ELECTROANALYTICAL CHEMISTRY OF NUCLEAR MATERIALS



Bhabha Atomic Research Centre, Mumbai, India

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Recommendations of the Viva Voce Board

As members of the Viva Voce Board, we certify that we have read the dissertation prepared by Shri R. Govindan entitled "Electroanalytical Chemistry of Nuclear Materials" and recommend that it may be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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(R.Govindan)

DECLARATION

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / diploma at this or any other Institution / University.

(R.Govindan)

List of Publications arising from the thesis

Journal

- "Determination of Lithium by Potentiometry using Fluoride Ion Selective Electrode", R. Govindan, D. Alamelu, Raju V. Shah, T.V. Vittal Rao, Y.R. Bamankar, A.R. Parab, K. Sashi Bhushan, R.M. Rao, S.K. Mukerjee and S.K. Aggarwal, *Anal. Methods*, 2010, 2, 1752-1755.
- "Determination of Lithium in Organic Matrix Using Coated Wire Lithium Ion Selective Electrode", R. Govindan, D. Alamelu, T.V. Vittal Rao, Y.R. Bamankar, S.K. Mukerjee, S.C. Parida and A.R. Joshi, *Indian Journal of Advances in Chemical Science*, 2014, 2 (2), 89-94.
- 3. "Development of Coated Graphite Gallium Ion Selective Electrode based on Aliquat 336", R. Govindan, D. Alamelu, S.C. Parida and A.R. Joshi, *Indian Journal of Advances in Chemical Science*, **2014**, *2* (2), 110-115.
- 4. "Determination of Uranium by Coated Graphite Uranyl Ion Selective Electrode", R.Govindan, D.Alamelu, U.M.Kasar, S.C.Parida and A.R.Joshi, *Indian Journal of Chemical Technology (Under Review)*.

Conferences

- 1. "Determination of lithium in organic matrix by potentiometric titration using fluoride ion selective electrode" R. Govindan, D. Alamelu, Raju Shah and S.K. Aggarwal, *DM-ELANTE-2008*, **2008**, P-27, 250-252.
- "Development of Coated Wire Ga(III) Ion Selective Electrode R.Govindan, J.L.Sharma, K.G.Kate, D.Alamelu, D.R.Ghadse, N.K.Shukla and A.R.Joshi *NUCAR-2011*, 2011, E-32, 577-578.

DEDICATIONS

I dedicate this dissertation to

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My beloved parents

Late Shri K.Ramamurthy

&

Late Smt.R.Rajalakshmi

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(R.Govindan)

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SYNOPSIS

Electroanalytical Chemistry of Nuclear Materials

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 nonmetallic 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:

$$\mathbf{E}_{\text{ion}} = \mathbf{E}^{\mathbf{0}}_{\text{ion}} \pm \mathbf{S} * \log \left(\mathbf{a}_{\text{ion}} \right) \tag{1}$$

 E^{0}_{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 CI⁻. 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 = RT / zF

- where R gas constant $(8.314 \text{ JK}^{-1}\text{mol}^{-1})$
 - 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 NH₄F 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 Li₂TiO₃ microspheres for ITER (International Thermonuclear Experimental Reactor) process and to standardize the various steps involved in the preparation of Li₂TiO₃ microspheres by internal-gelation route of sol-gel process. In recent years, Li based ceramics such as Li₂O, LiAlO₂, Li₂ZrO₃, Li₂TiO₃ and Li₄SiO₄ have received considerable importance as tritium breeders in Test Blanket Modules (TBMs) for fusion reactors. Recently, Li-meta-titanate (Li₂TiO₃) 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 UO2 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 Li⁷ instead of enriched Li⁶ which is actually to be used for the preparation of Li₂TiO₃ 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 solgel 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 Li₂TiO₃ 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 Li₂TiO₃ 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 3×10^{-5} M. The calibration slope of this lithium ion selective electrode was found to be 58.5 ± 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 Li₂TiO₃ 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_2TiO_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 Calibration curve of lithium ion selective electrode

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 $(UO_2Cl_4^{2-})$ 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 1×10^{-4} M to 1×10^{-1} M with a detection limit of 5×10^{-5} M in constant 6M chloride concentration. The calibration slope of this ion selective electrode was found to be -29.2 ± 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 UO₂ 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 GaCl₄⁻ 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 $1 \times 10^{-4} M - 1 \times 10^{-1} M$ of Ga(III) ions in constant chloride concentration of 6M with a detection limit of 2×10^{-5} M calibration slope of $-58.2 \text{ mV} \pm 1.0 \text{ mV/decade}$ change in concentration of Ga. Interference of Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Fe³⁺, Cr³⁺, Ni³⁺, Th⁴⁺, U(VI), OH, CO₃²⁻ and NO₃⁻ 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

- 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
- 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.

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Summary

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CHAPTER – 1

Introduction

1.1 Introduction

Nuclear energy is an important clean and environmental friendly source of energy. It has potential to meet the demands of energy for the coming few hundred years. India has embarked on a three stage nuclear power programme, which is based on utilization of natural uranium as nuclear fuel in the first stage using pressurized heavy water reactors, utilization of plutonium in the second stage using fast breeder reactors and utilization of thorium using advanced reactors in the third stage. The three-stage power programme is schematically shown in Figure 1.1.



Figure 1.1 Three stage Nuclear Fuel Programme

As is evident, natural uranium is the main component of fuel in the first stage of Indian nuclear power programme. The production of natural uranium based fuels involves various stages starting from its mining. A typical nuclear fuel cycle is given in Figure 1.2.



Figure 1.2 Nuclear Fuel cycle

Chemical quality control (CQC) is highly essential at various stages of nuclear fuel cycle. In CQC, depending on the content of element of interest in the matrix, it is considered as major, minor, trace or ultra-trace element. These classifications are based on the following guidelines.
Major:	>1 wt%
Minor:	<1 wt% and 0.01wt%
Trace:	<0.01wt% and >0.0001wt%
Ultra trace:	<0.0001 wt%

Chemical quality control provides a means to ensure that the quality of the fabricated fuel conforms to the chemical specifications for the fuel laid down by the fuel designer. These specifications are worked out for the major, minor, trace and ultra trace constituents as mentioned above which affect the fuel properties and hence its performance under conditions prevailing in an operating reactor.

The strategic importance of uranium, plutonium and thorium, calls for stringent conditions for their accounting, containment and disposal of wastes produced during their processing due to the radiological hazards associated with them. These requirements, as well as the CQC of nuclear materials, from feed materials to finished products, require accurate and precise determination of these elements. The fabrication of the fuel is an important step in the production of nuclear energy during the residence of the fuel in a nuclear reactor. The fuel has to meet stringent chemical specifications laid down by the fabricator. Chemical quality assurance, thus, forms an integral part of nuclear fuel fabrication. This involves measurements of the major constituents, fissile isotopic content, as well as trace impurities present.

There are different methods of chemical quality control such as:

- ➤ Heavy Metal Content viz., U, Th, Pu etc.
- Oxygen to Metal Ratio
- Moisture content
- ➤ Isotopic Composition

- ➢ Metallic impurities
- Non-Metallic Impurities viz., H, C, N, O, S etc.
- Total gas content
- Cover gas analysis

Electronalaytical techniques play an important role in the CQC of nuclear materials at various stages of fuel cycle. Although various analytical methods are reported, electroanalytical techniques such as potentiometry and amperometry are commonly employed for the accurate determination of uranium and plutonium because of their simplicity, reliability, fastness and simple, inexpensive instrumentation. The feed materials comprise of UO₂, PuO₂, ThO₂ etc., while the finished products are sintered pellets of UO₂, (U,Pu)O₂, (U,Pu)C, (U,Th)O₂, and ²³³U – Al – Zr and Pu – Ga alloys. While the fissile isotopic content (isotopic composition) is determined by thermal ionization mass spectrometry (TIMS), the uranium and plutonium contents are determined by redox titrimetry, and thorium content is determined by complexometric titration. Since electroanalytical techniques are widely employed in the above determinations, a brief description of the various electroanalytical techniques and their theoretical aspects is presented here.

1.2 Theoretical Considerations in Electro Analytical Chemistry

1.2.1 Electrochemical Cells

An electrochemical cell forms the basis of any electrode reaction. There are two types of electrochemical cells – galvanic (or voltaic) and electrolytic. Galvanic cell consists of two half cells and is capable of converting chemical energy into electrical energy. In an electrolytic cell, electrical energy from an external source is forced to flow through a cell effecting concentration changes in the system. If the galvanic emf is opposed by an equal applied emf, no current will flow through the cell and the potential generated at the interface of the indicator electrode will reflect the composition of the solution phase. However, it is possible to measure the potential of an indicator electrode (E_{ind}) if it is coupled with a reference electrode of known potential (E_{ref}). In an electrochemical cell

$$E_{cell} = E_{ind} + E_{ref} + E_j \tag{1.1}$$

where E_j is the liquid junction potential. In a properly designed system, E_{ref} is a constant and E_j is constant or negligible and hence the indicator electrode can give information about ion activities. Platinum and gold are the most common indicator electrodes while calomel, hydrogen, Ag / AgCl, Hg / Hg₂SO₄ are the most common reference electrodes.

1.2.2 Electrode Potential

According to IUPAC convention, the electrode potentials are the emf of the cells formed by combination of the individual half-cells with standard (or normal) hydrogen electrode (SHE or NHE).

Pt, H₂ (1 atm)
$$| H^+ || M^{n+} (a = 1) | M$$
 (1.2)

The emf of the cell is the difference between these half-cells. If all the substances participating in the reversible operation of the cell at a particular temperature are in their standard states, the free energy change of the cell reaction

$$\frac{n}{2}H_{2(g)} + M^{n+} \rightleftharpoons nH^{+} + M^{0}$$
(1.3)

is given by

$$\Delta G^0 = -n F E_{cell}^0 \tag{1.4}$$

where ΔG° = change in standard free energy, and F = Faraday

constant. For a spontaneous cell reaction, the ΔG° is negative. By convention, the standard potential, E° , of a hydrogen electrode at all temperatures is taken as zero.

1.2.3 Effect of concentration on electrode potential

When a metal is immersed in a solution containing its own ions, a potential difference is established between the metal and the solution. The potential difference E of the reaction

$$M \rightleftharpoons M^{n+} + ne \tag{1.5}$$

is given by the expression

$$E = E^{0} - \frac{RT}{nF} \ln \frac{1}{a_{M^{n+}}}$$
(1.6)

Where "R" is the gas constant, "T" is the absolute temperature, F is the Faraday constant, n is the charge of the ions, $a_{M^{n+}}$ is the activity of the ions in solution and E^0 is a constant dependent upon the metal. The equation can be simplified by introducing the known values of R and F and converting logarithm on base 10, and at 25°C

$$E = E^0 - \frac{0.0591}{n} \log \frac{1}{a_{M^{n+}}}$$
(1.7)

For many purposes in quantitative analysis, $a_{M^{n+}}$ is replaced by $C_{M^{n+}}$, the ion concentration (in moles / litre) and the equation becomes

$$E = E^0 - \frac{0.0591}{n} \log \frac{1}{C_{M^{n+}}}$$
(1.8)

This is a useful form of the Nernst equation, where E^0 is the standard electrode potential of the metal. When the activity of the ion M^{n+} is equal to unity (approximately true for a 1M solution), the electrode potential is equal to the standard electrode potential. The standard electrode potential is a quantitative measure of the readiness of the element to lose electrons, and hence the measure of the strength of the element as a reducing agent in aqueous solution. The more negative the potential of the element, the more powerful is its action as a reductant.

Electrode potential varies with the concentration of the ions in solution. When two electrodes of the same metal are immersed in solutions containing different concentrations of its ions, such a cell is called a concentration cell. The potential of the cell will be the algebraic difference of the two potentials, if liquid-liquid junction potential is eliminated with a salt bridge.

The simple electrochemical cell consists of a zinc rod dipping into zinc sulphate solution and a strip of copper in copper sulphate solution; the solutions being separated by keeping one in a porous pot and the other in a surrounding vessel. The cell may be represented as;

$$\operatorname{Zn} | \operatorname{ZnSO}_{4\,(\mathrm{aq})} \| \operatorname{CuSO}_{4\,(\mathrm{aq})} | \operatorname{Cu}$$
(1.9)

At the zinc electrode, zinc ions pass into solution leaving an equivalent negative charge on the metal. Copper ions are deposited at the copper electrode rendering it positively charged. By completing the external circuit, current (electrons) passes from Zn to Cu. The chemical reactions taking place in the cell are as follows:

- (a) Zinc electrode: $Zn \rightleftharpoons Zn^{2+} + 2e$;
- (b) Copper electrode : $Cu^{2+} + 2e \rightleftharpoons Cu$

The net chemical reaction can be represented as:

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$
 (1.10)

1.2.4 Oxidation – Reduction cells

In a system containing both an oxidizing agent and its reduction product, there will be equilibrium between them and electrons. If an inert electrode such as platinum is placed in a redox system, for example, containing Fe(III) and Fe(II) ions, it will assume a definite potential indicative of an equilibrium. The relative strength of oxidizing and reducing agents can be found out by measuring the standard potential of the cell in which the ratio of the activity of the oxidant to that of the reductant is unity, when measured against standard hydrogen electrode. In practice, the formal potentials determined under defined concentrations are very useful for predicting the possibilities of redox processes. The electrode potential which is established when an inert electrode is immersed in a solution containing both oxidant and reductant is given by the expression:

$$E = E^{0'} - \frac{RT}{nF} \ln \frac{a_{\text{Re}d}}{a_{Ox}}$$
(1.11)

which becomes

$$E_{25^{\circ}} = E^{0'} - \frac{0.0591}{n} \log \frac{[\text{Re}\,d]}{[Ox]}$$
 (1.12)

when values of R and F are substituted and activity is changed into concentration at 25°C. $E^{0'}$ is the formal potential of the system. If the concentrations of the oxidant and reductant are equal, $E_{25^{\circ}}$ becomes equal to E^{0} , the standard reduction potential. Most of the electroanalytical techniques are based upon electrode reactions involving oxidation and reduction in an electrolytic cell. An overview of the various electroanalytical techniques is given below.

1.3 Electroanalytical Techniques

1.3.1 Conductimetry

According to Ohm's law, the current I (amperes) flowing in a conductor is directly proportional to the applied electromotive force E (volts) and inversely proportional to the resistance R (ohms) of the conductor:

$$I = E / R \tag{1.13}$$

The reciprocal of the resistance is termed the conductance (G), which is measured in reciprocal ohms Ω^{-1} , for which the name siemens (S) is used. The resistance of a homogeneous material of length '*l*' and area of crosssection '*a*' is given by

$$R = \rho . \frac{l}{a} \tag{1.14}$$

where ρ is termed resistivity (specific resistance), a characteristic property of the material. The reciprocal of resistivity is the conductivity (specific conductance) κ , measured in units of $\Omega^{-1}cm^{-1}$.

1.3.2 Coulometry

Coulometry is an application of Faraday's First Law of Electrolysis, which states that the extent of chemical reaction at an electrode is proportional to the quantity of electricity passing through the electrode. The weight of the substance produced or consumed in an electrolysis involving Q coulombs is given by the expression

$$W = \frac{M_r \times Q}{96487 \ n} \tag{1.15}$$

where M_r is the relative atomic (or molecular) mass of the substance liberated or consumed.

1.3.3 Potentiometry

Potentiometric methods embrace two major types of analyses: (i) the direct measurement of an electrode potential from which the activity or concentration of an ion may be derived and (ii) the changes in the potential brought about through the addition of a titrant (potentiometric titration). For quantitative measurements, however, the latter finds wider application. In a potentiometric titration, the change in the potential of an indicator electrode in an electrochemical cell is used for the detection of the equivalence point of the titration. In addition to the establishment of the equivalence point, further information about the sample and its reaction may be obtained by the complete recording of a titration curve.

1.3.3.1 Location of the Equivalence Point

The critical problem in a titration is the recognition of the equivalence point. The titration curve can be obtained by plotting the cell emf vs. volume of the titrant. Over most of the titration range, the emf varies gradually, but near the end point the emf changes abruptly as the logarithm of concentration undergoes rapid change. The resulting curve will resemble Fig. 1.3(a). An endpoint may be located more precisely by plotting successive values of the rate of change of emf vs. titrant increment in the vicinity of the inflection point. The maximum on the first derivative curve Fig. 1.3(b) corresponds to the inflection point. The end point can be even more precisely located from the second derivative curve Fig. 1.3(c).

1.3.3.2 Sensitivity

Sensitivity of a potentiometric titration is limited by the accuracy of

measurement of the electrode potentials at low concentrations. A 10^{-2} N solution can be titrated with an accuracy of 0.1% while the accuracy for 10^{-3} N solution can be 1%. Other titration methods are needed for solutions more dilute than 10^{-3} N, the limiting concentration in potentiometric titration.



Volume of Titrant (V)

Figure 1.3 (c)

Figure 1.3 Potentiometric Titration Curves

1.4 History of Ion Selective Electrode Development

The historic discovery of selective potentiometric transducers was achieved by Cremer about one hundred years ago [1]. The pH selective glass electrode, which Cremer introduced, even after about 100 years, still remains a good example of an analytical tool. It would be difficult to surpass its excellent selectivity, its exceptionally broad range of dynamic response, the simplicity of its operation and its cost efficiency. Indeed, the pH sensitive glass membrane electrode is one of the most widely and most frequently used analytical tools even today. It took research scientists more than a half century to develop ion selective glass based potentiometric electrodes for the measurement of different ions. In 1957, Eisenmann became the first researcher to report the preparation of a well functioning sodium ion selective glass electrode [2]. The potentiometric response of membranes that consist of various non-glass materials have been investigated by several groups [3-5]. They have used corresponding silver halide membranes to measure ion activity response, which was very close to Nernstian and was also free of redox interferences, for chloride, bromide and iodide. In the 1950s several research groups studied the electrode potential function of different membranes prepared from ion exchanger materials through various techniques. Pungor and Hollos [6] were the first scientists to report the preparation of highly selective iodide electrodes with electrode potential response that was very close to Nernstian. Their initial report was about silver iodide containing paraffin membranes. Later heterogeneous membrane electrodes were prepared with cold, vulcanized silicon-rubber matrix materials. Soon after that initial report, Frant and Ross, the founders of Orion Company [7], developed their lanthanum fluoride crystal based fluoride selective electrodes.

The commercial success of the lanthanum fluoride crystal based fluoride selective electrode, as well as the scientific interest generated by it, lead to an extremely intensive research effort, which was focused on the development of

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new ion selective electrodes as well as the improvement of ion selective electrodes. These studies resulted in the invention of plasticized PVC based electrodes, the universal ion selective electrode form and the coated wire electrodes.

A major step in development of ion selective electrode was initiated by Pioda in 1969 who demonstrated that neutral organic molecules could be used effectively as active measuring materials (ionophore) in the preparation of membrane based ion selective electrodes [8] The first neutral ionophore molecule, the antibiotics valinomicin and nonactin, were borrowed from nature. But later good results were also achieved with synthetic ionophores. These studies lead to an intensive research effort aiming to design, prepare and try out different types of organic molecules in the preparation of ion selective potentiometric sensors. This work is in progress even today also at different laboratories of the world.

1.5 Principle of ion selective electrode

The sensing polymeric membrane allows only the ion of interest to pass from sample solution at outer membrane surface to an internal solution in contact with an inner membrane surface. The internal solution contains a fixed activity of the ion to which the membrane is permeable. When such an electrode is placed in a sample solution, there is a momentary flux of ions across the membrane in the direction of the solution containing the lower activity of mobile ion. since the ions carry a charge, an electrical potential is set up which opposes further ion migration and eventually as equilibrium is established in which the potential across the membrane is exactly equal to that required to prevent further net movement of ions. Changes in this membrane potential can be measured by making electrical contact to the inner filling solution with a suitable reference electrode and at the same time contacting the sample solution with a second reference electrode with proper bridge solution. A high input impedance voltmeter connected across the two reference electrodes leads will indicate a potential given by the Nernst equation. E = Constant + $(2.303 \text{RT/nF}) \log_{10} \text{A}$, where E is the potential in millivolts, developed across the measurement electrodes in the system. The constant term depends on the particular choice of reference electrodes used, on the choice of ion activity in the inner solution and also includes a small potential associated with the liquid-liquid junctions. RT/F is the Nernst factor, which depends on the temperature and has a value of 59.16 mV at 25°C. "A" is the activity (in the sample solution) of the ion to which the membrane is permeable and z is its charge including sign. In use, the electrode pair must first be calibrated with standard solutions of known activity. A plot of electrode potential versus log A of the standard solutions can then used as working curve to determine unknown sample activities.

1.6 Sensing Components in Ion-Selective Membrane

1.6.1 Membrane and its constituents

All characteristics of membrane based ISE are dictated by ion carriers in the membrane and its combination with other membrane constituents. Depending on ion of interest, we have to select proper ionophore and other membrane constituents. Also studies have to be carried out to optimize membrane composition for getting best response of ISE for the primary ion. Brief discussion about general characteristics of ionophore and other membrane constituents is given below.

Ion-selective-electrodes (ISEs) can be divided into three main groups, namely glass membrane, crystalline membrane (solid membrane) and polymeric membrane (liquid membrane). The most common glass membrane electrode is the glass pH electrode. This electrode incorporates both glass and reference electrode in one body. A crystalline membrane is commonly used for environmental monitoring of heavy metal ions such as copper, cadmium and silver. Both glass membrane and crystalline membrane have good selectivity but only a few ions can be measured using the approach.

A polymeric membrane is normally used to separate a filling solution containing a solution of the target ion and the test solution. It is commonly known as ion-selective membrane (ISM). This polymeric membrane consists of four components, in which the nature and the amount of each component have a great effect on the characteristics of the chemical sensors. The four basic membrane components are:

- **4** Polymeric matrix
- ↓ Ionophore (membrane active recognition)
- Plasticizer (membrane solvent)
- Lipophilic additive salt (Ionic additives)

One of the main advantages of a polymeric membrane is its high selectivity achieved by incorporating molecular recognition (an ion carrier). However, a polymeric membrane needs to be stable in order to be effective. Typically, the component of sensing membrane consists of 33% (w/w) polyvinyl chloride (PVC) as polymeric matrix, 66% plasticizer for homogenzing the matrix and 1% ionophore. The first membranes using neutral-carrier were prepared using silicon or PVC without the addition of lipophilic ionic sites. Later it was realized that these ISEs only exhibited a Nernstian response due to the presence of ionic impurities and other membrane components. It has been shown that membranes without ionic sites do not give any response to the target ion.

Shatkay (1967) was the first to use a polymer as a homogenous membrane matrix for an ion-selective membrane and PVC is a common material used as the polymer matrix. PVC is used as a matrix that gives the membrane mechanical strength and structural integrity but is not intended to be an active component in the membrane. Polyurethane (PU) is also used as a polymer matrix due to enhanced biocompatibility and its adhesive property; however they tend to result in higher detection limits.

1.6.2 Ionophore

The main component of electro active membrane is neutral or charged compound, which is able to complex ions reversibly and to transfer them through an organic membrane by a carrier translocation. This compound is called as an ionophore or an ion carrier. There are two kinds of ionophores, charged one (usually termed liquid exchanger) and neutral carriers. They are mobile in both free and complexed forms, so the mobilities of all species are part of the selectivity coefficient together with ion exchange equilibrium. The ionophore is an electron-rich complexing compound that can bind to a specific ion. It can be an ion exchanger (charged) or a neutral macrocyclic compound that has cavities to surround the target ions. The ionophore is the most important component in any polymeric membrane, as it is responsible for the selectivity and sensitivity of the sensor which depends on the binding between the ionophore and the target ion. The selectivity of an ISE towards other ions originates from the difference in binding strength between the ionophore and various ions. A good ionophore must complex the ion of interest with higher affinity than interfering ions and the complexation must be reversible. The ions will be transferred through an organic membrane by carrier translocation. A number of naturally occurring ionophores have been used as ISE membrane components such as valinomycin, crown ether, nonactin, ionomycin, nigericin and monensin. Since some of the natural ionophores have limited selectivity, many synthetic ionophores have also been synthesised. Ionophores require a fine-tuned balance between the free energies of ion-ligand interaction and ion hydration. The complex formation constants in membrane span several orders of magnitude, from 104 to 109 mol⁻¹kg for all 1:1 stoichiometric species. The lower limit is set by the requirement that, in order to make full use of selectivity of the ionophores, the ions must be present predominantly in complexed form, whereas the upper limit is determined by the fact that counter ions from the sample must not enter the sensing film, otherwise the co-extraction of the analyte ion and its counter-ion deteriorates the potentiometric response. The selectivity behavior of ISE is defined by the ion exchange constants which depend on the standard free energies of the respective ions in the aqueous and organic phases as well as on the selectivity of complexation. The former can be influenced, to some extent by choosing an appropriate plasticizer and polymer matrix for a given organic phase. Still, the most important means of realizing highly selective sensors is to use ligands that strongly complex the preferred ion and only weakly all the others. Notwithstanding, as mentioned above, there is an upper limit to the complex formation constant allowed.

