the sample droplet size generated. Whereas the direct sample injection process in the total consumption burner results in larger droplets of size ∼7 nL, the premix burner nebulizer produces droplets of size as small as 0.05 nL. The smaller droplets evaporate and eventually atomize much more easily. A typical design is shown in Figure. A three-slotted burner head, originally due to Boling, as shown in the figure, is the most common. It produces a wide flame, sufficient to accommodate the widest probe beam cross section. Atmospheric oxygen enters only the

edges of the flame, permitting optimum reducing conditions in the central portion of the flame. The atom population is uniform with height over a significant portion of the flame, making adjustments simple. Three-slot burners have been shown to exhibit less noise and



clog less easily with samples of significant dissolved solute content than most other designs. Past the nebulization point, most burner/nebulizer assemblies have baffles in their path that effectively remove the large droplets; these do not atomize as efficiently and result in local cooling of the flame.

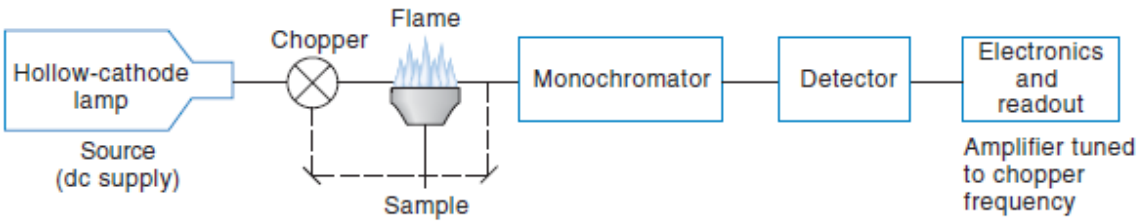
A flame should meet several desirable characteristics for use in flame emission applications: (a) it should provide sufficient energy for the sample to be atomized; for the metals determined presently by flame photometry, the propane-air flame is sufficient, (b) the flame should be nonturbulent so that atom population shows the least spatiotemporal variation, (c) by itself the flame should have minimum emission and absorption at the wavelengths of interest, and (d) the flame should be able to operate at low gas velocities so the emitting atoms remain in the view volume as long as possible. In addition, the flame operation should be safe and inexpensive.

Atomic Absorption Spectrometry

Since the number of atoms in the ground state far outweighs those in the excited state, one would normally think that the study of absorption by atoms in a flame will parallel or even precede flame emission spectroscopy studies. This in fact has not been the case because in flame AAS we encounter a problem that has no parallel in molecular absorption spectrometry. This is that the flame itself emits some (often a lot) of light at the wavelength(s) where we are trying to measure light absorption. Moreover, this background emission from the flame is not particularly constant over time; a simple subtraction of its contribution is not possible. Imagine a flashlight being aimed at a detector in an otherwise dark room. It is not difficult to tell when some of this light is being absorbed by species present in the light path; this is the situation in molecular spectroscopy.

On the other hand, if the same experiment is conducted in a brightly sunlit room (and moreover, clouds are occasionally passing by, changing the background light intensity), it would not be easy for the detector to tell minor changes in the light it is receiving from the flashlight because of the presence of absorbing species. This was the problem facing Australian spectroscopist Alan Walsh (see sidebar) as his colleague John Shelton reminded him. Walsh's solution was equivalent to turning the flashlight on and off at a constant and relatively high frequency and then filter the detector signal so we look only at this frequency. This process eliminates all other signals and looks only at the flashlight signal. This is no more complicated than being immersed in radio waves of all different frequencies but still being able to tune to the desired frequency
and listen to/watch one's favorite radio or TV station. Pulsing on and off light sources at high speeds reproducibly is only practical for solid-state sources that did not exist until recently. Walsh accomplished this by putting a motorized mechanical chopper in front of the light source. As the chopper rotates, it alternately blocks the beam and allows it to pass through.

The rotational speed basically controls the frequency with which the light is "turned on and off." (Walsh also proved the concept by using a sodium lamp powered at 50 Hz; this did not need a chopper.) The detector is tuned to this frequency. Walsh also recognized that he did not have monochromators that can provide resolution comparable to those of atomic absorption lines (he estimated the line width to be 2 pm). Such resolution will be needed to essentially exclude stray light. He chose therefore to use a light source that contained the analyte element of interest. A discharge is created; this results in the emission of line(s) characteristic of the element. (If more than one line is emitted, they are far enough apart for a simple monochromator, usually placed after the sample, to isolate the principal emission line of interest.) This line is used as the source light. In effect, the source itself functions as a very high-resolution monochromator, providing an extremely narrow source line. Note that a different lamp is needed for the analysis of each element. Note also that the temperature of the light source should not be very high, as temperature also causes broadening of the emitted line. A line much broader than the absorption line width will also effectively be stray light.



PRINCIPLES OF FLAME AAS

A simplified functional diagram of the first commercial flame AAS instrument (Perkin Elmer Model 303) is shown in Figure 17.4. The light source is a hollow cathode lamp that emits at the atomic absorption line of interest (more on this later). A mirror-equipped chopper alternately directs the beam through the flame and bypassing it, effectively providing a double-beam arrangement and compensating for any source drift. Modern AAS instruments mostly do not use such a double-beam arrangement, however. The drift of present-day light sources following a warm-up time is much smaller than drifts in the atomizer. Rather, the reference reading is often taken just before and after the sample is measured, thus effectively

providing a double beam in time arrangement. The sample solution is aspirated into a flame as in flame emission spectrometry, and the analyte element is converted to atomic vapor. The flame then contains atoms of that element. Some are thermally excited by the flame, but most remain in the ground state, as shown in Table These ground-state atoms can absorb radiation emitted by the source that is deliberately composed of that element so its characteristic lines are emitted. Atomic absorption spectrophotometry is identical in principle to absorption spectrophotometry described in the previous chapter. The absorption follows Beer's law. That is, the *absorbance* is directly proportional to the pathlength in the flame and to the concentration of atomic vapor in the flame. Both of these variables are difficult to determine, but the pathlength is essentially held constant in a given burner and flame conditions and the concentration of atomic vapor is directly proportional to the concentration of the analyte in the solution being aspirated. In practice, one calibrates the instrument response by aspirating samples of different concentration.

TYPES OF AAS INSTRUMENTATION

Broadly there are two types of AAS instrumentation in present use:

(a) Line source AAS (LS-AAS) instruments, and
(b) Continuum source AAS (CS-AAS) instruments

Either type can utilize flame or a graphite furnace (also called electrothermal) atom source. Walsh originally believed CS-AAS instruments would not be possible, not only because single-digit pm resolution is needed, but also because even if such resolution could be attained, there would not be enough light from a continuum source through such a narrow bandwidth. Technology has advanced to the point, however, that such instruments have become commercially available since 2004, equipped with a very high-power water-cooled Xenon lamp operated in a "hot-spot" mode, a very high-resolution double monochromator, and a CCD-array detector. They have the advantage that very many different lamp sources are not needed for the analysis of different elements. Bernhard Welz, perhaps the most ardent champion of AAS (see
Reference 8), simply calls CS-AAS "The better way to do AAS". As in molecular absorption spectrophotometry, the requirements for AAS include a light source, a beam path through the analyte (the flame or furnace), a monochromator, and a detector. As in molecular absorption spectroscopy with array detectors, the monochromator follows the sample. The various components of an atomic absorption spectrophotometer are described.

Atomic Absorption Spectroscopy was invented by Alan Walsh in 1950's for the qualitative determination of trace metals in liquids. The superiority of the technique over other is based on the fact that by this technique 50-60 elements can be determined without any interference from trace to big quantities.

All these elements can be detected here which fail to yield satisfactory result in flame photometry. Thus, it is a successful instruments for detection and estimation of metals and non-metals both types of pollution from factories.

The technique has also proved very helpful to both aqueous and non-aqueous solutions.

Note # 2. Principle of Atomic Absorption Spectroscopy:

When a solution having a mixture of metallic species is introduced into the flame, the solvent evaporates and vapour of metallic species is obtained. Some of metal atoms can be raised to an energy level sufficiently high to emit characteristics radiation of metal-a phenomenon that is used in flame photometry. Here a large amount of metal atoms remain in non-emitting ground state.

These ground state atoms of a particular element are receptive of light radiation of their own specific resonance wavelength. In this way, when a light of this wavelength passes through a flame, a part of light will be absorbed and this absorption will be proportional to the intensity of atoms in the flame.

So in atomic absorption spectroscopy the amount of light absorbed is determined because the absorption is proportional to the concentration of the element.

Note # 3. Advantages of Atomic Absorption over Flame Photometry:

(1) It does not suffer from spectral interference, which occurs in flame emission spectroscopy.

(2) It is independent of flame temperature.

(3) By atomic absorption technique, traces of one element can easily be determined in presence of high concentration of other elements.

(4) It has proved very successful in the analysis of bronze and copper alloys and in the determination of metals like platinum, gold etc.

Note # 4. Disadvantages of Atomic Absorption Spectroscopy:

Some of the disadvantages are summarized as follows:

(1) This technique has not proved very successful for the estimation of elements like V, Si, Mo, Ti and A1 because these elements give oxides in the flame.

(2) In aqueous solution, the anion affects the signal to a noticeable degree.

(3) A separate lamp is needed for the determination of each element. Attempts are being made to overcome this difficulty by using a continuous source.

Note # 5. Instruments of Atomic Absorption Spectroscopy:

The apparatus consist of:

(1) Radiant Source.

(2) Atomizer

(3) Monochromator

(4) Lenses and Slits and

(5) Detectors.

The main components used in the instrument can be described as follows:

(1) Radiant Sources:

Generally a hydrogen lamp is used as continuous source of radiation.

(2) Atomizer:

Generally burners are used to break the liquid sample into droplets which are then allowed to enter into flame. The droplets are then evaporated and sample element is left in residue. The residue is then decomposed by flame. Thus in this process the sample is reduced to atoms.

(3) Hollow Cathode Lamp:

For atomic absorption spectroscopy the radiation source is a hollow cathode lamp

It consists of the following parts:

(i) Cathode: is made of the element to be determined or coated with it.

(ii) Anode Anode is made of tungsten, zinconium or nickel.

(iii) Window is made of Pyrex glass depending on wavelength of emitted radiation.

(iv) The lamp is filled with neon or argon gas.

These gases emit sharp line spectra.

Generally these lamps are constructed for individual elements but multi-element lamps have also been prepared for all purposes.

The hydrogen lamp is a hollow cathode lamp.

A hollow cathode lamp emits more than one composite line for each element but the required spectral line can be separated by means of a relatively low dispersion monohromator. Most of lines are non-absorbing lines because they involve transition other than from ground state. The most intense absorption line is selected to provide maximum intensity.

The inlet and exit slit widths of monochromator should be narrow to isolate the particular line being used; the requirements depend on:
(1) Focal length,

(2) Grating ruling of Monochromator.

(4) Monochromator:
Generally the monocchromators are gratings and prisms.

(5) Filters or slits:
Filters or slits are used for isolation of required spectral line if element has a simple line spectrum. Filter photometers are used for determination of potassium, sodium calcium, magnesium etc. in samples.

(6) Detectors:
Generally photomultipliers are used as detectors. In some instruments two filters and two detectors are used to compensate the fluctuation in the sources.

Note # 6. Experimental Techniques of Atomic Absorption Spectroscopy:
First of all, a meter is adjusted to read zero absorbance or 100% transmittance when a blank solution is sprayed into the flame and light of hollow cathode lamp passes on to photomultiplier tube. Now the solution to be investigated is introduced, a certain part of light is absorbed resulting in decrease of light intensity falling on photomultiplier. This gives a deflection in the meter needle which is noted immediately.

As this is a comparative method hence standard solutions of elements are used to make a calibration curve from which the concentration of sample elements can be calculated.

Note # 7. Interference of Atomic Absorption Spectroscopy:
(1) Chemical Interference:

In practice, it has been found that phosphate ions interfere with determination of calcium and magnesium. This interference can be reduced by adding a salt of lanthanum.

(2) Ionisation Interference:

Ionisation interference is caused due to alkali metals which need low energy for ionization. For example, a loss in petrochemicals sensitivity results due to splitting of a free metal atom into a positive ion and an electron

$M = M^{+} + e^{-}$

(3) Role of Solvent:

Solvent plays an important part to interfere in the determination of conc. of metals. The results have shown that metals in aqueous solution yield lower absorbance readings than same concentration of such metals when present in the organic solvent.

(4) Dissociation of Metal Compounds:

Some metals like Al, Ti etc. when subjected to flame give oxides in place of metal atoms and thus complicate the system.

(5) Spectral Interferences:

Sometimes interference occurs due to overlapping of any radiation with that of characteristic radiation of sample element, e.g. potassium doublet (4044, 2047Å), manganese triplet (4031, 4033 and 4035Å).

This interference can be removed by working with AC amplifiers in the technique.

Note # 8. Applications of Atomic Absorption Spectroscopy:

(i) Quantitative Analysis:

As we know that each element has its own characteristic emission spectrum, hence the intensity of the lines is compared with standard and the concentration can be easily evaluated from the graph (Fig. 3).

Suppose the intensity of unknown element is C, then the concentration is evaluated by drawing a perpendicular on the line (calibration curve) and from the point it cuts the curve. A perpendicular is drawn on the x-axis. The value from (0 to 0) will give the concentration of unknown in moles per litre.

In atomic adsorption spectroscopy, the same method is followed for determining the concentration of the element in an unknown solution.

(ii) Method of Standard Addition:

If calibration graph is linear, the sample concentration can be calculated by adding known amount of the test element to the sample. This gives a section of calibration graph above the unknown sample concentration and the resulting straight line can be extrapolated back to zero signal intensity.

The concentration scale is determined by standard additions and unknown concentration is given by the point at which extrapolated line crosses concentration axis.

(iii) Quantitative Analysis:

Generally first a curve is plotted between absorbance valve vs. concentration of standard samples of the element. A linear curve is obtained.

From this curve, the concentration of unknown is evaluated by knowing absorbance value only from the following equation:

$A = S \times C$

or Absorbance = Slope × Concentration

As it is very sensitive technique hence it gives more accurate results than many analytical methods.

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram (μg dm–3) in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level. Atomic absorption spectrometry has many uses in different areas of chemistry.

Clinical analysis. Analysing metals in biological fluids such as blood and urine.

Environmental analysis. Monitoring our environment – *eg* finding out the levels of various

elements in rivers, seawater, drinking water, air, petrol and drinks such as wine, beer and fruit drinks.

Pharmaceuticals. In some pharmaceutical manufacturing processes, minute quantities of a catalyst used in the process (usually a metal) are sometimes present in the final product. By using AAS the amount of catalyst present can be determined.

Industry. Many raw materials are examined and AAS is widely used to check that the major elements are present and that toxic impurities are lower than specified – *eg* in concrete, where calcium is a major constituent, the lead level should be low because it is toxic.

Mining. By using AAS the amount of metals such as gold in rocks can be determined to see whether it is worth mining the rocks to extract the gold.

Figure 2

How it works

Atoms of different elements absorb characteristic wavelengths of light. Analysing a sample to see if it contains a particular element means using light from that element. For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the sample. In AAS, the sample is atomised – *ie* converted into ground state free atoms in the vapour state – and a beam of electromagnetic radiation emitted from excited lead atoms is passed through the vaporised sample. Some of the radiation is absorbed by the lead atoms in the sample. The greater the number of atoms there is in the vapour, the more radiation is absorbed. The amount of light absorbed is

proportional to the number of lead atoms. A calibration curve is constructed by running several samples of known lead concentration under the same conditions as the unknown. The amount the standard absorbs is compared with the calibration curve and this enables the calculation of the lead concentration in the unknown sample. Consequently an atomic absorption spectrometer needs the following three components: a light source; a sample cell to produce gaseous atoms; and a means of measuring the specific light absorbed.

