Department of Field Crops …….

College of Agriculture…….

University of Salahaddin…….

Subject : Analytical Chemistry

Course Book – (First Year Classes) / First Course..Group (2).

Lecturer's name Prof. (Ass.) Dr. Dheyaa Jirjees Yaqoob,

Academic Year: 2022 /2023

Course Objective:-

Our major goal is to provide the student with the appreciation for the entire analytical process. I believe that selection of the most suitable of several available methods of analysis requires an awareness of all aspects of the problem. In this connection my believe is that an understanding of theory upon which an analysis is based provides the best guide in distinguishing between those experimental variables that are crucial to success and those which do not require so much care. The general organization of the subject matter has also been retained. This course is devoted to volumetric analysis with emphasis being placed upon the equilibrium aspects of this topic. This topic takes a large look at the entire analytical process, with the aim of introducing the student to the formidable problems of selecting a method of all of which must precede the final measurement, not only but the course provide flexibility to solving problems of volumetric analysis. Furthermore, insofar as possible, I will attempt to make the various sections independent of one another. I hope that these measures will provide the student with a variety of topic from which to choose those best suited for his needs and permit him to rearrange the order of presentation according to the described mythology of his instructor. The general organization of the subject matter has also been retained. A preliminary section is concerned with general aspects of quantitative analysis, a review of fundamental concepts and others. There is a part concerned with volumetric analysis with emphasis being placed upon the equilibrium aspects of this topic. In order to provide flexibility a more material than would ordinarily be covered in introductory analytical courses have been included. Entirely new sets of problems have been prepared in this course. Finally changes in subject matter have been extensive in my revision. Some topics have been condensed and others reorganized to make room for new material.

Methods of Teaching:-

Different methods of teaching conducted to gain the objectives of the course, such as: - a.) General review of previous lecture to refresh some information regarding the new studying. b.) Performing activities between the instructor and the students. c.) Black board presentation. d.) Power point presentation. e.) Practical part (lab expts.).

Grading – Exams:-

Your final grade will be derived as follows: Students are required to conduct: (1) **Two close book exams** in any course in the theoretical part in analytical chemistry throughout the semester. Each test will be scheduled for **90** minutes, and out of **(100%)** then it will be transferred to **(40%)** of your grade, **(25%)** on writing test, while **(15%)** for practical part. The final exam, is comprehensive in all course outlines and will be **(60%)** of your grade. **(20%)** practical and **(40%)** theoretical.

(2) **Quizzes:** About **(6)** quizzes will be given throughout the semester, they will be given at the end of the class period and last **15** minutes out of **(3%)** of your grade.

(3) **Participation, activity and reports (4%).**

Course Program:-

1. Basic principles of quantitative analysis, how can you express concentrations of solutions?
2. Principles of volumetric analysis.
3. Precipitation Titrations.
4. Oxidation – Reduction System.
5. Theory of neutralization.
6. Complex Formation Titrations.
7. Precipitation equilibrium (The solubility product).
8. Gravimetric Analysis.
9. Volumetric Methods involving iodine.

Syllabus of analytical course:-

Weeks	Issue
1st week 2nd weeks	Basic principles of quantitative analysis. The expression of solutions concentration with examples and problems.
3rd+4th + 5th weeks	Principles of volumetric analysis and scope of applications.
6th + 7th+8th + 9th weeks	Oxidation – Reduction System & Precipitation Titrations.
10th + 11th+12th weeks	Theory of neutralization, pH calculations and buffer solutions.
13th + 14th+15th weeks	Complex Formation Reactions. Models of titration curves. The application of solubility product constant. & Gravimetric analysis.
16th week.	Volumetric Methods involving iodine.

Note: These syllabus may be subjected to changes and the students will be notified well in advanced.

References:

1- "Chemistry", M. Mcelrey & J. Sadler , 1988 .
2- "General Chemistry", Hary. H.Sisler and A.W. Davidson,10th Ed. 1965.
3- "Chemistry", D. E. Goldberg , 1988.
4- "Chemical Analysis", C,R.N. Srouts and H.N.Wilson, vol. 2, 1962.
5- "Chemical Calculation", Sidney W. Benson , 1966.
6- "A text Book of Quantitative Inorganic Analysis", Arthur I. Vogel 3rd Ed. (1961).
7- "Analytical chemistry", Gary. D. Christtian, 4th. Ed. 1986.
8- "Analytical Chemistry", R. S. Porter , vol. 3 1974.
9- "Analytical Chemistry", J. D. Dick , 1973.
10-"Advanced Inorganic Chemistry", Cotton and Wilkinson, 1980.
11-"Fundamentals of physical Chemistry".
12- Internet Researches and studies.
13- "Analytical Chemistry: Principles and Techniques"**,** Hargis, L. G., (1988), Prentice-Hall, Inc., New-Jersy, p 424-427.

