Electroanalytical chemistry is a fascinating branch of chemistry in many areas of science. Electroanalytical chemistry has wide applications in various fields for the chemical analysis with respect to major, minor, trace and ultra-trace constituents in different matrices and hence is considered to be one of the very important branches of electrochemistry. Electroanalytical techniques and electrochemical processes play a crucial role in the entire nuclear fuel cycle which comprises the determination of various elements of interest in nuclear technology at various stages of the fuel cycle. Electroanalytical chemistry encompasses various analytical techniques based on the measurements of one or more electrical quantities namely voltage, current, resistance, conductance – whose magnitude may be directly correlated with the amount of the analyte present in the sample. These analytical methods can be categorized as potentiometry, amperometry, coulometry, conductometry etc. depending upon the variable measured, while other parameters are kept constant. Electroanalytical chemistry plays a major role in the area of nuclear science and technology. Nuclear energy is an important source of electricity production of the future as the limited deposits of the fossil fuels are fast depleting, in addition to the environmental concerns. Nuclear energy is produced in nuclear reactors through the process of fission. For the satisfactory performance of a nuclear reactor, the nuclear fuel has to meet stringent specifications laid down by the reactor designer. This necessitates the chemical quality assurance at different stages of fuel fabrication, from starting material to finished product. The various specifications to be checked during chemical
quality assurance include fertile and fissile content of nuclear fuel, metallic and non-metallic trace elements, O/M ratio (oxygen/metal ratio for oxide fuel), carbon content (for carbide fuel), moisture etc. Uranium, thorium and plutonium constitute the major components of the nuclear fuel. Electroanalytical methods based on redox reactions such as potentiometry, amperometry, coulometry etc. are widely employed for determining the amounts of uranium and plutonium in the fuel. Selection of the method depends upon the nature of sample matrix, dissolution procedure and precision and accuracy required. However, other points like availability of equipment, robustness and simplicity of the method, generation of minimum analytical waste, time involved and cost of analysis etc. are also considered while employing a particular method routinely. Ion selective electrode methods satisfy majority of these requirements and, therefore, have been used for various types of analyses.

Potentiometry involving ion selective electrodes also form an important branch of electroanalytical chemistry, where it is possible to develop suitable ionophores which can be employed for determining the ions of the element of interest with required precision and accuracy, in the presence of other interfering ions. Due to this, ion selective electrodes can also cater an important role in the chemical characterization of the nuclear fuel materials and which can be employed for the quantitative determination of uranium, thorium with respect to third generation of nuclear fuel viz. AHWR etc. In view of the versatility of ion selective electrodes over the past four decades, efforts are continued to develop improved and alternate electrochemical methodologies for various applications in nuclear technology.

The work in the thesis is described in 5 Chapters. First Chapter gives an introduction to electroanalytical chemistry with emphasis on to the fundamental
aspects of ion selective electrodes. This Chapter also emphasizes the scope of the present work. In the Second Chapter, a new, indirect method based on titrimetry which was developed for the determination of Lithium present in Organic impurities using fluoride ion selective electrode with potentiometric end-point detection is described. In the Third Chapter the development of coated wire Lithium ion selective electrode and its application for the determination of lithium present in organic impurities is discussed. Fourth Chapter deals with the development and application of coated graphite uranyl ion selective electrode for determination of uranium in nuclear fuels viz. UO₂, (U,Th)O₂. Fifth Chapter presents studies carried out for the development of coated graphite gallium ion selective electrode and its application to analysis of gallium (ppm level) in pure nickel.

Chapter – I

Introduction

Ion selective electrode (ISE) plays a vital role in the determination of various ions with respect to nuclear materials. There are various types of ion selective electrodes available viz. (i) solid state ISE (ii) liquid membrane based ISE (iii) gaseous based ISE (iv) enzyme based ISE etc. The basic principle of ISE remains the same while utilizing different kinds of ion selective electrodes. The advantage of working with ion selective electrodes (ISE) is that it is possible to obtain meaningful data about individual substances using economical systems. Ion selective electrodes are electrochemical sensors that can be used directly in the mg/L range and below. Analysis with ISE is by using the procedures employed for potentiometry (i.e.) the signal is measured in the form of potentials or more precisely as potential differences, or voltages in mV. An ion selective measuring system basically consists of the ISE
reacting on an ion of interest and a reference electrode that are jointly immersed in the sample to be measured. This combination is called a measuring chain. This measuring instrument must be very highly resistive in order to fulfill the conditions of a potentiometric measurement. The measurements currents should be low enough so that no polarization occurs and the electrodes are not damaged. For these reasons the electrode connections must be kept dry. Moisture can cause unwanted parallel connections and interferences.