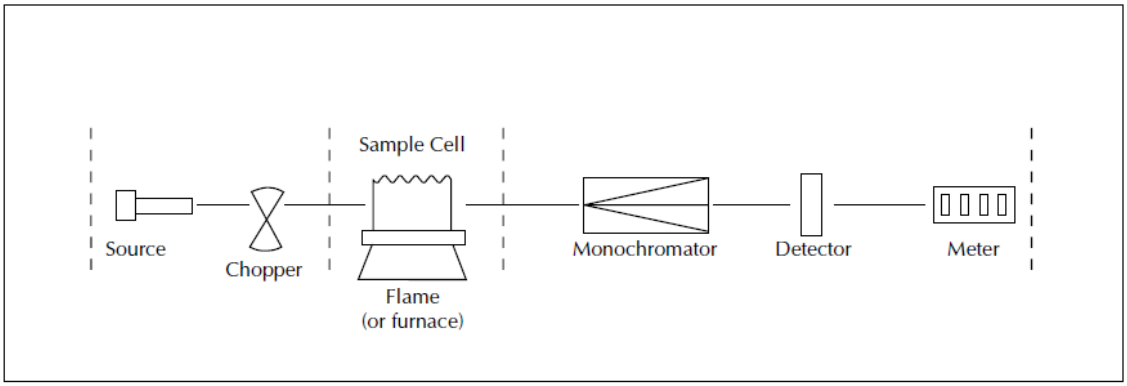
The light source

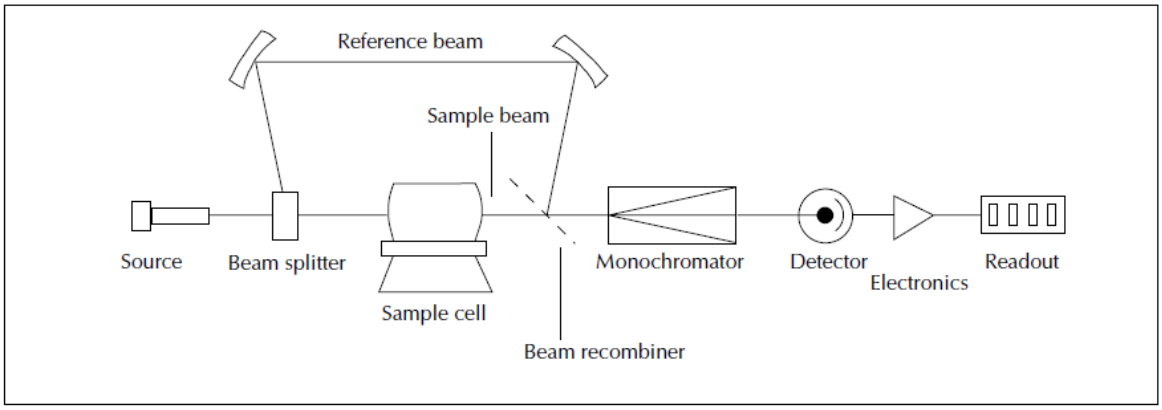
The common source of light is a 'hollow cathode lamp'. This contains a tungsten anode and a cylindrical hollow cathode made of the element to be determined. These are sealed in a glass tube filled with an inert gas – *eg* neon or argon – at a pressure of between 1 Nm–2 and 5 Nm–2. The ionisation of some gas atoms occurs by applying a potential difference of about 300–400 V between the anode and the cathode. These gaseous ions bombard the cathode and eject metal atoms from the cathode in a process called sputtering. Some sputtered atoms are in excited states and emit radiation characteristic of the metal as they fall back to the ground state – *eg* $Pb^* \rightarrow Pb + h$. The shape of the cathode concentrates the radiation into a beam which passes through a quartz window, and the shape of the lamp is such that most of the sputtered atoms are redeposited on the cathode.

A typical atomic absorption instrument holds several lamps each for a different element. The lamps are housed in a rotating turret so that the correct lamp can be quickly selected.

The optical system and detector

A monochromator is used to select the specific wavelength of light – *ie* spectral line – which is absorbed by the sample, and to exclude other wavelengths. The selection of the specific light allows the determination of the selected element in the presence of others. The light selected by the monochromator is directed onto a detector that is typically a photomultiplier tube. This produces an electrical signal proportional to the light intensity.





Double beam spectrometers

Modern spectrometers incorporate a beam splitter so that one part of the beam passes through the sample cell and the other is the reference *(Fig. 4)*. The intensity of the light source may not stay constant during an analysis. If only a single beam is used to pass through the atom cell, a blank reading containing no analyte (substance to be analysed) would have to be taken first, setting the absorbance at zero. If the intensity of the source changes by the time the sample is put in place, the measurement will be inaccurate. In the double beam instrument there is a constant monitoring between the reference beam and the light source. To ensure that the spectrum does not suffer from loss of sensitivity, the beam splitter is designed so that as high a proportion as possible of the energy of the lamp beam passes through the sample.

Atomisation of the sample

Two systems are commonly used to produce atoms from the sample. Aspiration involves sucking a solution of the sample into a flame; and electrothermal atomisation is where a drop of sample is placed into a graphite tube that is then heated electrically.

Some instruments have both atomisation systems but share one set of lamps. Once the appropriate lamp has been selected, it is pointed towards one or other atomisation system.

Flame aspiration

Figure 5 shows a typical burner and spray chamber. Ethyne/air (giving a flame with a temperature of 2200–2400 °C) or ethyne/dinitrogen oxide (2600–2800 °C) are often used. A flexible capillary tube connects the solution to the nebuliser. At the tip of the capillary, the solution is 'nebulised' – *ie* broken into small drops. The larger drops fall out and drain off while smaller ones vaporise in the flame. Only *ca* 1% of the sample is nebulised.

Electrothermal atomisation

Figure 6 shows a hollow graphite tube with a platform. 25 μl of sample (*ca* 1/100th of a raindrop) is placed through the sample hole and onto the platform from an automated micropipette and sample changer. The tube is heated electrically by passing a current through it in a pre-programmed series of steps. The details will vary with the sample but typically they might be 30–40 seconds at 150 °C to evaporate the solvent, 30 seconds at 600 °C to drive off any volatile organic material and char the sample to ash, and with a very fast heating rate (*ca* 1500 °C s-1) to 2000– 2500 °C for 5–10 seconds to vaporise and atomise elements (including the element being analysed). Finally heating the tube to a still higher temperature – *ca* 2700 °C – cleans it ready for the next sample. During this heating cycle the graphite tube is flushed with argon gas to prevent the tube burning away. In electrothermal atomisation almost 100% of the sample is atomised. This makes the technique much more sensitive than flame AAS.

Sample preparation

Sample preparation is often simple, and the chemical form of the element is usually unimportant. This is because atomisation converts the sample into free atoms irrespective of its initial state. The sample is weighed and made into a solution by suitable dilution. Elements in biological fluids such as urine and blood are often measured simply after a dilution of the original sample. The figure shows a flame atomic absorption spectrometer with an autosampler and flow injection accessory.

When making reference solutions of the element under analysis, for calibration, the chemical environment of the sample should be matched as closely as possible – *ie* the analyte should be in the same compound and the same solvent. Teflon containers may be used when analysing very dilute solutions because elements such as lead are sometimes leached out of glass vessels and can affect the results.

Background absorption

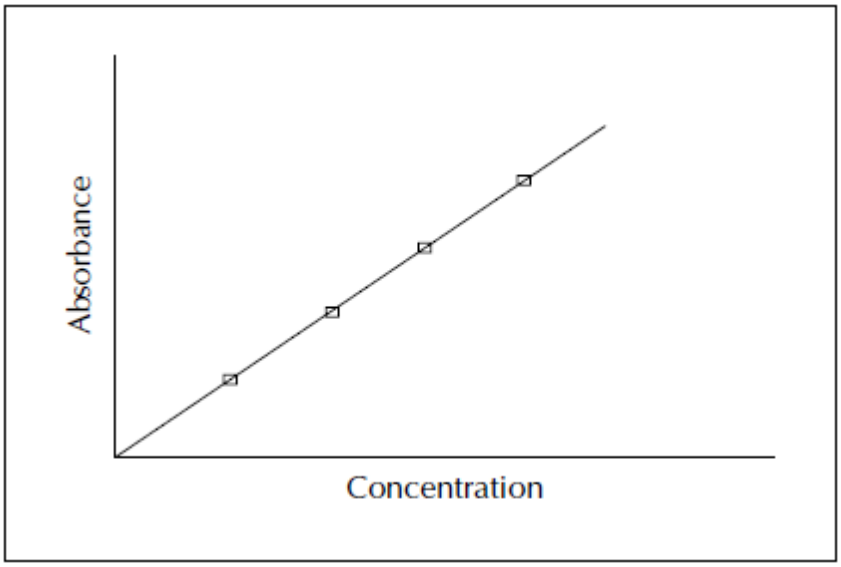
It is possible that other atoms or molecules apart from those of the element being determined will absorb or scatter some radiation from the light source. These species could include unvaporised solvent droplets, or compounds of the matrix (chemical species, such as anions, that tend to accompany the metals being analysed) that are not removed completely. This means that there is a background absorption as well as that of the sample.

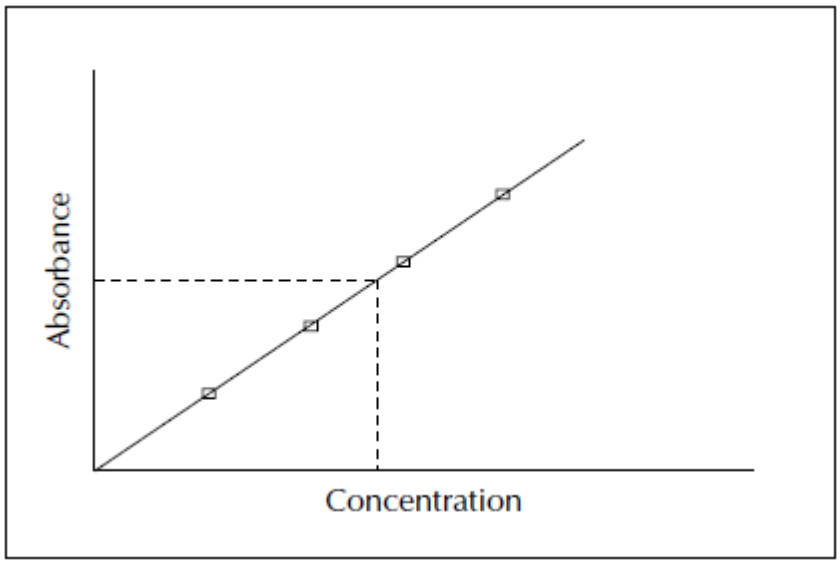
One way of measuring and correcting this background absorption is to use two light sources, one of which is the hollow cathode lamp appropriate to the element being measured. The second light source is a deuterium lamp. The deuterium lamp produces broad band radiation, not specific spectral lines as with a hollow cathode lamp. By alternating the measurements of the two light sources – generally at 50 –100 Hz – the total absorption (absorption due to analyte atoms plus background) is measured with the specific light from the hollow cathode lamp and the background absorption is measured with the light from the deuterium lamp. Subtracting the background from the total absorption gives the absorption arising from only analyte atoms.

Calibration

A calibration curve is used to determine the unknown concentration of an element – *eg* lead – in a solution. The instrument is calibrated using several solutions of known concentrations. A calibration curve is produced which is continually rescaled as more concentrated solutions are used – the more concentrated solutions absorb more radiation up to a certain absorbance. The calibration curve shows the concentration against the amount of radiation absorbed *(*The

sample solution is fed into the instrument and the unknown concentration of the element – *eg* lead – is then displayed on the calibration curve





Interferences and matrix modification

Other chemicals that are present in the sample may affect the atomisation process. For example, in flame atomic absorption, phosphate ions may react with calcium ions to form calcium pyrophosphate. This does not dissociate in the flame and therefore results in a low reading for calcium. This problem is avoided by adding different reagents to the sample that may react with the phosphate to give a more volatile compound that is dissociated easily. Lanthanum nitrate solution is added to samples containing calcium to tie up the phosphate and to allow the calcium to be atomised, making the calcium absorbance independent of the amount of phosphate.

With electrothermal atomisation, chemical modifiers can be added which react with an interfering substance in the sample to make it more volatile than the analyte compound. This

volatile component vaporises at a relatively low temperature and is removed during the low and medium temperature stages of electrothermal atomisation.

Colorimetry

Colorimetry is "the science and technology used to quantify and describe physically the human colour perception. It is similar to spectrophotometry, but is distinguished by its interest in reducing spectra to the physical correlates of color perception.

A colorimeter is a light-sensitive device used for measuring the transmittance and absorbance of light passing through a liquid sample. The device measures the **intensity** or concentration of the color that develops upon introducing a **specific** reagent into a **solution.**

In chemistry, they are especially used to measure colour absorption by solutions. The main **difference between colorimeter and spectrophotometer** is that **colorimeter** is a device which measures absorbance of specific colours, whereas a **spectrometer** measures transmittance or reflectance as a function of wavelength.

optics **filters** are **used** in the **colorimeter** to select the wavelength which the solute absorbs the most, in order to maximize accuracy. If it is necessary to operate in the [ultraviolet]range then some modifications to the **colorimeter** are needed.

A **blank** solution is a solution containing little to no analyte of interest, usually **used** to calibrate instruments such as a **colorimeter.**

A **colorimeter** is an instrument that compares the amount of light getting through a solution with the amount that can get through a sample of pure solvent. A**colorimeter** contains a photocell is able to detect the amount of light which passes through the solution under investigation.

In physical and analytical **chemistry**, **colorimetry** or **colourimetry** is a technique "**used** to determine the concentration of colored compounds in solution." ... The concentration of a sample can be calculated from the intensity of light before and after it passes through the sample by using the Beer–Lambert law.

Working Principle

The colorimeter is based on Beer-Lambert's law, according to which the absorption of light transmitted through the medium is directly proportional to the medium concentration.

In a colorimeter, a beam of light with a specific wavelength is passed through a solution via a series of lenses, which navigate the colored light to the measuring device. This analyzes the color compared to an existing standard. A microprocessor then calculates the absorbance or percent transmittance. If the concentration of the solution is greater, more light will be absorbed, which can be identified by measuring the difference between the amount of light at its origin and that after passing the solution.

To determine the concentration of an unknown sample, several sample solutions of a known concentration are first prepared and tested. The concentrations are then plotted on a graph against absorbance, thereby generating a calibration curve. The results of the unknown sample are compared to that of the known sample on the curve to measure the concentration.

Applications

Besides being used for basic research in chemistry laboratories, colorimeters have many practical applications such as testing water quality by screening chemicals such as chlorine, fluoride, cyanide, dissolved oxygen, iron, molybdenum, zinc and hydrazine. They are also used to determine the concentrations of plant nutrients such as ammonia, nitrate and phosphorus in soil or hemoglobin in blood. Colorimetry is also used in color printing, textile manufacturing and paint manufacturing for precise quality inspection.

SUGGESTED MATERIALS

1. Svehla, G. (2002). Vogel's Qualitative Inorganic Analysis (VII Edition). Singapore: Pearson Education.
2. Christian, G. D. (2007). *Analytical Chemistry* (VI Edition). United States: John Wiley & Sons.
3. Skoog, D. A., West, D. M., Holler, F. J., & Crouch, S. R. (2014). *Fundamentals of Analytical Chemistry* (IX Edition). United States of America: Cengage Learning.

Section-A
(Online examination)
20x1= 20 Marks

Possible questions

1. Explain the Theoretical and practical aspects of colorimetric analysis.
2. Compare and contrast Flame emission and atomic absorption spectroscopy
3. Describe the terms (i) emission methods (ii) absorption methods (iii) fluorescence methods of spectroscopy
4. Explain the principle and applications of atomic absorption spectroscopy
5. Explain the principle and applications of Flame emission spectroscopy
6. What is meant by an atomizer. Write notes on flame atomizers and electrothermal atomizers
7. What are the advantages of atomic absorption spectrometry over flame photometry.
8. Detail in detail about the source and atomizers for atomic spectroscopy

UNIT II

S.No	Question	a	b	c	d	Answer
1.	In atomic absorption spectroscopy	does not suffer from spectral interference	dependent of flame temperature	traces of one element cannot easily be determined in presence of high concentration of other elements.	Not successful in the analysis of bronze and copper alloys	does not suffer from spectral interference
2.	In atomic absorption spectroscopy	suffer from spectral interference	independent of flame temperature	traces of one element cannot easily be determined in presence of high concentration of other elements.	Not successful in the analysis of bronze and copper alloys	independent of flame temperature
3.	In atomic absorption spectroscopy	suffer from spectral interference	dependent of flame temperature	traces of one element can easily be determined in presence of high concentration of other elements.	Not successful in the analysis of bronze and copper alloys	traces of one element can easily be determined in presence of high concentration of other elements.

4.	In atomic absorption spectroscopy	suffer from spectral interference	dependent of flame temperature	traces of one element cannot easily be determined in presence of high concentration of other elements.	successful in the analysis of bronze and copper alloys	successful in the analysis of bronze and copper alloys
5.	This does not suffer from spectral interference	atomic absorption spectroscopy	UV-Visible spectrometer	IR spectrometer	Gas chromatography	atomic absorption spectroscopy
6.	Which is independent of flame temperature	atomic absorption spectroscopy	UV-Visible spectrometer	IR spectrometer	colorimeter	atomic absorption spectroscopy
7.	traces of one element can easily be determined in presence of high concentration of other elements in	atomic absorption spectroscopy	UV-Visible spectrometer	IR spectrometer	colorimeter	atomic absorption spectroscopy
8.	Which instrument is successful in the analysis of bronze and copper alloys	atomic absorption spectroscopy	UV-Visible spectrometer	IR spectrometer	Gas chromatography	atomic absorption spectroscopy
9.	One among the disadvantages of atomic absorption spectroscopy is	elements like V, Si, Mo, Ti and A1 cannot be estimated because these elements give oxides in the flame.	not suffer from spectral interference	is independent of flame temperature	traces of one element can easily be determined in presence of high concentration of other elements	elements like V, Si, Mo, Ti and A1 cannot be estimated because these elements give oxides in the flame.

