CHAPTER – 1

INTRODUCTION
Potassium is an alkali metal which is abundant and widely disseminated in Nature constituting 2.58% of known terrestrial matter. Sir Humphry Davy discovered potassium in 1807 AD in London. This was the first metal to be isolated by electrolysis. Its name comes from the Latin word Kalium.

It is a soft silvery-white lustrous metal which can be easily cut with a knife. It is highly reactive which tarnishes readily in air due to the formation of a layer of potassium oxide on the surface of the metal. However, because of its high reactivity it is not found naturally in its elemental state. Further, potassium compounds do not occur in workable deposits and are not found concentrated in one location. It is feebly radioactive which is present to the extent of 0.012% emitting beta-rays.

Most minerals containing potassium are sparingly soluble and the metal is difficult to obtain from them. Certain minerals such as sylvite, sylvinite and carnallite, are found in deposits formed by evaporation of old seas or lakes and potassium salts can be easily recovered from them. Potassium is also found in the ocean in small amounts compared with sodium.
Potassium is essential to human and animal life and it is toxic for certain levels. One of its natural isotopes is radioactive. Although its radioactivity is mild, it may be one natural cause of genetic mutation in man. Potassium is used in organic chemistry as a powerful reducing agent.

In biological field it is considered to be an essential trace element that is known for its beneficial effects, deficiency and toxicity in human beings. In agriculture it plays a vital role in plants growth and reproduction. It is equally important for human beings to take as a mineral. Potassium is one of the electrolytes that we all require to maintain health. The greatest demand for potassium compounds is in fertilizers and soils. Many other potassium salts are of great importance including the nitrate, carbonate, chloride, bromide, cyanide and sulfate.

Potassium is needed for growth, building muscles, transmission of nerve impulses, heart activity etc. Potassium, together with sodium - potassium inside the cell and sodium in the fluid surrounding the cell, work together for the nervous system to transmit messages as well as regulating the contraction of muscles.
Deficiency of potassium causes kidneys to excrete any excesses but deficiencies are seldom found in people on normal diets although most people could look at increasing their potassium intake. A deficiency may result in fatigue, cramping legs, muscle weakness, slow reflexes, acne, dry skin, mood changes, irregular heartbeat. It is advisable to increase potassium intake for bodybuilders, since potassium is needed to maintain the muscles in good form, controlling the muscle actions. Potassium is lost in excessive sweating and urine. A great way to include this in the diet is to have a banana, citrus fruit or even a dash of apple cider vinegar. Potassium is found in fruits and vegetables as well as whole grains, citrus fruit, molasses, fish and unprocessed meats.

The minimum dosage of potassium that a human being requires per day is 3500 milligrams to ward off serious deficiency of this particular nutrient. In the therapeutic use of this nutrient, the dosage is usually increased considerably, but the toxicity level must be kept in mind. Potassium is well absorbed, but is not stored in large quantities in the body.

The estimation of potassium is required in the analysis of rocks, minerals, soils, ashes of plants, waters, brines, saline residues, fertilizers and many technical products. It is of particular importance in the analysis of fertilizers and soils.
Hypokalaemia (lowered plasma $[K^+]$), hyperkalaemia (increased plasma $[K^+]$) and hyperkaluria (increased urinary excretion of $K^+$) are again indicative of a variety of conditions and hence the clinical measurement of $[K^+]$ is also of great importance.
Determination of the molecular forms (Speciation) in which an element exists becomes one of the basic requirements in many chemical investigations nowadays. This information is particularly useful in studies related to environmental, toxicological and physiological investigations. Most speciation schemes rely on element-specific detection. Speciation analysis refers to the determination of chemical forms of metals and metalloids including metalloorganic compounds.

Potassium is the one of the most important metals to trace in biological and agriculture fields. The excess or deficiency of this metal causes severe health disorders like fatigue, cramping legs, muscle weakness, slow reflexes, acne, dry skin, mood changes, irregular heartbeat etc. in humans and animals. In agriculture it plays a vital role in plants growth and reproduction. There is a greatest demand for potassium compounds is in fertilizers and in soils. And also it is required in the analysis of rocks, minerals, soils, ashes of plants, waters, brines, saline residues and many technical products.
In order to aware the people of its significance, it is very essential to estimate the amount of potassium in blood, serum, rocks, minerals, soils, fertilizers, waters and brines etc. which gives a valuable information to educate and create awareness in the people while selecting the agricultural crops or while selecting the fertilizers etc.

