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# UNIT 14 INTRODUCTION TO ANALYTICAL INSTRUMENTS

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## 14.1 INTRODUCTION

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This is the last Unit of this course. In this Unit we have just introduce you to different analytical instrument and their evolution. The details of these instruments you will study in different courses of this programme.

After brief introduction of evolution of analytical balance we will familiarize you to colorimeter, photometer and spectrophotometer. Next we will discuss about the spectrography and atomic absorption. Although there is a separate course on electro analytical methods. We will discuss about the evaluation of different electro analytical methods and in the last we will learn about the role of computers in analytical instruments

### Objective

- understand the evolution of analytical instruments,
- understand the basic idea about the colorimeter, photometer and spectrophotometer,
- explain basic idea the flam photometry and atomic absorption and
- describe briefly about electro analytical methods.

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## 14.2 ANALYTICAL INSTRUMENTS AN INTRODUCTION

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Analytical instruments are directed towards understanding the chemical composition of matter. “What are the elements present? What are the compounds present? In what quantities are they present?” Thus it gathers both quantitative information of matter.

Qualitative analysis was based on boiling points, melting points, solubility in solvents, refractive indices and colour reactions with suitable reagents. Quantitative analysis was based on gravimetric and tetrimetric methods. There was interest only on the major constituents, which could be determined by gravimetry and volumetry. This was the picture till the beginning of the twentieth century. Minor constituents had no role in this scheme and traces were not even thought of. The above scenario

completely changed when it began to be realized that traces impurities decide the properties of materials.

From 1920 onwards, attention was turned towards development of analytical methods based on physical properties as light absorption, emission, fluorescence, electrode potential, began to be exploited for analysis. This gave rise of instrumental methods of analysis. The methods are listed in Table 1.1. Highly efficient methods of separation chromatography, ion exchange, solvent extraction-helped in isolation the analysis if interest in a more efficient manner than the conventional methods. A happy combination of separation methods with that of measurement based on physical properties gave rise to better methods of analysis.

The instrumental methods and the physical/chemical properties on which they are based are given in Table 1.1.

**Table 1.1: Physical/Chemical Property**

1. Optical

<b>Principle</b>	<b>Analytical Technique</b>
Absorption of radiation	Photometry
	Spectrophotometry
	Atomic Absorption
Emission of radiation	Flame photometry
	Emission spectroscopy
	Fluorescence
Scattering of radiation	Turbidimetry
	Nephelometry
Diffraction of radiation	X ray diffraction
	Electron diffraction

2. Electrochemical methods

<b>Principle</b>	<b>Analytical Techniques</b>
Measurement of potential of electrode or change in potential	Potentiometry
Measurement of mass of substance deposited on electrode	Electrogravimetry
Change of conductivity	
Measurement of conductivity or change in conductivity of a solution	Conductimetry
Change in diffusion current with respect to potential	Voltammetry/polarography

3. Mass to change determination                      Mass spectrometry

4. Radioactivity Measurements                      Radioanalytical methods

The measurement of mass is fundamental in Analytical chemistry. Practically all determinations depend directly or indirectly on the measurement of mass. This is the basis of gravimetry. Even for titrimetric measurements, the concentrations of standard solutions are expressed in terms of molarity, molality and normality, which are based on mass.

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### 14.3 ANALYTICAL BALANCE

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The Analytical balance for measurement of mass was the first analytical instrument to be used by analytical chemists. This involved the comparison of the unknown mass of an object with a known mass, related to a standard mass, defined in terms of primary standard unit of mass-the international kilogram, a Plotinum-Rhodium alloy preserved in the International Bureau of Weights and Measures in France.

In the beginning two pan balances were used. In these balances, the mass of the unknown was counterbalanced by standard weights in the other pan. Subsequently, the single pan balance, based on substitution weighing, was introduced. Since the weighing process is much faster and more convenient with a single pan balance, the single pan balance soon replaced the double pan balance.