The ion selective electrode provides an electrochemical potential that is influenced by the concentration of the ion type to be measured. The reference electrode, however, is intended to build up an electrochemical potential that does not depend on the composition of the sample to be measured. The difference of these potentials, the voltage displayed by the meter, can be described by the Nernst equation:

\[ E_{\text{ion}} = E^0_{\text{ion}} \pm S \times \log(a_{\text{ion}}) \quad (1) \]

\( E^0_{\text{ion}} \) is a fixed value given by the measuring system. The slope \( S \) defines how much the measurement signal is increased or reduced when the concentration changes. Its theoretical value is referred to as the Nernst slope and is 59.16 mV at 25°C for simply charged ions such as ammonium or nitrate. The arithmetic sign depends on the charge of the measured ions, a plus is for positively charged cations, e.g. \( K^+ \), a minus for anions such as \( Cl^- \). The activity “a” is the active concentration of an ion type that takes into account the influence of other ions in the sample and thus describes a considerable part of the matrix effect. Due to their positive charge, cations produce a
positive slope of the line, anions a negative slope. The slope can be specified more exactly with $S = \frac{RT}{zF}$

where $R$ gas constant (8.314 JK$^{-1}$mol$^{-1}$)

$T$ temperature in Kelvin (298 K)

$z$ valency of the ions

$F$ Faraday constant (96485 Cmol$^{-1}$)

Here the influence of the temperature becomes clear. The theoretical value of the slope (so-called Nernst slope), is - according to amount -59.16 mV for 25 °C for simply charged ions, i.e. with a change of the activity by the factor 10 the voltage changes by this amount.

Though the name of ion selective electrode specifically measures the relevant ions and there are other ions which are sometime equally interfering during the analysis while using ISE. This is explained on the basis of selectivity co-efficient.

The key area of this research work is to utilize (i) commercially available ISE (ii) to fabricate and utilize the non-commercially available ISE. A combination fluoride ISE, commercially available ISE was utilized for the determination of lithium present in organic impurities (indirectly) by titration of samples and standard with known excess of 0.5M NH$_4$F and the free F$^-$ ions was measured. In the second case, various types of non-commercially available ISE viz., Li-ISE, U-ISE and Ga-ISE in the form of coated wire ISE were developed by optimization of several experimental parameters and were then employed for the determination of respective elements (directly) in the standards and samples after suitable treatment of the sample (if necessary). These non-commercially available coated types ISE were studied for their
(a) dynamic range (b) detection limit (c) life time (d) dynamic response (e) application for the nuclear materials.

Chapter – II

**Determination of Lithium by Titrimetry using Fluoride Ion Selective Electrode employing potentiometric end point detection**

A simple and fast technique would be desirable for the determination of lithium present along with organic impurities during the preparation of Li$_2$TiO$_3$ microspheres for ITER (International Thermonuclear Experimental Reactor) process and to standardize the various steps involved in the preparation of Li$_2$TiO$_3$ microspheres by internal-gelation route of sol-gel process. In recent years, Li based ceramics such as Li$_2$O, LiAlO$_2$, Li$_2$ZrO$_3$, Li$_2$TiO$_3$ and Li$_4$SiO$_4$ have received considerable importance as tritium breeders in Test Blanket Modules (TBMs) for fusion reactors. Recently, Li-meta-titanate (Li$_2$TiO$_3$) was proposed as an important material for TBM because of its good chemical stability and possibility of tritium recovery at relatively low temperature. Sol-Gel process is promising for obtaining ceramic nuclear fuel materials such as UO$_2$ as well as non-nuclear materials in the form of microspheres (pebbles). Sol gel process was hence developed for the preparation of Li containing ceramic materials in the form of pebbles of required size and characteristics as well as with the required Li:Ti stoichiometry. For ITER process, the initial study is being carried out using natural Li$^7$ instead of enriched Li$^6$ which is actually to be used for the preparation of Li$_2$TiO$_3$ microspheres.