Generally potassium is detected in its compounds by the characteristic lialac colouration, which it imparts to non-luminous flame when burned and by spectroscopic methods\(^3\).

The determination is a very difficult task despite the appearance of new methods. The following are the different new methods that are in use for potassium estimation.

a. Flame photometry

b. Atomic absorbance spectroscopy
c. Colorimeter
d. Spectrophotometer
e. Ion spectroscopy

f. Ion chromatography
g. Electrochemical methods etc.
FLAME PHOTOMETRY

A traditional and simple method for determining sodium and potassium in agricultural and biological fluids involves the technique of emission flame photometry. This relies on the principle that an alkali metal salt drawn into a non-luminous flame will ionise, absorb energy from the flame and then emit light of a characteristic wavelength as the excited atoms decay to the unexcited ground state. The intensity of emission is proportional to the concentration of the element in the solution. A photocell detects the emitted light and converts it to a voltage, which can be recorded. Since Na+ and K+ emit light of different wavelengths (colours), by using the appropriate colour filters, the emission due to Na+ and K+ (and hence their concentrations) can be specifically measured in the same sample. One drawback of flame photometers is that they respond linearly to ion concentrations over a narrow concentration range. Hence, suitable dilutions are to be prepared.

Flame photometry is also named as flame emission spectroscopy because of the use of a flame to provide the energy of excitation to atoms introduced into the flame. It provides high sensitivity and high reliability for the determination of elements in the first two columns of the periodic table. Among these elements are sodium, potassium, lithium calcium, magnesium, strontium, and barium. And it is also successful in determining
the transition elements, such as copper, iron and manganese. By making a wavelength scan of the emission spectrum, it is also possible to do qualitative analysis by employing flame photometer.

This method is less reliable than atomic absorption spectroscopy. It cannot provide information about the molecular structure of compound present in the sample solution. Non-radiating elements such as carbon, hydrogen and halides cannot be detected.

**ATOMIC ABSORBANCE SPECTROSCOPY**

Atomic absorption spectroscopy is an analytical technique based on the absorption of radiant energy by atoms. In this method when a dispersion of the atoms of a sample is produced in a flame, some of these atoms get thermally excited and emit characteristic radiation as they return to the ground level. Most of them, however, remain in the ground state. When a beam of light is made to pass through the flame, a portion of it will be absorbed by dispersed atoms. It is possible to find a series of absorption bands corresponding to the energy levels of the atoms sprayed into the flame. The wavelength of the bands is characteristic of the atoms of the element concerned and the absorbance of the band proportional to the concentration of the atoms in the flame.
In atomic absorption spectroscopy both ionization and chemical interferences may occur. These interferences are caused by other ions in the sample, and result in reduction of the number of neutral atoms in the flame. Ionization is a problem with the technique because ions have inherently different electron band structures than unionized atoms of the same element. Therefore, ions do not absorb light of the same characteristic frequencies. This leads to artificially low absorbance and concentration data. The ability to measure very low elemental concentrations is also hindered by ionization. Alkali elements such as potassium are especially prone to ionization when they enter the flame. This method is expensive and time-consuming.

COLORIMETER

Instrument used for measuring absorption in the visible region is generally called colorimetry. The term colorimeter designates an instrument for absorption measurements in which the human eye serves as the detector. One or more color comparison standards are required. It is the simplest form, where human eye acts as a measuring instrument. This involves comparison by visual means of the colour of an unknown solution, with the colour produced by a single standard or a series of standards. The comparison is made by obtaining a match between colour of the unknown and that of a particular standard by comparison with a series of standards.
In earlier days, visual methods were commonly employed for all colorimetric measurements, but now photoelectric methods have largely replaced them and are used almost exclusively for quantitative colorimetric measurements. Any method involving measurement of colour in the visual region of the electromagnetic spectrum (400-700 μm) is referred to as the colorimetric method.

This method is simple in construction and operation. They are used for a great deal of analytical work, where high accuracy is not required. The disadvantage is that a range of filters is required to cover different wavelength regions. Also the spectral bandwidth of these filters is large in comparison with that of the absorption band being measured. And also the inability of the eye to compare light intensities.