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### 14.4 COLORIMETER, PHOTOMETER, SPECTROPHOTOMETER

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In this unit we will introduce you to colorimeter, photometer and spectrophotometer. In Unit 2 of MCH-003 course of this programme you will study about these instruments in details

#### 14.4.1 Colorimeter

The so-called instrumental methods of analysis can be traced to colorimetry and flame photometry analysis. Colorimetry is based on comparing the color produced by an unknown amount of the substance with the same color produced by a known amount of the same substance.

The color of the test solution in a Nessler tube diluted to a fixed volume is compared with a series of standards of the same component, similarly prepared. In a variation of the method, the height of the liquid in one tube is adjusted so that when the tubes are observed vertically the color intensities in the tubes are equal. (Duboseq method) The concentration in one of the tubes being known, the concentration in the other can be calculated from the respective lengths of the columns by the relationship

$$c_1h_1 = c_2h_2$$

Where as  $h_1$  and  $h_2$  represent the heights of the column of solutions, when balanced.  $c_1$  and  $c_2$  are the concentrations, one of them being known.

For convenience, artificial color standards as Lovibond glasses, salt solutions of ferric chloride in hydrochloric acid (yellow), aqueous cobalt chloride (pink), aqueous copper sulphate (blue) and aqueous potassium dichromate (orange) were also used. These artificial standards had to be standardized against known amount of the substance.

#### 14.4.2 Photometer

Then came the development of photometers in which the eye was replaced by a photoelectric cell, which produces a current, the intensity of which gives a measure of the light falling on the photocell. They measure the light absorption by the solution concerned. Basically these instruments consists of a light source, a suitable light filter to obtain an approximately monochromatic light, a glass cell to hold the solution of measurement, photoelectric cell, and a measuring device to record the reponse of the photoelectric cell. A refinement of the photoelectric photometer was the incorporation of two photoelectric cells instead of one. This design took care of fluctuations in the intensity of light source. Examples of single photocell instruments were the Unicam SP 300 and 1400 Hilger Biochem. Instruments with two phtocells were Hilger Spekkon H 760, Fischer Lumetron 420.

The photo cells, which are light sensitive devices were of two types- photo emissive and barrier cells. The photo emissive cell is basically a glass tube, internally coated with a thin sensitive layer of Cesium oxide or Potassium oxide along with silver oxide. These emit electrons when light falls on it, which can be speeded up to a suitable anode, mounted in the centre of the tube. The flow of electrons results in a current, which can be measured and is related to the intensity of light falling on the photocell. The photo multiplier uses a series of positively charged anodes, at increasing potentials, by which the initial current can be considerably increased leading to better sensitivity. The cathode and anode are connected to a voltage source. In the barrier layer cell, the voltage source is disposed of. The cell consists of a metal base plate of iron upon which is deposited a thin layer of semi conducting selenium, which is covered by a thin layer of transparent material. When light falls on the selenium layer, electrons are released, which the base plate is positive and the transparent plate is negative. By connecting the two to a galvanometer, current can be detected and measured, which is proportional to the intensity of light. The current output of the barrier cell is dependent upon the wavelength of incident light.

In the beginning, optically filters were used in colorimeters and photometers, for isolating the desired spectral region from the source emission. These were of colored glass or colored gelatin coated on glass and possessed the property of transmitting light from a specified region of the spectrum, the other components being preferentially absorbed. These filters were from Koak, Ilford, Corning etc.

#### 14.4.3 Spectrophotometer

In course of time, the more sophisticated spectrometers came to the market. These instruments enable the measurement of transmittance at various wavelengths. They may be considered as refined photoelectric photometers employing continuously variable and near monochromatic light. The monochromator is an essential part of the spectrophotometer, which is not present in the photometer. The monochromator splits the light beam entering through the slit into wavelengths of the light beam. The dispersion is achieved by using a glass/quartz prism or a grating. Prisms show greater dispersion in the short wavelength region than in the long wavelength region. On the other hand, grating shows about the same dispersion through out the spectrum. In view of the possible variations of the operating current of light source, two cell photometers were proposed based on the premise that fluctuations will affect two cells equally and this will be compensated. The two cells are to be selected on the basis of similarity in spectral response and should be matched as closely as possible.