10.	One among the disadvantages of atomic absorption spectroscopy is	In aqueous solution, the anion affects the signal to a noticeable degree	not suffer from spectral interference	is independent of flame temperature	traces of one element can easily be determined in presence of high concentration of other elements	In aqueous solution, the anion affects the signal to a noticeable degree
11.	One among the disadvantages of atomic absorption spectroscopy is	A separate lamp is needed for the determination of each element	not suffer from spectral interference	is independent of flame temperature	traces of one element can easily be determined in presence of high concentration of other elements	A separate lamp is needed for the determination of each element
12.	One of the advantages of atomic absorption spectroscopy is	A separate lamp is needed for the determination of each element	In aqueous solution, the anion affects the signal to a noticeable degree	elements like V, Si, Mo, Ti and A1 cannot be estimated because these elements give oxides in the flame.	not suffer from spectral interference	not suffer from spectral interference
13.	One of the advantages of atomic absorption spectroscopy is	A separate lamp is needed for the determination of each element	In aqueous solution, the anion affects the signal to a noticeable degree	elements like V, Si, Mo, Ti and A1 cannot be estimated because these elements give oxides in the flame.	is independent of flame temperature	is independent of flame temperature

14.	One of the advantages of atomic absorption spectroscopy is	A separate lamp is needed for the determination of each element	In aqueous solution, the anion affects the signal to a noticeable degree	elements like V, Si, Mo, Ti and A1 cannot be estimated because these elements give oxides in the flame.	traces of one element can easily be determined in presence of high concentration of other elements	traces of one element can easily be determined in presence of high concentration of other elements
15.	In atomic absorption spectroscopy hydrogen lamp is used as a	Radiation source	Atomiser	Monochromator	Detector	Radiation source
16.	In atomic absorption spectroscopy Hollow Cathode Lamp is used as a	Radiation source	Atomiser	Monochromator	Detector	Radiation source
17.	Which is used as the cathode in the Hollow Cathode Lamp	element to be determined	Tungsten	Zirconium	Nickel	element to be determined
18.	Which is used as an anode in Hollow Cathode Lamp	element to be determined	Tungsten	Mercury	Sodium amalgam	Tungsten
19.	Which is used as an anode in Hollow Cathode Lamp	element to be determined	Zirconium	Mercury	Sodium amalgam	Zirconium
20.	Which is used as an anode in Hollow Cathode Lamp	element to be determined	Nickel	Mercury	Sodium amalgam	Nickel
21.	The window present in the Hollow Cathode Lamp was made up of	Corning glass	wood	Pyrex glass	Fiber glass	Pyrex glass
22.	The lamp present in Hollow Cathode Lamp is filled with	Neon	Hydrogen	Nitrogen	oxygen	Neon
23.	The lamp present in Hollow Cathode Lamp is filled with	Argon	Hydrogen	Nitrogen	oxygen	Argon
24.	In the Hallow cathode lamp	These gases emit	These gases emit	These gases emit	These gases emit	These gases emit

	The lamp is filled with neon or argon gas because	sharp line spectra	broad line spectra	band spectra	split line spectra	sharp line spectra
25.	A hollow cathode lamp emits more than one composite line for each element but the required spectral line can be separated by means of a	relatively low dispersion monohromator	Fine holes	Reflection through a mirror	Refraction through a glass slabe	relatively low dispersion monohromator
26.	The ions which interfere with determination of calcium and magnesium.	Nitrate ions	Phosphate ions	Chloride ions	Bromide ions	Phosphate ions
27.	The phosphate ions interfere with determination of calcium and magnesium in atomic absorption spectroscopy. It is minimised by using	Lanthanum	Lutecium	Chromium	vanadium	Lanthanum
28.	The phosphate ions interfere with determination of calcium and magnesium in atomic absorption spectroscopy. It is a	Chemical interference	Ionisation Interference	Role of a solvent	Dissociation of metal compounds	Chemical interference
29.	The interference caused due to alkali metals is	Chemical interference	Ionisation Interference	Role of a solvent	Dissociation of metal compounds	Ionisation Interference
30.	Metals in aqueous solution yield lower absorbance readings than same concentration of such metals when present in the organic	Chemical interference	Ionisation Interference	Role of a solvent	Dissociation of metal compounds	Role of a solvent

	solvent.					
31.	Some metals like Al, Ti etc. when subjected to flame give oxides in place of metal atoms. This is a	Chemical interference	Ionisation Interference	Role of a solvent	Dissociation of metal compounds	Dissociation of metal compounds
32.	An example for ionisation interference in AAS is	Some metals like Al, Ti etc. when subjected to flame give oxides in place of metal atoms	Metals in aqueous solution yield lower absorbance	The interference caused due to alkali metals is	The phosphate ions interfere with determination of calcium and magnesium	The interference caused due to alkali metals is
33.	An example for interference due to a solvent in AAS is	Some metals like Al, Ti etc. when subjected to flame give oxides in place of metal atoms	Metals in aqueous solution yield lower absorbance	The interference caused due to alkali metals is	The phosphate ions interfere with determination of calcium and magnesium	Metals in aqueous solution yield lower absorbance
34.	An example for interference due to Dissociation of metal compounds in AAS is	Some metals like Al, Ti etc. when subjected to flame give oxides in place of metal atoms	Metals in aqueous solution yield lower absorbance	The interference caused due to alkali metals is	The phosphate ions interfere with determination of calcium and magnesium	Some metals like Al, Ti etc. when subjected to flame give oxides in place of metal atoms
35.	The interference occurs due to overlapping of any radiation with that of characteristic radiation of sample element. It is called	Spectral interfrence	Chemical interference	Ionisation Interference	Role of a solvent	Spectral interfrence
36.	In the spectral interference	Doublet	Triplet	Singlet	Quartet	doublet

	potassium appear as a					
37.	In the spectral interference Manganese appear as a	Doublet	Triplet	Singlet	Quartet	Triplet
38.	In the applications of AAS, an example for Clinical analysis	finding out the levels of various elements in rivers,	check that the major elements are present in raw materials	Analysing metals in biological fluids such as blood and urine	amount of metals such as gold in rocks	Analysing metals in biological fluids such as blood and urine
39.	In the applications of AAS, an example for environmental analysis	finding out the levels of various elements in rivers,	check that the major elements are present in raw materials	Analysing metals in biological fluids such as blood and urine	amount of metals such as gold in rocks	finding out the levels of various elements in rivers,
40.	In the applications of AAS, an example for Industrial applications	finding out the levels of various elements in rivers,	check that the major elements are present in raw materials	Analysing metals in biological fluids such as blood and urine	amount of metals such as gold in rocks	check that the major elements are present in raw materials
41.	In the applications of AAS, an example for Mining applications	finding out the levels of various elements in rivers,	check that the major elements are present in raw materials	Analysing metals in biological fluids such as blood and urine	amount of metals such as gold in rocks	amount of metals such as gold in rocks
42.	In the applications of AAS, an example for pharmaceutical applications	finding out the levels of various elements in rivers,	check that the major elements are present in raw materials	Analysing metals in biological fluids such as blood and urine	Amount of catalyst present may be determined	Amount of catalyst present may be determined
43.	In AAS finding out the levels of various elements in rivers is an example for	Clinical analysis	environmental analysis	Mining applications	Pharmaceutical application	environmental analysis
44.	In AAS checking that the major elements are present in raw materials	Clinical analysis	environmental analysis	Industrial application	Pharmaceutical application	Industrial application
45.	In AAS Analysing metals in	Clinical analysis	environmental	Industrial	Pharmaceutical	Clinical analysis

	biological fluids such as blood and urine is an example for		analysis	application	application	
46.	In AAS Amount of catalyst present may be determined	Clinical analysis	environmental analysis	Industrial application	Pharmaceutical application	Pharmaceutical application
47.	A drop of sample is placed into a graphite tube that is then heated electrically. Is called	Flame aspiration	electrothermal atomisation	Photomultiplier detection	Monochromator system	electrothermal atomisation
48.	sucking a solution of the sample into a flame	Flame aspiration	electrothermal atomisation	Photomultiplier detection	Monochromator system	Flame aspiration
49.	The science and technology used to quantify and describe physically the human colour perception is called.	colorimetry	Fluorimetry	Spectrophotometry	Radiometry	colorimetry
50.	The device measures the **intensity** or concentration of the color that develops upon introducing a **specific** reagent into a **solution. The technique is called**	colorimetry	Fluorimetry	Spectrophotometry	Radiometry	colorimetry
51.	**colorimeter** is a device which measures	absorbance of specific colours	measures transmittance as a function of wavelength.	measures reflectance as a function of wavelength.	Absorbance of light	absorbance of specific colours
52.	Absorbed wavelengths in atomic absorption spectrum appear as	Dark background	Dark lines	Light background	Light lines	Dark lines
53.	Lines which appear in	Same	different	Very different	Far apart	Same

	absorption and emission spectrum are					
54.	Background in atomic absorption spectrum is	Bright	dark	brown	purple	Bright
55.	Which of the following is not a step in AAS	A caliberation curve is constructed	Atoms absorb light	Particles are absorbed on to a stationary phase	A solution is vapourised	Particles are absorbed on to a stationary phase
56.	The measurement taken by a AAS is	Volume	mass	Concentration	Absorbance	Absorbance
57.	What are the black lines in absorption spectra produced by?	The emission of light as electrons move from higher energy levels to lower energy levels.	The emission of light as electrons move from lower energy levels to higher energy levels.	The absorption of light as electrons move from lower energy levels to higher energy levels.	The absorption of light as electrons move from higher energy levels to lower energy levels.	The absorption of light as electrons move from lower energy levels to higher energy levels.
58.	**An emission spectrum is observed as**	black lines on a coloured background.	A smooth curve	coloured lines on an uncoloured background	identical to a continuous spectrum	black lines on a coloured background.
59.	Atomic-emission spectroscopy (AES) is an analytical method for quantitating	Elements in solids or liquids	Atmospheric gases.	Organic molecules in aqueous solution	Polymeric solutions	Elements in solids or liquids
60.	The purpose of the high-energy flame, discharge, or plasma source is to	Desolvate the sample	Excite the analyte atoms	Destabilise the molecules	Atomize the sample	Atomize the sample

Unit-IV

Electrochemical Methods of Analysis: Cyclic voltammetry, coulometry and amperometry-principle and applications.

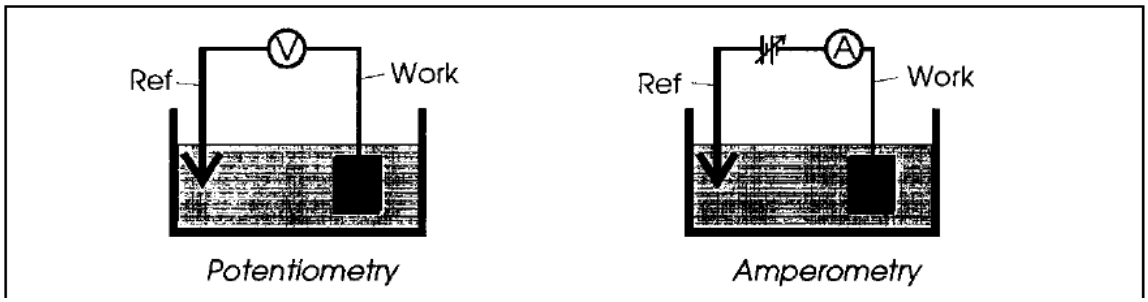
Thermal characterization techniques: Principle and applications of differential thermal analysis (DTA), differentials scanning calorimetry (DSC) and thermogravimetric analysis (TGA) thermometric titration.

Cyclic Voltammetry

Introduction

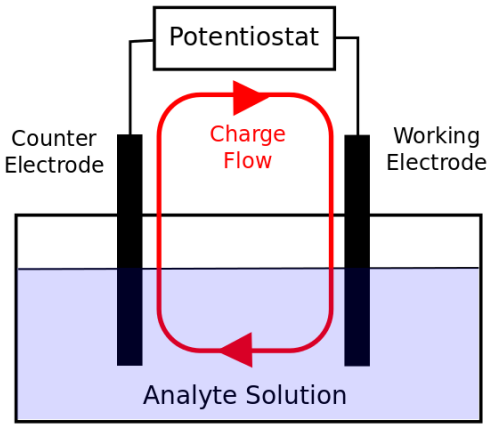
Electrochemical analyses can be thought of in terms of two broad classes of measurement, one in which the potential that develops between two electrodes is measured (potentiometry) and another in which the current that flows between two electrodes is measured (amperometry). In potentiometry, it often proves helpful to arrange things such that the current is very low (e.g., by placing a high-resistance voltmeter in series between two electrodes). The electrochemical potential of one electrode (the reference electrode) is usually fixed, so the measured cell potential can be interpreted in terms of an equilibrium half-cell reaction involving an analyte species in contact with the other electrode (the working electrode). In favorable cases, one can use data from potentiometric measurements to calculate analyte concentrations directly from the Nernst equation. Potentiometry is a simple and straightforward analytical method, and is routinely used to solve many problems in the analysis of electrochemically active and/or charged analytes.

An important assumption in potentiometry is that the measured potential accurately reflects the equilibrium position of a well-defined electrochemical cell reaction. Often this is not the case, however, and potentiometric methods cannot be used. In many situations, it is instead more appropriate to control the potential of the working electrode (relative to a reference electrode) and to measure the resulting current. (Recall that current is simply the flow rate of electrons in a circuit; an ampere of current corresponds to a coulomb of charge flowing per second.) The magnitude of the resulting current and its dependence on the applied potential then provide the analytical information. An experiment in which the potential applied to the working electrode is swept at a constant sweep rate and the resulting current measured as a function of potential is called a voltammetry experiment, and much of the recent interest in electroanalytical chemistry stems from the use of voltammetry to obtain analytical (e.g., concentration), thermodynamic (e.g., redox potentials and equilibrium constants), kinetic (e.g., rate constants for reactions involving electrogenerated species) and mechanistic information about chemical systems in which redox chemistry plays a role.

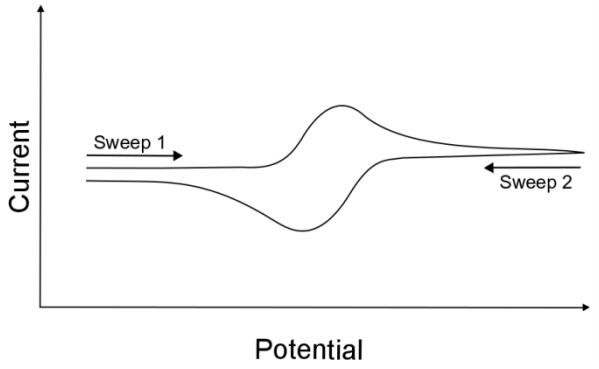


Before we define cyclic voltammetry, what is voltammetry? For our purposes, voltammetry is any experiment where we expose a solution of an analyte to an electrode, change the electrode potential, and observe the current that flows in response.

In other words, we make a circuit out of a solution containing a molecule that we are interested in studying (analyte), change the voltage (electrode potential) on one of the electrodes, and see what voltage is required to transfer electrons (cause current to flow) between the electrode and our molecule of interest. Incorporating our analyte into a circuit is as easy as dipping two electrodes into our analyte solution. These two electrodes are connected to a potentiostat, which is an instrument that controls the voltage (potential) of each electrode. Voltammetry is a sensitive analytic technique that informs us about the thermodynamics and kinetics of electron transfer for a given analyte.