**SPECTROPHOTOMETER**

A spectrophotometer is an instrument which isolates monochromatic radiation in a more efficient and versatile manner than colour filters used in filter photometers. In these instruments, light from the source is made into a parallel beam and passed to a prism or diffraction grating, where the light source is made into a parallel beam and passed to a prism or diffraction grating, where the light of different wavelengths is dispersed at different angles. This diffracted light is passed through the sample. The amount of
light reaching the detector of the spectrophotometer is generally very smaller than that available for a colorimeter. The detector current is amplified electronically and displayed directly on an indicating meter or in digital form. These instruments have the advantage in speed of measurement. This technique is used to measure absorbance, concentration, percent transmission and differential absorbance reading. The light sources in the spectroscopy will differ according to the sample absorbance wavelength region. And named according the source wave length like visual spectrophotometer for visible region and infrared spectrophotometer for infrared region etc. This method has two types of errors categorized as instrument errors and non-instrument errors.

ION SPECTROSCOPY

Ion spectroscopy is a powerful technique applied to surface characterization. The two techniques usually adopted are ion-scattering spectroscopy (ISS) and secondary-ion mass spectroscopy. Ions are formed by bombarding gas atoms with electrons. The positive ions are accelerated and focused on the sample at an angle of 45°. Ions are scattered in all directions. However, only those electrons which are in a selected small solid angle are received in the 127° electrostatic analyzer. The detector can be a channel electron multiplier or a solid state silicon device. To obtain the
spectra, the back-scattered primary ions are sampled by the cylindrical mirror analyzer and their kinetic energies are measured.

The ion-scattering spectroscopy is sensitive to every element heavier than helium, since the lightest isotope used as a primary ion is $^3$He and the scattering element must be heavier than the scattering gas. The specificity (ability to separate two particular elements) will vary depending on the scattering gas used. The detection limit of ISS is probably of the order of $10^{-3}$ % of a monolayer. This method is expensive and time-consuming.

**ION CHROMATOGRAPHY**

Ion chromatography is a useful technique for the measurement of various ionic species in solution. It is based on the principles of chromatography separation, and detection methods, the most common method uses conductivity suppression. The conductometric application of ion chromatography can be applied to cations, it is well suited for the detection of inorganic anions, as other methods during its time of development were insensitive and time consuming.

The ion chromatography is suited for the analysis of a variety of inorganic and organic anions and cations. The most important fields of application of ion chromatography are the environmental analysis, for the
determination of anions and cations in all kinds of water, including sea and continental water and waste water and the power plant chemistry, for the evaluation of the water, steam and condensate quality.

Conductometric suppression of analyte has been a remarkable improvement of the method. It allows more sensitive detection of the conductivity difference between an anions and the mobile phase eluent. Because the concentration of eluent is so high relative to that of the anions, it is often difficult to detect the slight drops in highly conductive eluent as less conductive anions pass through the detection cell. Since its development, conductometric detection has become a common means of detecting anions, such as the seawater component, sulfate and others. Sodium, potassium, magnesium, and calcium can be analysed with ion chromatography in precipitation. Ion chromatography has no special advantage concerning sensitivity, precision and accuracy over the spectroscopic methods. And also this method is expensive.

ELECTROCHEMICAL INSTRUMENTS

The determination of an ion or molecule by direct potentiometric measurement is rapid and simple 12. The comparision of the potential developed by the indicator electrode in the test solution and the potential when immersed in one or more standard solutions of the analyte. Because
most indicator electrodes are selective, preliminary separations steps are
seldom required. In addition, direct potentiometric measurements are rapid
and readily adapted to the continuous and automatic monitoring of ion
activities. There are many instruments based on the electrochemical cell
theory such as, conductivity meters, voltammetry, polar graphs,
coulometers etc.¹³

In voltammetry and polarography, the measurement is carried out
via a current produced from prior electrolytic process, handled under
controlled conditions of mass transport at appropriately small polarizable
electrodes. In these methods the concentration is related with the intensity
when definite voltage functions are applied. The qualitative information is
obtained from the peak potential and the quantitative information from the
diffusion-current. Polarography with microscopic microelectrodes is used
to study the chemical process going on inside organs of living species such
as mammal brains.