The most common source used for visible and near ultra violet and near infra red region was the tungsten filament incandescent lamp, operating at a temperature of 2870K to optimize the output whit at the same time, increasing the life of the lamp. For the ultra violet region, the best source of continuous ration was the hydrogen discharge tube.

The use of ultra violet and visible spectrometry instrumentation gave an impetus to analytical methods. Simultaneously, the theory behind Spectrophotometry was also developed which helped in understanding the technique and enabled in proposing new and better methods of higher sensitivity.

#### 14.4.4 Infrared Spectrophotometer

Infrared spectrophotometry came into the field of analytical methods much later, although William Herschel, in 1800, had reported that radiation existed beyond the red region of the solar spectrum, which heated up substances. Unfortunately, he was not aware that this absorption could reveal the modular structure of substances. It was left to William W. Coblentz, who collected and first published the IR specter of nearly 131 substances. The specters were subsequently interpreted on the basic of the vibrational-

## Estimations Based On Precipitation and Gravimetry

rotational modes of the molecules of the substances. It became apparent that the spectrum represented a veritable wealth of information about the basic characteristics of the molecule, is the nature of atoms, their spatial arrangement and their chemical linkage forces. In fact, it became a fingerprint of the molecule.

Several changes in the UV-Visible spectrophotometers were necessary before IR instrumentation became possible. Many substances such as glass and quartz absorbed in the IR region and could not be used and had to be replaced with front surface mirrors.

Parabolic mirrors were used to bring energy of all wavelengths to focus at one point. Both gratings and prisms were found useful for dispersing the energy, with a preference for prisms so as not to lose energy in height in higher order spectra. Thus prisms of NaCl, CsBr,  $\text{CaF}_2$ , CsBr were found useful. Since most of these materials were soluble in water, the instruments had to be carefully protected from high relative humidity.

Globar (Silicon Carbide) and Nernst Glower (oxides of Rare Earths) which emit in the IR region, when heated, replaced the tungsten lamp of the visible spectro photometer. Similarly, the photosensitive detectors had to be replaced by heat sensitive devices as Thermocouples, Bolometers, Thermistors, Golay thermal detector.

### 14.4.5 Flame Photometer

Along with color comparison in solutions, one of the earliest methods of detection of elements was the characteristic color imparted to flames when certain salts as NaCl, KBr were introduced. The intensity of the color was found to vary with the concentration of the substance. This was the basis on which flame photometers were built. A small volume of the sample solution was sprayed into the flame in a controlled manner. At the high temperature of the flame, water evaporated off; salts were dissociated into constituent atoms and ions. The excited atoms, on de excitation, emitted characteristic spectra, which were dispersed using a monochromator. A photocell with a read out device measured the intensity of the isolated radiation. Similar to the color photometry, two types of instruments were built-flame photometer and flame spectrophotometer. In the former, a filter interposed between the flame and the detector transmitted only the high intensity spectral line of the element, which can be detected. Flame photometers were generally used for the analysis sodium, potassium, lithium, and calcium. In the flame spectrophotometer, light from the burner passes on to a monochromator with the desired resolving power. The isolated radiation from the element of interest falls on a photocell in conjunction with a photomultiplier device and finally a meter as a readout device. Because of the high resolving power of the monochromator, a number of other elements, besides those mentioned, can be determined.

One of the earliest commercial flame photometer was the EEL flame photometer. The flame was produced from butane or propane and compressed air. The light emitted from the flame was collected by a reflector and focused by a lens on to an optical filter, suitable for sodium potassium, lithium and calcium lines. The current generated by the photocell is detected by a galvanometer. One of the earliest flame spectrophotometer, Unicam SP 900 housed a sample compartment, burner unit, monochromator, detector with an amplifier and a galvanometer. Acetylene or propane was used along with air for the flame. The sample was drawn through polythene capillary under the action of compressed air, fed into the atomizer and sprayed as a fine mist into the flame. The monochromator was a fused silica prism. The detector is a photo multiplier tube with red sensitive photocell for measurement of wavelengths up to 1020 nm. Detail about the flame photometry you will study in Unit 7 of MCH-003 course.