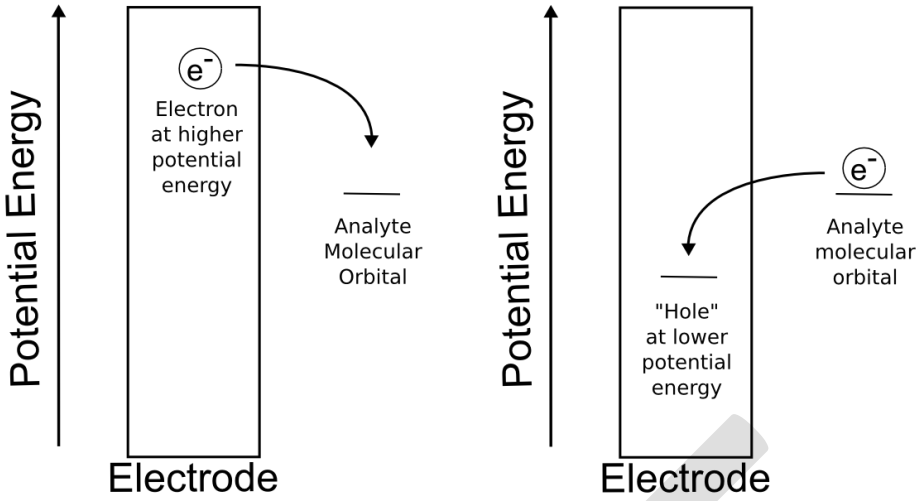


If we were to only sweep (change the electrode potential) in one direction and stop, the experiment would be referred to as a "linear sweep voltammogram," but if we tell the potential sweep to reverse directions when the potential reaches a certain value and return to the starting potential, we are now performing "cyclic" voltammetry and collecting a "cyclic voltammogram," or "CV". We refer to the range of potentials that are accessed while collecting a CV as the potential window.



In chemistry, we should be comfortable with thinking about the change in the potential energy of a molecule during molecular transformations in the context of acid dissociation, ligand binding, or conformational changes. We should also have no problem comprehending that a given molecule has a different potential energy than an identical molecule to which one electron has been added. We might also be familiar with the concept of band theory, which describes the potential energy of electrons within solids. In fact, electrode potential can be thought of as the potential energy of electrons in the electrode. *Most electron transfers can be understood by thinking about the potential energies of the analyte and the electrons in the electrode*

If our analyte is redox–active, it will exchange an electron with an electrode when it reaches certain potentials. Our redox–active analyte will undergo reduction (accept an electron from the electrode) when the potential energy of the electrons in the electrode is higher than the potential energy of the empty molecular orbital on the analyte, so it is energetically favorable for an electron to transfer from the electrode to the analyte. Conversely, our analyte will undergo oxidation (losing an electron to the electrode) when the highest energy electron in the molecule is at a higher potential energy than the electrons in the electrode, and it becomes energetically favorable for it to transfer from the molecule to the electrode. *In both of these cases, electrons are transferred in order to minimize the potential energy of the total system.* We can use the potentiostat to change the electrode potential and observe where we see current flowing in order to learn about the electron transfer energetics of our analyte.



Voltammetry refers to the measurement of current that result from the application of potential. Unlike potentiometric measurements, which employ only two electrodes, voltammetric measurements utilise a three electrode electrochemical cell. The use of three electrodes (working, auxiliary and reference) along with the potentiostat instrument allows accurate application of potential functions and measurement of the resultant current.

Cyclic voltammetry is a method for investigating the electrochemical behaviour of a system. It was first reported in 1938. Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, on the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. Cyclic voltammetry is often the first experimental approach performed in an electroanalytical study, since it offers rapid location of redox potentials of the electroactive species and convenient evaluation of the effect of media upon the redox process.

Basic principles of Cyclic Voltammetry A cyclic voltammogram is obtained by applying a linear potential sweep (that is, a potential that increases or decreases linearly with time) to the working electrode. As the potential is swept back and forth past the formal potential, E°, of an analyte, a current flows through the electrode that either oxidizes or reduces the analyte. The magnitude of this current is proportional to the concentration of the analyte in solution, which allows cyclic voltammetry to be used in an analytical determination of concentration. The equipment required to perform cyclic voltammetry consists of a conventional three-electrode potentiostat connected to three electrodes (working, reference and auxiliary) immersed in a test solution. The potentiostat applies and maintains the potential between the working and reference electrode while at the same time measuring the current at the working electrode. Charge flows between the working electrode and the auxiliary electrode. A

recording device (such as a computer or plotter) is used to record the resulting cyclic voltammogram as a graph of current versus potential.

CV is a potential sweep technique. It involves sweeping the electrode potential between potential limits Ei and E2 at a known sweep rate (also called scan rate). On reaching limit E2 the sweep is reversed to Ei to obtain a cyclic scan. The CV scan is a plot of current verses potential and indicates the potential at which redox process occur. The potential axis is also a time axis that is related to scan rate. The excitation signal for CV is a linear potential scan with triangular waveform. This triangular potential excitation signal sweeps the potential of an electrode between two values, sometimes called the switching potential. The current measured during this process is often normalised to the electrode surface area and referred to as the current density. The current density is then plotted against the applied potential, and the result is referred to as a cyclic voltammogram. A peak in the measured current is seen at a potential that is characteristic of any electrode reaction taking place. The peak width and height for a particular process may depend on the sweep rate, electrolyte concentration and the electrode material

Applications of Cyclic Voltammetry

CV has become a very popular technique for electrochemical studies of new systems, and has proved as a sensitive tool for obtaining information about fairly complicated electrode reactions . CV methods have found to have extensive applications for the evaluation of thermodynamic and kinetic parameters such as number of electrons change (n), heterogeneous rate constant (ko), entropy (S), Gibb's free energy (G) and diffiision coefficient (Do) etc., of a number of redox reactions and associated chemical reactions. These methods are especially useful in both oxidation and reduction process and to study the multiple electron transfer in an electrochemical reaction.

In a potentiometric method of analysis we determine an analyte's concentration by measuring the potential of an electrochemical cell under static conditions. Dynamic techniques, in which current passes through the electrochemical cell, also are important electrochemical methods of analysis. In this section we consider coulometry.

Coulometry is based on an exhaustive electrolysis of the analyte. By exhaustive we mean that the analyte is completely oxidized or reduced at the working electrode or that it reacts completely with a reagent generated at the working electrode. There are two forms of coulometry: **controlled-potential coulometry**, in which we apply a constant potential to the electrochemical cell, and **controlled-current coulometry**, in which we pass a constant current through the electrochemical cell.

During an electrolysis, the total charge, Q, in coulombs, passing through the electrochemical cell is proportional to the absolute amount of analyte by **Faraday's law**

$$Q=nFNA$$

where n is the number of electrons per mole of analyte, F is Faraday's constant (96487 C mol^{-1}), and N_A is the moles of analyte. A coulomb is equivalent to an A·sec; thus, when passing a constant current, i, the total charge is

$$Q=ite$$

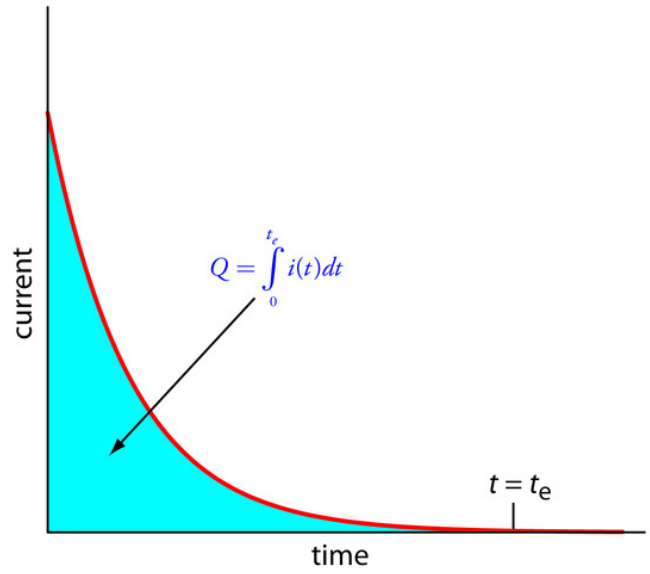
where t_e is the electrolysis time. If the current varies with time, as it does in controlled-potential coulometry, then the total charge is

$$Q=\int teoi(t)dt$$

In coulometry, we monitor current as a function of time and use either equation the above equations to calculate Q. Knowing the total charge, we then use equation 11.25 to determine the moles of analyte. To obtain an accurate value for N_A, all the current must be used to oxidize or reduce the analyte. In other words, coulometry requires 100% current efficiency—or an accurately measured current efficiency established using a standard—a factor that we must be consider when designing a coulometric method of analysis.

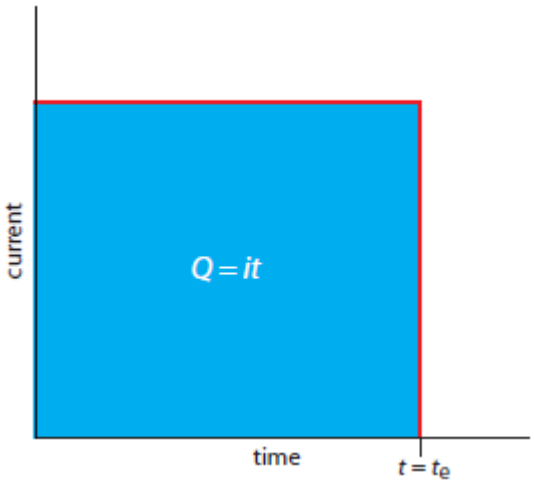
Controlled-Potential Coulometry

The easiest way to ensure 100% current efficiency is to hold the working electrode at a constant potential, chosen so that the analyte reacts completely without simultaneously oxidizing or reducing an interfering species. As electrolysis progresses the analyte's concentration decreases, as does the current. The resulting current-versus-time profile for controlled-potential coulometry is shown in Figure. Integrating the area under the curve from $t = 0$ to $t = t_e$ gives the total charge. In this section we consider the experimental parameters and instrumentation needed to develop a controlled-potential coulometric method of analysis.



Controlled-Current Coulometry

A second approach to coulometry is to use a constant current in place of a constant potential, which produces the current-versus-time profile shown in Figure 11.30. Controlled-current coulometry has two advantages over controlled-potential coulometry. First, the analysis time is shorter because the current does not decrease over time. A typical analysis time for controlled-current coulometry is less than 10 min, compared to approximately 30–60 min for controlled-potential coulometry. Second, because the total charge is simply the product of current and time, there is no need to integrate the current-time curve.



Quantitative Applications

Coulometry is used for the quantitative analysis of both inorganic and organic analytes.

- Used in the determination of the thickness of the metallic coatings.
- Used in the determination of the total anti-oxidant capacity of the anti-oxidants
- Used in the determination of the total carbon in ferrous and non-ferrous metals.
- Used in the determination of the picric acid.
- Used in the separation of the nickel and cobalt.
- Used in the analysis of the radioactive materials.
- Used in the determination n-values of the organic compounds.
- Used in the determination of the environment pollutants.

Coulometric Titrations

Constant coulometric method is commonly known as the coulometric titration. In coulometric titrations, the reagent is generated electrically and determined by the current and by the time. It should be of 100% efficiency and the reagent generated should react with the sample solution. The main principle involved in the coulometric titration is the generation of the titrant by electrolysis. Then a large amount of titrant solution is added to the sample solution. Then the sample solution is electrolysed at the anode surface. As the electrolysis proceeds, the anode potential is increased. Then the addition of the titrant solution decreases the potential by decreasing the current. The end point is determined by the any of the end point detection method.

Example: The sample solutions containing the ferrous ions are added to the excess amount of the Ce (III) ion solution.

$Fe^{+2} \longrightarrow Fe^{+3} + e^{-}$

$Ce^{+4} + Fe^{+2} \longrightarrow Ce^{+3} + Fe^{+3}$

The following are the advantages of the coulometric titrations:

- Standard solutions are not required.
- Reagent is generated.
- No need of the dilution of the sample solution.
- The method is readily adopted than other methods.

The following are the limitations of the coulometric titrations:

- Generation is difficult.
- Inferences are more.

The detection of the end points in the coulometric titrations is done by the following:

1. By the chemical indicators: These are added to the sample solution. The only requirement for these reagents should be electroinactive.
2. Examples:
    - Methyl orange
    - Dichlorofluorescein
    - Eosin
3. Potentiometric end point detection method: When the pair of electrodes are placed in the sample solution it shows the potential difference by the addition of the titrant or by the change in the concentration of the ions. To measure the electromotive force of the electrode, system is measured by the potentiometer or by the electronic voltameter.
4. Amperometric method: This method is mainly based on the current produced which is directly proportional to the concentration of the electroactive substance.
5. By the spectrophotometric method.

Amperometry

The detection of ions presence on solution on the basis of electric current or change in electric current is called as Amperometry. For example, for the detection of chlorine can be carried out by using amperomerty. No doubt there are other methods also available for the detection of chlorine like calorimeter which measures the chlorine level optically.

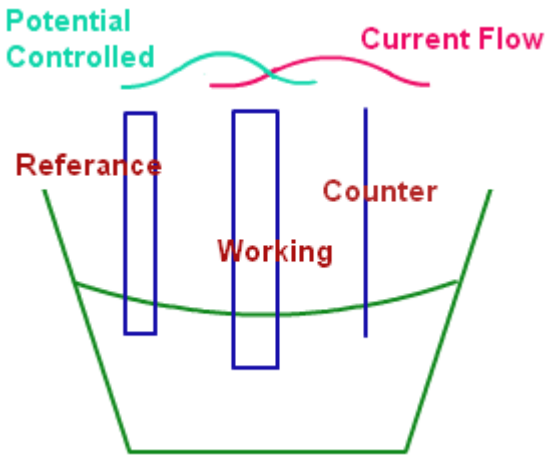
When chlorine is added to water it hydrolyzes and forms HOCl which further dissociates into respective ions.

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

$$HOCl\ (aq) \rightarrow OCl^-\ (aq) + H^+(aq)$$

In an amperometric method for the detection of chlorine a fixed voltage applied between two electrodes whereas the reaction takes place at the working electrode that is cathode and reduction of chlorine (HOCl) back to chloride (Cl^-) takes place and chlorine generate at the anode.

Since, the current flow in amperometric sensor is due to chlorine, hence the amount of current flow is directly proportional of chlorine presented to the sensor.



Amperometry Principle

Amperometry analysis is a type of voltammetric analysis which is widely used in food processing industries.

A voltammetric analyses is done by using a certain setup of a measuring chamber which contains three electrodes.

- **Working electrode (microelectrode)**

- **Reference electrode**
- **Auxiliary electrode**

1. Apart from these electrodes, there is a voltage source and a devices for measuring current and voltage – voltmeters and ammeter.
2. The method is based on the principle that the measurements of changes in time (τ) in the current (I) flowing through the system of electrodes in relation to potential (E) applied to the working electrode.
3. The change registered in the current allow drawing the $\mathbf{I(\tau) = f[E(\tau)]}$ relationship which is known the voltammogram.
4. If the same measurements of the current are carried out at constant potential, then it becomes a classical amperometric system.
5. Amperometric measurements completed in stirred solution or with rotating electrode which is also termed as hydrodynamic amperometry.
6. The best use of Amperometry apparatus is to detected dissolved oxygen which is reduced at the measuring electrode.
7. By using a micro- potentiotat the potential of the measuring electrode is kept at a constant which is main characteristic for the oxygen reduction in Amperometry technique.
8. Hence, the diffusion limited current is directly proportional to the oxygen concentration

Amperometric titration is a type of titration in which the determination of the equivalence point is done by measuring the electric current which produced by the titration reaction. For the estimation of equivalence point and end point in any titration, apart from titration indicators, amperometry can also be used.

If we take a solution containing the analyte, X with some conductive buffer and applied an electrolytic potential to the solution by using a working electrode, then the value of measured current will depend on the concentration of the analyte. This magnitude of measured current can be used to determine the concentration of the analyte and this form is called as amperometry.

However, the measurement of current depends on several other variables, and it is not always possible to control all of these variables at the same time, hence this limits the precision of

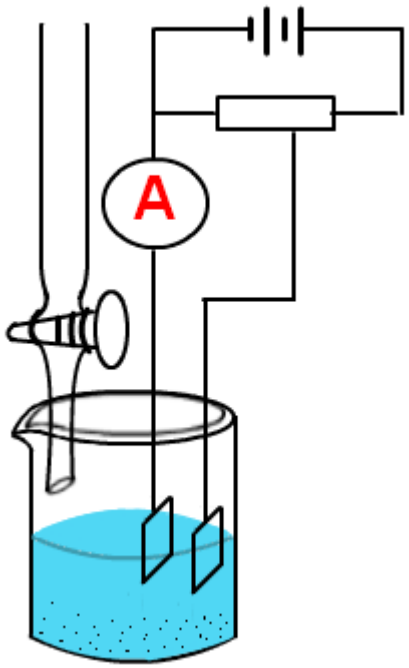
direct amperometry. Now the applied potential on working electrodes will decide the mode of reaction.

If the applied potential is sufficient to reduce the given analyte, then the concentration of analyte which is close to the working electrode will decrease. Hence more analyte will diffuse slowly in the solution which is close to the working electrode and restoring the concentration.