1.6.3 Plasticizer

A plasticizer is an important component in an ISE membrane. It is added to increase the plasticity i.e. turning the hard brittle plastic into a soft flexible elastomer by reducing the glass transition temperature (Tg) of the PVC to below room temperature. It should be inert and not form complexes with ions. The plasticizer also plays a role in dissolving the ionophore and lipophilic ionic additives in order to provide a homogenous and miscible system with the polymer matrix. For practical use as ISE membrane, leaching of the plasticizer should be avoided, otherwise it would affect the electrode performance over time. Leaching of the plasticizer from the membrane will increase the loss of ionophore and lipophilic additives. Common plasticizers used include adipates, phthalates, sebacates and phenyl ethers. Solvent polymeric membranes used in ion sensors are usually based on a matrix containing about 33% (w/w) of PVC and 66% of a membrane solvent i.e. plasticizer. Films with such a high amount of plasticizer have optimum physical properties and ensure relatively high mobilities of their constituents. In order to have homogeneous organic phase, the membrane solvent (plasticizer) must be physically compatible with the polymer. Otherwise, it excludes, yielding membranes of unstable composition. For various reasons, it also has an influence on the selectivity behavior. For a ligand-free ISE membrane based on an ion exchanger that is incapable of specific interactions, the selectivities are determined by the difference between the standard free energies of the ions in the aqueous and organic phases, which is only influenced by the plasticizer. On the other hand, selectivities of carrier based ISEs are highly influenced by the membrane solvent. For example the change in plasticizer from polar oNPOE to apolar dibutyl sebacate (DBS) or dioctyl sebacate (DOS) reduces the Ca²⁺ selectivity with the ionophore ETH 1001 by orders of magnitude [9, 10]. It has been assumed that this influence is due to the polarity of the plasticizer, which can be estimated from the interaction of charged species with a continuum of given dielectric constant. With more polar solvents, divalent ions are preferred over monovalent ones, the effect being especially pronounced with thin ligand layers [11].

1.6.4 Lipophilic additive

Lipophilic additive salts also known as ionic additives are ion exchangers. It is well established that the addition of a known quantity of lipophilic additive has greatly improved the electrode response time, stability, reproducibility and selectivity. It has also been shown that membranes without ionic sites do not respond to the concentration changes of the ion of interest. Therefore, it is a necessary for any membrane to have ion exchange sites in order to provide permselectivity. Initially, the main objective of adding a tetraphenyl borate salt to the membrane of a cation-selective electrode was to reduce the anionic interference observed in the presence of lipophilic anions like thiocyanate. Lipophilic additives also serve to lower the electrical resistance of the membrane, which is especially important for microelectrodes. The most common lipophilic salt additives used in ISEs are tetraphenyl borate salts for cation-selective electrodes and tetraalkyl ammonium salts for anion-selective electrodes. Since an ion cannot exist by itself in liquid membrane phase without violating the requirements of electro neutrality, it is necessary to provide a charged "site" of opposite sign as an addition to the solvent liquid. Also a prerequisite for obtaining a theoretical response with ISE membrane is their permselectivity which means that no significant amount of counter-ion may enter the membrane phase. To achieve this Donnan exclusion with electrically neutral carriers, counter ions (ionic sites) must be present in membrane. Although, neutral carrier based ISE membranes may work properly even when they contain only a very small amount of ionic sites (e.g., as impurities), the addition of a salt of a lipophilic ion is advisable and beneficial for various other reasons as well. The original motive for adding a tetraphenyl borate salt to the membrane of a cation selective electrode was to reduce the anionic interference observed in the presence of lipophilic anions like thiocyanate or perchlorate. At the same time, the electrical resistance of the membrane is lowered, which is especially important with microelectrodes. In charged carrier based ISE membranes, on the other side, ionic sites are not required to obtain a Nernstian response because the carrier itself induces the Donnan exclusion. However their presence is beneficial. In contrast to neutral carrier based membranes, they must bear the same charge as the anlyte ion. In general, the selectivity of ion complexation can only be fully exploited when these membranes contain ionic additives.

1.6.5 The polymer matrix

Originally, liquid ISE membranes were obtained by soaking porous materials (e.g., filter paper) with a solution of the ionophore in a water-immiscible, nonvolatile, viscous organic liquid [12]. Polymers as homogeneous membrane matrices came first in use with charged carriers [13]. The first neutral-carrier-based polymer ISE membranes were prepared with valinomycin in silicone rubber or PVC [14] but without adding lipophilic ionic sites. At that time, the polymer was considered to be just an inert matrix providing the necessary

physical properties, such as mechanical stability and elasticity. Nowadays, it is well-established that these ISEs only exhibit Nernstian response owing to the fortuitous presence of ionic impurities in PVC [15] and in other membrane components. It was demonstrated that membranes having no ionic sites at all do not give any electrode response. By radiotracer studies [16] as well as by ion exchange and atomic absorption [17], the total concentration of anionic impurities in cation-selective PVC membranes was found to be 0.5 and 0.05-0.6 mmol kg⁻¹. Recently, their electrochemically relevant concentration was determined more precisely by measuring potentiometric selectivity coefficients of a series of membranes that only differed in the amount of tetraphenylborate salt added. When prepared with commercially available PVC and o-NPOE, the membranes were shown to contain 0.016 mmol kg⁻¹ of anionic impurities. This is much less than the usually applied concentrations of ionophore and ionic additive (1-15 mmol kg⁻¹). Although the nature of the impurities in commercial PVC is not fully elucidated, it is established that some of them are compounds having sulfate or sulfonate groups. Impedance measurements seem to indicate that these anionic sites, which may come from emulsifier residues, are not covalently bonded to the polymer matrix. Of course, the kind and concentration of impurities may greatly vary with the source of PVC and be very different with other polymers. PVC is not the only polymer suitable for sensor membranes. As pointed out very early by Fiedler and Ruzicka [18], apart from having the necessary solubility, for a polymer to serve as sensor matrix, the most important factor is that its glass transition temperature (Tg) must be below room temperature. With polymers of high Tg (e.g., high molecular weight PVC: Tg 80°C), plasticizers must be used, while

with those of low Tg e.g., soft polyurethanes with a low content of crystalline units [19] silicone rubber or poly(vinylidene chloride) [20], polysiloxanes [21] was used avoiding the handicap of plasticizer leaching but, at the same time also losing the possibility to modify ion selectivities by varying the plasticizer. A number of other polymers have also been investigated. Although the polymer has only a slight effect on the performance of ISEs, detailed investigations show that it is not just an inert matrix but that it may influence various membrane properties. For example, the polarity of a membrane differs significantly from that the plasticizer alone. Thus the widely used plasticizers DOS and o-NPOE exhibit dielectric constants of 4.2 and 21, respectively, whereas the values for the corresponding membrane phases with 33% PVC are 4.8 and 14.299. As to the extent of ion pair formation, it is much lower in a DOS-PVC membrane than in DOS alone.

1.6.6 Potentiometric Measurements Using Ion-selective Electrodes

Potentiometric measurements are made using a potentiometer to determine the difference in potential between a working electrode and a reference electrode (EMF measurement). In potentiometric measurements, two electrodes need to be used as the absolute potential of an individual half-cell cannot be determined. The two electrodes are:

- an ion-selective electrode with membrane
- an external reference electrode

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Figure 1.4 Schematic representation of a typical potentiometric cell Ion-selective electrodes (ISEs) are electrodes that respond selectively to the activity (not concentration) of a particular ion sensed by the selective membrane. The conventional ISE consists of a Teflon tube filled with inner filling solution. The electrical contact is made via internal reference electrode (usually Ag/AgCl). The external reference electrode should be stable and has a fixed potential such as a Ag/AgCl or saturated calomel electrode (Fig. 1.4). The electrochemical cell of the ISE measurement (Fig.1.5) can be represented as:

	externa	al ref. electrode	// test solution / mer	nbrane / inner solution	int. re	ef. electrode	
Ag AgCl KCl (sat'd) test solution membrane inner solution AgCl Ag							
	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	
	E_1	E_2	E _J	E _M	E_4	E_5	

Figure 1.5 Electrochemical Cell

The potential of a membrane is generated when both electrodes are in contact with the sample solution. The primary ion is transferred from the sample solution to the membrane phase and a potential difference is generated by selective ion exchange at both interfaces. The measurement is made at zero current condition. In this condition, the transfer of primary ion from the solution to the membrane is equal to the transfer of ions from the membrane to the solution. The measured voltage is a difference of potentials and not possible to measure the absolute potentials. The voltage across the whole cell is the sum of different potential generated at all solid-solid, solid-liquid and liquid-liquid interfaces.

$$EMF = E_1 + E_2 + E_3 + E_4 + E_J + E_M$$
(1.16)

In an ideal condition, potentials of E_1 through E_4 are constant. Therefore, the electromotive force (EMF) across the galvanic cell can be expressed as:

$$EMF = E_{constant} + E_J + E_M$$
(1.17)

 E_M is the membrane potential which includes the phase boundary potentials (EPB) at both aqueous sample|membrane interfaces and the diffusion potential within the membrane (ED). E_J is the liquid junction potential created at the porous frit, practically used instead of the salt bridge (||) for which $E_J = 0$. It is important to note that this liquid junction potential that prohibits the true assessment of single ion activities with ion-selective electrodes. E_J originates from a separation of charge created on the interface due to the different mobilities of ions migrating at different rates. For ions of similar mobility E_J can be very small and it can be neglected. For an ISE, the E_D is zero if no ion concentration gradients occur. Then, the EMF is only dependent on the variation of the phase boundary potential at sample solution|membrane interface (E_{PB}):

$$EMF = E_{constant} + E_{PB}$$
(1.18)

1.6.7 The response mechanism

The basic theory of the response of solvent polymeric membrane electrodes was developed many decades ago [22-24]. However, the relevance of the various contributions to the membrane potential has been the subject of long-lasting debates [25,26]. Ion-selective electrode membranes are typically investigated under zero-current conditions in a galvanic cell such as the following (see **Figure 1.6**):

Hg | *Hg*₂*Cl*₂ | *KCl*(*sat.*) | 3 *M KCl* || *sample solution* || *liquid membrane* || *internal filling solution* | *AgCl* | *Ag*

Figure 1.6 Galvanic Cell Representations

The electromotive force (EMF) across this cell is the sum of all contributing individual potentials. Many of these are sample-independent, and the measured emf can usually be described as

$$EMF = E_{const} + E_J + E_M$$
 (1.19)

where E_M is the membrane potential, and E_J is the liquid junction potential at the sample/bridge electrolyte interface, which can either be kept reasonably small and constant under well-defined conditions or be estimated according to the Henderson formalism. It is important to note that it is this liquid junction potential that prohibits the true assessment of single ion activities with ionselective electrodes; the role of the reference electrode on the overall emf measurement should, therefore, not be overlooked [27]

1.6.8 Phase Boundary Potential

Since the membrane is usually interposed between the sample and an inner reference electrolyte, it is common to divide the membrane potential (E_M) into

three separate potential contributions, namely the phase boundary potentials at both interfaces and the diffusion potential within the ion-selective membrane. The potential at the membrane/inner filling solution interface can usually be assumed to be independent of the sample. Recent experimental evidence shows that the diffusion potential is negligible in most cases of practical relevance [28]. For ion-selective electrodes, the membrane internal diffusion potential is zero if no ion concentration gradients occur. This is often the case for membranes that show a Nernstian response. Therefore, the membrane potential E_M is

$$E_{\rm M} = {\rm Const} + E_{\rm PB} \tag{1.19}$$

where E_{PB} is the phase boundary potential at the membrane-sample interface, which can be derived from basic thermodynamic considerations. First, the electrochemical potential, $\mu^*_{(aq)}$ is formulated for the aqueous phase:

$$\mu^{*}_{(aq)} = \mu_{(aq)} + zF\Phi_{(aq)} = \mu^{\circ}_{(aq)} + RT \ln a_{I(aq)} + zF\Phi_{(aq)}$$
 (1.20)

and for the contacting organic phase:

$$\mu^{*}_{(\text{org})} = \mu_{(\text{org})} + zF\Phi_{(\text{org})} = \mu^{\circ}_{(\text{org})} + RT \ln a_{I(\text{org})} + zF\Phi_{(\text{org})}(1.21)$$

where μ is the chemical potential (μ° under standard conditions), z is the valency and a_1 the activity of the un-complexed ion I, Φ is the electrical potential, and R, T and F are the universal gas constant, the absolute temperature and the Faraday constant respectively. It is now assumed that the interfacial ion transfer and complexation processes are relatively fast and that, therefore, equilibrium holds at the interface so that the electrochemical potentials for both phases are equal. This leads to a simple expression for the

phase boundary potential:

$$E_{PB} = \Delta \Phi = -(\mu^{\circ}(\text{org}) - \mu^{\circ}(\text{aq}) / zF) + (RT/zF) \ln a_1(\text{aq}) / a_1(\text{org}) \quad (1.22)$$

Often, the term comprising of the standard chemical potentials is combined to the symbol k_1 ; i.e., $(k_1 = \exp(\{\mu^0 (aq) - \mu^0 (org)\}/RT)$. Apparently, a simple function of the phase boundary potential on sample ion activities is expected if a_I (org) is not significantly altered by the sample. Under the condition that $a_I(org)$ remains unaltered, it can, together with all other sample-independent potential contributions, be included in one term (E₀) and eq. (8) reduces to the well-known **Nernst** equation:

$$E = Constant + (2.303RT/nF) log_{10}A$$
 (1.23)

According to eq. (9) it is evident that the composition of the surface layer of the membrane contacting the sample must be kept constant in order to obtain an exact Nernstian response of the electrode [29]. Only within the extremely thin charge separation layer at the very interface, where electro neutrality does not hold, are sample-dependent changes in the concentrations of complex and ionophore and ionic sites allowed to occur.

1.6.9 Selectivity

The selectivity is clearly one of the most important characteristics of an ion selective electrode, as it often determines whether a reliable measurement in the target sample is possible. A theoretically thorough selectivity description allows researchers to identify the key parameters for optimizing the performance of potentiometric sensors, e.g., by adjusting weighing parameters (i.e., absolute membrane concentrations) or choosing different plasticizers or matrices. Virtually all selectivity considerations were based in the past on the semi empirical **Nicolskii-Eisenman** equation (N-E equation).

$$E = Constant + \frac{RT}{Z_A F} \ln\{a_A + \sum_{B \neq A}^{B} K_{A,B}^{Pot} (a_B)^{ZA/ZB}\}$$
(1.24)

where, a_A and z_A are the activity and charge of primary ion respectively similarly, a_B and z_B are activity and charge of a interfering ion respectively. $K_A^{pot}{}_{,B}^{pot}{}_{,B}$ is the selective coefficient of ISE for primary ion over interfering ion. For extremely selective electrodes, the **Nicolskii** coefficient $K_{A,B}^{pot}{}_{,B}$ is negligibly small and the total activity term in the parentheses in the above equation approaches a_A . If interference is observed, a lower activity a_A of the mixed sample will give the same response as the activity a_A of the solution containing no interfering ions. This equation has a symmetrical form with respect to the primary and interfering ions and assumes the **Nernstian** electrode response not only to the primary but also to interfering ions.

1.7 Determination of Selectivity Coefficients. $K_{A,B}^{Pot}$

1.7.1 Classical Procedures

The IUPAC commission, in 1976, recommended the use of two different procedures to determine the **Nicolskii** coefficients of ISEs, namely the fixed interference method (FIM) and the separate solution method (SSM) [30].

1.7.1.1 Fixed interference method

The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with solutions of constant level of interference, a_B , and varying activity of the primary ion, a_A . The potential values obtained are plotted against the activity of the primary ion. The intersection of the

extrapolation of the linear portions of this curve will indicate the value of a_A which is to be used to calculate *K* from the equation:

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{Z_A/Z_B}}$$
(1.25)

where both z_A and z_B have the same signs, positive or negative.

1.7.1.2 Separate solution method

The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with each of two separate solutions, one containing the ion A at the activity a_A (but no B), the other containing the ion B at the same activity $a_B = a_A$ (but no A). If the measured values are E_1 and E_2 , respectively, the value may be calculated from the equation:

$$\log K_{A,B}^{Pot} = \frac{(Z_A F)(E_2 - E_1)}{2.303 RT} + (1 - (Z_A / Z_B) \log a_A)$$
(1.26)

This method is recommended only if the electrode exhibits a **Nernstian** response. It is less desirable because it does not represent the actual conditions under which the electrodes are used. It has been reported by many researchers that some discrepancies were found among selectivity coefficients determined under different conditions, e.g., with different activities of the primary and/or interfering ions and/or by different methods [31-36] also with ions of different charge [37]. This suggests that selectivity coefficient is not a physical constant but a value which changes according to experimental conditions.

1.7.1.3 A method independent of the N-E equation: Matched potential method

In this method, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion which gives the same potential change in a reference solution. To determine the selectivity coefficient, one would measure the change in potential as a function of the primary ion activity (concentration). The interfering ion would then be added to an identical reference solution until the same potential change is obtained. The change in potential must be produced in a constant initial background of the primary ion and must be the same in both cases (**Figure 1.7**). This method is totally independent of the N-E equation, accurate and reliable selectivity coefficients obtained even when ions of unequal charge are involved. This method, therefore, has a sound analytical basis to judge obtained values of $K_{A,B}^{Pot}$ to be realistic.



Figure 1.7 Determination of selectivity coefficients by matched potential method

1.7.2 Detection limit of ISE

Every ion-selective electrode has a lower and upper detection limit where the response starts to deviate significantly from a **Nernstian** electrode slope. Generally, they fall into activity ranges where the electrode starts to lose sensitivity towards the primary ion. According to the IUPAC recommendation

of 1976, the detection limit is defined by the intersection of the two extrapolated linear calibration curves (Figure 1.8). There are two main possible explanations for the apparent loss of Nernstian response slope at low primary ion activities, namely (a) the perturbation of the interfacial sample activity by the membrane and (b) interference by other competing ions in the sample. The most likely reason for the first effect is the constant release of a low amount of primary ions from the membrane into the sample, thereby inducing a local nonzero primary ion activity at the interface. Although the Nernst equation is still valid in this case, the ion activity at the interface is considerably higher than in the bulk, so the response of the electrode becomes insensitive to sample activity changes. The continuous release of small amounts of ions from ISE membranes has indeed been observed [38]. For cation-selective membranes (anion-selective electrodes can be treated in complete analogy), the upper detection limit is a consequence of a coextraction process of primary cation and interfering anions from the sample into the ion-selective membrane, thereby leading to a loss of membrane permselectivity (Donnan failure) [39].



Figure 1.8 Definition of the upper and lower detection limits of an ion-selective electrode according to the IUPAC recommendations

1.7.3 Measurement range

The measurement range of ISEs is defined as the activity ratio of upper and lower detection limit and approximately corresponds to the range where the electrode responds according to the **Nernst** equation. The semi-quantitative relationships have been established to estimate the maximum possible measurement range of carrier-based ion-selective electrodes.

1.7.4 Response Time

The time which elapses between the instant when an ion-selective electrode and a reference electrode (ISE cell) are brought into contact with a sample solution (or at which the activity of the ion of interest in a solution is changed) and the first instant at which the emf/time slope (\mathbf{E} / \mathbf{t}) becomes equal to a limiting value selected on the basis of the experimental conditions and/or requirements concerning the accuracy is referred to as response time [40].

1.7.5 Issues related to practical application of ISE

1.7.5.1 Reference electrode

In all ion selective electrode measurements, potential has to be measured with respect to reference electrode. There are several reference electrodes but for practical convenience only Ag/AgCl reference electrode or calomel electrode is employed in ISE measurements. Brief discussion about details of functioning of these electrodes is given below.

1.7.5.1.1 Ag/AgCl reference electrode: A silver wire covered with a layer of silver chloride responds to the chloride activity of the contiguous solution according to

$$\Delta E = \Delta E^{\circ} - \frac{2.303 \ RT}{F} \log a_{Cl} -$$
(1.27)

If the sample solution has a constant chloride ion activity, then this silver wire can be dipped directly into the test solution to construct a cell without liquid junction. But in all other practical cases, an approximately 0.1 to 3 M KCl solution is inserted between the internal Ag/AgCl and the sample solution by means a salt bridge. Since solubility of AgCl in concentrated KCl solution is considerably high (10^{-2} mol/L) , the KCl solution used should be saturated with AgCl by adding enough AgCl. Due to relatively large solubility of AgCl in 3M KCl solution, Ag⁺ ion passes through the salt bridge diaphragm into a sample solution along with K⁺ and Cl⁻ ions. Thus this electrode should not be employed directly for the determination Ag⁺, K⁺ and Cl⁻ ions. Also, Ag⁺ reacts with various ions like Br⁻, I⁻, S²⁻ etc., to form insoluble salts. These insoluble precipitates deposit in canals of the diaphragm and block the necessary electrolytic contact between the test solution and the reference electrode solution. The best way of avoid these problems is to use an Ag/AgCl reference electrode in conjunction with a double salt bridge. Any inert electrolyte with about the same transport number for cation and anion which does not interfere with the indicator electrode or react with ions present in the sample solution can be chosen as a second outer salt bridge electrolyte (for example KNO₃, (NH₄)₂SO₄, CH₃COOLi etc.,).

1.7.5.1.2 Calomel Electrode: Calomel electrode comprises a non-attackable element, such as platinum in contact with mercury, mercurous chloride (calomel) and a neutral solution of KCl of known concentration and saturated with calomel. The electrode potential represented as

$$\Delta E = \Delta E^{\circ} - \frac{2.303 \, RT}{2F} \log a_{Cl} -$$
(1.28)

The calomel electrode containing saturated KCl solution is commonly used because it is easy to prepare and maintain. However, it is temperature sensitive; electrode potential varies due to Cl⁻ activity change in solution. For accurate measurements, 0.1 M KCl solution is used as inner filling solution.

1.7.6 Activity coefficient

As ISE gives the response for activity of an ion, it is very important to calculate the activity of an ion in solution where the response was measured. The activity or effective concentration of ion X depends on the ionic strength of the medium and it is defined as

$$\mathbf{a}_{\mathbf{x}} = [\mathbf{X}] \boldsymbol{\gamma}_{\mathbf{x}} \tag{1.29}$$

where a_x is the activity of an ion X, [X] is its molar concentration and γ_X is a dimensionless quantity called the activity coefficient. The activity coefficient

and thus activity of ion vary with ionic strength of the solution. In 1923, P. Debey and E.Huckel [41] used the ionic atmosphere model, to derive an equation that permits the calculation of activity coefficient of ions from their charge and their average size [42]. This equation know as the **Debey-Huckel equation**.

$$-\log \gamma_X = -\frac{0.51 Z_X^2 \sqrt{\mu}}{1+3.3 a_X \sqrt{\mu}}$$
(1.30)

where γ_X is activity coefficient of the ion, Z_X is the charge on the ion, μ is ionic strength of the solution and a_X is the diameter of the hydrated ion X in nanometers.

Unfortunately, considerable uncertainty exists regarding the magnitude of a_x for various ions. The above equation modified [17] which can be used to calculate activity coefficient of any ion

$$-\log \gamma_X = 0.51 Z_X^2 \left[\frac{\sqrt{\mu}}{(1+1.5\sqrt{\mu})} - 0.2 \mu \right]$$
 (1.31)

where μ is the ionic strength of the solution and z_x is the valency of ion.