**SAQ 1**

Fill the following blanks

- i) The color of the test solution in a .....diluted to a fixed volume is compared with a series of standards of the same component, similarly prepared.
- ii) Examples of single photocell instruments were ..... and .....
- iii) These instruments enable the measurement of transmittance at various.....
- iv) The light emitted from the flame was collected by a.....

**14.5 SPECTROGRAPHY**

The flame furnishes only low energy, resulting in the excitation of only a few elements. In order to cover more elements, other sources of excitation as the AC arc, DC arc and the high voltages spark, were introduced. Each of them had its advantages and disadvantages. The sample under investigation was used as one of the electrodes, if it was a conductor. Otherwise, the sample was placed in a small cavity of a carbon or graphite electrode. The other electrode was of pure metal rods as copper or silver. The essential parts, besides the arc or spark consist of a slit, an optical system and a photographic plate or a series of photo detectors. The optical system houses the monochromator, which is a prism or grating. One of the earliest spectrograph to be built was the Hilger Quartz spectrograph. The radiation emitted by the sample in the excitation source (Arc/spark), passed through a narrow slit to a lens and further to a quartz prism, which disperses the radiation to the constituent wavelengths. A second lens focused the images on a photographic plate. The spectrograph was provided with a scale graduate in wavelengths which was illuminated and printed directly on the spectrograph place. The lengths of the instrument form were about 4 ft. An optical bar, made of steel was attached to the base of the instrument, which was parallel to the optical axes. For quantitative analysis, the intensity of the lines as reflected by the blackening on the photographic plate was compared with that of standards. The photograph has been replaced by a set of photomultiplier tubes, suitably placed record the different wavelengths from the dispersed spectra.

Besides flame and spectrographs for atomization, many other atomizers have been proposed over the years. These are indicated in Table 14.1

**Table 14.1: Type of atomizers and atomization temperature**

Atomisers	Temp (C°)
Flame	1700-3100
Electric arc	4000-5000
Electric spark	40,000
Inductively coupled plasma	4000-6000
Direct current plasma	4000-6000
Glow discharge plasma	400-6000

The plasma sources have become the most important and most widely used source for atomic emission. The advantage of the plasma source is their lower inter element interference, as a result of the high temperature of the plasma. Another advantage is that under single set of excitation condition spectra of dozens of elements can be recorded simultaneously. A third advantage is that elements that form refractory compounds can be analyzed in plasma sources. Among them, the most widely used is the Inductively Coupled Plasma.

## SAQ 2

What is the length of spectrographic instrument?

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## 14.6 INDUCTIVELY COUPLED PLASMA

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Once Plasma became a reality, which could reach high temperatures, attempts were made to use plasma as a source for atomization. There were many ways in which Plasmas could be produced- Inductively Coupled Plasma, DC plasma, Micro wave induced plasma and Glow Discharge Plasma. Among these, ICP has proved to be the most popular. The plasma is generally obtained using Argon.

A stream of Argon gas is made to flow through the specially designed torch (Fassel torch) which consists of three concentric tubes. The sample solution, introduced using a nebulizer, is carried by the Argon flow through the innermost tube. Surrounding the tube at the top is the induction coil powered by radio frequency generator. Argon ions and electrons gain sufficient power from the magnetic field generated by the coil. The interaction causes the ions and electrons, confined within innermost tube of three concentric quartz tubes, to flow in a closed annular path. This results in Ohmic heating resulting in high temperatures of the order of 6,000 to 10,000°K. Atomisation of the sample takes place. Because of the high temperature, it is almost complete, unlike the flame, Arc and Spark. Due to the presence Argon, oxidation is prevented, enhancing the lifetime of the atoms. Two types of ICP instruments have been developed –Sequential and Simultaneous. As the name suggests, in the former, the measurement is made at a single wavelength followed by another. On the other hand, the latter measures the Intensities at all wavelengths simultaneously. Grating monochromators are used for dispersion and photomultiplier tubes for detection of intensities of emission. Instead of photomultiplier, charged coupled detectors have been developed for measurement recently. Almost all elements can be determined by ICP. For elements as B, P, N, S, C, vacuum spectrometer is necessary as their emission lies in the UV region.