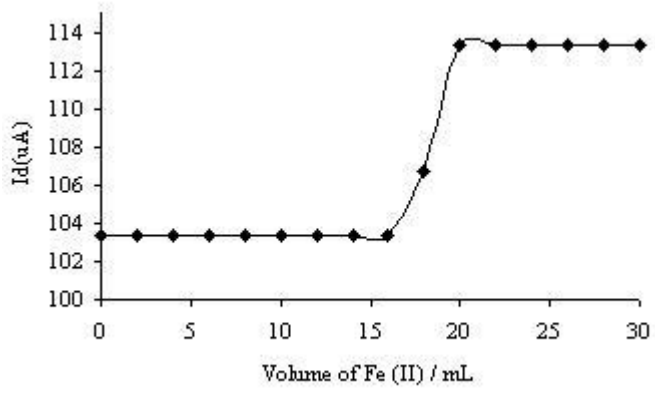
On the other hand, If the applied potential is more, the concentration of analyte which is close to the working electrode will depend on the rate of diffusion. In this a case, the current is called as diffusion limited. The concentration of the analyte will decrease in solution due to reduction of it on working electron.

This reduction in concentration of analyte takes place with a very slow speed which depends on the size of the working electrode. If there is any other ion of molecule present in solution the concentration of the analyte will decreases due to reaction with other substance as well as due to applied potential.

After equivalence point when enough titrant has been added to react with the analyte, the excess titrant reduced at the working electrode. Since each species has a certain diffusion characteristics and different half-reaction, after equivalence point the slope of current versus added titrant will have a different slope. This inflection in slope marks the equivalence point as the change in pH marks the equivalence point in an acid-base titration.



Example of amperometric titration is the titration if cerium (IV) ions against iron(II) which carried out at 1.8 V while the amperometric titration of $KMnO_4$ with Fe (II) was performed at 1.2 V. The inflection point in curve denotes the equivalence point in titration.



Advantage of Amperometry titration

1. In amperometry titration, a few current measurements at constant applied voltage before and after the end point are sufficient to estimate the equivalence point and end point.

2. Amperometry titration is useful for such case in which the solubility relations like potentiometric are unsatisfactory. For example, in precipitation titration or in acid-base titration.

3. A amperometric titration can be carried out at low dilutions also at which many other titration are no longer yield accurate results.

4. 'Foreign' salts do not create any interference in amprometric titration. They are usually added as the supporting electrolyte for the elimination of the migration current.

5. No change in temperature is observed during titration and this titration is independent of the characteristics of the capillary.

Principle of Differential Thermal Analysis (DTA)

A technique in which the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.

Description of DTA

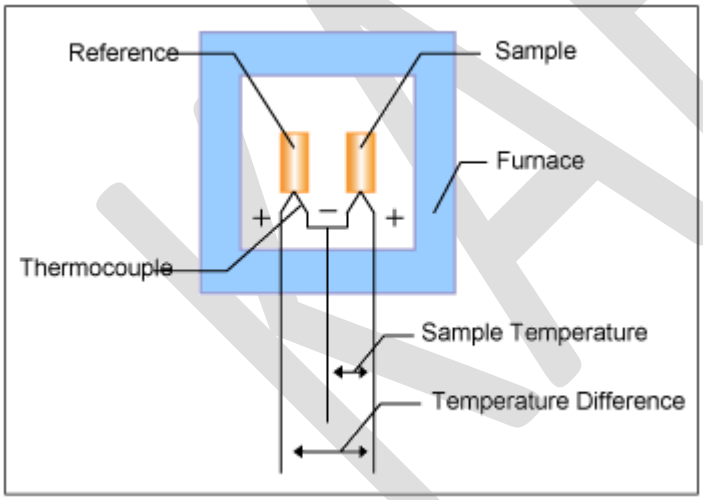


Figure 1. Block diagram of DTA

Figure 1 shows the block diagram of DTA.
The sample and the reference are placed symmetrically in the furnace. The furnace is controlled under a temperature program and the temperature of the sample and the reference are changed. During this process, a differential thermocouple is set up to detect the temperature difference between the sample and the reference.
Also, the sample temperature is detected from the thermocouple on the sample side.

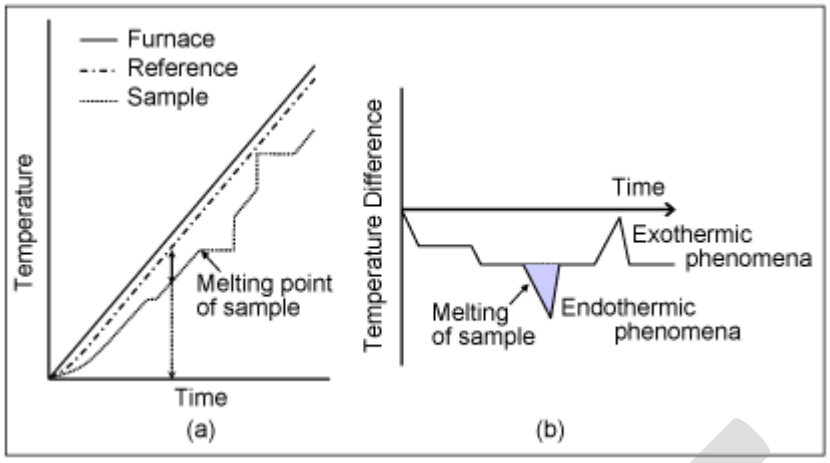


Figure 2 Measurement principles of DTA

Graph (a) shows the temperature change of the furnace, the reference and the sample against time.
Graph (b) shows the change in temperature difference (ΔT) against time detected with the differential thermocouple.
ΔT signal is referred to as the DTA signal.

Matters that do not change in the measurement temperature range (usually α-alumina) are used as reference.

When the furnace heating begins, the reference and the sample begin heating with a slight delay depending on their respective heat capacity, and eventually heat up in according to the furnace temperature.
ΔT changes until a static state is reached after the heating begins, and after achieving stability, reaches a set amount compliant with the difference in heat capacity between the sample and the reference. The signal at the static state is known as the baseline.

When the temperature rises and melting occurs in the sample, for example, the temperature rise stops as shown in graph (a) and the ΔT increases. When the melting ends, the temperature curve rapidly reverts to the baseline.
At this point, the ΔT signal reaches the peak, as shown in graph (b).
From this, we can detect the samplefs transition temperature and the reaction temperature from the ΔT signal (DTA signal).
In graph (b), the temperature difference due to the samplefs endothermic change is shown as a negative direction and the temperature difference due to the samplefs exothermic change is shown as a positive direction.

Principle of Differential Scanning Calorimetry (DSC)

DSC is the generic term for the following two measurement methods.

- **Heat Flux DSCs**
  A technique in which the temperature of the sample unit, formed by a sample and reference material, is varied in a specified program, and the temperature difference between the sample and the reference material is measured as a function of temperature.

- **Power Compensation DSC**
  A technique in which difference of thermal energy that is applied to the sample and the reference material per unit of time is measured as a function of the temperature to equalize their temperature, while temperature of the sample unit, formed by the sample and reference material, is varied in a specified program.

Description of DSC

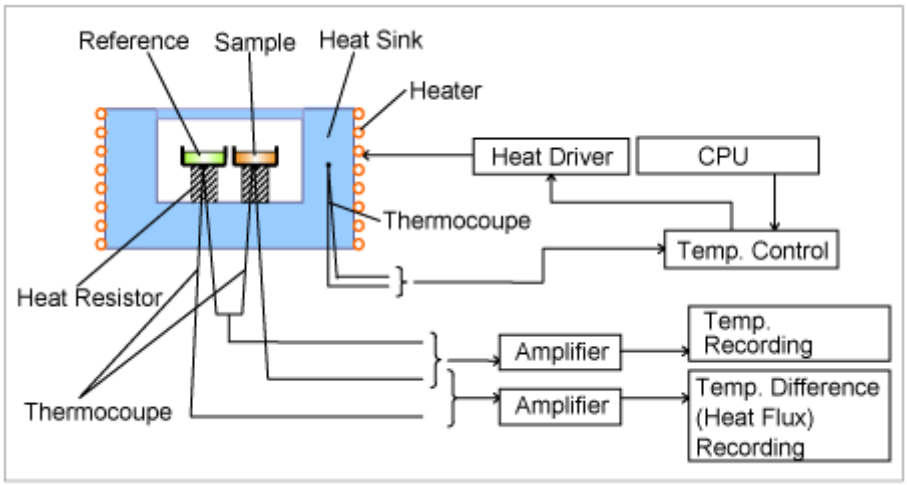


Figure 1. Block diagram of Heat Flux DSC

DSC is a commercially available instrument which has two (2) types: Heat Flux Type and Power Compensation Type. Figure 1 shows the block diagram of Heat Flux DSC as an example. Heat Flux DSC comprises the sample and reference holder, the heat resistor, the heat sink, and the heater. Heat of heater is supplied into the sample and the reference through heat sink and heat resistor. Heat flow is proportional to the heat difference of heat sink and holders. Heat sink has the enough heat capacity compared to the sample. In case the sample occurs endothermic or exothermic phenomena such as transition and reaction, this endothermic or exothermic phenomena is compensated by heat sink. Thus the temperature difference between the sample and the reference is kept constant. The difference the amount of heat supplied to the sample and the reference is proportional to the temperature difference of both holders. By calibrating the standard material, the unknown sample quantitative measurement is achievable.

DSC enables the measurements of the transition such as the glass transition, melting, and crystallization. Furthermore, the chemical reaction such as thermal curing, heat history,

specific heat capacity, and purity analysis are also measurable. Recently, with the development of the highly-functional polymeric material, these thermal properties analysis needs are increasing dramatically. DTA and DSC detect the temperature differences between the sample and the reference; however, DSC can perform the quantitative measurement of the amount of heat on top.

Principle of Thermogravimetry (TG)

A technique in which the mass of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.

A method in which thermogravimetry and differential thermal analysis are combined and measured simultaneously by a single apparatus.

Description of TG/DTA

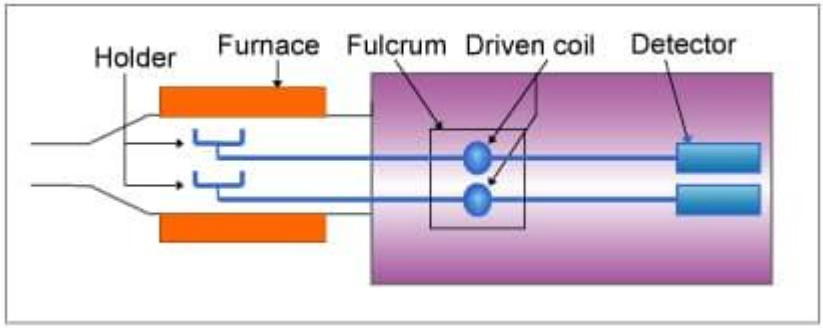


Figure 1. Block diagram of horizontal differential TG/DTA

Figure 1 shows the The balance beams for the sample and the reference are located in the furnace. The masses of the sample and the reference are measured by the sensitivity-calibrated drive coils separately. The mass difference is sent as TG signal. By the differential mass measurement, the effects of the beam expansion, the convection flow, and buoyant force are cancelled. Thus the highly sensitive thermogravimetry measurement is achieved. The mass measurement of the sample and the reference by the independent drive coils enables the easy adjustment of the TG baseline drift electrically.

Also, thermocouple is located in each holder which enables the simultaneous DTA signal output.

TG can be utilized for the analysis of the thermal decomposition, the oxidization, the dehydration, the heat resistance, and kinetics analysis. By combining with the other measurement technique, variety of information can be achieved from one sample. In particular, TG/DTA simultaneous measurement instrument is most common.

SUGGESTED MATERIALS

1. Svehla, G. (2002). Vogel's Qualitative Inorganic Analysis (VII Edition). Singapore: Pearson Education.
2. Christian, G. D. (2007). *Analytical Chemistry* (VI Edition). United States: John Wiley & Sons.
3. Skoog, D. A., West, D. M., Holler, F. J., & Crouch, S. R. (2014). *Fundamentals of Analytical Chemistry* (IX Edition). United States of America: Cengage Learning.

Section-A

(Online examination)

20x1= 20 Marks

Possible questions

1. What are the principles and applications of Cyclic voltammetry
2. What are the principles and applications of coulometry
3. What are the principles and applications of amperometry
4. Explain the Principle and applications of differential thermal analysis (DTA)
5. Explain the Principle and applications of differentials scanning calorimetry (DSC)
6. Explain the Principle and applications of thermogravimetric analysis (TGA)
7. Compare and contrast differentials scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

KARPAGAM ACADEMY OF HIGHER EDUCATION

CLASS: IMSc CHEMISTRY COURSE NAME: ANALYTICAL CHEMISTRY

COURSE CODE: 18CHP205B UNIT: I (Quantitative Inorganic Analysis) BATCH:2018-2020

Analytical Chemistry

S.No	Question	a	b	c	d	Answer
1.	In Electrochemical analyses, one in which the potential that develops between two electrodes is measured is called	potentiometry	amperometry	Coulometry	TGA	potentiometry
2.	In Electrochemical analyses, the current that flows between two electrodes is measured	potentiometry	amperometry	Coulometry	TGA	amperometry
3.	Potentiometry is related to	Chemical reactions	Photochemical reactions	Electrochemical reactions	rearrangements	Electrochemical reactions
4.	The use of voltammetry is to obtain analytical information like	redox potentials and equilibrium constants	rate constants for reactions	mechanisms	concentration	concentration
5.	The use of voltammetry is to obtain Thermodynamic information like	redox potentials and equilibrium constants	rate constants for reactions	mechanisms	concentration	redox potentials and equilibrium constants
6.	The use of voltammetry is to obtain Thermodynamic information like	redox potentials and equilibrium constants	rate constants for reactions	mechanisms	concentration	rate constants for reactions
7.	Any experiment where we expose a solution of an analyte to an electrode, change the electrode	voltammetry	Complexometric titration	TGA	Differential scanning calorimetry	voltammetry

	potential, and observe the current that flows in response.					
8.	The analytic technique that informs us about the thermodynamics and kinetics of electron transfer for a given analyte	voltammetry	Complexometric titration	TGA	Differential scanning calorimetry	voltammetry
9.	Voltammetry is a technique which informs about the	thermodynamics and kinetics of electron transfer for a given analyte	Decomposition temperature of an analyte	Thermal stability of a substance	Functional groups present in the compound	thermodynamics and kinetics of electron transfer for a given analyte
10.	If we were to only sweep (change the electrode potential) in one direction and stop, the experiment would be referred to as	a "linear sweep voltammogram	"cyclic" voltammetry	Thermal gravimetric analysis	Scanning electron microscopy	a "linear sweep voltammogram
11.	if we tell the potential sweep to reverse directions when the potential reaches a certain value and return to the starting potential, the experiment would be referred to as	a "linear sweep voltammogram	"cyclic" voltammetry	Thermal gravimetric analysis	Scanning electron microscopy	"cyclic" voltammetry
12.	The technique which deals with an exhaustive electrolysis of the analyte	a "linear sweep voltammogram	"cyclic" voltammetry	Thermal gravimetric analysis	coulometry	coulometry
13.	Coulometry is a technique which deals with	an exhaustive electrolysis of the analyte	thermodynamics and kinetics of electron transfer for a given analyte	Decomposition temperature of an analyte	Thermal stability of a substance	an exhaustive electrolysis of the analyte

14.	In coulometry	The analyte is completely oxidized or reduced at the working electrode	Gives the thermodynamics and kinetics of electron transfer for a given analyte	Gives the Decomposition temperature of an analyte	Gives the Thermal stability of a substance	The analyte is completely oxidized or reduced at the working electrode
15.	In coulometry	it reacts completely with a reagent generated at the working electrode.	Gives the thermodynamics and kinetics of electron transfer for a given analyte	Gives the Decomposition temperature of an analyte	Gives the Thermal stability of a substance	it reacts completely with a reagent generated at the working electrode.
16.	The coulemetry in which we apply a constant potential to the electrochemical cell it is called	controlled-potential coulometry	controlled-current coulometry	"cyclic" voltammetry	Amperometry	controlled-potential coulometry
17.	In coulemetry in which we pass a constant current through the electrochemical cell. It is called	controlled-potential coulometry	controlled-current coulometry	"cyclic" voltammetry	Amperometry	controlled-current coulometry
18.	In controlled-potential coulometry	we apply a constant potential to the electrochemical cell	we pass a constant current through the electrochemical cell.	an exhaustive electrolysis of the analyte takes place	The analyte is completely oxidized or reduced at the working electrode	we apply a constant potential to the electrochemical cell
19.	In controlled-current coulometry	we apply a constant potential to the electrochemical cell	we pass a constant current through the electrochemical cell.	an exhaustive electrolysis of the analyte takes place	The analyte is completely oxidized or reduced at the working electrode	we pass a constant current through the electrochemical cell.
20.	Q=nFNA is called	Faradays law of electrolysis	Ionic product of water	Solubility product	Kolrauches law	Faradays law of electrolysis