1.7.7 Liquid junction potentials

A liquid junction potential develops across the boundary between two electrolyte solutions that have different compositions. Liquid junction potential cannot be eliminated and only could be minimized and kept constant under well defined conditions. The magnitude of the liquid junction potential can be minimized by placing a salt bridge between the two solutions. The salt bridge is more effective if the mobilities of the negative and positive ions in the bridge are nearly equal and if their concentrations are large. It is important to note that it is this liquid junction potential that precludes the true assessment of single ion activities with ion-selective electrodes. For practical purposes, liquid junction potentials calculated employing **Henderson formalism** [44,45].

$$E_{j,k}^{H} = -\frac{RT}{F} \left[\frac{\sum \frac{C_{i,k}\lambda_{i}^{\infty}}{Z_{i}} - \sum_{i} \frac{C_{i,r}\lambda_{i}^{\infty}}{Z_{i}}}{\sum_{i} C_{i,k}\lambda_{i}^{\infty} - \sum_{i} C_{i,r}\lambda_{i}^{\infty}} \right] \ln \frac{\sum_{i} C_{i,k}\lambda_{i}^{\infty}}{\sum_{i} C_{i,r}\lambda_{i}^{\infty}}$$
(1.32)

where C_i is the concentration of ions in equivalents per dm³, λ_i^{∞} is the limiting equivalent ionic conductance at infinite dilution. The values of the limiting equivalent conductance taken from literature and they are given in Table1.1.

Table 1.1 Equivalent conductivities of ions for infinite dilution at 25 °C

Cation	Cation Equivalent Anion		Equivalent conductance	
H^+	349.81	OH	-198.6	
Li ⁺	38.68	F	-55.4	
Na ⁺	50.10	Cl	-76.35	
\mathbf{K}^+	73.50	Br	-78.14	
Rb ⁺	77.81	I	-76.84	
Cs ⁺	77.26	NO ₃	-71.46	
$\mathrm{NH_4}^+$	73.55	HCO ₃	-44.50	
Mg^{+2}	53.05	CH ₃ COO ⁻	-40.90	
Ca ⁺²	59.50	SO4	-80.02	
Sr ⁺²	59.45	CO ₃ ²⁻	-69.3	
Ba^+	63.63	Formate	-54.59	

1.8 Recent Advancements in the field of Ion Selective Electrodes

Potentiometric sensors employ ionophore agents like crown compounds and calixarenes and they are usually applied to ion monitoring. Molecular imprinting techniques has enabled a larger range of molecules to be screened, *e.g.*, pesticides, drugs, antibiotics, *etc. although* much work is still needed to implement ISEs into general practice for the analysis of the latter. The field of potentiometric sensors has gone through a revolution in the last ten years with a major effort focused in the theoretical developments which has led not only to a deeper understanding of these devices, but significantly in dramatic improvements in the detection limits, which has opened up new opportunities in environmental monitoring. For instance, reference highlights the importance of the diffusion potential and its variation from sample-to-sample and over time. Theoretical models offer tools to tackle and predict the latter aspect which would be extremely beneficial for engineering more robust ISEs.

Solid-Contact Ion-Selective Electrodes (SC-ISEs) are more convenient for remote monitoring than liquid filled ISEs as they are compatible with microfabrication technologies and they are easier to miniaturize. In a SC-ISE, the internal reference electrode and the inner filling solution are replaced by a solid material which should be nonpolarizable upon the input current of the measuring amplifier and have suitable redox and ion-exchange properties.

Despite these advantages, it should be noted that the control of the ion fluxes across the SC-ISEs membrane cannot be established in the same way as in inner liquid filling ISE. For instance, incorporation of a complexing agent into the SC layer, conditioning steps, increasing polymer content or using different polymeric membranes may help in achieving this control. Conducting

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Polymers (CPs) have received particular attention as solid contact despite unresolved issues around the effects of the polymer chemical/redox layer properties on the sensor's analytical performance. Conducting polymer based SC-ISEs have produced significant results for the detection of lead at concentrations comparable with the current legislation requirements.

For example, significant results in the detection of lead have been achieved in Diamond's group. Employing screen printed electrodes as substrates for poly(3,4-ethylenedioxythiophene) SC-ISEs, and coupling the latter electrodes to solid state reference electrodes (SC-REs) lead concentrations down to ppb levels in real samples were detected when standard addition methodology was employed. These results are significant because obtained with real samples and the good correlation shown with the ICP-MS method. Researchers from the same group showed that the calibration trends of these sensors are significantly distorted upon exposure with environmental samples. This finding may indicate that sensors can be used only in combination with the standard addition method to compensate for the matrix effect although the latter may give rise to anomalous super Nernstian responses. It was also shown that Electrochemical Impedance Spectroscopy (EIS) may represent a powerful self-diagnostics for remotely deployed chemical sensors in order to decide when sensor calibration is needed.

Poly(3-octylthiophene) (POT) has been used as solid contact because of its hydrophobicity to improve membrane adhesion and limit water uptake particularly in combination with polyacrylate membranes which improved the limit of detection (LOD) in several cases by reducing ion diffusivities. Formation of a water layer at the POT/electrode interface does not occurs

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while the incorporation of water (in form of nanodroplets) occurs within the membrane but at a slower rate than ISEs based on PVC membranes requiring ~ 450 hours to reach equilibration. Therefore, it has been suggested that silicone membranes may represent a significant option to polyacrylate ones although poor solubility of ionophores and high bulk impedance are the main drawbacks.

While effects of layer deposition, *e.g.*, dropcast *vs.* electrodeposition, oxidation state of CP, ion content, have been analyzed at some extent nanostructured conducting polymers in the solid contact has not been extensively investigated and it may represent an interesting research line. For instance, Lindfors *et al.* used polyaniline (PANI) nanoparticles as solid contact in combination with a silicone membrane for the detection of silver showing enhanced selectivity than ones reported for PVC and polyacrylate membranes. Kisiel used polypyrrole microcapsules as solid contact of Ca-ISEs showing that the control of the electrolyte composition of the microcapsules can tune the LOD. It should be also noted that the type of CP used as solid contact may be important in relation to the ion analyte. For instance, a comparison of PANI and PEDOT commercial dispersions in SC-ISEs highlights the importance of the CP redox state during the analysis for silver but not for lead.

Chemical and photochemical sensitivity of CPs has motivated investigations of other materials as solid contact. Single-walled carbon nanotubes (SWCNT) thanks to their hydrophobicity and lack of redox capacity appear promising. However, Pb-ISEs based on SWCNT dispersed in poly(ethylene-*co*-acrylic acid) showed only slightly submicromolar LOD and no report on real water sample was presented. Single-piece solid contact ISEs with polymer-Multi-

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Walled Carbon Nanotubes (MWCNTs) applied for the detection of sodium, copper, potassium and calcium did not show submicromolar detection limits. Ordered macroporous carbon solid contact on the other hand allowed the preparation of ISEs for the monitoring of potassium and silver with LOD of 1.6×10^{-7} M and 4.0×10^{-11} M respectively. Considering that potassium is an important electrolyte in sweat and that silver concentration above 0.17 µg L⁻¹ are considered toxic to fish these results could be significant for wearable and environmental applications, respectively. Finally, very recently potentiometric strip cells were produced on screen printed substrates and applied to test potassium in saliva samples although diluted with buffer (to equalize ionic strength and pH). These strips contained SWCNT-based SC-ISEs and SC-REs, employed polyacrylate membranes and they were plugged into a 2-way edge connector. The values of potassium were determined using a calibration plot generated with the measurement of 5 standard solutions and validated with AAS showing no statistical difference.

Ionic liquids (IL) were also applied to ISEs replacing ionic additives, ionophores, plasticizers in the membrane phase [90] and, perhaps more significantly, they were used as solid contact (after gellation in PVC membrane) providing double layer capacitance to stabilize sensor response. The latter sensors could detect 40 ppm of lead in spiked tap, river and waste water using standard addition method in good correlation with the data obtained from anodic stripping voltammetry. Graphite modified with hydroquinone was used as solid contact in ISEs and the ratio of the surface confined redox species (= a_{ox}/a_{red}) was tuned to 1 to improve the stability of the potential of the solid contact.

Among the limits fixed by the Water Framework Directive for four heavy metals, *i.e.*, lead, cadmium, mercury and nickel, it appears that research on ISEs has been largely focused on lead at the required nano-molar level and potentiometric detection at these levels for other important toxic ions, *e.g.*, manganese and arsenate, has so far not been reported or it is below the environmental policy requirements, *e.g.*, Cr(VI). In this regard it is worthwhile to note that the measurement of cadmium at 1 ppb levels, *i.e.*, compatible with some water regulation policies, in concentrated NaCl samples (simulating sea water) with ISE was reported. A pre-concentration step at a bismuth-coated electrode and subsequent release in a different media allowed this measurement, however, these sensors were not tested in real sea water samples.

In spite of extensive research in the area, it seems that obtaining SC-ISEs with reproducible standard potentials is still a great challenge and it should be noted that most of the ISEs designs described above rely yet on the use of standard macroelectrodes. In this regard, encouraging results employing screen printed electrodes have been recently obtained. For instance, Saltisza *et al.* prepared Pb-ISEs which show superimposing calibration curves down to 10 nM ranges. In addition, Musa *et al.* prepared a solid state ISE for pH using screen printing technology and a photo-polymerizable ion selective membrane deposited directly on the carbon surface but their performances upon exposition to real samples was not investigated.

1.8.1 The Miniaturization of ISEs

Ultra-Microelectrodes (UMEs) have received enormous interest thanks to several favorable characteristics, *e.g.*, compatibility with small sample,

reduced amount of material used per device, and the great demand for miniaturized sensors and their use was also applied to potentiometry measurements. For example, potentiometric ion selective microelectrodes for pH and silver have been reported but are based on glass pipette microelectrodes which limit their applicability as environmental and wearable sensors due to the cost and fragility. It should be also noted that the miniaturization of the ISEs may cause lower potential stability because of the smaller redox or double-layer capacitances, the leakage of membrane components, the adherence and the exfoliation of membranes and overall, a trade-off in decreasing the size of the electrode may exist.

Despite the benefits of microelectrodes and microelectrodes arrays, their manufacture is still complex and the long term-stability sometimes problematic. To date, convincing designs of low-cost ion-selective microelectrodes which can be easily mass-produced and are applicable to environmental monitoring and wearable applications seem to be missing. Finally, multi-calibration in an array becomes complicated and time consuming as the array response pattern becomes important and, as each electrode drifts, the pattern is unstable in use. In conclusion there is still much work to do in order to develop low cost and reliable potentiometric micro- and microarray sensors for untreated samples.

The recent efforts in the field of ion selective electrodes were concentrated on the fundamental understanding of the membrane processes involved, the development of newer applications of available electrode systems as well as the design of new ion sensors.

In the last few years, the development of new ion selective electrodes was

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mainly directed towards special electrodes (gas sensing electrodes enzyme substrate electrodes) as well as liquid membrane electrodes.

Liquid membrane sensors offer a wide range of accessible ion selectivity. In these electrodes, mobile ion selective sites (e.g. an ion selective ligand dissolved in an appropriate solvent) are interposed between the sample solution and a reference system for a microelectrode and a more conventional ion electrode. By incorporating the mobile sites into solvent impregnated PVC, systems of high electro-motive and mechanical stability with electrode lifetimes of more than one year may be obtained. Since a miniaturization of liquid membrane electrodes is easily realized and since such tools are attractive for bio-medical applications, efforts were directed towards the design of ion selective ligands for alkali and alkaline earth metal cations [206-246].

1.9.2 Coated Wire Ion Selective Electrode

Polymeric membrane based ion-selective electrodes (ISEs) have been very extensively studied over many years, and ISEs for more than 60 analytes have been described so far. In the last decade, the field has undergone a renaissance and the performance of ISEs has dramatically improved in terms of selectivity and detection limit. These improvements have fuelled renewed interest in pursuing application fields that were previously considered unreachable e.g. environmental analysis. For example, Pb²⁺-selective electrodes have been successfully used for the determination of lead and lead speciation in Zurich drinking water. More recently, Cs⁺-selective electrodes were applied in the determination of caesium in natural waters, while bio-uptake studies were successfully carried out with Pb²⁺- and Cd²⁺-selective electrode. The

miniaturization of ISEs, while simultaneously preserving their selectivity and sensitivity, is a crucial step in the next phase of ISE evolution. Traditionally, in so-called coated-wire ISEs, the ion-selective membrane is placed directly on a solid electronically conductive support, thereby removing the need for an inner solution. The need to measure analytes in smaller sample volumes has driven research efforts in two different directions. The coated wire electrode (CWE) uses components of conventional ISEs except that no internal aqueous filling solution is used. Instead, a conductor is directly coated with an ionresponsive membrane (usually PVC based). This conductor can be metallic or graphite-based and be of any convenient geometric shape (i.e., wire, disk, cylinder, thin film, etc.). It was also proved that it is possible to fabricate sensors by directly contacting the membrane with a wire (so called coatedwire electrodes) to form an ohmic contact. Such systems are found to exhibit complex behaviour (time and temperature dependences), requiring frequent recalibration, but they are extremely simple to construct. An example is a silverselective electrode, that has been designed by attaching a wire to the back of graphite/PTFE disc, on the front side of which the silver halide is rubbed in to the surface. Another exemplary coated-wire electrode was prepared by simply coating a wire with a membrane film of PVC containing an ion-exchanger. However, in these devices, it was observed that the long term potential stability was quite limited, and they were useful only in specific applications such as capillary electrophoresis or in flow-injection analysis. The development of coated wire electrodes has recently been reviewed and includes information on multisensor probes that can be used in seawater analysis. A more extensive review covers coated wire electrodes and the

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technology of polymer-coated as well as solid contact devices that make up this ever expanding field. Copper-selective wire electrodes can be prepared by treating bare copper wire with either gaseous or aqueous-based hydrogen sulfide. Sodium and potassium levels were measured in human urine and serum simultaneously by using a pair of coated wire electrodes that utilized crown ethers as the selective agents. An aluminum wire electrode that is coated with PVC plasticized with 2-nitrophenyl alkyl ether was used for the potentiometric titration of singly charged anthraquinone dyes. Beside metallic conductors, graphite has been used with good success for making coated-type electrode devices. Graphite rods and powders have been formed into electrodes that are coated with chemically modified polymer films. Instead of using PVC as the polymer, several different polymers and modified polymers were tested. Poly(acrylic acid), and modified poly(vinylbenzyl chloride) containing substituted amines were used to form both cation- and anionresponsive electrodes. The potentiometric response and studies of similar polymer-film, chemically modified graphite electrodes have been published. Interest in these and other forms of coated-type electrodes has caught the attention of industrial firms as the number of patents rise ISEs are attractive for routine monitoring of water samples since they are cost-effective and miniaturizable devices that have very low power demand and can provide unique information on the speciation of analytes. The development of coated wire ion-selective electrodes (CW-ISEs) is in line with current trends in analytical chemistry towards micro fabrication and mass production of durable chemical sensors. This integrates CW-ISE and the evaluation of the practical applicability in nuclear materials. Ion-selective electrodes prepared by coating

polymer films containing electroactive species have been incorporated on a metallic substrate and have proven to be effective for a wide variety of inorganic and organic anions and cations.

In this thesis, the elements viz., determination of lithium, uranium and gallium are discussed. Though there are several methods based on sophisticated instruments available for their determination, electroanalytical techniques such as use of either ion selective electrodes or coated wire ion selective electrodes finds exclusive role for their determination as these methods are very simple, precise, does not require expensive instruments, require no extra reagents and cost effective measurement. In addition, these ion selective electrodes can be fabricated indigenously as and when required. The accuracy of this method using ion selective electrode is found to be better than 2%. Since last three decades there is a tremendous improvement in the application of ion selective electrodes for the determination of various elements. Coated wire ion selective electrode. The characteristic studies of these coated wire ion selective electrode were explained in chapter 3, 4 and 5.

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

A modified methodology was developed for the determination of lithium based on the precipitation of Li by adding a known excess of NH_4F solution, followed by determining excess fluoride using ISE. The method was then adopted for the determination of lithium in the various process streams generated during Li₂TiO₃ preparation where significant amount of organic constituents are present along with lithium. The method is simple and rapid and an accuracy of about 0.5% can be achieved for the determination of Li in the range of 1 to 3 mg in the organic matrix.

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

Coated wire lithium ion selective electrode was fabricated using lithium ionophore-VI, 2-nitrophenyl octyl ether (NPOE) and potassium tetrakis(p-chlorophenyl)borate (KTpClPB) on platinum wire. Lithium ion selective lectrode was giving Nernstian response from 10⁻¹M to 10⁻⁴M with a detection limit of 3×10^{-5} M. The calibration slope of this lithium ion selective electrode was found to be 58.5 ± 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 in complex chemical matrix containing hexamethylene tetramine, formaldehyde, urea and ammonium nitrate etc. which are the wash streams generated during the sol–gel process employed for preparation of Li₂TiO₃ microspheres.

1.8.5 Determination of uranium using coated graphite uranium ion selective electrode

A coated graphite uranyl ion selective electrode was developed by depositing a membrane comprising Aliquat – 336 loaded with uranyl tetrachloride dianion $(UO_2Cl_4^{2-})$ and poly vinyl chloride (PVC) on graphite rod. 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

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Nernstian response over uranyl concentration range from 1×10^{-4} M to 1×10^{-1} M with a detection limit of 5×10^{-5} M in constant 6M chloride concentration. The calibration slope of this ion selective electrode was found to be -29.2 ± 1.0 mV. The selectivity coefficients of this electrode with respect to the different metal ions were determined by matched potential method. The electrode was employed for determining Uranium in presence of Thorium (Th to U amount ratio=25), which gives a promising application to the simple approach for the (Th,U)O₂ based nuclear fuel. This coated uranyl ion selective electrode can be used for consecutive four months without losing Nernstian response.

1.8.6 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 GaCl₄ 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 1×10^{-4} M- 1×10^{-1} M of Ga(III) ions in constant chloride concentration of 6M with a detection limit of 2×10^{-5} M calibration slope of -58.2 mV \pm 1.0 mV/decade change in concentration of Ga. Interference of Li⁺, Na⁺, K⁺, Ca²⁺, 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.

CHAPTER - 2

Determination of lithium by titrimetry using fluoride ion selective electrode employing potentiometric end point detection

2.1 Introduction

Determination of elemental concentrations is of great importance in various fields of nuclear science and technology. These data are required for chemical quality assurance of various ingredients used in the processing of industrial materials. Elemental determination is also of interest in nuclear industry as a part of the chemical quality assurance of nuclear fuels, for obtaining their fissile content. In this chapter, a method has been developed for the determination of lithium in organic impurities which was the wash solution resultant from the preparation of Li₂TiO₃ microspheres by internal sol-gel route. Before proceeding to the development of method for the determination of Lithium in organic impurities, a brief description about the International Thermonuclear Experimental Reactor (ITER) and the necessity for the preparation of Li₂TiO₃ microspheres and its characteristics are discussed below.

2.2 International Thermonuclear Experimental Reactor (ITER)

ITER is an international nuclear fusion research and engineering project, which is currently building the world's largest experimental Tokamak nuclear fusion reactor adjacent to the Cadarache facility in the south of France. The ITER project aims to make the long-awaited transition from experimental studies of plasma physics to full-scale electricity-producing fusion power plants. ITER is a step towards future production of electricity from fusion energy. ITER will produce at least ten times more energy than the energy required to operate it. In future demo or commercial reactors based on fusion, this energy can be converted to electricity. The ITER partners are presently the People's Republic of China, the European Union, India, Japan,

the Republic of Korea, the Russian Federation and the United States of America.

The main fusion reaction is:

$$D + T \rightarrow (^{4}He + 3.52 \text{ Mev}) + (n + 14.1 \text{ Mev})$$
 (2.1)

In a fusion reactor, insitu production of tritium is carried out by exploiting the following reaction:

Lithium-6 isotope in farious forms are used for this purpose. One way is to use Li-6 in the blanket of a thermonuclear reactor by exploiting the fast neutrons (n) generated from the D-T fusion (Eq. 2.1).

Since the products of reaction given in Eq. 2.2 will release total energy of 4.8 MeV inside the blanket, the engineering of the second step (Eq. 2.2) must provide removal and recovery of tritium needed for (Eq. 2.1) and of the heat which is an important fraction (21.4%) of the overall process. One of the research lines to make this process (Eq. 2.2) feasible for the Fusion Reactor is based on blanket engineering concepts using Li-ceramics in a way similar to that developed for the fission reactor power plants using U-Pu oxide ceramics as fuels [46].

Lithium based oxide ceramics such as Li₂TiO₃, Li₂ZrO₃ and Li₄SiO₄ have been proposed as tritium breeding materials for fusion reactor blankets [47-50]. Among them, lithium titanate (Li₂TiO₃) shows the best chemical stability in air and the most excellent tritium release characteristics at lower temperature. Moreover, it displays acceptable mechanical strength and low activation [51-54]. For the preparation of lithium-containing ceramic powders, several synthetic techniques including solid state reaction, co-precipitation, solution combustion process and sol-gel process are available [55-56]. In Bhabha Atomic Research Centre (BARC), Sol-Gel is one of the well studied processes for the preparation of gel microspheres of UO₂, ThO₂, (U, Pu)O₂, (Th, U) O_2 etc. [57]. Sol-Gel process was hence developed for the preparation of Li containing ceramic materials of required size and characteristics [58]. In the Sol-Gel process, the Gel particle is actually made of Ti - hydroxide network in which Li ion is trapped. Sol-Gel process is promising for obtaining ceramic nuclear fuel materials such as UO₂ as well as non-nuclear materials in the form of microspheres (pebbles). In recent years, Li based ceramics such as Li_2O , $LiAIO_2$, Li_2ZrO_3 , Li_2TiO_3 and Li_4SiO_4 have received considerable importance as tritium breeders in Test Blanket Modules (TBMs) for fusion reactors. Li₂O is promising for obtaining suitable tritium breeding ratio (TBR) but not used because of its high sensitivity towards moisture. Recently, Limeta-titanate (Li₂TiO₃) 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 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. The concentration of Li ion needs to be optimum (1.65 M) in the Gel so that the ultimate product is stoichiometric Li₂TiO₃. The Gel particle once produced is washed with ⁶Li containing organic solution to remove unreacted and unused materials, while maintaining Li/Ti stoichiometry in Gel. The number of washings required need be standardized so that the Li concentration in Gel does not deviate from the expected value. The washed solutions which contain enriched Li⁶ also needed be analyzed for Li content

prior to the recovery process.

The process required a simple and robust technique, which is capable of Li determination to standardize the various steps of the sol-gel process. Determination of inorganic constituents in an organic matrix (HMTA, urea, etc.) by the conventionally used techniques such as ICPMS, ICP-OES, TXRF etc. requires removal of organics. Whenever the organic components are difficult to remove by conventional methods such as evaporation, combustion methods are employed which can lead to loss of volatile inorganic components like Li, which is unacceptable in the sol-gel process. Moreover, the mixture containing HMTA and NH_4NO_3 becomes explosive upon heating [59]. Among the other methods, acid – base titration or flame photometer [60] method can be used, but is not suitable as a fast approach and solution also needs be diluted to ppm level. It was, therefore, considered worthwhile to investigate the possibility of employing simple titrimetry using fluoride ion selective electrode for the determination of Li. A simple and fast technique would be desirable for the determination of Li to standardizing the various steps in the sol-gel process. Conventional analytical methods such as ICP-AES, AAS etc. cannot be employed directly in an organic matrix containing HMTA, urea, etc. 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. An acid-base titration method after separation of Li using cation exchange separation is also possible, but is not suitable as a fast approach. It was, therefore, considered worthwhile to investigate the possibility of employing potentiometric titration for the determination of Li. Recently, a

simple methodology was reported for the stoichiometric analysis of lithium carbonate, a raw material for the solid-state synthesis of lithium metazirconate (Li₂ZrO₃). The reported methodology consisted of decomposition of the Li₂CO₃ sample in hydrochloric acid, drying and dissolving in ethanol. Li was determined by titrating with ammonium fluoride in water–ethanol (1+1). The results were compared with those obtained from titration with 0.1 M NaOH after cation exchange separation of Li and a precision of 0.3–0.4% was reported. There is a great interest in International Thermonuclear Experimental Reactor (ITER) which uses lithium compounds for tritium breeding. Among the probable candidates like Li₂O, LiAlO₂, Li₂ZrO₃ and Li₄SiO₄, Li₂TiO₃ is attractive from the view point of tritium recovery at low temperature and chemical stability.