**Voltammetry and polarography techniques** are excellent methods for
trace and ultra-trace analysis of inorganic and organic substances and
compounds due to their low detection in ppb/ppt range with high accuracy
and high precision as well as the possibility of multi-element detection.
Chemical sensors are miniaturized analytical devices which can deliver real-time and on-line information on the presence of specific compounds or ions in complex samples. Usually an analyte recognition process takes place followed by the conversion of chemical information into an electrical or optical signal. Among various classes of chemical sensors ion-selective electrodes (ISE) are one of the most frequently used potentiometric sensors during laboratory analysis as well as in industry, process control, physiological measurements, and environmental monitoring. The principle of ion-selective electrodes operation is quite well investigated and understood.

An ion-selective membrane is the key component of all potentiometric ion sensors. It establishes the preference with which the sensor responds to the analyte in the presence of various interfering ions from the sample. If ions can penetrate the boundary between two phases, then an electrochemical equilibrium will be reached, in which different potentials in the two phases are formed. If only one type of an ion can be exchanged between the two phases, then the potential difference formed between the phases is governed only by the activities of this target ion in these phases. When the membrane separates two solutions of different ionic activities \( (a_1 \text{ and } a_2) \) and provided the membrane is only permeable to this
single type of ion the potential difference (E) across the membrane is described by the Nernst equation:

\[ E = \frac{RT}{zF} \ln \left( \frac{a_2}{a_1} \right) \]

If the activity of the target ion in phase 1 is kept constant, the unknown activity in phase 2 \((a_1 = a_x)\) is related to \((E)\) by:

\[ E = \frac{RT}{zF} \ln \left( \frac{a_x}{a_1} \right) = \text{const} + S \cdot \log(a_x) \]

where \(S = 59.16/z\) [mV] at 298 K and \(z_x\) - the charge of the analyte. The potential difference can be measured between two identical reference electrodes placed in the two phases. In practice the potential difference i.e. the electromotive force is measured between an ion selective electrode and a reference electrode, placed in the sample solution. It is important to note that this is a measurement at zero current i.e. under equilibrium conditions. Equilibrium means that the transfer of ions from the membrane into solution is equal to the transfer from the solution to the membrane. The measured signal is the sum of different potentials generated at all solid-solid, solid-liquid and liquid-liquid interfaces.

The common methods applied for speciation of organometals are separation of the species by chromatography, followed by detection and determination of the element with a specific detector such as atomic absorption spectrometry or mass spectrometry. These methods are expensive and time-consuming. Electroanalytical methods have much more
to offer in terms of species-selective detection than spectroscopic methods. Potentiometry with ion-selective electrodes is in principle well suited to speciation studies because of its selective response to free ions in aqueous solutions. The selectivity of these electrodes is based on interface molecular recognition process.

During last three decades, a number of ion-selective electrodes with polymeric membranes have been reported\textsuperscript{24-32}. Among the various ligands available for ion-selective electrodes such as crowns, podands, cryptands and spherands, the calixarenes met many of the requirements that an ionophore should satisfy for the use in ion-selective electrodes\textsuperscript{33}. A number of calixarene derivatives containing pendant ether, amide, ketonic and ester groups have been incorporated as neutral carriers into ion-selective electrodes sensitive to sodium, potassium and cesium ions\textsuperscript{34-38}.

Advantages of ion selective electrode are simple to do, inexpensive, rapid, rugged and selective. And also it has some disadvantages that they are not really an identification tool, more of a quantification tool, not as selective as some voltammetric techniques and not a tool to study electron transfer rxns.
When compared to many other analytical techniques, ISEs are inexpensive, simple to use, rapid, rugged and selective and, unlike the flame photometer have a linear response over a wide concentration range. However, they have some disadvantages that require attention if good results are to be obtained.

Many of them are not entirely ion-specific. For example, the sodium electrode also responds to potassium ions, of course with less sensitivity. This means that Na⁺ will be overestimated if a high concentration of K⁺ is present. Mathematical techniques have been devised to compensate for this.

They underestimate high concentrations because of "crowding" of the ions at the membrane – some just don't get "seen". The activity coefficient is a measure of this: activity equals concentration at low values, but it is less than concentration at high values. ISEs measure activity.

This method is not really an identification tool, more of a quantification tool, not as selective as some voltammetric techniques and not a tool to study electron transfer rxns.