Though there are several methods available for the determination of lithium in inorganic matrix, but there is no suitable method available to determine lithium
present containing organic impurities. Conventional analytical methods such as ICP-AES, AAS etc. cannot be employed directly in an organic matrix containing HMTA, urea, etc. as they require removal of organics before analysis. Normally employed methodologies for destruction of organic components cannot be employed in the sol-gel process, since it has been reported that the mixture containing HMTA and NH₄NO₃ while heating may be explosive in nature. It was, therefore, considered worthwhile to investigate the possibility of employing potentiometric titration for the determination of Li. A titration method using potentiometric end point was developed for the determination of lithium in ethanol medium using ammonium fluoride as titrant and combination fluoride ion selective electrode as an indicator electrode for end point detection. Synthetic mixtures were prepared employing LiNO₃, with and without the organic constituents and the effect of the presence of the organic constituents for interference studies. Furthermore, synthetic mixtures containing varying amounts of lithium were prepared in an aqueous solution of 0.5 M NH₄OH containing the different organic constituents, namely HMTA (0.75 M) and urea (0.75M). Concentrations of the different components were higher than those actually used (0.25M) for gel preparation, to find out interferences, if any, during the determination of lithium by this method. 0.1 mL of each of these standard solutions was added to 15 mL of absolute ethanol which was used as a titration medium. Lithium present was converted to LiF using 0.5M NH₄F solution and the end point was detected from the variation in EMF measured Vs volume of 0.5M NH₄F. Orion Make Combination fluoride ion selective electrode was used to detect the free F⁻. Titrations were performed in sol-gel wash solutions for the determination of lithium in the same manner as above. The titrations were possible only in alcohol medium owing to high solubility of LiF in aqueous medium. Though it is reported that the NH₄F
titrant is to be mixed in ethanol+water mixture (1:1), in this work, we found that it is sufficient to mix the titrant in pure water. The precision of the measurements for samples containing 1 to 3 mg of Li was found to be better than 0.5%. The developed methodology was then employed for the determination of concentration of lithium (Li) in a complex organic mixture containing hexamethylenetetramine (HMTA), formaldehyde and ammonium nitrate, which are the wash streams generated in the sol-gel process employed for preparation of Li₂TiO₃ microspheres. The concentration data profile agreed with the isotopic profile obtained by thermal ionization mass spectrometry.

Figure 1 shows that the data obtained from the sequential washings of lithium titanate sol-gel particles in two sets of experiments. The samples in P-I set were from microspheres which were washed without any digestion. Samples in P-II set from washings of microspheres which were digested at 60°C for 17 hours in an oven. Both P-I as well as P-II set of samples were washed using 1.55M LiOH and 6% NH₄OH. The non-digested samples (P-I) show higher amount of lithium leached from the microspheres during the washings while the digested samples (P-II) show less leaching from the sol-gel particles as expected.
Figure 1 Lithium concentration determined in wash solutions obtained after washing of Li$_2$TiO$_3$ microspheres

Chapter – III

Determination of Lithium in Organic Matrix by coated wire Lithium ion selective electrode

The lithium determination (indirectly) in Chapter–2 containing organic impurities using combination fluoride ion selective electrode requires adjustment of pH between 5-7 as the fluoride ion selective electrode can function only in the pH range of 5-7. Moreover, this titration method is time consuming and can be cumbersome when the response is sluggish at the end-point. Therefore, a direct method was developed for the determination of lithium in the wash solution obtained during the preparation of Li$_2$TiO$_3$ microspheres. This could be achieved by fabricating
non-commercially available coated wire lithium ion selective electrode (Figure 2). This lithium ion selective electrode was fabricated using commercially available Lithium ionophore-VI (name of the ionophore need to be given), 2-nitrophenyl octyl ether (NPOE) as plasticizer and potassium tetrakis (p-chlorophenyl) borate (KTpClPB) as additive using PVC (Poly Vinyl Chloride) matrix on platinum wire.

Figure 2 Coated Wire Li-Ion Selective Electrode

Figure 3 shows the calibration data for of the coated wire lithium ion selective electrode. Lithium ion selective electrode was giving Nernstian response from $10^{-1}$M to $10^{-4}$M with a detection limit of $3 \times 10^{-5}$M. The calibration slope of this lithium ion selective electrode was found to be $58.5 \pm 1.0$ mV/decade. The selectivity coefficients of this electrode with respect to the different ions were determined by matched potential method. This lithium ion selective electrode was then used for the determination of lithium containing hexamethylene tetramine, formaldehyde, urea and ammonium nitrate etc. which are the wash streams generated during the sol–gel process employed for preparation of Li$_2$TiO$_3$ microspheres. The method was adopted
for the determination of lithium using coated wire lithium ion selective electrode in the various process streams generated during Li$_2$TiO$_3$ preparation where significant amount of organic constituents are present along with lithium. The lithium concentration data in the wash streams was obtained by coated Lithium ion selective electrode was found to be better than 2%. These studies were found to be highly useful in the optimization of the washing conditions in sol-gel process for obtaining phase pure lithium titanate sol-gel particle. The methodology developed in this work is fast and precise and can be employed on a routine basis for lithium determination in solutions containing organic constituents.