2.3 Preparation of lithium titanate microspheres

The lithium titanate microspheres (**Figure 2.1**) were obtained by the internal gelation process. Natural Lithium nitrate and titanium chloride solutions were mixed with 3M solution containing a mixture of HMTA/Urea at 0°C to obtain feed solution. This feed solution was then dispersed as droplets through a stainless steel capillary of 0.8 to 1.0 mm internal diameter into a glass column in which hot silicone oil pre-heated to 90°C was circulated. These droplets get hardened (gelled microspheres) as they travel down the column. The gelled microspheres were separated from oil, washed initially with CCl₄ (4 to 5 times), to remove the adhering silicone oil, dried and then digested in 1.55M LiOH at 60° C in an air oven for 16 to 18 hours. Washing with 1.55M LiOH was done 6 to 7 times to remove the reaction products and unused chemicals from the microspheres to prevent their cracking during sintering of the

microspheres. The microspheres were then dried at 100°C. In order to study the pickup/leaching of Li from the microspheres during the washing, LiOH used for washing was prepared from depleted ⁶Li.



Figure 2.1 Sol-gel process flow-sheet for Li₂TiO₃ microspheres preparation

2.4 Determination of Lithium by Potentiometry using Fluoride Ion Selective Electrode

A potentiometric method was developed for the determination of Lithium in ethanol medium using ammonium fluoride as titrant and fluoride ion selective electrode for end point detection. 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 chemical mixture containing hexamethylenetetramine (HMTA), formaldehyde and ammonium nitrate, which are the wash streams generated in the sol-gel process employed for preparation of LiTiO₂ microspheres. The concentration data profile agreed with the isotopic profile obtained by Thermal Ionization Mass Spectrometry. Determination of elemental concentrations is of great importance in various fields of science and technology. These data are required for chemical quality assurance of various ingredients used in the processing of industrial materials. Elemental determination is also of interest in nuclear industry as a part of the chemical quality assurance of nuclear fuels, for obtaining their fissile content. A simple and fast technique would be desirable for the determination of Li to standardizing the various steps in the sol-gel process. Conventional analytical methods such as ICP-AES, AAS etc. cannot be employed directly in an organic matrix containing HMTA, urea, etc. 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. An acid – base

titration method after separation of Li using cation exchange separation is also

possible, but is not suitable as a fast approach. It was, therefore, considered worthwhile to investigate the possibility of employing potentiometric titration for the determination of Li.

Recently, a simple methodology was reported for the stoichiometric analysis of lithium carbonate, a raw material for the solid-state synthesis of lithium metazirconate (Li_2ZrO_3). The reported methodology consisted of decomposition of the Li_2CO_3 sample in hydrochloric acid, drying and dissolving in ethanol. Li was determined by titrating with ammonium fluoride in water–ethanol (1 + 1). The results were compared with those obtained from titration with 0.1 M NaOH after cation exchange separation of Li and a precision of 0.3–0.4% was reported.

2.4.1 Experimental

In the present work, a modified methodology was developed for the determination of lithium. In this work, the determination of lithium is based on the precipitation of Li by adding a known excess of NH_4F solution, followed by determining excess fluoride using ISE. The method was then adopted for the determination of lithium in the various process streams generated during Li_2TiO_3 preparation where in addition to Li, significant amount of organic constituents are present. The Li concentration data in the wash streams was then compared with isotope profile obtained by Thermal ionization mass spectrometry (TIMS). The method is simple and rapid and an accuracy of about 0.5 % can be achieved for the determination of Li in the range of 1 to 3 mg in the organic matrix.

2.4.1.1 Instrument / Reagents Required

A combination fluoride ion selective electrode (M/s. Orion) and an Orion 5-Star ion analyzer were employed to measure the potential developed during the titration. A magnetic stirrer was employed throughout the experiment for continuous stirring of the electrolytic solution during analysis. 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 Li were prepared in an aqueous solution of 0.5 M NH₄OH containing the different organic constituents, namely HMTA (0.75 M) and urea (0.75 M). 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 Li by this method. All the chemicals used were of A.R. grade.

2.4.1.2 Potentiometric Titration of Li⁺ Vs. NH₄F using F⁻ ISE

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 was precipitated using 0.5M NH₄F solution and the end point was detected from the variation in EMF measured Vs volume of 0.5 M NH₄F. F⁻ ion selective electrode was used to detect the free F⁻. Titrations were also performed for the 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) [61,62], in this work, we found that it is sufficient to mix the titrant in pure water.

2.5 Determination of ⁶Li/⁷Li atom ratio by thermal ionization mass spectrometry (TIMS)

The atom ratios of Li in different wash samples were determined using a Finnigan MAT 261 (Bremen, Germany) Thermal Ionization Mass Spectrometer with multiple Faraday cup detectors employing $Li_2BO_2^+$ ions for analysis [61] since simultaneous multicollection using Li⁺ ions was not possible due to the large relative mass difference in the two isotopes of Li (16%). The sample solution was first mixed with high purity boric acid (NIST-SRM-951) so as to obtain a mole ratio around 2 for B/Li. The solution was then loaded on to the single filament assembly of high purity rhenium filament. The solution was slowly dried at a heating current of 1.5A for 5 minutes. The filament current was then increased to 2A and maintained for 10 minutes to convert the loaded mixture into Li compound which gives high intensity of $Li_2BO_2^+$ ions during TIMS analysis [63]. The intensity of the ions corresponding to m/z 56 and 57 were measured by employing static made of multicollection. In order to ascertain that there is no interference in the determination of lithium due to the presence of organic constituents, potentiometric titrations were carried out using the two solutions of known Li concentration (as LiNO₃), one aqueous and the other containing the organics (0.75 M HMTA and 0.75 M urea). It was found that the concentration of Li in the two samples matched within 0.5% of the expected values which proved the absence of any significant interference.

2.6 Results and Discussion

Table 2.1 shows the data on the determination of lithium in synthetic mixtures containing organic components (HMTA, urea). It can be seen that the results agree well with those of the expected values in the synthetic samples. The

precision of the method was also ascertained by repetitive determination of Li in one of the samples and was found to be better than 0.5%. The above method was then employed for determining the lithium concentrations in the wash solutions of the sol-gel process of Li₂TiO₃. As explained earlier, the washing of the microspheres was done using LiOH, the pH of the titration medium varied significantly during the analysis of these samples. We also observed that the Li hydroxide wash solutions containing HMTA were in the pH working range of the fluoride ISE (namely 5 to 7), while those samples without HMTA, the pH was above 11. Since the pH range of the F⁻ ISE's is limited (pH 5 to 7), it was not possible to employ the same approach for all the wash solutions. In order to analyze all samples within the pH range of the fluoride electrode, two methodologies were investigated, (i) adjusting the pH using known volume of 0.5 M HNO₃ and (ii) employing a titrant solution containing the buffer solution (TISAB III supplied by M/s. Orion for the F-ISE's). The response of the electrode was sluggish when the ionic strength adjuster was used, which resulted in identification of the end point of titration difficult. So for the wash solutions with pH higher than 11, the pH adjustment was carried out using known amounts of 0.5 M HNO₃.

Table 2.1

Determination of lithium from solutions of synthetic mixtures (containing 0.75 M HMTA + 0.75 M Urea) using fluoride ion selective electrode (ISE) (Solution with 1.4 M Li was taken as a standard)

Sample	Li concentration (M)			
	Determined	Expected	Λ /D	
	using F ⁻ ISE	(B)	A/D	
	(A)			
Li-MIX – 1	0.852±0.020	0.84±0.02	1.014	
Li-MIX - 2	1.00±0.02	1.00±0.02	1.001	
Li-MIX – 3	0.78±0.02	0.78±0.02	1.001	
Li-MIX - 4	0.89±0.02	0.89±0.02	1.002	
Li-MIX- 5	1.79±0.04	1.80±0.04	0.997	

The developed potentiometric method was employed for studying the leaching/pick up of lithium from/by the LiTiO₂ microspheres. Any leaching or pickup that occurs during the washing would change the ${}^{6}\text{Li}/{}^{7}\text{Li}$ isotope ratio of the wash solution, due to the difference in the isotopic signatures of lithium in the two systems. Figure 2.2 shows the data obtained for the successive wash solutions by using F⁻ ISE. It can be seen that washing the microspheres with 1.55 M LiOH, leads to significant leaching of Li⁺ from the pebbles to the wash liquid at the first stage of washing. Subsequently, small amount of leaching of Li⁺ from the microspheres (pebbles) was observed, finally reaching to a

saturation level. The data on the TIMS analyses of the wash solutions are given in Table 2.2. The Table also contains the details on the ion current data of the major peak at m/z 57. The isotopic ratio of Li in the sample was then obtained using the formula [61]

$$\frac{{}^{6}Li}{{}^{7}Li} = \frac{1}{2} \left[R_{\frac{56}{57}} - \frac{{}^{10}B}{{}^{11}B} \right]$$
(2.3)

Where ${}^{6}\text{Li}/{}^{7}\text{Li} = \text{Isotopic ratio of lithium in the sample}$

 $R_{56/57}$ = Measured intensity ratio of the ions at m/z 56 & 57

 ${}^{10}\text{B}/{}^{11}\text{B}$ = Isotopic ratio of boron used for TIMS analysis (NIST-SRM-951)

Table 2.2

Data on the TIMS analysis of different lithium solutions

Sample	Ion intensity	Ion intensity	⁶ Li/ ⁷ Li	Remarks
	(in mV) at	ratio	atom ratio	
	m/z 57	(56/57)		
Li-I	295	0.40242	0.0776	Natural Li used for
		(0.02 %)		preparation of pebbles
Li-II	355	0.33504	0.0438	Depleted ⁶ Li used for
		(0.1 %)		washing
OD-1	33.45	0.35902	0.0558	Wash solutions after
		(2.36%)		overnight digestion
OD-2	298.6	0.33830	0.0455	
		(0.24 %)		
OD-3	323.3	0.33546	0.0440	
		(0.10 %)		
OD-4	924.4	0.33754	0.0451	
		(0.06 %)		
OD-5	122.0	0.33517	0.0439	
		(0.0417)		
OD-6	670.2	0.33642	0.0446	
		(3.6 %)		
OD-7	1186.0	0.33541	0.0440]
		(0.15 %)		

Note: The isotope ratio of ${}^{10}\text{B}/{}^{11}\text{B}$ in the samples was taken from the certified value in NIST-SRM-951 (0.2473 ± 0.1%) and was used to calculate ${}^{6}\text{Li}/{}^{7}\text{Li}$ atom ratio from the observed ion intensity ratio at m/z 56/57.

It can be seen from the TIMS data that there is a significant change in the isotopic ratio of lithium in the first two stages of washings, in comparison to that of the solution (Li-II) (depleted lithium) which was used for washing. After two washings, no significant change in the isotopic ratio of Li was observed. Thus the leaching of lithium from pebbles during first two stages of washings was confirmed by employing mass spectrometry data as well. Also, it was confirmed that there is no significant change in the isotopic ratio of Li in the wash solutions was observed.

The data on the change in the isotopic ratios in the different wash solutions with respect to that of the stock are also shown in Figure 2.2. It can be clearly seen that there is significant leaching of lithium during the first two washings, and it becomes insignificant from the third washing onwards. These studies indicate that further increase in the amount of lithium in wash liquid might be helpful in minimizing the loss of Li from the microspheres as well as leaching of Li from the microspheres. This is essential to maintain the required Li to Ti stoichiometry in the final product.



Figure 2.2 Data on Li concentration (M) by ISE and ⁶Li/⁷Li atom ratio by TIMS in different wash solutions

2.7 Conclusions

The results from these experiments demonstrate the usefulness of the present method for lithium determination in complex chemical matrix containing various organic constituents. These studies would be highly useful in the optimization of the washing parameters in sol-gel process for obtaining phase pure lithium titanate pebbles. In addition to maintaining the stoichiometry, the investigations would also be helpful to reduce the loss of enriched Li⁶. This is desirable due to the high cost of enriched Li⁶ as well as the strategic importance of this isotope. The ISE 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.

CHAPTER – 3

Determination of Lithium in Organic Matrix by

Coated Wire Lithium Ion Selective Electrode

3.1. Introduction

In the last chapter, a potentiometric method was developed for the determination of Lithium in ethanol medium using ammonium fluoride as titrant and fluoride ion selective electrode for end point detection. A thought was given to determine Lithium directly by using Coated wire Lithium ion selective electrode. This was fabricated using commercially available Lithium ionophore-VI, 2-nitrophenyl octyl ether (NPOE) and potassium tetrakis(pchlorophenyl)borate (KTpClPB) on platinum wire. Lithium ion selective electrode was giving Nernstian response from 10⁻¹M to 10⁻⁴M with a detection limit of 3×10^{-5} M. The calibration slope of this lithium ion selective electrode was found to be 58.5 ± 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 in complex chemical matrix containing hexamethylene tetramine, formaldehyde, urea and ammonium nitrate etc. which are the wash streams generated during the sol-gel process employed for preparation of Li₂TiO₃ microspheres. There are many literatures available on Lithium ion selective electrode [64-69] which are mostly used in a pharmaceutical line for the determination of lithium in serum blood. Recently, Lithium ion selective electrode was employed to measure the cardiac output of the patients in intensive care using lithium dilution method [70]. Most of this Lithium ion selective electrodes are liquid membrane based electrodes and being used for the above mentioned purpose. So far, there is no literature available for the determination of lithium in samples containing complex chemical mixture using coated wire lithium ion selective electrode. A method

has been developed for the determination of lithium by potentiometry using commercially available fluoride ion selective electrode by the current author [71]. Coated wire Lithium Ion Selective Electrode (Li-ISE) is exclusively developed for the determination of lithium in complex chemical mixture containing hexamethylene tetramine, formaldehyde, urea and ammonium nitrate etc. which are the wash streams generated in the sol-gel process (Li^6) employed for preparation of Li₂TiO₃ microspheres. Lithium isotope plays an important role in nuclear industry for the production of tritium during nuclear fusion reaction. The proposed fuel for fusion reactor is based on lithium-6 in which Li^6 fuel would generate tritium by the following ${}^6Li(n,\alpha)T$ nuclear reaction inside the blanket of the thermonuclear reactor by exploiting the fast neutrons (n) coming from the D-T fusion reaction. The washed solutions which contain enriched Li⁶ also needed to be analyzed for Lithium content prior to the recovery process. Thus the method required a simple and robust technique, which is capable of Lithium determination to standardize the various steps of the sol-gel process. Determination of Lithium in a complex chemical mixture containing HMTA, urea etc. by the conventionally used techniques such as ICPMS, ICP-OES, TXRF etc., requires removal of organics. It was therefore considered worthwhile to investigate the possibility of determination of Lithium using coated wire Lithium ion selective electrode. In the present work, the fabrication of coated wire lithium ion selective electrode, calibration, interference studies, lifetime of the electrode and its application to the analysis of lithium in complex organic matrix are demonstrated. The method adopted for the determination of lithium using coated wire lithium ion selective electrode in the various process streams

generated during Li_2TiO_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%.

3.2 Experimental

3.2.1 Regents / Instruments Required

Lithium ionophore (VI), Fluka Make, Poly Vinyl Chloride (PVC), Fluka Make, A.R. Grade 2-nitrophenyl octyl ether (NPOE), A.R. Grade potassium tetrakis (p-chlorophenyl) borate (KTpClPB), A.R. Grade Anhydrous LiCl, A.R. Grade Anhydrous LiOH, A.R. Grade Anhydrous LiNO₃, A.R. Grade Urea, A.R. Grade Hexamethylene tetramine. Double Distilled water was used for the preparation of all reagents and standards. Orion 5-Star ion analyzer was employed to measure the potential developed using Lithium ion selective electrode and Double Junction Calomel Reference Electrode during the analysis. A magnetic stirrer was employed throughout the experiment for continuous stirring of the electrolytic solution during analysis.

3.2.2 Preparation of Li⁺ Standards

The Lithium stock solution (1M) was prepared by dissolving 4.240g LiCl in 100 ml using double distilled water. From this stock, Li^+ standard solutions of different concentrations in the range of 10^{-1} M to 10^{-5} M were prepared by subsequent dilution suing double distilled water.

3.2.3 Loading of LiCl on Lithium Ionophore (VI) and Construction of Li-ISE

Initially, 29.6 mg of commercially available Li ionophore (VI) was dissolved in 5 ml 2-nitrophenyl octyl ether (NPOE). To this 2.5 ml of 5M Lithium Chloride was added and equilibrated for one hour and the organic mixture was allowed to settle for few hours. The organic layer containing lithium was then separated from aqueous solution. Then, 300 mg of PVC was dissolved in 2-3 ml Tetrahydrofuran. To this ~700 mg of organic mixture containing Lithium ionophore (VI), NPOE loaded with lithium chloride having ~5 mg of potassium tetrakis (p-chlorophenyl) borate (KTpClPB) as an additive was mixed thoroughly using magnetic stirrer till slurry is formed. Then using Ptwire (the central portion of the Pt-wire was encapsulated using glass tube) such that one end was used for membrane coating and the other end was used for electrical contact. This slurry was coated on the Pt-wire and the electrode was allowed to dry for two days (**Figure 3.1**). The lithium ion selective electrode was conditioned in 0.1M LiCl for few hours prior to analysis.



Figure 3.1 Coated Wire Li- ion selective electrode

3.2.4 Preparation of Lithium Titanate Microspheres

The lithium titanate microspheres were obtained by the internal gelation process. Natural lithium nitrate and titanium chloride solutions were mixed with 3M solution containing a mixture of HMTA/urea at 0°C to obtain feed solution. This feed solution was then dispersed as droplets through a stainless steel capillary of 0.8 to 1.0 mm internal diameter into a glass column in which hot silicone oil pre-heated to 90°C was circulated. These droplets get hardened (gelled microspheres) as they travel down the column. The gelled microspheres were separated from oil, washed initially with CCl₄ (4 to 5 times), to remove the adhering silicone oil, dried and then digested in 1.55 M LiOH at 60°C in an air oven for 16 to 18 h. Washing with 1.55 M LiOH was done 6 to 7 times to remove the reaction products and unused chemicals from the microspheres to prevent their cracking during sintering. The microspheres were then dried at 100°C. In order to study the pickup/leaching of Li from the microspheres during the washing, LiOH used for washing was prepared from depleted 6Li. During the preparation of Li₂TiO₃ (with enriched Li⁶) by sol-gel process, the microspheres are washed with Li⁶ containing organic mixture (0.54M NH₄NO₃+0.24M NH₄Cl+0.075M HMTA + 0.075M Urea + LiOH) so that leaching of Li⁶ from the sol-gel particles during washing can be minimized.

3.3 Results and Discussion

3.3.1 Calibration Curve for Li ISE

Figure 3.2 shows the calibration curve of lithium ion selective electrode and it has been observed that the lithium ion selective electrode was responding satisfactorily to the lithium standard solutions in the range 1×10^{-4} M to

 1×10^{-1} M with a detection limit of 3×10^{-5} M. The calibration slope (S) of this Slithium ion selective electrode was found to be 58.5 ± 1.0 mV/decade. The response behavior of the electrode did not show any significant change with time, which would not affect the analytical results when fresh calibration is employed for measurements. Hence it can be seen that the electrode can be used with fair amount of reproducibility.



Figure 3.2 Calibration curve of lithium ion selective electrode

The integrity of the electrode was tested with various lithium salts as the same will be used as a feed material for the preparation of lithium titanate microspheres. Figure 3.3 shows the calibration curve for different lithium salts viz., LiOH, LiNO₃ and LiCl using lithium ion selective electrode. The slope of the lithium ion selective electrode in all the three salts was well within the limits.



Figure 3.3 Calibration curves for different lithium salts

3.3.2 Potentiometric Selectivity

The influence of interfering ions on the response behavior of ion selective electrodes is usually described in terms of selectivity coefficients. The selectivity coefficients for lithium with respect to variety of interfering ions were described by matched potential method (MPM) [72-74]. In this method, 5 mL of 1 x 10^{-3} M Li⁺ was taken in a beaker and its potential was measured using lithium ion selective electrode. The potential was then slowly varied in small increments (~5 mV) by addition of standard lithium solution (1x10⁻²M).

After every addition, the stabilized potential was recorded and corresponding increase in lithium concentration Aa_A) was calculated. In the second set of experiments, potential of 5 mL of 1×10^{-3} M Li⁺ was varied in similar increments by addition of standard solution of impurity ion (a_B) prepared. Concentration of lithium ion throughout the impurity ion addition was adjusted to 1×10^{-3} M by adding required amount of lithium solution of known concentration. From the increase in concentrations of lithium io $Aa(_A)$ and concentration of impurity ion (a_B) required to carry out the same change in potential, selectivity coefficients were calculated as follows:

Selectivity Coefficient =
$$\Delta a_A / a_B$$
 3.1

where A is lithium ion; B is impurity ion Δa_A = Increase in concentration of lithium ion to get certain change in potential; a_B = Concentration of impurity ion required to get the same change in potential.

3.3.3 Interference Studies

Interference of presence of HMTA, Urea, NH₄⁺ Na⁺ and K⁺, ions on the potential measurement of lithium standard solution using coated wire lithium ion selective electrode was investigated by adopting matched potential method. The potential of the solution containing constant initial concentration (1x10⁻³M) of primary ion i.e. Li⁺, was varied by about 30 mV in four to five increments either by adding lithium std. solution or impurity ion solution. The selectivity coefficient obtained from these studies is summarized in **Table 3.1**. The results clearly showed that the impurity ions studied have negligible interference in lithium measurement. Among the various ions studied, HMTA

was found to have highest selectivity coefficient indicating interference at high concentrations.

S.No.	Impurity ion	Selectivity Coefficient
1	Urea	8.24 x 10 ⁻²
2	$NH4^+$	3.54 x 10 ⁻³
3	HMTA	9.97 x 10 ⁻¹
4	Na^+	3.42 x 10 ⁻³
5	\mathbf{K}^+	3.48 x 10 ⁻³

Table 3.1 Selectivity coefficient of impurities using coated wire Lithium ISE

3.3.4 Response of Coated Wire Li-ISE

The response of lithium ion selective electrode in one month time was given in **Figure 3.4**. It was found that the response of the electrode was found to be working satisfactory. In addition response time is another important factor for any ion selective electrode. Thus, in the case of all electrodes, the average response time required for the electrodes to reach a potential response within ± 1 mV of final equilibrium values after successive immersion in a series of solutions each having a 10-fold difference in concentration was measured. In
this study, the practical response time was recorded by changing solutions with different low-to-high lithium concentration. As can be seen, in the concentration range, the electrode reaches equilibrium response within few minutes. The measurement sequence was from the lower $(1 \times 10^{-3} \text{M})$ to the higher $(1 \times 10^{-2} \text{M})$ concentration. Characteristic performance of coated wire lithium ion selective electrode was shown in **Table 3.2**.



Figure 3.4 Response of Li ion selective electrode in one month since fabrication

3.3.5 Life Time of Coated Wire Li-ISE

The coated lithium ion selective electrode was calibrated almost every day and it can be seen from the **Figure 3.5** that the ion selective electrode could be conveniently used for consecutive four months without losing their Nernstian response. Later to that period, the response of the electrodes deteriorated and the behavior deviated more from the Nernstian slope. Drift in the value of E^0 was observed over time, but the overall drift in E^o value was found to be less than 5% and this could be attributed to the following reasons: (i) by nonuniform coating of membrane on Pt-wire (ii) deterioration of membrane due to aging of the PVC matrix etc. It was found that the drift in E^o could be improved by conditioning of lithium ion selective electrode before analysis overnight.