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## 14.7 ATOMIC ABSORPTION

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Molecular absorption spectrometers and atomic emission spectrometry had already established themselves in the fields of absorption and emission respectively. Therefore, it was rather strange that atomic absorption took such a long time before it became a reality as an analytical technique. It was the pioneering work of Alan Walsh and his colleagues in CSIRO, Australia in 1950s that paved the way for atomic absorption methods. Working on his experience of using a modulated light source in IR spectrometry, Walsh decided to experiment with a flame for atomization, removing the emission spectrum by modulating the light from the source and using a detection system tuned to the modulation frequency. Since the width of atomic absorption lines is very narrow, of the order of less than nm, the line width of the radiation emitted by the source for excitation of the atom had to be still narrower. Even highest quality monochromators had bandwidths, significantly greater than the width mentioned. Walsh solved the problem of source, by using the emission lines of the same element,

whose determination is desired. Thus for determination of sodium, he used a compound of sodium as the cathode material, which could emit the sodium, he used a compound of sodium as the cothode material, which would emit the sodium line at 589.0 nm. This gave rise to the concept of Hollow cathode lamps, consisting of a cylindrical cathode of the element or its compound, whose determination is desired and a tungsten anode in an evacuated tube. In order to eliminate interference caused by flame emission, the output of the source was modulated so that its intensity fluctuates at constant frequency. Thus the detector received two types of signals, one due to absorption by the atoms and a continuous one from the flame. The de signal from was removed by a filter and the ac signal was passed on for further amplification.

The next major step in AAS came with the work of Boris V.L'vov. He was interested in developing absolute AAS methods that would not require calibration. He knew that flame would not be suitable because of incomplete atomization of the element of interest. The alternative was to use a furnace and expect complete vaporization and atomization of the sample Based on Massamnn's furnace design, the first commercial Graphite Furnace was introduced into the market in 1970. In order to overcome the problems associated with strong matrix effects and non selective interferences, L'vov introduced sample on to a thin pyrolytic graphite boat, kept on a platform in the middle of the furnace, which made it possible to atomize the sample at almost constant temperature conditions. A major advantage was that this arrangement could handle solid samples as well.

In spite of the fact that only one element could be analyzed at one temperature within a short span of less than half a decade, atomic absorption spectrometry has overtaken many other analytical techniques. In a few favorable cases as AS, Ab, Bi, Ge, Se and Te, they can be volatilized as their hydrides and introduced into the light plate for measurement. Similarly Hg which has a high vapor pressure can be volatilized as elemental Hg and measured Over 60 elements can be analyzed with high sensitivity and free from almost all interferences. In unit 9 of MCH-003 you will study about atomic absorption in detail.

### **SAQ 3**

Who discovered the atomic absorption and when?

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## **14.8 ELECTRO ANALYTICAL METHODS**

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In this section we will give brief introduction of electro analytical methods. There is a separate course (MCH-004) on electro analytical methods in which you will study in details about this methods.

An important class of analytical methods falls under electro analytical methods. The basis of all of them stems from the famous Nernst equation, which relates the potential developed by an electrode in contact with a solution of its own ions to the concentration.

If one more electrode is introduced into the solution and the electrodes are connected externally it forms an electrochemical cell. There are many ways in which the electrochemical cell can be used for a variety of techniques. Some of the important ones are i) Potentionmetry in which the potential of the electrode in contact with a solution of its ions is a measure of the concentration ii) Electrogravimetry, in which the element of interest is deposited on an electrode and weighed iii) Coulometry,



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Gravimetry**

which is based on the number of coulombs required to complete the reaction at the electrode iv) Voltammetry which relates the diffusion current as a function of potential in an unstirred solution of the element of interest v) Polarography, which is Voltammetry at a micro electrode, normally the dropping mercury electrode vi) Conductimetry in which the reciprocal of electrical resistance of a solution is related to the concentration of ions in solution.