21.	Coulometry requires	50% current efficiency	100% current efficiency	75% current efficiency	10% current efficiency	100% current efficiency
22.	Coulometry requires	50% current efficiency	an accurately measured current efficiency	75% current efficiency	10% current efficiency	an accurately measured current efficiency
23.	In controlled-potential coulometry, Integrating the area under the curve from t = 0 to $t = t_e$ gives	The total oxidation potential	The total Reduction potential	Electromotive force	the total charge.	the total charge.
24.	A typical analysis time for controlled-current coulometry is	less than 10 min	30 min	30–60 min	120 min	less than 10 min
25.	A typical analysis time for controlled-potential coulometry	less than 10 min	30 min	30–60 min	120 min	30–60 min
26.	The analysis time is shorter for controlled-current coulometry than controlled-potential coulometry because	The potential does not decrease over time	the current decreases over time	the current does not decrease over time	the current increases over time	the current does not decrease over time
27.	the total charge is obtained in controlled-current coulometry is	Integrating the area under the curve from t = 0 to $t = t_e$	the product of current and time	The sum of current and time	Dividing the current by time	the product of current and time
28.	the thickness of the metallic coatings may be determined by	Coulometry	voltametry	Calorimetery	Differential scanning calorimetry	Coulometry
29.	the total anti-oxidant capacity of the anti-oxidants may be determined by	Coulometry	voltametry	Calorimetery	Differential scanning calorimetry	Coulometry
30.	the total carbon in ferrous and non-ferrous metals may be determined by.	Coulometry	voltametry	Calorimetery	Differential scanning calorimetry	Coulometry

31.	The reagent is generated electrically and determined by the current and by the time.	Coulometric Titrations	Complexometric titrations	In cyclic voltametry	Calorimetry	Coulometric Titrations
32.	Which is not an advantage of coulometry	Standard solutions are not required	Reagent is generated	No need to dilute the samples	Reagent Generation is difficult.	Reagent Generation is difficult.
33.	Which is the disadvantage of coulometry	Standard solutions are not required	Reagent is generated	No need to dilute the samples	Inferences are more	Inferences are more
34.	The detection of ions presence on solution on the basis of electric current or change in electric current is called as	Coulometric Titrations	Complexometric titrations	In cyclic voltametry	Amperometry	Amperometry
35.	which is widely used in food processing industries.	Coulometric Titrations	Complexometric titrations	In cyclic voltametry	Amperometry	Amperometry
36.	A voltammetric analyses is done by using a certain setup of a measuring chamber which contains	Working electrode, reference electrode and auxillary electrode	Working electrode, reference electrode	Working electrode, reference electrode	microelectrode	Working electrode, reference electrode and auxillary electrode
37.	a type of titration in which the determination of the equivalence point is done by measuring the electric current which produced by the titration reaction	Coulometric Titrations	Complexometric titrations	In cyclic voltametry	Amperometry titrations	Amperometry titrations
38.	a few current measurements at constant applied voltage before and after the end point are sufficient to estimate the	Coulometric Titrations	Complexometric titrations	In cyclic voltametry	Amperometry titrations	Amperometry titrations

	equivalence point and end point. This is an advantage of					
39.	A technique in which the difference in temperature between the sample and a reference material is monitored against time or temperature	Differential Thermal Analysis	Differential scanning calorimetry	Thermogravimetric analysis	cyclic voltametry	Differential Thermal Analysis
40.	A technique in which the temperature of the sample unit, formed by a sample and reference material, is varied in a specified program, and the temperature difference between the sample and the reference material is measured as a function of temperature.	Differential Thermal Analysis	Differential scanning calorimetry	Thermogravimetric analysis	cyclic voltametry	Differential scanning calorimetry
41.	A technique in which the mass of the sample is monitored against time or temperature	Differential Thermal Analysis	Differential scanning calorimetry	Thermogravimetric analysis	cyclic voltametry	Thermogravimetric analysis
42.	a differential thermocouple is set up to detect the temperature difference between the sample and the reference in	Differential Thermal Analysis	Differential scanning calorimetry	Thermogravimetric analysis	cyclic voltametry	Differential Thermal Analysis
43.	In DTA When the furnace heating begins, the reference and the sample begin heating with a slight change in	delay depending on their respective heat capacity	delay depending on their respective melting point	delay depending on their respective boiling point	delay depending on their respective freezing point	delay depending on their respective heat capacity
44.	the glass transition, melting,	Differential	Differential	Thermogravimetric	cyclic voltametry	Differential

	and crystallization can be determined using	Thermal Analysis	scanning calorimetry	analysis		scanning calorimetry
45.	thermal curing, heat history, specific heat capacity, and purity analysis are also measurable using	Differential Thermal Analysis	Differential scanning calorimetry	Thermogravimetric analysis	cyclic voltametry	Differential scanning calorimetry
46.	Differential scanning calorimetry we can measure	the glass transition, melting, and crystallization	Entropy of the compound	Rate constant of a reaction	Boiling point of a compound	the glass transition, melting, and crystallization
47.	Differential scanning calorimetry we can measure	thermal curing, heat history, specific heat capacity, and purity analysis	Entropy of the compound	Rate constant of a reaction	Boiling point of a compound	thermal curing, heat history, specific heat capacity, and purity analysis
48.	utilized for the analysis of the thermal decomposition, the oxidization, the dehydration, the heat resistance, and kinetics analysis	Differential Thermal Analysis	Differential scanning calorimetry	Thermogravimetric analysis	cyclic voltametry	Thermogravimetric analysis
49.	'Foreign' salts are added during amprometric titration	To eliminate migration current	To make the titration independent of the characteristics of the capillary.	To find the equivalence point	To precipitate the compound	To eliminate migration current
50.	Which of the following is true	The area under a DTA peak represents the enthalpy of the change	In DTA both the reference and the sample undergoes change with temperature	DTA stands for Direct Thermal Analysis	The area under a DTA peak represents the heat capacity of the compound	The area under a DTA peak represents the enthalpy of the change
51.	The DTA plot of calcium oxalate in air shows an upward peak	Formation of calcium oxide	Formation of calcium carbonate	Burning of CO	Elimination of water	Burning of CO

	due to					
52.	In the heat vs temperature plot of DSC of a polymer the glass transition is represented by	A gradual slope	A hump	glass transition temperature cannot be determined	A kink	A kink
53.	Differential scanning calorimetry is a technique to measure	Specific heat	Impact energy	Thermal expansion	Electrical conductivity	Specific heat
54.	Differential scanning calorimetry comes under the category of	Spectral analysis	Morphological analysis	Thermal analysis	Geological analysis	Thermal analysis
55.	DTA is a	Spectral analysis	Morphological analysis	Thermal analysis	Geological analysis	Thermal analysis
56.	TGA is a	Spectral analysis	Morphological analysis	Thermal analysis	Geological analysis	Thermal analysis
57.	Which is not true regarding amperometric titrations	a few current measurements at constant applied voltage before and after the end point are sufficient to estimate the equivalence point	Not suitable for precipitation titration or in acid-base titration.	'Foreign' salts are added to eliminate migration current	A amperometric titration can be carried out at low dilutions	Not suitable for precipitation titration or in acid-base titration.
58.	Which is not true regarding amperometric titrations	a few current measurements at constant applied voltage before and after the end point are not sufficient to estimate the equivalence point	suitable for precipitation titration or in acid-base titration.	'Foreign' salts are added to eliminate migration current	A amperometric titration can be carried out at low dilutions	a few current measurements at constant applied voltage before and after the end point are not sufficient to estimate the equivalence point
59.	Which is not true regarding amperometric titrations	a few current measurements at	suitable for precipitation	'Foreign' salts are added to generate	A amperometric titration can be	'Foreign' salts are added to generate

		constant applied voltage before and after the end point are sufficient to estimate the equivalence point	titration or in acid-base titration.	migration current	carried out at low dilutions	migration current
60.	Loss of water of crystallisation will be represented in DSC plot as	Downward slope	Upward slope	Downward peak	Upward peak	Downward peak

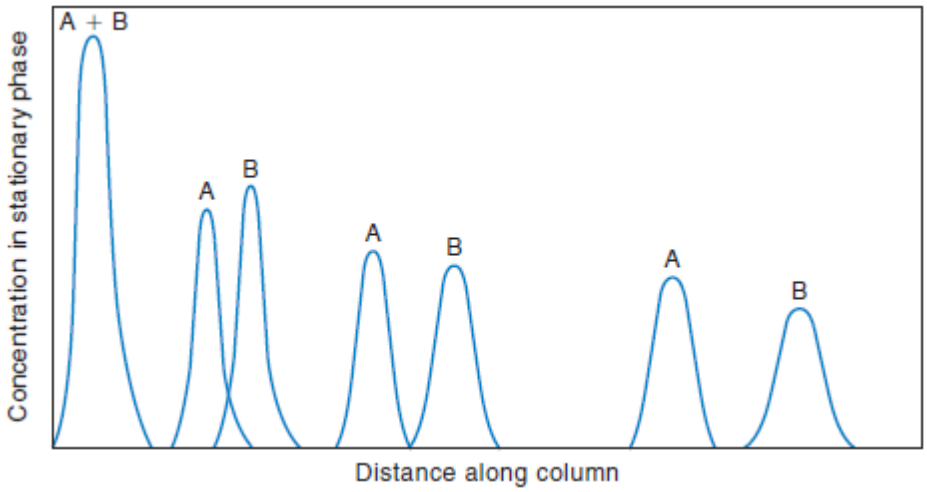
UNIT- V

Chromatographic Methods: Classification – techniques and applications in column, size-exclusion, ion exchange, paper and thin layer chromatography.
Gas chromatography and high performance liquid chromatography (HPLC)-principle, equipment design, sample injection system, columns, detectors and applications.

Principles of Chromatographic Separations

Chromatographic retention of a compound is often associated with the establishment of an equilibrium between the stationary phase and the mobile phase, but in reality, chromatography is a dynamic process, and true equilibrium may not be reached.

While the mechanisms of retention for various types of chromatography differ, they are all based on the dynamic distribution of an analyte between a fixed stationary phase and a flowing mobile phase. Each analyte will have a certain affinity for each phase. A small volume of sample is placed at the top of the column, which is filled with particles constituting the stationary phase and the solvent. Rather than an equilibrium-based "plate view" of chromatography, many hold that a "rate view" of chromatography to be more rigorous: in this view, the partition ratio is simply the ratio of the time a solute spends in the stationary phase to that it spends in the mobile phase. More solvent, functioning as mobile phase, is added to the top of the column and percolates through the column. The individual components interact with the stationary phase to different degrees, and the distribution is given in terms of the idealized equilibrium relationship represented by Equation. The distribution of the analyte between the two phases is governed by many factors: the temperature, the type of compound, and the stationary and mobile phases. As Equation implies, solutes with a large K value will be retained more strongly by the stationary phase than those with a small K value. The result is that the latter will move along the column (be eluted) more rapidly. The band broadens and decreases in amplitude as it travels down the column. This broadening of the injected rectangular wave sample pulse into a Gaussian peak is intrinsic to the chromatographic process,



Distribution of two substances, A and B, along a chromatographic column in a typical chromatographic separation.

and is not due to the lack of attaining equilibrium, parabolic profile of laminar flow or any other nonideal characteristics. The areas under the respective peaks, proportional to the analyte masses, remain the same. Band-broadening effects are treated below. Figure illustrates the distribution of two species A and B along a column as they move down the column. A plot of the concentrations of the analytes as they emerge from the column and as a function of time (or, less commonly, as a function of the volume of the mobile phase passed through the column) is called a chromatogram. A flow-through detector is placed at the end of the column to automatically measure the eluted compounds and print out a chromatogram of the peaks for the separated substances. Although there are several different forms of chromatography, this simplified model typifies the mechanism of each. That is, *there is nominally an equilibriumbetween two phases, one mobile and one stationary*. (True equilibrium is never really achieved.) By continually adding mobile phase, the analytes will distribute between the two phases and eventually be eluted, and if the distribution is sufficiently different for the different substances, they will be separated.

Classification of Chromatographic Techniques

Chromatographic processes can be classified according to the type of equilibration process involved, which is governed by the type of stationary phase. Various bases of equilibration

are: (1) adsorption, (2) partition, (3) ion exchange, and (4) size dependent pore penetration. More often than not, solute stationary-phase–mobilephase interactions are governed by a combination of such processes.

ADSORPTION CHROMATOGRAPHY

The stationary phase is a solid on which the sample components are adsorbed. The mobile phase may be a liquid (*liquid–solid chromatography*) or a gas (*gas–solid chromatography*); the components distribute between the two phases through a combination of sorption and desorption processes. Thin-layer chromatography (TLC) is a special example of adsorption chromatography in which the stationary phase is planar, in the form of a solid supported on an inert plate, and the mobile phase is a liquid.

PARTITION CHROMATOGRAPHY

The stationary phase of partition chromatography is usually a liquid supported on a solid or a network of molecules, which functions virtually as a liquid, bonded on the solid support. Again, the mobile phase may be a liquid (*liquid–liquid partition chromatograpy*) or a gas (*gas–liquid chromatography*, GLC). In the normal mode of operations of liquid–liquid partition chromatography, a polar stationary phase (e.g., cyano groups bonded on silica gel) is used, with a nonpolar mobile phase (e.g., hexane). When analytes (dissolved in the mobile phase) are introduced into the system, retention increases with increasing polarity. This is called **normal-phase chromatography**. If a nonpolar stationary phase is used with a polar mobile phase, the retention of solutes decreases with increasing polarity. This mode of operation is termed **reversed-phase chromatography** and is presently the most widely used mode. “Normal-phase” chromatography significantly predates the reversed-phase mode, and was originally called liquid chromatography. Only after “reversed-phase” chromatography came along, the need arose to distinguish between the two, and the older version, still more prevalent then, was termed “normal-phase.”

ION EXCHANGE AND SIZE EXCLUSION CHROMATOGRAPHY

Ion exchange chromatography uses supports with ion exchange functionalities as the stationary phase. The mechanism of separation is based on ion exchange equilibria. Hydrophobic interactions play a strong role in most ion exchange separations nevertheless, particularly in anion exchange chromatography. In size exclusion chromatography, solvated molecules are separated according to their size by their ability to penetrate into porous pockets and passages in the stationary phase. Some types of chromatography are considered together as a separate technique, such as *gas chromatography* for gas–solid and gas–liquid chromatography. In every case, successive equilibria determine to what extent the analyte stays behind in the stationary phase or moves along with the eluent (mobile phase). In column chromatography, the column may be packed with small particles that act as the stationary phase (adsorption chromatography) or are coated with a thin layer of liquid phase (partition chromatography). In gas chromatography, the most common form today is a capillary column in which a virtual liquid phase, often a polymer, is coated or bonded on the wall of the capillary tube.

GAS CHROMATOGRAPHY

Gas chromatography (GC) is one of the most versatile and ubiquitous analytical techniques in the laboratory. It is widely used for the determination of organic compounds. The separation of benzene and cyclohexane (bp 80.1 and 80.8◦C) is extremely simple by gas chromatography, but it is virtually impossible by conventional distillation. Although Martin and Synge invented liquid–liquid chromatography in 1941, the introduction of gas–liquid partition chromatography by James and Martin a decade later had a more immediate and larger impact for two reasons. First, as opposed to manually operated liquid–liquid column chromatography, GC required instrumentation for application, which was developed by collaboration among chemists, engineers, and physicists; and analyses were much more rapid and done on a small scale. Second, at the time of its development, the petroleum industry badly needed improved analytical monitoring and immediately adopted GC. Within a few short years, GC was used for the analysis of almost every type of organic compound. Very complex mixtures can be separated by this technique. There are two types of GC: **gas–solid (adsorption) chromatography** and **gas–liquid (partition) chromatography**. The more

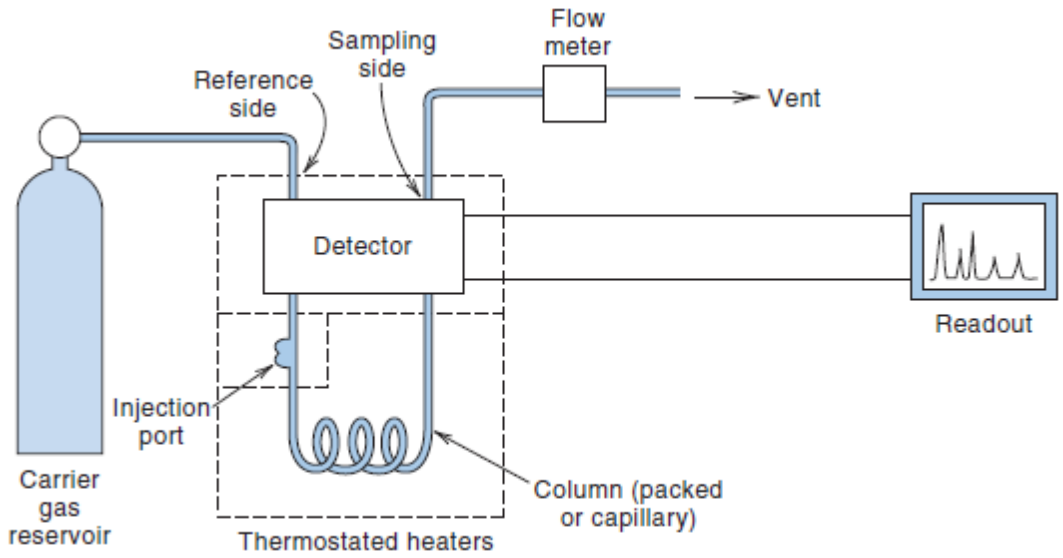
important of the two is gas–liquid chromatography (GLC), used in the form of a capillary column.