Figure 3.5 Lifetime of Li-ion selective electrode

Properties	Values / range
Optimized Membrane	Lithium ionophore (VI) loaded
Composition	with 5M LiCl, 2-nitrophenyl
	octyl ether (NPOE) as plasticizer
	and potassium tetrakis(p-
	chlorophenyl)borate (KTpClPB)
	as an additive : PVC (70:30)
Electrode type	Coated wire lithium ion selective
	electrode using Pt wire
Conditioning time	One hour prior to use in 10 ⁻¹ M
	Li ⁺
Linear range (M)	$1x10^{-4} - 1x10^{-1}$
Slope (mV/decade)	58.5 ± 1.0
Detection Limit	3.0x10 ⁻⁵ M
Response time	< 100 sec.

Table 3.2 Response characteristics of the coated wire lithium ion selective electrode

3.3.6 Analytical Applications of Coated Wire Li-ISE

In order to ascertain that there is no significant interference in the determination of lithium due to the presence of organic matrix using coated lithium ion selective electrode, all the washing sample containing Li (natural) received from the preparation of Li_2TiO_3 microspheres were diluted prior to lithium analysis. It was observed that the concentration of Li in the mixture

matched within 2% of the expected values which proved the absence of any significant interference owing to organic constituents. **Table 3.3** shows the data on the determination of lithium in synthetic mixtures containing organic components (HMTA, urea). The precision of the method was also ascertained by repetitive determination of Li in one of the samples and was found to be better than 0.5%.

 Table 3.3 Determination of lithium in from solutions of synthetic mixture (containing

 HMTA+Urea) using coated wire lithium ion selective electrode

Sample	Coated Li ISE	Expected (B)	A/B
	(*) (M)		
Li-Mix-1	1.541±0.031	1.535±0.031	1.007
Li-Mix-2	1.537±0.031	1.551±0.031	0.992
Li-Mix-3	1.554±0.031	1.542±0.031	1.009
Li-Mix-4	1.569±0.031	1.558±0.031	1.012
Average			1.005
			±0.020

[(*) Results based on the average of triplicate measurements]

3.3.7 Storage of Coated Wire Li-ISE

The advantage of coated wire lithium ion selective electrode is such that it can be stored in air unlike other liquid membrane based electrodes which needs to be stored in respective solution.

3.4. Conclusion

The results from the above experiments demonstrate the usefulness of the coated wire lithium ion selective electrode for the determination of lithium in complex chemical mixture containing various organic materials and solvent. 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 rapid and precise and can be employed on a routine basis for lithium determination in solutions containing organic constituents.

CHAPTER – 4

Determination of Uranium using Coated

Graphite Uranium Ion Selective Electrode

4.1 Introduction

Determination of uranium concentration is of great importance in nuclear industry due to the application of the uranium dioxide as a fuel in nuclear reactors. It is important to determine the concentration of uranium at various stages of the fuel cycle with high precision and accuracy due to its strategic importance. Several analytical methods based on different physico-chemical methods are widely applied for the determination of uranium. These include redox titrimetry, spectrophotometry, mass spectrometry, fluorimetry, ICP-AES etc. However, many of these methods require expensive instrumentation, wellcontrolled experimental conditions, frequent maintenance etc. and are also difficult to employ for on line measurements. The electrochemical sensors have many advantages such as ease of fabrication, high sensitivity, simple instrumentation and in some cases also offer high selectivity in presence of interfering ions. This analytical technique also provides an accurate, rapid, cost effective method of analysis and has a high potential for on line applications. In this Chapter, the development of a simple, fast and robust method for the determination of uranium in nuclear fuel samples viz. sintered UO₂ and (U,Th)O₂, employing coated graphite uranium ion selective electrode is described. Determination of uranium is required during fabrication of the fuel at all stages, from feed materials to finished products, to ensure that the fuel meets the stringent specifications required by the designer [75-77]. Though many methods are available for the determination of uranium, some aspects have to be considered while choosing the appropriate method. The method should (i) give the required precision and accuracy with a small sample amount to minimise the radiation dose to the analyst, (ii) be free of interferences from constituent elements of the fuel, (iii) have minimum analytical waste generated and (iv) be amenable to easy recovery of the fissile materials from the analytical wastes.

4.1.1 Determination of Uranium in Nuclear Fuel

There are several methods reported for the determination of uranium [78-115] by different electroanalytical techniques such as potentiometry, amperometry and coulometry. In these methods, uranium is reduced to U(IV) by a suitable reductant and U(IV) is then titrated with a standard oxidant such as $K_2Cr_2O_7$ or Ce(IV) using suitable electrometric end point detection. Since U(VI) / U(IV) couple is irreversible, a reversible couple such as Fe(III) / Fe(II) is introduced as an intermediate to locate the end point. Fe(III) oxidizes U(IV) to U(VI) getting itself reduced to equivalent amount of Fe(II). This Fe(II) is then titrated with the standard oxidant. $K_2Cr_2O_7$, being a primary standard, is preferred as the titrant in comparison to Ce(IV).

4.1.1.1 By Davies and Gray Method using Potentiometric end point

Among the various redox methods, the Davies and Gray method is commonly used for uranium determination in plutonium bearing samples due to its tolerance towards plutonium, iron and HNO₃. In this method, uranium is reduced to U(IV) by an excess of Fe(II) in conc.H₃PO₄ medium (10M), followed by selective oxidation of the excess Fe(II) by HNO₃ in presence of Mo(VI) as catalyst and subsequent titration of U(IV) with standard K₂Cr₂O₇ after dilution with 1M H₂SO₄. Originally the method was intended for 200 – 300 mg U. Several modifications have been incorporated and reported to allow the analysis of samples containing smaller amounts of uranium, with improved precision. Sharpening of end point has been achieved by introducing V(IV) in the medium during dilution. End point detection is done using potentiometry.

Aluminium–clad, Al (20 wt %)– 233 U–Zr plate fuel were fabricated for KAMINI reactor at IGCAR, Kalpakkam. Chemical quality assurance of this fuel as well as recovery of 233 U from analytical waste is mandatory. However, presence of the highly complexing phosphate ions in the analytical waste solutions generated by Davies and Gray method, makes the recovery of 233 U and Pu difficult and cumbersome. Further, the fuel sample being an alloy, is normally dissolved in a non-oxidizing acid like HCl and these chloride ions interfere in the potentiometric titration making the end point detection difficult. This necessitates the removal of chloride ions. In order to overcome the above limitations of Davies and Gray method, it was necessary and worthwhile to develop a new method, devoid of phosphate ions usage and which would tolerate the presence of chloride ions in the medium.

4.1.1.2 By Davies and Gray Method using Amperometric end point

Uranium can be determined using the above method and only difference is that the end point is being determined amperometrically.

4.1.1.3 Determination of Uranium using Ti(III) reduction method

U(VI) can be reduced to U(IV) using Ti(III) and followed by titration of U(IV) with $K_2Cr_2O_7$ using amperometric end point. This method is preferred in presence of Pu(IV) for sequential determination of both U and Pu.

4.1.1.4 Determination of Uranium by Controlled Potential coulometry

Uranium can be determined by well known method using controlled potential coulometry. In this method, initially the impurities are reduced at +0.085V and followed by reduction of U(VI) to U(IV) on Hg electrode at -0.325V in HClO₄ medium.

4.2 Determination of Uranium by Coated Graphite Uranyl Ion Selective Electrode

Most of the electrochemical sensors reported in literature for uranium determination are based on use of liquid membrane consisting of uranium sensitive ionophore for the separation of sample solution from internal standard solution [116,117]. The potential difference developed across the liquid membrane due to difference in uranium concentration between the internal standard solution and the external sample solution was measured in reference to a standard reference electrode. The construction, use and maintenance of these liquid membrane electrodes require significant expertise and require good electrical isolation between the internal standard solution. A coated ion selective electrode on the other hand, does not require internal reference solution and hence is usually very simple to prepare and convenient to use.

The development of coated wire ion selective electrode started four decades ago by Freiser [118]. Coated wire ion selective electrode contain ion selective membrane made up of compound of anionic complex of metal ion of interest to be determined and large hydrophobic cation impregnated in poly vinyl chloride [PVC] [119]. Among the various hydrophobic cations, use of Aliquat-336 has been reported for determination of various metal ions like iron, copper, mercury, zinc, bismuth, cobalt etc. [120-125] The major advantage in the use of Aliquat 336 is that it acts not only as an ionophore but also as a plasticizer thus avoiding the use of extra additive for the fabrication of the membrane.

A coated graphite uranyl ion selective electrode was developed by depositing a membrane comprising Aliquat-336 loaded with uranyl tetrachloride dianion $(UO_2Cl_4^{2-})$ and poly vinyl chloride (PVC) on graphite rod. 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 1×10^{-4} M to 1×10^{-1} M with a detection limit of 5x10⁻⁵M 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 were determined by matched potential method. The electrode was employed for determining Uranium in presence of Thorium (Th to U amount ratio=25), which gives a promising application to the simple approach for the $(Th,U)O_2$ based nuclear fuel. This coated uranyl ion selective electrode can be used for consecutive four months without losing Nernstian response. The development of a coated uranyl ion selective electrode using graphite rod which is inexpensive as compared to other metals viz., Pt, Ag etc. used for the preparation of ion selective electrodes. The uranyl ion selective electrode was prepared using Aliquat 336 loaded with anionic chloro complex of uranium. The effect of membrane composition, electrolyte composition on the response of uranyl ion selective electrode were studied and optimized for the analytical performance. The useful life of electrode was also studied. The interference due to the presence of various cations and anions were also studied. The dynamic response of the electrode was also evaluated. Determination of uranium in sintered UO₂ pellets as well as synthetic mixture containing uranium and thorium were also performed.

Using Aliquat 336 in the present work, uranyl chloride anions are extracted according to the following exchange reaction:

 $4R_3N+CH_3Cl(org) + UO_2Cl_4^{2-}(aq) \rightarrow (R_3NCH_3) 4UO_2Cl_4(org) + 4Cl^{-}(aq) (4.1)$

4.2.1 Experimental

4.2.1.1 Reagents Employed

Aliquat-336 (tricaprylylmethylammonium chloride) Sigma Aldrich Make, USA, Poly Vinyl Chloride (PVC), Fluka Make, Nuclear grade U_3O_8 , Spectroscopy grade high purity graphite rod, A.R. Grade Tetrahydro furan (THF), A.R. Grade nitric acid, A.R. Grade hydrochloric acid, A.R. Grade lithium chloride, A.R. Grade Thorium Nitrate were used. Double distilled water was used for preparation of all standard uranium solutions. A.R. grade salts of different cations were also employed for the interference studies.

4.2.1.2 Preparation of standard uranium solution

The uranium stock solution was prepared by dissolving known amount of nuclear grade U_3O_8 in concentrated nitric acid followed by conversion of uranyl nitrate to uranyl chloride by repeated evaporation almost to dryness using 6M HCl. The resultant uranyl chloride residue was dissolved in 6M HCl and the stock solution was standardized for uranium using titrimetry [126]. Standard solutions in the concentration range from 10^{-1} M- 10^{-5} M were prepared by subsequent dilution using 5.9M LiCl+0.1M HCl mixture. The total chloride ion concentration in both the standard and the unknown solution was maintained at 6M.

4.2.1.3 Loading of Aliquat 336 with Uranium

About 5 ml Aliquat 336 (in chloride medium) was equilibrated with 5 ml of uranyl stock solution and the mixture was stirred on a magnetic stirrer for about 3-4 hours and allowed to settle overnight. The organic phase containing Aliquat 336 loaded with uranyl tetrachloride dianion $UO_2Cl_4^{2-}$ was then separated and used for the preparation of ion selective electrode.

4.2.1.4 Construction of Electrode

Coated uranyl ion selective electrode was prepared using the technique as reported in the literature. The spectroscopic grade high purity graphite rod (5mm OD and 100mm length) was taken and the central portion of the rod was encapsulated in a glass tube such that one end of the electrode could be used for membrane coating and the other end for emf measurements. The membrane coating methodology consisted of mixing required weighed amounts of the Aliquat 336 loaded with uranyl tetrachloride dianion $UO_2Cl_4^{2-}$ [127] and PVC in the suitable amount of solvent namely Tetrahydrofuran (THF). One end of the graphite rod was repeatedly dipped into this mixture until a uniform, adhesive coating was obtained on the graphite rod. The electrodes were then dried in air for one week. Figure 4.1 shows freshly prepared uranyl ion selective electrodes as well as used ones. Uranyl ion selective electrodes having different membrane composition i.e. with Aliquat 336: PVC in the ratio of 80:20, 70:30 and 60:40 were prepared for optimizing the electrode composition. The coated graphite uranyl ion selective electrode was conditioned at least for one hour in 0.1M uranyl solution prior to analysis. The coated uranyl ion selective electrode was stored in air after its use.



Figure 4.1 Coated Graphite Uranyl Ion Selective Electrode

4.2.1.5 Instruments Used

A 4-Star ion meter (Orion Make) and double junction reference electrode (DJRE) (M/s. pH Products Company, Hyderabad) were used for emf measurement. The secondary salt bridge solution in DJRE was 5.9M LiCl and 0.1M HCl.

4.2.2 Results and discussion

4. 2.2.1 Calibration Curve for Uranyl ion selective electrode

Figure 4.2 shows the calibration curves of three different uranyl ion selective electrodes which were fabricated under identical condition on the same day. It was shown that all the three electrodes were responding satisfactorily to the uranyl standard solutions in the range 1×10^{-4} M to 1×10^{-1} M. The difference in the sensitivity i.e. mV/ decade change in concentration can be attributed to the small differences during the fabrication of these three electrodes. However, the response behavior of the electrode was found not to change significantly with time, which would not affect the analytical results when fresh calibration is employed for measurements. Hence it can be seen that the electrodes can be used with fair amount of reproducibility.



Figure 4.2 Performance of identical coated graphite Uranyl ISE

4.2.2.2 Optimization of Electrode Composition

Figure 4.3 shows the responses of uranyl ion selective electrodes in different ratios of Aliquat 336 loaded with $UO_2Cl_4^{2-}$ and PVC viz. 80:20, 70:30 and 60:40. It can be seen that the uranium ion selective electrode in the ratio of 70:30 gave better slope (S= -29.2) than the other compositions viz. 80:20 (S= -26.8); 60:40 (S= -23.7) and hence the composition 70:30 was employed for all the subsequent studies. The ratio of 90:10 did not yield a suitable membrane for studies and the ratio of 50:50 was found to be giving unstable reading during emf measurements and hence was not employed in this study.



Figure 4.3 Optimization of electrode composition using Aliquat 336 and PVC

4.2.2.3 Optimization of the Electrolyte Composition for Determination of U

It was necessary to control the chloride concentration in the electrolyte (i.e. LiCl+HCl mixture) for standards as well as samples in order to have uniform ionic strength and to keep the fraction of uranyl anionic complexes at constant value. Chloride ion concentration could be maintained either by using only HCl or solution of highly soluble chloride salt (e.g. LiCl) or by their mixture. Preliminary experiments of using either only HCl or only LiCl solution to maintain chloride concentration to 6M gave inconsistent results even after maintaining the salt bridge solution as pure HCl and pure LiCl. Studies were carried out for optimizing the amounts of LiCl+HCl for maintaining the Cl⁻ ion concentration. Best results were obtained using 5.9 M LiCl+0.1 HCl and

all measurements were carried out using uranyl standards and unknown samples in this electrolyte.

4.2.2.4 Potentiometric Selectivity

The influence of interfering ions on the response behavior of ion selective electrodes is usually described in terms of selectivity coefficients. The selectivity coefficients for uranium with respect to variety of interfering ions were described by matched potential method (MPM). In this method, 5 mL of 1×10^{-4} M U in 0.1M H⁺+6M Cl⁻ was taken in a beaker and its potential was measured using uranyl ion selective electrode. The potential was then slowly varied in small increments (~5 mV) by addition of standard uranyl solution $(1x10^{-2}M)$. After every addition, the stabilized potential was recorded and corresponding increase in uranyl concentration $\Delta (a_A)$ was calculated. In the second set of experiments, potential of 5 mL of 1x10⁻⁴M U in 0.1M H⁺+6M Cl was varied in similar increments by addition of standard solution of impurity ion (a_B) prepared in 0.1M H⁺+6M Cl⁻. Concentration of uranyl ion throughout the impurity ion addition was adjusted to 1×10^{-4} M by adding required amount of uranyl solution of known concentration. From the increase in concentrations of uranyl ion (a_{A}) and concentration of impurity ion (a_{B}) required to carry out the same change in potential, selectivity coefficients were calculated as follows:

Selectivity Coefficient = $\Delta a_A / a_B$ 4.2

where A is uranyl ion; B is impurity ionAa $_{A}$ = Increase in concentration of uranyl ion to get certain change in potential; a_{B} = Concentration of impurity ion required to get the same change in potential.

4.2.2.5 Interference Studies

Interference of presence of Th(IV), Fe(III), Na(I), K(I), Ca(II), Ba(II) and Mg(II) ions on the potential measurement of uranyl solution using coated graphite uranyl ion selective electrode of a typical membrane composition of 70% Aliquat-336 loaded with $UO_2Cl_4^{2-}$, 30% PVC was investigated by adopting matched potential method. The potential of the solution containing constant initial concentration (1x10⁻⁴M) of primary ion i.e. U, was varied by about 30 mV in four to five increments either by adding uranyl solution or impurity ion solution prepared in 6M CI⁻. The selectivity coefficient obtained from these studies is summarized in **Table 4.1**. The results clearly showed that the impurity ions studied have negligible interference in uranyl measurement. Among the various ions studied, Fe(III) was found to have highest selectivity coefficient indicating interference at high concentrations.

S.No.	Impurity ion	Selectivity Coefficient
1	Na(I)	1.87 x 10 ⁻³
2	K(I)	4.84 x 10 ⁻³
3	Ca(II)	1.37 x 10 ⁻³
4	Ba(II)	3.10 x 10 ⁻⁴
5	Mg(II)	1.17 x 10 ⁻³
6	Fe(III)	1.47
7	Th(IV)	4.87 x 10 ⁻³

 Table 4.1 Selectivity coefficient of cationic impurities using coated wire Uranyl ISE

4.2.2.6 Interference due to anionic impurities

Since the present work involves measurement of anionic complex of uranium, the presence of various anionic impurities viz., OH^- , CO_3^{2-} , NO_3^- ions were also investigated. It was observed that there was no significant interference due to the presence of above anionic impurities during the determination of uranium in sintered UO₂ pellets and synthetic mixture containing uranium and thorium. The results are tabulated in **Table 4.2**.

 Table 4.2
 Selectivity coefficient of anionic impurities using coated wire Urayl ISE

S.No.	Impurity ion	Selectivity
		Coefficient
1	OH	1.19 x 10 ⁻³
2	CO ₃ ²⁻	8.70 x 10 ⁻⁴
3	NO ₃ -	3.20 x 10 ⁻⁴

4.2.2.7 Response of Uranyl ion selective electrode

The response time is an important factor for any ion selective electrode. Thus, in the case of all electrodes, the average response time required for the electrodes to reach a potential response within ± 1 mV of final equilibrium values after successive immersion in a series of solutions each having a 10fold difference in concentration was measured. In this study, the practical response time was recorded by changing solutions with different low-to-high uranyl concentration. The actual potential Vs. time was shown in **Figure 4.4**. As can be seen, in the concentration range, the electrode reaches equilibrium response within few minutes. The measurement sequence was from the lower $(1x10^{-4}M)$ to the higher $(1x10^{-1}M)$ concentration. Characteristic performance of coated graphite uranyl ion selective electrode was shown in **Table 4.3**.



Figure 4.4 Dynamic Response of Uranyl Ion Selective Electrode

Table 4.3 Response characteristics of the coated	l graphite
uranyl ion selective electrode	

Properties	Values / range
Optimized Membrane	Aliquat 336 loaded with $UO_2Cl_4^{2-}$: PVC (70:30)
Composition	
Electrode type	Coated graphite uranyl ion selective electrode
Electrolyte medium (6M Cl-)	5.9M LiCl+0.1M HCl for all standards and samples
Conditioning time	One hour prior to use
Linear range (M)	$1 \times 10^{-4} - 1 \times 10^{-1}$
Slope (mV/decade)	-29.2 ± 1.0
Detection Limit	$5.0 \times 10^{-5} M$
Response time	2-3 min.

4.2.2.8 Life time of uranium ion selective electrode

The uranyl ion selective electrodes were calibrated almost every day and it can be seen from the **Figure 4.5** that the uranyl ion selective electrode could be conveniently used for consecutive four months without losing their Nernstian response. Later to that period, the response of the electrodes deteriorated and the behavior deviated more from the Nernstian slope. Drift in the value of E^0 was observed over time, but the overall drift in E^o value was found to be less than 5% and this could be attributed to the following reasons: (i) by nonuniform coating of membrane on graphite rod (ii) deterioration of membrane due to aging of the PVC matrix etc. It was found that the drift in E^o could be improved by conditioning of uranyl ion selective electrode before analysis overnight.



Figure 4.5 Lifetime of coated graphite Uranyl Ion Selective Electrode

4.2.3. Analytical applications of the electrode

Since the interest of this work was to study the suitability of this electrode for uranium samples from nuclear fuel cycle (either as pure oxide or in (Th,U)O₂ pellets), different samples of UO₂ pellets were analyzed using this methodology. From the study of Th(IV) as an interfering ion confirmed that uranium determination is possible in (U,Th)O₂ nuclear fuel proposed for Advanced Heavy Water Reactor (AHWR) [16]. This is due to the fact that Th(IV) does not form anionic complex at 6M Cl⁻ concentration whereas uranium forms UO₂Cl₄²⁻ at 6M Cl⁻ and hence online determination of uranium in presence of thorium was found to be feasible using this coated graphite uranyl ion selective electrode. Further, it was observed that uranium can be determined in presence of thorium when thorium to uranium amount ratio ~150.

The results obtained using the coated graphite uranyl ion selective electrode was compared with that obtained using ICP-AES. **Table 4.4** shows the comparison of the results obtained for determination of uranium in pure sintered UO_2 pellets. The values obtained by coated graphite uranyl ion selective electrode are in well agreement with the results obtained by ICP-AES. The precision of the measurement by using coated graphite uranyl ion selective electrode were also found to be better than 2%.

Sample	Coated Graphite (*)	ICP-AES (*)	ISE / ICP-AES
	Uranyl ISE (mg/ml)	(mg/ml)	
Α	2.131±0.043	2.135±0.043	0.998
В	6.689±0.134	6.698±0.134	0.999
С	3.489±0.070	3.504±0.070	0.996
D	0.321±0.006	0.322±0.006	0.997
Average			0.998 ± 0.010

TADIC T-T Determination of Oramum in Sintered 0.07 Same	2 samples
--	-----------

[(*) Results based on tr4iplicate measurements]

Since India has large reserves of thorium, several rector concepts which can employ thoria are being studied. An Advanced Heavy Water Reactor (AHWR) [16] is already under consideration for utilization of thorium as MOX either with uranium or plutonium. Hence it was of interest to employ this coated graphite uranyl ion selective electrode for determining uranium in presence of thorium (where thorium to U amount ratio ~25). A synthetic mixture in 6M Cl⁻ medium consisting of U:Th in the range of 1:25 was prepared and analyzed for uranyl content using coated graphite uranyl ion selective electrode with that of the expected values is shown in **Table 4.5.** It was evident from the **Table 4.5** that there is no significant interference due to thorium in uranium determination.

Sample	Coated Graphite	Expected
	Uranyl ISE	(µg/ml)
	(µg/ml) (*)	
Α	48.30±0.97	48.60±0.97
В	52.20±1.04	52.10±1.04

Table 4.5 Determination of Uranium in synthetic mixture of U:Th

[(*) Results based on triplicate measurements]

4.3 Storage of uranium ion selective electrode

The advantage of coated uranium ion selective electrode is such that it can be stored in air unlike other liquid membrane based electrodes which needs to be stored in respective solution.

4.4 Conclusions

Coated graphite uranyl ion selective electrodes have been prepared. A coated graphite uranyl ion selective electrode exhibits linear Nernstian response over uranyl concentration range of 1×10^{-4} M - 1×10^{-1} M in constant chloride concentration of 6M obtained from 5.9M LiCl+0.1M HCl with a slope of - 29.2±1.0 mV/concentration decade and a detection limit of 5 x 10⁻⁵M for the Aliquat 336 loaded UO₂Cl₄²⁻ and PVC composition in the ratio of 70:30. The life time of the electrode was found to be four months with consistent use. The response time during the emf measurement was about less than 2 minutes for uranium standards in the range from 1×10^{-5} - 1×10^{-4} M and less than 30 seconds

for the uranium standards in the range of 1×10^{-3} M to 1×10^{-1} M. This coated graphite uranyl ion selective electrode was successfully employed for the online determination of uranium in sintered UO₂ samples as well as synthetic (U,Th)O₂ samples. The technique is highly attractive due to the fact that simple instrumentation and was also cost effective.