![Figure 3](image)

**Figure 3** Calibration curve of lithium ion selective electrode

\[
S = 58.5 \times 10^{-1} \times 10^{-4} \text{M}
\]
Chapter – IV

Determination of Uranium using coated graphite uranium ion selective electrode

Several methods are available for the determination of uranium in nuclear fuels using potentiometry, amperometry and coulometry etc. but little literature is available for the determination of uranium in nuclear fuels using ion selective electrodes. The current work was carried out for the development of ion selective electrode for determination of uranium in presence of thorium (U:Th ratio = 1:25 for AHWR fuel) using coated graphite uranyl ion selective electrodes as there are only few methods available for the determination of uranium in presence of thorium. Coated graphite uranyl ion selective electrode (Figure 4) was developed by depositing a membrane comprising Aliquat-336 loaded with uranyl tetrachloride dianion ($\text{UO}_2\text{Cl}_4^{2-}$) and poly vinyl chloride (PVC) on graphite rod.

Figure 4 Coated Graphite Uranyl Ion Selective Electrode
Figure 5 shows the performance of identical coated graphite uranyl ion selective electrodes which was fabricated on the same day. The drift in potential is due to the fact that these coating of membrane were done manually, the thickness as well as coating was found to be different for the same set of electrodes.

The coated uranyl ion selective electrode having Aliquat-336 loaded with uranyl tetrachloride dianion and PVC in the ratio 70:30 was found to exhibit linear Nernstian response over uranyl concentration range from $1 \times 10^{-4}$M to $1 \times 10^{-1}$M with a detection limit of $5 \times 10^{-5}$M in constant 6M chloride concentration. The calibration slope of this ion selective electrode was found to be $-29.2 \pm 1.0$ mV. The selectivity coefficients of this electrode with respect to the different metal ions as well as anions were determined by matched potential method. This coated uranyl ion selective electrode can be used for consecutive four months without losing Nernstian response [36-48]. The electrode was then employed for determining U in sintered UO$_2$ pellets as well as in presence of thorium. The results are encouraging.

Figure 5 Performance of identical coated graphite uranyl ion selective electrode
Chapter – V

Development of coated graphite Gallium ion selective electrode

Coated graphite Gallium ion selective electrode was developed by depositing a membrane comprising of Aliquat-336 loaded with Gallium in the form GaCl$_4^-$ and poly vinyl chloride in the ratio of 70:30. Specific properties of the electrodes were studied including calibration curve, slope, detection limit, concentration range, response time and life time. The effect of chloride concentration was investigated. This coated graphite Gallium ion selective electrode exhibits linear Nernstian response over gallium concentration range of 1x10$^{-4}$M-1x10$^{-1}$M of Ga(III) ions in constant chloride concentration of 6M with a detection limit of 2x10$^{-5}$ M calibration slope of -58.2 mV ± 1.0 mV/decade change in concentration of Ga. Interference of Li$^+$, Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, Fe$^{3+}$, Cr$^{3+}$, Ni$^{3+}$, Th$^{4+}$, U(VI), OH$^-$, CO$_3^{2-}$ and NO$_3^-$ on electrode response have also been investigated. The selectivity coefficients of this electrode with respect to the different ions were determined by matched potential method. This coated graphite gallium ion selective electrode can be used for consecutive three months without losing Nernstian response.
Summary and Highlights of the present work

1. A titrimetry method has been developed for the determination of lithium in wash solution resulting during the preparation of lithium meta titanate (Li₂TiO₃) microspheres using fluoride ion selective electrode with potentiometric end point detection for the first time.

2. Coated wire Lithium ion selective electrode was developed for the purpose of determining lithium in the organic matrix after suitable treatment of the sample during the preparation of lithium meta titanate (Li₂TiO₃) microspheres.

3. A method was developed for the determination of uranium in sintered UO₂ pellets and in the synthetic mixture containing uranium and thorium (AHWR type fuel) using coated graphite uranium ion selective electrode.

4. Coated graphite gallium ion selective electrode was developed and the performance of the electrode was checked.