Performing GC Separations

Analyte in the vapor state In gas chromatography, the sample is converted to the vapor state a gas) by injection into a heated port, and the eluent is a gas (the **carrier gas**). The stationary phase is generally a nonvolatile liquid or a liquid-like phase supported on or bonded to a capillary wall or inert solid particles such as diatomaceous earth (kieselguhr—derived from skeletal remains of microscopic marine single-celled algae, consisting mainly of silica); the kieselguhr is usually calcined to increase particle size, creating what is known as firebrick, sold as Chromosorb P orW, for example. There are a large number of liquid phases available, and it is by changing the liquid phase, rather than the mobile phase, that different separations are accomplished. The most important factor in gas chromatography is the selection of the proper column (stationary phase) for the particular separation to be attempted. The nature of the liquid or solid phase will determine the exchange equilibrium with the sample components; and this will depend on the solubility or adsorbability of the analytes, the polarity of the stationary phase and sample molecules, the degree of hydrogen bonding, and specific chemical interactions. Most separation protocols have been developed empirically, however, theoretical approaches as well as suitable software are now available.

A schematic diagram of a gas chromatograph is given in Figure and a picture of a modern GC system is shown in Figure The sample is rapidly injected by means of a hypodermic syringe through a septum or from a gas sampling valve. Typically, the injected sample first goes into the inlet/inlet liner and then the carrier gas carries it (or if split, a portion of it—often done with capillary columns to avoid overloading) to the column. The sample injection port, column, and detector are heated to temperatures at which the sample has a vapor pressure of at least 10 torr, usually about 50◦C above the boiling point of the highest boiling solute. The injection port and detector are usually kept somewhat warmer than the column to promote rapid vaporization of the injected sample and prevent sample condensation in the detector. For packed columns, liquid samples of 0.1 to 10 μL are injected, while gas samples

of 1 to 10mL are injected. Gases may be injected by means of a gas-tight syringe or through a special gas inlet chamber of constant volume (gas sampling valve). For capillary columns, volumes of only about 1/100 these sizes must be injected because of the lower capacity (albeit greater resolution) of the columns. Sample splitters are included on chromatographs designed for use with capillary columns that deliver a small fixed fraction of the sample to the column, with the remainder going to



Schematic diagram of gas chromatograph.

waste. They usually also allow splitless injection when packed columns are used (split/splitless injectors). Separation occurs as the vapor constituents equilibrate between carrier gas and the stationary phase. The carrier gas is a chemically inert gas available in pure form such as argon, helium, or nitrogen. A highly dense gas gives best efficiency since diffusivity is lower, but a low-density gas gives faster speed. The choice of gas is often dictated by the type of detector. Gas chromatography always uses flow-through detectors that automatically detect the analytes as they elute from the column; the majority of GC detectors are destructive. The sample emerges from the column at a constant flow rate. A variety of detectors are used, the specific response is dependent upon the analyte (see below). Some detectors contain a **reference side** and a **sampling side**. The carrier gas is passed through the

reference side before entering the column and emerges from the column through the sampling. The difference in response of the sampling side relative to the reference side is processed as the analytical signal. The signal, representing the chromatographic peaks is acquired and displayed by a data system as a function of time. By measuring the **retention time** (the minutes between the time the sample is injected and the time the chromatographic peak appears) and comparing this time with that of a standard of the pure substance, it may be possible to identify the peak (agreement of retention times of two compounds does not guarantee the compounds are identical). The area under the peak is proportional to the concentration, and so the amount of substance can be quantitatively determined. The peaks are often very sharp (narrow in their temporal width, this requires fast detectors) and, if so, the peak height can be compared with a calibration curve prepared in the same manner. Chromatography data handling systems usually have automatic detection of peaks, readout of the peak area and/or peak height, as well as the retention time.

With complex mixtures, it is not a simple task to identify the many peaks. Instruments are commercially available in which the gaseous effluent is fed into a mass spectrometer where they are ionized, sorted on the basis of their mass-to-charge ratio, and identified based on mass/charge ratio mass (as well as and fragmentation pattern). This important analytical technique is called **gas chromatography–mass.** The mass spectrometer is a sensitive selective detector, and when a capillary GC column (very high resolution) is used (capillary GC–MS), this technique is capable of identifying and quantifying very complex mixtures of trace substances. For example, hundreds of compounds may be identified in sewage effluents, and traces of complex drugs in urine or blood or pollutants in water can be determined. GC-GC offers yet an order of magnitude greater peak capacity, some 4000 compounds have been identified in cigarette smoke. For best sensitivity, though, some of the element or compound-type specific detectors listed later offer exquisitely low detection limits.

What Compounds Can Be Determined by GC?

Many, many compounds may be determined by gas chromatography, but there are limitations. They must be volatile and stable at operational temperatures, typically from 50 to 300◦C. GC is useful for:

- All gases
- Most nonionized organic molecules, solid or liquid, containing up to about 25 carbons
- Many organometallic compounds (volatile derivatives of metal ions may be prepared)

If compounds are not volatile or stable, often they can be derivatized to make them amenable to analysis by GC. GC cannot be used for macromolecules nor salts, but these can be determined by HPLC and ion chromatography.

Gas Chromatography Columns

The two types of columns used in GC are **packed columns** and **capillary columns**. Packed columns came first and were used for many years. Capillary columns are more commonly used today, but packed columns are still used for applications that do not require high resolution or when increased capacity is needed.

PACKED COLUMNS

Columns can be in any shape that will fill the heating oven. Column forms include coiled tubes, U-shaped tubes, and W-shaped tubes, but coils are most commonly used. Typical packed columns are 1 to 10m long and 0.2 to 0.6 cm in diameter. Well-packed columns may have 1000 plates/m, and so a representative 3-m column would have 3000 plates. Short columns can be made of glass or glass/silica-lined stainless steel, but longer columns may be made of stainless steel or nickel so they can be straightened for filling and packing. Columns are also made of Teflon. For inertness, glass is still preferred for longer columns. The resolution for packed columns increases only with the square root of the length of the column. Long columns require high pressure and longer analysis times and are used only when necessary (e.g., analytes that are poorly retained require more stationary phase to achieve adequate retention). Separations are generally attempted by selecting columns in

lengths of multiples of 3, such as 1 or 3 m. If a separation isn't complete in the shorter column, then the next longer one is tried.

The column is packed with small particles that may themselves serve as the stationary phase (adsorption chromatography) or more commonly are coated with a nonvolatile liquid phase of varying polarity (partition chromatography). Gas–solid chromatography (GSC) is useful for the separation of small gaseous species such as H2, N2, CO2, CO, O2, NH3, and CH4 and volatile hydrocarbons, using high surface area inorganic packings such as alumina *(*Al2O3*)* or porous polymers (e.g., Porapak Q—a polyaromatic cross-linked resin with a rigid structure and a distinct pore size).

The gases are separated by their size due to retention by adsorption on the particles. Gas–solid chromatography is preferred for aqueous samples. The solid support for a liquid phase should have a high specific surface area that is chemically inert but wettable by the liquid phase. It must be thermally stable and available in uniform sizes. The most commonly used supports are prepared from diatomaceous earth, a spongy siliceous material. They are sold under many different trade names. Chromosorb P is a pink-colored diatomaceous earth prepared from crushed firebrick. Chromosorb W is diatomaceous earth that has been heated with an alkaline flux to decrease its acidity; it is lighter in color. Chromosorb G was the first support expressly developed for GC, combining the good efficiency and handling characteristics of Chromosorb G while having the low adsorptive properties of Chromosorb W. Generally, all of the above are available in non-acid washed, acid washed, and silanized with dimethylchlorosilane (DMCS, this greatly reduces polarity) and in high-performance versions (HP, controlled uniform fine particles). Chromosorb 750 is a very inert and efficient support that is acid washed and DMCS treated. Chromosorb T is useful for separating permanent gases and small molecules, it is largely based on fluorocarbon (Teflon) particles. Chromosorb P is much more acidic than Chromosorb W, and it tends to react with polar solutes, especially those with basic functional groups.

Column-packing support material is coated by mixing with the correct amount of liquid phase dissolved in a low-boiling solvent such as acetone or pentane. About a 5 to 10% coating (wt/wt) will give a thin layer. After coating, the solvent is evaporated by heating and stirring;

the last traces may be removed in a vacuum. A newly prepared column should be conditioned at elevated temperature by passing carrier gas through it for several hours, preferably before connecting detectors or other downstream components. The selection of liquid phases is discussed below. Particles should be uniform in size for good packing and have diameters in the range of 60 to 80 mesh (0.25 to 0.18 mm), 80 to 100 mesh (0.18 to 0.15 mm), or 100 to 120 mesh (0.15 to 0.12 mm). Smaller particles are impractical due to high pressure drops generated.

CAPILLARY COLUMNS——THE MOST WIDELY USED

In 1957 Marcel Golay in his equation predicted increased number of plates in a narrow open-tubular column with the stationary phase supported on the inner wall. Band broadening due to multiple paths (eddy diffusion) would be eliminated. And in narrow columns, the rate of mass transfer is increased since molecules have small distances to diffuse. Higher flow rates can be used due to decreased pressure drop, which decreases molecular diffusion. Golay's work led to the development of various **open-tubular columns** that today provide extremely high resolution and have become the mainstay for gas-chromatographic analyses. These columns are made of thin fused silica *(*SiO_2*)* coated on the outside with a polyimide polymer for support and protection of the fragile silica capillary, allowing them to be coiled. The polyimide layer is what imparts a brownish color to the columns, and it often darkens on use. The inner surface of the capillary is chemically treated to minimize interaction of the sample with the silanol groups (Si–OH) on the tubing surface, by reacting the Si–OH group with a silane-type reagent (e.g., DMCS). Capillaries can also be made of stainless steel or nickel. Stainless steel interacts with many compounds and so is deactivated by treatment with DMCS, producing a thin siloxane layer to which stationary phases can be bonded. Stainless steel columns, though less common, are more robust than fused silica columns and are used for applications requiring very high temperatures.

The capillaries are 0.10 to 0.53mm internal diameter, with lengths of 15 to 100m and can have several hundred thousand plates, even a million. They are sold as coils of about 0.2m diameter (Figure 20.4). Capillary columns offer advantages of high resolution with narrow peaks, short analysis time, and high sensitivity (with detectors designed for capillary GC) but

are more easily overloaded by too much sample. Split injectors by and large alleviate the overloading problem.

There are three types of open-tubular columns. **Wall-coated open-tubular** (WCOT) columns have a thin liquid film coated on and supported by the walls of the capillary. The walls are coated by slowly passing a dilute solution of the liquid phase through the columns. The solvent is evaporated by passing carrier gas through the columns. Following coating, the liquid phase is cross-linked to the wall. The resultant stationary liquid phase is 0.1 to 0.5 μm thick. Wall-coated open-tubular columns typically have 5000 plates/m. So a 50-m column will have 250,000 plates.

In **support coated open-tubular** (SCOT) columns, solid microparticles coated with the stationary phase (much like in packed columns) are attached to the walls of the capillary. These have higher surface area and have greater capacity than WCOT columns. The tubing diameter of these columns is 0.5 to 1.5 mm, larger than WCOT columns. The advantages of low pressure drop and long columns is maintained, but capacity of the columns approaches that of packed columns. Flow rates are faster and dead volume connections at the inlet and detector are less critical. Sample splitting is not required in many cases, so long as the sample volume is 0.5 □L or less. If a separation requires more than 10,000 plates, then a SCOT column should be considered instead of a packed column.

The third type, **porous layer open-tubular** (PLOT) columns, have solid-phase particles attached to the column wall, for adsorption chromatography. Particles of alumina or porous polymers (molecular sieves) are typically used. These columns, like packed GSC columns, are useful for separating permanent gases, as well as volatile hydrocarbons. The resolution efficiency of open-tubular columns is generally in the order: WCOT > SCOT > PLOT. Wide-bore (0.5-mm) open-tubular columns have been developed with thicker stationary liquid phases, up to 5 □m, that approach the capacity of SCOT and packed columns, but their resolution is decreased. Many

wide-bore columns are only available with thicker films. Columns can tolerate a limited amount of analyte before becoming overloaded, causing peak distortion and broadening, and shifts in retention time. Sample capacity ranges are from approximately 100 ng for a 0.25-

mm-i.d. column with 0.25-μm-thick film, up to 5 μg for a 0.53-mm-i.d. column with a 5-μm-thick stationary phase.

Gas Chromatography Detectors

Since the initial experiments with gas chromatography were begun, a large number of detectors have been developed. Some are designed to respond to most compounds in general, while others are designed to be selective for particular types of substances. We describe some of the more widely used detectors. Table lists and compares some commonly used detectors with respect to application, sensitivity, and linearity. The original GC detector was the **thermal conductivity**, or **hot wire**, **detector** (TCD). As a gas is passed over a heated filament wire, the temperature and thus the resistance of the wire will vary according to the thermal conductivity of the gas. Typically it is deployed in a referenced configuration: The pure carrier is passed over one filament, and the effluent gas containing the sample constituents is passed over another.

These filaments are in opposite arms of aWheatstone bridge circuit that generates a voltage as the resistance of the sensing filament changes. So long as there is only carrier gas in the effluent, the resistance of the wires will be the same. But whenever a sample component elutes, a small resistance change will occur in the effluent arm. The change in the resistance, which is proportional to the concentration of the sample component in the carrier gas, is registered by the data system. The TCD is particularly useful for the analysis of gaseous mixtures, and of permanent gases such as CO2.

TABLE 20.3
Comparison of Selected Gas-Chromatographic Detectors

Detector	Application	Sensitivity Range
Thermal conductivity	General, responds to all substances	Fair, 5–100 ng, 10 ppm–100%
Catalytic combustion	Very similar to the FID	Fair, very similar to TCD
Flame ionization	All organic substances; some oxygenated products respond poorly. Good for hydrocarbons	Very good, 10–100 pg, 10 ppb–99%
Flame photometric	Sulfur compounds (393 nm), phosphorus compounds (526 nm)	Very good, 10 pg S, 1 pg P
Flame thermionic	All nitrogen- and phosphorus-containing substances	Excellent, 0.1–10 pg, 100 ppt–0.1%
Rubidium silicate bead	Specific for nitrogen- and phosphorus-containing substances	Excellent
Argon ionization (β-ray)	All organic substances; with ultrapure He carrier gas, also for inorganic and permanent gases	Very good; 0.1–100 ng, 0.1–100 ppm
Electron capture	All substances that have affinity to capture electrons; no resonse for aliphatic and naphthenic hydrocarbons	Excellent for halogen containing substancs, 0.05–1 pg, 50 ppt—1 ppm
Vacuum UV absorption	Nearly all substances but inert gases and nitrogen	Excellent down to pg levels
Mass spectrometry	Nearly all substances. Depends on ionization method	Excellent

Hydrogen and helium carrier gases are preferred with thermal conductivity detectors because they have a very high thermal conductivity compared with most other gases, and so the largest change in the resistance occurs in the presence of sample component gases (helium is preferred for safety reasons). The thermal conductivity of hydrogen is 53.4 × 10−5 and that of helium is 41.6 × 10−5 cal/◦C-mol at 100◦C, while those of argon, nitrogen, carbon dioxide, and most organic vapors are typically one-tenth of these values. The advantages of thermal conductivity detectors are their simplicity and approximately equal response for most substances. Also, their response

is very reproducible. They are not the most sensitive detectors, however. Most organic compounds form ions in a flame, generally cations such as CHO+. This forms the basis of an

extremely sensitive detector, the **flame ionization detector** (FID). The ions are measured (collected) by a pair of oppositely charged electrodes. The response (number of ions collected) depends on the number of carbon atoms in the sample and on the oxidation state of the carbon. Those atoms that are completely oxidized do not ionize, and the compounds with the greatest number of low oxidation state carbons produce the largest signals. This detector gives excellent sensitivity,permitting measurement of components in the ppb concentration range. The FID is

about 1000 times more sensitive than the TCD. However, the dynamic range is more limited, and samples of pure liquids are generally restricted to 0.1 μL or less. The carrier gas is relatively unimportant. Helium, nitrogen, and argon are most frequently employed. The flame ionization detector is insensitive to most inorganic compounds, including water, and so aqueous solutions can be injected (but only if you have a compatible column). If oxygen is used as the flame support gas in place of air, then many inorganic compounds can be detected because a hotter flame is produced that can ionize them.