Computers plays a pivotal role in instrumentation. The interfacing of instruments with computers has vastly increased our ability to measure. But
the attempts to design and develop the computer based systems for the measurement are rather scarce particularly in India though they offer many advantages. Hence, the need to design and develop a computer based system for measurement.
Section 1.3

ROLE OF COMPUTERS IN INSTRUMENTATION

Instrumentation has its origins in the attempts to measure, monitor or record various physical, chemical, biological or engineering phenomena. Historically, instrumentation had its roots in mechanical and hydraulic systems, but rapidly moved to electrical and electronic devices\textsuperscript{39}.

The art of measurement is a wide discipline in both engineering and science, encompassing the areas of detection, acquisition, control and analysis of data\textsuperscript{40}. It involves the precise measurement and recording of a physical, chemical, mechanical, optical and electrical parameters. Measurement plays a vital role in every branch of scientific research and industrial processes interacting basically with control systems, material sciences, and other branches of science and technology which resulted in the development of many sophisticated and high precision measuring devices and systems, catering to varied measurement problems in such disciplines as aeronautics, science and technology, space, medicine, oceanography, and industry in general\textsuperscript{41}.

With the invention of the microprocessor and microcomputer the measurement of any parameter became easy now a day, by interfacing the
system with microcomputer, which measures, stores and display the data read from the system. And also it is used to control the system.

Computer plays a pivotal role in instrumentation. Computer interactions with analytical instruments are of two types, passive, and active. In passive applications, the computer does not participate in the control of experiment but is used only for data handling, processing, storing, file searching, or display. In active interaction, the output from the computer controls sequence of steps required for operation of the instrument. The part of the time is devoted to data collection, the rest of the being employed for data processing and control. Thus active applications are real-time operations.

Not only instrumentation and measurement are playing an increasingly important role in technological society but also computers are playing an increasingly important role in instrumentation. The reason for this is that most physical quantities can be converted into electrical signals by means of transducers and these signals are processed and converted into digital form for automatic analysis and storage. The interfacing of instruments with computers has vastly increased our ability to measure and thereby our ability to find nature's answers to new questions.
There are many advantages for a computer-based instrument. The computer based measurement offers CRT text read-out, updating measurement readings, scale factors, general calculations, waveform scaling, time-frequency conversion, scale factor calculation, controlling and coordinating modules within an instrument etc.

Another useful feature is auto or self calibration. Self-calibration can also be extended to complete waveforms in waveforms processing instruments. These instruments have the provision to store and print the data. Processing and Analysis of data is another important feature of these instruments. There is a provision for real time measurements.

Another important advantage in using computers is their self-test ability. A computer with appropriate software can easily locate the failure in the board level, or perhaps the section or chip level and also it helps in rectifying the faults. Automated instruments offer a major economic advantage because of their savings in labour costs.

Another major advantage of automated instruments is their speed, which is frequently significantly greater than that of manual devices. Another advantage of automation is that a well-designed analyzer can
usually produce more reproducible results over a long period of time than can an operator employing a manual instrument.

We are living in a world that can do nothing without computers. So completely we are dominated by that term and the major nations of the world would shut down without it.

Despite the advances in other fields, by its very ubiquitousness, the 21st century belongs to the field of computers and instrumentation 42.
Section 1.4

PURPOSE AND SCOPE OF THE PRESENT STUDY

Amongst the various analytical techniques available, the use of ion-selective membrane electrodes is a well-established analytical technique. Good ion-selective electrodes possess many advantages over the traditional methods of analysis as they provide accurate, reproducible, fast and often selective determination of various ionic species. And also the ion-selective electrodes allow non-destructive, on line monitoring of particular ion in small volume of sample without any pretreatment. Hence, the use of ISEs is increasing day by day in medicinal, environmental, agricultural and industrial fields.

The automation of the analytical instruments such as potassium measurement systems and pH meters with computers delivers a great advantage in measuring the different parameters without manual attention. It also provides to control the system and it is capable to store data. The stored data can be used to analyze the properties of the liquid under investigation at any time you want. The display helps us in selecting user-friendly menu options. And also it indicates the improper circuits actions due to the faulty adjustments.
No doubt, several investigators developed the conventional potassium measurement systems, both analog and digital. But the attempts to design and develop the computer based systems for the measurement of potassium are rather scarce particularly in India though they offer many advantages. Hence, in the present study, an attempt is made to design and develop a computer based system for measuring potassium concentration.