CHAPTER – 5

Development of Coated Graphite Gallium

Ion Selective Electrode

5.1 Introduction

Gallium finds application in nuclear as well as non-nuclear fields. Uranium rich Ga-U alloys and compounds are technologically important materials. Uranium rich GaU alloys have been found to show magnetic and electrical transport. Gallium/Indium compounds such as Gallium nitride, Gallium arsenide, Indium antimonide, Indium arsenide, Indium phosphide and Indium Gallium arsenide are extensively used in electronics industry as semiconducting materials. Gallium is also a component in low melting alloys to stabilise allotropes of plutonium and as heat exchanger in nuclear reactors. An alloy of In, Ag and Cd has been used in nuclear control rods. Due to high neutron absorption cross-section of In (270 barns), it has also added recently as one of the specification elements in nuclear fuels. Thus, in view of the importance of Gallium and Indium in many applications, it becomes imperative to analyse these elements in a variety of matrices. Gallium compounds (GaN, GaAs) are used as semiconductors, especially in lightemitting diodes, while the new photovoltaic compound, Cu(In,Ga)(Se,S)₂, is reported to be useful in solar panels as alternative to crystalline silicon. Gallium readily alloys with most metals, and is used as a component in lowmelting alloys. In particular, it is used to stabilize the allotropes of plutonium. Ga-U and Ga-Pu systems have been studied for the development of new metal fuel reactors with respect to their thermodynamic stability for high temperature applications. Gallium is known to degrade the properties of many metallic materials via corrosion, embrittlement, or intermetallic phase formation. In view of these, sensitive and reliable methods for the determination of trace and minor concentrations of gallium are required.

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Gallium is normally used for nuclear alloy fuels along with plutonium metal for strategic applications. However, plutonium has many allotropic forms, ranging from alpha to epsilon [129]. Amongst these the delta phase is stable at 320° to 440°C and is important because of its desirable properties [130]. Alloying plutonium with a small amount of gallium (1–2%) stabilizes the delta phase of plutonium at room temperature and provides substantial corrosion protection in atmosphere [131] Pu-Ga alloy thus formed is found to be one of the alternate reference materials for plutonium. Accurate determination of gallium, therefore, forms an important part of the chemical characterization of this Pu-Ga alloy.

There are several methods available for the determination of gallium viz., spectrophotometry [132], chromatography [133], ICP-AES [134], ICP-MS [135], calorimetry [136], AAS [137], and polarography [138] etc. However these methods require expensive instruments, well-controlled experimental conditions. The use of electrochemical sensors on the other hand has the advantages of use of simple instruments, rapid and easy, applicable over concentration range from milligram to microgram, enhanced sensitivity and good selectivity. A few methods have been reported in the literature for the determination of gallium by potentiometry using ion selective electrode [139,140]. Many of these ion selective electrodes are prepared with organic ion-exchangers having large sized molecules and with neutral carriers. These membranes are sensitive to a large number of ions than the glass and solid state membranes. Among this Ca^{2+} , K^+ ion electrodes are commercially available. The need for the determination of many heavy metals in the environment has prompted the development of a number of different

ionophores. Since there are no investigations about gallium membrane electrodes prepared using Aliquat 336; the aim of this study was to construct, characterize and use some of them in potentiometric determination of gallium ions. Their optimum working conditions for the determination of gallium were investigated and the interference studies have been made. The selectivity coefficient of this electrode with respect to the different ions were determined by matched potential method. This electrode has been used for the determination of gallium ions using direct method. Prior to fabrication and use of gallium ion selective electrode, let us look into the various methods available for the determination of gallium in experimental solutions. However, the following methods can be adopted for the determination of gallium in Pu-Ga alloy type fuels only after the separation of plutonium from Pu-Ga solutions.

5.2 Methods for Determination of Gallium

For gallium determination, many methods including gravimetry, colorimetry, mass spectrometry, fluorimetry, flame photometry, radiometry and titrimetry are reported in literature. An overview of these methods is given below.

5.2.1 Gravimetric Methods

Gravimetric methods involve precipitation of gallium as insoluble compounds of known composition and their determination as the stable Ga_2O_3 . Some of the approaches used are given below.

(i) <u>Precipitation with ammonium hydroxide</u> [141]: Gallium was precipitated as Ga(OH)₃ by ammonium hydroxide. Excess of ammonia should be avoided as gallium hydroxide is soluble in NH₄OH.

- (ii) <u>Precipitation with sulphite</u> [142,143]: Gallium is precipitated as Ga(OH)₃ by solid sodium sulphite or from aqueous solution of ammonium bisulphate. The precipitate is heated to above 813°C and weighed as Ga₂O₃.
- (iii) <u>Precipitation with urea</u> [144,145]: $Ga(OH)_3$ is precipitated from dilute H₂SO₄ with urea followed by determination as Ga_2O_3 after hydrolytic decomposition of basic gallium sulphate at 475°C.
- (iv) <u>Precipitation with aniline</u> [146]: Gallium is precipitated as $Ga(OH)_3$ by aniline from boiling solutions, heated to >550°C and determined as Ga_2O_3 . The method was used for the determination of gallium in presence of iron.
- (v) <u>Precipitation with pyridine in presence of NH_4Cl [147]: Gallium was precipitated as gallium hydroxide with pyridine. Separation from alkali and alkaline earth metals was possible.</u>
- (vi) <u>Precipitation with cupferron (ammonium nitrosophenyl hydroxylamine)</u> [148]: The precipitate was ignited to oxide at temperature above 745°C. Fe(II) did not interfere. Gallium was determined in presence of many folds of aluminium by this method.
- (vii) <u>Precipitation with camphoric acid</u> [149–151]: Gallium was precipitated quantitatively by camphoric acid or sodium camphorate. The precipitate was ignited and weighed as Ga₂O₃. Many metal ions did not interfere. Indium, iron(III) and aluminium (>10 mg) were found to interfere.
- (viii) <u>Precipitation with 8-quinolinol or 5,7-dibromo-8-quinolinol</u> [152-154]: It was highly unspecific as many metal ions interfered.
- (ix) <u>Precipitation with tannin (digallic acid)</u> [155]: Precipitation of gallium with tannin was used for its determination, but Iron and aluminium were found to interfere.

(x) <u>Electrodeposition</u> [156-157]: Gallium was deposited electrolytically on a platinum cathode from an alkaline solution in presence of hydrazine sulphate and was determined as metal. Platinum interfered by getting deposited on the cathode after anodic dissolution.

Although gravimetric methods are convenient, they require large sample size (100 mg or more) for accurate determination in addition to inherent problems such as solubility of the precipitate, co-precipitation of other ions etc. Ga_2O_3 is also hygroscopic in nature.

When gallium amount in the sample solution is small, gravimetric methods are unsuitable for its determination. Mass Spectrometry, Colorimetry, Flame Photometry, Fluorimetry, Emission Spectroscopy and Radiochemical methods are employed when gallium is present in a few micrograms.

5.2.2 Polarography

In acid solutions, the polarographic wave for gallium was observed very close to the reduction wave of hydrogen [158]. This made the polarographic determination of gallium rather difficult.

According to Vinogradova and Chudinova [159], in salicylate solution (>0.003M) at pH 2.8 to 3.4, gallium gave an irreversible wave with a half-wave potential of -0.88V vs. S.C.E., the wave height was proportional to gallium concentration in the range of 0.028 to 0.0014 M.

5.2.3 Colorimetric Methods

Absorptiometric and fluorimetric methods were reported for gallium determination with Rhodamine B [160-162]. Rhodamine B chlorogallate was extracted into chlorobezene – carbon tetrachloride mixture after adding TiCl₃

to suppress the reagent blank. One to 10 μ g of Ga was determined with an error of 5 to 10%.

Malachite Green chlorogallate [163] was extractable into benzene from 6 to 6.5N HCl. One to 5 μ g of Ga was determined by measuring the absorbance of the extract. The method was selective and use of isopropyl ether extraction prior to determination made the method very useful.

5.2.4 Fluorimetric Methods [164-166]

Fluorescence of gallium 8-quinolinate in chloroform was the basis of a fluorimetric method. When chloroform extraction was made from an aqueous solution of pH 2.6 to 3.0, no metal-oxinate other than indium and scandium were found to fluoresce. The intensity of the fluorescence of indium and scandium were much weaker and separation of GaCl₃ by ether extraction was useful prior to determination.

Rhodamine B chlorogallate extract in benzene was used for the fluorimetric determination of 0.2 to $2.0 \ \mu g$ of Ga.

5.2.5 Flame Photometry

In 1875, Boisbaudran discovered gallium by a flame–spectrographic method [167]. Bode and Fabian [168] developed flame photometric method for determination of traces of gallium in bauxite, clay, aluminium and zinc blend. Gallium was separated by ether extraction, estimated in dilute acid solution after adding acetone, which enhanced the intensity of the gallium lines.

5.2.6 Mass Spectrometry

Isotope Dilution–Thermal Ionization Mass Spectrometry (ID–TIMS) is a highly precise and accurate method for the determination of gallium in trace levels (nanogram to microgram amounts) [169]. But the requirement of costly instrumentation and enriched isotope of Ga to be used as a tracer in isotope dilution restricts the use of mass spectrometry for regular analytical work.

5.2.7 Spectrophotometric Methods

Phenylfluorone reacts with Ga(III) in presence of hexadecylpyridinium bromide and pyridine to form a water-soluble chelate with an absorption maximum at 570 nm in pH range of 4.0 to 5.5 [170]. At this wavelength the Beer's law is obeyed upto 4.3×10^{-6} M Ga. The method has high sensitivity and can be used for Ga determination at microgram level.

5.2.8 Radiochemical Methods

Determination of traces of gallium was also reported by neutron activation. Ga-72, which has a half-life of 14.2 hrs, is frequently used for Ga determination.

5.2.9 Titrimetric Methods [171-205]

Titrimetric methods are commonly used, when gallium is present in milligram amounts in the samples. Various titrimetric methods are reported, and some of the common methods are given below.

5.3 Determination of Gallium using EDTA as a Titrant

Ethylenediaminetetraacetic acid (EDTA) has wide applications in chemical analysis because of its strong complexing ability and commercial availability. EDTA complexes with metal ions of charge 2 (M^{2+}) are stable in alkaline or slightly acidic solution whilst complexes with ions of charge 3 or 4 (M^{3+} or M^{4+}) exist in solutions of much higher acidity. In the EDTA titration, a metal ion-sensitive indicator was often employed to detect the end point. The end point of the titration also detected by electrometric techniques such as

potentiometry or amperometry. But, EDTA was a very unselective reagent because it complexed with numerous cations of different charges.

Gallium was also determined by complexing with EDTA either by direct titration at pH 2 to 4 or by back-titration, the pH range for the back-titration was wider. Metal indicators reported for direct titration included Cu-PAN, pyrocatechol violet, gallocyanin, morin and 8-quinolinol. Many procedures were proposed for back-titration of gallium. Metal indicators like xylenol orange, eriochrome black T, pyrocatechol violet, potassium thiocyanate, pyrogallol red etc. were used for back-titration depending upon the reagent used. Back-titration of gallium with zinc in acetate solution of pH 4 to 6 using potentiometric end point was also reported. Separation of gallium from other metal ions and masking of interfering ions was required for satisfactory results.

5.3.1 Titration with Potassium Ferrocyanide

Potassium ferrocyanide forms compounds with many metal ions due to its strong complexing ability. Since the ferricyanide-ferrocyanide system is reversible, it was used as a redox titrant for many metal ions. End point of such titration was detected either with the help of redox indicators, or by electroanalytical methods like potentiometry or amperometry. Kirschman and Ramsey and Ato studied the potentiometric titration of gallium with standard potassium ferrocyanide solution containing potassium ferricyanide. In 0.0015 to 0.005N HCl, the composition of the precipitate formed corresponded to the formula $Ga_4[Fe(CN)_6]_3$. Ato determined 5 to 20 mg of Ga while Kirschman and Ramsey titirated 33 to 130 mg of Ga.

The use of dead-stop end point (biamperometry) in the titration of 0.05 to 0.17 millimoles of gallium with a standard potassium ferrocyanide solution was reported. The optimum conditions for the experiments were pH of 2.0 and temperature of 50°C, when the potential difference across the Pt wire electrodes was 230 mV. Chloride, sulphate and perchlorate ions did not interfere, while presence of ammonium ions gave slightly high results.

Belcher proposed the use of redox indicators like 3,3'-dimethyl naphthidine and / or 3,3'-dimethyl naphthidine disulphonic acid in the titration with $K_4Fe(CN)_6$ in presence of small amounts of $K_3Fe(CN)_6$ and determined 0.74 to 2.94 mg of Ga with uncertainty of $\pm 0.25\%$.

5.3.2 Titration with Potassium Bromate

Gallium was precipitated as the 8-quinolinate and the precipitate was dissolved in HCl. The 8-quinolinol which combined with gallium was titrated with std. KBrO₃ in presence of KBr. KI was added, and the liberated iodine was titrated with standard thiosulphate solution using starch as indicator. Gallium in amounts of 14 to 28 mg was determined with uncertainty of \pm 0.21%.

5.4 Development of Coated Graphite Gallium Ion Selective Electrode based on Aliquat 336

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⁺, Ca²⁺, Mg²⁺, Ba²⁺, Fe³⁺, Cr³⁺, Ni³⁺, Th⁴⁺, U(VI), OH⁻, CO₃²⁻ and NO₃⁻ 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.

5.4.1 Experimental

5.4.1.1 Reagents employed

Aliquat-336 (tricaprylylmethylammonium chloride) Sigma Aldrich Make, USA, Poly Vinyl Chloride (PVC), Fluka Make, High Purity Ga Metal (99.99%), Spectroscopy grade high purity graphite rod, A.R. Grade Tetrahydro furan (THF), A.R. Grade Nitric acid, A.R. Grade Hydrochloric acid, A.R. Grade anhydrous Lithium chloride were used. Double distilled water was used for preparation of all standard gallium solutions.

5.4.1.2 Instruments used

A 4-Star ion meter (Orion Make) and double junction reference electrode (DJRE) (M/s. pH Products Company, Hyderabad) were used for emf measurement. The secondary salt bridge solution in DJRE was 5.5M LiCl and 0.5M HCl. Magnetic Stirrer is used for stirring purpose.

5.4.1.3 Preparation of Ga stock solution

Stock solution of Gallium in 7M HCl was prepared by dissolving 99.99% pure gallium metal in a mixture of concentrated HCl and HNO₃ and the nitrate was

evaporated almost to dryness using conc. hydrochloric acid. The residue gallium chloride in the form of $GaCl_4^-$ was then dissolved in 7M HCl and made up to a known concentration.

5.4.1.4 Loading of Aliquat 336 with Gallium

About 2-3 ml Aliquat 336 (in chloride form) was equilibrated with 5 ml of Gallium Stock solution. The mixture was stirred on a magnetic stirrer for about 5 hours and allowed to settle overnight. The organic phase containing Aliquat 336 loaded with $GaCl_4^-$ was separated and used for preparation of ion selective electrodes using spectroscopy pure graphite rod. The amount of gallium loaded on Aliquat-336 was ~300mg/ml.

5.4.1.5 Construction of Electrode

Coated graphite gallium ion selective electrode was prepared using the technique as reported in the literature. The spectroscopic grade high purity graphite rod (5 mm OD and 100 mm length) was taken and the central portion of the rod was encapsulated in a glass tube such that one end of the electrode could be used for membrane coating and the other end for emf measurements. The membrane coating methodology consisted of mixing required weighed amounts of the Aliquat 336 loaded with GaCl⁴ and PVC in the suitable amount of solvent namely Tetrahydrofuran (THF). One end of the graphite rod was repeatedly dipped into this mixture until a uniform, adhesive coating was obtained on the graphite rod. The electrodes were then dried in air for 48 hours. Gallium ion selective electrodes having different membrane composition i.e. with Aliquat 336: PVC in the ratio of 80:20, 70:30 and 60:40 were prepared for optimizing the electrode composition. The coated graphite gallium ion selective electrode was conditioned at least for one hour in 10⁻

¹M Gallium solution prior to analysis.

Using Aliquat 336 in the present work, gallium chloride anions are extracted according to the following exchange reaction:

$$4R_{3}N+CH_{3}Cl(org) + GaCl_{4}^{-}(aq) \rightarrow (R_{3}NCH_{3}) 4GaCl_{4}(org) + 4Cl^{-}(aq) \qquad 5.1$$

5.4.1.6 Preparation of Standard Solutions

Gallium standard solutions of different concentration in the range of 10⁻¹M to 10⁻⁶M were prepared from the original stock of Ga solution in mixture containing varying concentration of LiCl and HCl.

5.4.1.7 EMF Measurements

To measure the potential of the standard/test solution, about 10 ml of Ga sample solution was taken in a beaker. Ga ion selective electrode and double junction reference electrode were dipped in the solution and EMF of the cell was measured using 4-star Orion ion meter. Care was taken that during all the measurements entire coated part of the electrode was immersed in the solution. The solution was continuously stirred before the measurement was done. This Gallium ion selective electrode was conditioned by soaking in 1x10⁻¹ M Ga solution prior to use. The salt bridge solution namely saturated KCl (primary junction) and 5.5M LiCl+0.5M HCl mixture (secondary junction) were regularly changed in the reference electrode before emf measurements.

5.4.2 Results and Discussion

5.4.2.1 Calibration Curve for Coated Graphite Ga-ISE

Figure 5.1 shows the calibration curve of coated graphite gallium ion selective electrode. It was shown that the electrode was responding satisfactorily to the

gallium standard solutions in the range from 1×10^{-4} M to 1×10^{-1} M. The response behavior of the electrode was found not to change significantly with time, which would not affect the analytical results when fresh calibration is employed for measurements. Hence it can be seen that this electrode can be used with fair amount of reproducibility.



Figure 5.1 Calibration Curve of Coated Graphite Ga-ISE

5.4.2.2 Optimization of Electrode Composition

Figure 5.2 shows the responses of gallium ion selective electrodes in different ratios of Aliquat 336 loaded with $GaCl_4^-$ and PVC viz. 80:20, 70:30 and 60:40. It can be seen that the gallium ion selective electrode in the ratio of 70:30 gave better slope (S= -58.2) than the other compositions viz. 80:20 (S= -56.6); 60:40 (S= -55.5) and hence the composition 70:30 was employed for all the subsequent studies. The ratio of 90:10 did not yield a suitable membrane for

studies and the ratio of 50:50 was found to be giving unstable reading during emf measurements and hence was not employed in this study.



Figure 5.2 Optimization of electrode composition using

GaCl₄⁻ loaded Aliquat 336 and PVC

5.4.2.3 Optimization of the Electrolyte Composition for Coated Graphite Ga-ISE

It was necessary to control the chloride concentration in the electrolyte (i.e. LiCl+HCl mixture) for standards as well as samples in order to have uniform ionic strength and to keep the fraction of gallium anionic complexes at constant value. Chloride ion concentration could be maintained either by using only HCl or solution of highly soluble chloride salt (namely LiCl) or by their mixture. **Figure 5.3** shows the study of various electrolyte composition viz., LiCl, HCl or mixture of LiCl+HCl (i.e. total chloride concentration 5M, 6M or 7M).



Figure 5.3 Study of Electrolyte Composition using LiCl or HCl or mixture of LiCl+HCl (Cl⁻ Conc.: 5M, 6M, 7M)

Figure 5.4 shows the experiments carried out by using either only HCl or only LiCl solution to maintain chloride concentration to 7M but gave inconsistent results even after maintaining the secondary salt bridge solution as pure HCl and pure LiCl. Nernstian Slope (S) was not satisfactory as the curve was not linear in both the cases which ruled out the use of either HCl or LiCl at 7M as an electrolyte for Ga-standards and samples.



Figure 5.4 Calibration Curve at Chloride Concentration 7M (HCl or LiCL)

Similar studies were carried out by using mixture of LiCl and HCl at varying compositions viz., at 5M, 6M and 7M (**Figure 5.5 & 5.6**). Best results were obtained using 5.5 M LiCl+0.5 HCl and all measurements were carried out using gallium standards and unknown samples in this electrolyte. Though the slope (S) of the electrode were found to be near Nernstian at chloride concentration using LiCl+HCl (6.5M+0.5M [S= -55]; 5.9M+0.1M [S= -54.3]; 5M+1M [S= -54.7] and 4.5M+0.5M [S= -54.3];), it was optimized to use the gallium electrode at chloride concentration using LiCl+HCl at (5.5M+0.5M) as the slope [S= -58.2] was found to be very much satisfactory.



Figure 5.5 Calibration Curve at Chloride Concentration 7M (LiCl+HCl)



Figure 5.6 Calibration Curve at Chloride Concentration 6M / 5M (LiCl+HCl)

5.4.2.4 Potentiometric Selectivity

The influence of interfering ions on the response behavior of ion selective electrodes is usually described in terms of selectivity coefficients. The selectivity coefficients for gallium with respect to variety of interfering ions were described by matched potential method (MPM). In this method, 5 mL of 1 x 10⁻⁴M Ga in 0.5M HCl+5.5M LiCl was taken in a beaker and its potential was measured using gallium ion selective electrode. The potential was then slowly varied in small increments (~5 mV) by addition of standard gallium solution $(1 \times 10^{-2} \text{M})$. After every addition, the stabilized potential was recorded and corresponding increase in gallium concentration (Δa_A) was calculated. In the second set of experiments, potential of 5 mL of 1x10⁻⁴M gallium in 0.5M HCl+5.5M LiCl was varied in similar increments by addition of standard solution of impurity ion (a_B) prepared in 0.1M H⁺+6M Cl⁻. Concentration of gallium ion throughout the impurity ion addition was adjusted to 1x10⁻⁴M by adding required amount of gallium solution of known concentration. From the increase in concentrations of gallium ion Aa_A and concentration of impurity ion (a_B) required to carry out the same change in potential, selectivity coefficients were calculated as follows:

Selectivity Coefficient = $\Delta a_A / a_B$ 5.1

where A is gallium ion; B is impurity ion Δa_A = Increase in concentration of gallium ion to get certain change in potential; a_B = Concentration of impurity ion required to get the same change in potential.

5.4.2.5 Interference Studies due to Cationic Impurities

Interference in presence of Na^+ , K^+ , Ca^{2+} , Ba^{2+} , Mg^{2+} , Fe^{3+} , Cr^{3+} , Ni^{3+} , Th^{4+} and U(VI) ions on the potential measurement of gallium solution using coated graphite gallium ion selective electrode of a typical membrane composition of 70% Aliquat-336 loaded with GaCl₄, 30% PVC was investigated by adopting matched potential method. The potential of the solution containing constant initial concentration (1x10⁻⁴M) of primary ion i.e. Gallium, was varied by about 30 mV in four to five increments either by adding gallium standard solution or impurity ion solution prepared in 6M Cl⁻. The selectivity coefficient obtained from these studies is summarized in **Table 5.1**. The results clearly showed that the impurity ions studied have negligible interference in gallium measurement.

S.No.	Impurity ion	Selectivity Coefficient
1	Na(I)	2.26×10^{-3}
2	K(I)	3.18 x 10 ⁻³
3	Ca(II)	4.75 x 10 ⁻⁴
4	Ba(II)	2.31 x 10 ⁻³
5	Mg(II)	3.23 x 10 ⁻³
6	Fe(III)	3.86 x 10 ⁻²
7	Cr(III)	1.43 x 10 ⁻²
8	Ni(III)	4.52×10^{-3}
9	Th(IV)	2.47 x 10 ⁻³
10	U(VI)	2.73 x 10 ⁻²

Table 5.1 Selectivity coefficient of cationic impurities using coated wire Gallium ISE

5.4.2.6 Interference due to Anionic Impurities

Since the present work involves measurement of anionic complex of gallium, the presence of various anionic impurities viz., OH^{-} , CO_{3}^{2-} , NO_{3}^{-} ions were also investigated. It was observed that there was no significant interference due to the presence of above anionic impurities during the determination of gallium. The results are tabulated in **Table 5.2**.