The **catalytic combustion detector** (CCD) responds much like an FID in regard to the type of compounds it responds to and has the sensitivity of a TCD. The detector is very small (typically 1 cm diameter). The sensor element consists of a Pt wire coil embedded in an alumina ceramic containing noble metal catalysts. It is well suited for use with an air-carrier GC application; with other carrier gases, air is added prior to passage over the detector.

The **flame thermionic detector** is essentially a two-stage flame ionization detector designed to give an increased specific response for nitrogen- and phosphoruscontaining substances. A second flame ionization detector is mounted above the first, with the flame gases from the first passing into the second flame. The two stages are divided by a wire mesh screen coated with an alkali salt or base such as sodium hydroxide. This detector is also known as a nitrogen–phosphorous detector (NPD).

The **electron capture detector** (ECD) is extremely sensitive for compounds that contain electronegative atoms and is selective for these. It is similar in design to the β-ray detector, except that nitrogen or methane doped with argon is used as the carrier gas. These gases have low excitation energies compared to argon and only compounds that have high electron

affinity are ionized, by capturing electrons. Many ECDs operate with helium as the carrier gas, using nitrogen as a makeup gas in the detector.

GC-VUV

An emerging technology for gas chromatography detection is vacuum ultraviolet (VUV) spectroscopy. Involving the absorption of light ranging in wavelength from approximately 120–200 nm, VUV spectroscopy has historically been limited to investigations at specialized synchrotron facilities, where these short-wavelength photons could be harnessed from electrons accelerated to extremely high kinetic energies. Very few accounts can be found of VUV spectroscopy in textbooks and in the literature. Only recently, have manufacturers devised bench-top devices with this capability that utilize a standard deuterium light source. The windows of the lamp and flow cell are made from MgF2, which allows for the transmission of low wavelength VUV radiation (for more on such materials). The biggest advantages of vapor phase VUV spectroscopy are that all molecules absorb in this region of the electromagnetic spectrum and when measurements are made in the gas phase, absorption features are sharp (in solution, interactions with solvent blur spectral absorption features); every molecule has a unique spectrum, which can be used to unequivocally assign its identity.

HPLC

PRINCIPLES

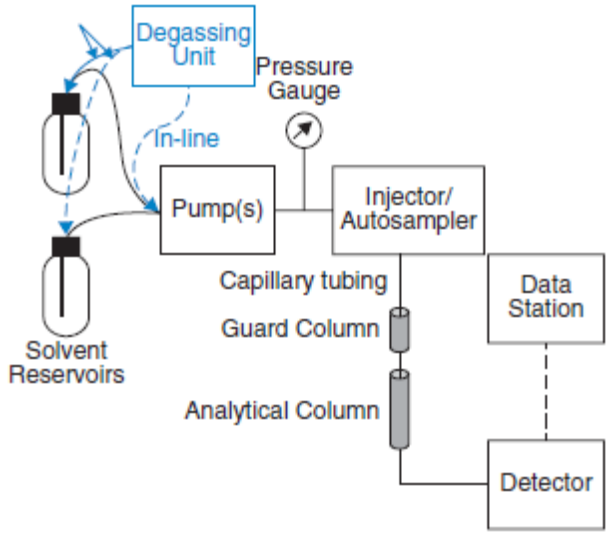
Figure 21.1 shows the basic components of an HPLC system and Figure illustrates a modern HPLC instrument. These instruments tend to be assembled in modular form, unlike most GC instruments, allowing the user to readily change different components. In HPLC, analytes are separated based on their differential affinity between a solid stationary phase and a liquid mobile phase. The kinetics of distribution of solutes between the stationary and the mobile phase is largely diffusion-controlled. Compared to gases, the diffusion coefficient of analytes in liquids is 1000 to 10,000 times slower. To minimize the time required for the interaction of the analytes between the mobile and the stationary phase, two criteria should be met. First, the packing particles should be small and as uniformly and densely packed as possible. This criterion is met by uniformly sized spherical particles and results in a smaller *A* value in the van Deemter equation (smaller eddy diffusion). Second, the stationary phase should be effectively a thin uniform film with no stagnant pools and provide a small *C* value (more rapid mass determinant of *H* in HPLC. Because molecular diffusion in liquids is small, the *B* term in Equation 19.13 is small. Hence, the detrimental increase in *H* at slow flow rates is much less pronounced than what was generically shown in Fig.

Equipment for HPLC

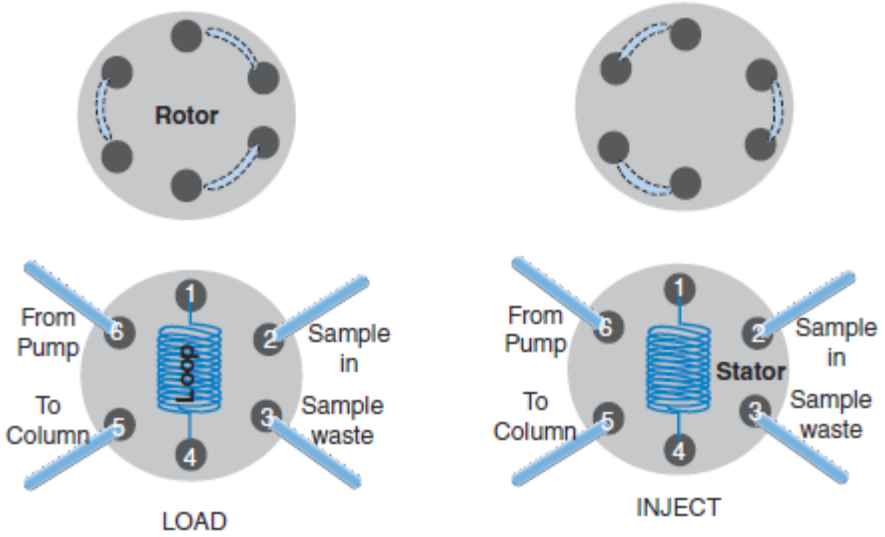
Any HPLC system must have a minimum of four components: a pump, an injector, a separation column, and a detector. Commonly a computer system is used to acquire the data and to control the other components; an autosampler is also a commonly used accessory in busy laboratories.

Solvent Delivery System. While the principal component of the solvent delivery system is the pump, other important ancillary components are an inlet filter, a solvent degassing system, and a pulse dampener.

Pumps for solvent delivery. All HPLC pumps are positive displacement pumps that rely on the incompressibility of liquids. Within limits of their pressure capabilities, they ideally provide a constant flow rate, independent of solvent viscosity or column backpressure. The most commonly used pump for HPLC is the reciprocating pump. In its simplest configuration, this comprises of a small cylindrical piston chamber equipped with two one-way check valves.



2. Sample Injection System. Most HPLC injection systems consist of 6-port loop-type injection valves or variations thereof. An injector of this type consists of a "stator," to which external connections are made and an internal disk-shaped "rotor", and is shown schematically in Figure with the perspective from the rear of the injector. We will label the ports 1 through 6 clockwise from the top of the injector. The ports are threaded and all connections with tubes to the external world are made with appropriately threaded nuts and compression ferrules.



3. Column. Straight lengths of stainless steel tubing with highly polished (typical RMS surface roughness <0.2 μm, often electropolished) interior walls are most commonly used as column housing (Figure 21.10). "Standard" bore columns usually mean an inner diameter of 4.6 mm, although 4 and 2.1mm bore columns are also common.

4. Detectors. Generally Desirable Criteria for HPLC detectors and Data Acquisition. Low noise and high sensitivity promotes good detection limits and are thus desirable in all detectors. As a single chromatographic run on a complex sample can last a significant time (≥ 1 hour), it is highly desirable that the detector baseline does not drift substantially. As column efficiency increases, peaks become narrower and span a smaller range of time; this necessitates that the detector must respond fast and the resulting data must be acquired with a sufficiently fast time resolution. This also requires that the detector cell volume be sufficiently small and of a geometry that the entire passage to and through the cell contributes little to overall band dispersion. If any of these criteria are not met, the acquired chromatogram will display a poorer separation than what was actually achieved at the column exit.

Universal and quasi-universal detectors. A mass spectrometer and a refractive index (RI) detector are both truly universal detectors. **A refractive index (RI) detector** is a bulk property detector; any change in its composition is reflected in the RI. The RI detector has two major shortcomings: (1) RI changes considerably with temperature; as a result all good RI detectors use a thermostated optical block, and the entrance liquid is thermally equilibrated before it enters the detection cell.

From the beginning days of HPLC, the most commonly used detection mode has been UV absorbance measurement. In early years, a fixed wavelength absorbance detector that utilized an Hg lamp emitting at 254 nm and equipped with a band pass filter that allowed the transmission of only this line was much used. Especially with the advent of near-monochromatic LEDs with emission wavelengths into deep UV, it will be even easier today to fabricate such dedicated single wavelength detectors with high performance, and they will be useful in niche applications. In practice, all HPLC systems are presently sold with **variable wavelength UV-visible absorbance detectors**. The simplest of these detectors requires manual selection of wavelength and the absorbance at a single wavelength is monitored. At the other extreme, **photodiode array (PDA) detectors** (also called a **diode array detector** or **DAD**) can monitor
a large range of wavelengths, even the entire spectrum, on a near-continuous basis. Photodiode array spectrometers have been discussed in detail —the HPLC detector version is equipped with an appropriate flow cell (some are based on a LCW) and optimized for fast data throughput. Because of its versatility, the PDA is presently the most used HPLC detector.

Fluorescence detectors are among the most sensitive detectors used in HPLC. A small minority of compounds exhibit native fluorescence and thus this is a rather selective mode of detection. However, it is also common to derivatize specific class of compounds, either before separation or in a postcolumn fashion after separation. Common reactions for making fluorescent derivatives of amino acids/amines and alcohols.

SUGGESTED READINGS:

Text Books:

1. Svehla, G. (2002). *Vogel's Qualitative Inorganic Analysis* (VII Edition). Singapore: Pearson Education.
2. Christian, G. D. (2007). *Analytical Chemistry* (VI Edition). United States: John Wiley & Sons.
3. Skoog, D. A., West, D. M., Holler, F. J., & Crouch, S. R. (2014). *Fundamentals of Analytical Chemistry* (IX Edition). United States of America: Cengage Learning.

Section-A
(Online examination)
20x1= 20 Marks

Possible questions

1. Explain the techniques and applications of column chromatography
2. What are the techniques and applications of size-exclusion chromatography
3. Discuss the techniques and applications of ion exchange chromatography
4. Explain the techniques and applications of paper chromatography
5. What are the techniques and applications of thin layer chromatography
6. Discuss the instrumentation and applications of Gas chromatography
7. Discuss the instrumentation and applications of liquid chromatography (HPLC)
8. Discuss in detail about the principle, equipment design, sample injection system, columns, detectors and applications of HPLC.

UNIT V

S.No	Question	a	b	c	d	Answer
1.	Chromatography is based on the	Different rate of movement of the solute in a column	Separation of one solute from other constituents by being captured on the adsorbent	Different rate of movement of the solvent in the column	Movement of adsorbents in a solvent	Different rate of movement of the solute in a column
2.	In gas chromatography, the basis for separation of the components is the difference in	Partition coefficients	conductivity	Molecular weight	Molarity	Partition coefficients
3.	In reverse phase chromatography, the stationary phase is made	non-polar	polar	Either polar or non polar	Neutral	non-polar
4.	Ion exchange chromatography is based on the	Electrical mobility of ionic species	Adsorption chromatography	Partition chromatography	Electrostatic attraction	Electrostatic attraction
5.	Which of the following statements about chromatography is correct?	Paper chromatography and gas chromatography are both routinely used for qualitative analysis only.	Paper chromatography is usually considered to be quantitative only, while gas chromatography can be qualitative or quantitative	Paper chromatography is usually considered to be qualitative only, while gas chromatography can be qualitative or quantitative.	Paper chromatography and gas chromatography are both routinely used for quantitative analysis only.	Paper chromatography is usually considered to be qualitative only, while gas chromatography can be qualitative or quantitative.
6.	In gas chromatography, the	from the Rt value of	measurement of	comparison of the	comparison of the	comparison of the

	concentration of a substance can be determined by	the substance.	the height of the peak produced by the substance.	area under the peak produced by the substance with the areas under the peaks produced by standard.	Rt of the substance with that of a standard	area under the peak produced by the substance with the areas under the peaks produced by standard.
7.	High performance liquid chromatography (HPLC) cannot be used to	identify the various pigments from a leaf extract.	separate organic pesticides.	determine the caffeine content in coffee samples.	determine the mercury content in a fish sample.	determine the mercury content in a fish sample.
8.	Which of the following statements about paper Rf and gas chromatography Rt is correct?	The Rf and Rt values of a substance are determined solely by the interaction of the substance with the stationary phase.	A substance with a long retention time in gas chromatography is likely to have a high Rf value in paper chromatography.	A high Rf value is indicative of a substance that adsorbs strongly onto the stationary phase.	A long retention time in gas chromatography is indicative of a substance with a strong adsorption on to the stationary phase.	A long retention time in gas chromatography is indicative of a substance with a strong adsorption on to the stationary phase.
9.	Thin layer chromatography can be used to distinguish between different amino acids. If a particular amino acid has low solubility in the mobile phase used, then the other amino acid	will spend more time dissolved in the mobile phase than attached to the stationary phase.	will have a low Rf value.	will move at a speed close to that of the solvent.	must have a high molecular mass.	will have a low Rf value.
10.	Column chromatography separates molecules according to their	Molecular size	Solubility	Polarity	Matrix	polarity
11.	Chromatography is a physical method that is used to separate and analyse _____	Simple mixtures	Complex mixtures	Viscous mixtures	metals	Complex mixtures
12.	In which type of chromatography, the stationary phase held in a narrow tube and the mobile	Column chromatography	Planar chromatography	Liquid chromatography	Gas chromatography	Column chromatography

	phase is forced through it under pressure					
13.	In chromatography, the stationary phase can be _____ supported on a solid	Solid or liquid	Liquid or gas	Solid only	Liquid only	Solid or liquid
14.	In chromatography, which of the following can the mobile phase be made of	Solid or liquid	Liquid or gas	Gas only	Liquid only	Liquid or gas
15.	Which of the following cannot be used as adsorbent in Column adsorption chromatography	Magnesium oxide	Silica gel	Activated alumina	Potassium permanganate	Potassium permanganate
16.	Which of the following types of chromatography involves the separation of substances in a mixture over a 0.2mm thick layer of an adsorbent	Gas liquid	column	Thin layer	paper	Thin layer
17.	In Column chromatography, the stationary phase is made of _____ and the mobile phase is made of _____	Solid, liquid	Liquid, liquid	Liquid, gas	Solid, gas	Solid, liquid
18.	In Thin layer chromatography, the stationary phase is made of _____ and the mobile phase is made of _____	Solid, liquid	Liquid, liquid	Liquid, gas	Solid, gas	Solid, liquid
19.	In which of the following type of paper, chromatography does the mobile phase move horizontally over a circular sheet of paper?	Ascending paper chromatography	Descending paper chromatography	Radial paper chromatography	Ascending – descending chromatography	Radial paper chromatography
20.	Liquid chromatography can be performed in which of the following ways?	Only in columns	Only on plane surfaces	Either in columns or on plane surfaces	Neither in columns nor on plane surfaces	Only in columns
21.	Gas chromatography can be performed in which of the	Only in columns	Only on plane surfaces	Either in columns or on plane	Neither in columns nor on plane	Only in columns

	following ways?			surfaces	surfaces	
22.	Which of the following types of chromatography involves the process, where mobile phase moves through the stationary phase by the influence of gravity or capillary action?	High Pressure Liquid Chromatography	Gas Chromatography	Planar Chromatography	Column Chromatography	Column Chromatography
23.						
24.						
25.						
26.						
27.						
28.						
29.						