The Scope of Analytical Chemistry: Methods of Quantitative Analysis

A complete chemical description of a sample of matter establishment not only of the types of species present but also of their amounts. These are the questions to which analytical chemistry is directed. Qualitative analysis comprises the tests that enable the chemist to determine what species are present, and perhaps their state of combination as well. Quantitative analysis provides the means for determining how much of some component is present in a unit quantity of sample. Qualitative analysis and quantitative analysis resemble one another in some respects and are quite different in others. Both require the measurement of some chemical or physical property of the system, which in turn can be related to the information desired. Both also require preliminary treatment steps to ensure that the analytical observation, when it is made, measures only the component of interest. In contrast to these similarities, many problems confronting the analyst are unique only to quantitative measurement. Here, for example, he must work with the aim of keeping losses of the component he seeks to a tolerable minimum during the preliminary phases of the analysis. It is ordinarily a requirement that the reaction on which the he bases his analysis will proceed to essential completion with the formation of a single product. Quantitative information is not a prerequisite for a successful qualitative analysis. On the other hand, a qualitative description of the sample is ordinarily essential to selection of a suitable quantitative method.

The Importance of Analytical Chemistry

Historically, analytical chemistry has always occupied a vital position in the development of the field. The successful elucidation of the process of combustion by Lavoisier was due mainly to his employment of a balance in his investigation; he was among the first to recognize the immense power of quantitative measurement in chemical research. The atomic concept of matter dates at least to ancient Greece, and certainly was not original with John Dalton. Dalton's contribution above all, was to introduce a quantitative aspect to this notion – an aspect that could be verified by actual experiment. In a very real sense, then, chemical analysis provided the support necessary to convert the atomic theory from a philosophical abstraction into something of physical significance. Early chemistry was principally analytical in nature. Only as the body of experimental fact increased did it become possible for the chemist to specialize according to his interest – in other fields. Analytical chemistry thus assumed the supporting rule of an indispensible tool in advancing the state of knowledge in the fields of inorganic, organic, and physical chemistry. Analytical techniques are employed by the physicist in identifying the products of a high energy bombardments. The rule of analytical chemistry in modern industry is difficult to overestimate. Virtually every item of commerce has been subjected to analytical testing at one or more stages in its manufacture. The clothes we wear, the food we eat, the drugs we require, the automobiles we drive – all these and more require the aid of analytical chemistry to assure the production of goods having uniform quality and characteristics. Finally, above and beyond these practical considerations, the study of quantitative analysis requires development of systematic and orderly work habits as well as intellectually honest observations; these traits are worthy of cultivation regardless of one's ultimate field of endeavor.

Steps in the Determination of Concentration

It is important to recognize that the final measurement is but one step in a sequence of operations that leads to the knowledge of the concentration of a component in a sample of matter. Thus it is useful to identify the several steps needed. **1.** Choice of method, **2.** Sampling, **3.** Preparation of the Laboratory Sample for Analysis, **4.** Procurement of a Measured Quantity of the Sample, **5.** Solution of the Sample, **6.** Separation of Interfering Substances, **7.** The Completion of the Analysis, **8.** Calculations and Interpretation of Results.

From a historical standpoint, the majority of early analytical methods were either gravimetric or volumetric procedures; for this reason these are sometimes known as *classical* methods of analysis. Procedures based on the measurement of optical, electrical, thermal, and other properties were developed later and as a group are sometimes termed *instrumental* methods. In many respects this dual classification is unfortunate, for it implies that classical and instrumental methods are basically different. In reality, fundamental differences between the two categories do not exist; both are based upon the correlation of a physical measurement with concentration; both employ an instrument for this measurement; to the extent that neither is specific, preliminary separation steps are needed for both types of analyses. The classification of methods as classical or instrumental is thus founded largely on chronological development.