Table 5.2 Selectivity coefficient of anionic impurities using coated wire Gallium ISE

S.No.	Impurity ion	Selectivity Coefficient
1	OH	2.83 x 10 ⁻³
2	CO ₃ ²⁻	4.32 x 10 ⁻³
3	NO ₃ ⁻	3.89 x 10 ⁻³

5.4.2.7 Response of Ga-ISE

The response time is an important factor for any ion selective electrode. Thus, in the case of all electrodes, the average response time required for the electrodes to reach a potential response within $\pm 1 \text{ mV}$ of final equilibrium values after successive immersion in a series of solutions each having a 10-fold difference in concentration was measured. In this study, the practical response time was recorded by changing solutions with different low-to-high gallium concentration. The measurement sequence was from the lower (1x10⁻⁴M) to the higher (1x10⁻³M) concentration. Characteristic performance of coated graphite gallium ion selective electrode was shown in **Table 5.3**.

Table 5.3 Response characteristics of the coated graphite

11.	•	1 . •	1	. 1
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Properties	Values / range
Optimized Membrane Composition	Aliquat 336 loaded with GaCl ₄ ⁻ : PVC (70:30)
Electrode type	Coated graphite Gallium ion selective electrode
Electrolyte medium (6M Cl ⁻)	5.5M LiCl+0.5M HCl for all standards and samples
Conditioning time	One hour prior to use
Linear range (M)	$1 \times 10^{-4} - 1 \times 10^{-1}$
Slope (mV/decade)	-58.2 ± 1.0
Detection Limit	$2.0 \times 10^{-5} M$
Response time	< 100 seconds

5.4.2.8 Life Time of Ga-ISE

The gallium ion selective electrode was calibrated almost every day and it can be seen from the **Figure 5.7** that the gallium ion selective electrode could be conveniently used for consecutive three months without losing their Nernstian response. Later to that period, the response of the electrodes deteriorated and the behavior deviated more from the Nernstian slope. Drift in the value of E^0 was observed over time, but the overall drift in E^0 value was found to be less than 5% and this could be attributed to the following reasons: (i) by nonuniform coating of membrane on graphite rod (ii) deterioration of membrane due to aging of the PVC matrix etc. It was found that the drift in E° could be improved by conditioning of gallium ion selective electrode before analysis overnight.



Figure 5.7 Lifetime of Ga-ISE

5.4.2.9 Analytical Application of Ga-ISE

Coated Graphite ion selective electrode can be conveniently used for the determination of gallium in standard reference material for nickel - BCS-CRM 346 Nickel Alloy IN 100 wherein the certified value of Gallium is 50.6 ppm (Table 5.4) and for BCS-CRM 345 Nickel Alloy IN 100 the specification of Ga is 8.2 ppm. This Gallium ion selective electrode can be used to determine gallium in presence of plutonium in Pu-Ga alloy without separation of plutonium from gallium by reducing Pu (IV) to Pu (III) using ascorbic acid.

 Table 5.4
 Determination of Gallium in standard reference material for nickel

	Coated Graphite (*)	Expected
Sample	Gallium ISE (µg/ml)	(µg /ml)
BCS-CRM 346 Nickel		
Alloy IN 100	49.7±0.99	50.60±1.01

BCS-CRM 346 Nickel Alloy IN 100

[(*) Results based on triplicate measurements]

5.4.3 Storage of Coated Graphite Ga-ISE

The advantage of coated graphite gallium ion selective electrode is such that it can be stored in air unlike other liquid membrane based electrodes which needs to be stored in respective standard solution.

5.4.4 Conclusion

The above studies revealed that coated graphite rod Ga-ISE exhibits linear Nernstian response over gallium concentration range of 1 x 10^{-4} M - 1 x 10^{-1} M of Ga(III) ions in constant chloride concentration of 6M with a calibration slope of -58.2mV \pm 1.0 mV/decade change in concentration of Ga.

Summary

Potentiometry involving ion selective electrodes 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 cater an important role in the chemical characterization of the nuclear fuel materials and which can be employed for the quantitative determination of various elements viz. (i) determination of lithium by either by titrimetry or coated Li-ISE for ITER process, (ii) determination of uranium in sintered UO₂ and (U,Th)O₂ with respect to third generation of nuclear fuel viz. AHWR using U-ISE, (iii) development of method for the determination of gallium in pure metal samples or alloy such as Pu-Ga samples.

- 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. The ISE methodology developed in the work is fast and precise and can be employed on a routine basis for lithium determination in solutions containing organic constituents. The results from the experiments demonstrate the usefulness of the present method. These studies would be highly useful in the optimization of the washing parameters in sol-gel process for obtaining phase pure lithium titanate pebbles. In addition to maintaining the stoichiometry, the investigations would also be helpful to reduce the loss of enriched Li⁶. This is desirable due to the high cost of enriched Li⁶ as well as the strategic importance of this isotope.
- 2. Coated wire Lithium ion selective electrode was developed for the purpose of

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determining lithium in the organic matrix after suitable treatment of the sample during the preparation of lithium meta titanate (Li₂TiO₃) microspheres. The results obtained from the experiments based on indigenously developed Li-ISE demonstrate the usefulness of the coated wire Li-ISE for the determination of lithium in complex chemical mixture containing various organic materials and solvent. As explained above, 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 rapid and precise and can be employed on a routine basis for lithium determination in solutions containing organic constituents.

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. This indigenously developed coated graphite uranyl ion selective electrode exhibits linear Nernstian response over uranyl concentration range of 1×10^{-4} M - 1×10^{-1} M in constant chloride concentration of 6M obtained from 5.9M LiCl+0.1M HCl with a slope of -29.2±1.0 mV/concentration decade and a detection limit of 5 x 10⁻⁵M for the Aliquat 336 loaded UO₂Cl₄²⁻ and PVC composition in the ratio of 70:30. The life time of the electrode was found to be four months with consistent use. The response time during the emf measurement was about less than 2 minutes for uranium standards in the range from 1×10^{-5} - 1×10^{-4} M and less than 30 seconds for the uranium standards in the range of 1×10^{-3} M to 1×10^{-1} M. This coated graphite uranyl ion selective electrode was successfully employed for the online determination of uranium

in sintered UO_2 samples as well as synthetic (U,Th) O_2 samples. The technique is highly attractive due to the fact that simple instrumentation and was also cost effective.

4. Coated graphite gallium ion selective electrode was developed and the performance of the electrode was checked. This indigenously developed coated graphite Ga-ISE exhibits linear Nernstian response over gallium concentration range of 1 x 10^{-1} M-1 x 10^{-4} M of Ga(III) ions in constant chloride concentration of 6M with a calibration slope of -58.2mV \pm 1.0 mV/decade change in concentration of Ga. This Ga-ISE can be adopted for the determination of gallium in Pu-Ga samples without separating the Pu matrix.

The following Table summarizes the method developed for elements viz., Li, U and Ga and their applicability in nuclear field along with performance of the method.

Element /	Method	Remarks
Applicability	5	
Lithium for	By titrimetry	Li $: 1 - 3 \text{ mg}$
ITER process	using NH ₄ F	Accuracy : Better than 0.5%
Lithium for	By coated Li-ISE	Optimized Membrane Composition :
ITER process		Lithium ionophore (VI) loaded with 5M LiCl, 2-
		nitrophenyl octyl ether (NPOE) as plasticizer and
		potassium tetrakis(p-chlorophenyl)borate
		(KTpClPB) as an additive : PVC (70:30)
		Linear range (M) $: 1x10^{-4} - 1x10^{-1}$
		Detection Limit $: 3.0 \times 10^{-5} M$
		Slope (mV/decade) : 58.5 ± 1.0
		Accuracy : better than 2%
Uranium for	By coated U-ISE	Optimized Membrane Composition :
sintered UO ₂ &	Aliquat 336 loaded with $UO_2Cl_4^{2-}$: PVC	
AHWR		Linear range (M) : $1x10^{-4} - 1x10^{-1}$
samples		Detection Limit $: 5.0 \times 10^{-5} M$
$(U,Th)O_2$		Slope (mV/decade) : -29.2 ± 1.0
		Accuracy : better than 2%
Gallium for	By Ga-ISE	Optimized Membrane Composition :
pure metallic Aliquat 3		Aliquat 336 loaded with $GaCl_4^-$: PVC (70:30)
sample and		Linear range (M) $: 1x10^{-4} - 1x10^{-1}$
alloy (Pu-Ga		Detection Limit $: 2.0 \times 10^{-5} M$
alloy)		Slope (mV/decade) : -58.2 ± 1.0
		Accuracy : better than 2%

References

- [1] M. Cremer, Electromotoric properties of textures, Z. Biol., 29 (1906) 562.
- [2] G. Eisenmann, D.O. Rudin and J.V. Casby, Glass electrode for measuring sodium ion, Science, 126 (1957) 831.
- [3] H.J.C. Tandeloo, A new and easy method for the potentiometric determination of calcium concentrations in solutions, J. Biol. Chem., 113 (1936) 333.
- [4] R.S.Anderson, The attempted use of crystals as calcium electrodes J. boil. Chem., 115 (1936) 323.
- [5] I.M. Kolthoff and H.L. Sanders, Electric Potentials at Crystal Surfaces, and at Silver Halide Surfaces in Particular, J. Amer.Chem.Soc., 59 (1937) 416.
- [6] E. Pungor and E. Hollos Rokosinyi, Application of membrane electrodes for the assay of ion concentrations, Acta Chim. Acad.Sci. Hung., 27 (1961) 63.
- [7] M.S. Frant and J.W. Ross, Electrode for sensing fluoride ion activity in solution, Science, 154 (1966) 1553.
- [8] L.A.R. Pioda. V. Stankova and W. Simon, Highly Selective Potassium Ion Responsive Liquid-Membrane Electrode, Anal. Lett., 2 (1969) 665.
- [9] D. Ammann, R. Bissig, M. Guggi, E. Pretsch, W. Simon, I.J. Borowitz, L. Weiss, Preparation of Neutral Ionophores for Alkali and Alkaline Earth Metal Cations and their application in ion selective membrane electrodes, Helv. Chim. Acta, 58 (1975) 1535.
- [10] P. Anker, E. Wieland, D. Ammann, R.E. Dohner, R. Asper, W. Simon, Neutral carrier based ion-selective electrode for the determination of total calcium in blood serum, Anal. Chem., 53 (1981) 1970.
- [11] W.E. Morf, W. Simon, Abschätzung der Alkali- und Erdalkali-Ionenselektivität von elektrisch neutralen träger-antibiotica (carrier-antibiotica) and

modellverbindungen,

Helv. Chim. Acta, 54 (1971) 2683.

- [12] J.L. Mcnay, P.G. Dayton, Potassium ion specific electrode with high selectivity for potasdsium over sodium, Science, 167 (1970) 987.
- [13] A. Shatkay, Ion specific membranes as electrodes in determination of activity of calcium, Anal. Chem., 39 (1967) 1056.
- [14] U. Fiedler, J. Ruzicka, Selectrode-The universal ion-selective electrode : Part VII. A valinomycin-based potassium electrode with nonporous polymer membrane and solid-state inner reference system, Anal. Chim. Acta, 67 (1973) 179.
- [15] G. Horvai, E. Graf, K. Toth, E. Pungor, R.P. Buck, Plasticized poly(vinyl chloride) properties and characteristics of valinomycin electrodes. 1. High-frequency resistances and dielectric properties, Anal.Chem., 58 (1986) 2735.
- [16] A.P. Thoma, A.V. Nauer, S. Arvanitis, W.E. Morf, W. Simon, Mechanism of neutral carrier mediated ion transport through ion-selective bulk membranes, Anal. Chem., 49 (1977) 1567.
- [17] E. Lindner, E. Graf, Z. Nigreisz, K. Toth, E. Pungor, R.P. Buck, Responses of site-controlled, plasticized membrane electrodes, Anal. Chem., 60 (1988) 295.
- [18] S.C. Ma, M.E. Meyerhoff, Membrane receptors for the IgG_4 subclass on human basophils and mast cells, Mikrochim. Acta, 1 (1990) 197.
- [19] E. Lindner, V.V. Cosofret, S. Ufer, R.P. Buck, W.J. Kao, M.R. Neuman, J.M. Anderson, Ion-selective membranes with low plasticizer content: Electroanalytical characterization and biocompatibility studies, J.of Biomed. Mater. Res., 28 (1994) 591.
- [20] V.J. Wotring, P.K. Prince, L.G. Bachas, Evaluation of poly(vinylidene

chloride) as a matrix for polymer membrane ion-selective electrodes, Analyst, 116 (1991) 581.

- [21] D.N. Reinhoudt, J.F.J. Engbersen, Z. Brozka, V. vanden, G.W.N. Honig,
 H.A.J. Holterman, U.H. Verkerk, Development of Durable K⁺-Selective
 Chemically Modified Field Effect Transistors with Functionalized
 Polysiloxane Membranes, Anal. Chem., 66 (1994) 3618.
- [22] W.E. Morf, The Principles of Ion-Selective Electrodes and of Membrane Transport; Elsevier: New York, 1981.
- [23] T. Theorell, An Attempt to Formulate a Quantitative Theory of Membrane Permeability Proc. Soc. Exp. Biol. Med., 33 (1935) 282.
- [24] K.H. Meyer, J.F. Sievers, La perméabilité des membranes I. Théorie de la perméabilité ionique, Helv. Chim. Acta, 19 (1936) 649.
- [25] E. Pungor, Working mechanism of ion selective electrodes, Pure Appl. Chem.,64 (1992) 503.
- [26] W.E. Morf, W. Simon, Cation-Response Mechanism of Neutral Carrier Based Ion-Selective Electrode Membranes, Helv. Chim. Acta, 69 (1986) 1120.
- [27] H. Sigel, A. D. Zuberbuhler, O. Yamauchi, Comments on potentiometric pH titrations and the relationship between pH-meter reading and hydrogen ion concentration, Anal. Chim. Acta, 255 (1991) 63.
- [28] E. Bakker, M. Nagele, U. Schaller, E. Pretsch, Applicability of the phase boundary potential model to the mechanistic understanding of solvent polymeric membrane-based ion-selective electrodes, Electroanalysis, 7 (1995) 817.
- [29] K. Tohda, Y. Umezawa, S. Yoshiyagawa, S. Hashimoto, M. Kawasaki, Cation Permselectivity at the Phase Boundary of Ionophore-Incorporated Solvent

Polymeric Membranes As Studied by Optical Second Harmonic Generation, Anal. Chem., 67 (1995) 570.

- [30] G.G. Guilbault, R.A. Durst, M.S. Frant, H. Freiser, E.H. Hansen, T.S. Light, E. Pungor; G. Rechnitz, N.M. Rice, T.J. Rohm, W. Simon, J.D.R. Thomas, IUPAC Technical Reports and Recommendations, Pure Appl. Chem., 48 (1976) 127.
- [31] Y. Umezawa (Ed.), "Handbook of Zon-Selective Electrodes: Selectivity Coefficients", CRC Press Inc., Boca Raton, FL (1990).
- [32] G.J. Moody, R.B. Oke and J.D.R. Thomas, A calcium-sensitive electrode based on a liquid ion exchanger in a poly(vinyl chloride) matrix, Analyst, 95 (1970) 910.
- [33] G.J.Moody and J.D.R. Thomas, Selectivity ratios/coefficients of selective ion sensitive electrodes, Talanta, 18 (1971) 1251.
- [34] C.J.Coetzee and H. Freiser, Liquid-liquid membrane electrodes based on ionassociation extraction systems, Anal. Chem., 41 (1969) 1128.
- [35] A.C. Wilson and K.H. Pool, An improved ion-selective electrode for perchlorate, Talanta, 23 (1976) 387.
- [36] A. Hulanicki and Z. Augustowska, Selectivity coefficient changes for liquidmembrane electrodes, Anal. Chim. Acta, 78 (1975) 261.
- [37] J. B. Harrel, A. D. Jones and G. R. Choppin, Liquid ion-exchange membrane electrode for polyvalent cations, Anal. Chem., 41 (1969) 1459.
- [38] P. Buhlmann, S. Yajima, K. Tohda, K. Umezawa, S. Nishizawa, Y. Umezawa, Studies on the phase boundaries and the significance of ionic sites of liquid membrane ion-selective electrodes, Electroanalysis, 7 (1995) 811.
- [39] W.E. Morf, G. Kahr, W. Simon, Reduction of the Anion Interference in Neutral

Carrier Liquid-Membrane Electrodes Responsive to Cations, Anal. Lett. 7 (1974) 9.

- [40] R.P. Buck, E. Lindner, Recommendations for nomenclature of ionselective electrodes (IUPAC Recommendations 1994), Pure Appl. Chem., 66 (1994) 2527.
- [41] C.W. Outhwaite, The linear extension of the Debye-Hückel theory of electrolyte solutions, Chemical Physics Letters, 5 (1970) 77.
- [42] J. Kielland, Individual Activity Coefficients of Ions in Aqueous Solutions, J.Amer.Chem.Soc., 59 (1937) 1675.
- [43] S. Kamata, A. Bhale, Y. Fukunage, A. Murata, Copper (II) selective electrode using thiuram disulfide neutral carriers, Anal. Chem. 60 (1988) 2464.
- [44] P. Henderson, Z. physik. Chem., 59 (1907) 118.
- [45] G. Wilczek-vera, E. Rodil, J.H. Vera, On the Activity of Ions and the Junction Potential. Revised Values for All Data, AIChE J., 50 (2004) 445.
- [46] C.E. Johnson, Tritium behavior in lithium ceramics, J. Nuclear Mat., 270 (1999) 212.
- [47] C.E. Johnson, G.W. Hollenberg, N. Roux and H. Watanabe, Current experimental activities for solid breeder development, Fusion Eng. Des. 8 (1989) 145.
- [48] P.A. Finn, K. Kurasawa, S. Nasu, K. Noda, T. Takahashi, H. Takeshita, T. Tanifuji and H. Watanabe, Proceedings of the 9th IEEE Symposium on Engineering Problems of Fusion Research, 2 (1981) 1200.
- [49] N. Roux, G. Hollenberg, C. Johnson, K. Noda and R. Verrall, Summary of experimental results for ceramic breeder materials, Fusion Eng. Des., 27 (1995) 154.

- [50] J.D. Lulewicz and N. Roux, First results of the investigation of Li₂ZrO₃ and Li₂TiO₃ pebbles, Fusion Eng. Des., 39–40 (1998) 745.
- [51] C. Alvani, S. Casadio, V. Contini, A. Di Bartolomeo, J.D. Lulewicz and N. Roux, Li₂TiO₃ pebbles reprocessing, recovery of Li⁶ as Li₂CO₃, J. Nucl. Mater., 307–311 (2002) 837.
- [52] J.P. Kopasz, J.M. Miller and C.E. Johnson, Tritium release from lithium titanate, a low-activation tritium breeding material, J. Nucl. Mater., 212–215 (1994) 927.
- [53] N. Roux, J. Avon, A. Floreancing, J. Mougin, B. Rasneur and S. Ravel, Lowtemperature tritium releasing ceramics as potential materials for the ITER breeding blanket, J. Nucl. Mater., 233–237 (1996) 1431.
- [54] C.H. Jung, J.Y. Park, S.J. Oh, H.K. Park, Y.S. Kim, D.K. Kim and J.H. Kim, Synthesis of Li₂TiO₃ ceramic breeder powders by the combustion process, J. Nucl. Mater., 253 (1998) 203.
- [55] O. Renoult, J.P. Boilot, J.P. Korb and M. Boncoeur, Lithium sol-gel ceramics for tritium breeding applications, J. Nucl. Mater., 223 (1995) 126.
- [56] O. Renoult, J.P. Boilot and M.J. Boncoeur, Alkoxide–Hydroxide route for the preparation of γ-LiAlO₂-based ceramics, J. Am. Ceram. Soc., 77 (1994) 249.
- [57] V.N. Vaidya, S.K. Mukerjee, J.K. Joshi, R.V. Kamat, D.D. Sood, A study of chemical parameters of the internal gelation based sol-gel process for uranium dioxide, J. Nucl. Mater., 148 (1987) 324.
- [58] S. Suryanarayana, N. Kumar, Y.R. Bamankar, V.N. Vaidya, D.D. Sood, Fabrication of UO₂ pellets by gel pelletization technique without addition of carbon as pore former, J. Nucl. Mater., 230 (1996) 140.

- [59] Ashok Kumar, T.V. Vittal Rao, S.K. Mukerjee, V.N. Vaidya, Recycling of chemicals from alkaline waste generated during preparation of UO₃ microspheres by sol–gel process, J.Nucl. Mater., 350 (2006) 254.
- [60] M.S.Y. Haddadin, S. Khattari D. Caretto, and R.K. Robinson, Potential intake of lithium by the inhabitants of different regions in Jordan, Pak. J. Nutrition, 1 (2002) 39.
- [61] M. Taddia and M. Mattioli, Inorg. Chim. Acta, 360 (2007) 1226.
- [62] C.B. Stubblefield and R.O. Ricardo, J. Chem. Eng. Data, 17 (1972) 491.
- [63] B.P. Datta, P.S. Khodade, A.R. Parab, A.H. Goyal, S.A. Chitambar and H.C. Jain, Int. J. Mass Spectrom. Ion Processes, 116 (1992) 87.
- [64] Robert Y. Xie and Gary D. Christian, Anal. Chem., 58(8) (1986) 1807.
- [65] Jun Ho Sim, Kyoung Moon Lee, Joung Su Lee, Dong Hoe Cho, Hakhyun Nam, and Geun Sig Cha, Lithium ion-Selective electrode with improved lifetime, Bull. Korean Chem. Soc., 22(7) (2001) 765.
- [66] Anthony Okorodudu, Robert W. Burnett, Robert B. McComb, and George N. Bowers, Jr., Evaluation of three first-generation ion-selective electrode analyzers for lithium, Clin. Chem., 36(1) (1990) 104.
- [67] You Ra Kang, Kyoung Moon Lee, Hakhyun Nam, Geun Sig Cha, Sung Ouk Jung and Jae Sang Kim, Lithium ion-selective electrodes employing tetrahydrofuran-based 16-Crown-4 derivatives as neutral carriers, Analyst, 122 (1997) 1445.
- [68] Victor P. Y. Gadzekpo, James M. Hungerford, Azza M. Kadry, Yehia A. Ibrahim, and Gary D. Christian Lipophilic lithium ion carrier in a lithium ion selective electrode, Anal. Chem., 57 (1985) 493.

- [69] Roger L Bertholf, M. Geraldine Savory, Kathy Winbome, Judy C. Hundley, George M. Plummer and John Savory, Lithium determined in serum with an ion-selective electrode, Clin. Chem., 34(7) (1988) 1500.
- [70] M.M. Jonas, F.E. Kelly, R.A.F. Linton, D.M. Band, T.K. O'Brien, N.W.F. Linton, J.Clin. Monitoring and Computing, 15 (1999) 525.
- [71] R. Govindan, D. Alamelu, Raju V. Shah, T.V. Vittal Rao, Y.R. Bamankar, A.R. Parab, K. Sasi Bhushan, S.K. Mukerjee and S.K. Aggarwal, Determination of lithium by potentiometry using fluoride ion selective Electrode, Anal. Methods, 2 (2010) 1752.
- [72] G. Horvai, The matched potential method, a generic approach to characterize the differential selectivity of chemical sensors, Sensors and Actuators, B 43 (1997) 94.
- [73] V.P.Y. Gadzekpo, G. Christian, Determination of selectivity coefficients of ion selective electrodes by a matched-potential method, Anal Chim Acta, 164 (1984) 279.
- [74] Yoshio Umezawa, Kayoko Umezawa and Hitoshi Sato, Selectivity coefficients for ion-selective electrodes-recommended methods for reporting $K_{A,B}^{pot}$ values. Pure Appl Chem, 67 (1995) 507.
- [75] M.V. Ramaniah, Pure and Appl. Chem., Vol. 54, No.4 (1982) 889.
- [76] M.V. Ramaniah, P.R. Natarajan and P. Venkataramana, Radiochimica Acta, 22 (1975) 199.
- [77] C. Ganguly, P.V. Hegde, G.C. Jain, U. Basak, R.S. Mehrotra, S. Majumdar and P.R. Roy, Nuclear Technology, 72 (1986) 59.
- [78] C.J. Rodden, "Analysis of Essential Nuclear Materials", USAEC Division of Technical Information (1964).