The earliest potentiometric measurement was that of the hydrogen ion measurement using a glass electrode. Besides the glass electrode, a number of ion sensitive electrodes have been developed – Solid state electrodes, Ion Exchange membrane electrodes, Molecular selective membrane electrode, Biocatalytic membrane electrode, Ion selective field effect transistor. For measurement of potential one more electrode was needed to complete the circuit. The second electrode was the reference electrode, with a constant potential value – Saturated Calomel Electrode, Silver- Silver Chloride electrode. For carrying out the cell voltage measurement, electronic voltammeters, with high input impedance, which allows only very small current to flow through the circuit or better a potentiometer circuit, which exactly balances the voltage produced, was developed.

The instrumentation slightly differed for the techniques. For electrogravimetry, the equipment needed was simple – a power supply, a voltmeter, an ammeter, a pair of electrodes of which one is platinum and a vessel to hold the solution of interest. Under Coulometry, two variations were developed – i) Potentiostatic ii) Amperostatic. In the former, the assembly consisted of an electrolysis cell, Platinum gauze working electrode, a platinum counter electrode, a saturated calomel reference electrode in contact with the solution through a salt bridge. An electronic circuit was assembled to maintain the potential of the working electrode constant. An integrator was provided to determine the number of coulombs required for the reaction. In amperostatic coulometry, the set up consists of a Constant current source, a voltmeter by which current can be indirectly measured, a cell housing a rectangular Pt electrode and an auxiliary electrode.

**SAQ 4**

What are the different ways to use electrochemical cell?

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**14.9 ROLE OF COMPUTERS IN ANALYTICAL INSTRUMENTATION**

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The computer has now become an indispensable tool in analytical instrumentation. In order to appreciate the functioning of the computer in the measurement process, one must look at the basics of measurement. The measurement one is interested about a particular substance – mass volume, intensity of light – reside in non-electrical domains. With the advent of electronic signal processors, and transducers, it is now possible to convert information from non-electrical domains. Any measurement process thus depends on inter domain conversion. For example, one is interested in the concentration of substance a in a solution. The intensity of light absorption or emission from the solution can be related to the concentration. This intensity can be converted to an electrical domain using a photosensitive device, which produce an electrical signal, which after due processing can be converted back to the

non electrical domain as concentration of the substance A. Information, as the magnitude, one of the electrical quantities as current, voltage etc, is encoded in analog domains. The data thus generated in analog form is converted to digital form. Most of the analytical instruments, today have data domain converters as analog to digital converters along with microprocessor and computers.

The analog to digital converter where the measurement of a specific physical and chemical property of the substance, is obtained in digital form as a number, related to the concentration of the substance. This is further processed in the microprocessor, which is a large integrated circuit made up of thousands of transistors, resistors, diodes and other circuit elements, miniaturized to be accommodated in a silicon chip. Microprocessor functions as the mathematical component. In addition, it finds use in the control of the analytical instruments. Microprocessor is in fact, the central processing unit of a computer.

By connecting a computer to an analytical instrument, it is possible to automate the functions, leading to rapid data acquisition, possibility of repetitive measurements and better reproductively. Another important advantage of the computer is that of tremendous computational and data handling capabilities.

Hardware, which consists of physical entities as disk drives, printer, clocks, data acquisition modules along with software as programs, instructions make up the computer. Both are equally important.

Communication with a computer is done through the software. This consists of a series of instructions, which actually is the operation of a series of electronic switches in the off or on position (0 and 1). This binary machine code language can be understood by the machine. To avoid the tedious and time consuming operation of machine coding, assembly languages have been developed in which the switch setting steps are assembled into groups, designated by mnemonics. For example, the mnemonic for subtract can be SUB, which is 101 in machine language. Assembly languages are still tedious. To overcome that, many high level languages such as BASIC, FORTRAN, PASCAL, C have been developed. The instructions in high-level languages are translated to assembly languages and further to machine language.