Classification of Methods of Quantitative Analysis

Ultimately in every quantitative analysis, there is a final measurement whose magnitude can be related to the amount of the species being determined. It is convenient to classify the methods of quantitative analysis according to the nature of this final measurement. Thus, in a gravimetric analysis the final measurement involves the determination of a weight; in a volumetric analysis it involves the measurement of a volume.

The final measurement in a colorimetric analysis consist of establishing indirectly the amount of radiant energy that has been absorbed by the sample. Electroanalytical methods are based upon the determination of some electrical property as the final step. A classification of common quantitative techniques on this basis are shown in **Table (1)**.

Table (1): Classification of common analytical methods.

General Classification	Subclassification	Quantity Measured
Gravimetric	Direct method	Weight of compound containing species
	Indirect method	Loss of weight due to volatilization of species
Volumetric	Titration methods	Volume of solution that is chemically equivalent to the species sought
	Gas analysis	Volume of a gaseous species produced or consumed
Optical	Emission spectroscopy	Radiation emitted by species
	Absorption spectroscopy including colorimetry	Radiation absorbed by a species
	Polarimetry	Rotation of polarized light by species
	Refractometry	Refractive index of species
	Turbidimetry, nephelometry	Scattering of radiation by species in suspension
Electro-analytical	Potentiometry	Potential of an electrode in equilibrium with the species
	Conductimetry	Conductance of a solution of the species
	Coulometry	Quantity of electricity equivalent to the species
	Polarography	Current associated with reaction at a polarizable electrode
	High-frequency methods	Capacitance of solution of species
Miscellaneous	Mass spectroscopy	Mass-to-charge ratio of decomposition products of species
	Radiochemical methods	Radioactive decay of species
	Thermal-conductivity methods	Thermal conductance of species
	Enthalpy titrations	Heat of reaction of species

Examples of semester Examination (Typical Questions).

Q1/ calculate the pH and the capacity toward acid added for a solution containing 12 mM of acetic acid + 8 mM of CH_3COONa, total volume = 100 ml, pKa = 4.74

Q2/ Explain with reasons and equations, **(Mohr method): 1)** Attention must be paid to the acidity of the medium. **2)** The medium is not made strongly alkaline. **3)** The AgCl ppt, tends to form first before Ag_2CrO_4 in the titration mixture.

Q3 / Detection of an endpoint involves the observation of some property of the solution. Explain.

Q4/ calculate pH of 0.1M of $AgNO_3$ **(two methods)**, pKb AgOH = 3.96
$AgNO_3 + H\text{-}OH \rightleftarrows AgOH + HNO_3$

Q5/ Consider the titration of (50) ml (0.1) F NaCl with (0.1) F $AgNO_3$. Calculate (pAg) and (pCl) with respect to (49.95, 50, 52.5 mL) volumes added of $AgNO_3$. Will you expect the titration curve for the process? Ksp AgCl = $1.82 * 10^{-10}$ (mol^2/L^2) at 25°C.

Q6/ Correct the underlined statements

1) The Kw is called the ion product constant for **ether**.
2) Buffer solution is added to resist change in **Kw.**
3) Base capacity is a number of **kilograms of weak acid/L** added to cause rising of pH by unity.
4) If the medium is made strongly alkaline in **(Fajan)** method; Ag^+ will precipitate as its oxide.
5) Precipitation titrations are based on **accepting of electrons.**
6) $CaCO_3$ is a primary standard used to standardize **NaCl** solution.

Q7/NaCl with an assay of (99.86%) is used to standardized $AgNO_3$ solution. Assuming 241.5 mg of NaCl requires (47.56 ml) of $AgNO_3$ to reach (e.p), calculate (N) of $AgNO_3$ by adjusting the exact weight and exact equivalent weight of NaCl. Mwt. of NaCl = 58.44

Q8/ Calculate the pH & pOH of $3.2*10^{-14}$ F $Ba(OH)_2$?

Q9/ calculate the pH of solution prepared by the addition of (20 ml, 0.1M NaOH) to (30 ml, 0.15M) acetic acid, pKa (acid) = 4.76

Q10/ Enumerate the desirable characteristics of a volumetric analysis.

Q11/ Explain **(with three important equations)** the mechanism of **Volhard method**. Give reason with equation for the addition of the indicator after all AgI is precipitated completely.