- [79] C.J. Rodden, , "The Analytical Chemistry of the Manhattan Project, McGraw Hill Co., New York (1950).
- [80] Selected Measurement Methods for Plutonium and Uranium in Nuclear Fuel Cycle, R.J. Jones (Ed), USAEC Report, TID 7029 (1963).
- [81] Annual Book of ASTM Standards, Part 45, C 696 (1975) 176.
- [82] Annual Book of ASTM Standards, Vol. 12.01, C 698 (1985) 7 .
- [83] Selected Measurement Methods for Plutonium and Uranium in Nuclear FuelCycle, C.J. Rodden (Ed), 2nd Edn, USAEC Report, TID 7029 (1972).
- [84] V.K. Markov, Proc. IAEA Progress in Safeguards Techniques, Karlsruhe, Vol. II (1970) 3; Eng. Trans. USAEC Report LA-Tr-71-24 (1970).
- [85] G.W.C. Milner, G. Philips and A.J. Füde, Chemical analysis of Ceramic materials containing Uranium and Plutonium arising from the development of Nuclear fuels, Talanta, 15 (1968) 1241.
- [86] C.W. Sill, and H.E. Peterson, Anal. Chem. 24, (1952) 1175.
- [87] H. Kramer, USAEC Report NBL-159 (1955) 28.
- [88] L.H. Baetsle and A.C. Demildt, Analyst, 83 (1958) 23.
- [89] C.R. Walker and O.A. Vita, Anal. Chim. Acta, 49 (1970) 391.
- [90] V. Mareska, Microtitrimetric determination of uranium in HNO₃ in presence of excess iron, magnesium and aluminium, Talanta, 19 (1972) 212.
- [91] W. Davies and W. Gray, A Rapid and Specific Titrimetric Method for the Precise Determination of Uranium using Fe(II) Sulphate as Reductant, Talanta, 11 (1964) 1203.
- [92] A.R. Eberle, M.W. Lerner, C.G. Goldbeck and C.J. Rodden, Titrimetric determination of uranium in products, fuel and scrap materials after ferrous ion reduction in phosphoric acid, USAEC Report, NBL – 252 (1970).

- [93] Mary John, S. Vaidyanathan, P. Venkataramana and P.R. Natarajan, Anal–58, Convention of Chemists, Bangalore (1976).
- [94] R.T. Chitnis, R.T. Kulkarni, S.G. Rege and A. Mukherjee, J. Radioanal. Chem., 45 (1978) 331.
- [95] L. Pszonicki, Precise determination of Uranium in high purity uranium compounds – Reduction with Aluminium metal in presence of cadmium ions in conc. hydrochloric acid, Talanta, 13 (1966) 403.
- [96] J. Molinowski and G.B. Cook, Analyst, 83 (1958) 9.
- [97] C.L. Rao, G.M. Nair, N.P. Singh, M.V. Ramaniah and N. Srinivasan, Z. Anal. Chem., 234 (1971) 126.
- [98] G. Gopalarao, Seetarama Raju Sagi, A new reductimetric reagent: Iron(II) in a strong phosphoric acid medium, Talanta, 9 (1962) 715.
- [99] J. Cherry, UKAEA Report PG-R-827 (1968).
- [100] P.R. Nair, Mary Xavier, Keshav Chander and S.K. Aggarwal, "Recent Studies in Electroanalytical Methodologies for the Determination of Uranium", International Society of Electrochemistry, Kita Kyushu, Japan P–1 (1998).
- [101] P.H. Chadwick, and I.R. McGowan, Determination of Plutonium and Uranium in mixed oxide fuels by sequential redox titration, Talanta, 19 (1972) 1335.
- [102] J. Corpel, and F. Regnaud, Anal. Chim. Acta, 27 (1962) 36.
- [103] Lewis, K., Amperometric Determination of Uranium after reduction with Fe(II) in Phosphoric Acid, Report NBL–272.
- [104] Mary Xavier, "Biamperometry for the Characterization of Nuclear Fuel Materials", Invited talk, Workshop cum Seminar on Electro analytical Chemistry and Allied Topics (ELAC–2000) 131.
- [105] J.E. Harrar, A.J. Bard, Electroanalytical Chemistry, 8 (1975) 128.

- [106] Plock, C.E. and W.S. Polkinghorne, Talanta, 14, 1356 (1967).
- [107] G.W.C. Milner, A.J. Wood, G. Phillips and G.J. Weldrick, Z. Anal. Chem., 224 (1967) 346.
- [108] G.W.C. Milner, and G. Phillips, "Coulometry in Analytical Chemistry", Pergammon Press (1967) 19.
- [109] H.S. Sharma, Invited talk, Workshop cum Seminar on Electro analytical Chemistry and Allied Topics (ELAC – 2000)
- [110] C.J. Rodden, Private Communication, 1959.
- [111] N.H. Furman, and J.B. Heberling, USAEC, MDDC–1622 (1947).
- [112] F.S. Grimaldi, USAEC, AECD–1815 (1948).
- [113] N. Kano, Nippon Kagasu Zasshi, 43 (1922) 550.
- [114] R.C. Lopez, and L.E. Delgado, Anales fis. y. quim (Madrid) 38 (1942) 40.
- [115] C. Yoshimura, Nippon Kagasu Zasshi, 74 (1953) 448.
- [116] Saad S.M. Hassan, Mounir M. Ali, Amr M.Y. Attawiya, PVC membrane based potentiometric sensors for uranium determination, Talanta, 54 (2001) 1153.
- [117] Jayshree Ramkumar, B. Maiti, Nafion-coated uarnyl selective electrode based on calizarene and tri-n-octyl phosphine oxide, Sensors and Actuators, B 96 (2003) 527.
- [118] Freiser H. Coated Wire Ion Selective Electrodes, Principles and Practice,J. Chem Soc Faraday Trans., 1 82 (1986) 1217.
- [119] Cattrall R.W., Henry Freiser. Coated Wire Ion Selective Electrodes, Anal Chem, 43(13) (1971) 1905.
- [120] R.W. Cattrall Chin-Poh Pul, Coated Wire Ion Selective Electrode for the Determination of Iron (III), Anal Chem, 47 (1975) 93.

- [121] R.W. Cattrall, Chin-Poh Pul, A Coated-wire ion selective electrode responsive to chlorocuprate(II) ions, Anal Chim Acta, 83 (1976) 355.
- [122] R.W.Cattrall, Chin-Poh Pul, Coated Wire Ion Selective Electrode for the Determination of Mercury (II), Anal Chem, 48 (1976) 552.
- [123] R.W. Cattrall Chin-Poh Pul, A coated wire ion-selective electrode for the determination of Zn (II), Anal Chim Acta, 87(2) (1976) 419.
- [124] P.W. Alexander, P. Joseph Jose Selective potentiometric determination of Bi(III) with a coated wire electrode, Talanta, 28(12) (1981) 931.
- [125] R.W. Cattrall, G.L. Lee, I.C. Hamilton, Coated-wire ion selective electrodes responsive to chlorocobaltate (II) ions. Anal Chim Acta, 116(2) (1980) 391.
- [126] R.T. Chitnis, R.T. Kulkarni, S.G. Rege, A. Mukherjee, Volumetric method for the determination of uranium in the active process solutions. J. Radioanal and Nucl Chem, 45(2) (1978) 331.
- [127] P.K. Mohapatra, D.S. Lakshmi, D. Mohan, V.K. Manchanda, Uranium pertraction across a PTFE flatsheet membrane containing Aliquat 336 as the carrier, Separation and Purification Technology, 5 (2006) 24-30.
- [128] R.K. Sinha, A. Kakodkar, Design and development of the AHWR—the Indian thorium fuelled innovative nuclear reactor, Nucl Engg and Design, 236(7-8) (2006) 683.
- [129] Plutonium Handbook, A Guide to the Technology, O.J. Wick, Gordon and Breach, Science Publishers, New York, 1 (1967) 147.
- [130] Plutonium Handbook, ibid, p 36.
- [131] Plutonium Handbook, ibid, p 156.

- [132] Zygmunt Marczenko and Helena Kalowska, Sensitive Spectrophotometric Determination of Gallium with Eriochrome Cyanine R and Cetyltrimethylammonium ions, Mickrochimica Acta [Wien], 2 (1979) 507.
- [133] M.S. Gidwani, S.K. Menon, Y.K. Agrawal, React. Funct. Polym., 53 (2002)143.
- [134] H.F. Koch, L.A. Girard, D.M. Roundhill, At. Spectrosc., 20, (1999) 30.
- [135] M. Martin, F.X. Olivier, Anal. Chem., 70 (1998) 2639.
- [136] C.G.S. Queiroz, M.L. Guia, A.C. Magalh, Thermochim. Acta, 351 (2000) 33.
- [137] Hideji Tanaka, Akiko Mitani, Kensaku Okamoto, Hideyoshi Morita and Shigeru Shimomura, Determination of gallium by AAS using tantalum carbide-coated graphite tube, Nunseki Kagaku, 46(11) (1997) 875.
- [138] S. Puri, R.K. Dubey, M.K. Gupta, B.K. Puri, Anal. Lett., 31 (1998) 841.
- [139] Nobutaka Yoshikuni, Hiromi Takeno and Koichi Oguma, Preparation of Gallium ion selective electrode by use of anion-exchange resin and its application to chemical analysis of industrial materials Bunseki Kagaku Abstracts, 50(11) (2001) 753.
- [140] Sabry K. Mohamed, Anal. Chim. Acta, 562 (2006) 204.
- [141] T. Dupuis, and C. Duval, Anal. Chim. Acta, 3 (1949) 324.
- [142] W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, Applied Inorg. Analysis, 2nd ed., Wiley, New York, Chapter-30 (1953).
- [143] G. Rienäcker, and H.G. Jerschkewitz, 'Gallium" in W. Fresenius and G. Gander Handbuch der analytischen Chemie, 2nd ed., Springer-Verlag, Berlin, 3 (1956) 141.
- [144] H.H. Willard, and H.C. Fogg, J. Am. Chem. Soc., 59 (1937) 1197.

- [145] L. Gordon, M.L. Salutsky and H.H. Willard, Precipitation from homogenous solutions, Wiley, New York, (1959) 23.
- [146] L. Moser, and A. Brukl, Monatsh., 55 (1930) 14.
- [147] Ivanov-Emin, B.N. and E.A. Ostroumov, Zavodskaya Lab., 12 (1946) 674.
- [148] E.Z. Gastinger, Anal. Chem., 140 (1953) 244.
- [149] S. Ato, , Sci. Papers, Inst. Phys. Chem. Res., Tokyo (1930) 22.
- [150] S. Ato, ibid, 15 (1931) 289.
- [151] G.W.C. Milner, A.J. Wood and J.L. Woodhead, Analyst, 79 (1954) 272.
- [152] W. Geilmann and F.W. Wrigge, Z. Anorg. U. Allgem. Chem., 209 (1932) 129.
- [153] T. Moeller, and A.J. Cohen, Anal. Chem., 22 (1950) 686.
- [154] E. Gastinger, Z. Anal. Chem., 140 (1953) 252.
- [155] I.M. Kolthoff, P.J. Elving, Treatise on Anal. Chem., 2 (1962) 14.
- [156] E. Reichel, Z. Snal. Chem., 87 (1932) 321.
- [157] E. Reichel, Z. Snal. Chem., 89 (1932) 411.
- [158] A.I. Zelyanskaya, N.V. Bausova and L. Ya. Kukalo, Trudy Inst. Metallurg. Ural'sk. Fil. Akad. Nauk, SSSR, Analyt. Abstr. 6 (1959) 3906.
- [159] E.N. Vinogradova, and N.N. Chudinova, Zavodskaya Lab., 22 (1956) 1280.
- [160] H. Onishi, and E.B. Sandell, Anal. Chim. Acta, 13 (1955) 159.
- [161] F. Chulkin, and J.P. Riley, Analyst, 83 (1958) 208.
- [162] V.S. Saltykova, and E.A. Fabrikova, Zhur. Anal. Khim., 13 (1958) 63.
- [163] S. Sakuraba, Talanta, 37, No.6 (1990) 637.
- [164] Jankovsky, Talanta, 2 (1959) 29.
- [165] Sandell, E.B., Anal. Chem., 19 (1947) 63.
- [166] Y. Nishikawa, Nippon Kagaku Zasshi., 79 (1958) 631.

- [167] M. Ishibashi, T. Shigematsu and Y. Nishikawa, Nippon Kagaku Zasshi., 78 (1957) 1139.
- [168] Weeks, M.E., Discovery of the Elements, 5th ed., J. Chem. Education, Easton, Pa, (1948) 400
- [169] H. Bode, and H. Fabian, Z. Anal. Chem. 170 (1959) 387.
- [170] S.A. Chitamber, A.R. Parab, P.S. Khodade, S. Jeyakumar, A.H. Goyal and H.C. Jain, Proceedings of Xth ISMAS National Symp. on Strategic and Hitech metals extraction and process charact. (1994).
- [171] F.J. Welcher, The Analytical uses of Ethylenediamine tetraacetic acid, Van Nostrand, Princeton, (1958) 176.
- [172] J.T. Baker, C. Chemcal, N.J. Phillipsburg, The EDTA Titration (1957) 28.
- [173] H. Flaschka, and H. Abdine, Chemist Analyst, 45 (1956) 58.
- [174] G. Schwarzenbach, Die komplexometrische Titration, 2nd ed., F. Enke, Stuttgart (1956).
- [175] V. Suk, and M. Malat, Chemist Analyst, 45 (1956) 30.
- [176] H. Specker, and E. Bankmann, Z. Anal. Chem., 149 (1956) 97.
- [177] V. Patrovsky, Chem. Listy, 47 (1953) 1338.
- [178] R.H.A. Crawley, Anal. Chim. Acta, 19 (1958) 540.
- [179] C.N. Reilley, R.W. Schmid and D.W. Damson, Anal. Chem., 30 (1958) 953.
- [180] H.D. Kirchman, and J.B. Ramsey, J. Am. Chem. Soc., 50 (1928) 1632.
- [181] S. Ato, Sci. Papers, Inst. Phys. Chem. Res., Tokyo, 10 (1929) 1.
- [182] N.R. Fetter, and D.F. Swine hart, Anal. Chem., 28 (1956) 122.
- [183] R. Belcher, A.J. Nutten and W.I. Stephen, J. Chem. Soc., (1952) 2438.
- [184] J.T. Stock, Amperometric Titrations, Wiley, New York (1958) 327.
- [185] O.W. Rollins, and C.K. Deischer, Anal. Chem. 26 (1954) 769.

- [186] W.H. Cone, L.C. Cady, J. Am. Chem. Soc., 49 (1927) 356.
- [187] I.M. Kolthoff, Chem. Weekbl., 24 (1927) 203.
- [188] I.M. Kolthoff, E.A. Pearson, Ind. Eng. Chem., Anal. Ed., 4 (1932) 147.
- [189] Mary R. Richardson, Alexander Bryson, Analyst, 78 (1953) 291.
- [190] T.D. Parks, O.D. Smith and S.B. Radding, Anal. Chim. Acta, 10 (1954) 485.
- [191] Verzijl, Ejah and I.M. Kolthoff, Rec. Trav. Chim. Pays-Bas, 43 (1924) 380.
- [192] E. Z. Brennecke, Anal. Chem., 86 (1931) 173.
- [193] A.Mayer, G. Bradshaw, J. Deutschman, Analyst, 78 (1953) 367.
- [194] I.A. Sheka, I.S. Chaus, T.T. Mityureva, Chemistry of Gallium, Elsevier, Amsterdam (1966) 266.
- [195] D.F. Swinehart, Anal. Chem., 23 (1951) 380.
- [196] P.R.Nair, Mary Xavier and S.K. Aggarwal, 18th Annual Convention of Indian Council of Chemists, North Maharashtra Univ., Jalgaon (1999).
- [197] P.R. Nair, Mary Xavier and S.K. Aggarwal, Workshop cum Seminar on Electro analytical Chemistry and Allied Topics (ELAC-2000), Paper-17 (2000).
- [198] J.M. Donaldson, UKAEA, AWRE, Aldermaston, Private communication to J.T. Byrne, The Dow Chemical Co. 1959.
- [199] G.N. Lypka, and A. Chow, Anal. Chim. Acta, 60 (1972) 65.
- [200] F.J. Miner and R.P. DeGrazio, Ion Exchange Separation and Volumetric Det. of Gallium in Pu –Ga Alloys, Anal Chem., 37(8) (1965) 1071.
- [201] K.A. Kraus, F. Nelson and G.W. Smith, J. Phys. Chem., 58 (1954) 11.
- [202] J.J. Katz and G.T. Seaborg, Chemistry of the Actinide Elements, Wiley, New York (1957) 264.
- [203] K.A. Kraus, F. Nelson, Anion exchange studies of the fission products, ORNL, Oak Ridge, 9B, 1.

- [204] W.B. Wilkinson, Argonne National Laboratory Report No.4109 (1948).
- [205] A.M. Dymov and A.P. Savotsin, Analytical Chemistry of Gallium, Ann Arbor Science Publisher, London (1970).
- [206] O.D. Renedo, M.A. Alonso-Lomillo, M.J.A. Martínez, Talanta, 73 (2007) 202.
- [207] B.J. Privett, J.H. Shin, M.H. Schoenfisch, Analytical Chemistry, 80 (2008) 4499.
- [208] E. Bakker, E. Pretsch, Angewandte Chemie International Edition, 46 (2007) 5660.
- [209] E. Bakker, V. Bhakthavatsalam, K.L. Gemene, Talanta, 75 (2008) 629.
- [210] J. Bobacka, Electroanalysis, 18 (2006) 7.
- [211] J. Bobacka, A. Ivaska, A. Lewenstam, Electroanalysis, 15 (2003) 366.
- [212] J. Bobacka, A. Ivaska, in: S. Cosnier, A. Karyakin (Eds.)
 Electropolymerization. Concepts, Materials, and Applications, Wiley VCH, Weinheim, Germany, 2010, pp. 173-187.
- [213] J. Bobacka, A. Ivaska, in: S. Alegret, A. Merkoçi (Eds.) Comprehensive Analytical Chemistry, Vol. 49, Elsevier, Amsterdam, 2007, pp. 73-86.
- [214] J. Bobacka, A. Ivaska, A. Lewenstam, Chemical Reviews, 108 (2008) 329.
- [215] E. Lindner, R. Gyurcsányi, Journal of Solid State Electrochemistry, 13 (2009) 51.
- [216] U. Guth, F. Gerlach, M. Decker, W. Oelßner, W. Vonau, Journal of Solid State Electrochemistry, 13 (2009) 27.
- [217] A.J. Bard, L.R. Faulkner, in: Electrochemical methods: fundamentals and applications, Wiley India Pvt. Ltd., 2006, pp. 74-81.
- [218] S. Amemiya, in: C.G. Zoski (Ed.) Handbook of electrochemistry, Elsevier, Amsterdam, 2007, pp. 261-294.
- [219] P.R. Unwin, in: A.J. Bard, M. Stratmann, P.R. Unwin (Eds.) Encyclopedia of Electrochemistry: Instrumentation and electroanalytical chemistry, Wiley-VCH, Weinheim, Germany, 2003, pp. 7-13.
- [220] E. Bakker, M.E. Meyerhoff, in: A.J. Bard, G.S. Wilson, M. Stratmann (Eds.) Encyclopedia of Electrochemistry, Bioelectrochemistry, Wiley-VCH, Weinheim, Germany, 2002, pp. 277-307.
- [221] M.J. Whitcombe, D. Lakshmi, in: S. Cosnier, A. Karyakin (Eds.) Electropolymerization. Concepts, Materials and Applications, Wiley-VCH,

Weiheim, Germany, 2010, pp. 133-151.

- [222] T.S.C.R. Rebelo, S.A.A. Almeida, J.R.L. Guerreiro, M.C.B.S.M. Montenegro, M.G.F. Sales, Microchemical Journal, 98 (2011) 21.
- [223] A. Ceresa, A. Radu, S. Peper, E. Bakker, E. Pretsch, Analytical Chemistry, 74 (2002) 4027.
- [224] A. Radu, A.J. Meir, E. Bakker, Analytical Chemistry, 76 (2004) 6402.
- [225] T. Sokalski, T. Zwickl, E. Bakker, E. Pretsch, Analytical Chemistry, 71 (1999) 1204.
- [226] M. Fibbioli, W.E. Morf, M. Badertscher, N.F. de Rooij, E. Pretsch, Electroanalysis, 12 (2000) 1286.
- [227] M. Telting-Diaz, E. Bakker, Analytical Chemistry, 73 (2001) 5582.
- [228] A. Radu, D. Diamond, in: S. Alegret, A. Merkoçi (Eds.) Comprehensive Analytical Chemistry, Vol. 49, Elsevier, Amsterdam, 2007, Ch. 2.
- [229] A. Radu, S. Peper, E. Bakker, D. Diamond, Electroanalysis, 19 (2007) 144.
- [230] E.J. Parra, P. Blondeau, G.A. Crespo, F.X. Rius, Chemical Communications, 47 (2011) 2438.
- [231] F. Faridbod, P. Norouzi, R. Dinarvand, M. Ganjali, Sensors, 8 (2008) 2331.
- [232] C.M. McGraw, T. Radu, A. Radu, D. Diamond, Electroanalysis, 20 (2008) 340.
- [233] M. Pawlak, E. Grygolowicz-Pawlak, E. Bakker, Analytical Chemistry, 82 (2010) 6887.
- [234] J.-P. Veder, R. De Marco, G. Clarke, R. Chester, A. Nelson, K. Prince, E. Pretsch, E. Bakker, Analytical Chemistry, 80 (2008) 6731.
- [235] M. Vázquez, P. Danielsson, J. Bobacka, A. Lewenstam, A. Ivaska, Sensors and Actuators B: Chemical, 97 (2004) 182.
- [236] T. Lindfors, L. Hofler, G. Jagerszki, R.E. Gyurcsanyi, Analytical Chemistry, 83 (2011) 4902.
- [237] T. Lindofors, J. Szucs, F. Sundfors, R.E. Gyurcsanyi, Analytical Chemistry, 82 (2010) 9425.
- [238] W. Plieth, in: Electrochemistry for materials science, Elsevier, Hungary, 2008, pp. 323-363.
- [239] G. Bidan, in: S. Cosnier, A. Karyakin (Eds.) Electropolymerization: Concepts, Materials and Applications, John Wiley & Sons, Germany, 2010, pp. 1-26.
- [240] T.F. Otero, J. Arias-Pardilla, in: S. Cosnier, A. Karyakin (Eds.)

Electropolymerization: Concepts, Materials and Applications, John Wiley & Sons, Germany, 2010, pp. 241-245.

- [241] M.A. Vorotyntsev, V.A. Zinovyeva, D.V. Konev, in: S. Cosnier, A. Karyakin (Eds.) Electropolymerization: Concepts, Materials and Applications, John Wiley & Sons, Germany, 2010, pp. 27-50.
- [242] A. Michalska, M. Wojciechowski, W. Jędral, E. Bulska, K. Maksymiuk, Journal of Solid State Electrochemistry, 13 (2009) 99.
- [243] J. Guo, S. Amemiya, Analytical Chemistry, 78 (2006) 6893.
- [244] J. Sutter, E. Lindner, R.E. Gyurcsányi, E. Pretsch, Analytical and Bioanalytical Chemistry, 380 (2004) 7.
- [245] S. Anastasova-Ivanova, U. Mattinen, A. Radu, J. Bobacka, A. Lewenstam, J. Migdalski, M. Danielewski, D. Diamond, Sensors and Actuators B: Chemical, 146 (2010) 199.
- [246] A. Radu, S. Anastasova-Ivanova, B. Paczosa-Bator, M. Danielewski, J. Bobacka, A. Lewenstam, D. Diamond, Analytical Methods, 2 (2010) 1490.