FORTRAN was specifically designed for scientific applications. Similarly, Microsoft Excel, has many basic statistical functions, such as mean, standard deviation, median, mode. Least square fit, ANOVA etc. Several equation solvers as Maple, Mathcad have been introduced which are relevant to analytical chemistry programs such as Chem. Windows and Chemdraw are available for drawing organic structures. For curve fitting, we have programs as Peak Fit. GRAMS/32 is capable of analyzing and translating data files generated by more than hundred analytical instruments. Fourier transformation, data smoothing, curve fitting and mathematical operations such as differentiation, integration, interpolation can be carried out by GRAMS32 of data handling, processing, storing and display.

Data storage is also an important function of the computer. For example, the data generated in a few minutes by a GC/MS may be spectra of a number of compounds, each compound having a number of peaks. The data has to be stored, before processing to identify the peaks and assigning it to possible compounds, based on a search of files spectra.

The computer has been designed to play not only a passive role, but also an active role. This is used for real time operations as wavelength setting in a spectrophotometer, the rate of addition of reagents, the rate of heating etc. for example, in a graphite furnace AAS, it includes pipetting out a known volume of sample solution, transferring it to the furnace, setting the temperatures of drying,

ashing etc followed by the measurement of the emission signal. The computer collects the data and prints out the concentration of the element of interest.

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## **14.10 SUMMARY**

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In this Unit we have deeply discussed following points

- Evaluation of different analytical instruments
- Colorimetry is based on comparing the color produced by an unknown amount of the substance with the same color produced by a known amount of the same substance.
- Then came the development of photometers in which the eye was replaced by a photoelectric cell, which produces a current, the intensity of which gives a measure of the light falling on the photocell. They measure the light absorption by the solution concerned.
- In course of time, the more sophisticated spectrometers came to the market. These instruments enable the measurement of transmittance at various wavelengths. They may be considered as refined photoelectric photometers employing continuously variable and near monochromatic light.

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## **14.11 TERMINAL QUESTIONS**

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1. What are the different ion sensitive electrodes?
2. What are the general uses of flame photometer?
3. What are the advantages of plasma source?

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## **14.12 ANSWERS**

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### **Self Assessment Questions**

1. i) Nessler tube ii) Unicam SP 300 and 1400 Hilger Biochem iii) wavelengths iv) reflector
2. four feet
3. Alan Walsh and his colleagues in CSIRO, Australia in 1950s
4. i) Potentionmetry in which the potential of the electrode in contact with a solution of its ions is a measure of the concentration ii) Electrogravimetry, in which the element of interest is deposited on an electrode and weighed iii) Coulometry, which is based on the number of coulombs required to complete the reaction at the electrode iv) Voltammetry which relates the diffusion current as a function of potential in an unstirred solution of the element of interest v) Polarography, which is Voltammetry at a micro electrode, normally the dropping mercury electrode vi) Conductimetry in which the reciprocal of electrical resistance of a solution is related to the concentration of ions in solution.

### **Terminal Question**

1. Glass electrode, Solid state electrodes, Ion Exchange membrane electrodes and Molecular selective membrane electrode

2. Flame photometers are generally used for the analysis Sodium, Potassium, Lithium, Calcium.
3. The advantage of the plasma source is their lower inter element interference, as a result of the high temperature of the plasma. Another advantage is that under single set of excitation condition spectra of dozens of elements can be recorded simultaneously. A third advantage is that elements that form refractory compounds can be analyzed in plasma sources.

### **Further Readings**

1. Vogel's Textbook of Quantitative Chemical Analysis, 5th Ed., By G.H. Jefferey, J. Bassett, J. Mendham, and R.C. Denney, ELBS – Longman.
2. Fundamentals of Analytical Chemistry, 7th Ed., By D.A. Skoog, D.M. West and F.J. Hooler, Sounders College Publishing.
3. Quantitative Analysis, 5th Ed., by R.A. Day, Jr. and A.L. Underwood, Prentice – Hall of India.
4. Basic Concepts of Analytical Chemistry, 2nd Ed., By S.M. Khopkar, New Age Publishers.
5. Comprehensive Analytical Chemistry, Vol. IA, Edited By C.L. Willson and D.W. Wilson, Elsevier Publishing Company.



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